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### Fluorene based amorphous hole transporting materials for solution processed organic light-emitting diodes

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### ABSTRACT

For an organic light-emitting diode (OLED), enhancing hole injection into the emissive layer for charge balance is a priority to achieve efficient device performance, while solution processing enables organic devices to be fabricated cost-effectively with a large area-size via continuous roll-to-roll manufacturing. However, a limited number of small molecules-based hole-transporting materials (HTMs) were reported with the solution process feasibility and high performance. Here, we demonstrate a series of low cost, efficient and solution processable small molecule HTMs, namely, 2,7-Di(4-fluorophenyl)-9,9-diethylfluorene (Fl-PyEyF), 2,7-Di(3,5-difluorophenyl)-9,9diethylfluorene (di-Fl-PyEyF) and 2,7-Di(2,4,6-trifluorophenyl)-9,9-diethylfluorene (tri-FlPyEyF), designed by using two fluorophenyl, difluorophenyl or trifluorophenyl fragments as common end capping groups with 9,9-Diethylfluorenes cores, respectively, for highly efficient OLEDs. The glass transition temperatures of the molecules were estimated to be higher than 80 °C, which can provide morphologically stable amorphous thin films. All the molecules possess good solubility in common organic solvents. Moreover, all the synthesized molecules have not only appropriate highest occupied molecular orbital energy levels for good hole injection ability, but also sufficient lowest unoccupied molecular orbital for electron blocking capability, adequate ionization potentials (6.15 eV) and suitable triplet energies, which make them suitable hole transporting materials. The current efficiency of a conventional iridium(III) bis(4phenylthieno[3,2-c]pyridinato-N,C-2') acetylacetonate based phosphorescent yellow OLED device increases from 40.2 to 61.0 cd/A, an increment of 51.7% by substituting the conventional HTM, N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB), with the tri-Fl-PyEyF counterpart. These findings suggest that the reported materials can serve as potential molecular HTMs in solution-processed OLED.

### 1. Introduction

After three decades of extensive research, noteworthy development has been made in organic electroluminescent materials and device architecture for energy-efficient organic lightemitting diodes (OLEDs). As a result, mass-produced OLED television screens, mobile displays and lighting panels are now enthusiastically available in our daily life [1–7]. OLEDs bring the several unique benefits, such as superior image quality, ease of fabrication, conformability to curved structures, low power consumption, high-speed video rate, low-cost, wide viewing angle, wide color gamut, mechanical robustness, surface emission, and transparency [1–13]. Now, most prominent electronics companies, such as Apple, Samsung and Google, switched to OLED based displays in their recent products, i.e. iPhone X [14], Galaxy S8 [15] and Pixel [2,16] respectively. Moreover, several other companies including Philips/OLED Works, Osram, LG, and Konica Minolta already offer OLED based lighting panels. Regrettably, almost all these commercially available products are fabricated via vacuum deposition because of its superlative features, such as enabling multilayer deposition, precise control of layer thickness and good thin film integrity, which are highly essential for an

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efficient and stable device. The manufacturing process is highly expensive and possesses some serious drawbacks like low throughput, poor scalability, complicated color patterning process, huge material consumption, and difficulty in uniform film deposition of materials over a large area while maintaining high pixel resolution.17 Therefore, a facial solution process to fabricate organic/polymeric emitting and transporting materials are in great demand for commercially profitable and large-area production of OLEDs by using inkjet printing or roll-to-roll printing [17-19]. The state-of-the-art high-performance OLED devices routinely integrated electron- and hole transporting materials (ETMs and HTMs) as n-type and p-type contacts respectively, which play a key role in decreasing the energy-barrier between the electrode and organic layers. They assist to generate balance light-emitting charge-carriers in the emissive layer (EML) and hence minimizes undesired recombination losses at the interfaces [20-24]. A broad range of high triplet energy  $(E_t)$  ETMs have been already developed, whereas only a few organic HTMs have been realized and incorporated in OLED devices. Organic HTMs mainly consist of a small molecule conducting polymers. Usually, as an excellent hole transporting material, should exhibit: (1) good hole mobility, (2) morphologically stable thin film, (3) high triplet energy for triplet exciton confinement, (4) high glass transition temperature, (5) low crystallization at high temperature, (6) an appropriate ionization potential to ensure a low energy barrier for hole injection from the anode into the emissive layer, and (7) adequate energy levels of HOMO for effective hole injection [20-24]. In the past few years, several small molecules based HTMs have been synthesized and applied in OLEDs, including triphenylamine (TPA)-based [25-28], carbazole-based [23,29-33], azepine and phenoxazine [34,35], and tolylamino cyclohexane derivatives [36], because of their high hole mobility, electron confining ability and amorphous film forming property. Amongst, arylamine derivatives, such as N,N'-diphenyl-N,N'-bis(1-naphthyl)-(1,1'-biphenyl)-4, 4'diamine (NPB), N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)benzidine (TPD) and 1,1-bis((di4-tolylamino)phenyl)-cyclohexane (TAPC) are the most famous HTMs in the early stage and belongs to the benzidine family [37-39]. An amine-based HTM, 4,4',4"tris(diphenylamino)triphenylamine (TDATA) [40], 4,4',4"-tris[(3-methylphenyl)phenylamino)]triphenylamine (MTDATA) [41] and 4,4',4"-tris (N-3-methylphenyl-N-phenylamino)triphenylamine (m-MTDATA) [42] with high glass transition temperature are another kinds of successful example. Furthermore, (9,9'-bis(4-vinylbenzyl)-9H,9'H-3,3'-bicarbazole) (VvPvMCz) [43,44], 1,3-Bis(N-carbazolyl)benzene (mCP) [45], 3, 6-bis(4-vinylphenyl)-9ethylcarbazole (VPEC) [46] and 4,4',4"-tris(carbazol-9-yl)triphenylamine (TCTA) [47] are commonly used as the hole transport layer (HTL) and consists of carbazole and amine moieties. In the molecular design aspect, the carbazole moiety has several commendable properties including easy modification, chemical stability, and large triplet energy. Our group has considerable experience in synthesizing HTMs using carbazole-containing designs and their electroluminescent (EL) applications. For example, in 2014, G. Krucaite et al. reported the phenyl, naphthyl or biphenyl disubstituted 9-alkylcarbazole based HTLs, amongst, Alq3 based OLED device using 3,6-diphenyl-9-ethylcarbazole as hole transporting layer demonstrated a turn-on voltage of 5 V, a maximum brightness of 9800 cd/m<sup>2</sup>, and maximum current efficiency of 22.5 cd/A [28]. In 2017, Sudhir et al. demonstrated the naphthyl and phenyl substituted 9-(2-phenylvinyl) carbazole based HTLs, which displayed 40% higher current efficiency than that of NPB, for Ir(ppy)<sub>3</sub> based device [12]. Recently, Grigalevicius et at. stated two low-cost 9-(2,2-diphenylvinyl) carbazole-based derivatives with aryl substitutions, which exhibited better performance than those of the widely used hole transporting material, TAPC based device for the same device structure [29].

Among numerous strategies to design high performance conjugated small molecules, the introduction of fluorine atom into the donor and acceptor units has been recently attracted a lot of attention owing to its superb features such as i) downshift of the molecular orbital energy levels without sacrifice of optical bandgap due to strong electronegativity of fluorine [48,49], ii) enhancement of the non-covalent interaction and intermolecular aggregation of H–F and C–F which improve the thin film morphology [50], and iii) reduced steric hindrance due to the small size of fluorine atoms and its van der Waals radius i.e. 1.35 Å [51, 52]. Small size of fluorine atom also endows the molecule backbones greater planarity and facilitates charge transport [51,52]. Nevertheless, the fluorination of small molecules also creates some detrimental effects on the compound such as low solubility in the common organic solvent, an inappropriate molecular energy level and large aggregation of compound in thin film state [53,54]. Therefore, the degree of fluorination should be optimized to achieve a high performance.

In this study, we demonstrate a series of 9,9-diethylfluorenes derivatives, substituted with two fluorophenyl, difluorophenyl or trifluorophenyl fragments as an efficient solution processable hole transporting materials for OLED devices. These HTMs exhibit excellent solubility in common organic solvents and robust thermal stability. Taking conventional PO-01 emitter based yellow phosphorescent device, for example, at  $100 \text{ cd/m}^2$ , the current efficiency (CE) dramatically increases from 31.7 to 54.4 cd/A and power efficiency (PE) from 17.3 to 31.5 lm/W, an increment of 72 and 82% respectively, is observed, as NPB is replaced by tri-Fl-PyEyF. This improvement is strictly attributed to the incorporation of triFI-PyEyF that intended the rational hole mobility, smooth surface morphology, sufficiently high triplet energies, effective electron confinement, charge transport, carrier recombination, and charge balancing in the emissive layer. The high efficiencies of the yellow PhOLEDs suggest great potential of the new 9,9-diethylfluorenes based electroactive materials for OLED applications.

#### 2. Results and discussion

### 2.1. Synthesis

The synthesis of dual fluorophenyl, difluorophenyl or trifluorophenyl substituted 2,7-diaryl 9,9-diethylfluorenes derivatives, Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF was carried out by a multi-step synthetic route as shown in Scheme 1 and reported in our earlier work [55]. In brief, the key bromo intermediate 2,7-dibromo-9,9-diethylfluorene (1) was synthesized by alkylation of commercially available 2, 7-dibromofluorene with ethyl iodide. 2,7-Diaryl-9,9diethylfluorenes (3–5) were then prepared by Suzuki reaction [56] of the 2. 7-dibromo-9,9diethylfluorene and an excess of 4-fluorophenyl boronic acid, 2,4-difluorophenyl boronic acid or 2,4,6-trifluorophenyl boronic acid, respectively. The synthesized derivatives all were identified by mass spectrometry and <sup>13</sup>C NMR spectroscopy [55]. The data were found to be in good agreement with the proposed structures. The materials were soluble in common organic solvents and their thin films could be prepared by spin coating which facilitates simple solution processing techniques for device fabrication. GK41.

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, δ, ppm) of Fl-PyEyF: 162.34, 159.51, 148.17, 142.78, 138.24, 135.15, 123.44, 118.44, 117,09, 117.02, 107.20, 107.17, 107.13, 99.61, 99.58, 99.53, 49.82, 31.25, 7.11. (Supplementary information, Page 15).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, δ, ppm) of di-Fl-PyEyF: 164.67, 162.21, 151.22, 144.96, 144.87, 144.78, 141.24, 138.15, 126.19, 121.44, 120.44, 110,09, 110.02, 109.90, 109.83, 102.63, 102.38, 102.13, 56.52, 32.82, 8.62. (Supplementary information, Page 16).

<sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, δ, ppm) of tri-Fl-PyEyF: 13C NMR spectrum (CDCl<sub>3</sub>, δ, ppm): 167.14, 165.32, 154.63, 148.12, 144.35, 142.41, 129.22, 113.19, 113.13, 106.52, 106.39, 106.14, 58.25, 35.18, 10.12. (Supplementary information, Page 17).

### 2.2. Photophysical properties

The optical properties of the organic compounds Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF dyes were examined by measuring absorption



Scheme 1. Schematic illustration of the synthesis of the two fluorophenyl, difluorophenyl or trifluorophenyl substituted with 9,9-diethylfluorenes derivatives with based hole transporting materials (HTMs), Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF.

and emission spectra in  $10^{-5}$  M tetrahydrofuran (THF) solutions in ambient environments. The ultraviolet–visible (UV–vis) and photoluminescence (PL) spectra of the compounds are displayed in Fig. 1 and the relevant data are listed in Table 1. The optical band gaps (*Eg*) were estimated from the intersections of the absorption and emission spectra. The compounds Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF show *Eg* of 3.46 eV, 3.49 eV, and 3.81 eV, respectively.

#### 2.3. Electrochemical properties

The electrochemical properties of all the synthesized compounds were characterized by cyclic voltammetry. The highest occupied molecular orbital (HOMO) energy levels were calculated by using the oxidation potentials obtained from the cyclic voltammograms, as shown in Fig. 2. The oxidation potentials of the compounds are cited in contrast to the internal standard i.e. ferrocene. All the dyes exhibited more positive oxidation potentials when compared to those of with ferrocene, suggesting the facile deletion of electrons from the molecules. The estimated HOMO levels of compounds Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF are 5.68, 5.83 and 5.96 eV, respectively, and their corresponding lowest unoccupied molecular orbital (LUMO) energy levels are 2.23, 2.34 and 2.15 eV, that are calculated from the difference between HOMO energy level and *E*g. All the calculated data are listed in Table 1.

#### 2.4. Theoretical calculations

Theoretical calculation (by using Density Functional Theory (DFT) at B3LYP/6-31g (d) basis set) were executed to further understand the correlation between electronic structure and photophysical properties of the compounds [57]. The optimized geometry of the synthesized compounds is shown in Fig. S1. The electron density distributions of the frontier molecular orbitals are also shown in Fig. S2. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbitals (LUMO) are distributed on total molecular structure. The calculated HOMO/LUMO values of these molecules are -5.49/-1.32 eV for FL-PyEyF, -5.57/-1.40 eV for di-Fl-PyEyF, and 5.65/-1.14 eV for tri-Fl-PyEyF, respectively (Table S1). It can be clearly seen from Fig. S3 and Table S1 that the HOMO values of all the synthesized compounds are ranging from -5.49 to -5.66 eV, which are in between HTL (TAPA, -4.91 eV) and emissive layer (FIrpic, -5.91 eV). Thus, these synthesized derivatives may have the good hole transport ability in the OLED

device [58]. Time-Dependent DFT (TD-DFT) calculation were also been performed to find out the excited energy level locations (singlet and triplet) of the compounds in gas and solution phase and the corresponding data is summarized in Table S1. The simulated gas-phase, as well as DCM phase absorption spectra of the compounds, were shown in Fig. S4. It can be observed that the absorption spectra of the synthesized derivatives have an intense peak in the range of around 320-330 nm, which are assigned to the  $\pi$ - $\pi$ \* transitions. The absorption spectra clearly show that there is a blue-shift in absorption spectra in tri-Fl-PyEyF and compared to Fl-PyEyF and di-Fl-PyEyF, which is due to the increasing the electron-with drawing 'F' atoms on the terminal phenyl ring. The calculated vertical excitation wavelengths, their oscillator strength (f) and orbital contribution of each individual compound are sequentially listed in Table S2, Table S3 and Table S4. In addition, atomic coordinates of all the synthesized compounds are given in the supplementary information. (Supplementary information, Tables S5, S6, and S7).

### 2.5. Ionization potentials

The solid-state ionization potential is also one of the essential parameters of HTMs that need to be taken into consideration before fabricating the OLED devices, which gives a precise approximation of the HOMO energy level of the materials. Ip of thin layers of the synthesized compounds Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF are measured by the electron photoemission method. The photoemission spectra of thin amorphous films of these compounds are presented in Fig. 3. The established Ip values of the molecules FL-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF are 6.15, 6.16, and 6.08 in eV, respectively. The characteristic demonstrates that hole transporting layer of compounds Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF should be well suited for application in optoelectronic devices to ensure efficient hole transfer at the interface. It is important to note that Ip of all the synthesized compounds are higher than that of N,N'-di(1-naphthyl)-N,N'-diphenyl-(1,1'biphenyl)-4,4'-diamine (NPB) i.e.  $5.32 \pm 0.3$  Ev [59,60] resulting comparatively higher hole-injecting and transporting properties in the multilayer OLED devices.

### 2.6. Hole-only device of HTMs

Another important property is the ability of the HTMs to transport holes, which can be quantified by measuring the current density vs.



**Fig. 1.** The ultraviolet–visible (UV–vis) and photoluminescence (PL) spectra of dual fluorophenyl, difluorophenyl or trifluorophenyl substituted 2,7-diaryl-9,9-diethylfluorenes based HTMs, (a) Fl-PyEyF, (b) di-Fl-PyEyF and (c) tri-Fl-PyEyF. All the data were measured by dissolving the HTMs in THF.

voltage plot of the hole only devices (HOD). To investigate the electrical properties of the reported HTMs, HODs were fabricated with the following structure: ITO/PEDOT: PSS (35 nm)/Fl-PyEyF, di-Fl-PyEyF, tri-Fl-PyEyF, or NPB/LiF/Al (100 nm). In this case, a control device using NPB instead of the newly synthesized HTMs was also fabricated. The structure of the HOD and a plot of the current density-voltage characteristics of the device are shown in Fig. 4. The results obtained from the HOD measurement revealed that the newly synthesized compounds possess better hole transport mobility than that of NPB based control part device.

The reason beside this may be fluorination of the molecules which leads to an optimal thin film morphology that balances charge separation and transfer as well as facilitates charge collection, an enhanced domain purity, the formation of hierarchical domain size and a directional vertical phase gradation [61]. It is also believed that mobility of the molecules highly hinged with molecular packing [62–64]. Lower intermolecular spacing distance will result in very dense molecular packing which enables better charge transport, hence high mobility [62–64]. The introduction of fluorine atom, steepening the potential energy surface in the region near the equilibrium structure, will significantly increases the planarity of the structure and decrease intermolecular spacing distance [65]. Furthermore, all the synthesized compounds possess either deeper or almost similar HOMO levels as compared to NPB which facilities more injection of hole into the designed hole only devices for these molecules, hence higher hole mobility.

### 2.7. Electroluminescent properties

To explore the hole injecting and transporting characteristics of synthesized HTMs Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF, conventional yellow phosphorescent OLED devices were fabricated with following general device configuration ITO/PEDOT: PSS/HTL/EML/TPBi/

LiF/Al. In the designed device architecture, ITO and Al work as the anode and cathode, respectively. PEDOT: PSS and LiF employed as the hole- and electron-injection layers, respectively, and TPBi is an electron transporting layer. Two well-known materials 4,4'-di (9 H-carbazol-9-yl) biphenyl (CBP) and PO-01 were utilized as a bipolar host and phosphorescent yellow emitter, respectively. Furthermore, the control OLED device was also fabricated with NPB HTM to compare the results. The schematic energy-level diagram of all the studied OLED devices is shown in Fig. 5.

The electroluminescent characteristics of conventional PO-01 based vellow phosphorescent OLED devices fabricated with newly synthesized HTMs, i.e. Fl-PyEyF, di-Fl-PyEyF, tri-Fl-PyEyF and NPB based controlled HTM device are displayed in Fig. 6 and obtained results are summarized in Table 2. Fig. S5 demonstrates the normalized EL spectra of all the devices that are collected at 100  $cd/m^2$ , i.e., identical for all the employed HTMs. The control OLED device demonstrates the maximum PE, CE and brightness of 25.1 lm/W, 40.2 cd/A and 10,940 cd/m<sup>2</sup>, respectively. The Fl-PyEyF based OLED device shows a maximum CE of 49.4 cd/A, which is 22.9% higher than that of the control OLED device. Furthermore, the PE at 100 and 1000 cd/m<sup>2</sup> are noticeably enhanced from 20.5 lm/W and 13.5 lm/W to 27.4 lm/W and 17.9 lm/W, respectively, as shown in Fig. 6. In addition, di-Fl-PyEyF and tri-Fl-PyEyF based OLED devices show a maximum CE of 58.7 cd/A (PE = 38.2 lm/W) and 61.0 cd/A (PE = 39.5 lm/W), respectively, which are 46% (52%) and 52% (57%) higher than the NPB based device. The di-Fl-PyEyF containing device showed a PE of 33.2 lm/W, a CE of 53.4 cd/ A and an external quantum efficiency (EQE) of 17.1% at 100  $cd/m^2$ , however, 35.3 lm/W, 56.3 cd/A and 17.4% were observed for the tri-Fl-PyEyF containing device at the same brightness. The reason why the tri-Fl-PyEyF based device showed the highest efficiency among all the studied HTMs may be attributed to effective electron and exciton confinement within the emissive layer, high hole mobility and suitable molecular orbital energy levels.

The confinement of electron and hole in the desired emitting zone of an OLED has been known as one of the key factors affecting the performance of it [66,67], which can be achieved by employing high triplet energy host material as well as other functional layers including a hole and electron transporting layers [68,69]. The triplet energies of the HTLs used in this study are 2.69, 2.69, 2.73, and 2.30 eV for Fl-PyEyF, di-Fl-PyEyF, tri-Fl-PyEyF, and NPB respectively, which are also displayed in Fig. 7 along with the triplet energies of PO-01 and CBP. It should be noted that all the designed HTMs confines the triplet excitons within the emitting layer most effectively when compared with NPB based device. In NPB based control device, exciton energy enthusiastically transfers from host CBP to the HTL (NPB), ensuing in lower device efficiency. Furthermore, both the Fl-PyEyF and di-Fl-PyEyF HTMs have a similar triplet energy level (2.69 eV) but the efficiency of di-Fl-PyEyF Table 1

Photophysical, thermal, electrochemical, and electrical characteristics of the hole transporting materials.

Compound	$\lambda_{max}$ , nm ( $\epsilon_{max}$ , $M^{-1}$ cm <sup>-1</sup> $\times$ 10 <sup>3</sup> ) <sup>a</sup>	$\lambda_{em}^{b}$ [nm]	$T_m^{c}$ [°C]	Tg <sup>d</sup> [°C]	$T_d^{e}$ [°C]	HOMO <sup>f</sup> [eV]	LUMO <sup>f</sup> [eV]	Band Gap <sup>g</sup> [eV]
Fl-PyEyF	308 (24.3), 334 (26.6)	378	109	82	279	-5.58	-2.23	3.46
di-Fl-PyEyF	308 (24.2), 329 (26.4)	382	218	182	272	-5.83	-2.34	3.49
tri-Fl-PyEyF	298 (28.8)	353	152	89	260	-5.96	-2.15	3.81

 $^{\rm a}$  Measured in THF solution with concentration  $10^{-5}$  M.

<sup>b</sup> Photoluminescent peak.

<sup>c</sup> Melting temperature;<sup>48</sup>.

<sup>d</sup> Glass transition temperature;<sup>48</sup>

<sup>e</sup> Decomposition temperature;<sup>48</sup>.

<sup>f</sup> HOMO and LUMO were calculated from the redox potentials measured by cyclic voltammetry (CV) method. The semi-oxidation potential ( $E_{1/2}^{ox}$ ) was calculated from ( $E_{p1} + E_{p2}$ )/2–0.48, where 0.48 is the correct value obtained from the oxidation system as the Ferrocenium/Ferrocene (Fc<sup>+</sup>/Fc) was added as the internal standard. The energy of HOMO was then obtained from the  $E_{HOMO} = -(E_{1/2}^{ox} + 4.8)$ . The energy of LUMO was estimated by subtracting the bandgap from the HOMO energy level, [ $E_{LUMO} = -E_{HOMO} + Eg$ ].

<sup>g</sup> Optical band gap.



Fig. 2. Cyclic voltammograms of the compounds (a) Fl-PyEyF, (b) di-Fl-PyEyF and (c) tri-Fl-PyEyF.

based device is marginally higher than that of Fl-PyEyF based device. The reason beside this may be high hole mobility and the deeper HOMO level of di-Fl-PyEyF based device when compared with Fl-PyEyF device.



Fig. 3. Electron photoemission spectra of Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF thin films.



Fig. 4. Current density vs voltage curves of hole-only devices for Fl-PyEyF, di-Fl-PyEyF tri-Fl-PyEyF and NPB.

Similar observation also reported in the literature [70,71] For example, Lee et al. reported that OLED device performance is very sensitive to the mobility and triplet energy of HTMs. Given that the OLED device with TAPC HTM shows high efficiency when compared with TPD and  $\alpha$ -NPD owing to its higher triplet energy amongst [70]. Goushi et al. also found analogous consequences in their green phosphorescent devices where they observed a noteworthy difference in efficiency even with the small difference in the triplet energies of HTMs. They also suggested that triplet exciton diffusion at the interface of hole transport and emissive layers can be controlled by employing suitable high triplet energy HTL [71].

The hole injecting characteristics of HTMs in OLED device also highly depend on energy barriers between them and emissive layer. For efficient hole injection and transportation to the emission zone, reducing



**Fig. 5.** Schematic energy levels diagram of the solution-processed yellow OLED device containing the spin-coated films of four different HTMs, NPB, Fl-PyEyF, di-Fl-PyEyF, and tri-Fl-PyEyF. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

the hole injection barrier is a successful approach, which can be achieved by ladder type cascading of HTMs [72]. The resultant device structure displays energy barriers of -0.50, -0.51, -0.43, and -0.33 eV

or 0.40, 0.39, 0.47, and 0.56eV for holes to enter from the HTMs NPB, Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF to host CBP or guest PO-01, respectively. Amongst all the studied HTMs, the tri-Fl-PyEyF favors



**Fig. 7.** Proposed energy transfer mechanism in the designed OLED device and triplet energy level of HTLs, CBP, and PO-01. Triplet energy is strongly confined by HTMs FI-PyEyF, di-FI-PyEyF, and tri-FI-PyEyF when compare with conventional HTM, i.e., NPB.



Fig. 6. OLED characteristics using different HTMs. (a) Current density and (b) luminance as a function of voltage. (c) Power and (d) Current efficiency as a function of luminance.

### Table 2

Effect of HTMs Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF on the EL characteristics of PO-01 based phosphorescent OLED devices fabricated by solution process.

HTL	@ 100 cd/m <sup>2</sup> /1	1000 cd/m <sup>2</sup> /Maximum valu		Maximum Luminance (cd/m <sup>2</sup> )		
	OV[V]	PE[lm/W]	CE[cd/A]	EQE[%]	CIE <sub>xy</sub> coordinates	
NPB	5.2/6.4/-	20.5/13.5/25.1	37.1/28.3/40.2	15.5/9.0/-	(0.53, 0.46)	10,940
Fl-PyEyF	4.9/6.1/-	27.4/17.9/29.0	46.6/34.7/49.4	16.7/10.7/-	(0.53, 0.46)	10,913
di-Fl-PyEyF	4.7/6.1/-	33.2/21.9/38.2	53.4/39.0/58.7	17.1/12.2/-	(0.53, 0.47)	12,060
tri-Fl-PyEyF	4.6/5.8/-	35.3/25.6/39.5	56.3/42.1/61.0	17.4/12.4/-	(0.53, 0.47)	13,400

more efficient hole injection into the host and guest, hence the highest brightness and low turn on voltage obtained when compared with other counterparts. Although there is lowest energy barrier for the hole to enter from the HIL to HTM for the Fl-PyEyF based OLED device, but it exhibits poor performance, the reason beside this may be i) low hole mobility, ii) low triplet energy and iii) high hole injection barrier towards the host or guest.

As a final point, this study demonstrates that developing new solution processable HTMs with high hole mobility, appropriate molecular orbital energy level and high triplet energy may be a more productive approach to achieving high-performance low-cost OLEDs than merely monitoring the charge transport properties and molecular orbital energy of the emissive layer. Our results also line up with the previously reported solution processable small molecule hole transporting materials.

### 3. Conclusion

In conclusion, a series of solution-processable dual fluorophenyl, difluorophenyl and trifluorophenyl fragments substituted 9.9-Diethylfluorenes cores based HTMs, Fl-PyEyF, di-Fl-PyEyF and tri-Fl-PyEyF have been designed, synthesized and successfully employed in highly efficient phosphorescent OLED devices, as alternatives to the routinely employed NPB. All the molecules exhibited high thermal stability, high triplet energy, outstanding solubility in common organic green solvents, appropriate molecular orbital energy level, and suitable ionization potential to work as a hole transporting layer in OLEDs. The hole-transport properties of all the HTMs are shown to be better than that exhibited by NPB. The tri-Fl-PyEyF based yellow phosphorescent OLED device revealed a maximum PE of 39.5 lm/W and CE of 61.0 cd/A, that improves by 55.8 and 52.8%, respectively, compared to the NPB based control OLED device. Excellent hole injecting and transporting abilities, adequate HOMO-LUMO and triplet energy level, reduced hole injection barrier for host and guest, and significantly confinement of light emitting exciton in the desired recombination are the key factors behind higher device performances. This study will open an avenue towards realization of high efficiency in OLED devices by molecular and device engineering of hole transporting materials instead of the emissive layer with solution process feasibility.

### Declaration of competing interest

There are no conflicts of interest to declare.

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### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.orgel.2020.105633.

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### 1. Introduction

Ever since the discovery of electric light, by Edison in 1879, artificial lighting has empowered human beings to work around-the-clock and has developed a highly productive and modern society. In hindsight, exposure to artificial white light at night, as the work culture demands it, disrupts the age-old established circadian rhythmic clock due to the presence of blue light, which triggers specialized cells in the eye's retina.<sup>1-3</sup> It is a proven fact that the circadian disruption causes sleep disorders, obesity, and diabetes by suppression of melatonin secretion resulting in various types of cancer in men and women.<sup>4-6</sup> However, it is equally essential to have white light during the daytime to stimulate our biological clock owing to its ability to stimulate cortisol by the presence of blue emission.<sup>1–5</sup> The prolonged absence of white light during daytime proves to be detrimental to human health causing depression and even the development of suicidal tendencies.

## High efficiency color-temperature tunable organic light-emitting diode

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Rhythmic lighting with varying color-temperature and brightness like that of diurnal sunlight has now been recognized to be extremely crucial to human health. In this study, we demonstrate a high-efficiency and high light-quality organic light-emitting diode (OLED) with color temperature tunable from the 1700 K of dusk-hue, 1900 K of candles and 2500 K of incandescent bulbs to 3000 K of warm-white light. The color-temperature tunable OLED device was achieved by utilizing a hybrid system and inserting a carrier modulation layer (CML) between the emission layers. In addition, the electron-rich charge transport properties of EML-1, facilitated *via* a 3:1 composition ratio of the 3P-T2T host to TPD-15 co-host, played a crucial role in tuning the desirable low-color temperature of the fabricated OLED devices. The current efficiency, power efficacy, and spectrum resemblance index (SRI) of the studied OLED are 40.2 cd/A, 40.3 lm W<sup>-1</sup> and 82.2 at 1000 cd m<sup>-2</sup>, respectively. The resultant devices show great potential to advance the study and development of physiologically friendly lighting and enable a successful commercial OLED lighting product in the market.

All these have raised great concern internationally, and physicians have hence been calling for the development of a smart lighting source which provides a color temperature tunable emission because of its direct impact on human physiology and psychology.<sup>1,7-10</sup> According to the National Human Activity Pattern Survey (NHAPS), people spend on average 87% of their lives indoors, often without exposure to natural daylight.<sup>11</sup> Artificial light makes it hard to tune into the natural rhythms of the day. For example, for home lighting, not only does the home environment need to be bright but it should also be pleasant; however, it can only be achieved via smart lighting that has the ability to tune the color temperature suitable to our needs. Therefore, the adaption of a color temperature tunable light source is the way forward to enhance the quality of human life and minimize the light hazards caused by artificial lighting.

Since 1996, efforts have been made by the scientific community to develop a color temperature (CT) tunable organic light-emitting diode (OLED). The first color-tunable OLED was demonstrated by Burrows *et al. via* a two- or three-color stacked OLED (SOLED), in which each color element could be controlled independently.<sup>12,13</sup> However, in 2009, Jou *et al.* achieved a real breakthrough by fabricating a sunlight style CT tunable single-junction OLED device, having a color temperature span ranging from 2300 to 8200 K that mimicked the daylight-chromaticity of the natural sunlight. These remarkable results were obtained *via* novel device engineering, in which a 3 nm hole modulation layer



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Fig. 1 The recent published data for OLED devices with color temperature, power efficacy, and CRI parameters.

(HML) was inserted between the red and green emissive layers and the enhanced power efficacy of the CT-OLED was achieved by using a double HML.<sup>14,15</sup> In 2013, they successfully demonstrated a low color temperature tunable OLED with CT span ranging from 1580 to 2600 K, covering that of dusk-hue (2500 K) and candlelight (1900 K), and provided a physiologically friendly, blue hazard-free, high-quality light source with a color rendering index (CRI) of 91.<sup>16</sup> Novel device engineering demonstrated that color temperature and chromaticity tunability of OLED devices can be achieved by regulating the recombination zone in the emissive layer, which greatly depends on energy transfer between host and guest under the influence of the different electric field.<sup>17-20</sup> However, another approach to fabricate CT tunable OLED devices is to use the stacked tandem device architecture. In 2014, Joo et al. employed the capping layer to enhance the emission of the upper transparent OLED of the stacked color-tunable white organic light-emitting diodes.<sup>21</sup> Weaver et al. demonstrated a color-tunable OLED lighting panel size of  $15 \times 15$  cm<sup>2</sup> based on RGB monochrome stripes that exhibited a CT ranging from 2700 K to 4000 K with an enhanced power efficacy of 63  $\text{lm W}^{-1}$  by employing a 20 mm thick out-coupling block and diffuser sheet.<sup>22</sup> In 2017, Oliva's group adopted a parallel configuration of tandem CT-OLEDs, where the top and bottom subunits were connected through silver metal that acts as an interlayer to control the CT via the applied voltage. The silver interlayer helps to reduce the device operating voltage of the OLED device.<sup>23</sup> In 2018, Lee et al. fabricated a color-tunable OLED by using three vertically stacked basic colors of blue, green and red, which can be independently controlled.<sup>24</sup> We have summarized the data of some color tunable-OLED devices including the stacked OLEDs (SOLEDs) and single device OLEDs in Fig. 1.

The literature survey indicates the importance of the color temperature tunable OLED device; however, the structure of the adapted device inherited some drawbacks – particularly stacked tandem CT-tunable devices needed a high operating voltage along with the complex fabrication process of interconnecting layers, which can adversely affect the color stability of the device. To overcome this drawback, a hybrid OLED device structure consisting of phosphorescent and fluorescent emissive layers could be more useful.<sup>25–29</sup> Herein, to make color temperature tunable OLED lighting with low driving voltage

and high power efficacy, we choose to use a hybrid device architecture comprising of phosphorescent green and red emitters as the first emissive layer (EML-1) to provide a high luminance and a fluorescent blue emitter as the second emissive layer (EML-2) to adjust the color temperature. The combination of EML-1 and -2 enables us to fabricate natural light color OLED devices.

### 2. Experimental

### 2.1. Materials and the device fabrication method

All the devices were fabricated on a 150 nm thick indium tin oxide (ITO) substrates with a size of  $10 \times 10$  cm<sup>2</sup> having active pixel size of  $2 \times 2$  mm<sup>2</sup>, which act as an anode layer. The ITO substrates were cleaned with detergent and dried in an oven followed by oxygen and argon plasma treatment for 120 seconds and subsequently transferred to the thermal evaporation deposition chamber for device fabrication. In this study, we fabricated the color temperature tunable OLED devices by employing two different emissive layers (EMLs) with the first emissive layer (EML-1) designed to emit red and green and the second emissive layer (EML-2) designed to emit blue light. The carrier modulating layer (CML), having hole dominated charge carriers, was inserted between the two EMLs. The specific details of the studied OLED devices are described as follows.

### 2.2. Device structures

Fig. 2 shows the device architecture and energy diagram of the studied Devices 1 and 2. A 150 nm ITO anode layer, an 18.75 nm 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4-TCNQ) doped in a 4,4',4"-tris(N-(naphthalen-2-yl)-N-phenylamino)triphenylamine (2T-NATA) hole injection layer (HIL) with 4 wt% p-type doping, a 20 nm TPD-15 hole transport layer (HTL), a 19 nm EML-1 comprised of 5 wt% bis(2-(naphthalen-2yl)pyridine)(acetylacetonate)iridium(III) (Ir(npy)2acac) and 10 wt% bis(2-(3,5-dimethylphenyl)quinoline-C2,N'(acetylacetonato) iridium(III) (Ir(mphq)<sub>2</sub>(acac)) co-doped in the 3P-T2T and TPD-15 co-host system with various deposition rates (0.6 Å  $s^{-1}$  + 0.6 Å  $s^{-1}/$ 0.9 Å  $s^{-1}$  + 0.3 Å  $s^{-1}$ ), a 3 nm TPD-15 carrier modulation layer (CML), an 8 nm EML-2 with 5 wt% of IDE-102 doped in tb-AND, a 17.5 nm electron-transporting layer (ETL) consisting of 2,7-bis(2,20-bipyridine-5-yl)triphenylene (Bpy-TP2) co-doped with Liq, a 1 nm electron injection layer (EIL) of Liq, and 150 nm thick aluminum as a cathode electrode were used to fabricate OLED Devices 1 and 2.

The device architecture and the energy diagram of Devices 2 and 3 are shown in Fig. 3. The device architecture was similar for both with the same materials of HIL, HTL, CML, ETL, EIL and cathode (Al) with exact layer thicknesses. However, for device-3, in EML-2 the light blue fluorescence emitter IDE-102 was replaced with 1,4-bis[2-[4-[*N*,*N*-di(*p*-tolyl)amino]phenyl]-vinyl]benzene (DSB) as the deep blue emitter.

Devices 4 to 6 were fabricated with the same materials of HIL, HTL, ETL, EIL and cathode (Al) with exact layer thicknesses. However, the EML was modified by changing the EML-1



Fig. 2 (a) Schematic structure and (b) energy level diagram of Devices 1 and 2; Device 1 (a : b) = 1 : 1 and Device 2 (a : b) = 3 : 1.

thickness to 6, 4 and 2 nm and the corresponding EML-2 thickness to 21, 23, and 25 nm for Devices, 4, 5 and 6, respectively. A 3 nm CML comprised of 3P-T2T co-doped with TPD-15 was kept constant for all three devices. The device architecture and the energy level diagram are shown in Fig. 4.

### 2.3. Device characterization

The luminance, CIE chromatic coordinates and EL spectrum were measured by using a Minolta CS-1000 spectroradiometer. A Keithley 238 electrometer was used to measure the current-voltage (I-V) characteristics. The OLED device lifetime was measured with Chroma (Model 58131). The emission area of all the resultant devices was 4 mm<sup>2</sup> and the luminance in the forward direction was measured.

### 3. Results and discussion

In order to achieve the low color temperature at initial driving voltage (turn-on voltage) and color temperature tunability *via* 

increasing the applied driving voltage, we devised a strategy to control the main recombination zone such that it can be distributed in the phosphorescent emissive layer and close to the interface between EML-1 and CML, so that the blue emitter only harvests a few excitons while suppressing the luminescence contribution of the blue light. Besides, the CML or the main emissive layer needs to increase the injection of the holes with respect to an increase in applied voltage, so that the variation of the color temperature is more obvious.<sup>30-33</sup> The two EMLs are separated by employing the CML in between them. The CML is comprised of two materials and was optimized via controlling the evaporation rate. The optimized CML plays a crucial role in controlling the recombination zone in EMLs, which depends on the applied voltage. This peculiar device arrangement will be expected to emit color temperature tunable natural light that follows the locus of the black body radiation curve.

Based on these requirements, we designed several experiments with different conditions. In the device concept design, 2T-NATA doped with 4 wt% of F4-TCNQ was used as a HIL which assists in Published on 08 November 2019. Downloaded by National Tsing Hua University on 11/27/2019 8:40:55 AM.



Fig. 3 (a) Schematic structure and (b) energy level diagram of Devices 2 and 3; The EML-2 is doped with the light blue emitter IDE-102 (Device 2) and the deep blue emitter DSB (Device 3).

reducing the driving voltage and enhances the hole injection efficiency.<sup>34,35</sup> TPD-15 was employed as a HTL. The first emitting layer (EML-1) consisted of phosphorescent materials, *i.e.* 3P-T2T as the host and TPD-15 as the co-host. The former one possesses excellent electron mobility and the latter one has inherited high hole-mobility, enabling the hole-transfer process effectively.<sup>36–38</sup>  $Ir(mphq)_2(acac)$  and  $Ir(npy)_2(acac)$  were employed as red and green emitters, respectively. The second emissive layer (EML-2) was composed of a fluorescent blue material (light blue or deep blue). Bpy-TP2 was selected as an electron transporting material, which can effectively block the holes coming through EML-2. The ETL was co-doped with Liq to decrease the electron injection barrier height between ETL and EIL. The EIL was made up of Liq. To control the electron- and hole-recombination zone, we inserted the CML between EML-1 and EML-2.

In the first set of experiments, we studied the effect of 3P-T2T host and TPD-15 co-host composition ratios of the EML-1 on the color temperature of OLED devices. We have fabricated Devices 1 and 2 with 1:1 and 3:1 composition ratios of host and co-host, respectively. The device structure and the corresponding energy level diagram are shown in Fig. 2a and b. In the second set of experiments, to investigate the effect of the

deep blue emitter on the electroluminescence characteristics and color temperature of the OLED devices, we fabricated Device 3 with the DSB emitter in EML-2 and compared the results with Device 2 in which EML-2 was doped with a light blue emitter (Fig. 3a and b). In the third set of experiments, the EML-1 thickness was varied from 6, 4 and 2 nm while the EML-2 thickness was changed to 21, 23 and 25 nm for Devices 4, 5 and 6, respectively. A 3 nm CML prepared from TPD-15 doped with 3P-T2T was used for all the three devices. The total thickness of the emissive layer was maintained at 30 nm. The device engineering was meant to optimize the low color temperature and enhance the span of color temperature variation. The composition ratio of the host and co-host in EML-1 was kept constant at 3:1 unless otherwise stated.

Electroluminescence characteristics of Devices 1 and 2 are summarized in Table 1. It shows that the composition ratio of the host and co-host in EML-1 has a profound effect on EL characteristics of the OLED. It is found that the 3:1 host and co-host composition ratio in EML-1 (Device 2) produced a power efficacy of 28.8 lm  $W^{-1}$ , which is 4.6 times higher than the power efficacy obtained for the 1:1 host and co-host composition ratio (Device 1) at 1000 cd m<sup>-2</sup>. A similar trend



Fig. 4 (a) Schematic structure and (b) energy level diagram of Devices 4, 5 and 6, wherein EML-1 (x) and EML-2 (y) thicknesses for Device 4 are x = 6 nm, y = 21 nm; for Device 5, x = 4 nm, y = 23 nm; and for Device 6, x = 2 nm, y = 25 nm.

is noticed for current efficiency and EQE, which show 4.3 and 4-fold increments, respectively, in Device 2 as compared to Device 1. It is important to note that the color temperature drastically reduced from 7483 K to 1781 K with the change in CIE coordinates from (0.29, 0.33) to (0.57, 0.40) as the host and co-host composition in EML-1 is changed from 1:1 to 3:1 (Devices 1 and 2). Fig. 5 shows the chromaticity and color temperature characteristics of Devices 1 and 2. The CIE diagram reveals that the color temperature of both devices can be varied with respect to applied voltage suggesting the CT tunable ability of the fabricated OLED device. For the 1:1 composition ratio of 3P-T2T host and TPD-15 co-host in EML-1 (Device 1), the CT varied from 7483 K to 9357 K as the applied bias voltage was increased from 3.4 to 4.1 V with minute variation in the color rendering index (CRI) and the spectrum resemblance index (SRI) from 63.8 to 64.8 and 84.2 to 85.4, respectively.39,40 Electroluminescence spectra with respect to applied bias voltage are illustrated in Fig. 6a for Device 1. Remarkably, the increase in EL intensity in the blue emission region obtained by an increase in applied voltage indicates that the charge carrier recombination zone shifted towards the EML-2 leading to significantly high blue emission. The dominant blue emission of Device 1 resulted in a high color temperature. However, for the 3:1 composition ratio of 3P-T2T and TPD-15 in EML-1 (Device 2), the CT drastically reduced from 7483 K to 1781 K and it extended to 1877 K with CRI and SRI varying from 58.5 to 64.3 and 77.6 to 80.6, respectively, followed by an increase in bias voltage from 3.2 to 3.9 V. The obtained CIE (x, y) coordinates for Device 2 (0.57, 0.40) evinced domination of orange-red emission over blue emission. It is important to note that the CIE coordinates follow the locus of black body radiation whereas the CIE coordinates of Device 1 deviated from the locus of black body radiation because of strong blue emission over orange-red emission (Fig. 6). The EL spectra recorded at different bias voltages are shown in Fig. 6b. The major emission peak is observed in the 600-700 nm wavelength region along with small blue emission, which rendered a low color temperature of 1781 K.

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Table 1 Effects of EML-1 host and co-host materials ratio on the power efficacy (PE), current efficiency (CE), external quantum efficiency (EQE), CIE coordinate, color temperature (CT), color rendering index (CRI), and spectrum resemblance index (SRI) of the studied color-temperature tunable OLEDs at 1000, 3000 and 5000 cd m<sup>-2</sup>

	Ratio of	Driving voltage (V)	PE (lm W <sup>-1</sup> )	$\begin{array}{c} \text{CE} \\ (\text{cd } \text{A}^{-1}) \end{array}$	EQE (%)	CIE	CT (K)	CRI	SRI	Max.
Device	host/co-host		(a) (cc) (cc) (a) (a) (a) (a) (a) (a) (a) (a) (a) (a							
1	1:1	3.4/3.8/4.1	6.2/6.3/6.1	6.7/7.6/7.9	3.4/3.8/4.0	(0.29, 0.33)/ (0.28, 0.33)/ (0.27, 0.33)	7483/8788/ 9357	63.8/64.5/64.8	84.2/85.2/85.4	51 900
2	3:1	3.2/3.6/3.9	28.8/24.3/20.6	29.2/27.9/25.4	13.6/13.0/11.8	(0.57, 0.40)/ (0.55, 0.40)/ (0.54, 0.40)	1781/1838/ 1877	58.5/61.9/64.3	77.6/79.4/80.6	37 400



**Fig. 5** Chromaticity and color temperature characteristics of Devices 1 and 2, which show a color temperature tunable emission between low-and high-applied voltages. Specifically, Device 2 shows a lower color temperature than Device 1.

The typical shift in the EL spectra of Devices 1 and 2 is attributed to OLED device architecture and the composition of EML-1. Specifically, in Device 1, at a low bias voltage (3 V), both blue and orange-red emissions contributed with marginal difference; however, as the bias voltage increased with a step of 0.5 V, the blue emission started to dominate over orange-red emission and it showed a leap forward at 6 V, revealing that at the initial bias voltage, the charge carrier recombination zones occurred in both EMLs. However, as the bias voltage increased, hole-charge carriers started to cross over to EML-1 and accumulated between CML and EML-2 which caused a shift in the recombination zone in EML-2 and at the interface of EML-1/ CML. An expansion of EL spectra in the blue region at higher bias voltage is ascribed to the extension of the recombination zone because of the efficient hole injection from the anode.<sup>41</sup>

The main cause of the shifting of the recombination zone towards the CML and EML-2 is the 50% presence of TPD-15 in the EML-1, which possesses high hole-mobility. As a result, EML-1 is dominated by hole-charge carriers.42 In EML-2, the fluorescent host tb-AND also has high hole mobility as compared with electron mobility, and hence the whole device is dominated by hole charge carriers rather than electron charge carriers. Because of the unbalanced charge carrier injection, with a slight increase in bias voltage, holes greatly accelerated towards the cathode and started to accumulate in the CML and EML-2 enabling maximum recombination at the CML and EML-2. Therefore, the blue region dominated EL spectra are obtained at high-applied bias voltage. On the other hand, even though holes and electrons are accelerated at high bias voltages the injection of electrons into EML-1 is restricted by the CML (Fig. 2), and hence, the recombination zone is shifted to EML-2. It is also important to note that blue dye has high triplet energy as compared with red dye; therefore, at high-applied voltage,



Fig. 6 Electroluminescence spectra of (a) Device 1 and (b) Device 2 at various applied voltages.



Fig. 7 (a) Power efficacy, (b) external quantum efficiency, (c) luminance, (d) current density, and (e) current efficiency of the studied devices with different host and co-host materials ratio in EML-1.

rapid triplet energy transfer occurred from guest to host that assisted in increasing the rate of exciton formation in the EML-2. In the case of Device 2, the composition ratio of the host to co-host was 3:1 (3P-T2T:TPD-15), and hence the electron mobility of EML-1 ( $>10^{-3}$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>) is higher than that of EML-2. Due to this, balanced hole and electron injection is done into the EML-1, and the major recombination of injected electron-hole charge carriers occurred in EML-1 and therefore, the EL spectra obtained for Device 2 are dominated by orange-red emission (Fig. 6b). However, it is observed that as the bias voltage increased, the blue-light emission in EL started to appear and increased with the applied voltage. The emission of blue light at the highapplied voltage in Device 2 is attributed to the electron-hole recombination zone formed near to the interface of CML and EML-2. The weak recombination zone formed at the CML/ EML-2 interface was assisted by the accelerated hole charge carriers that cross over from EML-1 and CML even though the hole mobility of EML-1 is lower.

A detailed study of EL characteristics of Devices 1 and 2 is done and is presented in Fig. 7. Since EML-2 is comprised of the IDE-102 fluorescence emitter, we obtained low power efficacy, current efficiency, and EQE (Fig. 7). However, the current density of Device 1 is higher as compared to Device 2 due to the superior hole-charge carrier mobility of EML-1. As the composition ratio of 3P-T2T and TPD-15 is changed to 3:1 in EML-1, the hole-mobility of EML-1 significantly reduced resulting in low current density of Device 2 with respect to Device 1. Owing to the low hole-charge carrier mobility, the recombination zone is mainly established in the EML-1 and the interface of CML and EML-2. The EML-1 is made up of phosphorescent green and red emitters enabling strong orange-red emission spectra with weak blue emission. The phosphorescent emitter also enabled us to achieve high power

Table 2Effects of 2nd EML emitters on the power efficacy (PE), current efficiency (CE), external quantum efficiency (EQE), CIE coordinate, colortemperature (CT), color rendering index (CRI), and spectrum resemblance index (SRI) of the studied color-temperature tunable OLEDs at 1000, 3000 and5000 cd  $m^{-2}$ 

	and FMI	Driving voltage (V)	$\stackrel{\rm PE}{({\rm lm}~{\rm W}^{-1})}$	$\begin{array}{c} { m CE} \\ { m (cd} \ { m A}^{-1} { m )} \end{array}$	EQE (%)	CIE	CCT (K)	CRI	SRI	Max.	
Device	emitter				@1000/3000/5000 cd m <sup>-2</sup>						
2	IDE-102	3.2/3.6/3.9	28.8/24.3/20.6	29.2/27.9/25.4	13.6/13.0/11.8	(0.57, 0.40)/ (0.55, 0.40)/ (0.54, 0.40)	1781/1838/ 1877	58.5/61.9/64.3	77.6/79.4/80.6	37 400	
3	DSB	3.2/3.6/3.8	26.7/22.6/19.5	26.9/25.7/23.7	12.9/12.4/11.4	(0.57, 0.39)/ (0.55, 0.39)/ (0.55, 0.39)	1763/1800/ 1825	58.9/61.2/62.9	77.0/78.9/80.3	38 500	



Fig. 8 Chromaticity and color temperature characteristics of Devices 2 and 3, which show a color temperature tunable emission between lowand high-applied voltages.

efficacy, current efficiency, and EQE, as shown in Fig. 7. It is important to note that, Device 1 provided a maximum luminance of 51 900 cd m<sup>-2</sup>, which is 38% higher than that provided by Device 2 (37 400 cd m<sup>-2</sup>). The enhanced luminance occurred because of the high recombination rate.

We have also investigated the effect of the blue emitter on the color temperature and electroluminescence spectra of the device. For this purpose, we replaced the light blue emitter IDE-102 with the deep blue emitter DSB (Device 3) in EML-2 and fabricated the OLED devices with the same parameter as of Device 2. The EL data of Devices 2 and 3 are tabulated in Table 2. The CIE coordinates of Devices 2 and 3 are presented in Fig. 8. The CIE coordinates of both devices move along the black body radiation curve with the change in bias voltage. This reveals that once an appropriate host, co-host and emitter combination of EML-1 is optimized then it is easy to change the light or deep blue emitter of the EML-2 to obtain the natural-style light, which follows black body radiation. Electroluminescence spectra obtained with different bias voltages for both devices are presented in Fig. 9a and b. It is found that the intensity of blue-green (in the 500 nm band) emission for the deep blue emitter (Device 3) is lower as compared to that for

the light blue emitter (Device 2). It can be reasonably inferred that if the deep blue emitter is used, the electroluminescence characteristics of the fabricated device can be improved by slightly increasing the concentration of the green emitter in the EML-1. Generally, it is expected that the light blue emitter can give higher luminous efficiency than the deep blue counterpart. Nevertheless, in the present study, we saw a minute difference in electroluminescence characteristics, color temperature and light quality when the light blue emitter is replaced with the deep blue emitter (Fig. 10 and Table 2).

Based on the results of the above two sets of experiments, we slightly modified the device structure through the complementary change in EML-1 and EML-2 thicknesses and composition change in the CML layer via mixing 3P-T2T and TPD-15 in 3:1 ratio, while keeping its thickness at 3 nm constant, to further improve the power efficiency and achieve an extended color temperature span. The schematic device structure and the corresponding energy level diagram are shown in Fig. 4. As described above, we analyzed the EL characteristics of Devices 4, 5 and 6 and the data obtained are summarized in Table 3. A power efficacy of 40.3  $\text{lm W}^{-1}$ , current efficiency of 40 cd  $A^{-1}$ , and EQE of 18.8% were achieved for Device 5. The results obtained for Device 5 show that the power efficacy increased by 8 and 35.6% as compared to Devices 4 and 6, respectively. A similar trend is noticed for EQE, which revealed 10 and 38.2% enhancement for Device 5 in comparison with Devices 4 and 6, respectively.

As shown in Fig. 11, the CIE color coordinates for Devices 4–6 follow the black body radiation curve as the color temperature changed with applied bias voltage. EL spectra recorded with the change in bias voltage are presented in Fig. 12a–c for Devices 4–6. A low color temperature of 1791 K with an extended range up to 2597 K was obtained for Device 4. In the case of Device 5, a color temperature span of 1881 K to 2843 K was recorded whereas for Device 6 the color temperature span was greatly increased from 2219 K to 4217 K. The results obtained suggest that the thickness of EML-1 and EML-2 plays a pivotal role in tuning and extension of the color temperature range of OLED devices. As the thickness of EML-1 decreased from 6 to 2 nm, the color temperature span increased because



Fig. 9 Electroluminescence spectra of (a) Device 2 and (b) Device 3 at various applied voltages.



Fig. 10 (a) Power efficacy, (b) external quantum efficiency, (c) luminance, (d) current density, and (e) current efficiency of the studied devices containing light blue (IDE-102) and deep blue (DSB) emitters in EML-2.

 Table 3
 Effects of EML-1 and EML-2 thicknesses on device performance, while the weight ratios of red/green and blue dye are fixed. Amongst Devices

 4, 5 and 6, Device 5 has a color temperature (CT) of 1892 K which is close to candle-light and has the highest power efficacy (PE)

	1st/2nd FMI	Driving voltage (V)	PE (lm W <sup>-1</sup> )	$\begin{array}{c} { m CE} \ ({ m cd} \ { m A}^{-1}) \end{array}$	EQE (%)	CIE	CT (K)	CRI	SRI	Max.
Device	thicknesses (Å)		(a) 1000/3000/5000 cd m <sup>-2</sup>							
4	60/210	3.1/3.6/3.8	37.2/30.9/27.7	36.9/34.7/ 32.8	17.0/16.0/15.1	(0.57, 0.41)/(0.56, 0.41)/(0.55, 0.41)	1800/1848/ 1872	61.8/64.6/66.1	80.3/81.4/82	52 170
5	40/230	3.1/3.6/3.8	40.3/32.2/28.1	40.0/36.3/ 33.7	18.8/16.4/15.2	(0.56, 0.42)/ (0.54, 0.42)/ (0.53, 0.41)	1892/1961/ 2001	65.8/68.7/70.3	82.2/83.3/83.9	41 500
6	20/250	3.3/3.7/4.0	29.7/23.6/19.4	30.9/27.7/ 24.9	13.6/12.2/11.0	(0.51, 0.42)/(0.48, 0.41) (0.47, 0.41)	2304/2467/ 2650	74.2/76.8/78.6	85.6/86.4/87.0	29 300



Fig. 11 Chromaticity and color temperature characteristics of Devices 4, 5 and 6, which show a color temperature tunable emission between low- and high-applied voltages.

of significant reduction in the charge carrier recombination in EML-1. Nevertheless, at low applied voltage, the recombination zone is mainly localized in EML-1, *i.e.* the green-red emissive region. At high-applied voltage, however, hole injections are accelerated, which resulted in an extension of the recombination zone into the EML-2. Due to the large number of holes that crossed over from EML-1 and CML to EML-2 a significant increase of blue emission appeared in EL spectra at highapplied voltage, as illustrated in Fig. 12c. This leads to an increase in the color temperature of the OLED devices at highapplied voltages because blue emission is mainly responsible for the increase in the color temperature of the OLED device. Due to the strong variation of blue light emission in EL with respect to the applied voltage, the color temperature of Device 6 showed a wide color temperature tunable range as compared with Devices 4 and 5. The power efficacy, EQE, luminance, J-V curve, and current efficiency plots for Devices 4-6 are given in Fig. 13a-e.



Fig. 12 Electroluminescence spectra of (a) Device 4, (b) Device 5 and (c) Device 6 at various applied voltages.



Fig. 13 (a) Power efficacy, (b) external quantum efficiency, (c) luminance, (d) current density, and (e) current efficiency of the studied devices with varied EML-1 and EML-2 thicknesses.

It is noticed that the power efficacy of Device 6 is significantly low as compared to that of Devices 4 and 5. We believe that the low power efficacy stems from the drift in the triplet excited states into the fluorescent system due to the long diffusion length and long lifetime of the phosphorescent emitter or they might be quenched due to being too densely accumulated in the thin EML-1 (2 nm thickness).<sup>43,44</sup> And therefore, apart from power efficacy, EQE and current efficiency are also low as compared to the rest of the mentioned devices. This peculiar device arrangement allows us to control exciton distribution between two EML regions which facilitates the charge carrier balance and thereby obtain high power efficacy and EQE for the fabricated device. It also provides us a degree of freedom to achieve a desirable output by applying different bias voltages. Based on these data, we can speculate that Device 5 has a suitable thickness of the phosphorescent layer and the proportion of blue light can be increased *via* regulating the charge carrier recombination zone enabling the requisite efficiency. From the experimental results, it is confirmed that the thickness of EML-1 and EML-2 is optimized to fabricate high efficacy OLED devices with a wide color temperature span.

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Fig. 14 Lifetime study of devices carried out under a constant current of  $100 \text{ mA cm}^{-2}$  at room temperature.

The CML plays a vitally important role in controlling the concentration of charge carriers and separates the two recombination zones enabling a wide color temperature span.

We have performed a lifetime study on large area size OLED panels (active pixel size of  $2 \times 2 \text{ mm}^2$ ) with a color temperature tunable feature under accelerated conditions.<sup>45</sup> The luminance decay recorded under accelerated conditions is shown in Fig. 14. Taking Device 4 for example, it showed a half lifetime, LT<sub>50</sub>, of 28 hours under an accelerated testing condition at a constant current of 100 mA cm<sup>-2</sup> and an initial luminance of 26078 nits. On changing to the typical operation luminance, i.e. 1000 nits, it showed an LT<sub>50</sub> of 18925 hours. Similarly, Devices 5 and 6 showed LT<sub>50</sub> of 25 and 28 hours at the initial luminance of 21461 and 19169 nits, respectively, and the corresponding LT<sub>50</sub> values at 1000 nits are 11204 and 10019 hours. The reason why Device 4 showed better stability as compared with Devices 5 and 6 may be due to the balanced injection of charge carriers. In the case of Devices 5 and 6, the respective EML-1 thicknesses were just 4 and 2 nm and as a result, there is not only unbalanced charge injection but also significant reduction of the charge carrier recombination zone in EML-1 that adversely affected the brightness of the OLED devices. On the other hand, the recombination zone is significantly large for Device 4 due to the 6 nm thick EML-1, which is dominated by electron charge carriers because of the relatively high electron mobility of the 3P-T2T host material. Therefore, Device 4 shows high brightness and stability as compared with Devices 5 and 6. The device lifetime data obtained for Devices 4, 5 and 6 are tabulated in Table 4.

In summary, a color temperature tunable OLED with a simple device structure and good efficacy can be realized. The color temperature is tunable from 1881 K (3 V) to 2843 K (6 V)

 Table 5
 Effect of color temperature on the maximum permissible retina

 exposure limit (MPE) and melatonin suppression sensitivity (MSS) of studied devices

Device	Driving voltage	Color temperature	MPE(s)	MSS (%)
1	3.0/6.0	6202/14349	1587/938	16.31/27.22
2	3.0/6.0	1758/2708	18927/4213	2.07/6.79
3	3.0/6.0	1750/2436	16 331/2958	2.36/9.63
4	3.0/6.0	1791/2597	57 853/3938	1.29/7.38
5	3.0/6.0	1881/2843	50 943/3187	1.39/8.93
6	3.0/6.0	2219/4217	17 782/1939	2.42/14.08



Fig. 15 Specimen sample of a low color temperature (1766 K to 1842 K) OLED desktop lamp (panel size of 5 cm  $\times$  15 cm) having power efficacy of 47.8 lm W<sup>-1</sup> and 37.8 lm W<sup>-1</sup> at 1000 and 2000 cd m<sup>-2</sup>, respectively.

along with the CIE coordinates from (0.56, 0.42) to (0.44, 0.39). The fabricated OLED devices have high power efficacy and external quantum efficiency; particularly, for Device 5, a power efficacy of 40.34 lm W<sup>-1</sup>, a current efficiency of 40.22 cd A<sup>-1</sup>, a color temperature of 1892 K, and a spectrum resemblance index (SRI) of 88.2 at 1000 cd m<sup>-2</sup> were achieved. We have calculated the maximum permissible exposure (MPE) limit and melatonin suppression sensitivity (MSS) of the fabricated OLED devices and the obtained data are tabulated in Table 5. The best values of MPE and MSS were found to be 50 943 s and ~1.4% for Device 5, respectively. The obtained data of MPE and MSS

 Table 4
 Summary of the lifetime testing data obtained under accelerated condition driven with a constant current of 100 mA cm<sup>-2</sup> at room temperature for Devices 4, 5 and 6

Device no.	Voltage at $t_0$ (V)	Luminance at $t_0$ (cd m <sup>-2</sup> )	CCT at $t_0$ (K)	CCT at $t_{50}$ (K)	$LT_{50}$ (hours)	$LT_{50}$ (1000 cd m <sup>-2</sup> ) (hours)
Device 4	5.01	26 078	2176	2075	28.75	18 925
Device 5	5.00	21 461	2365	2280	25.08	11 204
Device 6	5.23	19169	3511	3143	28.08	10 019

confirm that the light emission from the fabricated OLED devices is benign and healthy, which is a unique feature of these OLED devices.<sup>46,47</sup> With the help of the studied devices, we have successfully fabricated a color temperature tunable OLED lamp as shown in Fig. 15.

## 4. Conclusion

In conclusion, high-efficiency, high light purity, good MPE and MSS, and color-temperature tunable OLED lighting was demonstrated in this study. The fabricated OLED devices exhibited color temperature tunability from the 1700 K of dusk-hue, 1900 K of candles and 2500 K of incandescent bulbs to 3000 K of warm-white light. The wide span of color temperature was achieved by utilizing a hybrid device architecture, coupled with a carrier modulation layer (CML) inserted between two emission layers. The device lifetime of 18 925 hours is demonstrated. We have chosen a long-life organic material, using a very simple component structure, making it easy to produce large size color temperature tunable OLED lighting panels.

## Conflicts of interest

There are no conflicts to declare.

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### Modification effect of hole injection layer on efficiency performance of wet-processed blue organic light emitting diodes

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#### ABSTRACT

We examined the performance of solution-processed organic light emitting diodes (OLEDs) by modifying the hole injection layer (HIL), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS). Atomic force microscopy (AFM) showed morphological changes with surface roughness ( $R_{RMS}$ ) of 1.47, 1.73, and 1.37 nm for pristine PEDOT: PSS, PEDOT: PSS modified with a 40 v% deionized water and with a 30 v% acetone, respectively. The surface hydrophobicity of the acetone modified PEDOT:PSS HIL layer was decreased by 34% as comparing with the water modified counterpart. Electrical conductivity was increased to two orders of magnitude for the water and acetone modified PEDOT:PSS as compared to pristine. We observed a low refractive index and high transmittance for the modified HILs. We fabricated and explored electroluminescent properties of bis[2-(4,6-diffuorophenyl)pyridinato-C2,N](picolinato)iridium(III) (FIrpic) based sky blue device by utilizing HIL with and without modification. The changes in electrical conductivity, surface roughness, refractive index, and transmittance of the modified HILs strongly influenced the performance of devices. By utilizing a 30% acetone modified HIL, the power efficiency was increased from 14.2 to 24.2 lm/W, an increment of 70% and the EQE from 8.5 to 13.1% at 100 cd/m<sup>2</sup>, an increment of 54%. The maximum luminance also increased from 11,780 to 18,190 cd/m<sup>2</sup>. The findings revealed herein would be helpful in designing and fabricating high efficiency solution processed OLEDs.

### 1. Introduction

OLEDs are extensively used both in displays technology and making entry into healthy indoor lighting applications [1] [–] [4]. Examples include smartphone displays, television screens, computer monitors, MP3 players, and GPS devices, etc. [5,6]. OLEDs are not only superior in terms of physical properties but also allow to fabricate devices via solution process that is advantageous over existing technologies and might reduce the production cost [7]. The solution process technology has a degree of freedom over the physical deposition techniques, that permits to fabricate OLED devices via a roll to roll process, inkjet printing, and slot die coating methods, incredibly enhancing the scale-up feasibility of OLED devices on a large area and profoundly reducing the product cost [6]. Moreover, these techniques are more compatible with the flexible substrates, which are tempting to develop attractive electronic gadgets [8,9]. Fabricating high-efficiency OLED devices via solution process techniques is hence vitally important.

In general, a typical solution processed OLED device structure is made up of hole injection and transport layers (HIL/HTL), emissive layer (EML) and electron transport layer (ETL) excluding anode and cathode electrodes [10,11]. To fabricate highly efficient OLED devices, one has a wide variety of choices to select the EML and ETL materials according to requirements. However, very few choices are left in selecting appropriate molecule HTLs because of their high solubility in commonly used

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solvents making them more difficult to deposit the layers one over another [12]. To date, PEDOT: PSS is the widely used HIL in solution processed OLED devices due to its compatibility with the organic solvent along with excellent electronic properties [13] [-] [15]. An alternative to PEDOT:PSS is p-type metal oxide semiconductor materials, but many of these materials require high processing temperature and hence unfit to fabricate flexible OLED devices [12]. Moreover, most of metal oxide semiconductors possess low hole-mobility as compared to PEDOT:PSS and forbid to deposit a HTL layer more than few nanometers. On the other hand, PEDOT:PSS is available in aqueous form and readily used to deposit at room temperature and having superior electronic properties and more importantly, its chemical composition can be easily tailored according to the requirement of application [13]. Therefore, PEDOT:PSS is emerged as one of the most suitable material to fabricate highly efficient solution processed OLED devices [16,17]. PEDOT: PSS is an intricate material, from chemical, morphological and electronic point of view. Favorable alteration of these properties can influence the optoelectronic device performances [18] [-] [20].

There are many studies discussing the physical properties changes of PEDOT: PSS with the addition of co-solvents [21] [–] [25]. De Kok et al. reported that with increasing the pH of PEDOT: PSS, the device lifetime diminished [26]. According to Snaith et al. addition of glycerol to PEDOT: PSS solution prior to spin coating reduced the sheet resistivity of thin film [27]. Syed et al. employed sodium citrate modified PEDOT: PSS as a hole transporting layer for the efficiency enhancement of solar cell [28]. Zhang et al. investigated the change in thermoelectric properties with the addition of both organic solvents and water as co-solvent in PEDOT: PSS [29]. Pathak et al. examined the conductivity increment with the addition of graphene oxide and solvents, and found the solvent addition to wash away insulating PSS from the substrate surface after spin coating and annealing [30].

Some studies revealed the performance of the solution processed devices, in which the HIL is metal oxide blended or bilayer with PEDOT: PSS. Zhang et al. reported an efficient ultraviolet (UV) OLED with PEDOT:PSS/MO<sub>x</sub>, the device showed an external quantum efficiency (EQE) of 4.6% [31]. Zheng et al. reported a UV OLED with an EQE of 4.4% by utilizing PEDOT:PSS blended with MoO<sub>x</sub> as the HIL [32]. Lian et al. utilized blend of magnetic nano particles PEDOT:PSS to fabricate efficient OLEDs [33]. Yadav et al. reported a blend of V<sub>2</sub>O<sub>5</sub>-PEDOT:PSS HIL for high efficiency OLEDs [34].

"Hole carrier mobility is one of the key parameters to achieve an efficient blue OLED device. Apart from the hole mobility of hole injection/transport material, triplet energy, work function, molecular orbital energy levels, charge injection/migration barrier, recombination, and exciton generation process across the successive layers significantly contributing to the overall device performance [35] [-] [37]. In 2015, Kim et al. proposed high hole mobility and compatible molecular orbital level (5.1 eV) that keen important for excellent hole injection layer (HIL) in the OLED applications [38]. Lee and coworkers demonstrated an improved hole injection for blue phosphorescent OLEDs using solution deposited SnOx NPs decorated ITO anodes with enhanced work function and hole injection capability [39]. Liu et al. demonstrated improved deep-blue PLED efficiencies with the optimization of both the optical and electrical performance through an optimal top-to-bottom HOMO energy level arrangement and improved hole mobility [40]. Furthermore, the studied device shows improved device performance because high hole mobility causes accumulation of holes near the EML/ETL interface, resulting in triplet-polaron or triplet-triplet annihilation leads to enhanced blue efficiency [41-43].

In the present study, we tuned the electrical conductivity, surface roughness, refractive index, transmittance, and film-forming property of PEDOT: PSS by the addition of deionized water and acetone. The modified PEDOT: PSS was employed as HIL in phosphorescent sky blue OLED device structure to study its effect on electroluminescence properties. The reason for selecting FIrpic as emissive material is because of the sky blue emission. The demand for efficient and long lifetime blue Table 1

Resistivity and Conductivity measurement of pristine and modified PEDOT: PSS.

HIL	Resistivity (Ω. cm)	Conductivity (S/cm)
Pristine 40 v% DI water 30 v% ACE	$\begin{array}{c} 1.13\times 10^{-2}\\ 2.47\times 10^{-4}\\ 2.58\times 10^{-4}\end{array}$	$\begin{array}{c} 8.84 \times 10^{1} \\ 4.05 \times 10^{3} \\ 1.13 \times 10^{3} \end{array}$

OLEDs are always increasing. All the devices that consist of the modified HIL showed better performance compared to the pristine counterpart. The best EL properties were observed in a device with a 30% acetone in HIL. The power efficiency was increased from 14.2 to 24.2 lm/W, an increment of 70% and the EQE from 8.5 to 13.1% at 100 cd/m<sup>2</sup>, an increment of 54%. The maximum luminance also increased from 11,780 to 18,190 cd/m<sup>2</sup>.

### 2. Experimental

PEDOT: PSS aqueous solution [CLEVIOS P VP AI4083] was purchased from Heraeus. The modification of PEDOT:PSS was done by adding optimized amount of deionized water (DI water, 40 v%) and acetone (ACE, 30 v%) [ECHO Chemical Co., Ltd.]. Electrical conductivity of modified PEDOT:PSS solution was investigated by EUTECH PC300 CyberScan Portable pH/Conductivity/TDS Meter. Surface morphology analysis of modified and pristine HIL s was characterized by using atomic force microscopy (AFM, Bruker) under tapping mode. The water contact angles of thin films were measured by First-Ten-Angstroms FTA-100 series (Chi 608) instrument using deionized water droplets of about 6  $\mu$ L. Ellipsometer was used to determine the refractive index (n) [Radiation Technology Co., Ltd.] of pristine and modified PEDOT:PSS layer.

The OLED device fabrication process was started with spin coating of pristine and modified PEDOT: PSS at 4000 rpm for 20 s on a pre-cleaned indium tin oxide (ITO) anode. The emissive layer solution was prepared by dissolving the host Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) and guest (FIrpic 20%) molecules in toluene solvent at 50 °C for 90 min with stirring using a magnetic stirrer. The prepared solution was spin coated at 2500 rpm for 20 s inside a nitrogen-filled glove box. The electron transporting layer (2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-*H*-benz-imidazole), (TPBi) bought from, Shine Materials Technology Co., Ltd), electron injection layer of lithium fluoride (LiF, Shine Materials Technology Co., Ltd), were deposited via thermal evaporation under less than  $10^{-6}$  Torr.

OLED characteristics of all the fabricated devices were investigated in ambient atmosphere without encapsulation. Luminance, CIE chromatic coordinates and electroluminescence spectrum of the resulting sky-blue OELDs were measured using Photo Research PR-655 spectra scan. Keithley 2400 electrometer with minol was used to measure the current-voltage (I–V) characteristics. The emission area of the devices was kept to 9 mm<sup>2</sup>, and the luminance in the forward direction was measured.

#### 3. Results and discussion

### 3.1. Characterizations of pristine and modified PEDOT: PSS

The electronic properties of pristine and modified PEDOT: PSS were examined via a resistivity and conductivity measurement. Electrical conductivity and resistivity of the modified and pristine PEDOT: PSS tabulated in Table 1. The measured electrical conductivities were found to be  $8.84 \times 10^1$ ,  $4.05 \times 10^3$ , and  $1.13 \times 10^3$  S cm<sup>-1</sup> for pristine, modified with 40 v% DI water and 30 v % PEDOT: PSS HIL., respectively. The electrical conductivity of PEDOT: PSS increased with the addition of water and acetone. The electrical conductivity of PEDOT:PSS is increasing with the addition of polar cosolvents. Lee and Na et al.



Fig. 1. Surface morphologies of the layer of PEDOT: PSS (a) without modification (b) modified by adding 40 v% DI water and (c) modified by adding 30 v% ACE.



Fig. 2. Static contact angles of water drop on thin films (a) Pristine PEDOT: PSS, (b) PEDOT: PSS modified with DI water, and (c) PEDOT: PSS modified with acetone.

fabricated a highly conductive PEDOT:PSS thin film by adding DMSO as a cosolvent in their independent research works [44,45]. Palumbiny et al. improved the electrical conductivity of PEDOT:PSS by the addition of ethylene glycol cosolvent [46]. Solvation plays a crucial role in the conductivity increment. Acetone solvates PEDOT and water solvates PSS chain selectively, which results in synergetic effect and subsequently reduces the Coulombic repulsions and increases the conductivity [47].

The surface morphologies of thin films; pristine modified with 40 v% deionized water and with 30 v% acetone PEDOT:PSS HIL are shown in Fig. 1. The film showed surface roughness of ( $R_{RMS}$ ) 1.47, 1.73, and 1.37 nm for pristine, modified with 40 v% DI water and with 30 v% acetone PEDOT: PSS layer, respectively. The film surface morphologies are not showing any drastic change after modification.

We examined the water contact angles in order to measure the hydrophilic property and spread-ability of pristine and modified PEDOT: PSS on ITO. Fig. 2 shows the static contact angles of water drop on the thin films of both pristine and modified PEDOT: PSS thin films. The contact angle measurement showed 15°, 58°, and 38°, respectively, for pristine PEDOT: PSS, PEDOT: PSS modified with 40 v% DI water and 30 v% acetone. This means, the DI water modified PEDOT: PSS (Fig. 2(b)) is more hydrophobic compared to pristine and acetone modified PEDOT: PSS. The spreading ability of pristine and 30 v% acetone modified



Fig. 3. Refractive indices of pristine and modified PEDOT: PSS thin films.

PEDOT: PSS is higher compared to DI water modified PEDOT: PSS, low water contact angle indicates the hydrophilic property of HIL that enhances the film forming property.

Fig. 3 shows the refractive indices of the pristine, modified with 40 v



Fig. 4. Transmittance of thin films with and without modification of PEDOT: PSS.

% of DI water, and 30 v % of acetone PEDOT:PSS HIL. High refractive indices of pristine PEDOT:PSS are noticed in the visible region. Refractive indices of 30 v% acetone added PEDOT:PSS decrease drastically as compared to DI water modified PEDOT:PSS.

Fig. 4 shows transmittance spectra recorded in the visible region for pristine and modified PEDOT:PSS thin films. It is very clear from the experimental data that 40 v% DI water and 30 v% acetone modified PEDOT: PSS evince higher transmittance compared to pristine PEDOT: PSS over the visible wavelengths region. At lower wavelengths between 400 and 450 nm, the transmittance is higher. The thin films showed 96, 98.5 and 97% transmittance respectively for pristine PEDOT: PSS, 40 v% DI water modified PEDOT: PSS, and 30 v% acetone modified PEDOT: PSS. The transmittance increased with decrease in film thickness. The

thickness was 35, 25, and 29 nm respectively for pristine PEDOT:PSS, DI water modified PEDOT:PSS and acetone modified PEDOT:PSS.

### 3.2. Electroluminescent properties

To investigate the influence of physical and optical properties of modified PEDOT:PSS, blue OLED devices were fabricated. Fig. 5 show a schematic representation of a modification of PEDOT: PSS and energy level diagrams of blue OLEDs devices. D1 was fabricated with pristine PEDOT: PSS HIL and other two devices by utilizing modified PEDOT: PSS i.e. D2 was fabricated by employing PEDOT: PSS modified with 40 v % of DI water and D3 was fabricated with PEDOT: PSS modified with 30 v% of acetone., The pristine and modified HIL layers were deposited via spin coating on ITO substrate. Effect of modification of the HIL layer on electroluminescence parameters of fabricated blue OLED devices is summarized in Table 2. Performance of OLED devices with different ratios of water and acetone modified PEDOT:PSS as HIL showed in Table S2.

Addition of solvents strongly influenced the device performance. Optimum addition of DI water (40% DI water, D2) showed better performance compared to the reference device, D1. The device showed PE increment of 40% from 14.2 to 19.9 lm/W, external quantum efficiency (EQE) showed an increment of 24%, from 8.5 to 10.6% at 100 cd/m<sup>2</sup>, compared to the reference device, D1. D2 showed a low operating voltage of 4.2 V compared to D1, 4.4 V. Among all devices, PEDOT: PSS modified with 30% acetone (D3) showed the best performance both at low luminance and higher luminance, compared to all other devices fabricated. In D3 the power efficiency increased from 14.2 to 24.2 lm/W, an increment of 70%, EQE showed an increment of 54%, from 8.5 to 13.1% at 100 cd/m<sup>2</sup>, comparing to the device without HIL modification. The maximum luminance also showed an increment from 11,780 to 18,190 cd/m<sup>2</sup>.



Fig. 5. Schematic diagram of the energy-levels of a sky-blue OLED containing PEDOT: PSS as hole injection material, whose solution is modified by adding either deionized water or acetone. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

### Table 2

Effect of modified hole injection layer on the operation voltage(OV), power efficiency(PE), current efficiency(CE), external quantum efficiency (EQE), CIE coordinates, and maximum luminance of the studied sky-blue OLEDs.

Device	DI H <sub>2</sub> O [ratio%]	ACE [ratio%]	OV [V]	PE [lm/W]	CE [cd/A]	EQE [%]	CIE coordinates [cd/m <sup>2</sup> ]	Max Luminance
			@100/1000/1	10000 cd/m <sup>2</sup>				
D1	_	-	4.4/4.9/7.3	14.2/12.8/3.1	20.0/20.0/7.1	8.5/8.6/-	(0.18, 0.40)/(0.18, 0.40)/-	11780
D2	40	-	4.2/4.8/7.0	19.9/14.0/3.7	26.4/21.2/8.3	10.6/8.5/-	(0.18, 0.42)/(0.18, 0.41)/-	12760
D3	-	30	3.9/4.6/6.3	24.2/18.2/6.3	30.5/26.5/12.6	13.1/11.6/5.5	(0.17, 0.39)/(0.17, 0.39)/(0.17, 0.38)	18190



Fig. 6. Electroluminescent characteristics of solution processed OLED devices with pristine or modified HIL (a) current density vs voltage, (b) luminance vs voltage, (c) power efficiency vs luminance, and (d) current efficiency vs luminance.



Fig. 7. EQE of solution processed OLEDs with pristine or modified HIL.

Fig. 6 showing the electroluminescent characteristics of solution processed sky blue OLEDs with pristine or modified HIL. From Fig. 6(a), it is clear that, D2 and D3 showed a low turn on voltage compared to D1. The turn on voltage may be influenced by change in conductivity with modification. Current density also following the same trend (Fig. 6(b)). The efficiency roll-off of all the three devices is showed in Fig. 6(c) and (d). Fig. 7 showing the EQE increment with the modification in HIL.

Fig. 8 showing the EL spectra of devices D1, D2 and D3. In the case of deionized water modified HIL, the device showing a slight bathochromic shift compared to the reference device, D1. In the case of acetone modified HIL, the device showing similar emission like reference device D1.

The better performance of device with acetone modified HIL may attributed to different factors. The increment in conductivity of modified HIL influenced the device performance. Hole mobility also improved with the addition of acetone, which may facilitate the exciton formation and thereby improvement in device performance. Compared with the surface roughness of DI water modified HIL, acetone modified HIL showed a less surface roughness. The low surface roughness can reduce



**Fig. 8.** Modification effect of hole injection layer on the EL spectra at 100 cd/ $m^2$ . EL spectra of the studied sky-blue OLEDs with PEDOT: PSS (HIL) with and without modification. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 3

Outcoupling efficiency enhancement of acetone modified PEDOT:PSS device performance for various luminescence  $(100/1000/10000 \text{ cd/m}^2)$  compared with pristine PEDOT:PSS.

@100/1000/10000 cd/m <sup>2</sup>							
Outcoupling Enhancement (%)							
PE [lm/W] 70.4/42.1/103.2	CE [cd/A] 52.5/32.5/77.4	EQE [%] 54.1/34.8/-	Max Luminance [cd/m <sup>2</sup> ] 54.4				

the dielectric breakdown of thin films [48]. Low refractive index of acetone modified HIL is one of the key factor, which improved the device performance [49]. Outcoupling efficiency enhancement of acetone modified PEDOT:PSS device performance for various luminescence (100/1000/10000 cd/m<sup>2</sup>) compared with pristine PEDOT:PSS shown in Table 3.

Numerous studies have been reported that a film possessing a lower refractive index, a hole-transport layer with reduced optical density but slightly reduced hole-transport characteristics. The device based on reduced-index layer show an improved efficiency compared to reference devices (PEDOT:PSS). It strongly discovers that efficiency improvement is only to some extent due to enhanced outcoupling resulting directly from the reduced refractive index but primarily due to a change of the width of the emission zone [18,49–51].

The transmittance increment of modified HIL, compared to pristine PEDOT: PSS also influenced the device performance. The less water of acetone modified PEDOT:PSS compared to DI water modification also plays a role in the efficiency improvement. The increment in electrical conductivity may played a vital role in the improvement of device performance. Kim et al. utilized a high conductive Zno/CNT HTL for the performance of OLEDs [52]. Gu et also improved the conductivity of PEDOT:PSS by associating it with CNT and ethylene glycol and the device showed a better performance [53].

#### 4. Conclusion

Modified PEDOT:PSS utilized for the fabrication of sky blue OLEDs. PEDOT: PSS modified with 40 v% deionized water and with 30 v% acetone, respectively showed better performance. We fabricated and explored electroluminescent properties of Bis[2-(4,6-difluorophenyl) pyridinato-C2,N](picolinato)iridium(III) (FIrpic) based sky blue device by utilizing HIL with and without modification. The changes in electrical conductivity, surface roughness, refractive index and transmittance of modified HIL strongly influenced the performance of devices. By utilizing a 30% acetone modified HIL, the power efficiency was increased from 14.2 to 24.2 lm/W, an increment of 70% and the EQE from 8.5 to 13.1% at 100 cd/m<sup>2</sup>, an increment of 54%. The maximum luminance also increased from 11,780 to 18,190 cd/m<sup>2</sup>.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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#### Appendix A. Supplementary data

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# Short Alkyl Chain Engineering Modulation on Naphthalene Flanked Diketopyrrolopyrrole toward High-Performance Single Crystal Transistors and Organic Thin Film Displays

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Studying multi-purpose applications of a specific material is a challenging topic in the organic electronics community. In this work, through molecular engineering and smart device structure design strategy, high performance in transistors and thin film display devices is simultaneously achieved by applying a simple new dye molecule, naphthalene flanked diketopyrrolopyrrole (DPPN), as the active layer material. Short alkyl chains (hexyl or octyl side groups for H-DPPN and O-DPPN, respectively) are adapted to improve the hole mobility in organic thin film transistors (OTFTs) and single crystal transistors (SCTs). Specifically, H-DPPN shows a similar hole mobility in either OTFTs or SCTs, while O-DPPN exhibits a dramatically enhanced mobility, reaching 0.125 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in SCTs. Additionally, a smart organic light emitting diode (OLED) device is designed by using DPPN molecule as the dopant with a host matrix. The promising external quantum efficiencies of 4.0% and 2.3% are achieved for H-DPPN and O-DPPN fabricated OLEDs. Overall, in this work, it is reported that DPP-based small molecules can simultaneously function well in both transistors and thin film displays with high device performance through molecular and smart device engineering.

### 1. Introduction

Diketopyrrolopyrrole (DPP) derivatives have proven to be an important class of high-performance organic semiconductors that can be used as active materials in various types of electronic devices.<sup>[1-7]</sup> As representative examples, the power conversion efficiency (PCE) of organic photovoltaic (OPV) devices have reached more than 12% by using some DPP derivatives as the active layer materials.<sup>[8,9]</sup> In DPP semiconductors for organic thin film transistors (OTFTs), impressive hole mobilities exceeding 10 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> have been demonstrated.<sup>[1]</sup> Recently, DPP materials are being exploited in more applications like OLEDs, sensors, photodetectors, and memory devices.<sup>[2,10–17]</sup> Flanking groups substituted at the 3- and 6-position of the DPP core play significant roles in the

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optoelectronic properties of resultant materials.<sup>[18]</sup> Flanking moieties such as thiophene, furan, selenophene, thiazol, thienothiophene, phenyl, and pyridyl groups have been reported.<sup>[19,20]</sup> Thiophene flanked DPP (DPPT) is one of the most promising building blocks to construct high-performance materials for both OTFTs and OPVs. We previously reported the polymer, PDPP-TNT, consisting of DPPT and naphthalene.<sup>[21,22]</sup> The introduction of conjugation-extended naphthalene promoted strong intermolecular interactions and resulted in favorable  $\pi$  stacking between polymer backbones. Thus, a high hole mobility of  $\approx 1.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  was observed in OTFTs and a promising PCE of 4.7% was obtained in OPVs as donor mixing with PC71BM. Simultaneously achieving high performance in both OPVs and OTFTs is feasible, because the good charge carrier transport for a molecule is also a beneficial factor for improving both the short-circuit current  $(I_{SC})$  and fill factor (FF) when it is used in active layer of OPV devices.<sup>[23]</sup> In addition to DPPT, other DPP derivatives based semiconductors also successfully demonstrated high performance in electronic devices.<sup>[24-26]</sup>

It is worth mentioning that phenyl flanked DPP (DPPh) has been proven to be a great choice of luminescent material for OLEDs and related applications.<sup>[10]</sup> One reason making DPPh a promising molecule is that the dihedral angles between the phenyl groups and the DPP core (estimated to be around 40°) to some extent weaken the  $\pi$  stacking which minimizes the fluorescence quenching in solid state.<sup>[27]</sup> Recently, we reported novel naphthalene flanked DPP (DPPN) with different alkyl chains as a new member in the DPP family.<sup>[28]</sup> Compared with five- or six-membered ring DPPs, the fused aromatic ring of naphthalene resulted in a more extended  $\pi$ -conjugation leading to a larger intermolecular orbital overlap and thus facilitated the charge transport. Our primary attempt has demonstrated that n-decyl substituted DPPN (D-DPPN) monomer showed the highest hole mobility of 0.019 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in OTFTs as the active semiconductor directly, without any further functionalization. It is believed that there is still room to further improve the mobility by decreasing the length of side chains. Moreover, shorter chains substituted DPPN monomers are more suitable for growing single crystals, which prompted us to study their intrinsic charge carrier transport behavior by fabricating single crystal transistors (SCTs). Naphthalene, a common acene type of benzene derivative that has been proven to form J-aggregation in solid state, can be used as a building block in materials that can retain efficient emission and thus lead to high photoluminescence quantum yield.<sup>[29]</sup> Our DPPNs were observed to show strong luminescence under a laboratory lamp thus could be also promising in related devices like OLEDs.

In this work, *n*-hexyl and *n*-octyl alkylated DPPN compounds, H-DPPN and O-DPPN, were synthesized and their thermal, optical, and electronic properties were studied. The hole mobility of OTFTs was further enhanced by decreasing the length of side chains to *n*-octyl (O-DPPN) but dropped then for shorter *n*-hexyl H-DPPN. Moreover, single crystals for both materials were successfully grown and the fabricated SCTs indicated their high intrinsic hole transporting property. Due to the strong luminescence feature under laboratory UV light, we also fabricated OLED devices by using H-DPPN and O-DPPN as the dopant mixed with tris(4-carbazoyl-9-ylphenyl) amine (TCTA) host and achieved promising performance with external quantum efficiencies (EQEs) of 4.0% and 2.3% respectively. It is well known that compact packing of molecules can induce strong and plentiful intermolecular interactions that generally facilitate charge transport in OTFTs. However, the interactions will also quench the solid-state luminescence, which makes it difficult to achieve both high mobility in OTFTs and high EQE in OLEDs. Nevertheless, in our current scenario, we have achieved high performance in both OTFTs and OLEDs via smart device and molecular engineering approaches. This is the first report of novel flanking group naphthalene attached DPP based small molecules, which can simultaneously function well in several different electronic devices, and the afforded high performance is encouraging for the future advancement of organic electronics.

### 2. Results and Discussion

Our previous report on DPPNs has demonstrated that a linear and short side alkyl chain enhances charge carrier mobility; in particular, the obtained hole mobility was higher.<sup>[28]</sup> We perform a systematic study to investigate this type of material further, in particular, to find the most suitable side chains for this series of DPPN compounds. In this work, we continuously shorten the side chains to synthesize *n*-hexyl and *n*-octyl substituted DPPN based small molecular materials namely H-DPPN and O-DPPN. Besides, both materials are expected to show versatility for use in various electronic devices considering the structural advantages: i) higher hole mobility is expected according to our previous report; ii) monomers with short side chains are more feasible to grow single crystals, being beneficial for SCTs fabrication; iii) as an analogue of DPPh, H-DPPN, and O-DPPN solutions were observed to be highly fluorescent under the laboratory UV lamp (Figure S1, Supporting Information), demonstrating their potential in OLEDs. As per our previous report, the synthetic route to H-DPPN and O-DPPN is shown in Figure 1a.<sup>[30]</sup> The alkylation of NH-DPPN was performed in the presence of n-hexyl or n-octyl bromide, respectively, at 120 °C in dimethylformamide (DMF) with anhydrous potassium carbonate (K<sub>2</sub>CO<sub>3</sub>) as the base. The purity and structures of H-DPPN and O-DPPN were characterized with <sup>1</sup>H, <sup>13</sup>C NMR spectra, and high-resolution mass spectrometry (HRMS).

The thermogravimetric analysis (TGA, Figure S2a in the Supporting Information) indicated that both H-DPPN and O-DPPN appear to possess excellent thermal stability with the decomposition temperature (Td, 5% weight loss) of 340 and 348 °C, respectively. These values are high enough to perform annealing or other thermal processing required for devices fabrication. The differential scanning calorimetry (DSC, Figure S2b-d: Supporting Information) demonstrated that small variation in side chains on DPPN has dramatic influence on their crystallinity. H-DPPN undergoes a classic melting transition at 162 °C (91.22 J g<sup>-1</sup>) and a crystalline transition at 102 °C (72.74 J g<sup>-1</sup>). However, O-DPPN shows a different behavior in that an endothermic peak at 119 °C followed by a cold crystallization at 125 °C (18.96 J g<sup>-1</sup>) was observed before the material was completely melted at 147 °C (79.80 J g<sup>-1</sup>). This feature is an indication of the melting and secondary recrystallization of the amorphous area. The crystallinity peak is observed at about 84 °C







Figure 1. a) The synthetic route to H-DPPN and O-DPPN. b) UV-vis absorption spectra of H-DPPN and O-DPPN in both chloroform solutions and thin films. c) Photoluminescence (PL) spectra of H-DPPN and O-DPPN in chloroform solutions. d) Photoelectron spectroscopy in air (PESA) measurements of H-DPPN and O-DPPN films.

during cooling process with the enthalpy of 29.59 J g<sup>-1</sup>. The original DSC analysis labelled with enthalpy values are present in Figure S3 in the Supporting Information.

The UV-vis absorption spectra (Figure 1b) of both compounds in solutions are well overlapped due to the similar molecular backbone and the absence of interchain interactions. This observation has also been confirmed by density functional theory (DFT) modelling where both molecules exhibit the same visible peak position (503 nm, Figure S4a: Supporting Information). The measured absorption maximum in solution is located around 487 nm, which is attributed to the intramolecular charge transfer (ICT) from naphthalene to the DPP core. This peak was red-shifted to 502 and 503 nm for H-DPPN and O-DPPN thin films, respectively, due to the molecular aggregation. In thin films, both materials only exhibit H-aggregation which follows a similar trend to that observed in our previous work, namely, that the shorter the side chains, the stronger the H-aggregation.<sup>[28]</sup> After annealing the thin films at 100 and 130 °C for 10 min (Figure S5a,b: Supporting Information), the J-aggregation of H-DPPN has been enhanced, whereas for O-DPPN, not only the J-aggregation was enhanced after 100 °C annealing, an extra absorption peak and a red-shifted spectrum are observed. After annealing at 130 °C, the spectrum went back to the dominant H-aggregation, but the red shift remains the same. This phenomenon is consistent with the DSC analysis, since the secondary recrystallization of the amorphous area of O-DPPN promoted further aggregation and caused the change from J- to H-aggregation. The bandgaps of both compounds are calculated from the onset of thin film spectra (559 and 565 nm for H-DPPN and O-DPPN, respectively) to be 2.22 and 2.19 eV. In solutions, both materials show a strong PL emissive peak at 558 nm (Figure 1c and Figure S5c: Supporting Information). In thin films, aggregation caused quenching was observed for both materials with a dominant emissive peak at 388 and 422 nm for H-DPPN and O-DPPN, respectively, under excitation wavelength of 325 nm. Upon exciting at 502 or 503 nm, both compounds exhibited weak emission with a peak located at around 610 nm (Figure S5d: Supporting Information).

The highest occupied molecular orbital (HOMO) energy levels are determined through photoelectron spectroscopy in air (PESA) measurements to be -5.40 and -5.39 eV respectively as shown in Figure 1d. In our previous publication,<sup>[28]</sup> we observed that the side chains on DPPN can have a significant influence on the energy levels (despite of same conjugated backbone) due to the different solid state stacking, which is supported by the significant color variation. However, for H-DPPN and O-DPPN, the HOMOs are only slightly changed. This can be further confirmed from the similar color appearance of both compounds and the similarity of the absorption spectra in solutions and thin films. The lowest unoccupied molecular orbital (LUMO) energy levels are estimated from the difference between optical bandgaps and HOMOs to be -3.18 and -3.20 eV for H-DPPN and O-DPPN, respectively.

DFT calculations were employed to investigate the electronic structure and molecular geometry of H-DPPN and O-DPPN. As shown in Figure S6 (Supporting Information), both molecules







Figure 2. Transfer curves of OTFTs based on a) H-DPPN and b) O-DPPN thin films. Transfer curves of SCTs based on c) H-DPPN and d) O-DPPN crystals with the corresponding optical device structure images in the insets. Optical images of e) H-DPPN and f) O-DPPN single crystals. X-ray determined unit cells of g) H-DPPN and h) O-DPPN crystals.

have same HOMO and LUMO distributions, which are found to be localized at the entire molecular backbone that can be beneficial to facilitate the intramolecular charge carrier transport. The computed molecular HOMO levels are -5.35 eV for both molecules, which is in an excellent agreement with the experimental results. The calculated bandgaps (2.62 eV) and LUMO (-2.73 eV) values are higher than the experimental values which could be attributed to the fact that the measured onset of optical absorption is affected by vibrational broadening while the computed levels are at the equilibrium geometry, as well as errors due to approximations used. The optimized backbone conformation indicates the same dihedral angles of 37° and 31° for both molecules (Figure S6, Supporting Information). Since both H-DPPN and O-DPPN solutions have shown strong fluorescence under a UV lamp, the relatively large dihedral angles can, to some extent, restrain the emission quenching effect in solid state, demonstrating their promise for application in OLEDs.

Top gate bottom contact (TG/BC) OTFT devices were fabricated to evaluate the electrical properties of newly synthesized H-DPPN and O-DPPN semiconductors. The representative device schematic and transfer curves after annealing at 100 °C or 120 °C are shown in Figure S7 (Supporting Information) and **Figure 2**a,b. The hole mobility values ( $\mu_h$ ), threshold voltage ( $V_{th}$ ), subthreshold swing (SS) and on/off ratio ( $I_{on}/I_{off}$ ) extracted from transfer curves at the saturation regime are summarized in **Table 1**.

It was found that the devices annealed at 100 °C exhibited better performance with a highest hole mobility of 0.01 cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup> for H-DPPN and 0.05 cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup> for O-DPPN. This performance is better than some reported alkylated thiophene DPP monomers in solution processed thin film transistors as compared in Table S1 (Supporting Information).<sup>[31]</sup> When the thin films were annealed at 120 °C, the mobility decreased to 0.006 and 0.001 cm<sup>2</sup>  $V^{-1}$  s<sup>-1</sup>, respectively. By comparing with

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 Table 1. Summary of TG/BC structured OTFT device performance.



Material	T <sub>anneal</sub> [°C]	$\mu_h^{\text{ave.}} \times 10^{-2} \ [\text{cm}^2 \ \text{V}^{-1} \ \text{s}^{-1}]$	$\mu_h^{max.} \times 10^{-2} \ [cm^2 \ V^{-1} \ s^{-1}]$	SS [V dec <sup>-1</sup> ]	V <sub>th</sub> [V]	$I_{\rm on}/I_{\rm off}  [ imes  10^6]$
H-DPPN	100	$\textbf{0.66} \pm \textbf{0.27}$	1.02	$\textbf{0.95}\pm\textbf{0.20}$	$20.1\pm4.1$	$\textbf{0.43} \pm \textbf{0.49}$
	120	$\textbf{0.23}\pm\textbf{0.19}$	0.61	$\textbf{0.77} \pm \textbf{0.17}$	$23.5 \pm 1.8$	$\textbf{0.54}\pm\textbf{0.63}$
O-DPPN	100	$\textbf{4.29} \pm \textbf{1.38}$	5.03	$-4.70\pm1.0$	$-8 v.9 \pm 2.6$	$\textbf{0.63} \pm \textbf{0.13}$
	120	$\textbf{0.04}\pm\textbf{0.06}$	0.16	$5.62\pm5.60$	-	$\textbf{0.13} \pm \textbf{0.27}$

our reported compounds, O-DPPN was observed to show the best performance and H-DPPN shows an even worse mobility than D-DPPN (0.019 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>).<sup>[28]</sup> From the polarized microscopic images shown in Figure S8 (Supporting Information), it is clear that the films of both materials easily form large crystalline domains, which is beneficial for charge carrier transport. However, the H-DPPN film has many defects while the O-DPPN film is smoother that contributed to the higher hole mobility. Upon annealing at 120 °C, the defects become more obvious in H-DPPN film which caused a decreased hole mobility, while the crystal domains did not change much, that is consistent with the high melting point >160 °C observed from the DSC curve. From the AFM (atomic force microscope) images of H-DPPN and O-DPPN films annealed at 120 °C, similar phenomenon is observed as shown in Figure S9 (Supporting Information). For the O-DPPN film, the crystal domains were broken, and a culletshaped film was observed. After 120 °C annealing, the amorphous area experienced melting process, which, we assume, caused the broken of crystalline regions of O-DPPN films. This phenomenon can easily cause disconnection along the conducting channel and thus result in a large decrease in mobility. Microstructure, defects, and domain walls are thus critical determinants of mobility in these materials. Computed estimates of charge transfer rates (see the Supporting Information) also point the critical role of domains and microstructure: while the computed single crystal charge hopping rate between neighboring molecules is higher for H-DPPN than for O-DPPN, the packing of H-DPPN favors 1D hopping pathways, while the packing of O-DPPN favors 2D pathways (Figure S10, Supporting Information). The low-dimensional hopping paths imply strong dependence of the measured bulk rate on crystal domain size, whereby domain boundaries are expected to be a significant bottleneck to transport in particular because ideal crystal transport is lowdimensional. The grain boundaries are expected to be a more significant bottleneck in H-DPPN due to 1D transport in the ideal crystal, explaining the better measured mobility with O-DPPN.

To investigate the intrinsic charge transport behavior, transistor devices based on H-DPPN or O-DPPN single crystals were fabricated. By drop-casting a H-DPPN ( $0.1 \text{ mg mL}^{-1}$ ) solution in chlorobenzene on bare Si/SiO<sub>2</sub> wafer and after solvent evaporation, well-defined ribbon-shaped crystals were grown in three days (Figure 2e). Since ill-defined clusters of O-DPPN were grown in chlorobenzene, we screened the solvent species and used a mixed solvent (chloroform:ethyl acetate = 1:2) to grow ribbon-shaped crystals (Figure 2f) by drop-casting method (0.05 mg mL<sup>-1</sup>). The optical images of H-DPPN and O-DPPN single crystals are also present in Figure S11 (Supporting Information) with a same scale plate for better comparison. The single crystals were annealed in vacuum at 80 °C to remove residual solvent before devices fabrication. Drain and source electrodes (40 nm) were deposited on H-DPPN and O-DPPN crystals by thermal evaporation of a gold film with the "Au stripe mask".<sup>[32]</sup> The transfer curves and optical images (insets) of fabricated devices are shown in Figure 2c,d. The electrical characteristics of all devices were measured under ambient conditions. From the saturation regime of the transfer characteristics, the mobility is calculated by linear fitting of the dependence of  $(I_{DS})^{1/2}$  versus  $V_G$ . The mobility of the best devices for O-DPPN crystals is up to 0.125 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, over ten times higher than that of H-DPPN crystals. The  $I_{on}/I_{off}$ ratio of the best device for O-DPPN crystals was measured to be 10<sup>6</sup>, five orders of magnitude higher than that of H-DPPN crystals. These results further demonstrated that O-DPPN crystals exhibit much better charge transport behaviors compared with H-DPPN.

To better understand the difference between single crystals for H-DPPN and O-DPPN, we grew H-DPPN and O-DPPN single crystals as shown in Figure S12 (Supporting Information). Their structures and unit cells were determined through X-ray diffraction as shown in Figure S13 (Supporting Information) and Figure 2g,h. H-DPPN and O-DPPN crystallize in the space groups  $P2_1/c$  and  $P2_1/n$ , respectively. In the crystal structure of H-DPPN, the molecules stack in chain to chains, with the principal interaction being an offset face-to-face  $\pi$ - $\pi$ interaction between adjacent naphthalene units (3.278 Å). In the O-DPPN crystal structure, chains of stacked O-DPPN molecules (vertical offset 2.760 Å) interact with adjacent chains via weak naphthalene CH- $\pi$  interactions (3.808 Å) between neighboring naphthalene units. CH- $\pi$  interactions (2.695 Å) are also observed between naphthalene rings and adjacent alkyl chains. Obviously, the favorable backbone stacking in Figure 2h for O-DPPN crystals explained its higher mobility in SCTs. The comparison of single crystal data of H-DPPN and O-DPPN with thiophene, selenophene, and phenyl DPPs (with hexyl side chains) indicate that DPPN compounds exhibit a much closer  $\pi$  stacking than other DPP derivatives as compared in Table S1 (Supporting Information).<sup>[33]</sup> That is a highly favorable feature for intermolecular charge carrier transport. We also performed large-scale calculations on crystals and clusters of H-DPPN and O-DPPN to estimate the effect of solid-state packing on electronic properties. First, density functional tight binding (DFTB) and time-dependent DFTB (TD-DFTB) were benchmarked to DFT and TD-DFT in single-molecule calculations. The results are given in Table S2 and Figure S4 (Supporting Information), showing that while (TD)-DFTB results in somewhat different values of the HOMO, LUMO energies, the gap, and the visible absorption peak from DFT (as is expected given that the DFTB parameterization is based on GGA calculations), it can be used for qualitative assessment and is reliable for comparison between the two molecules and between different molecular







Figure 3. DFTB-computed unit cells (delimited by the box) of crystalline a) H-DPPN and c) O-DPPN. Molecular clusters of b) H-DPPN and d) O-DPPN.

environments. We therefore compared properties computed in periodic crystals and clusters to those of the molecules.

The unit cells of H-DPPN and O-DPPN crystals are shown in Figure 3a,c. Experimental structures were used as a starting point of optimizations. Clusters were cut preserving the optimized geometry of the periodic calculation (Figure 3b,d). The DFTB-optimized cell parameters are given in Table S3 (Supporting Information). As TD-DFTB calculations had to be done with the  $\Gamma$  point, a supercell with 10 molecules was then optimized for O-DPPN to make  $\Gamma$  point calculations sufficiently accurate (for H-DPPN, the unit cell is big enough for a  $\Gamma$  point calculation). The calculated HOMO, LUMO values and the gap for crystals and clusters are also shown in Table S2 (Supporting Information). For crystals, they show stabilization of the HOMO about 0.3 eV for H-DPPN and  $\approx$ 0.4 eV for O-DPPN. The band gap becomes about 0.3 eV lower in H-DPPN versus O-DPPN, while the HOMO-LUMO gap is practically the same at the single-molecule level. While the absolute values of HOMO and LUMO in periodic systems are generally not directly comparable to molecular levels, changes in the gap are comparable and indicate stronger effects of aggregation on the gap with H-DPPN. The cluster calculations result in higher HOMO values versus single molecules, by 0.2–0.3 eV. They confirm the decrease in the gap in H-DPPN versus O-DPPN due to aggregate state effects, by 0.36 eV, similar to the results of the periodic calculations. Both periodic and cluster calculations indicate a slightly (≈0.1 eV) lower HOMO of O-DPPN in solid state versus H-DPPN even though molecular HOMO are nearly identical. The calculations also clearly confirmed the  $\pi$ stacking between naphthalene for O-DPPN, while H-DPPN tends to stack parallel.

A family of DPP molecules is gaining significant importance in OLED technology because of its high fluorescent quantum yield, thermal and photostability.<sup>[10,27]</sup> In the present study, H-DPPN and O-DPPN were used to fabricate yellowish orange OLED by using cost-effective solution processing. Specifically, the device structure is shown in Figure S14 (Supporting Information) where PEDOT:PSS is employed as a hole injecting and transporting layer (HIL/HTL), the emissive layer (EML) is composed of TCTA host doped with 2 wt% H-DPPN or O-DPPN orange emitter, TPBi is used as an electron transporting layer (ETL), and LiF/Al acts as a cathode. The energy level diagram of all used materials is shown in Figure 4a. The I-V curve as shown in Figure 4b exhibits well-defined diode characteristics, revealing that the fabricated OLED behaves as a rectifying device. The forward bias current for both devices rises with the increase of applied bias voltage, however, the reverse bias current remained significantly low (not shown in *I-V* curve), suggesting both OLEDs act as rectifying diodes. The rapid increase in forward-bias current is observed for O-DPPN based OLED, implying a small sheet resistance of the device, whereas H-DPPN OLED has a high sheet resistance.

The difference in high forward bias current is attributed to differences in charge carrier mobility of the corresponding molecules.<sup>[34]</sup> From the OTFTs and SCTs study, it is confirmed that O-DPPN possesses a higher mobility compared to H-DPPN. The influence of hole mobility is vividly observed in OLED device turn-on voltage as shown in Figure 4c which is the plot of luminescence versus applied voltage. The O-DPPN based OLED requires a 3.0 V to emit 10 cd m<sup>-2</sup> luminescence, whereas to get the same luminescence, 3.8 V is needed for H-DPPN emitter OLED (0.8 V more). However, the power www.advancedsciencenews.com





**Figure 4.** a) Energy level diagram of studied OLED device. b) Current–voltage (J–V), c) luminance, d) power efficiency, and e) current efficiency of studied OLED devices based on TCTA host doped with 2 wt% H-DPPN or O-DPPN molecules. f) Electroluminescence (EL) spectra of the fabricated OLED devices at 100 cd m<sup>-2</sup>. Inset picture is the photograph of the working O-DPPN based OLED device.

efficiency obtained for H-DPPN OLED is 8.8 lm W<sup>-1</sup> which is 27% higher than that of O-DPPN (6.5 lm W<sup>-1</sup>) based device at 100 cd m<sup>-2</sup> (Figure 4d) and a similar trend is noticed for current efficiency (Figure 4e). **Table 2** details electroluminescent properties of the fabricated OLEDs. The maximum power efficiency, current efficiency, and EQE were found to be 8.3 lm W<sup>-1</sup>, 11.8 cd A<sup>-1</sup>, and 4.0%, respectively, at 100 nits, for the H-DPPN based OLED. The overall performance of the H-DPPN OLED is superior to the O-DPPN counterpart, except the maximum luminance. To emphasize the advantage of DPPN compound in OLEDs, we compared the EQE values with other DPP derivatives (Table S1, Supporting Information). Also as the dopant for a host material, the device fabricated with TAPC (4,4'-cyclohexylidenebis[*N*,*N*-bis(4-methylphenyl)benzenamine])

host doped with 10 wt% furan flanked DPP exhibited a much lower EQE value of  $0.7\%.^{[27]}$  Although this value is

Table 2. OLED device parameters with TCTA host doped with 2 wt% DPPNs.

Dopant <sup>a)</sup>	OV [V]	PE [lm W <sup>-1</sup> ]	CE [cd A <sup>-1</sup> ]	EQE [%]	CIE/(x,y)	Max. L [cd m <sup>-2</sup> ]
	@100/1000 cd m <sup>-2</sup>					
H-DPPN	4.5/5.2	8.3/4.7	11.8/7.8	4.0/2.7	(0.50,0.48)/(0.49,0.47)	5371
O-DPPN	3.5/4.5	6.5/4.5	7.3/6.5	2.3/2.0	(0.49,0.48)/(0.48,0.48)	6065

<sup>a)</sup>OV: Operating Voltage; PE: Power Efficiency; CE: Current Efficiency; EQE: External Quantum Efficiency; CIE 1931 Color Coordinates; Max. L: Maximum Luminance.


further enhanced to 12.1% by introducing a second dopant (9-[2,8]-9-carbazole-[dibenzothiophene-S,S-dioxide]-carbazole, initialized as 2d), it is not competitive since the 2d doped TAPC shows a EQE value of 15%.<sup>[35]</sup>

Figure 4f shows the normalized electroluminescent (EL) spectra of two OLED devices. Each one was made with 2 wt% H-DPPN and O-DPPN molecules doped in the TCTA host, obtained at 100 nits. The main emission peak is obtained at 570 nm for both devices, which corresponds to the absorbance band of H-DPPN and O-DPPN molecules, confirming the direct excitation of DPP cores. The CIE (x,y) coordinate of EL spectra (0.50, 0.48) evidences that the fabricated OLED devices generate greenish-yellow light. However, emission noticed at 400-450 nm originates from the TCTA host molecules. The EL spectrum of O-DPPN OLED is narrower than that of the H-DPPN counterpart, suggesting the recombination zone of the injected charge carriers is narrower as compared to H-DPPN based OLED. To explain this behavior, it is important to consider the charge carrier mobility of O-DPPN and H-DPPN. It is a well-known fact that the OLED device with a TCTA host with TPBi ETL is a hole charge carrier-dominated device and therefore the charge carrier recombination zone is mainly available at the interface of the emissive layer (EML) and the electron transporting layer (ETL).<sup>[36]</sup> O-DPPN possesses a higher hole mobility allowing for more efficient hole injection and transport through the EML layer up to the ETL interface, resulting in a narrower recombination zone. On the other hand, the H-DPPN molecule has a slightly lower hole-mobility that assists to widen the charge carrier recombination zone up to the interface of the HTL and EML.<sup>[34,37]</sup> As a result of this, we have obtained higher power and current efficacy and EQE for H-DPPN based OLED compared to the O-DPPN counterpart.

#### 3. Conclusions

To summarize, we designed and synthesized two naphthalene flanked DPP dye based versatile materials, namely, H-DPPN and O-DPPN. It was found that, through molecular engineering and smart device structure design, high performance can be achieved in both transistors and thin film displays, which is encouraging for researchers working on organic electronics. DPPNs with different side chains were first reported by our group, and in this work, we demonstrated that the octyl side chain is most suitable for this series of molecules due to its highest hole mobility of 0.05 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> in OTFTs. The better performance was ascribed to the uniform morphology with a highly crystalline nature. Molecule with short side chains allows growing single crystals for SCTs. O-DPPN shows a largely enhanced performance with mobility of up to 0.125 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> which is 10 times higher than that of H-DPPN. This is attributed to the stacking mode suggested by X-ray determined unit cells and DFTB computations. H-DPPN crystals appear to stack in 1D chain with a face to face  $\pi$ - $\pi$  interaction that lacks favorable backbone stacking for charge carrier transport. However, obvious backbone stacking from X-ray diffraction for O-DPPN crystals and naphthalene-naphthalene stacking from DFTB calculations are observed. This is a favorable feature for better charge carrier transport, explaining its higher hole



mobility in SCTs. Additionally, as the analogue of phenyl DPP, H-DPPN and O-DPPN also exhibit potential in OLEDs. To avoid the emission quenching effect of pristine DPPN film in the active layer, we smartly modified the OLED device structure by using the DPPN molecule as a dopant for TCTA. H-DPPN based OLED shows better performances with maximum power efficiency, current efficiency, and EQE of 8.3 lm W<sup>-1</sup>, 11.8 cd  $A^{-1}$ , and 4.0%, respectively, at 100 nits. Overall, in this work, we have clearly disclosed the versatility of two DPPN molecules in various types of electronic devices. Especially, simultaneously achieving high performance in both transistors and thin film displays through molecular engineering and smart device structure design is a new scenario in organic electronics community which is expected to advance the future development of electronic devices.

#### **Supporting Information**

Supporting Information is available from the Wiley Online Library or from the author.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

#### **Author Contributions**

Q.L. is responsible for the materials synthesis, properties characterization as well as managing the final manuscript preparation. S.C., J.-H.J., H.-S.C., and M.R.N. are responsible for the OLED device fabrication and characterization. H.Z., Y.Z., and W.H. are responsible for the single crystal transistors fabrication and characterization. H.S. and Y.-Y.N. are responsible for the thin film transistors fabrication and characterization. A.B. and J.M. are responsible for the X-ray determined single crystal data. S.M. and Y.C. are responsible for the DFT and DFTB calculations. K.F. is responsible for the PESA measurement. S.E.B. reviewed and revised the manuscript. P.S. conceived and directed the project. All authors have reviewed or commented on the final version of the manuscript.

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#### **Keywords**

molecular engineering, naphthalene flanked diketopyrrolopyrrole, smart device structure design, thin film displays, transistors

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# 3.3.2.1 Research Paper Published in UGC Approved Journals

# Growth and Characterization of Barium Oxalate Crystals by Single Diffusion Gel Method

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## ABSTRACT

Barium oxalate crystals were grown by agar-agar gel through the single diffusion technique. The tendency of barium oxalate crystals to cylindrical growth was demonstrated. The optimum growth conditions barium oxalate was achieved by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. The crystal structure of grown material was determined by X-ray diffraction technique and was found to be monoclinic with lattice parameters 'a' = 6.6562 Å, b = 8.0464 Å, c = 2.8090 Å,  $\beta$ =  $96.832^{\circ}$ , and V =  $149.38 \text{ Å}^3$ . The FTIR spectrum indicates OH and carbonyl group along with the presence of metal-oxygen bond. Morphology of grown crystals, investigated by scanning electron microscopy, exhibited compact grains including small and large sizes. Since the grown crystals are transparent, they show strong absorption in the ultra violet region above 290 nm wavelength.

Keywords: Crystal growth, Barium oxalate, X-ray spectroscopy, FTIR, and SEM.

#### 1. Introduction

A solid which consist of atoms or other microscopic particles arranged in a periodic manner in all directions is called as a crystal. The strong influence of single crystals in the present day technology is evident from the recent advancements ultra-small electronic gadgets. Crystals of different materials have several applications such as they are used in semiconductor devices like electrical diodes, photodiodes, transistors, integrated circuits, magnetic devices like tape heads, transformer cores, superconductors, optoelectronics, quantum electronics, quantum and nonlinear optics, telecommunication etc. hence today's demand is to grow large crystals with good quality, high purity and symmetry. With this demanding requirement it is important to study the growth of single crystals and hence, investigation of their physical properties towards the fulfillment of device fabrication is crucial for both academic as well as applied research. Therefore, enormous amount of toil and treasure has been lavished on the development of crystal growth techniques. The in-depth explanation of various techniques can be obtained in the literature [1-6]. There are three major stages involved in this research. The first is the production of pure materials and improved equipment's associated with the preparation of these materials.

Second one is the production of single crystals first in the laboratory and then extending it to commercial level. The third is the characterization and utilization of these crystals in devices.

In present study, we have adopted the agar-agar gel technique to grow the barium oxalate single crystals. We have successfully grown the cylindrical transparent barium oxalate single crystals and studied their physical properties.

#### 2. Experimental

In the present work, barium oxalate crystals were grown by single diffusion technique. The growth of barium oxalate crystals was carried out in agar-agar gel by adopting the similar technique as reported (Dalal and Saraf 2009) [10]. Barium chloride (BaCl<sub>2</sub>, 99.9%), oxalic acid (H<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, 99%), Agar-Agar powder (C<sub>14</sub> H<sub>24</sub> O<sub>9</sub>) were used as the starting materials. All chemicals were of AR grade. The borosilicate glass tubes were used as crystallization apparatus. The glass tubes used for single diffusion were of 25 cm in length having outer diameter of 2.5cm outer diameter and 250ml beaker. The solution of 0.5, 1.0, 1.2, 1.5, and 2M concentrations were prepared and stored in clean glassware. Agar-agar gel was prepared by mixing (0.5 to 2.0gm) of agar powder in 100ml double distilled water at boiling temperature. Barium chloride of concentration 0.5 to 2M and oxalic acid of concentration 0.5 to 2M were used as reactants.

The prepared solution of oxalic acid were transferred into the test tube followed by addition of appropriate volume of agar gel and then kept undisturbed for aging period of few days. After setting and aging over the setgel, the solution of barium chloride (desire volume and molarity) which is the reactant, was poured gently along the wall and allowed to diffuse into the gel medium. The open end of test tube was closed with cotton plug to protect from dust particles and kept undisturbed at room temperature.

We keenly observed the reaction and noticed that a thin precipitation layer was formed on the surface of the gel. This precipitate band increased gradually and diffusion proceeded into the gel. After 5 to 6 days nucleation process observed at the interstitial sides inside the test tube and then some transparent, star, platy shapes crystals were noticed. The crystals were harvested by washing them carefully with acetone. Prismatic, opaque, and platy shaped crystals were obtained with maximum size of a  $3 \times 4 \times 2$  mm<sup>3</sup>. The reaction which leads to the growth of crystals is expressed as

#### $BaCl_2 + H_2C_2O_4 \longrightarrow BaC_2O_4 + 2HCl$

The optimum conditions for growing a well-defined crystals are given in table 1.

Sr. No	Conditions	Single Diffusion
1	Percentage of gel	1%
2	Con. of Barium Chloride	1M
3	Volume of Barium Chloride	5 ml
4	Con. of Oxalic acid	1M
5	Volume of oxalic acid	10 ml
6	Gel setting period	24 hours
7	Gel aging period	32 days
8	Temperature	Room temperature
9	Quality	Star shaped, Needle shaped, Platy shaped
10	Size	1 to 5 cubic mm

Table 1. The optimum condition established for growth of barium oxalate crystals

#### 3. Growth kinetics

The growth of barium chloride was observed while growing in a test tube and effect of various parameters such as percentage of gel, concentration of first and second reactants, reversing and aging periods were studied.

#### 3.1 Effect of aging period

To observe the effect of aging period on the growth of barium oxalate crystals. The aging period changes from 24 to 48 hours, while other parameters kept constant. We have found 24 hours aging period indicating the fast growth rate.

#### 3.2 Effect of percentage of gel

To observe the effect of percentage of gel on the growth of crystals, all other parameters were kept constant except the percentage of the gel. It was found that for lower percentage (0.5%) of gel, the growth was slow and form small particles which were in large in number. When percentage of gel increased from 1.0 to 1.5% dendrite shaped crystals growth was observed. The size and appearance of growing crystals found more precise for 1.0% of gel as compare to other percentage of gel. As shown in Fig.1 (a)–(e) good, transparent crystals of barium oxalate having cubic to cylindrical shaped crystals were obtained.





Fig 1(e)

Figure 1 (a-e): Photographs of barium oxalate grown crystals.

#### 4. Result and discussion

#### 4.1 X-ray diffraction studies

X-ray diffractogram is useful method to analyze the crystal structure of unknown material. X-ray diffractogram of gel grown barium oxalate crystals was recorded using powder rotation photograph method on Minislex Regaku X-ray diffract meter at Dept. of Physics at Shivaji University Kolhapur. The sample was rotated in the range  $10^{0}$  - $80^{0}$  (2 $\theta$ ), scanning speed was kept  $2^{0}$ / min and chart speed was 2 cm/ min. X-ray diffractogram of barium oxalate is shown in fig. 2.

From the diffraction pattern, "d" values and (h, k, l) planes were computed. Calculated "d" values are well matched with the reported ones. The unit cell parameters and system calculated by the computed program are given in table 2. These parameters satisfy the conditions for monoclinic system. i.e.  $a \neq b \neq c$  &  $\alpha \neq \beta \neq \gamma$ .



Figure 2: X-ray diffraction pattern of as grown barium oxalate single crystal.

#### 4.2 Fourier transform infrared (FTIR)

The Fourier transform infrared (FT-IR) spectrum of barium oxalate was recorded at room temperature in the spectral range of 500 – 4500 cm<sup>-1</sup> by KBr pellet method using SHIMADZU spectrophotometer at the department of Physics, Shivaji University Kolhapur. Figure 3 shows the FTIR spectrum of barium oxalate. A few of the prominent vibrational modes are empirically assigned here. The bands around 2950 to 3650cm<sup>-1</sup> are attributed to asymmetric and symmetric –OH stretching of water. The – OH stretching frequency of barium oxalate appeared at 2923cm<sup>-1</sup>. The moderate absorption around the 3500 to 3200cm<sup>-1</sup> is probably due to stretching of alcohol group. The fundamental FT-IR frequencies observed in all barium oxalate crystals [11]. Table 3 shows FTIR spectral and vibrational assignments of barium oxalate.



Figure 3. FTIR of Barium oxalate crystal

Table 3. FT – IR spectral and vibrational assignments of barium oxalate.

Wave number cm <sup>-1</sup>	Intensity	Assignments	
3640 - 3610	S,sh	O – H Stretch	
3500 - 3200	S,b	O–H Stretch	
3330 - 3270	n,s	C=C -H Stretch	
3300 - 2500	m	O –H Stretch	
3000 - 2850	m	H-C = O Stretch	
1710 - 1665	S	C = O stretch	
1370 -1350	S	C – H rock	
1000 -650	m	= C- H bend	
700 - 610	b	C –H bend	

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## Scanning Electron Microscopy (SEM)

In the present work powdered sample of barium oxalate crystals was examined by using SEM technique at the Dept. of Physics Shivaji University Kolhapur. The study of the surface of the crystal gives valuable information about its internal structure. Figure 4 (a) illustrates SEM photographs of single crystals of barium oxalate crystal. High resolution SEM image is shown in Figure 4 (b). It is observed that due to growth conditions voids are created at the grain boundary. SEM images revealed that the growth of barium oxalate crystals consist of flat layered particles as well as spherical small grains. The individual flat grains possessed sharp edge [13].



Figure 4: SEM images of as grown (a) barium oxalate crystal and (b) high resolution image.

# UV-Vis Absorption spectroscopy

Absorption spectrum of barium oxalate crystals was obtained by a SHIMADZU UV-2450, UV- Vis spectrophotometer at the Dept. of Physics Shivaji University Kolhapur. Figure 5 shows UV-Vis absorption spectrum of barium oxalate crystal. Spectrum shows that the barium oxalate crystal allows to pass the entire visible and IR wavelengths and absorbs only ultra-violate wavelengths and therefore, the absorption coefficient is high at low wavelengths and high at short wavelengths. Since it is transparent crystal for wide range of wavelength (350-900 nm), the barium oxalate crystals can be used for second and third harmonic generations of the 1064 nm radiation [14-15]. Optical band gap energy of the as-grown barium oxalate crystals is calculated using the following simple conversion equation;

Band gap energy (ev) =  $\frac{1240}{\lambda (nm)}$ 

The band gap energy of barium oxalate crystal is found to be 4.06ev and tabulated in table 4.

Table 4: the band gap energy of Barium oxalate crystals.

Crystal	$\Lambda(nm)$	Band gap Energy(ev)
Barium oxalate	305.00	4.06



Figure 5: Optical absorption spectra of as-grown barium oxalate crystal.

## 5 Conclusions

From systematic investigation on the single diffusion gel growth of the barium oxalate crystals. Best conditions have been established to get good crystals.

1) Gel method is found suitable for growing barium oxalate crystals.

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- 2) The growth of barium oxalate crystals was accomplished by allowing diffusion of barium chloride solution through ager-ager gel impregnated with oxalic acid in single diffusion gel tube system, with all growth conditions. Barium oxalate crystals possessed cubic and cylindrical shapes
- 3) The crystals obtained in ager-ager gel with average size of  $3 \times 4 \times 2$  mm<sup>3</sup> in single diffusion.
- 4) Different habits of barium oxalate crystals can be obtained by changing parameters like gel density, gel aging pH of gel, concentration of reactant etc.
- 5) The 'd' values of grown material obtained from the XRD are well matches with POWD Programmed.
- 6) The FTIR, studies suggested different characteristics features and morphology of grown crystals.
- 7) UV-Vis absorption spectra of barium oxalate crystal showed 4.06 eV optical band gap energy.

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# Physical and Morphological Study of Barium Oxalate Crystals Grown by Agar-Agar Gel Method

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# ABSTRACT

Barium oxalate crystals were grown by agar-agar gel through the single diffusion technique. The tendency of barium oxalate crystals to cylindrical growth was demonstrated. The optimum growth conditions barium oxalate was achieved by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. The crystal structure of grown material was determined by TGA, DTA, DSC and EDAX.

Keywords: Crystal growth, Barium oxalate, TGA, DTA, DSC, and EDAX.

# Introduction

The growth of crystal occurs not only in the crust of Earth or in laboratory but also in a living body. Many crystals, particularly, bio-materials and proteins, cause various ailments and health related problems. The urinary stones are usually composed of either pure or mixed crystals of calcium oxalate, brushite, struvite, and hydroxyapatite and carbonate apatite [1]. Arthropathies, i.e., bone and joint diseases, are caused by crystals such as hydroxyapatite, calcium pyrophosphate and monosodium urate monohydrate [2]. There are other crystals which play important role in various ailments, for instance, f.c.c. type ferritin crystals in development of cataract [3] and cholesterol crystals for cardiovascular diseases and gall stones [4]. This bio-crystallization occurring in human body causes suffering and it is not desirable to occur. This has been discussed in detail by the predecessors of the present author [5-7]. There are several micro-organisms which synthesize crystals, for example, magneto-tactic bacteria synthesizing magnetite [8], chrysophytes [9] diatoms and act in opoda synthesizing siliconous materials and S. layer bacteria synthesizing gypsum and calcium carbonate surface layers [10]. Calcite crystals are found in mollusk shells [11] and as a component in gall stones [12]. The earlier crystal growth study was divided into two parts :(1) The study of the equilibrium between the crystal and surrounding medium(2) The study of the kinetics of growth.

# Experimental

Experimental procedure 5 gm of agar-agar powder was dissolved in to hot double distilled water mixed with 0.5 M to 1 M barium chloride solution was incorporated then again the mixture was stirred to make homogenous mixture. The crystallizing vessel were used essentially consist of standard glass tube having inner diameter 2.5 cm and the length 25 cm. Gelling mixture poured in glass test tubes. These tubes were hermitically sealed to prevent evaporation and contamination of the exposed surface by dust particles of atmosphere or atmospheric

impurities and were kept undisturbed. Usually in 3 to 4 days the gel was to be set which depends on the environmental temperature. It was observed that the mixture in a glass tube was initially transparent and slowly turned light white. The water slowly evaporated and gel was completely set. After ensuring firm gel setting, it was kept for aging for 3 to 4 days. After that 0.5 M to 1 M solution of oxalic acid was added as a supernatant over the set get. Nucleation was observed after 5 to 6 days and crystals started to grow. White color, larger size, transparent and shining crystals were obtained in the gel, as shown in fig.1, Optimum condition tabulated in table 1, [13].

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							8-0			8	

Concentration of agar-agar gel	5 %			
Concentration of reactant, strontium chloride	1M			
Concentration of supernatant, oxalic acid	1 M			
Room temperature	27 <sup>0</sup> C			
Gel aging period	4 days			
Growth period	25 - 40 days			
Quality of crystals	White colour, larger size $(1mm \times 1mm)$			
	transparent, shining crystals			





Fig.1 (a) Barium crystal inside the test tube (b) Opaque and shiny crystals

#### **Result and Discussion-**

## Thermo-Gravimetric Analysis (TGA)

TGA was carried out at Department of Physics, Shivaji University Kolhapur, TGA curve for barium oxalate is shown in figuer.2. From the thermo gram of barium oxalate one can observe that

i) The compound is stable up to  $50^{\circ}$ C.

ii) 5.165% weight loss in temperature range  $50^{\circ}$ C. To  $172^{\circ}$ C may be due to dehydration of water molecule and up to  $172^{\circ}$ C there is no further loss of weight.

iii) 25.68% weight loss in temperature range 172°C to 277°C from the dehydrated compound corresponds to loss of CO.

iv) 36.68% weight loss in temperature range 277°C to 435°C corresponds to loss of CO<sub>2</sub>.

v) 13.45% weight loss in temperature range  $435^{\circ}$ C to  $478^{\circ}$ C.

v) The residue remains stable from  $478^{\circ}$ C and decompose the material. [14-16].



Figure 2 TGA of Barium oxalate crystal grown by agar-agar gel

TGA data indicates that the grown crystals contains water molecule,

Stage	Temperature	Observed %	Calculated %	Loss of molecule
	range	weight loss	weight loss	in stage
Ι	50°C-172°C	5.165%	5.045%	H <sub>2</sub> O
II	172°C-277°C	25.68%	25.8%	It may be CO
III	277°C-435°C	36.68%	35.99%	CO <sub>2</sub>
IV	435°C-478°C	13.45 <mark>%</mark>	<mark>1</mark> 3.56%	

 Table 2
 TGA Data of Barium oxalate

## Differential Thermal Analysis (DTA)

DTA was carried out at Department of Physics, Shivaji University Kolhapur.DTA curve for barium oxalate is shown in figure3. From the thermo gram of barium oxalate one can observe that.

In DTA curve of barium oxalate by agar-agar gel at 37.51°C an endothermic peak is observed due to the loss of bulk of water of crystallization. The decomposition of oxalate is observed at the onset due to complete dehydration. In DTA curve the exothermic peaks at 153.°C to 154.54°C shows the decomposition of oxalate. Loss of weight at the temperature range 153.°C relates to the loss of water of crystallization which is endothermic in character.

Loss of weight at the temperature 250.07<sup>o</sup>C endothermic peak is observed that means the weight loss with respect to temperature of the grown crystals was further supported by DTA results. DTA data is shown in table- 3



## Figure 3 DTA of Barium oxalate

Table no.3 DTA data of barium oxalate

Peak recorded	Peak	Nature	$\Delta H(J/gm)$	
	height		PITR	
37.51 <sup>o</sup> C	-0.600	Endothermic	-0.6406	
154.54 <sup>0</sup> c	-0.5	Exothermic	-0.5344	
250.07 <sup>0</sup> c	-0.4	Endothermic	-0.4613	

# Differential Scanning Calorimeter (DSC)

DSC was carried out at Department of Physics, Shivaji University Kolhapur, The DSC thermogram was recorded in the temperature range from  $25^{\circ}$ C to  $450^{\circ}$ C.Microcrystalline (powdered) samples of barium oxalate crystals were taken for DSC studies and the weight of the sample 8.5230mg.The sample was hold for 10 min in air to evaporate water due to moisture and then heated from  $25^{\circ}$ C to  $450^{\circ}$ C.at the rate 10c/min in Air .After reaching the temperature of  $450^{\circ}$ C,the sample was hold for I minute at  $450^{\circ}$ C and then again cooled from  $450^{\circ}$ C to  $25^{\circ}$ C at the rate of 10C/min in Air.

The DSC curve for barium oxalate gel grown crystal shown in figure 4. And the DSC data collected from this curve is tabulated in the table 4.

# Step-I

i) The initiation temperature is 225°C and equilibrium temperature 277°C.At 225°C (initiation temperature) initiation of phase change start & is completed at peak endo-down temperature of 250.07°C(transition temperature). The temperature at which the sample and the reference come to the thermal equilibrium by thermal diffusion appears to be at 277°C. The peak appeared in the DSC curve at 154.54°C indicates the phase transformation due to loss of water molecules and formation of stable anhydrous barium oxalate. This is the good agreement with the TGA curve,

ii) Area under the curve is 5707.384 mJ.

iii) Heat of transisiton  $\Delta$ H i.e. enthalpy change of transisiton 517.56 J/g which 0.51756kJ/mole. Since molecular weight is 1g/mole,  $\Delta$ Htr =  $\Delta$ Hf i.e. heat of phase transformation is also 0.5756 kJ/mole, where  $\Delta$ Hf is enthalpy change of new phase transformation or it is called heat of phase formation.

#### Step-II

- i) The initiation temperature is  $430^{\circ}$ C and equilibrium temperature is  $450^{\circ}$ C.At  $430^{\circ}$ C (initiation temperature) initiation of phase change starts and is completed at peak endo- down temperature of 438.76°C (transition temperature). The temperature at which the sample and the reference come to the thermal equilibrium diffusion appears to be 450°C. The further phase transition occurs at temperature 438.76°C due to the loss of carbon and H<sub>2</sub>O and formation of stable barium oxalate. This is good agreement with TGA Curve.
  - ii) Area under the curve is 232.43mJ.
- iii) Heat of transition  $\Delta$ H i.e. enthalpy change of transition 21.99J/g which is 0.02199KJ/mole. Since molecular weight is 1 g/mole, Hence  $\Delta$ Htr =  $\Delta$ Hf i.e. heat of phase transformation is also 0.02199KJ/mole. Where  $\Delta$ Hf enthalpy change of new phase transformation or it is called heat of phase formation. DSC data is shown in table-4.



Figure 4 DSC curve for Barium oxalate

Sample	Weight of the sample	Stage	Change in the enthalpy(ΔH)	Transition temperature (Tr)
Barium oxalate	0.8523gm	Ι	0.51756KJ/mole	250.07 <sup>0</sup> C
		II	0.02199KJ/mole	438.76 <sup>0</sup> C

DSC data is shown in table-4

## Energy Dispersive Analysis by X-rays (EDAX) -

Energy Dispersive analysis by X-ray (EDAX) is used for the quantitative analysis of barium oxalate and is also called as elemental analysis. Fig 5& Table No 5 shows, in present work elemental analysis of gel grown barium oxalate crystals was Department of Physics, Shivaji University Kolhapur. It conclude that the (weight **JETIR2104299** 741

& atomic %) of copper (Cu) in the grown crystal measured by EDAX are very close with the values calculated from the molecular formula.[17-20]



# eZAF smaryt quant Results

Element	Weight%	Atomic%	Net.Int	Error	%	K	Z	R	Α	F
						ratio				
Ck	7.36	34.64	443.18	7.82	0.05	0.05	1.47	0.75	0.47	1.00
Ok	8.71	30.80	991.30	7.87	0.05	0.05	1.42	0.77	0.39	1.00
Barium	83.93	34.56	5594.20	2.05	0.80	0.80	0.91	1.07	1.03	1.03

#### Conclusions -

The present work reports the growth and characterization of barium oxalate single crystals. We have demonstrated the formation of barium oxalate single crystals in agar-agar gels. Barium oxalates exhibits microrod-like and spherulites growth (flower) shape are observed. Further to obtain good quality single crystals of barium oxalate, both reactants –barium chloride and oxalic acid were interchanged. With barium chloride incorporated gels result only fibers. These facts have been explained by taking in account the interaction of the reactants ions with the sodium and silica ions. The effect of temperature on growth of barium oxalate crystals showed that there is a decrease in nucleation density at higher temperature which is due to the increases of the aqueous solubility of barium oxalate.

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# INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

# Growth and Characterization of Cobalt Oxalate Crystal by Ager-Ager Gel Method

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#### Abstract

We have grown the cobalt oxalate crystals by adopting single diffusion technique via agar-agar gel. The tendency of cobalt oxalate crystals to form splices, twins, spherulites and dendrites was demonstrated. The growth dynamic of cobalt oxalate was studied by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. Physical properties of the grown crystals were analyzed by XRD, and FTIR techniques and the results are discussed.

**KEYWORDS**: Gel, Crystal, Gel Growth, Crystal Growth, XRD, and FTIR

## Introduction

Crystals grown by the gel method has gained interest in the research community because it is cheap and easy to grow single crystals of alkaline-earth metal oxalates[1] and transition metal oxalates [2]. These materials have interesting properties like low solubility in water [3], decomposition before freezing point [4], interesting optoelectronic properties. Their role in analytical chemistry and subsequently in industries [5, 6] has created an opportunity for the researcher to investigate every scientific aspect of these materials. Therefore, efforts are being made to investigate and study the physical and chemical properties of these materials. Recently, there are reports on the growth of mixed-ligand complex formation using cadmium oxalate [7]. In the present study, we have presented the optimization of growth parameters to grow the cobalt oxalate single crystals using the agar gel method.

#### **Materials and Methods**

Materials used to grow the cobalt oxalate crystals are cobalt chloride, oxalic acid, and agar-agar gel. All the chemicals used for the experiment were used without any further purification. Sodium silicate glass test-tubes were used as crystallizing vessels. The test-tubes were filled with the first reactant (cobalt chloride) of desired volume and morality. The second reactant, oxalic acid having a concentration range of 0.5 to 1.0 M, was poured along the walls of the test-tube into the set-gel, and allowed to diffuse into the gel medium. The open end of the tube was closed with cotton plugs and kept undisturbed. The said procedure was carried out at room temperature. The ions of the supernatant solution reacted with ions of the first reactant via capillaries formed in gel medium. After six to seven days, nucleation kick-started at the gel-solution interface. The chemical reaction that occurred between the two reactants is given as follows:

 $CoCl_2 + H_2C_2 O_4 \longrightarrow CoC_2O_4 + 2HCL$ 

The diamond-shaped opaque crystals were obtained in the test-tube. The crystals were harvested by washing them carefully with acetone and collected for further characterization. Table 1 shows the optimized crystal growth parameters for the cobalt oxalate crystals.

	Sr.No	Co <mark>nditio</mark> n Single Diffusion	<b>Condition Single Diffusion</b>
	1	Percentage of gel	2.0 %
	2	Concentration of cobalt chloride	1.0M
~~	3	Concentration of oxalic acid	1.0M
5	4	Volume of cobalt chloride	5.0 ml
1	5	Volume of oxalic acid	15 ml
~	6	Gel setting period	34 Hours
	7	Gel aging period	4 days



Figure 1:(a) in situo growth of Cobalt oxalate crystals in test-tube and (b) optical photograph of cobalt oxalate crystals

#### Result and discussion

The crystal structure analysis of the grown cobalt oxalate crystal was done via X-ray diffraction. X-ray pattern was recorded from the range of 10 to 80 degrees. The occurrence of highly resolved intense peaks at specific Bragg angles 20 indicates the high crystallinity of the grown material and revealed monoclinic structure. The obtained crystal data has been compared with the JCPDS data and it closely matched with the reported JCPDS no. 037-0719. The unit cell parameters ('a' = 5.39820 Å, 'b' = 5.03100 Å, and 'c' = 5.73590Å) are close to the reported cell parameters of CoC2O4.2H2O, indicating the monoclinic phase of cobalt oxalate crystal. Comparative data is tabulated in Table 2 for the gel-grown cobalt oxalate crystal.

Table 2. Comparison of unit cel	l parameters of cobalt oxalate.
---------------------------------	---------------------------------

Parameters	Calculated	JCPDS data
System	Monoclinic (P)	Monoclinic
а	9∙67638 Å	6·4534 Å
b	6·7156 Å	7.5009 Å
С	8.6822 Å	10·940 Å





### 4.2 Fourier transform infrared (FTIR) Spectra

The Fourier transform infrared (FTIR) spectrum of cobalt oxalate was recorded at room temperature in the spectral range 500 – 4500cm<sup>-1</sup> by KBr pellet method using SHIMADZU spectrophotometer at the department of Physics, Shivaji University Kolhapur. Figure 3 shows the FTIR spectrum of cobalt oxalate. The spectrum shows various frequencies of vibrational modes which confirm the presence of oxalate in the crystal.



Figure 3: FTIR of Cobalt oxalate grown crystal

The sharp peak at 3300.18 cm<sup>-1</sup> is attributed to the stretching of O–H group, indicating the presence of water of crystallization or water of hydration. However the peak at 1710. 00 cm<sup>-1</sup> to 1665.00cm<sup>-1</sup> correspond to  $\alpha,\beta$ -unsaturated aldehydes, and ketones. The two identical sharp peaks around 1367.93 and 1327.43 cm<sup>-1</sup> correspond to an asymmetric and symmetric stretch of C–H rock, respectively. Thus the FTIR spectroscopy confirmed the growth of cobalt oxalate crystals due to the presence of water of crystallization.

#### **Conclusions**

Cobalt oxalate crystals were grown by gel method using agar- agar gel in well size and shape. XRD powder diffraction patterns and analysis shows the crystalline nature of crystal with monoclinic phase. Different functional groups revealed by FTIR show the metal bond and different vibrations in the sample.

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# INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

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# Thermal and Morphological Study of Transition Metal Cobalt Oxalate Crystal Grown By Agar-Agar Gel Technique

H. S. Pawar<sup>1</sup>, S. J. Nandre<sup>2</sup>, S. D. Chavhan<sup>3</sup> and R. R. Ahire<sup>3</sup>

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## ABSTRACT

In this article, we have reported fabrication of various morphological of cobalt oxalate. Cobalt oxalate crystals were grown by agar-agar gel through the single diffusion technique. The tendency of cobalt oxalate crystals to spherulites growth was demonstrated. Also Liesegang ring are observed. The cobalt oxalate preparation method was played crucial role on the crystal structure and its morphology. The optimum growth conditions cobalt oxalate was achieved by controlling the parameters like, concentration of gel, concentration of reactants, aging period and reversing of reactants. The crystal structure of grown material was determined by TGA, DTA and EDAX.

Keywords: Crystal growth, cobalt oxalate, TGA, DTA and EDAX.

# **Introduction:**

Growth of crystal ranges from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days and to months. The starting points are the historical works of the inventors of several important crystal growth techniques and their original aim. Crystals are used in semiconductor physics, engineering, as electro-optic devices etc., so there is an increasing demand for crystal [1-5]. For years, Natural specimens were the only source of large, well-formed crystals. The growth of crystals generally occurs by means of following sequence of process. Diffusion of the molecules of the crystallizing substance through the surrounding environment. Diffusion of these molecules over the surface of the crystal to special sites on the surface. Today almost all naturally occurring crystals of interest have been synthesized successfully in the laboratory [6-9]. It is now possible only by crystal growth techniques.

#### **Materials and Methods**

Materials used to grow the cobalt oxalate crystals are cobalt chloride, oxalic acid, and agar-agar gel. All the chemicals used for the experiment were used without any further purification. Sodium silicate glass test-tubes were used as crystallizing vessels. The test-tubes were filled with the first reactant (cobalt chloride) of desired volume and morality. The second reactant, oxalic acid having a concentration range of 0.5 to 1.5 M, was poured along the walls of the test-tube into the set-gel, and allowed to diffuse into the gel medium. The open end of the tube was closed with cotton plugs and kept undisturbed. The said procedure was carried out at room temperature. The ions of the supernatant solution reacted with ions of the first reactant via capillaries formed in gel medium. After six to seven days, nucleation kick-started at the gel-solution interface. The chemical reaction that occurred between the two reactants is given as follows:

 $CoCl_2 + H_2C_2 O_4 \longrightarrow CoC_2O_4 + 2HCL$ 

The diamond-shaped, spherulites, opaque crystals were obtained in the test-tube. The crystals were harvested by washing them carefully with acetone and collected for further characterization. Table 1 shows the optimized crystal growth parameters for the cobalt oxalate crystals.

Table 1 shows the Optimum condition of cobait oxalate crystal							
Sr.No	Condition Single Diffusion	Condition Single Diffusion					
1	Percentage of gel	2.0 %					
2	Concentration of cobalt chloride	1.0M					
3	Concentration of oxalic acid	1.0M					
4	Volume of cobalt chloride	5.0 ml					
5	Volume of oxalic acid	15 ml					
6	Gel setting period	34 Hours					
7	Gel aging period	4 days					

## Table 1 shows the Optimum condition of cobalt oxalate crystal

**Liesegang rings** - are a phenomenon seen in many, if not most, chemical systems undergoing a precipitation reaction under certain conditions of concentration and in the absence of convection. Rings are formed when weakly soluble salt are produced from reaction of two soluble substances, one of which is dissolved in a gel medium [10]. The phenomenon is most commonly seen as rings in a Petri dish or bands in a test tube; however, more complex patterns have been observed, such as dislocations of the ring structure in a Petri dish, helices', and Saturn rings in a test tube [11]. Despite continuous investigation since rediscovery of the rings in 1896, the mechanism for the formation of Liesegang rings is still unclear.





Fig. 1(a) Shows the spherulites cobalt oxalate crystals (b) Shows the formation of Liesegang rings Result and Discussion-

**Thermogravimetric Analysis (TGA) of Cobalt Oxalate-** The thermogram of cobalt oxalate crystal were obtained with the help of SDT Q600 V20.9 Build 20. TGA/DTA/DSC thermal analyser available at Materials Characterization Laboratory Department of Materials Science and Engineering, Yonsei University,Room No.B307,Engineering Hall 2,50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Republic of Korea. The TGA curve of cobalt oxalate agar-agar gel grown crystal is as shown in fig (2), the percentage of the weight loss in the different stages of decomposition of cobalt oxalate are presented in the table (2). There is good agreement between the observed and calculated weight. The four stages of decomposition are described as below: In the first stage decomposition occurs in the temperature range 30°C to 177°C in which weight loss of 17.46% agrees very well with the calculated weight loss 17.58%. Thus it is clear that the crystals are hydrate and the weight loss calculation clearly indicate that cobalt oxalate crystals have nine water molecule as water of crystallization. It is notice that the sample losses water of hydration and becomes anhydrous at 177°C.

In the second stage of decomposition in the temperature range  $200^{\circ}$ C to  $247^{\circ}$ C, the total weight loss 3.411% is seen which is due to the loss 3C and 3H<sub>2</sub>O this is well agreement with calculated weight loss of 3.50%. Then an anhydrous cobalt decomposes into cobalt oxalate.

In the third stage of decomposition total weight loss 36.88% was observed in the temperature range 247°C to 260°C which corresponds to the loss of 2CO. This weight loss agrees very well with the calculated weight loss 37.00%. Thus cobalt oxalate further decomposes into cobalt carbonate.

Finally in the temperature range  $892^{\circ}$ C to  $930^{\circ}$ C, total weight loss of 2.538% was obtained. This loss is attributed to the loss of CO<sub>2</sub>. This is in well agreement with the calculated weight loss of 2.8%. Thus the cobalt carbonate finally turns into cobalt oxide at  $930^{\circ}$ C. Which is confirmed by residual weight up to the end of analysis 2.538%. This is in good agreement with calculated residual weight of 2.80%.[12-14]



Fig.2 Shows the TGA Curve of Cobalt oxalate crystal grown by agar-agar gel technique

Stage	Temperature range <sup>0</sup> C	Observed Weight loss %	Calculated Weight loss %	Loss of Molecule in stage
I	30-177 <sup>0</sup> C	17.46%	17.58%	9H <sub>2</sub> O
II	200-247 <sup>0</sup> C	3.41%	3.50%	3C and 3H <sub>2</sub> O
III	247-260 <sup>0</sup> C	36.88%	37.00%	2CO
IV	892-930 <sup>0</sup> C	2.538%	2.80%	$CO_2$

Table 2 Summarized data of TGA results of decomposition process of cobalt oxalate crystals

# Differential Thermal Analysis (DTA) -

The DTA curve for cobalt oxalate agar- agar gel grown crystal is as shown in figure(3) and the DTA data collected from this curve is tabulated in the table(3). In DTA curve we observe two endothermic peak at  $208.25^{\circ}$ C and  $919^{\circ}$ C and one exothermic peak at  $310^{\circ}$ C are due to decomposition of hydrated cobalt oxalate into anhydrous cobalt oxalate. In the first stage of decomposition, peak at  $208.25^{\circ}$ C is attributed to loss of first

 $4H_2O$  molecules immediately followed by another endothermic peak at  $919^{\circ}C$  which corresponds  $2H_2O$  molecules. The endothermic peaks observed in the DTA curve corresponds to the total weight loss of Nine water molecule in TGA curve [15-17].

Peaks recorded	Nature
208.25°C	Endothermic
919ºC	Endothermic
310°C	Exothermic

#### Table 3 DTA data of Cobalt oxalate

The exothermic peak at  $310^{\circ}$ C due to the decomposition of anhydrous cobalt oxalate into cobalt oxalate. The exothermic peak attributed to the loss of 4C molecule and endothermic at  $208.25^{\circ}$ C is attributed to the loss of 3 water molecules. The endothermic peak at  $919^{\circ}$ C is due to the decomposition of cobalt oxalate carbonate to cobalt oxide which is attributed to the loss of 2CO<sub>2</sub>.





#### Energy Dispersive Analysis by X-rays (EDAX) -

The chemical composition of as grown crystals is analyzed by Energy Dispersive X-ray Analysis (EDX). Fig. 4 shows the EDX spectrum which confirms the presence of expected elements O,C and Cu. The stoichiometric composition was computed using experimental and theoretical results of EDX. Energy Dispersive analysis by X-ray (EDAX) is used for the quantitative analysis of cobalt oxalate and is also called as elemental analysis. It conclude that the (weight & atomic %) of copper (Cu) in the grown crystal measured by EDAX are very close with the values calculated from the molecular formula.[18-22].



#### Figure 2EDAX of Cobalt oxalate

#### Table 4 EDAX of cobalt oxalate

Element	Weight%	Atomic%	Net.Int	Error	%	K	Ζ	R	Α	F
						ratio				
Ck	2.22	9.46	44.68	19.14	0.01	0.05	1.33	0.84	0.21	1.00
Ok	2.41	7.71	<mark>2</mark> 27.93	10.39	0.01	0.05	1.28	0.86	0.42	1.00
Cobalt	95.37	82.83	6779.47	1.88	0.97	0.80	0.98	1.01	1.0	1.03

#### **Conclusions** -

The present work reports the growth and characterization of cobalt oxalate single crystals. We have demonstrated the formation of cobalt oxalate single crystals in agar-agar gels. Cobalt oxalates exhibits star shaped, opaque and spherulites growth (flower) shape are observed. Further to obtain good quality single crystals of cobalt oxalate, both reactants –cobalt chloride and oxalic acid were interchanged. With cobalt chloride incorporated gels result only fibers. These facts have been explained by taking in account the interaction of the reactants ions with the sodium and silica ions. The effect of temperature on growth of cobalt oxalate crystals showed that there is a decrease in nucleation density at higher temperature which is due to the increases of the aqueous solubility of cobalt oxalate.

#### **Conclusions-**

Transition metal cobalt (II) oxalate crystal was grown by gel method using agar agar gel in well size and shape.Red –pink colour crystal were observed. In contrast bigger and better shape of red pink block crystal of cobalt oxalate observed, however, longer growth time was needed to grow the crystal.

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# Liquid Exfoliation of Decagonal Quasicrystals and Its Light Out-Coupling Performance in Organic Light-Emitting Devices

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Decagonal quasicrystals are receiving considerable attention because of their unique crystallographic structure, electrical, magnetic, and mechanical properties. Hence, anisotropic decagonal nano-quasicrystals (NQCs) will have potential applications in multifunctional devices. Here, the decagonal NQCs are prepared from an anisotropic bulk sample by liquid exfoliation via the ultrasonic process at room temperature. The NQCs have high transmittance and are incorporated into green organic light-emitting diodes via solution and dry processes for light outcoupling. The overall device performance is markedly enhanced with NQC incorporation. A power efficacy of 31.4 lm W<sup>-1</sup> is achieved at 1000 cd m<sup>-2</sup> with a 37% increment for the solution-processed device. For the dry-processed device, 66.4 lm W<sup>-1</sup> is obtained with an increment of 108%. These NQCs can be made free standing, providing OLED devices an extremely convenient and effective measure for maximizing out-coupling of the generated light, near 80% of which would otherwise be trapped and wasted within.

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1. Introduction

Quasicrystals are unusual crystals with nonperiodicity, but they retain long-range ordering with lack of translational symmetry. Quasicrystals are classified according to their symmetry (8-, 10-, and 12-fold) and quasi-periodicity (one (1D), two (2D), and three (3D) dimension). They have unique structural, mechanical, physical, and chemical properties.<sup>[1–3]</sup> Further, size reduction of quasicrystals leads to high strength.<sup>[4]</sup>

Nowadays, 2D atomically thin-layered materials have potential applications in electronics and semiconductor technologies because of their unique physical, optical, and electrical properties.<sup>[5,6]</sup> 2D layered materials are stacked by van der Waals interlayer (weak) bonding and able to exfoliate into few or atomic thin layers with a

crystalline nature.<sup>[7]</sup> Similarly, a large area of mono- and fewlayers of 2D quasicrystals have been prepared from the 3D icosahedral Al-Pd-Mn quasicrystal by liquid exfoliation.<sup>[8]</sup> The stability of the Al-Pd-Mn quasicrystal was retained after the exfoliation with icosahedral symmetry. Still, the exfoliation technique is not explored in other quasicrystals with different symmetry. Particularly, decagonal quasicrystal shows its unique nature with two-dimensional quasiperiodic planes, whereas Al-Co-Cu based alloys stand out as a stable decagonal quasicrystal with a wide composition range.<sup>[9]</sup> The stability of the quasicrystal was found to increase with increasing Co concentration and a stable decagonal single crystal grown in the Al-Cu-Co alloys.<sup>[10,11]</sup> The bulk Al-Co-Cu quasicrystal has high electrical conductivity in both the periodic and quasiperiodic direction, and behaves like a metallic conductor.<sup>[12]</sup> Since the decagonal quasicrystals (Al-Co-Cu) show two-dimensional quasiperiodicity and one-dimensional periodicity in bulk, it is more convenient to exfoliate stable quasicrystal with a few layers of thickness. In general, one- to three-dimensional (1D, 2D, and 3D) quasicrystals have attracted significant interest in various applications. In particular, photonic quasicrystals have been used to improve the targeted spectrum efficiency.<sup>[13-15]</sup> The photonic quasicrystal structure guides to couple out the trapped light in the waveguide because of the total internal reflection.<sup>[16]</sup> In addition, quasicrystal-structured substrates have also been implemented to enhance the efficiency of OLED applications.<sup>[17–19]</sup> However, until now, the direct use of quasicrystal materials in OLED applications has not been examined.

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In addition, organic light-emitting diodes (OLEDs) continue to play a pivotal role in modern lighting and display technologies. The advantageous features specifically associated with OLEDs, such as low turn-on voltage, diffused light emission, high to low color temperature tunability, rapid response time, excellent color gamut, and flexibility have been integrated and reinforced in state-of-art electronic gadgets. However, high-efficiency OLED devices have vet to materialize. A major limiting factor is the failure to extract all emitted light. The internal loss of the light of up to 40-60% is mainly due to the large differences between the refractive indices of the indium tin oxide (ITO)/organic laver and glass substrate and air.<sup>[20-23]</sup> To minimize these losses, the surface plasmonic method<sup>[24]</sup> and various light extraction methods have been adopted, such as Bragg diffraction grating,<sup>[25]</sup> low-index grids,<sup>[26]</sup> and nanostructured surface substrates.<sup>[27]</sup> However, most of the available methods are expensive as well as too complex, for large-scale production .<sup>[26,28,29]</sup>

In the present study, a novel approach of the Al–Co–Cu based nano-quasicrystal is designed and developed for OLED application. Nano-size quasicrystals (Al–Co–Cu) are synthesized by liquid exfoliation via the ultrasonic-assisted process. Nanoquasicrystals are used for external light out-coupling and significant improvements of OLED power efficiencies, EQE, and luminance are achieved.

#### 2. Results and Discussion

# 2.1. Structure and Composition Analysis of Bulk and Exfoliated Quasicrystals

The x-ray diffraction (XRD) patterns of the Al-Co-Cu quasicrystal are shown in Figure 1a, with the sharp Bragg diffraction patterns indicating the stability of the decagonal quasicrystals. The diffraction patterns of the decagonal quasicrystals are identified with six independent indices according to Mukhopadhyay et al.<sup>[30]</sup> report. Different diffractions with various compositions were reported, such as Co concentration containing Al-Co-Cu quasicrystals with icosahedral and decagonal quasicrystal patterns.<sup>[9]</sup> Increasing Co concentration leads to a single decagonal quasicrystal phase. In the present study, Al-Co-Cu quasicrystal was prepared with high Co concentration and also annealed for a long time to obtain a stable quasicrystal phase. According to the crystal growth studies,<sup>[10,11]</sup> the decagonal quasicrystal plane is stacked along the ten-fold axis and then they are grown along the periodic direction [000001] and perpendicular to the quasiperiodic directions. After the liquid exfoliations (Figure 1a), the obtained sample retained the decagonal quasicrystals' nature without secondary phases. The relative intensity of the



Figure 1. a) Powder XRD pattern of bulk and exfoliated quasicrystals, b,c) TEM mapping of exfoliated quasicrystals and d) High-magnification image of exfoliated quasicrystal and height profile (inserted).
pared to the (000004) plane in a are pla

(101100) plane increased as compared to the (000004) plane in exfoliated samples. Moreover, no significant change in peak position was found in the exfoliated quasicrystal as compared with the bulk quasicrystal. The XRD result indicates the quasicrystal nature increased after exfoliation as the thickness of the layer decreased. The obtained results differ from the 2D Al–Mn–Pd quasicrystals, which were exfoliated from 3D icosahedra quasicrystal.<sup>[8]</sup> The exfoliated decagonal quasicrystals show similar behavior to that reported in the few layer 2D transmission metal chalcogenides.<sup>[31,32]</sup>

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The bright field transmission electron microscope (TEM) image of the exfoliated quasicrystal is shown in the Figure 1b. A sheetlike morphology with an  $\approx$ 325 nm lateral size of quasicrystals was observed. The elemental mapping of the exfoliated quasicrystal confirmed the presence of the Al, Co, and Cu elements and their uniform distribution in the sample. The average elemental composition of the sample is determined to be 68.89 at% of Al-17.79 at% of Co-13.3 at%. Cu had slightly higher Al content as compared with the prepared bulk quasicrystal. The highmagnification image of the thin layers of 2D quasicrystal images is shown in Figure 1c. Nonhomogeneity in the surface was found and the nano-quasiparticles were placed on the sheet morphology. The nano-quasicrystal is unstable under high-resolution beam conditions and lost its structural properties. However, it is not deformed into the crystalline nature and became amorphous.

For more information of the exfoliation quasicrystals, a thin layer was chosen for TEM analysis. Bright field image and elemental mapping of the exfoliated quasicrystal, as shown in Figure 1d, show the exfoliated decagonal quasicrystal consists of a few layers of nanosheets. In addition, small-sized nanoparticles are observed on the top of the nanosheets. The elements are distributed uniformly in the nanoparticles, although their composition shows excess Al.

In contrast, lower concentrations of Co and Cu with Al-rich conditions were observed in a few layers of the nanosheets, as reported in the 2D Al-Mn-Pd quasicrystals.<sup>[8]</sup> In case of Al-Mn-Pd,<sup>[8]</sup> the atomic positions of all the elements (Al, Mn, and Pd) were calculated using density functional theory (DFT) calculations, whereas the thin atomic layer Al sheet formed initially, Mn and Pd atoms later formed on top of the Al sheet to stabilize the structure. However, they did not clearly report the elemental distribution on the Al sheet in the experimental details. The present study observed Al sheet formation with Co and Cu distribution from the energy dispersive X-ray analysis (EDAX) Map. It is concluded that Co and Cu are formed on the top of the Al sheet to form a stable quasicrystal nature. In addition, small nano-quasicrystals found on the sample with higher Co and Cu concentration. From the XRD result, no significant shift in exfoliated nano-quasicrystal occurs by varying the Co and concentrations, indicating large size nano-quasicrystals are more dominant than small nanoquasicrystals in the diffraction pattern. The Co and Cu deficiency might lead to more defects in nanolayered quasicrystals. The concentration of Co and Cu increased with increasing thickness of the nanostructured quasicrystals up to the bulk limit.

The AFM image of exfoliated quasicrystals drop coasted on the ITO/glass substrate is shown in **Figure 2**a. Exfoliated quasicrystals with various height distributions from 5 to 35 nm were observed with different surface morphology. The lateral size of the nanoparticles also varies from 100 to 600 nm and they

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are placed on top of the quasi-nanosheets. The obtained nanodecagonal quasicrystal morphology and size differ from the 2D flakes of the Al–Mn–Pd.<sup>[8]</sup> The decagonal QCs could grow up to a few mm in size in single crystal form.<sup>[10]</sup> During the sonication, the large size particles were broken into nanoparticles and also removed during the centrifuge with high speed. The NQCs dispersion in 3D view is shown in Figure 2b. A large number of NQCs are distributed from 5 to 15 nm height with a maximum density of around 9 nm and distributed up to 35 nm, as shown in Figure 2c. The thickness of the NQCs is comparable with the TEM results.

Wavelength-dependent transmission and the absorption of ITO, as well as external out-coupling of NQC on the ITO/glass substrate are shown in Figure 2d. Almost more than 90% of the transmission was demonstrated at a wavelength of 500–580 nm in the emission region of the emitter (PO-01). The corresponding absorption was observed in all the samples, indicating the NQCs did not observe a significant wavelength in the green emission region. Hence, the effect of surface plasmonic polarization could be ruled out. This indicates scattering of light at a low wavelength by NQCs became more transparent at a high wavelength in the measured range, particularly, in the green light region. The NQC-like particles might scatter the light and the NQC sheets became transparent.

# 2.2. OLED Device Performance with Quasicrystal Incorporation in External Approach via Solution Process

**Figure 3**a,b represents the schematic illustration of the decagonal nano-quasicrystals utilized device structures. To clearly understand the nano-quasicrystals' role, both solution-processed (Figure 3a) and the dry-processed (Figure 3a) device were fabricated with NQC. The NQCs were deposited on the rear side of the substrate for external out-coupling.

A comparison of the electroluminescent characteristics of the solution and dry-processed OLED devices with and without quasicrystals in terms of power efficiency ( $\eta_p$ ), current efficiency ( $\eta_c$ ), and external quantum efficiency (EQE) at 100, 1000, and 10 000 values of each parameters is summarized in **Table 1**. D1 and D2 represent OLED devices without and with NQCs in solution process.

The performance of the device with nano-quasicrystal (D2) improved with a power efficiency of  $31.4 \text{ Im W}^{-1}$  (Figure 4a), current efficiency of  $31.1 \text{ cd A}^{-1}$  (Figure 4b), and EQE of 13.1% at 1000 cd m<sup>-2</sup>. Overall power efficiency, current efficiency, and EQE increased to 37 and 31%, respectively, as compared to the device fabricated (D1) without quasicrystals. The plot of luminance versus the applied bias voltage shown in Figure 4c shows a decrease in the operating voltage of the device with nano-decagonal quasicrystal. The luminance increased with NQCs and reached a maximum at 18 800 cd m<sup>-2</sup>, as compared to the device (16 430 cd m<sup>-2</sup>) without NQCs.

# 2.3. OLED Device Performance with Quasicrystal Incorporation in External Approach via Dry Process

Devices D3 and D4 represent without and with NQCs prepared from the dry process. The best performance was observed for the



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Figure 2. a) AFM image of exfoliated quasicrystal b) 3D view, c) statistical density of NQCs with high profile, and d) transmittance and absorption versus wavelength spectrum of NQC on/back side of the ITO/glass substrate.



Figure 3. Modified decagonal nano-quasicrystals as external out-coupling in a) solution process and b) dry process.

Table 1. Effect of decagonal nano-quasicrystals on green devices performance from the perspectives of operation voltage (OV), power efficiency (PE), current efficiency (CE), external quantum efficiency (EQE), CIE coordinates, and maximum luminance.

Fabrication process	Device	OV [V]	Power efficiency $[Im W^{-1}]$	Current efficiency [cd $A^{-1}$ ]	EQE [%]	Max Lumi. [cd m <sup>-2</sup> ]
			@100/1000/10 000 [cd m <sup>-2</sup> ]			
Solution	D1(W/O)	3	32.1/22.9/7.1	30.51/26.4/8.98	11/10/4.9	16 430
Processed	D2 (W/NQC)	3.2	47.9/31.4/10.2	47.04/31.1/10.1	15.2/13.1/6.9	18 800
Enhancement [%]	_	-	49/37/44	50.17/17.6/13	38/31/41	_
Dry	D3 (W/O)	3	50.1/31.8/11.4	56.8/47.3/26.4	15.4/12/7.1	18 740
Processed	D4 (W/NQC)	2.8	58.3/66.4/32.5	53.2/70.8/55	14.6/19.5/15.2	37 000
Enhancement [%]	_	-	16/108/41	-/50/108	-/63/114	-



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Figure 4. a,d) power efficiency, b,e) current efficiency, and c,f) luminance of OLED devices in solution and dry process, respectively.

external out-coupled NQCs fabricated device (D4), as measured by a power efficiency (Figure 4d) of  $66.4 \,\mathrm{lm} \,\mathrm{W}^{-1}$ , current efficiency (Figure 4e) of  $70.8 \,\mathrm{cd/A}$ , and EQE of 19.5% at  $1000 \,\mathrm{cd} \,\mathrm{m}^{-2}$ . The obtained power efficiency, current efficiency, and EQE increased in corresponding luminance values by 108%, 50%, and 63%, respectively, as compared to the OLED without a quasicrystal (D3). A significant enhancement of device performance at high luminance has been reported in various lightcoupling methods.<sup>[33–36]</sup> The performance of OLED device with NQCs is less at  $100 \,\mathrm{cd} \,\mathrm{m}^{-2}$  and it enhanced at high luminance.

The luminance versus applied voltage graph (Figure 4f and Table 1) shows the operating voltage of the decagonal nano-quasicrystals with external coupling (D4) is lower than the normal device (D3), indicating the QC nanoparticles help to reduce the operating voltage of the fabricated OLED devices by out-coupling. The luminance enhanced with NQCs and reached a maximum at 37 000 cd m<sup>-2</sup>, as compared to the device (18760 cd m<sup>-2</sup>) without NQCs. Similarly, the luminance was enhanced by external out-coupling in lens-free OLED devices.<sup>[33,37]</sup> The superior out-coupling performance of the decagonal nano-quasicrystal device is attributed to scattering 1) by large size NQCs, 2) by defects in the few layer NQCs via light propagation.

**Figure 5** shows the normalized electroluminescent spectra of all the devices with and without the quasicrystals. The peaks of the emission spectra for the green OLED devices reveal the emission from all devices in the green region. The nature of the EL spectra emission seems to be very similar to all green OLED devices.

#### 3. Conclusion

For the first time, decagonal nano-quasicrystals are prepared by liquid exfoliations and their decagonal quasicrystal nature is



Figure 5. Normalized electroluminescence (EL) spectra as a function of wavelength of the studied OLED devices via solution and dry process.

confirmed. The NQCs are successfully incorporated into external out-coupling via solution and dry process for green light OLED devices. The incorporation of nano-quasicrystals improved the power efficiency (37% and 108%), current efficiency (17.6% and 50%), and EQE (31% and 60%), by improving light out-coupling performance at 1000 cd m<sup>-2</sup> in solution and dry process, respectively.

The maximum luminance with NQCs is achieved at 37 000 cd m<sup>-2</sup> as compared to the device (18760 cd m<sup>-2</sup>) without NQCs in dry process. This is a low cast and free standing nano-quasicrystal with scalable method for light out-coupling applications in OLED devices as compared with quasicrystal-patterned devices. In general, different quasicrystals have various

crystallographic dimensions with symmetry and a band gap, which can be explored in the future. The novel application of decagonal nano-quasicrystals in the OLED devices is the ideal platform for different quasicrystal materials in optoelectronic applications.

#### 4. Experimental Section

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For preparing bulk quasicrystal (Al<sub>66.5</sub>Co<sub>19.5</sub>Cu<sub>14</sub>), high-purity elemental metals of Al (99.999%), Co (99.95%), and Cu (99.9%) were weighed according to the stoichiometry and arc-melted in an argon atmosphere. The arc-melted sample was then placed in a graphite crucible and sealed inside a quartz tube under a vacuum of  $10^{-2}$  Pa. The sealed sample was then annealed at 900 °C for 15 days, which was followed by water quenching. A total of 10 mg of prepared quasicrystal in powder form was placed in DMF *N*,*N*-dimethylformamide solvent (50 mL) and sonicated for 60 h. Following sonication, the sample was centrifuged at 5000 rpm for 10 min to separate and remove the unexfoliated quasicrystals. The exfoliated sample with the DMF solution was then dispersed in ethanol and drop casted on a glass substrate for XRD, on a Si substrate for TEM analysis.

XRD was carried out on all samples for phase identification using D2 (Bruker, USA). The morphology and elemental analysis (EDS) of the quasicrystals were performed using a FEI Talos F200X (FEI, USA). The topological information was carried out by AFM(Bruker, Dimension ICON, USA) in the tapping mode at room temperature under ambient conditions. Transmission spectrum was obtained using a UV-vis spectro-photometer U-3010 (Hitachi, Japan).

For solution process, the quasicrystal containing DMF solution of 400  $\mu L$  was drop cast on the bottom of the glass substrate at 180 °C in a glove box under a nitrogen atmosphere. Later, PEDOT:PSS as a hole injection/transport layer, and EML solution CBP and Ir(ppy)\_2(acac) were spin coated on the ITO/glass substrate for 20 s at 4000 and 2500 rpm, respectively, in a nitrogen-filled glove box. The depositions of TPBi as an electron transport layer, LiF as an electron injection layer, and Al as a cathode layer were carried out using a high-vacuum thermal evaporator.

For dry process, the quasicrystal containing DMF solution of 400  $\mu$ L was drop cast on the bottom of the glass substrate at 180 °C in a glove box under a nitrogen atmosphere. On ITO-coated glass substrate, 5 nm 1,4,5,8,9,11-hexaazatriphenylene-hexacarbonitrile (HAT-CN) as a hole injection layer (HIL), a 35 nm di-[4-(*N*,*N*-ditolylamino)-phenyl]cyclohexane (TAPC) as a hole transport layer (HTL), CBP, TPBi, LiF, and Al were fabricated via sequential thermal evaporation for both the organic and inorganic materials under high vacuum (10<sup>-6</sup> Torr) conditions. A reference device was fabricated without quasicrystals.

*Device Characterizations*: The characterization of the final device was done in an ambient atmosphere without encapsulation. The current–voltage– luminance characterization was carried out using a computer-interfaced Keithley 2400 electrometer and Minolta CS-100 A luminance–meter. Emission spectra were recorded by a PR-655 spectroradiometer. The emission area of the OLED device was 0.09 cm<sup>2</sup>, calculated from the overlapping of the ITO and Al electrodes.

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#### **Conflict of Interest**

The authors declare no conflict of interest.

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#### Keywords

light out-coupling, nano-quasicrystals, OLEDs

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# Synthesis and characterization of ZnO nanoparticles by sol-gel method.

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## Abstract

Zinc oxide nanoparticles were prepared by sol-gel technique via two different approaches having by employing zinc sulphate and sodium hydroxide. In the first approach, NaOH was added dropwise with regular interval (ZnO-A) whereas in the second approach NaOH was directly mixed with ZnSO4 solution (ZnO-B). The physical properties of the synthesized nano-particles were studied by X-ray diffraction technique and scanning electron microscope to investigate the structure and morphology of the material, respectively. It was observed that the both the grown ZnO particles revealed the crystalline properties. From the Debye-Scherrer formula , the particle size of ZnO-A was found to be 10nm whereas for ZnO-B it was found to be 7.7 nm. The SEM morphology exhibited the grown particles have uniformity. The synthesized ZnO particles could be used for various opto-electronic devices.

## Keywords: Debye-Scherrer Formula, sol-gel, FWHM, Whatman filter paper.

## Introduction

Due to diverse technological applications, ZnO has been an active area of research for more than half a century. It has many interesting optoelectronics properties such as wide band gap (~3.37 eV), a large excitation binding energy of 60 meV and high dielectric constant. Therefore, it can be used in the fabrication of electronics and optical devices such as UV/blue laser (Jhonson*et al* 2001), light-emitting diodes (LEDs), Solar Cells, and Organic light-emitting diodes (OLEDs). The size dependent optical properties of this material are very interesting and it can also be tailored with annealing temperature.

Because of these properties, it can be used for the wide range of applications like fabrication of switching element, transistors (Arnold et al 2002) and detectors. It is transparent to the most of the solar spectrum, therefore widely used for window material in solar cells, optical waveguide, light modulators and optical sensors. Therefore the controlled synthesis of good quality ZnO nanostructures, nano crystals (Singh & Gopal 2008a), nano wires, nano belts and other nano architecture are very important. Several routes are employed to synthesis the ZnO nano materials particularly solvothermal (Dev*et al* 2006), thermal evaporation (Pan *et al* 2001, Kong *et al* 2004), solid state pyrolysis (Wang *et al* 2003), chemical vapour deposition (Fay *et al*2005; Xiang *et al* 2007), molecular beam epitaxy (Agashe*et al* 2004)

and laser ablation (Singh *et al* 2008) etc. These technologies are very expensive and difficult to use for large area fabrication. Therefore, to overcome these difficulties, we have adopted the low-cost sol-gel technique to grow the ZnO nanomaterials.

In this paper we report the characterization of ZnO nanomaterial synthesized by ZnO different method using hydroxide route. Structural and surface morphology properties have been studied by using X- Ray Diffraction and Scanning Electron Microscope techniques.

#### EXPERIMENTAL

ZnO is prepared by conventional precipitation method using sodium hydroxide and zinc sulphate solutions. Calcinations of zinc hydroxide gives zinc oxide in powder form. For the preparation of zinc hydroxide, sodium hydroxide solution is mixed with sodium suphate solution in two ways, in the first approach (i.e. ZnO-A) sodium hydroxide is mixed drop wise with zinc sulphate solution and for second approach (ZnO-B) it has been mixed in one-shot with the same.

First of all homogeneous solution of NaOH is prepared by dissolving 1.6 g of NaOH (Merk Specialties Private Ltd, India) in 40 g of distilled water. The pH value of NaOH was found 11.57. The recorded humidity and temperature during experiment was found 29% and 34.5<sup>o</sup>C respectively.

Similarly, a homogeneous solution of ZnSO<sub>4</sub> (Chemical Corporation of India) in 120 ml of water. Then NaOH solution was mixed drop wise with regular interval of time with continuous stirring for 35 min. The mixture was allowed to stir for next 30 minute more and left it for another 48 hours. The obtained product was filtered using Whatman filter paper and washed properly with deionised water to remove all the sulphate ions etc. The white precipitate containing zinc hydroxide was spread on the glass substrate. The glass substrate was placed in an oven and alternate heating and cooling was applied. First of all it was heated at 150°C for one hour then allowed to cool for 30 minute. The process of heating for one hour and subsequent cooling for 30minute was repeated for five times. Hence after total heating for five hour, ZnO-A is collected in powder form.

Similarly in method (B) again similar solution of NaOH and ZnSO<sub>4</sub> as in method (A) having same pH value and at room temperature were prepared. In this method NaOH solution was allowed to mix in one-shot in ZnSO<sub>4</sub> solution. The mixture was allowed to stir continuously for 12 hour then left for 72 hour. After 72 hour the mixture was filtered out by Whatman filter paper and washed properly through with deionised water to remove all the sulphate ions etc. After washing properly the residue i.e. zinc hydroxide was spread on a glass substrate. After applying similar process of heating and cooling as in method (A) i.e. subsequent heating for 1 hour and cooling for 30 minute for five times, ZnO-B is collected in powder form.

#### **RESULT AND DISCUSSION**

#### Surface morphology study by SEM:

The morphology of synthesized powder was investigated with scanning electron microscope (SEM, Edex). Figure 1(a) and (b) show the morphology of the ZnO film prepared by sol-gel technique for both methods. Method (A) and method (B) give the ZnO nanomaterial in the form of cluster and nanosheets showed in figure 1(a) and 1(b) respectively. The image obtained by SEM shows that the particle prepared by method (A) exist in cluster form whereas that obtained in method (B) does not exist in cluster form. The particles prepared by this process are named as ZnO- A and ZnO –B.



Figure 1(a): SEM image of ZnO - A prepared by method - A



Figure 1(b): SEM image of ZnO - B prepared by method - B

#### **Crystal Structure study by XRD:**

The crystalline property of synthesized powder was investigated with XRD (Mini Flex, Rinku Corporation, Japan). The X-ray diffraction data were recorded with Cu K<sub> $\alpha$ </sub> radiation have wavelength 1.5 418 Å. The intensity data was collected over the range 10<sup>0</sup> to 70<sup>0</sup>. The most intense peak (Fig.2 a and b) were considered for the sample ZnO- A and ZnO –B. the peaks are very intense which shows that the the grown material is crystalline in nature. The peak of ZnO –B is more intense with respect to ZnO- A. it shows that ZnO –B is more crystalline than ZnO- A. by calculating the FWHM values of the above sample, the sizes of the crystals are calculated by Debye Scherer Formula (Vermeulen*et al* 2007). The size of ZnO- A and ZnO –B were found 10nm and 7.7 nm respectively. The size of the particle prepared by the method as for ZnO –B is more fine with respect to ZnO- A.

The size of the crystal in the direction perpendicular to the reflecting plane is given by Debye Scherer Formula



$$D = \frac{k\lambda}{\beta cos\theta}$$

Where k is constant its value lies from 0.89 to 1.39 depending on the specific geometry of the scattering object. For two dimensional lattices the value of k was found to be 0.89 while that of three dimensional lattices is 1.3.  $\beta$  is the FWHM of the peak in radians,  $\theta$  is the diffraction peak position and  $\lambda$  is the wavelength of the x-rays used.

The experimental result was found to be

For ZnO- A:  $2\theta$ = 12.56,  $\theta$  = 6.28,  $\beta$  (FWHM)=0.01396(in radian), K=0.89. Size of ZnO-A, **D**<sub>1</sub>- **10.0nm** 

For ZnO –B:  $2\theta$ = 12.40,  $\theta$  = 6.20,  $\beta$  (FWHM)=0.01815(in radian), K=0.89. Size of ZnO-B, D1- **7.7nm** 

## Conclusion

Synthesis method plays an important role in monitoring structural properties of materials as shown by the Scanning Electron Microscope and X-ray Diffraction study of ZnO nanomaterials. It was found that the particle of ZnO-B is highly crystalline and size of particle is also very fine with respect to the sample prepared by method –A. This morphological change due to difference in applied physical parameters i.e. due to different sedimentation time and stirring time. So, by changing synthesis method we can obtain different types of ZnO nanomaterials and change the crystallinity of ZnO nanomaterials.

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