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# Synthesis, optical properties, and blue electroluminescence of fluorene derivatives containing multiple imidazoles bearing polyaromatic hydrocarbons

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## ABSTRACT

Fluorene decorated with multiple imidazole units in a non-conjugated fashion and featuring polyaromatic hydrocarbons such as anthracene or pyrene were synthesized and characterized as blue emitters suitable for application in organic light-emitting diodes. The optical absorption and emission peak profiles remained unaltered on increasing the imidazole loading on fluorene. But the molar extinction coefficient progressively increased on introduction of additional imidazole unit attributable to the increment in the chromophore density. Replacement of phenyl group at the C-2 of imidazole nucleus with polyaromatic hydrocarbons such as anthracene and pyrene led to a red-shift in the absorption and emission spectra due to their characteristic absorption features. All the compounds exhibited high thermal decomposition temperature in the range 395–509 °C showing significant thermal robustness. The anthracene and pyrene derivatives were demonstrated as efficient blue emitters in 4,4'-di(9*H*-carbazol-9-yl)-1,1'-biphenyl host for multilayered organic light-emitting diodes.

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# 1. Introduction

Organic materials suitable for application in organic lightemitting diodes (OLEDs) have been intensively studied due to their potential application in electroluminescent devices used in high-resolution, full-color, and flat-panel displays.<sup>1</sup> To achieve practical utility for such devices, organic or organometallic materials exhibiting emission in one of the three primary colors (blue, green, or red), high electroluminescence (EL) efficiencies, good thermal stabilities, and excellent charge-carrier injection/transport abilities are required. Though the green- and red-emitting diodes<sup>2,3</sup> have been demonstrated with satisfactory functionalities, the performance of blue-emitting diodes remains below required excellence limits. It is partially due to their intrinsic electronic features such as wide band gap and low lying HOMO energy level, which retard the injection of charge carriers in the molecular layer of blueemitting materials. So the researchers are actively involved in the design and the synthesis of blue-emitting materials with color purity in emission and good charge injection/transport capabilities remains active.

Variety of organic compounds containing functional chromophores such as styrylarylene,<sup>4</sup> fluorene,<sup>5</sup> fluoranthene,<sup>6</sup> quinoline,<sup>7</sup> quinoxaline,<sup>8</sup> anthracene,<sup>9</sup> carbazole,<sup>10</sup> triarylamines,<sup>11</sup> and pyrene<sup>12</sup> have been designed and synthesized toward realizing efficient blue OLEDs. Among the various blue-emitting materials reported, anthracene<sup>9</sup> and pyrene containing<sup>12</sup> molecular materials have emerged as efficient blue emitters in OLEDs because of their unique optical and electrochemical properties. But the drawback with the anthracene and pyrene derivatives are their unwanted longer-wavelength emission and emission-quenching in the solid state or concentrated solutions attributed to excimer formation by  $\pi-\pi$  stacking interactions.<sup>13</sup> This drawback can be eliminated either by structural alternations or by the use of appropriate device architectures. Structurally, introduction of sterically demanding alkyl or aryl units or non-planar structural elements at the lateral position of the conjugation backbone has been found to impede the aggregation propensity of such derivatives and enhances the OLED performance.<sup>12c,14</sup> Further employing device architectures in which the emitting dye is doped in a host matrix composed of hole and/or electron-transporting or hole/electron blocking materials were also found to be beneficial for deep-blue emission. This kind of concentration dilution in solid solutions effectively suppresses the aggregation and the correct choice of host will ensure efficient







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energy transfer to the emitting material to give efficient OLED performance.<sup>12d,15</sup>

2,4,5-Trisubstituted imidazoles possess non-coplanar structure, which is beneficial to retard aggregation.<sup>16</sup> So the use of arylated imidazoles as an emitting chromophore in a molecular design will be beneficial for favorable properties such as emission color purity. photoluminescence quantum yield, and thermal stability.<sup>17</sup> Imidazole and arene-fused imidazole units such as benzimidazole.<sup>18</sup> pyridoimidazole,<sup>19</sup> pyrrolloimidazole,<sup>20</sup> fluorenoimidazole,<sup>21</sup> phe-nanthroimidazole,<sup>22</sup> pyrenoimidazole,<sup>23</sup> etc. have been used in the construction of multifunctional organic materials and appropriately exploited for application in organic light-emitting diodes or dye-sensitized solar cells. In this work, we report the synthesis and optical, electrochemical, and thermal characterization of six fluorene-bridged non-conjugated bis- and tris-imidazoles. The imidazole chromophores were connected to the fluorene core via a methylene linkage at C2 and C7 or C2, C5, and C7 positions of the fluorene nucleus. Tri-substituted fluorene derivatives are relatively scarce and their use in OLEDs remains unexplored.<sup>24</sup> To impart desirable emission properties, polyaromatic hydrocarbons such as anthracene or pyrene are introduced at the C2 position of imidazole nucleus. Due to the fused and rigid structure they are expected to play a beneficial role to improve the thermal stability of the final compounds. The molecules were designed to inherit the absorption and the emission properties of polyaromatic hydrocarbons and exhibit additional charge transporting capabilities attributable to the imidazole unit.

### 2. Results and discussion

## 2.1. Synthesis and characterization

The synthetic pathway employed to synthesize the fluorenebridged non-conjugated bis- and tris-imidazoles is shown in Scheme 1. The non-conjugated imidazoles **4** and **6** were obtained by N-alkylation of **3** with bis- and tris-bromomethylated fluorenes **2** and **5**,<sup>24</sup> under phase transfer catalytic conditions. The *N*unsubstituted imidazoles (**3**) required were constructed from the corresponding diketones and aryl aldehydes as reported in our earlier publication.<sup>25</sup>

# 2.2. Photophysical properties

The photophysical properties of the compounds were investigated by measuring absorption and emission spectra in a series of solvents of varying polarity *viz.* toluene (Tol), dichloromethane (DCM), chloroform (CHCl<sub>3</sub>), *N*,*N*-dimethylforma-mide (DMF), acetonitrile (ACN), and methanol (MeOH) at the concentration of  $2 \times 10^{-5}$  M and  $2 \times 10^{-6}$  M, respectively. The absorption spectra of the imidazoles (**4a**–**4c** and **6a**–**6c**) recorded in toluene are displayed in Fig. 1 and the absorption parameters are listed in Table 1.



Fig. 1. Absorption spectra of 4a-4c and 6a-6c recorded in toluene.

Compounds containing 2,4,5-triphenylimidazole units (**4a** and **6a**) exhibited poorly resolved absorption peaks originating from fluorene and phenyl units below 320 nm. A hump observed at ~310 nm for all the compounds is attributed to the fluorene localized  $\pi - \pi^*$  transition.<sup>26</sup> Other derivatives (**4b**, **4c**, **6b**, and **6c**) displayed signature peaks attributable to the anthracene<sup>27</sup> and pyrene<sup>27b</sup> chromophores. Consequently, the anthracene containing



Scheme 1. Synthesis of non-conjugated fluorene-bridged imidazoles (4a-4c and 6a-6c).

Tuble 1						
Absorption	properties	of 4a-4	c and 6a-	- <b>6c</b> in	different	solvents

Dye	$\lambda_{abs}$ , nm ( $\epsilon \times 10^3$ , N	$I^{-1} \text{ cm}^{-1}$ )					
	Tol	DCM	CHCl <sub>3</sub>	DMF	ACN	MeOH	
4a	312 (42.5)	311 (40.9)	311 (39.3)	311 (39.8)	310 (39.0)	310 (33.7)	
	300 (47.1)	284 (62.9)	284 (64.1)	283 (59.3)	281 (65.9)	279 (67.6)	
6a	307 (61.4)	307 (58.4)	307 (56.4)	307 (57.3)	306 (56.3)	307 (49.9)	
		285 (83.9)	285 (85.2)	285 (78.8)	284 (85.4)	284 (89.5)	
4b	389 (16.5)	389 (17.0)	395 (15.1)	389 (16.6)	387 (17.3)	387 (16.8)	
	371 (16.0)	370 (17.3)	376 (18.6)	371 (17.2)	369 (17.6)	369 (18.0)	
	312 (28.0)	354 (11.8)	362 (14.6)	355 (11.6)	353 (11.8)	352 (12.5)	
		311 (27.8)	311 (26.8)	311 (25.9)	311 (25.9)	311 (24.4)	
6b	390 (22.9)	390 (23.3)	392 (22.7)	390 (22.9)	388 (23.3)	389 (23.2)	
	373 (22.8)	372 (24.3)	375 (25.6)	372 (23.9)	370 (24.6)	370 (25.8)	
		356 (16.6)		356 (16.0)	354 (16.8)	353 (17.9)	
4c	347 (50.1)	345 (55.5)	350 (57.6)	347 (53.8)	344 (55.9)	343 (59.5)	
	312 (45.0)	312 (45.5)	311 (37.3)	311 (44.5)	310 (44.3)	310 (40.7)	
		278 (96.2)	280 (91.6)	278 (93.4)	277 (97.7)	276 (93.7)	
6c	347 (71.6)	346 (77.0)	349 (78.9)	347 (75.9)	344 (77.4)	344 (80.6)	
	310 (53.5)	309 (53.8)	280 (118.5)	308 (55.7)	277 (127.1)	311 (46.5)	
	. ,	278 (118.6)		278 (123.2)	268 (107.5)	277 (125.3)	
		()				267 (104.7)	

derivatives (**4b** and **6b**) showed most red-shifted absorption. On comparing the bis-imidazoles with the corresponding trisimidazoles the following salient features emerge: (a) absorption peaks mainly arise from the localized electronic transitions and the inter-chromophoric electronic interactions are negligible (b) molar extinction coefficients of the absorption peaks attributable to aryl units (phenyl, anthracene, or pyrene) progressively increased with the number of imidazole units on fluorene. The increment in the chromophore density on incorporation of additional imidazole moiety on fluorene nucleus is responsible for this hike in optical intensity. The absorption profile of the compounds was insensitive to the solvent polarity, which indicates that the effect due to the interaction of the dyes with the solvent molecules in the ground state is less important.

The emission spectra of the compounds recorded for toluene solutions are shown in Fig. 2 and the relevant data compiled in Table 2 for other solvents also. The emission peak values followed a trend as per the nature of the aryl unit on imidazole: benze-ne<pyrene<anthracene. This is reminiscent of an order expected for the unsubstituted aromatic segments. It appears that the electronic delocalization from the aromatic segment into the imidazole unit is very limited. The bis- and tris-imidazoles showed similar emission profiles. Lophine derivatives showed emission in the



Fig. 2. Emission spectra of 4a-4c and 6a-6c recorded in toluene.

UV-region while the anthracene and pyrene derivatives emitted in blue-region.

Though the lophine derivatives (4a and 6a) did not display alternations in the emission profile on changing the solvent polarity, the anthracene (4b and 6b) and pyrene (4c and 6c) derivatives exhibited prominent positive solvatochromism (Table 2). The later observation suggests the stabilization of excited state in polar solvents for the anthracene and pyrene derivatives. Though there is no inherent bipolar character in these molecules, it is probable that electronic excitation induces significant change in the dipole moment for the molecules. Consequently the interaction of induced molecular dipole with the solvent dipole is more favorable in polar solvents with appreciable polarizability. Interestingly, a blue shift in emission profile was observed for the anthracene and pyrene derivatives when recorded in methanol. As this blue shift is not seen for the lophine derivatives, we believe that hydrogen bonding interaction with the solvent may not be a plausible reason. Alternatively, pronounced hydrophobicity of the pyrene and anthracene derivatives may be responsible for this unusual shift. Due to this probably an 'oil in water' effect is operating and bringing the fluorophores together and leading to aggregates, which cause blue shift in emission. The Stokes shifts of the lophine (4a and 6a) and pyrene (4c and 6c) derivatives are significantly larger than those observed for the anthracene derivatives (4b and 6b). This probably suggests a reasonable structural reorganization in the excited state for the former compounds.<sup>28</sup>

The emission spectra recorded for the solid films (Fig. 3) of the compounds are slightly red-shifted than those observed in toluene and dichloromethane solutions but exhibit close resemblance to those observed in acetonitrile solutions. This probably indicates that the dielectric constants for the solid films are approximately close to that in corresponding acetonitrile solutions. It is very interesting to note here that the red-shifted emission peaks observed for anthracene<sup>29</sup> and pyrene<sup>29a,30</sup> excimers are not observed for these derivatives. This clearly highlights the importance of the present design in inhibiting the aggregation.

Photoluminescence quantum yields determined for the compounds by using 2-aminopyridine ( $\Phi_{\rm F}$ =60% in 0.1 N H<sub>2</sub>SO<sub>4</sub>)<sup>31</sup> and coumarin-1 ( $\Phi_{\rm F}$ =99% in ethyl acetate)<sup>32</sup> as standard are slightly high (see Table 2) for the anthracene (**4b** and **6b**) and pyrene (**4c** and **6c**) derivatives when compared to the lophine analogs (**4a** and **6a**), which indicates the importance of anthracene and pyrene acting as main fluorophore in these compounds. The exceptional fluorescence quantum efficiency observed for the pyrene

Table 2	
Emission properties and Stokes shift observed for the compounds in the different solve	ents

Dye	$\lambda_{ m em},{ m nm}(arPhi_{ m F},\%)^{ m a}$						Stokes shift, cm <sup>-1</sup>						
	Tol	DCM	CHCl <sub>3</sub>	DMF	ACN	MeOH	Film	Tol	DCM	CHCl <sub>3</sub>	DMF	ACN	MeOH
4a	383 (na)	382 (6) <sup>b</sup>	385 (5) <sup>b</sup>	384 (4) <sup>b</sup>	382 (2) <sup>b</sup>	381 (3) <sup>b</sup>	383	5942	5976	6180	6113	6080	6011
6a	383 (na)	381 (4) <sup>b</sup>	383 (4) <sup>b</sup>	384 (3) <sup>b</sup>	382 (1) <sup>b</sup>	378 (2) <sup>b</sup>	388	6464	6327	6464	6532	6502	6118
4b	456 (61)	464 (65)	456 (60)	479 (52)	476 (47)	453 (56)	469	3777	4155	3387	4830	4831	3765
6b	456 (59)	462 (63)	457 (58)	475 (49)	473 (42)	455 (52)	475	3711	3996	3628	4588	4632	3729
4c	440 (90)	449 (79)	447 (76)	462 (75)	460 (69)	444 (72)	460	6091	6714	6200	7173	7331	6632
6c	440 (88)	449 (75)	448 (73)	459 (72)	458 (67)	443 (71)	459	6091	6630	6332	7032	7236	6496

na=not analyzed.

<sup>a</sup> Coumarin-1 ( $\Phi_F$ =99% in ethyl acetate) as reference.

 $^{\rm b}$  2-Aminopyridine ( $\Phi_F\!\!=\!\!60\%$  in 0.1 N H\_2SO\_4) as reference.



Fig. 3. Emission spectra of the spin cast films of 4a-4c and 6a-6c.

derivatives indicates that these compounds may be suitable for application as emitting dopants in organic light-emitting diodes.

Since the compounds containing anthracene and pyrene units displayed solvent dependent excited state properties, we have attempted to correlate the Stokes shift with Lippert–Mataga equation,<sup>33</sup> and  $E_{\rm T}(30)$  parameters of the solvents.<sup>34</sup> The Lippert–Mataga plots of Stokes shift against the orientation polarizability map the general interaction of dye molecules with the polar and nonpolar solvents (Fig. 4(a)). A linear correlation in the Lippert–Mataga plot is indicative of the presence of general solvent–solute interactions while a deviation from linearity suggests a solvent specific interactions such as hydrogen bonding,

aggregation, or photochemical reactions. Near linear trend observed for most of the solvents with the exception of methanol for the reason described before (vide supra). The plot of Stokes shifts versus the  $E_T(30)$  parameter displayed for compounds **6b** and **6c** in Fig. 4(b) further supports the positive solvatochromic behavior of the compounds.

# 2.3. Electrochemical properties

The electrochemical characteristics of the compounds were examined by using cyclic voltammetric (CV) and differential pulse voltammetric (DPV) techniques. The redox potentials were calibrated using ferrocene as internal standard in each measurement and the pertinent data compiled in Table 3. The pyrene containing imidazoles showed three irreversible oxidation peaks while the lophine and anthracene derivatives displayed single irreversible oxidation wave (Fig. 5). The oxidation potential of the compounds followed a trend reminiscent of the nature of C2 substituent in the imidazole ring: phenyl>anthracene>pyrene. It is fairly in agreement with the electron-richness of the aryl unit. The HOMO energy of these derivatives was calculated by using ferrocene as a reference  $(4.8 \text{ eV})^{35}$  and ranges from 5.52 to 5.71 eV. The LUMO energy was calculated from HOMO energy and optical band gap estimated from the intersection of absorption and emission profiles, which ranges from 1.97 to 2.71 eV.

### 2.4. Thermal properties

The thermal properties of the compounds were investigated by thermogravimetric analysis and the data are presented in Fig. 6 and Table 3. The thermal decomposition temperature of the compounds falls in the range 395–509 °C. Pyrene containing derivatives (**4c** 



Fig. 4. Correlation of solvent-induced Stokes shift with (a) orientation polarizability and (b)  $E_{\rm T}(30)$  parameter for compounds **6b** and **6c** (data for methanol are omitted from linear correlation).

# Table 3 Thermal and electrochemical properties of the compounds

_							
	Dye	$T_{\mathbf{d}}, ^{\circ}\mathbf{C}^{\mathbf{a}}$	$T_{\text{onset}}, ^{\circ}\text{C}^{b}$	$E_{\rm ox}$ , V <sup>c</sup>	HOMO, eV <sup>d</sup>	LUMO, eV <sup>e</sup>	$E_{0-0}^{f}$
	4a	395	336	0.85	5.65	1.97	3.68
	6a	401	345	0.84	5.64	1.97	3.67
	4b	461	382	0.77	5.57	2.57	3.00
	6b	459	407	0.91	5.71	2.71	3.00
	4c	509	406	0.72, 0.98,	5.52	2.39	3.13
				1.22			
	6c	494	418	0.72, 0.80,	5.52	2.39	3.13
				1.21			

<sup>a</sup> Heating rate 10 °C/min in nitrogen.

<sup>b</sup> Temperature corresponding to 5% weight loss.

<sup>c</sup> Oxidation potentials with reference to the ferrocene, which was used as an internal standard

<sup>d</sup> Deduced from the equation HOMO= $E_{ox}$ +4.8.

<sup>e</sup> Deduced from the equations LUMO=HOMO- $E_{0-0}$ .

<sup>f</sup> Derived from the optical edge.



Fig. 5. Differential pulse voltammograms recorded for selected compounds 4a, 6a, 4b, and 6b in dichloromethane.



Fig. 6. Thermogravimetric traces observed for the compounds.

and **6c**) showed higher  $T_d$  than the corresponding anthracene (**4b** and **6b**) and lophine (**4a** and **6a**) derivatives. This observation reveals that the rigid polyaromatic substituents are responsible for the thermal stability of these compounds. Pyrene containing molecular materials demonstrated as potential hole transporting/

emitting materials have displayed pronounced thermal stability attributable to the rigidity of pyrene segment.<sup>12b,36</sup> All the compounds were found to be crystalline in nature and did not display inflection in the differential scanning calorimetric traces attributable to the glass transition temperature.

### 2.5. Electroluminescent characteristics

The electroluminescent characteristics of the blue-emitting compounds **4b**, **6b**, **4c**, and **6c** were investigated by employing them as dopant in a multilayered OLED device with the configuration: ITO/PEDOT:PSS/CBP+**4b** or **4c** or **6b** or **6c** (10%)/TPBI/LiF/Al where 125 nm ITO (indium tin oxide) was the anode, 35 nm poly(3,4-ethylene-dioxythiophene)–poly-(styrenesulfonate)

(PEDOT:PSS) served as a hole-injection layer, 36 nm **4b/6b/4c/6c** (10 wt%) doped in 4,4'-bis(9*H*-carbazol-9-yl)biphenyl (CBP) as a solution processed emitting layer, 32 nm 1,3,5-tris(*N*-phenyl-benzimidazol-2-yl)benzene (TPBI) as an electron-transporting layer, 0.7 nm LiF as an electron injection layer and 150 nm Al as a cathode.

Alignment of the energy levels in the materials used for the fabrication of the devices, the current density–voltage (I–V) plots and luminance–current density (L–I) characteristics of the OLEDs fabricated using these dyes are shown in Fig. 7. The device performance and EL emission characteristics are summarized in Table 4. The bright-blue EL spectra (Fig. 8) observed for the devices using anthracene-based dyes (**4b** and **6b**) are broad and structureless with the maximum peak at 448 nm and CIE coordinates of x=0.16 and y=0.14 while the devices containing pyrene-based dyes showed EL at 432 nm with CIE coordinates very close to the National Television Standards Committee (NTSC) standard blue values. The EL spectra observed for the dyes are slightly blue shifted (~8 nm) than those recorded in toluene, which clearly results due to the dilution effect arising from the uniform dispersion of the dyes in CBP.

The driving voltages (at 10  $cd/m^2$ ) observed for the anthracene derivatives (4b and 6b) were slightly lower than those realized for devices based on pyrene derivatives (4c and 6c). This probably points an effective charge transport in the molecular layers of the former compounds arising due to the lower LUMO (Fig. 7(a)) observed for them, due to which electron injection from the electrontransporting layer is favored. Compound 6b showed best device performance exhibiting a maximum luminance of 2060 cd/m<sup>2</sup> as well as maximum power and current efficiencies of 1.0 lm/W and 2.3 cd/A, respectively. This may be attributed to the efficient capturing of energy by this molecule from the CBP excitons generated due to its reasonable alignment of energy levels (Fig. 7(a)). Compound **4c** exhibited deep-blue electroluminescence with moderate current-voltage-luminance characteristics (maximum luminance of 1280 cd/m<sup>2</sup> and power and current efficiencies of 0.7 lm/W and 1.7 cd/A). The efficiency of the devices showed slight roll-off from a low current density to a higher current density. The efficiency increased from bis- to tris-derivative for anthracene containing compounds while reverse result was observed for the pyrene analogs (Table 4).

#### 3. Conclusions

In summary, a series of non-conjugated fluorene-bridged bisand tris-imidazole derivatives have been synthesized and characterized by their spectral, thermal, and electrochemical properties. Polyaromatic hydrocarbons present on the imidazole nucleus play vital role to determine the absorption and emission properties of these blue-emitting compounds. Anthracene and pyrene containing derivatives exhibited blue photoluminescence with high quantum yield and thermal stability. The solution processed OLED



Fig. 7. (a) Energy level diagram of the materials used in the devices (b) the current density–voltage (I–V) and (c) luminance–current density (L–I) curves of the devices using 4b, 4c, 6b, and 6c as dopants.

Device performance characteristics of the OLEDs fabricated using 4b, 6b, 4c, and 6c

Dye	Drive voltage, V <sup>a</sup>	Power efficiency, lm/W <sup>b</sup>	Current efficiency, cd/A <sup>b</sup>	Max. luminance, cd/m <sup>2</sup>	EL peak, nm	CIE(x,y)
4b+CBP	6.4	0.6/0.4	1.5/1.3	1550	448	0.16, 0.14
6b+CBP	6.1	1.0/0.7	2.3/2.1	2060	448	0.16, 0.14
4c+CBP	7.1	0.7/0.4	1.7/1.2	1280	432	0.16, 0.09
6c+CBP	7.0	0.5/-	1.2/-	827	432	0.16, 0.08

<sup>a</sup> At 10 cd/m<sup>2</sup>.

<sup>b</sup> At 100 cd/m<sup>2</sup> and 1000 cd/m<sup>2</sup>.



Fig. 8. The electroluminescence spectra observed for the devices containing 4b, 6b, 4c, and 6c as dopants.

devices based on these derivatives, **4b**, **6b**, **4c**, and **6c**, as dopant were successfully fabricated and found to exhibit decent device parameters. They showed blue electroluminescence with CIE coordinates of x=0.16 and y=0.14 for **4b** and **6b**, x=0.16 and y=0.09 for **4c** and x=0.16 and y=0.08 for **6c**. The results suggest that these compounds are promising emitting materials for the blue OLEDs. Further studies to use these materials as hosts for suitable triplet emitters, in solution processed electrophosphorescent devices are currently being pursued.

# 4. Experimental section

# 4.1. Materials and methods

Chemicals were purchased from commercial sources and used as received. Solvents were dried and distilled prior to use by standard procedure. Column chromatography purification was performed with the use of silica gel (230–400 mesh, Rankem) as the stationary phase in a column with 40 cm long and 3.0 cm diameter. <sup>1</sup>H NMR and <sup>13</sup>C NMR were recorded in CDCl<sub>3</sub> on a Bruker AV 500 O FT-NMR spectrometer operating at 500.13 and 125.77 MHz, respectively. High-resolution mass spectrometric measurements were carried out using ESI mass spectrometer. The IR spectra were recorded on THERMO NICOLET NEXUS FT-IR spectrometer. UV-vis spectra were recorded at room temperature in quartz cuvettes using UV-1800 Shimadzu spectrophotometer. Fluorescence measurements were carried out on RF-5301-PC Shimadzu Spectrofluorimeter. Quantum yield of the dyes was calculated by following standard procedure and using 2-aminopyridine  $(\Phi_{\rm F}=0.60 \text{ in } 0.1 \text{ N } \text{H}_2\text{SO}_4)^{31}$  or coumarin-1 ( $\Phi_{\rm F}=0.99$  in ethyl acetate)<sup>32</sup> as reference. Corrections due to dye absorption and refractive indices of the solvents used for measurement were incorporated in the calculation. The cyclic voltammetric (CV) and differential pulse voltammetric (DPV) measurements were carried out on a CHI 620C electrochemical analyzer in dichloromethane by using 0.1 M tetrabutylammonium perchlorate as supporting electrolyte. The experiments were performed at room temperature in nitrogen atmosphere with a convenient three-electrode cell consisting of a platinum wire as auxiliary electrode, a non-aqueous Ag/ AgNO<sub>3</sub> reference electrode, and a glassy carbon working electrode. The highest occupied molecular orbital (HOMO) energy levels of organic materials were measured from the oxidation potential obtained from cyclic voltammetry and lowest unoccupied molecular orbital (LUMO) energy levels were determined from the HOMO energy levels and optical band gap estimated from the intersection of absorption and emission. Thermogravimetric analyses were performed on Perkin-Elmer (Pyris Diamond) at a heating rate of 10 °C/min under a flow of nitrogen.

### 4.2. Synthesis and characterization

Compounds 2,7-bis(bromomethyl)-9,9-diethyl-9*H*-fluorene (**2**) and 2,4,7-tris(bromomethyl)-9,9-diethyl-9*H*-fluorene (**5**) were synthesized by following reported procedures.<sup>24</sup>

4.2.1. 1,1'-(9,9-Diethyl-9H-fluorene-2,7-diyl)bis(methylene)bis(2,4,5triphenyl-1H-imidazole) (4a). A mixture of 2,7-bis(bromomethyl)-9,9-diethyl-9H-fluorene (0.41 g, 1 mmol), 2,4,5-triphenyl-1H-imidazole (0.65 g, 2.2 mmol), BTEAC (0.20 g), 10 mL of 50% sodium hydroxide, and 5 mL of benzene was refluxed for 24 h. After completion of the reaction, the reaction mixture was poured into beaker containing hot water. It was allowed to stand overnight in a hood. The solid formed was extracted with CH<sub>2</sub>Cl<sub>2</sub>, dried over Na<sub>2</sub>SO<sub>4</sub>, and purified by flash column chromatography on silica gel (10% EtOAc/  $CH_2Cl_2$ ) to give the title compound as white solid (0.45 g, 54%);  $R_f(5\%)$ EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) 0.48; mp 194–196 °C; IR (KBr) 3058, 2926, 2860, 1596, 1491, 1451, 1376, 1255, 1129, 837, 746, 698 cm<sup>-1</sup>;  $\delta_{\rm H}$ (500.13 MHz, CDCl<sub>3</sub>) 7.70-7.71 (4H, m), 7.62 (4H, d, / 8.5 Hz), 7.49 (2H, d, J 8.0 Hz), 7.29-7.40 (16H, m), 7.24 (4H, t, J 7.5 Hz), 7.16-7.18 (2H, m), 6.82 (2H, d, J 8.0 Hz), 6.71 (2H, s), 5.19 (4H, s), 1.80 (4H, q, J 7.0 Hz), 0.13 (6H, t, J 7.0 Hz); δ<sub>C</sub> (125.77 MHz, CDCl<sub>3</sub>) 150.3, 148.1, 140.4, 138.1, 136.7, 134.5, 131.1, 131.0, 130.1, 129.1, 129.0, 128.9, 128.7, 128.6, 128.1, 126.8, 126.4, 124.8, 120.5, 119.9, 56.0, 48.5, 32.6, 8.3;  $\delta_{\rm C}$ DEPT 45 (125.77 MHz, CDCl<sub>3</sub>) 131.1, 129.1, 129.0, 128.9, 128.7, 128.6, 128.1, 126.8, 126.4, 124.8, 120.5, 119.9, 48.5, 32.6, 8.3; HRMS (ESI): MNa<sup>+</sup>, found 861.3926. C<sub>61</sub>H<sub>50</sub>N<sub>4</sub>Na (M+Na) requires 861.3933.

4.2.2. 1,1'-(9,9-Diethyl-9H-fluorene-2,7-diyl)bis(methylene)bis(2-(anthracen-9-yl)-4,5-diphenyl-1H-imidazole) (**4b**). The title compound was synthesized by following similar procedure described for **4a** by using 2,7-bis(bromomethyl)-9,9-diethyl-9H-fluorene (0.41 g, 1 mmol) and 2-(anthracen-9-yl)-4,5-diphenyl-1H-imidazole (0.87 g, 2.2 mmol). The crude product was purified by flash column chromatography (10% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) to give pale-yellow solid (0.71 g, 68%);  $R_f$  (5% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) 0.32; mp 223–225 °C; IR (KBr) 3058, 2951, 2927, 2860, 1598, 1490, 1416, 1377, 1255, 1130, 827, 752, 697 cm<sup>-1</sup>;  $\delta_{\rm H}$  (500.13 MHz, CDCl<sub>3</sub>) 8.56 (2H, s), 8.02–8.04 (4H, m), 7.88–7.90 (4H, m), 7.66–7.68 (4H, m), 7.44–7.48 (8H, m), 7.36 (10H, s), 7.21–7.24 (4H, m), 7.14–7.17 (2H, m), 6.93 (2H, d, *J* 8.0 Hz), 6.27 (2H, s), 6.20 (2H, d, *J* 7.5 Hz), 4.74 (4H, s), 1.39 (4H, q, *J* 7.5 Hz), -0.26 (6H, t, *J* 7.5 Hz);  $\delta_{\rm C}$  (125.77 MHz, CDCl<sub>3</sub>) 149.9, 144.9, 139.9, 138.3, 135.3, 134.7, 132.2, 131.5, 131.4, 131.3, 129.5, 129.2, 129.0, 128.7, 128.2, 126.9, 126.8, 126.4, 125.9, 125.8, 125.4, 124.6, 121.2, 119.0, 55.5, 48.8, 32.1, 8.3;  $\delta_{\rm C}$  DEPT 45 (125.77 MHz, CDCl<sub>3</sub>) 131.3, 129.2, 129.0, 128.7, 128.2, 126.9, 126.8, 126.4, 125.9, 125.8, 125.4, 125.4, 121.2, 119.0, 48.8, 32.1, 8.3; HRMS (ESI): MNa<sup>+</sup>, found 1061.4554. C<sub>77</sub>H<sub>58</sub>N<sub>4</sub>Na requires 1061.4559.

4.2.3. 1,1'-(9,9-Diethyl-9H-fluorene-2,7-diyl)bis(methylene)bis(4,5*diphenyl-2-(pyren-1-yl)-1H-imidazole)* (**4***c*). The title compound was synthesized by following similar procedure described for 4a by using 2,7-bis(bromomethyl)-9,9-diethyl-9H-fluorene (0.41 g, 1 mmol) and 4,5-diphenyl-2-(pyren-1-yl)-1H-imidazole (0.92 g, 2.2 mmol). The crude product was purified by flash column chromatography (10% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) to give light-yellow solid (0.72 g, 66%); R<sub>f</sub> (5% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) 0.28; mp 220–222 °C; IR (KBr) 3056, 2956, 2927, 2857, 1599, 1466, 1418, 1342, 1322, 1248, 1132, 1069, 974, 819, 769, 748, 698 cm  $^{-1}; \delta_{\rm H}(500.13\,{\rm MHz},{\rm CDCl}_3)$  8.30 (2H, d, J 9.5 Hz), 8.24 (4H, d, J 7.5 Hz), 8.13-8.17 (8H, m), 8.03-8.08 (4H, m), 7.73 (4H, d, J 8.0 Hz), 7.37-7.41 (10H, m), 7.29 (4H, t, J 7.5 Hz), 7.18-7.22 (4H, m), 6.49 (2H, d, / 8.0 Hz), 6.33 (2H, s), 5.02 (4H, s), 1.48 (4H, q, / 7.5 Hz), -0.19 (6H, t, J 7.5 Hz);  $\delta_{C}$  (125.77 MHz, CDCl<sub>3</sub>) 149.9, 147.2, 140.1, 138.3, 136.0, 134.6, 132.0, 131.3, 131.2, 131.2, 130.9, 130.7, 129.8, 129.0, 128.8, 128.7, 128.4, 128.4, 128.2, 127.3, 126.9, 126.5, 126.3, 125.7, 125.6, 125.4, 125.1, 124.9, 124.8, 124.5, 120.7, 119.4, 55.7, 48.6, 32.2, 8.1; δ<sub>C DEPT 45</sub> (125.77 MHz, CDCl<sub>3</sub>) 131.2, 129.0, 128.8, 128.69, 128.40, 128.36, 128.2, 127.3, 126.9, 126.5, 126.3, 125.7, 125.6, 125.1, 124.8, 124.5, 120.7, 119.4, 48.6, 32.2, 8.1; HRMS (ESI): MNa<sup>+</sup>, found 1109.4565. C<sub>81</sub>H<sub>58</sub>N<sub>4</sub>Na requires 1109.4559.

4.2.4. 1,1',1"-(9,9-Diethyl-9H-fluorene-2,4,7-triyl)tris(methylene) tris(2,4,5-triphenyl-1H-imidazole) (6a). The title compound was synthesized by following similar procedure described for 4a by using a mixture of 2,5,7-tris(bromomethyl)-9,9-diethyl-9H-fluorene (0.50 g, 1 mmol), 2,4,5-triphenyl-1H-imidazole (0.98 g, 3.3 mmol), BTEAC (0.30 g), 10 mL of 50% sodium hydroxide, and 5 mL of benzene. The crude product was purified by flash column chromatography (30% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) to give cream colored solid (0.71 g, 62%); *R*<sub>f</sub> (10% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) 0.19; mp 180–182 °C; IR (KBr) 3056, 2928, 2864, 1599, 1498, 1456, 1379, 1259, 1135, 832, 741, 692 cm<sup>-1</sup>;  $\delta_{\rm H}$  (500.13 MHz, CDCl<sub>3</sub>) 7.62–7.64 (2H, m), 7.55–7.57 (2H, m), 7.48-7.51 (4H, m), 7.45-7.47 (2H, m), 7.36-7.41 (5H, m), 7.33-7.35 (1H, m), 7.27-7.31 (2H, m), 7.18-7.23 (12H, m), 7.10-7.17 (12H, m), 7.06-7.09 (2H, m), 7.00-7.02 (2H, m), 6.68 (1H, dd. J 8.0 Hz, 1.5 Hz), 6.62 (1H, s), 6.5-6.51 (2H, m), 5.33 (2H, s), 5.13 (2H, s), 5.09 (2H, s), 1.67–1.72 (4H, m), –0.07 (6H, t, J 7.5 Hz);  $\delta_{C}$ (125.77 MHz, CDCl<sub>3</sub>) 151.0, 150.7, 148.1, 147.7, 139.9, 138.5, 138.4, 138.3, 137.1, 136.5, 136.3, 134.4, 134.3, 133.4, 131.1, 131.01, 130.97, 130.9, 130.9, 130.7, 130.02, 129.99, 129.04, 129.01, 128.93, 128.85, 128.8, 128.7, 128.61, 128.58, 128.5, 128.4, 128.1, 128.0, 127.0, 126.93, 126.85, 126.44, 126.40, 126.3, 124.9, 122.7, 122.1, 120.6, 119.7, 55.6, 48.3, 46.3, 32.7, 8.1; δ<sub>C DEPT 45</sub> (125.77 MHz, CDCl<sub>3</sub>) 131.1, 131.0, 130.9, 129.04, 129.01, 128.94, 128.86, 128.8, 128.7, 128.61, 128.58, 128.5, 128.4, 128.1, 128.0, 127.96, 126.93, 126.9, 126.44, 126.40, 126.3, 124.9, 122.7, 122.1, 120.6, 119.7, 48.3, 46.3, 32.7, 8.1; HRMS (ESI): MNa<sup>+</sup>, found 1169.5262. C<sub>83</sub>H<sub>66</sub>N<sub>6</sub>Na requires 1169.5247.

4.2.5. 1,1',1"-(9,9-Diethyl-9H-fluorene-2,4,7-triyl)tris(methylene) tris(2-(anthracen-9-yl)-4,5-diphenyl-1H-imidazole) (**6b**). The title compound was synthesized by following similar procedure described for **6a** using a mixture of 2,5,7-tris(bromomethyl)-9,9diethyl-9H-fluorene (0.50 g, 1 mmol) and 2-(anthracen-9-yl)-4,5diphenyl-1H-imidazole (1.31 g, 3.3 mmol). The crude product was purified by flash column chromatography (25% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) to give yellow solid (1.13 g, 78%); Rf (10% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) 0.28; mp 233-235 °C; IR (KBr) 3065, 2959, 2932, 2869, 1603, 1491, 1417, 1375, 1259, 1122, 820, 757, 692 cm<sup>-1</sup>;  $\delta_{\rm H}$  (500.13 MHz, CDCl<sub>3</sub>) 8.55 (1H, s), 8.36 (1H, s), 8.01-8.03 (2H, m), 7.84-7.88 (4H, m), 7.76 (1H, s), 7.68-7.72 (6H, m), 7.61 (2H, d, J 8.5 Hz), 7.28-7.47 (22H, m), 7.11-7.24 (14H, m), 6.88 (2H, t, / 7.5 Hz), 6.79 (2H, t, / 7.5 Hz), 6.19 (1H, s), 5.98 (1H, s), 5.87 (1H, d, / 8.0 Hz), 5.74 (1H, d, / 8.0 Hz), 5.51 (1H, s), 4.76 (2H, s), 4.58 (2H, s), 4.51 (2H, s), 0.89-0.95 (4H, m), –0.86 (6H, t, J 7.5 Hz); δ<sub>C</sub> (125.77 MHz, CDCl<sub>3</sub>) 150.0, 149.8, 145.2, 144.9, 144.8, 138.6, 138.5, 138.2, 138.0, 135.5, 135.3, 134.6, 134.49, 134.46, 134.4, 132.1, 131.6, 131.43, 131.38, 131.36, 131.3, 131.24, 131.22, 131.19, 131.1, 131.0, 130.9, 130.8, 130.4, 130.1, 129.5, 129.41, 129.36, 129.14, 129.07, 128.9, 128.8, 128.7, 128.64, 128.55, 128.31, 128.28, 127.1, 126.90, 126.89, 126.8, 126.6, 126.5, 126.0, 125.9, 125.7, 125.5, 125.4, 125.2, 125.0, 124.8, 124.41, 124.35, 124.0, 120.9, 120.4, 118.6, 54.2, 48.6, 48.2, 44.6, 32.0, 7.9; δ<sub>C DEPT 45</sub> (125.77 MHz, CDCl<sub>3</sub>) 131.4, 131.24, 131.22, 129.41, 129.36, 129.14, 129.07, 128.9, 128.8, 128.7, 128.64, 128.56, 128.31, 128.28, 127.1, 126.90, 126.89, 126.8, 126.60, 126.56, 126.5, 126.0, 125.9, 125.7, 125.5, 125.4, 125.2, 125.0, 124.8, 122.6, 120.9, 120.4, 118.62, 48.6, 48.2, 44.6, 32.0, 7.9; HRMS (ESI): MNa<sup>+</sup>, found 1470.6237. C<sub>107</sub>H<sub>78</sub>N<sub>6</sub>Na requires 1470.6219.

4.2.6. 1.1'.1"-(9.9-Diethyl-9H-fluorene-2.4.7-trivl)tris(methylene) tris(4.5-diphenvl-2-(pvren-1-vl)-1H-imidazole) (6c). The title compound was synthesized by following similar procedure described for 6a using a mixture of 2,5,7-tris(bromomethyl)-9,9-diethyl-9H-fluorene (0.50 g, 1 mmol) and 4,5-diphenyl-2-(pyren-1-yl)-1H-imidazole (1.39 g, 3.3 mmol). The crude product was purified by flash column chromatography (30% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) to give cream colored solid (1.05 g, 69%); R<sub>f</sub> (10% EtOAc/CH<sub>2</sub>Cl<sub>2</sub>) 0.25; mp 210–212 °C; IR (KBr) 3055, 2954, 2925, 2853, 1598, 1461, 1419, 1340, 1329, 1241, 1139, 1061, 979, 829, 772, 751, 691 cm<sup>-1</sup>;  $\delta_{\rm H}$  (500.13 MHz, CDCl<sub>3</sub>) 8.09-8.25 (8H, m), 7.99-8.06 (7H, m), 7.84-7.95 (7H, m), 7.79 (1H, t, J 7.5 Hz), 7.54–7.74 (12H, m), 7.28–7.31 (3H, m), 7.07–7.25 (19H, m), 6.59(1H, d, J 8.0 Hz), 6.42(1H, s), 5.97-6.00(2H, m), 5.81(1H, s), 5.08 (2H, s), 4.86 (2H, s), 4.74 (2H, s), 1.01–1.08 (4H, m), -0.84 (6H, t, J 8.0 Hz); δ<sub>C</sub> (125.77 MHz, CDCl<sub>3</sub>) 150.0, 147.6, 147.3, 147.23, 139.17, 138.6, 138.4, 136.3, 136.1, 135.4, 134.79, 134.77, 132.7, 132.08, 132.05, 131.8, 131.33, 131.30, 131.17, 131.15, 131.1, 131.0, 130.93, 130.86, 130.8, 130.7, 130.41, 130.36, 130.2, 129.9, 129.4, 129.2, 129.1, 128.9, 128.8, 128.6, 128.5, 128.4, 128.1, 127.6, 127.4, 127.2, 127.1, 126.7, 126.5, 126.3, 126.1, 126.0, 125.83, 125.76, 125.64, 125.57, 125.5, 125.4, 125.3, 125.1, 125.0, 124.8, 124.7, 124.6, 124.3, 122.1, 122.0, 120.3, 119.6, 54.8, 48.7, 48.3, 45.6, 32.2, 7.6; δ<sub>C DEPT 45</sub> (125.77 MHz, CDCl<sub>3</sub>) 131.2, 131.1, 131.01, 129.95, 129.4, 129.2, 129.1, 129.0, 128.93, 128.88, 128.8, 128.6, 128.5, 128.4, 128.3, 128.1, 127.6, 127.4, 127.2, 127.1, 126.9, 126.8, 126.7, 126.5, 126.3, 126.1, 126.0, 125.83, 125.76, 125.64, 125.57, 125.5, 125.3, 124.8, 124.73, 124.65, 122.1, 122.0, 120.3, 119.6, 48.7, 48.3, 45.6, 32.2, 7.8; HRMS (ESI) MNa<sup>+</sup>, found 1542.6229. C<sub>113</sub>H<sub>78</sub>N<sub>6</sub>Na requires 1542.6219.

#### 4.3. OLED device fabrication and characterization

The OLED device was fabricated on the pre-cleaned glass substrate and composed of a 125 nm layer indium tin oxide as anode, 35 nm poly(3,4-ethylene-dioxythiophene)—poly-(styrenesulfonate) (PEDOT:PSS) as hole-injection layer (HIL), emissive layer (EML), TPBI as electron-transporting layer, a 0.7 nm LiF electron injection layer (EIL), a 150 nm Al layer as cathode. The aqueous solution of PEDOT:PSS was spin coated at 4000 rpm for 20 s to form a 40 nm HIL layer. A series of EMLs, doped in 4,4'-bis(9*H*-carbazol9-yl)biphenyl (CBP), were presented and deposited by spin-coating at 2500 rpm for 20 s, TPBI layer was deposited on it. Subsequently, lithium fluoride and aluminum cathode were thermally evaporated at  $1.0 \times 10^{-5}$  Torr.

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### Supplementary data

Absorption and emission spectra of the dyes recorded in different solvents, NMR (<sup>1</sup>H and <sup>13</sup>C) spectra are provided in Supplementary data. Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2013.01.046. These data include MOL files and InChiKeys of the most important compounds described in this article.

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