Substitution effect of super hydrophobic units: A new strategy to design deep blue fluorescent emitters

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Fluorescent deep-blue emitters consisting of arylamine chrysene have attracted immense commercial interest in organic light-emitting devices (OLEDs). Herein, we endeavor to design emitters with super hydrophobic groups, namely trifluoromethoxy (−OCF3) or trifluoromethylsufanyl (−SCF3) substituted on 6,12-diarylamino chrysene. Surprisingly, the new materials show highly efficient and substantial blue shift in fluorescence spectra with more pure color quality, higher thermostability and better moisture resistant properties. Astonishing electroluminescence performance is envisioned by promoting the molecular design based on experience and theoretical calculations along with the single crystal X-Ray analysis. The CIE coordinate values for 6, 12-diamine- N,N,N’ N’-tetra-p-trifluoromethoxyphenyl)chrysene (DATPC-OCF3) and 6,12-diamine-N,N,N’ N’-tetra-p-trifluoromethylsulphanylphenyl)chrysene (DATPC-SCF3) are (0.14, 0.09) and (0.15, 0.06), respectively, which exactly match with the National Television System Committee (NTSC) and High-Definition Television requirements for unprecedented deep-blue emission.

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1. Introduction

Since Tang et al. first demonstrated a multilayer device structure to achieve high efficiency in 1987 [1], organic light-emitting diodes (OLEDs) have been the most promising technology for the third generation displays [2]. However, pure blue emitter with high luminescent efficiency (4–5 cd/A) and suitable Commission Internationale de L’Eclairage (CIE) coordinates of (0.12–0.15, 0.06–0.10) are still challenging [3,4]. Therefore, it is highly desirable to obtain a stable and high-performance blue emitter to make OLEDs with three primary colors. Although thermally activated delayed fluorescence (TADF) and phosphorescent OLEDs have recently obtained higher efficiency, fluorescent emitters are more competitive because of the more credible device performance and easier fabrication [5]. At present, only conventional fluorescent emitters have managed to realize large scale industrial production. High efficiency roll-off at high luminance and shorter lifetime are inherent drawbacks of TADF and phosphorescent OLEDs [6]. Fluorescent deep-blue emitters, arylamine substituted chrysene [7], are so far reported to be the best blue dopant material in OLEDs [8,9]. However, blue fluorescence emitters have external quantum efficiency (EQE) almost below 3% [10], low color purity and unstable lifetime, which are urgent problems to solve in all blue OLEDs [11].

Our work focuses on the design and development of an emitting material, comprising the prominent class of chrysene, to achieve tuned deep-blue color emission. In particular, we endeavor to accomplish novel high efficient deep blue emitters with super moisture resistant characteristics. Although tuning deep blue emission of the chrysene chromophores has been demonstrated through various substituted groups, only a little research work has been conducted to address the stability of emitting materials. It is widely accepted that one of the degradation pathways of OLEDs is electrochemical oxidation and reduction processes [12], most likely due to the oxygen and water effects. Thus, designing moisture resistant molecules with intrinsic hydrophobic properties will be
Scheme 1. Structures of DATPC, DATPC-OCF$_3$ and DATPC-SCF$_3$.

Scheme 2. Synthesis of 6,12-diphenylaminechrysene (DATPC) and its derivatives (DATPC-OCF$_3$ and DATPC-SCF$_3$).
Trifluoromethoxy (−OCF3) or trifluoromethylsulfonyl (−SCF3) groups, because of their super hydrophobic property have been remarkably used in agrochemicals, medical imaging and pharmaceuticals [14], owing to their high Hansch hydrophobicity parameter (πR) of 1.04 and 1.44, respectively (compared to trifluoromethyl group with πR = 0.88). Moreover, a relatively small overlap integral between the adjacent molecules is needed to realize fluorescent blue emission [15]. According to the equation, $E_g(\text{eV}) = \frac{1240}{\lambda (\text{nm})}$, if we want to obtain a deep blue colored emitter, the bandgap should be increased. In other words, one useful strategy to get deep blue fluorescence is to introduce strong electron withdrawing groups to redistribute active electron density [16,17], or bulky substituents to obtain steric separation. The matter of rejoice is that −OCF3 and −SCF3 are also strong electron withdrawing groups [18]. Recently, the Jongwook Park group designed deep blue fluorescent emitters using the triphenylamine substituted chrysene achieving impressive high EQE [8]. However, 6,12-diarylamine chrysene (DATPC) may be due to the fact that arylamine groups do not nescence spectra as compared to 6,12-diarylamine chrysene hardly makes any blue shift in luminescence spectra as compared to 6,12-diarylamine chrysene (DATPC) [19]. The narrower full width at half maximum (FWHM) (49–50 nm) of absorption and fluorescence spectra as compared to DATPC (63 nm) imply higher color purity. Single layer undoped devices achieve maximum external quantum efficiency (EQE) of 3.05% and the CIE coordinate values of (0.14, 0.09) and (0.15, 0.06) for DATPC-OCF3 and 6,12-diamine-N,N,N,N′,N′,N′-tetra(p-trifluoromethoxyphenyl)chrysene (DATPC-SCF3) are illustrated in Scheme 1 and their synthesis techniques are summarized in Scheme 2. The Density Functional Theory (DFT) calculation along with the single crystal X-ray analysis establish the correctness of design strategy. DATPC-OCF3 and DATPC-SCF3 show substantial blue shift in UV−vis absorption and fluorescence spectra.

The narrower full width at half maximum (FWHM) (49–50 nm) of absorption and fluorescence spectra as compared to DATPC (63 nm) imply higher color purity. Single layer undoped devices achieve maximum external quantum efficiency (EQE) of 3.05% and the CIE coordinate values of (0.14, 0.09) and (0.15, 0.06) for DATPC-OCF3 and DATPC-SCF3, respectively, which exactly meet the High-Definition Television ITU-R BT.709 requirement of CIE (0.15, 0.06) for deep-blue emission [11]. Based on the aforementioned facts, we report a simple fabrication process to obtain deep-blue and highly efficient novel emitter. The Narrower full width at half maximum (FWHM) (49–50 nm) of absorption and fluorescence spectra as compared to DATPC (63 nm) imply higher color purity. Single layer undoped devices achieve maximum external quantum efficiency (EQE) of 3.05% and the CIE coordinate values of (0.14, 0.09) and (0.15, 0.06) for DATPC-OCF3 and DATPC-SCF3, respectively, which exactly meet the High-Definition Television ITU-R BT.709 requirement of CIE (0.15, 0.06) for deep-blue emission [11]. Based on the aforementioned facts, we report a simple fabrication process to obtain deep-blue and highly efficient novel emitters for OLEDs by incorporating super hydrophobic units of −OCF3 or −SCF3 substituted in 6,12-diarylamine chrysene.

### 2. Results and discussion

#### 2.1. Theoretical calculations, the single crystal X-Ray analysis, physical and optical properties

DFT calculations (B3LYP/6-31G* as basis set) of the DATPC complexes were carried out to evaluate the effect of −OCF3 and −SCF3 substitution and the results are summarized in Fig. 1 and Table 1. As shown in Fig. 1, −OCF3 and −SCF3 substituent groups withdraw the HOMO electron to diphenylamine group, separating HOMO, LUMO electron concentrate on chrysene core. The theoretically predicted and experimental values of the bandgap ($E_g$) of DATPC are 3.4 eV and 2.81 eV, respectively. Actually, DATPC has sky blue-colored emission and according to $E_g(\text{eV}) = \frac{1240}{\lambda (\text{nm})}$, if one wants to get a deep blue color emitter, the bandgap of new molecules should be wider than that of DATPC. Further comparison of the theoretical and experimental values of bandgaps of DATPC, DATPC-OCF3 and DATPC-SCF3 in Table 1, reveals that the values of their bandgaps follow the order: DATPC < DATPC-OCF3 < DATPC-SCF3. It indicates fluorescence emission sustaining blue shift from DATPC to DATPC-SCF3. Oxygen and sulfur atoms possess two additional pairs of non-bonding electrons [20], which lowers the HOMO more than the LUMO, it may be the net effect which causes the bandgap to increase. The enlarged bandgap is also attributed to slightly decreased intramolecular conjugation length [21,22]. Most importantly, −OCF3 and −SCF3 substitution is probably unique one to fine-tune and engineer the bandgap in order to achieve deep blue emission in highly efficient OLED materials.

The crystal structures of DATPC-OCF3 and DATPC-SCF3 are shown in Fig. 2 (a) and (b). Whereas for DATPC, it proved to be unfeasible to obtain the single crystal due to its instability. From single crystal X-ray structures, the corresponding dihedral angles between chrysene and phenyl groups of DATPC-OCF3 and DATPC-SCF3 are 87.61° and 89.43°, which are almost equal to right-angle. The DFT calculation shows that the torsion angles for DATPC, DATPC-OCF3 and DATPC-SCF3 are 77.77°, 85.04° and 87.54°, respectively, which are in good agreement and confirm the same order with the single crystal data. Thus, the bulky −OCF3 and −SCF3 substituents coincide with the former idea of steric separation to beneficial for the stability of the OLEDs [13]. Considering the above issues, we strategically introduce super hydrophobic groups substitution to realize highly efficient deep blue luminescence.

**Table 1**

<table>
<thead>
<tr>
<th>Compound</th>
<th>DFT calculation (eV)</th>
<th>Experimental data (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>HOMO</td>
<td>LUMO</td>
</tr>
<tr>
<td>DATPC</td>
<td>−4.80</td>
<td>−1.40</td>
</tr>
<tr>
<td>DATPC-OCF3</td>
<td>−5.21</td>
<td>−1.79</td>
</tr>
<tr>
<td>DATPC-SCF3</td>
<td>−5.49</td>
<td>−1.95</td>
</tr>
</tbody>
</table>

*The S0 states of the compounds calculated using B3LYP/6-31G* basis set.

**Notes:**

A. HOMO obtained from cyclic voltammetry.

B. LUMO obtained from the HOMO and the optical bandgap.
realize high efficiency. Fig. 2 (c), (d) and (e) are the optimized dimer aggregation structures of DATPC, DATPC-OCF3 and DATPC-SCF3 by Spartan molecular modeling method. The aggregation overlap integrals of all the three dimers are very low and nearly no $\pi-\pi$ interaction is observed. Combined with the single crystal X-ray, Fig. 3 (a) and (b) are the highly-ordered molecular packing details of DATPC-OCF3 and DATPC-SCF3 respectively. This herringbone cross-lamination arrangement of chrysene core is significantly beneficial to reduce transportation distance of the excitons. In the case of DATPC-OCF3, the shortest intermolecular distance is 3.47 Å (from hydrogen atom to fluorine atom). For DATPC-SCF3, the shortest distance between two adjacent molecules is 2.55 Å (from hydrogen atom to fluorine atom). In fact, these shorter distances promote intermolecular exciton transfer. The intermolecular chrysene-chrysene distances obtained from single X-ray crystal data of DATPC-OCF3 and DATPC-SCF3 are 3.434 Å and 3.330 Å, respectively, where it is generally accepted that high-efficient intermolecular interaction often occurs within effective distance smaller than 4.0 Å [23,24]. The head-to-head aggregation subserves the exciton transfer between adjacent molecules to promote blue emission and prevents exciton quenching. In conclusion, $-\text{OCF}_3$ and $-\text{SCF}_3$ substituents decrease the packing.

The UV–vis absorption wavelengths of DATPC-OCF3 (383 nm) and DATPC-SCF3 (378 nm) in their solution states are about 22–27 nm blue shifted than that of DATPC (405 nm) shown in Fig. 4 (a). The fluorescence emission spectra show emission peaks at 440 nm (DATPC-OCF3) and 435 nm (DATPC-SCF3), which are 37–42 nm blue shifted than that of DATPC (477 nm). FWHM values of the fluorescence emission are 51 nm and 48 nm for DATPC-OCF3 and DATPC-SCF3, respectively, which are over 12 nm narrower as compared to that of DATPC (63 nm). Photoluminescence quantum yield (PLQY) in solution state of DATPC-OCF3 and DATPC-SCF3 are 50% and 42%, respectively, while that of DATPC is 47%, for details in Fig. S1 (ESI). Fig. 4 (b) summarizes the UV–vis absorption and fluorescence emission spectra in solid state, with the same changing tendency as that of the solution state. The optical properties are listed in Table 2. The cyclic voltammetry (CV) are summarized in Fig. S2 (ESI). In conclusion, $-\text{OCF}_3$ and $-\text{SCF}_3$ substituent modification can provide deep blue emission as well as higher color purity. The differential scanning calorimetry (DSC) in Fig. S3 (ESI!) and thermogravimetric analysis (TGA) in Fig. S4 (ESI!) were carried out to evaluate the thermal properties of our new materials and are summarized in Table 2. From the thermal property data, it is suggested that the additional $-\text{OCF}_3$ and $-\text{SCF}_3$ substituents can improve thermostability of the corresponding compounds, that may otherwise attribute to the unstable arylamine structure [25,26].

To study the effect of substituents on the hydrophobic property, contact angle measurements were also carried out and listed in Fig. 5. The contact angles of DATPC, DATPC-OCF3 and DATPC-SCF3 are 88.56°, 103.55° and 90.00°, respectively, obtained from an average value of five reasonable distribution points. Evidently, the hydrophobic property is enhanced by $-\text{OCF}_3$ and $-\text{SCF}_3$ substituents, providing better device stability.
2.2. Electroluminescence properties

Although certain doped fluorescent OLEDs, which have been reported so far, can realize higher efficiency, undoped OLEDs are more attractive due to stable device performance and simple manufacturing processes [5]. Subsequently, blue undoped OLEDs with the structure [ITO/MoO3 (1 nm)/TCTA (60 nm)/DATPC derivative (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (200 nm)] were fabricated. The optical and physical properties of the resulting devices are summarized in Fig. 6 and Table 3. The EL spectra of DATPC derivative-based OLEDs are shown in Fig. 6 (a). The excimer emission peaks from new DATPC-OCF3 (435 nm) and DATPC-SCF3 (430 nm) are 25–30 nm shorter than that of DATPC (460 nm). FWHM value of DATPC-OCF3 (49 nm) and DATPC-SCF3 (50 nm) is 16 nm narrower than that of DATPC (66 nm). The EL spectra of DATPC-OCF3 and DATPC-SCF3 based OLED devices shows better blue color luminance and higher color purity. The EQE-current density curves of the devices are shown in Fig. 6 (b). The maximum EQE of DATPC-OCF3 and DATPC-SCF3 is obtained to be 2.70% and 3.05%, respectively, which is a significant improvement over that of DATPC (2.06%). Although EQE of DATPC-SCF3 is highest, it gets roll-off quickly with the increase in current density. In general, the possible reason may be the difference in electron and hole mobility [27] as the material’s energy barriers of hole-transporting and electron-transporting layer do not match very well. To further investigate this issue from the aspect of the concentration quenching effect, the time-resolved emission spectra were also recorded in Fig. S5 (ESI) and Table S1 (ESI). DATPC, DATPC-OCF3 and DATPC-SCF3 show exciton lifetimes of 3.7 ns, 3.4 ns and 2.0 ns, respectively, in solution state. The longer exciton lifetime can provide enough time for its transportation and aggregation in emitting layer, significantly for blue conventional fluorescence materials [28]. Fig. 6 (c) exhibits the CIE coordinate values for DATPC(0.17, 0.20), DATPC-OCF3 (0.14, 0.09) and DATPC-SCF3 (0.15, 0.06). It is noteworthy that we have unprecedentedly designed deep-blue emitters meeting the requirements of television displays with CIE coordinates of (0.14, 0.08) regulated by the National Television System Committee (NTSC); and High-Definition Television ITU-RBT.709 requiring CIE of (0.15, 0.06) for deep-blue emission [11]. Fig. 6 (d) shows OLED device structure incorporating DATPC, DATPC-OCF3 or DATPC-SCF3 as active emission layer. Tris(4-carbazoyl-9-ylphenyl)amine (TCTA) was applied as hole-transporting and exciton-blocking layer and 1,3,5-Tris(N-phenylbenzimidazol-2- yl)benzene (TPBi) was utilized as electron-transporting and exciton-blocking layer. In this article, we mainly focused on the innovation in material structure, and not too much...
on the exploration of device structure. But we believe that the roll-off problem of our new materials can be solved with a subsequent study to design appropriate device structure.

3. Experimental

3.1. Synthesis

DATPC, DATPC-OCF₃ and DATPC-SCF₃ were obtained from bromochrysene according to the reported procedure [8,29,30]. Compound 8 (diphenylamine) was obtained from chemical company.

Compound 3 [bis(4-trifluoromethoxyphenyl)amine]: Compound 1 (4-trifluoromethoxybromobenzene) (24.10 g, 0.1 mol) and compound 2 (4-trifluoromethoxyphenylamine) (17.71 g, 0.1 mol) were added to dry toluene solution (300 mL). 1,1'-Bis(diphenylphosphino)ferrocene (DPPF) (6.65 g, 12 mmol), [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride dichloromethane adduct [(DPPF)PdCl₂.CH₂Cl₂] (0.33 g, 0.4 mmol) and potassium tert-butoxide (KOTBu) (9.61 g, 0.1 mol) were added to the reaction mixture under nitrogen atmosphere. The reaction was stirred for 5 h at 120 °C. After completing the reaction, the mixture was poured into water (100 mL); the organic layer was extracted with ethyl acetate and distilled water. The obtained organic layer was isolated by silica gel column chromatography using the ethyl acetate: petroleum ether (1: 9) to get the oily product. Yield 67%. ¹H NMR (300 MHz, Chloroform-d) δ 7.15 (d, J = 8.4 Hz, 4H), 7.04 (d, J = 9.0 Hz, 4H), 5.72 (s, 1H). ¹³C NMR (126 MHz, Chloroform-d) δ 143.65, 142.07, 122.79, 119.09.

Compound 6 [bis(4-trifluoromethylsulanylphenyl)amine]: Compound 4 [4-(trifluoromethylsulanyl)bromobenzene] (21.42 g, 0.083 mol) and compound 5 [4-(trifluoromethylsulanyl)phenylamine] (19.31 g, 0.1 mol) were added to dry toluene solution (300 mL). 1,1'-Bis(diphenylphosphino)ferrocene (DPPF) (6.65 g, 12 mmol), [1,1'-bis(diphenylphosphino)ferrocene]palladium(II) dichloride dichloromethane adduct [(DPPF)PdCl₂.CH₂Cl₂] (0.33 g, 0.4 mmol) and potassium tert-butoxide (KOTBu) (9.61 g, 0.1 mol) were added to the reaction mixture under nitrogen atmosphere. The reaction was stirred for 5 h at 120 °C. After completing the reaction, the mixture was poured into water (100 mL); the organic layer was extracted with ethyl acetate and distilled water. The obtained organic layer was isolated by silica gel column chromatography using the ethyl acetate: petroleum ether (1: 9) to get the oily product. Yield 73%. ¹H NMR (300 MHz, Chloroform-d) δ 7.57 (d, J = 8.6 Hz, 4H), 7.13 (d, J = 8.7 Hz, 4H), 6.08 (s, 1H). ¹³C NMR

The UV–vis absorption (solid dots) and fluorescence (hollow dots) spectra of DATPC, DATPC-OCF₃ and DATPC-SCF₃ (a) in anhydrous chloroform solution (1 × 10⁻⁵ M); (b) in the vacuum-deposited films (50 nm) on glass substrates. Fig. 4.

Table 2: Optical and thermal properties of DATPC, DATPC-OCF₃, and DATPC-SCF₃.

<table>
<thead>
<tr>
<th>Compound</th>
<th>In Solution ¹</th>
<th>On Film ²</th>
<th>PLQY ³ (%)</th>
<th>Tg (°C)</th>
<th>Tm (°C)</th>
<th>Ta (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>UV (nm)</td>
<td>PL (nm)</td>
<td>FWHM (nm)</td>
<td>UV (nm)</td>
<td>PL (nm)</td>
<td>FWHM (nm)</td>
</tr>
<tr>
<td>DATPC</td>
<td>405</td>
<td>477</td>
<td>62.96</td>
<td>397</td>
<td>450</td>
<td>63.21</td>
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<tr>
<td>DATPC-OCF₃</td>
<td>383</td>
<td>440</td>
<td>50.79</td>
<td>385</td>
<td>438</td>
<td>51.10</td>
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<tr>
<td>DATPC-SCF₃</td>
<td>378</td>
<td>435</td>
<td>47.46</td>
<td>380</td>
<td>433</td>
<td>48.91</td>
</tr>
<tr>
<td></td>
<td>⁴×10⁻⁵M in anhydrous chloroform.</td>
<td>⁴Film thickness is 50 nm on the glass.</td>
<td>⁴The solution-state in anhydrous chloroform relative quantum yield using the 2-Aminopyridine in 0.1 M H₂SO₄ as the reference.</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fig. 5. Contact angles of (a) DATPC, (b) DATPC-OCF₃, and (c) DATPC-SCF₃ measured by 2 μL water spread over vacuum-deposited 50 nm films on the glass.
Compound 9 (DATPC): Compound 7 (6,12-dibromochrysene) (1.94 g, 5 mmol) and compound 8 (4.49 g, 20 mmol) were added to dry toluene solution (120 mL). Tris(dibenzylideneacetone)dipalladium(0) [Pd2(dba)3] (0.092 g, 0.1 mmol), tri-tert-butylphosphonium tetrafluoroborate [P(tBu)3HBF4] (0.029 g, 0.2 mmol) and potassium tert-butoxide (KOTBu) (1.68 g, 1.5 mmol) were added to the reaction mixture under nitrogen atmosphere. The reaction was stirred for 5 h at 110 °C. After completing the reaction, the mixture was poured into water (50 mL); the organic layer was extracted with dichloromethane and distilled water. The obtained organic layer was isolated by silica gel column chromatography using the dichloromethane: petroleum ether (1:3). Yield 19%. 1H NMR (300 MHz, Chloroform-d) δ = 8.55 (d, J = 8.8 Hz, 4H), 8.11 (d, J = 8.3 Hz, 2H), 7.59 (t, J = 7.6 Hz, 2H), 7.47 (t, J = 7.5 Hz, 2H), 7.21 (d, J = 7.6 Hz, 8H), 7.15 (d, J = 8.0 Hz, 8H), 6.96 (t, J = 7.2 Hz, 4H). 13C NMR (126 MHz, Chloroform-d) δ = 129.21, 129.18, 129.10, 126.96, 126.90, 126.85, 125.07, 124.99, 123.62, 121.95, 121.86, 121.77. HRMS(APCI): m/z calcd for C42H31N2 [M+H]+ 563.2482; found 563.2476.

Compound 10 (DATPC-SCF3): Compound 7 (4.10 g, 10.55 mmol) and compound 6 (8.57 g, 23.22 mmol) were added to dry toluene solution (150 mL). Tris(dibenzylideneacetone)dipalladium(0) [Pd2(dba)3] (0.25 g, 0.27 mmol), tri-tert-butylphosphonium tetrafluoroborate [P(tBu)3HBF4] (0.16 g, 0.55 mmol) and potassium tert-butoxide (KOTBu) (3.78 g, 39.30 mmol) were added to the reaction mixture under nitrogen atmosphere. The reaction was stirred for 5 h at 110 °C. After completing the reaction, the mixture was poured into water (50 mL); the organic layer was extracted with dichloromethane and distilled water. The obtained organic layer was isolated by silica gel column chromatography using the dichloromethane: petroleum ether (1:3). Yield 63%. 1H NMR (300 MHz, Chloroform-d) δ = 8.62–8.53 (m, 4H), 8.04 (dd, J = 8.3, 1.3 Hz, 2H), 7.67 (ddd, J = 8.4, 6.9, 1.4 Hz, 2H), 7.54 (ddd, J = 8.1, 6.9, 1.1 Hz, 2H), 7.17–7.05 (m, 16H). 13C NMR (75 MHz, Chloroform-d) δ = 146.63, 143.99, 142.22, 132.06, 130.17, 128.14, 127.67, 127.62, 124.75, 123.91, 122.74, 122.64, 122.40, 118.97. HRMS(APCI): m/z calcd for C46H27F12O4N2 [M+H]+ 899.1774; found 899.0159.

Compound 11 (DATPC-SCF3): Compound 7 (6,12-dibromochrysene) (1.94 g, 5 mmol) and compound 6 (8.57 g, 23.22 mmol) were added to dry toluene solution (120 mL). Tris(dibenzylideneacetone)dipalladium(0) [Pd2(dba)3] (0.25 g, 0.27 mmol), tri-tert-butylphosphonium tetrafluoroborate [P(tBu)3HBF4] (0.16 g, 0.55 mmol) and potassium tert-butoxide (KOTBu) (3.78 g, 39.30 mmol) were added to the reaction mixture under nitrogen atmosphere. The reaction was stirred for 5 h at 110 °C. After completing the reaction, the mixture was poured into water (50 mL); the organic layer was extracted with dichloromethane and distilled water. The obtained organic layer was isolated by silica gel column chromatography using the dichloromethane: petroleum ether (1:3). Yield 43%. 1H NMR (300 MHz, Chloroform-d) δ = 8.62–8.53 (m, 4H), 8.04 (dd, J = 8.3, 1.3 Hz, 2H), 7.67 (ddd, J = 8.4, 6.9, 1.4 Hz, 2H), 7.54 (ddd, J = 8.1, 6.9, 1.1 Hz, 2H), 7.17–7.05 (m, 16H). 13C NMR (75 MHz, Chloroform-d) δ = 146.63, 143.99, 142.22, 132.06, 130.17, 128.14, 127.67, 127.62, 124.75, 123.91, 122.74, 122.64, 122.40, 118.97. HRMS(APCI): m/z calcd for C46H27F12O4N2 [M+H]+ 899.1774; found 899.0159.

<table>
<thead>
<tr>
<th>Compound</th>
<th>CIE (x,y)</th>
<th>ELmax (nm)</th>
<th>EL FWHM (nm)</th>
<th>Va (V)</th>
<th>CEb (cd A–1)</th>
<th>EQEmax</th>
</tr>
</thead>
<tbody>
<tr>
<td>DATPC</td>
<td>(0.17, 0.20)</td>
<td>460</td>
<td>65.44</td>
<td>4.7</td>
<td>2.62</td>
<td>2.06</td>
</tr>
<tr>
<td>DATPC-OCF3</td>
<td>(0.14, 0.09)</td>
<td>435</td>
<td>48.75</td>
<td>5.5</td>
<td>1.71</td>
<td>2.70</td>
</tr>
<tr>
<td>DATPC-SCF3</td>
<td>(0.15, 0.06)</td>
<td>430</td>
<td>49.69</td>
<td>5.8</td>
<td>1.05</td>
<td>3.05</td>
</tr>
</tbody>
</table>

a Operating voltage.
b Current efficiency.
butoxide (KOTBu) (3.04 g, 31.65 mmol) were added to the reaction mixture under nitrogen atmosphere. The reaction was stirred for 5 h at 110 °C. After completing the reaction, the mixture was poured into water (50 mL); the organic layer was extracted with dichloromethane and distilled water. The obtained organic layer was isolated by silica gel column chromatography using the dichloromethane: petroleum ether (1: 3). Yield 71%. 1H NMR (300 MHz, Chloroform-d) δ = 8.68–8.58 (m, 4H), 7.98 (dd, J = 8.3, 1.3 Hz, 2H), 7.69 (dd, J = 8.4, 6.9, 1.4 Hz, 2H), 7.60–7.55 (m, 2H), 7.55–7.47 (m, 8H), 7.24–7.14 (m, 8H), 13C NMR (75 MHz, Chloroform-d) δ = 149.31, 141.29, 137.84, 131.93, 128.29, 127.82, 127.73, 124.29, 123.83, 123.11, 121.94, 116.68. HRMS(APCI)m/z calcd for C46H27F12N2S4[M+H]+ 963.0860; found: 963.8682.

3.2. General information

The 1H-NMR and 13C-NMR spectra were recorded on Bruker Avance 300 spectrometers. The high-resolution mass spectra (HRMS) were recorded on TOFMS(APCI), 4800 PLUS, ABI.

The theoretical calculation of the HOMO and LUMO energy levels and dimer structure were done by Spartan software at DFT B3LYP/6-31G* levels of theory. The Experimental data of HOMO and LUMO energy levels were calculated from redox potential in CV curve.

The UV–vis spectra were obtained by using a PerkinElmer Lambda 1050 UV/Vis/NIR spectrometer. The photoluminescence spectra were obtained by a PerkinElmer Luminescence spectrometer.

3.3. Single crystal X-ray diffraction

CCDC 1522077 and 1503591 contain the supplementary crystallographic data for DATPC-OFCF3 or DATPC-SCF3 respectively. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

4. Conclusions

This article investigates the effect of super hydrophobic and strong electron withdrawing groups –OCF3 and –SCF3 to realize highly efficient deep blue fluorescence with more pure color quality, higher thermostability and better moisture resistant properties. The photophysical and optoelectronic properties have been interpreted with the help of theoretical calculations based on the DFT approach along with molecular packing study of their single crystal X-ray analysis. Single layer undoped devices achieved the maximum EQE 3.05% and CIE coordinate values of (0.14, 0.09) and (0.15, 0.06) for DATPC-OCF3 and DATPC-SCF3 respectively, exactly meeting High-Definition Television ITU-R BT.709 requirement of CIE coordinates of (0.15, 0.06) for deep-blue emission. We believe the theory prior to experiment, accurately predicting the material's properties, can promote the experience in molecular formulation and designing.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2016.12.034.

References


