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## COMMUNICATION

## Highly Efficient Deep-Blue OLEDs Based on Hybridized Local and Charge-Transfer Emitters Bearing Pyrene as the Structural Unit

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A new family of hybridized local and charge-transfer (HLCT) emitters bearing pyrene structural unit has been developed. Deepblue OLEDs based on them achieved high brightness over 10000 cd m<sup>-2</sup>, high maximum external quantum efficiency over 10.5%, and high maximum exciton utilization efficiency approaching 100%, with CIE coordinates of (0.152, 0.065).

As deep-blue organic light-emitting diodes (OLEDs) can promote better color gamut and reduced power consumption in displays and lightings,<sup>1</sup> the development of high-performance deep-blue emitters, especially those capable of satisfying the required CIE coordinates (x, y) = (0.15, 0.06) defined by High-Definition Television (HDTV) ITU-RBT.709, is highly demanded.<sup>2</sup> However, despite their theoretical maximum exciton utilization efficiency (EUE<sub>max</sub>) of 100%, highly efficient and stable deepblue phosphorescent devices are quite scarce by far.<sup>2,3</sup>

To address these issues, several alternative strategies for utilizing triplet excitons via cheaper fluorescent materials, such as triplet-triplet annihilation (TTA), thermally activated delayed fluorescence (TADF), and hybridized local and charge-transfer (HLCT) have been proposed.<sup>4,5</sup> Currently, deep-blue TTA-OLEDs can show relatively high maximum luminance ( $L_{max}$ ) together with mild efficiency roll-off, but they often suffer from relatively low maximum external quantum efficiency (EQE<sub>max</sub>) due to their intrinsic low EUE<sub>max</sub> of  $\leq$  62.5%.<sup>6</sup> In contrast, deep-blue TADF-OLEDs can exhibit high EQE<sub>max</sub>s, but their  $L_{max}$  and efficiency roll-off are quite unsatisfactory.<sup>7</sup> For deep-blue HLCT-OLEDs, they

can exhibit both high  $L_{max}$  and insignificant efficiency roll-off, but their EQE<sub>max</sub>s are relatively low ( $\leq 8\%$ ),<sup>5b,6,8</sup> despite the high theoretical EUE<sub>max</sub> of 100% of HLCT-OLEDs.<sup>5b</sup> This should be ascribed to either the low photoluminescence (PL) efficiency ( $\varphi_{PL}$ ) of the emitters,<sup>8a,b</sup> or the low EUE of the devices.<sup>6a,8c-d</sup>

Owing to its large optical bandgap ( $E_g$ ), good thermostability and high TTA efficiency, pyrene has attracted much attention as the building block for deep-blue fluorophores.<sup>9</sup> Yet despite the fact that pyrene owns a large energy gap between its T<sub>2</sub> and T<sub>1</sub> states ( $\Delta E_{(T2-T1)} = 1.3 \text{ eV}$ ) that is good for the suppression of internal conversion (IC), and a small  $\Delta E_{(S1-T2)}$  (~0.2 eV) that is good for the promotion of reverse intersystem crossing (RISC) of the "hot excitons",<sup>10</sup> so far little effort has been devoted to the exploitation of pyrene-containing HLCT materials. A possible reason may lie in the symmetrically forbidden  $S_1 \rightarrow S_0$ transition nature hence low radiative decay rate constant ( $k_r$ , ~10<sup>6</sup> s<sup>-1</sup>) and low  $\varphi_{PL}$  (0.29) of pyrene unit.<sup>11</sup> Note that for traditional HLCT materials, to guarantee a relatively large  $k_r$ , a lower-lying highly fluorescent local excited singlet state (<sup>1</sup>LE) is indispensable.<sup>5b</sup>

Herein, we unveil that pyrene is a quite promising building block for deep-blue HLCT materials. To endow pyrene-based donor-acceptor-structured (D-A) materials with relatively high  $k_r$ , the twisting angle between the D and A units should be relatively small, so that a CT-featured excited singlet state (<sup>1</sup>CT) with relatively high radiative efficiency can be acquired. To ensure deep-blue PL emission, 9,9-dimethylthioxanthene-*S*,*S*dioxide (TXO<sub>2</sub>) with LUMO energy level of -2.33 eV is selected as the A moiety,<sup>12</sup> and pyrene is used as the D unit. The structure of the resultant **DP-TXO<sub>2</sub>** and **P-TXO<sub>2</sub>** is shown in



Figure 1. Molecular structure of the objective compounds.

Figure 1.

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Figure 2. a) UV-vis absorption and PL spectra (in Tol, 298 K), and phosphorescence spectra (in 2-Me-THF, 77 K) of DP-TXO<sub>2</sub>, P-TXO<sub>2</sub>, and TPP-TXO<sub>2</sub>; b) PL spectra of DP-TXO<sub>2</sub> in Hex, BE, Tol and DCM (298 K); c) Lippert-Mataga plots of the fluorescence maxima of DP-TXO<sub>2</sub>, P-TXO<sub>2</sub>, and TPP-TXO<sub>2</sub> against the solvent polarity parameters; d) transient PL decay curves of DP-TXO<sub>2</sub> in Hex, BE, and DCM at  $\lambda_{em}$  of 390 nm and 460 nm; e) PL spectra of a 1 wt.% DP-TXO<sub>2</sub>:PMMA film at 77-295 K; f) transient PL decay curves of a 1 wt.% DP-TXO<sub>2</sub>:PMMA film at 77-295 K ( $\lambda_{em}$  = 400 nm).

Excitingly, crystallographic analysis indicates that DP-TXO<sub>2</sub> and P-TXO<sub>2</sub> both show relatively small D-A twisting angles of 46-54° (Figure S1). This is appropriate to the formation of not only HLCT, but also highly radiative <sup>1</sup>CT states. As shown in Figure 2a, in toluene (Tol), DP-TXO<sub>2</sub> and P-TXO<sub>2</sub> show similar absorption maxima ( $\lambda_{abs}$  = 349 nm) with relatively high molar extinction coefficients (log  $\varepsilon$  > 4), and similar PL maxima ( $\lambda_{em}$  = 410 nm) with relatively high  $\varphi_{\rm PL}$  of 0.59 (Table 1). Analogous to most reported HLCT compounds,<sup>8b-d</sup> DP-TXO<sub>2</sub> and P-TXO<sub>2</sub> show more distinct positive solvatochromism in more polar solvents, and their Lippert-Mataga plots are nonlinear with their crossover points near the solvent polarity of butyl ether (BE) (Figures 2b, c, S2, S3). In hexane (Hex) and dichloromethane (DCM), DP- $TXO_2$  shows a single-exponential PL decay with lifetime ( $\tau$ ) of 15.7 and 2.4 ns, respectively (Figures 2d, S4). Judging from the presence and absence of vibronic bands in its PL spectra in Hex and DCM, the S<sub>1</sub> state of DP-TXO<sub>2</sub> should be of purely LE- and CT-feature in Hex and DCM, respectively. Based on the au and  $arphi_{\mathsf{PL}}$ data ( $\varphi_{PL}$ : 0.63 in Hex; 0.57 in DCM), the  $k_{r(LE)}$  and  $k_{r(CT)}$  of **DP**-**TXO<sub>2</sub>** is calculated to be  $4.0 \times 10^7$  and  $2.4 \times 10^8$  s<sup>-1</sup>, respectively. The much larger  $k_{\rm r(CT)}$  than  $k_{\rm r(LE)}$  verifies the higher radiative efficiency of the <sup>1</sup>CT than <sup>1</sup>LE state of **DP-TXO<sub>2</sub>**. But different from most HLCT fluorophores, 5b,8 DP-TXO<sub>2</sub> displays a bi- rather than single-exponential PL decay behavior in BE ( $\tau_1 \sim 2.0$  ns;  $\tau_2$ ~7.2 ns). As the radiative transition of  ${}^{1}LE$  state is less-allowed than that of <sup>1</sup>CT state, the shorter and longer  $\tau$  components observed in BE are tentatively assigned to the <sup>1</sup>CT and <sup>1</sup>LE states of **DP-TXO<sub>2</sub>**, respectively. These findings suggest the mixing of <sup>1</sup>LE and <sup>1</sup>CT states of **DP-TXO<sub>2</sub>** in BE. Note that this is the first direct experimental evidence for the state-mixing of <sup>1</sup>LE and <sup>1</sup>CT in HLCT compounds. In the case of **P-TXO<sub>2</sub>**, since only one decay component with  $\tau$  of 2.9 ns is found in DCM (Table S2), in combination with its  $\varphi_{PL}$  in DCM (0.68), the  $k_{r(CT)}$  of **P-TXO<sub>2</sub>** is determined to be 2.3 × 10<sup>8</sup> s<sup>-1</sup>, which is similar to that of **DP-TXO<sub>2</sub>**. But in both Hex and BE, **P-TXO<sub>2</sub>** shows a bi-exponential PL decay hence state-mixing of its <sup>1</sup>LE and <sup>1</sup>CT states (Table S2).

At 295 K, the doped film of 1 wt.% **DP-TXO**<sub>2</sub> in poly(methyl methacrylate) (PMMA) exhibits an unstructured PL band with  $\lambda_{em}$  of 414 nm (Figure 2e), and its PL decay curve shows a triexponential function with  $\tau_1 = 3.8$  ns,  $\tau_2 = 10.4$  ns, and  $\tau_3 = 33.2$  ns (Figure 2f, Table S3). According to its transient PL properties in BE, the  $\tau_1$  and  $\tau_2$  species are assigned to the <sup>1</sup>CT and <sup>1</sup>LE states of **DP-TXO**<sub>2</sub>, respectively. For the longest  $\tau_3$  component, as the content of **DP-TXO**<sub>2</sub> is as low as 1 wt.%, and the monitored  $\lambda_{em}$  (400 nm) is in the high-energy spectral region, the interference from the excimer should be suppressed effectively. Hence the  $\tau_3$  component with lifetime of 33.2 ns is tentatively assigned to the delayed fluorescence (DF) of **DP-TXO**<sub>2</sub>.

With decreasing temperature to 77 K, the PL intensity hence the overall  $\varphi_{PL}$  of the film sample depresses significantly (Figure 2e).<sup>13</sup> Since the  $\varphi_{PL(LE)}$  and  $\varphi_{PL(CT)}$  of **DP-TXO<sub>2</sub>** in Hex and DCM are comparable, the markedly lowered  $\varphi_{PL}$  of the **DP-TXO<sub>2</sub>**-based

Fable 1. Photophysical characteristics, thermal stability, and frontier molecular orbital energy level of the three compounds.												
Compd.	$\lambda_{abs}^{a)}[nm]$	$\log \epsilon^{a}$	$\lambda_{em} = \frac{a}{b}/c}{d} = \frac{\lambda_{em}}{b}$	<i>Φ</i> <sub>Pl</sub> a)/b)/c)/d)/e)/f)[%]	$T_d/T_g/T_m$ [°C]	$E_{g}^{g}$ [eV]	HOMO <sup>h)</sup> [eV]	LUMO <sup>i)</sup> [eV]				
DP-TXO <sub>2</sub>	349	4.58	410/473/447/444/462/453	59/35/48/41/15/27	378/177/299	3.21	-5.76	-2.55				
P-TXO <sub>2</sub>	349	4.50	410/470/423/426/452/443	59/46/48/45/19/27	388/ - /278	3.25	-5.70	-2.45				
TPP-TXO <sub>2</sub>	365	4.66	418/463/433/436/443/437	59/48/47/52/28/39	490/164/263	3.12	-5.68	-2.56				

<sup>a)</sup> In 2 × 10<sup>-6</sup> M Tol solutions at 295 K; <sup>b)</sup> in neat thin films; <sup>c)</sup> 12 wt.%-doped thin films in PMMA matrix; <sup>d)</sup> 12 wt.%-doped thin films in 26DCzPPy host matrix; <sup>e)</sup> 12 wt.%-doped thin films in TcTa:26DCzPPy (1:1) mixed host matrix; <sup>g)</sup> estimated from the onset of the absorption edge in DCM solution; <sup>h)</sup> calculated from the formula HOMO =  $-[E_{ox} - E(Fc/Fc^*) + 4.8]$  eV (in DCM solution); <sup>i)</sup> calculated from the formula LUMO = HOMO +  $E_{e}$ .

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Figure 3. The mechanism diagram of EL and molecular design. a) Traditional HLCT materials; and b) HLCT materials bearing pyrene subunits.

film should be mainly ascribed to the decreased contribution from the DF rather than the alteration in contribution from the <sup>1</sup>CT and <sup>1</sup>LE states of **DP-TXO<sub>2</sub>**. Meanwhile, the lowered  $\varphi_{PL}$  of **DP-TXO<sub>2</sub>** and the prolonged lifetime of the  $\tau_3$  species (from 33.2 to 60.3 ns, vide Table S4) upon cooling down verify the thermally activated nature of the DF species of **DP-TXO<sub>2</sub>**.<sup>14</sup> It is noteworthy that the quite short lifetime of the TADF species of **DP-TXO<sub>2</sub>** indicates the presence of very fast RISC processes in **DP-TXO<sub>2</sub>**. Actually, as shown in Table S5, the RISC rate constant ( $k_{RISC}$ ) of **DP-TXO<sub>2</sub>** is calculated to be as high as 7.3 × 10<sup>6</sup> s<sup>-1</sup>,<sup>4a,13-15</sup> which is not only good for the efficient harvesting of triplet excitons, but also favorable for the suppression of efficiency roll-off in OLED applications.<sup>7a</sup>

Nevertheless, the energy levels of <sup>1</sup>LE and <sup>1</sup>CT states of DP-**TXO<sub>2</sub>** are both ~ 3.2 eV, but that of its LE-featured T<sub>1</sub> state is only 2.0 eV (Figure 2a). Accordingly, the  $\Delta E_{ST}$  between <sup>1</sup>LE/<sup>1</sup>CT and T<sub>1</sub> is 1.2 eV, which is too large to promote fast RISC process between them. Consequently, the TADF in DP-TXO2 should be attributed to the RISC of the "hot exciton". To gain insight into the TADF mechanism of **DP-TXO<sub>2</sub>**, density functional theory (DFT) calculations are performed. As shown in Figure S9, DP-TXO<sub>2</sub> owns pseudo-degenerated S<sub>1</sub> and S<sub>2</sub>, T<sub>1</sub> and T<sub>2</sub>, and T<sub>3</sub> and T<sub>4</sub> states due to its symmetrical D-A-D structure. Both the S<sub>1</sub> and  $S_2$  states show a HLCT transition character; both the  $T_1$  and  $T_2$ states show a LE-dominated feature mainly confined to the pyrene moiety; while both T<sub>3</sub> and T<sub>4</sub> states possess a LEdominated feature. Because of the quite small  $\Delta E_{ST}$  (0.02 eV) and marked difference in the transition nature, relatively large spin-orbital coupling (SOC) elements hence large  $k_{RISC}$  between the  $S_1/S_2$  and  $T_3/T_4$  states of **DP-TXO<sub>2</sub>** can be expected.<sup>7b,15,16</sup>

Therefore, as depicted in Figure 3, our pyrene-containing objective compounds show a quite different HLCP/mechanism from that of traditional HLCT materials: 1) for traditional HLCT emitters, their <sup>1</sup>LE states are responsible for the large  $k_r$ , <sup>5b</sup> but for pyrene-containing ones, relatively large  $k_r$  is realized by an efficiently radiative <sup>1</sup>CT state; 2) for traditional HLCT materials, their RISC processes of the "hot exciton" occur from the <sup>3</sup>CT to <sup>1</sup>CT states, and are facilitated by hyperfine coupling (HFC), <sup>7b,17</sup> but for pyrene-containing ones, SOC is also an important driving force facilitating the RISC processes from the <sup>3</sup>LE<sub>Tn</sub> to <sup>1</sup>CT states.

To trigger small charge injection barriers and balanced charge injection and transportation, double-emissive layer OLEDs with structure of ITO/HAT-CN (6 nm)/HAT-CN (0.2 wt.%): TAPC (50 nm)/emitter: TcTa (12 wt.%, 10 nm)/emitter:26DCzPPy (12 wt.%, 10 nm)/Tm3PyP26PyB (50 nm)/LiF (1 nm)/Al (100 nm) are fabricated, in which DP-TXO2 or P-TXO2 acts as the emitter, 4,4',4"-tri(N-carbazolyl)tripheylamine (TcTa) and 2,6-bis(3-(9Hcarbazol-9-yl)phenyl)pyridine (26DCzPPy) serve as the hole- and electron-transporting hosts, 1,1-bis(4-(N,N-di(p-tolyl)amino) phenyl)cyclohexane (TAPC) and 1,3,5-tris(6-(3-(pyridine-3-yl) phenyl)pyridin-2-yl)benzene (Tm3PyP26PyB) act as the holeand electron-transporting materials, respectively (Figure S15). Although the two devices emit deep-blue electroluminescent (EL) with similar EL maxima ( $\lambda_{EL}$ ) of 443 nm and EQE<sub>max</sub> of 4%, their CIE coordinates are (0.154, 0.098) for DP-TXO<sub>2</sub>-based, and (0.160, 0.085) for P-TXO<sub>2</sub>-based devices (Table 2). Inferred from the more red-shifted PL spectrum and the lower  $arphi_{\mathsf{PL}}$  of the 12 wt.% **DP-TXO<sub>2</sub>**:TcTa film than those of the **P-TXO<sub>2</sub>**- based one (Figure S17, Table 1), the inferior chromaticity of the DP-TXO2based device is ascribed to the more serious exciplex-forming intermolecular interactions between the TcTa host and the pyrene subunit in **DP-TXO**<sub>2</sub> than that in **P-TXO**<sub>2</sub>.<sup>8a</sup> Nevertheless, taking into account that the  $\varphi_{PL}$ s of the 26DCzPPy-hosted and TcTa-hosted emitting layers are  $\leq$  0.45 and  $\leq$  0.19, respectively, the high EQE<sub>max</sub> of 4% of these devices implies the relatively high EUE<sub>max</sub> of these devices (> 40%, Table S10), indicative of the effective harvesting of triplet excitons in these devices.

To alleviate the intermolecular interactions between the pyrene subunit of the objective compounds and the TcTa host, a bulky 1,1':3',1"-terphenyl (TP)<sup>8a</sup> group is grafted at the pyrene moiety of **P-TXO**<sub>2</sub> to render **TPP-TXO**<sub>2</sub> (Figure 1). As depicted in Table 1, Figures 2a and S2, while the presence of the TP substituent will lead to slightly red-shifted absorption and PL



Figure 4. Electroluminescence (EL) characteristics of OLEDs based on DP-TXO<sub>2</sub>, P-TXO<sub>2</sub>, and TPP-TXO<sub>2</sub>. a) EL spectra at current density of 100 mA cm<sup>-2</sup>; b) current density-voltage-luminance (*I-V-L*) characteristics; c) EQE–luminance characteristics.

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Table 2. Summary of EL characterisation results of the objective compounds.

Dovico	$V_{\rm on}$	EQE <sup>a)/b)</sup>	L <sub>max</sub>	$CE_{max}$	CIE 1931				
Device	[V]	[%]	[cd m <sup>-2</sup> ]	[cd A <sup>-1</sup> ]	(x, y)				
DP-TXO <sub>2</sub>	3.3	4.0/3.5	9120	4.6	(0.154, 0.098)				
P-TXO₂	3.6	4.0/3.4	5730	3.0	(0.160, 0.085)				
TPP-TXO <sub>2</sub>	3.1	10.5/4.6	10480	11.1	(0.152, 0.065)				
<sup>a)</sup> Maximum external quantum efficiency; <sup>b)</sup> EQE at a luminance of 1000 cd m <sup>-2</sup> .									

bands than those of DP-TXO<sub>2</sub> and P-TXO<sub>2</sub> in solution, in both neat and doped films, TPP-TXO2 shows not only the best deepblue color purity, but also the highest  $\varphi_{PL}$ , verifying the lessened intermolecular interactions. More importantly, TPP-TXO2 has a much higher  $k_{RISC}$  of  $1.4 \times 10^7$  s<sup>-1</sup> than that of **DP-TXO<sub>2</sub>** or **P-TXO<sub>2</sub>** (Table S5). According to the DFT calculation results, the ultrahigh  $k_{\text{RISC}}$  of **TPP-TXO<sub>2</sub>** should originate from its quite small  $\Delta E_{(S1-1)}$ (0.04 eV) as well as the large SOC element due to the markedly different nature of its LE-dominated T<sub>2</sub> state (confined to the TP segment) and HLCT-featured S<sub>1</sub> state (localized in the TXO<sub>2</sub> and pyrene units) (Figure S11). Excitingly, the TPP-TXO<sub>2</sub>based OLED shows much enhanced EL performances than those based on DP-TXO<sub>2</sub> and P-TXO<sub>2</sub>, with more desirable color purity of CIE (0.152, 0.065) approaching the deep-blue standard defined by the European Broadcasting Union (EBU), together with much higher EQE<sub>max</sub> of 10.5% and  $L_{max}$  of 10480 cd m<sup>-2</sup>. Note that the high EQE<sub>max</sub> of 10.5% indicates that the ultra-high EUE<sub>max</sub> even can approach 100% in this device (Table S10). More fascinatingly, this device exhibits just moderate effciency rolloff, with EQE values of 4.6% at 1000 cd m<sup>-2</sup> and 2.8% at 10000 cd m<sup>-2</sup>. This should be attributeded to the quite fast RISC process of the emitter material TPP-TXO2.

Since pyrene is also a widely-used building block of TTA materials, to probe if TTA process contributes significantly to the total EL in these devices, magneto-electroluminescence (MEL) response of a **DP-TXO<sub>2</sub>**-based OLED is measured, because **DP-TXO<sub>2</sub>** owns the highest content of pyrene unit among these compounds. The MEL of the device increases sharply within the low-field regime (< 50 mT), then saturate in a higher B-field with increasing external magnetic field at varied applied bias (Figure S20). Accordingly, the emitting mechanism of **DP-TXO<sub>2</sub>** should not be TTA-dominant.<sup>18</sup>

In summary, we demonstrate that pyrene is a quite promising structural unit for the construction of high-performance HLCT emitters. Different from traditional HLCT emitters, in these pyrenecontaining HLCT materials, an efficiently radiative <sup>1</sup>CT state is responsible for the high  $k_r$  of these compounds, while the effective SOC between their  ${}^{1}CT$  and  ${}^{3}LE_{Tn}$  states may be an important factor responsible for the high  $k_{RISC}$  of these compounds. This represents a new molecular design strategy for HLCT emitters capable of showing both high  $k_r$  and high  $k_{RISC}$  through which ultra-high EUE could be realized. OLEDs based on one objective molecule of TPP-TXO2 can emit deep-blue light with decent color purity of CIE (0.152, 0.065) and  $\text{EQE}_{\text{max}}$  of 10.5%, together with high luminance of 10480 cd  $\text{m}^{\text{-2}}.$ This facile constructive strategy for HLCT OLED emitters can greatly extend the design rationales, which will light up the enthusiasm of scientists to develop more promising HLCT materials showing other emission colors.

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## **Conflicts of interest**

There are no conflicts to declare.

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Pyrene is a quite promising structural unit for HLCT emitters, and deep-blue OLED showing quite high brightness over 10000 cd m<sup>-2</sup> and EQE<sub>max</sub> over 10.5% has been achieved.