Supporting Information

Development of Red Exciplex for Efficient OLEDs by Employing a Phosphor as a Component

*Ming Zhang, Kai Wang,Cai-Jun Zheng,\*De-QiWang, Yi-Zhong Shi, Hui Lin, Si-Lu Tao, Xing Li,and Xiao-Hong Zhang\**

1. **Synthesis.**

**1,3-di(10H-phenoxazin-10-yl)benzene (13PXZB)**.

Toluene (20 ml) and tri-tert-butyl phosphine solution 10% in pentane (0.3 mL, 0.13 mmol) were added to a mixture of phenoxazine (403.1mg, 2.20 mmol), 1,3-dibromobenzene (235.9 mg, 1.00 mmol), palladium(II) acetate (6.7 mg, 0.03 mmol), sodium tertbutoxide (576.63 g, 6.00mmol). With stirring, the suspension was heated at 90°C for 12 h under nitrogen atmosphere. When cooled to room temperature, the mixture was extracted with dichloromethaneand dried over MgSO4. After the solvent had been removed, the residue was purified by column chromatography on silica gel using dichloromethane as the eluent to give a white solid, with an 83.6% yield (368 mg). 1H NMR (600 MHz, CDCl3) δ 7.82 (t, J = 7.9 Hz, 1H), 7.48 (dd, J = 7.9, 2.0 Hz, 2H), 7.40-7.39 (m, 1H), 6.69 (td, J = 7.8, 1.7 Hz, 5H), 6.66 (dd, J = 7.7, 1.7 Hz, 3H), 6.63 (td, J = 7.6, 1.8 Hz, 4H), 5.99 (dd, J = 7.8, 1.6 Hz, 4H). TOF-MS (EI) m/z: [M]+: calcd for C30H20N2O2 440.15; found, 440.15.

**2. Experimental section**

**2.1** **Materials sources.** All materials used were directly purchased from directly purchased from commercial sources, except 13PXZB which is newly designed and synthesized.

**2.2 General information.** 1H NMR data and mass spectral data were respectively measured with Bruker Advance-400 spectrometer and Finnigan 4021C gas chromatography-mass spectrometry instrument. The measurements of fluorescence quantum yields (PLQY), elemental analysis, and PL temperature-dependent transient decay lifetime were carried out at the Analysis and Test Center of Soochow University of Materials Chemistry institute. Cyclic voltammetry data were measured with CHI660E electrochemical analyzer, with a saturated calomel electrode (SCE), Pt disks, and 0.1M Bu4NPF6 respectively as the reference electrode, working electrode, and the supporting electrolyte, and the scan rate of 10 mV/s.

**2.3** **OLEDs fabrication.** The ITO coated glasses were cleaned and treated with UV-ozone for 15 minutes, and then organic materials were deposited in a vapor deposited instrument under the pressure of 4 × 10–4 Pa. The deposited rate of organic materials, LiF, and Al were controlled at 1-2 Å s–1, 0.1 Å s–1, and 10 Å s–1, respectively. The optical and electrical data of the devices were respectively recorded with a PR650 Spectrascan and Keithley 2400 SourceMeter under ambient atmosphere simultaneously. CE, PE, and EQE were calculated with the data of current, luminance and emission spectrum, assuming a Lambertian distribution.

**3. Determination of Φp ,Φd and *k*ISC.**

In this study, total PL quantum efficiency was determined by the emission intensity between in air (Iair) and in vacuum (Ivacuum) and Φtotal was calculated by the flowing equation:

 (1)

The Φprompt and Φdelayed were determined by using total PL quantum efficiency and the ratio between prompt and delayed components which was calculated from transient PL measurements. The intensity ratio between prompt (r1) and delayed (r2) components were determined using emission lifetime (τ1, τ2) and fitting parameter (Α1, Α2) as follow.

 (2)

 (3)

 (4)

Then, Φprompt and Φdelayed were determined using intensity ratio (r1, r2) and total emission quantum yield.

(5)

The energy difference (Δ*E*ST) and the triplet formation efficiency (ΦT) were evaluated using a Berberan-Santos plot[S2] from the temperature dependence results according to the above equation. Then, the intersystem crossing rate constant (*k*ISC), were estimated assuming that *k*ISC was independent of temperature

**3.1. Main kinetic parameters calculations.**

According to the literature, the main kinetic parameters of the two exciplexs were calculated by the following equations. Particularly, to conveniently evaluate the phosphor-based exciplexes, we neglect the phosphorescence decay.

 (6)

 (7)

 (8)

 (9)

 (10)

 (11)

 (12)



**Figure S1.** Cyclic voltammetry of a) 13PXZB, Ir(ppy)3 and PO-T2T in N,N-dimethylformamide (DMF); and b)mCP in acetonitrile (ACE). The HOMO levels of 13PXZB and Ir(ppy)3, LUMO level of PO-T2T (in DMF) are respectively calculated with equation: HOMO = − *e*(*E*ox + 4.52) and LUMO = − *e*(*E*red + 4.52). The HOMO level of mCP (in ACE) is calculated with equation: HOMO = − *e*(*E*ox + 4.62). *E*ox, *E*red are the onsets of oxidation and reduction curves, respectively.





**Figure S2.** Phosphorescence spectra of a) PO-T2T, b) Ir(ppy)3 and c) 13PXZB in 2-MeTHF at 77K.

 

**Figure S3.** Transient PL decay curves of the (a) PO-T2T:Ir(ppy)3 film; (b) PO-T2T:13PXZB film in the range of 100 ns at room temperatures by exciting at 300 nm.



**Figure S4. a)** PL spectra of PO-T2T:Ir(ppy)3 film at various temperature; b) PL spectra of PO-T2T:13PXZB film at various temperature; c) the transient PL decay curves of PO-T2T:Ir(ppy)3 film at various temperature; d) the transient PL decay curves of PO-T2T:13PXZB film at various temperature.

**Table S1.** Lifetime data extracted from the transient characterization of PO-T2T:Ir(ppy)3 film and PO-T2T:13PXZB film in different temperature.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| exciplex | T(k) | τ1 (ns) | A1 | τ2(μs) | A2 | Φtotal | Φp | Φd |
| PO-T2T:Ir(ppy)3 | 300 | 13.1 | 0.491 | 2.8 | 0.392 | 0.233 | 0.023 | 0.210 |
| 280 | 13.5 | 0.511 | 4.1 | 0.376 | 0.332 | 0.036 | 0.296 |
| 260 | 13.9 | 0.701 | 5.6 | 0.312 | 0.389 | 0.047 | 0.342 |
| 240 | 14.7 | 0.739 | 7.3 | 0.284 | 0.445 | 0.062 | 0.383 |
| 220 | 15.3 | 0.796 | 8.2 | 0.257 | 0.501 | 0.075 | 0.426 |
| 200 | 16.1 | 0.766 | 11.3 | 0.242 | 0.565 | 0.096 | 0.469 |
| PO-T2T:13PXZB | 300 | 17.2 | 0.545 | 13.9 | 0.555 | 0.086 | 0.010 | 0.076 |
| 280 | 17.8 | 0.694 | 14.1 | 0.306 | 0.114 | 0.014 | 0.100 |
| 260 | 18.3 | 0.673 | 15.3 | 0.327 | 0.122 | 0.015 | 0.107 |
| 240 | 18.9 | 0.713 | 15.9 | 0.287 | 0.127 | 0.018 | 0.109 |
| 220 | 19.6 | 0.762 | 16.2 | 0.298 | 0.134 | 0.021 | 0.113 |
| 200 | 20.1 | 0.785 | 17.8 | 0.235 | 0.142 | 0.027 | 0.115 |

**Table S2**. Transition rates of two exciplex at 300 K. The unit of transition rates is s-1.

|  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Exciplex | Φtotal | Φprompt | ΦTADF | τp (ns) | τd (μs) | kp | Kd | Krs | Knrs | KISC | KRISC | KnrT |
| PO-T2T:Ir(ppy)3 | 23.3 | 2.3 | 21.0 | 13.2 | 2.8 | 7.60×107 | 3.57×105 | 0.17×107 | 0.73×107 | 6.70×107 | 3.71×106 | 7.00×103 |
| PO-T2T:13PXZB | 8.6 | 1.0 | 7.6 | 17.1 | 13.9 | 5.84×107 | 7.21×104 | 0.06×107 | 0.85×107 | 4.93×107 | 6.17×105 | 1.04×104 |

 ****

**Figure S5.** Current density-voltage curves of hole- and electron-only devices based on a) 13PXZB; b) PO-T2T; c) PO-T2T:Ir(ppy)3. Hole-only devices: ITO/MoO3 (12 nm)/Materials (50 nm)/MoO3 (12 nm)/Al (100 nm); Electron-only devices: ITO/Al (40 nm)/LiF(1 nm)/Materials (50 nm)/LiF (1 nm)/Al (100 nm).



**Figure S6.** a) PE–EQE-luminance plots of the Device 2, b) Current density–luminance-voltage characteristics of Device 2; c) EL spectra of the Device 3 at different luminance; d) Current density–luminance-voltage characteristics of Device 3; c) PE–EQE-luminance plots of the Device 3.



**Figure S7.** EL spectra of the Device 1, 3 and 4.

**References**

[S1] T. Nakagawa, S.-Y. Ku, K.-T. Wong, C. Adachi, *Chem. Commun*. **2012**, *48*, 9580.

[S2] M. N. Berberan-Santos, J. M. M. Garcia, *J. Am. Chem. Soc.* **1996**, *118*, 9391.