

## Supporting information

# **Dibenzo[a,c]phenazine-11,12-dicarbonitrile (DBPzDCN) Acceptor based Thermally Activated Delayed Fluorescent Compound for Efficient Near-Infrared Electroluminescent Devices**

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## 1. Analysis of Rate Constants

According to references S1-4, the rate equation for singlet and triplet exciton densities ( $[S_1]$  and  $[T_1]$ ) is described by

$$\frac{d[S_1]}{dt} = -(k_{r,S} + k_{nr,S} + k_{ISC})[S_1] + k_{RISC}[T_1] \quad (1)$$

$$\frac{d[T_1]}{dt} = -(k_{r,T} + k_{nr,T} + k_{RISC})[T_1] + k_{ISC}[S_1] \quad (2)$$

where  $k_{r,S}$ ,  $k_{nr,S}$  and  $k_{ISC}$  are the rate constants of radiative decay (fluorescence), intrinsic non-radiative decay (internal conversion) and ISC for the singlet excitons, respectively.  $k_{r,T}$ ,  $k_{nr,T}$ , and  $k_{RISC}$  are the rate constants of radiative decay (phosphorescence), intrinsic non-radiative decay and RISC of the triplet exciton, respectively.

The general solution for  $[S_1]$  is then:

$$[S_1] = C_p e^{-k_p t} + C_d e^{-k_d t} \quad (3)$$

where  $C_p$  and  $C_d$  are the intensities of the prompt and delayed fluorescence, respectively;  $k_p$  and  $k_d$  represent the decay rate constants for prompt and delayed fluorescence, respectively, and have the relationship of <sup>[S1-S3]</sup>

$$k_p, k_d = \frac{k_{r,S} + k_{nr,S} + k_{ISC} + k_{nr,T} + k_{RISC}}{2} \times \left( 1 \pm \sqrt{1 - \frac{4(k_{r,S} + k_{nr,S} + k_{ISC})(k_{nr,T} + k_{RISC}) - 4k_{ISC}k_{RISC}}{(k_{r,S} + k_{nr,S} + k_{ISC} + k_{nr,T} + k_{RISC})^2}} \right) \quad (4)$$

$$k_p + k_d = k_{r,S} + k_{nr,S} + k_{ISC} + k_{r,T} + k_{nr,T} + k_{RISC} \quad (5)$$

$$k_p k_d = (k_{r,S} + k_{nr,S} + k_{ISC})(k_{r,T} + k_{nr,T} + k_{RISC}) - k_{RISC} k_{ISC} \quad (6)$$

When there are negligible deactivation channels from  $T_1$ , the values of  $k_{r,S}$ ,  $k_{nr,S}$  and  $k_{ISC}$  are significantly larger than those of  $k_{r,T}$ ,  $k_{nr,T}$  and  $k_{RISC}$ . Generally,  $k_p \gg k_d$ , then  $k_p$  and  $k_d$

can be experimentally determined from prompt and delayed fluorescence decay time constants  $\tau_p$ ,  $\tau_d$  as follows:

$$k_p = \frac{1}{\tau_p} = k_{r,S} + k_{nr,S} + k_{ISC} \quad (7)$$

$$k_d = \frac{1}{\tau_d} = k_{nr,T} + \left( 1 - \frac{k_{ISC}}{k_{r,S} + k_{nr,S} + k_{ISC}} \right) k_{RISC} \quad (8)$$

The PL quantum efficiency of prompt fluorescence ( $\Phi_p$ ) and delayed fluorescence ( $\Phi_d$ ) are expressed by

$$\phi_p = \frac{k_{r,S}}{k_{r,S} + k_{nr,S} + k_{ISC}} = \frac{k_{r,S}}{k_p} \quad (9)$$

$$\phi_d = \sum_{k=1}^{\infty} (\phi_{ISC} \phi_{RISC})^k \phi_p = \frac{\phi_{ISC} \phi_{RISC}}{1 - \phi_{ISC} \phi_{RISC}} \quad (10)$$

where  $\Phi_{ISC}$  and  $\Phi_{RISC}$  are the intersystem crossing efficiency and reverse intersystem crossing efficiency, respectively, which can be expressed by the follow equations

$$\phi_{ISC} = \frac{k_{ISC}}{k_{r,S} + k_{nr,S} + k_{ISC}} = \frac{k_{ISC}}{k_p} \quad (11)$$

$$\phi_{RISC} = \frac{k_{RISC}}{k_{RISC} + k_{r,T} + k_{nr,T}} \quad (12)$$

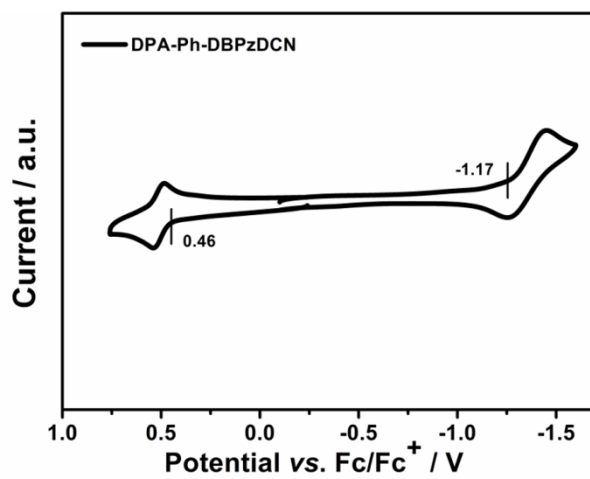
By assuming  $k_{r,T} + k_{nr,T} \ll k_{RISC}$ , i.e. most of triplet states can return to singlet states through RISC and thus  $\Phi_{RISC} \sim 1$  and major non-radiative losses occur in singlet states, via equations (7)-(12) one obtains.

$$\phi_{ISC} = \frac{\phi_d}{\phi_p + \phi_d} \quad (13)$$

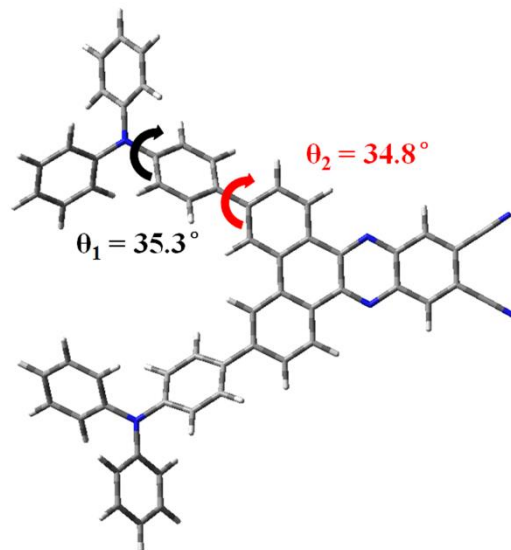
$$k_{ISC} = \frac{\phi_d}{\phi_p + \phi_d} k_p \quad (14)$$

$$k_{RISC} = \frac{k_d}{\left(1 - \frac{k_{ISC}}{k_p}\right)} = \frac{k_p k_d}{k_p - k_{ISC}} \quad (15)$$

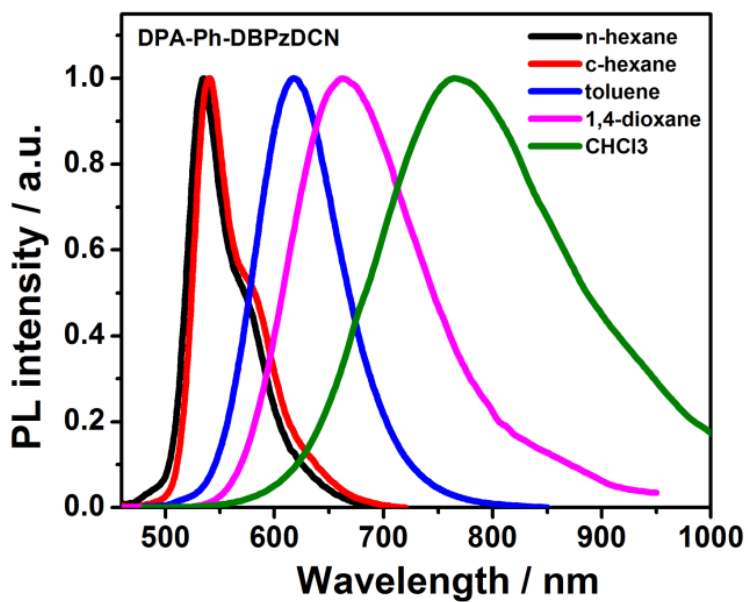
## 2. Figures



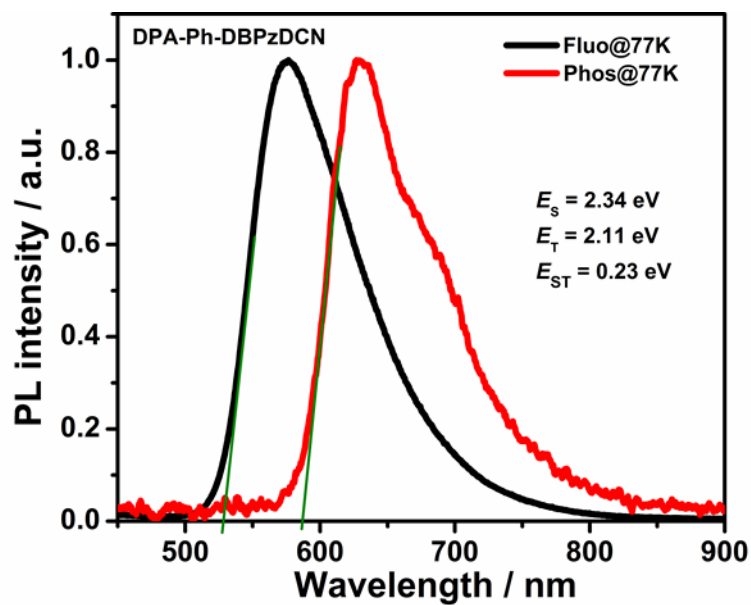
**Fig. S1** Cyclic voltammogram of DPA-Ph-DBPzDCN.



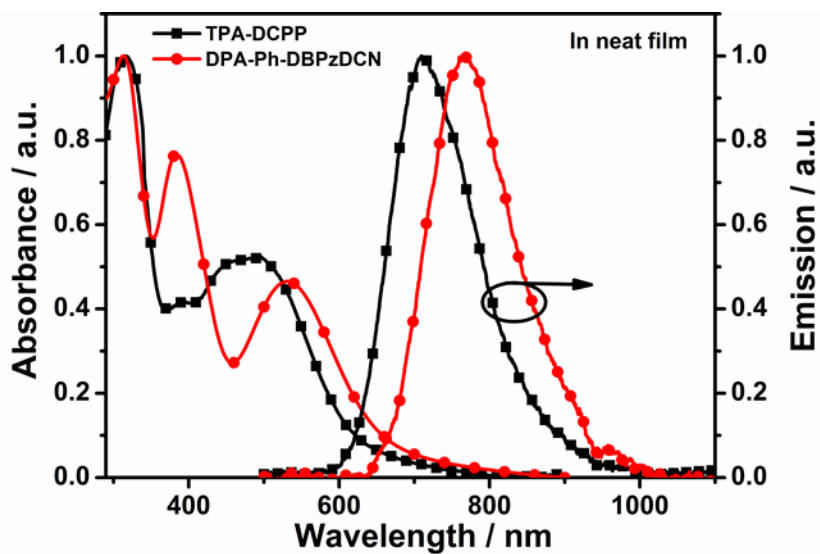
**Fig. S2** The  $S_0$  geometries of DPA-Ph-DBPzDCN optimized at the level of DFT/B3LYP/6-31G(d) in vacuum.



**Fig. S3** Normalized PL spectra of DPA-Ph-DBPzDCN in solvents with different polarity.



**Fig. S4** The fluorescence and phosphorescence spectra of DPA-Ph-DBPzDCN in toluene at 77 K.



**Fig. S5** The absorption and fluorescence spectra of TPA-DCPP and DPA-Ph-DBPzDCN in neat film.

### 3. Tables

**Table S1.** Thermal, electrochemical and TD-DFT calculation data of DPA-Ph-DBPzDCN.

compound	$T_g^a/T_d^b$ [°C]	HOMO/LUMO <sup>c)</sup> [eV]	HOMO/LUMO <sup>d)</sup> [eV]	$S_1/T_1^e$ [eV]	$\Delta E_{ST}^e$ [eV]	$f^e$
DPA-Ph-DBPzDCN	177/533	-5.21/-2.99	-5.26/-3.63	1.9257/1.777	0.1487	0.0744

<sup>a)</sup> Glass transition temperature; <sup>b)</sup> Decomposition temperature (5% weight loss); <sup>c)</sup> Estimated from DFT calculations; <sup>d)</sup> Measured by cyclic voltammetry in 0.1 M n-Bu<sub>4</sub>NPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> solution; <sup>e)</sup> Estimated from TD-DFT simulations.

**Table S2.** Photophysical properties of DPA-Ph-DBPzDCN.

compound	$\lambda_{abs, sol^a}/film^b$ [nm]	$\lambda_{PL, sol^a}/film^b$ [nm]	$\Phi_{PL, sol^c}/film^d$ [%]	$S_1/T_1^e$ [eV]	$\Delta E_{ST}^f$ [eV]
DPA-Ph-DBPzDCN	490/530	618/765	91/2	2.34/2.11	0.23

<sup>a)</sup> The longest peak wavelength of absorption and PL measured in toluene; <sup>b)</sup> The longest peak wavelength of absorption and PL measured in neat film; <sup>c)</sup> absolute PL quantum yield ( $\Phi_{PL}$ ) evaluated using an integrating sphere in toluene after N<sub>2</sub> bubbling; <sup>d)</sup>  $\Phi_{PL}$  of investigated molecule in neat film; <sup>e)</sup>  $S_1$  and  $T_1$  estimated from onsets of the fluorescence and phosphorescence spectra in toluene at 77K, respectively. <sup>f)</sup>  $\Delta E_{ST} = S_1 - T_1$ .

**Table S3.** The summary of rate constants for DPA-Ph-DBPzDCN films with different doping concentrations.

Concentration	$\lambda_{PL}$	$\Phi$	$\Phi_p/\Phi_d$	$\tau_p^a$ [ns]	$\tau_d$ [us]	$k_p$ [ $\times 10^7 s^{-1}$ ]	$k_d$ [ $\times 10^4 s^{-1}$ ]	$k_{r,S}$ [ $\times 10^7 s^{-1}$ ]	$k_{nr,S}$ [ $\times 10^7 s^{-1}$ ]	$k_{ISC}$ [ $\times 10^7 s^{-1}$ ]	$k_{RISC}$ [ $\times 10^4 s^{-1}$ ]
6 wt%	674	0.39	0.31/0.08	14.3	296.5	7.0	0.34	2.2	3.4	1.4	0.43
10 wt%	690	0.32	0.29/0.03	21.5	145.8	4.7	0.69	1.3	2.9	0.44	0.76
20 wt%	705	0.25	0.23/0.02	23.9	121.9	4.2	0.82	0.96	2.9	0.33	0.89
30 wt%	728	0.14	0.13/0.01	25.3	101.1	4.0	0.99	0.51	3.2	0.28	1.1

<sup>a)</sup> Average lifetime calculated by  $\tau_{av} = \sum A_i \tau_i^2 / \sum A_i \tau_i$ , where  $A_i$  is the pre-exponential for lifetime  $\tau_i$ .

#### 4. Reference:

- [S1] M. A. Baldo, and S. R. Forrest, Transient analysis of organic electrophosphorescence: I. Transient analysis of triplet energy transfer. *Phys. Rev. B*, 2000, **62**, 10958.
- [S2] K. Goushi, K. Yoshida, K. Sato and C. Adachi, *Nat. Photonics*, 2012, **6**, 253.
- [S3] H. Wang, L. Xie, Q. Peng, L. Meng, Y. Wang, Y. Yi and P. Wang, *Adv. Mater.*, 2014, **26**, 5198.
- [S4] K.-C. Pan, S.-W. Li, Y.-Y. Ho, Y.-J. Shiu, W.-L. Tsai, M. Jiao, W.-K. Lee, C.-C. Wu, C.-L. Chung, T. Chatterjee, Y.-S. Li, K.-T. Wong, H.-C. Hu, C.-C. Chen and M.-T. Lee, *Adv. Funct. Mater.*, 2016, **26**, 7560.