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\textsubscript{1}] and [T\textsubscript{1}]) is described by

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

\[
\frac{d[T_1]}{dt} = -\left(k_{r,T} + k_{nr,T} + k_{RISC}\right)[T_1] + k_{ISC}[S_1]
\] 
(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:

\[
[S_1] = C_p e^{-k_p t} + C_d e^{-k_d t}
\] 
(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 \([S1\textsuperscript{S3}]\)

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

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

\[
k_p^2 k_d = \left(k_{r,S} + k_{nr,S} + k_{ISC}\right)\left(k_{r,T} + k_{nr,T} + k_{RISC}\right) - k_{RISC}k_{ISC}
\] 
(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:

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

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

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

$$\phi_p = \frac{k_{r,S}}{k_{r,S} + k_{nr,S} + k_{ISC}} = \frac{k_{r,S}}{k_p}$$  \hspace{1cm} (9)

$$\phi_d = \sum_{k=1}^{\infty} (\Phi_{ISC} \Phi_{RISC})^k \phi_p = \frac{\Phi_{ISC} \Phi_{RISC}}{1 - \Phi_{ISC} \Phi_{RISC}}$$  \hspace{1cm} (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

$$\phi_{ISC} = \frac{k_{ISC}}{k_{r,S} + k_{nr,S} + k_{ISC}} = \frac{k_{ISC}}{k_p}$$  \hspace{1cm} (11)

$$\phi_{RISC} = \frac{k_{RISC}}{k_{RISC} + k_{r,T} + k_{nr,T}}$$  \hspace{1cm} (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.

$$\phi_{ISC} = \frac{\phi_d}{\phi_p + \phi_d}$$  \hspace{1cm} (13)
\[ k_{ISC} = \frac{\phi_d - k_p}{\phi_p + \phi_d} \]  

\[ k_{RISC} = \frac{k_d}{\left(1 - \frac{k_{ISC}}{k_p}\right) - k_p - k_{ISC}} \]  

(14)

(15)

2. Figures

![Cyclic voltammogram of DPA-Ph-DBPzDCN.](image)

**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.

![Fluorescence and phosphorescence spectra of DPA-Ph-DBPzDCN](image)

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

![Absorption and fluorescence spectra of TPA-DCPP and DPA-Ph-DBPzDCN](image)
3. Tables

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

<table>
<thead>
<tr>
<th>compound</th>
<th>$T_g$/$T_d$ $^b$</th>
<th>HOMO/LUMO$^a$</th>
<th>HOMO/LUMO$^d$</th>
<th>$S_1/T_1$ $^e$</th>
<th>$\Delta E_{ST}$ $^f$</th>
<th>$f$ $^e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPA-Ph-DBPzDCN</td>
<td>177/533</td>
<td>-5.21/-2.99</td>
<td>-5.26/-3.63</td>
<td>1.9257/1.777</td>
<td>0.1487</td>
<td>0.0744</td>
</tr>
</tbody>
</table>

$^a$) Glass transition temperature;  $^b$) Decomposition temperature (5% weight loss);  $^c$) Estimated from DFT calculations;  $^d$) Measured by cyclic voltammetry in 0.1 M n-Bu$_4$NPF$_6$ in CH$_2$Cl$_2$ solution;  $^e$) Estimated from TD-DFT simulations.

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

<table>
<thead>
<tr>
<th>compound</th>
<th>$\lambda_{\text{abs,sol/film}}^{\text{sol/film}}$ $^b$</th>
<th>$\lambda_{\text{PL,sol/film}}^{\text{sol/film}}$ $^b$</th>
<th>$\Phi_{\text{PL,sol/film}}^{\text{sol/film}}$ $^c$</th>
<th>$S_1/T_1$ $^e$</th>
<th>$\Delta E_{ST}$ $^f$</th>
</tr>
</thead>
<tbody>
<tr>
<td>DPA-Ph-DBPzDCN</td>
<td>490/530</td>
<td>618/765</td>
<td>91/2</td>
<td>2.34/2.11</td>
<td>0.23</td>
</tr>
</tbody>
</table>

$^a$) The longest peak wavelength of absorption and PL measured in toluene;  $^b$) The longest peak wavelength of absorption and PL measured in neat film;  $^c$) Absolute PL quantum yield ($\Phi_{\text{PL}}$) evaluated using an integrating sphere in toluene after N$_2$ bubbling;  $^d$) $\Phi_{\text{PL}}$ of investigated molecule in neat film;  $^e$) $S_1$ and $T_1$ estimated from onsets of the fluorescence and phosphorescence spectra in toluene at 77K, respectively.  $^f$) $\Delta E_{ST} = S_1 - T_1$.

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

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$\lambda_{\text{PL}}$</th>
<th>$\Phi$</th>
<th>$\Phi_{\text{r}}/\Phi_{\text{d}}$</th>
<th>$\tau_\text{av}$ $^a$</th>
<th>$\tau_0$</th>
<th>$k_{\text{e}}$ $\times 10^5$ s$^{-1}$</th>
<th>$k_{\text{d}}$ $\times 10^5$ s$^{-1}$</th>
<th>$k_{\text{a,S}}$ $\times 10^5$ s$^{-1}$</th>
<th>$k_{\text{ISC}}$ $\times 10^5$ s$^{-1}$</th>
<th>$k_{\text{RISC}}$ $\times 10^4$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 wt%</td>
<td>674</td>
<td>0.39</td>
<td>0.31/0.08</td>
<td>14.3</td>
<td>296.5</td>
<td>0.34</td>
<td>2.2</td>
<td>3.4</td>
<td>3.4</td>
<td>1.4</td>
</tr>
<tr>
<td>10 wt%</td>
<td>690</td>
<td>0.32</td>
<td>0.29/0.03</td>
<td>21.5</td>
<td>145.8</td>
<td>0.69</td>
<td>1.3</td>
<td>2.9</td>
<td>0.44</td>
<td>0.76</td>
</tr>
<tr>
<td>20 wt%</td>
<td>705</td>
<td>0.25</td>
<td>0.23/0.02</td>
<td>23.9</td>
<td>121.9</td>
<td>0.82</td>
<td>0.96</td>
<td>2.9</td>
<td>0.33</td>
<td>0.89</td>
</tr>
<tr>
<td>30 wt%</td>
<td>728</td>
<td>0.14</td>
<td>0.13/0.01</td>
<td>25.3</td>
<td>101.1</td>
<td>0.99</td>
<td>0.51</td>
<td>3.2</td>
<td>0.28</td>
<td>1.1</td>
</tr>
</tbody>
</table>

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

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4. Reference:


