Oxadiazole- and triazole-based highly-efficient thermally activated delayed fluorescence emitters for organic light-emitting diodes

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1. Preparation of 10-(4-(5-phenyl-1,3,4-oxadiazol-2-yl)phenyl)-10H-phenoxazine (PXZ-OXD)

To a solution of 2-(4-bromophenyl)-5-phenyl-1,3,4-oxadiazole (1.20 g, 3.98 mmol, synthesized by a reported method\textsuperscript{s1}), phenoxazine (802 mg, 4.38 mmol) and potassium carbonate (1.81 g, 13.1 mmol) in toluene (30 mL) was added, with stirring, a solution of palladium(II) acetate (29.2 mg, 0.13 mmol) and tri-\textit{tert}-butylphosphine (97.1 mg, 0.48 mmol) in toluene (30 mL). The mixture was stirred and heated under reflux for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over MgSO\textsubscript{4}, and concentrated \textit{in vacuo}. Purification of the residue by column chromatography (eluent: toluene/ethyl acetate = 10:1) afforded 1.52 g of PXZ-OXD. The yield was over 94%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]
\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) \(\delta = 5.98(d, 2H), 6.64(t, 2H), 6.69(t, 2H), 6.72(d, 2H), 7.55(m, 5H), 8.17(d, 2H), 8.38(d, 2H)\); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 300MHz) \(\delta = 113.3, 115.7, 121.9, 123.3, 127.0, 129.2, 129.7, 131.8, 131.9, 133.7, 142.4, 144.0\).

[MS]
MALDI-MS \textit{m/z} Calcd for C\textsubscript{26}H\textsubscript{17}N\textsubscript{3}O\textsubscript{2}: 403; found: 403.

[Element analysis]
Calcd for C\textsubscript{26}H\textsubscript{17}N\textsubscript{3}O\textsubscript{2}: C, 77.41; H, 4.25; N, 10.42; found: C, 77.58; H, 4.18; N, 10.42.
2. Preparation of 2,5-bis(4-(10H-phenoxazin-10-yl)phenyl)-1,3,4-oxadiazole (2PXZ-OXD)

To a solution of 2,5-bis(4-bromophenyl)-1,3,4-oxadiazole (630.8 mg, 1.66 mmol, synthesized by a reported method\textsuperscript{52}), phenoxazine (668.7 mg, 3.65 mmol) and potassium carbonate (1.52 g, 11.0 mmol) in toluene (25 mL) was added, with stirring, a solution of palladium(II) acetate (25.0 mg, 0.11 mmol) and tri-\textit{tert}-butylphosphine (81.0 mg, 0.40 mmol) in toluene (25 mL). The mixture was stirred and heated under reflux for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over MgSO\textsubscript{4}, and concentrated \textit{in vacuo}. Purification of the residue by column chromatography (eluent: chloroform) afforded 965.2 mg of 2PXZ-OXD. The yield was over 99\%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

\[\text{[NMR]}\]
\textsuperscript{1}H NMR (CDCl\textsubscript{3}, 300 MHz) \(\delta = 5.99(d, 4H), 6.61(t, 4H), 6.68(m, 8H), 7.57(d, 4H), 8.39(d, 4H)\); \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 300MHz) \(\delta = 113.3, 115.8, 121.9, 123.3, 129.7, 131.9, 133.7, 142.6, 144.0, 164.2\).

\[\text{[MS]}\]
MALDI-MS \textit{m/z} Calcd for C\textsubscript{38}H\textsubscript{24}N\textsubscript{4}O\textsubscript{3}: 584; found: 584.

\[\text{[Element analysis]}\]
Calcd for C\textsubscript{38}H\textsubscript{24}N\textsubscript{4}O\textsubscript{3}: C, 78.07; H, 4.14; N, 9.58; found: C, 78.02; H, 4.06; N, 9.56.
3. Preparation of 10-(4-(4,5-diphenyl-4H-1,2,4-triazol-3-yl)phenyl)-10H-phenoxazine (PXZ-TAZ)

To a solution of 3-(4-bromophenyl)-4,5-diphenyl-1,2,4-triazole (1.00 g, 2.66 mmol, synthesized by a reported method), phenoxazine (537 mg, 2.93 mmol) and potassium carbonate (1.21 g, 8.79 mmol) in toluene (20 mL) was added, with stirring, a solution of palladium(II) acetate (20.2 mg, 0.09 mmol) and tri-tert-butylphosphine (64.7 mg, 0.32 mmol) in toluene (20 mL). The mixture was stirred and heated under reflux for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over MgSO₄, and concentrated in vacuo. Purification of the residue by column chromatography (eluent: toluene/ethyl acetate = 1:1) afforded 1.01 g of PXZ-TAZ. The yield was over 79%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR]

$^1$H NMR (DMSO, 300 MHz) $\delta$ = 5.79(d, 2H), 6.67(t, 2H), 6.70(t, 2H), 6.74(d, 2H), 7.39(d, 2H), 7.41(m, 6H), 7.46(d, 2H), 7.52(d, 2H), 7.67(d, 2H); $^{13}$C NMR (CDCl₃, 300 MHz) $\delta$ = 113.2, 115.6, 121.6, 123.2, 126.7, 127.8, 128.5, 128.8, 129.8, 130.2, 131.0, 131.3, 133.9, 134.6, 140.4, 143.9.

[MS]

MALDI-MS m/z Calcd for C₃₂H₂₂N₄O: 478; found: 478.

[Element analysis]

Calcd for C₃₂H₂₂N₄O: C, 80.32; H, 4.63; N, 11.71; found: C, 80.21; H, 4.58; N, 11.70.
4. Preparation of 10,10’-((4-phenyl-4H-1,2,4-triazole-3,5-diyl)bis(4,1-phenylene))-bis(10H-phenoxazine) 2PXZ-TAZ

To a solution of 3,5-bis(4-bromophenyl)-4-phenyl-4H-1,2,4-triazole (1.50 g, 3.30 mmol, synthesized by a reported method\textsuperscript{31}), phenoxazine (1.33 g, 7.26 mmol) and potassium carbonate (3.01 g, 21.8 mmol) in toluene (40 mL) was added, with stirring, a solution of palladium(II) acetate (49.4 mg, 0.22 mmol) and tri-tert-butylphosphine (161.9 mg, 0.80 mmol) in toluene (40 mL). The mixture was stirred and heated under reflux for one day. The cooled mixture was partitioned between chloroform and water. The organic layer was separated, and the aqueous layer was extracted with chloroform. The combined organic layers were washed with brine, dried over MgSO\textsubscript{4}, and concentrated \textit{in vacuo}. Purification of the residue by column chromatography (eluent: chloroform/hexane=1:4) afforded 1.52 g of 2PXZ-TAZ. The yield was over 70%. The compound was further purified by sublimation under reduced pressure for OLED fabrication.

[NMR] 1H NMR (CDCl\textsubscript{3}, 300 MHz) $\delta$ = 5.88(d, 4H), 6.57(t, 4H), 6.64(m, 8H), 7.30(m, 6H), 7.55(m, 3H), 7.68(d, 4H); 13C NMR (CDCl\textsubscript{3}, 300MHz) $\delta$ = 113.2, 115.6, 121.7, 123.2, 126.9, 127.8, 130.4, 131.1, 131.2, 133.8, 135.1, 140.5, 143.9, 154.3.

[MS] MALDI-MS $m/z$ Calcd for C\textsubscript{44}H\textsubscript{29}N\textsubscript{5}O\textsubscript{2}: 659; found: 659

[Element analysis] Calcd for C\textsubscript{44}H\textsubscript{29}N\textsubscript{5}O\textsubscript{2}: C, 80.10; H, 4.43; N, 10.62; found: C, 80.11; H, 4.37; N, 10.61.
5. Ultraviolet-visible and photoluminescence spectra

(a) Ultraviolet-visible (UV-Vis) and photoluminescence (PL) spectra of (a) PXZ-OXD, (b) 2PXZ-OXD, (c) PXZ-TAZ, and (d) 2PXZ-TAZ. UV-Vis spectra were measured using a UV-Vis spectrophotometer (UV-2550, Shimadzu, Japan). PL spectra were measured using spectrofluorometers (Fluoromax-4, Horiba Jobin Yvon, USA; FP-6500-A-ST, Jasco, Japan). Excitation wavelength was 330 nm.

Supplementary Fig. S1: Ultraviolet-visible (UV-Vis) and photoluminescence (PL)
6. Calculated and experimental absorption and emission wavelengths

Supplementary Table S1: Absorption ($\lambda_{ab}$) and emission wavelengths ($\lambda_{em}$) for PXZ-OXD, 2PXZ-OXD, PXZ-TAZ, and 2PXZ-TAZ were computed using time-dependent density functional theory (TD-DFT) at the CAM-B3LYP/cc-pVDZ level of theory. Solvent effects were taken into account by means of the polarizable continuum model.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{ab}$ (nm)</th>
<th>$\lambda_{em}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PXZ-OXD</td>
<td>416</td>
<td>390</td>
</tr>
<tr>
<td>2PXZ-OXD</td>
<td>439</td>
<td>397</td>
</tr>
<tr>
<td>PXZ-TAZ</td>
<td>366</td>
<td>372</td>
</tr>
<tr>
<td>2PXZ-TAZ</td>
<td>370</td>
<td>376</td>
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</table>
7. ORTEP diagram of the crystalline structure of 2PXZ-OXD

Supplementary Fig. S2: ORTEP diagram of the molecular structure of 2PXZ-OXD determined by single crystal X-ray diffraction. The torsion angle is 76.7°.
8. Calculated $S_1$ and $T_1$ excitation energies and $\Delta E_{ST}$

**Supplementary Table S2:** Calculated $S_1$ and $T_1$ excitation energies and the difference between them ($\Delta E_{ST}$) for PXZ-OXD, 2PXZ-OXD, PXZ-TAZ, and 2PXZ-TAZ. Calculation of $\Delta E_{ST}$ was carried out with TD-DFT at the CAM-B3LYP/cc-pVDZ level of theory. Oscillator strengths ($f$) of the $S_1$ states shown in parentheses.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$S_1$ energy (eV)</th>
<th>$T_1$ energy (eV)</th>
<th>$\Delta E_{ST}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PXZ-OXD</td>
<td>3.49 (0.0001)</td>
<td>2.84</td>
<td>0.65</td>
</tr>
<tr>
<td>2PXZ-OXD</td>
<td>3.40 (0.0000)</td>
<td>2.83</td>
<td>0.57</td>
</tr>
<tr>
<td>PXZ-TAZ</td>
<td>3.80 (0.0000)</td>
<td>2.83</td>
<td>0.97</td>
</tr>
<tr>
<td>2PXZ-TAZ</td>
<td>3.69 (0.0000)</td>
<td>2.83</td>
<td>0.86</td>
</tr>
</tbody>
</table>
9. Highest occupied and lowest unoccupied natural transition orbitals for the $S_1$ states of PXZ-OXD, PXZ-TAZ, and PXZ-2TAZ

Supplementary Fig. S3: Highest occupied and lowest unoccupied natural transition orbitals (NTOs) for the $S_1$ states of (a) PXZ-OXD, (b) PXZ-TAZ, and (c) PXZ-2TAZ calculated at the CAM-B3LYP/cc-PVDZ level of theory.
10. Temperature dependence of photoluminescence spectrum of 6 wt% 2PXZ-OXD:DPEPO film

Supplementary Fig. S4: Temperature dependence of photoluminescence spectrum of a 6 wt% 2PXZ-OXD:DPEPO film.
11. Photoluminescence characteristics of 6 wt% 2PXZ-TAZ:DPEPO film

(a)

![Absorption and PL spectra of a 6 wt% 2PXZ-TAZ:DPEPO film](image)

(b)

![Transient PL decay curves for the doped film measured at temperatures of 8 to 300 K](image)

(c)

![Fluorescence and phosphorescence spectra of the doped film measured at 8 K](image)

**Supplementary Fig. S5**: (a) Absorption and PL spectra of a 6 wt% 2PXZ-TAZ:DPEPO film. (b) Transient PL decay curves for the doped film measured at temperatures of 8 to 300 K. (c) Fluorescence and phosphorescence spectra of the doped film measured at 8 K. Black and red lines show fluorescence and phosphorescence spectra, respectively.
References

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1. $^1$H NMR spectrum of PXZ-OXD
2. $^1$H NMR spectrum of 2PXZ-OXD
3. $^1$H NMR spectrum of PXZ-TAZ
4. $^1H$ NMR spectrum of 2PXZ-TAZ