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Introduction

Following the invention of organic light-emitting diode (OLED) technology by C. W. Tang and S. A. VanSlyke in 1987,¹ OLEDs have attracted extensive attention in both academia and industry.^{2–6} Currently, OLEDs have demonstrated a wide range of applications in both display and lighting. So far, much progress has been made in the development of efficient emissive materials from fluorescent molecules,^{7–9} phosphorescent complexes,^{10–13} or thermally activated delayed fluorescent (TADF) compounds.^{14–18} Recently, Yersin *et al.* reported the fourth generation OLEDs based on rigidified molecules with an extremely small ¹CT–³CT energy difference of around 2 meV.¹⁹ However, the development of TADF emitters is currently a hot research topic because of their particular properties, such as the utilization of both singlet and triplet excitons, diversity in their structural modification and functionality, and absence of noble metals. Since TADF emitters can realize a

Highly efficient red thermally activated delayed fluorescence materials based on a cyano-containing planar acceptor[†]

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Two highly emissive materials (**W1** and **W2**) were designed and synthesized, where two *ortho*triphenylamine (TPA) groups were used as electron-donating units and one dibenzo[*a*,*c*]phenazine group was used as an electron-withdrawing motif. In **W1**, two additional cyano groups were attached to the dibenzo[*a*,*c*]phenazine unit to reinforce the electron-accepting strength. As a consequence, remarkable bathochromic shifts were observed in both the UV-vis absorption and photoluminescence spectra of **W1** relative to those of **W2**. Furthermore, the incorporation of cyano groups into **W1** led to a significant separation of the frontier molecular orbitals (FMOs), resulting in a small singlet-triplet splitting energy (ΔE_{ST}) and a strong intramolecular charge transfer (ICT) state. Notably, **W1** possessed higher photoluminescence quantum yields (PLQYs) and better device performance than **W2**. The organic light-emitting diodes (OLEDs) based on **W1** with a doping ratio of 10 wt% achieved a maximum external quantum (EQE) efficiency of 24.97%.

> 100% internal quantum efficiency (IQE), TADF OLEDs can achieve over 30% external quantum efficiencies (EQEs) with the hostdopant dispersion strategy.²⁰ However, efficient red TADF OLEDs are still highly desirable since red emitters generally suffer from severe non-radiative decay due to their small band gaps.

> Although Hatakeyama et al. successfully demonstrated a novel design strategy based on multi-resonance induced TADF emitters with coplanar structures,²¹ emitters with twisted donoracceptor (D-A) structures are the mainstream TADF materials owing to the easy realization of large separation of the lowest unoccupied molecular orbitals (LUMOs) and highest occupied molecular orbitals (HOMOs), thus resulting in a small singlettriplet energy difference ($\Delta E_{\rm ST}$). The twisted structure is a spontaneous outcome of steric hindrance between the D and A units. It is notable that the rotation of the σ bond between D and A usually leads to a broad electroluminescence (EL) spectrum and the variation in the overall electronic structure of a TADF molecule.22 Herein, we designed and synthesized two TADF molecules, where two ortho-TPA units are attached to the planar electron-withdrawing dibenzo[a,c]phenazine unit. Consequently, the rotation of the D-A σ bond in **W1** and **W2** is highly limited due to the increased repulsion interactions between D and A. In addition, the TPA unit intrinsically shows a certain degree of rotation flexibility relative to other rigidified donor units (for example, acridine), which will also lead to non-radiative decay. The crowded arrangement of these two ortho-TPA units in W1 and W2 will reduce the rotation flexibility greatly. In W1,

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there are two cyano groups grafted onto the dibenzo[*a*,*c*]phenazine unit to enhance the electron-accepting capability of the whole configuration, therefore tuning the emission into the deep red region. Xu *et al.* applied the gradient multi-inductive effect to achieve efficient ¹CT radiation by enhancing the overlap of the frontier molecular orbitals.²³ In comparison with **W2**, the introduction of multiple electron-withdrawing groups into **W1** leads to substantial CT character in both the singlet (S₁) and triplet (T₁) states, thus leading to a small ΔE_{ST} , which could be favorable for the reverse intersystem crossing (RISC). Notably, **W1**-based OLEDs demonstrate a highly efficient EL performance

with an EQE of 23.24% (620 nm) at the doping ratio of 15 wt%, and

24.97% (608 nm) at the doping concentration of 10 wt%.

Experimental

General information

All chemicals and reagents were used as received without further purification. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 400 spectrometer at room temperature. Matrix-assisted laser desorption/ionization time of flight mass spectrometry (MALDI-TOF-MS) was performed on a BRUKER ultrafleXtreme MALDI-TOF spectrometer. UV-vis absorption spectra were recorded on a PerkinElmer Lambda 750 spectrophotometer. PL spectra and phosphorescence spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on a TA DSC 2010 unit and a TA SDT 2960 instrument, respectively, at a heating rate of 10 °C min⁻¹ under nitrogen. The glass transition temperatures (T_{o}) were determined from the second heating scan. Cyclic voltammetry (CV) was performed on a CHI600 voltammetric analyzer at room temperature with ferrocenium-ferrocene (Fc/Fc⁺) as the internal standard at a scan rate of 100 mV s⁻¹.

Synthesis of *N*4,*N*4,*N*4''',*N*4"-tetraphenyl-[1,1':2',1"-terphenyl]-4,4',4",5'-tetraamine (1). A mixture of 4,5-dibromobenzene-1,2diamine (1.33 g, 5 mmol), 4-(diphenylamino)phenylboronic acid (3.63 g, 12.5 mmol), Pd(PPh₃)₄ (288.75 mg, 0.25 mmol), K₂CO₃ (2.76 g, 20 mmol), 1,4-dioxane (100 mL) and H₂O (10 mL) was heated at 85 °C for 24 hours under nitrogen. After cooling to room temperature, the solution was poured into water and extracted with DCM. The organic layer was dried over Na₂SO₄ and concentrated under reduced pressure. The residue was purified by column chromatography with PE/EA (2/1, v/v) to afford the compound **1** (2.88 g, 96%). ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.23 (t, *J* = 7.7 Hz, 8H), 6.98 (dd, *J* = 13.6, 5.2 Hz, 4H), 6.93 (d, *J* = 9.6 Hz, 4H), 6.83 (d, *J* = 8.2 Hz, 2H), 6.59 (s, 1H).

Synthesis of 4,4'-(2,7-dibromodibenzo[*a*,*c*]phenazine-11,12diyl)bis(*N*,*N*-diphenylaniline) (2). Compound 1 (654.5 mg, 1.1 mmol) and 2,7-dibromophenanthrene-9,10-dione (366 mg, 1 mmol) were dissolved in AcOH (30 mL) and heated at 125 °C overnight under nitrogen. After cooling down to room temperature, the mixture was subjected to filtration and washed with water. The crude product was re-crystallized in DCM to afford compound 2 (0.73 g, 79%). ¹H NMR (400 MHz, Chloroform-*d*): δ 9.52 (s, J = 2.2 Hz, 2H), 8.38 (m, J = 5.9 Hz, 4H), 7.90 (s, 2H), 7.29 (m, J = 8.1 Hz, 8H), 7.22 (d, J = 8.4 Hz, 4H), 7.15 (d, J = 8.0 Hz, 8H), 7.06 (t, J = 7.3 Hz, 8H).

Synthesis of 11,12-bis(4-(diphenylamino)phenyl)dibenzo[a,c]phenazine-2,7-dicarbonitrile (W1). 4,4'-(2,7-Dibromodibenzo[a,c]phenazine-11,12-divl)bis(N,N-diphenylaniline) (520 mg, 0.56 mmol) and CuCN (125 mg, 1.4 mmol) were dissolved in 1-methyl-2pyrrolidinone (20 mL). This reaction mixture was heated at 180 °C by microwave irradiation for 2 hours. After removing the solvent, the residue was purified by column chromatography with PE/DCM (2/3,v/v) as the eluent to afford the compound W1 (288 mg, 63%). ¹H NMR (400 MHz, chloroform-*d*): δ 9.73 (s, *J* = 1.8 Hz, 2H), 8.64 (d, J = 8.5 Hz, 2H), 8.37 (s, 2H), 8.03 (d, J = 8.4 Hz, 2H), 7.29 (m, J = 7.8 Hz, 8H), 7.22 (d, J = 8.3 Hz, 4H), 7.16 (d, J = 8.0 Hz, 8H), 7.07 (t, J = 7.4 Hz, 8H). ¹³C NMR (400 MHz, CDCl₃): δ 147.54, 147.50, 145.19, 142.12, 140.18, 133.61, 133.05, 132.08, 131.68, 130.91, 130.81, 129.62, 129.41, 124.80, 124.47, 123.32, 122.50, 118.39, 112.95. MALDI-TOF-MS: m/z calcd for C₅₈H₃₆N₆: 816.300, found: 816.591. Elemental analysis (%) for C₅₈H₃₆N₆: C, 85.27; H, 4.44; N, 10.29; found: C, 85.43; H, 4.41; N, 10.34.

Synthesis of 4,4'-(dibenzo[*a*,*c*]phenazine-11,12-diyl)bis(*N*,*N*diphenylaniline) (W2). The synthesis procedure of compound W2 was similar to that of compound 2. ¹H NMR (400 MHz, chloroform-*d*): δ 9.41 (d, *J* = 7.8, 1.6 Hz, 2H), 8.58 (d, *J* = 8.0 Hz, 2H), 8.36 (s, 2H), 7.85–7.78 (t, 2H), 7.76 (t, *J* = 7.7 Hz, 2H), 7.35– 7.26 (m, 8H), 7.22 (d, *J* = 8.4 Hz, 4H), 7.14 (d, *J* = 7.9 Hz, 8H), 7.05 (m, *J* = 7.9, 4.9 Hz, 8H). ¹³C NMR (400 MHz, CDCl₃): δ 147.58, 146.99, 143.24, 142.53, 141.54, 134.48, 131.97, 130.83, 130.42, 130.17, 129.67, 129.29, 127.90, 126.19, 124.53, 123.01, 122.90, 122.72. MALDI-TOF-MS: *m*/*z* calcd for C₅₆H₃₈N₄: 766.310, found: 766.591. Elemental analysis (%) for C₅₆H₃₈N₄: C, 87.70; H, 4.99; N, 7.31; found: C, 87.88; H, 4.818; N, 7.34.

Results and discussion

Scheme 1 describes the synthetic routes of **W1** and **W2**. The intermediate **1** was synthesized through the Suzuki coupling reaction between 4,5-dibromobenzene-1,2-diamine and (4-(diphenyl-amino)phenyl)boronic acid. The following condensation reactions of diamine **1** with 2,7-dibromophenanthrene-9,10-dione and phenanthrene-9,10-dione under acidic conditions produced **2** and **W2**, respectively. The substitution reaction of compound **2** with CuCN yielded the final product **W1**. The compounds **W1** and **W2** were fully characterized *via* ¹H/¹³C NMR spectroscopy (Fig. S1–S4, ESI†) and mass spectrometry.

The thermal stability of **W1** and **W2** was investigated by thermo-gravimetric analysis (TGA) measurements. As shown in Fig. 1, both **W1** and **W2** exhibit excellent thermal stability with the decomposition temperature of 521 °C and 480 °C, respectively. The temperature at 5% weight loss is defined as the decomposition temperature. This result would be beneficial for device fabrication *via* a vacuum deposition method. Furthermore, the differential scanning calorimetry (DSC) curves indicate that both compounds have a high glass transition temperature of 209 °C, which could help maintain the morphology of the light

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Scheme 1 Synthetic procedure of W1 and W2. (i) Pd(PPh₃)₄, K₂CO₃, 1,4-dioxane/H₂O, 85 °C, 24 h; (ii) AcOH, 125 °C, overnight; (iii) CuCN, NMP, 180 °C, MW, 2 h.



emitting layer at the device working stage. The electrochemical properties of **W1** and **W2** were studied by cyclic voltammetry. The HOMO energy levels are determined from the onsets of the oxidation potentials (Fig. S5 and S6, ESI[†]), and the LUMO energy levels are calculated by the difference between the HOMO and the corresponding band gap (E_g). It is interesting to note that the HOMO of **W1** (-5.08 eV) is slightly higher than

that of **W2** (-5.21 eV), which could be due to the π -conjugation between the donor and the strong acceptor in **W1**. The LUMO of **W1** is deeper than that of **W2** (Table 1) because of the introduction of the additional electron-withdrawing cyano group in **W1**, which is consistent with the simulation results (*vide infra*).

The UV-vis absorption and PL spectra of **W1** and **W2** are shown in Fig. 2. The strong absorption bands at around 300 nm

Table 1 Experimental properties of W1 and W2													
	Absorption ^a (nm)	PL^{a} (nm)	Φ^{b} (%)	S_1/T_1^c (eV)	$\Delta E_{\mathrm{ST}}^{d}$ (eV)	T_g/T_d^e (°C)	$E_{g}^{f}(eV)$	HOMO/LUMO ^g (eV)	$\tau_{\rm p}^{\ h} \left({\rm ns} \right)$	$\tau_{d}^{h}(\mu s)$			
W1	344, 484	580	57.1/93.7	2.18/1.94	0.24	209/521	2.29	-5.08/-2.79	29.42	67.62			
W2	317, 444	524	33.7/65.4	2.39/2.10	0.29	209/480	2.53	-5.21/-2.68	23.63	0.82			

^{*a*} Measured in toluene solution at room temperature. ^{*b*} Absolute PL quantum yield in neat film/in doped film (10% for **W1** and 15% for **W2**). ^{*c*} Singlet/triplet energies (S₁/T₁) estimated from onsets of the fluorescence and phosphorescence spectra in toluene at 77 K. ^{*d*} $\Delta E_{ST} = S_1 - T_1$. ^{*e*} T_g : glass transition temperature; T_d : decomposition temperature. ^{*f*} E_g : optical band gap energies were calculated from the corresponding absorption onsets in a toluene solution. ^{*g*} HOMO levels were calculated from CV data; LUMO levels were calculated from the HOMOs and E_gs . ^{*h*} τ_p/τ_d : prompt & delayed exciton lifetime for **W1** 10 wt%/**W2** 15 wt% doped in CBP host film.



are assigned to the π - π * transition, while the absorption bands observed at longer wavelengths (>400 nm) are attributed to the charge transfer transition from triphenylamine to the planar acceptor unit. As expected, W1 shows a red-shift in its UV-vis absorption spectrum relative to that of W2 due to the presence of a strong acceptor unit in W1. In W2, the CT absorption band displays a maximum molar extinction coefficient that is higher than that in W1, indicating the larger HOMO/LUMO overlap and higher CT transition probability in W2. Based on their absorption spectra, large oscillator strengths $(f)^{24}$ at around 0.2 are achieved for both the compounds, probably by virtue of their unique ortho-donor-planar-acceptor conjugation pattern. W1 and W2 manifest intense photoluminescence (PL) emission at 580 nm and 524 nm, respectively. In addition, W1 possesses a Stokes shift that is about 96 nm larger than that of W2 (80 nm), suggesting that a strong intramolecular ¹CT state exists in W1. Currently, one promising design strategy of efficient TADF materials is to introduce obvious CT character into the excitation state on account of the radiative nature of Frenkel excitons with strong Coulombic interactions.²⁵ Both W1 and W2 reveal solvent polarity-dependent emission properties. As depicted in Fig. S7 (ESI[†]), significant red-shifts are observed in their PL spectra when the solvent polarities are increased, which indicates that the singlet states exhibit substantial CT character. In addition, their broad and featureless PL emission spectra imply that the CT excitation state is present. Both W1 and W2 are also highly emissive in neat films with photoluminescence quantum yields (PLQYs) of 57.1% and 33.7%, respectively (Fig. S8, ESI[†]). The singlet/triplet energy levels of W1 (2.18/1.94 eV) and W2 (2.39/2.10 eV) are estimated from the onsets of the fluorescence and phosphorescence spectra in toluene at 77 K (Fig. S9 and S10, ESI⁺). As a result, W1 (0.24 eV) has a smaller $\Delta E_{\rm ST}$ than W2 (0.29 eV). Meanwhile, the transient PL decays are characterized to confirm the TADF feature, and the detailed data are presented in Table 1. The difference in delayed lifetime between W1 and W2 may result from the reduction in the energy transfer rate from hosts to guests.²⁶

To investigate the electronic structures of W1 and W2, density functional theory (DFT) calculations were performed using the Gaussian 09 B3LYP/6-31G(d) software package. As shown in Fig. 3, the HOMO and LUMO in both W1 and W2 are distributed over the ortho-TPA units and the planar acceptors, respectively. The electrostatic potential map of W1 shows that the electron-negative region is predominantly located on the cyano groups, while in W2 it is mainly around the phenazine N atoms (Fig. S11, ESI[†]). The introduction of cyano groups leads to a major separation of the relevant wave functions, resulting in a small $\Delta E_{\rm ST}$ in W1, which is consistent with the photophysical results. Nevertheless, there is a partial overlap between the HOMO and LUMO on the phenazine group for both compounds. W1 and W2 have similar HOMO energy levels since they have the same electron-donating groups. The LUMO energy level of W1 (-2.75 eV) is much deeper than that of W2 (-2.16 eV), which derives from the cyano groups with strong electron-withdrawing ability. The natural transition orbital (NTO) calculation reveals that in W1, the S_1 has substantial CT character and T_1 has a combination of a local excitation (LE) state and CT state. In W2, S1 predominantly exhibits CT character and T₁ is mainly a LE state. For organic TADF materials, the spinorbital coupling (SOC) also determines the rate of RISC from T_1 to S₁, although this coupling is relatively weak due to the absence of heavy atoms in most of them.²⁷ It is notable that the different spatial orbital occupation of S1 and T1 will result in a certain degree of SOC, hence contributing to the RISC process of W1 and W2.

To explore the electroluminescence properties of **W1** and **W2**, OLEDs based on these dopants were fabricated with a normal sandwiched configuration: ITO/HAT-CN (10 nm)/TAPC (40 nm)/TCTA (10 nm)/CBP: emitter (2–15 wt%, 20 nm)/TmPyPB (55 nm)/Liq (2 nm)/Al (120 nm). HAT-CN (1,4,5,8,9,11-hexaazatriphenylene-hexanitrile) and TAPC (1,1-bis[4-[N',N'-di(*p*-tolyl)amino]-phenyl]cyclohexane) were utilized as the hole-injecting layer (HIL) and hole-transporting layer (HTL), respectively. TCTA (4,4,4-tris(*N*-carbazolyl)triphenyl-amine) served as the excitonblocking layer, and TmPyPB (1,3,5-tri(m-pyrid-3-yl-phenyl)benzene) and Liq were used as the electron-transporting layer (ETL) and electron-injecting layer (EIL), respectively. In addition, in the emitting layer (EML), **W1** and **W2** were doped into the host (CBP) with 2/5/10/15 wt%. Fig. S12 (ESI†) shows the energy level diagram and corresponding molecular structures.

The EQE-current density curves of **W1** at different doping ratios are depicted in Fig. 4. A maximum EQE of 24.97% at the doping ratio of 10 wt% with an emission wavelength peak at 608 nm and corresponding Commission Internationale de L'Eclairage (CIE) coordinates of (0.61, 0.39) was achieved (Table 2). When the doping ratio was increased to 15 wt%, the emission wavelength red-shifted to 620 nm with CIE coordinates of (0.63, 0.37) and a maximum EQE of 23.24% was obtained. For the **W2**-based device, a maximum EQE of 8.69% was achieved at the doping ratio of 10% with the emission wavelength peak at 556 nm, corresponding to yellowish green light with CIE coordinates of (0.43, 0.55). The superior device efficiency of **W1** is attributed to its high PLQY (Table 1) as compared with that of **W2**. The inset of Fig. 4 shows the doping-ratio-dependent emission wavelengths are. This doping ratio-dependent red-shift is caused by

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Fig. 4 EQE-current density curves of **W1** (inset: EL spectra at 5 mA cm⁻²).

the large ground-state dipole moment of **W1**.²⁸ The polarity of EML changes as the doping ratio increases. The large redshift observed in

the emission spectra of **W1** (inset of Fig. 4) relative to that of **W2** agrees well with the fact that **W1** has a larger polarity than **W2**. The absence of host CBP emission around 400 nm in the EL spectra indicates the efficient energy transfer from the host to the dopant. Current density–voltage–luminance (*J–V–L*) characteristics of **W1** are shown in Fig. 5. The turn-on voltage is measured at 100 cd m⁻². As the doping ratio is increased from 10 wt% to 15 wt%, the turn-on voltages show a slight decrease from 4.14 V to 4.07 V, which could be due to the enhancement of carrier capture. As shown in Fig. 6, a maximum current efficiency (CE) of 40 cd A⁻¹ and power efficiency (PE) of 38.27 lm W⁻¹ could be achieved. This device performance based on **W1** is among the best reported results with similar emission wavelengths.²⁹

The electron and hole transporting properties of W1/W2 are shown in Fig. S16 and S17 (ESI[†]), respectively. W1 and W2 demonstrate similar hole transport behaviors. W1 shows better electron transport capability than W2, which could be due to the lower LUMO energy level and larger conjugation system of W1.

Table 2 Electroluminance performance of W1 doped device

Doping conc. [wt%]	$V^{a}(\mathbf{V})$	$\operatorname{CE}^{b}\left[\operatorname{cd}\operatorname{A}^{-1} ight]$	$\mathrm{PE}^{b}\left[\mathrm{lm}\;\mathrm{W}^{-1} ight]$	$\mathrm{EQE}^{b}[\%]$	$\operatorname{CIE}^{c}(x, y)$	$\lambda_{\mathrm{EL}}{}^{d} [\mathrm{nm}]$
10	4.14	40/15/7	38.3/11.6/3.9	24.97/8.73/3.88	0.61, 0.39	608
15	4.07	30/14/6	39.6/10.9/3.3	23.24/9.85/4.06	0.63, 0.37	620

^{*a*} Voltage at 100 cd m⁻². ^{*b*} Maximum/luminance at 100/luminance at 1000 cd m⁻². ^{*c*} Commission Internationale de L'Eclairage coordinates. ^{*d*} Measured at 5 mA cm⁻².



Fig. 5 Current density-voltage-luminance (J-V-L) characteristics of the doped OLEDs based on **W1**.



Fig. 6 Power/current efficiency vs. luminance relationships of the W1-based device.

Conclusions

In summary, two highly emissive materials (W1 and W2) with planar electron-withdrawing dibenzo[*a*,*c*]phenazine groups were synthesized. With the introduction of cyano groups into W1, its PLQY in the doped film could reach 93.7%. In contrast, the PLQY is only 65.4% for W2 without multiple acceptor units. Moreover, the partial localization of LUMO on the cyano groups in W1 leads to a large separation of FMOs and a small ΔE_{ST} . As a result, W1 showed superior device performance with a maximum EQE of 23.24% and emission wavelength peak at 620 nm, and 24.97% at 608 nm. So, the incorporation of a cyanocontaining planar acceptor into CT molecules demonstrates great promise for the design of efficient red TADF molecules.

Conflicts of interest

There are no conflicts to declare.

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