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A Multidisciplinary Journal Centering on Chemistry



European Chemical Societies Publishing

## **Accepted Article**

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This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemPlusChem 10.1002/cplu.202000703

Link to VoR: https://doi.org/10.1002/cplu.202000703

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## Highly Efficient Orange-Red Thermally Activated Delayed Fluorescence Compounds Comprising Dual Dicyano-Substituted Pyrazine/Quinoxaline Acceptors

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Abstract: The  $\pi$ -conjugation of the acceptors influences the properties of the excited state deeply, especially for red thermally activated delayed fluorescence (TADF) materials. Two orange-red TADF compounds comprised of dual dicyano-substituted pyrazine/quinoxaline acceptors have been designed and synthesized. **TPA-2DCNQ** (3,3'-((phenylazanediyl)bis(4,1-phenylene))bis(2phenylquinoxaline-6,7-dicarbonitrile) with extended  $\pi$ -conjugated quinoxaline as the acceptor exhibits higher photoluminescence quantum yields in doped films of 0.67~0.71. At the same time, a smaller energy splitting ( $\Delta E_{st}$ ) of the first singlet excited state and triplet excited state is also achieved, indicating that enlarging the πconjugation of the acceptor rationally is an effective approach to designing highly efficient long-wavelength TADF materials. Devices with TPA-2DCNQ as the emitter display maximum external quantum efficiencies (EQEs) of 12.6~14.0%, which are more than two times higher than those of TPA-2DCNPZ (6,6'-((phenylazanediyl)bis(4,1phenylene))bis(5-phenylpyrazine-2,3-dicarbonitrile) based ones.

#### Introduction

Organic light-emitting diodes (OLEDs) technology has drawn more and more attention in flat panel displays and solid-state lighting fields owing to their flimsy and flexile features.<sup>[1]</sup> Up to now, a mass of smartphones and televisions are equipped with OLED screens. However, red materials are always the short slab among the three-primary colors, due to the anabatic internal conversion (IC) coefficient managed by the energy gap law.<sup>[2]</sup> Red phosphor materials are widely used in the industry at present owing to the 100% exciton utilization efficiency (EUE).<sup>[3]</sup> The introduction of precious metals, such as Ir, Pt, etc., increases the costs and it is not eco-friendly. Thermally activated delayed fluorescence (TADF) mechanism was proposed by Adachi and coworkers.<sup>[4]</sup> Metal-free TADF materials can also achieve 100% EUE by reverse intersystem crossing (RISC) process of triplet excitons. High photoluminescence (PL) quantum yield (PLQY) and small energy splitting ( $\Delta E_{st}$ ) of the first excited singlet state (S<sub>1</sub>) and excited triplet state (T1) are crucial factors for high-performance TADF materials, but they are contradictory.<sup>[5]</sup> How to balance them for highly efficient TADF materials is the issue urgently need to be addressed.

The  $\pi$ -conjugated skeleton of the acceptor units has a deep influence on the excited state energy level of the compounds.<sup>[6]</sup> On the one hand, rigid  $\pi$ -conjugated skeleton can suppress harmful structural relaxation; on the other hand, the  $\pi$ -conjugation

of the acceptor units also influence the distribution of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), which influences the properties of the excited state.<sup>[7]</sup> The HOMO usually distributes on electron donor (D) units, and the LUMO mainly concentrates on electron acceptor (A) units in charge transfer type D-A materials. Rationally expanding the  $\pi$ -conjugated acceptors can enlarge the distribution of LUMO, and the centroid distance between HOMO and LUMO can be increased. As a result, the overlap of HOMO and LUMO will be decreased and smaller  $\Delta E_{st}$  will be obtained. Recently, a few efficient red TADF materials have been reported.<sup>[8]</sup> Wang and coworkers reported a large π-conjugated acceptor, *i.e.* phenanthro[4,5-abc]phenazine-11,12-dicarbonitrile. Compounds comprised of this acceptor showed around 80~90% PLQY in doped films, and the maximum external quantum efficiency (EQE) of the deep red devices were more than 20%.[9] The large  $\pi$ -conjugated acceptor seems has a positive impact on the efficient red TADF materials. However, a large π-conjugated acceptor usually causes  $\pi$ - $\pi$  stacking, which may induce serious aggregation induced quenching.<sup>[2c, 9b]</sup> So rationally modifying the degree of conjugate of acceptors is crucial.

In this contribution, two orange-red TADF compounds with dual dicyano-substituted pyrazine/quinoxaline as the acceptors and triphenylamine unit as the donor have been synthesized. TPA-2DCNQ (**Scheme 1**) with larger  $\pi$ -conjugated acceptor shows a deeper LUMO energy level and a less overlap of HOMO and LUMO. More importantly, a higher PLQY and a smaller  $\Delta E_{st}$  are achieved simultaneously compared with TPA-2DCNPZ (**Scheme 1**). Eventually, OLED devices with TPA-2DCNQ as emitter display maximum EQEs of 12.6~14.0%, which is more than 2 times higher than those of TPA-2DCNPZ based ones.

#### **Results and Discussion**

#### Synthesis

All raw materials were commercially purchased without further purification. The synthetic routes and molecular structures of TPA-2DCNPZ and TPA-2DCNQ is depicted in **Scheme 1**. Intermediates **1** was synthesized by Sonogashira cross coupling reaction. Then diketone derivative, intermediate **2**, was synthesized by potassium permanganate involved oxidation reaction in dilute acid solution. Intermediates **1** and **2** were synthesized referencing the reported literatures.<sup>[10]</sup> Finally, the

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Scheme 1. Synthetic steps to product TPA-2DCNPZ and TAP-2DCNQ. a) PPh<sub>3</sub>, Cul, (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub>, NEt<sub>3</sub>, reflux, 8 h, N<sub>2</sub> protection; b) KMnO<sub>4</sub>, HOAc, acetone/H<sub>2</sub>O, reflux, 2.5 h; c) HOAc, reflux, 6 h, N<sub>2</sub> protection.

target compounds TPA-2DCNPZ and TPA-2DCNQ were synthesized by cyclization reactions in acetic acid. They were characterized by the NMR (nuclear magnetic resonance) (Figure S1~S4), mass spectrometry (Figure S5~S6) and elemental analysis, which demonstrated the products were the target materials.

#### Thermal and electrochemical properties



Figure 1. TGA (a) and DSC (b) curves of TPA-2DCNPZ and TPA-2DCNQ.

The thermal properties of TPA-2DCNPZ and TPA-2DCNQ were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) in a nitrogen atmosphere. The decomposition temperatures (T<sub>d</sub>, corresponding to 5% weight loss) of TPA-2DCNPZ and TPA-2DCNQ were 417 and 513 °C, respectively, seen from **Figure 1a**. The glass transition temperatures (T<sub>g</sub>) of TPA-2DCNPZ and TPA-2DCNQ were 133 and 175 °C, respectively, obtained from **Figure 1b**. The high T<sub>d</sub> and T<sub>g</sub> values suggest that TPA-2DCNPZ and TPA-2DCNQ are stable under heating and they are applicable for OLEDs devices fabrication via vacuum deposition technique.

Cyclic voltammetry (CV) measurements were conducted to test the electrochemical properties of TPA-2DCNPZ and TPA-2DCNQ. They showed similar and reversible oxidation curves (**Figure 2**), because the redox reactions took place on triphenylamine units. The HOMO energy levels were calculated to be -5.45 and -5.42 eV, and the LUMO energy levels were calculated to be -3.05 and -3.16 eV, respectively, based on the absorption spectra of TPA-2DCNPZ and TPA-2DCNQ (**Figure 5**). The LUMO of TPA-2DCNQ is deeper than that of TPA-2DCNPZ because of the extended  $\pi$ -conjugated acceptor.<sup>[2c, 7b-c, 11]</sup>





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Figure 3. The configuration (a), cell structure (b), and intermolecular interactions of TPA-2DCNQ in single crystal.

#### Crystal structure analysis

The crystal of TPA-2DCNQ was obtained by solvent evaporation method using dichloromethane/methyl alcohol mixed solvents. The configuration of TPA-2DCNQ in crystal is shown in **Figure 3a**. The dihedral angles between phenyl bridge of triphenylamine and quinoxaline units are 13.1 and 61.3°, which will induce inhomogeneous distribution of LUMO on the dual dicyano-substituted quinoxaline acceptors. The cell structure and intermolecular interactions diagrams are shown in **Figure 3b** and **3c**. There are abundant hydrogen bond and C-H... $\pi$  intermolecular interactions, which is beneficial to suppress molecular vibration and rotation induced internal conversion effect, resulting in high PLQY of TPA-2DCNQ.

#### **Theoretical calculations**

Density functional theory (DFT) and time-dependent DFT (TD-DFT) calculations at the B3LYP/6-31G(d,p) level were applied for TPA-2DCNPZ and TPA-2DCNQ to get further insight into the geometrical and electronic structures of them. The optimized ground state configurations are shown in **Figure S7**. The two dicyano-substituted pyrazine units were nearly symmetrical, while the two dicyano-substituted quinoxaline units were not, which may be resulted from steric hindrance caused by the expanded  $\pi$ -conjugated skeleton. The dihedral angles between phenyl bridge of triphenylamine and acceptor units were named  $\theta_1$  and

 $\theta_1$ ', while those between acceptor units and single phenyl rings were named  $\theta_2$  and  $\theta_2'$ . The values of  $\theta_1$  and  $\theta_1'$  were around 37°, and those of  $\theta_2$  and  $\theta_2'$  were 37° for TPA-2DCNPZ and 41° for TPA-2DCNQ. The detailed data are shown in Table S1. The HOMO and LUMO distributions of TPA-2DCNPZ and TPA-2DCNQ are shown in Figure 4. For TPA-2DCNPZ, the HOMO was mainly concentrated on triphenylamine unit and slightly located at pyrazine units, the LUMO was mainly distributed over the acceptors and phenyl bridges of triphenylamine, resulting in a larger overlap of HOMO and LUMO. The HOMO of TPA-2DCNQ was mainly located at triphenylamine unit, while its LUMO was mainly distributed over the acceptors, the overlap of HOMO and LUMO was less than that of TPA-2DCNPZ. The overlap integrals of norm of HOMO and LUMO were 0.454 and 0.400, calculated via Multiwfn software package. The less overlap of HOMO and LUMO contributes smaller  $\Delta$ Est, which was calculated to be 0.368 eV for TPA-2DCNPZ and 0.299 eV for TPA-2DCNQ.

#### **Photophysical properties**

The ultraviolet-visible absorption spectra of TPA-2DCNPZ and TPA-2DCNQ are shown in **Figure 5**. The intense absorption bands at 294 and 322 nm of TPA-2DCNPZ should be attributed to the  $\pi$ - $\pi$ \* transitions of the aromatic amines and the pyrazine unit.<sup>[7c,11]</sup> The more intense absorption band of 360~553 nm was

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Figure 4. The HOMO and LUMO distributions and energy levels of TPA-2DCNPZ and TPA-2DCNQ by DFT and TDDFT calculations.



Figure 5. The absorption spectra of TPA-2DCNPZ and TPA-2DCNQ in dichloromethane ( $10^{-5}$  M).

assigned to intermolecular charge transfer (CT) from triphenylamine electron-donor unit to dicyano-substituted pyrazine. TPA-2DCNQ showed a similar and slightly red-shifted absorption spectrum, but a relatively lower CT absorption intensity. The molar absorption coefficient is positively associated with the transition dipole moment. The frontier molecular orbitals' overlap of TPA-2DNCPZ is larger than that of TPA-2DCNQ, indicating a higher transition dipole moment of TPA-2DCNPZ. The transition dipole moment and calculated absorption spectra of them are shown in **Figure S8**. TPA-2DCNPZ exhibited higher CT absorption intensity arisen from the higher transition dipole moment from S<sub>0</sub> to S<sub>1</sub>. The PL spectra of them in dilute toluene are shown in **Figure 6**. The energy levels of S<sub>1</sub> and T<sub>1</sub> were



Figure 6. The PL spectra of TPA-2DCNPZ (a) and TPA-2DCNQ (b) in toluene at 77 K ( $10^{-5}$  M).

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calculated based on the onset of the spectra at 77 K, which were 2.667, 2.270 eV and 2.562, 2.281 eV for TPA-2DCNPZ and TPA-2DCNQ, respectively, and the corresponding values of  $\Delta E_{st}$  were 0.397 and 0.281 eV. In order to explore the properties of TPA-2DCNPZ and TPA-2DCNQ in thin films, the doped films were prepared by vacuum evaporation with CBP (4,4'-bis(Ncarbazolyl)-1,1'-biphenyl) as the host. The doping concentrations were 5 wt%, 10 wt%, and 20 wt%. The PL emission peaks were located at 570, 581, and 600 nm for TPA-2DCNPZ, those for TPA-DCNQ were slightly red-shifted, which were located at 574, 593, and 609 nm, indicating the extended  $\pi$ -conjugated acceptors usually possess stronger ability of electron-withdrawing. Moreover, the redshift of TPA-2DCNQ based doped films' PL spectra was larger than that of TPA-2DCNPZ based ones from 5 wt% to 20 wt%, which could be contributed to the stronger intermolecular interactions of TPA-2DCNQ in high-concentration doped films.<sup>[2c]</sup> The doped films showed PLQYs of 0.35, 0.33, and 0.23 with the doping concentrations of TPA-2DCNPZ were 5 wt%. 10 wt%, and 20 wt%, respectively. TPA-2DCNQ doped films showed more than double PLQYs compared with those of TPA-2DCNPZ at the same doping concentrations, as shown in Figure 7. It's clearly that the extended  $\pi$ -conjugated acceptor contributed to the boost of the PLQY, the rigid skeleton of the acceptor was benefit to restrain the nonradiative process, which proved that the  $\pi$ -conjugated skeleton of the acceptors has an important impact on the luminescence properties of long-wavelength TADF materials. The extended *π*-conjugated skeleton from dicyanosubstituted pyrazine to dicyano-substituted guinoxaline not only obtained a stronger electron-withdrawing acceptor, but also a smaller  $\Delta E_{st}$  and higher PLQYs were achieved simultaneously. The results provide an approach to designing high-performance long-wavelength TADF materials.

To verify the TADF property of TPA-2DCNPZ and TPA-2DCNQ, the transient PL decay measurements of the doped films were carried out, and the transient PL decay measurements at different temperatures of the 10 wt% doped films were also performed. The results are shown in **Figure 8** and **Figure S9**. From **Figure S9**, all the transient PL decay curves exhibited delayed fluorescence lifetimes in the time range of 1 and 2 milliseconds, which indicated the TADF properties of them. The temperature-dependent transient PL decay curves showed that the proportions of delayed fluorescence were increased with increasing the test temperatures from 100~350 K, which further confirmed the TADF



**Figure 7.** The PL spectra and PLQYs of TPA-2DCNPZ and TPA-2DCNQ in doped films (host: CBP) with concentrations of 5wt%, 10 wt%, and 20 wt%.

Table 1. Photo physical constants of the doped films.											
films	<i>T</i> ⊵ [ns] <sup>[a]</sup>	<i>Т</i> тадғ [µs] <sup>[b]</sup>	φ <sub>Ρ</sub> [%] <sup>[c]</sup>	Φταdf [%] <sup>[d]</sup>	<i>k</i> ғ [*10 <sup>8</sup> s <sup>-1</sup> ] <sup>[е]</sup>	<i>k</i> ıс [*10 <sup>8</sup> s <sup>-1</sup> ] <sup>[f]</sup>	<i>k</i> ısc [*10 <sup>8</sup> s <sup>-1</sup> ] <sup>[g]</sup>	<i>k</i> risc [*10 <sup>4</sup> s <sup>-1</sup> ] <sup>[h]</sup>			
5 wt% TPA-2DCNPZ	6.80	295	0.294	0.056	4.32	8.02	2.36	0.42			
10 wt% TPA-2DCNPZ	6.55	249	0.284	0.046	4.33	8.80	2.14	0.44			
20 wt% TPA-2DCNPZ	5.70	197	0.204	0.026	3.57	11.96	2.00	0.27			
5 wt% TPA-2DCNQ	9.50	143	0.655	0.054	6.90	2.82	0.81	3.52			
10 wt% TPA-2DCNQ	11.16	134	0.622	0.048	5.57	2.74	0.64	3.35			
20 wt% TPA-2DCNQ	10.39	106	0.638	0.032	6.14	3.02	0.46	4.23			

[a]: The lifetime of prompt fluorescence. [b]: The lifetime of delayed fluorescence. [c]: The prompt component of the PL quantum efficiency. [d]: The delayed component of the PL quantum efficiency. [e]: The singlet radiative rate constant. [f]: The singlet internal conversion rate constant. [g]: The singlet intersystem crossing rate constant. [h]: The triplet reverse intersystem crossing rate constant.

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Figure 8. Temperature-dependent transient PL decay curves of TPA-2DCNPZ and TPA-2DCNQ in 10 wt% doped films.

properties of them. The photo physical parameters were calculated by formulas (see Supporting Information) and the results are listed in Table 1. The internal conversion rate was suppressed by the rigid extended π-conjugated acceptor of TPA-2DCNQ, and higher reverse intersystem crossing rate constants were simultaneously obtained resulted from the smaller  $\Delta E_{st}$ .

#### in these OLED devices are shown in Figure 9, and the relevant results are shown in Figure 10 and Table 2. The emission peaks of the EL spectra of TPA-2DCNPZ and TPA-2DCNQ were 576

#### **Electroluminescence properties**

The electroluminescence (EL) properties of TPA-2DCNPZ and TPA-2DCNQ were also measured by fabricating OLED devices with the structure of [ITO/ TAPC (50 nm)/ TCTA (5 nm)/ CBP: 10 wt% emitters (20 nm)/ TmPyPb (45 nm)/ LiF (1 nm)/ Al (100 nm)]. The ITO (indium tin oxide) and LiF/AI were applied as anode and cathode, respectively. TAPC and TCTA were hole-transport layers, while TmPyPb was electron-transport layer. The device structure, chemical formulas and energy levels of used materials

in these OLED devices are shown in <b>Figure 9</b> , and the relevant results are shown in <b>Figure 10 and Table 2</b> . The emission peaks of the EL spectra of TPA-2DCNPZ and TPA-2DCNQ were 576												
Table 2. EL performance of the devices.												
emitter	λ <sub>EL</sub> [nm]	CE <sub>max</sub> [cd A <sup>-1</sup> ] <sup>[a]</sup>	PE <sub>max</sub> [Im W <sup>-1</sup> ] <sup>[b]</sup>	EQE <sub>max</sub> [%] <sup>[c]</sup>	EQE <sub>100</sub> [%] <sup>[d]</sup>	EQE1000 [%] <sup>[e]</sup>						
10 wt% TPA- 2DCNPZ	576	10.4	6.6	4.4	1.8	1.0						
10 wt% TPA- 2DCNQ	596	21.5	30.2	13.6	6.4	2.6						

[a]: maximum current efficiency; [b]: maximum power efficiency; [c]: maximum EQE; [d]: EQE at 100 cd m<sup>-2</sup>; [e]: EQE at 1000 cd m<sup>-2</sup>.

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Figure 9. Device structure, chemical formulas and energy levels of used materials in device fabrication.

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Figure 10. EL spectra (a) and EQE-Luminance plots (b) of TPA-2DCNPZ and TPA-DCNQ based devices.

and 596 nm. The maximum external quantum efficiency (EQE) of TPA-2DCNPZ was 4.4%, which was 13.6% for TPA-2DCNQ. Both the higher rate of RISC (kRISC) and PLQY of the emitting layer of TPA-DCNQ contribute to the higher performance of the devices, proving the expending  $\pi$ -conjugated acceptors rationally is an effective designing strategy for long-wavelength TADF materials. Devices with the emitters' doping concentrations of 5 wt% and 20 wt% were also fabricated. The devices' performance was depicted in Figure S10~S11, the detailed data were summarized in Table S2. Devices based on 5 wt% doped emitters showed higher EQEs than those based on 10 wt% and 20 wt% doped emitters, which could be ascribed to the higher PLQYs of the doped films. It's worth to note that 20 wt% doped film of TPA-2DCNQ displayed higher kRISC than that of 10 wt% doped film as well as identical PLQY, but the device equipped with 20 wt% doped TPA-2DCNQ demonstrated a slightly lower EQE of 12.6%, which may be caused by the more unbalanced carrier migration, and the efficiency maybe improved by further optimization.

#### Conclusion

In conclusion, two orange-red TADF compounds comprised of dual dicyano-substituted pyrazine/quinoxaline acceptors were designed. The extended  $\pi$ -conjugated acceptor of TPA-DCNQ shows stronger electron-withdrawing ability and deeper LUMO energy level. With the larger  $\pi$ -conjugated skeleton, the overlap of HOMO and LUMO is decreased, resulting in a smaller  $\Delta E_{st}$  and higher rate of RISC. Moreover, the PLQY is also boosted with the larger rigid  $\pi$ -conjugated acceptor at the same time. Eventually, the OLED device with TPA-DCNQ showed highest EQEs of 12.6%~14.0%. The work proves that extending the  $\pi$ -conjugated acceptor rationally is an effective approach to designing highly efficient long-wavelength TADF materials.

#### **Experimental Section**

#### **General Information**

<sup>1</sup>H and <sup>13</sup>C NMR spectra were measured on Bruker AVANCE III 500 MHz spectrometer with tetramethylsilane as the internal standard. Mass spectra

was recorded on a Thermo Fisher ITQ1100 GC/MS mass spectrometer. Elemental analyses were performed on a flash EA 1112 spectrometer. Differential scanning calorimetric (DSC) measurements were performed on a NETZSCH DSC204 instrument at a heating rate of 10 K min<sup>-1</sup> under a nitrogen atmosphere. Thermogravimetric analyses (TGA) were performed on a TA Q500 thermogravimeter by measuring their weight loss while heating at a rate of 10 K min<sup>-1</sup> from 25 to 800 °C under nitrogen. Electrochemical measurements were performed with a BAS 100W Bioanalytical electrochemical work station, using platinum disk as working electrode, platinum wire as auxiliary electrode, and a porous glass wick Aq/Aq<sup>+</sup> as pseudo reference electrode with ferrocene/ferrocenium as the internal standard. The oxidation potentials were measured in CH2Cl2 solution containing 0.1 M of n-Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte at a scan rate of 50 mV s<sup>-1</sup>. The UV-Vis absorption spectra were recorded by a Shimadzu UV-2550 spectrophotometer. The emission spectra were recorded by a Shimadzu RF-5301 PC spectrometer. Both fluorescence and phosphorescent spectra at low temperature (77 K) were recorded by Ocean Optics QE Pro with a 365 nm Ocean Optics LLS excitation source. The absolute fluorescence quantum yields of films were measured on Edinburgh FLS 920 steady state fluorimeter utilizing an integrating sphere. Transient PL decay was investigated under vacuum using FLS 920 fluorescence lifetime measurement system.

#### Single Crystal Structure

Diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the  $\omega$ -scan mode with graphite monochromator Mo+Ka radiation. The structure was solved using SHELXT and refined with SHELXL. Non-hydrogen atoms were refined anisotropically. The positions of hydrogen atoms were calculated and refined isotropically. Deposition Number 2033403 (for TPA-2DCNQ) contains the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service www.ccdc.cam.ac.uk/structures.

#### **Theoretical calculation**

The ground state geometries of gas state were fully optimized by B3LYP method including Grimme's dispersion correction with 6-31G(d,p) basis set using Gaussian 09 software package.<sup>[12]</sup> HOMO and LUMO were visualized with Gaussview 6.0. The overlap integral of norm of HOMO and LUMO was calculated via Multiwfn software package.<sup>[13]</sup>

#### **Device fabrication**

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Glass substrates pre-coated with indium tin oxide (ITO) with a sheet resistance of 15  $\Omega$  per square were thoroughly cleaned in ultrasonic bath of tetrahydrofuran, detergent, deionized water, acetone and isopropyl alcohol and treated with plasma for 5 min in sequence. Organic layers were deposited onto the ITO-coated glass substrates by thermal evaporation under high vacuum (<5×10<sup>-4</sup> Pa). Cathode was patterned using a shadow mask with an array of 2.0 mm × 2.5 mm openings. Deposition rates are 1 Å s<sup>-1</sup> for organic materials, 0.1 Å s<sup>-1</sup> for LiF, and 5 Å s<sup>-1</sup> for AI, respectively. EL spectra and luminance intensities were recorded by Photo Research PR655. The current density and driving voltage characteristics were measured by Keithley 2400 simultaneously. External quantum efficiency was calculated from the current density, luminance, and EL spectrum, assuming a Lambertian distribution.

#### Synthesis

Synthesis of 6,6'-((phenylazanediyl)bis(4,1-phenylene))bis(5phenylpyrazine-2,3-dicarbonitrile) (TPA-2DCNPZ)

A mixture of intermediates **2** (1.53 g, 3.00 mmol) and diaminomaleonitrile (0.97 g, 9.00 mmol) were refluxed in 40.0 mL glacial acetic acid for 6 hours. After the reaction was completed, the reaction mixture was poured into ice water. After suction filtration, the residue was purified via silica gel column chromatography using petroleum ether/dichloromethane (1:1; v/v) as an eluent to give the product TPA-2DCNPZ as a red solid (1.20 g, 61.2%). <sup>1</sup>H NMR (500 MHz, Methylene Chloride-*d*<sub>2</sub>)  $\delta$  7.64 (dt, *J* = 7.1, 1.4 Hz, 4H), 7.57 – 7.43 (m, 10H), 7.43 – 7.37 (m, 2H), 7.29 – 7.23 (m, 1H), 7.22 – 7.15 (m, 2H), 7.10 – 7.00 (m, 4H). <sup>13</sup>C NMR (126 MHz, Methylene Chloride-*d*<sub>2</sub>)  $\delta$  155.00, 154.54, 149.40, 135.81, 131.26, 130.97, 129.90, 129.77, 129.53, 128.98, 128.80, 126.72, 125.75, 122.63, 113.51, 113.44. MS (*m*/z): 652.76 [M]<sup>+</sup> (calcd: 653.21). Anal. Calcd (100%) for C<sub>42</sub>H<sub>23</sub>N<sub>9</sub>: C, 77.17; H, 3.55; N, 19.28; Found: C, 77.18; H, 3.76; N, 19.12.

Synthesis of 3,3'-((phenylazanediyl)bis(4,1-phenylene))bis(2-phenylquinoxaline-6,7-dicarbonitrile) (TPA-2DCNQ)

The synthetic methods of TPA-2DNCQ were similar with those of TPA-2DCNPZ using compound 4,5-diaminophthalonitrile (1.42 g, 8.98 mmol) instead of diaminomaleonitrile. Finally, TPA-2DCNQ was obtained as a red solid (1.74 g, 69.3%). <sup>1</sup>H NMR (500 MHz, Methylene Chloride-*d*<sub>2</sub>)  $\delta$  8.62 (d, *J* = 6.3 Hz, 4H), 7.86 – 7.60 (m, 4H), 7.52 (dd, *J* = 7.9, 4.4 Hz, 7H), 7.47 (dd, *J* = 8.3, 6.7 Hz, 4H), 7.40 (t, *J* = 7.9 Hz, 2H), 7.27 – 7.15 (m, 2H), 7.13 – 7.01 (m, 4H). <sup>13</sup>C NMR (126 MHz, Methylene Chloride-*d*<sub>2</sub>)  $\delta$  157.38, 156.56, 148.89, 141.74, 141.37, 137.87, 136.76, 136.59, 131.33, 130.16, 129.77, 128.44, 126.31, 125.17, 122.64, 115.31, 114.05, 113.59. MS (*m/z*): 752.74 [M]<sup>+</sup> (calcd: 753.24). Anal. Calcd (100%) for C<sub>50</sub>H<sub>27</sub>N<sub>9</sub>: C, 79.67; H, 3.61; N, 16.72; Found: C, 79.78; H, 3.76; N, 16.88.

#### Acknowledgements

This work was partly supported by the Science Foundation of Jihua Laboratory.

**Keywords:** luminescence; organic light-emitting diodes;  $\pi$ conjugated acceptors; photophysics; thermally activated delayed fluorescence

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Higher PLQY of ~70% was obtained for TPA-2DCNQ with extended  $\pi$ -conjugated acceptors, which was twice over than that of TPA-2DCNPZ (~30%). The rates of RISC of TPA-2DCNQ were also around 10 times higher than that of TPA-2DCNPZ simultaneously. Ultimately, a higher EQE of TPA-2DCNQ of 13.6% was achieved, which was 3 times higher than that of TPA-2DCNPZ based one (4.4%). The results indicated that extending the  $\pi$ -conjugated skeleton of acceptors is an effective approach to high-performance long-wavelength TADF materials.