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Novel aggregation-induced emission and thermally activated delayed fluorescence materials based on thianthrene-9,9',10,10'-tetraoxide derivatives

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thianthrene-9.9'. Abstract: Two novel luminescent molecules based on 10.10'-tetraoxide derivatives, named tCzDSO2 and 3tCzDSO2, have been The compound tCzDSO2 emits intense synthesized and characterized. aggregation-induced emission (AIE) with a high photoluminescence quantum yields $(\Phi_{\rm F})$ of 0.92 at room temperature in the solid state. Simultaneously, by increasing the proportion of carbazole units, 3tCzDSO2 exhibits both AIE and thermally activated delayed fluorescence (TADF) in the solid state with $\Phi_{\rm F}$ of 0.19 in air and 0.41 in N₂ atmosphere. The two compounds also display a bathochromic effect due to their intramolecular charge transfer (ICT) attribute. The time-dependent DFT predicted the singlet and triplet splitting (ΔE_{ST}) values of tCzDSO2 and 3tCzDSO2 are 0.29 eV and 0.06 eV, respectively. The ΔE_{ST} of 3tCzDSO2 is small enough to allow efficient reverse intersystem crossing (RISC), leading to the TADF property at room temperature. As a result, the molecular design provides a simple and effective approach to integrate the features of AIE and TADF into one compound.

Key words: Thianthrene-9,9',10,10'-tetraoxide, Aggregation-induced emission, Thermally activated delayed fluorescence, Singlet-triplet splitting

Introduction

In the past decade, considerable efforts have been made toward the development of organic luminescent materials for fabricating high-performance organic light-emitting

(OLEDs).¹⁻⁶ However, most conventional luminophores built with diodes π -conjugated planar chromophores suffer from the notorious aggregation-caused quenching (ACO).^{7,8} The conventional luminescent materials exhibit strong luminescence in solution but weakened emission in their aggregated states, which depresses the device performances, hindering the evolution of OLEDs. Even though the doping method may alleviate the ACQ effect, but it requires hard-to-control techniques and may suffer from other adverse problems, such as phase separation and unstable emission colors at high voltages. In 2001, Tang et al discovered a novel phenomenon of AIE that prevents the ACO effect efficiently.⁹ The combination of AIE-active units and conventional ACQ building blocks has generated various luminogens with excellent solid-state emission, which function outstandingly as light-emitting layers for undoped OLEDs.¹⁰⁻¹⁴ However, common AIE luminescent materials can only harvest singlet excitons to realize a theoretical internal quantum efficiency of 25% due to spin-forbidden interactions, limiting the efficiency of OLEDs.

Thermally activated delayed fluorescence (TADF) materials have attracted much attention in recent years because both singlet and triplet excitons can be harvested to achieve high efficiency. For a TADF molecule, a small ΔE_{ST} is required to promote the up-conversion of triplet excited state to singlet excited state. Recently, a series of E-type TADF emitters with small ΔE_{ST} were developed by Adachi et al.¹⁵⁻²⁰ as an alternative to achieving external quantum efficiencies (EQEs) higher than conventional fluorescent emitters. To achieve high efficiency, the most commonly method was via bipolar compounds based on intramolecular charge transfer (ICT) within systems containing donor and acceptor moieties. In an ICT based compound, the highest occupied molecule orbital (HOMO) and lowest unoccupied molecule orbital (LUMO) would be localized at the donor and acceptor moieties, respectively. Thus, a small overlap between HOMO and LUMO leads to a small ΔE_{ST} . However, a common problem for TADF OLEDs is exciton concentration quenching caused by singlet-triplet and triplet-triplet annihilation, restricting the application of undoped OLEDs. To overcome this problem, a special compound with the features of TADF

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and AIE is required to ensure efficient triplet harvesting, and more importantly, to overcome the ACQ effect. Whereas, to the best of our knowledge, there has been few studies about AIE-active TADF compounds. Xu et al. have successfully synthesized an AIE-active TADF compound with a high photoluminescence quantum yield of 93.3%, which is the highest quantum yield for long-lifetime emitters.²¹ Then, they also synthesized a single white-light-emitting organic molecule with the features of AIE and TADF.²² Wang et al. have successfully developed the TADF device with maximum EQE value of 21.5% by using AIE-active TADF compound as an emitter.²³

In this work, we designed and synthesized two compounds, tCzDSO2 and 3tCzDSO2, which with the features of AIE and AIE-active TADF, respectively. Both of them have a typical D-A structure with thianthrene 9,9',10,10'-tetraoxide (DSO2) as an electron accepter and 3,6-Di-tert-butyl-9H-carbazole (tCz)/ carbazole dendrons (3tCz) as an electron donor unit. The tCzDSO2 emits intense AIE with a high $\Phi_{\rm F}$ of 0.92 due to the efficient elimination of ACQ effect. Meanwhile, compound 3tCzDSO2 exhibits not only AIE, but also TADF in the solid state, which can prevent the ACQ effect and utilize the triplet excitons efficiently. The TGA and DSC demonstrated that both of them have excellent thermal properties with high morphological stability. The higher decomposition temperature (T_d) and glass-transition temperature (T_g) of 3tCzDSO2 due to the higher molecular weight are favorable to improve the film-forming performance during device operation. In addition, the 3tCzDSO2 shows greater separation of the HOMO and LUMO orbitals in the DFT calculations. The ΔE_{ST} of tCzDSO2 and 3tCzDSO2 were calculated to be 0.29 eV and 0.06 eV, respectively. The transient photoluminescence (PL) decay showed compound 3tCzDSO2 have a long lifetime, indicating the triplet excited state can up-convert to singlet excited state by RISC. This change in ΔE_{ST} can be explained well in the modification of molecular structures. This work provides a simple and effective approach to obtain AIE-active TADF compound by reducing the ΔE_{ST} in the modification of molecular structures.

2. Experimental section

General information

All solvents and materials were used as received from commercial sources without further purification. ¹H NMR and ¹³C HMR spectra were recorded on a BRUKER AMX 300 MHz and 75 MHz instrument relative to $Si(CH_3)_4$ as internal standard. Molecular masses were determined by matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) using a BRUKER DALTONICS instrument, with a-cyano-hydroxycinnamic acid as a matrix. Absorption and photoluminescence emission spectra of the target compound were measured using a SHIMADZU UV-2450 spectrophotometer and a HORIBA FLUOROMAX-4 spectrophotometer, respectively. The solid PL quantum efficiency was measured with an integrating sphere under an excitation wavelength of 380 nm. Cyclic voltammetry were performed on a CHI750C voltammetric analyzer in CH₂Cl₂ solutions (10⁻³ M) (oxidation process) at a scan rate of 100 mV s^{-1} with a platinum plate as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the electrode. electrolyte counter The supporting was tetrabutylammonium hexafluorophosphate (0.1 M) and ferrocene was selected as the internal standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) curves were recorded with a Netzsch simultaneous thermal analyzer (STA) system (STA 409PC) and DSC 2910 modulated calorimeter under a dry nitrogen gas flow at a heating rate of 10 °C min⁻¹. The films preparation as follows: In a general procedure, the quartz plate substrates were precleaned carefully and treated by UV ozone for 4 min. The solutions with the concentration of 10 mg mL⁻¹ were spin coated onto the quartz plate substrate and dried in vacuum.

Quantum chemical calculations

The geometrical and electronic properties of tCzDSO2 and 3tCzDSO2 were performed with the Gaussian 09 program package. The calculation was optimized at the B3LYP/6-31G (d) level of theory. The molecular orbitals were visualized using

Gaussview 5.0.

Materials

The 3,6-Di-tert-butyl-9H-carbazole 1 and carbazole dendrons 2 were synthesized according to the literature methods.^{24,25}

Preparation of 2-bromo-thianthrene

To a stirred solution of thianthrene (3 g, 13.85 mmol) in THF (100 mL) at room temperature under N₂ was added Br₂ (4.64 g, 29 mmol). After the addition was completed the mixture was heated at 80°C for 5 h. Then, the reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried by anhydrous Na₂SO₄ and filtered. The product was isolated by silica gel column chromatography using hexane as eluent to afford a white solid (2.15 g, 50%).¹H NMR (300 MHz, CDCl₃, δ) : 7.23-7.26 (m, 2H), 7.30-7.36 (m, 2H), 7.45-7.48 (m, 2H), 7.61 (d, J = 2.0 Hz, 1H); ¹³C NMR (75 MHz, CDCl₃, δ) : 121.4, 127.7, 127.9, 128.8, 128.8, 129.6, 130.5, 131.2, 134.7, 134.8, 135.2, 137.7; MS (MALDI-TOF) [m/z]: calcd for C₁₂H₇BrS₂: 293.92, found: 293.80. Anal. Calcd (%) for C₁₂H₇BrS₂: C, 48.82; H, 2.38.

Preparation of 2-Bromo-thianthrene 9,9',10,10'-tetraoxide

To a stirred solution of 2-bromo-thianthrene (2 g, 6.80 mmol) in AcOH (50 mL) at room temperature was added 30% H₂O₂ (7.8 g, 68 mmol). Then, the mixture was heated at 110 °C for 2h. After this mixture cooled to room temperature, the reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried by anhydrous Na₂SO₄ and filtered. The product was re-crystallized from ethyl acetate to give a colorless solid (2.38 g, 97%).¹H NMR (300 MHz, CDCl₃, δ) : 7.83-7.86 (m, 2H), 7.94 (d, J= 5.1 Hz, 1H), 8.09 (d, J= 8.1 Hz, 1H), 8.24-8.27 (m, 2H), 8.37 (s, 1H); ¹³C NMR (75 MHz, DMSO, δ) : 125.8, 125.8, 126, 128.3, 128.4, 128.5, 134.8, 135, 137.7, 137.9, 139.6; MS (MALDI-TOF) [m/z]: calcd for C₁₂H₇BrO₄S₂: 359.22, found: 359.80. Anal. Calcd (%) for C₁₂H₇BrO₄S₂: C, 40.12; H, 1.96. found: C, 40.12; H, 1.97.

Preparation of 3,6-Di-tert-butyl-9-(9,9',10,10'-tetraoxo-5,10-dihydro-5,10thianthren-2-yl)-9H-carbazole (tCzDSO2)

2-Bromo-thianthrene 5,5,10,10-tetraoxide (1 g, 2.8 mmol), 3,6-Di-tert-butyl-9H-carbazole (0.93 g, 3.4 mmol), K₂CO₃ (0.48 g, 3.4 mmol), copper(I) iodide (0.006 g, 0.3 mmol), and 1,10-phenanthroline (0.006 g, 0.3 mmol) were added to 20 mL of dried DMF. The mixture was heated at 160 °C for 12 h under nitrogen atmosphere. After this mixture cooled to room temperature, the reaction mixture was extracted with dichloromethane and washed with water. The organic layer was dried by anhydrous Na₂SO₄ and filtered. The product was isolated by silica gel column chromatography using petroleum ether/ethyl acetate (3:1) as eluent to afford a bright green solid (1.08 g, 70%). ¹H NMR (300 MHz, DMSO, δ) :1.42 (s, 18H), 7.52 (t, J= 8.4 Hz, 4H), 8.08 (t, J= 4.5 Hz, 2H), 8.29-8.44 (m, 6H), 8.53 (d, J= 8.4 Hz, 1H); ¹³C NMR(75 MHz, DMSO, δ) :31.7, 34.6, 109.1, 117, 122, 123.9, 124.2, 125.9, 126, 128.5, 130.9, 134.9, 135, 137.4, 138.2, 138.4, 140.2, 142.7, 144.2; MS (MALDI-TOF) [m/z]: calcd for C₃₂H₃₁NO₄S₂: 557.72, found: 557.23. Anal. Calcd (%) for C₃₂H₃₁NO₄S₂: C, 68.91; H, 5.60; N, 2.51. found: C, 68.89; H, 5.59; N, 2.50.

Preparation of 3,6-bis(3,6-di-tert-butyl-9H-carbazole-9yl)-(9,9',10,10'-tetraoxo-5, 10-dihydro-5,10-thianthren-2-yl)-9H-carbazole (3tCzDSO2)

The synthetic method of 3tCzDSO2 was according to that of tCzDSO2 with a yield of 41.7%. ¹H NMR (300 MHz, DMSO, δ) :1.42 (s, 36H), 7.33 (d, J= 8.7 Hz, 4H), 7.48 (d, J= 6.9 Hz), 7.73 (d, J= 10.5 Hz, 2H), 7.88 (d, J= 8.7 Hz, 2H), 8.09-8.14 (m, 2H), 8.30 (s, 4H), 8.41-8.44 (m, 2H), 8.53 (d, J= 8.1 Hz, 1H), 8.66 (d, J= 8.1 Hz, 1H), 8.73 (s, 3H); ¹³C NMR (75 MHz, DMSO, δ) : 31.8, 34.4, 109.0, 110.8, 111.3, 114.5, 115.6, 116.6, 119.9, 122.6, 123.6, 124.6, 126.0, 126.1, 131.2, 132.4, 138.1, 138.8, 139.3, 141.9, 142.2; MS (MALDI-TOF) [m/z]: calcd for C₆₄H₆₁N₃O₄S₂: 1000.32, found: 999.65. Anal. Calcd (%) for C₆₄H₆₁N₃O₄S₂: C, 76.84; H, 6.15; N, 4.20. found: C, 76.81; H, 6.14; N, 4.18.

Results and discussion

Synthesis and characterization

The synthesis routes and chemical structures of tCzDSO2 and 3tCzDSO2 are shown

in Scheme 1. 2-bromo-thianthrene was prepared through bromination reaction. Then, 2-bromo-thianthrene was oxidized to 2-Bromo-thianthrene 9,9',10,10'-tetraoxide. The compounds tCzDSO2 and 3tCzDSO2 were synthesized by the classic Ullmann reaction. Finally, the products were purified by column chromatography to give the pure products. ¹H and ¹³C NMR spectroscopy, mass spectrometry, and elemental analysis were used to characterize the molecular structures.



Scheme 1 Synthetic routes and chemical structures of tCzDSO2 and 3tCzDSO2.

Thermal Properties

The thermal properties of tCzDSO2 and 3tCzDSO2 were investigated by using thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. According to Fig. 1, tCzDSO2 exhibited excellent thermal stability with a 5% weight-loss T_d as high as 371 °C, while T_d of 3tCzDSO2 is reached at a temperature of 432 °C. This value is about 61°C above tCzDSO2, which is attributed to the high molecular weight of 3tCzDSO2. In addition, the DSC curves record well-defined T_g of 110 °C (tCzDSO2) and 141 °C (3tCzDSO2). Simultaneously, no noticeable signals related to the crystallization or melting is observed in the DSC curves. Such excellent thermal properties with high morphological stability are favorable to improve the OLEDs performance during device operation.



Fig. 1 TGA curves of tCzDSO2 and 3tCzDSO2. Inset: Corresponding DSC traces.

Photophysical Properties

The photophysical properties of two compounds were measured by UV-vis absorption and photoluminescence (PL) spectra as shown in Fig. 2 and Table 1. As depicted in Fig. 2a, both compounds exhibit three major absorption bands locate at the 285 nm -295 nm, 324 nm - 347 nm and 388 nm - 410 nm in the UV-vis absorption. The absorption spectra of tCzDSO2 and 3tCzDSO2 exhibits two strong absorption peaks be attributed to the n-π* transitions at 285-295 nm can of in 3,6-Di-tert-butyl-9H-carbazole and carbazole dendrons. Meanwhile, the peak at 324 nm - 347 nm in two compounds are correspond to carbazole- and thianthrene 9,9',10,10'-tetraoxide-centered n- π^* transitions. The strong peak at 388 nm and the weak peak at 410 nm for tCzDSO2 and 3tCzDSO2 can be assigned to the ICT transitions. The optical bandgap (E_{σ}) can be estimated from the edge of the UV-vis absorption, giving the values of 2.82 eV and 2.58 eV for tCzDSO2 and 3tCzDSO2, respectively. Upon UV excitation, the PL spectra of tCzDSO2 and 3tCzDSO2 exhibit the peaks at 522 nm/554 nm and 544 nm/595 nm in the film/solution, respectively. Fig. 2b and Fig. 2c showed the ICT characteristics of the two compounds via their gradually red-shifted and broadened fluorescent emissions upon increasing the

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polarity of solvent, indicating the typical photoinduced ICT process and the effective electronic communication between the donor and acceptor units. The solid Φ_F of tCzDSO2 and 3tCzDSO2 are 0.92 and 0.19/0.41, respectively. Such high Φ_F can attribute to the suitable D-A molecular structures.





Fig. 2 (a) The absorption and emission spectra of tCzDSO2 and 3tCzDSO2 in flim and CH₂Cl₂. (b) PL spectra of tCzDSO2 in different solvents. (c) PL spectra of 3tCzDSO2 in different solvents.

	$T_{ m g}/$ $T_{ m d}$ a	$\lambda_{abs}{}^{b}$	$\lambda_{ m em}{}^b$	$\lambda_{\rm em}{}^c$	$\Phi_{\rm F}$ ^c	E_g^{d}	Eg ^e	HOMO/LUMO ^e	HOMO/LUMO ^f	ΔE_{ST}^{e}
	[°C]	$[nm]$ (log ϵ)	[nm]	[nm]	[%]	[eV]	[eV]	[eV]	[eV]	[eV]
tCzDSO2	371/110	284(6.5),292	553	520	92	3.39	2.82	-5.64/-2.25	-5.60/-2.78	0.29
		(6.49),325(6.								
		3),337(6.34),								
		388(6.34)								
3tCzDSO2	432/141	285(5.77),29	595	547	19/41	2.72	2.58	-5.18/-2.46	-5.32/-2.74	0.06
		5(5.78),334(
		5.3),346(5.3)								
		,397(4.69)								

 Table 1 Physical properties of the compounds

^{*a*} Measured by DSC/TGA at a heating rate of 10 °C mim⁻¹. ^{*b*} Measured in CH₂Cl₂ (10⁻⁵ M). ε denotes the molar extinction coefficient. ^{*c*} Measured in thin film on quartz substrate. ^{*d*} Estimated from the optical absorption edge, E_g =1240/ λ_{onset} . ^{*e*} Obtained from quantum calculations by using B3LYP/6-31G(d). ^{*f*} Calculated by HOMO = -(4.8+ E_{onset}^{OX}) eV, and LUMO = HOMO + E_g, where E_{onset}^{OX} is the onset potential of the oxidation.

AIE Properties

The photoluminescence spectra of tCzDSO2 and 3tCzDSO2 in aqueous THF with different THF/water ratios were shown in Fig. 3. Water was used as a nonsolvent for the compounds. The reason was that the compounds must aggregate in the aqueous mixtures with high water fractions (f_w). As shown in Fig. 3, emission of tCzDSO2 in the pure THF was very weak that only weak signal was recorded with maxima at 533 nm. Simultaneously, emission of 3tCzDSO2 in the pure THF was almost no PL signal was recorded. With increasing f_w , the PL intensities initially decrease due to the increased solvent polarity. Then, the PL intensities start to increase at the f_w of 60% and 70% for tCzDSO2 and 3tCzDSO2, respectively. At a high f_w of 90%, luminescence was significantly enhanced for tCzDSO2 and 3tCzDSO2. The PL intensities enhancement was induced by aggregation of molecules, thus testifying to their AIE active. Notably, in comparison with the commonly reported AIE moieties, such as tetraphenyl ethylene (TPE), silole and 9,10-distyrylanthracene, the two compounds belong to a new class of AIE compounds due to their novel structures.





Fig. 3 Photoluminescence (PL) spectra of tCzDSO2 (a) and 3tCzDSO2 (b) in THF/water mixtures with different amounts of water (f_w). $c = 10 \mu M$.

Electrochemical properties

The electrochemical properties of tCzDSO2 and 3tCzDSO2 were characterized by the electrochemical cyclic voltammetry (CV)using tetrabutylammonium hexafluorophosphate (TBAPF6) as the supporting electrolyte and ferrocene as the internal standard. As shown in Fig. 4, during the anodic scan in dichloromethane, tCzDSO2 and 3tCzDSO2 exhibited reversible oxidation behavior, which can be attributed to the oxidation of electron-donating 3,6-di-tert-butylcarbazole moiety and the introduction of two tert-butyl groups at the 3,6 positions of outlayer carbazole units, respectively. No reduction waves were detected. On the basis of the onset potentials for oxidation, the HOMO energy levels tCzDSO2 and 3tCzDSO2 were estimated to be -5.60 eV and -5.32 eV, respectively. The reason is that the HOMO of tCzDSO2 is mainly concentrated in the tCz and DSO2 units, while the HOMO of 3tCzDSO2 is distributed over the whole 3tCz moiety. Thus, the calculated HOMO value of 3tCzDSO2 is 0.28 eV higher than that of tCzDSO2, which better matches the work function of anode for the injection of holes. The results are further confirmed by DFT calculations. The LUMO energy levels tCzDSO2 and 3tCzDSO2 were estimated from the HOMO energy level and E_g were -2.78 eV and -2.74 eV.



Fig. 4 Oxidation part of the CV curves of tCzDSO2 and 3tCzDSO2 in dichloromethane.

Delayed fluorescence

The transient photoluminescence (PL) decay characteristics of two compounds in solid film were depicted in Fig. 5 and data was listed in Table S1. As shown in Fig. 5a and Table S1, tCzDSO2 only have a fast decay with a lifetime of 16 ns, which can be assigned to fluorescence. However, as depicted in Fig. 5b, 3tCzDSO2 have two-component decays, that is, a fast decay with a lifetime of 29 ns and a slow decay with a lifetime of 1.6 µs can be attributed to fluorescence and delayed fluorescence decay, respectively. Thus, the triplet excited state can up-convert to the singlet excited state by RISC. The results indicated that 3tCzDSO2 shows better solid-state triplet harvesting, which is favorable to improve the efficiency of OLEDs. The delayed component of 3tCzDSO2 showed remarkable temperature dependence when the temperature increased from 150 K to 300 K (see Fig. S1a), consistent with other TADF materials. Meanwhile, the delayed fluorescence emission for 3tCzDSO2 decreases with decreasing temperature (see Fig. S1b), confirming the thermally assisted mechanism. These results proved the presence of thermal activation energy for the delayed fluorescence.¹⁵ In addition, the $\Phi_{\rm F}$ of 3tCzDSO2 increased from 0.19 in air to 0.41 in N₂ atmosphere, also indicating the existence of delayed fluorescence.



Fig. 5 Transient PL decay profiles of tCzDSO2 (a) and 3tCzDSO2 (b) in solid films.

DFT calculations

The three-dimensional geometries and the frontier molecular orbital energy levels of tCzDSO2 and 3tCzDSO2 were calculated using density functional theory (DFT). The results were depicted in Table 1, and the HOMOs and LUMOs of two compounds were in shown in Fig.6. The geometries of two compounds in Fig.6 show that the thianthrene 9,9',10,10'-tetraoxide and carbazole are significantly twisted, resulting in a non-planar structure in each molecule. The HOMOs of the tCzDSO2 and 3tCzDSO2

are evenly delocalized over the outer 3,6-Di-tert-butyl-9H-carbazole and carbazole dendrons, respectively. The LUMOs are evenly delocalized over the thianthrene 9,9',10,10'-tetraoxide. However, in comparison with tCzDSO2, the 3tCzDSO2 shows greater separation of the HOMO and LUMO orbitals. To predict the energy difference (ΔE_{ST}) between the lowest S₁ and the lowest T₁ levels, Time dependent density functional theory (TD-DFT) calculations were performed, based on the ground state geometries when optimized by the DFT (B3LYP/6-31G(d)). The ΔE_{ST} values of tCzDSO2 and 3tCzDSO2 were 0.29 eV and 0.06 eV, respectively, confirming the smaller overlap between the HOMO and LUMO of 3tCzDSO2. The smaller ΔE_{ST} values of 3tCzDSO2 indicated a potentially high RISC, thus causing the TADF phenomenon.



Fig. 6 Optimized geometries and calculated HOMO and LUMO density maps for tCzDSO2 and 3tCzDSO2 by DFT calculations in Gaussian 09 at the B3LYP/6-31G (d) level.

Conclusion

In summary, two novel compounds, namely tCzDSO2 and 3tCzDSO2, composed of electron-donating 3,6-Di-tert-butyl-9H-carbazole (tCz)/carbazole dendrons (3tCz) and electron-accepting thianthrene 9,9',10,10'-tetraoxide, have been designed and synthesized. The compound tCzDSO2 exhibits intense AIE with a high Φ_F of 0.92 in

the solid state. Simultaneously, the compound 3tCzDSO2 exhibits AIE-active TADF, which provide the Φ_F of 0.19 and 0.41 in air and N₂ atmosphere, respectively. The ΔE_{ST} of tCzDSO2 and 3tCzDSO2 are 0.29 eV and 0.06 eV, respectively. The DFT calculations demonstrate that the ΔE_{ST} of 3tCzDSO2 was minimized by the increased proportion of carbazole units, which can induce the separating of the HOMO and LUMO. This report provides a simple and effective approach to obtain AIE-active TADF compound, and is significant for the potential application in nondoped OLED. Meanwhile, further studies about devices preparation are currently in progress in our laboratory.

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References

- M. Baldo, D. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. Thompson and S. Forrest, Nature, 1998, 395, 151.
- 2 Y. Zou, J. Zou, T. Ye, H. Li, C. Yang, H. Wu, D. Ma, J. Qin and Y. Cao, Adv. Funct. Mater., 2013,23, 1781.
- 3 L. Duan, J. Qiao, Y. Sun and Y. Qiu, Adv. Mater. 2011, 23, 1137.
- 4 J. Moorthy, P. Venkatakrishnan, P. Natarajan, D. Huang and T. Chow, J. Am. Chem. Soc. 2008, 130, 17320.
- 5 H. Sasabe, N. Toyota, H. Nakanishi, T. Ishizaka, Y. J. Pu and J. Kido, Adv. Mater., 2012, 24, 3212.
- 6 W. Jiang, H. Xu, X. Ban, G. Yuan, Y. Sun, B. Huang, L. Duan, and Y. Qiu, Org.

Lett., 2014, 16, 1140.

- 7 Y. Gong, Y. Tan, J. Liu, P. Lu, C. Feng, W. Yuan, Y. Lu, J. Z. Sun, G. He and M. Zhang, Chem. Commun., 2013, 49, 4009.
- 8 S. Kim, Q. Zheng, G. He, D. J. Bharali, H. Pudavar, A. Baev and P. Prasad, Adv. Funct. Mater., 2006, 16, 2317.
- 9 J. Luo, Z. Xie, J. Lam, L. Cheng, H. Chen, C. Qiu, H. Kwok, X. Zhan, Y. Liu, D. Zhu and B. Tang, Chem. Commun., 2001, 1740.
- 10 L. Chen, Y. Jiang, H. Nie, P. Lu, H. Sung, I. Williams, H. Kwok, F. Huang, A. Qin, Z. Zhao and B. Tang, Adv. Funct. Mater., 2014, 24, 3621.
- 11 J. Huang, N. Sun, Y. Dong, R. Tang, P. Lu, P. Cai, Q. Li, D. Ma, J. Qin and Z. Li, Adv. Funct. Mater., 2013, 23, 2329.
- 12 X. Du, J. Qi, Z. Zhang, D. Ma and Z. Wang, Chem. Mater., 2012, 24, 2178.
- 13 Y. Hong, J. Lam and B. Tang, Chem. Soc. Rev., 2011, 40, 5361.
- 14 Z. Zhao, Z. Wang, P. Lu, C. Chan, D. Liu, J. Lam, H. Sung, I. Williams, Y. Ma and B. Tang, Angew. Chem., Int. Ed., 2009, 121, 7744.
- H. Uoyama, K. Coushi, K. Shizu, H. Nomura and C. Adachi, Nature, 2012, 492, 234.
- 16 G. Mehes, H. Nomura, Q. Zhang, T. Nakagawa and C. Adachi, Angew. Chem., Int. Ed., 2012, 51, 11311.
- J. Li, T. Nakagawa, J. MacDonald, Q. Zhang, H. Nomura, H. Miyazaki and C. Adachi, Adv. Mater., 2013, 25, 3319.
- 18 Q. Zhang, J. Li, K. Shizu, S. Huang, S. Hirata, H. Miyazaki, and C. Adachi, J. Am. Chem. Soc., 2012, 134, 14706.
- Q. Zhang, B. Li, S. Huang, H. Nomura, H. Tanaka and C. Adachi, Nat. Photonics, 2014, 8, 326.
- H. Nakanotani, K. Masui, J. Nishide, T. Shibata and C. Adachi, Sci. Rep., 2014, 4, 2045.
- S. Xu, T. Liu, Y. Mu, Y. Wang, Z. Chi, C. Lo, S. Liu, Y. Zhang, A. Lien, and J. Xu, Angew. Chem. Int. Ed., 2014, 53, 1.
- 22 Z. Xie, C. Chen, S. Xu, J. Li, Y. Zhang, S. Liu, J. Xu, and Z. Chi, Angew. Chem.

Int. Ed., 2015, 54, 1.

- H. Wang , L. Xie , Q. Peng , L. Meng , Y. Wang , Y. Yi , and P. Wang, Adv. Mater.,
 2014, 26, 5198.
- 24 H. Zhang, S. Wang, Y. Li, B. Zhang, C. Du, X. Wan and Y. Chen, Tetrahedron, 2009, 6, 4455.
- 25 K. Albrecht and K. Yammoto, J. Am. Chem. Soc., 2009, 131, 2244.

By introducing more proportion of carbazole, the newly designed molecule 3tCzDSO2 integrates the features of AIE and TADF with extremely small ΔE_{ST} .

