Supporting Information

Engineering Excited-State Properties of Intramolecular and Intermolecular Charge Transfer Purely Organic Emitters towards High-Performance Fluorescent OLEDs

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1. Material Synthesis

1.1 General.

Other reagents without special instructions were purchased from commercial suppliers. 2-Bromophenylphenylsulfane (M1) and 2,7-dibromo-9*H*-hioxanthen-9-one (M2) were synthesized according to the literatures.^[S1]

1.2 Synthetic Routes



Scheme S1. Synthetic routes of DTPA and DAcDB.



Scheme S2. Synthetic routes of DSO2.



Scheme S3. Synthetic routes of DBr-DSO2



DBPA-DSO2

Scheme S4. Synthetic route of DBPA-DSO2.



Scheme S5. Synthetic route of DAc-DSO2.



Scheme S6. Synthetic route of DTPA-DSO2.



Scheme S7. Synthetic route of DAcDB-DSO2.

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2. Density Functional Theory (DFT) Computation

All of the simulations were performed using the Gaussian 09-B01 program package.^[52] Geometry character and transition property of these ICT molecules were computed by the density functional theory (DFT) and time-dependent density functional theory (TD-DFT). Considering that the ground state (S_0) geometry is less sensitive to the exchange correlation (XC), S_0 geometry was optimized using a B3LYP functional and 6-31G* basis set. A hybrid meta-generalized gradient-approximation (GGA) functional M06-2x was employed for TD-DFT calculation of excited state because of its testified effectiveness to provide intermediate results for ICT molecules.^[53] Through the advance of DFT computation by recent years, the ground and excited state property of ICT molecules could have been predicted quite precisely. However, it is still a tough task to credibly Fig. out these properties of inter-CT systems, which possess a long range interaction and much more complex accumulation modes of the separated donor and acceptor. Thereby, the DFT calculation was only employed to investigate the quantum chemical property of ICT emitters in this work.



Scheme S8. Molecular structures and spatial distributions of HOMOs and LUMOs of ICT molecules.

The spatial distributions of highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of these molecules are shown in Scheme S7, and the extracted key parameters from the DFT calculation are summarized in Table S1. The HOMOs and LUMOs are roughly distributed on the respective donor and acceptor moieties for these emitters, indicating their ICT property. The values of calculated HOMO levels of these molecules are around -5.0 \pm 0.2 eV, and their defined values are affected by the orbital components. The rather large orbital component of HOMO contributed from DSO2 fragment results in the lowest HOMO level for

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DBPA-DSO2. The changing trends are roughly consistent with the experimental values obtained from CV measurement. The oscillator strengths (*f*) of DTPA-DSO2 and DBPA-DSO2 are several orders of magnitude larger than those of DAcDB-DSO2 and DAc-DSO2, which could be ascribed to the discrepant exchange integral between their HOMO and LUMO levels. The dihedral angles between the donor and acceptor units of acridine-containing molecules are significantly larger than the phenylamine-containing molecules. A more compact molecular geometry of DAc-DSO2 yields much larger dihedral angles (close to 90°) than the other three ICT molecules, and this benefits in a much smaller singlet and triplet splitting energy (ΔE_{ST}). The calculated ΔE_{ST} values of these ICT emitters are in coincidence with the experimental results extracted from their PL spectral data.

Molecules	$lpha_{1}/lpha_{2}$ (°)	<i>I</i> 1/ <i>I</i> 2 (Å)	HOMO (eV)	LUMO (eV)	<i>S</i> ₁ (eV)	<i>T</i> 1 (eV)	f	ΔE _{st} (eV)
DTPA-DSO2	28.6/34.6	1.48/1.48	-4.98	-1.54	3.795	3.086	1.5192	0.709
DBPA-DSO2	n.a./n.a.	1.41/1.41	-5.20	-1.22	4.074	3.336	0.8722	0.738
DAc-DSO2	89.2/86.4	1.43/1.43	-4.99	-1.69	3.508	3.500	0.0000	0.008
DAcDB-DSO2	31.4/39.0	1.49/1.49	-4.86	-1.86	3.678	3.600	0.0002	0.078

Table S1. Summary of DFT computation data of ICT emitters.

3. Further Experimental Details

3.1 Device fabrication

OLEDs were grown on glass substrates pre-coated with a 95-nm-thin layer of indium tin oxide (ITO) with a sheet resistance of 10 Ω /square. The substrates were thoroughly cleaned in ultrasonic bath of acetone, isopropyl alcohol, detergent, deionized water, and isopropyl alcohol and treated with O₂ plasma for 20 min in sequence. Organic layers were deposited onto the ITO-coated substrates by high-vacuum (<5×10⁻⁴ Pa) thermal evaporation. Cathodes consisting of a 1-nm-thin layer of LiF followed by a 120-nm-thin layer of Al, were patterned using a shadow mask with an array of 3 mm × 3 mm openings. Deposition rates are 1~2 Å s⁻¹ for organic materials, 0.1 Å s⁻¹ for LiF, and 6 Å s⁻¹ for Al, respectively. For each batch of device fabrication, four devices with a same device conFig.uration were simultaneously obtained. EL spectra were recorded by a spectrophotometer (Photo Research, PR705). The current-density–voltage–luminance characteristics were measured using a Keithley source measure unit 2400 and a Minolta CS200 luminance meter, respectively. EQE was calculated from the luminance, current density, and EL spectrum, assuming a Lambertian distribution. The emissive area of all the devices is 0.09 cm⁻². The performances of each type device have been verified based on at least 4 devices, while the device performances of key devices including DAc-DSO2, DTPA-DSO2 and DBPA-DSO2 as an emitter have been confirmed based on at least 16 devices (>3 batches of fabrication).

3.2 Measurement Details of PL Emission Spectra

Steady-state and transient photoluminescence (PL) was measured with an Edinburgh FL980 fluorescence spectrophotometer. Transient PL spectra were carried out based on the time-correlated single photon counting (TCSPC) technique. The total detective channel amount for time-resolved PL measurements is 8000, so the temporal resolution depends on the selected time range for each measurement. The temporal resolution to measure nanosecond- and microsecond-scale transient PL data in this study is 0.0625 and 6.25 ns/channel, respectively. A picosecond light-emitting diode with a peak wavelength of 296.6 nm, a pulse width of 831.8 ps and a bandwidth of 10 nm was adopted as the excitation source in the transient PL emission experiment. Measurement of the lowest singlet and triplet state (S_1 and T_1) values of the investigated materials was performed using a spectrometer with the gate-delayed accessory (Horiba Jobin Yvon, FL-3). These values are extracted from their low-temperature emission spectra at 77 K frozen in toluene. The phosphorescence spectra with a 50 µs delay time were compared with the low-temperature emission spectra to exactly distinguish fluorescence and phosphorescence emission band. S_1 and T_1 values are calculated from the following equation: S_1 or $T_1 = hc/\lambda_{peak}$, where λ_{peak} corresponds to the highest emission peak of the fluorescence and phosphorescence emission band, respectively, *h* is the Plank constant, c is the speed of light in vacuum.

4. Other Supplementary Figures and Tables



Fig. S1 Excitation spectra of the developed ICT and inter-CT systems recorded at their corresponding emission peak, respectively.

Table S2 The fitting parameters of PL transient decay curves by the decay model: $I(t)=I_0 + A_1 exp(-t/\tau_1)$ or $I(t)=I_0 + A_1 exp(-t/\tau_1) + A_2 exp(-t/\tau_2)$.

			Prompt			Delayed		
	Sample	τ _{1 (ns)}	A ₁	proportion	$\tau_{2 (ns)}$	A ₂	proportion	χ^2
				(%)			(%)	
-	DTPA	2.44	983	100	-	-	-	0.579
	DAcDB	5.71	1016	100	-	-	-	0.267
	DSO2	0.46	1149	100	-	-	-	0.282
	DTPA:DSO2	3.61	750	65.7	11.1	127	34.3	0.271
	DAcDB:DSO2	6.88	867	72.9	33.1	66.8	27.1	0.798
	DTPA-DSO2	3.06	929	100	-	-	-	0.429
	DBPA-DSO2	2.71	901	100	-	-	-	0.527
	DAcDB-DSO2	4.11	741	49.9	19.1	159	50.1	1.108
	DAc-DSO2	25.5	930	44.8	2081	14.0	55.2	0.716
	DTPA:TmPyTZ	42.4	721	17.7	2307	61.5	82.3	1.161
	DAcDB:TmPyTZ	50.0	643	14.0	1992	99.6	86.0	1.276

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Fig. S2 PL emission spectra of (a) DSO2 and (b) AcB in toluene solution at room temperature (RT) and 77 K.



Fig. S3 Transient PL decay profiles of DAc-DSO2 thin films under various temperatures. The positive correlation of the fractions of long-lived decay components and the temperature confirms the TADF property of DAc-DSO2.



Fig. S4 Comparison of time-resolved PL emission spectra of the binary-mixed films at various sliced times (unit: ns) and the EL emission spectra of the devices thereof at 1 and 5 mA cm⁻²: (a) DAcDB:DSO2 and (b) DTPA:DSO2.



Fig. S5 (a) PL emission spectra and (b) transient PL decay curves of DAcDB:TmPyTZ and DTPA:TmPyTZ.



Fig. S6 (a) Current density-luminance versus voltage (J-V-L) and (b) external quantum efficiency versus luminance (EQE-L) characteristics (inset: EL spectra at 1 mA cm⁻²) of OLEDs with an inter-CT emitter in a configuration of ITO/ DTPA or DAcDB (60 nm)/DTPA:TmPyTZ or DAcDB:TmPyTZ (1:1, wt, 20 nm)/TmPyTZ (50 nm)/LiF (1 nm)/Al (150 nm).



Fig. S7 Cyclic voltammogram (CV) characteristics of the developed compounds measured in 0.1 M n-Bu₄NPF₆ in CH₂Cl₂:CH₃CN (4:1, v/v) solution. All these compounds were measured under the same experimental conditions. The redox potential ($E_{1/2}$) of ferrocene/ferrocenium (Fc/Fc⁺) was measured to be 0.47 V. Given that the redox potential of Fc/Fc⁺ has an absolute energy level of -4.80 eV compared to a vacuum, HOMO energy levels of the current materials could be estimated according to the following equation: HOMO = -e (E_{ox} +4.33) eV, where E_{ox} is the relevant oxidation potential. LUMO energy levels were estimated from their optical bandgaps (E_g^{opt}) and HOMOs using this equation: LUMO = HOMO+ E_g^{opt} .



Fig. S8 (a) TGA and (b) DSC thermograms of the developed materials recorded at a heating rate of 10 °C min⁻¹.



Fig. S9 Original ¹H NMR spectrum of DTPA.



Fig. S10 Original ¹³C NMR spectrum of DTPA.







Fig. S12 Original ¹H NMR spectrum of DAcDB.



Fig. S13 Original ¹³C NMR spectrum of DAcDB.



Fig. S14 Original HRMS spectrum of DAcDB.



Fig. S15 Original ¹H NMR spectrum of DSO2.



Fig. S16 Original ¹³C NMR spectrum of DSO2.



Fig. S17 Original HRMS spectrum of DSO2.

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Fig. S18 Original ¹H NMR spectrum of DBPA-DSO2.



Fig. S19 Original ¹³C NMR spectrum of DBPA-DSO2.



Fig. S20 Original HRMS spectrum of_DBPA-DSO2.



Fig. S21 Original ¹H NMR spectrum of DAc-DSO2.



Fig. S22 Original ¹³C NMR spectrum of DAc-DSO2.



Fig. S23 Original HRMS spectrum of DAc-DSO2.



Fig. S24 Original ¹H NMR spectrum of DTPA-DSO2.



Fig. S25 Original ¹³C NMR spectrum of DTPA-DSO2.



Fig. S26 Original HRMS spectrum of DTPA-DSO2.



Fig. S27 Original ¹H NMR spectrum of DAcDB-DSO2.



Fig. S28 Original ¹³C NMR spectrum of DAcDB-DSO2.



Fig. S29 Original HRMS spectrum of DAcDB-DSO2.



Fig. S30 Original ¹H NMR spectrum of DBr-DSO2 (2,7-dibromo-9,9'-spirobi[thioxanthene] 10,10,10',10'- tetraoxide).



Fig. S31 Original ¹³C NMR spectrum of DBr-DSO2.

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