Supporting Information

Tuning the organic persistent room-temperature phosphorescence

through aggregated states

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1. General Experimental Procedures

Materials

Dibenzofuran, 4-fluorobenzoyl chloride, anhydrous FeCl₃, carbazole and *tert*butoxide (*t*-BuOK) were purchased from Alfa Aesar and used as received. All other reagents and solvents (analytical grade) were purchased from Guangzhou Jincheng Company (China) and used without further purification. Ultra-pure water was used during the work-up procedures in the experiments.

Characterization

Proton and carbon NMR (¹H NMR and ¹³C NMR) spectra were collected from a Fourier transform nuclear magnetic spectrometer (Bruker AVANCE 400) (CDCl₃, tetramethyl silane ($\delta = 0$) as the internal standard). The mass spectra were obtained on thermo-spectrometers (DSQ & MAT95XP-HRMS). The UVvisible absorption spectrum was measured on a Hitachi U-3900 spectrophotometer. The photoluminescence (PL) spectra were detected with a spectrometer (FluoroLog-3) from HORIBA Instruments or a spectrometer system (Maya Pro2000) form Ocean Optics with a 310 nm Rhino LED as the excitation source. The persistent phosphorescent spectra were collected at a delayed time of 8 ms after the excitation source turn off. Powder wide-angle Xray diffraction (PXRD) measurements were measured by an X-ray diffractometer (Smart lab) with an X-ray source of Cu K α (λ = 0.15406 nm) at 40 kV and 30 mA, using a scan rate of 4° (2 θ) per min. The quantum chemistry calculations were performed with the Gaussian 09 software, at the B3LYP/6-31G (d) level of theory using the time-dependent density functional theory (TD-DFT) method. The exciton energies of the n-th singlet (S_n) and n-th triplet states (T_n) were obtained on the corresponding ground state geometries. The possible S_1 to T_n intersystem crossing (ISC) channels are believed to share part of the same transition orbital compositions. And the energy levels of T_n are considered to lie within the range of $E_{S1} \pm 0.3$ eV. Especially, two elements are mainly considered for the major ISC channels determination. First, the ratio of the same transition configuration in S₁ and T_n states should be large in all the transition orbital compositions. Second, the energy gap between S₁ and the specific T_n state should be small. The determination of minor ISC channels is vice versa.

The single-crystal X-ray diffraction data were collected, by using a Gemini A Ultra system (Agilent Technologies) or a Smart 1000 CCD (Bruker), with an X-ray source of Cu-K α radiation (λ = 1.54178 Å). The structure was solved by direct methods following the different Fourier syntheses. All non-hydrogen

atoms were anisotropically refined through least-squares on F^2 and assigned with the anisotropic thermal parameters, using the SHELXTL program suite. While the hydrogen atoms attached to carbon were placed in idealized positions and refined by using a riding model.

2. Synthesis



Scheme S1 Synthetic route for the DBF-BZ-Cz.

Synthesis of dibenzo[b,d]furan-2-yl(4-fluorophenyl)methanone (DBF-BZ).

Dibenzofuran (1.00 g, 5.95 mmol) and 4-fluorobenzoyl chloride (1.13 g, 7.13 mmol) were added into dichloromethane (DCM, 100 ml). Anhydrous FeCl₃ (1.16 g, 7.13 mmol) was added into the mixture slowly and heated at 40 °C for 5h. Then, the reaction mixture was cooled to room temperature and carefully poured into a diluted HCl solution. The precipitate was filtered, washed several times with water, and then dried over anhydrous Na₂SO₄. The crude product was purified by silica gel column chromatography with DCM/*n*-hexane (v/v = 1:2) as eluent. Compound DBF-BZ was obtained as a white solid in 76 % yield (1.31 g). EI-MS, *m*/*z*: [M]⁺ 290; calcd. for C₁₉H₁₁FO₂, 290.

Synthesis of 4-(9H-carbazol-9-yl) phenyl) (dibenzo [b,d]furan-2-yl) methanone (DBF-BZ-Cz).

To a solution of carbazole (0.69 g, 4.13 mmol) in dry DMF (50 ml), potassium *tert*-butoxide (1.16 g, 10.33 mmol) was added slowly, under an argon atmosphere. After the solution was stirred at room temperature for 20 mins, DBF-BZ (1.00 g, 3.44 mmol) was added. Then the reaction mixture was heated to 110 °C and stirred for an additional 6 h. After cooling to room temperature, the mixture was poured into ice/water mixture. The precipitate was filtered and washed with water (50 ml × 3). The crude product was purified by silica gel column chromatography using DCM/*n*-hexane (v/v = 1:1) as an eluent. And

compound DBF-BZ-Cz was obtained as a white solid in 82% yield (1.24 g). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 8.58-8.49 (d, J = 1.2 Hz, 1H), 8.19-8.08 (dd, J = 19.8, 8.0 Hz, 4H), 8.08-7.99 (dd, J = 13.0, 4.5 Hz, 2H), 7.80-7.73 (d, J = 8.3 Hz, 2H), 7.72-7.66 (d, J = 8.6 Hz, 1H), 7.65-7.61 (d, J = 8.2 Hz, 1H), 7.57-7.49 (dd, J = 13.6, 8.2 Hz, 3H), 7.48 – 7.38 (m, 3H), 7.32 (t, J = 7.4 Hz, 2H).¹³C NMR (100 MHz, CDCl₃) δ (ppm): 196.45, 160.14, 158.34, 142.96, 141.71, 137.94, 133.88, 133.19, 131.17, 129.47, 127.75, 127.59, 126.00, 125.24, 125.06, 124.90, 124.75, 122.50, 121.98, 121.85, 113.38, 113.00, 111.18. EI-MS, m/z: [M]⁺ 437; calcd. for C₃₁H₁₉NO₂, 437. HRMS, m/z: [M]⁺ 437.1414; calcd. for C₃₁H₁₉NO₂, 437.1410.

Preparation of the different aggregation/ polymorphs of DBF-BZ-Cz.

In a clean glass sample tube cover with a cap, 200 mg of DBF-BZ-Cz was dissolved in a mixture of DCM/*n*-hexane/ethyl alcohol (v/v/v = 1:1:1, 20 mL) and kept at room temperature for slow evaporation. After 5 days, a yellow colored single crystal (C-LY) along with a mixture of yellow (C-Y) and white solid (C-W) were obtained inside the bottle. Later, the excess of solution was poured out and solids were scratched from the inner surface using semi-micro spatula. They are finally separated by using long needles in good amount.



3. Supporting Figures

Fig. S1. The distribution of electron cloud of (up) LUMO and (down) HOMO of compound DBF-BZ-Cz: from left to right: idea molecule in vacuum, molecule in crystal C-LY and dimer in crystal C-LY. The energy levels and energy gaps were also inset.



Fig. S2. UV-vis absorption, fluorescence spectrum in THF solution (10⁻⁵ mol/L), and phosphorescence spectrum (77 K) of the compound DBF-BZ-Cz.



Fig S3. PXRD patterns of crystals C-LY, C-W and C-Y with different aggregated states.



Fig. S4. The intermolecular interactions inside the dimer in crystal C-LY.



Fig. S5. The ISC channels between the lowest singlet (S_1) and triplet states (T_n) of DBF-BZ-Cz monomer (a) and dimer (b) in its crystal C-LY. The red solid and dashed arrows represent major and minor ISC channels, respectively; the blue solid line represents energy levels between $S_1 \pm 0.4$ eV.



Fig. S6. Comparison of fractional free volume region in different compounds: (a) sulphonyl derivative (**7**), (b) carbonyl derivative (**15**), and DBF-BZ-Cz in crystal C-LY (monomer and dimer).

4. Supporting tables

Table S1. Calculated HOMO-1, HOMO, LUMO and LUMO+1 distributions of compound DBF-BZ-Cz in vacuum (gas) and in crystalline state (monomer and dimer) using TD-DFT method.

DBF-BZ-Cz	LUMO+1	LUMO	НОМО	HOMO-1
Ideal/Gas	\$~ \$ \$			
Crystal (Monomer)	₿_₽₽₽₽₽	J.	*** ***	
Crystal (Dimer)				

Table S2. The calculated energies of HOMO, LUMO, S_1 and T_1 orbitals and oscillator strength of transition for compound DBF-BZ-Cz both in vacuum and its crystalline state (monomer and dimer) using TD-DFT method.

State	E _{S1}	E _{T1}	ΔE _{ST}	Еномо	ELUMO	ΔEg	£	
State	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)	I(S0-s1)	I(S0-s2)
Ideal	2 211	0 706	0.42	E 409	1 9 2 6	2 672	0.251	0.005
(Vacuum)	3.211	2.780	0.42	-3.490	-1.020	3.072	0.231	0.005
Crystal	2 4 9 0	2 000	0.20	E 700	0.076	2 620	0 1000	0.000
(Monomer)	3.180	2.880	0.30	-5.706	-2.076	3.030	0.1920	0.006
Crystal	2 200	0.000	0.04	F 7F7	0.400	0.050	10.01	0.040
(Dimer)	3.200	2.890	0.31	-5./5/	-2.106	3.050	< 0.01	0.316

	Experimental data						
Compounds	S1 (eV)	T1 (eV)	T ₁ * (eV)	$\Delta E_{\rm ST}$ (eV)	Δ <i>E</i> _{TT} *(eV)		
Amorphous	2.96	2.93	-	0.03	-		
C-LY	2.87	2.68	2.41	0.19	0.27		
C-Y	2.57	2.39	2.20	0.18	0.19		
C-W	2.77	2.60	2.21	0.17	0.39		
THF solution	2.88	2.60	-	0.28	-		

Table S3. The experimental excited state energy levels for compound DBF-BZ-Cz in different aggregated states: solution, amorphous and crystalline states.

Table S4. Crystal data and structure refinements for the single crystal of C-LY.

Identification code	C-LY				
Empirical Formula	C ₃₁ H ₁₉ NO ₂				
Formula Weight	437.50				
Crystal system	Monoclinic				
Temperature	293 K				
Wavelength	1.5418 Å				
Space group	P-1				
	a = 8.10 (3) Å α = 90°				
	b = 30.67 (11) Å β = 91°				
	c = 8.89 (4) Å γ = 90°				
Unit cell dimensions	88.905(5)				
	80.763(6)				
	77.057(5)				
Volume	2212.89 (15) Å ³				
Z	4				
Density (calculated)	1.313 g/cm ³				
Absorption coefficient	1.000 mm ⁻¹				
F (000)	914.8024				

Crystal size	0.35 X 0.3 X 0.05 mm ³
Theta range for data collection	5.11-73.30°
Index ranges	-6≤h≤8, -10≤k≤10, -17≤l≤18
Reflections collected	4305
Independent Reflections	3173 [R(_{int}) = 0.0514]
Completeness to theta = 62.30°	66.49%
Absorption corrections	Spherical harmonics
Maximum and minimum transmission	1.0000 and 0.67446
Refinement method	Full-matrix least-square on F ²
Data/restraints/parameter	2810/2/307
Goodness-of-fit on F ²	1.1380
Final R indices [I $\geq 2\sigma$ (I)]	R ₁ = 0.057, wR ₂ = 0.16
R indices (all)	R ₁ = 0.075, wR ₂ = 0.188

^a R₁ = Σ | | F₀ | - | F_c | | Σ | F₀ | . ^b wR₂ = [Σ | w | F₀² - F_c²)²] / Σ _w (F₀²)²]^{1/2} Where, w = 1/[$\sigma^{2}(F_{0}^{2})$ +(aP)² ₊ bP] and P = (F₀² + 2F_c²)/3

Compound Normal Phosphorescence		pRTP
		0.769 s (548 nm)
		0.679 s (562 nm)
C-LY	-	0.756 s (597 nm)
		0.680 s (616 nm)
		0.666 s (653 nm)
	r ₁ = 18.05 μs (48.86%)	$0.445 \circ (EG4 \text{ pm})$
C-Y	<i>τ</i> ₂ = 0.71 μs (51.14%)	0.445 S (564 IIII)
	(470 nm)	0.430 S (613 nm)
	τ ₁ = 2.83 μs (68.80%)	$0.221 \circ (560 \text{ nm})$
C-W	<i>τ</i> ₂ = 14.16 μs (31.20)	0.321 \$ (560 mm)
	(450 nm)	0.323 S (600 nm)

Table S5. Life times of the cr	ystals C-LY, C-Y	' and C-W at ambier	t conditions.
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No.	Structures	FFV	Lifetime	Φ _P (%)	Reference
		/ %	/ s		
1		2.12	0.71	0.3	
2		2.30	1.28	0.6	
3		1.70	1.06	1.25	1
4		1.37	0.47	2.1	
5		7.75	0.21	0.08	
6		4.15	0.54	-	2
7		4.37	0.10	-	
8	OCH3 OSSO	7.10	0.20	-	3
9		9.64	0.36	-	4

Table S6. The fractional free volume (FFV) and phosphorescence lifetime ofreported organic materials.

10		5.76	0.82	2.64	
11		5.37	0.83	1.11	
12		2.07	0.10	2.3	
13	Br	2.51	0.10	6.8	5
14	cr	2.09	0.12	7.2	
15		1.44	0.47	1.4	6
16		0.67	0.29	3.5	
17		0.80	0.34	10.2	7
18		1.30	0.31	9.8	
19		1.50	0.76	-	This work

5. Structural Characterization.



Fig. S9. EI-mass spectrum of DBF-BZ-F.



Fig S10. EI-mass spectrum of DBF-BZ-Cz.



Fig. S11. High resolution mass spectrum of DBF-BZ-Cz.



Fig. S12. ¹H-NMR spectrum of DBF-BZ-Cz.



Fig. S13. ¹³C-NMR spectrum of DBF-BZ-Cz.

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