# **Supporting Information**

# Highly Efficient Ultralong Organic Phosphorescence through Intramolecular Space Heavy Atom Effect

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#### **Reagents and materials:**

1,4-dibromo-2,5-difluorobenzene, 9H-carbazole, Dibromobenzene, KOH, K<sub>2</sub>CO<sub>3</sub>, Cu, 18crown-6, dry DMF, were purchased from commercial sources without further purification.

# **Physical measurements:**

Nuclear magnetic resonance (<sup>1</sup>H NMR and <sup>13</sup>C NMR) spectra were obtained on a Bruker Ultra Shield plus 400 MHz spectrometer using CDCl<sub>3</sub>. Chemical shift was relative to tetramethylsilane (TMS) as an internal standard. Resonance patterns are reported with the notation s (singlet), d (double), t (triplet), q (quartet), and m (multiplet). UV-visble absorption spectra were measured by Shimadzu UV-1750. Steady-state PL/phosphorescence spectra were conducted using Hitachi F-4600 fluorescence spectrophotometer. The phosphorescence lifetimes were detected on Edinburgh FLSP920 fluorescence spectrophotometer equipped with a nanosecond hydrogen flash-lamp (nF920) and a microsecond flash-lamp (µF900), respectively. The PL quantum yield was obtained Hamamatsu C11347 Quantaurus-QY. The luminescent photos were taken by a Cannon EOS 700D camera at room temperature.

# Single crystal X-Ray Diffraction studies:

X-ray crystallography was achieved using a Bruker SMART APEX-II CCD diffractometer with graphite monochromated Mo-Kα radiation.

#### The preparation of the micro-crystals and RTP gel:

PDBCz micro-crystals were obtained by fast evaporation of PDBCz (10 mg) solution in mixed solvents of dichloromethane (2 mL)/ petroleum ether (0.5 mL) at 323 K. Then the obtained micro-crystals (10 mg) was doped into PDMS (10 mL) or ethoxyline resin (10 mL) to afford RTP gel for flexible or 3D patterns with corresponding molds, respectively.

#### **Computational Methods:**

For model systems, the oscillator strength of triplet states and the spin-orbit coupling (SOC) matrix elements between singlet and triplet states are given at TD-B3LYP/6-31G(d) level.

Synthesis:



Scheme S1. Synthetic routes of target compounds. (i) 1.0 equiv. 1,4-dibromo-2,5difluorobenzene, 2.5 equiv. 9H-carbazole, 4.0 equiv. KOH, DMF, 40 °C, 2 h; 110 °C, 4 h; (ii) 1.0 equiv. dibromobenzene, 3.0 equiv. 9H-carbazole, 6.0 equiv. K<sub>2</sub>CO<sub>3</sub>, 12.0 equiv. Cu, 0.82 equiv. 18-crown-6, dry DMF, 140 °C, 30 h.

9,9'-(2,5-dibromo-1,4-phenylene)bis(9H-carbazole) (PDBCz). 9H-carbazole (1.0 g, 6.0 mmol) and KOH (0.54 g, 9.6 mmol) were added into a glass flask and dissolved into dimethylformamide (40 mL) at 40 °C and stirred for 2 h. 1,4-dibromo-2,5-difluorobenzene (0.65 g, 2.4 mmol) was added to the mixture solution at 110 °C for 4 h, then cooled down to room temperature and filtered. The raw product was purified by silica column chromatography with dichloromethane and petroleum ether as eluents. White powders were collected at yields of 60%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.19 (d, *J* = 7.8 Hz, 4H), 8.01 (s, 2H), 7.54 -7.48 (m, 4H), 7.37 (dd, *J* = 11.1, 3.9 Hz, 4H), 7.27 (s, 2H), 7.25 (s, 2H). <sup>13</sup>C NMR

(100 MHz, CDCl<sub>3</sub>) δ 140.50, 138.32, 135.97, 126.30, 123.66, 123.18, 120.72, 120.62, 110.06; Anal. Calc. (%): C, 63.63; H, 3.20; N 4.95. Found (%): C, 63.71; H, 3.25; N, 4.90.

1,4-di(9H-carbazol-9-yl)benzene (PDCz). To a 100 mL two-neck round-bottom flask charged with 9H-carbazole (2.1 g, 12.7 mmol), 1,4-dibromobenzene (1.0 g, 4.2 mmol), Cu (1.6 g, 25.2 mmol), K<sub>2</sub>CO<sub>3</sub> (7.1g, 48.8 mmol) and 18-crown-6 (0.92 g, 3.5 mmol), dry DMF (45 mL) was injected and the mixture was stirred for 36 h at 150 °C. Then the reaction was cooled down to room temperature and filtered. The product was purified by silica column chromatography with methylene chloride and petroleum ether. White powders were collected at yields of 45%. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.20 (d, *J* = 7.8 Hz, 4H), 7.83 (s, 4H), 7.58 (d, *J* = 8.2 Hz, 4H), 7.53 – 7.46 (m, 4H), 7.38 – 7.32 (m, 4H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  140.78, 136.69, 128.39, 126.17, 123.60, 120.50, 120.31, 109.79; Anal. Calc. (%): C, 88.21; H, 4.94; N: 6.86. Found (%): C, 87.89; H, 5.17; N: 6.96



Figure S1. <sup>1</sup>H NMR spectrum of PDBCz in CDCl<sub>3</sub>.



Figure S2. <sup>13</sup>C NMR spectrum of PDBCz in CDCl<sub>3</sub>.



Figure S3. <sup>1</sup>H NMR spectrum of PDCz in CDCl<sub>3</sub>.



Figure S4. <sup>13</sup>C NMR spectrum of PDCz in CDCl<sub>3</sub>.



**Figure S5.** Lifetime decay profiles of emission bands at (a) 366, (b) 410 and (c) 430 nm for PDCz phosphor and (d) 330, (e) 403 and (f) 421 nm for PDBCz phosphor in solid state under ambient conditions.



**Figure S6.** a) Lifetime decay profile of emission bands at 420 nm and 600 nm of PDCz in crystal at 300 K. b) Lifetime decay profile of emission band at 595 nm of PDBCz in crystal at 300 K.



**Figure S7.** Phosphorescence spectra of (a) PDCz and (b) PDBCz crystals in vacuum (black solid line) and oxygen (red solid line) atmosphere.



**Figure S8.** Phosphorescence lifetime and efficiency chart of reported single-component organic phosphorescent materials and PDBCz in this work.<sup>1-6</sup>



Figure S9. The model selected as calculated SOC constant, calculated energy diagram and SOC ( $\xi$ ) of PDBCz with external heavy atoms effect.



Figure S10. Single crystal structures of PDBCz and PDCz with H-aggregation formation.



**Figure S11.** The NTOs for excited states at single crystal geometric structures of (a) PDCz, (b) PDBCz, and (c) Model are obtained by the density functional method at the B3LYP/6-31G(d) level.

From Figure S11, it is easily found that the lowest singlet and triplet excited states are governed by  $\pi \rightarrow \pi^*$  transition and remain unchanged from PDCz to PDBCz, subsequently resulting in a tiny varied  $\xi$  (S<sub>0</sub>, T<sub>1</sub>) and  $\xi$  (S<sub>1</sub>, T<sub>1</sub>). Additionally, this feature also caused the similar fluorescence and phosphorescence in these two compounds, including peak position and spectral shape (see Figure 2a). Instead of the higher triplet states dominated by  $\pi \rightarrow \pi^*$  transition in PDCz, these states in PDBCz involve extra  $n \rightarrow \pi^*$  transition that introduced by Br atom (Figure S11), thus the SOCs between S<sub>1</sub> and T<sub>n</sub> were hugely enhanced from PDCz to PDBCz. For example, the  $\xi$  (S<sub>1</sub>, T<sub>3</sub>) = 0.089 cm<sup>-1</sup> in PDCz was increased to  $\xi$  (S<sub>1</sub>, T<sub>3</sub>) = 3.809 cm<sup>-1</sup> in PDBCz.



**Figure S12.** Luminescent images of 3D patterns fabricated by PDBCz micro-crystals under room light or dark with the excitation UV lamp on and off.

**Table S1.** Photoluminescence lifetimes  $(\tau)$  and its percentage of PDCz and PDBCz.

	Fluorescence				Phosphorescence			
Compound	$\lambda_{em}(nm)$	$\tau_{a}\left(ns\right)$	τ (ns)	%	$\lambda_{em}(nm)$	$\begin{array}{c} \tau_a \\ (ms) \end{array}$	τ (ms)	%
PDCz	366	2.3	1.5/4.2	68.9/31.1	420	40.3	1.6/7.3/37.8/163.0	19.9/36.8/26.6/16.7
	410	10.2	3.3/13.1	29.9/70.1	558	560.0	104/604	8.8/91.2
	430	9.2	2.8/12.8	36.0/64.0	600	557.2	96.7/605.0	9.4/90.6
PDBCz	330	0.5	0.49	100	546	217.3	217.3	100
	403	0.8	0.6/1.5	73.0/27.0	510			
	421	0.9	0.6/2.0	79.5/20.5	595	218.8	218.8	100

 $\tau_a$  is average lifetime.

 Table S2 Dynamic photophysical parameters of ultralong organic phosphors.

Compound	$ au_{\mathrm{F,c}}$	$arPsi_{ m F}$	$ au_{ m P}$	$arPhi_{ m P}$	K <sub>F</sub>	K <sub>n,F</sub>	K <sub>ISC</sub>	K <sub>P</sub>	K <sub>n,P</sub>
	[ns]	[%]	[ms]	[%]	$[s^{-1}]^{a)}$	[s <sup>-1</sup> ] <sup>b)</sup>	[s <sup>-1</sup> ] <sup>c)</sup>	$[s^{-1}]^{d}$	[s <sup>-1</sup> ] <sup>e)</sup>
PDBCz	0.50	1.90	218	38.1	3.9×10 <sup>7</sup>	1.2×10 <sup>9</sup>	5.4×10 8	1.75	2.84
PDCz	11.0	59.5	560	2.50	5.4×10 <sup>7</sup>	3.5×10 <sup>7</sup>	5.1×10 7	0.04	1.74
<sup>a)</sup> $k_r^{Fluo} = \phi_{Fluo} / \tau_{Fluo};$ <sup>b)</sup> $k_{nr}^{Fluo} = (1 - \phi_{Fluo} - \phi_{Phos}) / \tau_{Fluo};$ <sup>c)</sup> $k_{isc} = \phi_{Phos} / \tau_{Fluo};$ <sup>d)</sup> $k_r^{Phos} = \phi_{Phos} / \tau_{Phos};$ <sup>e)</sup> $k_{nr}^{Phos} = (1 - \phi_{Phos}) / \tau_{Phos}$									

Table S3 Structure data of PDBCz and PDCz single crystals

Name	PDBCz	PDCz
Formula	$C_{30}H_{18}Br_2N_2$	C <sub>30</sub> H <sub>20</sub> N <sub>2</sub>
Wavelength (Å)	0.71073	0.71073
Space Group	P2(1)/n	Pbca
	a 8.4384(17),	a 8.194(2)
Cell Lengths (Å)	b 8.9213(18),	b 16.337(5)
	c 15.669(3)	c 31.464(8)
	α 90.00,	α 90.00,
Cell Angles (°)	β 99.33(3),	β 90.00,
	γ 90.00	γ 90.00
Cell Volume (Å <sup>3</sup> )	1164.0(4)	4212(2)
Z	18	8
Density (g/cm <sup>3</sup> )	1.616	1.288
F (000)	564	1712

$h_{max}, k_{max}, l_{max}$	10, 10, 18	9,19,37
CCDC	1866969	899423

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