Supporting Information

Carbazole&Benzoindole-based Purely Organic Phosphors: Comprehensive Phosphorescence Mechanism, Tunable Lifetime and Adavnced Encryption System

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1. Materials and General Methods

All the solvents and reactants were purchased from commercialized companies and used as received without further purification except for specifying otherwise.

¹H NMR and ¹³C NMR spectra was recorded on the 400 MHz (Bruker ARX400) at room temperature with DMSO- d_6 and CDCl₃ as the solvent and tetramethylsilane (TMS) as the internal standard. ESI high resolution mass-spectra (HRMS) were acquired on a Bruker Apex IV FTMS mass spectrometer. High Performance Liquid Chromatography (HPLC) was acquired on Shimadzu LC-20AT. The elution procedure was optimized as 65/35 (v/v) of acetonitrile/water for 30 min at 1.00 mL/min. The type of chromatographic column was ZORBAX SB-C₁₈ (Agilent, 150 mm \times 4.6 mm, 5 µm). HPLC-HRMS was recorded on the Thermo Fisher high resolution liquid chromatography mass spectrometry. Transient and delayed photoluminescence spectra were performed on the Hitachi F-7000 or Edinburgh Instruments FLS980 fluorescence spectrophotometer. Luminescence lifetime were acquired on the Edinburgh Instruments FLS980 fluorescence spectrophotometer or Deltaflex Fluorescence Lifetime Instrument (λ_{ex} =365 nm). Wide-angle X-ray diffraction (WAXD) experiments were performed on a Philips X'PertPro diffractometer with a 3 kW ceramic tube as the X-ray source (Cu Ka) and an X'celerator detector. Single crystal X-ray diffraction data were collected with a NONIUS KappaCCD diffractometer with graphite monochromator and Mo K α radiation [λ $(MoK\alpha) = 0.71073$ Å]. Structures were solved by direct methods with SHELXS-97 and refined against F2 with SHELXS-97.

TD-DFT calculations were conducted on Gaussian 09 program with a method similar to previous literature.¹ Ground state (S_0) geometry of CNCZBr was directly selected from single crystal structures and was used as molecular model without further optimization. On the basis of this, exciton energies in singlet (S_n) and triplet states (T_n) were estimated through a combination of TDDFT and B3LYP at the 6-311+G(p, d) level. Kohn-Sham frontier orbital analysis was subsequently performed based on the results of theoretical calculation to elucidate

the mechanisms of possible singlet-triplet intersystem crossings, in which the channels from S_1 to T_n are believed to share part of the same transition orbital compositions. Spin-orbital couplings (SOC) matrix elements were conducted through the Beijing Density Functional (BDF) program based on single crystal structures at the B3LYP/6- 311G* level. Herein, energy levels of the possible T_n states are considered to lie within the range of $ES_1 \pm 0.3$ eV².

2. Synthesis of targeted molecule



• Scheme S1. The general synthetic routes to Cz-Lab.



- CZPyBr
- Scheme S2. The general synthetic routes to target product.



• Scheme S3. The synthetic routes to 2-Bromo-N-phenylbenzenamine

Sodium tert-butoxide (961.0 mg, 10 mmol), Pd(OAc)₂ (33.7 mg, 0.15 mmol), (oxybis(2,1phenylene))bis(diphenylphosphine) (80.8 mg, 0.15 mmol) were added to a 100 mL shrek bottle. Then aniline (465.6 mg, 5 mmol) and o-bromoiodobenzene (1.4145 g, 5 mmol) which were dissolved in toluene (10 mL, AR grade) were added to the bottle. The mixed solution was refluxed at 110 °C for 12h in nitrogen atmosphere. After the reaction was over, the resultant mixture was cooled down to room temperature and the solvent was removed under reduced pressure. The crude product was purified by silica gel column using petroleum ether as the eluent to obtain pure product as colorless and transparent liquid. Yield: 89%.

¹H NMR (400 MHz, CDCl₃) δ = 7.57 (dd, J = 8.0, 1.4, 1H), 7.41 – 7.33 (m, 2H), 7.32 – 7.29 (m, 1H), 7.25 – 7.16 (m, 3H), 7.13 – 7.05 (m, 1H), 6.78 (td, J = 7.9, 1.6, 1H), 6.13 (s, 1H). ¹³C NMR (400 MHz, CDCl₃) δ = 141.62 (s), 133.01 (s), 129.48 (s), 128.12 (s), 122.73 (s), 120.92 (s), 120.30 (s), 115.82 (s), 112.21 (s).



• Scheme S4. The synthetic routes to 9H-carbazole

Potassium carbonate (1.1057 g, 8 mmol), Pd(OAc)₂ (26.9 mg, 0.12 mmol), Tricydohexylphosphine tetrafluoroborate (88.4 mg, 0.24 mmol) were added to a 100 mL shrek bottle. Then 2-Bromo-N-phenylbenzenamine (1g, 4 mmol) which was dissolved in DMAC (10 mL, AR grade) was added to the bottle. The mixed solution was refluxed at 130 °C for 16h in nitrogen atmosphere. After the reaction was over, the resultant mixture was cooled down to room temperature and the solvent was washed by Saturated brine and DCM for 2 times. The obtained solvent was removed under reduced pressure. The crude product was purified by silica gel column using petroleum ether as the eluent to obtain pure product as white powder. Yield: 60%.

¹H NMR (400 MHz, DMSO-*d*₆) δ = 11.24 (s, 1H), 8.11 (d, J = 7.8, 2H), 7.48 (d, J = 8.1, 2H), 7.37 (dd, J = 11.7, 4.7, 2H), 7.15 (t, J = 7.9, 2H).

¹³C NMR (400 MHz, CDCl₃) δ = 139.47 (s), 125.84 (s), 123.36 (s), 120.34 (s), 119.45 (s), 110.57 (s), 77.03 (s).



• Scheme S5. The synthetic routes to CNCZBr-Lab and CNCZBr-Cm.

Potassium tert-butoxide (0.3703 g, 3.3 mmol), carbazole (0.5016 g, 3 mmol) and 3-Bromo-5-fluorobenzonitrile (0.6003 g, 3 mmol) were added to a 100 mL shrek bottle. Then sealing the bottle and fill it with nitrogen. DMF (10 mL, AR grade) was add to the bottle and the mixed solution was refluxed at 110 °C for 24h in nitrogen atmosphere. The crude product was purified by silica gel column (using petroleum ether: DCM = 2:1 as the eluent) to obtain a white powder. Yield: 58%.

¹H NMR (400 MHz, CDCl₃) δ = 8.13 (d, J = 7.7, 2H), 8.01 (t, J = 1.9, 1H), 7.85 (dt, J = 5.2, 1.5, 2H), 7.49 – 7.42 (m, 2H), 7.41 – 7.31 (m, 4H).

¹³C NMR (400 MHz, CDCl₃) δ = 139.93 – 139.73 (m), 134.44 (s), 133.09 – 132.89 (m), 128.80 (s), 126.56 (s), 124.04 (d, J = 14.7), 121.25 (s), 120.69 (s), 116.59 (s), 115.58 (s), 109.19 (s).

HR-ESI-MS Calcd. For C₁₉H₁₁BrN₂ [M]⁺ : 346.01001. Found: 346.00998.



• Scheme S6. The synthetic routes to CZPyCb-Lab and CZPyCb-Cm.

Potassium tert-butoxide (1.3465 g, 12 mmol), carbazole (1.0033 g, 6 mmol) and 6-Fluoronicotinic acid (0.7055 g, 5 mmol) were added to a 100 mL shrek bottle. Then sealing the bottle and fill it with nitrogen. DMF (10 mL, AR grade) was add to the bottle and the mixed solution was refluxed at 110 °C for 24h in nitrogen atmosphere. After the reaction was over, the resultant mixture was cooled down to room temperature and the solvent was washed by deionized water and ethyl acetate. Then acetic acid (1.00 g, 16.6 mmol) was add to the water phase and white solid precipitated immediately. The pure produce was obtained by filtration as white powder. Yield: 66%.

¹H NMR (400 MHz, DMSO-*d*₆) δ = 13.49 (s, 1H), 9.21 (s, 1H), 8.58 – 8.46 (m, 1H), 8.26 (d, J = 7.7, 2H), 7.96 (dd, J = 19.0, 8.4, 3H), 7.50 (t, J = 7.7, 2H), 7.37 (t, J = 7.4, 2H). ¹³C NMR (400 MHz, DMSO) δ = 166.24 (s), 154.28 (s), 151.04 (s), 140.63 (s), 139.00 (s), 127.09 (s), 124.40 (d, J = 15.0), 122.13 (s), 120.93 (s), 118.49 (s), 112.39 (s). HR-ESI-MS Calcd. For C₁₈H₁₃N₂O₂ [M+H]⁺: 289.097048. Found: 289.097154. **CZPyCN:** Following the similar synthesis of CNCZBr, CZPyCN was obtained as white powder by using 2-Cyano-3-fluoropyridine in place of 3-Bromo-5-fluorobenzonitrile. Yield: 37%.

¹H NMR (400 MHz, CDCl₃) $\delta = 8.89$ (d, J = 4.7, 1H), 8.18 (d, J = 7.7, 2H), 8.02 (d, J = 8.2, 1H), 7.79 (dd, J = 8.2, 4.7, 1H), 7.48 (t, J = 7.7, 2H), 7.39 (t, J = 7.8, 2H), 7.21 (d, J = 8.2, 2H). ¹³C NMR (400 MHz, CDCl₃) $\delta = 150.16$ (s), 140.47 (s), 138.62 (s), 137.42 (s), 133.29 (s), 128.03 (s), 126.54 (d, J = 0.7), 124.28 (s), 121.48 (s), 120.79 - 120.59 (m), 115.16 (s), 109.52 (s).

HR-ESI-MS Calcd. For C₁₈H₁₂N₃ [M+H]⁺: 270.102765. Found: 270.102574.



• Scheme S7. The synthetic routes to CZPyAm-Lab and CZPyAm-Cm.

Potassium carbonate (1.2439 g, 9 mmol), 2-Cyano-3-fluoropyridine (0.3663 g, 3 mmol) and carbazole (0.5016 g, 3 mmol) were added to a 100 mL round-bottom flask. The mixed solution was refluxed at 160°C for 24h. The crude product was purified by silica gel column using DCM as the eluent to obtain pure product as wihte powder. Yield: 96%.

¹H NMR (400 MHz, CDCl₃) δ = 8.78 (d, J = 4.6, 1H), 8.16 (d, J = 7.6, 2H), 7.97 (d, J = 9.5, 1H), 7.72 (dd, J = 8.0, 4.6, 1H), 7.52 (s, 1H), 7.39 (t, J = 7.7, 2H), 7.31 (d, J = 7.0, 2H), 7.08 (d, J = 8.1, 2H), 5.41 (s, 1H).

¹³C NMR (400 MHz, DMSO-*d*₆) δ = 166.92 (s), 151.82 (s), 148.96 (s), 141.41 (s), 139.32 (s),
131.86 (s), 127.18 (s), 126.25 (s), 123.34 (s), 120.80 (s), 120.28 (s), 110.15 (s).
HR-ESI-MS Calcd. For C₁₈H₁₄N₃O [M+H]⁺: 288.113529. Found: 288.113139.

CZPyBr: Following the similar synthesis of CZPyAm, CZPyBr was obtained as white powder by using 2-Bromo-6-fluoropyridine in place of 2-Cyano-3-fluoropyridine. Yield: 14%. ¹H NMR (400 MHz, CDCl₃) δ = 8.08 (d, *J* = 7.6, 2H), 7.98 (t, J = 7.9, 1H), 7.85 (d, J = 8.2, 2H), 7.48 (d, J = 7.5, 1H), 7.26 (td, J = 7.4, 0.9, 2H), 7.23 – 7.12 (m, 3H). ¹³C NMR (400 MHz, CDCl₃) δ = 161.37 (s), 150.24 (s), 141.63 (s), 139.32 (s), 126.15 (s),

124.35 (s), 121.03 (s), 120.02 (s), 114.22 (s), 111.56 (s), 110.71 (s).



Figure S2. ¹³C NMR spectrum of 2-Bromo-N-phenylbenzenamine in CDCl₃.



























4. High-performance liquid chromatogram of CNCZBr-Cm and CNCZBr-Lab.

Figure S25. High-performance liquid chromatogram of CNCZBr-Cm at the concentration of 250 ppb (a), 250 ppm and meanwhile remove the principal component (b), 1000 ppm and meanwhile remove the principal component (c).



5. UV-vis absorption spectra of CNCZBr

Figure S26. UV–vis absorption spectra of CNCZBr-Cm (dark line) and CNCZBr-Lab (red line) in THF solution (10⁻⁵ M) (a) and crystal state (b) under ambient conditions.

6. PL spectra and decay profiles of CNCZBr



Figure S27. PL decay profiles of CNCZBr-Lab crystals at peaks of 500 nm (a) and 550 nm (b) at ambient conditions. (λ_{ex} =365 nm)



Figure S28. PL decay profiles of CNCZBr-Cm crystals at peaks of 500 nm (a), 550 nm (b), 600 nm (c) and 650 nm (d) at ambient conditions. (λ_{ex} =365 nm)



Figure S29. Steady-state PL spectra of CNCZBr-Lab (a) and CNCZBr-Cm (b) and decay profiles (c), (d) in PMMA films (1% wt.) at ambient conditions. (λ_{ex}=365 nm)



Figure S30. Steady-state PL spectra and delayed (Δt =0.1 ms) emission spectra of CNCZBr-Lab (a) and CNCZBr-Cm (b) and decay profiles (c - h) in PMMA films (1% wt.) at 77K. (λ_{ex} =365 nm)

7. XRD pattern of CNCZBr



2θ (°)

Figure S31. XRD pattern of CNCZBr-Lab (dark line) and CNCZBr-Cm (red line).

8. Data table of CNCZBr single crystal.

Identification code	CNCZBr
CCDC Number	2082252
Empirical formula	$C_{19}H_{11}BrN_2$
Formula weight	347.21
Temperature	273 К
Wavelength	0.71076 Å
Crystal system	triclinic
Space group	P -1
Unit cell dimensions	$a = 4.0288(4)$ Å, $\alpha = 87.368(4)^{\circ}$
	b = 10.1219(10) Å, β = 83.942(4)°.
	$c = 18.2137(17)$ Å, $\gamma = 85.116(4)^{\circ}$.
Volume	735.40(12)Å ³
Ζ	2
Density (calculated)	1.568 Mg/m ³
Absorption coefficient	2.792 mm ⁻¹
F(000)	348
Crystal size	-
Theta range for data collection	2.969 to 27.323°.
Index ranges	-5<=h<=5, -13<=k<=13, -23<=l<=23
Paflactions collected	2303
Independent reflections	2766 [P(int) = 0.0250]
Final R indices [1>2cigma(1)]	$P_1 = 0.0444 \text{ wP2} = 0.1274$
rmai ix indices [1/25igma(1)]	KI -0.0444, WK2 -0.12/4
R indices (all data)	R1 = 0.0536, wR2 = 0.1358

Table S1. Detailed data of CNCZBr single crystals.

9. TD-DFT results

Table S2. Triplet excited states of CNCZBr containing the same orbital transition components of S1.

Excited State	Energy (eV)	Transition configuration (%)	
Monomer	1		
T1	3.0644	H-5 \rightarrow L(2.3%), H-4 \rightarrow L(8.1%), H \rightarrow L(78.3%), H \rightarrow L+1(6.9%)	
T2	3.1508	H-5 \rightarrow L+9(2.2%), H-2 \rightarrow L+2(3.1%), H-1 \rightarrow L(2.7%), H- 1 \rightarrow L+2(76.8%), H \rightarrow L+4(8.2%)	
Т3	3.3316	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	
S1	3.4009	H→L(98.0%)	
T4	3.4187	H-3 \rightarrow L(5.6%), H-3 \rightarrow L+1(4.6%), H \rightarrow L(2.9%), H \rightarrow L+1(6.4%), H \rightarrow L+2(70.7%)	
Dimer			
T1	3.0252	H-1 \rightarrow L(17.8%), H \rightarrow L+1(21.9%), H \rightarrow L(22.8%), H \rightarrow L+1(20.3%)	
T2	3.0258	H-1 \rightarrow L(22.2%), H \rightarrow L+1(20.6%), H \rightarrow L(17.5%), H \rightarrow L+1(22.4%)	
T3	3.1495	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	
T4	3.1498	H-3 \rightarrow L+4(36.1%), H+3 \rightarrow L+5(40.1%), H-1 \rightarrow L+9(2.0%), H \rightarrow L+8(2.1%), H \rightarrow L+9(2.2%)	
T5	3.3248	$\begin{array}{ c c c c c c c c c c c c c c c c c c c$	
T6	3.3249	$ \begin{array}{c c} H-6 \rightarrow L(2.2\%), H-1 \rightarrow L(4.0\%), H-1 \rightarrow L+2(9.4\%), \\ H-1 \rightarrow L+3(13.3\%), H-1 \rightarrow L+4(4.9\%), \\ H-1 \rightarrow L+5(4.3\%), H \rightarrow L(5.6\%), H \rightarrow L+2(13.5\%), \\ H \rightarrow L+3(10.9\%), H \rightarrow L+4(4.0\%), H \rightarrow L+5(6.1\%) \end{array} $	
S1	3.3547	H-1 \rightarrow L+1(43.3%), H \rightarrow L(54.8%)	
Τ7	3.4104	$\begin{array}{c c} H-7 \rightarrow L+3(2.2\%), H-6 \rightarrow L(2.7\%), H-1 \rightarrow L+3(2.4\%), \\ H-1 \rightarrow L+4(28.8\%), H-1 \rightarrow L+5(7.5\%), H \rightarrow L+2(2.7\%), \\ H \rightarrow L+4(7.9\%), H \rightarrow L+5(25.8\%) \end{array}$	
Т8	3.4105	$\begin{array}{c c} H-7 \rightarrow L(2.5\%), H-6 \rightarrow L+3(2.3\%), H-1 \rightarrow L+2(2.7\%), \\ H-1 \rightarrow L+4(6.4\%), H-1 \rightarrow L+5(27.2\%), H \rightarrow L+3(2.4\%), \\ H \rightarrow L+4(27.2\%), H \rightarrow L+5(9.1\%) \end{array}$	
T9	3.6130	H-1 \rightarrow L+1(52.0%), H \rightarrow L(42.4%)	
T10	3.6138	H-1 \rightarrow L(42.6%), H \rightarrow L+1(52.0%)	

10. SOC values between S_1 and T_n of CNCZBr

Table S3. Spin-orbit coupling (SOC) values between S_n and T_n of monomer and dimer in crystal state.

<s<sub>n Hso T_n></s<sub>	Monomer (cm ⁻¹)	Dimer (cm ⁻¹)
S_0/T_1	237.97859	222.67682
S_1/T_1	117.82283	67.18102
S ₁ /T ₂	14.03838	58.60291
S ₁ /T ₃	240.41197	9.49140
S_1/T_4	265.05167	10.06255
S ₁ /T ₅	-	141.70828
S ₁ /T ₆	-	172.46362
S_1/T_7	-	224.33362
S_1/T_8	-	127.57123
S_1/T_9	-	129.33015
S_{1}/T_{10}	-	17.77588

11. Diagrams of the TD-DFT calculated energy levels of CNCZBr



Figure S32. Diagrams of the TD-DFT calculated energy levels and possible ISC channels of CNCZBr monomer (a) and dimer (b) between the singlet (S_1) and triplet (T_n) states. Molecular orbital distributions of CNCZBr monomer (c) and dimer (d).

12. PL spectra and decay profiles of CZPyCN, CZPyAm, CZPyCb, CZPyBr and their doped system.



Figure S33. Steady-state PL spectra and delayed ($\Delta t=0.1 \text{ ms}$) emission spectra of CZPyCN-Lab (a), Lab : Cm = 3 : 1 (b), Lab : Cm = 1 : 1 (c), Lab : Cm = 1 : 3 (d), CZPyCN-Cm (e) and decay profiles of all doped system (f). ($\lambda_{ex}=365 \text{ nm}$)



Figure S34. Steady-state PL spectra and delayed ($\Delta t=0.1 \text{ ms}$) emission spectra of CZPyAm-Lab (a), Lab : Cm = 3 : 1 (b), Lab : Cm = 1 : 1 (c), Lab : Cm = 1 : 3 (d), CZPyAm-Cm (e) and decay profiles of all doped system (f). ($\lambda_{ex}=365 \text{ nm}$)



Figure S35. Steady-state PL spectra and delayed ($\Delta t=0.1 \text{ ms}$) emission spectra of CZPyCb-Lab (a), Lab : Cm = 3 : 1 (b), Lab : Cm = 1 : 1 (c), Lab : Cm = 1 : 3 (d), CZPyCb-Cm (e) and decay profiles of all doped system (f). ($\lambda_{ex}=365 \text{ nm}$)



Figure S36. Steady-state PL spectra and delayed ($\Delta t=0.1 \text{ ms}$) emission spectra of CZPyBr-Lab (a), Lab : Cm = 3 : 1 (b), Lab : Cm = 1 : 1 (c), Lab : Cm = 1 : 3 (d), CZPyBr-Cm (e) and decay profiles of all doped system (f). ($\lambda_{ex}=365 \text{ nm}$)

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