Supporting Information

A Hydrogen Bonding Strategy to Strengthen Room Temperature Phosphorescence of Nitrogen-modified Benzocarbazole

Yanjun Zhao,[a] Xingda Zhang,[a] Tianya Zhang,[a] Liming Lin,[a] Lijuan Bu,[b] Zhimin Ma,[c] Mingxing Chen[c] and Zhiyong Ma[a]**

[a] Beijing State Key Laboratory of Organic-Inorganic Composites, College of Chemical Engineering, Beijing University of Chemical Technology, Beijing 100029, China. E-mail: mazhy@mail.buct.edu.cn

[b] Chinese PLA Center for Disease Control and Prevention, Beijing 100071, China.

[c] Beijing National Laboratory for Molecular Sciences, Key Laboratory of Polymer Chemistry and Physics of the Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China.

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.

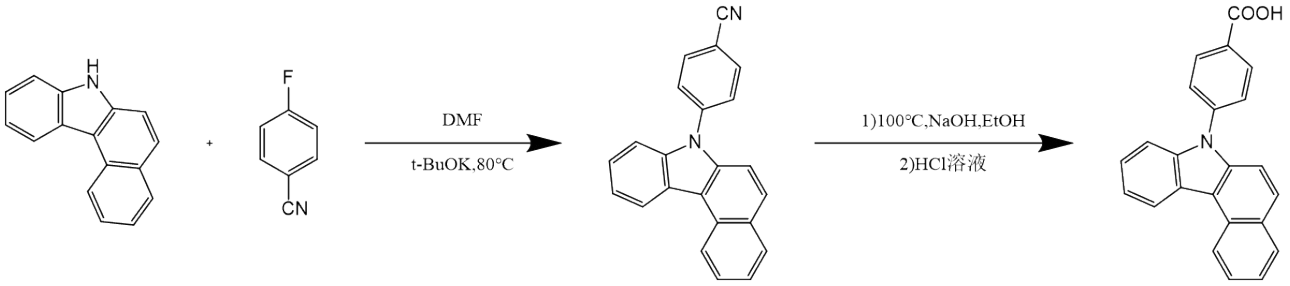
^{1}H NMR was recorded on the 400 MHz (Bruker ARX400) and ^{13}C NMR spectra were recorded on the Bruker 101 MHz spectrometer at room temperature with $CDCl_3$ as the solvent and tetramethylsilane (TMS) as the internal standard. ESI high resolution mass-spectra (HRMS) were acquired on a Bruker Apex IV FTMS mass spectrometer. UV-Vis spectra were acquired on the Hitachi U-3900H UV-Vis spectrophotometer. Transient and delayed photoluminescence spectra were performed on the Hitachi F-7000 or Edinburgh Instruments FLS980 fluorescence spectrophotometer equipped with a continuous xenon lamp (Xe1) and a microsecond flashlamp, respectively. Phosphorescence lifetime were acquired on the Edinburgh Instruments FLS980 fluorescence spectrophotometer (λ_{ex} = 365 nm) equipped with a microsecond flashlamp. The emission lifetime of the samples was determined by the Time Correlated Single Photon Counting (TCSPC) technique using an Edinburgh Instruments mini-tau lifetime spectrophotometer equipped with an EPL 375 pulsed diode laser.

TD-DFT calculations were conducted on Gaussian 09 program with a method similar to previous literature.[1] Ground state (S_0) geometries of BCz, NBCz, 2NBCz-1, 2NBCz-2, BCz-PhCOOH, NBCz-PhCOOH, 2NBCz-1-PhCOOH and 2NBCz-2-PhCOOH monomer were directly optimized in vacuum condition. 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. We have to emphasize that the computed singlet and triplet levels in this article refer to emission (excited state optimization). 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 were believed to share part of the same transition orbital compositions. Herein, energy levels of the possible T_n states were considered to lie within the range of $ES_1 \pm 0.3$ eV.[2] Spin-orbital couplings (SOC) matrix elements were conducted through the Beijing Density Functional (BDF) program based on optimized or single crystal structures at the B3LYP/6-311G* level.

2. Syntheses and characterizations

The synthesis methods of the substrates (NBCz and 2NBCz-2) used in this paper are the same as our previous work.[3] 2NBCz-1 is commercially available and was used after further purification. The detailed syntheses of BCz-PhCOOH, NBCz-PhCOOH, 2NBCz-1-PhCOOH and 2NBCz-2-PhCOOH are shown as follows.



Scheme S1. The synthetic route to BCz-PhCOOH.

BCz-PhCN: 7H-benzo[c]carbazole (250 mg, 1.15 mmol), sodium tert-butoxide (194 mg, 1.73 mmol), 4-fluorobenzonitrile (167 mg, 0.138 mmol), 2 mL DMF were added to a 10 mL Shrek bottle. The mixed solution was refluxed at room temperature for 12 h 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 and ethyl acetate (V_{PE}/V_{EA}, 10:1) as the eluent and pure product was obtained as white powder. Yield: 71%.

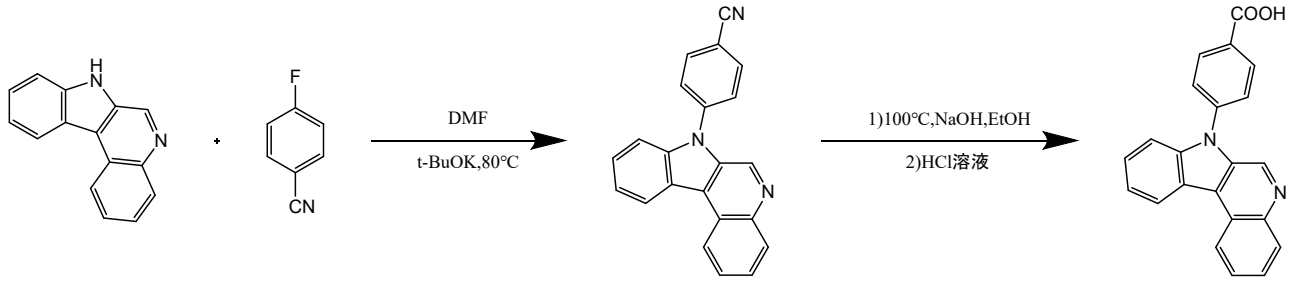
^{1}H NMR (400 MHz, DMSO-d_6) δ 8.90 (d, J = 8.4 Hz, 1H), 8.75 (dd, J = 7.1, 2.0 Hz, 1H), 8.24 – 8.16 (m, 2H), 8.16 – 8.09 (m, 1H), 8.04 – 7.90 (m, 3H), 7.79 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.66 (d, J = 8.9 Hz, 1H), 7.61 – 7.38 (m, 4H).

BCz-PhCOOH: BCz-PhCN (159.19 mg, 0.5 mmol) and NaOH (300 mg, 7.5 mmol) were placed in a 25 mL round-bottom flask, followed by the addition of 2.5 mL ethanol and 2.5 mL deionized water. A magnetic stir bar was added, and a spherical condenser was installed. The mixture was refluxed at 100 °C for 24 h. After the reaction was complete, the flask was cooled to room temperature, and 1.25 mL HCl was added for acidification until the pH was 1-2. The reaction was continued for another 2 h, then filtered under vacuum, washed with deionized water, and dried in a vacuum drying oven for 24 h to obtain a white product. Yield: 23%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.16 (s, 1H), 8.91 (d, J = 8.3 Hz, 1H), 8.76 (dd, J = 7.1, 1.8 Hz, 1H), 8.34 – 8.22 (m, 2H), 8.12 (d, J = 8.1 Hz, 1H), 8.00 (d, J = 9.0 Hz, 1H), 7.89 – 7.73 (m, 3H), 7.67 (d, J = 8.9 Hz, 1H), 7.62 – 7.41 (m, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.24, 140.75, 139.47, 137.98, 131.78, 130.74, 129.70, 129.48, 128.27, 127.95, 127.66, 125.51, 124.01, 123.84, 123.63, 122.57, 121.81, 115.51, 112.02, 110.80.

HR-ESI-MS Calcd. For $C_{23}H_{15}NO_2$ $[M+H]^+$: 338.110. Found: 338.3423.



Scheme S2. The synthetic route to NBCz-PhCOOH.

NBCz-PhCN: 7H-indolo[2,3-c]quinoline (109.13 mg, 0.5 mmol), sodium tert-butoxide (84.15 mg, 0.75 mmol), 4-fluorobenzonitrile (72.66 mg, 0.6 mmol), 2 mL DMF were added to a 10 mL Shrek bottle. The mixed solution was refluxed at room temperature for 12 h 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 and ethyl acetate (V_{PE}/V_{EA}, 1:1) as the eluent and pure product was obtained as white powder. Yield: 68%.

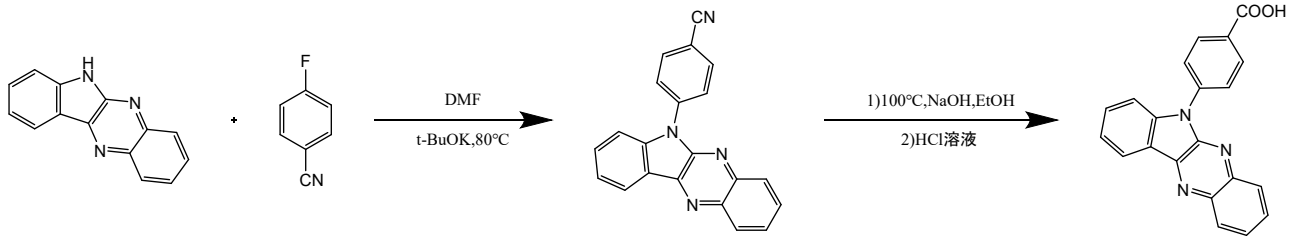
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.20 (s, 1H), 8.94 (dd, J = 8.3, 1.4 Hz, 1H), 8.86 (d, J = 8.0 Hz, 1H), 8.28 – 8.20 (m, 3H), 8.07 (d, J = 8.5 Hz, 2H), 7.85 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.77 (ddd, J = 8.3, 6.9, 1.4 Hz, 1H), 7.71 – 7.66 (m, 2H), 7.57 (ddd, J = 8.1, 5.1, 3.0 Hz, 1H).

NBCz-PhCOOH: NBCz-PhCN (31.94 mg, 0.1 mmol) and NaOH (60 mg, 1.5 mmol) were placed in a 25 mL round-bottom flask, followed by the addition of 2.5 mL ethanol and 2.5 mL deionized water. A magnetic stir bar was added, and a spherical condenser was installed. The mixture was refluxed at 100 °C for 24 h. After the reaction was complete, the flask was cooled to room temperature, and 1.25 mL HCl was added for acidification until the pH was 1-2. The reaction was continued for another 2 h, then filtered under vacuum, washed with deionized water, and dried in a vacuum drying oven for 24 h to obtain a white product. Yield: 25%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.33 (s, 1H), 9.41 (s, 1H), 9.09 (d, J = 8.2 Hz, 1H), 8.98 (d, J = 8.1 Hz, 1H), 8.44 – 8.24 (m, 3H), 7.98 (dq, J = 8.3, 2.0 Hz, 3H), 7.94 – 7.87 (m, 1H), 7.77 (dt, J = 15.7, 5.1 Hz, 2H), 7.64 (ddd, J = 8.1, 6.7, 1.3 Hz, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.05, 142.83, 138.96, 134.94, 133.25, 131.97, 131.92, 131.63, 131.46, 130.21, 129.86, 127.91, 126.65, 125.16, 124.92, 123.74, 123.63, 123.30, 121.04, 112.25.

HR-ESI-MS Calcd. For $C_{22}H_{14}N_2O_2$ $[M+H]^+$: 339.1055. Found: 339.1149.



Scheme S3. The synthetic route to 2NBCz-1-PhCOOH.

2NBCz-1-PhCN: 6H-indolo[2,3-b]quinoxaline (109.6 mg, 0.5 mmol), sodium tert-butoxide (84.15 mg, 0.75 mmol), 4-fluorobenzonitrile (72.66 mg, 0.6 mmol), 2 mL DMF were added to a 10 mL Shrek bottle. The mixed solution was refluxed at room temperature for 12 h 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 and ethyl acetate (V_{PE}/V_{EA}, 10:1) as the eluent and pure product was obtained as white powder. Yield: 63%.

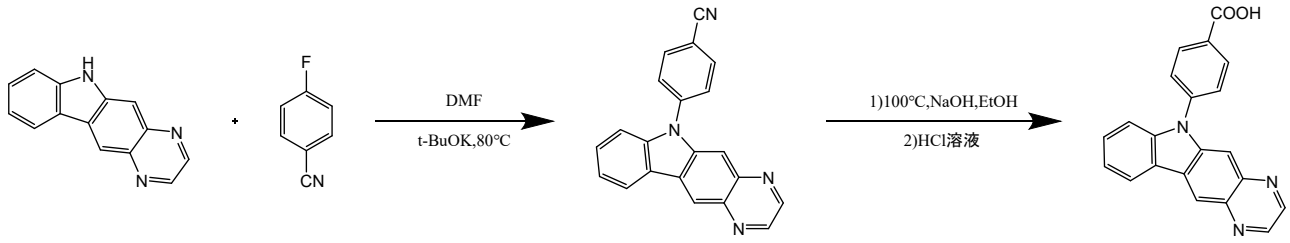
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 7.7 Hz, 1H), 8.41 – 8.35 (m, 1H), 8.15 – 8.09 (m, 1H), 8.07 – 7.95 (m, 4H), 7.80 (dtd, *J* = 8.0, 6.9, 5.1 Hz, 2H), 7.72 (dt, *J* = 7.8, 1.0 Hz, 1H), 7.66 (dt, *J* = 8.3, 0.9 Hz, 1H), 7.54 (ddd, *J* = 8.0, 7.2, 1.1 Hz, 1H).

2NBCz-1-PhCOOH: 2NBCz-1-PhCN (32 mg, 0.1 mmol) and NaOH (60 mg, 1.5 mmol) were placed in a 25 mL round-bottom flask, followed by the addition of 2.5 mL ethanol and 2.5 mL deionized water. A magnetic stir bar was added, and a spherical condenser was installed. The mixture was refluxed at 100 ^{o}C for 24 h. After the reaction was complete, the flask was cooled to room temperature, and 1.25 mL HCl was added for acidification until the pH was 1-2. The reaction was continued for another 2 h, then filtered under vacuum, washed with deionized water, and dried in a vacuum drying oven for 24 h to obtain a white product. Yield: 23%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.20 (s, 1H), 8.50 (d, *J* = 7.7 Hz, 1H), 8.33 (dd, *J* = 8.2, 1.7 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 2H), 8.08 – 8.02 (m, 1H), 8.00 – 7.88 (m, 2H), 7.86 – 7.74 (m, 3H), 7.68 – 7.59 (m, 1H), 7.56 – 7.52 (m, 1H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 167.69, 167.22, 145.68, 144.24, 140.23, 139.76, 139.35, 132.16, 131.27, 130.39, 129.76, 129.53, 129.46, 128.26, 127.46, 127.33, 122.89, 122.71, 119.87, 111.30.

HR-ESI-MS Calcd. For $C_{21}H_{13}N_3O_2$ $[M+H]^+$: 340.1008. Found: 340.1097.



Scheme S4. The synthetic route to 2NBCz-2-PhCOOH.

2NBCz-2-PhCN: 6H-pyrazino[2,3-b]carbazole (109.6 mg, 0.5 mmol), sodium tert-butoxide (84.15 mg, 0.75 mmol), 4-fluorobenzonitrile (72.66 mg, 0.6 mmol), 2 mL DMF were added to a 10 mL Shrek bottle. The mixed solution was refluxed at room temperature for 12 h 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 and ethyl acetate (V_{PE}/V_{EA}, 5:1) as the eluent and pure product was obtained as white powder. Yield: 56%.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.88 (d, J = 3.4 Hz, 3H), 8.37 (d, J = 7.7 Hz, 1H), 8.06 (s, 1H), 8.03 – 7.96 (m, 2H), 7.91 – 7.84 (m, 2H), 7.61 (ddd, J = 8.4, 7.1, 1.2 Hz, 1H), 7.53 – 7.43 (m, 2H).

2NBCz-2-PhCOOH: 2NBCz-2-PhCN (32 mg, 0.1 mmol) and NaOH (60 mg, 1.5 mmol) were placed in a 25 mL round-bottom flask, followed by the addition of 2.5 mL ethanol and 2.5 mL deionized water. A magnetic stir bar was added, and a spherical condenser was installed. The mixture was refluxed at 100 ^{o}C for 24 h. After the reaction was complete, the flask was cooled to room temperature, and 1.25 mL HCl was added for acidification until the pH was 1-2. The reaction was continued for another 2 h, then filtered under vacuum, washed with deionized water, and dried in a vacuum drying oven for 24 h to obtain a white product. Yield: 20%.

^{1}H NMR (400 MHz, DMSO-d_6) δ 13.25 (s, 1H), 9.17 – 8.84 (m, 3H), 8.60 (d, J = 7.7 Hz, 1H), 8.34 – 8.18 (m, 2H), 8.04 – 7.81 (m, 3H), 7.64 (t, J = 7.7 Hz, 1H), 7.53 (dd, J = 17.7, 8.2 Hz, 1H), 7.45 (td, J = 7.4, 3.7 Hz, 1H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 167.26, 145.37, 143.71, 143.20, 142.01, 141.61, 138.06, 131.92, 130.14, 129.59, 128.67, 126.89, 122.96, 122.70, 121.75, 120.57, 110.43, 105.94, 40.53.

HR-ESI-MS Calcd. For $C_{21}H_{13}N_3O_2$ $[M+H]^+$: 340.1008. Found: 340.1121.

3. NMR spectra and HR-MS of mentioned molecules

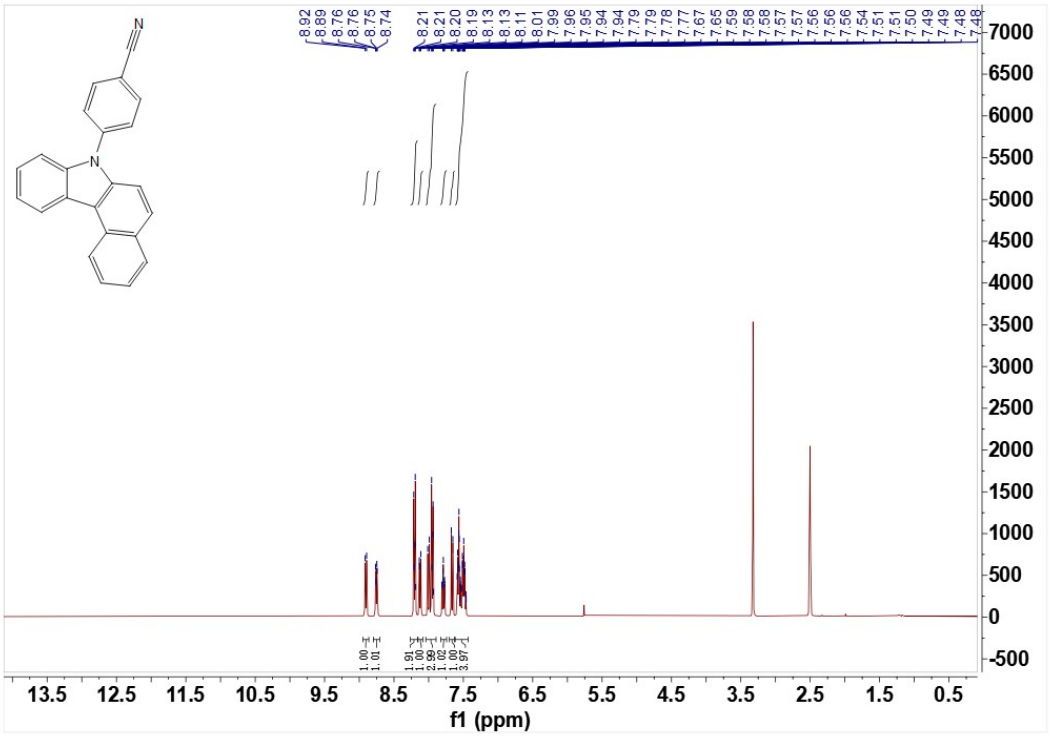


Figure S1. [1]H NMR spectrum of **BCz-PhCN** in DMSO-d_6.

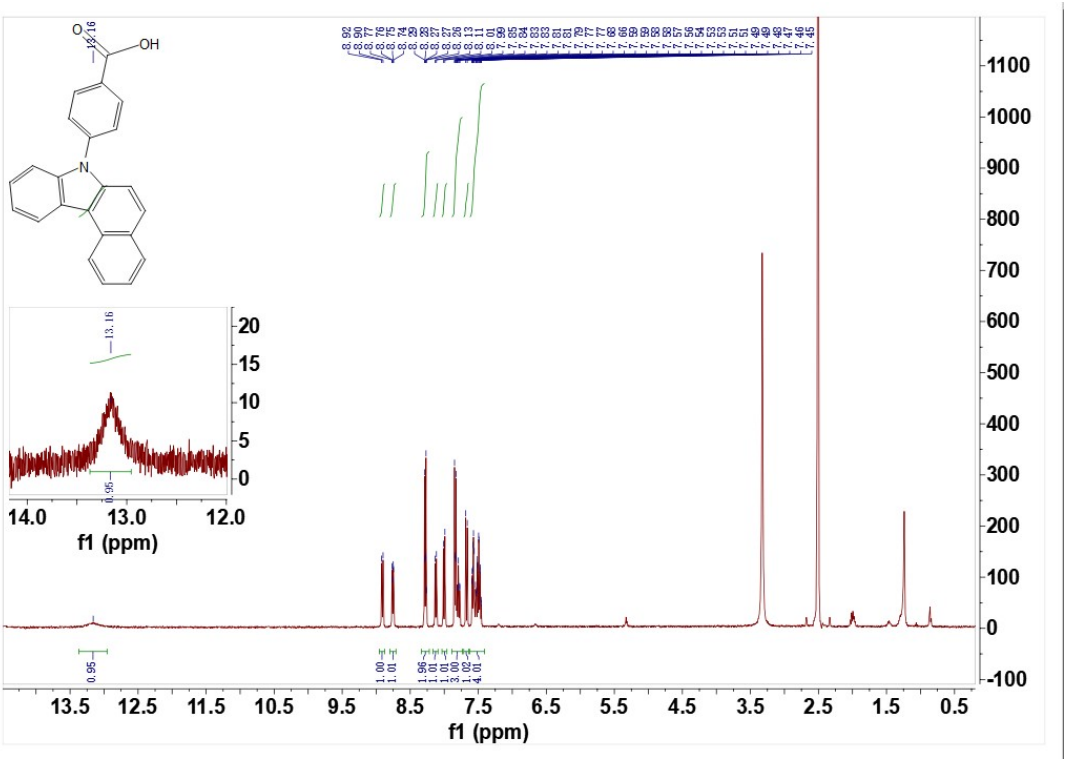


Figure S2. [1]H NMR spectrum of **BCz-PhCOOH** in DMSO-d_6.

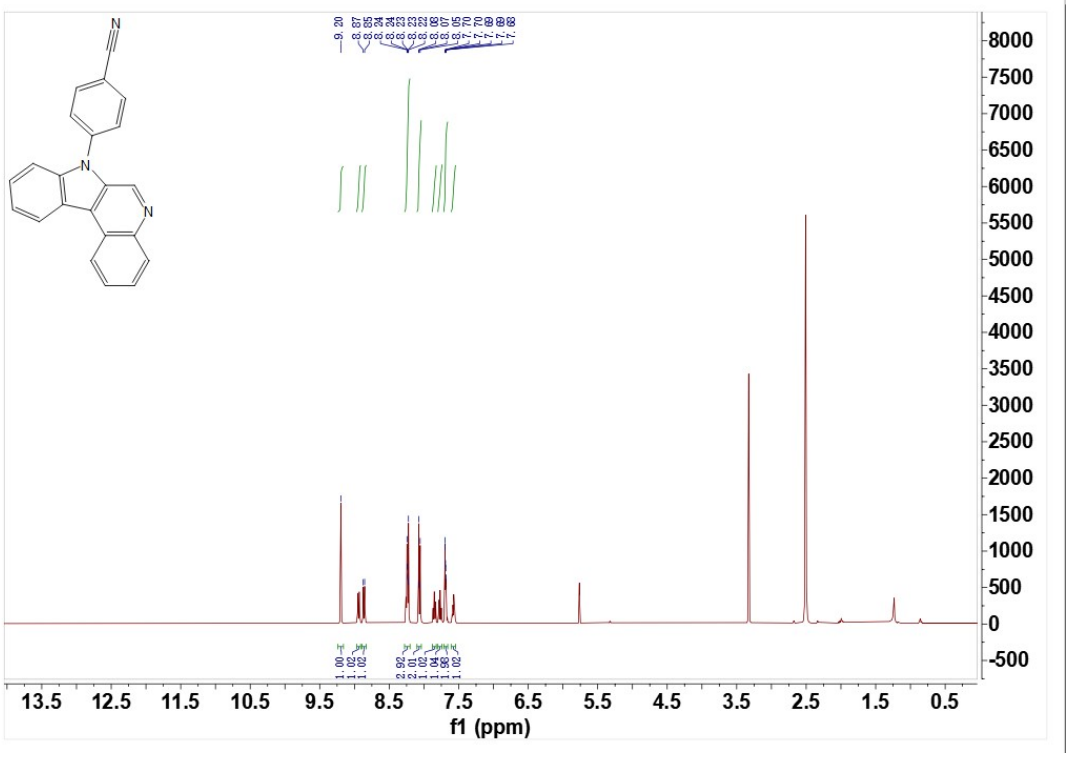


Figure S3. ^{1}H NMR spectrum of **NBCz-PhCN** in DMSO-d_6.

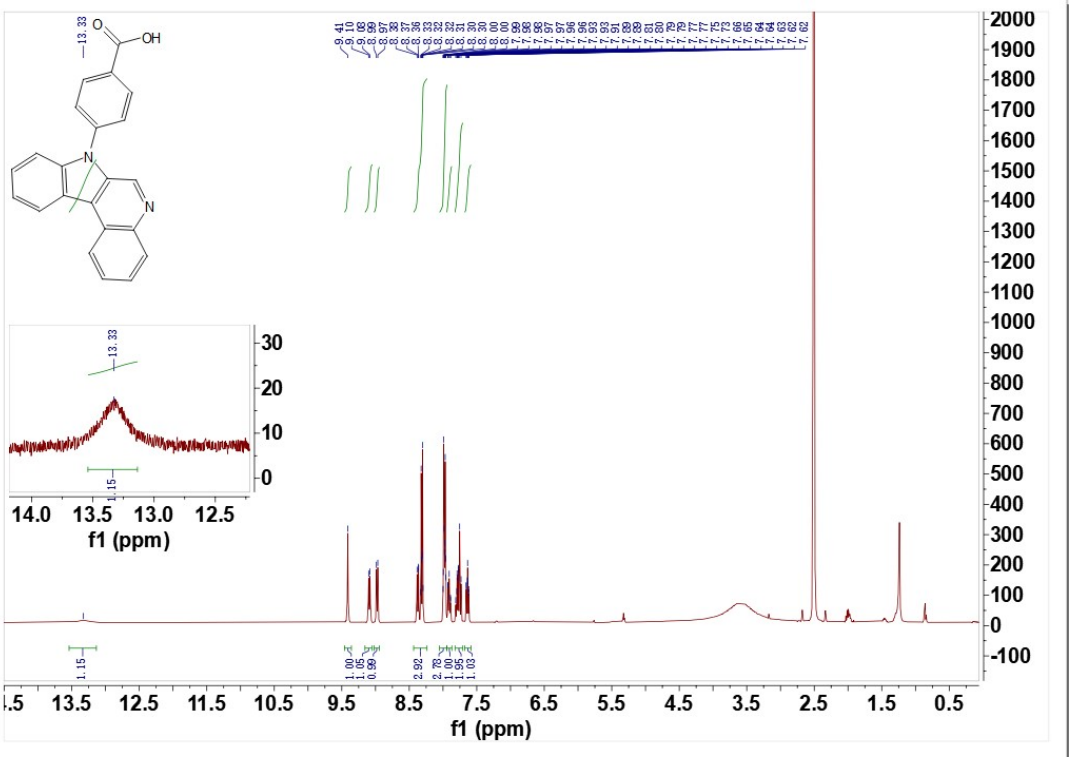


Figure S4. ^{1}H NMR spectrum of **NBCz-PhCOOH** in DMSO-d_6.

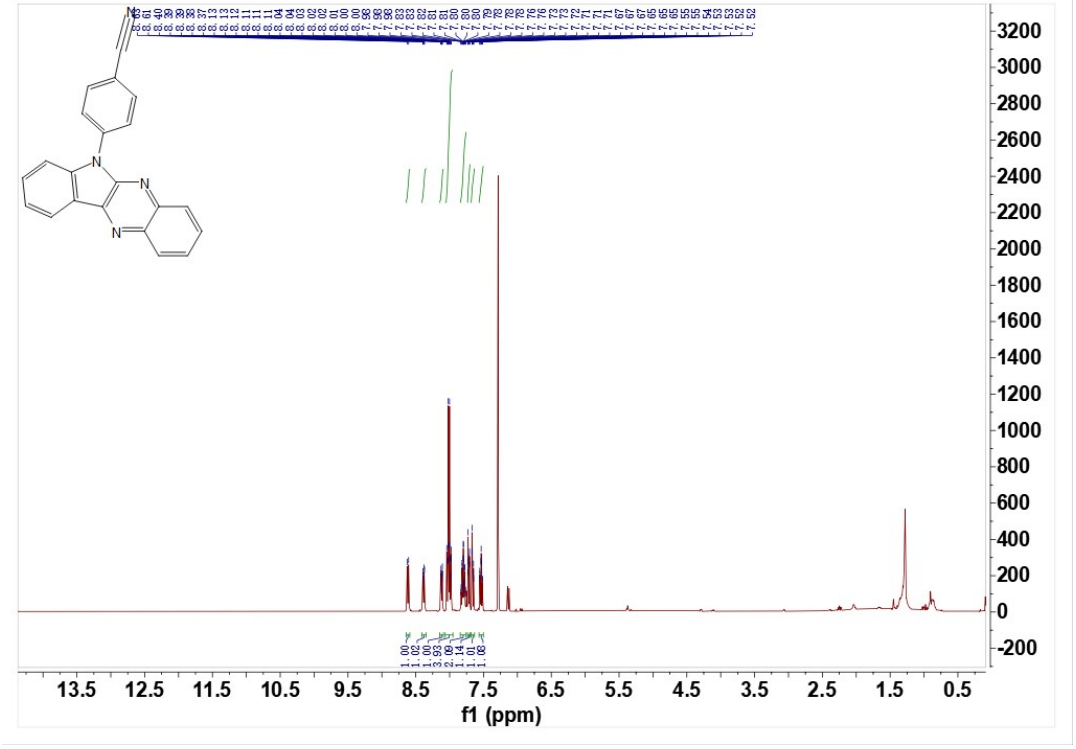


Figure S5. ^{1}H NMR spectrum of **2NBCz-1-PhCN** in $CDCl_3$.

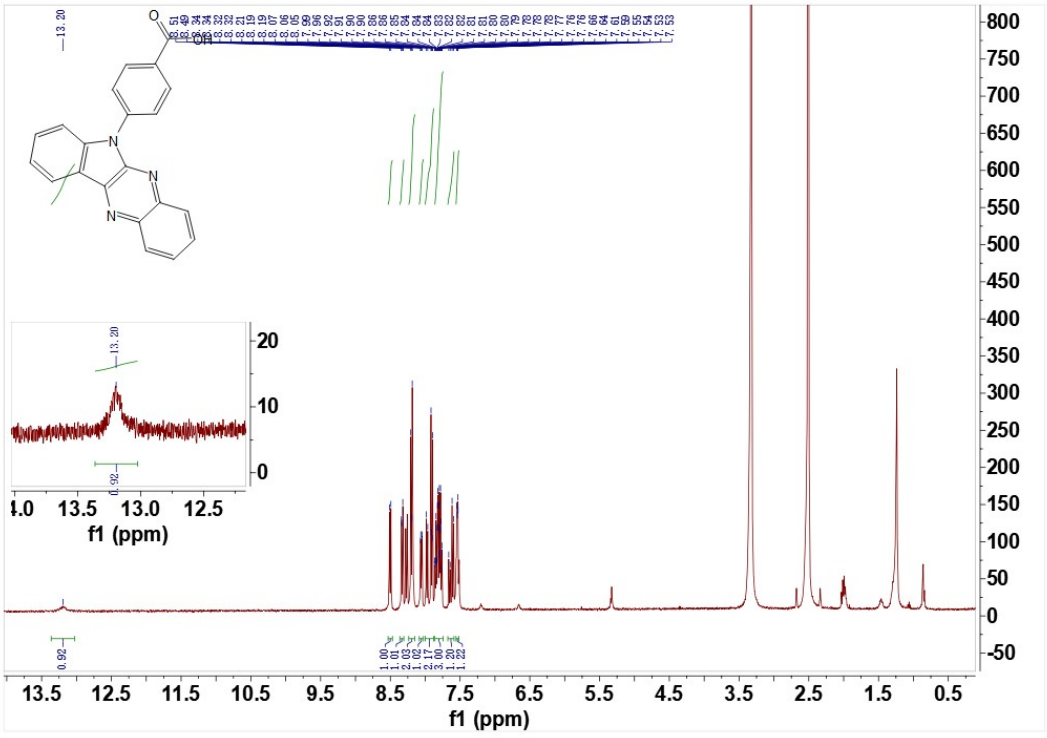


Figure S6. ^{1}H NMR spectrum of **2NBCz-1-PhCOOH** in DMSO-d_6.

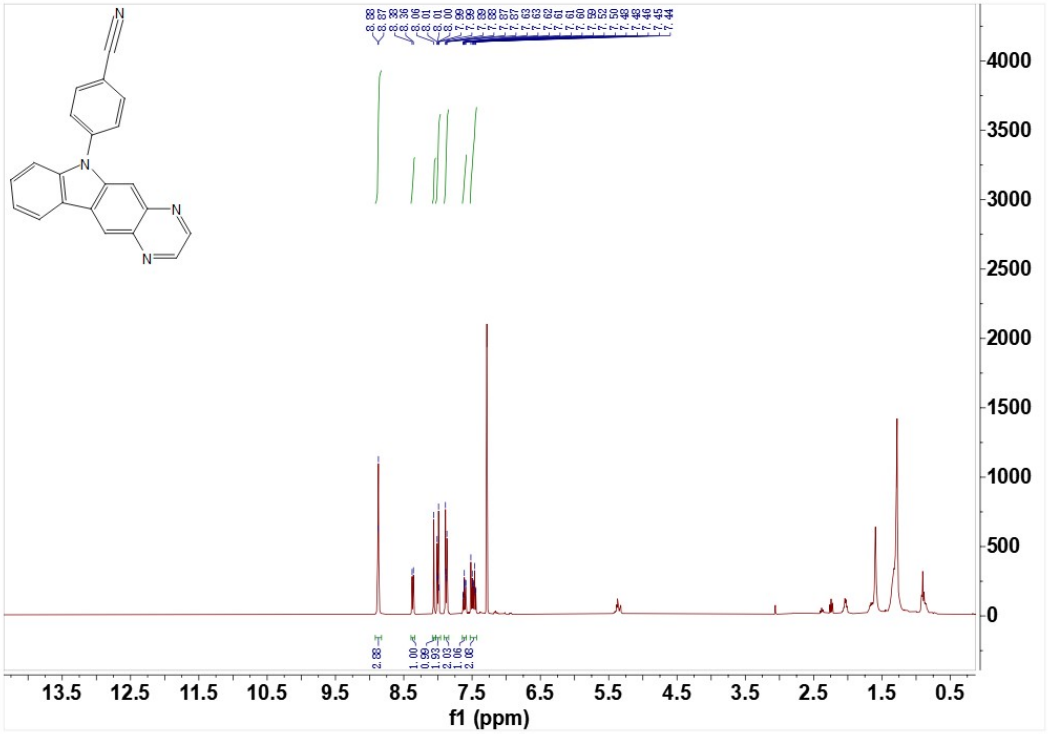


Figure S7. ^{1}H NMR spectrum of **2NBCz-2-PhCN** in $CDCl_3$.

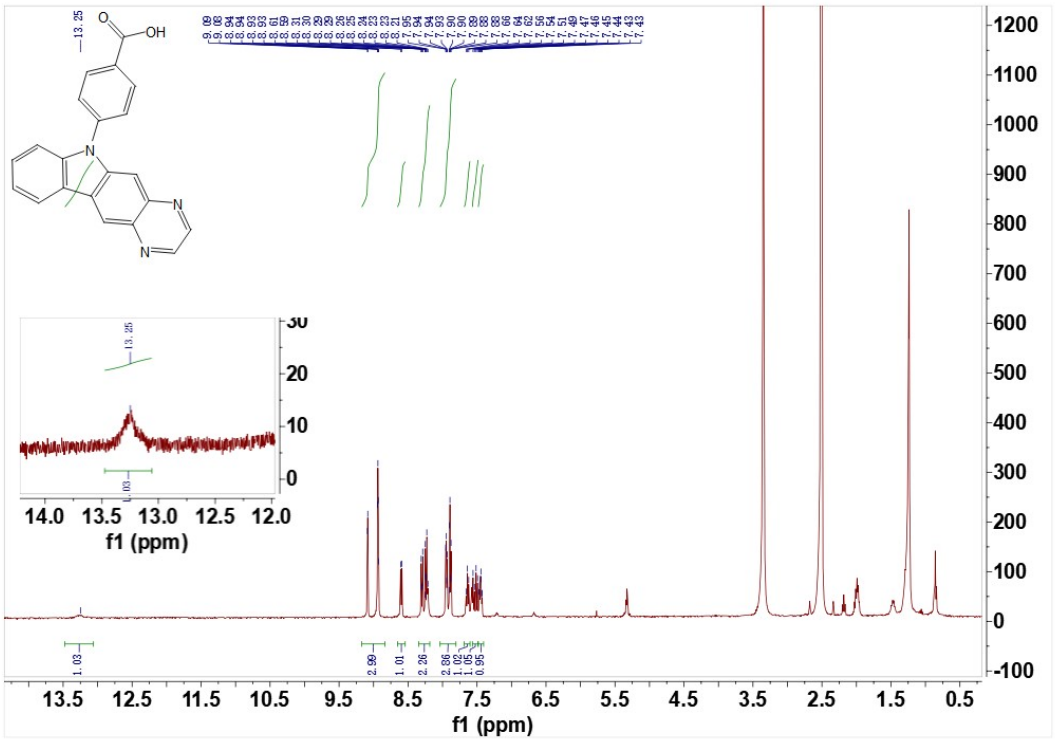


Figure S8. ^{1}H NMR spectrum of **2NBCz-2-PhCOOH** in DMSO-d_6.

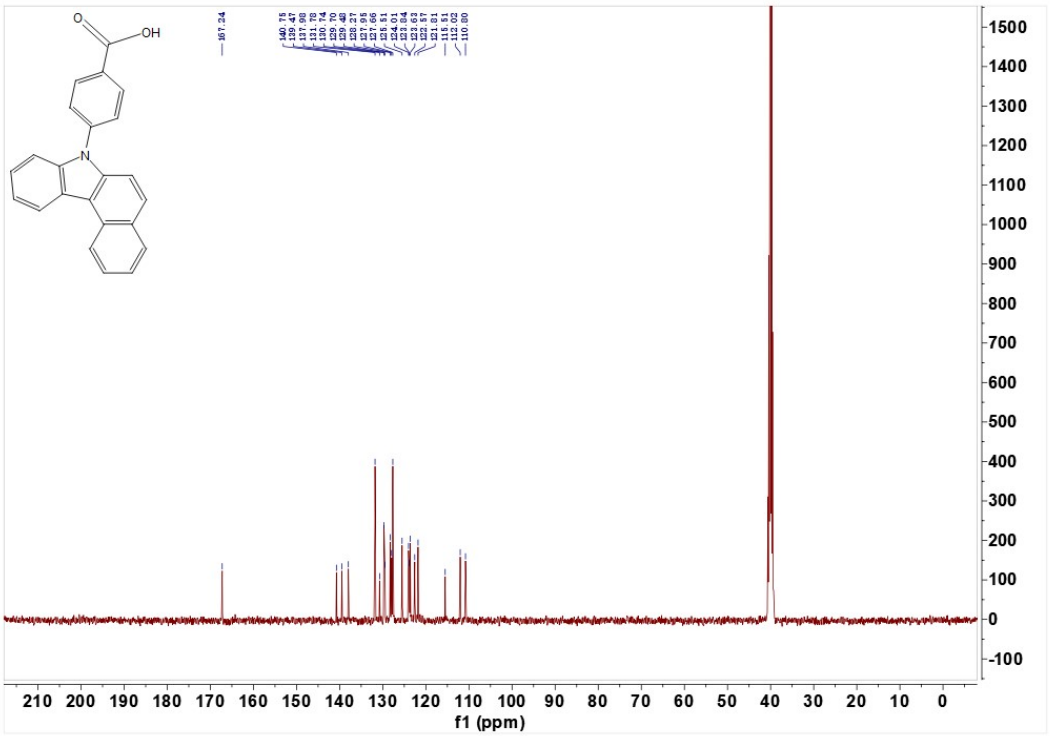


Figure S9. ^{13}C NMR spectrum of **BCz-PhCOOH** in DMSO-d_6.

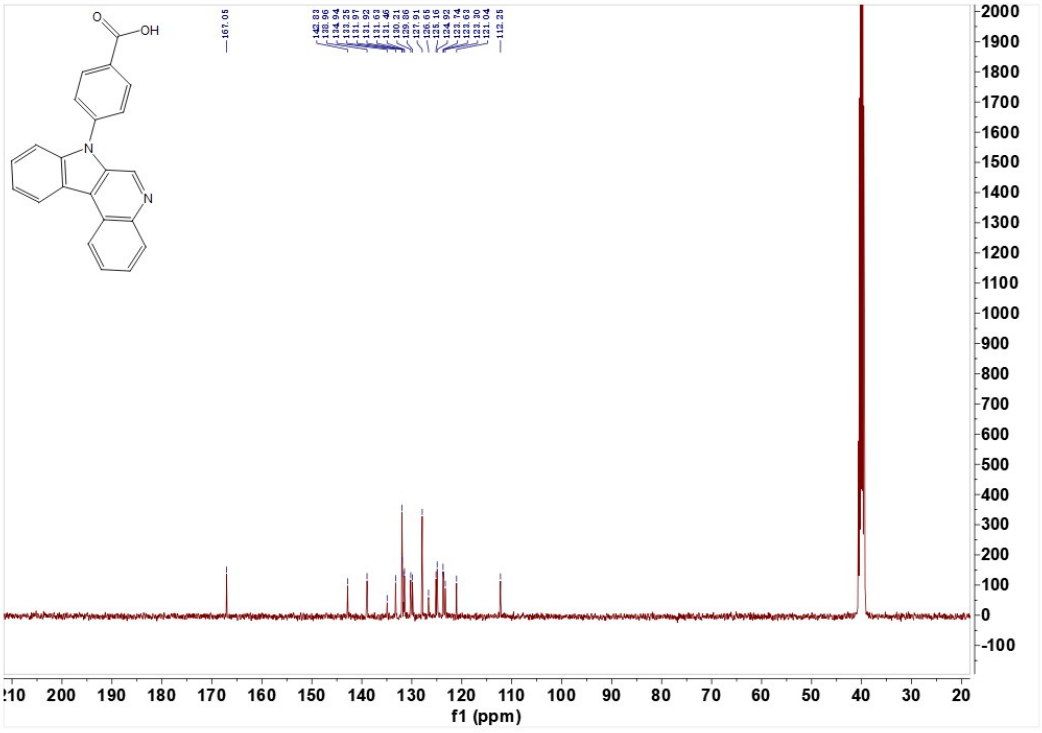


Figure S10. ^{13}C NMR spectrum of **NBCz-PhCOOH** in DMSO-d_6.

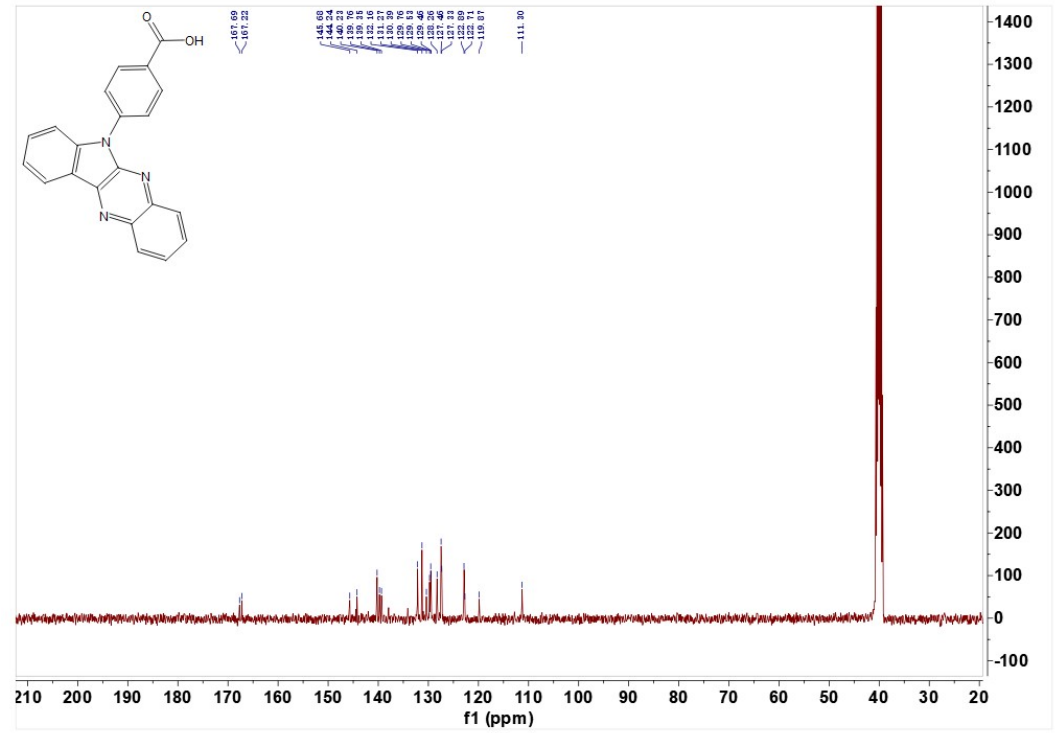


Figure S11. ^{13}C NMR spectrum of **2NBCz-1-PhCOOH** in DMSO-d_6.

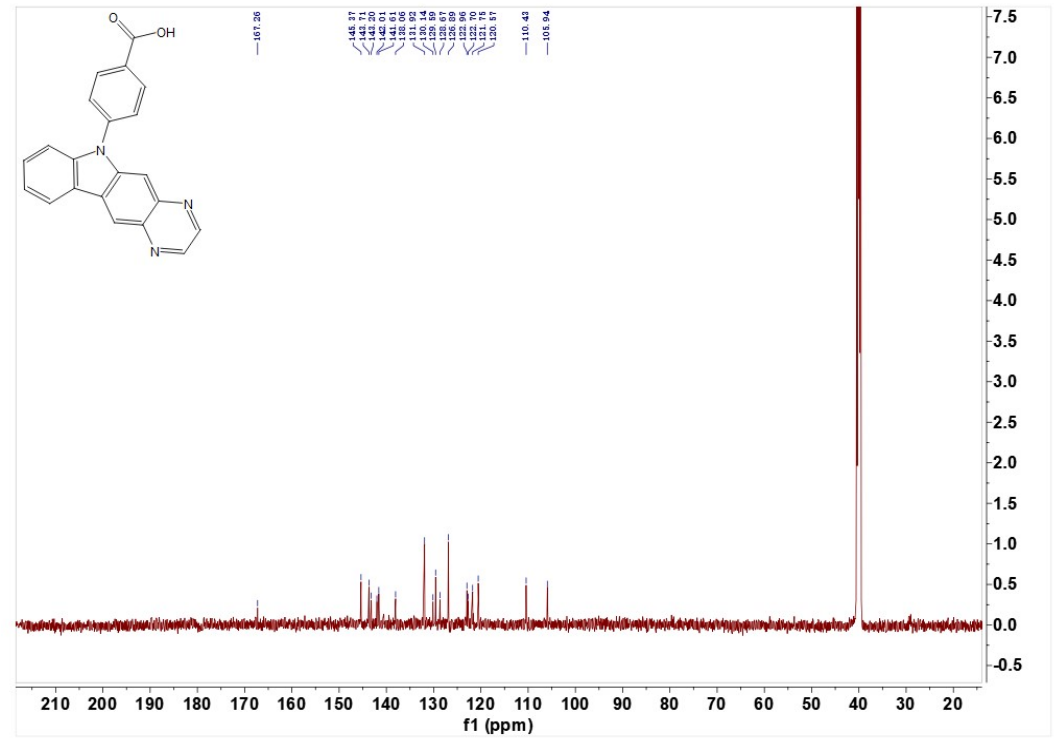


Figure S12. ^{13}C NMR spectrum of **2NBCz-2-PhCOOH** in DMSO-d_6.

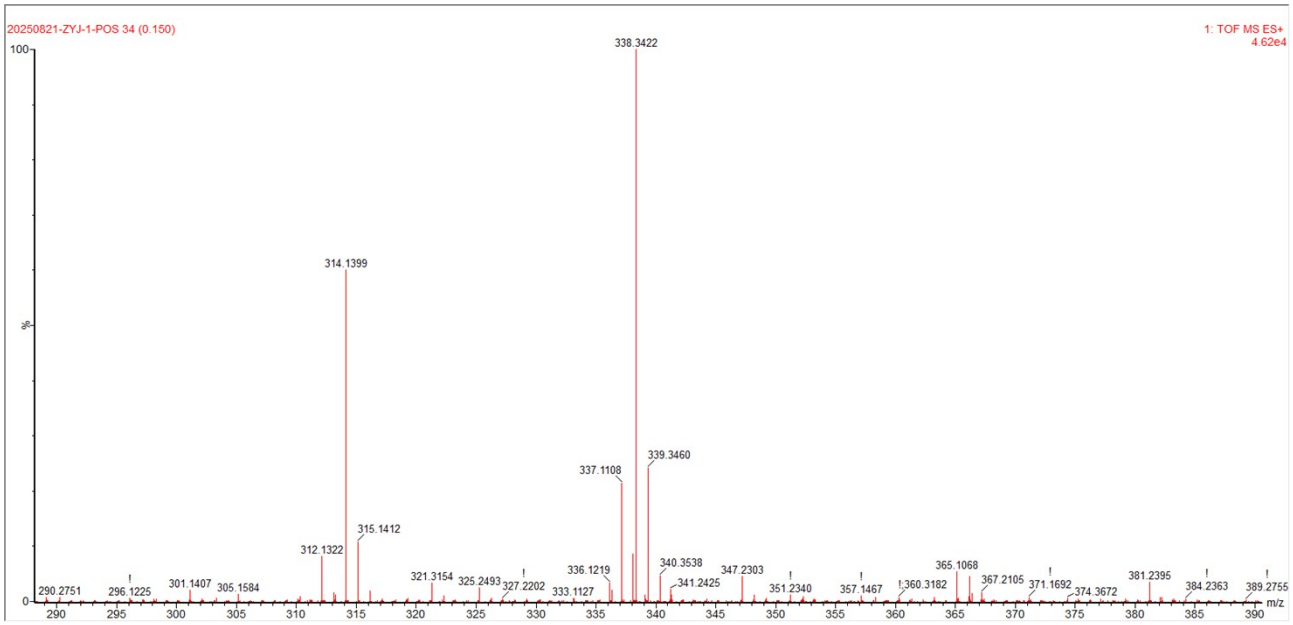


Figure S13. HR-MS spectrum of **BCz-PhCOOH**.

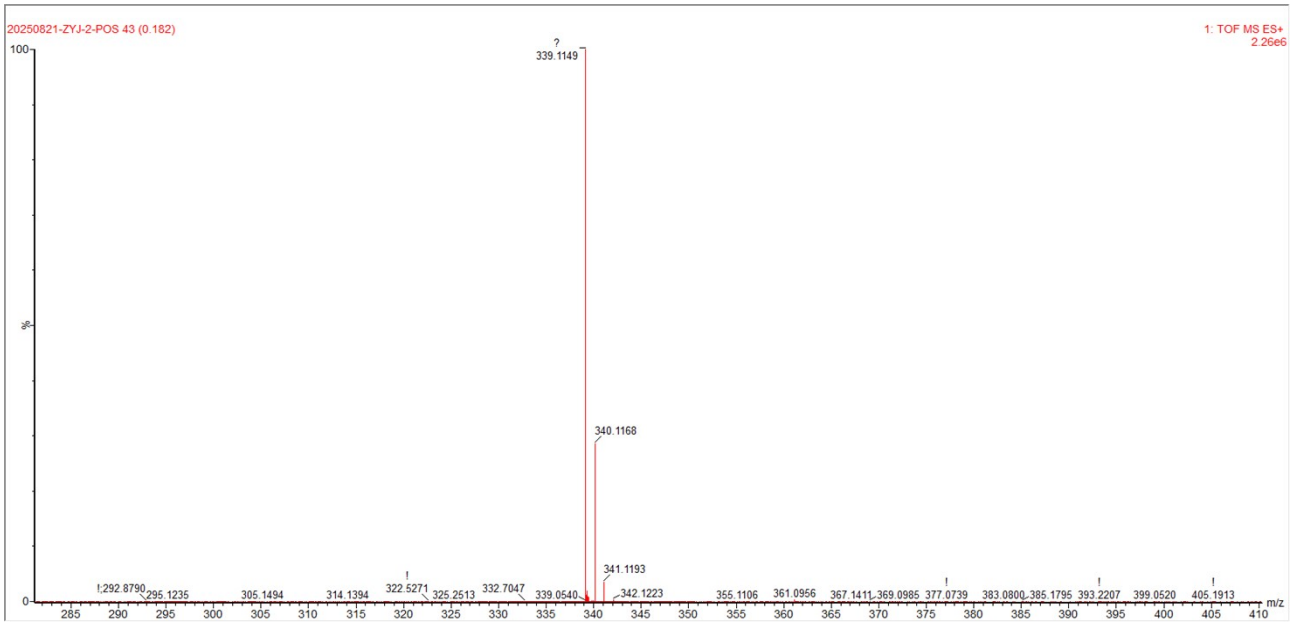


Figure S14. HR-MS spectrum of **NBCz-PhCOOH**.

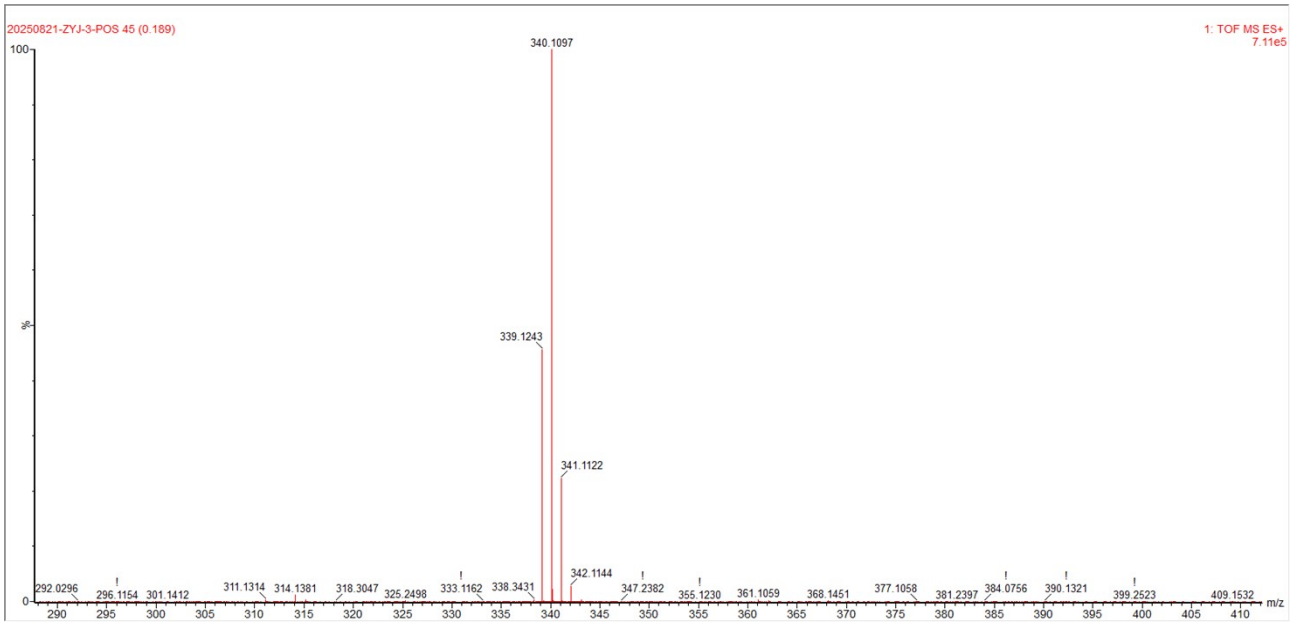


Figure S15. HR-MS spectrum of **2NBCz-1-PhCOOH**.

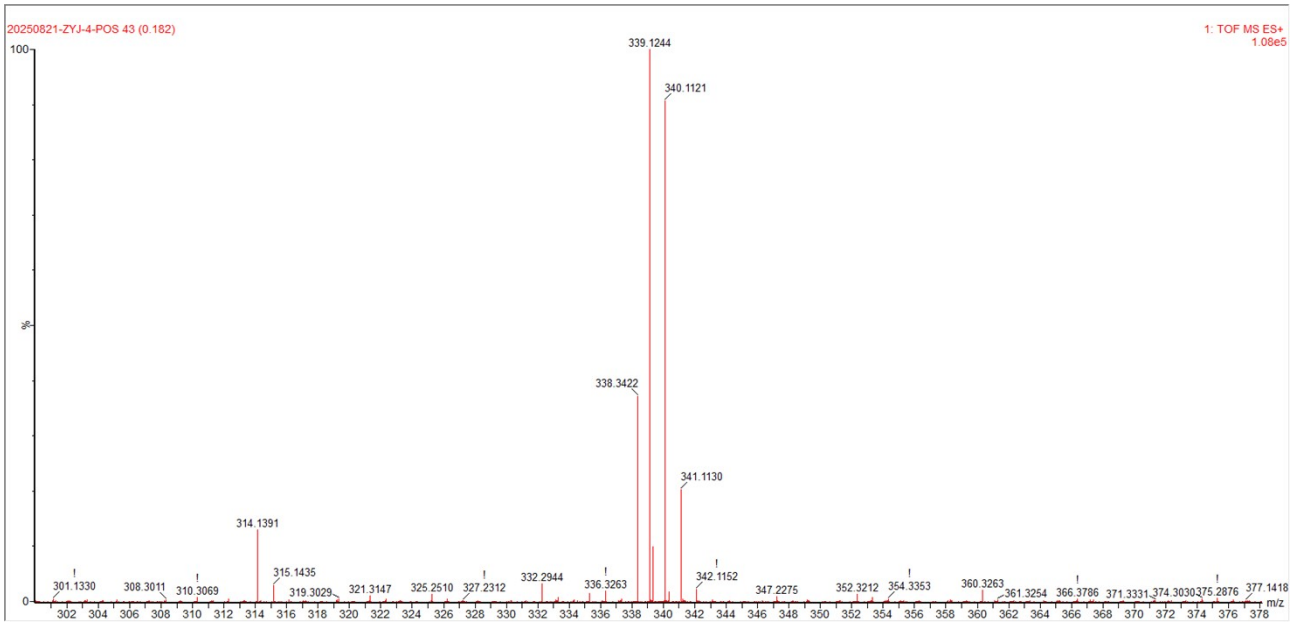


Figure S16. HR-MS spectrum of **2NBCz-2-PhCOOH**.

4. Photopysical properties in the solution

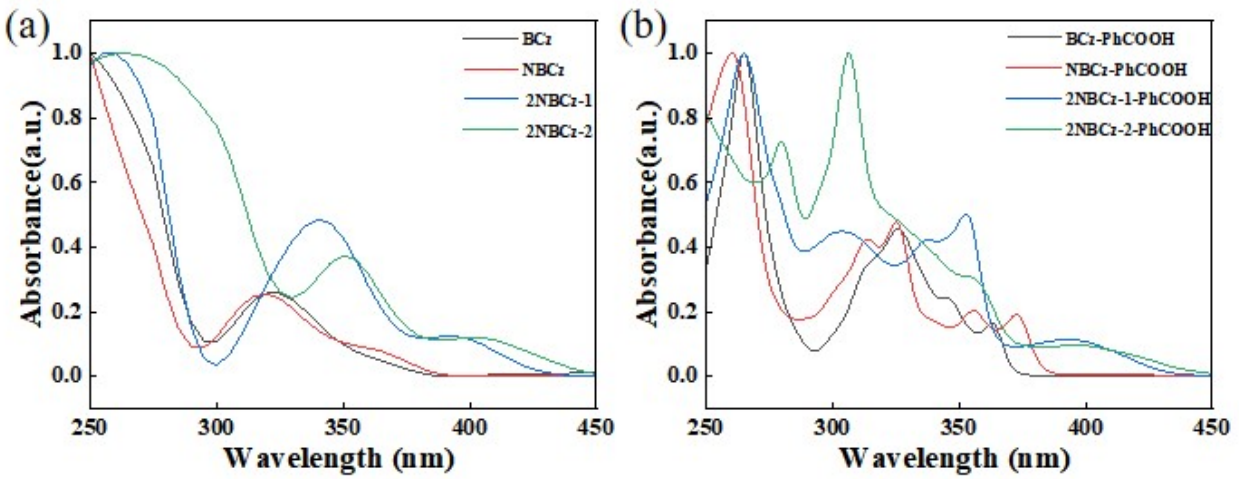


Figure S17. Absorption spectra of (a) BCz, NBCz, 2NBCz-1 and 2NBCz-2, (b) BCz-PhCOOH, NBCz-PhCOOH, 2NBCz-1-PhCOOH and 2NBCz-2-PhCOOH in THF solution (20 μM).

5. Photophysical properties in the solid state.

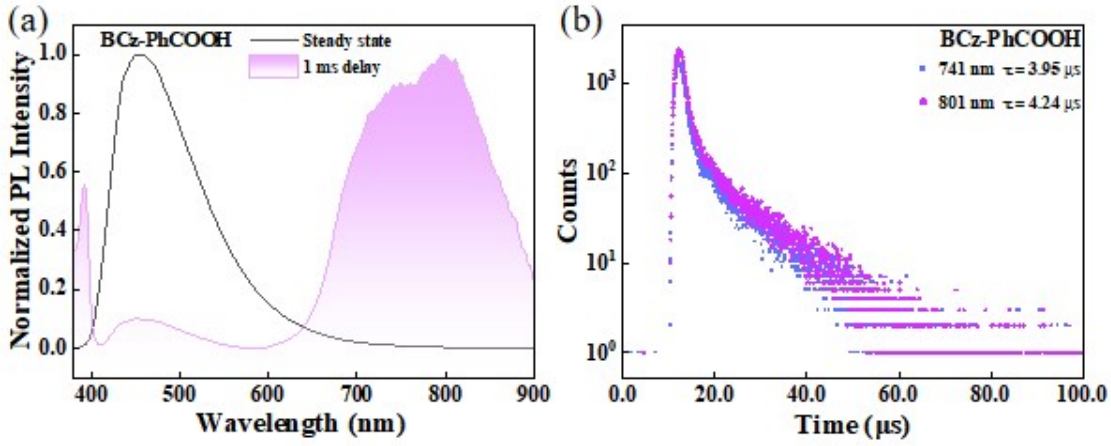


Figure S18. (a) Steady-state and 1 ms-delayed PL spectra of BCz-PhCOOH powder, and (b) decay spectra at ambient condition (λ_{ex} = 365 nm).

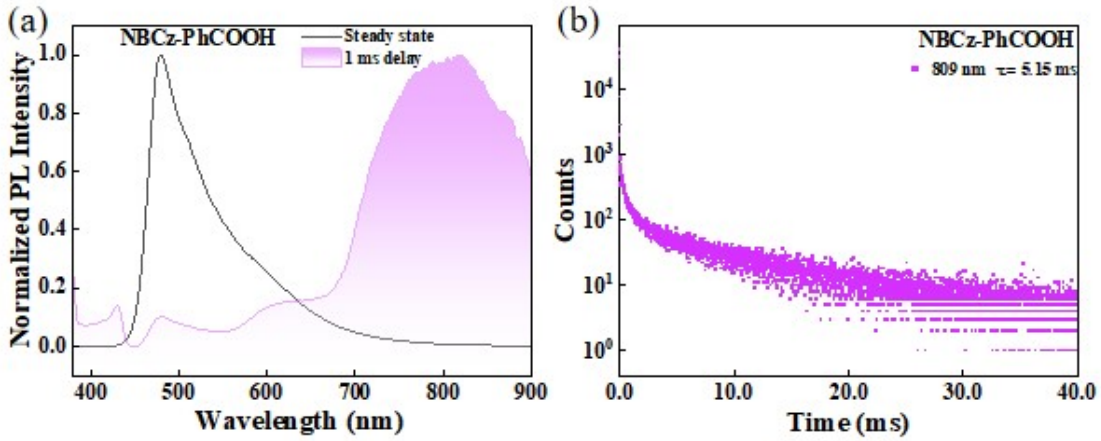


Figure S19. (a) Steady-state and 1 ms-delayed PL spectra of NBCz-PhCOOH powder, and (b) decay spectra at ambient condition (λ_{ex} = 365 nm).

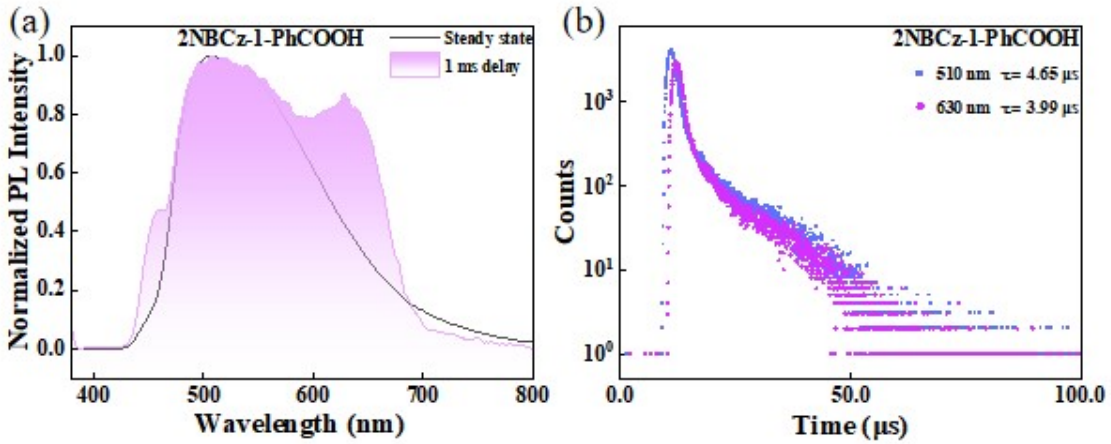


Figure S20. (a) Steady-state and 1 ms-delayed PL spectra of 2NBCz-1-PhCOOH powder, and (b) decay spectra at ambient condition (λ_{ex} = 365 nm).

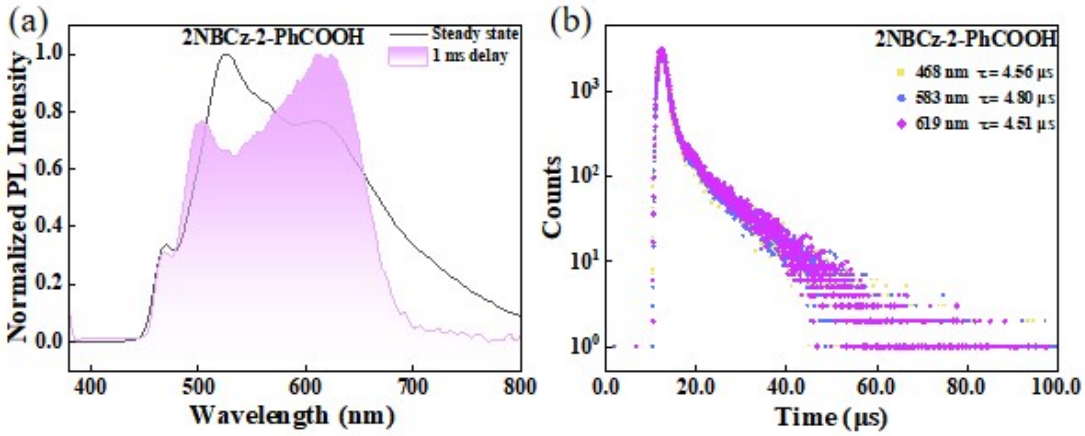


Figure S21. (a) Steady-state and 1 ms-delayed PL spectra of 2NBCz-2-PhCOOH powder, and (b) decay spectra at ambient condition (λ_{ex} = 365 nm).

6. Photophysical properties in the PVA film

Table S1. Phosphorescence quantum yield of the PVA films.

sample	Phosphorescence quantum yield (%)
BCz	14.86
BCz-PhCOOH	21.09
NBCz	15.36
NBCz-PhCOOH	17.41
2NBCz-1	0.98
2NBCz-1-PhCOOH	22.74
2NBCz-2	0.85
2NBCz-2-PhCOOH	1.73

7. Chemical shift of BCz-PhCOOH and BCz-PhCOOH@PVA

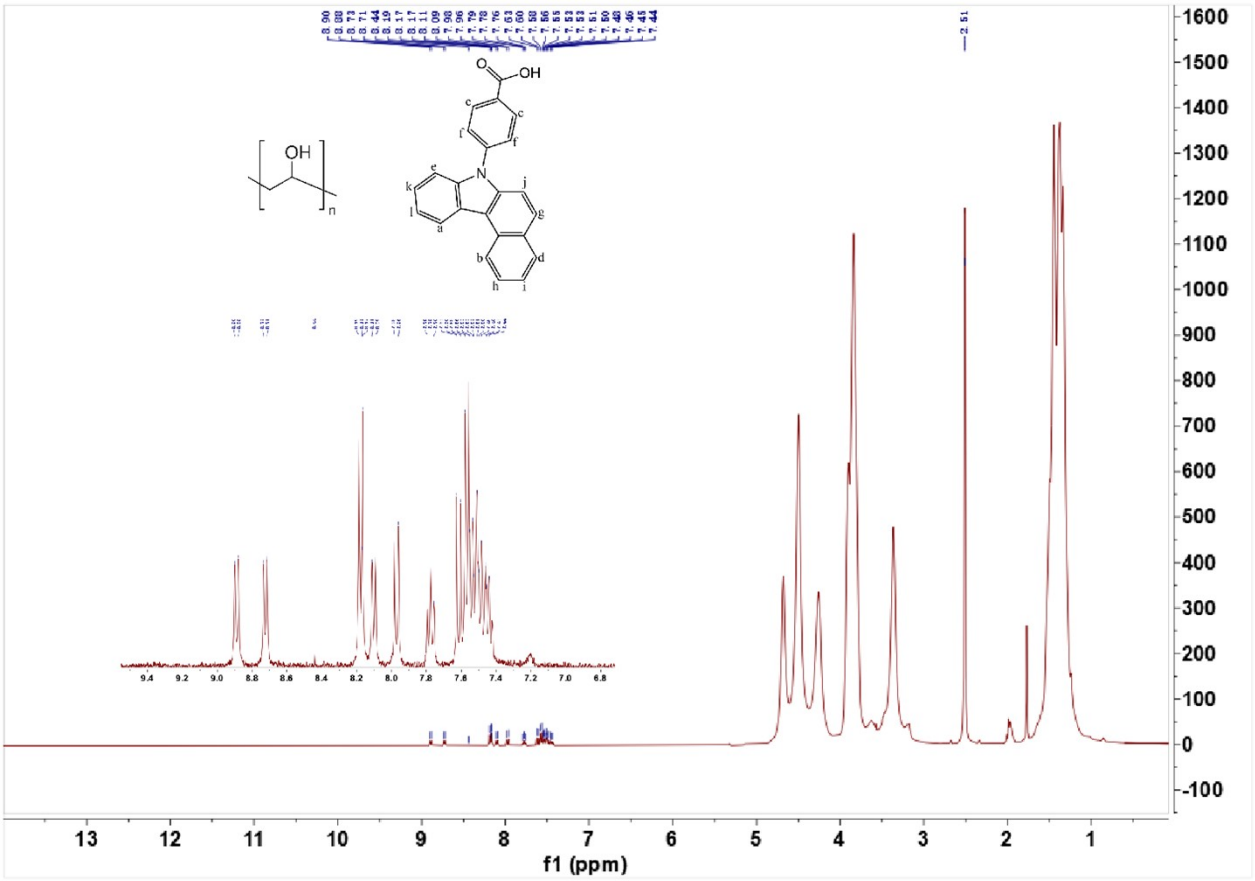


Figure S22. ^{1}H NMR spectrum of BCz-PhCOOH@PVA films in DMSO-d_6.

Table S2. Chemical shift of BCz-PhCOOH and BCz-PhCOOH@PVA.

Chemical shift (ppm)	BCz-PhCOOH	BCz-PhCOOH@PVA
a	8.92	8.90
b	8.77	8.73
c	8.29	8.18
d	8.13	8.11
e	8.01	7.98
f	7.85	7.77
g	7.79	7.62
h	7.68	7.57
i	7.59	7.55
j	7.57	7.50
k	7.51	7.48
l	7.47	7.43

8. HOMO and LUMO

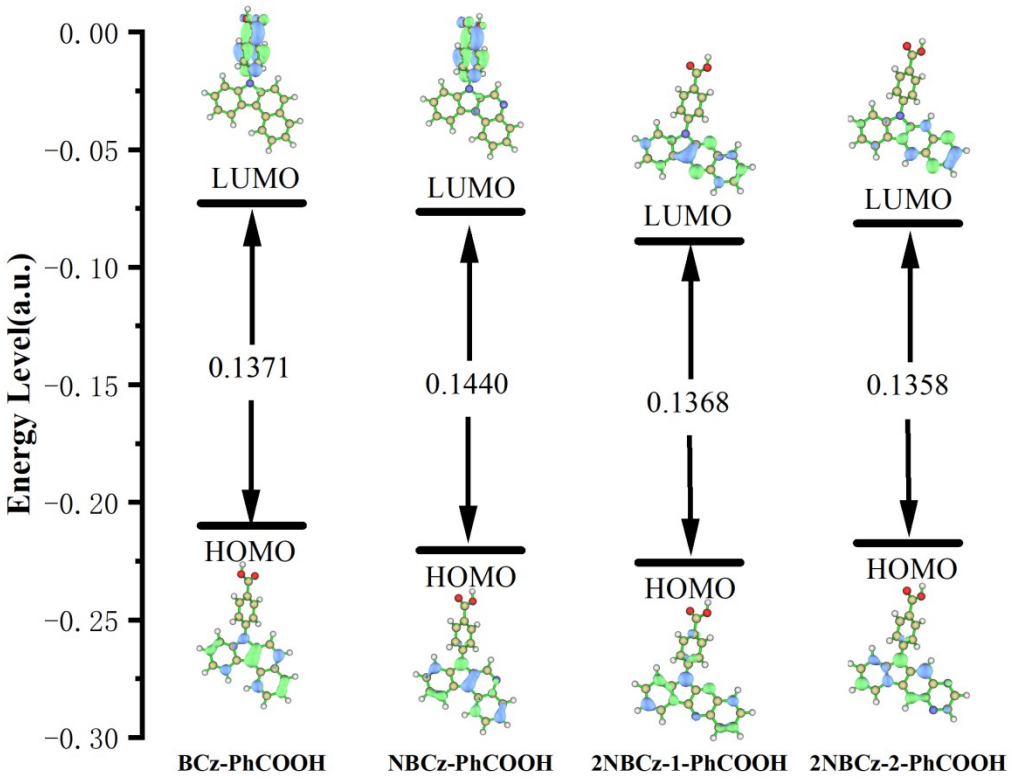


Figure S23. The HOMO and LUMO of the single molecule in the BCz-PhCOOH, NBCz-PhCOOH, 2NBCz-1-PhCOOH and 2NBCz-2-PhCOOH.

9. TD-DFT results

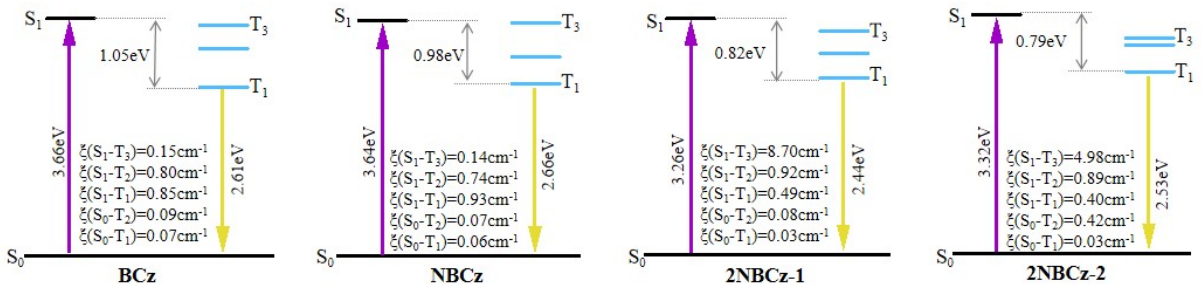


Figure S24. Energy levels and spin-orbit coupling matrix elements (ξ) of BCz, NBCz, 2NBCz-1, and 2NBCz-2 based on TD-DFT.

Table S3. TD-DFT calculated singlet and triplet excited states transition configurations of **BCz**.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.6101	H-1→L (6.30), H→L (81.95)
T_2	3.1996	H-2→L (3.33), H-2→L+2 (2.49),H-1→L (75.23), H→L (8.95), H→L+1 (2.03), H→L+2 (2.62)
T_3	3.5629	H-3→L (19.26), H-2→L (4.15), H-1→L (10.69), H-1→L+4 (4.23), H→L+1 (35.36), H→L+2 (15.78)
S_1	**3.6645**	**H-1→L (10.03), H-1→L+1 (3.45), H→L (82.29)**
T_4	3.8392	H-3→L (8.71), H-3→L+1 (4.11), H-2→L (4.29), H-1→L+1 (9.37), H-1→L+2 (10.72), H-1→L+4 (2.74),H→L (5.33), H→L+1 (25.53), H→L+2 (19.58)
S_2	**3.8957**	**H-1→L (72.47), H→L (11.10), H→L+1 (13.56)**

Table S4. TD-DFT calculated singlet and triplet excited states transition configurations of **NBCz**.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.6568	H-1→L (18.36), H→L (70.27), H→L+1 (2.76)

T_2	3.0789	H-2→L (3.69), H-2→L+2 (2.27), H-1→L (64.51), H→L (22.69), H→L+1 (2.05)
T_3	3.5941	H-4→L (26.51), H-2→L (12.50), H-1→L (6.44), H-1→L+1 (5.83), H-1→L+4 (4.98), H→L+1 (12.55), H→L+2 (17.89)
S_1	**3.6366**	**H-1→L (4.67), H-1→L+1 (3.58), H→L (88.62)**
T_4	3.7593	H-3→L (91.68), H-3→L+8 (4.09)
T_5	3.8530	H-4→L (13.67), H-4→L+2 (2.21), H-2→L (30.60), H-1→L (4.93), H-1→L+2 (14.67), H→L+1 (9.29), H→L+2 (11.95)

Table S5. TD-DFT calculated singlet and triplet excited states transition configurations of **2NBCz-1**.

Excited State	Energy (eV)	Transition configuration (%)
T1	2.4413	H-2→L (3.17), H-1→L (15.57), H→L (73.46)
T2	2.7842	H-1→L (77.32), H→L (18.12)
T3	3.0963	H-3→L (94.30), H-3→L+5 (2.39)
S1	**3.2620**	**H→L (96.57)**
T4	3.4059	H-2→L (70.69), H→L (4.89), H→L+1 (7.90), H→L+3 (5.84)

Table S6. TD-DFT calculated singlet and triplet excited states transition configurations of **2NBCz-2**.

Excited State	Energy (eV)	Transition configuration (%)

T1	2.5285	H-4→L (4.18), H-1→L (11.77), H→L (75.73), H→L+2 (2.80)
T2	2.8947	H-4→L (2.09), H-3→L (6.68), H-1→L (72.70), H→L (14.74)
T3	2.9862	H-2→L (90.88), H-2→L+1 (5.09)
S1	**3.3213**	**H→L (94.94)**
T4	3.5057	H-4→L (4.59), H-3→L (9.78), H-3→L+2 (3.05), H-1→L+1 (2.31), H-1→L+4 (4.87), H→L+1 (50.24), H→L+2 (14.07)
S2	**3.5118**	**H-1→L (90.03), H→L+1 (7.02)**
S3	**3.5512**	**H-2→L (97.74)**

Table S7. TD-DFT calculated singlet and triplet excited states transition configurations of **BCz-PhCOOH**.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.5991	H→L+1 69.2%, H-1→L+1 11.1%, H→L 8.4%
T_2	2.9846	H→L 49.2%, H-1→L 30.4%, H-4→L 11.3%
T_3	3.1949	H-1→L+1 70.5%, H→L+1 14.9%
S_1	**3.2372**	**H→L 98.4%**
T_4	3.3108	H-1→L 49.9%, H→L 37.6%
S_2	**3.4629**	**H-1→L 98.3%**
T_5	3.5713	H→L+3 29.1%, H-3→L+1 18.9%, H→L+4 14.9%, H-1→L+1 8.4%
S_3	**3.6458**	**H→L+1 81.3%, H-1→L+1 10.5%**
T_6	3.8090	H-4→L 44.7%, H-5→L+2 20.4%, H-1→L 14.0%

Table S8. TD-DFT calculated singlet and triplet excited states transition configurations of **NBCz-**

PhCOOH.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.6435	H→L+1 46.2%, H-1→L+1 22.6%, H→L 15.9%
T_2	3.0416	H→L 35.8%, H-1→L+1 29.2%, H-1→L 16.4%
T_3	3.0691	H→L+1 38.0%, H→L 23.9%, H-1→L+1 18.7%, H-5→L 6.9%
S_1	**3.4136**	**H→L 96.3%**
S_2	**3.5735**	**H→L+1 89.3%**
T_4	3.5894	H-4→L+1 20.8%, H→L+4 13.3%, H-1→L 10.2%, H-1→L+3 6.9%, H→L+3 6.6%, H-3→L+1 5.1%
T_5	3.6465	H-1→L 41.9%, H→L 15.1%, H-1→L+1 13.6%, H-5→L 7.8%
T_6	3.6913	H-2→L+1 50.8%, H-3→L+1 25.9%, H-2→L 9.6%
S_3	**3.7386**	**H-1→L 94.7%**
T_7	3.8566	H-5→L 14.9%, H-3→L+1 10.6%, H-1→L+1 9.7%, H-1→L 9.0%, H-6→L+2 7.8%, H-2→L+1 7.1%, H→L+3 7.0%, H-1→L+4 6.7%

Table S9. TD-DFT calculated singlet and triplet excited states transition configurations of **2NBCz-1-PhCOOH**.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.4254	H→L 70.6%, H-1→L 17.4%
T_2	2.7510	H-1→L 73.0%, H→L 20.6%
T_3	3.0553	H-2→L 73.7%, H-3→L 19.2%

S_1	**3.1242**	**H→L 97.4%**
T_4	3.1495	H→L+1 68.4%, H-5→L+1 8.0%, H-4→L+1 6.2%
T_5	3.3715	H-3→L 56.8%, H-2→L 14.3%, H→L+2 5.6%, H→L 5.2%
S_2	**3.5507**	**H-2→L 76.9%, H-3→L 20.7%**
T_6	3.7133	H→L+2 29.2%, H-6→L 14.0%, H-1→L+2 9.1%
S_3	**3.7316**	**H→L+1 87.5%, H-1→L 9.4%**

Table S10. TD-DFT calculated singlet and triplet excited states transition configurations of **2NBCz-2-PhCOOH**.

Excited State	Energy (eV)	Transition configuration (%)
T_1	2.3810	H→L 78.3%, H-1→L 7.0%, H-3→L 6.2%
T_2	2.7550	H-2→L 86.9%, H-2→L+2 5.2%
T_3	3.0126	H→L+1 45.6%, H-1→L 31.2%, H→L 7.6%
T_4	3.1049	H-1→L 43.4%, H→L+1 35.4%
S_1	**3.1605**	**H→L 97.7%**
S_2	**3.3407**	**H-2→L 95.4%**
S_3	**3.4137**	**H→L+1 98.7%**
T_5	3.6242	H→L+2 63.5%, H-3→L 19.5%
T_6	3.7826	H-4→L+1 17.7%, H-1→L+1 10.6%, H-1→L+2 8.1%, H→L+5

7.7%, H→L+1 7.4%, H-5→L+3 7.2%, H-5→L+1 5.9%

References

[1] J. A. Li, J. Zhou, Z. Mao, Z. Xie, Z. Yang, B. Xu, C. Liu, X. Chen, D. Ren, H. Pan, G. Shi, Y. Zhang, Z. Chi, *Angew. Chem. Int. Ed.* **2018**, 57, 6449.
[2] Z. An, C. Zheng, Y. Tao, R. Chen, H. Shi, T. Chen, Z. Wang, H. Li, R. Deng, X. Liu, W. Huang, *Nat. Mater.* **2015**, 14, 685.
[3] H. Jin, X. Zhang, J. Ma, L. Bu, C. Qian, Z. Li, Y. Guan, M. Chen, Z. Ma, Z. Ma, *ACS Appl. Mater. Interfaces* **2023**, 15, 54732.