Electronic supporting information

Functional Tails Decisive Photoluminescence Emissions and the Advanced Applications in the Field of Time-Resolved Information Input and Erasure

Haowen Huang, Yasong Cao, Zhonghua Zhao, Jiatong Xu, Cheng Zeng, Richao Shen, Jiawei Lv, Ziqiang Lei and Hengchang Ma*

Key Laboratory of Polymer Materials of Gansu Province, Key Laboratory of Eco-Environment-Related Polymer Materials Ministry of Education, College of Chemistry and Chemical Engineering, Northwest Normal University, Lanzhou 730070, PR China

*E-mail: mahczju@hotmail.com

Table of Contents

1. EXPERIMENTAL SECTION

2. RESULTS

1 EXPERIMENTAL SECTION

1.1 Materials and Chemicals.

The regents used in experiments including *N*,*N*-dimethylformamide (DMF, 98%), ultrapure water (water purifier, Resistivity of 18 mΩ*cm), tetrahydrofuran (THF, 99%), petroleum ether (PE, 98%), ethyl acetate (EA, 98%), dichloromethane (DCM, 98%), hexane (98%), isopropanol (IPA, 99%), dimethyl sulfoxide (DMSO, 99%). Unless other noted, all reagents used in the experiments are purchased from commercial sources without further purification. The materials used in experiments including 9H-carbazole (Cz, 97%), thiourea (99%), 1-bromooctane (99%), 1,8-dibromooctane (99%), 8-bromooctan-1-ol (98%), 8-bromooctanoic acid (98%), potassium hydroxide (KOH, 99%), sodium hydroxide (NaOH, 99%). The progress of all reactions was monitored by TLC using glass plates precoated with silica gel 60 F254 to a thickness of 0.5 mm. Column chromatography is performed on a silica gel (400 mesh) using petroleum ether and dichloromethane as eluents. They are purchased from Energy Chemical, Bide Pharmaceuticals and MERYER.

1.2 Measurements and Methods.

^{1}H NMR (600 MHz), ^{13}C NMR (150 MHz) spectra is recorded on MERCURY spectrometer at 25 ^{o}C in $CDCl_3$ or DMSO-d_6. All chemical shifts (δ) are reported in ppm and coupling constants (J) in Hz. High resolution mass spectra (HRMS) are recorded using Thermoscientific Q Exactive instruments under electrospray ionization (ESI) conditions. UV-visible absorption spectra (UV) are recorded on a TU-1901 spectrometer. Solid-state quantum yield is measured using a Hamamatsu C11347 Quantaurus-QY integrating sphere. Steady-state fluorescence/phosphorescence spectra and excitation spectra are measured using Hitachi F-4600. The lifetime and time-resolved emission spectra are obtained on Edinburgh FLS 1000 fluorescence spectrophotometer equipped with a xenon arc lamp (Xe 900), a nanosecond hydrogen flash-lamp (nF 920), a microsecond flash-lamp (μF 900) respectively. X-ray crystallography is achieved using a SuperNova X-ray single crystal diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å) or Cu-Kα radiation (λ = 1.54184 Å) [2,3].

1.3 The synthesis route of Cz derivatives

Synthesis of 9-(8-bromooctyl)-9H-carbazole (Cz-C$_8$-Br). [1,4] Cz (5.00 g, 167 g/mol, 6.00 mmol), 1,8-dibromopropane (8.13 mL, 270 g/mol, 9.00 mmol) and KOH (5.00 g, 56 g/mol, 18.00 mmol) are added to a 250 mL round-bottom flask with 50 mL acetone as solvent. The mixture is stirred at 25 ^{o}C for 24 h. DCM is added and organic phase is washed by water for three times. Organic layer is dried over $MgSO_4$. The solvent is removed by rotary evaporation, and the residue is purified by flash column chromatography using PE/EA (V/V: 1/300) as eluent to give colorless oil as product with a yield of 62%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.14 (d, J = 7.7 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.44 (s, 2H), 7.26 (d, J = 14.8 Hz, 2H), 4.31 (d, J = 7.2 Hz, 2H), 3.40 (d, J = 13.7 Hz, 2H), 1.94 - 1.86 (m, 2H), 1.81 (d, J = 14.4 Hz, 2H), 1.41 (d, J = 22.5 Hz, 4H), 1.32 (s, 4H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.42, 125.58, 122.82, 120.35, 118.72, 108.63, 43.01, 33.93, 32.69, 28.91, 28.58, 28.03, 27.18 ppm. ESI$^+$ HRMS m/z calcd for $C_{20}H_{24}BrN$ 357.1078 [M].

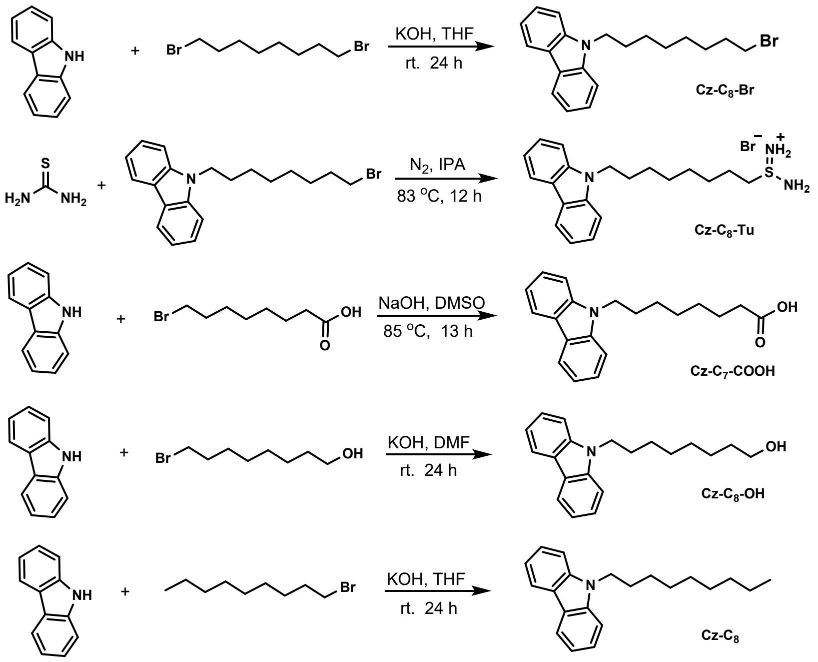
2-(8-(9H-carbazol-9-yl)octyl)thiouronium (Cz-C_8-Tu).[2,4] To a 100 mL round-bottom flask charged with Cz-C_8-Br (3.50 g, 357 g/mol, 20.00 mmol), thiourea (1.49 g, 76 g/mol, 40.00 mmol) with 40 mL IPA as solvent, the mixture solution is heated to 83 °C and reflux for 12 h under an argon atmosphere. The product is then filtered, washed three times with DCM, and placed in an oven at 45 °C overnight to give white solid powder as the title compounds with a yield of 92%. ^{1}H NMR (600 MHz, DMSO-*d*$_6$) δ 9.08 - 8.86 (m, 4H), 8.15 (d, *J* = 7.8 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.2 Hz, 2H), 7.20 (d, *J* = 7.5 Hz, 2H), 4.38 (d, *J* = 6.9 Hz, 2H), 3.07 (d, *J* = 7.2 Hz, 2H), 1.78 (d, *J* = 6.3 Hz, 2H), 1.52 (d, *J* = 6.6 Hz, 2H), 1.26 (td, *J* = 17.8, 14.9, 4.4 Hz, 8H) ppm. ^{13}C NMR (150 MHz, DMSO-*d*$_6$) δ 140.05, 125.71, 122.08, 120.33, 118.68, 109.29, 30.10, 28.71, 28.53, 28.34, 28.28, 27.78, 26.52 ppm. ESI$^+$ HRMS m/z calcd for $C_{21}H_{28}N_3S^+$ 354.1999 [M].

8-(9H-carbazol-9-yl)octanoic acid (Cz-C_7-COOH).[4] Cz (5.00 g, 167 g/mol, 25.10 mmol), NaOH (3.60 g, 40 g/mol, 75.00 mmol) are added to a 100 mL round-bottom flask with 25 mL DMSO as solvent. Heating the mixture to 85 °C and stirring continuously for 30 min, then 8-bromooctanoic acid (8.00 g, 222 g/mol, 30.20 mmol) is added portion by portion within 30 min. The mixture is cooled to room temperature and stired overnight, pouring into 200 mL water, filtering and collecting the filtrate. Then the solution is adjusted with hydrochloric acid (HCl) to pH = 3 to produce a white precipitate, the product is obtained by filtered and separated, washed three times with water, is dried at 40 °C with a yield of 65%. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 2H), 7.51 - 7.44 (m, 2H), 7.39 (s, 2H), 7.22 (d, *J* = 7.8 Hz, 2H), 4.30 (d, *J* = 14.4 Hz, 2H), 2.31 (d, *J* = 7.5 Hz, 2H), 1.88 (d, *J* = 14.0 Hz, 2H), 1.57 (d, *J* = 7.4 Hz, 2H), 1.33 (td, *J* = 14.9, 7.7 Hz, 7H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 179.60, 125.57, 122.81, 120.33, 118.71, 42.99, 33.85, 29.02, 28.88, 27.09, 24.53 ppm. ESI$^+$ HRMS m/z calcd for $C_{20}H_{23}NO_2$ 309.1688 [M].

Synthesis of 8-(9H-carbazol-9-yl)octanoic acid (Cz-C_8-OH).[1.3,4] KOH (3.00 g, 56 g/mol, 90.00 mmol) and carbazole (3.00 g, 167 g/mol, 30.00 mmol) are added to a 100 mL round-bottom flask with 20 mL DMF as solvent and slowly stirred at 25 °C for 1 h, then 8-bromooctan-1-ol (5.60 g, 209 g/mol, 45.00 mmol) is added to the mixture and slowly stirred at 25 °C for 24 h, the mixture is poured into water, filtered and air dried, then the sample is dissolved in DCM, $MgSO_4$ is used to remove the residual water, filtered again and concentrated under reduced pressure to obtain the crude product. The crude product is purified by column chromatography using PE/EA (V/V: 1/80) as eluent to afford the Cz-C_8-OH as yellow oil (4.2 g, yield 47.6 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.7 Hz, 2H), 7.49 - 7.45 (m, 2H), 7.42 (s, 2H), 7.23 (d, *J* = 7.9 Hz, 2H), 4.30 (d, *J* = 14.5 Hz, 2H), 3.61 (d, *J* = 13.2 Hz, 1H), 1.88 (d, *J* = 7.4 Hz, 2H), 1.55 - 1.51 (m, 2H), 1.39 (d, *J* = 7.7 Hz, 2H), 1.32 (dd, *J* = 20.5, 4.8 Hz, 7H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 122.81, 120.34, 118.66, 108.64, 62.93, 43.04, 32.68, 29.35, 28.93, 27.22, 25.63 ppm. ESI$^+$ HRMS m/z calcd for $C_{20}H_{26}NO$ 296.2010 [M+H].

Synthesis of 9-octyl-9H-carbazole (Cz-C_8).[4] KOH (3.00 g, 56 g/mol, 90.00 mmol) is added to a 100 mL round-bottom flask with 40 mL THF as solvent and mixed at room temperature for 15 min, then carbazole (3.00 g, 167 g/mol, 30.00 mmol) is added and slowly stirred for 1 h, 1-bromooctane (5.19 g, 192 g/mol, 45.00 mmol) is added to the mixture and slowly stirred at room temperature for 24 h, then the mixture is poured into water, filtered and air dried, then the sample is dissolved in DCM, $MgSO_4$ is used to remove the residual water, and the solution is concentrated under reduced pressure to obtain the crude product. The crude product is purified by column chromatography using PE/EA (V/V: 1/300) as eluent to afford the title compound as yellow oil (2.82 g, yield 56.2 %). ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.16 (d, J = 7.7 Hz, 2H), 7.54 - 7.49 (m, 2H), 7.45 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 7.2 Hz, 2H), 4.32 (d, J = 7.3 Hz, 2H), 1.94 -1.88 (m, 2H), 1.46 - 1.25 (m, 12H), 0.92 (s, 3H) ppm. ^{13}C NMR (150 MHz, $CDCl_3$) δ 140.50, 125.61, 122.89, 120.39, 118.75, 108.71, 108.71, 43.11, 31.88, 29.46, 29.03, 27.39, 22.69, 14.15 ppm.

2 RESULTS



Scheme S1. The sythesis route of Cz-C_8-Br, Cz-C_8-Tu, Cz-C_7-COOH, Cz-C_8-OH and Cz-C_8.

2.1 NMR data spectra

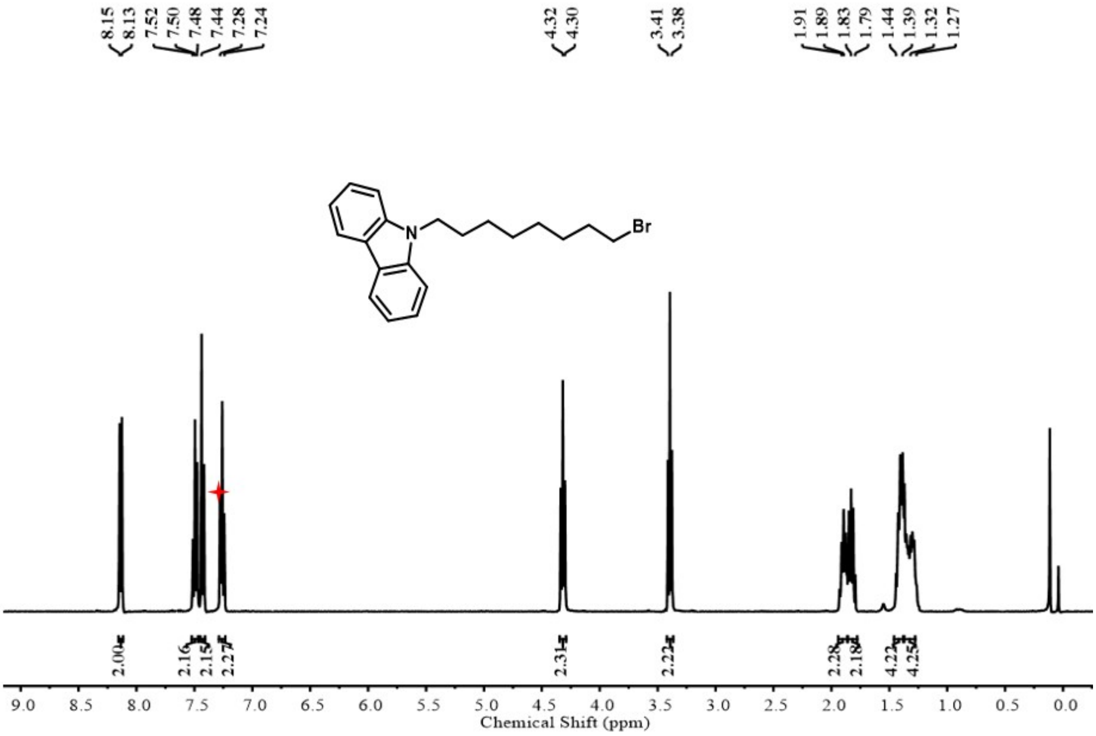


Figure S1. ^{1}H NMR spectra of Cz-C_8-Br (in $CDCl_3$).

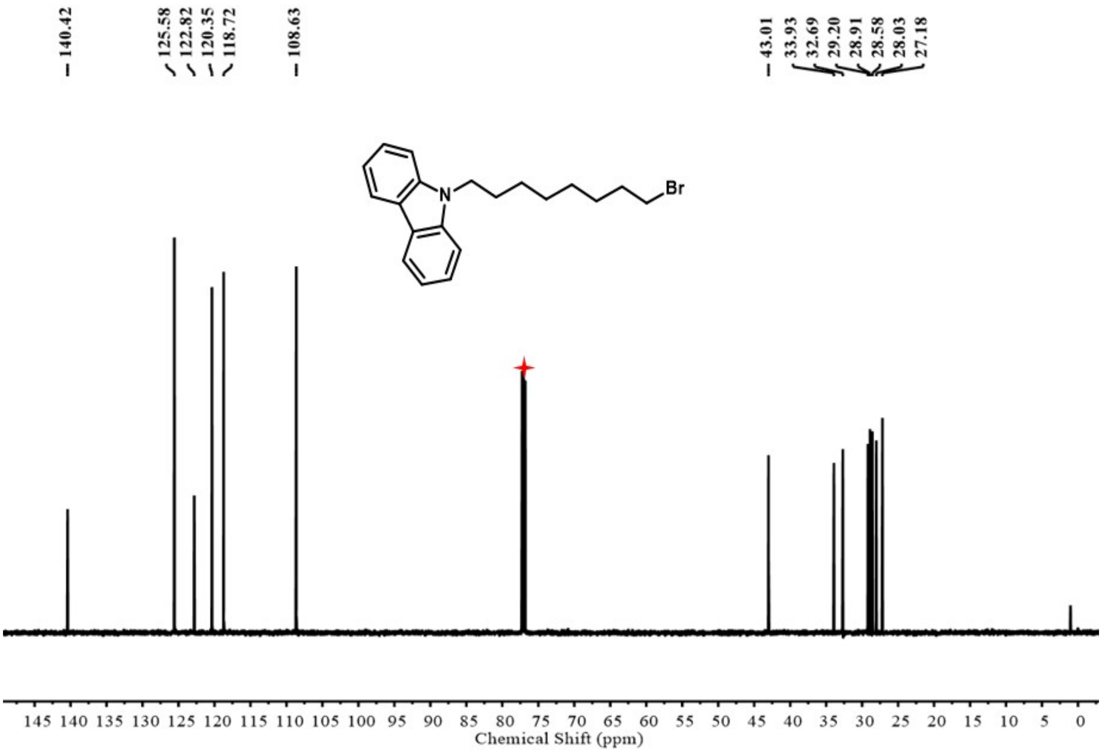


Figure S2. ^{13}C NMR spectra of Cz-C_8-Br (in $CDCl_3$).

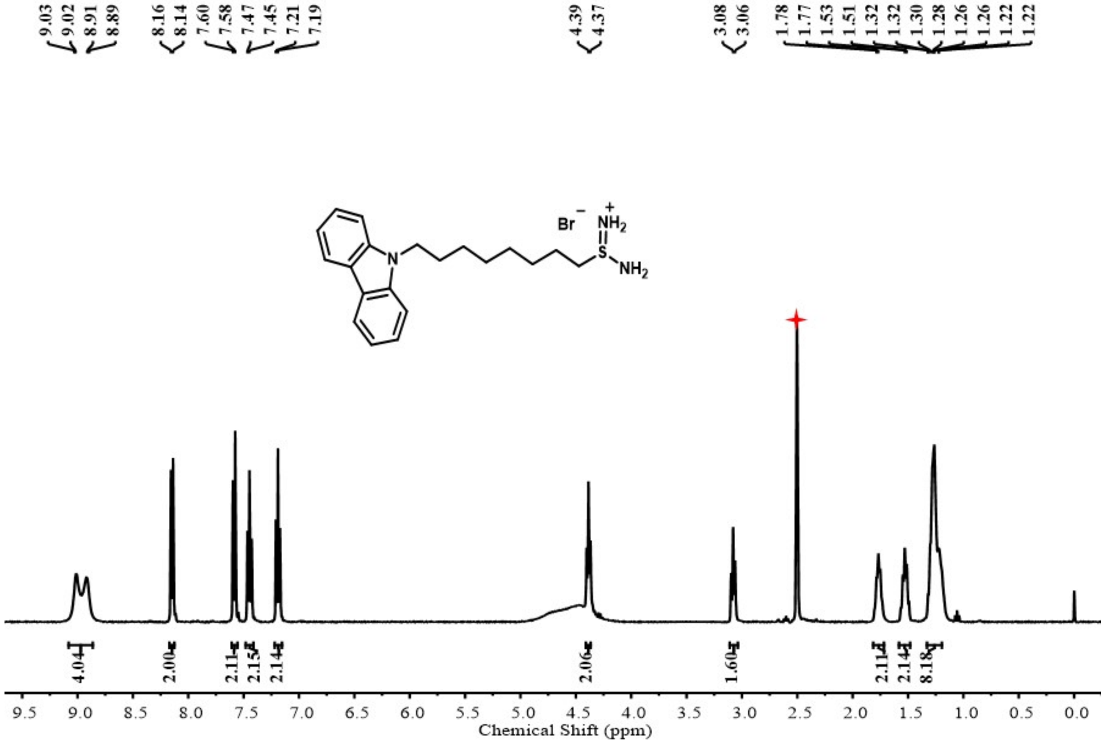


Figure S3. ^1H NMR spectra of Cz-C_8-Tu (in DMSO-*d*$_6$).

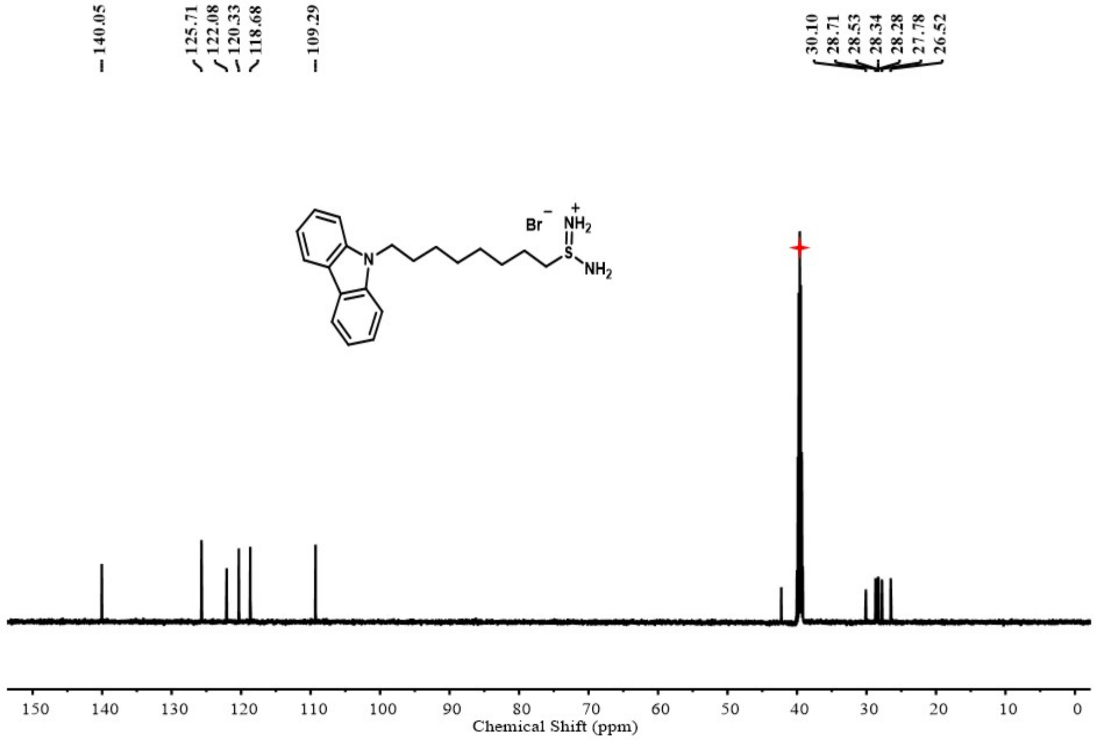


Figure S4. ^{13}C NMR spectra of Cz-C_8-Tu (in DMSO-*d*$_6$).

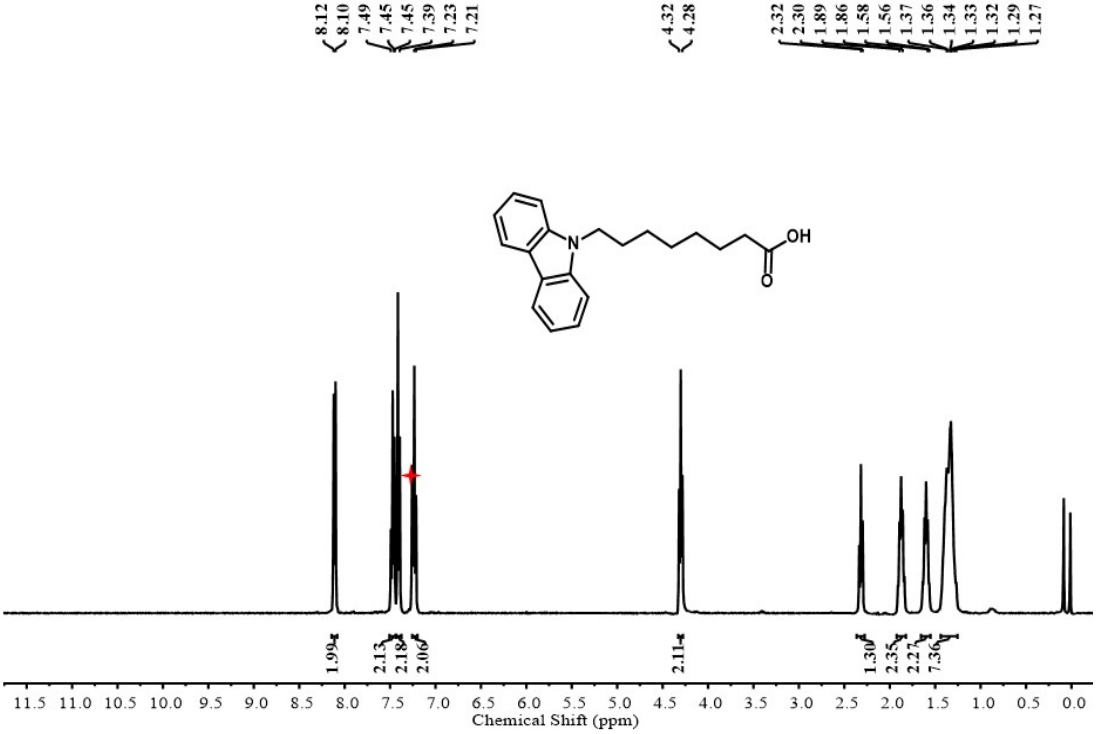


Figure S5. ^{1}H NMR spectra of **Cz-C$_7$-COOH** (in CDCl$_3$).

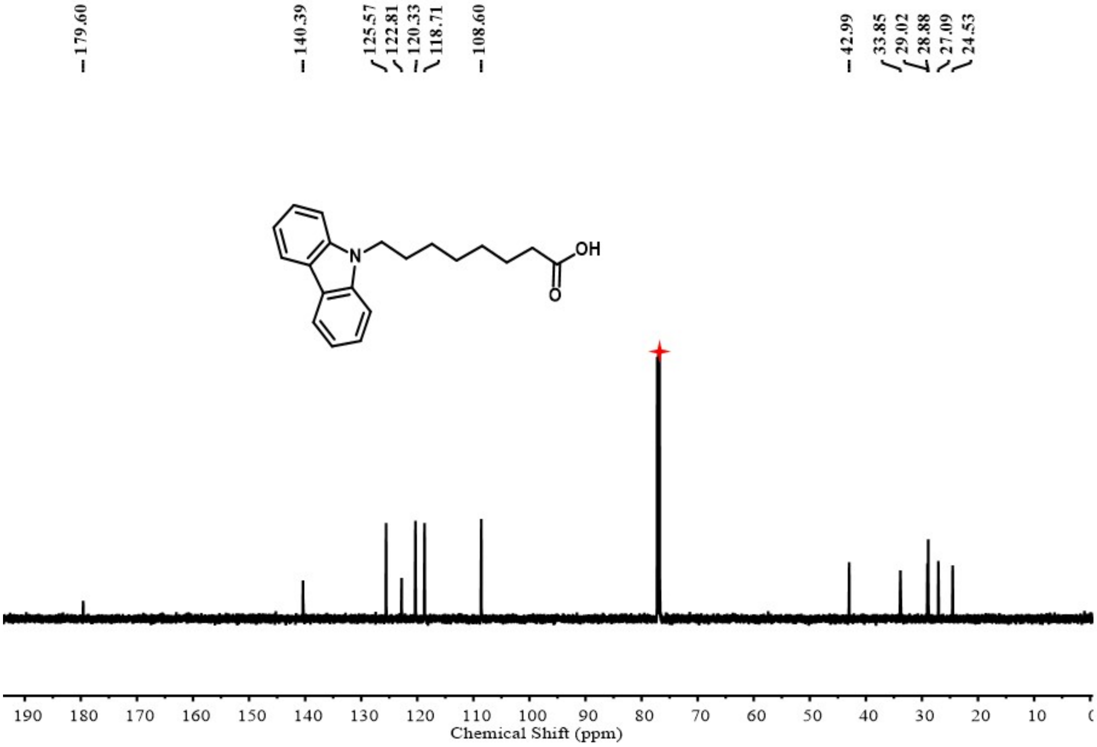


Figure S6. ^{13}C NMR spectra of Cz-C$_7$-COOH (in CDCl$_3$).

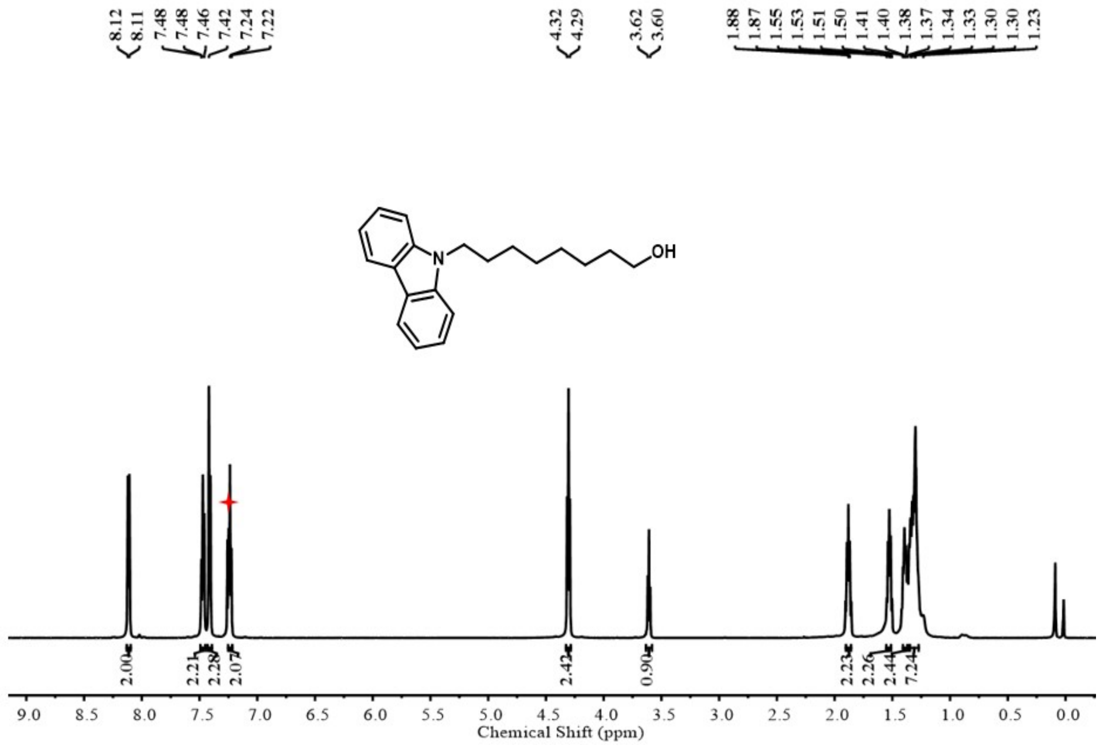


Figure S7. ^{1}H NMR spectra of Cz-C_8-OH (in $CDCl_3$).

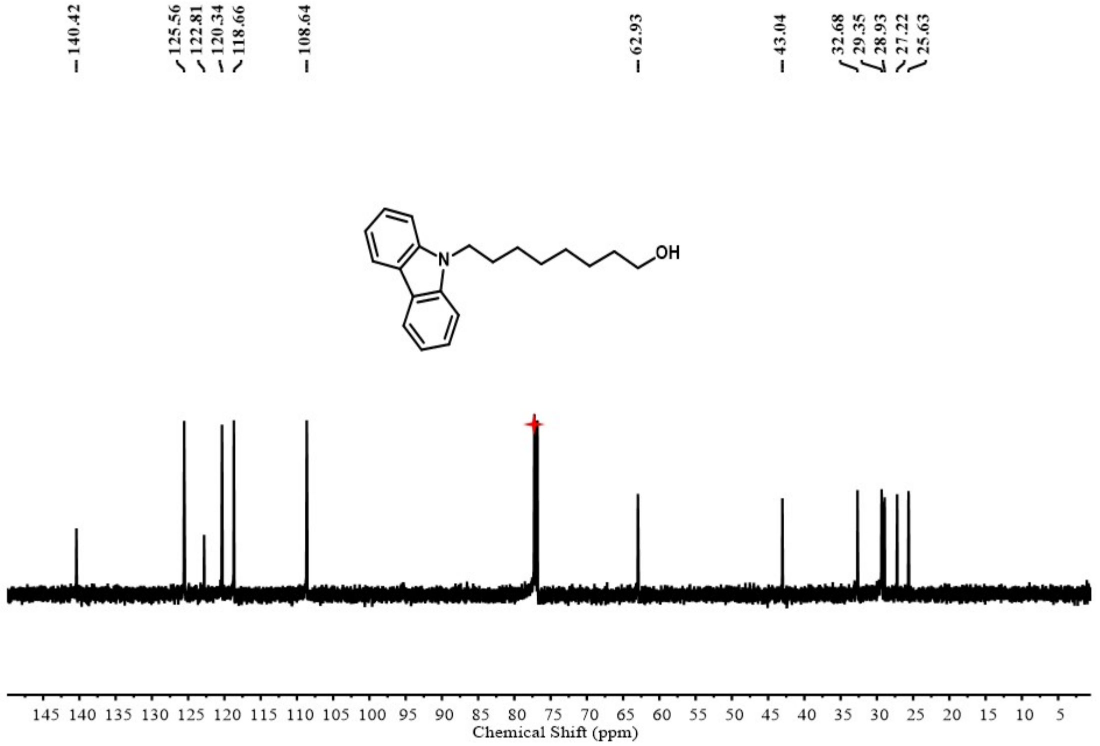


Figure S8. ^{13}C NMR spectra of Cz-C_8-OH (in $CDCl_3$).

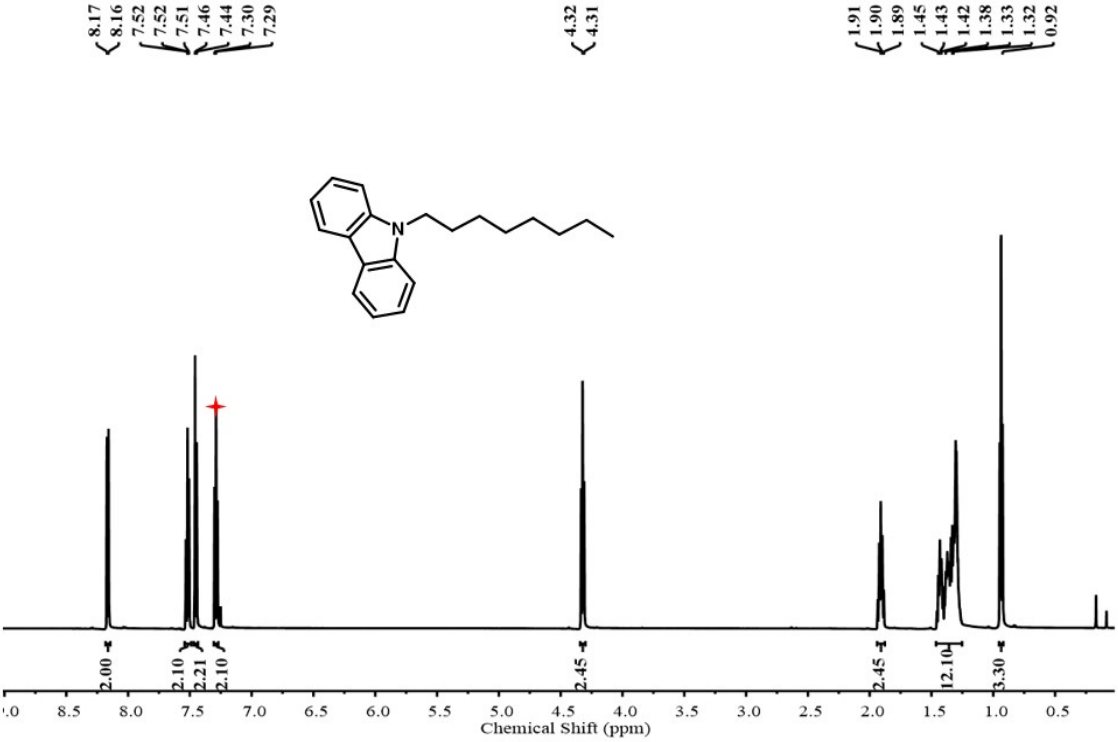


Figure S9. ^{1}H NMR spectra of Cz-C_8 (in $CDCl_3$).

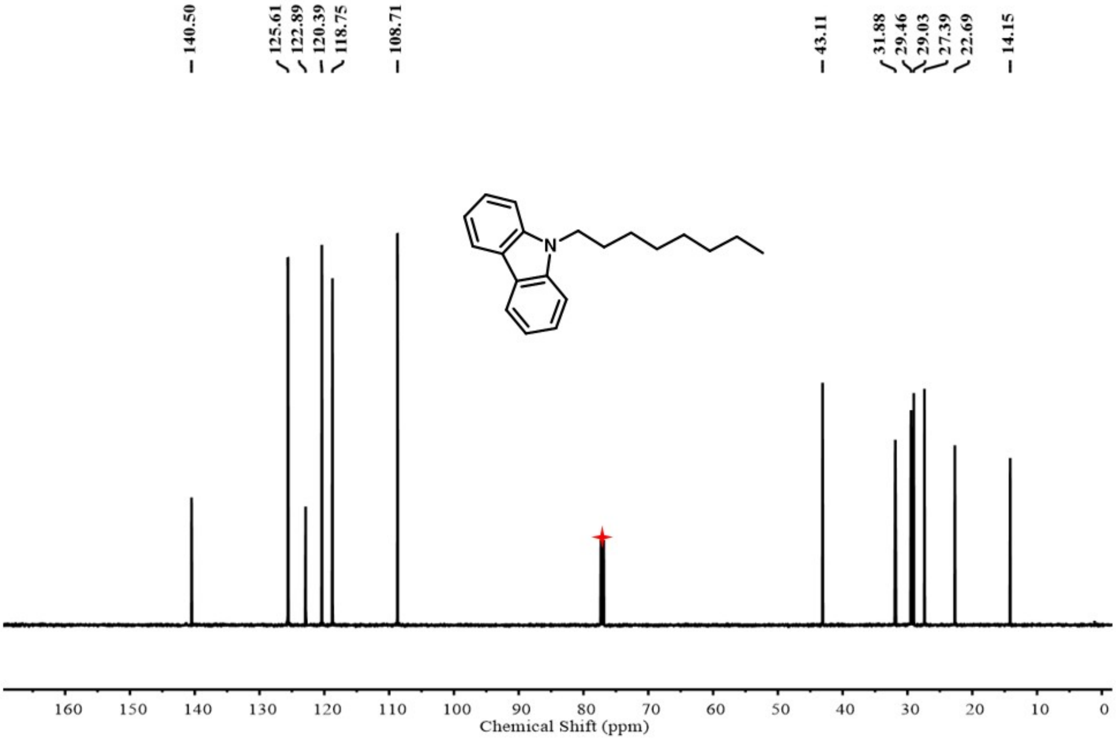
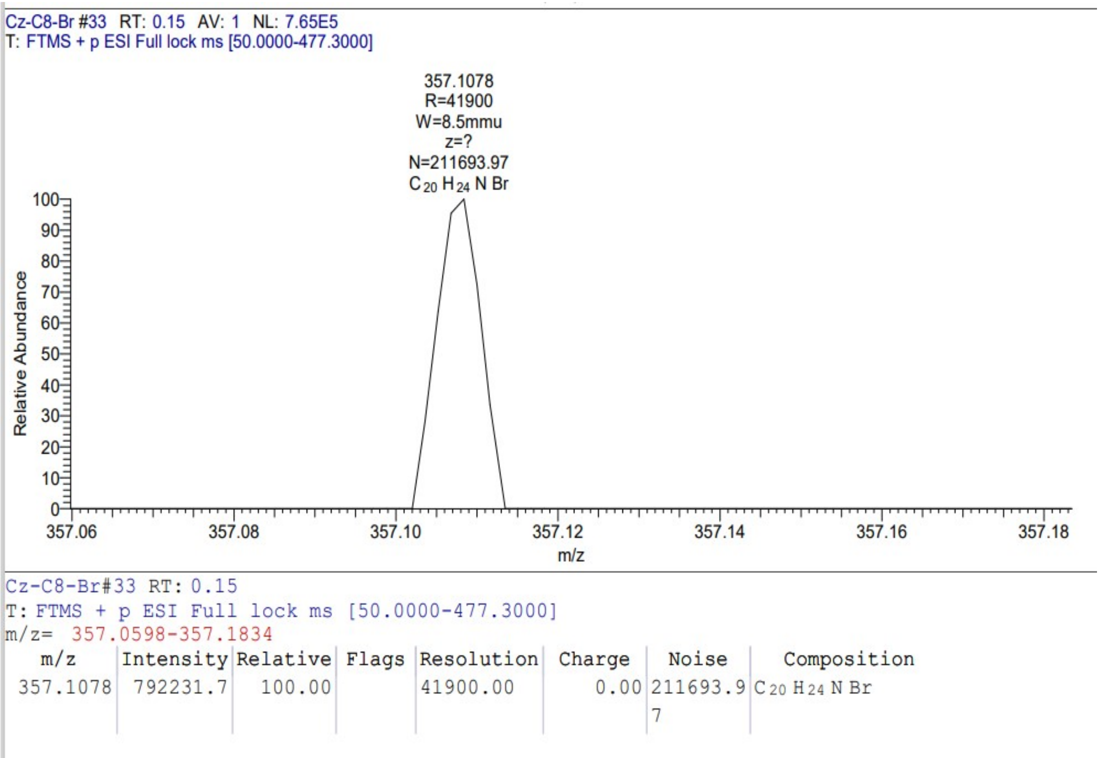


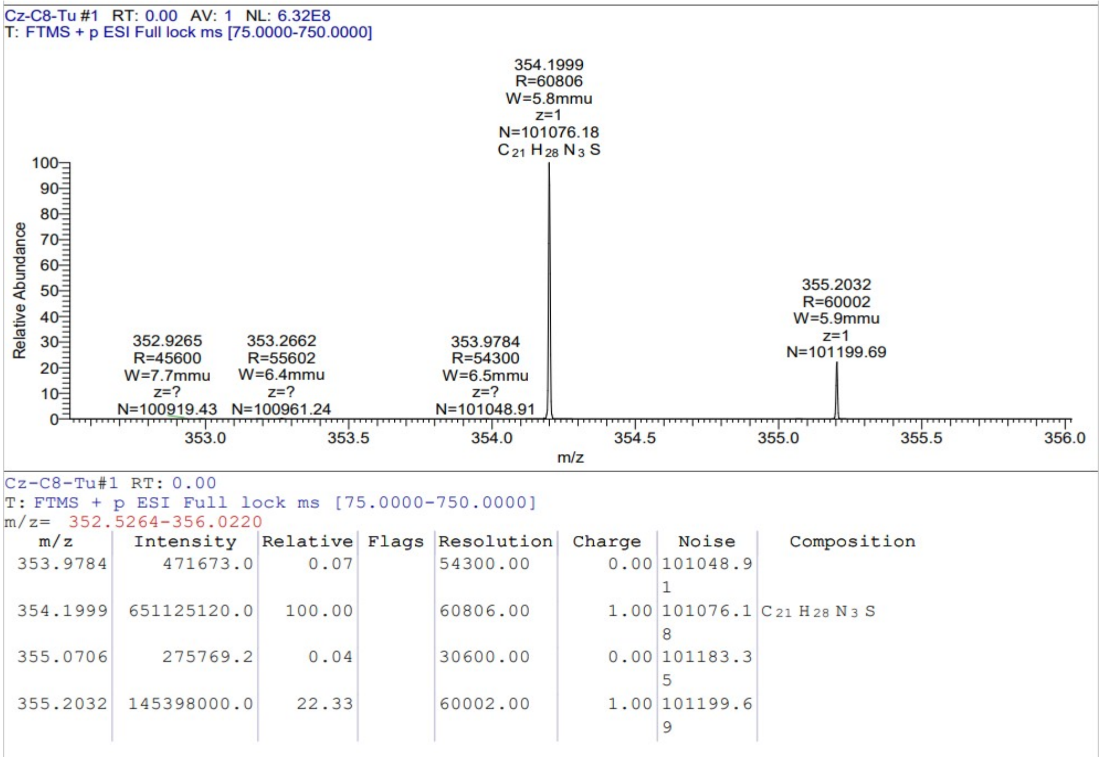
Figure S10. ^{13}C NMR spectra of Cz-C_8 (in $CDCl_3$).

2.2 HRMS data spectra



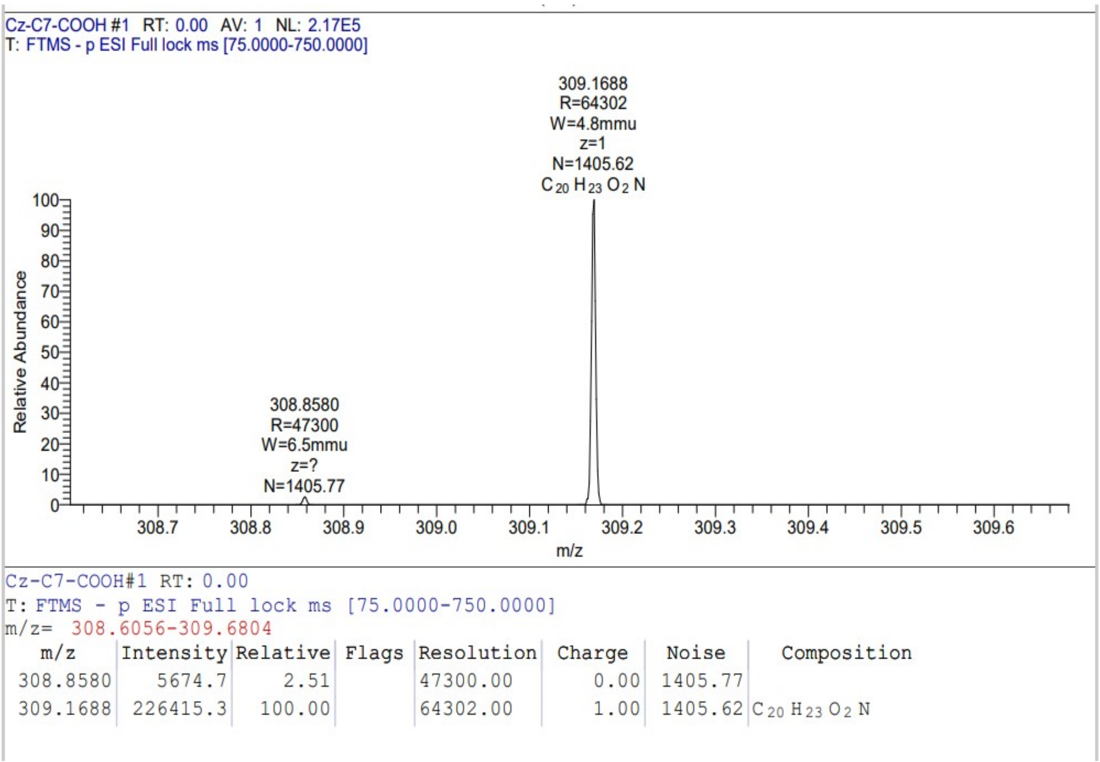
```
Cz-C8-Br#33 RT: 0.15
T: FTMS + p ESI Full lock ms [50.0000-477.3000]
m/z= 357.0598-357.1834
   m/z    Intensity Relative Flags Resolution  Charge   Noise   Composition
357.1078  792231.7   100.00        41900.00      0.00 211693.9 C20 H24 N Br
                                                      7
```

Figure S11. HRMS spectrum of compound Cz-C_8-Br.



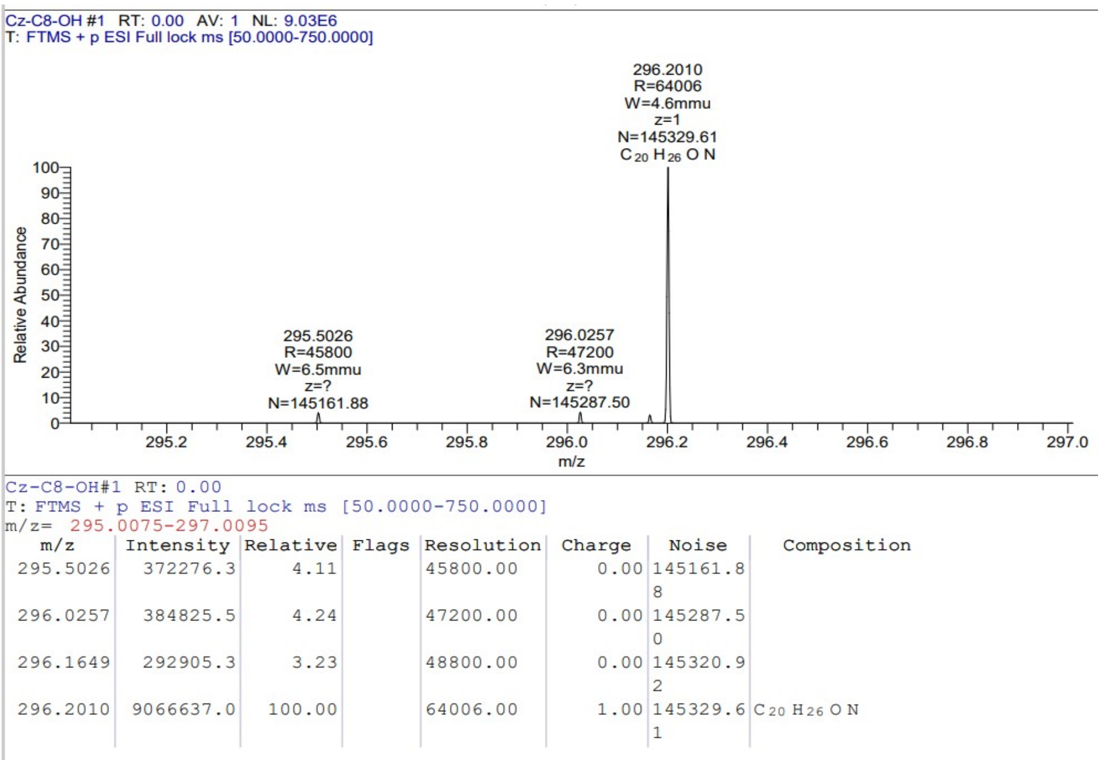
```
Cz-C8-Tu#1 RT: 0.00
T: FTMS + p ESI Full lock ms [75.0000-750.0000]
m/z= 352.5264-356.0220
   m/z       Intensity  Relative Flags Resolution  Charge   Noise     Composition
353.9784      471673.0      0.07       54300.00      0.00 101048.9
                                                          1
354.1999   651125120.0    100.00       60806.00      1.00 101076.1  C21 H28 N3 S
                                                          8
355.0706      275769.2      0.04       30600.00      0.00 101183.3
                                                          5
355.2032   145398000.0     22.33       60002.00      1.00 101199.6
                                                          9
```

Figure S12. HRMS spectrum of compound Cz-C_8-Tu.



```
Cz-C7-COOH#1 RT: 0.00
T: FTMS - p ESI Full lock ms [75.0000-750.0000]
m/z= 308.6056-309.6804
   m/z    Intensity Relative Flags Resolution  Charge   Noise    Composition
 308.8580    5674.7     2.51       47300.00      0.00  1405.77
 309.1688  226415.3   100.00       64302.00      1.00  1405.62 C 20 H 23 O 2 N
```

Figure S13. HRMS spectrum of compound Cz-C$_7$-COOH.



```
Cz-C8-OH#1 RT: 0.00
T: FTMS + p ESI Full lock ms [50.0000-750.0000]
m/z= 295.0075-297.0095
   m/z    Intensity  Relative Flags Resolution   Charge  Noise    Composition
 295.5026   372276.3     4.11       45800.00       0.00 145161.8
                                                        8
 296.0257   384825.5     4.24       47200.00       0.00 145287.5
                                                        0
 296.1649   292905.3     3.23       48800.00       0.00 145320.9
                                                        2
 296.2010  9066637.0   100.00       64006.00       1.00 145329.6 C 20 H 26 O N
                                                        1
```

Figure S14. HRMS spectrum of compound Cz-C$_8$-OH.

2.3 Fluorescence and phosphorescence spectra studies

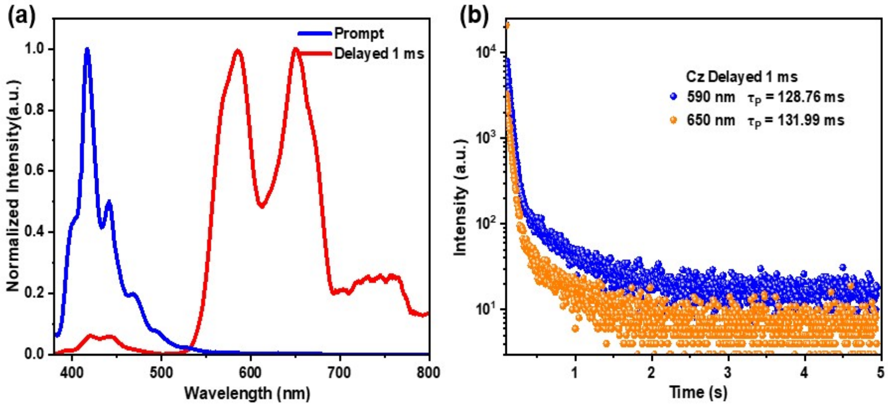


Figure S15. (a) Prompt and delayed PL spectra of Cz under ambient conditions. **(b)** Time-resolved phosphorescent decay curves of Cz at 550 nm and 600 nm under ambient conditions.

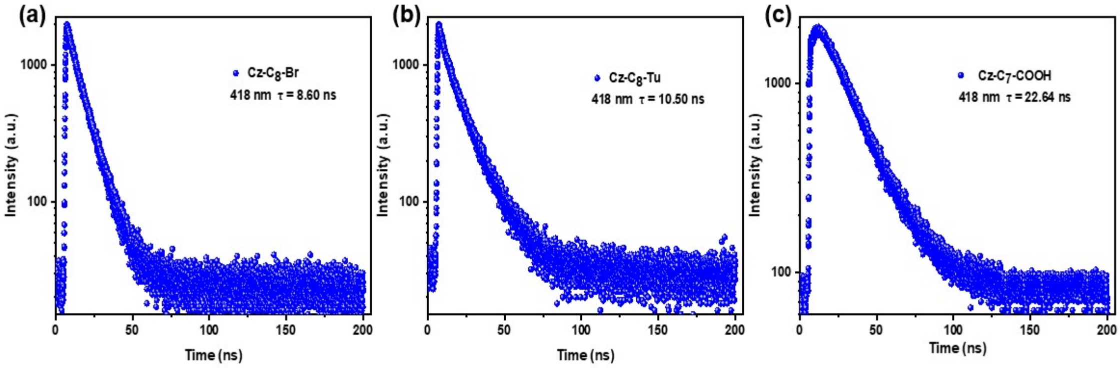


Figure S16. Time-resolved fluorescent decay curves of **(a)** Cz-C_8-Br, **(b)** Cz-C_8-Tu and **(c)** Cz-C_7-COOH under ambient conditions.

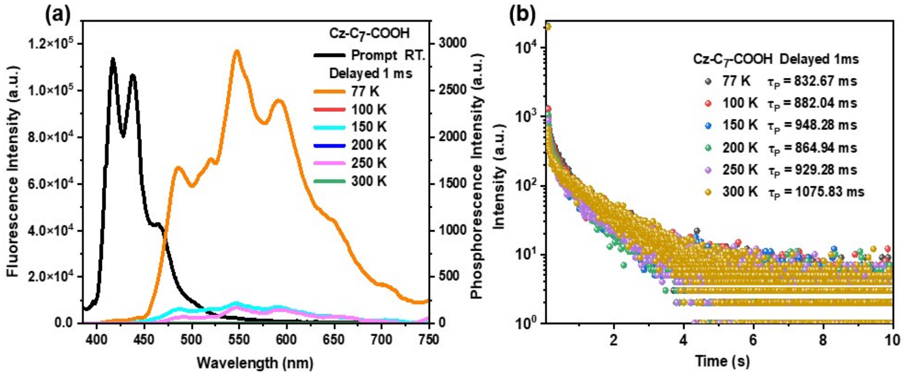


Figure S17. (a) Prompt and delayed PL spectra of Cz-C_7-COOH at 77 - 300 K. **(b)** Time-resolved phosphorescent decay curves of Cz-C_7-COOH at 77 - 300 K.

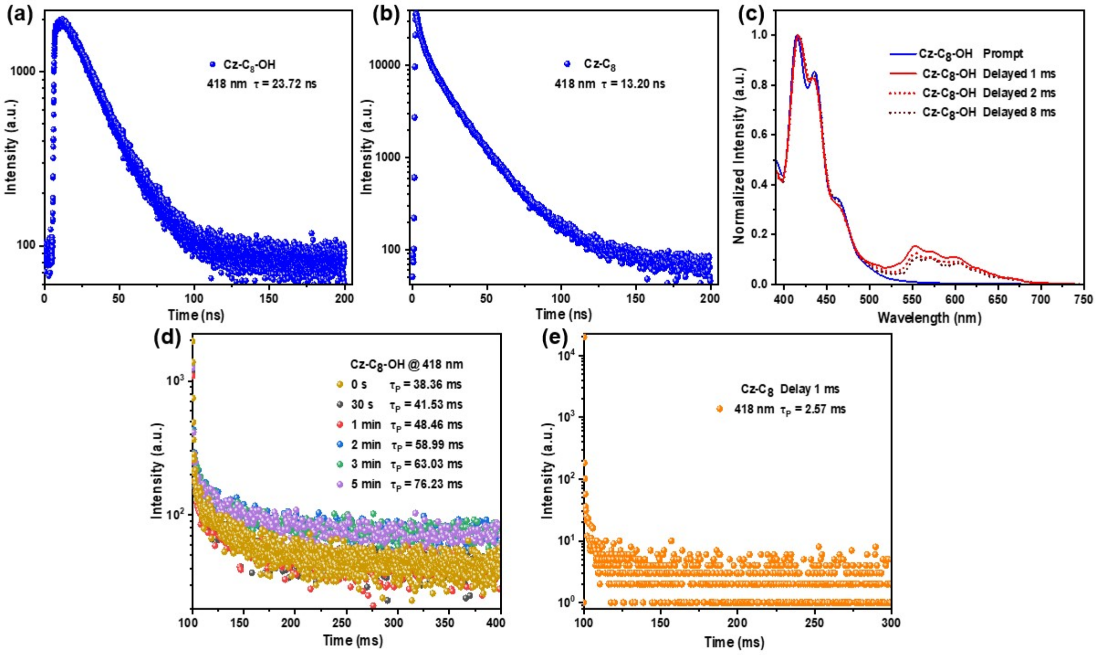


Figure S18. Time-resolved fluorescent decay curves of **(a)** Cz-C_8-OH, **(b)** Cz-C_8. **(c)** Prompt and delay different times (1 ms, 2 ms, 8 ms) PL spectrum of Cz-C_8-OH under ambient conditions. **(d)** Lifetime decay profiles at 418 nm after different photoactivation times ranging from 0 to 5 min under ambient conditions. **(e)**Time-resolved phosphorescent decay curves of Cz-C_8 at 418 nm under ambient conditions.

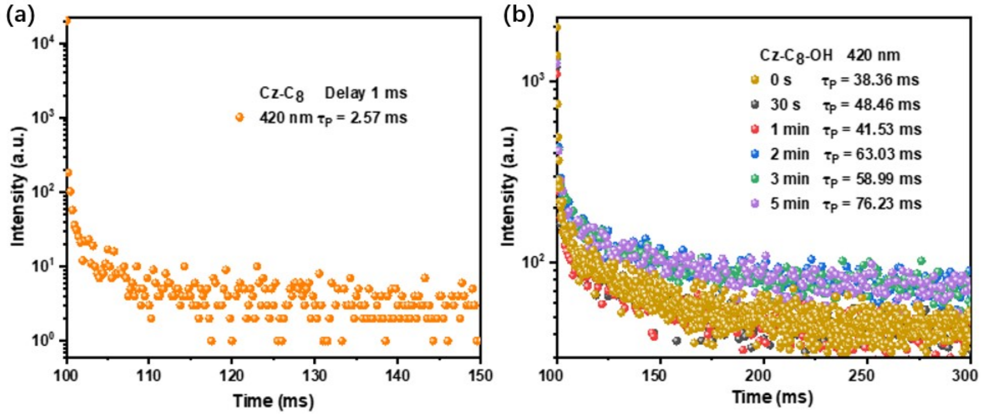


Figure S19. DF lifetime decay curves of **(a)** Cz-C_8 and **(b)** Cz-C_8-OH under ambient conditions (λ_{ex} = 360 nm, delayed = 1 ms).

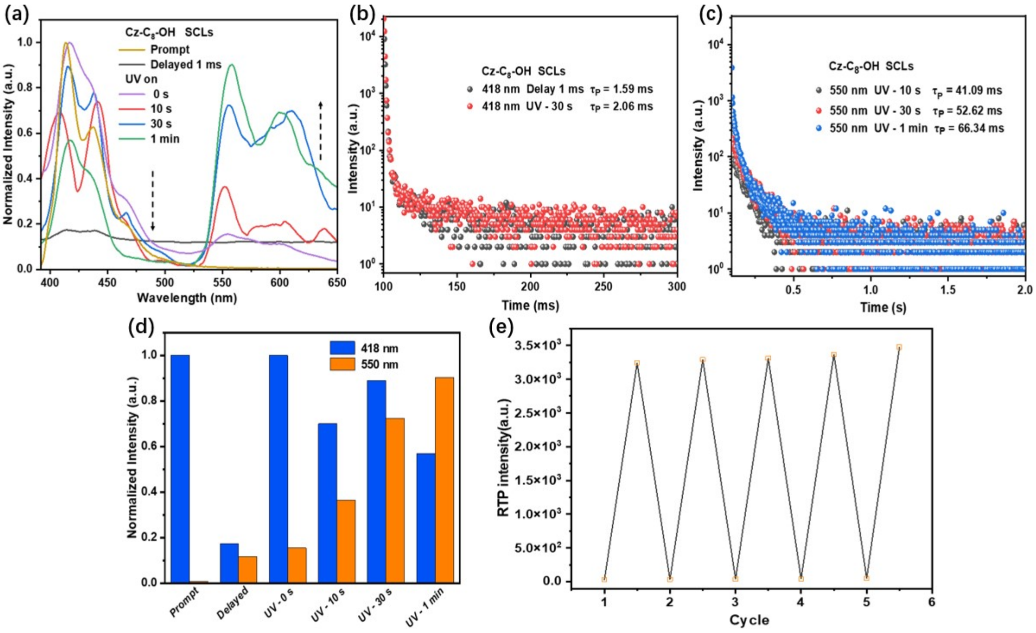


Figure S20. The photophysical properties of Cz-C_8-OH (SCLs). **(a)** Delay spectra of Cz-C_8-OH (SCLs) irradiated with photoluminescence and UV light for different times and **(b)** corresponding bar graphs (λ_{ex} = 360 nm, delayed = 1 ms) under ambient conditions; （**c**）Reversibility investigation of the Cz-C_8-OH(SCLs) by monitoring phosphorescence emission at 550 nm after repeated photoactivation and heating; Lifetime decay curves of Cz-C_8-OH(SCLs) at **(d)** 418 nm and **(e)** 550 nm under ambient conditions.

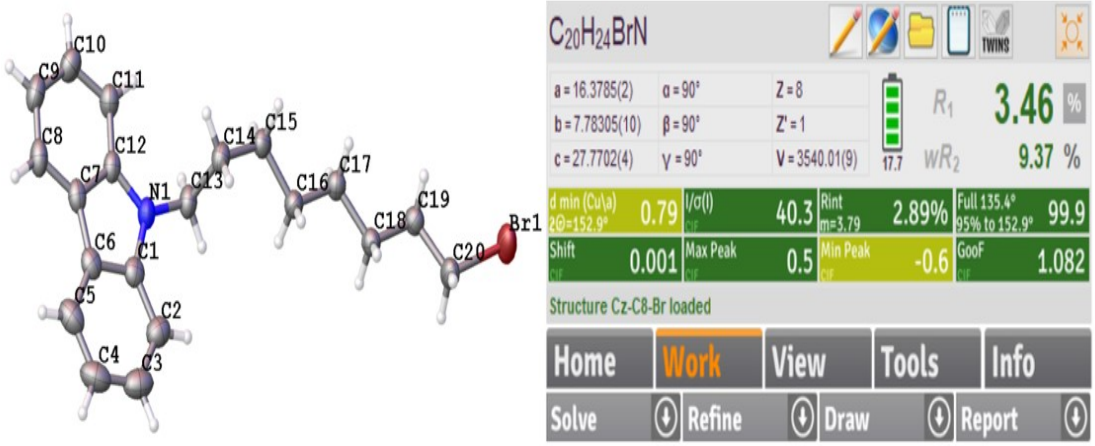
2.4 Single crystal analysis

Table S1.

Name	**Cz-C$_8$-Br**	**Cz-C$_7$-COOH**	**Cz-C$_8$-Tu**
Formula	$C_{20}H_{24}BrN$	$C_{20}H_{23}NO_2$	$C_{21}H_{28}N_3S,Br$
Wavelength(Å)	1.54184	0.71073	1.54184
Space Group	P *b c a*	P-1	P 21/c
Cell Lengths (Å)	**a** 16.37740 (3)	**a** 8.07454 (4)	**a** 13.7731 (1)
	b 7.78421 (13)	**b** 10.62940 (6)	**b** 9.33470 (1)
	c 27.76550 (6)	**c** 11.24710 (7)	**c** 16.8784 (2)
Cell Angles (°)	α 90.00	α 102.30 (5)	α 90.00
	β 90.00	β 109.67 (5)	β 98.84 (1)
	γ 90.00	γ 103.45 (5)	γ 90.00
Cell Vloume (Å^3)	3539.68 (12)	838.08 (9)	2144.27 (4)
Z	8	2	4
Density (g/cm^3)	1.345	1.226	1.346
F(000)	1488.0	332.0	904.0
h$_{max}$,k$_{max}$,l$_{max}$	20,4,30	10,15,14	17,11,21
R（all data）	$R_1 = 0.0388$	$R_1 = 0.0771$	$R_1 = 0.0314$
	$wR_2 = 0.0937$	$wR_2 = 0.1252$	$wR_2 = 0.1139$
Temperature(K)	150 (10)	303.8 (10)	150
CCDC	2305881	2305879	2305882

Crystal data of Cz-C$_8$-Br, Cz-C$_7$-COOH and Cz-C$_8$-Tu.

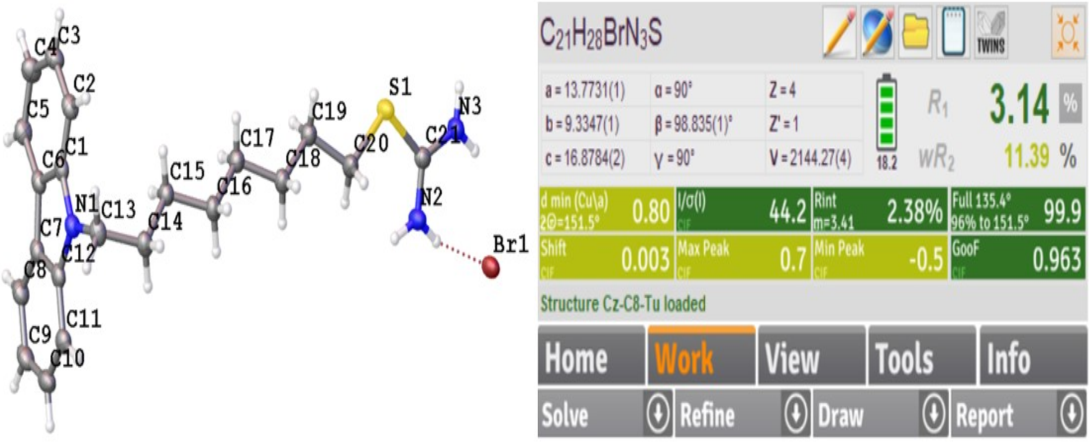
2.5 Research data of molecular structure



$C_{20}H_{24}BrN$

a = 16.3785(2) α = 90° Z = 8
b = 7.78305(10) β = 90° Z' = 1
c = 27.7702(4) γ = 90° V = 3540.01(9)
17.7
R_1 3.46 %
wR_2 9.37 %
d min (Cu\a) 2Θ=152.9° 0.79
I/σ(I) 40.3
Rint m=3.79 2.89%
Full 135.4° 95% to 152.9° 99.9
Shift 0.001
Max Peak 0.5
Min Peak -0.6
GooF 1.082
Structure Cz-C8-Br loaded

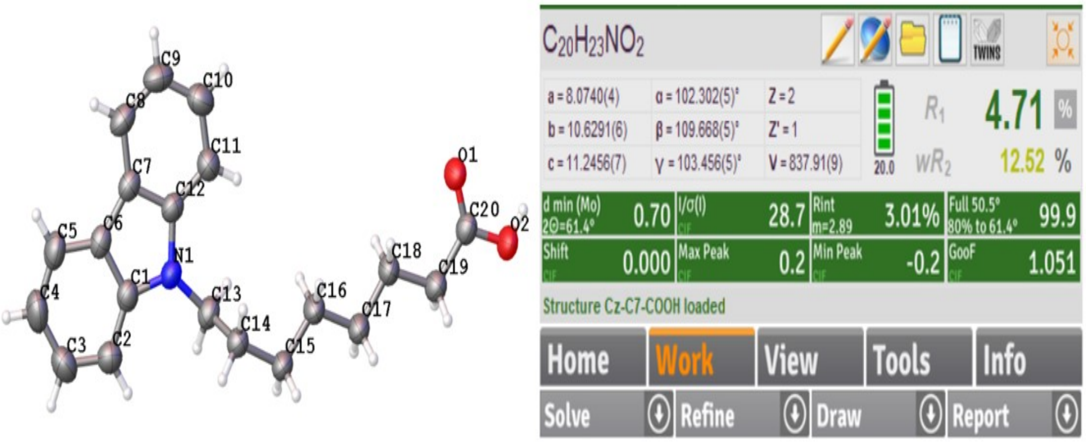
Figure S21. ORTEP-style illustration of Cz-C$_8$-Br with probability ellipsoids **(left)** and corresponding crystal resolution **(right)**.



$C_{21}H_{28}BrN_3S$

a = 13.7731(1) α = 90° Z = 4
b = 9.3347(1) β = 98.835(1)° Z' = 1
c = 16.8784(2) γ = 90° V = 2144.27(4)
18.2
R_1 3.14 %
wR_2 11.39 %
d min (Cu\a) 2Θ=151.5° 0.80
I/σ(I) 44.2
Rint m=3.41 2.38%
Full 135.4° 96% to 151.5° 99.9
Shift 0.003
Max Peak 0.7
Min Peak -0.5
GooF 0.963
Structure Cz-C8-Tu loaded

Figure S22. ORTEP-style illustration of Cz-C$_8$-Tu with probability ellipsoids **(left)** and corresponding crystal resolution **(right)**.



$C_{20}H_{23}NO_2$

a = 8.0740(4) α = 102.302(5)° Z = 2
b = 10.6291(6) β = 109.668(5)° Z' = 1
c = 11.2456(7) γ = 103.456(5)° V = 837.91(9)
20.0
R_1 4.71 %
wR_2 12.52 %
d min (Mo) 2Θ=61.4° 0.70
I/σ(I) 28.7
Rint m=2.89 3.01%
Full 50.5° 80% to 61.4° 99.9
Shift 0.000
Max Peak 0.2
Min Peak -0.2
GooF 1.051
Structure Cz-C7-COOH loaded

Figure S23. ORTEP-style illustration of Cz-C$_7$-COOH with probability ellipsoids **(left)** and corresponding crystal resolution **(right)**.

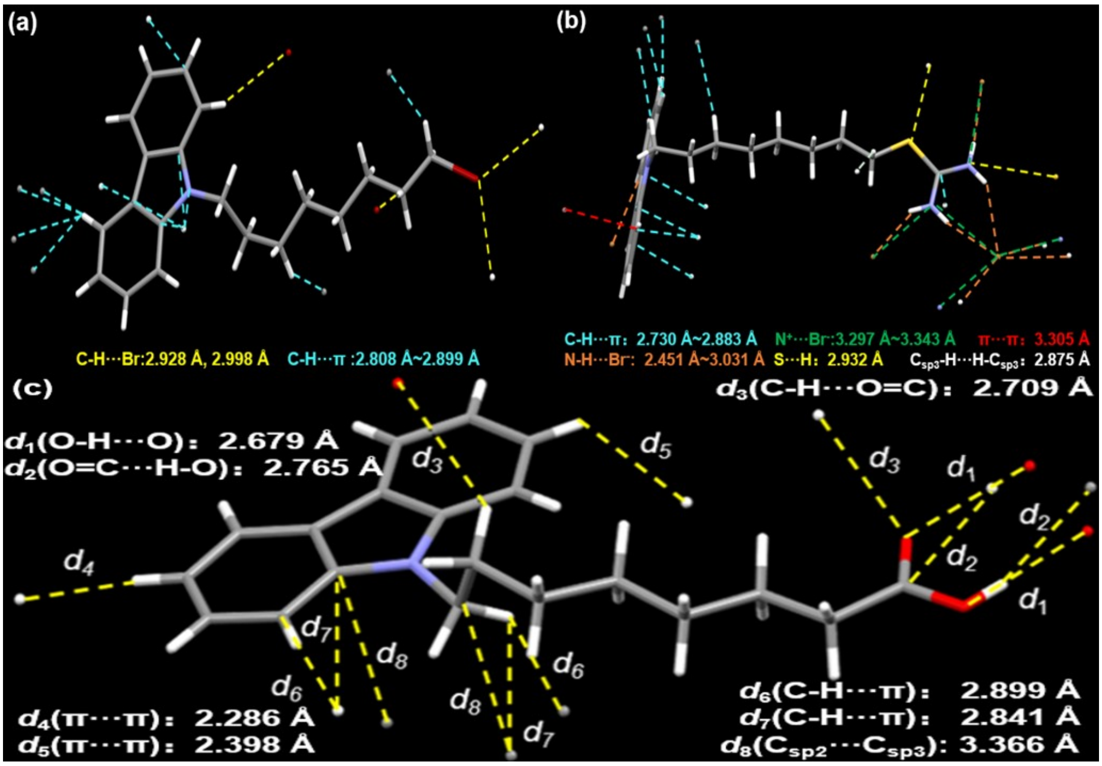


Figure S24. Molecular configuration of **(a)** Cz-C_8-Br, **(b)** Cz-C_8-Tu and **(c)** Cz-C_7-COOH in single crystals.

2.6 Pattern display and information encryption application

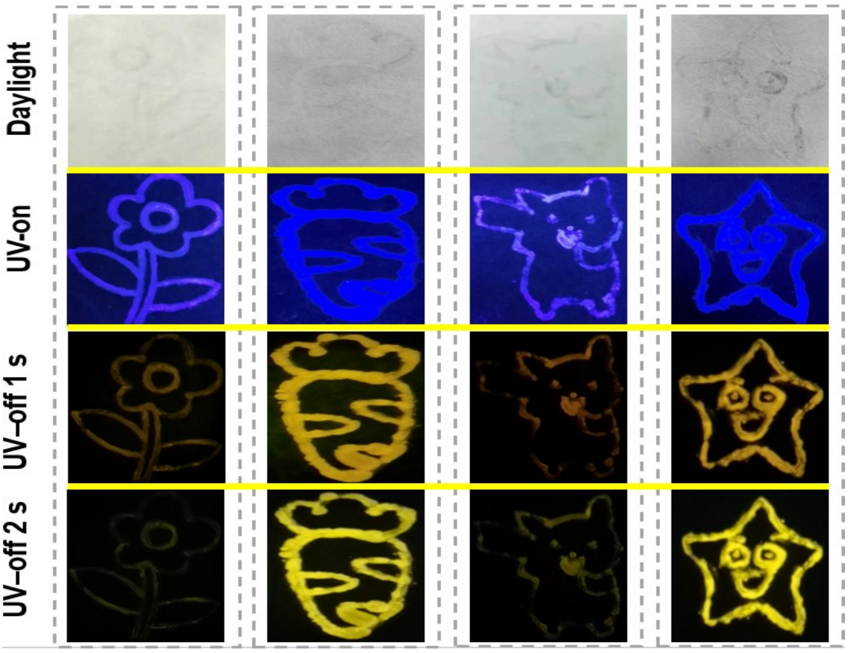


Figure S25. The 'flower', 'carrot', 'cartoon' and 'star' are displayed in exquisite patterns of fluorescence and afterglow under the condition of daylight, UV lamp on or off , respectively.

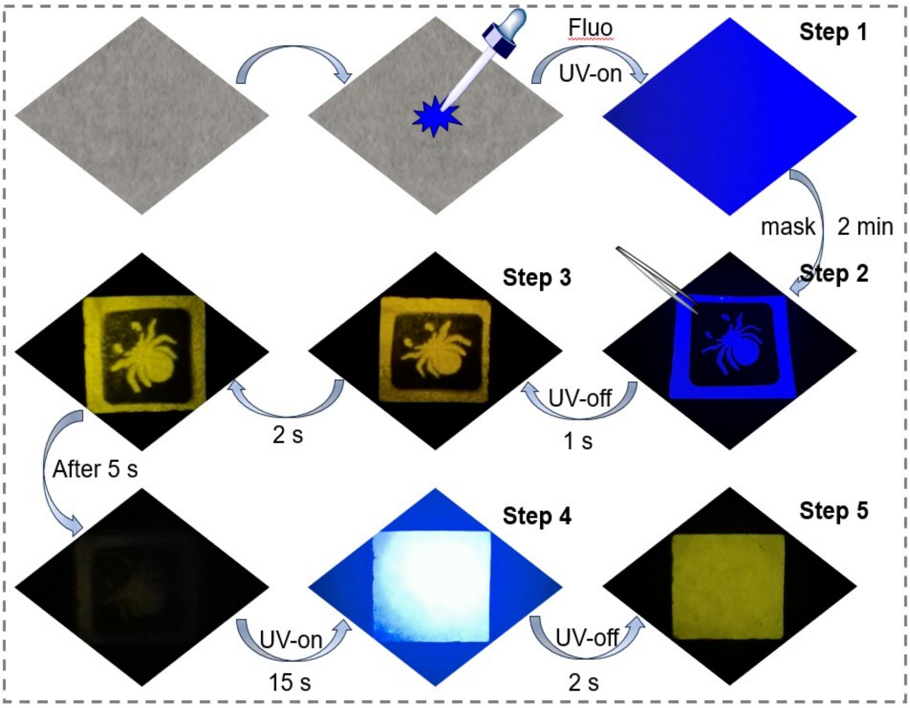


Figure S26. Data input and erasure processes that rely on UV lamp excitation.

3 REFERENCES

1 Q. Huang, X. Mei, Z. Xie, D. Wu, S. Yang, W. Gong, Z. Chi, Z. Lin and Q. Ling, *J. Mater. Chem. C*, 2019, **7**, 2530-2534.

2 J.-C. Yang, Z. Fu, H. Ma, T. Wang, Q. Li, K. Wang, L. Wu, P. Chen, H.-T. Feng, B. Z. Tang, *ACS Mater. Lett.* 2023, **5** (5), 1441-1449.

3 X. Wang, H. Ma, M. Gu, C. Lin, N. Gan, Z. Xie, H. Wang, L. Bian, L. Fu, S. Cai, Z. Chi, W. Yao, Z. An, H. Shi, W. Huang. *Chem. Mater.* 2019, **31** (15), 5584-5591.

4 S. Samal, Barry C. Thompson, *ACS Macro Lett.* 2021, **10** (6), 720-726.