Electronic Supplementary Information (ESI)

Ultralong Blue Room-temperature Phosphorescence by Cycloalkyl Engineering

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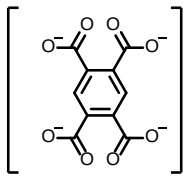
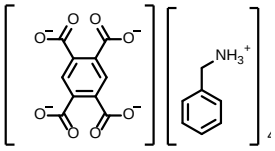
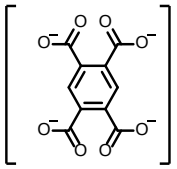
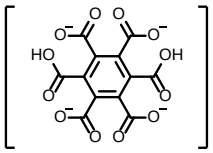
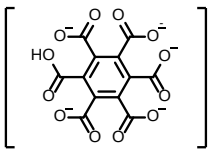
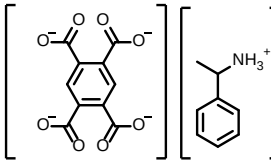
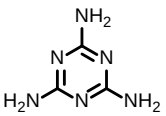
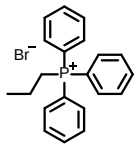
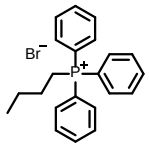
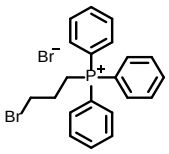
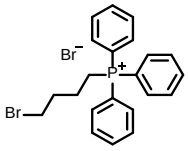
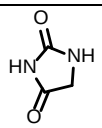
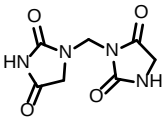
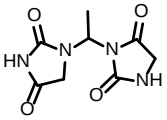
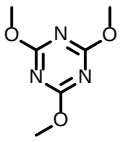
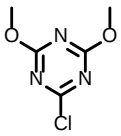
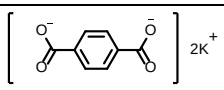
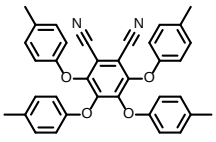
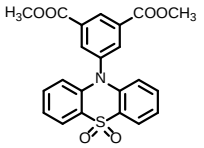
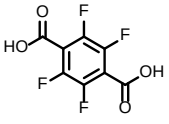
Table S1. Phosphorescence wavelengths (λ_{em}) and lifetimes (τ) of pure organic materials with blue RTP emission in literatures reported previously (Phosphorescence wavelengths :400~485 nm).

Sample	Molecular structure	λ_{em} (nm)	τ (ms)	References
B-1 (TSP)		447	168.39	
B-2 (TMP)		464	136.29	
B-3 (TPP)		420	132.61	*Nat. Mater.*, 2021, 20, 1539-1544
B-4 (HSM)		407	199.17	
B-5 (HPM)		410	101.20	
B-6 (TNP)		454	184.91	
B-7 (MEL)		465	580	*Anal. Chem.*, 2021, 93, 4075-4083

B-8 (TPP-3CB)		480	157	
B-9 (TPP-4CB)		480	200	
B-10 (TPP-3C2B)		480	159	*Adv. Mater.*, 2020, 32, 2001026
B-11 (TPP-4C2B)		480	164	
B-12 (HA)		456	1113.0	
B-13 (MDHA)		450	928.2	*Mater. Horiz.*, 2020, 7, 2105-2112
B-14 (EDHA)		450	491.5	
B-15 (TMOT)		465	580	
B-16 (DMOT)		430	2450	*Nat. Photon.*, 2019, 13, 406-411
B-17 (DPT)		456	174.31	*Angew. Chem. Int. Ed.*, 2018, 57, 678-682.
B-18 (TOP)		416	290.28	*J. Phys. Chem. Lett.*, 2018, 9, 3808-3813
B-19 (CS-2COOCH$_3$)		430	91	*Chem. Sci.*, 2020, 11, 833-838
B-20 (TFTPA)		484	17.93	*Chem. Sci.*, 2015, 6, 4438-4444

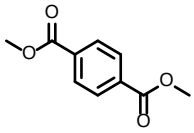
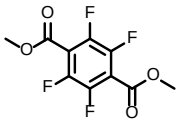
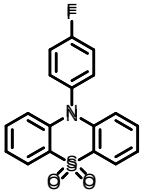
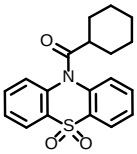
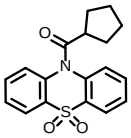
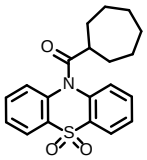
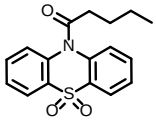
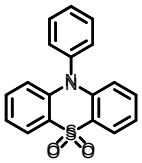
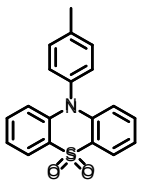
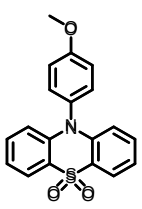
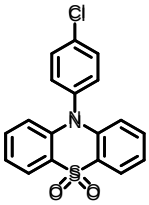
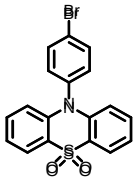
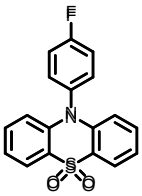
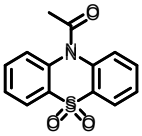
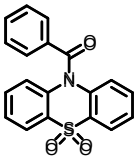
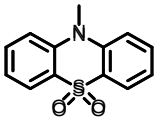
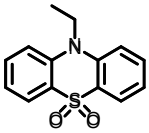
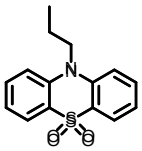
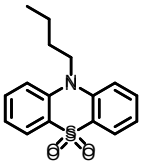
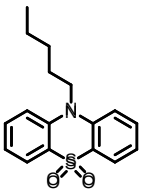
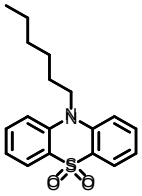
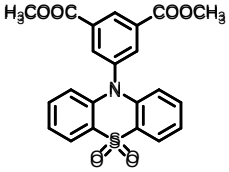
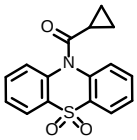
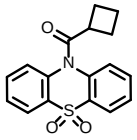
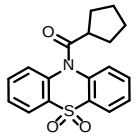
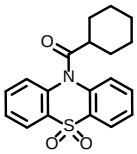
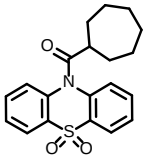
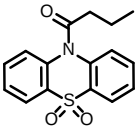
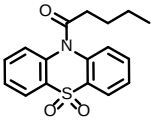
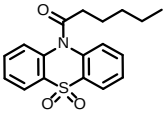
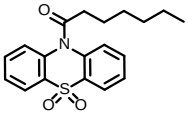
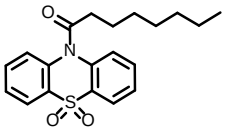
B-21 (DMTPA)		420	2.69	
B-22 (DMTFTPA)		484	9.12	
B-23 (CzS-F)		483	410	*Nat. Commun.*, 2018, 9, 840
***C*$_6$-CsO**		471	1116.10	this work
***C*$_5$-CsO**		403	51.96	this work
***C*$_7$-CsO**		409	60.75	this work
***N*$_4$-CsO**		471	249.43	this work

Table S2. Phosphorescence wavelengths (λ_{em}) and lifetimes (τ) of RTP emission in reported phenothiazine-5,5-dioxide based RTP materials.

Sample	Molecular structure	λ_{em} (nm)	τ (ms)	References
1-CsO (CzS-H)		525	188	
2-CsO (CzS-CH$_3$)		516	96	*Nat. Commun.*, 2018, 9, 840
3-CsO (CzS-OCH$_3$)		509	88	

4-CsO (CzS-Cl)		500	256	
5-CsO (CzS-Br)		525	268	
B-23 (CzS-F)		483	410	
7-CsO (DOPEO)		514	876	*Angew. Chem. Int. Ed.*, 2019, 58, 6645-6649
8-CsO (DOPPMO)		490	455	
9-CsO (Cs-CH_3)		515	245	
10-CsO (Cs-C_2H_5)		515	92	
11-CsO (Cs-C_3H_7)		490	327	*Mater. Chem. Front.*, 2019,3, 1391-1397
12-CsO (Cs-C_4H_9)		509	181	
13-CsO (Cs-C_5H_{11})		516	205	

14-CsO (Cs-C_6H_{13})		510	–	
B-19 (CS-2$COOCH_3$)		430	91	*Chem. Sci.*, 2020, 11, 833-838
***C*$_3$-CsO**		515	470.16	this work
***C*$_4$-CsO**		516	808.05	this work
***C*$_5$-CsO**		403	51.96	this work
***C*$_6$-CsO**		471	1116.10	this work
***C*$_7$-CsO**		409	60.75	this work
***N*$_3$-CsO**		515	989.06	this work
***N*$_4$-CsO**		471	249.43	this work
***N*$_5$-CsO**		438	0.27	this work
***N*$_6$-CsO**		450	0.74	this work

***N*$_7$-CsO**		452	_	this work

1. Experiment section

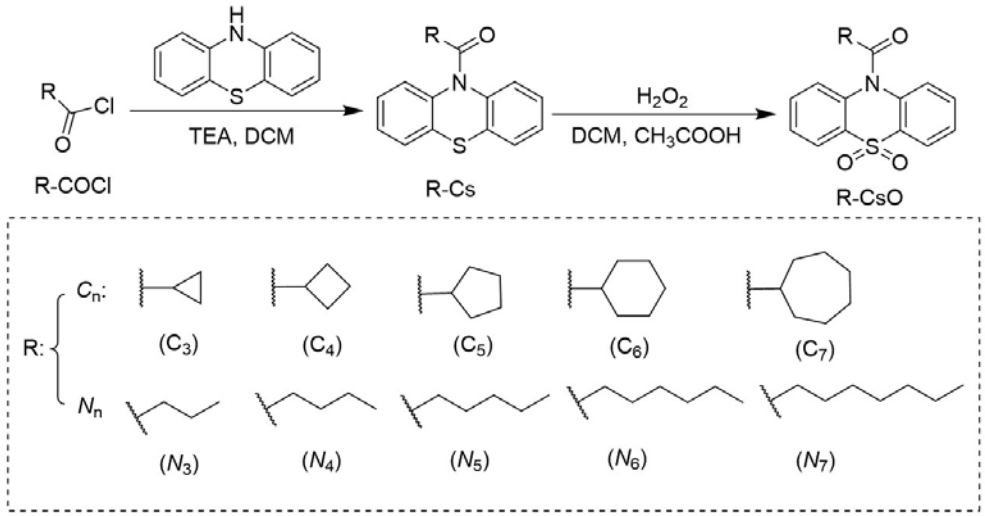
1.1 Materials

All starting chemicals were purchased from commercial sources and used without further purification. Column chromatography was carried out on silica gel using 200-300 mesh.

1.2 Instruments

^{1}H and ^{13}C NMR spectra were characterized on a Bruker Avance III HD 400 MHz using tetramethylsilane as internal standard. Mass spectra were recorded on a LCQadvantage mass spectrophotometer. Elemental analyses were conducted on a RARIO EL III. Photoluminescence spectra, phosphorescence spectra at room temperature and 77 K were determined on a Hitachi F-4600 fluorescence spectrophotometer. UV-vis spectra were measured on a Shimadzu UV-2550 spectrometer. Lifetimes and quantum yields were measured with FLS980 spectrometer. The single-crystal X-ray diffraction data were conducted in a Bruker Smart Apex CCD diffractometer. The powder X-ray diffraction patterns were characterized by D8 Advanced (Bruker) using Cu-Kα radiation. Size distribution of nanoparticles by Dynamic Light Scattering (DLS) were measured on Brookhaven instrument. The phosphorescent intensities of nanoparticles and bioimaging were recorded on IVIS® imaging system.

1.3 Synthetic procedures



Scheme S1 Synthetic routes of C_n-CsO and N_n-CsO series.

The general procedure for the synthesis of C_n-Cs and N_n-Cs series.

Phenothiazine (1.0 equiv.) and triethylamine (1.0 equiv.) were dissolved in dichloromethane (DCM) (50 mL) and then stirred at room temperature for 15 min. Then acyl chloride (2.0 equiv.) was added dropwise, the reaction mixture was refluxed at 50 °C for 24 h. After being cooled to room temperature, the mixture was washed by $NaHCO_3$ saturated aqueous solution (50 mL×3), 5% HCl (50 mL×3), and H_2O (50 mL×2) in sequence, extracted with DCM for three times (chloroform, a controlled drug, is not convenient to buy, so dichloromethane is selected). The combined organic extracts were dried over anhydrous Na_2SO_4 and the solvent was removed by rotary evaporation. The crude product was purified by silica gel column

chromatography using petroleum ether (PE) and DCM (2:1 v/v) as eluent to afford a solid product.

***C*$_3$-Cs：** White solid (0.97 g, 72.36%). mp: 99 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.62-7.60 (dd, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.47-7.44 (dd, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.35-7.31 (td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.25-7.21 (td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 1.86-1.79 (m, 1H), 1.13-1.10 (m, 2H, -CH_2-), 0.83-0.79 (m, 2H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.35, 139.41, 133.30, 128.20, 127.73, 127.19, 126.92, 13.09, 9.74. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{16}H_{14}NOS$, 268.4; found: 268.1. Anal. Cacld for $C_{16}H_{13}NOS$: C, 71.88; H, 4.90; N, 5.24. Found: C, 71.81; H, 4.82; N, 5.50.

***C*$_4$-Cs：** White solid (1.34 g, 59.61%). mp: 131 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.49-7.47 (d, *J* = 8.0 Hz, 2H, -ArH), 7.45-7.42 (dd, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.35-7.31 (td, *J* = 4.0, 1.5 Hz, 2H, -ArH), 7.26-7.22 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 3.54-3.45 (m, 1H), 2.24 (br, 2H, -CH_2-), 1.84-1.71 (m, 4H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 174.29, 139.34， 128.09, 127.32, 127.04, 38.55, 25.88, 17.85. MS (ESI), m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}NOSNa$, 304.4; found: 303.9. Anal. Cacld for $C_{17}H_{15}NOS$: C, 72.57; H, 5.37; N, 4.98. Found: C, 72.51; H, 5.31; N, 5.12.

***C*$_5$-Cs：** White solid (2.64 g, 68.84%). mp: 128 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.44-7.42 (dd, *J* = 8.0, 1.4 Hz, 2H, -ArH), 7.38-7.36 (dd, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.27-7.22 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.17-7.13 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 3.08-3.00 (m, 1H), 1.73-1.67 (br, 2H, -CH_2-), 1.62-1.53 (m, 4H, -CH_2-), 1.42-1.36 (m, 2H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ176.1, 139.69, 134.07, 128.23, 127.80, 127.31, 127.00 , 42.08, 31.22, 26.67. MS (ESI), m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}NOSNa$, 318.4; found: 318.0. Anal. Cacld for $C_{18}H_{17}NOS$: C, 73.19; H, 5.80; N, 4.74. Found: C, 73.38; H, 5.75; N, 4.78.

***C*$_6$-Cs：** White solid (3.12 g, 59.29%). mp: 135 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.51-7.49 (dd, *J* = 8.0, 1.4 Hz, 2H, -ArH), 7.47-7.45 (dd, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.36-7.31 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.26-7.22 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 2.77-2.69 (m, 1H), 1.73-1.67 (m, 4H, -CH_2-), 1.52-1.42 (m, 2H, -CH_2-) 1.27-1.02 (m, 4H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 175.54, 139.56, 133.99, 128.32, 127.68, 127.29, 127.03, 41.31, 29.90, 26.04, 25.92. MS (ESI), m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}NOSNa$, 332.4; found: 331.9. Anal. Cacld for $C_{19}H_{19}NOS$: C, 73.75; H, 6.19; N, 4.53. Found: C, 73.70; H, 6.21; N, 4.75.

***C*$_7$-Cs：** White solid (1.89 g, 58.72%). mp: 88 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.50-7.48 (dd, *J* = 8.0, 1.3 Hz, 2H, -ArH), 7.47-7.45 (dd, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.36-7.31 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.26-7.22 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 2.95-2.88 (m, 1H), 1.76 (br, 2H, -CH_2-), 1.69-1.65 (m, 4H, -CH_2-), 1.49-1.44 (m, 4H, -CH_2-), 1.27-1.23 (m, 2H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.75, 139.59, 134.07, 128.30, 127.84, 127.28, 127.02, 41.95, 31.80, 28.57, 26.90. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{20}H_{22}NOS$, 324.5 found: 324.2. Anal. Cacld for $C_{20}H_{21}NOS$: C, 74.27; H, 6.54; N, 4.33. Found: C, 74.13; H, 6.57; N, 4.46.

***N*$_3$-Cs：** White solid (1.89 g, 70.59%). mp: 77 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.51-7.49 (dd, *J* = 8.0, 1.4 Hz, 2H, -ArH), 7.47-7.45 (dd, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.36-7.31 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.26-7.22 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 2.44-2.40 (t, *J* = 8.0 Hz, 2H, -CH_2-), 1.63 - 1.54 (m, 2H, -CH_2-), 0.87-0.83 (t, *J* = 8.0 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.21, 139.51, 133.78, 128.26, 127.84, 127.30, 127.08, 36.55, 19.11, 13.82. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NOS$, 270.4 found: 270.1. Anal. Cacld for $C_{16}H_{15}NOS$: C, 71.34; H, 5.61; N, 5.20. Found: C, 71.22; H, 5.43; N, 5.26.

***N*$_4$-Cs:** White solid (1.95 g, 68.90%). mp: 86 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.51-7.49 (dd, *J* = 8.0, 1.4 Hz, 2H, -ArH), 7.47-7.45 (dd, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.35-7.31 (td, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.26-7.22 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 2.46-2.42 (t, *J* = 8.0, Hz, 2H, -CH_2-), 1.57 - 1.50 (m, 2H, -CH_2-), 1.29-1.20 (m, 2H, -CH_2-), 0.83-0.79 (t, *J* = 8.0, Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.39, 139.52, 133.77, 128.26, 127.83, 127.30, 127.08, 34.30, 27.79, 22.56, 13.90. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{17}H_{18}NOS$, 284.4 found: 284.1. Anal. Cacld for $C_{17}H_{17}NOS$: C, 72.05; H, 6.05; N, 4.94. Found: C, 72.24; H, 6.02; N, 5.18.

***N*$_5$-Cs:** White solid (2.62 g, 88.28%). mp: 119 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.51-7.49 (dd, *J* = 8.0, 1.4 Hz, 2H, -ArH), 7.47-7.45 (dd, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.35-7.31 (td, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.26-7.22 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 2.45-2.42 (t, *J* = 8.0 Hz, 2H, -CH_2-), 1.59 - 1.52 (m, 2H, -CH_2-), 1.22 - 1.18 (m, 4H, -CH_2-), 0.84 - 0.81 (t, *J* = 8.0, Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.40 139.52, 133.78, 128.26, 127.83, 127.29, 127.07, 34.56, 31.61, 25.38, 22.72, 14.05. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{18}H_{20}NOS$, 298.4 found: 298.2. Anal. Cacld for $C_{18}H_{19}NOS$: C, 72.69; H, 6.44; N, 4.71. Found: C, 72.71; H, 6.43; N, 4.81.

***N*$_6$-Cs:** White solid (2.75 g, 88.42%). mp: 100 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.51-7.49 (dd, *J* = 8.0, 1.4 Hz, 2H, -ArH), 7.47-7.45 (dd, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.35-7.31 (td, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.26-7.22 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 2.46-2.42 (t, *J* = 8.0 Hz, 2H, -CH_2-), 1.58 - 1.51 (m, 2H, -CH_2-), 1.26 - 1.14 (m, 6H, -CH_2-), 0.85-0.82 (t, *J* = 8.0 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.42, 139.53, 133.79, 128.26, 127.83, 127.29, 127.07, 34.58, 31.86, 29.10, 25.67, 22.86, 14.18. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{19}H_{22}NOS$, 312.4 found: 312.1. Anal. Cacld for $C_{19}H_{21}NOS$: C, 73.27; H, 6.80; N, 4.50. Found: C, 73.26; H, 6.76; N, 4.48.

***N*$_7$-Cs:** White solid (2.70 g, 83.20%) mp: 61 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 7.51-7.49 (dd, *J* = 8.0, 1.4 Hz, 2H, -ArH), 7.47-7.45 (dd, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.35-7.31 (td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.26-7.22 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 2.45-2.42 (t, *J* = 8.0 Hz, 2H, -CH_2-), 1.58-1.51 (m, 2H, -CH_2-), 1.25-1.19 (m, 8H, -CH_2-), 0.87-0.83 (t, *J* = 8.0 Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.42, 139.53, 133.80, 128.25, 127.83, 127.29, 127.07, 34.57, 32.03, 29.37, 29.32, 25.71, 22.99, 14.22. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{20}H_{24}NOS$, 326.5 found: 326.2. Anal. Cacld for $C_{20}H_{23}NOS$: C, 73.81; H, 7.12; N, 4.30. Found: C, 73.96; H, 7.16; N, 4.55.

The general synthetic route of *C*$_n$-CsO and *N*$_n$-CsO series.

The above collected *C*$_n$-Cs and *N*$_n$-Cs product (3.0-10.0 mmol) was dissolved in the mixture of DCM (20 -30 mL), acetic acid (30-40 mL) and H_2O_2 (5-10 mL) in a 100 mL flask, respectively. Then the mixture was refluxed at 70 °C for 24 h. After being cooled to room temperature, the reaction mixture was washed with H_2O (50 mL×2), extracted with DCM for three times. The organic extracts were dried over anhydrous Na_2SO_4, and the solvent was removed the solvent by rotary evaporation. The product was further purified by column chromatography using petroleum ether/ DCM (1:1 v/v) as eluent to afford a solid product.

***C*$_3$-CsO:** White solid (0.51 g, 84.95%). mp: 216 °C; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.02-8.00 (dd, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.91-7.89 (dd, *J* = 8.0, 1.1 Hz, 2H, -ArH), 7.65 - 7.61 (td, *J* = 8.0, 1.4 Hz, 2H, -ArH), 7.51-7.47 (td, *J* = 8.0, 1.1 Hz, 2H, -ArH), 1.96-1.90 (m, 1H), 1.24 - 1.20 (m, 2H, -CH_2-), 0.97-0.92 (m, 2H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 172.31, 140.20, 134.75, 132.89, 127.76, 127.27, 124.04, 14.56, 10.93. MS (ESI), m/z: $[M+Na]^+$ calcd for $C_{16}H_{13}NO_3SNa$, 322.3 found: 322.1. Anal. Cacld for $C_{16}H_{13}NO_3S$: C, 64.20; H, 4.38; N, 4.68. Found: C, 63.70; H, 4.23; N, 4.69.

***C*$_4$-CsO：** White solid (0.53 g, 47.56%). mp: 227 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.00-7.97 (dd, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.76-7.74 (dd, *J* = 8.0, 1.1 Hz, 2H, -ArH), 7.65-7.61 (td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.52-7.48 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 3.69-3.61 (m, 1H), 2.41 - 2.31 (m, 2H, -CH_2-), 1.93 - 1.73 (m, 4H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 173.49, 140.20, 135.08, 132.99, 127.53, 127.46, 124.10, 39.40, 25.89, 17.84. MS (ESI), m/z: $[M+Na]^+$ calcd for $C_{17}H_{15}NO_3SNa$, 336.4 found: 336.1. Anal. Cacld for $C_{17}H_{15}NO_3S$: C, 65.16; H, 4.82; N, 4.47. Found: C, 65.18; H, 4.71; N, 4.62.

***C*$_5$-CsO：** White solid (1.13 g, 75.22%). mp: 231 °C. ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.00-7.98 (dd, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.79-7.76 (dd, *J* = 8.0 1.1 Hz, 2H, -ArH), 7.65-7.60 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.51-7.47 (td, *J* = 8.0, 1.1 Hz, 2H, -ArH), 3.29-3.21 (m, 1H), 1.92 - 1.83 (m, 2H, -CH_2-), 1.79 - 1.67 (m, 4H, -CH_2-), 1.55 - 1.45 (m, 2H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 175.65, 140.54, 135.37, 132.92, 127.83, 127.42, 124.16, 43.33, 31.53, 26.55. MS (ESI), m/z: $[M+Na]^+$ calcd for $C_{18}H_{17}NO_3SNa$, 350.4 found: 350.1. Anal. Cacld for $C_{18}H_{17}NO_3S$: C, 66.04; H, 5.23; N, 4.28. Found: C, 65.99; H, 5.15; N, 4.31

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***C*$_6$-CsO：** White solid (0.71 g, 80.73%). mp: 254 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.01-7.98 (dd, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.76-7.74 (dd, *J* = 8.0, 1.1 Hz, 2H, -ArH), 7.65-7.61 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.52-7.48 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 2.91-2.83 (tt, *J* = 11.5, 3.4 Hz, 1H), 1.88 - 1.83 (m, 2H, -CH_2-), 1.75-1.70 (m, 2H, -CH_2-), 1.63 - 1.47 (m, 3H, -CH_2-), 1.28 - 1.05 (m, 3H, -CH_2-); ^{13}C NMR (100 MHz, CD_2Cl_2) δ 175.00, 140.41, 135.28, 132.90, 127.66, 127.43, 124.22, 42.62, 29.85, 25.90, 25.73. MS (ESI), m/z: $[M+Na]^+$ calcd for $C_{19}H_{19}NO_3SNa$, 364.4 found: 364.2. Anal. Cacld for $C_{19}H_{19}NO_3S$: C, 66.84; H, 5.61; N, 4.10. Found: C, 66.78; H, 5.58; N, 4.32.

***C*$_7$-CsO：** White solid (0.91 g, 71.99%). mp: 209 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.01-7.98 (dd, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.75-7.73 (dd, *J* = 8.0, 1.1 Hz, 2H, -ArH), 7.65 - 7.61 (td, *J* = 8.0, 4.0 Hz, 2H, -ArH), 7.51-7.47 (td, *J* = 8.0, 1.1 Hz, 2H, -ArH), 3.07-3.00 (m, 1H), 1.94 - 1.87 (m, 2H, -CH_2-), 1.78 - 1.69 (m, 4H, -CH_2-), 1.54 - 1.45 (m, 4H, -CH_2-), 1.35-1.25 (m, 2H, -CH_2-). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 176.15, 140.46, 135.31, 132.87, 127.75, 127.41, 124.22, 43.43, 31.77, 28.63, 26.66. MS (ESI), m/z: $[M+Na]^+$ calcd for $C_{20}H_{21}NO_3SNa$, 378.5 found: 378.2. Anal. Cacld for $C_{20}H_{21}NO_3S$: C, 67.58; H, 5.96; N, 3.94. Found: C, 67.43; H, 5.92; N, 4.04.

***N*$_3$-CsO：** White solid (0.78 g, 69.66%). mp: 205 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.00-7.98 (dd, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.76-7.74 (dd, *J* = 8.0, 1.1 Hz, 2H, -ArH), 7.65-7.61 (td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.52-7.48 (td, *J* = 8.0, 1.1 Hz, 2H, -ArH), 2.59-2.55 (t, *J* = 8.0, Hz, 2H, -CH_2-), 170-1.61 (m, 2H, -CH_2-), 0.90-0.86 (t, *J* = 8.0, Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 171.69, 140.41, 135.45, 132.97, 128.07, 127.55, 124.17, 37.50, 18.93, 13.72. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{16}H_{16}NO_3S$, 302.4 found: 302.1. Anal. Cacld for $C_{16}H_{15}NO_3S$: C, 63.77; H, 5.02; N, 4.65. Found: C, 63.73; H, 4.96; N, 4.72.

***N*$_4$-CsO：** White solid (0.76 g, 67.89%). mp: 182 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.00-7.98 (dd, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.76-7.74 (dd, *J* = 8.0, 1.1 Hz, 2H, -ArH), 7.65-7.61 (td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.52-7.48 (td, *J* = 8.0, 1.1 Hz, 2H, -ArH), 2.61-2.57 (t, *J* = 8.0, Hz, 2H, -CH_2-), 1.65-1.58 (m, 2H, -CH_2-), 1.32-1.23 (m, 2H, -CH_2-), 0.84 (t, *J* = 8.0, Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 171.82, 140.42, 135.45, 132.96, 128.05, 127.54, 124.17, 35.32, 27.51, 22.48, 13.88.

MS (ESI), m/z: $[M+H]^+$ calcd for $C_{17}H_{18}NO_3S$, 316.4 found: 316.1. Anal. Cacld for $C_{17}H_{17}NO_3S$: C, 64.74; H, 5.43; N, 4.44. Found: C, 64.78; H, 5.40; N, 4.58.

***N*$_5$-CsO：** White solid (0.97 g, 62.73%). mp: 161 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.00-7.98 (dd, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.76-7.74 (dd, *J* = 8.0, 1.1 Hz, 2H, -ArH), 7.65-7.61 (td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.52-7.48 (td, *J* = 8.0, 1.1 Hz, 2H, -ArH), 2.60-2.56 (t, *J* = 8.0, Hz, 2H, -CH_2-), 1.67-1.60 (m, 2H, -CH_2-), 1.25 - 1.23 (m, 4H, -CH_2-), 0.86 - 0.82 (t, *J* = 8.0, Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 171.84, 140.43, 135.45, 132.96, 128.06, 127.53, 124.17, 35.57, 31.50, 25.13, 22.71, 14.02. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{18}H_{20}NO_3S$, 330.4 found: 330.0. Anal. Cacld for $C_{18}H_{19}NO_3S$: C, 65.63; H, 5.81; N, 4.25. Found: C, 65.67; H, 5.77; N, 4.41.

***N*$_6$-CsO：** White solid (1.09 g, 66.05%). mp: 143 °C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.00-7.98 (dd, *J* = 8.0, 1.5 Hz, 2H, -ArH), 7.76-7.74 (dd, *J* = 8.0,, 1.1 Hz, 2H, -ArH), 7.65-7.61(td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.52-7.48 (td, *J* = 8.0, 1.1 Hz, 2H, -ArH), 2.60-2.56 (t, *J* = 8.0, Hz, 2H, -CH_2-), 1.66-1.59 (m, 2H, -CH_2-), 1.24-1.22 (m, 6H, -CH_2-), 0.86 - 0.82 (t, *J* = 8.0, Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 171.85, 140.43,135.46, 132.95, 128.06, 127.53, 124.18, 35.62, 31.85, 29.03, 25.42, 22.83, 14.15. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{19}H_{22}NO_3S$, 344.4 found: 344.1. Anal. Cacld for $C_{19}H_{21}NO_3S$: C, 66.45; H, 6.16; N, 4.08. Found: C, 66.48; H, 6.17; N, 4.23.

***N*$_7$-CsO：** White solid (1.62 g, 64.07%). mp: 136°C; ^{1}H NMR (400 MHz,CD_2Cl_2) δ 8.00-7.98(dd, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.76-7.74 (dd, *J* = 8.0, 1.1 Hz, 2H, -ArH), 7.65-7.61 (td, *J* = 8.0, 1.6 Hz, 2H, -ArH), 7.52-7.48 (td, *J* = 8.0, 1.1 Hz, 2H, -ArH), 2.60 - 2.56 (t, *J* = 8.0, Hz, 2H, -CH_2-), 1.66-1.59 (m, 2H, -CH_2-), 1.26-1.20 (m, 8H, -CH_2-), 0.86-0.83 (t, *J* = 8.0, Hz, 3H, -CH_3). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 171.86, 140.43, 135.46, 132.95, 128.06, 127.53, 124.17, 35.61, 32.00, 29.32, 25.46, 22.97, 14.21. MS (ESI), m/z: $[M+H]^+$ calcd for $C_{20}H_{24}NO_3S$, 358.5 found: 358.1. Anal. Cacld for $C_{20}H_{23}NO_3S$: C, 67.20; H, 6.49; N, 3.92. Found: C, 67.20; H, 6.46; N, 3.94.

1.4 Bioimaging experiment

Preparation of nanoparticles

***C*$_6$-CsO (or *C*$_4$-CsO, *N*$_3$-CsO)** crystal (1 mg) and PEG-b-PPG-b-PEG (F127) (10 mg) were dissolved into THF solution (1.0 mL). Then THF was removed with a gentle nitrogen flow. The deionized water (3.0 mL) was added and the mixture was sonicated by a microtip-equipped probe sonicator (Scientz-IID) for 20 min. The generated nanoparticle solution (about 0.33 mg/mL) was stored in dark at low temperature.

***In vitro* phosphorescent imaging of nanoparticles**

The phosphorescent intensities of nanoparticles were measured on an IVIS® imaging system after nanoparticles were irradiated using an UV lamp (365 nm) for 30 s. The IVIS system was set in bioluminescence mode with open filter setting (exposure time: 10 s).

***In vivo* phosphorescent imaging**

The healthy nude mice were anesthetized by 2 % isoflurane in oxygen and placed into the box of IVIS instrument. Then, 50 μL prepared nanoparticles were injected into the mice, which was irradiated by a UV lamp (365 nm) for 30 s. Then the phosphorescent bioimaging were acquired using IVIS instrument in bioluminescence mode with open filter setting (exposure time: 10 s) after the light excitation was stopped.

Phosphorescent imaging of lymph node

The prepared nanoparticles (50 μL) were injected into the forepaws of live mice. After 2 h post-injection, the mice were irradiated by a handheld UV lamp (365 nm) for 30 s and then imaged with IVIS instrument in bioluminescence mode with open filter setting (exposure time: 10 s) after the light excitation was stopped.

Cytotoxicity Assay

In vitro cytotoxicity of the C_4-CsO NPs, C_6-CsO NPs and N_3-CsO NPs against HeLa cells were evaluated by cell counting kit-8 (CCK-8) assay (HY-K0301, MEDCHEMEXPRESS). Briefly, HeLa cells were seeded in 96-well plates with 1×10^4 cells per well. Then, cells were exposed to each kind of nanoparticles at the concentrations of 6.25, 12.5, 25, 50, 100 μg/mL^{-1}, respectively, at 37 °C, 5% CO_2. After 24 h incubation, the wells were washed twice with 1×PBS. The culture medium diluted 1:10 with CCK-8 assay was added 110 μL into each well and incubated for another 4 hours. Then the mediums were transferred to a new 96-well cell culture plate and the absorbance was measured by a microplate reader scanning at 450 nm.

2. Additional data and spectra

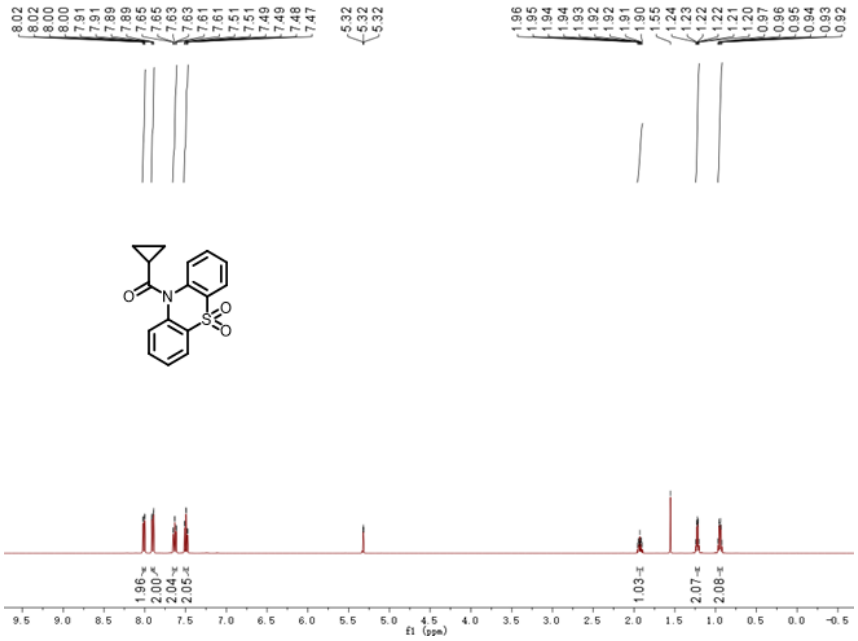

Figure S1. ^{1}H NMR spectrum of ***C*$_3$**-CsO.

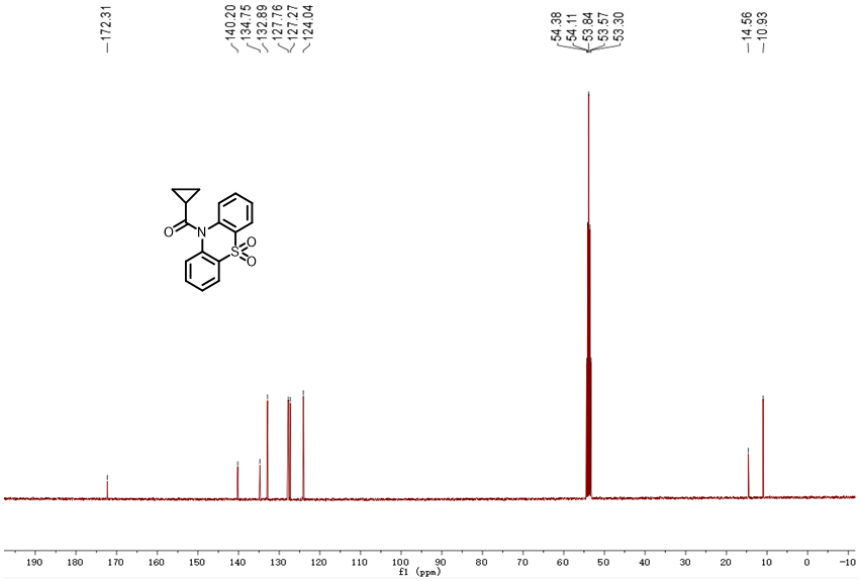

Figure S2. ^{13}C NMR spectrum of ***C*$_3$**-CsO.

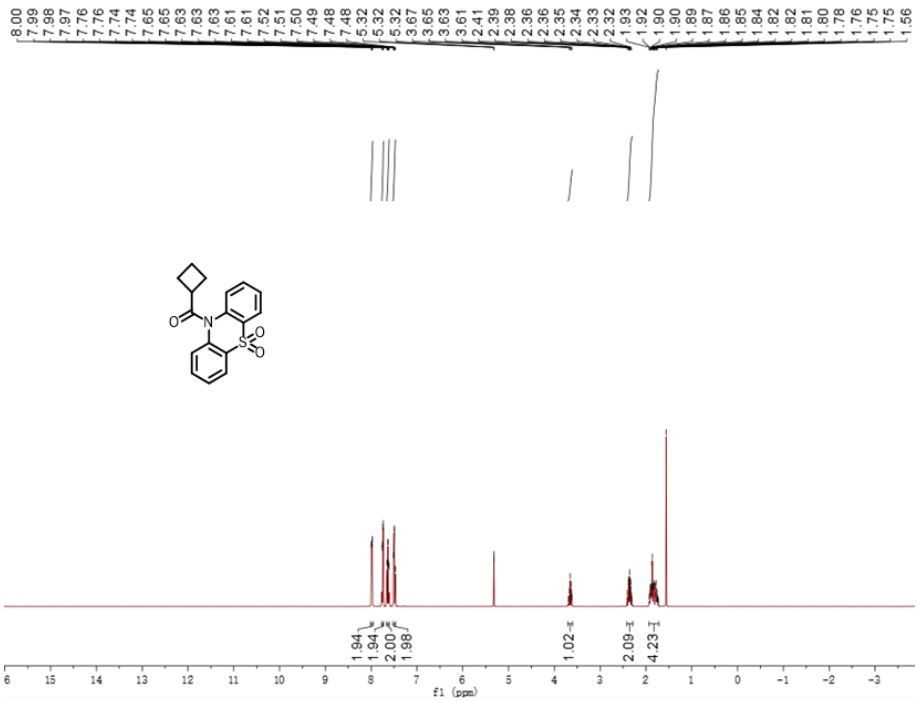

Figure S3. ^{1}H NMR spectrum of ***C*$_4$**-CsO.

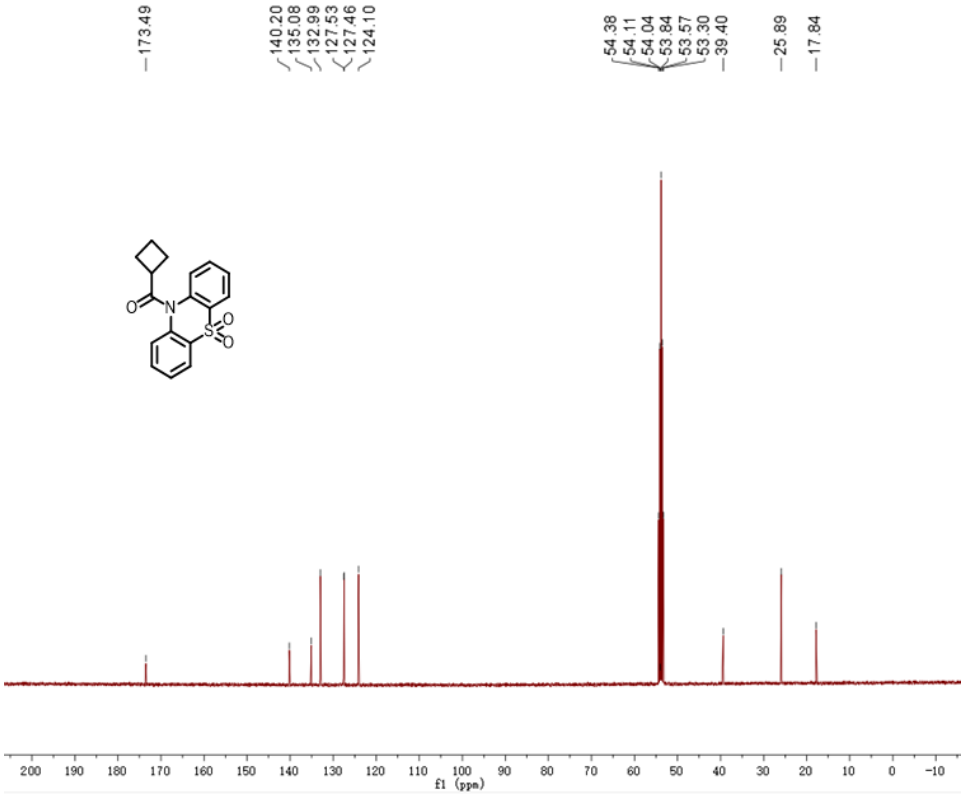

Figure S4. ^{13}C NMR spectrum of ***C*$_4$**-CsO.

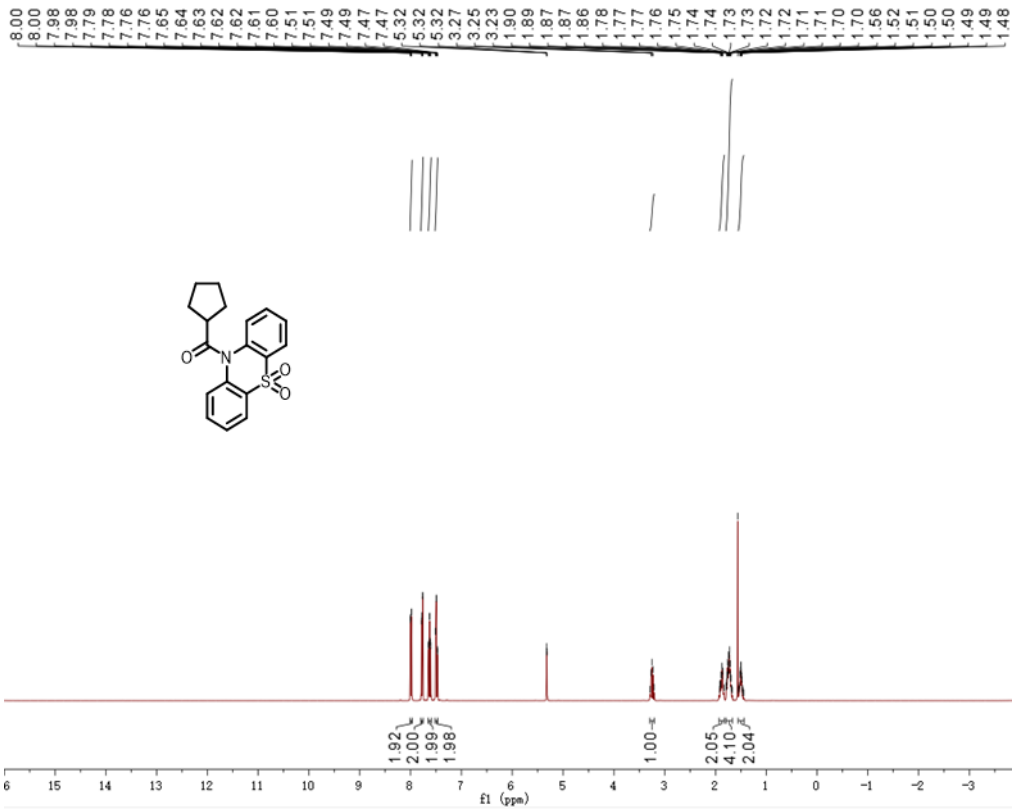

Figure S5. ^{1}H NMR spectrum of ***C*$_5$-CsO**.

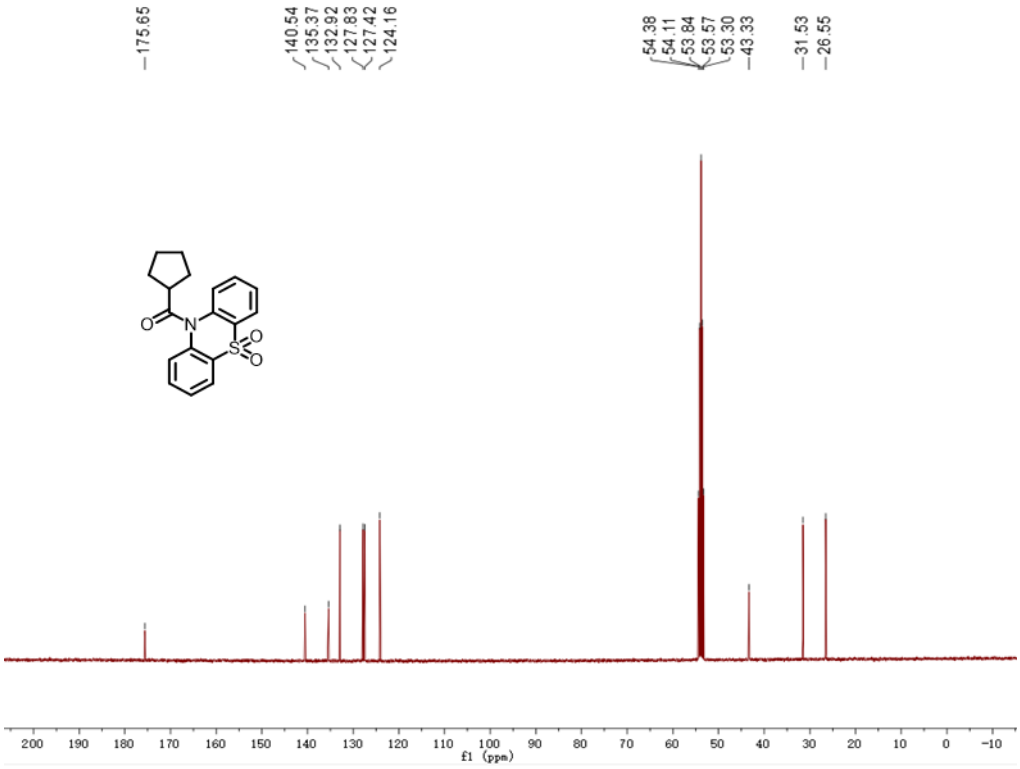

Figure S6. ^{13}C NMR spectrum of ***C*$_5$-CsO**.

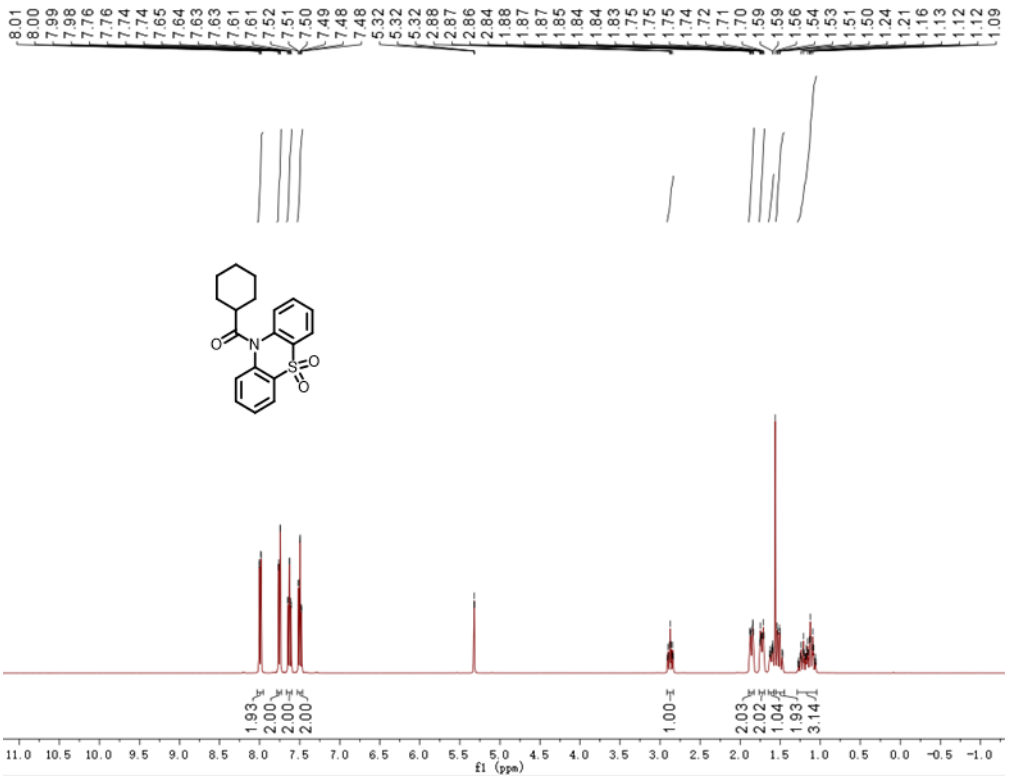

Figure S7. ^{1}H NMR spectrum of ***C*$_6$**-CsO.

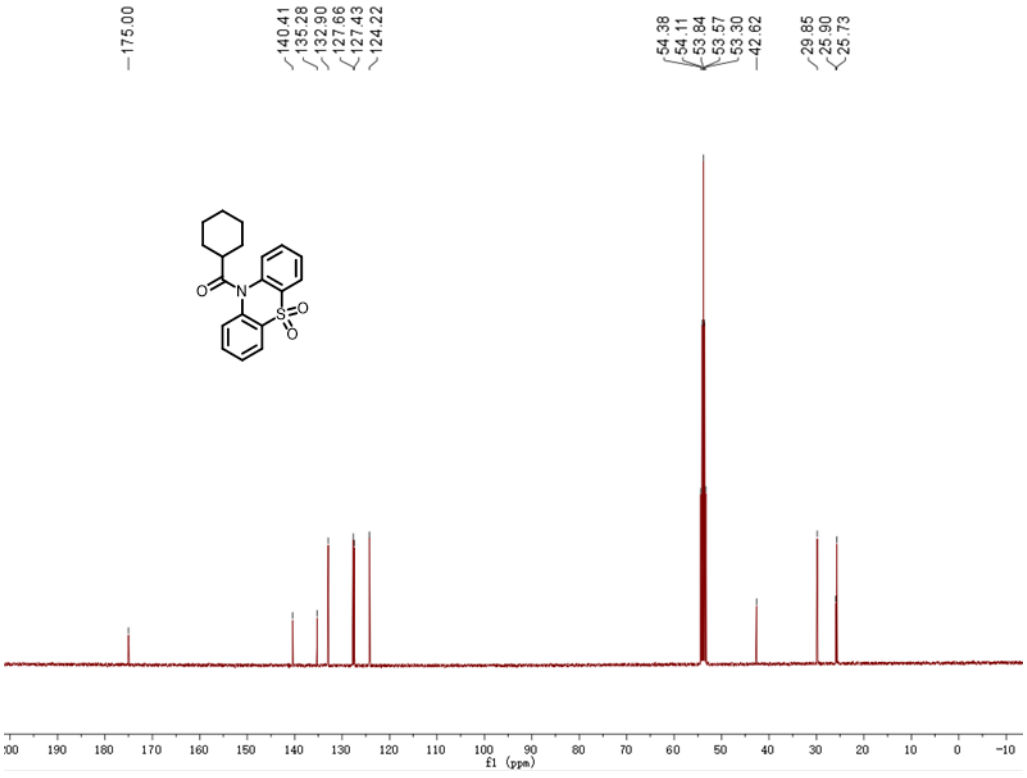

Figure S8. ^{13}C NMR spectrum of ***C*$_6$**-CsO.

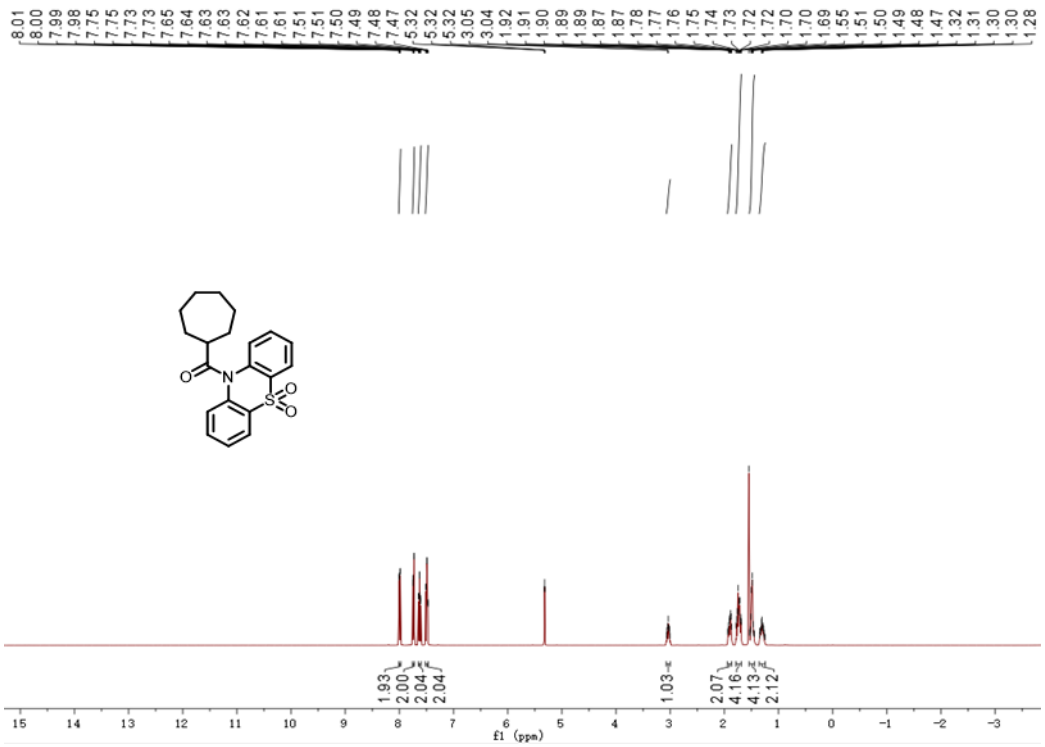

Figure S9. ^{1}H NMR spectrum of ***C*$_7$-CsO.

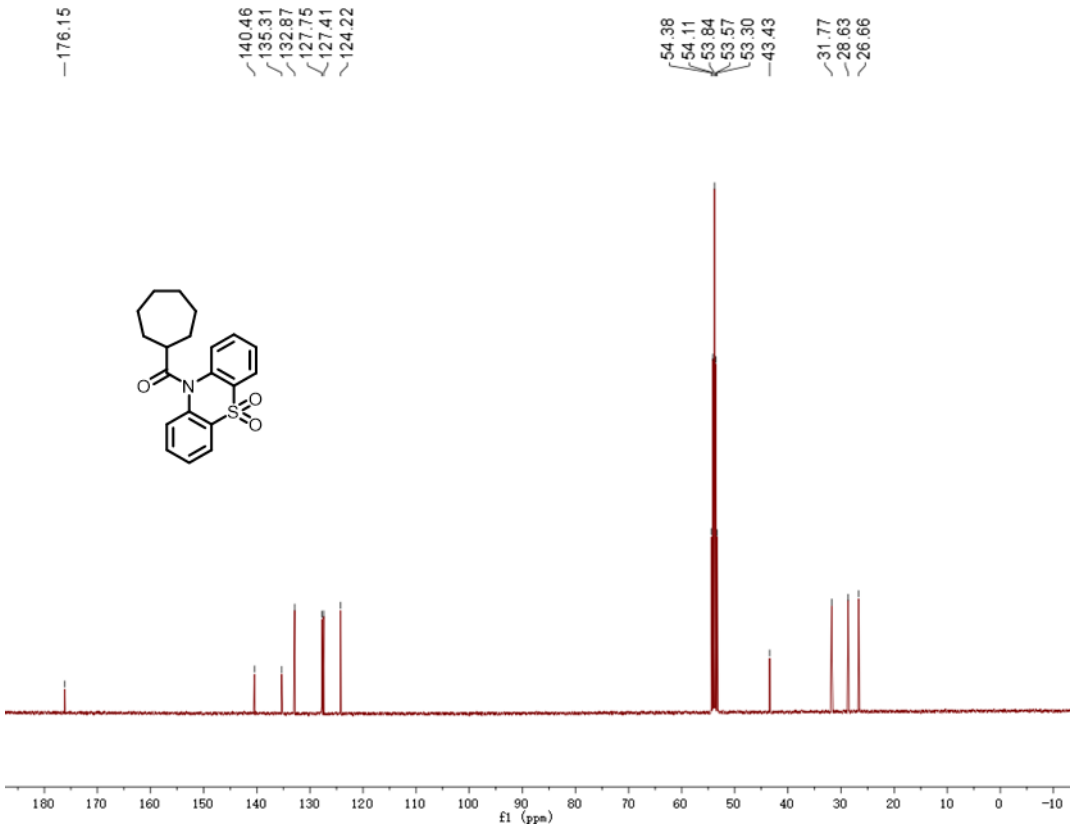

Figure S10. ^{13}C NMR spectrum of ***C*$_7$-CsO.

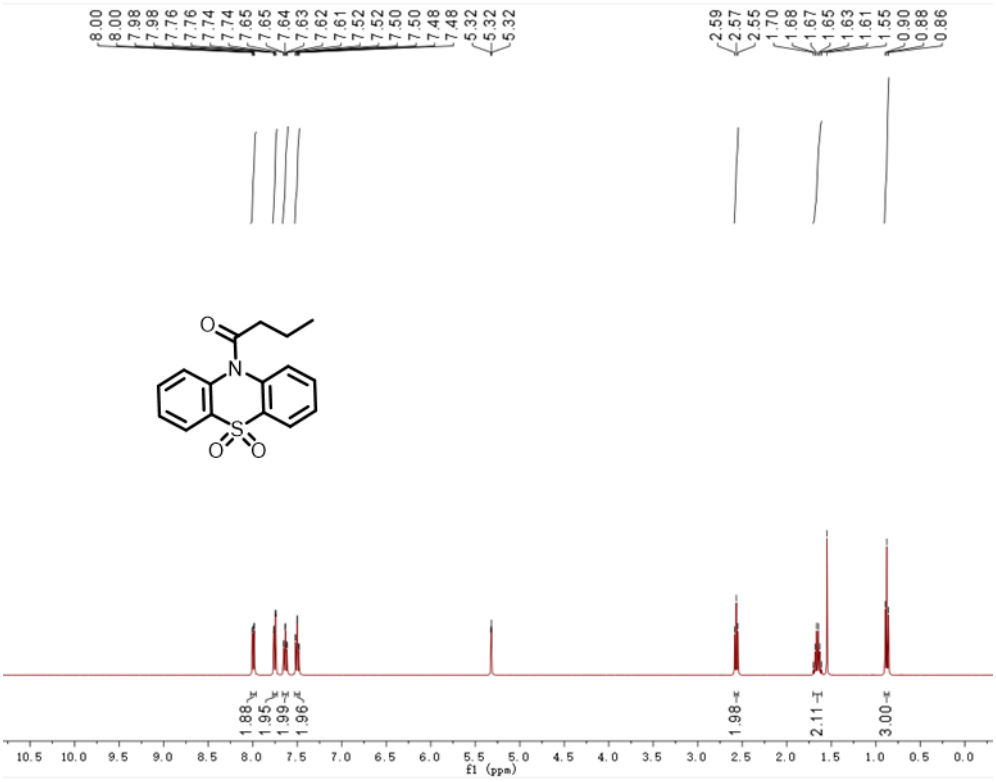

Figure S11. ^{1}H NMR spectrum of ***N*$_3$**-CsO.

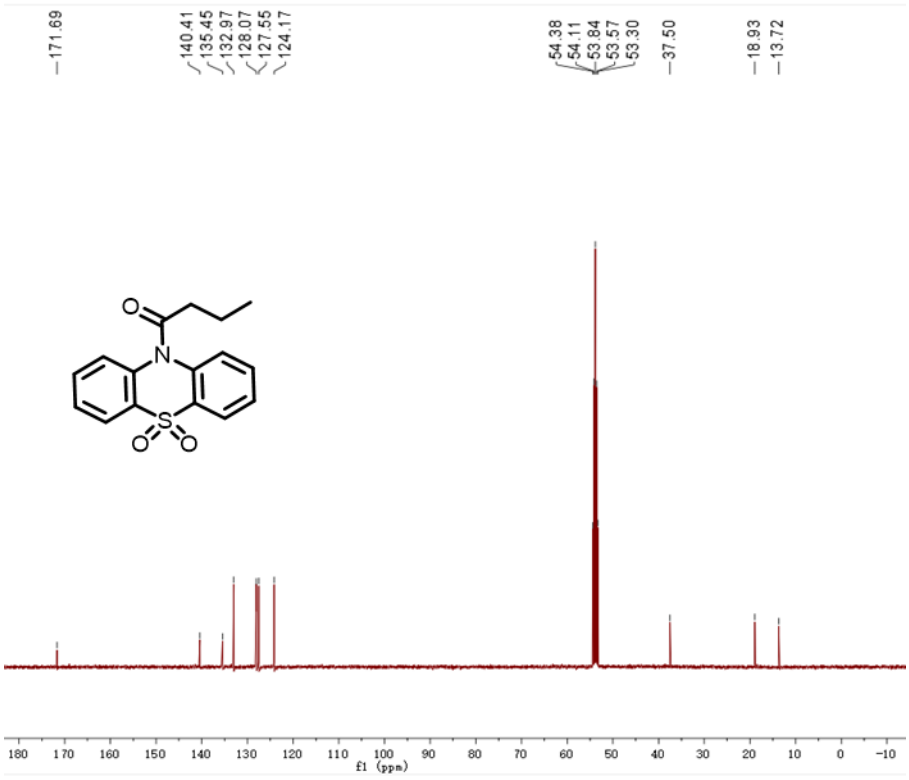

Figure S12. ^{13}C NMR spectrum of ***N*$_3$**-CsO.

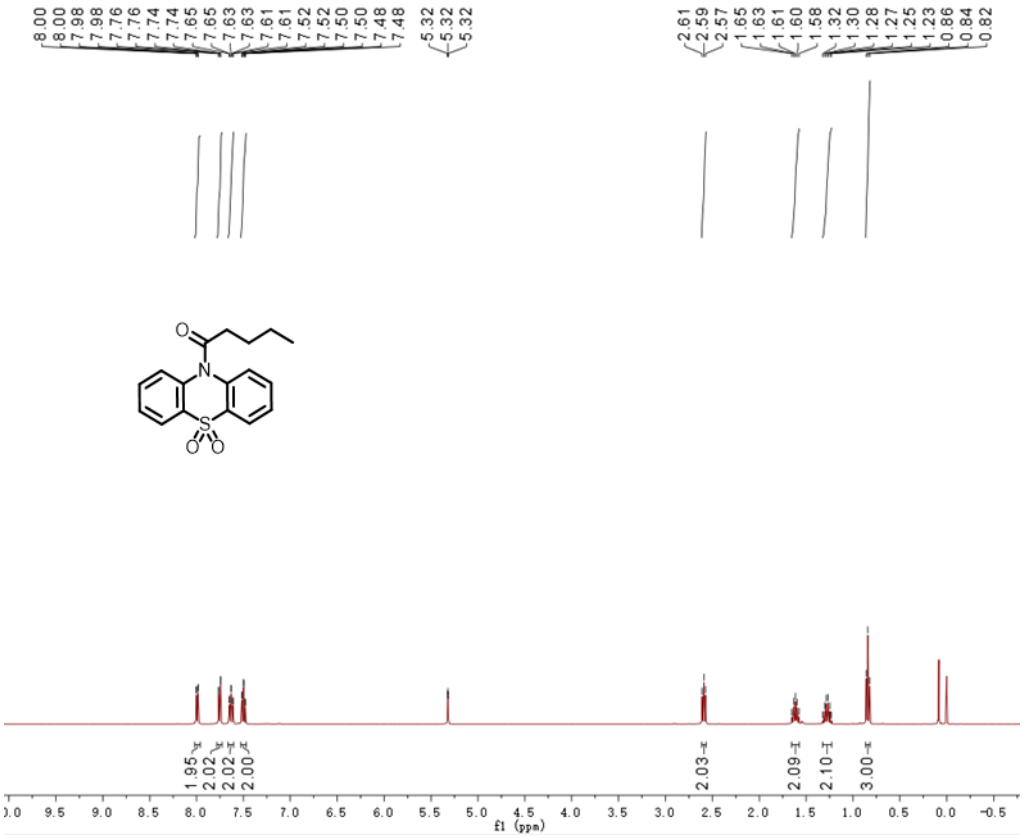

Figure S13. ^{1}H NMR spectrum of ***N*$_4$**-CsO.

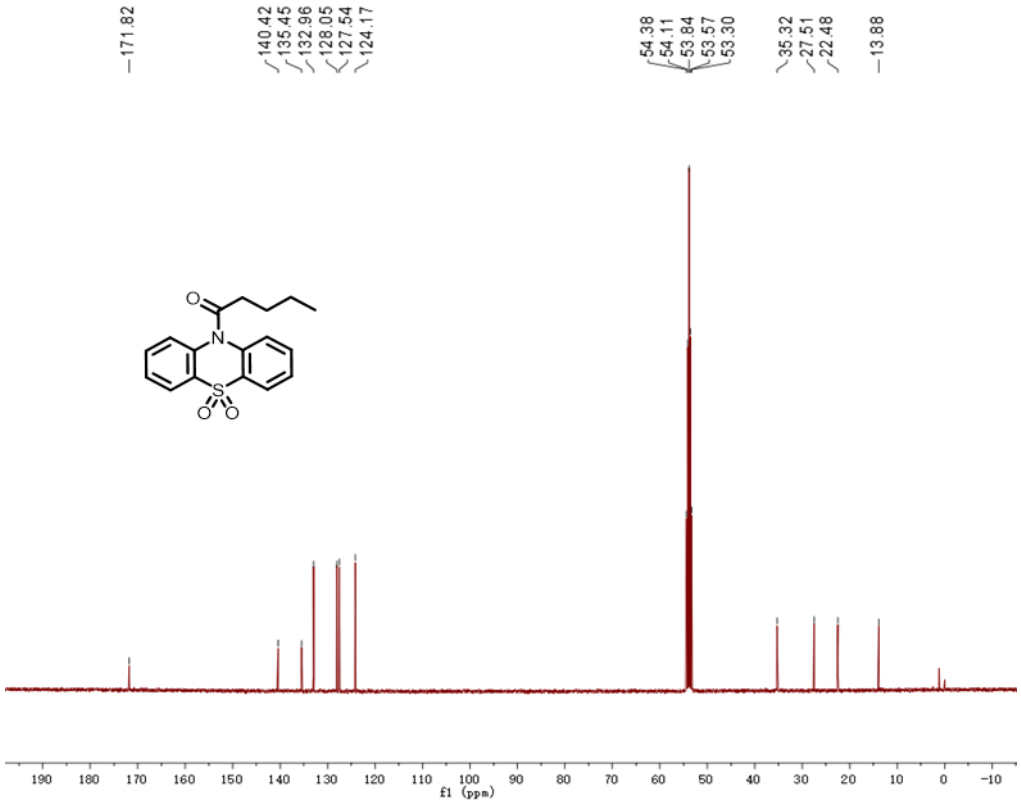

Figure S14. ^{13}C NMR spectrum of ***N*$_4$**-CsO.

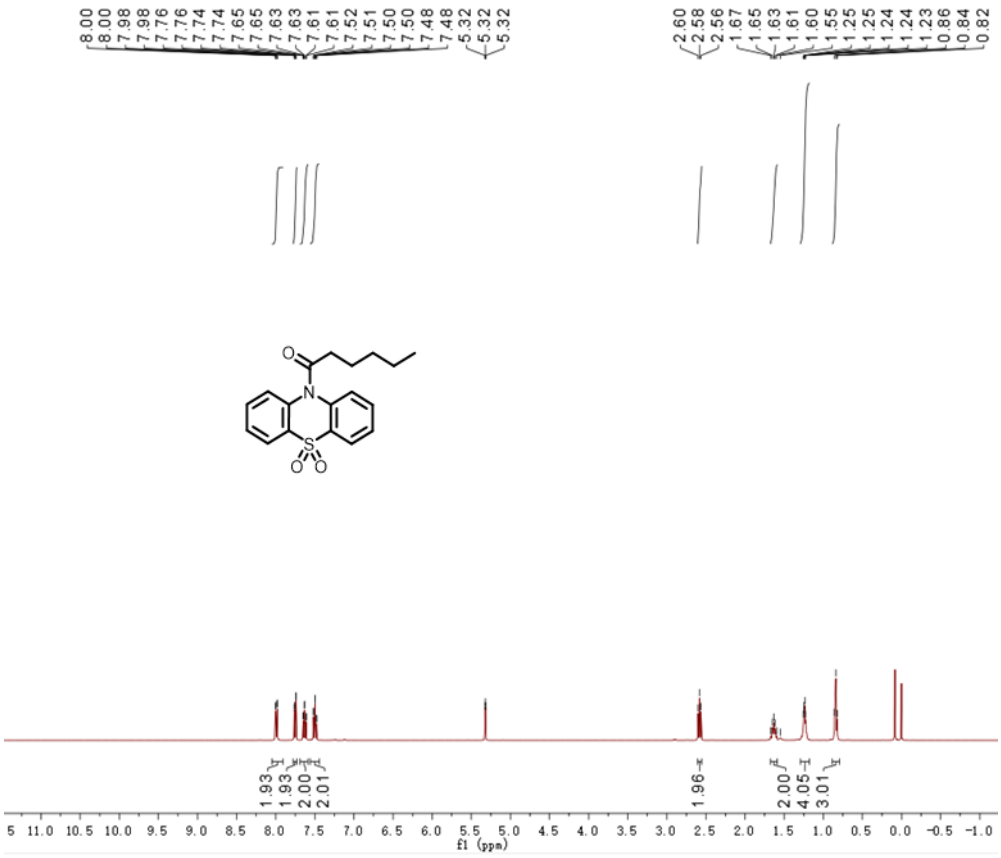

Figure S15. ^{1}H NMR spectrum of $\boldsymbol{N_5}$-CsO.

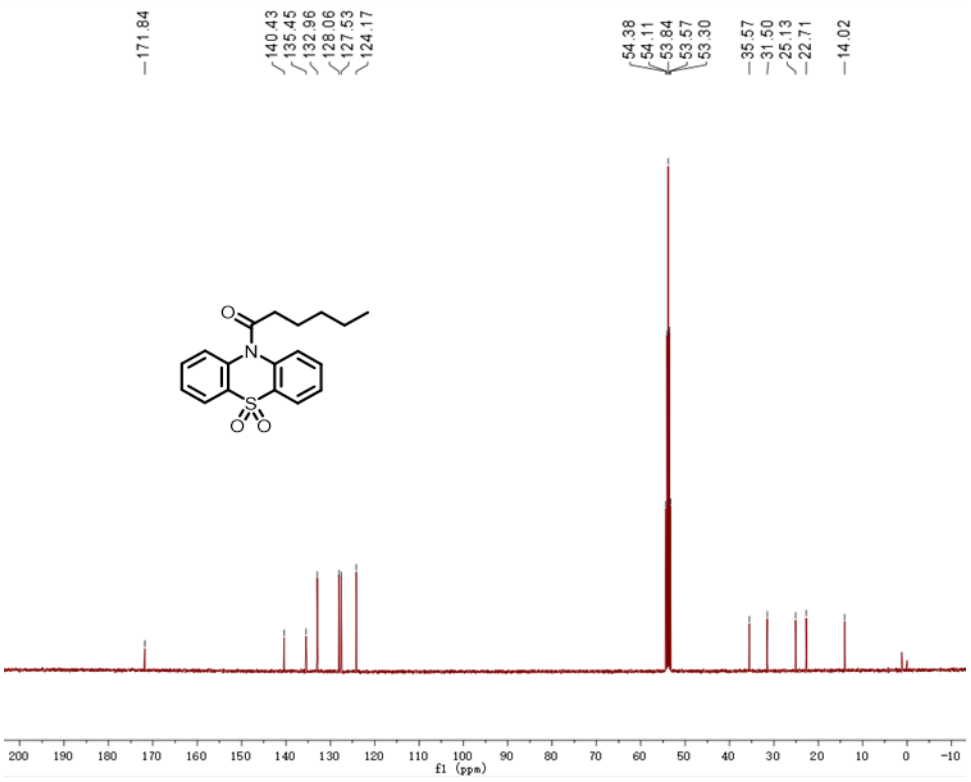

Figure S16. ^{13}C NMR spectrum of $\boldsymbol{N_5}$-CsO.

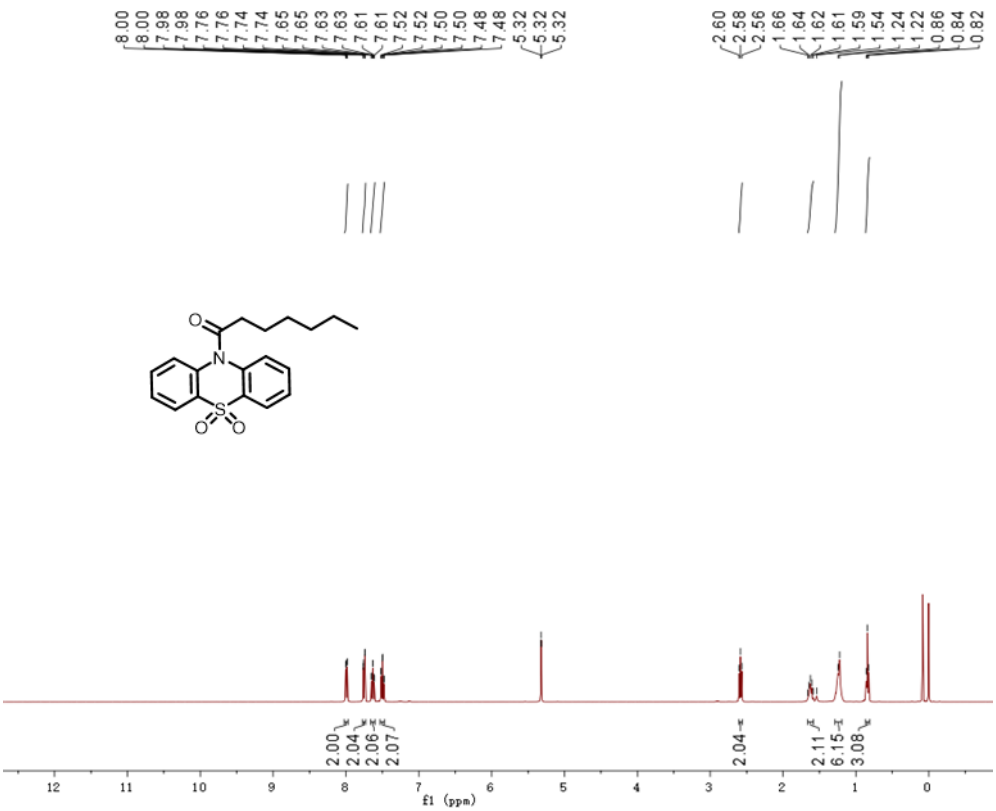

Figure S17. ^{1}H NMR spectrum of $\boldsymbol{N_6}$-CsO.

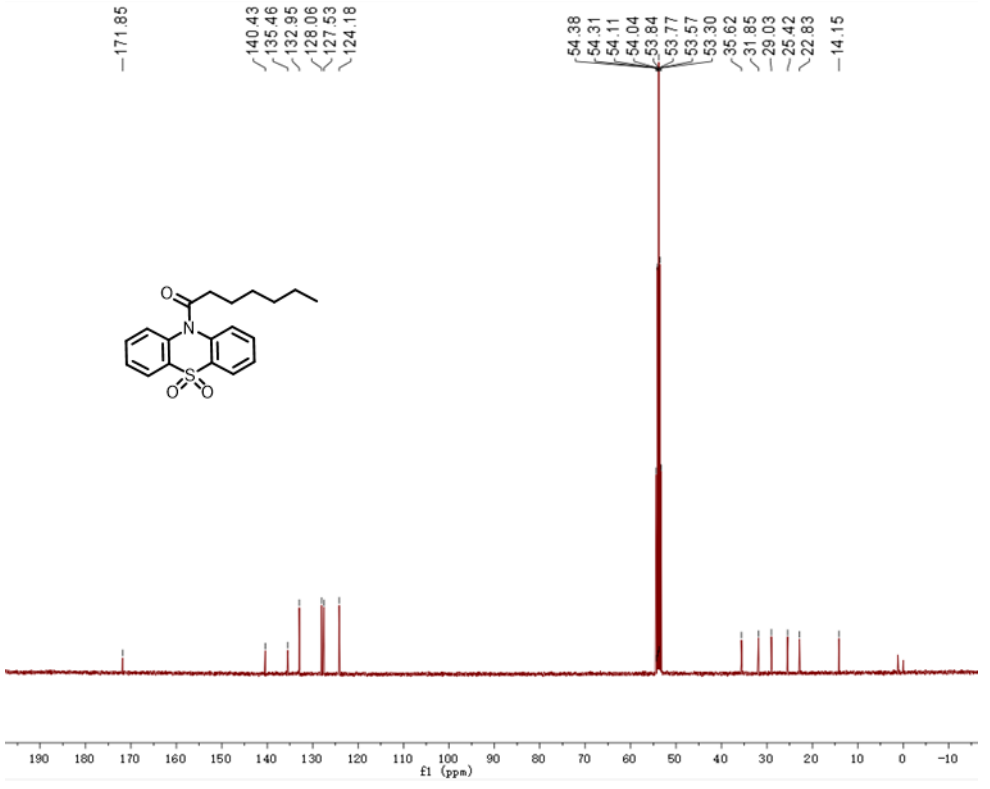

Figure S18. ^{13}C NMR spectrum of $\boldsymbol{N_6}$-CsO.

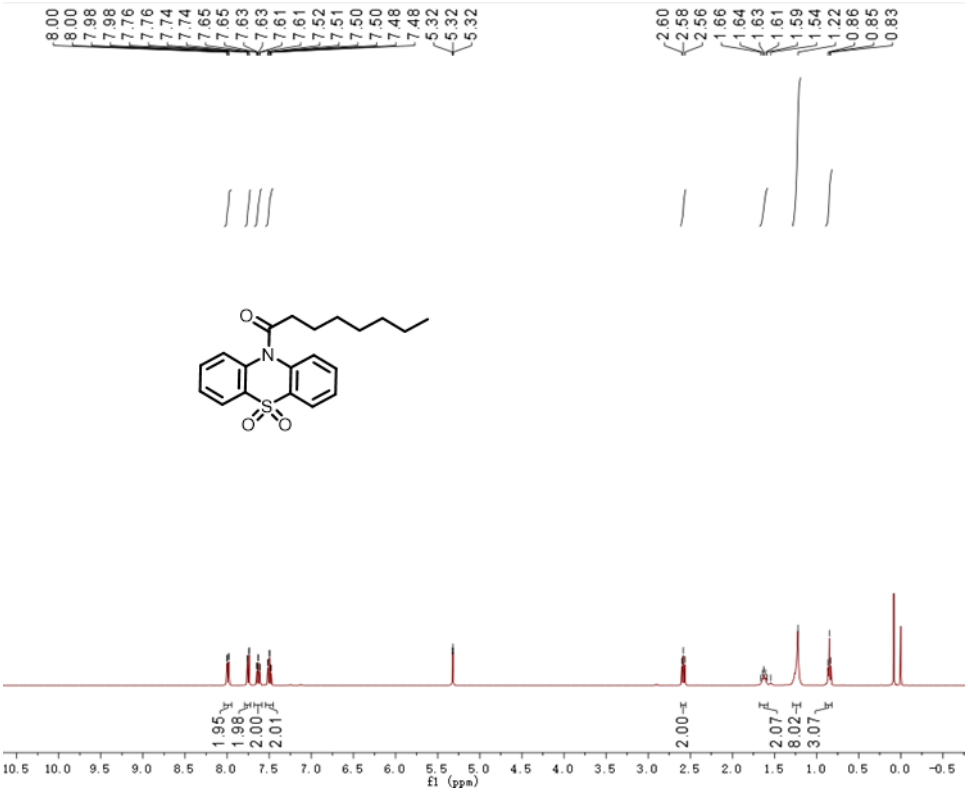

Figure S19. ^{1}H NMR spectrum of ***N*$_7$-CsO**.

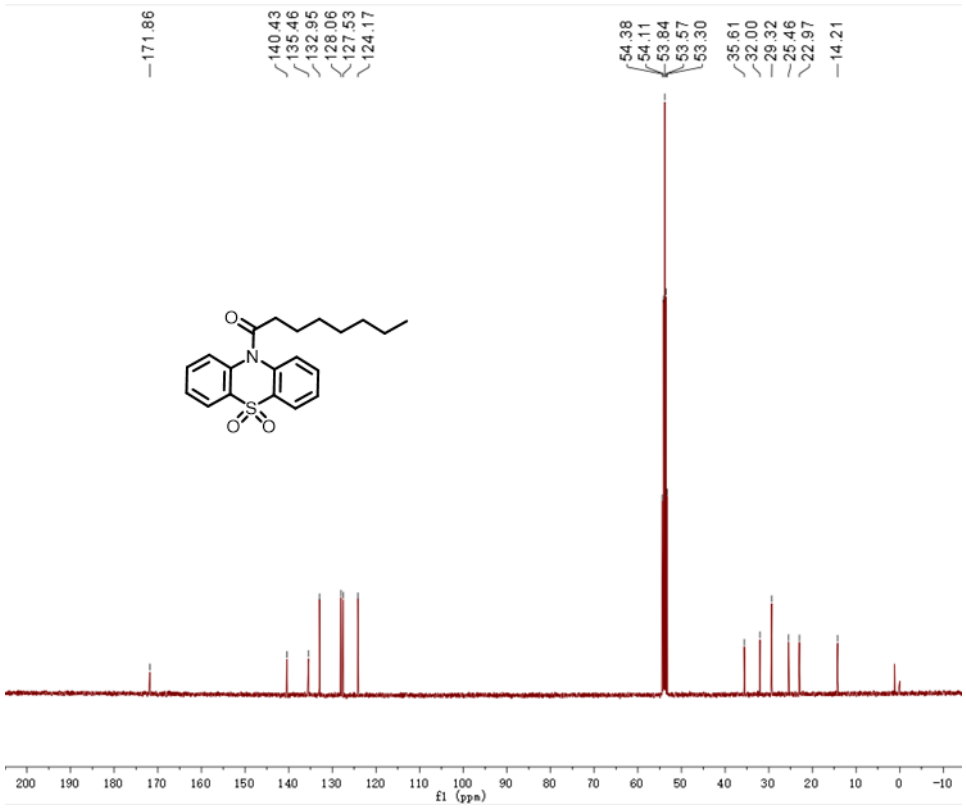

Figure S20. ^{13}C NMR spectrum of ***N*$_7$-CsO**.

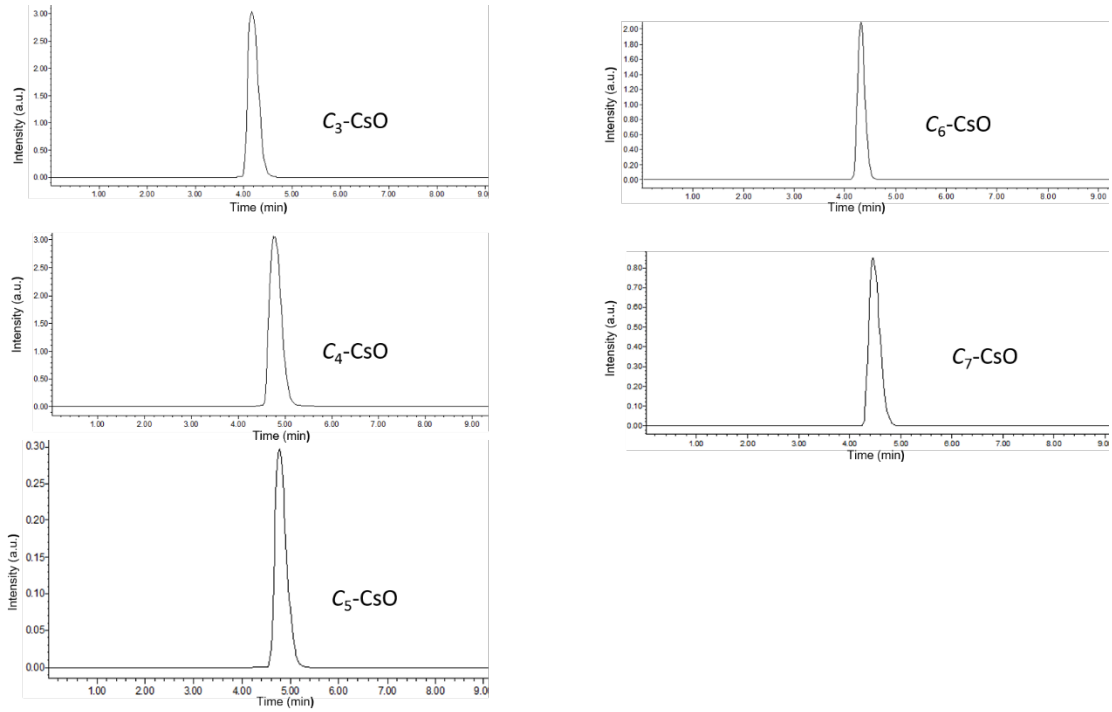

Figure S21. HPLC curves of C_n-C_SO compounds.

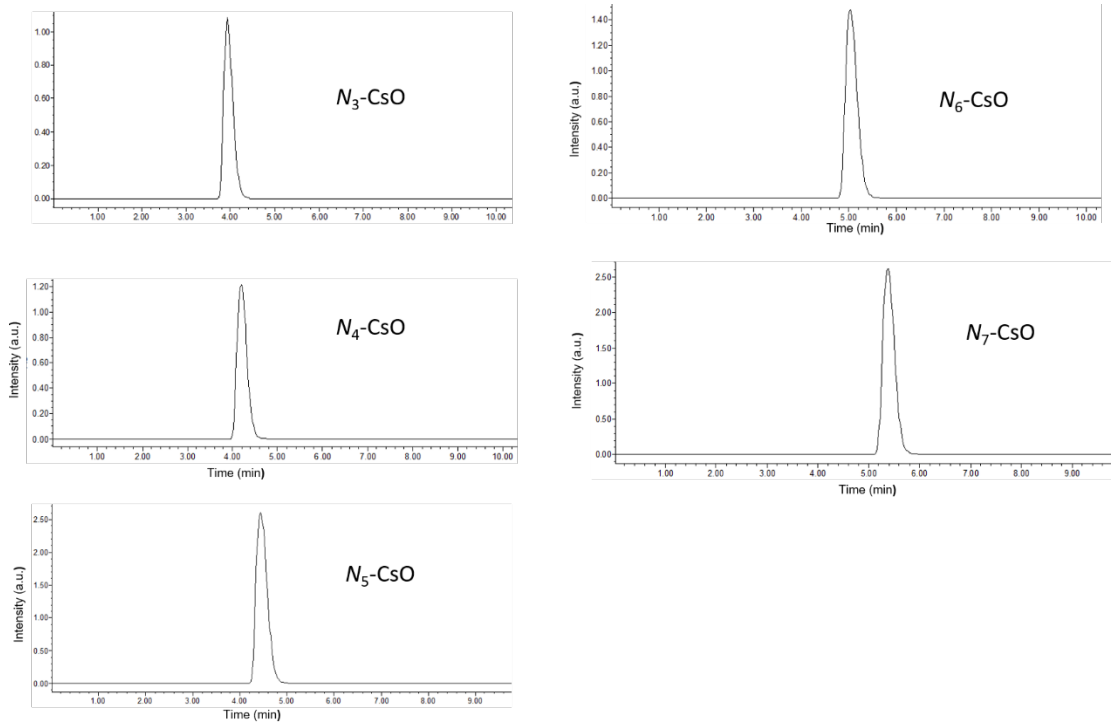

Figure S22. HPLC curves of N_n-C_SO compounds.

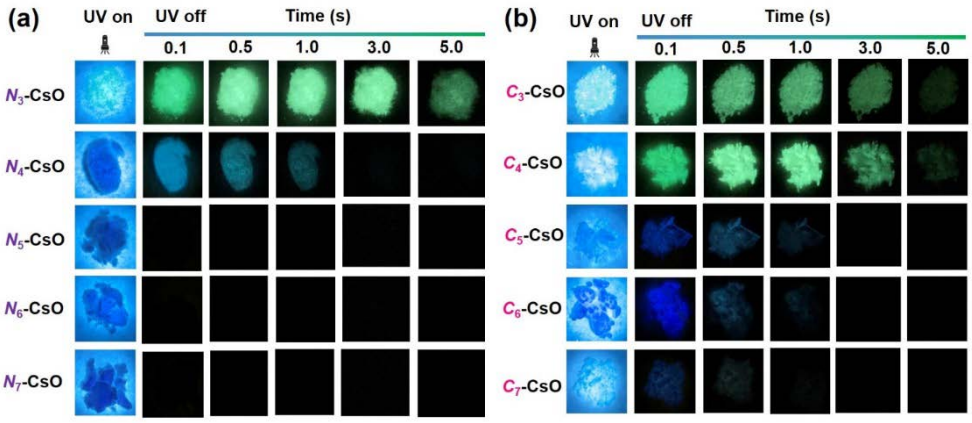

Figure S23. The phosphorescence photographs of N_n-CsO (a) and C_n-CsO crystals (b) taken at UV (365 nm) on and off at room-temperature.

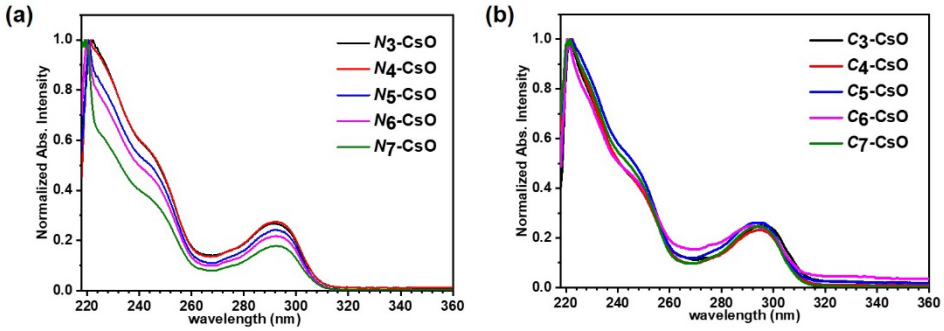

Figure S24 Absorption spectra of (a) N_n-CsO and (b) C_n-CsO series in dichloromethane solution (concentration: 20 μM).

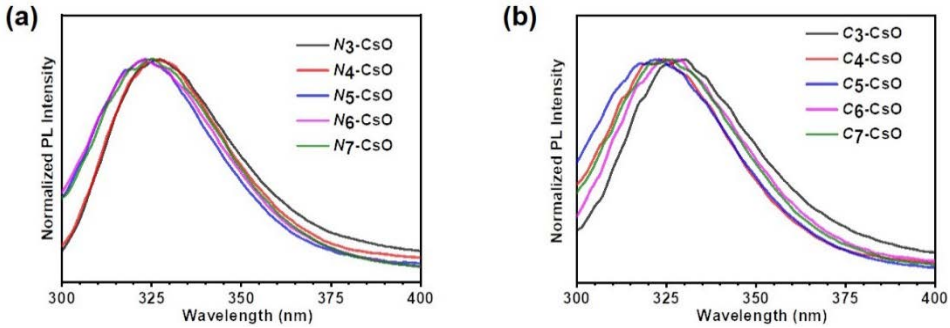

Figure S25 PL spectra of (a) N_n-CsO and (b) C_n-CsO series (1 wt%) doped in PMMA films at room temperture (λ_{ex}: 280 nm).

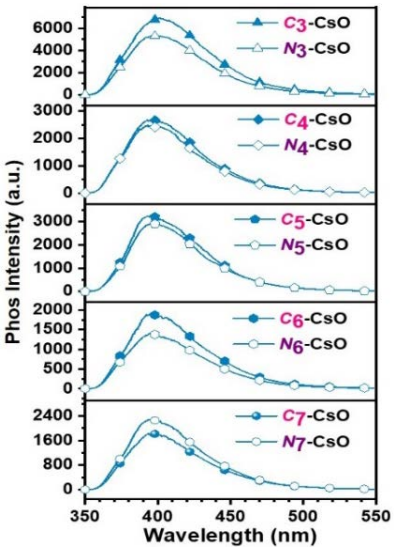

Figure S26 Phosphorescence spectra of N_n-C$_S$O and C_n-C$_S$O series (1 wt%) doped in PMMA films at 77 K (λ_{ex} : 305 nm).

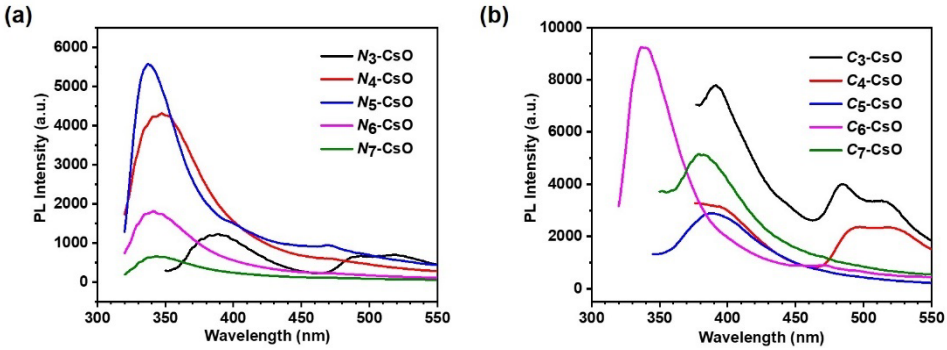

Figure S27 PL spectra of (a) N_n-C$_S$O and (b) C_n-C$_S$O crystals at room temperature.

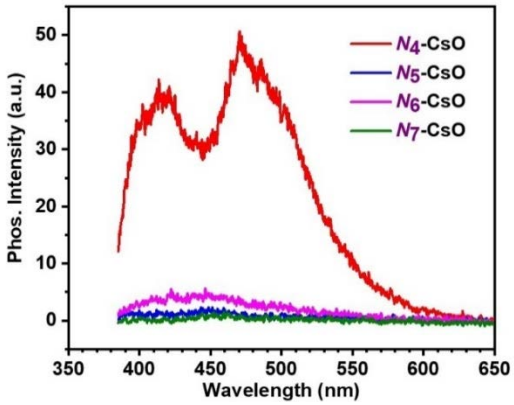

Figure S28 Phosphorescence spectra of N_4-C$_S$O, N_5-C$_S$O, N_6-C$_S$O and N_7-C$_S$O crystals at room temperature.

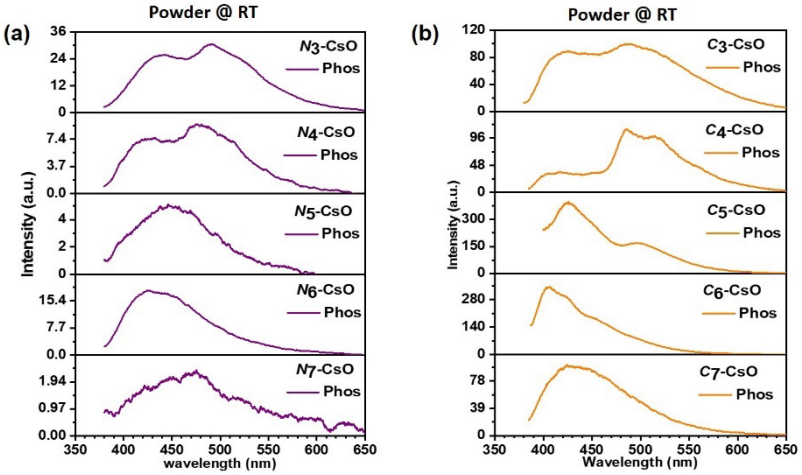

Figure S29 Phosphorescence spectra of (a) N_n-CsO and (b) C_n-CsO powders at room temperature (λ_{ex} : 365 nm).

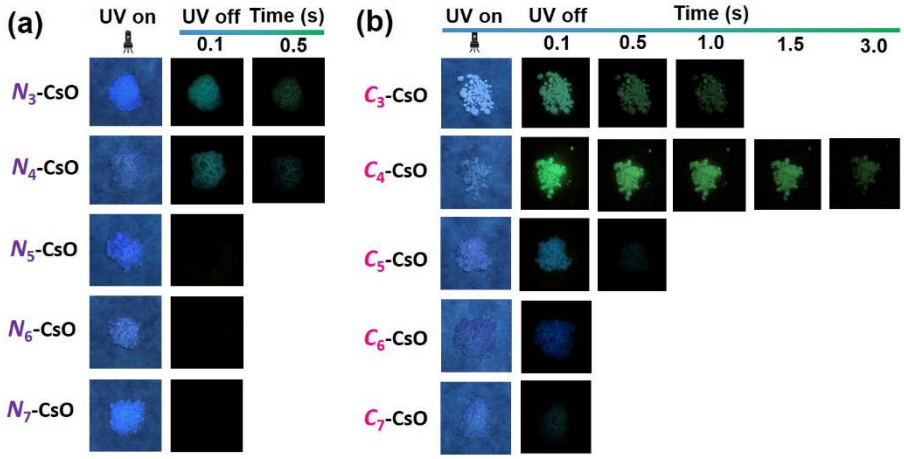

Figure S30. The phosphorescence photographs of (a) N_n-CsO and (b) C_n-CsO powders taken at UV (365 nm) on and off at room-temperature.

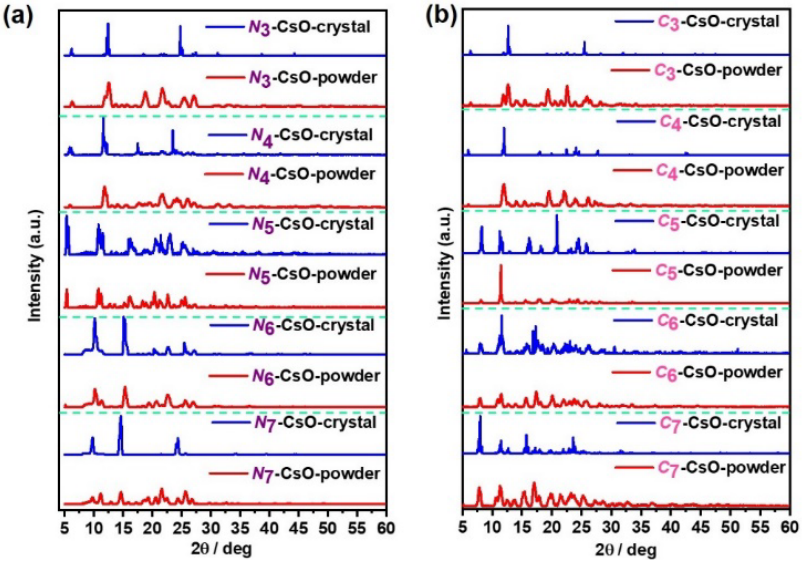

Figure S31 XRD patterns in different states for (a) N_n-CsO and (b)C_n-CsO series.

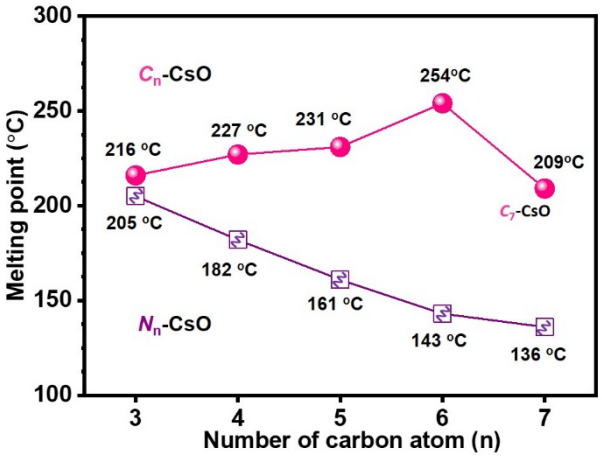

Figure S32 The melting points of C_n-C$_S$O (Top) and N_n-C$_S$O (Bottom).

Table S3 Photophysical data of C_n-C$_S$O compounds.

Sample	λ_{abs}[a] (nm)	λ_{PL}[b] (nm)	$\lambda_{Phos.}$[c] (nm)	λ_{PL}[d] (nm)	$\lambda_{Phos.}$[d] (nm)	$\tau_{Phos.}$[d] (ms)	Φ_{PL}[d] (%)
C_3-CsO	221, 295	329	402	391,484,515	489,515	453.63, 470.16	14.82
C_4-CsO	222, 295	325	400	395,494,522	489,516	807.15, 808.05	27.63
C_5-CsO	222, 296	324	395	392	403	51.96	9.02
C_6-CsO	220, 292	328	398	338	406,471,496	176.10, 1116.10, 1180.42	11.36
C_7-CsO	221, 294	326	398	379	409	60.75	42.83

a: Solution (20μM) at RT; b: Film at RT; c: Film at 77 K; d: Crystal at RT.

Table S4 Photophysical data of N_n-C$_S$O compounds.

Sample	$\lambda_{abs.}$[a] (nm)	λ_{PL}[b] (nm)	$\lambda_{Phos.}$[c] (nm)	λ_{PL}[d] (nm)	$\lambda_{Phos.}$[d] (nm)	$\tau_{Phos.}$[d] (ms)	Φ_{PL}[d] (%)
N_3-CsO	222, 291	327	405	390, 491, 519	486, 515	962.04, 989.06	10.18
N_4-CsO	221, 292	326	399	351	417,471	95.78, 249.43	4.54
N_5-CsO	221, 292	324	397	339	438	0.27	7.82
N_6-CsO	220, 292	325	396	338	450	0.74	5.82
N_7-CsO	219, 292	324	400	343	—	—	6.76

a: Solution (20μM) at RT; b: Film at RT; c: Film at 77 K; d: Crystal at RT.

Table S5 Structural data of single crystals based on CsO-derivatives (*C*$_3$-CsO — *C*$_7$-CsO).

Sample name	***C*$_3$-CsO**	***C*$_4$-CsO**	***C*$_5$-CsO**	***C*$_6$-CsO**	***C*$_7$-CsO**
CCDC Number	2123021	2123066	2123076	2123079	2123080
Formula	$C_{16}H_{13}NO_3S$	$C_{17}H_{15}NO_3S$	$C_{18}H_{17}NO_3S$	$C_{19}H_{19}NO_3S$	$C_{20}H_{21}NO_3S$
Wavelength (Å)	0.71073	1.34139	0.71073	0.71073	0.71073
Space Group	P21/c	P21/c	P21/n	P21/c	P21/n
Cell Lengths (Å)	a=13.992(2) b=8.8276(14) c=11.4697(18)	a=14.7399(9) b=8.7025(5) c=11.3772(7)	a=6.5733(12) b=15.503(3) c=15.682(3)	a=16.316(3) b=8.9933(16) c=11.873(2)	a=6.7394(16) b=16.651(4) c=15.824(4)
Cell Angles (º)	α=90 β=93.099(2) γ=90	α=90 β=91.586(1) γ=90	α=90 β=99.411(3) γ=90	α=90 β=107.627(3) γ=90	α=90 β=98.498(4) γ=90
Cell Volume (Å^3)	1414.6(4)	1458.84(15)	1576.6(5)	1660.4(5)	1756.3(7)
Z	4	4	4	4	4
Density (g/cm^3)	1.406	1.427	1.379	1.366	1.344
F(000)	624.8	656.0	688.0	720.0	752.0
h_{max}, k_{max}, l_{max}	20,13,17	17,10,13	9,22,22	24,13,17	9,23,22

Table S6 Structural data of single crystals based on CsO-derivatives (*N*$_3$-CsO — *N*$_6$-CsO).

Sample name	***N*$_3$-CsO**	***N*$_4$-CsO**	***N*$_5$-CsO**	***N*$_6$-CsO**
CCDC Number	2123082	2123083	2123084	2123085
Formula	$C_{16}H_{15}NO_3S$	$C_{17}H_{17}NO_3S$	$C_{18}H_{19}NO_3S$	$C_{19}H_{21}NO_3S$
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073
Space Group	P21/c	Pbca	Pbca	P21/c
Cell Lengths (Å)	a=14.404(3) b=8.8302(19) c=11.556(3)	a=8.855(2) b=11.597(3) c=29.990(7)	a=8.938(2) b=11.559(3) c=32.801(8)	a=17.879(10) b=8.882(5) c=11.605(7)
Cell Angles (º)	α=90 β=98.595(4) γ=90	α=90 β=90 γ=90	α=90 β=90 γ=90	α=90 β=103.340(11) γ=90
Cell Volume (Å^3)	1453.3(5)	3079.7(12)	3388.7(14)	1793.1(18)
Z	4	8	8	4
Density (g/cm^3)	1.377	1.360	1.291	1.269
F(000)	632.0	1328.0	1392.0	724.0
h_{max}, k_{max}, l_{max}	21,13,17	11,14,37	11,14,41	22,11,14

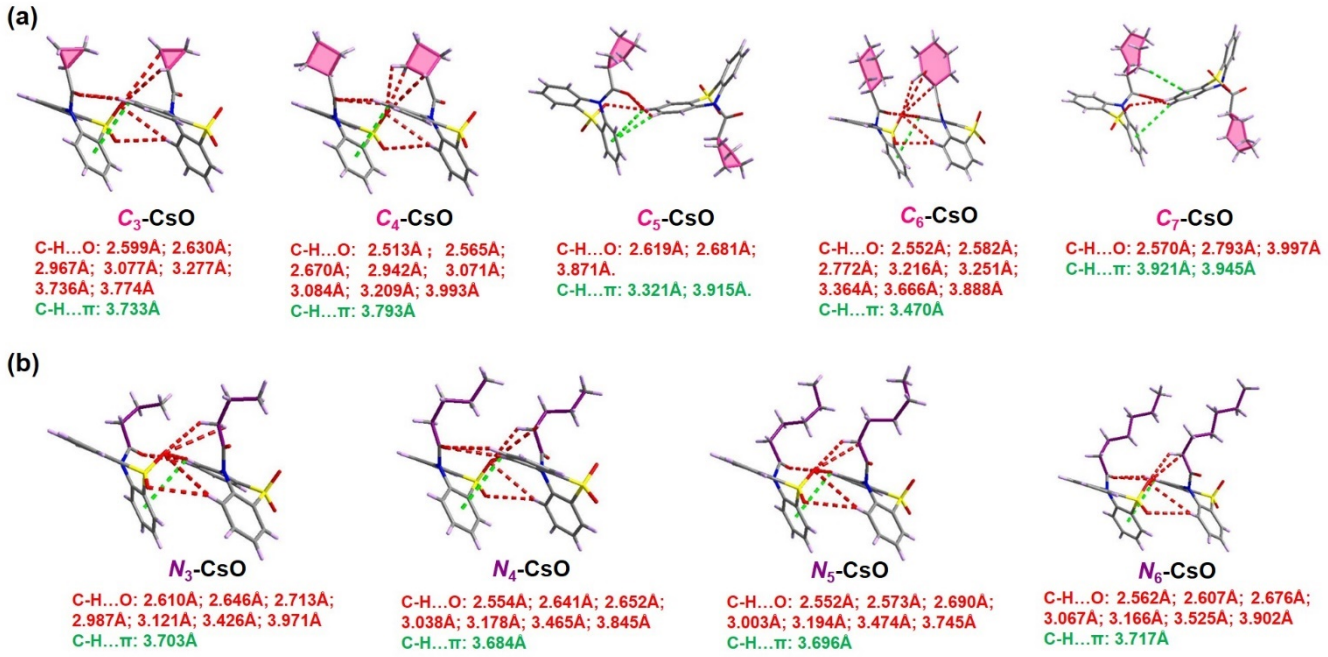

Figure S33 Intermolecular interaction of dimers in single crystals.

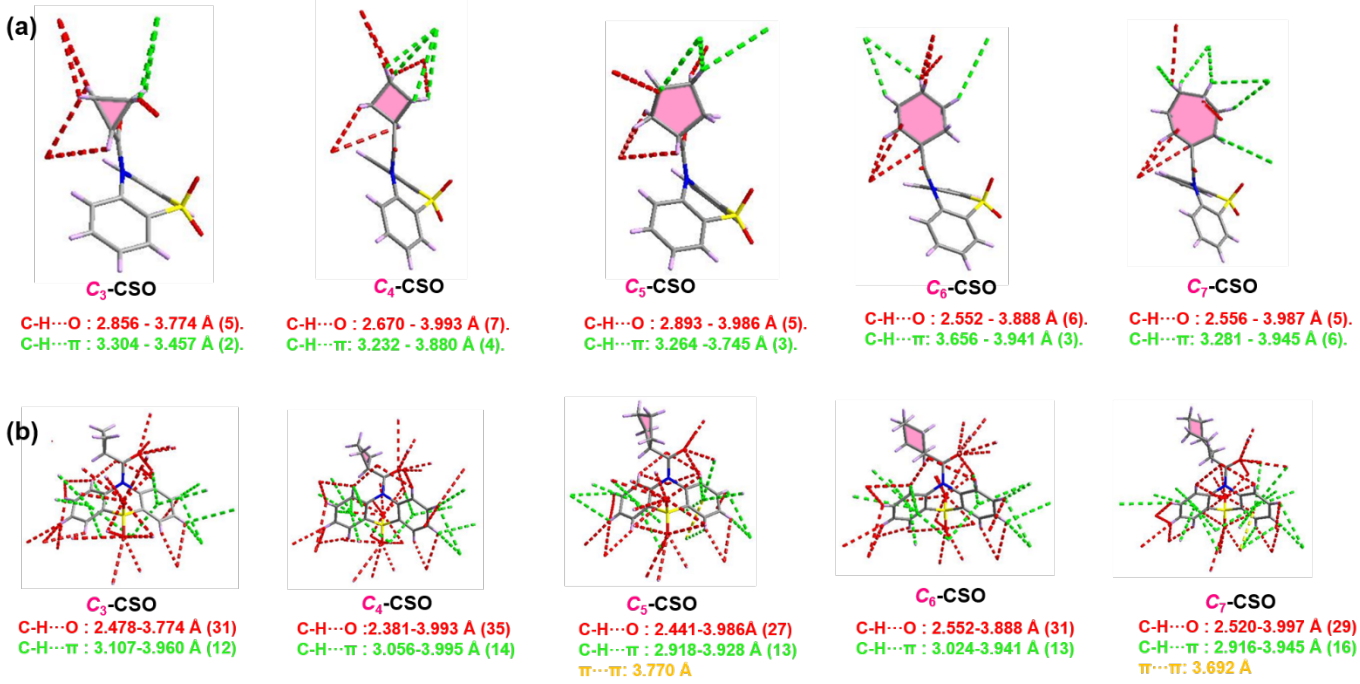

Figure S34 (a) Intermolecular interactions formed by cycloalkyl (C_n) substituents as heads; (b) Intermolecular interactions formed by phenothiazine and carbonyl groups as tails.

Table S7 The detail data of intermolecular interactions formed by cycloalkyl (C_n) substituents as heads

Sample	C-H…O (Å)	C-H…π (Å)
C_3-CsO	2.856, 3.012, 3.334, 3.736, 3.774	3.304, 3.457
C_4-CsO	2.670, 2.979, 3.036, 3.071, 3.843, 3.897, 3.993	3.232, 3.548, 3.607, 3.880
C_5-CsO	2.893, 3.158, 3.599, 3.741, 3.986	3.264, 3.506, 3.745
C_6-CsO	2.552, 2.780, 3.251, 3.556, 3.613, 3.888	3.656, 3.928, 3.941
C_7-CsO	2.556, 3.676, 3.793, 3.867, 3.987	3.281, 3.488, 3.491, 3.701, 3.944, 3.945

Table S8 The detail data of intermolecular interactions formed by phenothiazine and carbonyl groups as tails.

Sample	C-H…O (Å)	C-H…π (Å)	π…π (Å)
C_3-CsO	2.478(2),2.599(2),2.631(2),2.789(2),2.799(2),2.842(2),2.856,2.881(2),2.967(2),3.012,3.077(2),3.257(2),3.277(2),3.334,3.575(2),3.702(2),3.736,3.774	3.107(2),3.153(2),3.304,3.457,3.651(2),3.733(2)，3.960(2)	
C_4-CsO	2.381(2),2.513(2),2.565(2),2.670,2.673(2),2.704(2),2.712(2),2.859(2),2.943(2),2.979,3.036,3.071,3.085(2),3.200(2),3.209(2),3.526(2),3.753(2),3.843,3.897,3.982(2),3.993	3.056(2),3.078(2),3.232,3.548,3.573(2),3.607,3.792(2),3.880,3.995(2)	
C_5-CsO	2.441(2),2.459(2),2.619(2),2.681(2),2.819(2),2.893,2.954(2),2.996(2),3.158,3.190(2),3.213(2),3.216(2),3.369(2),3.599,3.741,3.871(2),3.986	2.918(2),3.264,3.321(2),3.506,3.733(2),3.745,3.915(2), 3.928(2)	3.770
C_6-CsO	2.552,2.582(2),2.611(2),2.772(2),2.799(2),2.780,2.856(2),2.864(2),3.069(2),3.216,3.251,3.283(2),3.364(2),3.551(2),3.556,3.613,3.641(2),3.666(2), 3.888	3.024(2),3.279(2),3.470(2),3.650(2),3.656,3.722(2),3.928,3.941	
C_7-CsO	2.520(2),2.556,2.570(2),2.575(2),2.793(2),2.895(2),2.928(2),3.004(2),3.178(2),3.210(2),3.322(2),3.468(2),3.676, 3.793,3.867,3.987,3.997(2)	2.916(2),3.281,3.488,3.491,3.701, 3.733(2),3.868(2),3.890(2),3.921(2), 3.944,3.945	3.692

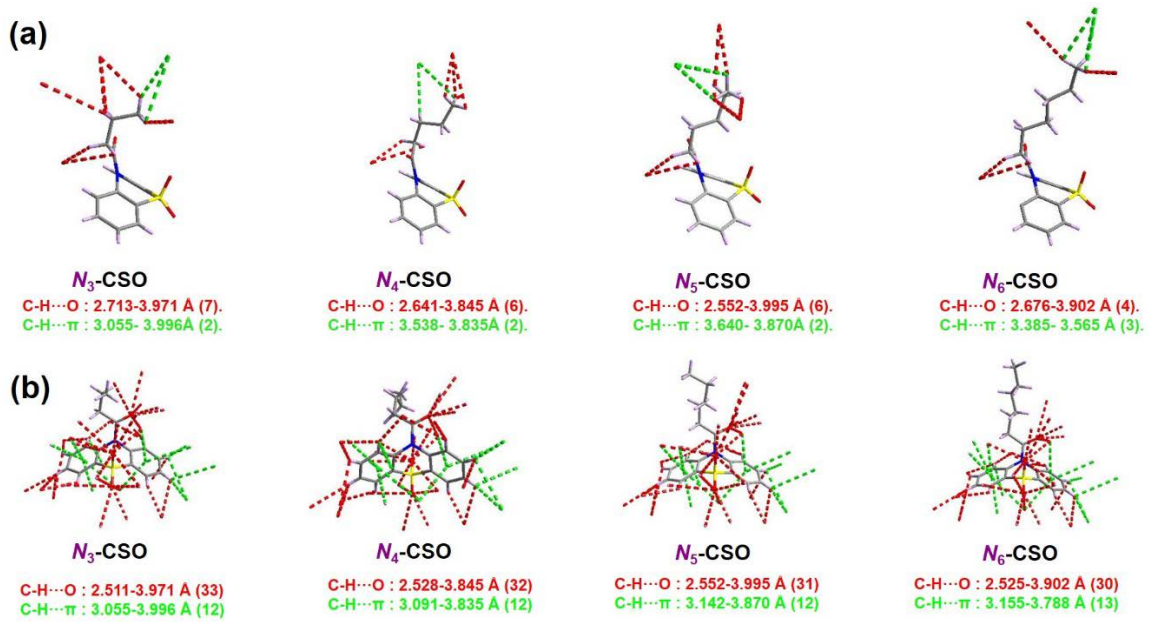

Figure S35 (a) Intermolecular interactions formed by alkyl (N_n) substituents as heads; (b) Intermolecular interactions formed by phenothiazine and carbonyl groups as tails.

Table S9 The detail data of intermolecular interactions formed by alkyl (N_n) substituents as heads

Sample	C-H…O (Å)	C-H…π (Å)
N_3-CsO	2.713, 3.102, 3.302, 3.372, 3.457, 3.899, 3.971	3.055, 3.996
N_4-CsO	2,641, 2.736, 3.225, 3.574, 3.632, 3.845	3.538, 3.835
N_5-CsO	2.552, 2.707, 3.701, 3.745, 3.797, 3.995	3.640, 3.870
N_6-CsO	2.676, 3.101, 3.420, 3.902	3.385, 3.525, 3.565

Table S10 The detail data of intermolecular interactions formed by phenothiazine and carbonyl groups as tails

Sample	C-H…O (Å)	C-H…π (Å)
N_3-CsO	2.511(2), 2.610(2), 2.646(2), 2.713, 2.749(2), 2.771(2), 2.812(2), 2.857(2), 2.987(2), 3.102, 3.121(2), 3.157(2), 3.302, 3.372, 3.426(2), 3.457, 3.591(2), 3.644(2), 3.899, 3.971	3.055, 3.105(2), 3.155(2), 3.686(2), 3.703(2), 3.825(2), 3.996.
N_4-CsO	2.528(2), 2.554(2), 2.641, 2.652(2), 2.736, 2.748(2), 2.762(2), 2.874(2), 2.946(2), 3.038(2), 3.160(2), 3.178(2), 3.225, 3.465(2), 3.574, 3.599(2), 3.632, 3.676(2), 3.845	3.091(2), 3.180(2), 3.538, 3.684(2), 3.692(2), 3.799(2), 3.835
N_5-CsO	2.552, 2.555(2), 2.573(2), 2.690(2), 2.707, 2.768(2), 2.828(2), 2.859(2), 2.986(2), 3.003(2), 3.156(2), 3.194(2), 3.474(2), 3.606(2), 3.701, 3.719(2), 3.745, 3.797, 3.995	3.142(2), 3.215(2), 3.640, 3.696(2), 3.744(2), 3.793(2), 3.870
N_6-CsO	2.525(2), 2.556(2), 2.562(2), 2.607(2), 2.676, 2.739(2), 2.782(2), 2.854(2), 2.958(2), 3.067(2), 3.101, 3.624(2), 3.702(2), 3.140(2), 3.166(2), 3.420, 3.902	3.155(2), 3.204(2), 3.385, 3.525, 3.565, 3.717(2), 3.725(2), 3.788(2),

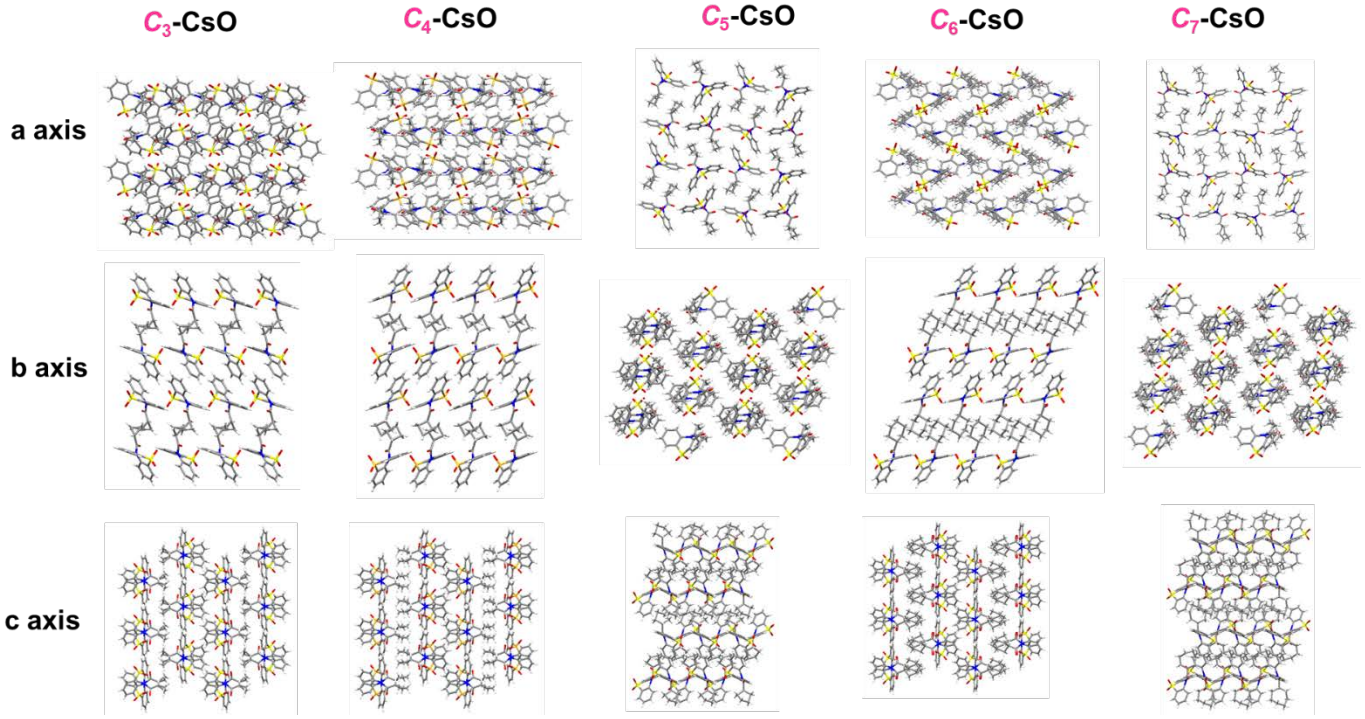

Figure S36 Molecular packing in C_n-CsO crystals along a, b and c axis.

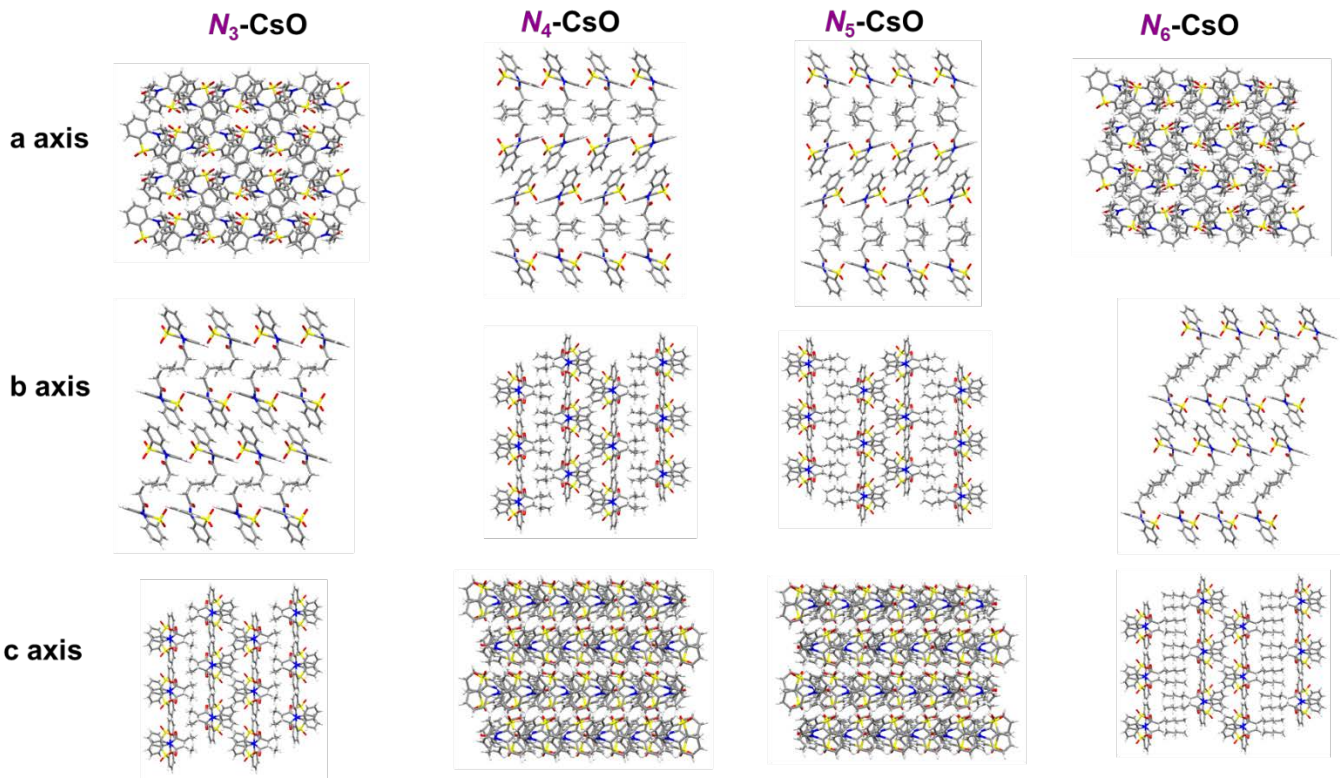

Figure S37 Molecular packing in N_n-CsO crystals along a, b and c axis.

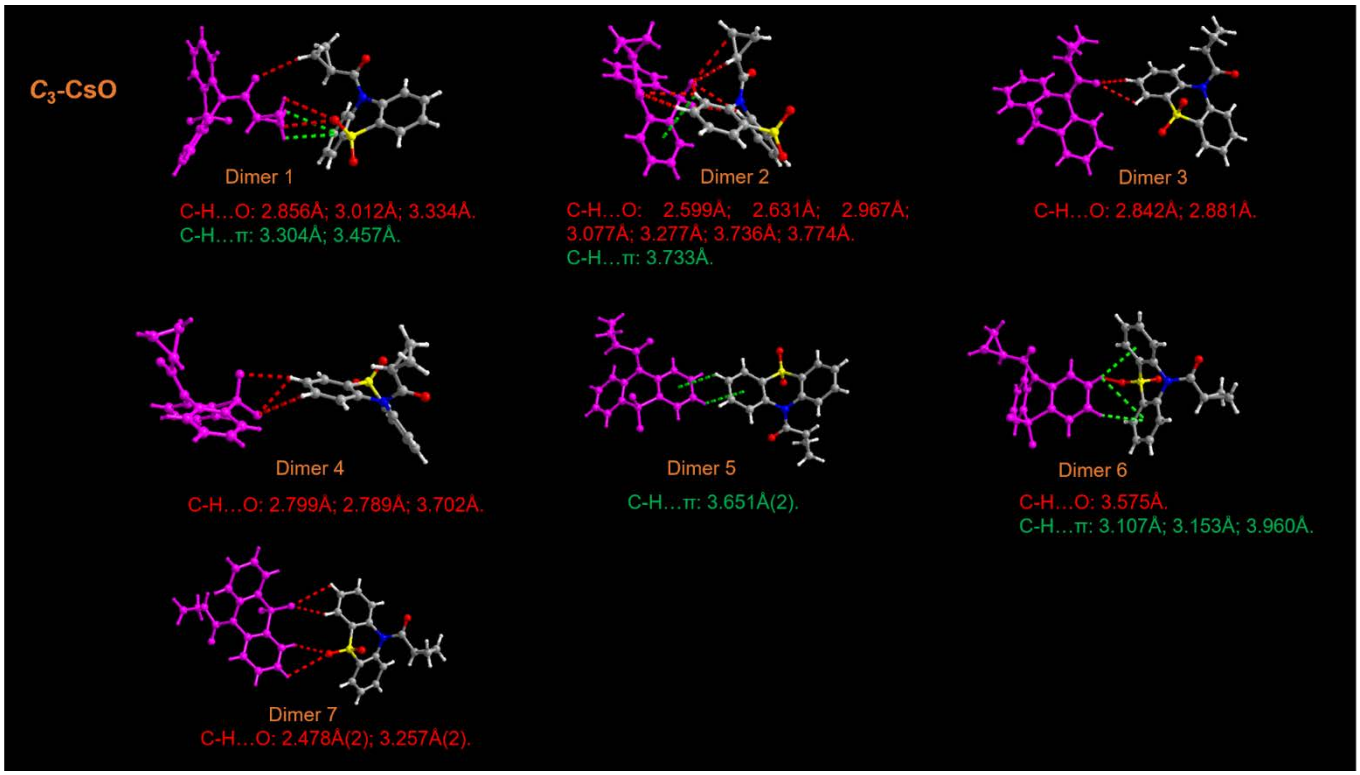

Figure S38 Intermolecular interactions in adjacent molecules in C_3-CsO crystal.

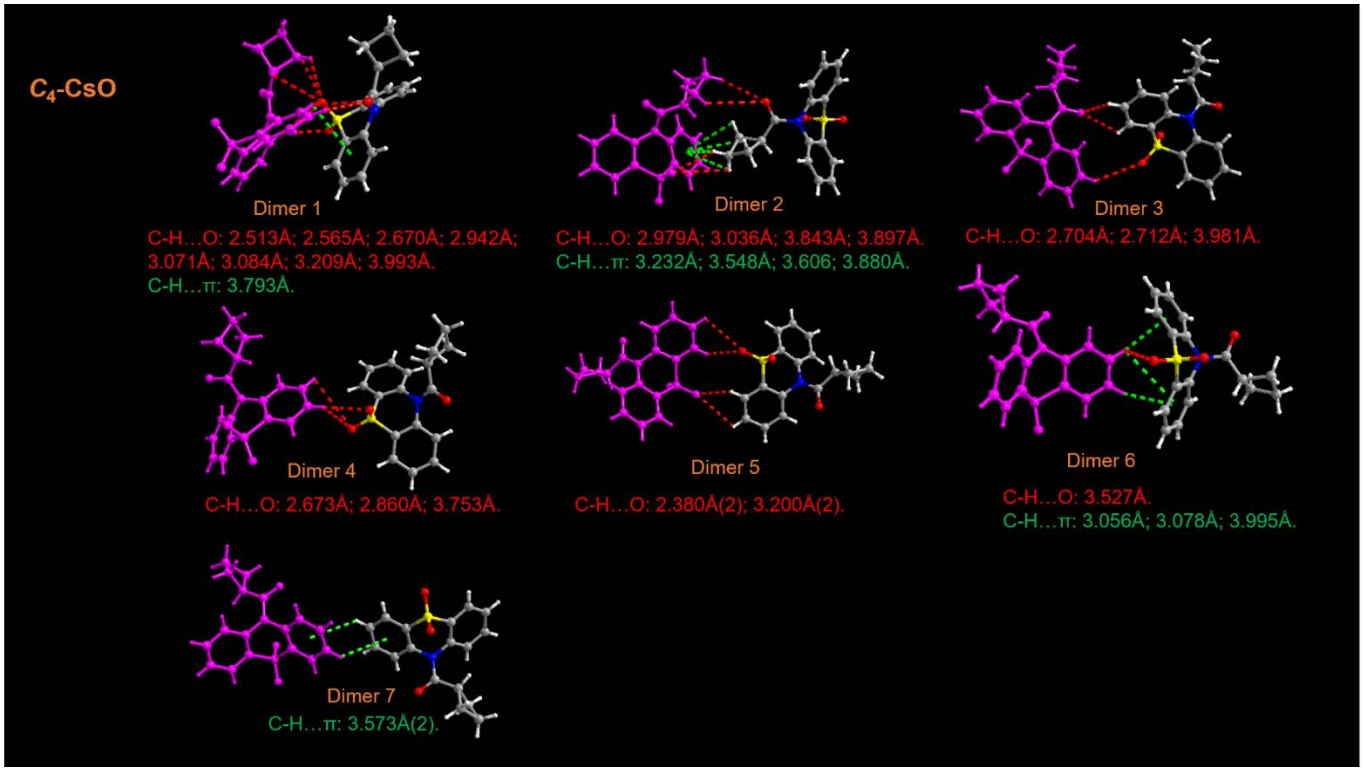

Figure S39 Intermolecular interactions in adjacent molecules in C_4-CsO crystal.

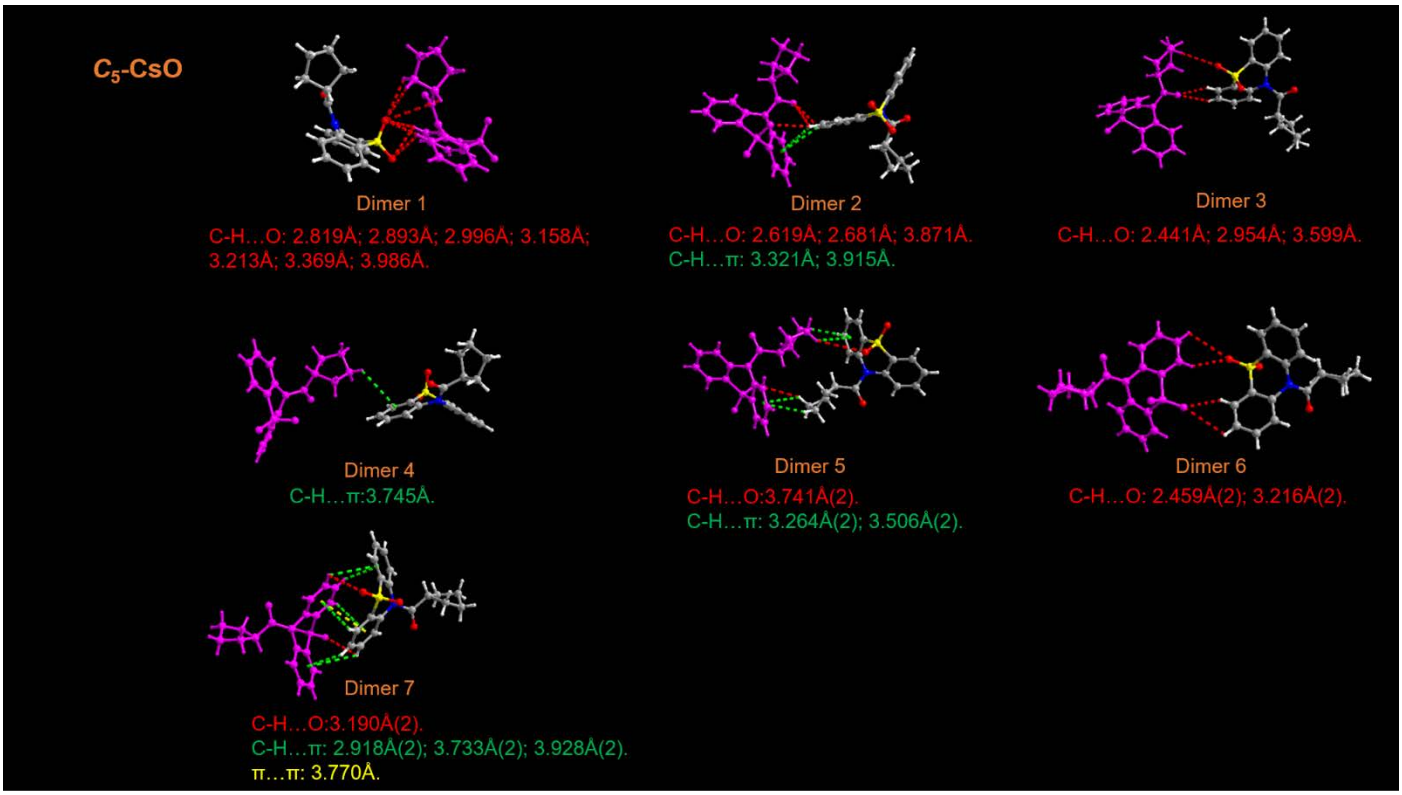

Figure S40 Intermolecular interactions in adjacent molecules in C_5-CsO crystal.

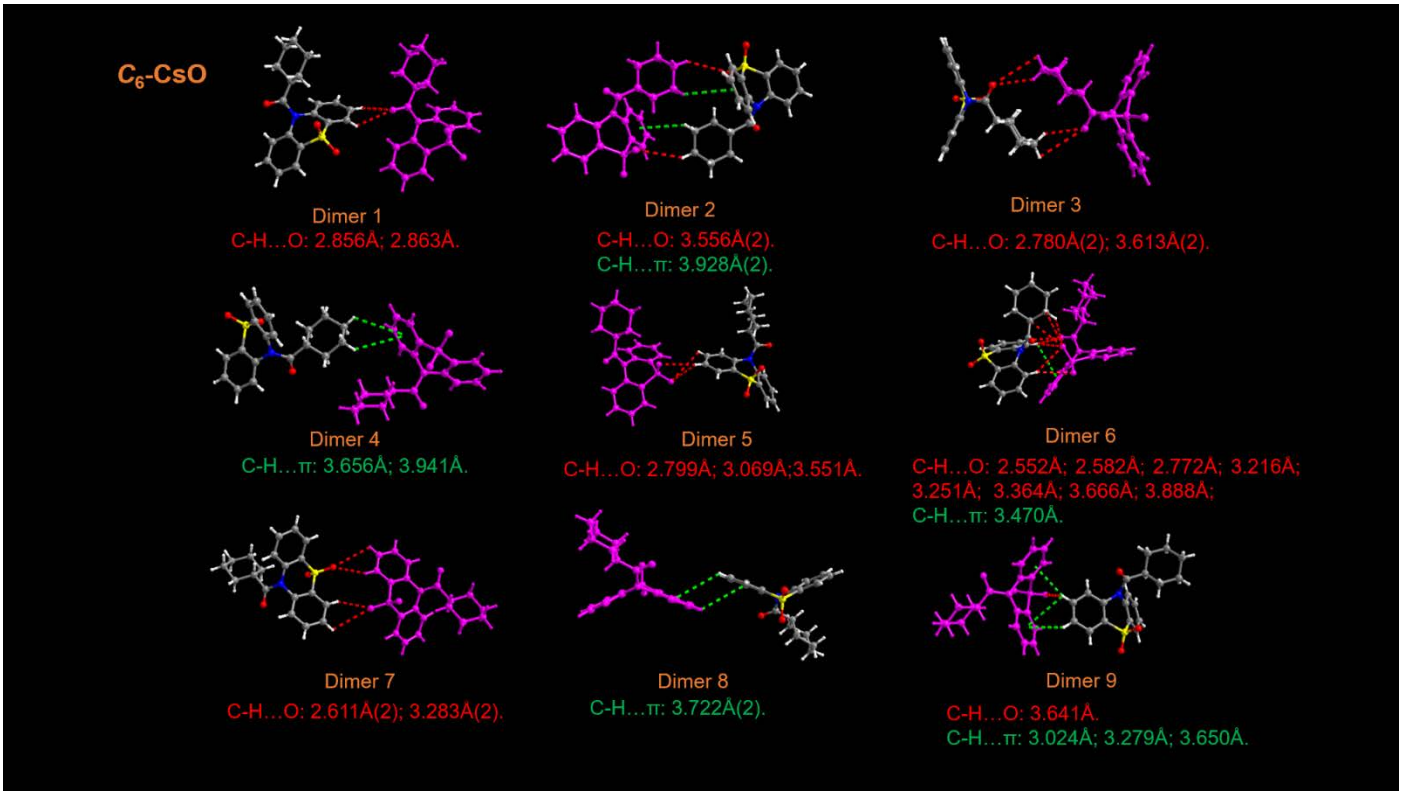

Figure S41 Intermolecular interactions in adjacent molecules in C_6-CsO crystal.

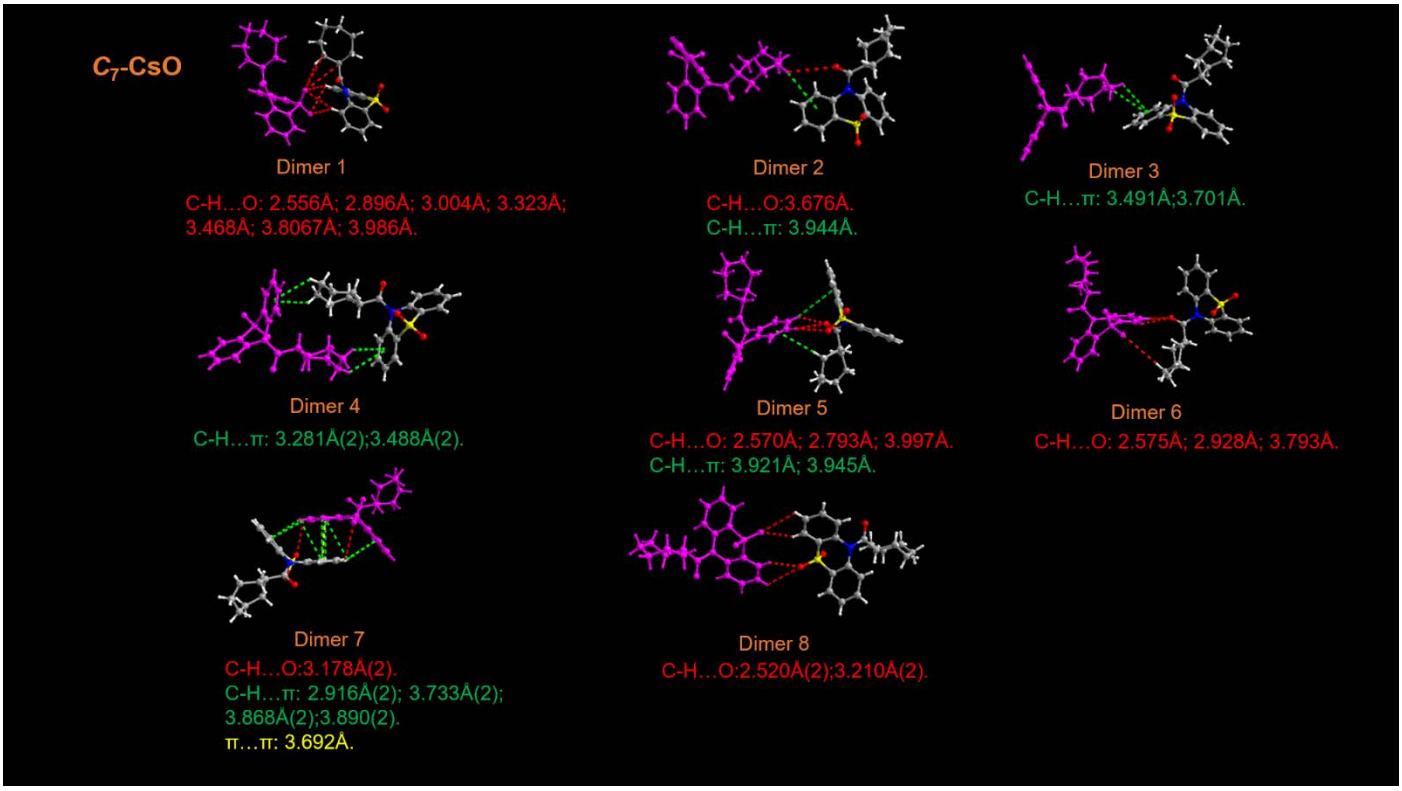

Figure S42 Intermolecular interactions in adjacent molecules in C_7-CsO crystal.

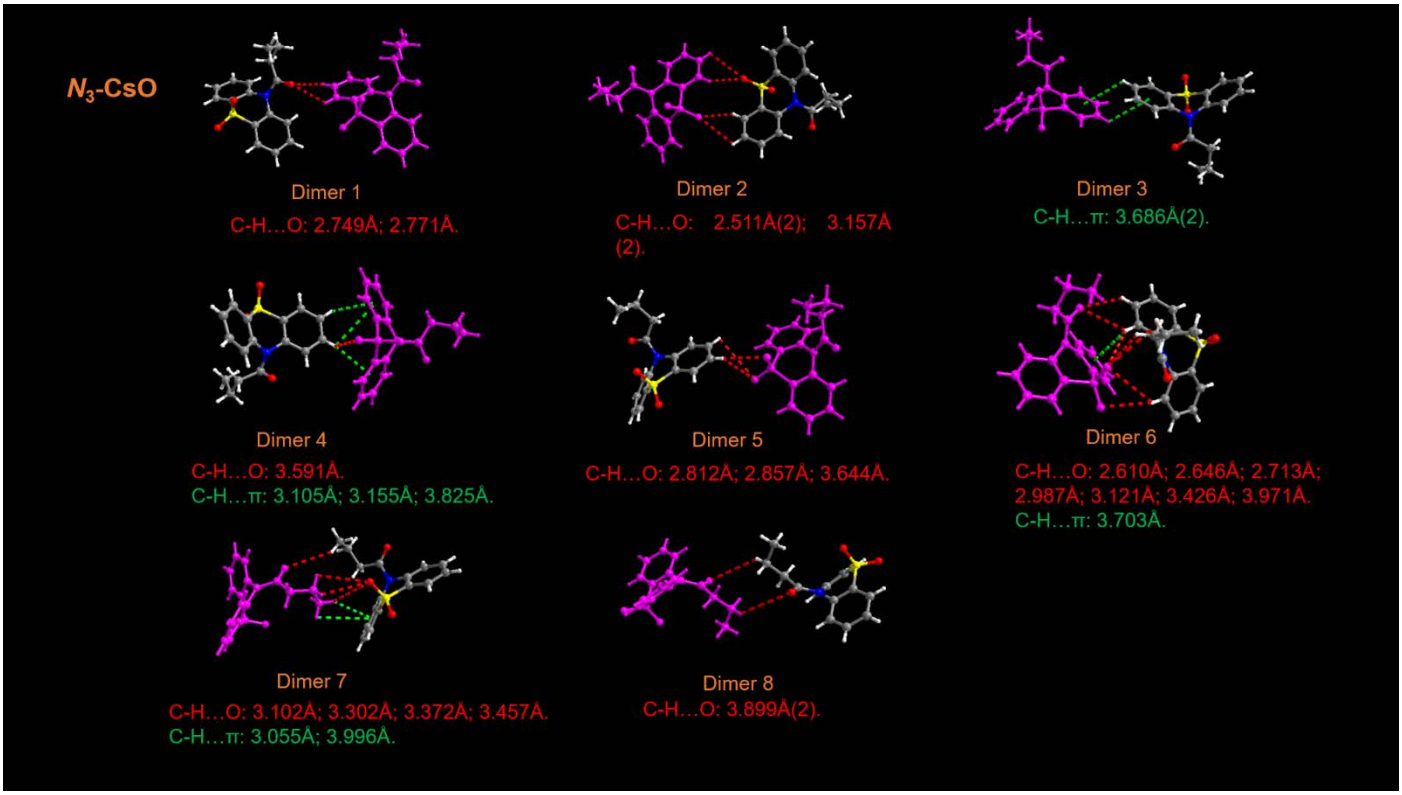

Figure S43 Intermolecular interactions in adjacent molecules in N_3-CsO crystal.

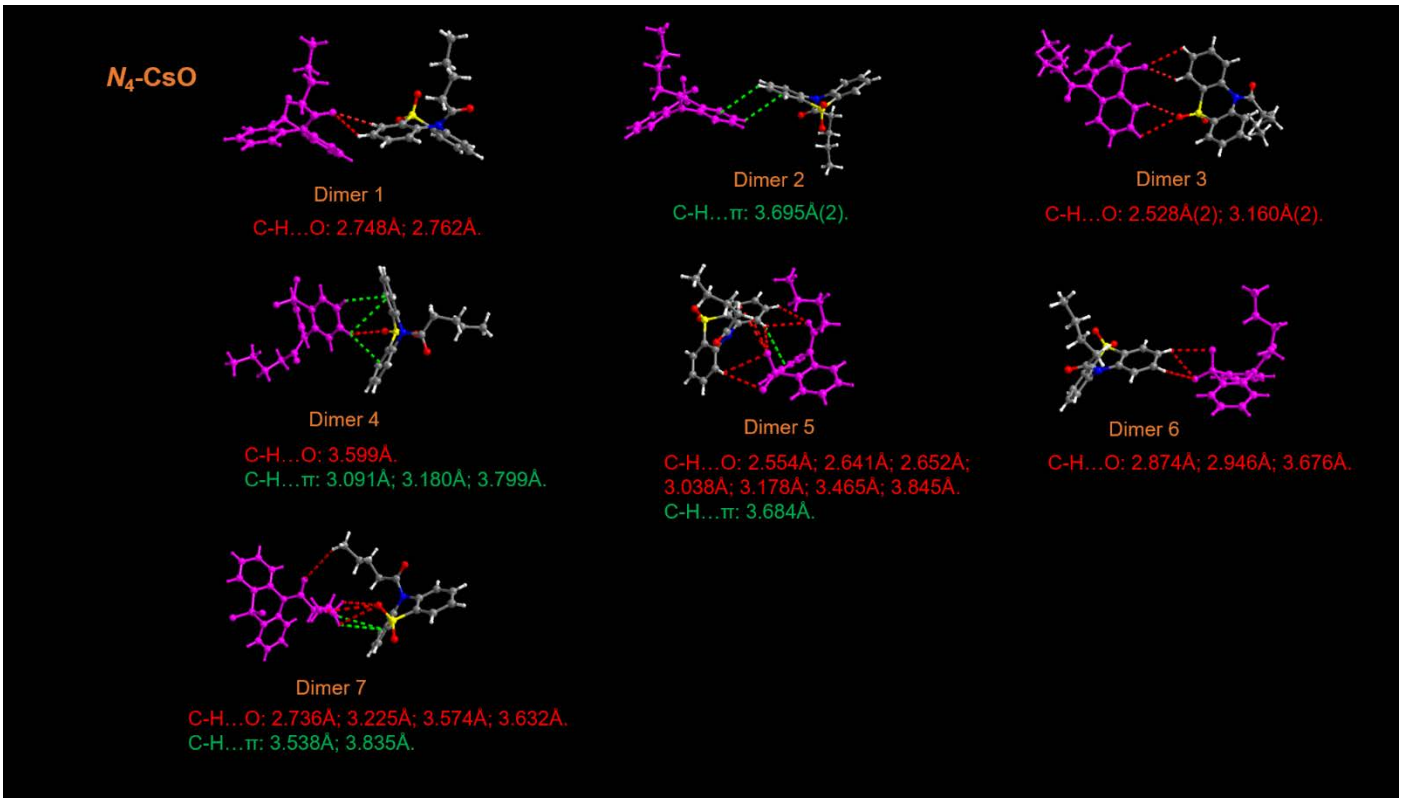

Figure S44 Intermolecular interactions in adjacent molecules in N_4-CsO crystal.

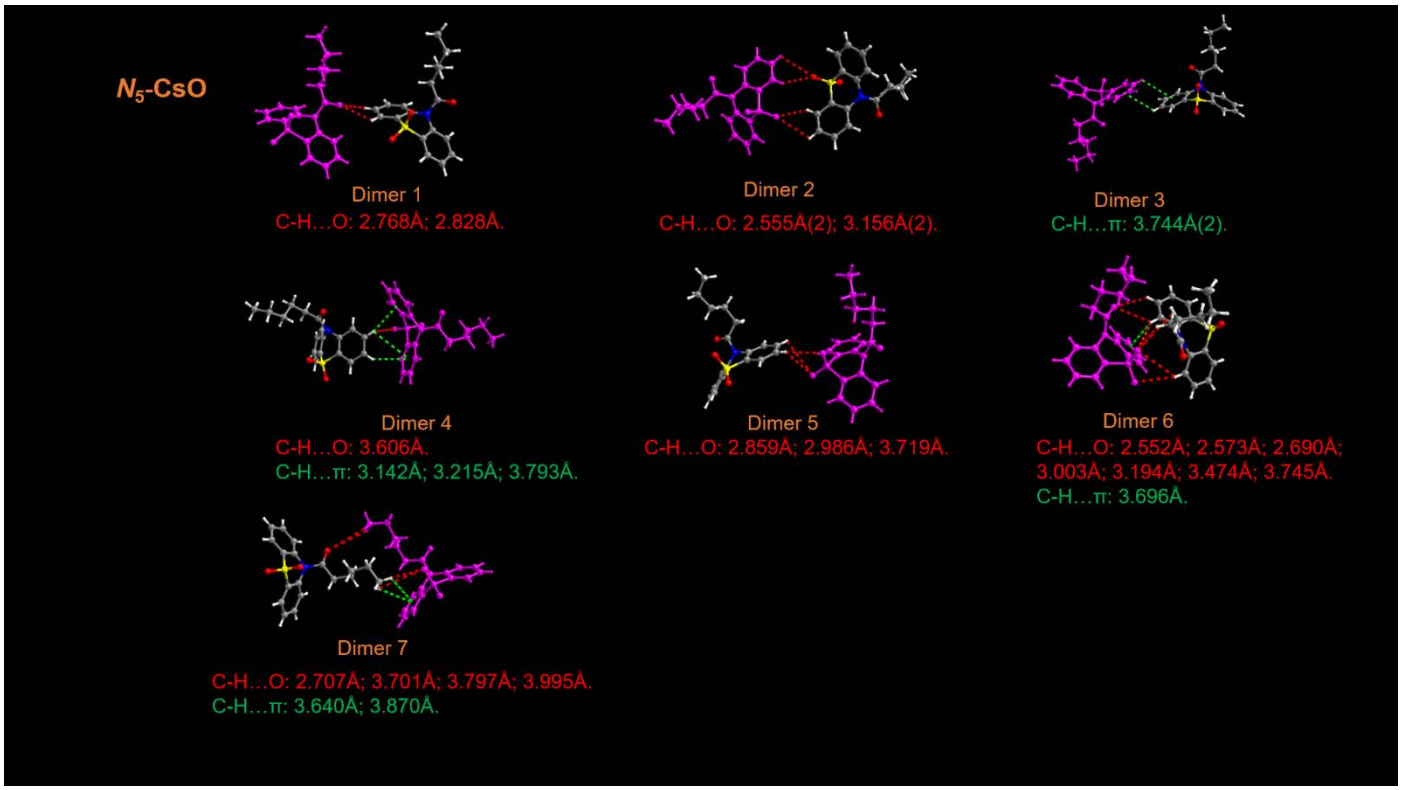

Figure S45 Intermolecular interactions in adjacent molecules in N_5-CsO crystal.

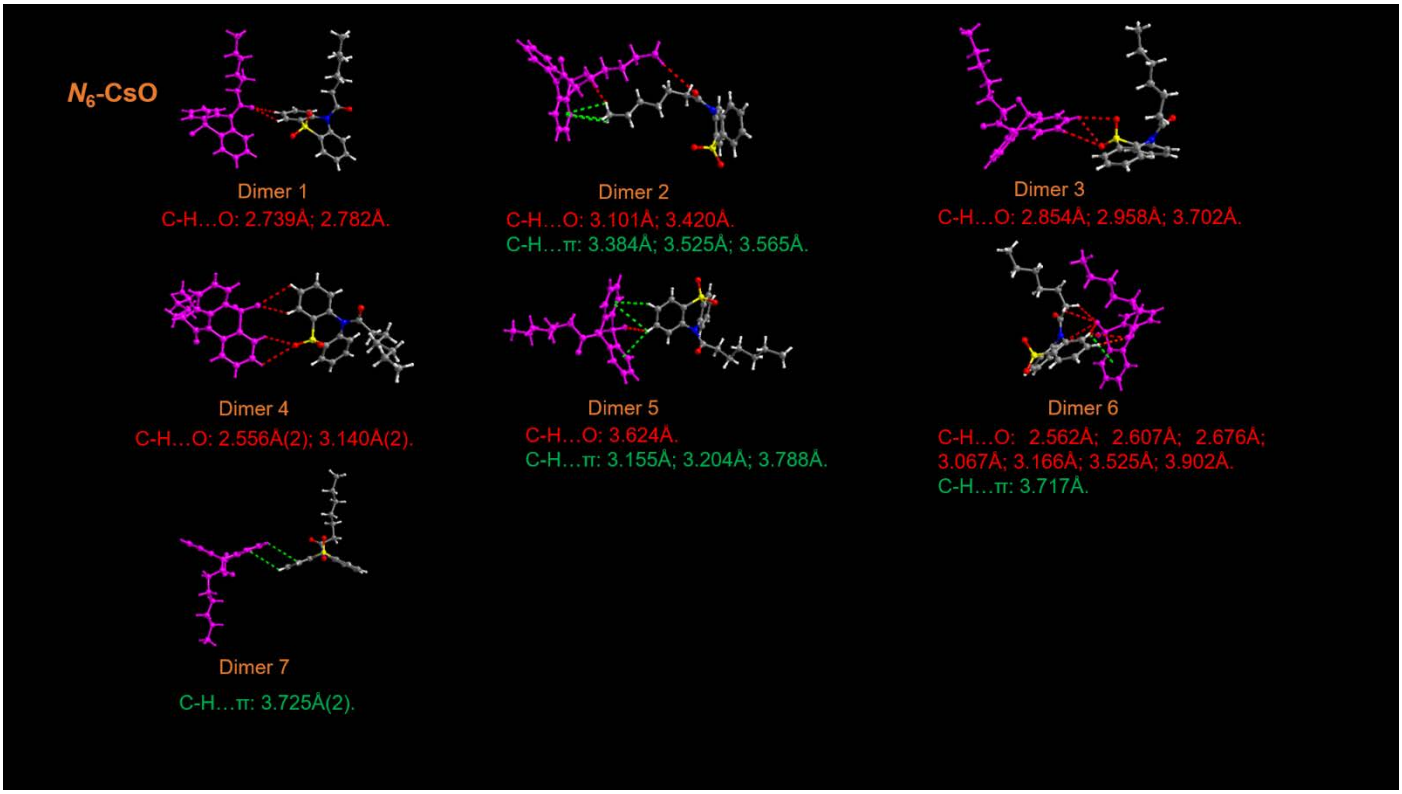

Figure S46 Intermolecular interactions in adjacent molecules in N_6-CsO crystal.

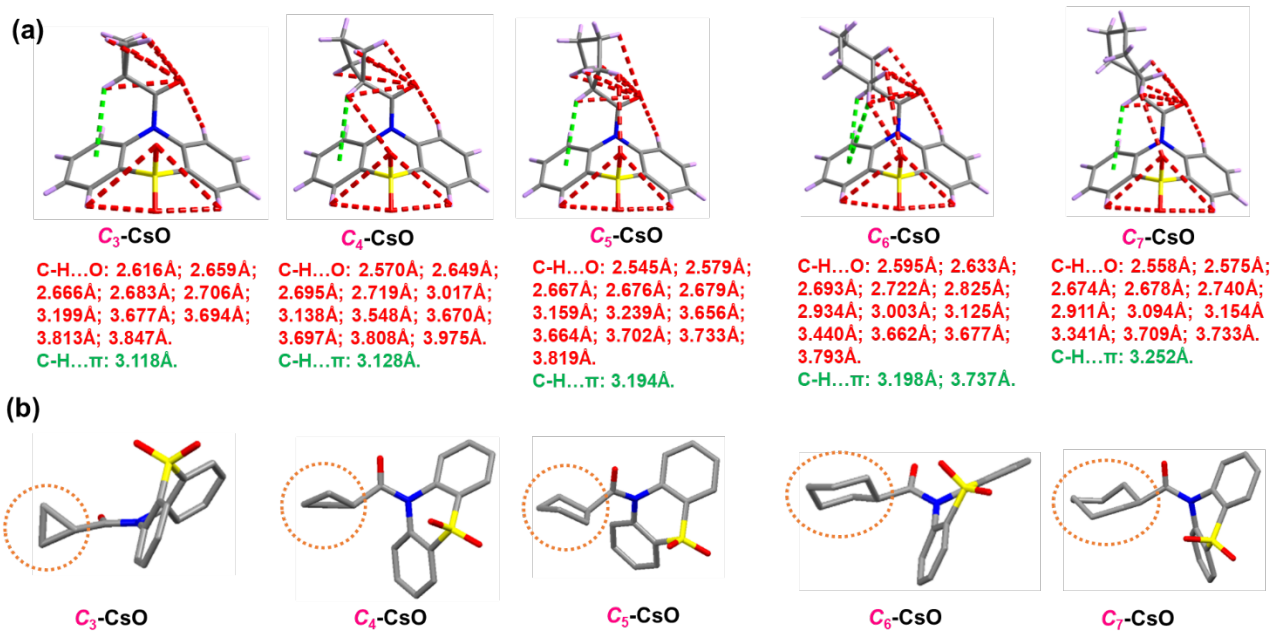

Figure S47 (a) The intramolecular interactions in C_n -CsO crystals; (b) The conformations of cycloalkyl moieties in C_n -CsO crystals.

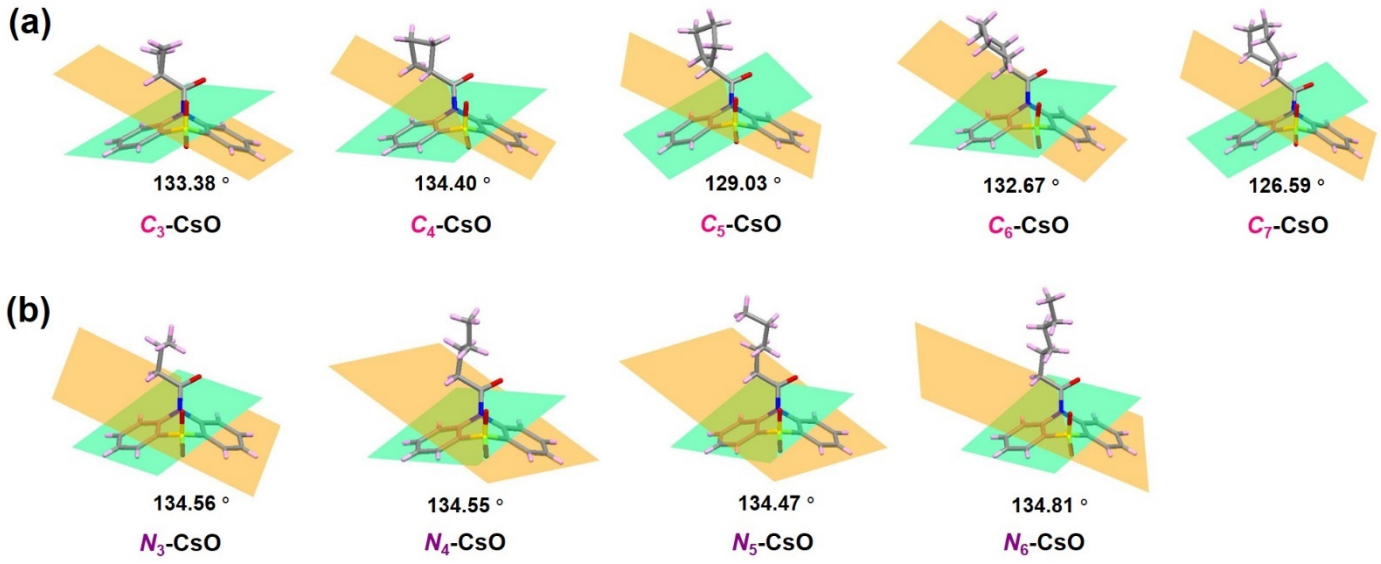

Figure S48 The dihedral angles between two benzene rings in phenothiazine moiety.

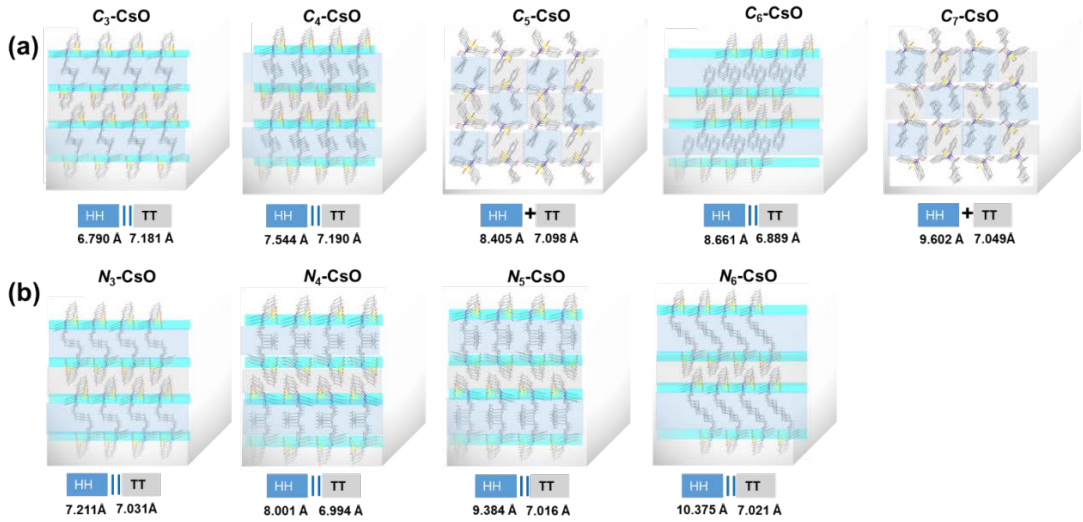

Figure S49 Molecular packing as well as the distances with head-to-head and tail-to-tail arrangnement among layers in C_n-CsO crystals.

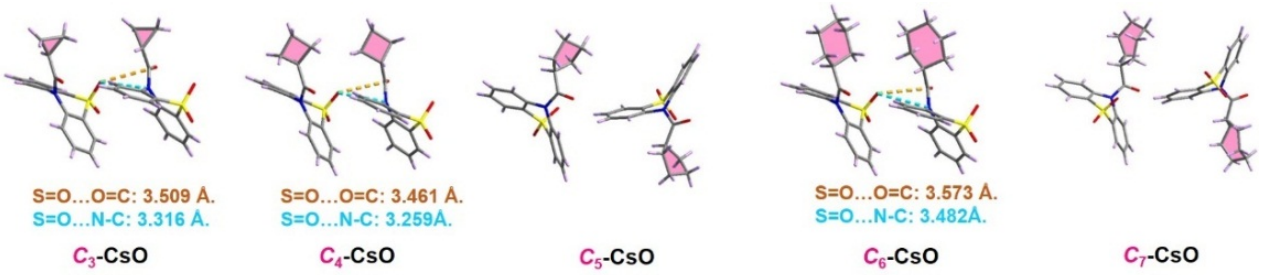

Figure S50 Intermolecular coupling of C_n-CsO dimers in single crystals.

Table S11 Energy levels of excited states of C_n-CSO dimers.

Compound	C_3-CSO	C_4-CsO	C_5-CsO	C_6-CsO	C_7-CsO
ΔE_{st} (eV)	0.3055	0.2332	0.6206	0.295	0.6490
S_1 (eV)	3.9406	3.8093	4.2333	3.9214	4.3152
T_1 (eV)	3.6351	3.5761	3.6127	3.6264	3.6662
T_2 (eV)	3.6402	3.5808	3.6208	3.6279	3.6703
T_3 (eV)	3.657	3.640	3.6516	3.6696	3.682
T_4 (eV)	3.6606	3.6416	3.6555	3.6743	3.6822
T_5 (eV)	3.9401	3.8108	4.0237	3.9194	4.0608
T_6 (eV)	4.0237	3.9575	4.0399	3.9829	4.0694
T_7 (eV)	4.0856	4.014	4.2332	4.0301	4.3077
T_8 (eV)	4.2964	4.0597	4.2853	4.1116	4.3168
T_9 (eV)		4.2135	4.3029	4.2452	4.3238
T_{10} (eV)			4.4311		4.4619
T_{12} (eV)			4.4324		4.4644
T_{13} (eV)			4.4645		4.4929
T_{14} (eV)			4.4664		4.4937
T_{15} (eV)			4.5125		4.5932
T_{16} (eV)					4.5951

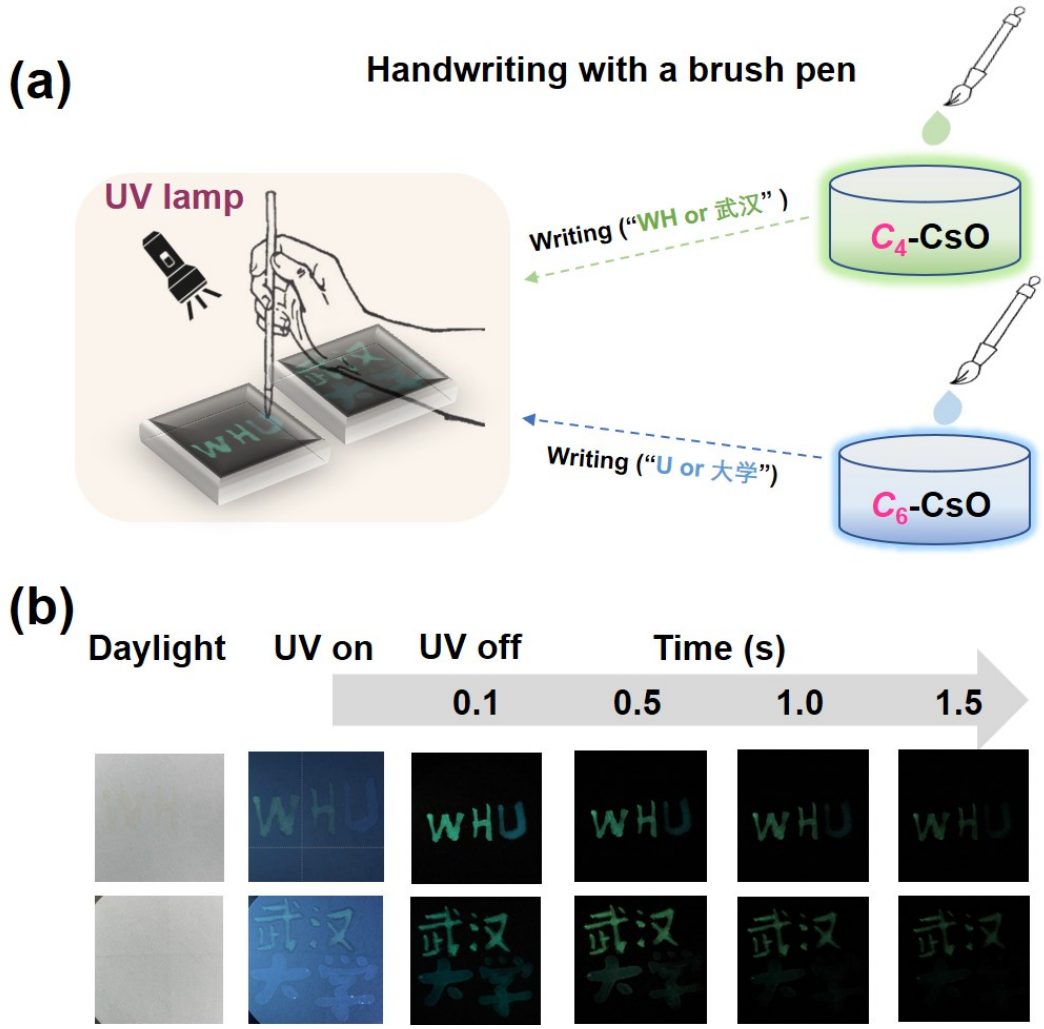

Figure S51 (a) The schematic diagram of anti-counterfeiting application. The letters "WHU" (the acronyms of Wuhan University) and chinese characters "武汉大学" are written by a brush pen, in which the "WH" and "武汉" is written with C_4-CsO in dichloromethane (DCM) solution as an ink, "U" and "大学" is written with C_6-CsO in dichloromethane (DCM) solution as an ink; (b) The phosphorescence photographs of the letters "WHU" and chinese characters "武汉大学" were taken at UV (365 nm) on and off under room-temperature.

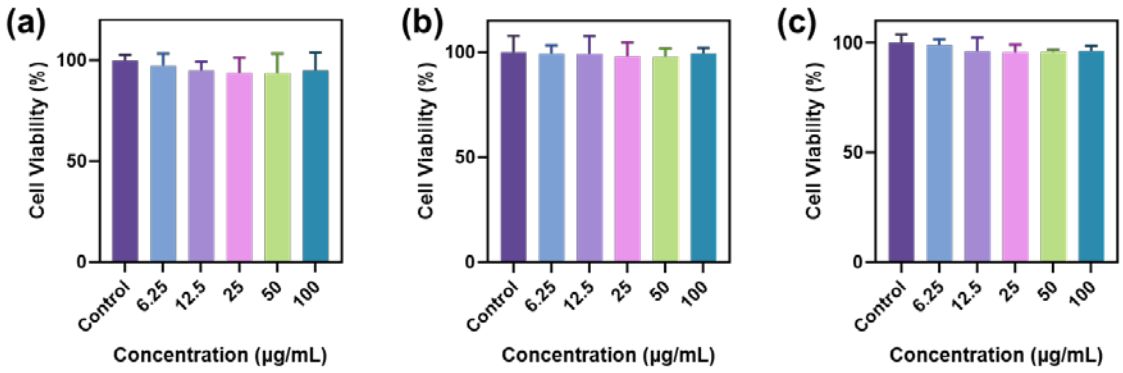

Figure S52 Cytotoxicity of C_4-CsO NPs (a), C_6-CsO NPs (b) and N_3-CsO NPs (c) against HeLa cells. The HeLa cells were incubated with C_4-CsO NPs, C_6-CsO NPs and N_3-CsO NPs at various concentrations for 24 h.

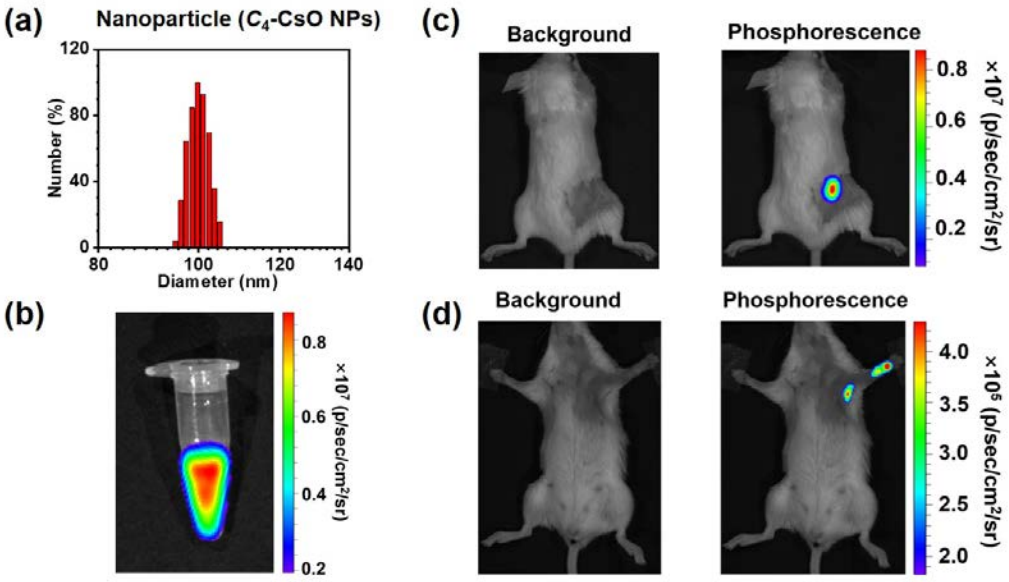

Figure S53 (a) The size distribution of organic nanoparticles based on C_4-CsO; (b) phosphorescence image of C_4-CsO NPs detected by IVIS instrument; The *in vivo* phosphorescence imaging of (c) subcutaneous tissue and (d) lymph node in living mice after injection of C_4-CsO NPs. (power density of UV light: 50 mW/cm^2)

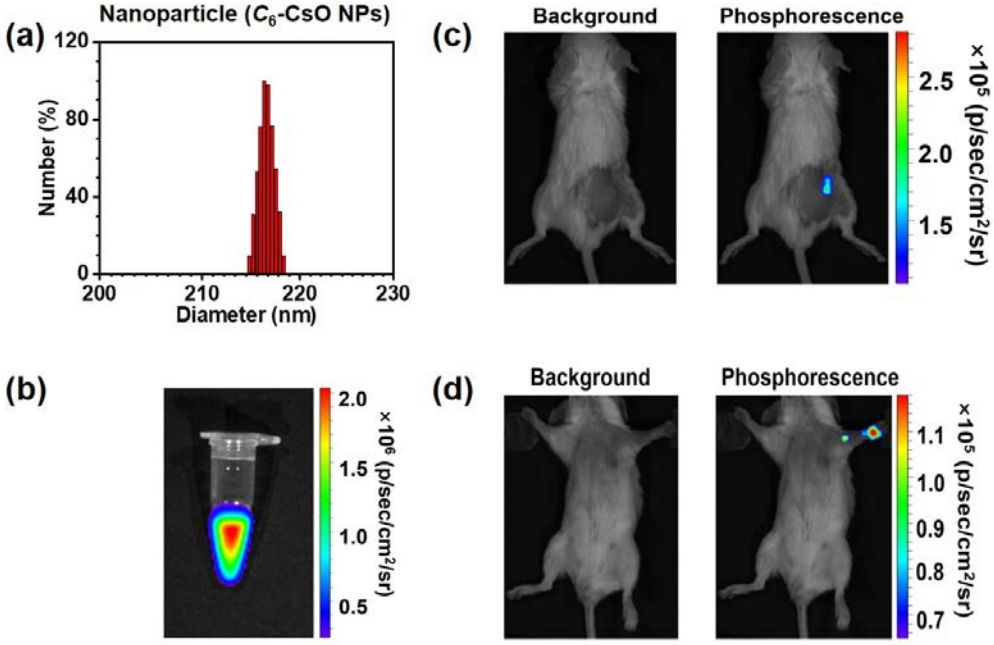

Figure S54 (a) The size distribution of organic nanoparticles based on C_6-CsO; (b) phosphorescence image of C_6-CsO NPs detected by IVIS instrument; The *in vivo* phosphorescence imaging of (c) subcutaneous tissue and (d) lymph node in living mice after injection of C_6-CsO NPs. (power density of UV light: 50 mW/cm^2)

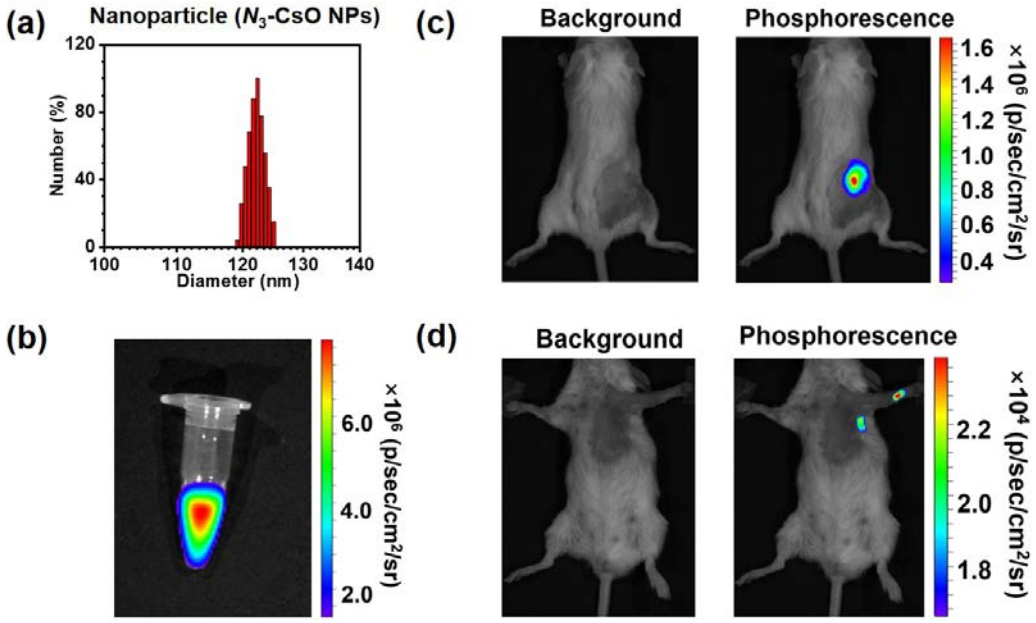

Figure S55 (a) The size distribution of organic nanoparticles based on N_3-CsO; (b) phosphorescence image of N_3-CsO NPs detected by IVIS instrument; The *in vivo* phosphorescence imaging of (c) subcutaneous tissue and (d) lymph node in living mice after injection of N_3-CsO NPs. (power density of UV light: 50 mW/cm^2)