Electronic Supporting Information

The odd-even effect of alkyl chain in organic room temperature phosphorescence luminogens and the corresponding in *vivo* imaging

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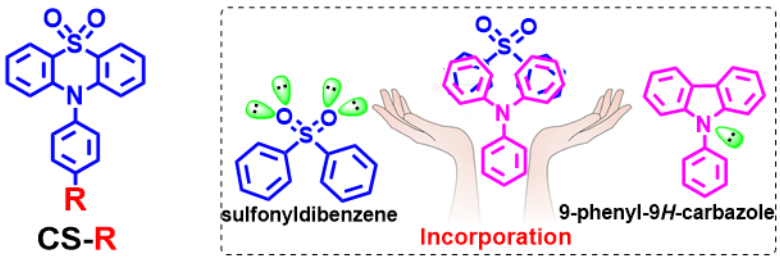
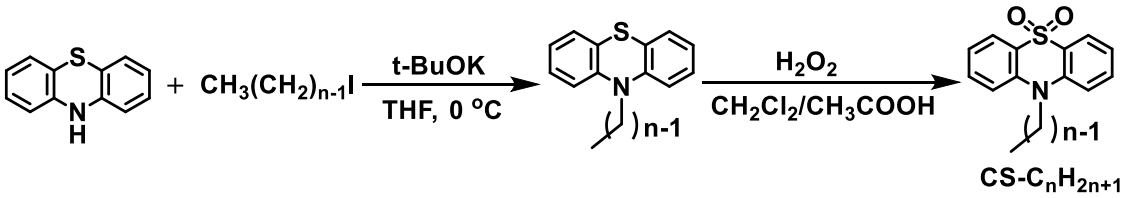


R	OCH_3	CH_3	H	Br	Cl	F
Abbreviation	CS-OCH_3	CS-CH_3	CS-H	CS-Br	CS-Cl	CS-F
τ (solid, RT)	88 ms	96 ms	188 ms	268 ms	256 ms	410 ms
λ_p (solid, RT)	509 nm	516 nm	525 nm	525 nm	500 nm	483 nm

Chart S1 The previous work based on 10-phenyl-10H phenothiazine 5,5-dioxide derivatives with RTP effect.



Scheme S1 The synthetic routes of the six target luminogens.

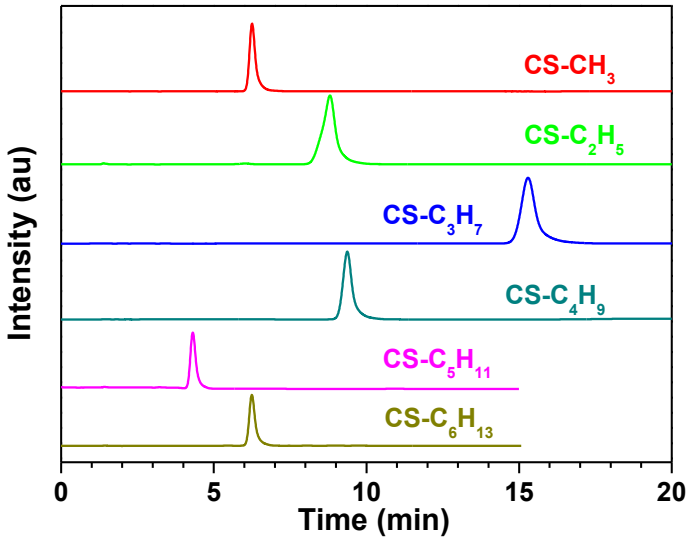


Figure S1 HPLC spectra of the six target compounds.

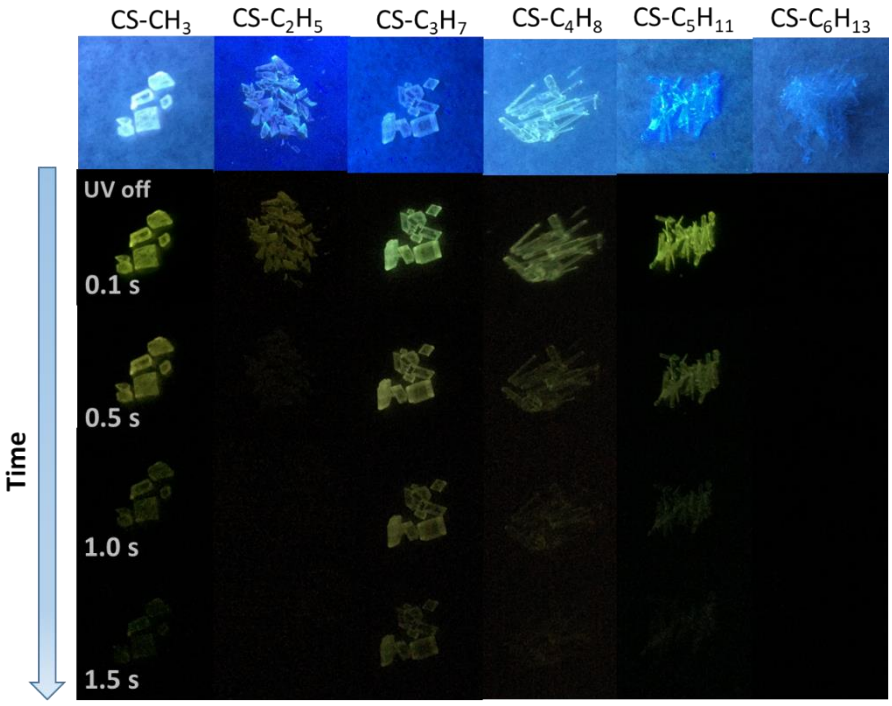


Figure S2 The RTP behaviors of the six luminogens.

Table S1 The photophysical data of CS-CH_3, CS-C_2H_5, CS-C_3H_7, CS-C_4H_9, CS-C_5H_{11} and CS-C_6H_{13} in solutions and crystals.

Compound	λ_{abs} [a] (nm)	λ_F [b] (nm)	τ_F [b] (ns)	λ_P [b] (nm)	τ_P [b] (ms)	λ_P [c] (nm)	τ_P [c] (ms)	Φ_{PL} [b] (%)
CS-CH_3	332	384	0.99	515	245	396, 405	253	3.83
CS-C_2H_5	335	398	0.65	476,515	92	393,407	273	3.50
CS-C_3H_7	335	385	0.90	414,435,490	327	395,407	268	5.68
CS-C_4H_9	335	385	0.71	509	181	391,407	269	2.99
CS-C_5H_{11}	336	382	0.66	415,442,516	205	395,405	246	5.51
CS-C_6H_{13}	336	378	0.86	510	/	391,406	249	2.93

[a] Observed from absorption spectra in dilute dichloromethane solution. [b] Determined in crystal at room temperature. [c] Determined in solution at 77K.

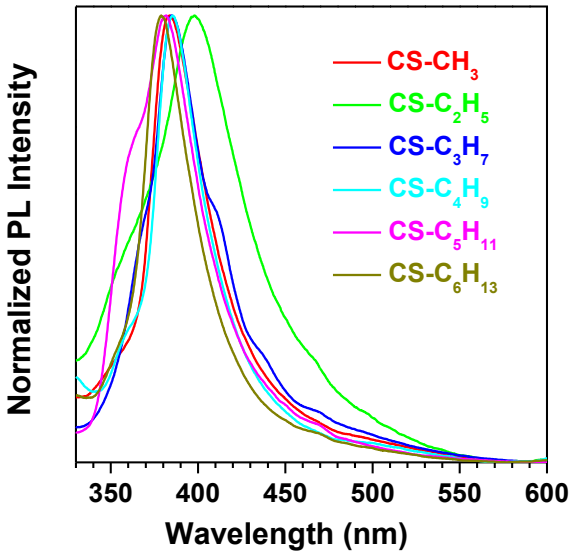
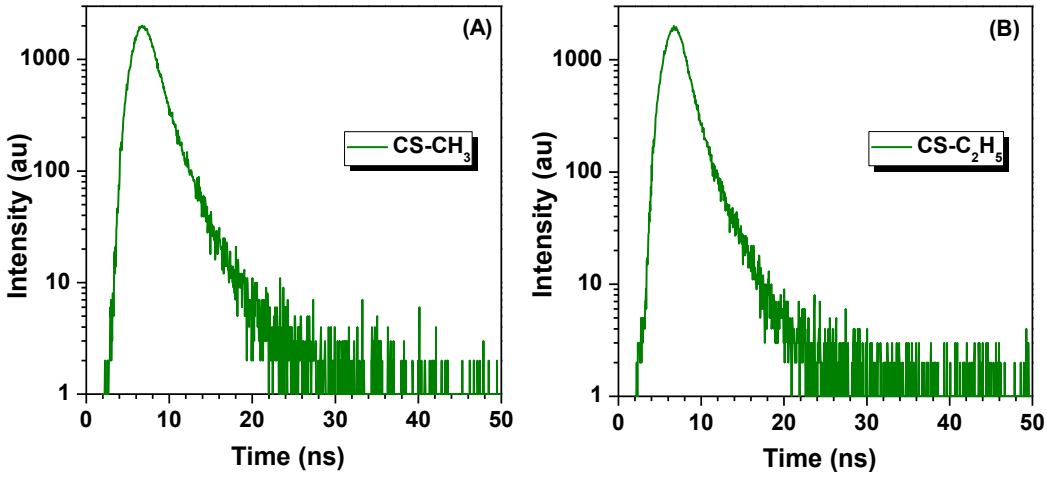


Figure S3 The normalized fluorescence spectra of the six luminogens in crystal state.



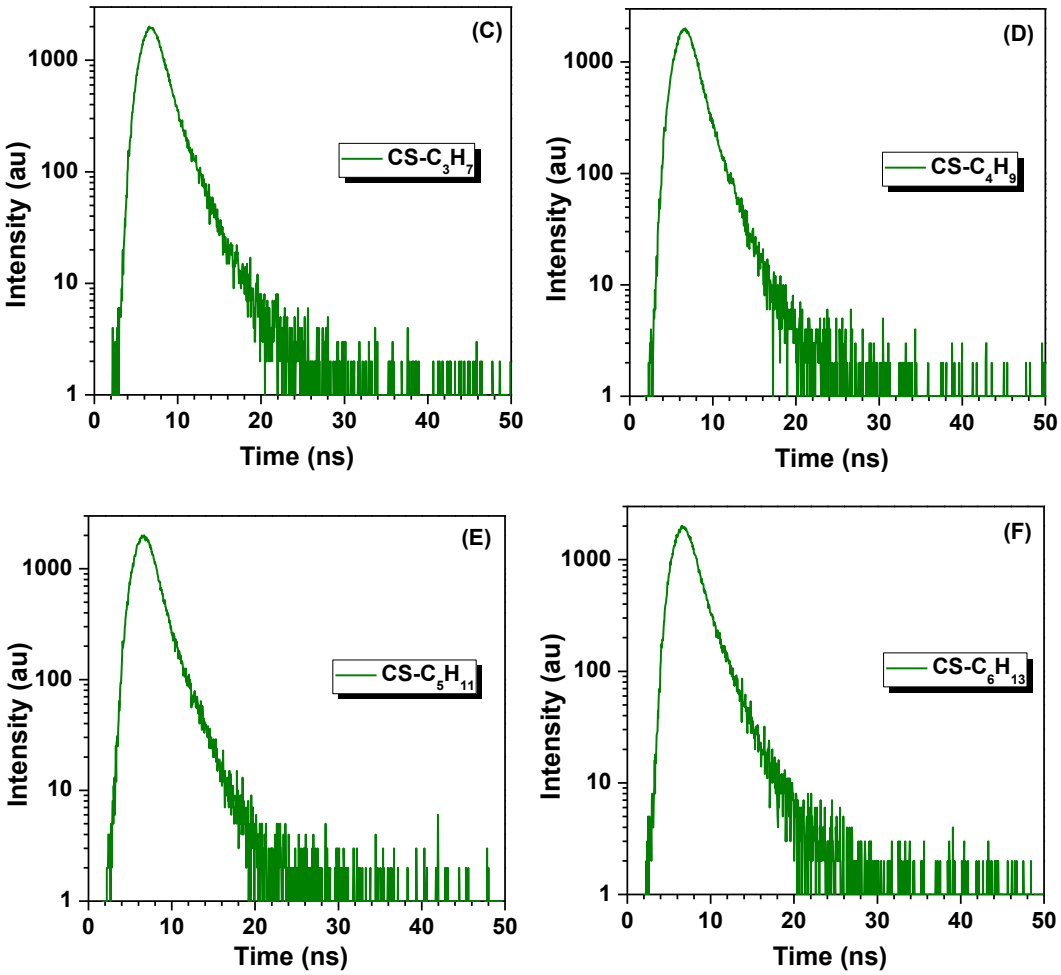


Figure S4 Time-resolved PL-decay curves for their fluorescence in crystal state of CS-CH_3 @384 nm **(A)**, CS-C_2H_5 @398 nm **(B)**, CS-C_3H_7 @385 nm **(C)**, CS-C_4H_9 @385 nm **(D)**, CS-C_5H_{11} @382 nm **(E)** and CS-C_6H_{13} @378 nm **(F)**.

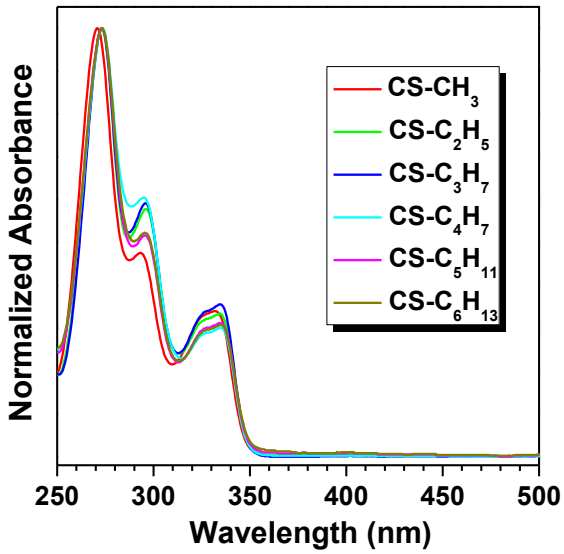


Figure S5 The UV-visible absorption spectra of the six luminogens in THF solutions.

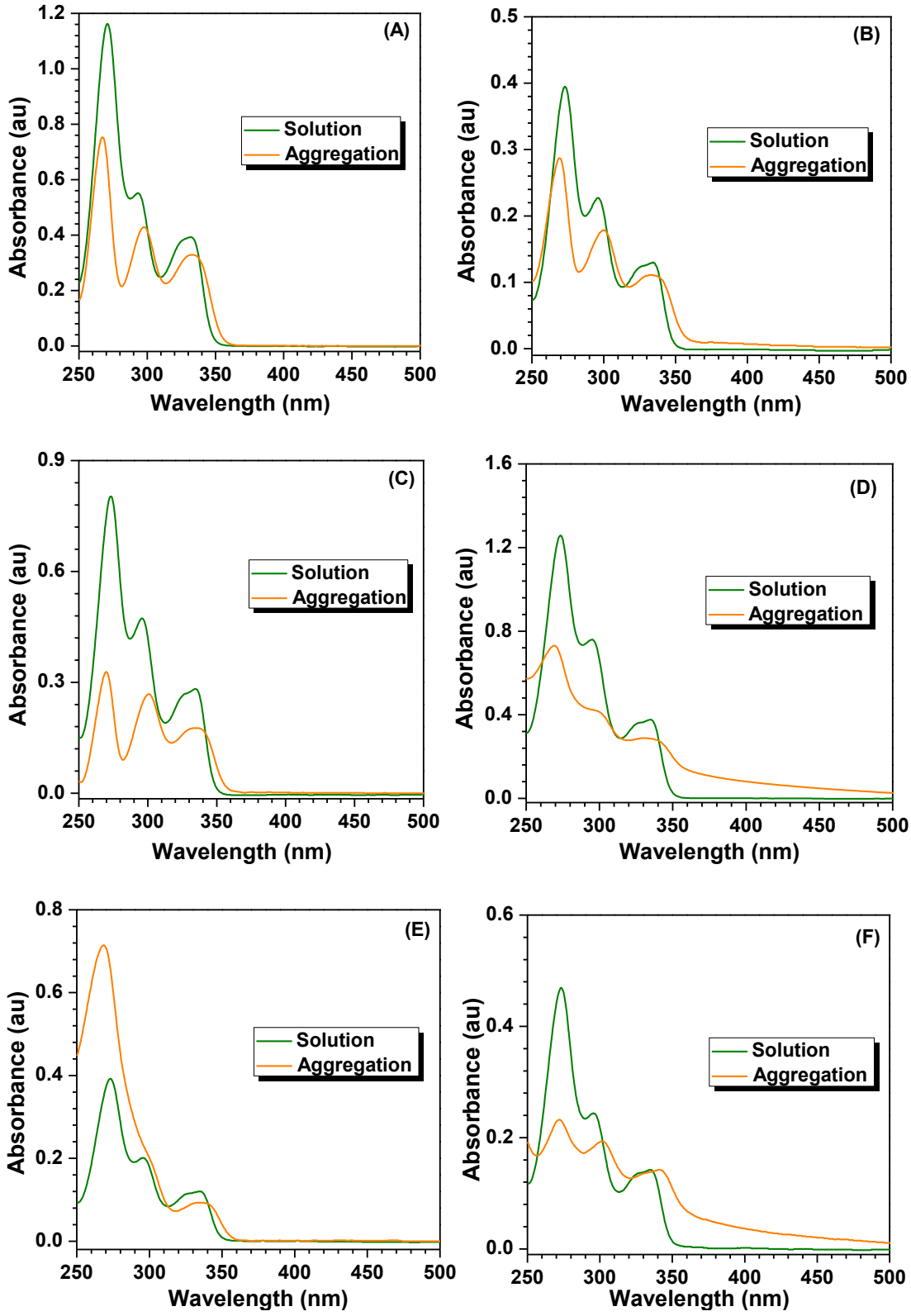


Figure S6 The UV-visible absorption spectra of THF solutions and aggregations (THF/water mixtures with f_{water} = 99%) of CS-CH_3 **(A)**, CS-C_2H_5 **(B)**, CS-C_3H_7 **(C)**, CS-C_4H_9 **(D)**, CS-C_5H_{11} **(E)** and CS-C_6H_{13} **(F)**.

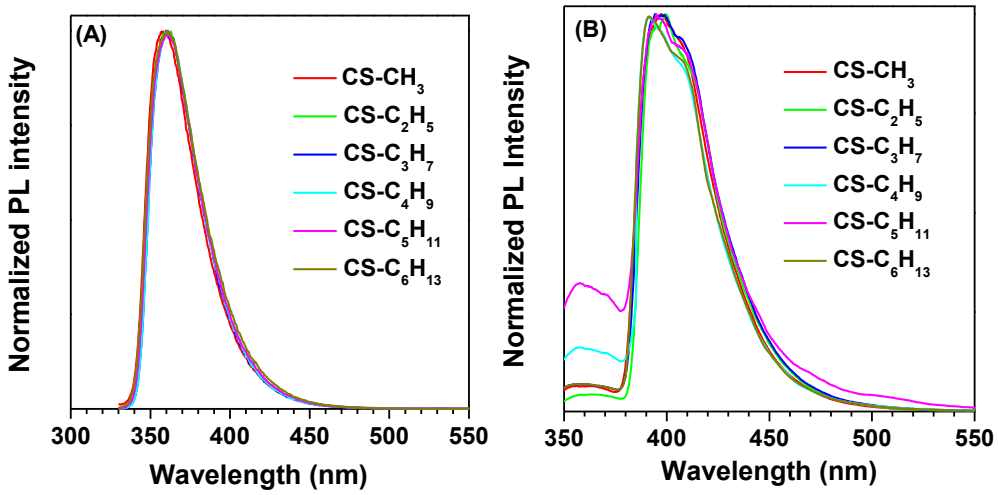


Figure S7 (A) Steady-state photoluminescence spectra of the six target luminogens in THF solution at room temperature; (B) Steady-state photoluminescence spectra of the six target luminogens in dichloromethane solution at 77K, concentration: 10^{-5} M.

Table S2 Structural data of single crystals of CS-CH_3, CS-C_2H_5, CS-C_3H_7, CS-C_4H_9, CS-C_5H_{11} and CS-C_6H_{13}.

Name	**CS-CH_3**	**CS-C_2H_5**	**CS-C_3H_7**	**CS-C_4H_9**	**CS-C_5H_{11}**	**CS-C_6H_{13}**
Formula	**$C_{13}H_{11}NO_2S$**	**$C_{14}H_{13}NO_2S$**	**$C_{15}H_{15}NO_2S$**	**$C_{16}H_{17}NO_2S$**	**$C_{17}H_{19}NO_2S$**	**$C_{18}H_{21}NO_2S$**
Wavelength (Å)	**0.71073**	**1.54184**	**1.54184**	**1.54184**	**0.71073**	**0.71073**
Space Group	**P21/n**	**P21/n**	**P-1**	**P 21/c**	**P21/n**	**R3c**
Cell Lengths (Å)	**a=8.78316(19)** **b=11.4642(2)** **c=11.1048(2)**	**a=7.9027(3)** **b=11.1576(4)** **c=13.5298(6)**	**a=7.7584(7)** **b=9.0839(8)** **c=10.0043(9)**	**a=18.9325(7)** **b=9.4253(3)** **c=17.2146(6)**	**a=11.377(3)** **b=9.712(3)** **c=13.362(4)**	**a= 26.477(7)** **b= 26.477(7)** **c= 12.475(3)**
Cell Angles (o)	**α=90** **β=91.3006(19)** **γ=90**	**α=90** **β=93.338(4)** **γ=90**	**α=109.128(8)** **β=97.408(8)** **γ=103.752(8)**	**α=90** **β=114.976(4)** **γ=90**	**α=90** **β=95.331(4)** **γ=90**	**α=90** **β=90** **γ=120**
Cell Volume ($Å^3$)	**1117.88(4)**	**1190.97(8)**	**630.39(10)**	**2784.58(19)**	**1470.0(7)**	**7574(4)**
Z	**4**	**4**	**2**	**8**	**4**	**18**
Density (g/cm^3)	**1.457**	**1.446**	**1.440**	**1.371**	**1.362**	**1.245**
F(000)	**512.0**	**544.0**	**288.0**	**1216.0**	**640.0**	**3024.0**
h_{max}, k_{max}, l_{max}	**10,14,13**	**9,13,16**	**9,10,11**	**22,11,20**	**15,13,18**	**32,32,15**
CCDC Number	**1879164**	**1879165**	**1879166**	**1879167**	**1879168**	**1879169**

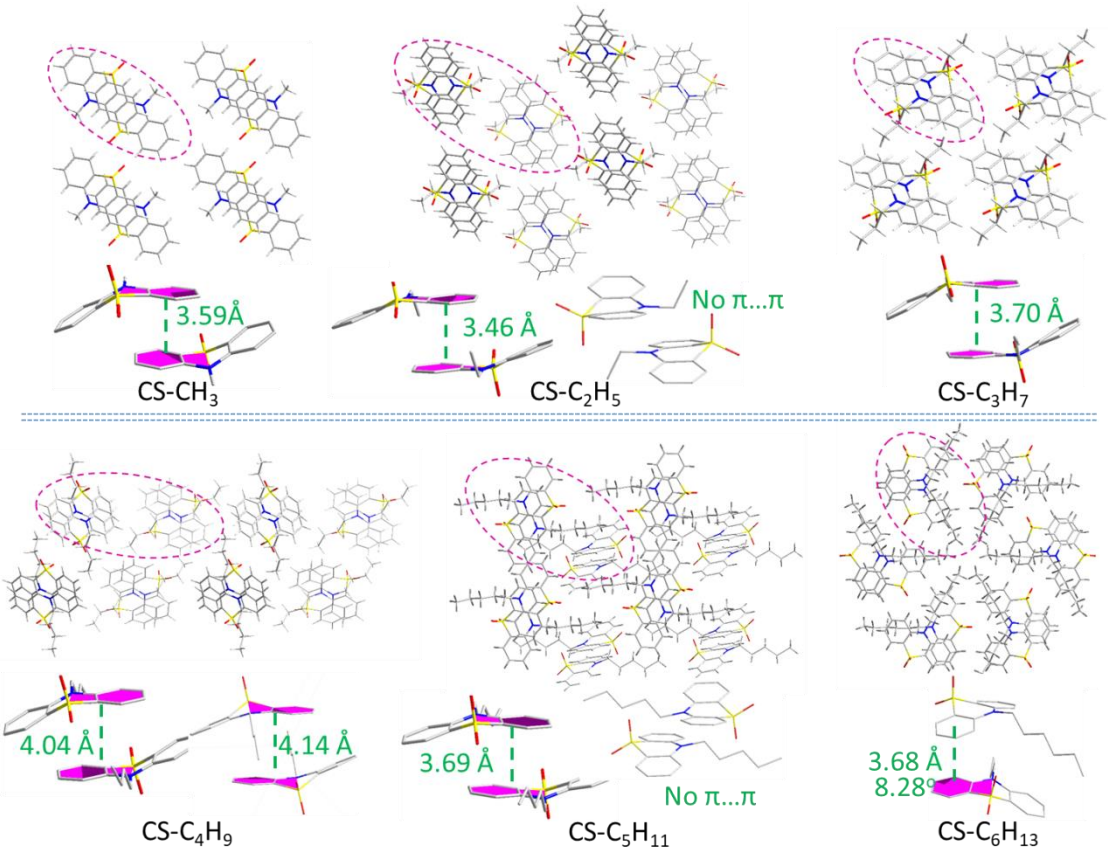


Figure S8 Single-crystal structures of the six luminogens. Entire (upper) and local (down) packing modes of the crystals: the local packing pictures were selected from the parts in cycles of corresponding entire ones.

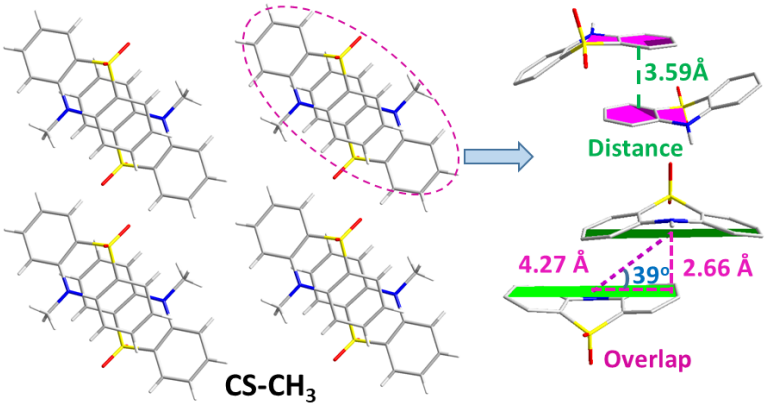


Figure S9 Analyses of single crystal for CS-CH_3 with the π-π distance and overlap labeled.

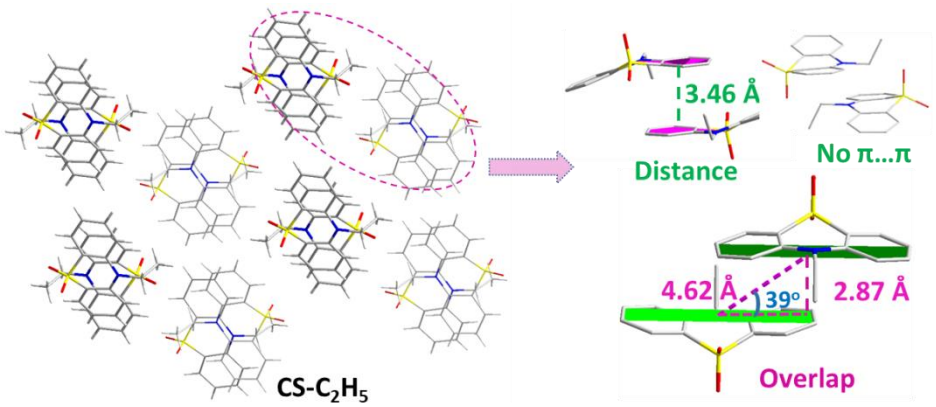


Figure S10 Analyses of single crystal for CS-C_2H_5 with the π-π distance and overlap labeled.

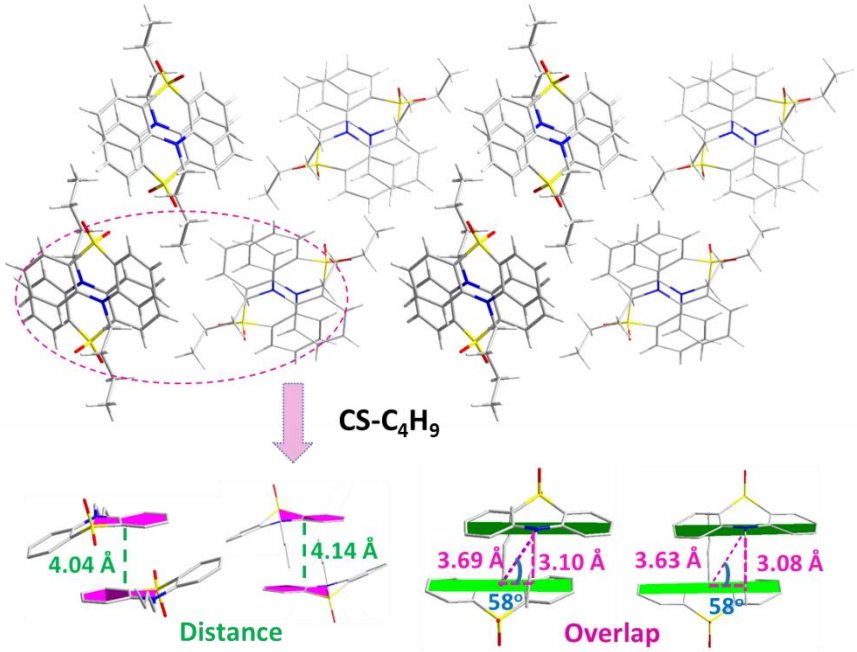


Figure S11 Analyses of single crystal for CS-C_4H_9 with the π-π distance and overlap labeled.

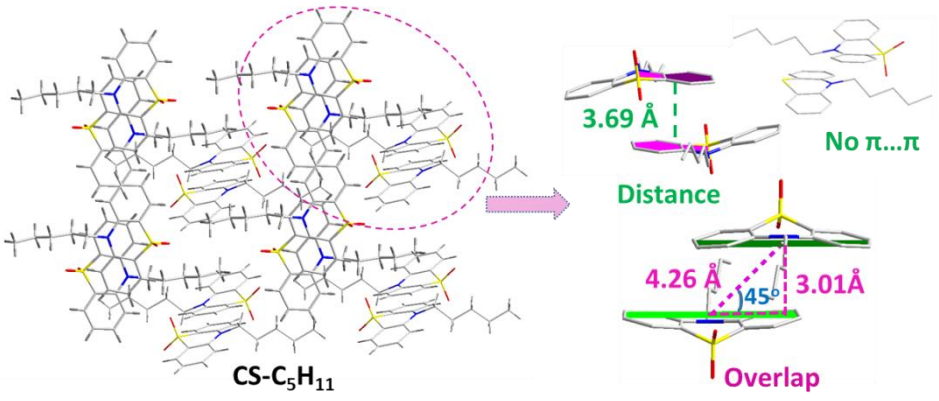


Figure S12 Analyses of single crystal for CS-C_5H_{11} with the π-π distance and overlap labeled.

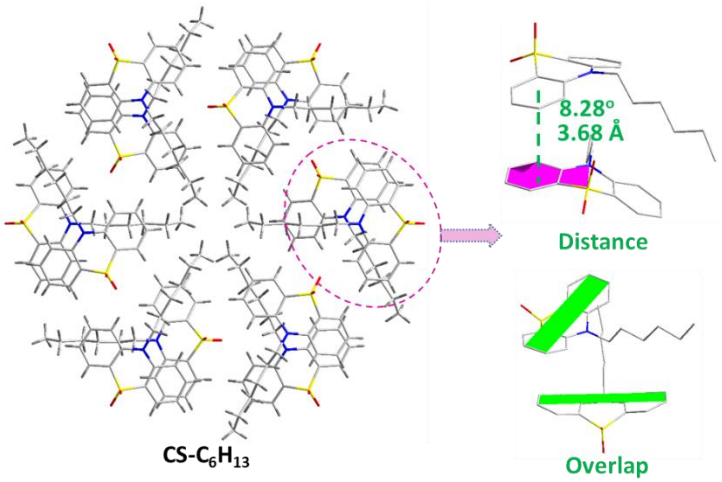


Figure S13 Analyses of single crystal for CS-C_6H_{13} with the π-π distance and overlap labeled.

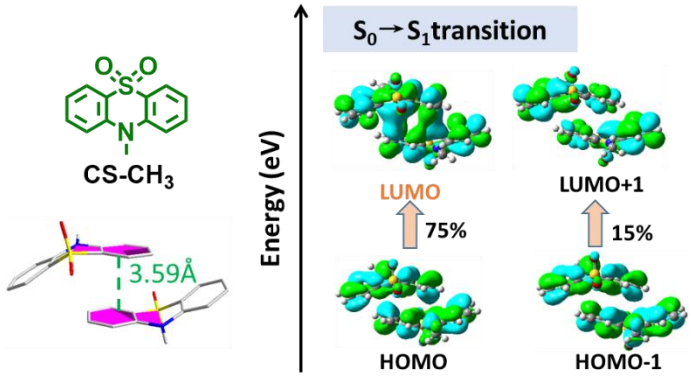


Figure S14 The energy transitions for S_0 to S_1 state of CS-CH_3 estimated by TD-DFT calculations at the m062x/6-31g* level and the frontier molecular orbits with intermolecular interaction of π-electron cloud labeled in orange.

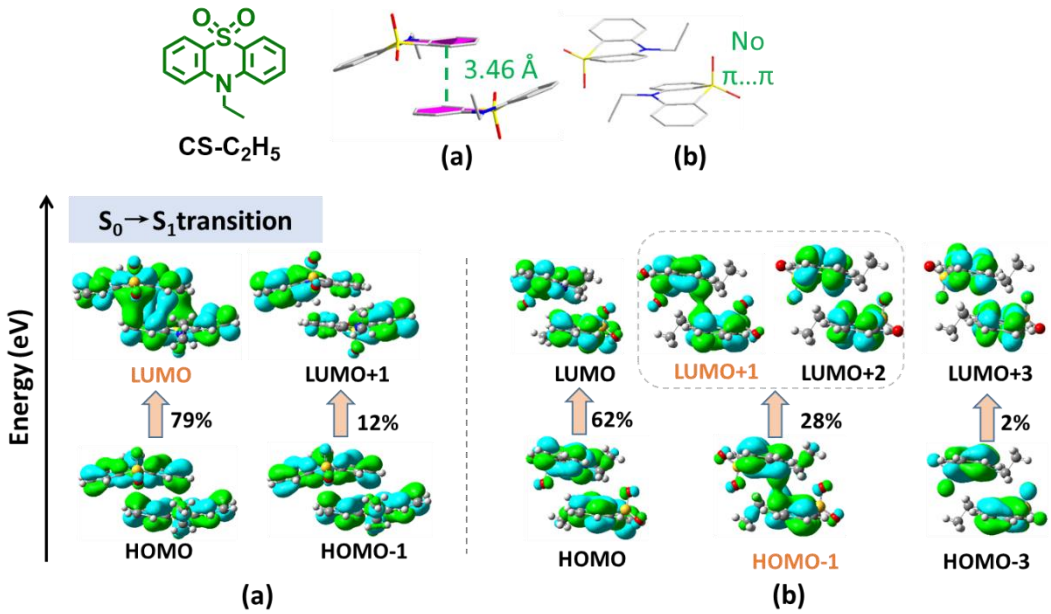


Figure S15 The energy transitions for S_0 to S_1 state of CS-C_2H_5 estimated by TD-DFT calculations

at the m062x/6-31g* level and the frontier molecular orbits with intermolecular interaction of π-electron cloud labeled in orange.

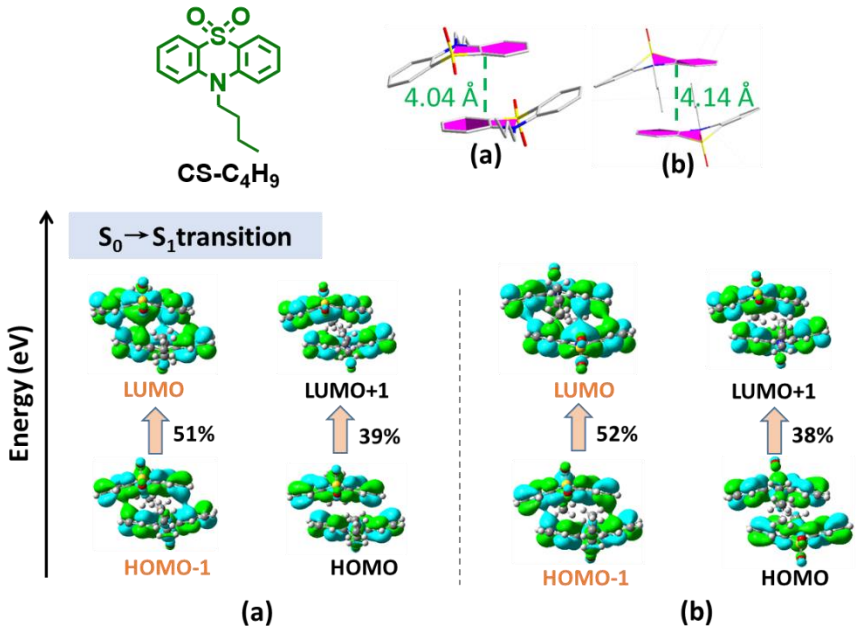


Figure S16 The energy transitions for S_0 to S_1 state of CS-C_4H_9 estimated by TD-DFT calculations at the m062x/6-31g* level and the frontier molecular orbits with intermolecular interaction of π-electron cloud labeled in orange.

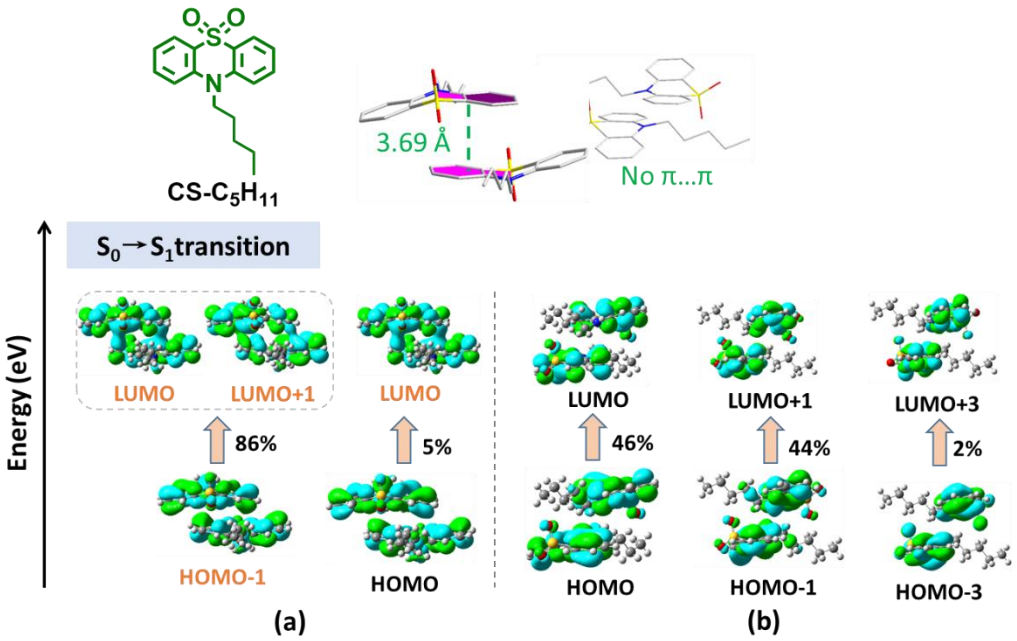


Figure S17 The energy transitions for S_0 to S_1 state of CS-C_5H_{11} estimated by TD-DFT calculations at the m062x/6-31g* level and the frontier molecular orbits with intermolecular interaction of π-electron cloud labeled in orange.

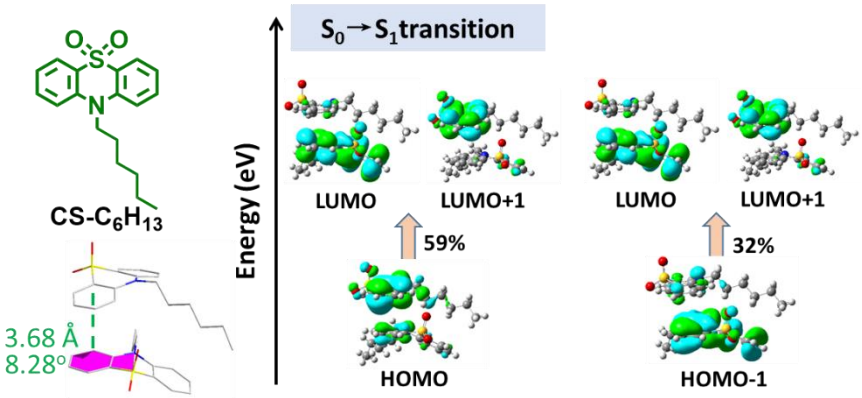


Figure S18 The energy transitions for S_0 to S_1 state of CS-C_6H_{13} estimated by TD-DFT calculations at the m062x/6-31g* level and the frontier molecular orbits with intermolecular interaction of π-electron cloud labeled in orange.

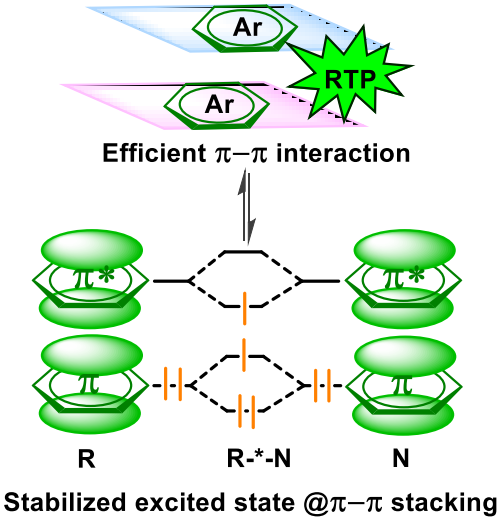


Figure S19 The proposed RTP mechanism based on the classical perturbation theory.

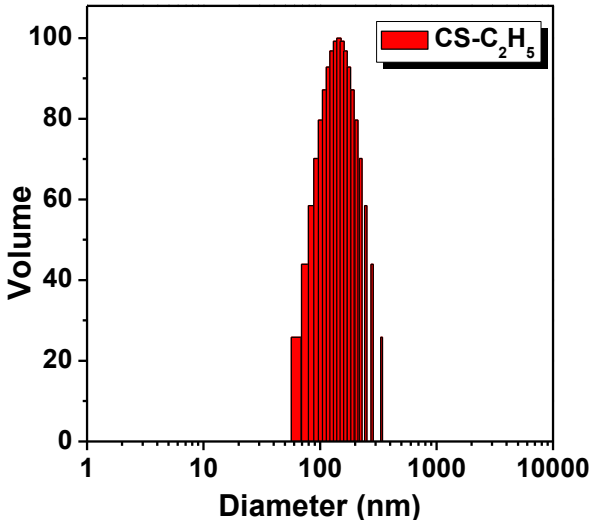


Figure S20 Particle size distribution of CS-C_2H_5 NPs.

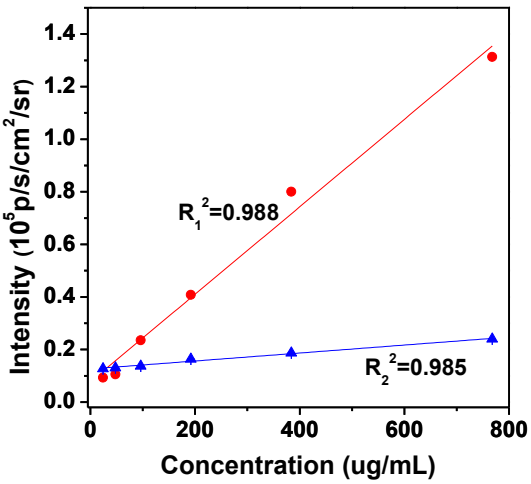


Figure S21 The ultralong phosphorescence intensities as a function of the concentrations of CS-C_3H_7 and CS-C_2H_5.

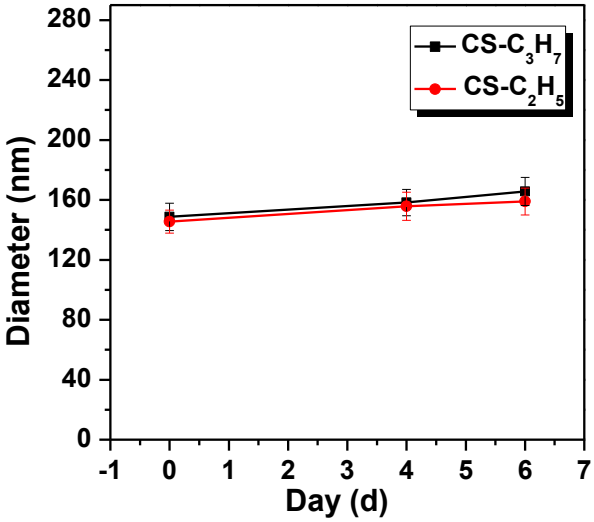


Figure S22 The diameters of CS-C_3H_7 and CS-C_2H_5 NPs after storage at 4 ℃ in dark for 4 and 6 days, respectively.

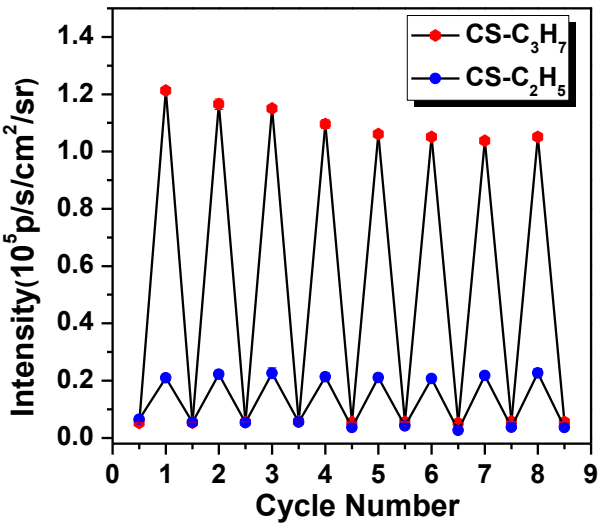


Figure S23 The ultralong phosphorescence intensities of CS-C_3H_7 and CS-C_2H_5 NPs solutions as a function of the cycle number of light activation.

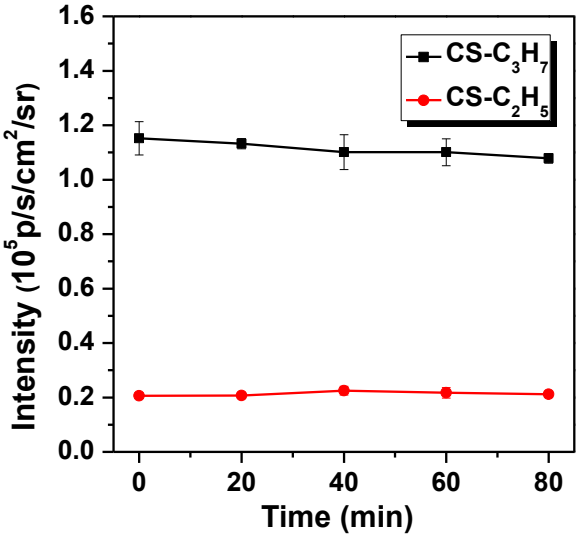


Figure S24 The ultralong phosphorescence intensities of CS-C_3H_7 and CS-C_2H_5 NPs under continuous light irradiation for 80 min (the power density: 10 mW cm^{-2}).

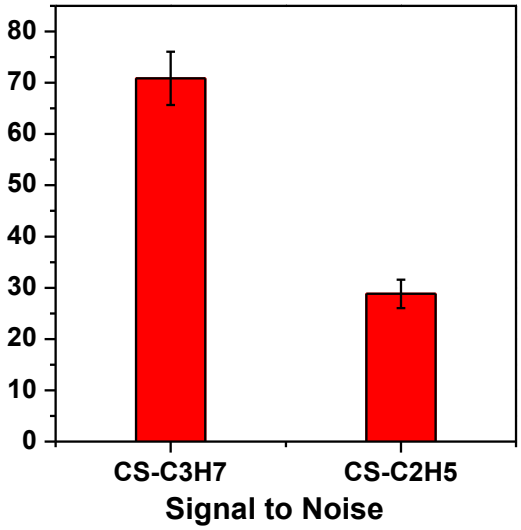


Figure S25 The signal to noise of CS-C_3H_7 and CS-C_2H_5 NPs for in *vivo* imaging.

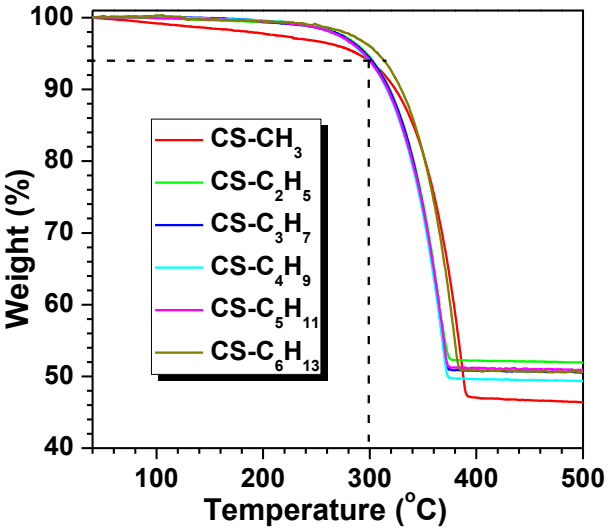


Figure S26 TGA curves of the six target compounds.

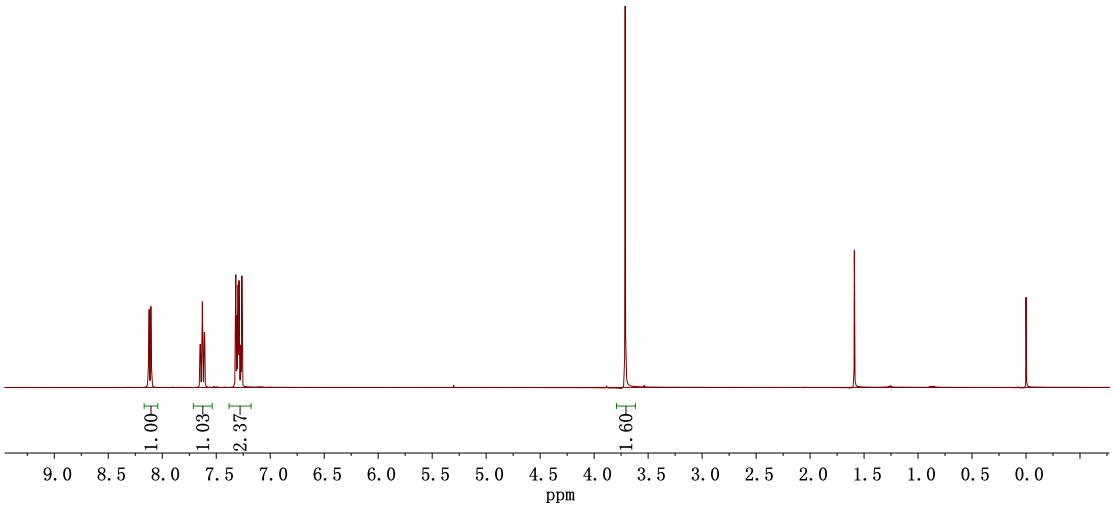


Figure S27 ^{1}H NMR spectrum of CS-CH_3.

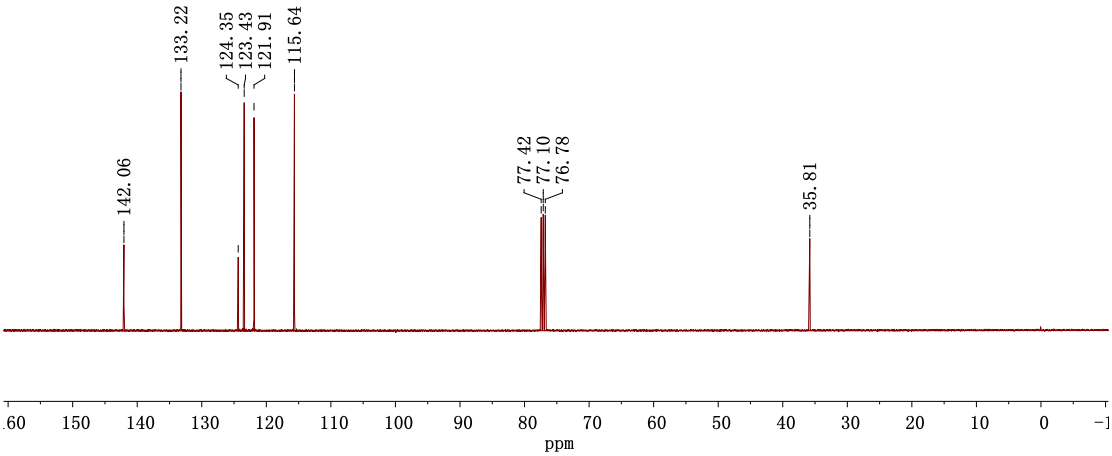


Figure S28 ^{13}C NMR spectrum of CS-CH_3.

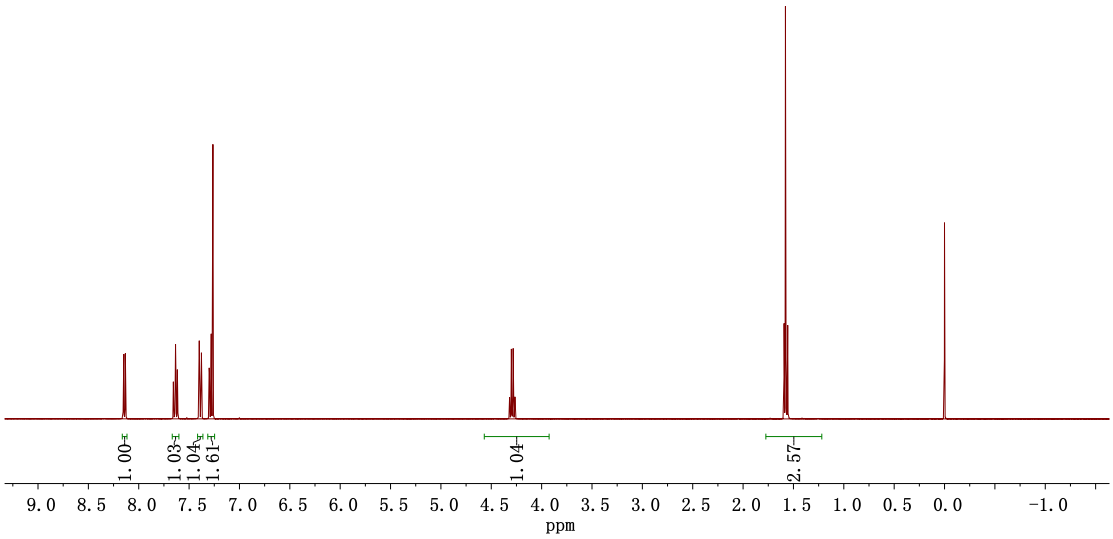


Figure S29 ^{1}H NMR spectrum of CS-C_2H_5.

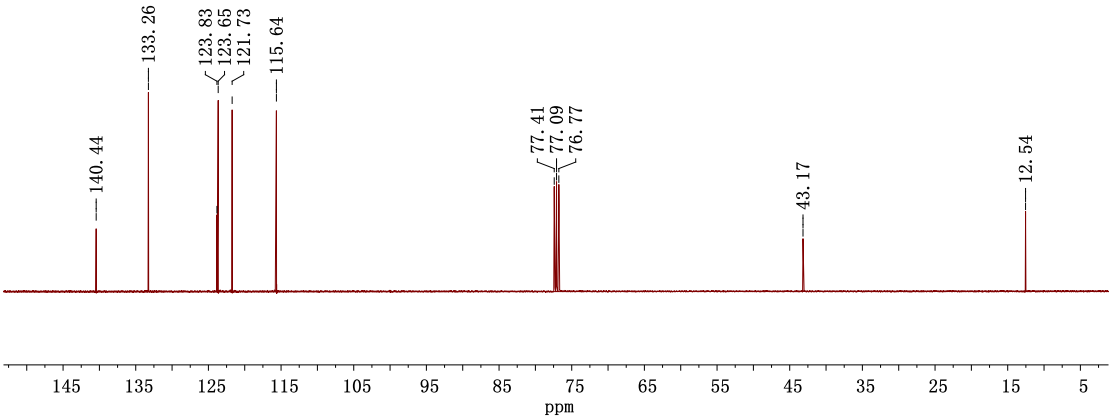


Figure S30 ^{1}C NMR spectrum of CS-C_2H_5.

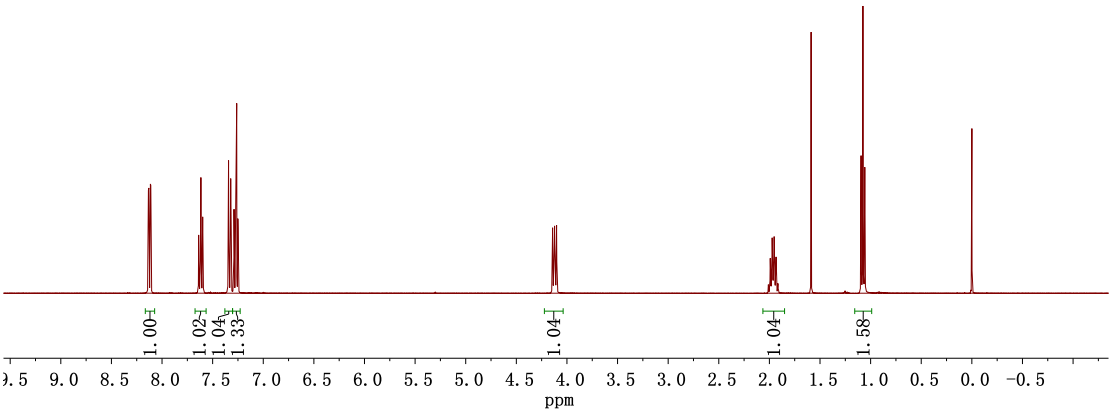


Figure S31 ^{1}H NMR spectrum of CS-C_3H_7.

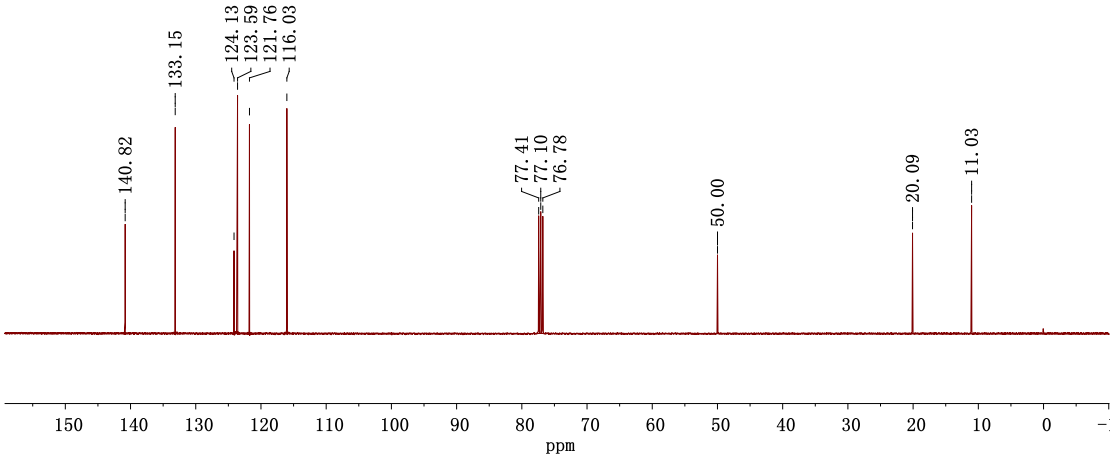


Figure S32 ^{13}C NMR spectrum of CS-C_3H_7.

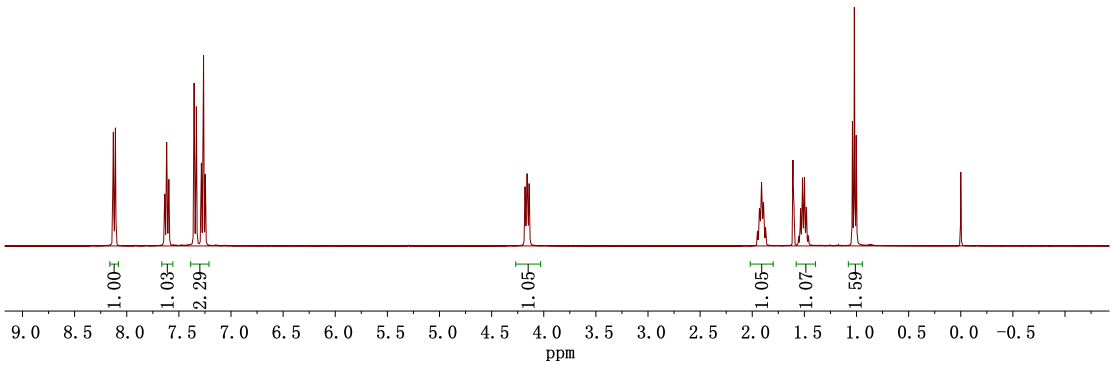


Figure S33 ^{1}H NMR spectrum of CS-C_4H_9.

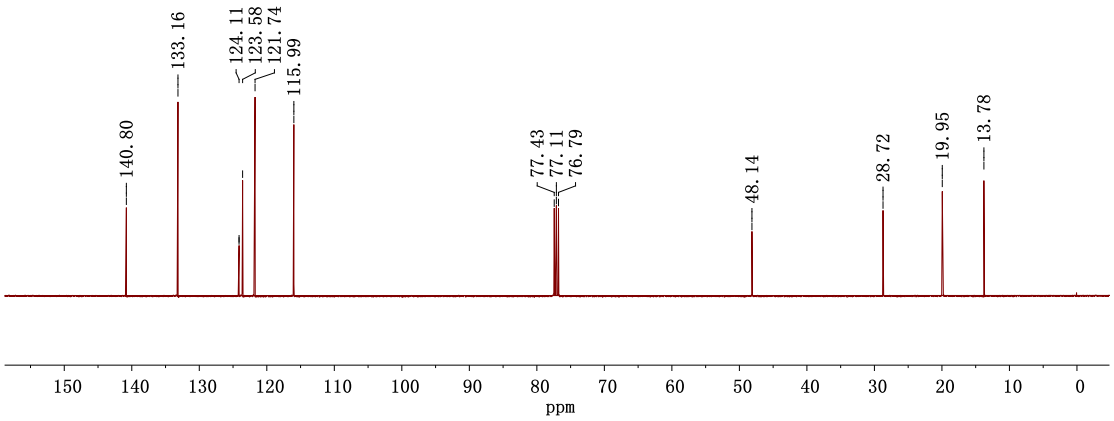


Figure S34 ^{13}C NMR spectrum of CS-C_4H_9.

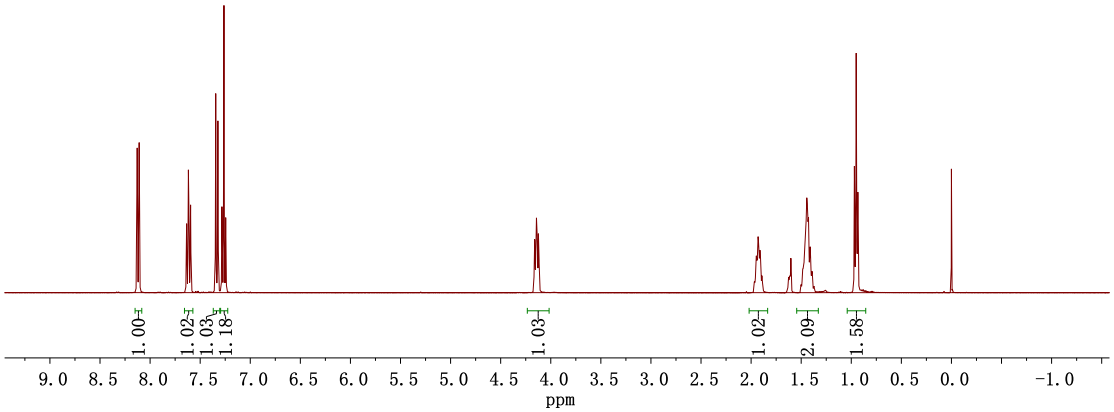


Figure S35 ^{1}H NMR spectrum of CS-C_5H_{11}.

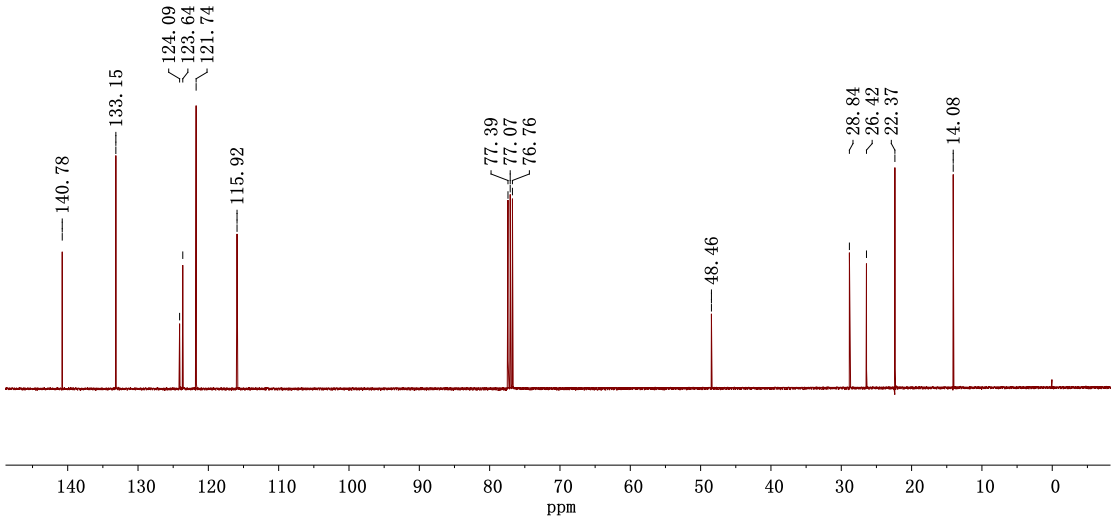


Figure S36 ^{13}C NMR spectrum of CS-C_5H_{11}.

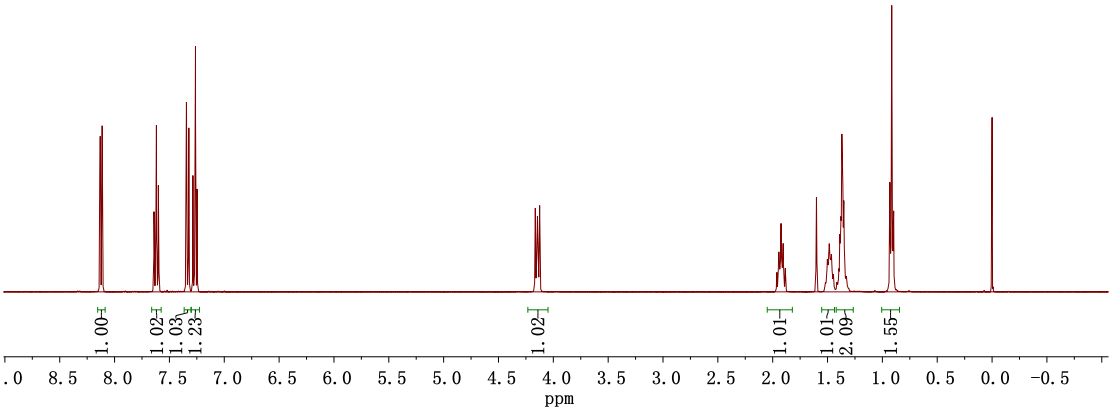


Figure S37 ^{1}H NMR spectrum of CS-C_6H_{13}.

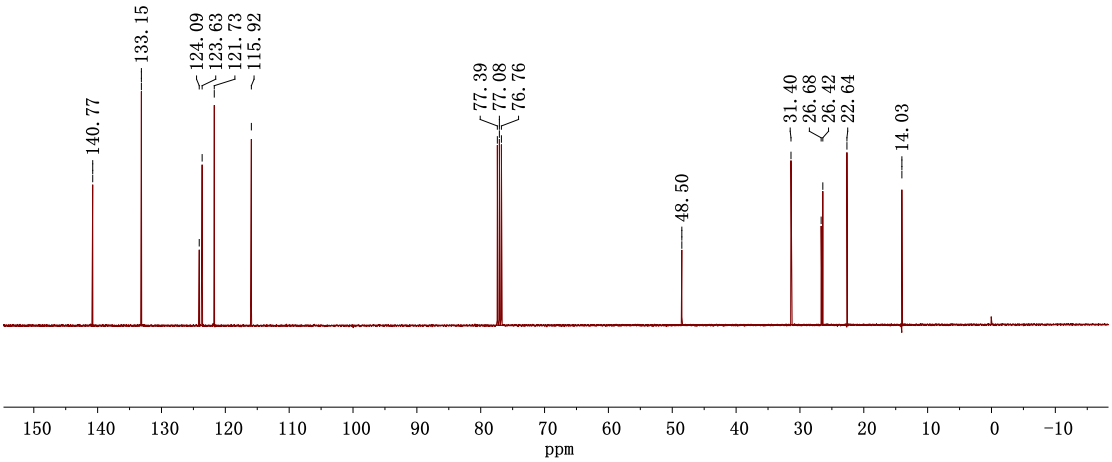


Figure S38 ^{13}C NMR spectrum of CS-C_6H_{13}.

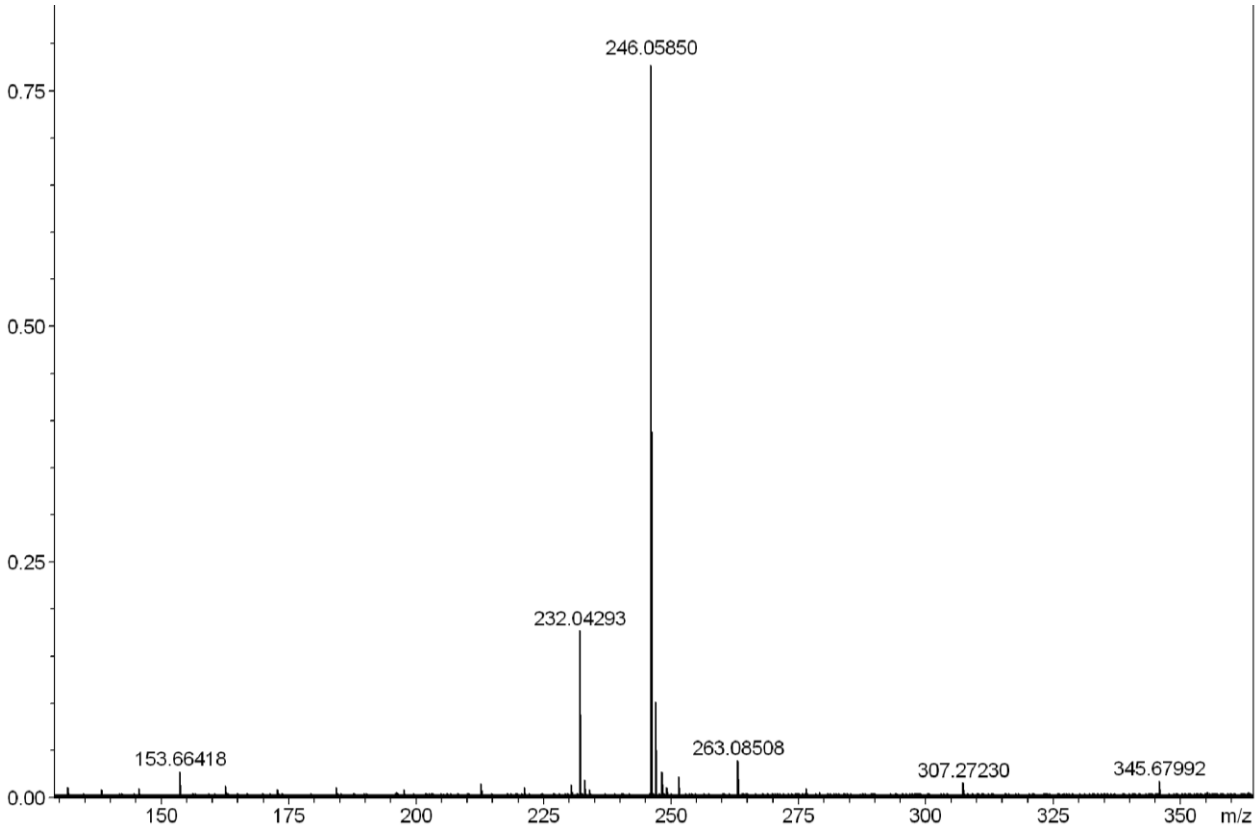


Figure S39 HRMS spectrum of CS-CH_3.

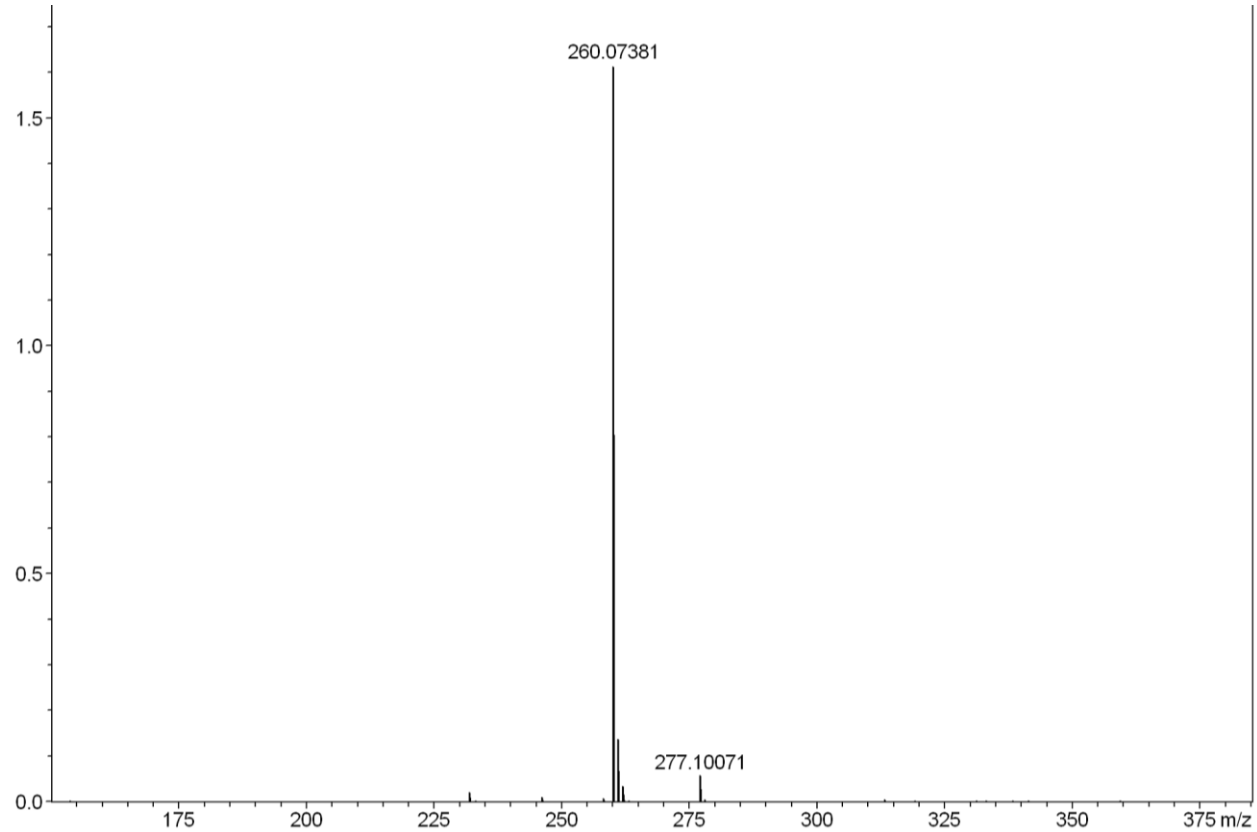


Figure S40 HRMS spectrum of CS-C_2H_5.

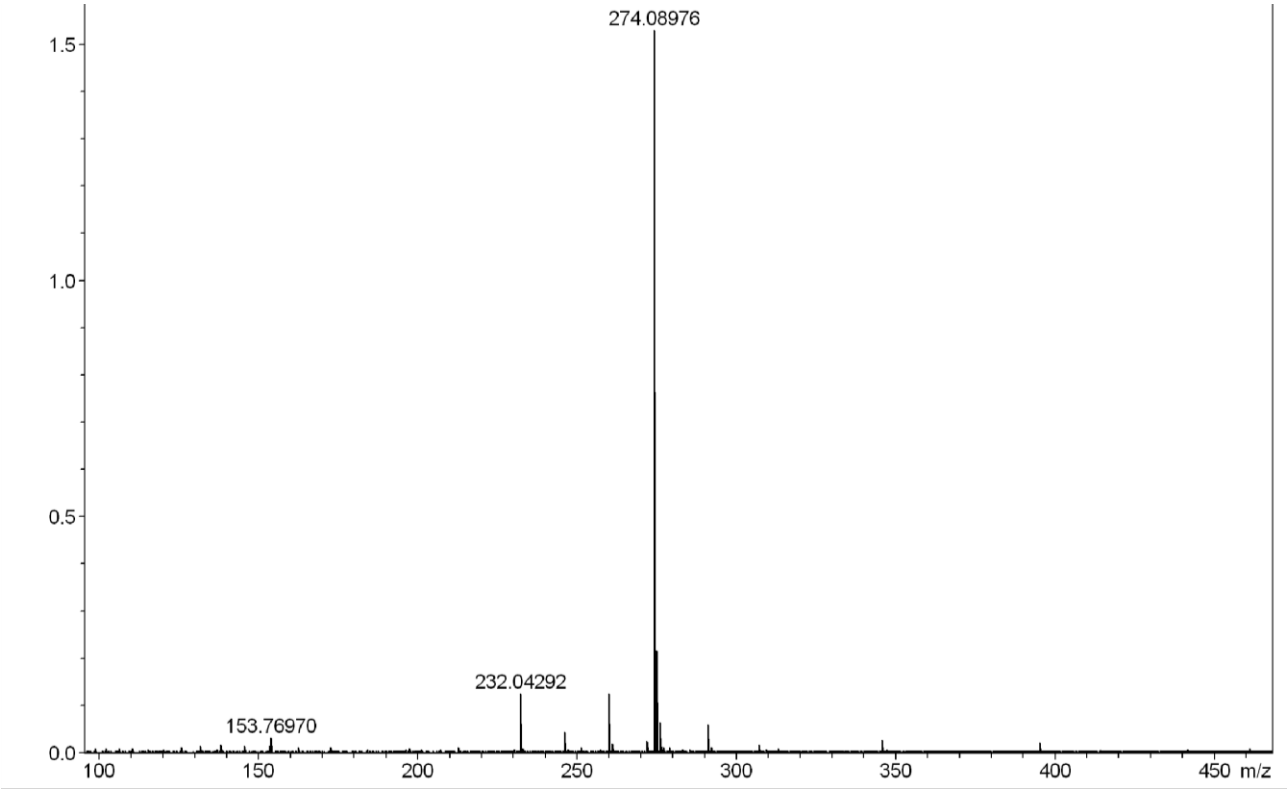


Figure S41 HRMS spectrum of CS-C_3H_7.

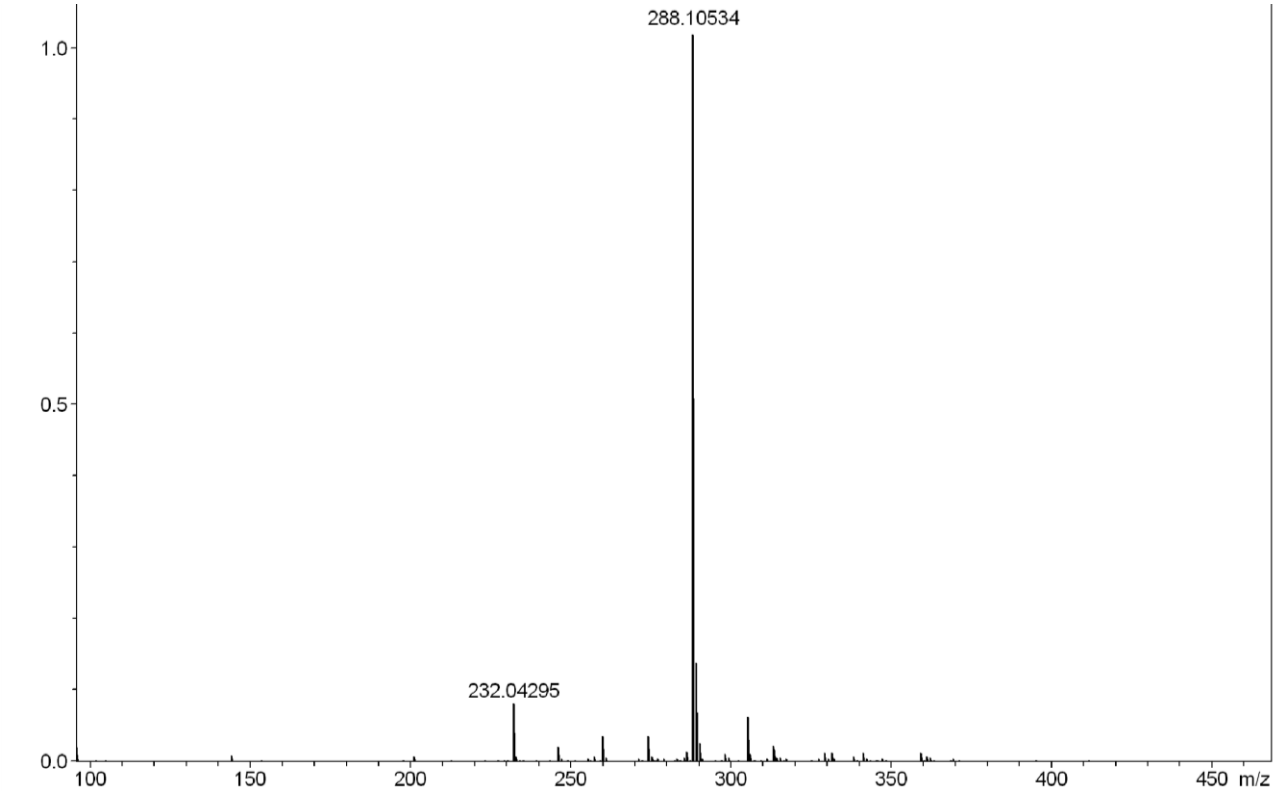


Figure S42 HRMS spectrum of CS-C_4H_9.

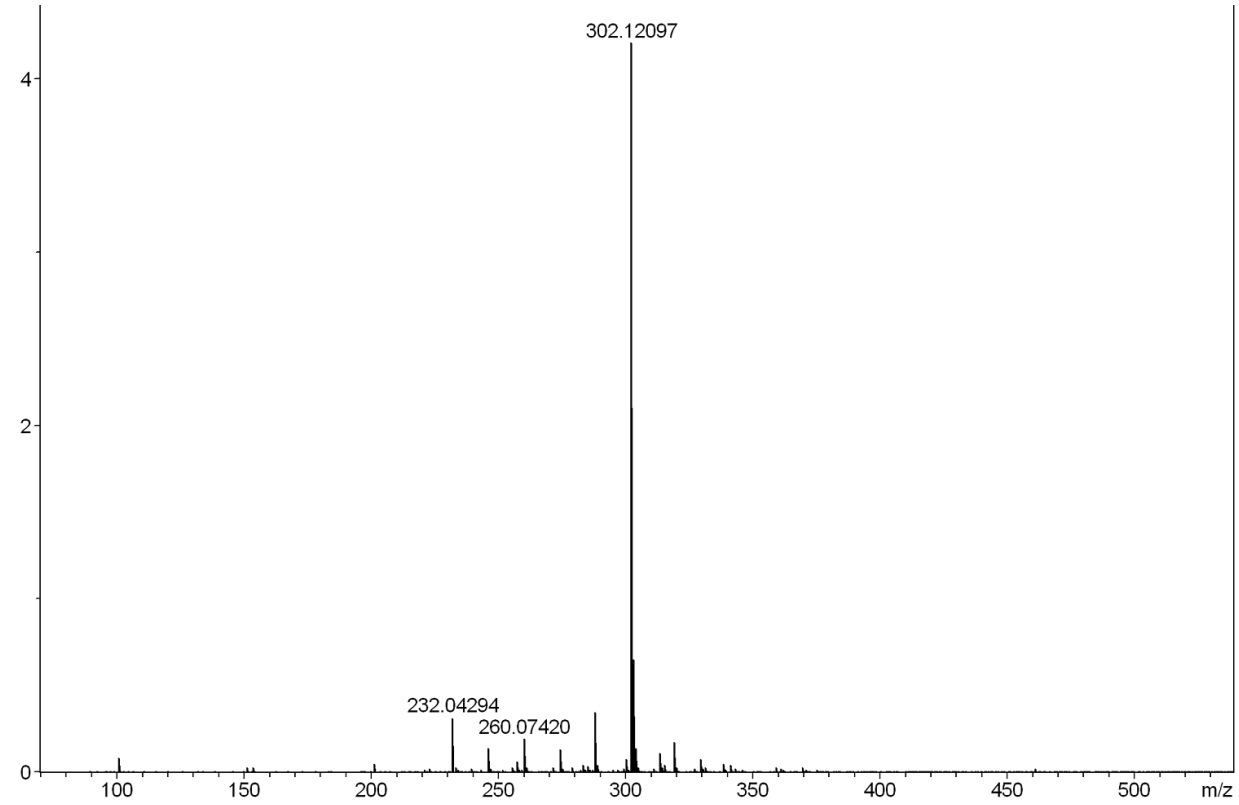


Figure S43 HRMS spectrum of CS-C_5H_{11}.

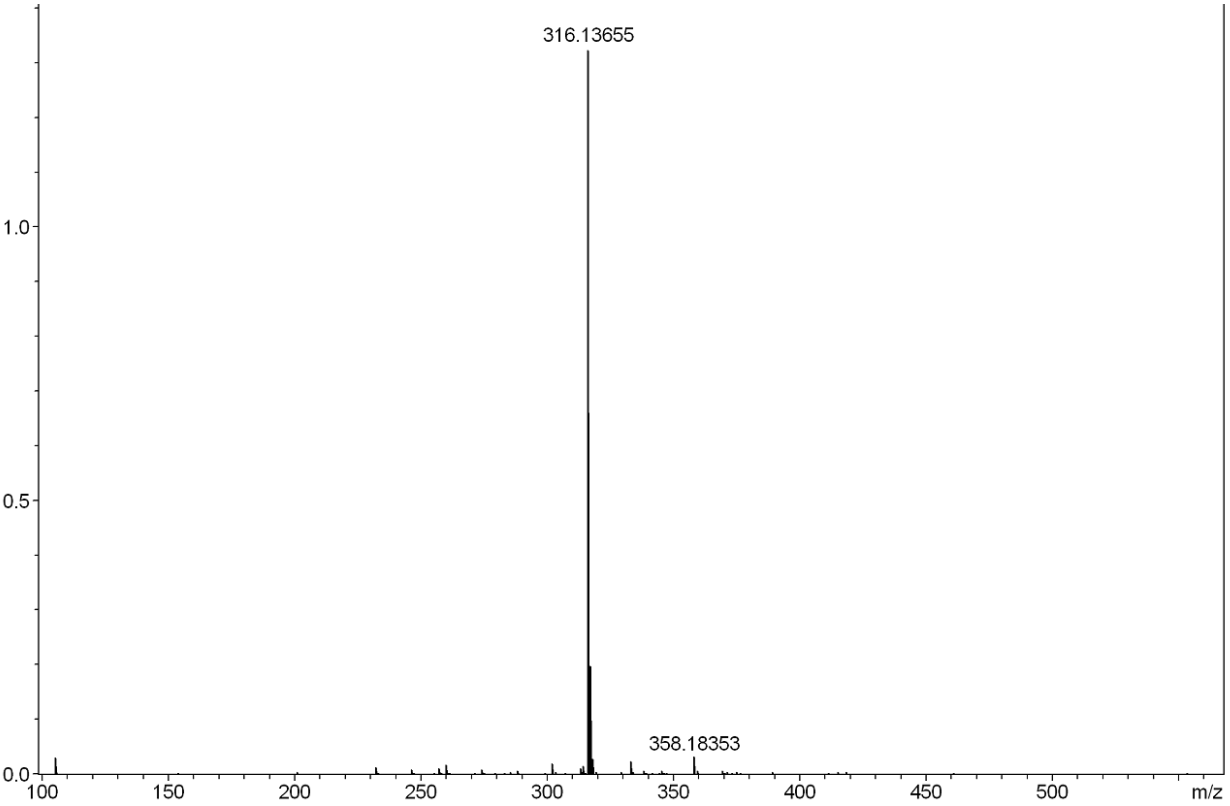


Figure S44 HRMS spectrum of CS-C_6H_{13}.