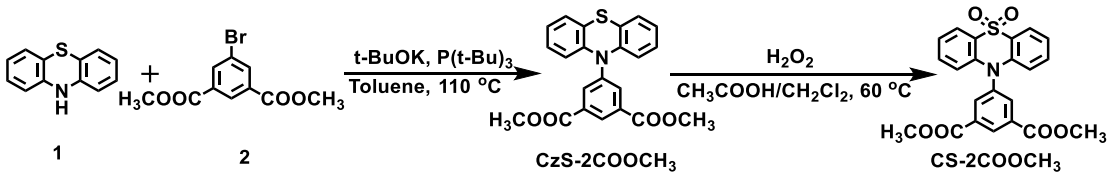
Electronic Supporting Information

Persistent organic room temperature phosphorescence: What is the role of molecular dimers?

Yunsheng Wang,[a] Jie Yang,*[a] Yu Tian,[a] Manman Fang,[a] Qiuyan Liao,[b] Liwei Wang,[a] Wenping Hu,[a] Ben Zhong Tang,*[ac] and Zhen Li*[abd]

Synthesis



Scheme S1 The synthetic route of compound CS-2$COOCH_3$.

CzS-2$COOCH_3$: Compound 1 (1.99 g, 10 mmol), compound 2 (3.28 g, 12 mol), potassium tert-butoxide (1.68 g, 15 mmol), palladium acetate (0.11 g, 0.5 mmol) and tri-tert-butylphosphine in toluene solution (0.5 mL, 0.25 mmol) were dissolved in toluene (100 mL) in a Schlenk tube.[1] The resultant mixture was refluxed for 12 hours under argon, then extracted with dichloromethane. The combined organic extracts were dried over anhydrous Na_2SO_4 and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel using petroleum ether/dichloromethane (v/v = 2:1) as eluent to afford a light yellow solid in a yield of 35%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.70 (s, 1H, ArH), 8.23 (s, 2H, ArH), 7.12-7.14 (d, 2H, ArH), 6.91-6.96 (m, 4H, ArH), 6.34-6.36 (d, 2H, ArH), 3.95 (s, 6H, -CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 165.6, 143.2, 142.6, 134.0, 133.1, 129.1, 127.4, 127.1, 123.6, 123.3, 118.0, 52.6. HRMS (EI), m/z: $[M+Na]^+$, calcd. for $C_{22}H_{17}NNaO_4S$, 414.0776; found, 414.0750. Anal. Calcd for $C_{22}H_{17}NO_4S$: C, 67.50; H, 4.38; N, 3.58. Found: C, 67.48; H, 4.46; N, 3.40.

CS-2$COOCH_3$: Compound CzS-2$COOCH_3$ was dissolved in dichloromethane (90 mL), acetic acid (45 mL) and H_2O_2 (2 mL). After reacting for another 24 hours at 60 °C, the reaction mixture was extracted with dichloromethane and further purified by column chromatography using petroleum ether/ethyl acetate (v/v = 5:1) as eluent to afford a white solid in a yield of 90%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ (ppm): 8.95 (s, 1H, ArH), 8.30 (s, 2H, ArH), 8.19-8.21 (d, 2H, ArH), 7.39-7.43 (t, 2H, ArH), 7.27-7.31 (t, 2H, ArH), 6.52-6.54 (d, 2H, ArH), 3.99 (s, 6H, -CH_3); ^{13}C-NMR (100 MHz, $CDCl_3$) δ (ppm): 164.8, 140.4, 139.5, 136.2, 134.2, 133.0, 131.8, 123.7, 123.2, 122.6, 116.9, 52.9; HRMS (EI), m/z: $[M+Na]^+$, calcd. for $C_{22}H_{17}NNaO_6S$, 446.0674; found, 446.0681. Anal. calcd for $C_{22}H_{17}NO_6S$: C, 62.40; H, 4.05; N, 3.31. Found: C, 62.58; H, 4.24; N, 3.15.

Characterization

^{1}H NMR spectra and ^{13}C NMR spectra were recorded on a 400 MHz Bruker AVANCE III spectrometer. Elemental analyses of carbon, hydrogen and nitrogen were measured on a vario EL cube. High resolution mass spectrum was measured on a UHPLC/Q-TOF MS. High-performance liquid chromatogram spectrum was recorded on Agilent 1100 HPLC. UV-vis spectra were measured on a Shimadzu UV-2700. Photoluminescence spectra and excitation spectra were performed on a Hitachi F-4600 fluorescence

spectrophotometer. The powder X-ray diffraction patterns were recorded by Rigaku Smartlab9KW. The single-crystal X-ray diffraction data of CS-2COOCH$_3$ were collected in XtaLAB SuperNova X-ray diffractometer. Fluorescence quantum yields and lifetimes were determined with FLS980 spectrometer.

The Gaussian 09 program was utilized to perform the TD-DFT calculations. The ground state (S_0) geometries were obtained from the single crystal structure and no further geometry optimization was conducted in order to maintain the specific molecular configurations and corresponding intermolecular locations. The natural transition orbit (NTO) of T_1 state and HOMO/LUMO of CS-2COOCH$_3$ were evaluated by the TD-b3lyp/6-31g*.

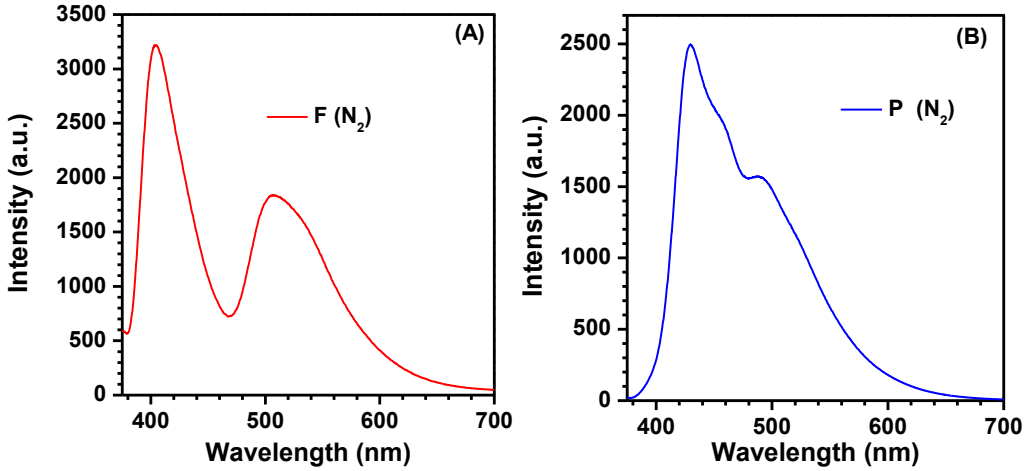


Figure S1 (A) The steady state PL spectra of CS-2COOCH$_3$ crystal under N_2 atmosphere; (B) The RTP spectrum, acquired after 10 ms delay, of CS-2COOCH$_3$ crystal under N_2 atmosphere.

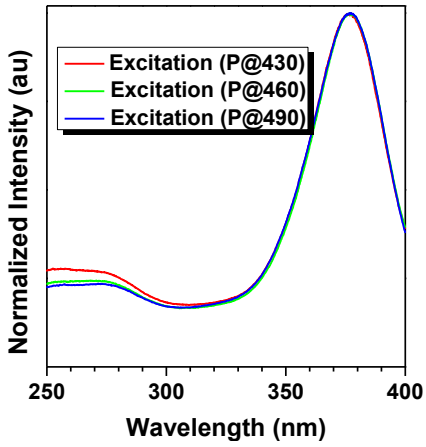


Figure S2 The excitation spectra of room temperature phosphorescence at 430, 460 and 490 nm.

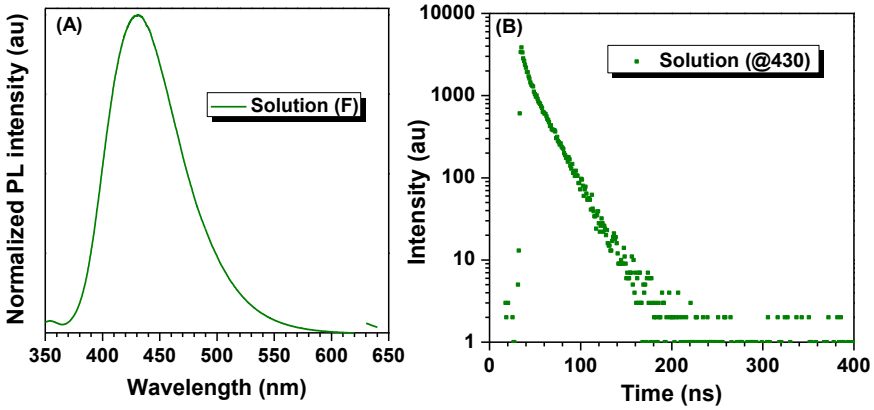


Figure S3 (A) The normalized PL spectrum of CS-2COOCH$_3$ in THF solution; (B) The PL decay curve of CS-2COOCH$_3$ in THF solution.

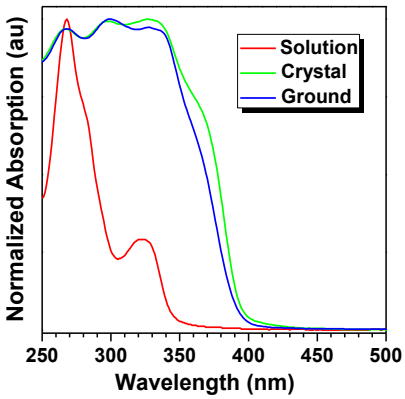


Figure S4 The UV-vis absorption spectra of CS-2COOCH$_3$ in different states, including THF solution, crystal and ground states.

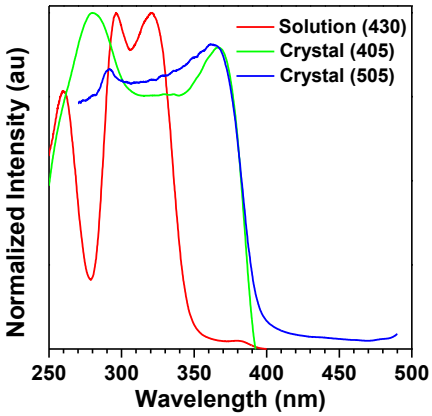


Figure S5 The normalized excitation spectra of CS-2COOCH$_3$ in THF solution and crystal states.

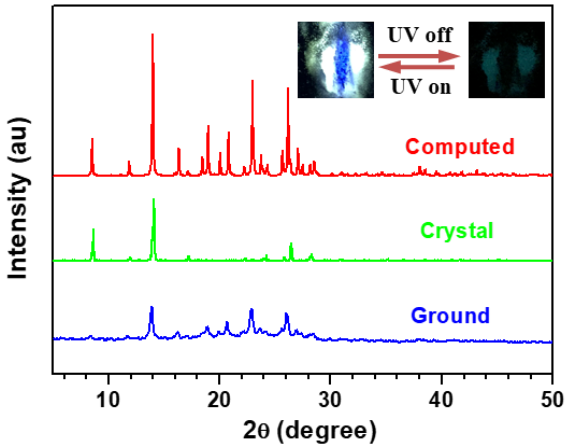


Figure S6 The computed XRD data (as derived from X-ray crystallography) and powder X-ray diffraction (PXRD) of CS-2COOCH$_3$ in crystal and ground states. Inset: the photo of CS-2COOCH$_3$ before and after turning off the 365 nm UV-irradiation, in which the CS-2COOCH$_3$ crystal is RTP active while the ground one is RTP non-active.

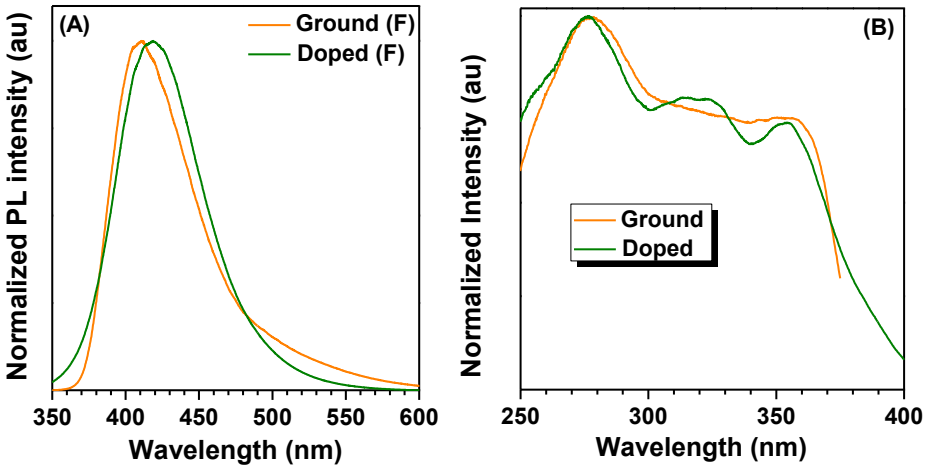


Figure S7 (A) The normalized PL spectra of CS-2COOCH$_3$ in ground state and doped in PMMA film; (B) The corresponding excitation spectra of CS-2COOCH$_3$ in ground state and doped in PMMA film.

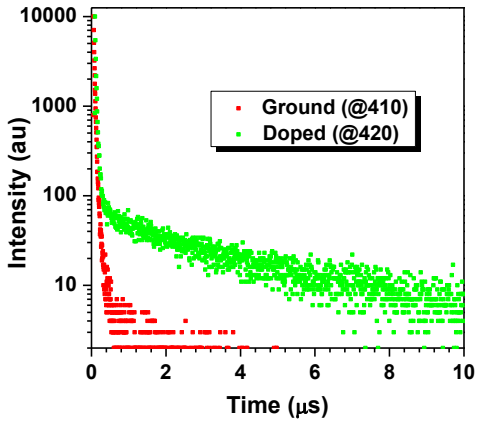


Figure S8 The PL decay curves of CS-2COOCH$_3$ in ground state and doped in PMMA film.

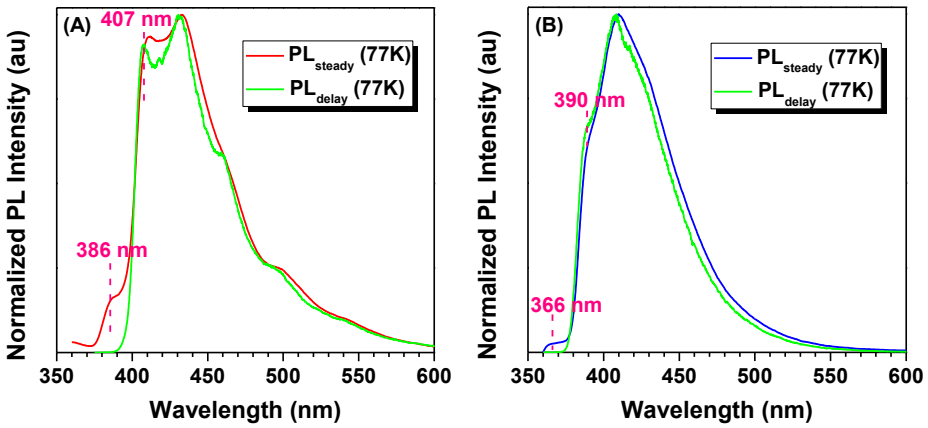


Figure S9 (A) The steady state PL spectrum and the delayed (10 ms) one of CS-2COOCH$_3$ crystal at 77 K; (B) The steady state PL spectrum and the delayed (10 ms) one at 77 K, when CS-2COOCH$_3$ was doped in PMMA film with mass fraction about 5%.

Table S1 Structure data of single crystals of CzS-2COOCH$_3$ and CS-2COOCH$_3$.

Name	CzS-2COOCH$_3$	CS-2COOCH$_3$
Formula	$C_{22}H_{17}NO_4S$	$C_{22}H_{17}NO_6S$
Wavelength (Å)	1.54184	1.54184
Space Group	P n m a	P 21 21 21
Cell Lengths (Å)	a=6.6807(2) b=19.9408(7) c=14.2683(4)	a=5.76005(7) b=15.96476(18) c=20.7187(2)
Cell Angles (o)	α=90 β=90 γ=90	α=90 β=90 γ=90
Cell Volume (Å3)	1900.80(10)	1905.25(4)
Z	4	4
Density (g/cm3)	1.368	1.476
F(000)	816	880
hmax, kmax, lmax	7,23,17	6,19,24
CCDC Number	1963173	1944189

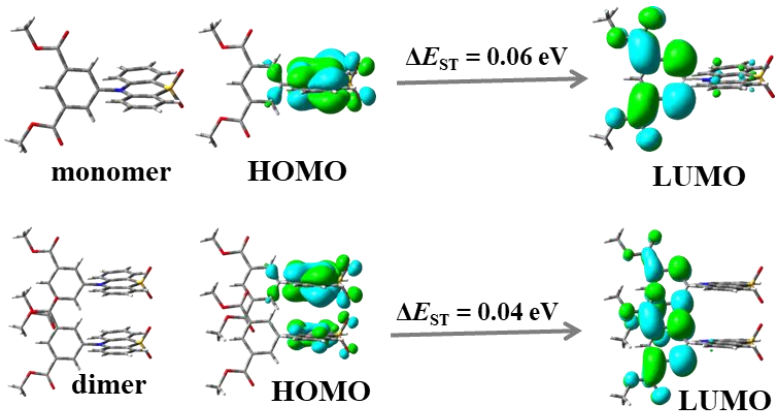


Figure S10 The HOMO and LUMO electron cloud distributions of CS-2COOCH$_3$ in monomer and dimer.

Table S2 The calculated fluorescence radiation rate and non-radiation rate of CS-2COOCH$_3$ in different states.

state	emission	Φ_F	τ_F	k_r	k_{nr}
doped	@420 nm	10.40%	0.97 μs	$10.72*10^4$ /s	$9.24*10^5$ /s
Crystal	monomer@405 nm	3.34%	1.27 μs	$2.63*10^4$ /s	$7.61*10^5$ /s
	excimer@505 nm	4.62%	10.6 μs	$0.44*10^4$ /s	$0.90*10^5$ /s

The radiation rate and non-radiation rate were estimated by the two equations below:
$\Phi_F \approx k_r/(k_r + k_{nr})$; $\tau_F \approx 1/(k_r + k_{nr})$

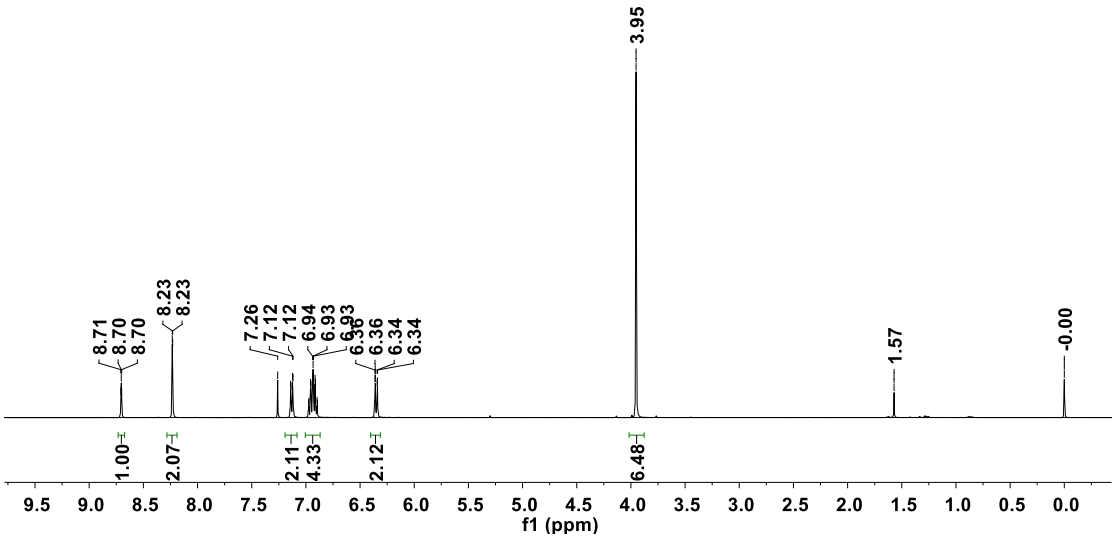


Figure S11 The ^{1}H NMR spectrum of CzS-2COOCH$_3$.

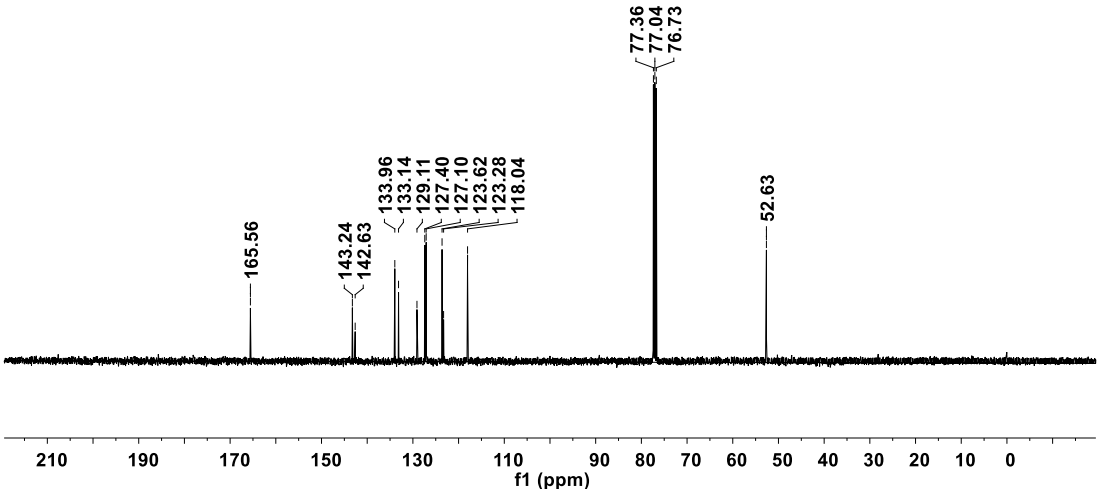


Figure S12 The ^{13}C NMR spectrum of CzS-2COOCH$_3$.

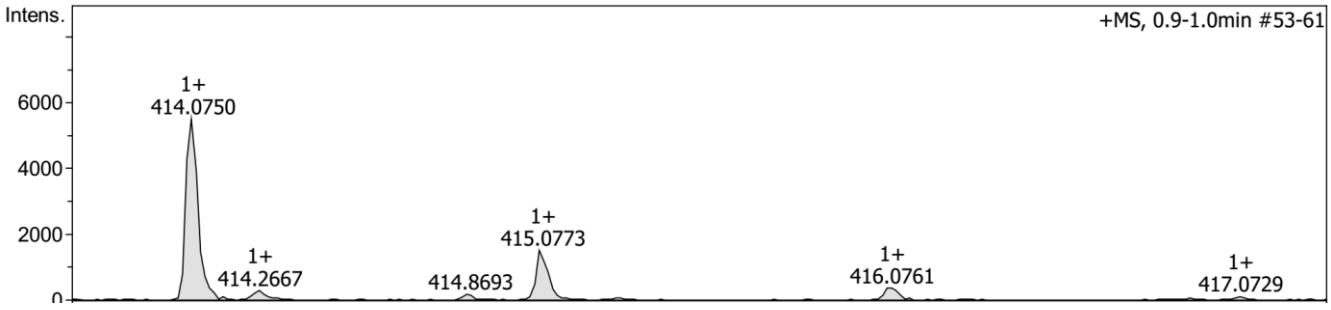


Figure S13 The HRMS spectrum of CzS-2COOCH$_3$.

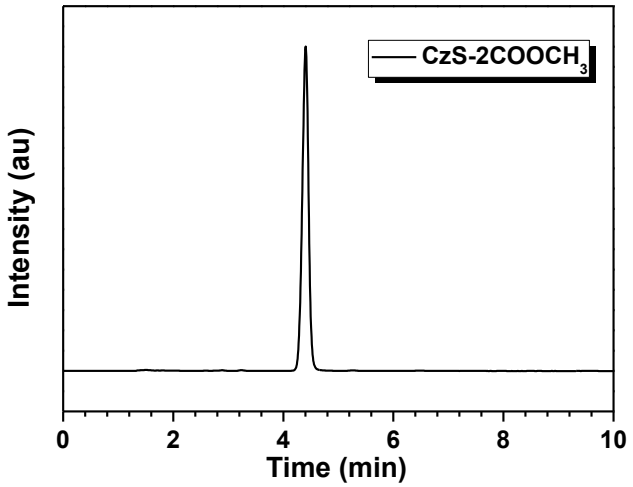


Figure S14 The HPLC spectrum of CzS-2COOCH$_3$.

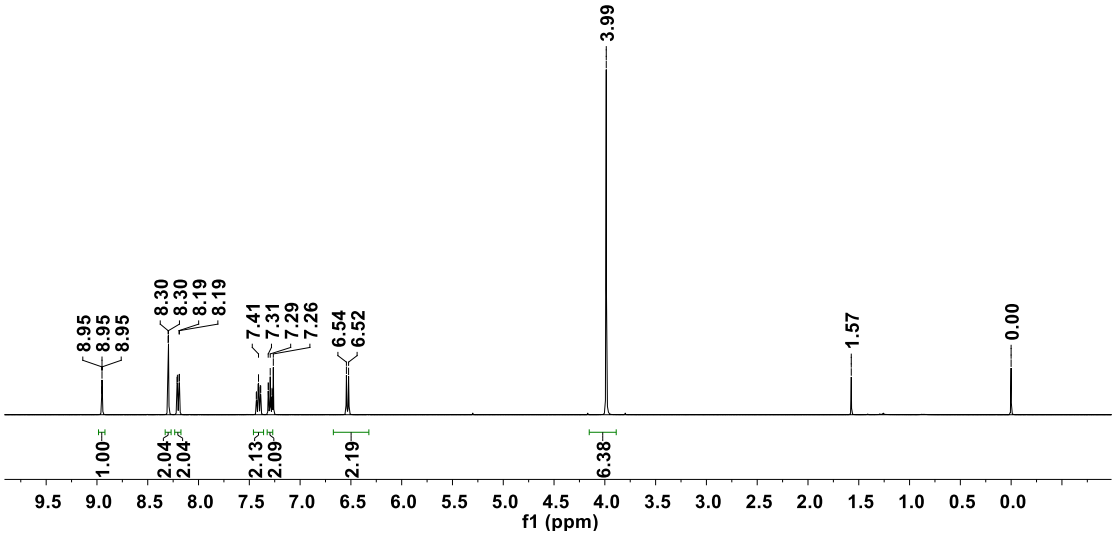


Figure S15 The ^{1}H NMR spectrum of CS-2COOCH$_3$.

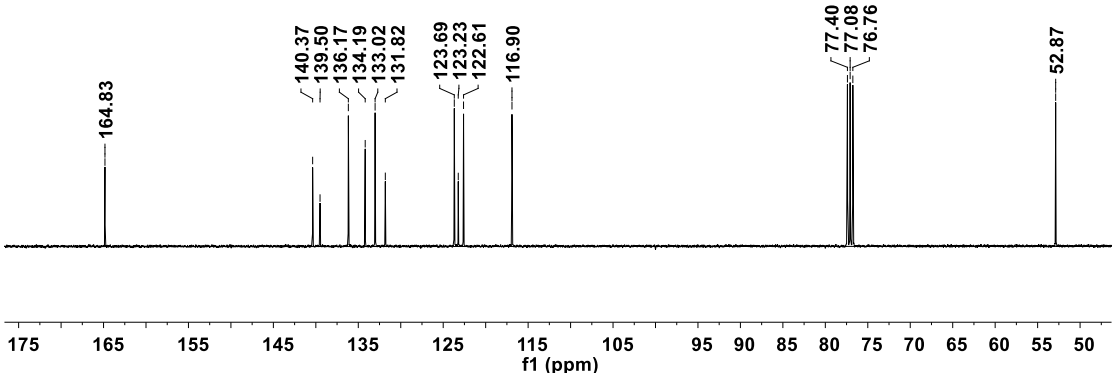


Figure S16 The ^{13}C NMR spectrum of CS-2COOCH$_3$.

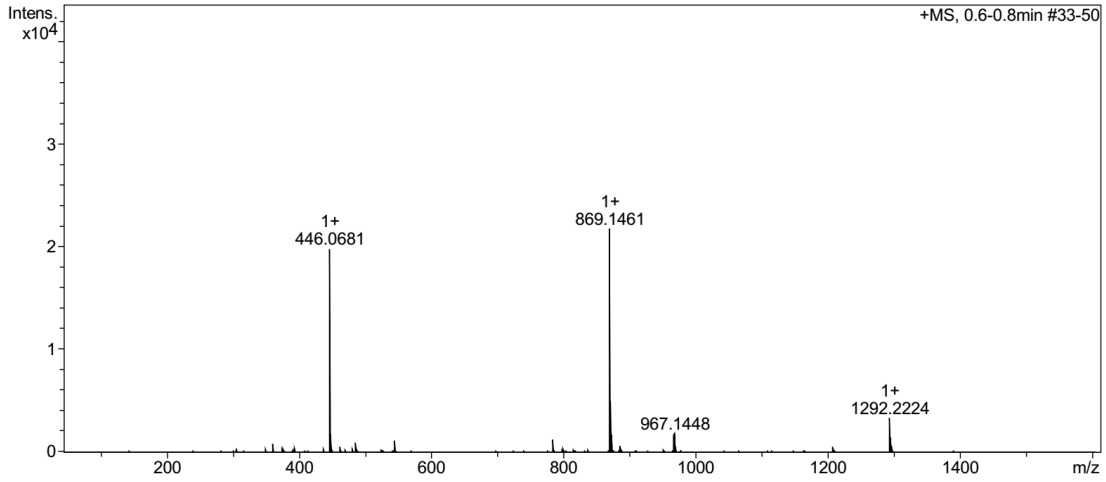


Figure S17 The HRMS spectrum of CS-2COOCH$_3$.

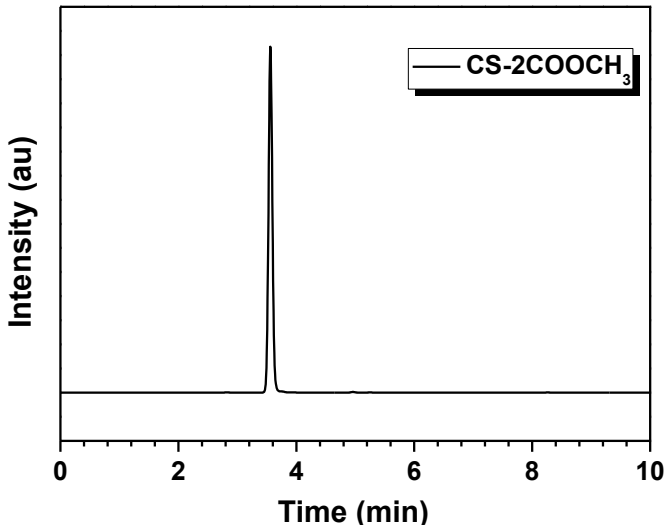


Figure S18 The HPLC spectrum of CS-2COOCH$_3$.

Table S3 The atomic coordinates for CS-2COOCH$_3$ monomer

O	5.29790000	10.16980000	5.89890000
O	4.17730000	11.08080000	7.60550000
C	5.09400000	11.09060000	6.83860000
H	5.50040000	13.02670000	8.52160000
H	5.32850000	15.59230000	7.05960000
C	4.31200000	9.11250000	5.83430000
H	4.19420000	8.73060000	6.70750000
H	4.61050000	8.43440000	5.22480000
H	3.47620000	9.47310000	5.52720000
C	6.15040000	12.15170000	6.81190000
C	7.11020000	12.23810000	5.81420000
C	6.13550000	13.08880000	7.84490000
C	8.04060000	13.27320000	5.83340000
H	7.13210000	11.60460000	5.13370000
C	7.06470000	14.10640000	7.85900000
C	9.12720000	13.40680000	4.81890000
C	8.00320000	14.21540000	6.85230000
N	7.05900000	15.07450000	8.93210000

O	9.19340000	12.33990000	4.02490000
O	9.86800000	14.35340000	4.75510000
H	8.61040000	14.92040000	6.85670000
C	8.02680000	14.94130000	9.93210000
C	6.18900000	16.16420000	8.81220000
C	10.21770000	12.37180000	3.01190000
C	8.20370000	15.88550000	10.95080000
C	8.87710000	13.82090000	9.94080000
C	6.14350000	17.20110000	9.75130000
C	5.32030000	16.25740000	7.70920000
H	11.05250000	12.63270000	3.40870000
H	9.97570000	13.00470000	2.33180000
H	10.30760000	11.49920000	2.61970000
S	7.20260000	17.29790000	11.12930000
C	9.21010000	15.73670000	11.90730000
H	8.77630000	13.16110000	9.29200000
C	9.85590000	13.69130000	10.89860000
C	5.26320000	18.27380000	9.60200000
C	4.45730000	17.32690000	7.58100000
O	6.44080000	17.18100000	12.34260000
O	8.00550000	18.47920000	11.00580000
C	10.04200000	14.64310000	11.88270000
H	9.31840000	16.38280000	12.56600000
H	10.40720000	12.94240000	10.88240000
H	5.25120000	18.95150000	10.23840000
C	4.41640000	18.33630000	8.52450000
H	3.89160000	17.36940000	6.84420000
H	10.71660000	14.54530000	12.51630000
H	3.82420000	19.04720000	8.43050000

Table S4 The atomic coordinates for CS-2COOCH$_3$ dimer

O	5.29790000	10.16980000	5.89890000
O	3.43250000	12.33970000	4.02490000
O	4.17730000	11.08080000	7.60550000
N	1.29780000	15.07490000	8.93210000
O	4.10700000	14.35380000	4.75510000
C	2.26590000	14.94140000	9.93210000
C	2.27960000	13.27320000	5.83340000
C	1.30380000	14.10630000	7.85900000
C	0.38960000	12.15170000	6.81190000
C	2.44270000	15.88560000	10.95080000
C	1.34920000	12.23840000	5.81420000
H	1.37100000	11.60510000	5.13370000
C	5.09400000	11.09060000	6.83860000
C	3.11610000	13.82080000	9.94080000
H	3.01520000	13.16120000	9.29200000
C	0.37450000	13.08910000	7.84490000

H	5.50040000	13.02670000	8.52160000
C	3.36610000	13.40670000	4.81890000
C	2.24230000	14.21550000	6.85230000
H	2.84960000	14.91990000	6.85670000
H	5.32850000	15.59230000	7.05960000
C	4.28100000	14.64320000	11.88270000
H	4.95580000	14.54480000	12.51630000
C	3.44910000	15.73650000	11.90730000
C	4.09500000	13.69120000	10.89860000
H	4.64640000	12.94290000	10.88240000
C	4.45680000	12.37190000	3.01190000
H	5.29160000	12.63300000	3.40870000
H	4.21490000	13.00430000	2.33180000
H	4.54650000	11.49880000	2.61970000
C	4.31200000	9.11250000	5.83430000
H	4.19420000	8.73060000	6.70750000
H	4.61050000	8.43440000	5.22480000
H	3.47620000	9.47310000	5.52720000
C	0.42800000	16.16420000	8.81220000
C	0.38250000	17.20110000	9.75130000
C	-0.44070000	16.25740000	7.70920000
S	1.44160000	17.29790000	11.12930000
C	-0.49780000	18.27380000	9.60200000
H	-0.43270000	15.59250000	7.05960000
C	-1.30370000	17.32690000	7.58100000
O	0.67980000	17.18100000	12.34260000
O	2.24450000	18.47920000	11.00580000
H	-0.50980000	18.95150000	10.23840000
C	-1.34460000	18.33630000	8.52450000
H	-1.86940000	17.36940000	6.84420000
H	-1.93680000	19.04720000	8.43050000
C	-0.66710000	11.09070000	6.83860000
O	-0.46320000	10.17000000	5.89890000
O	-1.58370000	11.08100000	7.60550000
C	-1.44890000	9.11290000	5.83430000
H	-1.56700000	8.73100000	6.70750000
H	-1.15050000	8.43400000	5.22480000
H	-2.28480000	9.47330000	5.52720000
C	6.15040000	12.15170000	6.81190000
C	7.11020000	12.23810000	5.81420000
C	6.13550000	13.08880000	7.84490000
C	8.04060000	13.27320000	5.83340000
H	7.13210000	11.60460000	5.13370000
C	7.06470000	14.10640000	7.85900000
C	9.12720000	13.40680000	4.81890000
C	8.00320000	14.21540000	6.85230000
N	7.05900000	15.07450000	8.93210000
O	9.19340000	12.33990000	4.02490000

O	9.86800000	14.35340000	4.75510000
H	8.61040000	14.92040000	6.85670000
C	8.02680000	14.94130000	9.93210000
C	6.18900000	16.16420000	8.81220000
C	10.21770000	12.37180000	3.01190000
C	8.20370000	15.88550000	10.95080000
C	8.87710000	13.82090000	9.94080000
C	6.14350000	17.20110000	9.75130000
C	5.32030000	16.25740000	7.70920000
H	11.05250000	12.63270000	3.40870000
H	9.97570000	13.00470000	2.33180000
H	10.30760000	11.49920000	2.61970000
S	7.20260000	17.29790000	11.12930000
C	9.21010000	15.73670000	11.90730000
H	8.77630000	13.16110000	9.29200000
C	9.85590000	13.69130000	10.89860000
C	5.26320000	18.27380000	9.60200000
C	4.45730000	17.32690000	7.58100000
O	6.44080000	17.18100000	12.34260000
O	8.00550000	18.47920000	11.00580000
C	10.04200000	14.64310000	11.88270000
H	9.31840000	16.38280000	12.56600000
H	10.40720000	12.94240000	10.88240000
H	5.25120000	18.95150000	10.23840000
C	4.41640000	18.33630000	8.52450000
H	3.89160000	17.36940000	6.84420000
H	10.71660000	14.54530000	12.51630000
H	3.82420000	19.04720000	8.43050000
H	-0.26040000	13.02700000	8.52160000
H	3.55740000	16.38280000	12.56600000

Reference

(1) (a) X. Ding, C. Chen, L. Sun, H. Li, H. Chen, J. Su, H. Li, H. Li, L Xu and M. Cheng, *J. Mater. Chem. A*, 2019, **7**, 9510-9516; (b) J. Yang, X. Zhen, B. Wang, X. Gao, Z. Ren, J. Wang, Y. Xie, J. Li, Q. Peng, K. Pu and Z. Li, *Nat. Commun*., 2018, **9**, 840.