Methylation-effect in Prolonging the Pure Organic Room Temperature Phosphorescence Lifetime

General experimental procedures

Materials. Benzenesulfonyl chloride, 4-toluene sulfonyl chloride, 2,4,6-trimethylbenzenesulfonyl chloride, fluorobenzene, iron chloride and carbazole purchased from Alfa Aesar were used without any further purification. All the solvents were purchased from Guangzhou chemical reagents factory.

Characterizations. ^{1}H NMR and ^{13}C NMR spectra were obtained on Bruker AVANCE 400 spectrometer in acetone-d_6 and CDCl$_3$. The mass spectra were measured by thermospectrometers (DSQ & MAT95XP-HRMS). UV-Vis absorption spectra were measured on Hitachi U-3900 spectrophotometer. Photoluminescence spectra, lifetime and quantum yield were measured on SHIMADZU FR-5301pc and Horiba JY FL-3 spectrometer equipped with a calibrated integrating sphere. Phosphorescence spectra were obtained on Ocean Optics QE65 Pro. Single crystals X-ray diffraction data were collected from Agilent Technologies Gemini A Ultra system with Cu-Kα radiation (λ = 1.54178 Å) at 293(10) K. The structures were resolved and refined using direct methods with OLEX2. The quantum chemistry calculations were performed at the B3LYP/6-31+G* level in the Gaussian 09 software for monomers and dimers. The fraction free volume was calculated through Materials Studio software from Accelrys Inc. All the models for calculation are extracted from single crystals.

Synthesis of the 1M and 3M. Compounds **1M** and **3M** were synthesized according to our previous work[1] as showed in Figure S1.
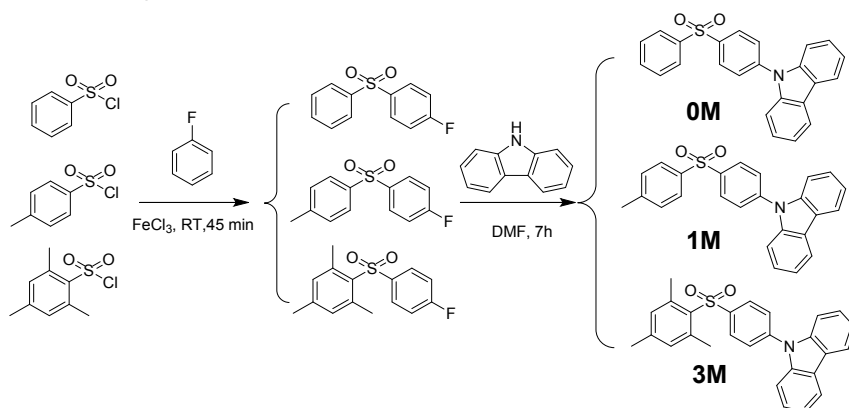

Figure S1. The synthetic route for compounds **0M**, **1M**, and **3M**.

9-(4-tosylphenyl)-9H-carbazole (1M):

^{1}H-NMR (400 MHz): δ 8.27 (m, 2H), 8.22 (m, 2H), 7.98 (m, 2H), 7.91 (m, 2H), 7.49 (t,4H), 7.43 (d, 2H), 7.32 (m, 2H), 2.44 (s, 3H). ^{13}C-NMR (100 MHz): δ 144.6, 142.4, 140.3, 140.1, 130.3, 129.5, 128.0, 127.2, 126.4, 124.1, 121.0, 120.6, 109.7, 21.8. EI-MS m/z: [m]$^+$ calcd for C$_{25}$H$_{19}$NO$_2$S, 397, found 397. HRMS m/z: [m]$^+$ calcd for C$_{25}$H$_{19}$NO$_2$S, 397.1136, found 397.1133.

9-(4-(mesitylsulfonyl)phenyl)-9H-carbazole (3M):

^{1}H-NMR (400 MHz): δ 8.09 (d, 2H), 8.02 (m, 2H), 7.78 (m, 2H), 7.39 (d, 2H), 7.31 (d, 2H), 7.19 (m, 2H), 6.99 (s, 2H), 2.55 (s, 6H), 2.20 (s, 2H). ^{13}C-NMR (100 MHz): 143.8, 142.3, 141.9, 141.8, 140.3, 140.2, 138.6, 138.1, 133.7, 132.5, 132.1, 128.3, 126.9, 126.4, 124.0, 120.9, 120.6, 109.7, 23.1, 21.7, 21.2. EI-MS m/z: [m]$^+$ calcd for $C_{27}H_{23}NO_2S$, 425, found 425. HRMS m/z: [m]$^+$ calcd for $C_{25}H_{19}NO_2S$, 425.1449, found 425.1442.
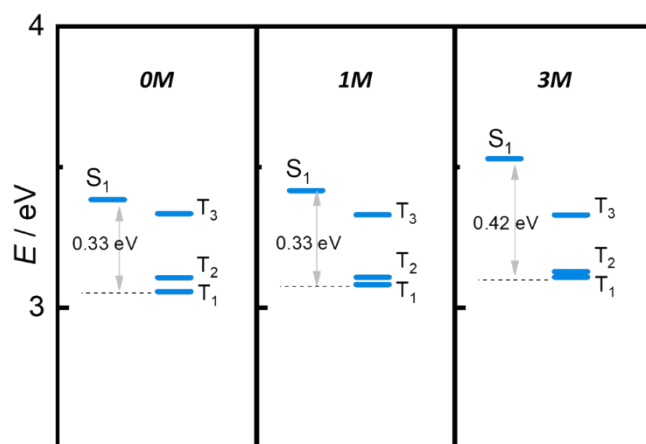
Figure S2. Energy level distribution of the isolated molecules simulated in a cavity of a THF solvent and using the polarizable continuum model.
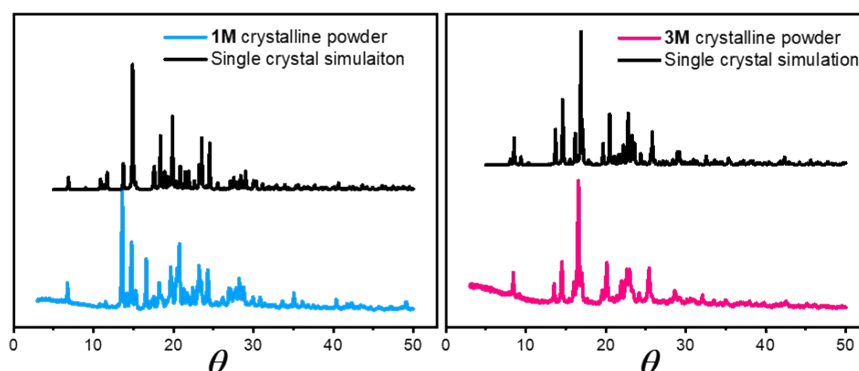
Figure S3. PXRD of **1M** and **3M** crystalline powder (indicating the crystalline powder and single crystal lattice have the same packing mode for similar diffraction peaks).
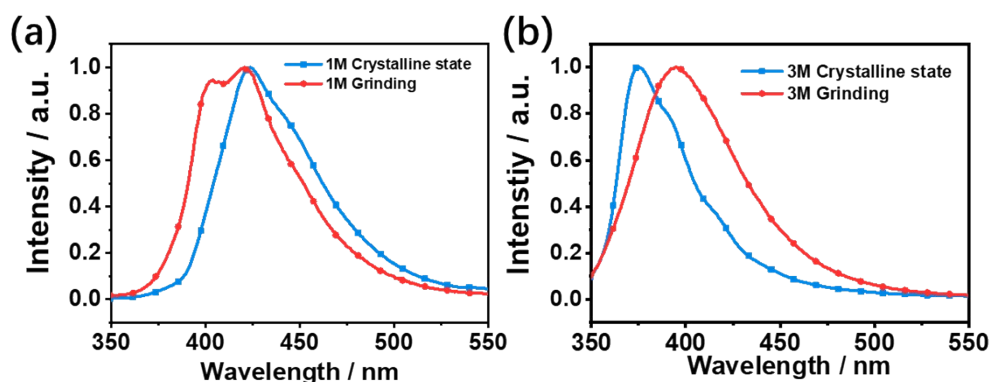

Figure S4. The PL spectra before and after grinding of the crystalline samples of (a) **1M** and (b) **3M**.
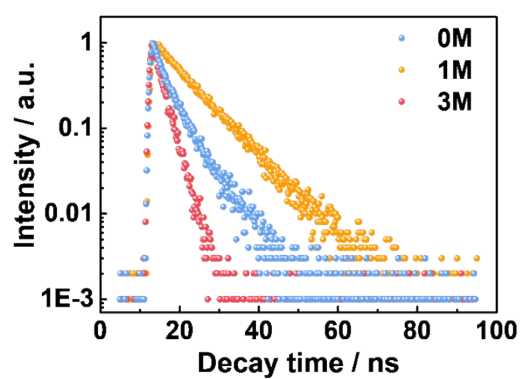
Figure S5. Fluorescence decay curves of **0M** (406 nm), **1M** (423 nm), **3M** (376 nm).
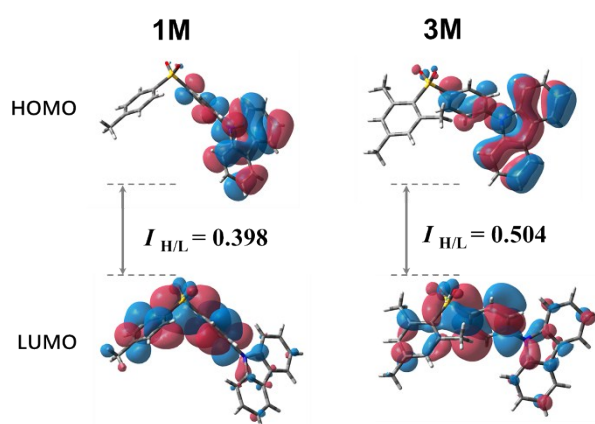

Figure S6. The HOMO and LUMO of **1M** and **3M**, and overlap integral extents $I_{H/L}$.
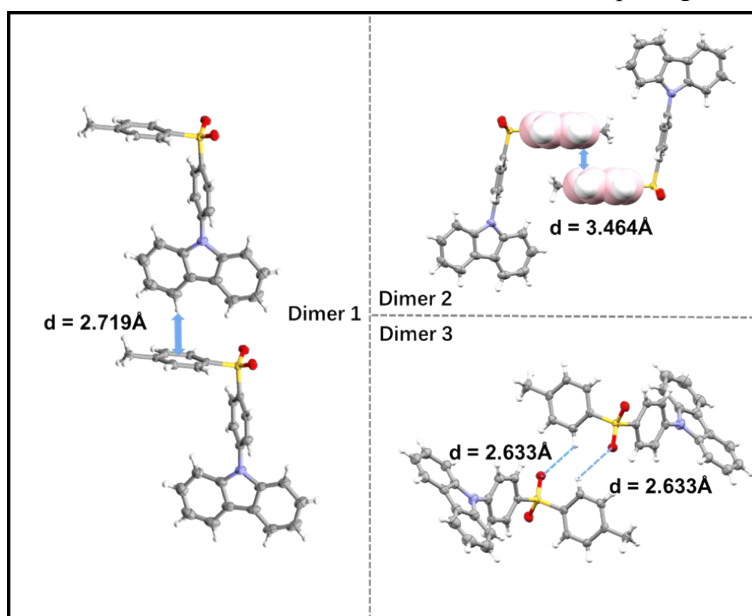

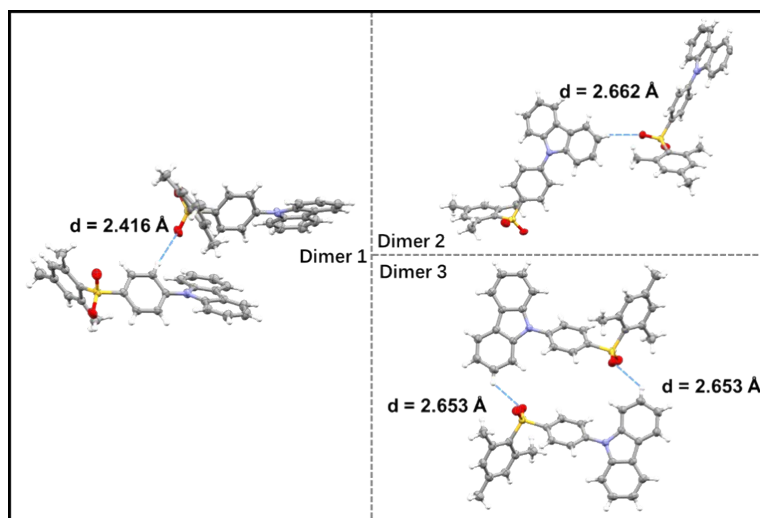**Figure S7.** Dimers extracted from **1M** single crystal.

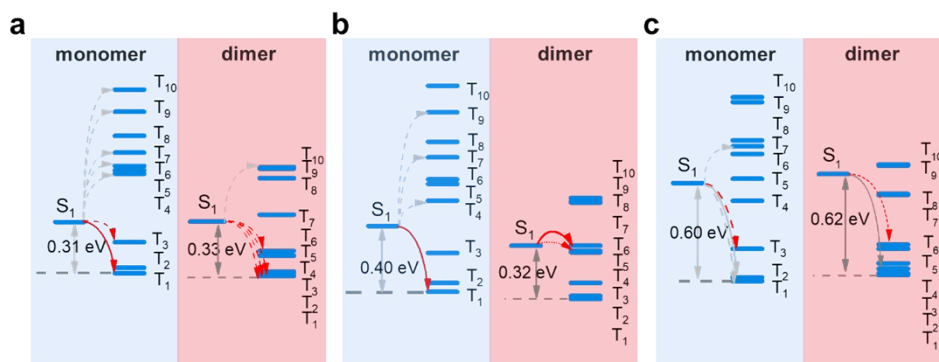**Figure S8.** Dimers extracted from **3M** single crystal.

Figure S9. The ISC channels between the lowest singlet (S_1) and triplet states (T_n) of (a) **0M**, (b) **1M**, and (c) **3M**. The red solid and dashed arrows represent major and minor ISC channels, respectively; the grey dashed line represents channels with little matched or above the lowest singlet state, the grey solid line represents energy gap over 0.5 eV.
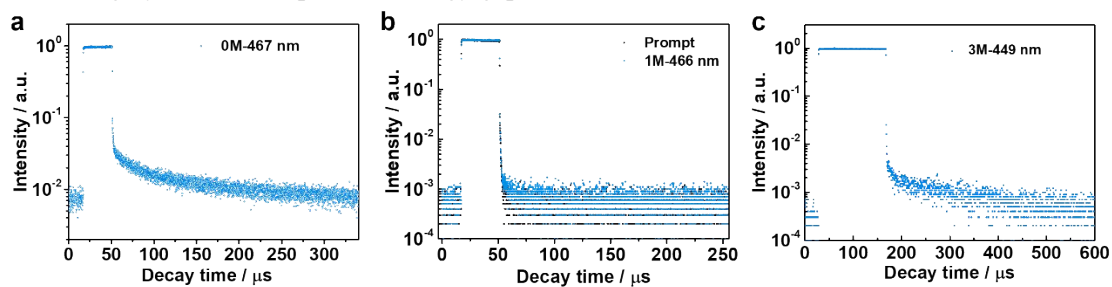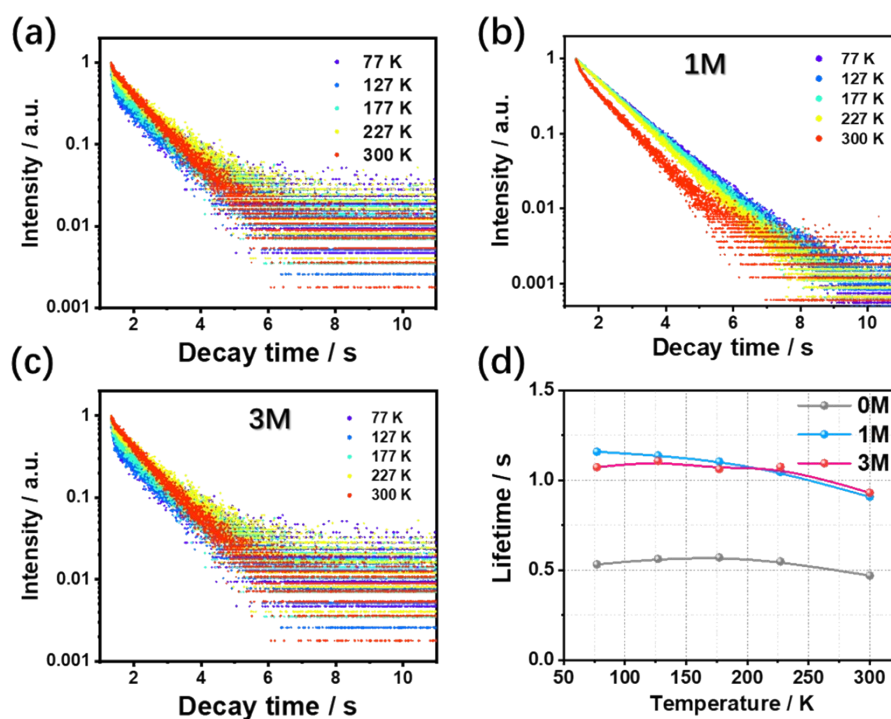

Figure S10. Normal phosphorescence decay curves of (a) **0M** (467 nm), (b) **1M** (466 nm) and (c) **3M** (449 nm) at ambient conditions.

Table S1. Lifetime of the crystalline powder at ambient conditions.

Compound	Fluorescence	Normal phosphorescence	Long-lived phosphorescence	Φ_F	Φ_P
0M	4.88 ns (406 nm)	τ_1=11.2 μs (11.77%) τ_2=62.0 μs (62.33%) τ_3= 2.98 μs (25.90%) (467 nm)	0.36 s (565 nm)	29.1%	1.50%
1M	9.19 ns (423 nm)	Not detected	0.82 s (546 nm)	72.5%	2.64%
3M	2.64 ns (376 nm)	τ_1=3.80 μs (7.48%) τ_2=143 μs (92.52%) (449 nm)	0.83 s (542 nm)	51.1%	1.11%

Figure S11. The temperature dependent long-lived phosphorescence decay curves of (a) **0M** (565 nm), (b) **1M** (546 nm), (c) **3M** (542 nm), and (d) temperature-dependent lifetime of **0M**, **1M** and **3M** in vacuum.

Table S2. The long-lived phosphorescence lifetime of **1M** and **3M** at different temperatures in vacuum.

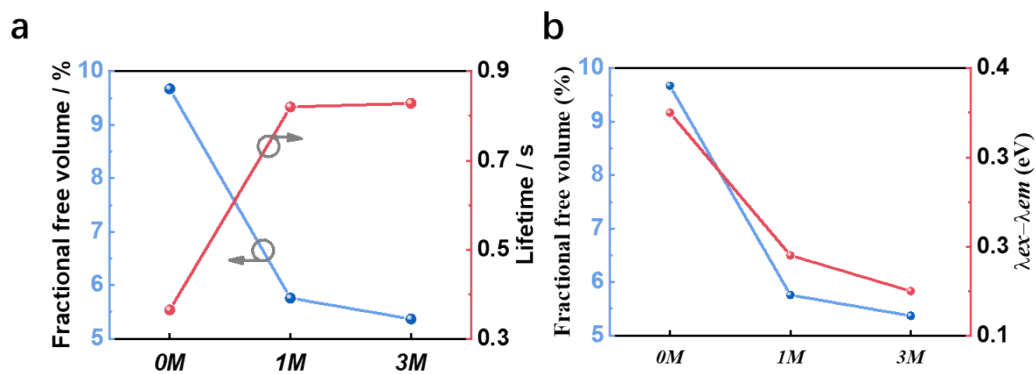| Lifetime / s	77 K	127 K	177 K	227 K	300 K
0M	0.53	0.56	0.57	0.55	0.47
1M	1.16	1.14	1.10	1.04	0.91
3M	1.07	1.11	1.06	1.07	0.93

Figure S12. (a) Fractional free volume and lifetime, and (b) fractional free volume and $\Delta E_{ex\text{-}em}$ of **0M**, **1M**, and **3M**.
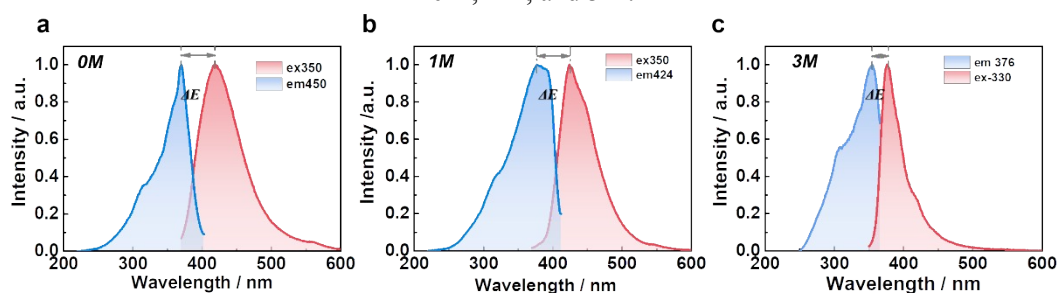

Figure S13. The excitation (blue) and emission (red) spectra of (a) **0M**, (b) **1M**, and (c) **3M** in the crystalline state.
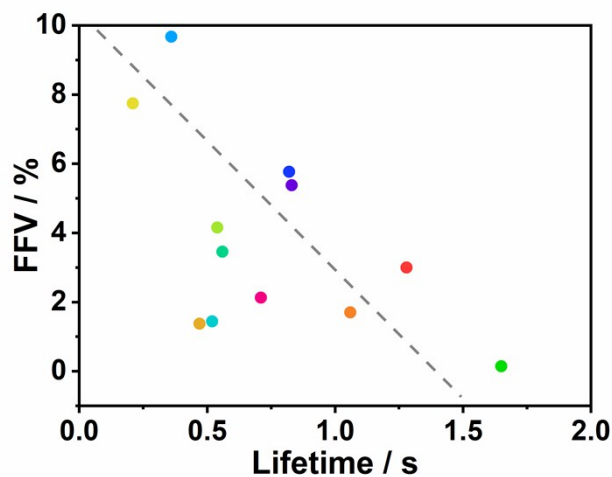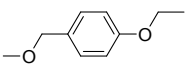

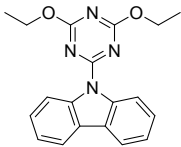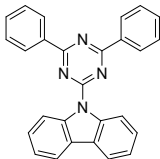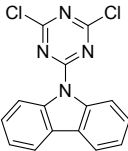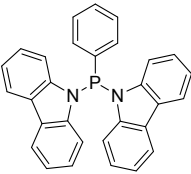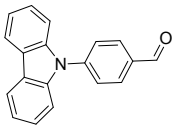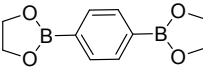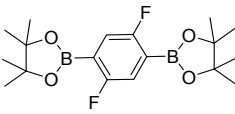**Figure S14.** The negative correlation for FFV and lifetime of the typically reported compounds (dashed line represents a negative trend).

Table S3. The FFV and lifetime of the typically reported compounds.
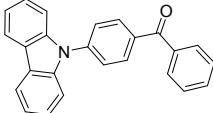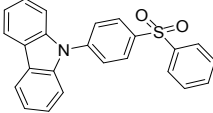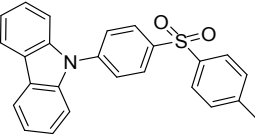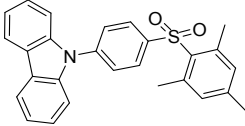
No.	Structures	FFV / %	Lifetime / s	Reference
1		2.12	0.71	Nature Materials. 2015, 14(7):685-690.

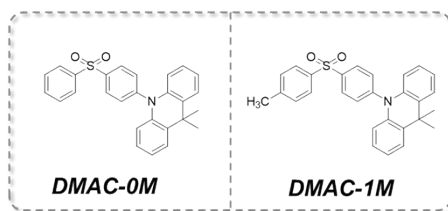|				
2		2.30	1.28	
3		1.70	1.06	
4		1.37	0.47	
5		7.75	0.21	
6		4.15	0.54	Chemical Communications. 2015, 51(52):10381-10384.
7		0.14	1.65	Journal of the American Chemical Society. 2017, 139(7):2728-2733.
8		3.46	0.56	
9		1.44	0.52	Advanced Materials. 2015, 27(40):6195-6201.
10		9.64	0.36	Angewandte Chemie International Edition. 2016, 55(6):2181-2185.
11		5.76	0.82	This work
12		5.37	0.83	

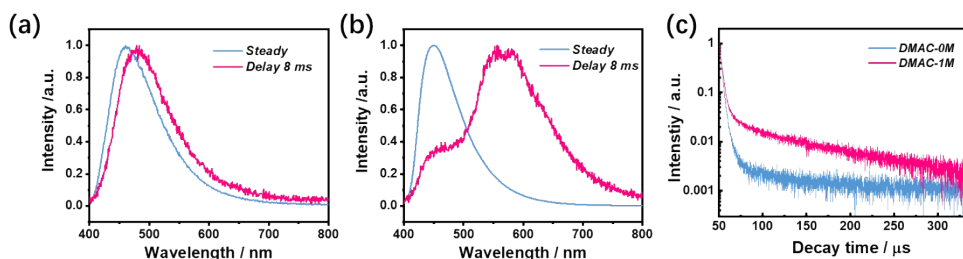**Figure S15.** The chemical structures of **DMAC-0M** and **DMAC-1M**.

Figure S16. The steady-state PL and phosphorescence spectra (delay time = 8 ms) of (a) **DMAC-0M** and (b) **DMAC-1M**, and (c) the corresponding phosphorescence decay curves.
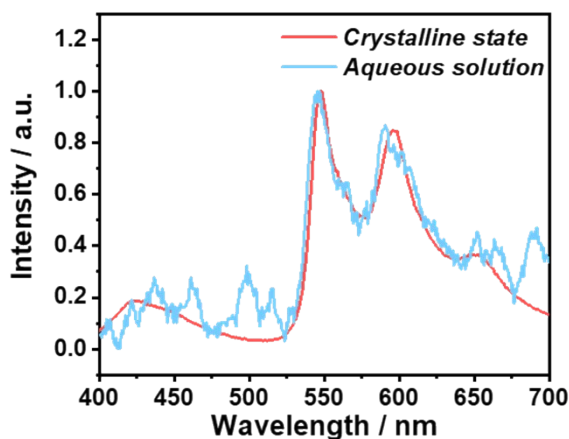

Figure S17. Phosphorescence spectra of **1M** in the crystalline state and aqueous solution (delay time = 8 ms).

We have demonstrated the potential applications of **1M** in bioimaging, and the aqueous solutions were prepared according to the previous work.[2] The **1M** powder (0.25 mg) was added into 5 mL F127 (PEG-B-PEG, 3.33 mg / mL) aqueous solution and the resulting mixture was treated with an ultrasonic bath for 15 mins at room temperature. The obtained aqueous solution was stored in the refrigerator (4 °C) after filtered. The corresponding aqueous solution exhibits relatively weak long-lived phosphorescence and cannot be observed easily with the naked eye, however, it can be detected with a CCD spectrometer with 8 ms delay.

Table S4. Structure data of **0M**, **1M**, and **3M** single crystals.

Name	0M	1M	3M
Formula	$C_{24}H_{17}NO_2S$	$C_{25}H_{19}NO_2S$	$C_{27}H_{23}NO_2S$
Wavelength (Å)	1.54178	1.54184	1.54184

Space group	P 21/n	P 21/c	C 2/c
Cell Length (Å)	a = 9.513 (2) b = 11.961 (3) c = 17.047 (5)	a = 13.4762 (3) b = 15.1134 (3) c = 10.0992 (2)	a = 21.0963 (7) b = 12.9096 (3) c = 15.8774 (4)
Cell Angeles (°)	α = 90 β = 99.69 (3) γ = 90	α = 90 β = 107.105 (2) γ = 90	α = 90 β = 101.148 (3) γ = 90
Cell Volume (Å^3)	1912.0 (9)	1965.93 (7)	4242.5 (2)
Z	4	4	8
Density (g/cm^3)	1.332	1.343	1.332
F(000)	800.0	832.0	1792.0
h_{max}, k_{max}, l_{max}	11, 14, 21	16, 18, 12	26, 16, 19
T_{min}, T_{max}	0.754, 0.718	0.6444, 0.952	0.725, 0.970
CCDC Number	1402470	1833075	1833083

The crystal structures above have been deposited at the Cambridge Crystallographic Data Centre.
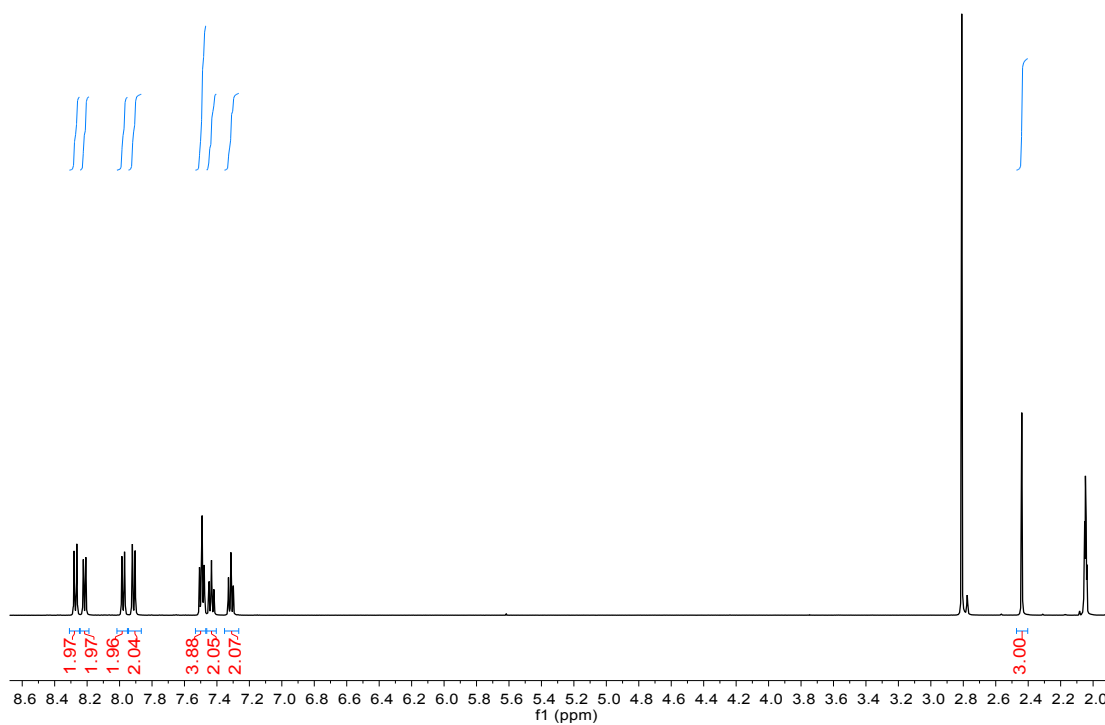

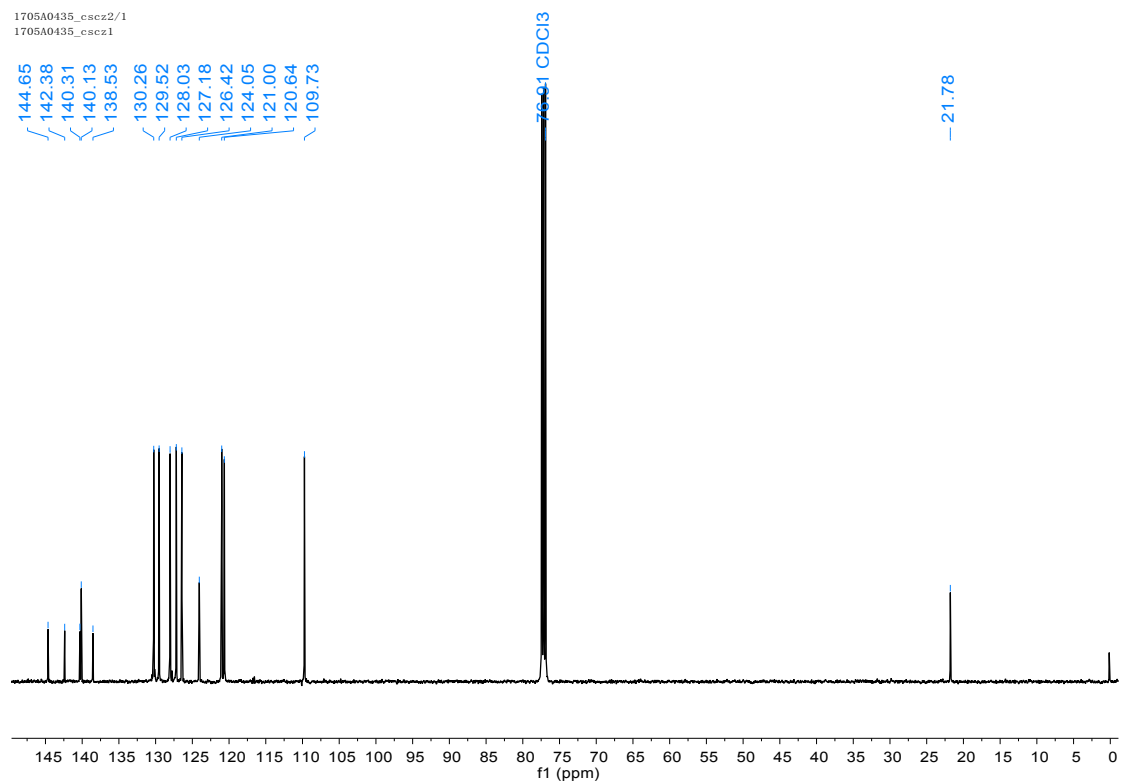**Figure S18.** ^{1}H NMR spectrum of compound **1M**.

Figure S19. ^{13}C NMR spectrum of compound **1M**.
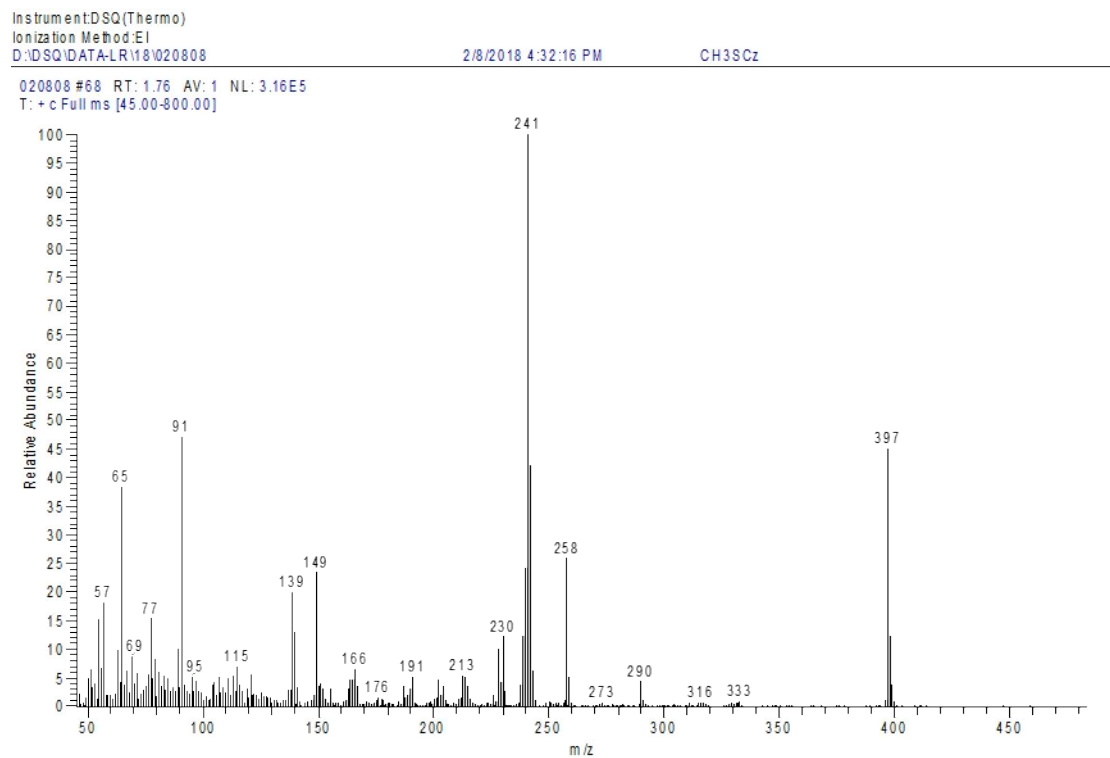
Figure S20. EI-MS of **1M**.
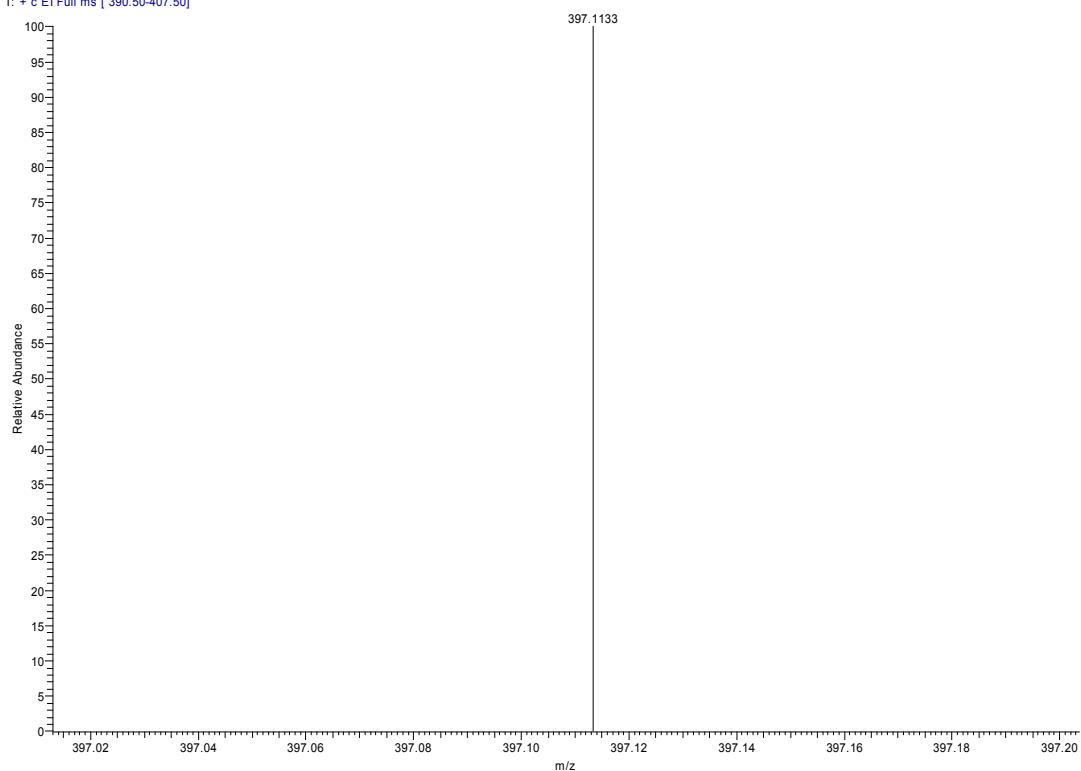
Figure S21. HRMS spectrum of compound **1M**.

1706A0152_3C−1/1
1706A0152_1C
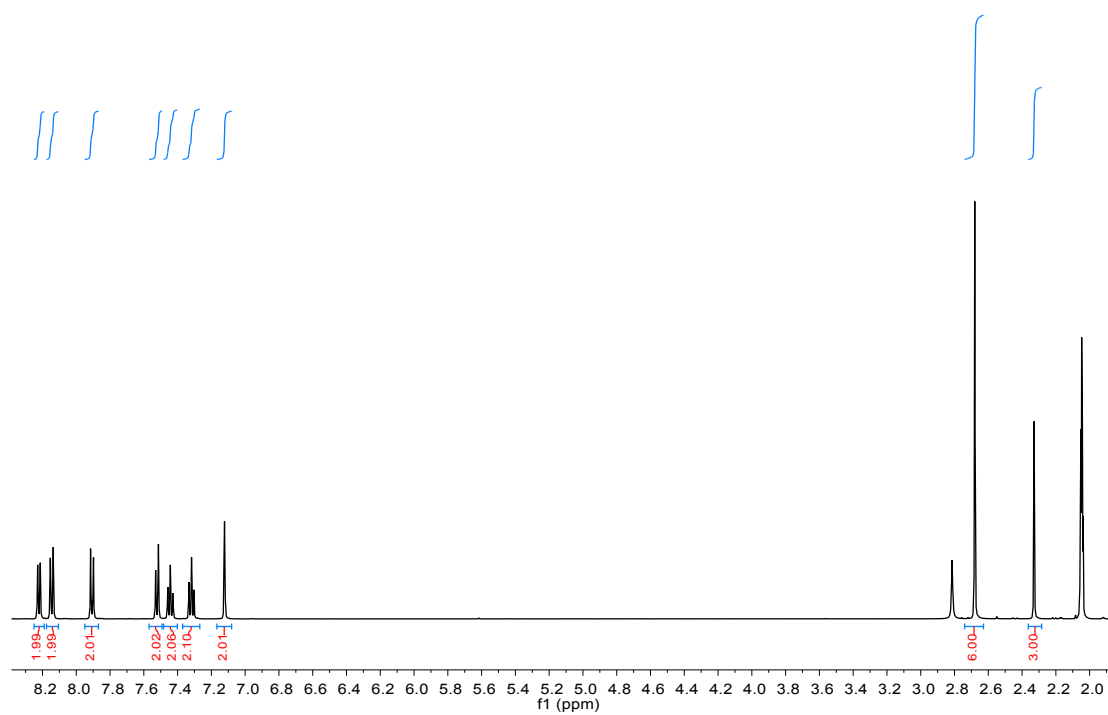
Figure S22. ^{1}H NMR spectrum of compound **3M**.

11
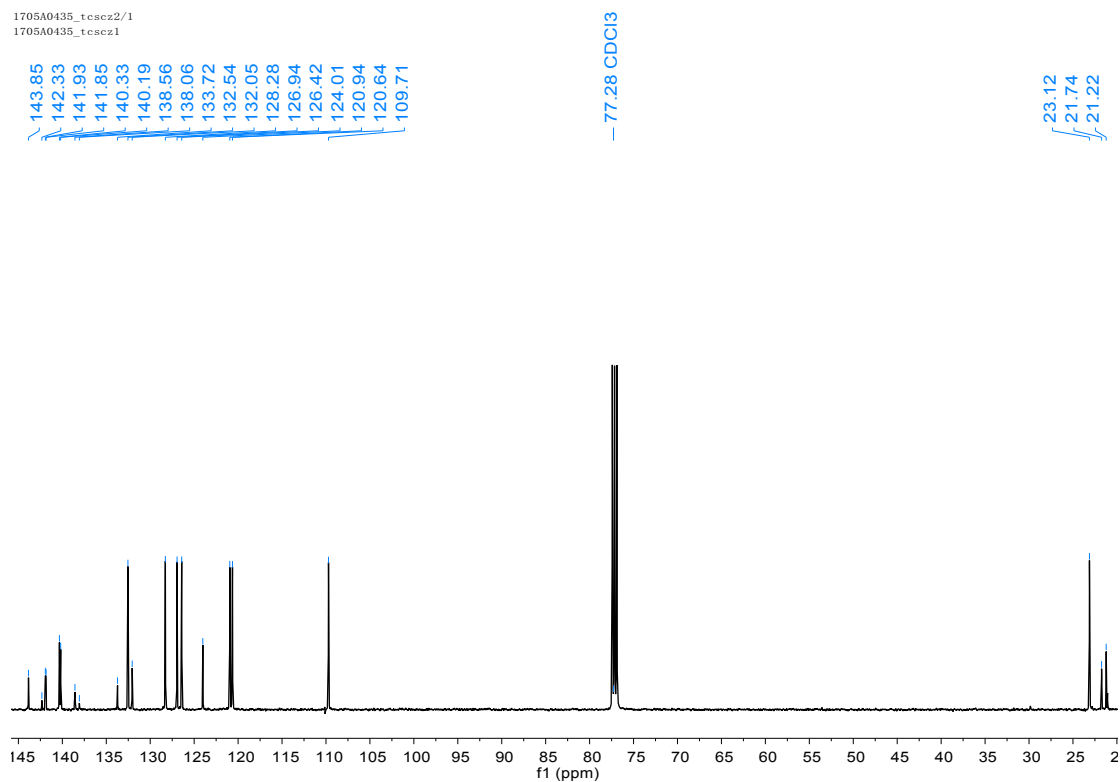
Figure S23. ^{13}C NMR spectrum of compound **3M**.

Instrument:DSQ(Thermo)
Ionization Method:EI
D:\DSQ\DATA-LR\18\020809   2/8/2018 4:39:39 PM   t-CH3SCz

020809 #61 RT: 1.58 AV: 1 NL: 1.05E5
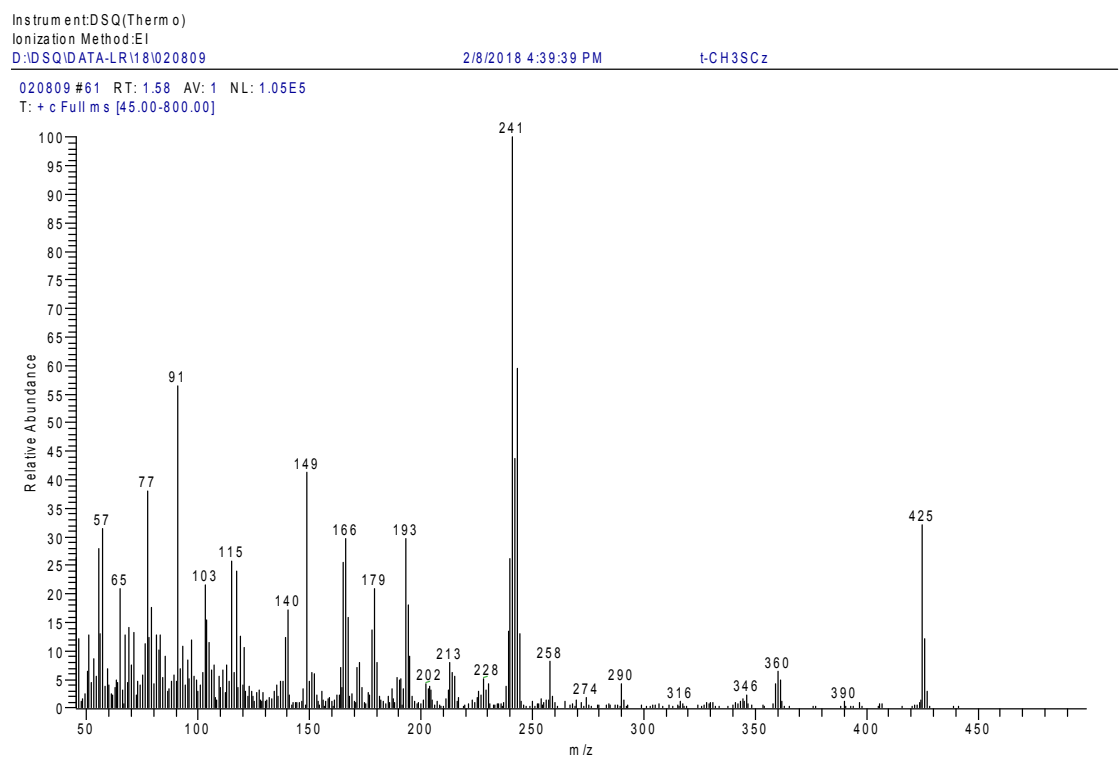T: + c Full ms [45.00-800.00]

Figure S24. EI-MS of **3M**.

020902-t-c3 #8 RT: 0.33 AV: 1 NL: 1.10E5
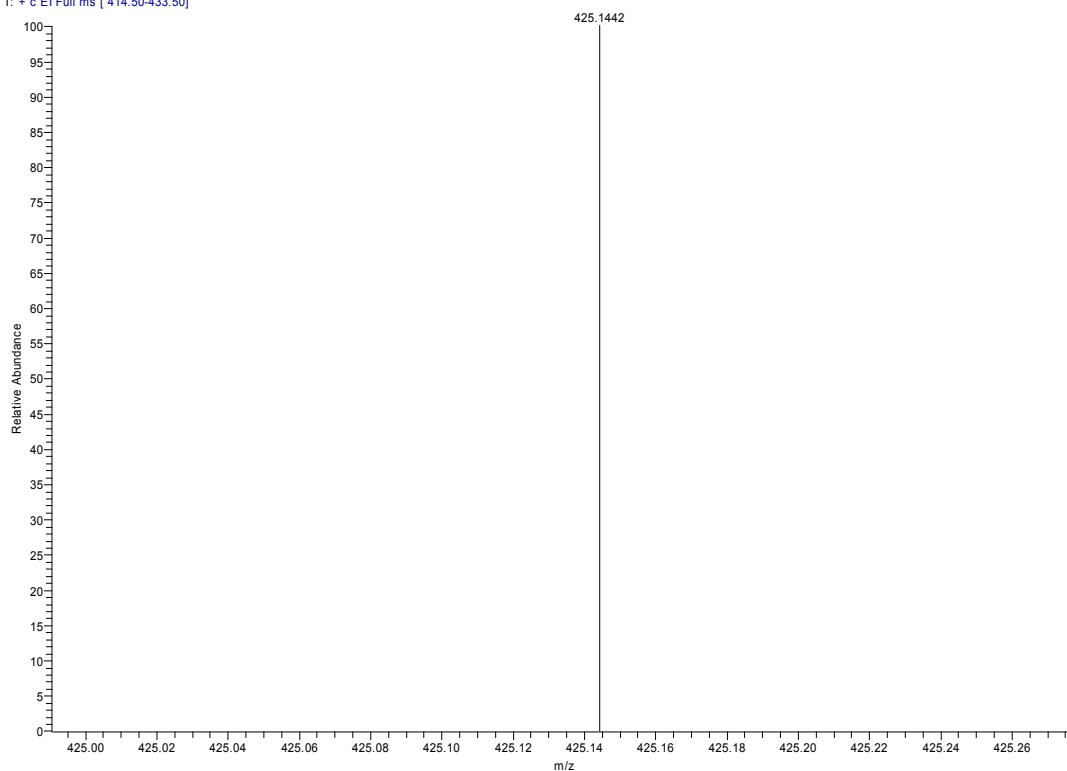T: + c EI Full ms [414.50-433.50]

Figure S25. HRMS spectrum of compound **3M**.

Reference

[1] Z. Yang, Z. Mao, X. Zhang, D. Ou, Y. Mu, Y. Zhang, C. Zhao, S. Liu, Z. Chi, J. Xu, Y. C. Wu, P. Y. Lu, A. Lien and M. R. Bryce, *Angew. Chem. Int. Ed.*, 2016, **55**, 2181.

[2] X. Zhen, Y. Tao, Z. An, P. Chen, C. Xu, R. Chen, W. Huang and K. Pu, *Adv. Mater.*, 2017, **29**, 1606665.