

## Supporting information

Xinping Ge<sup>a,ξ</sup>, Xiaoping Gan<sup>a,b,ξ</sup>, Shun Yao<sup>a</sup>, Kang Wang<sup>a</sup>, Weiju Zhu<sup>a</sup>, Jianhua Yu<sup>a</sup>,  
Jieying Wu<sup>a</sup>, Yupeng Tian<sup>a</sup>, Hongping Zhou<sup>a\*</sup>

<sup>a</sup>College of Chemistry and Chemical Engineering, Anhui University and Key Laboratory of  
Functional Inorganic Materials Chemistry of Anhui Province, 230601, Hefei, P.R. China

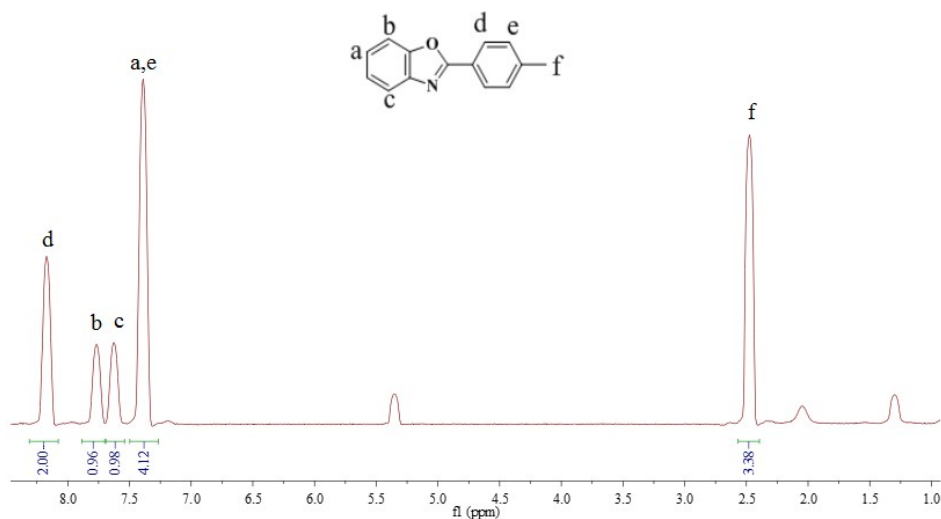
<sup>b</sup>Department of Applied Chemistry, School of Science, Anhui Agricultural University, 230036  
Hefei, P. R. China.

Corresponding author. Fax: +86-551-63861279; Tel: +86-551-63861279

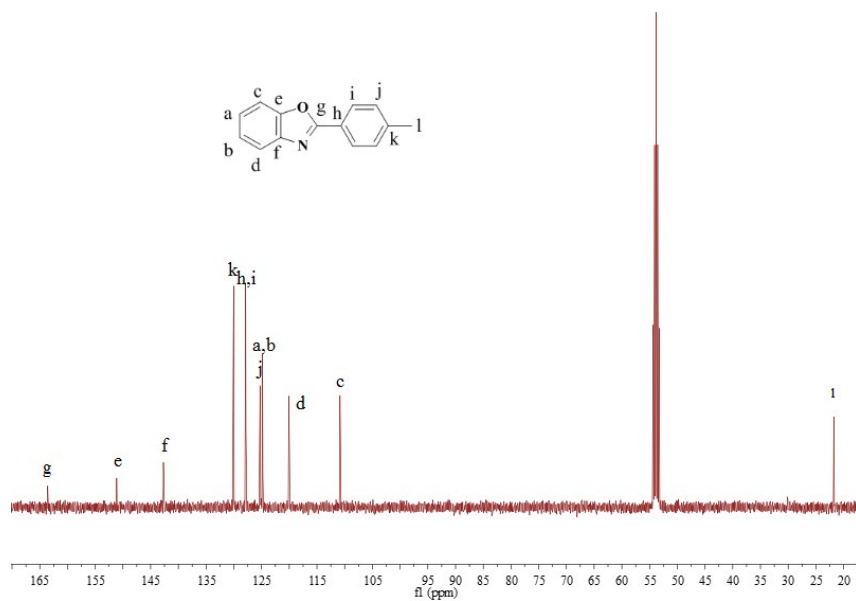
E-mail address: [zhpzhp@263.net](mailto:zhpzhp@263.net)

ξ: These authors contributed equally to this work and should be considered co-first authors

**Figure S1a:** <sup>1</sup>H NMR, <sup>13</sup>C NMR and MS spectra of **M1**.

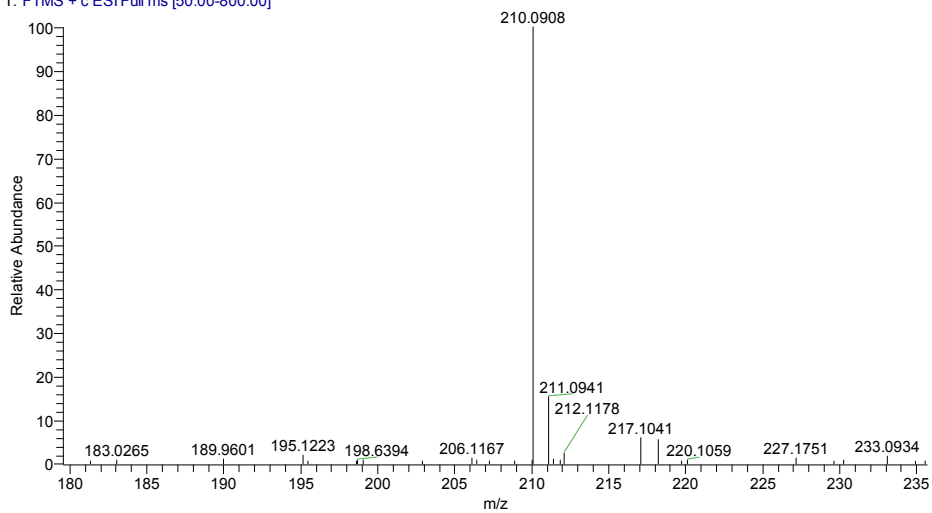


The <sup>1</sup>H NMR (400MHz) spectra of the **M1** in CD<sub>2</sub>Cl<sub>2</sub>



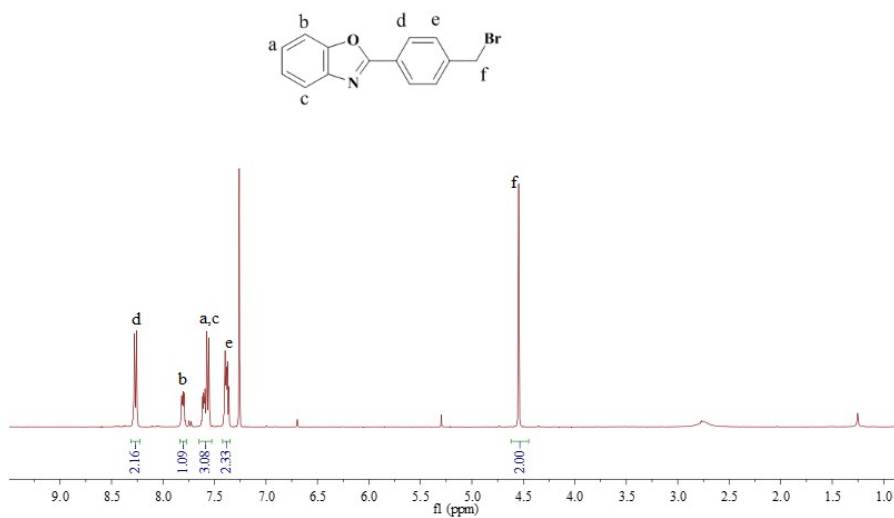
The  $^{13}\text{C}$  NMR (100 MHz) spectra of the **M1** in  $\text{CD}_2\text{Cl}_2$

log1 #22 RT: 0.21 AV: 1 NL: 1.32E7  
T: FTMS + c ESI Full ms [50.00-800.00]

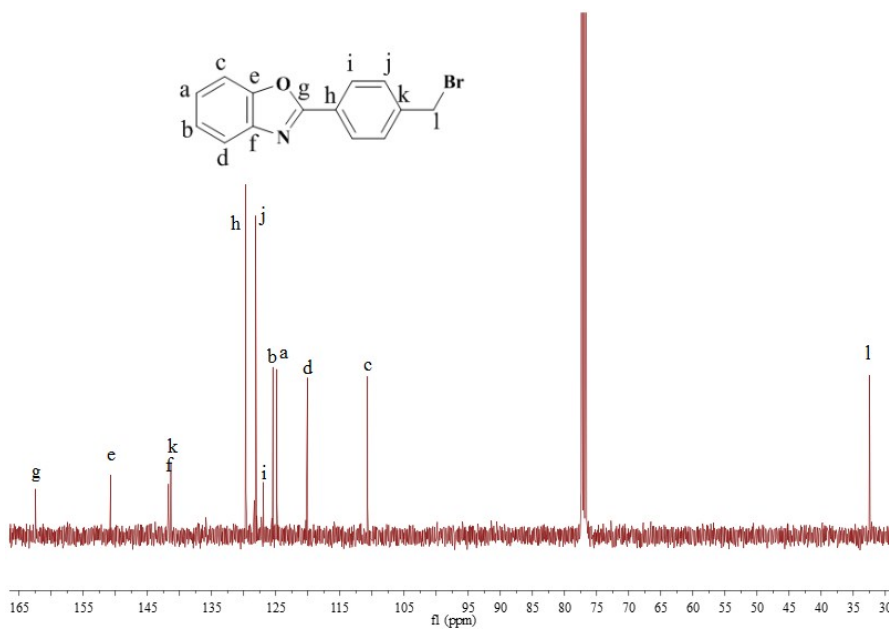


ESI MS of **M1**

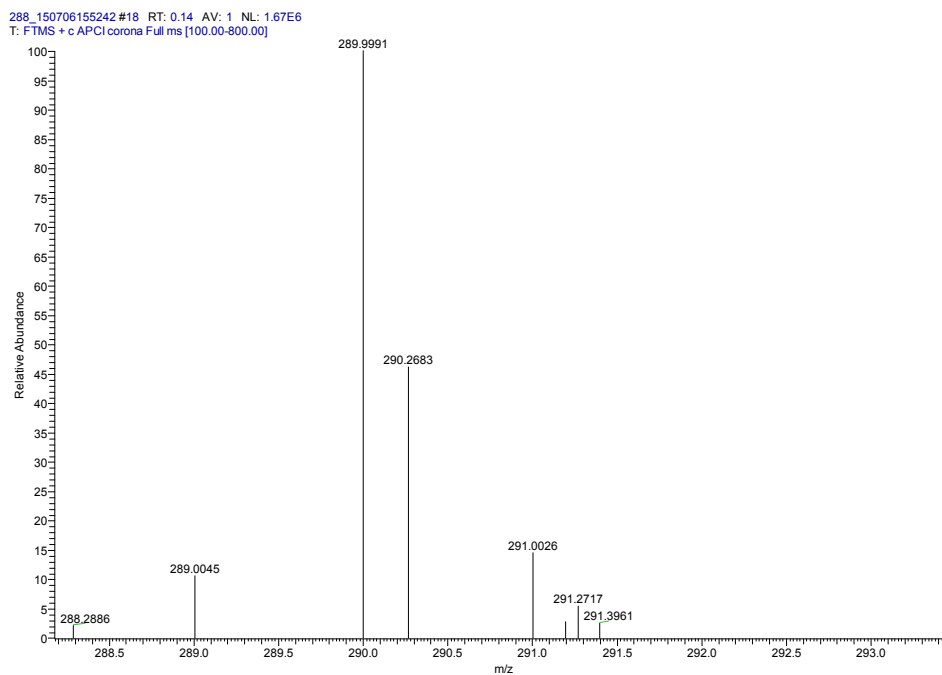
**Figure S1b:**  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS spectra of **M2**.



The  $^1\text{H}$  NMR (400MHz) spectra of the **M2** in  $\text{CDCl}_3$

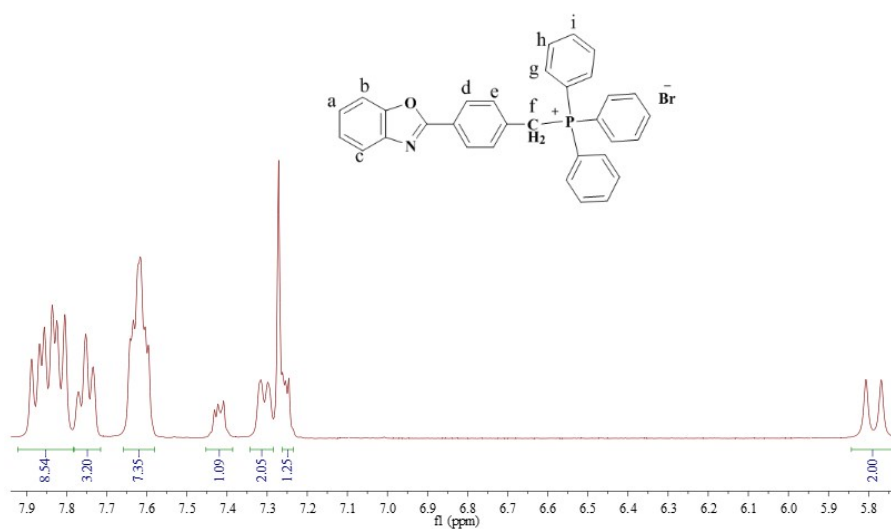


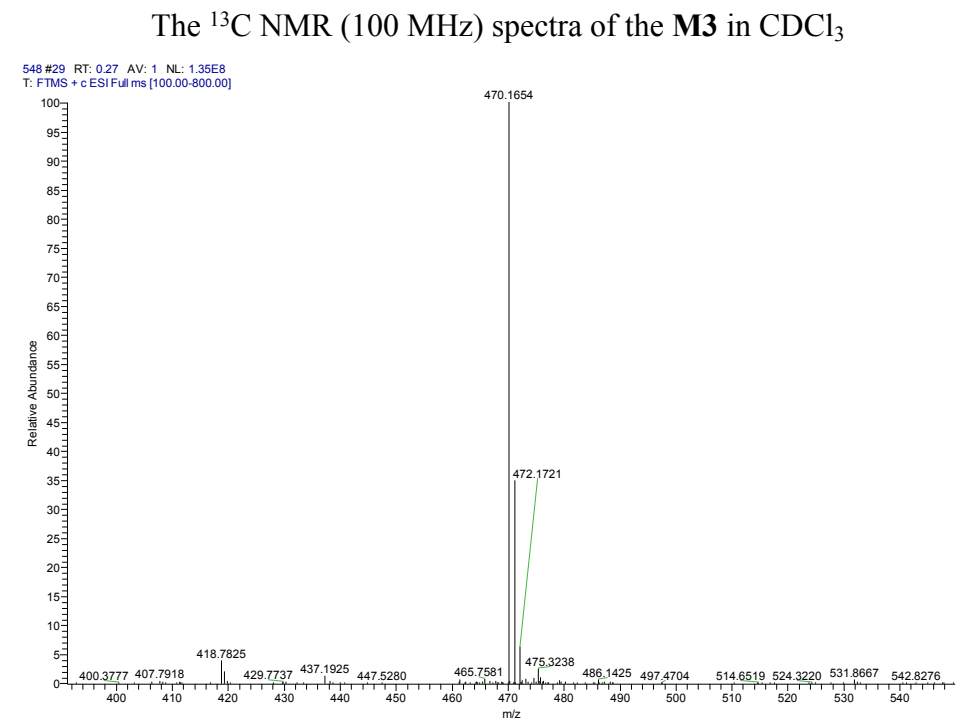
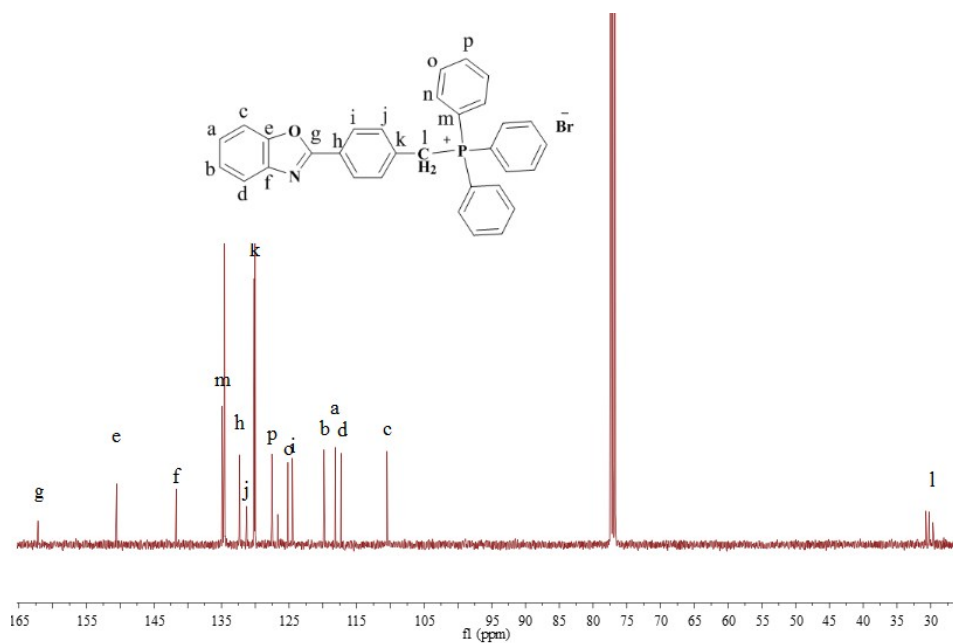
The  $^{13}\text{C}$  NMR (100 MHz) spectra of the **M2** in  $\text{CDCl}_3$



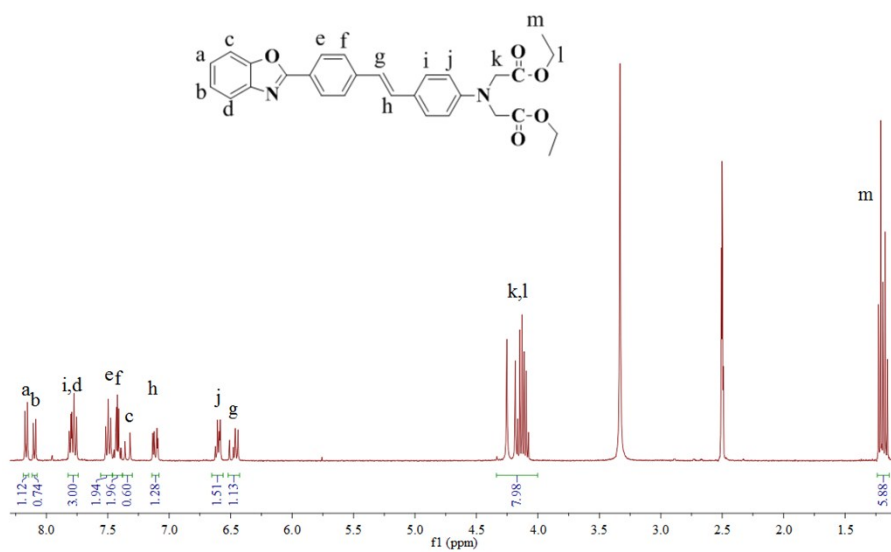
APCI MS of **M2**

**Figure S1c:**  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS spectra of **M3**.

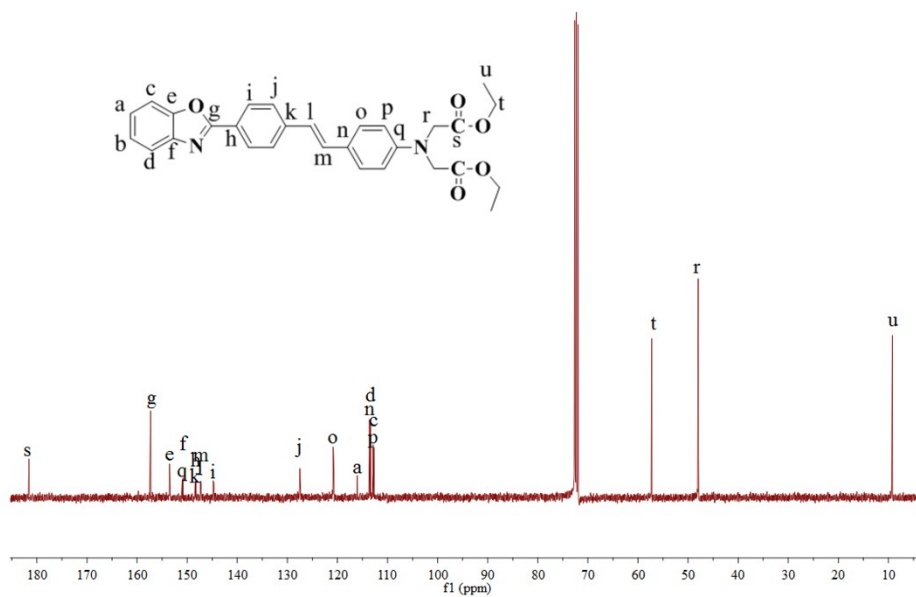




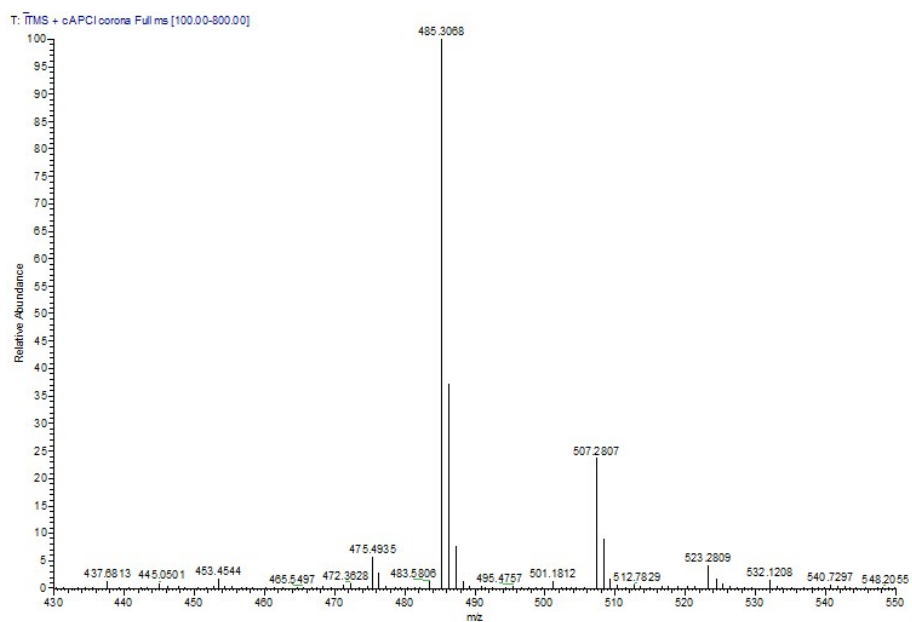
**Figure S1d:**  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS spectra of **T1**.



The  $^1\text{H}$  NMR (400MHz) spectra of the **T1** in  $\text{DMSO-}d_6$

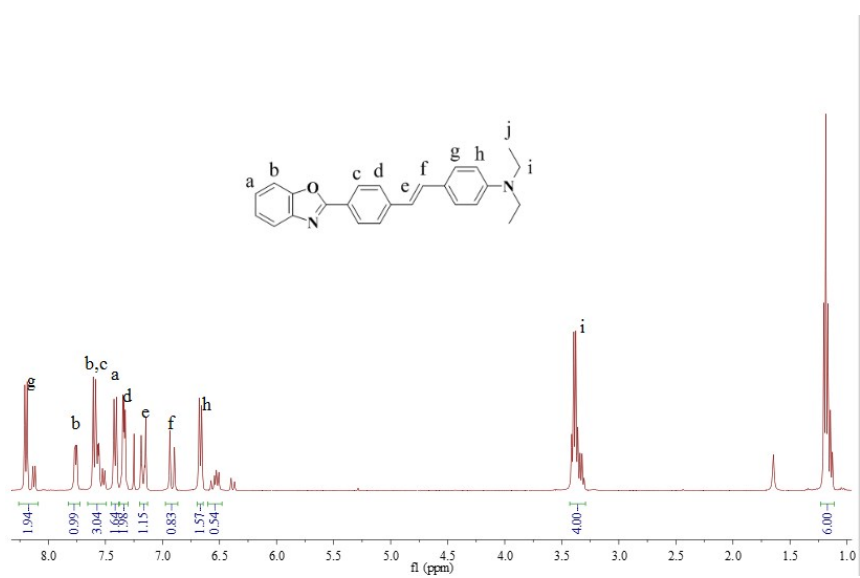


The  $^{13}\text{C}$  NMR (100 MHz) spectra of the **T1** in  $\text{DMSO-}d_6$

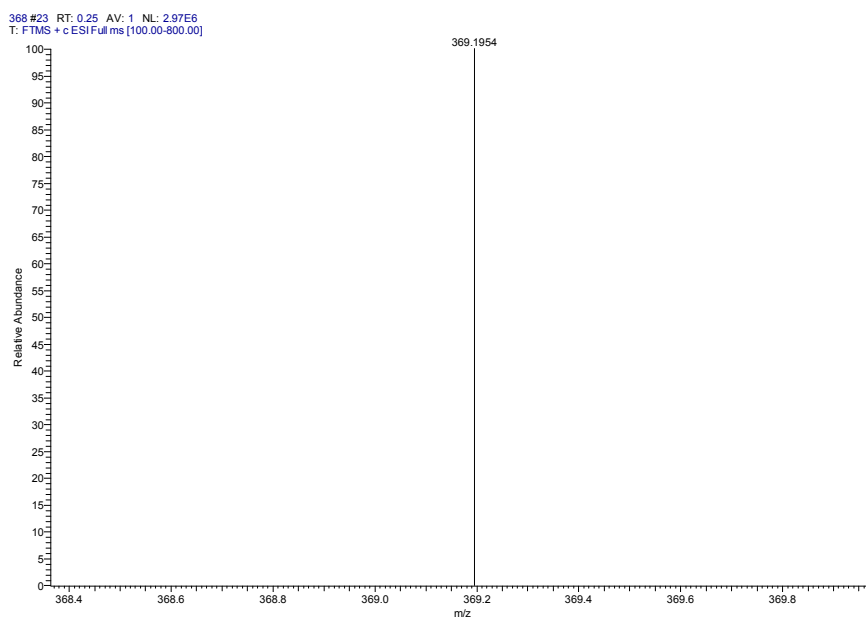
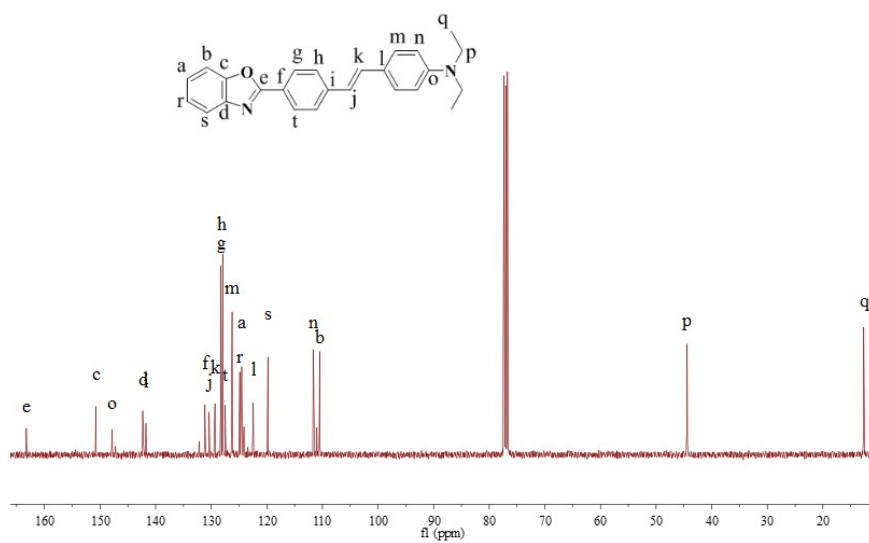


APCI MS of T1

Figure S1e:  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS spectra of T2.

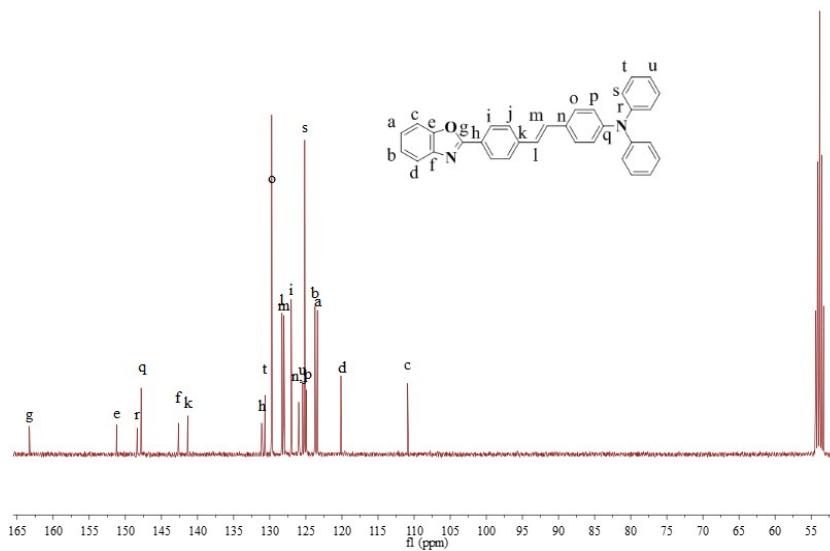
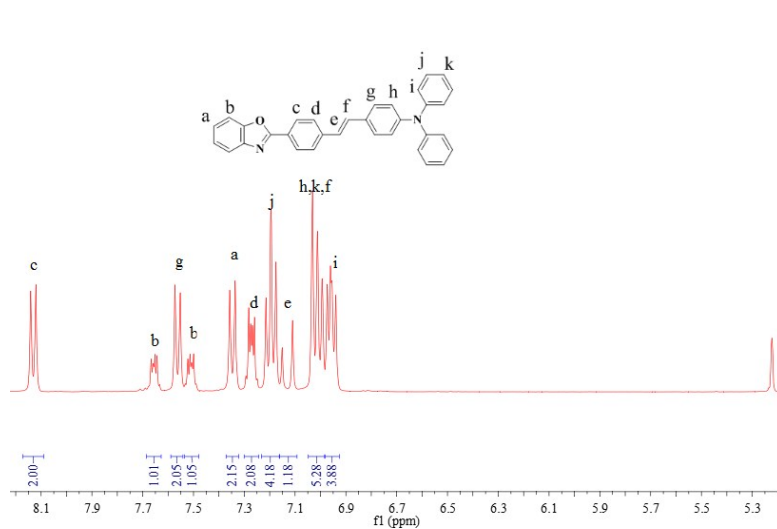


The  $^1\text{H}$  NMR (400MHz) spectra of the T2 in  $\text{CDCl}_3$

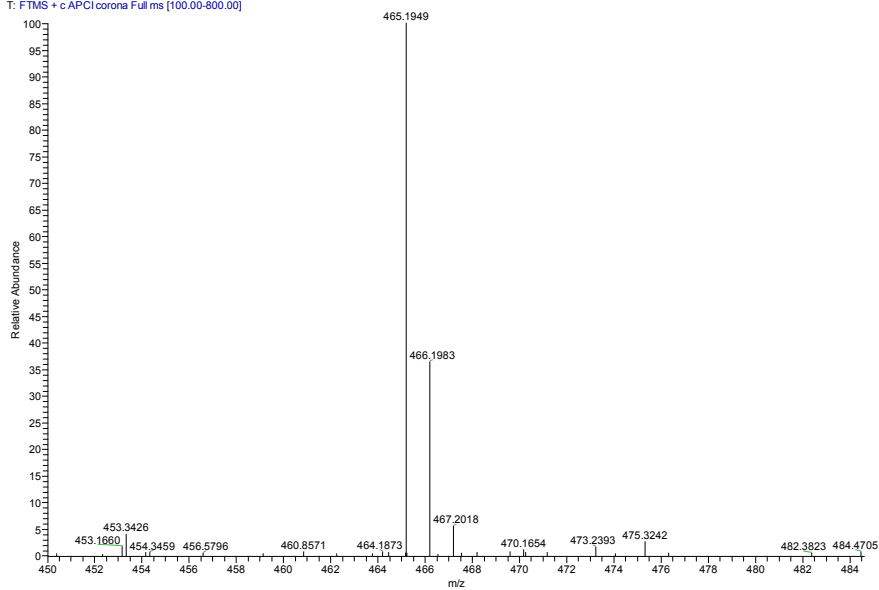


**Figure S1f**  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS spectra of **T3**.



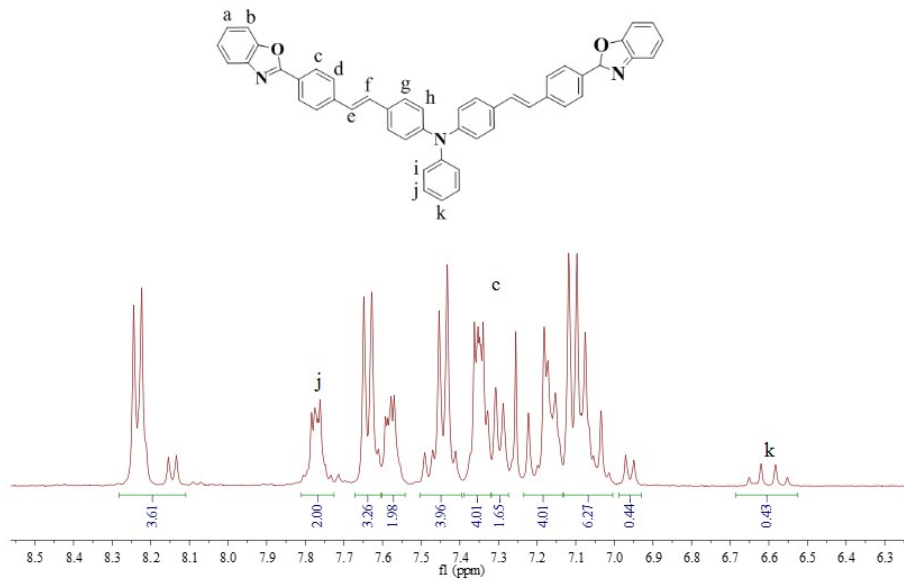


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T: FTMS + c APCI corona Full ms [100.00-800.00]

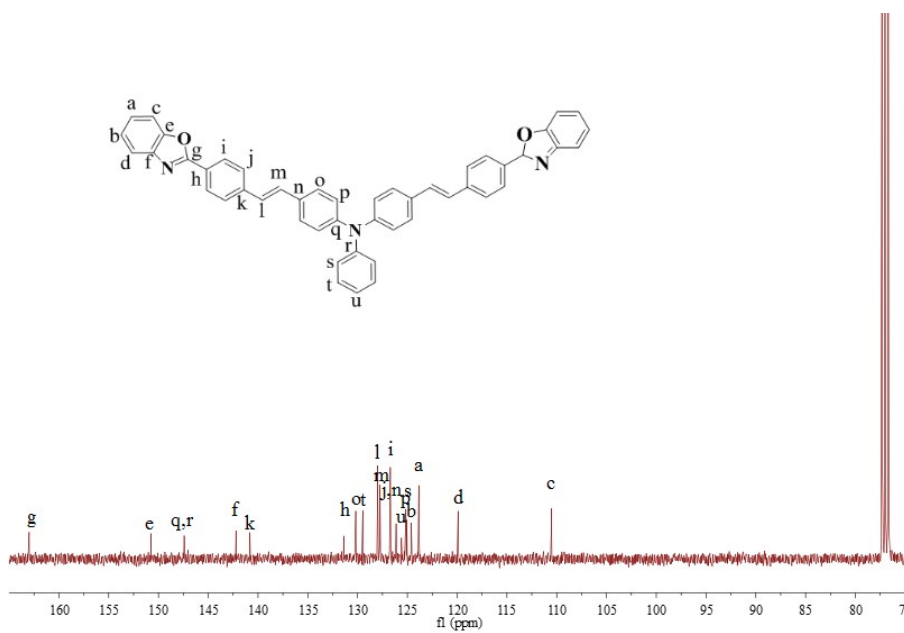


## APCI MS of T3

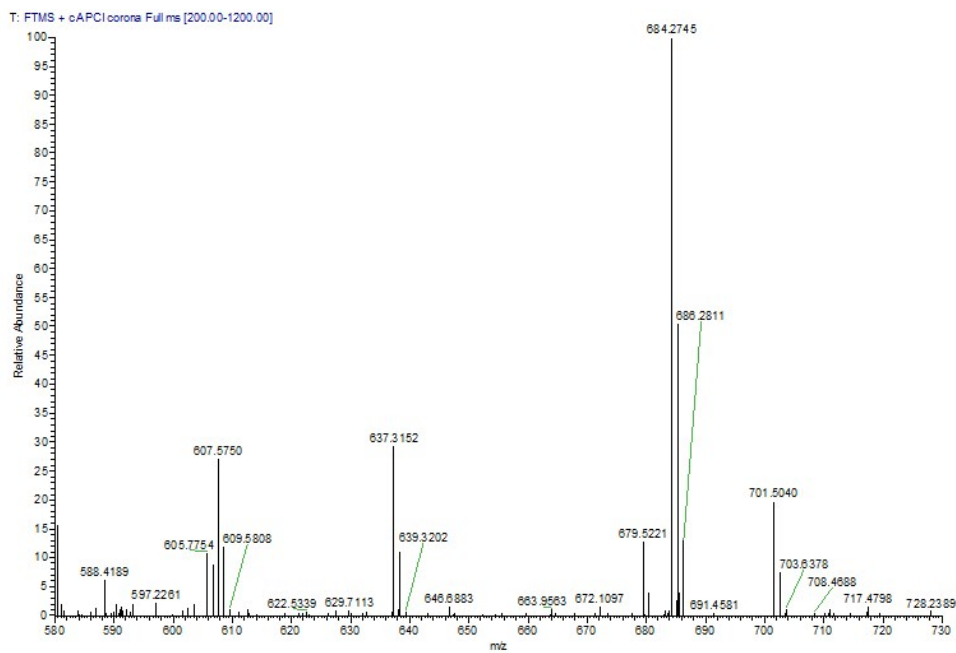
Figure S1g:  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS spectra of T4.



The  $^1\text{H}$  NMR (400 MHz) spectra of the T4 in  $\text{CDCl}_3$

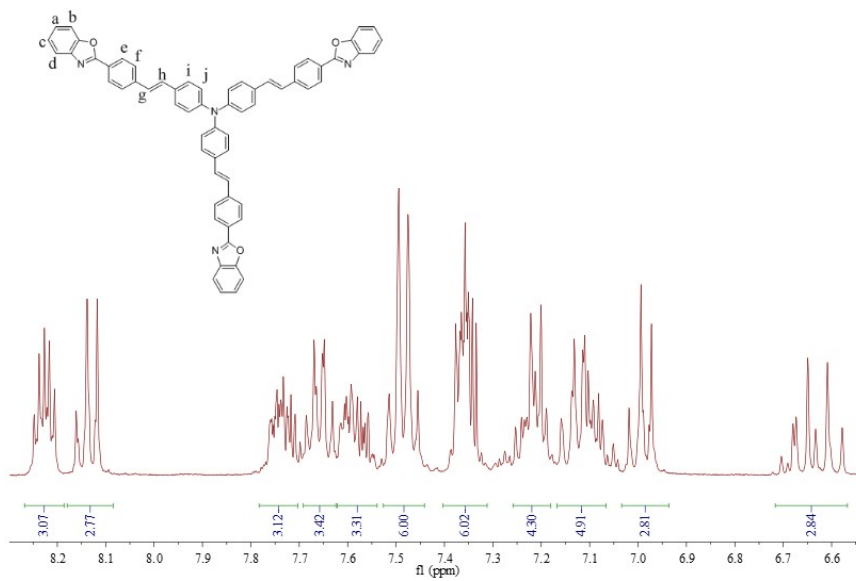


The  $^{13}\text{C}$  NMR (100 MHz) spectra of the T4 in  $\text{CDCl}_3$

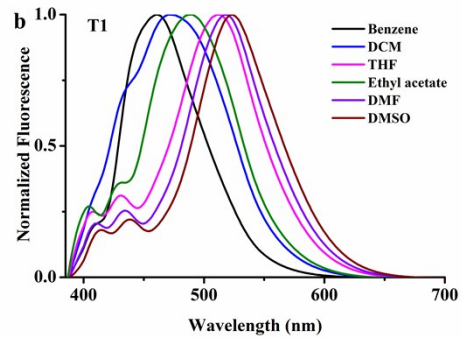
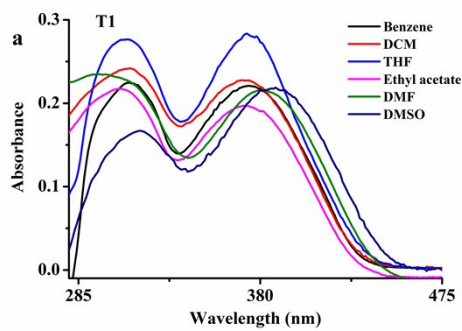
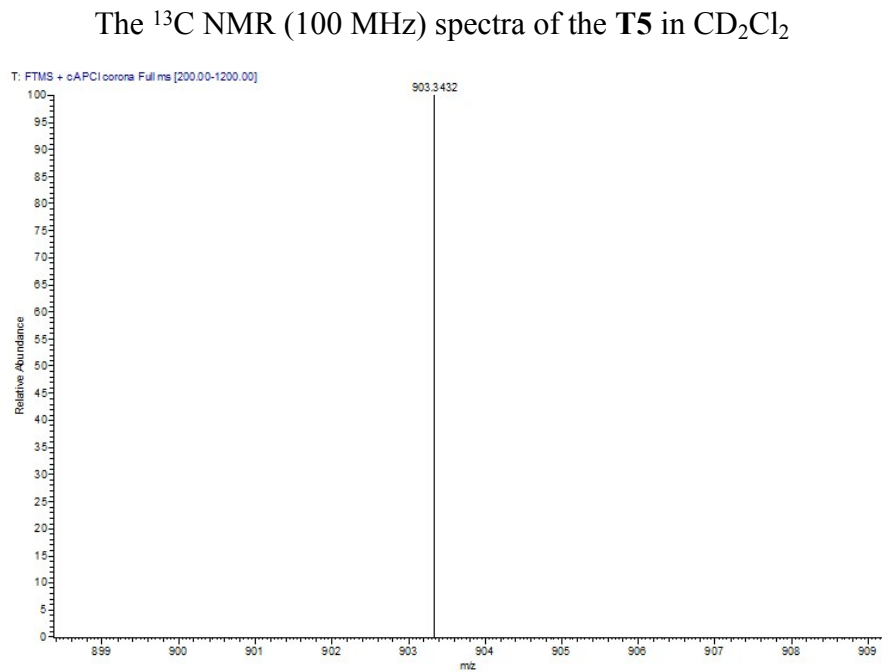
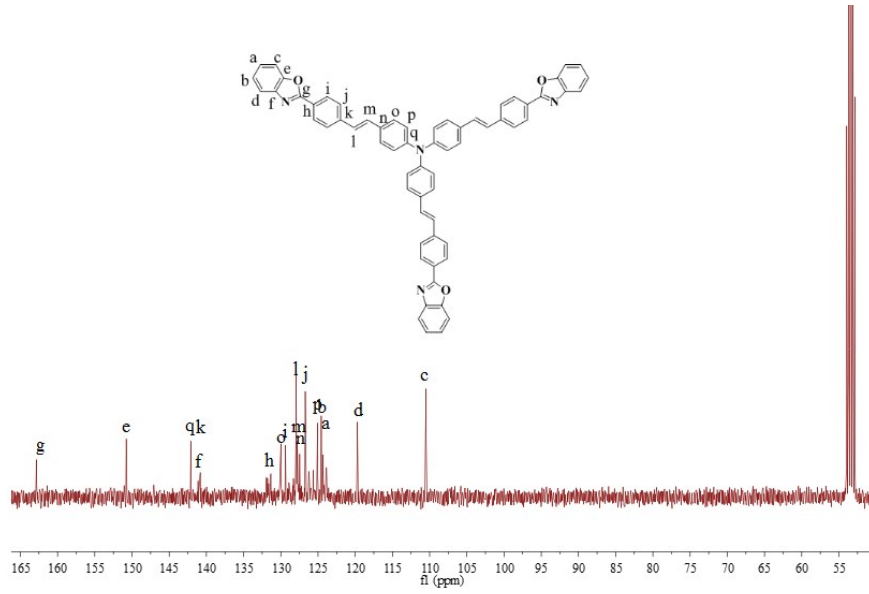


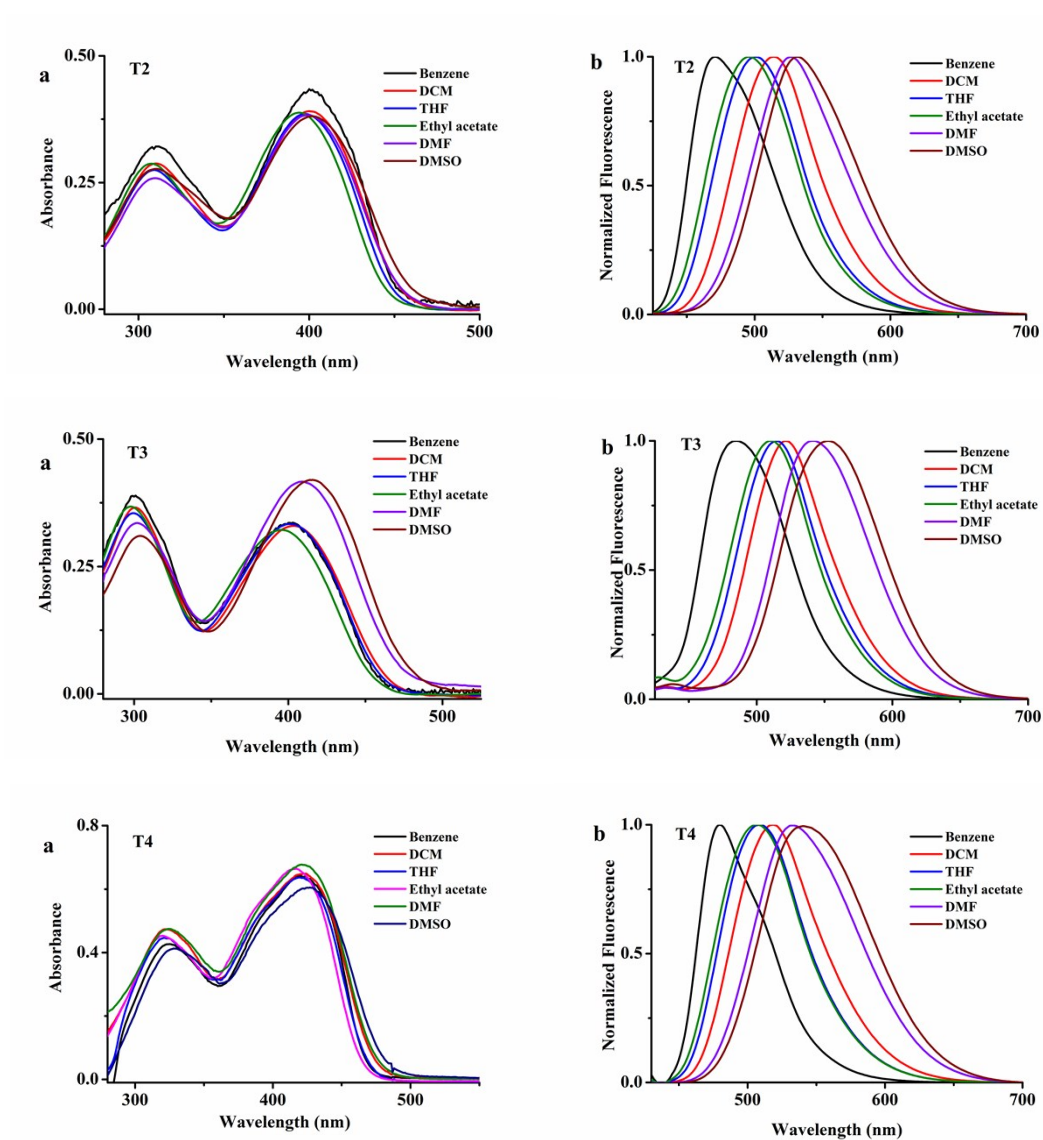
APCI MS of T4

Figure S1h:  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and MS spectra of T5.

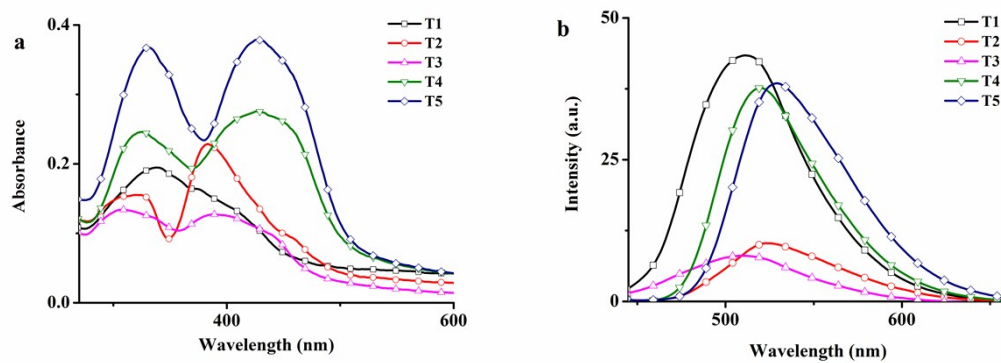


The  $^1\text{H}$  NMR (400MHz) spectra of the T5 in  $\text{CD}_2\text{Cl}_2$





**Fig. S2.** (a) Linear absorption spectra of **T1-4** in different organic solvents; (b) Normalized one photon fluorescence spectra of **T1-4** in different organic solvents.



**Fig. S3.** (a)-(b) OPA and OPEF spectra of **T1-5** in aqueous solution ( $c = 1.0 \times 10^{-5}$  mol/L).

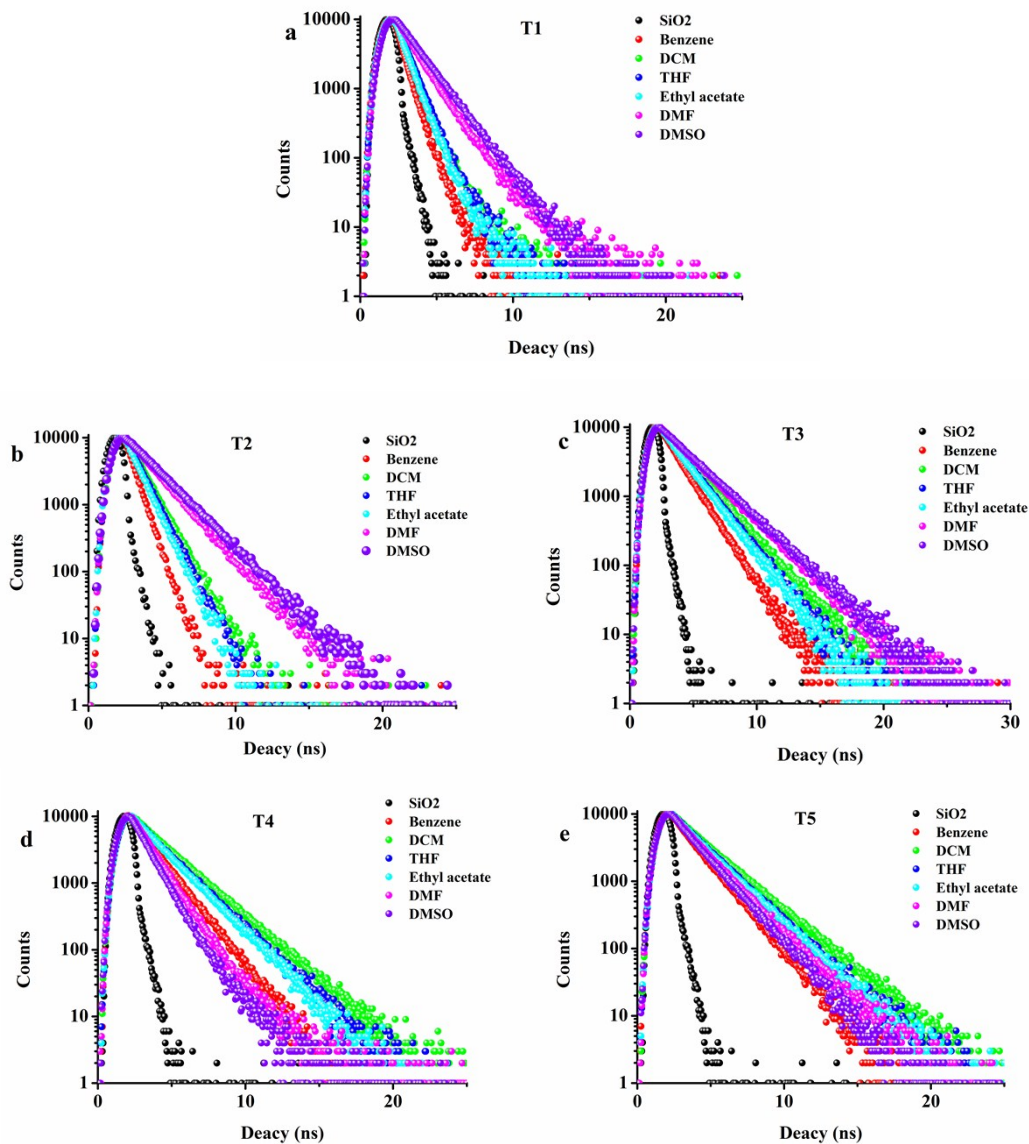


Fig. S4. (a)-(e) Fluorescence lifetime of T1-5 in different solvents.

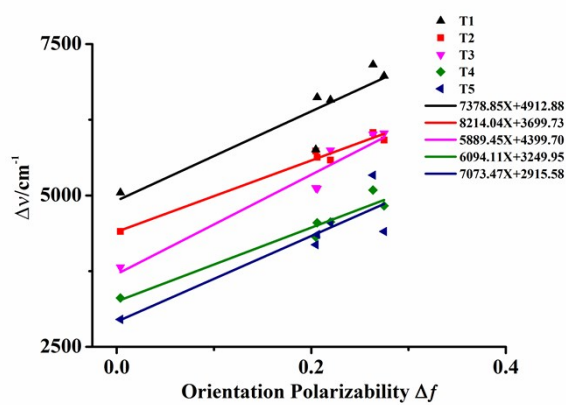
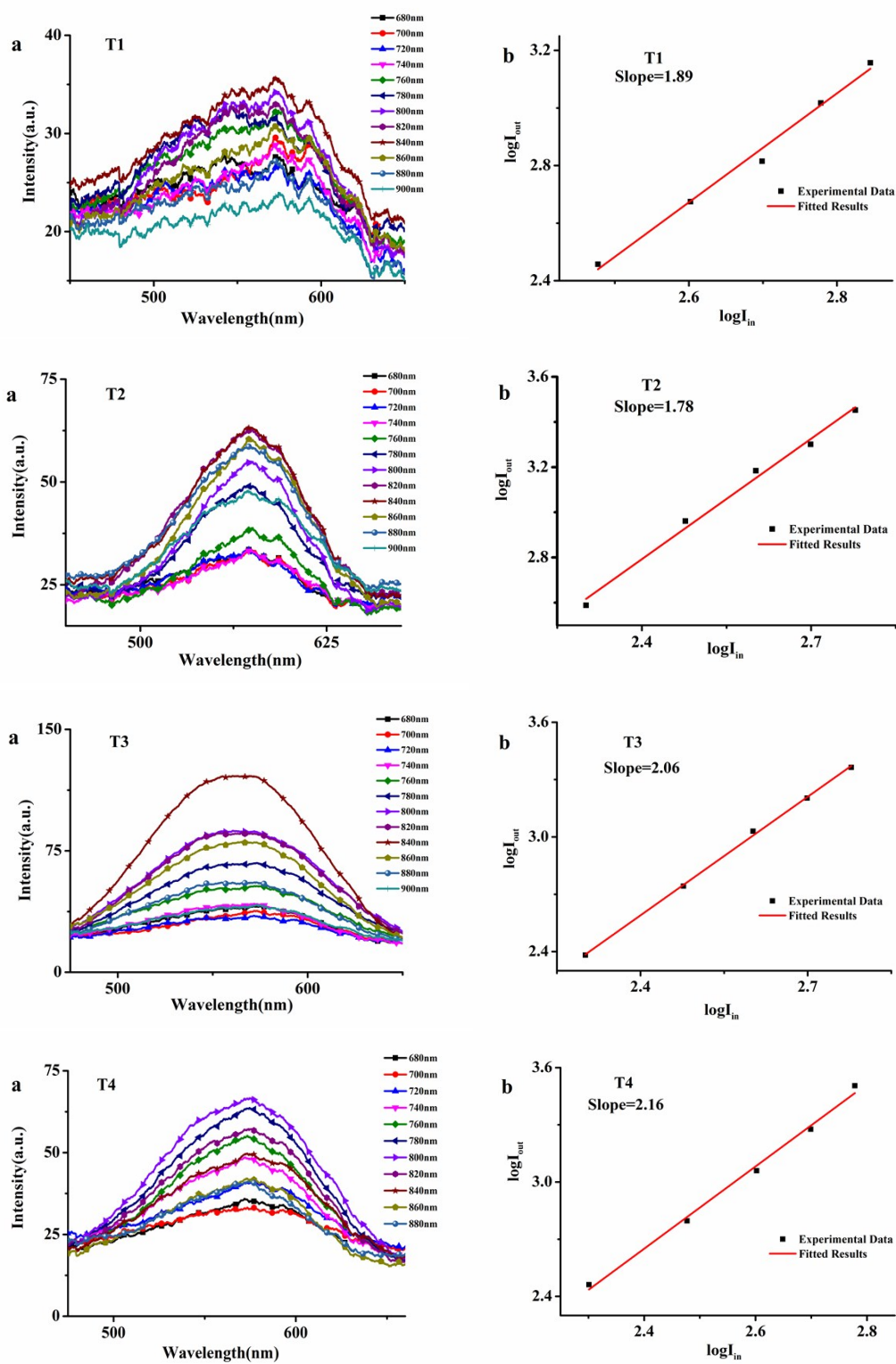
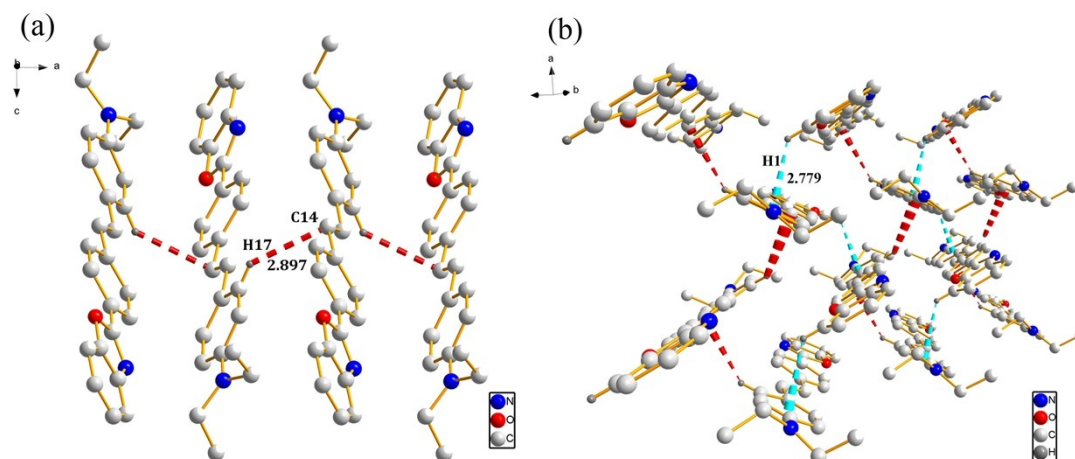


Figure S5. Lippert-Mataga plots for T1-5.

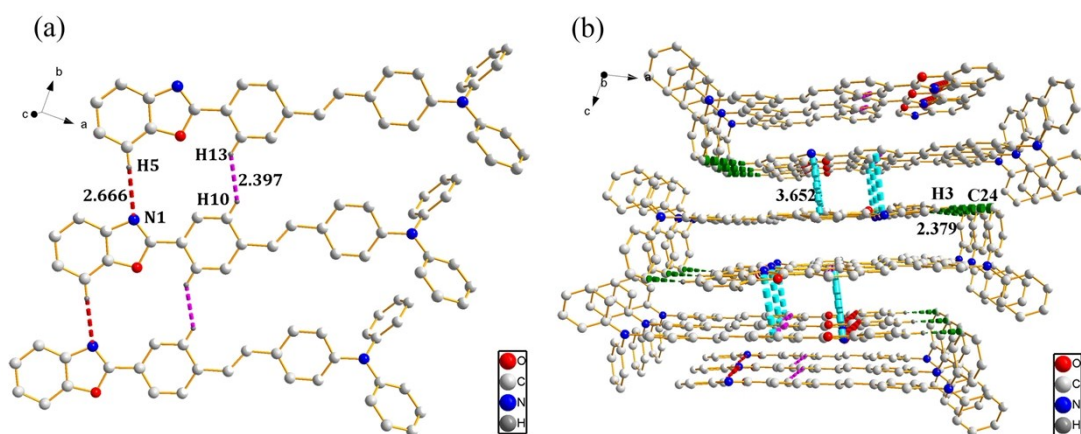




**Figure S6.** (a) The TPEF spectra of **T1-4** in DMF (500 mW,  $c = 5 \times 10^{-4}$  mol L<sup>-1</sup>); (b) Output fluorescence ( $I_{out}$ ) versus the square of input laser power ( $I_{in}$ ) for **T1-4** in DMF.

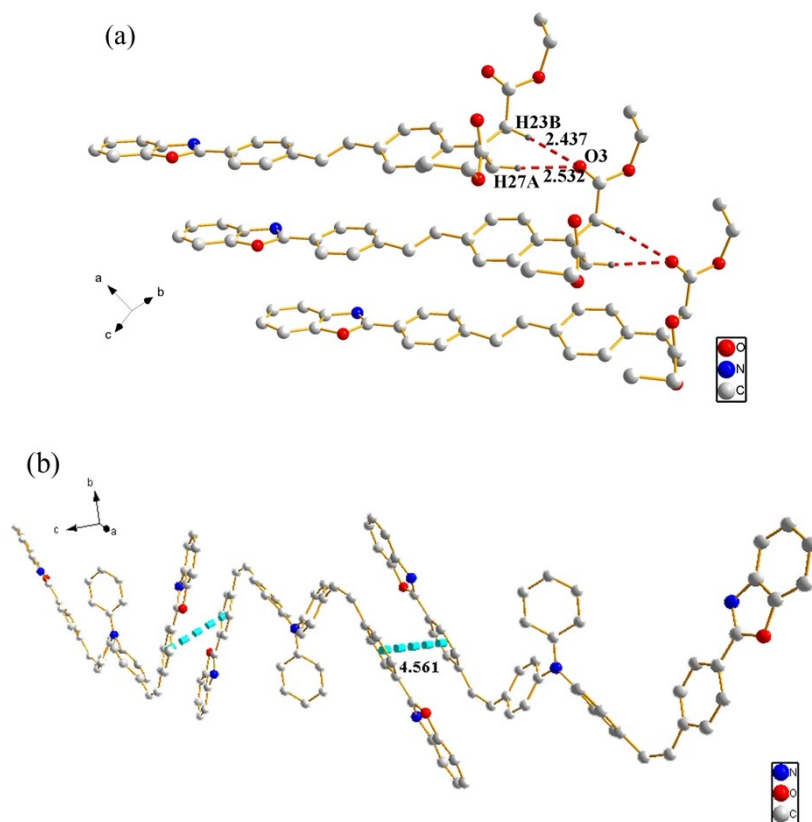


**Figure S7.** (a) One-dimensional structure of **T2** showing the C-H... $\pi$  (red) along the a-axis; (b) Three-dimensional structure of **T2** showing the C-H... $\pi$  stacking (blue-green) along the b-axis. Hydrogen atoms except H1 and H17 are omitted for clarity.

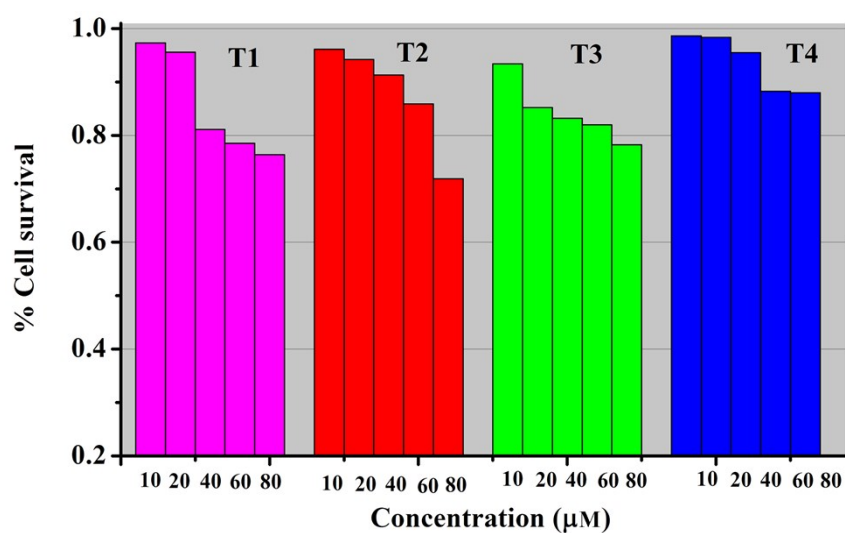


**Fig. S8.** (a) One-dimensional structure of **T3** showing the C-H...N (red), C-H...H-C (red violet) along the b-axis; (b) Two-dimensional structure of **T3** showing the C-H... $\pi$  (green),  $\pi$ ... $\pi$  (blue-green), stacking along the c-axis. Hydrogen atoms except H5, H10, H13 and H3 are omitted for clarity.

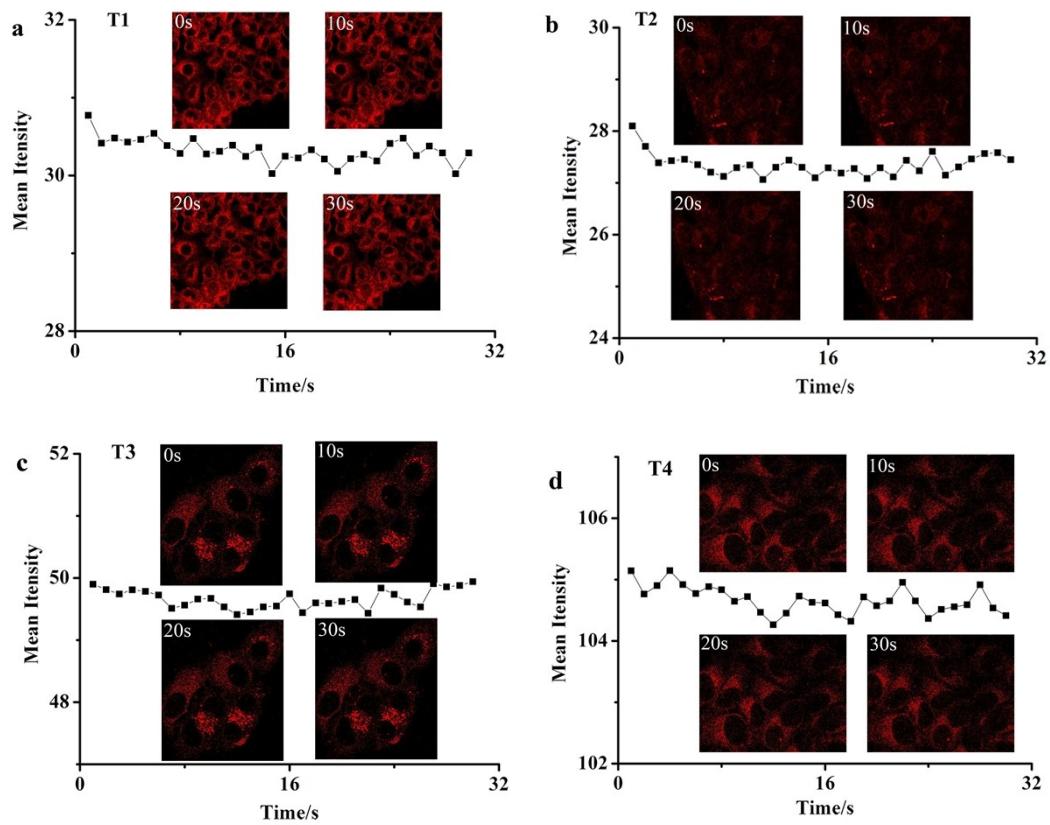




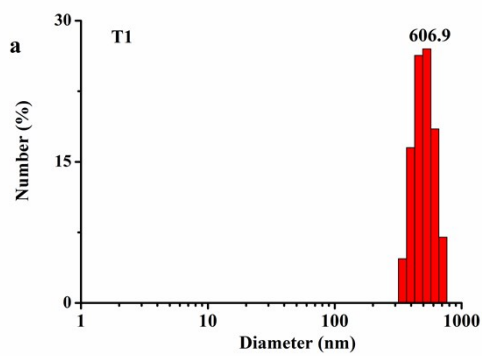
**Fig. S9.** (a) One-dimensional structure of **T1** showing the C-H $\cdots$ O (red) along the a-axis; (b) One-dimensional structure of **T4** showing the  $\pi\cdots\pi$  (blue-green) along the a-axis. Hydrogen atoms except H23B and H27A are omitted for clarity.

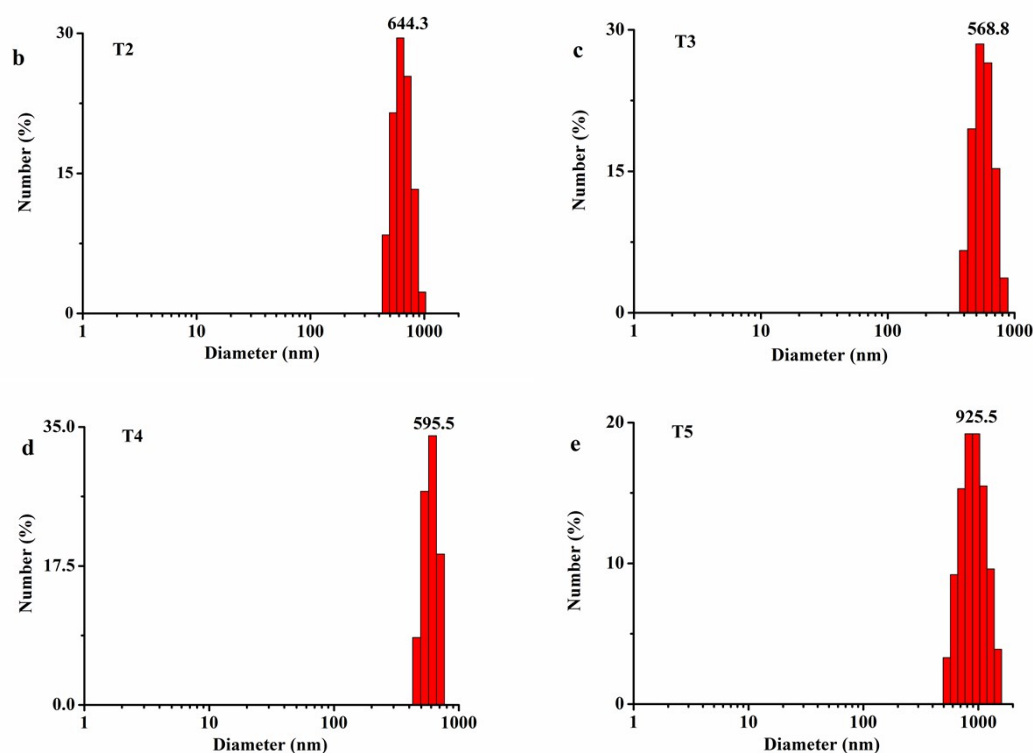


**Figure S10.** MTT assay of HepG2 cells treated with compounds **T1-4** at different concentrations for 24 h.



**Figure S11.** Time series showing luminescence intensity of **T1-4** in a HepG2 cytosol region ( $30\mu\text{M}$ , 30 min) under laser exposure over 30s, inset images from time point 0, 10, 20 and 30s.





**Figure S12.**(a)-(e) Particle size distributions of **T1-5** in water/DMF (v/v=99:1).

**Table S1**

Photophysical data of **T1-5** in different solvents.

Compounds	Solvents	$\lambda_{\max}^{[a]}$	$\lambda_{\max}^{[b]}$	$\Phi^{[c]}$	$\Delta\nu^{[d]}$	$\lambda_{\max}^{[e]}$	$\lambda_{\max}^{[f]}$	$\sigma^{[g]}$ (GM)	$\sigma_{\text{eff}}^{[h]}$ (GM)	$\tau^{[i]}$
<b>T1</b>	Benzene	374	445	0.10	4266					0.54
	DCM	370	478	0.11	6107					0.73
	THF	373	483	0.12	6106					0.76
	Ethyl acetate	373	484	0.10	6148					0.69
	DMF	380	517	0.21	6836	840	572	328	68	1.25
	DMSO	387	520	0.21	6879					1.46
	H <sub>2</sub> O	372	512	0.04	7350					1.00
<b>T2</b>	Benzene	400	472	0.13	3814					0.61
	DCM	398	516	0.22	5746					1.06
	THF	398	500	0.21	5126					0.93
	Ethyl acetate	395	495	0.18	5114					0.91
	DMF	400	527	0.36	6025	840	573	369	134	1.73
	DMSO	402	530	0.53	6008					1.97

<b>T3</b>	H <sub>2</sub> O	380	525	0.02	7268					0.82
	Benzene	401	487	0.55	4404					1.44
	DCM	407	520	0.55	5339					2.04
	THF	397	514	0.56	5734					1.84
	Ethyl acetate	395	508	0.48	5631					1.78
	DMF	412	543	0.57	5856	840	564	694	356	2.41
<b>T4</b>	DMSO	420	552	0.55	5694					2.53
	H <sub>2</sub> O	379	513	0.06	6892					0.94
	Benzene	415	481	0.64	3306					1.44
	DCM	419	518	0.54	4561					2.20
	THF	416	507	0.58	4315					1.96
	Ethyl acetate	412	507	0.54	4548					1.88
<b>T5</b>	DMF	422	530	0.19	4829	800	574	1214	232	1.24
	DMSO	423	539	0.15	5088					1.07
	H <sub>2</sub> O	430	520	0.04	4025					0.49
	Benzene	425	486	0.63	2953					1.57
	DCM	423	524	0.46	4557					2.32
	THF	423	514	0.53	4185					2.07
<b>T5</b>	Ethyl acetate	420	514	0.49	4354					2.03
	DMF	431	545	0.26	4853	740	581	2702	712	1.85
	DMSO	430	558	0.21	5335					1.72
	H <sub>2</sub> O	427	529	0.04	4516					0.48

<sup>[a]</sup> Absorption peak position nm ( $c = 1.0 \times 10^{-5}$  mol L<sup>-1</sup>, nm), <sup>[b]</sup> Peak position of OPEF ( $c = 1.0 \times 10^{-5}$  mol L<sup>-1</sup>, nm), excited at the absorption maximum, <sup>[c]</sup> Quantum yields determined by using fluorescein ( $c = 1.0 \times 10^{-5}$  mol L<sup>-1</sup>) as the standard, <sup>[d]</sup> Stocks' shift in cm<sup>-1</sup>, <sup>[e]</sup> Maximum two-photon excitation wavelength ( $5 \times 10^{-4}$  mol L<sup>-1</sup>, nm). <sup>[f]</sup> TPEF peak position in nm pumped by femtosecond laser pulses at 500 mw at their maximum excitation wavelength. <sup>[g]</sup> 2PA cross section, <sup>[h]</sup> Effective 2PA cross section, <sup>[i]</sup> Fluorescence lifetime (ns).

**Table S2**

Crystal data of compounds **T1**, **T2**, **T3** and **T4**.

Compounds	<b>T1</b>	<b>T2</b>	<b>T3</b>	<b>T4</b>
Empirical formula	C <sub>30</sub> H <sub>29</sub> NO <sub>5</sub>	C <sub>25</sub> H <sub>24</sub> N <sub>2</sub> O	C <sub>33</sub> H <sub>24</sub> N <sub>2</sub> O	C <sub>24</sub> H <sub>16.50</sub> N <sub>1.50</sub> O
Formula weight	483.54	368.46	464.54	341.89

Crystal system	Triclinic	Orthorhombic	Monoclinic	Monoclinic
Space group	P-1	P2(1)2(1)2(1)	C2/c	C2/c
a[Å]	5.0966(11)	7.589(2)	53.673(5)	22.153(3)
b[Å]	12.219(3)	9.368(3)	6.554(6)	9.690(14)
c[Å]	20.093(4)	28.167(8)	14.323(14)	17.251(3)
$\alpha$ [°]	96.803(3)	90.000	90.000	90.000
$\beta$ [°]	96.243(3)	90.000	103.843(10)	95.937(2)
$\gamma$ [°]	97.956(3)	90.000	90.000	90.000
$V$ [Å <sup>3</sup> ]	1220.5(4)	2002.5 (10)	4891.9 (8)	3683.2(9)
Z	2	4	8	8
$T$ [K]	296(2)	296(2)	296(2)	296(2)
$D_{\text{calcd}}$ [g·cm <sup>-3</sup> ]	1.316	1.222	1.262	1.233
F(000)	512	784	1952	1432
$\mu$ [mm <sup>-1</sup> ]	0.089	0.075	0.076	0.063
$\theta$ range[°]	1.03-25.68	2.29-25.00	0.78-25.00	1.85-25.68
Total no. data	4539	14162	16661	12667
No. unique data	1963	3519	4295	3242
$R_{\text{int}}$	0.0838	0.0531	0.0355	0.0267
$R_1$	0.1781	0.1291	0.0770	0.0454
$wR_2$	0.2072	0.2426	0.1484	0.1330
GOF	1.199	1.048	1.043	1.031

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