Supporting Information for the following manuscript:

A New Tetrathiafulvalene-phenoxynaphthacenequinone Dyad: Switching on the Intramolecular Electron-transfer with UV Light Irradiation and Metal Ion Coordination

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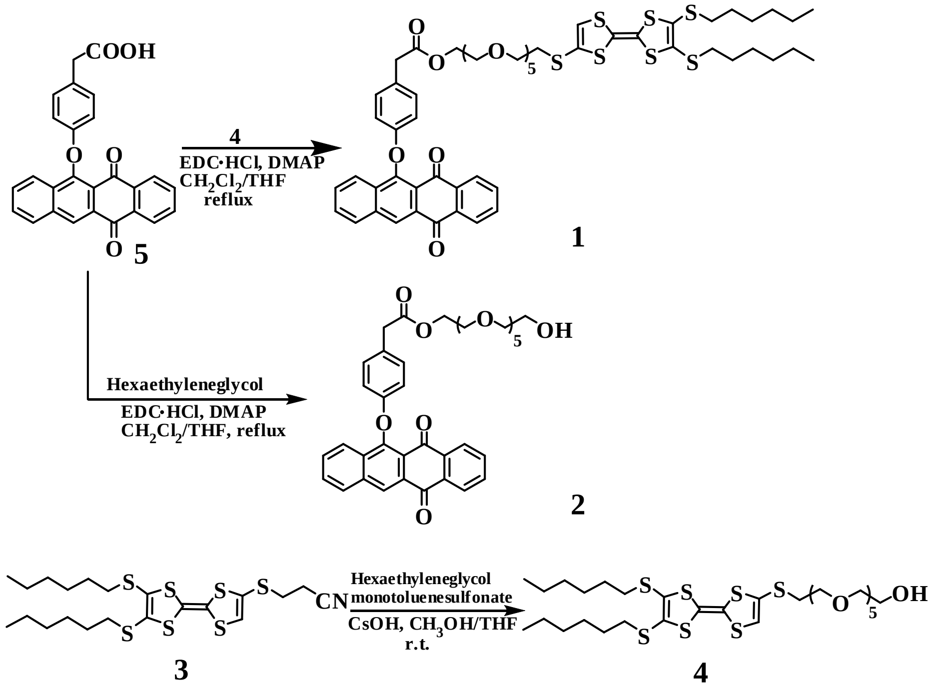
Contents

1. Synthesis and characterization of dyad 1 and compounds 2 and 4

Materials and characterization techniques: All solvents were purified and dried following standard procedures unless otherwise stated. ^{1}H-NMR, ^{13}C-NMR, MS (including HRMS), absorption and ESR spectra were measured with conventional spectrometers. Cyclic voltammetric measurements were performed in a standard three-electrode cell, with glassy carbon as the working electrode and platinum wire as auxiliary electrode, and Ag/AgCl electrode (saturated KCl) as the reference electrode； n-Bu$_4$NPF$_6$ (0.1 M) was used as supporting electrolyte.

Photoisomerization experiments: A solution of dyad **1** in a quartz cell (path length, 1.0 cm) was degassed thoroughly and kept in dark at room temperature for the UV light irradiation experiment. Light irradiation was carried out using a PLS-SXE300UV xenon arc lamp (Beijing Trusttech Co. Ltd). The UV light (310 nm) and visible light (500 nm) were selected by passing through the proper light filters. The distance between the center of the quartz cell and the lamp was 4.0 cm; at this position the light intensity without passing through the filters was ca. 18 mW/cm^2.



Scheme S1. The chemical structure and synthetic approach for compound **1** and **2**

Synthesis of compound 4: Under N$_2$ atmosphere, a solution of CsOH· H$_2$O（0.079 g, 0.47 mmol）in 2.0 mL of anhydrous degassed MeOH was dropped into a solution of compound **3** ^{S1}(0.203 g, 0.39 mmol) in 30 mL of anhydrous degassed THF over a period of 10 min.. The mixture was stirred for 30 min., followed by addition of a solution of hexaethyleneglycol-monotoluenesulfonate (0.166 g, 0.38 mmol) in 15 mL of anhydrous degassed THF. After being stirred overnight at room temperature, the residue was purified by silica gel column chromatography using the mixture of dichloromethane and methanol (v:v= 50:1) as eluant. Compound **4** (195 mg) was obtained as an orange-red oil in 68.4％yield. ^{1}H NMR(400 MHz, $CDCl_3$): δ 3.72-3.60 (22H, m), 2.94 (2H, t, J = 6.16), 2.81 (4H, br), 2.55 (1H, s), 1.64-1.58 (4H, m), 1.41 (4H, br), 1.29 (8H, br), 0.88 (6H, t, J = 5.86). ^{13}C NMR(100 MHz, $CDCl_3$): δ 128.06, 127.89, 126.69, 123.20, 113.91, 108.89, 72.77, 70.78, 70.56, 69.87, 61.87, 36.49, 35.38, 31.52, 29.92, 28.40, 22.76, 14.29. HR-MS (EI): calcd for $C_{30}H_{52}O_6S_7$, 732.1809; found, 732.1815.

Synthesis of compound 2: Under N_2 atmosphere, to a mixture of compound **5** [S2](200 mg, 0.49 mmol), hexaethyleneglycol (1.23 mL, 4.90 mmol) and DMAP (120 mg, 0.98 mmol) in 10 mL of anhydrous degassed THF, EDC·HCl (188 mg, 0.98 mmol) in 2.0 mL of anhydrous CH_2Cl_2 was added dropwise at 0 °C. Then the solution was stirred overnight at r.t. After removing the solvent, the residue was dissolved in 50 mL of CH_2Cl_2 and washed with water (50 mL × 3). The organic layer was dried over Na_2SO_4, filtered and evaporated. Compound **2** (110 mg) was obtained as bright yellow solid in yield of 33％ after purification via column chromatography. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (1H, s), 8.35-8.34 (1H, m), 8.23-8.21 (2H, m), 8.16 (1H, d, J = 7.98), 7.76-7.74 (2H, m), 7.74 (1H, t, J = 7.8), 7.66 (1H, t, J = 7.68), 7.21 (2H, d, J = 8.11), 6.84 (2H, d, J = 8.10), 4.23 (2H, br), 3.71-3.59 (24H, m). ^{13}C NMR (100 MHz, $CDCl_3$): 182.98, 181.23, 171.82, 158.41, 152.45, 136.17, 135.53, 134.48, 133.83, 133.61, 131.79, 130.78, 130.43, 130.31, 130.10, 127.78, 127.56, 127.39, 127.18, 125.12, 121.12, 115.09, 72.64, 70.68, 70.44, 69.18, 64.11, 61.86, 40.42. HR-MS (*m/z*): calcd for $C_{38}H_{40}O_{11}$, 672.2571; found, 672.2578.

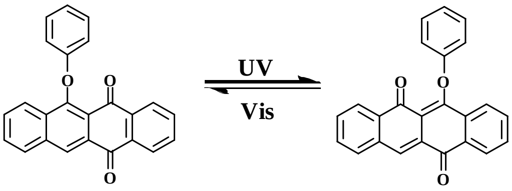
Synthesis of dyad 1: Under N_2 atmosphere, to a mixture of compound **5** [S2](160 mg, 0.39 mmol), compound **4** (140 mg, 0.19 mmol) and DMAP (48 mg, 0.39 mmol) in 10 mL of anhydrous degassed THF, EDC·HCl (75 mg, 0.39 mmol) in 5 mL anhydrous CH_2Cl_2 was added dropwise at 0 °C. Then, the solution was stirred overnight at room temperature. After removing the solvent, the residue was dissolved in 20 mL of CH_2Cl_2 and washed with water (20 mL × 3). The organic layer was dried over Na_2SO_4, filtered and evaporated. Compound **1** was obtained as bright yellow solid in yield of 89% after purification via column chromatography. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.85 (1H, s), 8.34-8.32 (1H, m), 8.23-8.20 (2H, m), 8.14 (1H, d, J = 8.1), 7.77-7.74 (2H, m), 7.72 (1H, d, J = 7.5),7.65 (1H, t, J = 7.74), 7.20 (2H, d, J = 8.58), 6.83 (2H, d, J = 8.58), 4.23 (2H, t, J = 4.68), 3.68-3.58 (22H, m), 2.92 (2H, t, J = 6.48), 2.80 (4H, w), 1.62-1.60 (4H, m), 1.42-1.36 (4H, m), 1.30-1.25 (8H, w), 0.88 (6H, t, J = 6.00). ^{13}C NMR (150 MHz, $CDCl_3$): 182.83, 181.10, 171.70, 158.28, 152.30, 136.03, 135.38, 134.36, 133.72, 133.47, 131.65, 130.67, 130.32, 130.20, 129.99, 127.66, 127.41, 127.28, 127.07, 124.99, 122.99, 120.98, 114.97, 70.58, 69.65, 69.06, 63.99, 40.30, 36.29, 35.14, 31.31, 29.71, 28.21, 22.55, 14.06; HR-MS: calcd for $C_{56}H_{66}O_{10}S_7$, 1122.2715; found: 1122.2695.

Reference:

S1. X. Guo, D. Zhang, H. Zhang, Q. Fan, W. Xu, X. Ai, L. Fan, D. Zhu, *Tetrahedron*, 2003, **59**, 4843.

S2. Z. Fang, S. Z. Wang, Z. F. Yang, B. Chen, F. T. Li, J. Q. Wang, S. X. Xu, Z. J. Jiang, T. R. Fang, *J. Photochem. Photobiol. A,* 1995, **88**, 23.

2. Theoretical calculations for the *trans* and *ana* forms of PNQ



trans-PNQ ***ana-PNQ***

Coordination Data of *trans*-PNQ in the optimized geometry (DTF-B3LYP, 6-31g(d)); total energy = -1148.6779 ha:

		X	Y	Z
1	C	0	0	0
2	C	0	2.557546	0
3	C	1.436287	2.522192	0
4	C	1.405329	-0.027126	0.03887
5	C	-0.62584	3.80424	-0.02175

6	C	2.177005	3.68312	-0.039027
7	C	1.554055	4.951556	-0.087781
8	C	0.125393	5.019171	-0.078017
9	C	-0.508463	6.288229	-0.122239
10	C	0.245899	7.440284	-0.172714
11	C	1.660195	7.37681	-0.181016
12	C	2.300251	6.158358	-0.139369
13	C	-0.712813	-1.20589	-0.005507
14	C	2.081588	-1.253596	0.072539
15	C	-0.034962	-2.42071	0.028596
16	C	1.364987	-2.445689	0.067978
17	C	2.191264	1.233088	0.038172
18	C	-0.77351	1.281656	-0.032951
19	O	-1.997184	1.248924	-0.096518
20	O	3.418309	1.217195	0.065213
21	O	-1.988265	3.950221	-0.073973
22	C	-2.771916	3.745965	1.051736
23	C	-4.139162	3.58834	0.821094
24	C	-2.260892	3.764393	2.349381
25	C	-5.0018	3.447382	1.904772
26	C	-3.138828	3.615201	3.425956
27	C	-4.507852	3.458643	3.212646
28	H	3.259552	3.602554	-0.037242
29	H	-1.591182	6.332507	-0.121053
30	H	-0.247494	8.40754	-0.20691
31	H	2.239246	8.295163	-0.221232
32	H	3.385452	6.100384	-0.146689
33	H	-1.796184	-1.161513	-0.035789
34	H	3.166127	-1.241846	0.100575
35	H	-0.594512	-3.352168	0.025093
36	H	1.891504	-3.395761	0.094343
37	H	-4.499203	3.56593	-0.202009
38	H	-1.197614	3.896208	2.520578
39	H	-6.066036	3.32067	1.724966
40	H	-2.742057	3.628711	4.437702
41	H	-5.184114	3.345013	4.054926

Coordination Data of *ana*-PNQ in the optimized geometry (DFT-B3LYP, 6-31g(d); total energy = -1148.6633 ha:

1	C	-2.0849	-1.087699	-0.3593
2	C	0.306399	-0.3966	-0.3068
3	C	0.661899	-1.7338	0.154099
4	C	-1.778	-2.3953	0.080999
5	C	1.3988	0.577499	-0.597299

6	C	1.962299	-2.0819	0.3742
7	C	3.0582	-1.1747	0.159599
8	C	2.7933	0.1297	-0.3204
9	C	3.850699	1.0181	-0.541999
10	C	5.162799	0.626099	-0.2908
11	C	5.431899	-0.6648	0.1849
12	C	4.390399	-1.5577	0.407199
13	C	-3.424799	-0.7553	-0.6287
14	C	-2.7982	-3.3377	0.243799
15	C	-4.4288	-1.705	-0.4689
16	C	-4.119299	-2.9987	-0.032
17	C	-0.3773	-2.7762	0.3873
18	C	-1.0224	-0.095799	-0.517199
19	O	-0.094699	-3.898999	0.802499
20	O	1.189999	1.6982	-1.0601
21	O	-1.4649	1.1138	-0.9617
22	C	-1.380399	2.2645	-0.1873
23	C	-1.501299	3.471399	-0.8744
24	C	-1.2795	2.232399	1.2025
25	C	-1.513999	4.6641	-0.1559
26	C	-1.287499	3.4375	1.908399
27	C	-1.4054	4.6547	1.237699
28	H	2.1637	-3.0918	0.7206
29	H	3.616199	2.0107	-0.9123
30	H	5.979599	1.320999	-0.4649
31	H	6.4566	-0.9693	0.3795
32	H	4.594	-2.5605	0.774
33	H	-3.6623	0.2464	-0.966599
34	H	-2.5243	-4.3293	0.589
35	H	-5.4593	-1.436399	-0.6842
36	H	-4.9083	-3.734999	0.0931
37	H	-1.5668	3.456199	-1.956999
38	H	-1.1982	1.2859	1.726999
39	H	-1.6023	5.6063	-0.6898
40	H	-1.2082	3.4167	2.9921
41	H	-1.412799	5.587499	1.793899

Table S1 HOMO and LUMO energies of *trans*-PNQ and *ana*-PNQ via DFT calculations

	***trans*-PNQ**	***ana*-PNQ**
HOMO energy	**-5.99 eV**	**-5.82 eV**
LUMO energy	**-2.58 eV**	**-3.02 eV**

3. The absorption spectra of dyad 1 after UV light irradiation and further visible light irradiation for different times

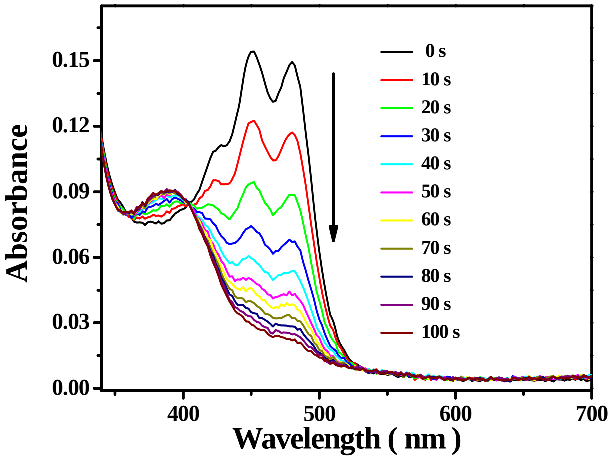


Figure S1. Absorption spectra of dyad **1** (1.0×10^{-5} M in CH_2Cl_2) after UV light (310 nm) irradiation for 110 s and further visible light (500 nm) irradiation for 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 s.

4. Variation of the absorbance at 479 nm *vs.* the UV light irradiation time for dyad 1 and compound 2

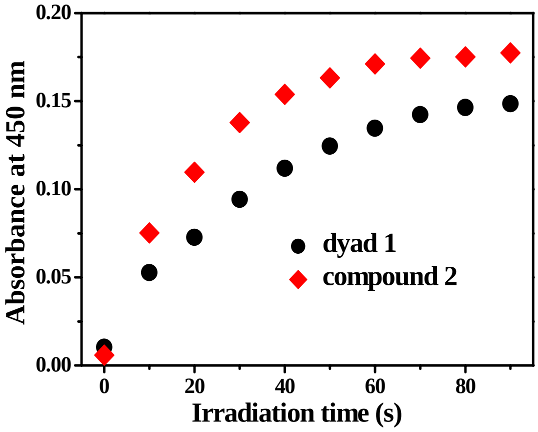
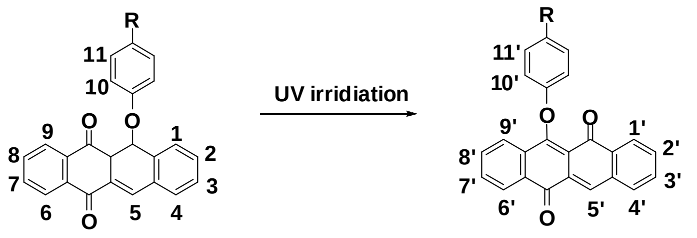


Figure S2. Variation of the absorbance at 450 nm *vs.* the UV light (310 nm) irradiation time for **1** (1.0×10^{-5} M in CH_2Cl_2) and **2** (1.0×10^{-5} M in CH_2Cl_2).

5. Variation of ^{1}H-NMR of dyad 1 and compound 2 upon UV light irradiation for different times



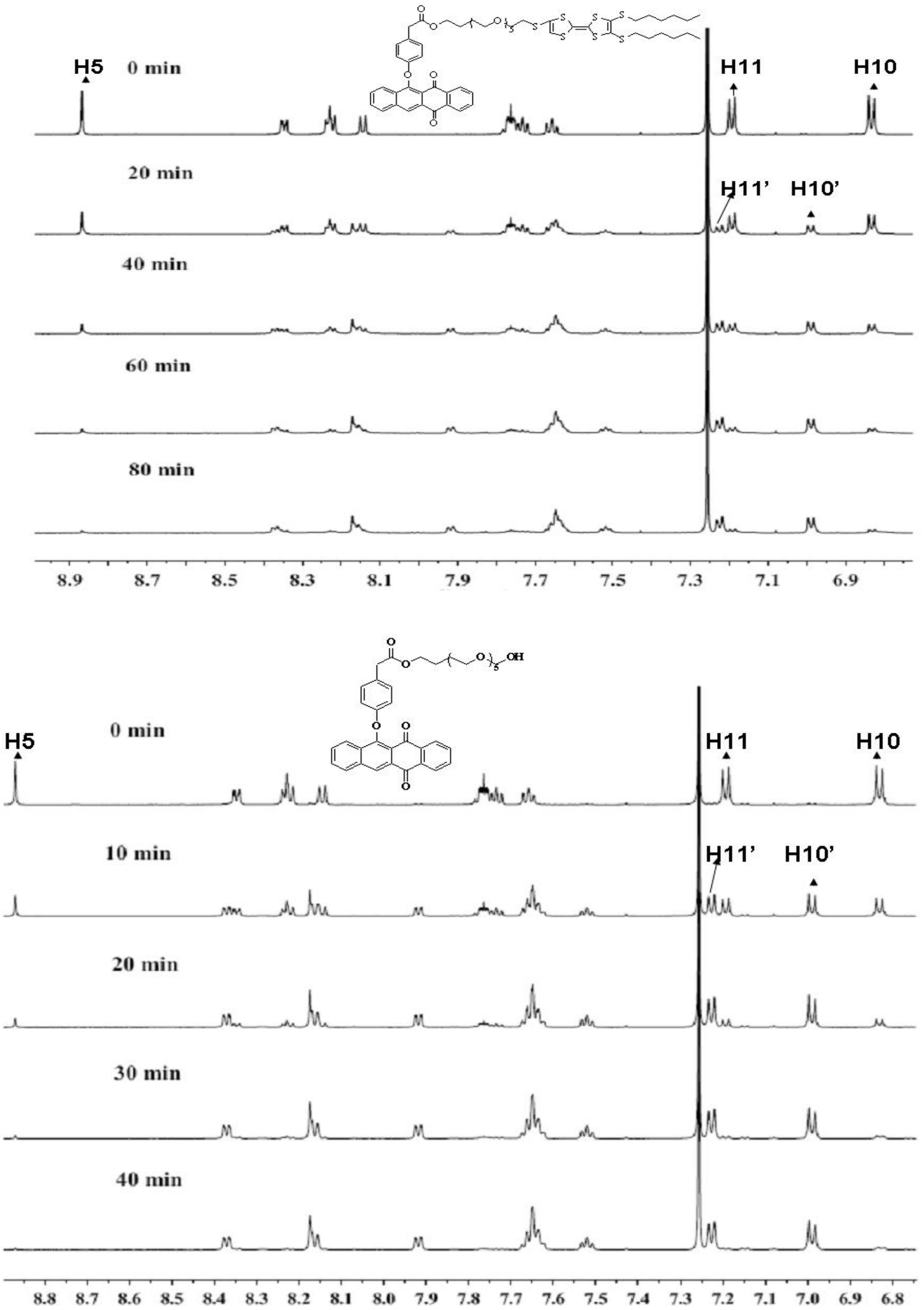


Figure S3. Variation of ^{1}H-NMR spectra of dyad **1** and compound **2** in degassed $CDCl_3$ (9.0×10^{-3} M) upon UV light (310 nm) irradiation for different times at room temperature.

6. Absorption spectra of 1，2 and 3

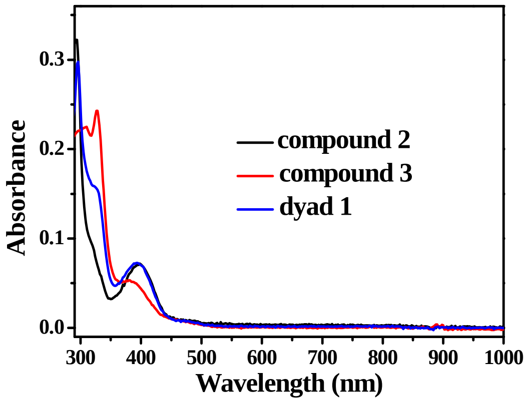


Figure S4. Absorption spectraof **1** (blue), **2** (black) and **3** (red) recorded in CH_2Cl_2 (1.0×10^{-5} M) at room temperature, respectively.

7. Cyclic voltammograms of dyad 1 before and after UV light irradiation

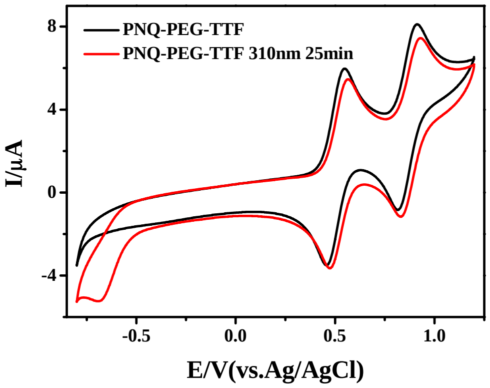


Figure S5. Cyclic voltammograms of dyad **1** (1.0×10^{-3} M) in degassed CH_2Cl_2 before (black) and after (red) UV light (310 nm) irradiation for 25 min.; the scan rate is 50 mVs^{-1}.

8. Absorption spectra of dyad 1 in the presence and absence of metal ions before UV light irradiation

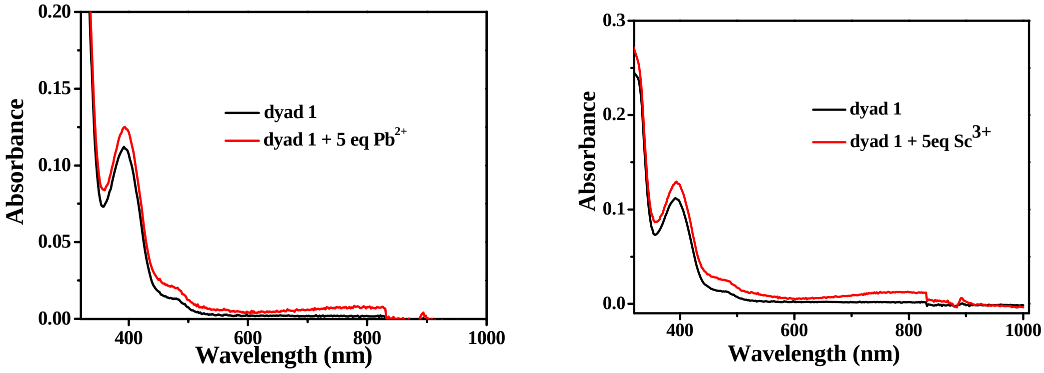


Figure S6. Absorption spectra of dyad **1** in the presence and absence of 5.0 eq. of Pb^{2+} (left) and Sc^{3+} (right) before UV light irradiation.

9. Absorption spectra of compound 3 in the absence and presence of Fe^{3+} in CH_2Cl_2

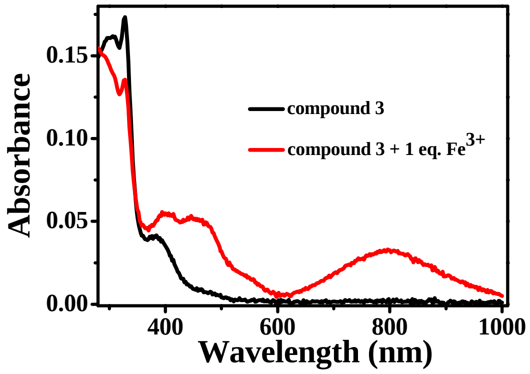
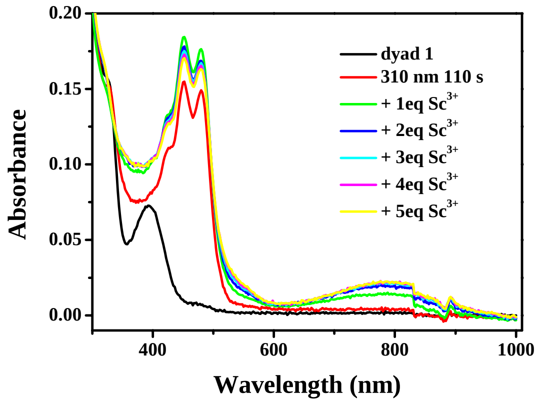
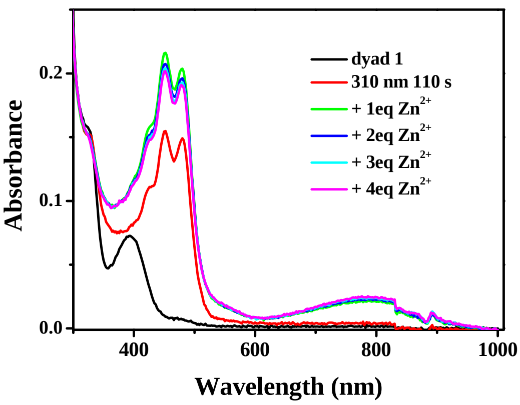
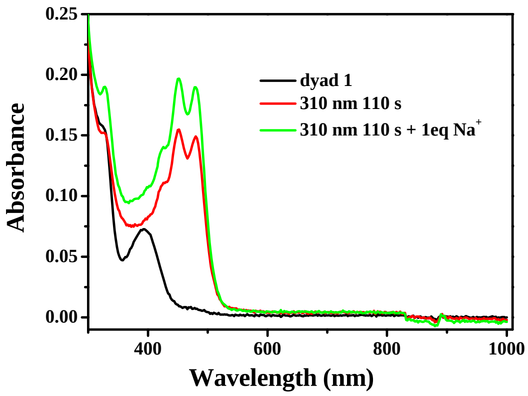


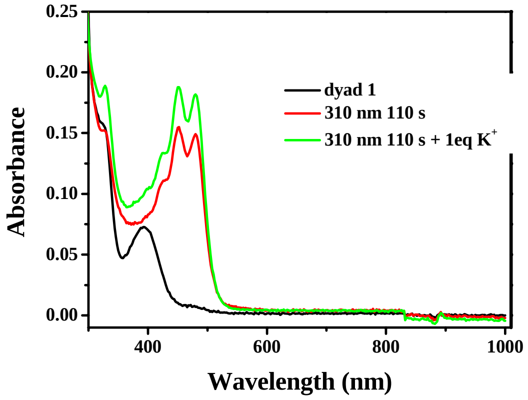
Figure S7. Absorption spectra of compound **3** (1.0×10^{-5} M) in CH_2Cl_2 in the absence and presence of 1.0 eq. of Fe^{3+} [Fe $(ClO_4)_3$].

10. The absorption spectra of dyad 1 after UV light irradiation and further addition of different amounts of metal ions









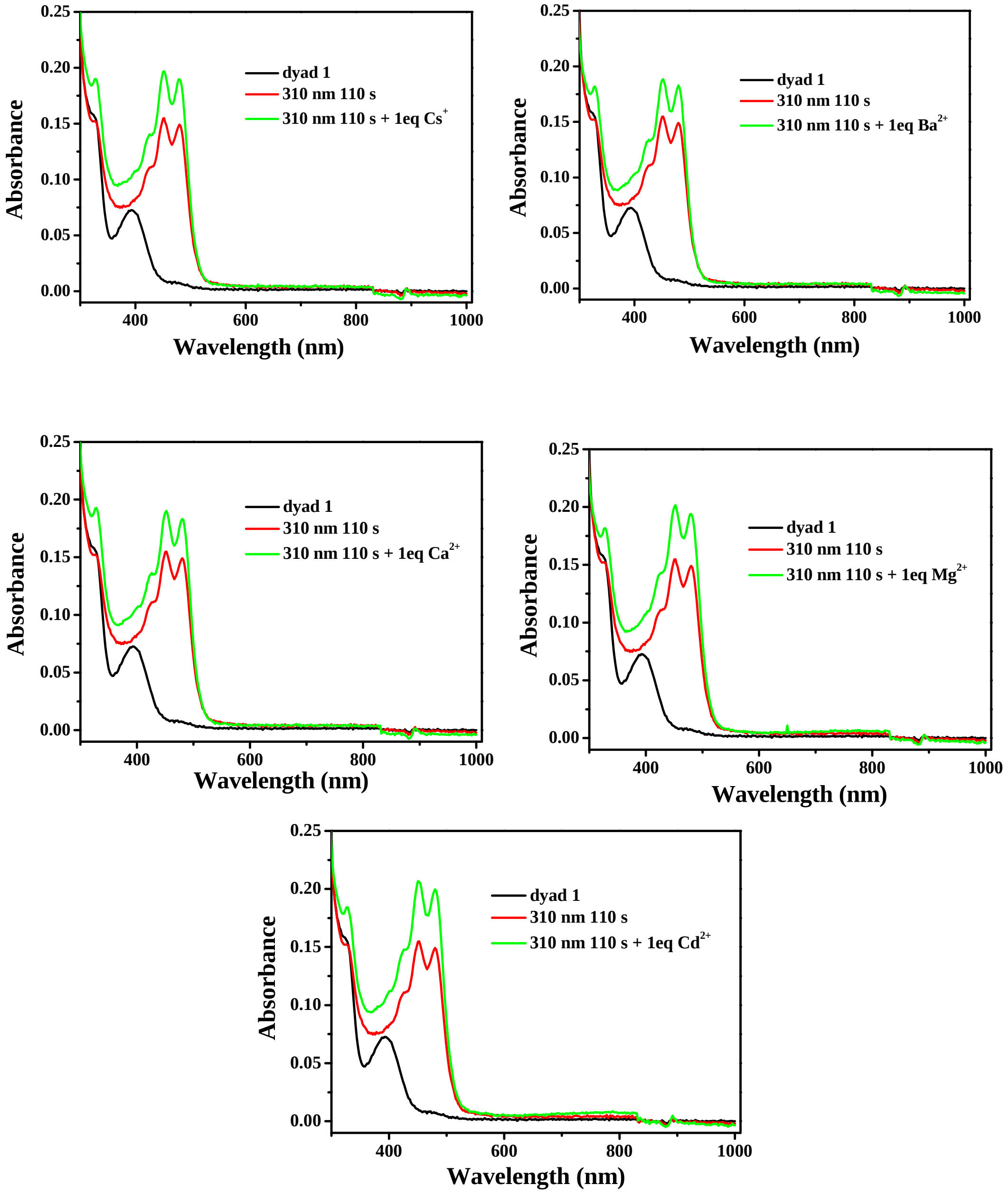


Figure S8. Absorption spectra of dyad **1** recorded in CH_2Cl_2 (1.0×10^{-5} M) after UV light (310 nm) irradiation for 110 s and further addition of different amounts of metal ions: $Sc^{3+}[Sc(SO_3CF_3)_3]$, $Zn^{2+}[Zn(ClO_4)_2]$, $Na^{+}(NaClO_4)$, $K^{+}(KClO_4)$, $Cs^{+}(CsClO_4)$, $Ba^{2+}[Ba(ClO_4)_2]$, $Ca^{2+}[Ca(ClO_4)_2]$, $Mg^{2+}[Mg(ClO_4)_2]$ and $Cd^{2+}[Cd(ClO_4)_2]$, respectively.

11. The ESR spectra of dyad 1 in the presence of Sc^{3+}/Zn^{2+} after UV light irradiation

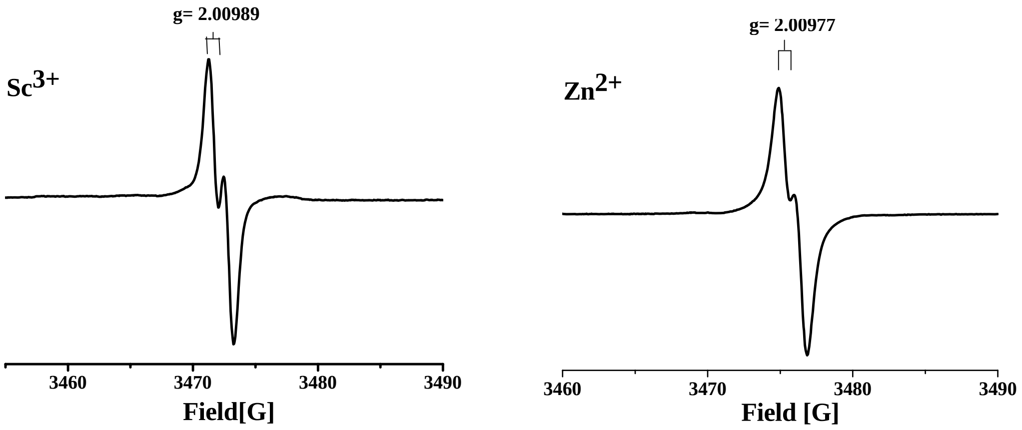


Figure S9. The ESR spectra of dyad **1** (1.0×10^{-3} M) in CH_2Cl_2 after UV light (310 nm) irradiation for 25 min. in the presence of 5.0 eq. of Sc^{3+} and 4.0 eq. of Zn^{2+}, respectively; the spectra were recorded at room temperature and the solutions were degassed before measurement.

12. Absorption spectra of dyad 1 in the presence of metal ions after UV light irradiation for different times

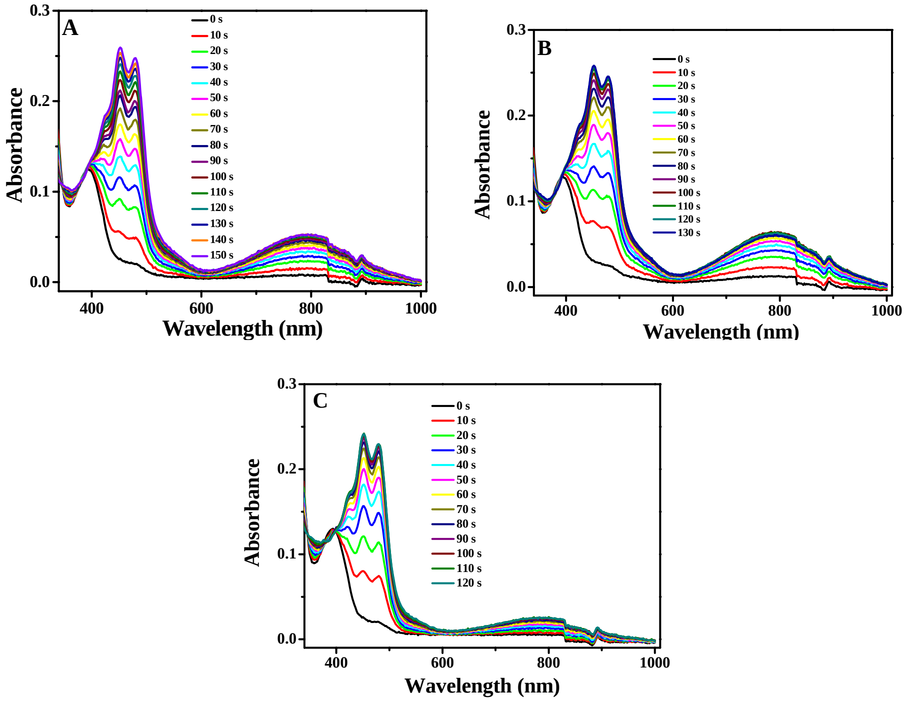


Figure S10. Absorption spectra of dyad **1** (1.0×10^{-5} M in CH_2Cl_2) in the presence of certain amounts of metal ions after UV light (UV 310 nm) irradiation for different times: (A) Pb^{2+} (5.0 eq.), (B) Sc^{3+} (5.0 eq.), (C) Zn^{2+} (4.0 eq.); the solutions were degassed before UV light irradiation and experiments were carried out at room temperature.

13. Cyclic voltammograms of compound 2 after UV light irradiation and further addition of metal ions

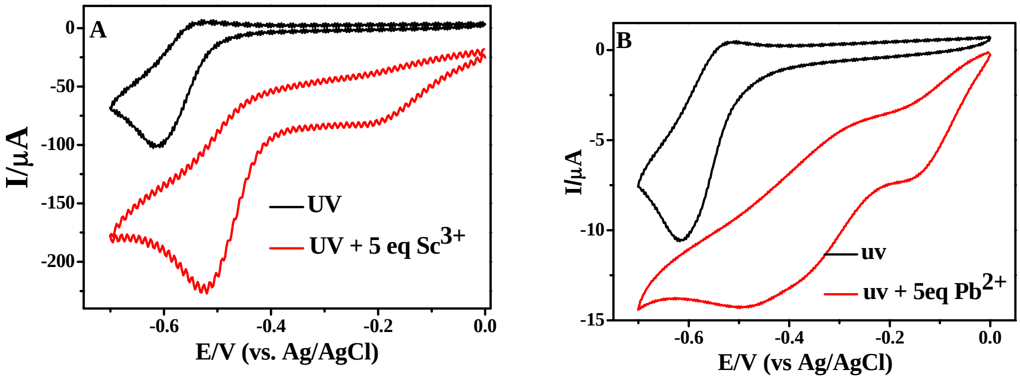


Figure S11. Cyclic voltammograms of **2** (1.0×10^{-3} M in CH_2Cl_2) after UV light (310 nm) irradiation for 25 min. and further addition of Sc^{3+} (A) and Pb^{2+} (B); the scan rate was 50 mVs^{-1}.

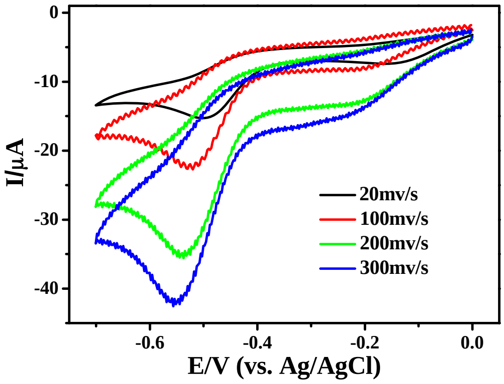


Figure S12. Cyclic voltammograms of compound **2** (1.0×10^{-3} M in CH_2Cl_2) after UV light irradiation in the presence of 5.0 eq. of Sc^{3+} at scan rates of 20, 100, 200 and 300 mV/s, respectively.

According to previous report (*J. Chem.. Soc. Perkin Trans. II*, **1985**, 371-378 and *Bull. Chem. Soc. Jpn.* **1983**, *56*, 2220-2227), the width of the cathodic wave ($E_{red}^{p/2} – E_{red}^{p}$) in such an irreversible system is known to depend on the transfer coefficient β according to equation (1), where *F* is the faraday constant and the other notations are conventional.

$E_{red}^{p/2} - E_{red}^{p} = 1.857\ RT/\beta F$ ....(1)

According to equation (2), the reduction potential E_{red}^{0} can be evaluated from the intercept of the linear correlation between E_{red}^{p} and $4(1 - 2\beta)$. β value is obtained from the cyclic voltammogram by using equation (1).

$E_{red}^{p} = E_{red}^{0} - 4(1 - 2\beta)\Delta G_0^{\ddagger}/F$.......................... .(2)

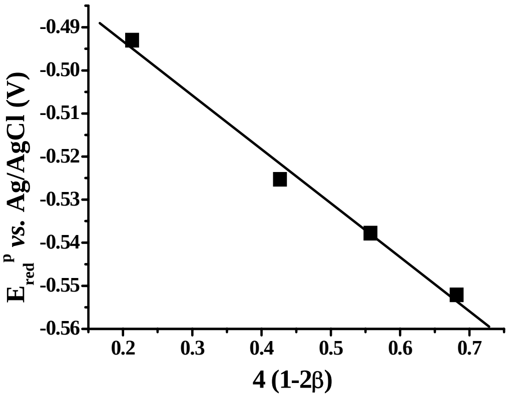


Figure S13. The plot of the cathodic-peak potential E_{red}^{p} (vs. Ag/AgCl) of compound **2** (1.0 ×10^{-3} M) after UV light irradiation in the presence of 5.0 eq. of $Sc^{3+}[Sc(SO_3CF_3)_3]$ vs. 4(1-2β); the reduction potential of compound **2** in the presence of Sc^{3+} was estimated to be -0.47.

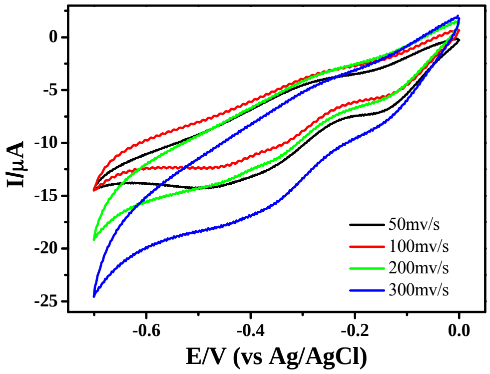
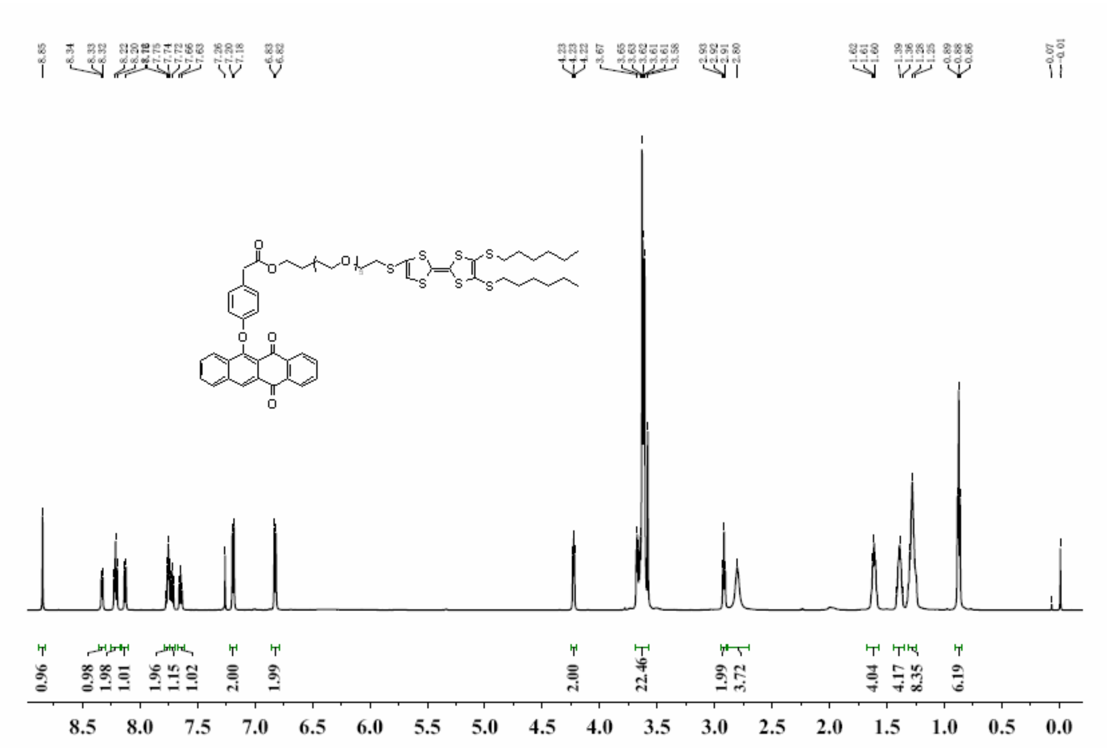


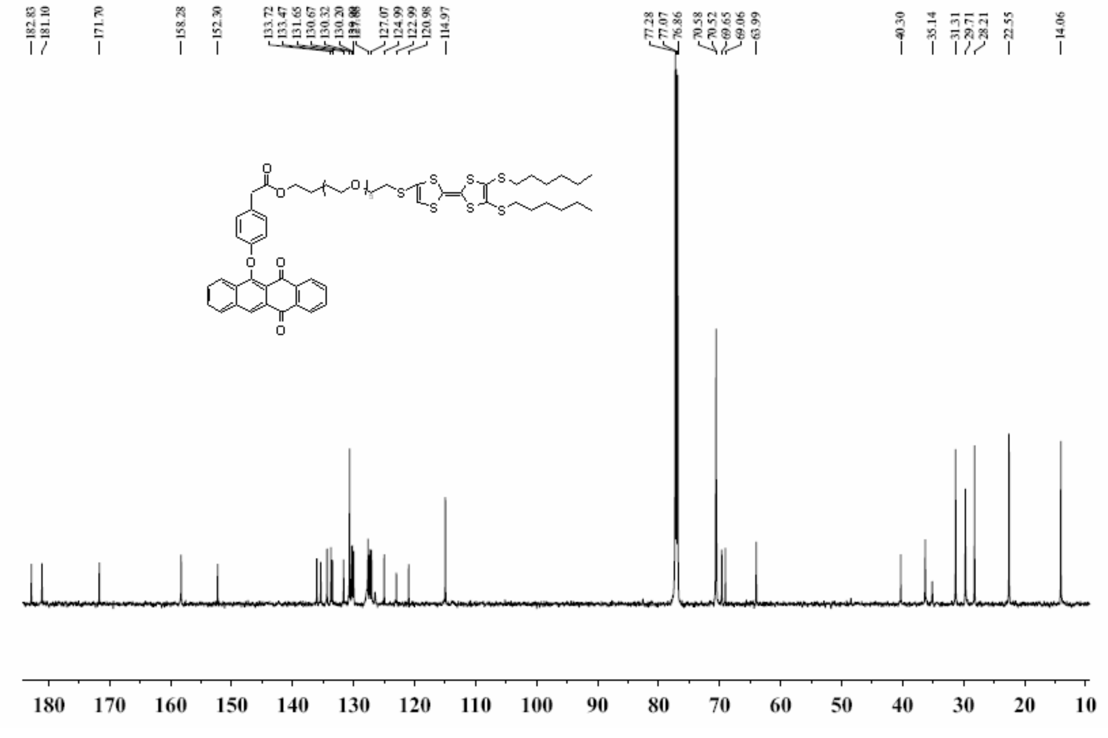
Figure S14. Cyclic voltammograms of compound **2** (1.0 ×10^{-3} M in CH_2Cl_2) after UV light irradiation in the presence of 5.0 eq. of Pb^{2+} at scan rates of 50, 100, 200 and 300 mV/s, respectively.

14. ^{1}H-NMR and ^{13}C-NMR spectra of dyad 1

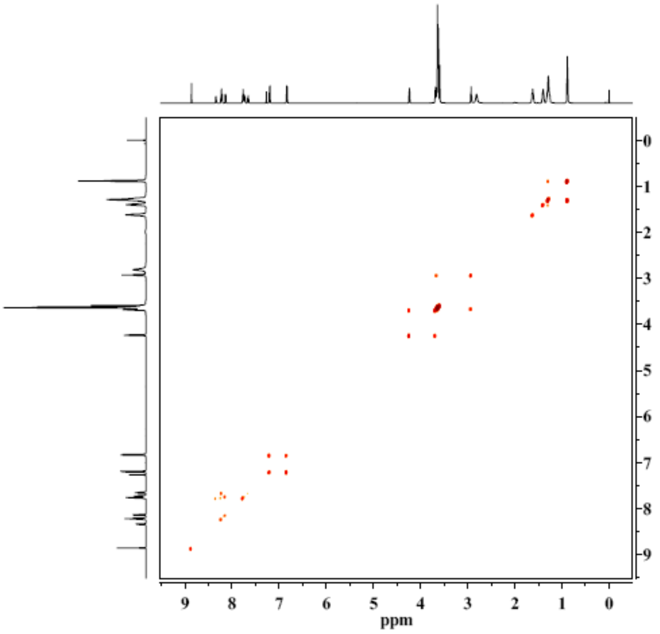
^{1}H-NMR


8.85
8.34
8.33
8.32
8.22
8.20
8.18
8.16
7.75
7.74
7.72
7.66
7.63
7.26
7.20
7.18
6.83
6.82
4.23
4.23
4.22
3.67
3.65
3.63
3.62
3.61
3.61
3.58
2.93
2.92
2.91
2.80
1.62
1.61
1.60
1.39
1.36
1.28
1.25
0.89
0.88
0.86
0.07
-0.01
O
S
0.96
0.98
1.98
1.01
1.96
1.15
1.02
2.00
1.99
2.00
22.46
1.99
3.72
4.04
4.17
8.35
6.19
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0

^{13}C-NMR


182.83
181.10
171.70
158.28
152.30
133.72
133.47
131.65
130.67
130.32
130.20
127.88
127.07
124.99
122.99
120.98
114.97
77.28
77.07
76.86
70.58
70.52
69.65
69.06
63.99
40.30
35.14
31.31
29.71
28.21
22.55
14.06
O
S
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10

^1H-^1H COSY of dyad 1.



^1H-^{13}C HMBC of dayd 1