Supporting information for publication

"A phenothiazine-based colorimetric chemodosimeter for the rapid detection of cyanide anion in organic and aqueous media"

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General

Phenothiazine (PTZ), hexadecyltrimethylammonium bromide or Cetrimonium bromide (CTAB), *n*-butyl bromide, tetracyanoethylene (TCE) and triton X-100 were purchased from Alfa Aesar, UK. All other chemicals and reagents received were of highest purity and used without further purification. Fisher Scientific FS60 ultrasonic bath cleaner (150 W) was used for performing sonication. The Fourier transform infrared spectroscopy (FTIR) was carried out on a Perkin-Elmer system 2000. The ^{1}H NMR and ^{13}C NMR were recorded on a nuclear magnetic resonance spectrometer (Bruker Cryomagnet, Oxford) operated under 600 MHz (^{1}H) and 150 MHz (^{13}C), respectively at room temperature. The chemical shifts (δ ppm) are referenced to the respective solvents and splitting patterns are designed as s (singlet), d (doublet), t (triplet), m (multiplet), dd (doublet of doublets), td (triplet of doublets) and bs (broad singlet). The UV-vis absorption spectroscopy was carried out using a JASCO V-570 instrument and the absorption maxima are expressed in nanometers (nm). The high resolution electrospray ionization mass spectrometric analyses were carried out in a Finnigan MAT 95 XP spectrometer. The column chromatography was carried out using silica gel (100-200 mesh). The TLC analysis was carried out on double coated silica Merk plates. The solvents used were of analytical grade and used without further purification unless otherwise mentioned.

Synthetic experimental:

Synthesis of 10-Butyl-10H-phenothiazine (**2**)

nC_4H_9Br (4.1 g, 30 mmol) was added to a stirred solution of phenothiazine (4.97 g, 25 mmol), hexadecyltrimethylammonium bromide (365 mg, 1 mmol), and NaOH (1.5 g, 37.5 mmol) in acetone (40 mL). The reaction mixture was heated to reflux for 12 h under nitrogen atmosphere. After completion of the reaction, the mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was washed with water and extracted with dichloromethane (3 × 50 mL). The combined organic fractions were dried over anhydrous $MgSO_4$. The solvent was removed and the residue was purified by column chromatography using *n*-heptane as an eluent. Yield: 3.315 g (52%) of a light green liquid; ^{1}H NMR (600 MHz, 25°C, $CDCl_3$): δ = 7.22-7.24 (m, 4H, Ar), 7.00 (t, *J*= 7.2 Hz, 2H, Ar), 6.94 (d, *J*= 7.5 Hz, 2H, Ar), 3.92 (t, *J*= 7.1 Hz, 2H, -N-CH_2), 1.85-1.90 (quin, 2H, -CH_2), 1.51-1.58 (sex, 2H, -CH_2) and 1.03 (t, *J*= 7.4 Hz, 3H, -

CH_3); ^{13}C NMR (150 MHz, 25°C, $CDCl_3$): δ = 145.2 C, 127.2 CH, 127.0 CH, 124.8 C, 122.1 CH, 115.2 CH, 46.9 N–CH_2, 28.8 CH_2, 20.0 CH_2 and 13.7 CH_3.

Synthesis of 10-Butyl-3-tricyanovinyl-10H-phenothiazine (**PCP 1**)

10-Butyl-10*H*-phenothiazine **2** (0.766 g, 3 mmol) was dissolved in anhydrous DMF-THF (10 mL, 1:1, v/v) and resulting mixture was stirred at room temperature. To this stirred solution, TCNE (0.384 g, 3 mmol) was added and heated to reflux for 6 h under nitrogen atmosphere. After completion of the reaction, the mixture was cooled to room temperature and the solvent was evaporated under reduced pressure. The residue was washed with cold water and extracted with dichloromethane (2 × 50 mL). The combined organic fractions were dried over anhydrous $MgSO_4$. The solvent was evaporated and crude was purified by column chromatography (dicholoromethane: *n*-hexane; 1:1 v/v). **PCP 1** was obtained as blue amorphous powder. Yield: 0.437 g (41%); IR (KBr, cm^{-1}): 2215 (CN), 1595, 1571, 1494, 1463, 1404, 1342, 1279, 1188; UV-vis (DCM, λ_{max}/nm): 330, 405 and 600; ^1H NMR (600 MHz, 25°C, $(CD_3)_2SO$): δ = 7.80 (d, *J*= 8.4 Hz, 1H, Ar), 7.66 (bs, 1H, Ar), 7.24 (d, *J*= 8.2 Hz, 2H, Ar), 7.14 (t, *J*= 8.8 Hz, 2H, Ar), 7.04 (t, *J*= 7.2 Hz, 1H, Ar), 3.97 (t, *J*= 6.6 Hz, 2H, -N-CH_2), 1.66-1.68 (m, 2H, -CH_2), 1.38-1.41 (m, 2H, -CH_2) and 0.88 (t, *J*= 6.7 Hz, 3H, -CH_3); ^{13}C NMR (150 MHz, 25°C, $(CD_3)_2SO$): δ = 150.7 C, 141.2 C, 137.3 C, 131.2 CH, 128.3 CH, 127.3 CH, 126.8 CH, 124.5 CH, 123.3 CN, 122.5 CN, 121.2 CN, 116.9 CH, 115.7 CH, 114.4 C, 113.1 C, 112.8 C, 86.0 C, 47.1 N–CH_2, 28.1 CH_2, 19.1 CH_2, and 13.4 CH_3; Anal Calc. for $C_{21}H_{16}N_4S$: Calcd C; 70.76, H; 4.52, N; 15.72. Found C; 70.75, H; 4.51, N; 15.70.

Synthesis of 3-tricyanovinyl-10H-phenothiazine (**4**)

Compound **4** was prepared by modification of known procedure.[1] In brief; TCNE (1.2 g, 9.3 mmol) was added to a stirred solution of phenothiazine (1.86 g, 9.3 mmol) in DMF (10 mL). The reaction mixture was heated at 90°C for 4 h under nitrogen atmosphere. After completion of the reaction, the mixture was cooled to room temperature and poured into crushed ice-water bath. The precipitate was filtered on Buckner funnel and washed repeatedly with water (2 × 100 mL) followed by methanol (50 mL). The as-obtained blue needles were dried under high vacuum for 6 h and stored in a dry box prior to use. Yield: 2.37 g (85%); mp 230 °C; IR (KBr, cm^{-1}): 3321 (NH),

2223 (CN), 1602, 1573, 1503, 1470, 1348, 1286, 1201, 1168; UV-vis (DCM, λ_{max}/nm): 325, 400 and 600; ^{1}H NMR (600 MHz, 25°C, $(CD_3)_2SO$): δ = 10.06 (s, 1H, N–H), 7.62 (dd, $J_{1,2}$= $J_{3,4}$= 2.3 Hz, $J_{1,3}$= 8.7 Hz, 1H, Ar), 7.49 (d, J= 2.0 Hz, 1H, Ar), 7.01-7.04 (dt, 1H, Ar), 6.93 (dd, $J_{1,2}$= $J_{3,4}$= 1.4 Hz, $J_{1,3}$= 7.7 Hz, 1H, Ar), 6.85-6.88 (dt, 1H, Ar), 6.74 (d, J= 8.7 Hz, 1H, Ar), and 6.72 (dd, $J_{1,2}$= $J_{3,4}$= 1.2 Hz, $J_{1,3}$= 7.9 Hz, 1H, Ar); ^{13}C NMR (150 MHz, 25°C, $(CD_3)_2SO$): δ = 147.7 C, 137.0 C, 136.0 C, 132.4 CH, 128.1 CH, 126.2 CH, 125.8 CH, 124.4 CH, 122.1 CN, 117.9 CN, 116.2 CH, 115.7 C, 114.5 CH, 113.7 C, 113.4 C, and 81.9 C; Anal Calc. for $C_{17}H_8N_4S$: Calcd C; 67.98, H; 2.68, N; 18.65. Found C; 67.94, H; 2.66, N; 18.64.

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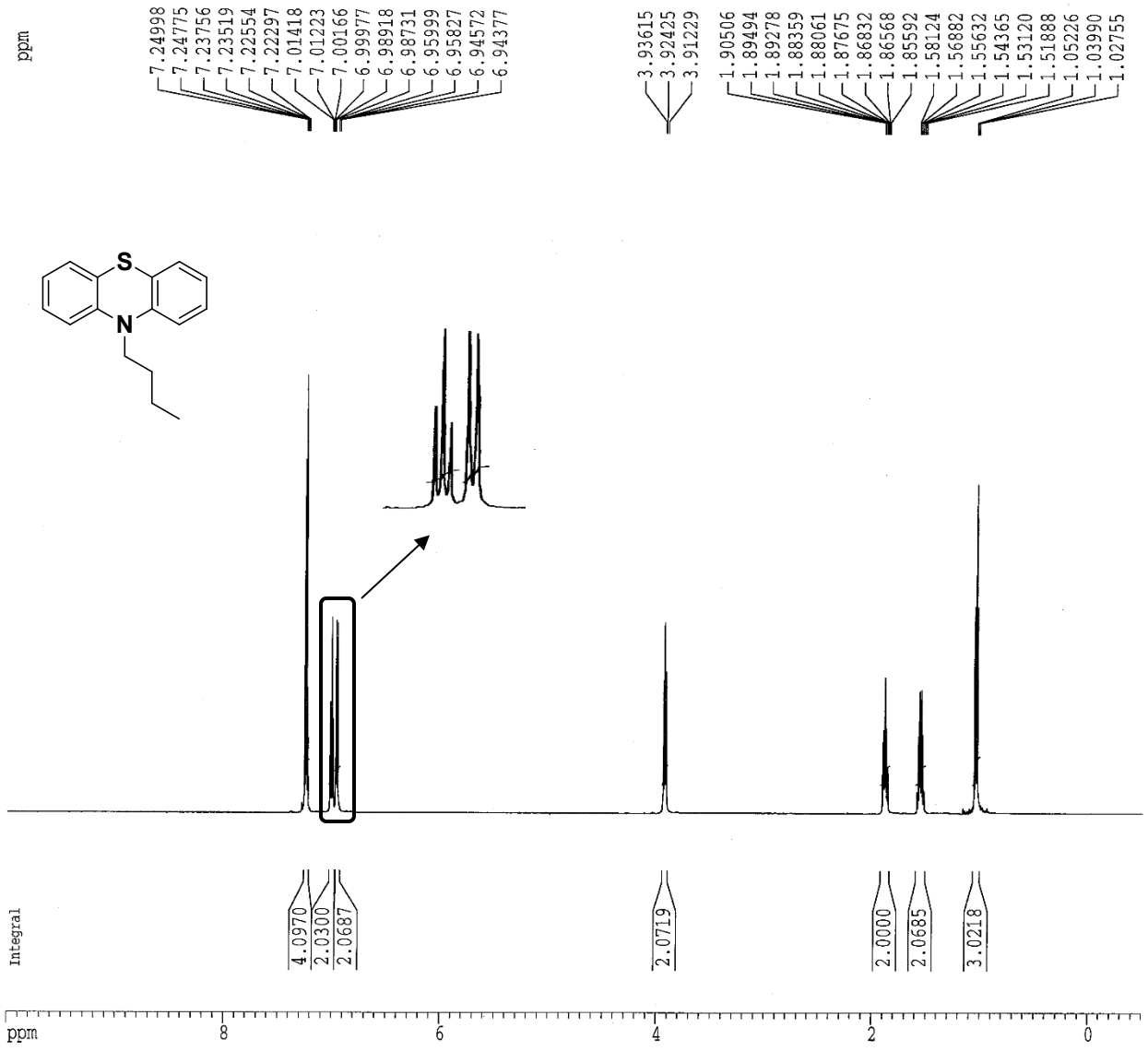

Figure S1 ^{1}H NMR spectrum of compound **2** in $CDCl_3$

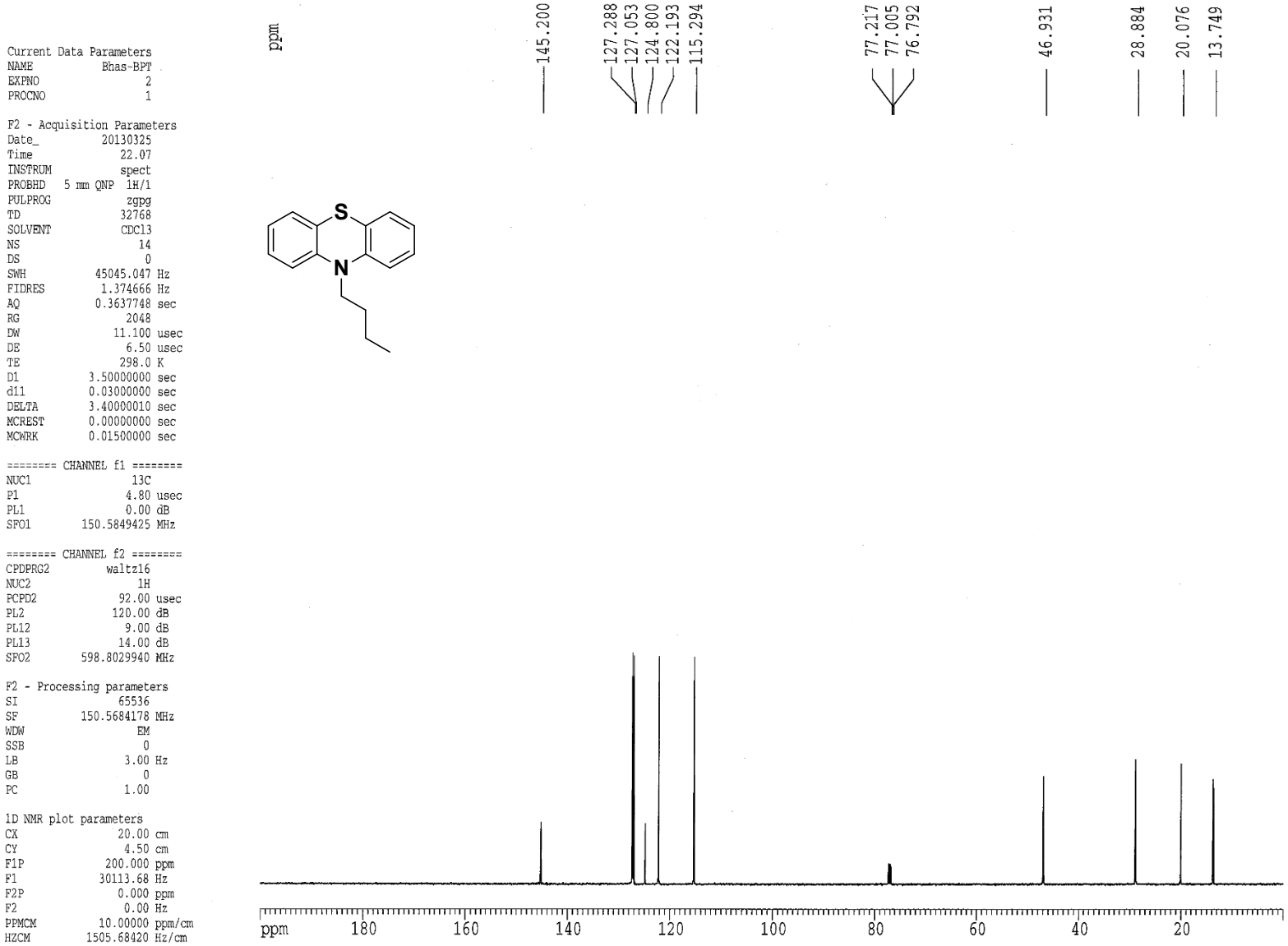

Figure S2 ^{13}C NMR spectrum of compound **2** in $CDCl_3$

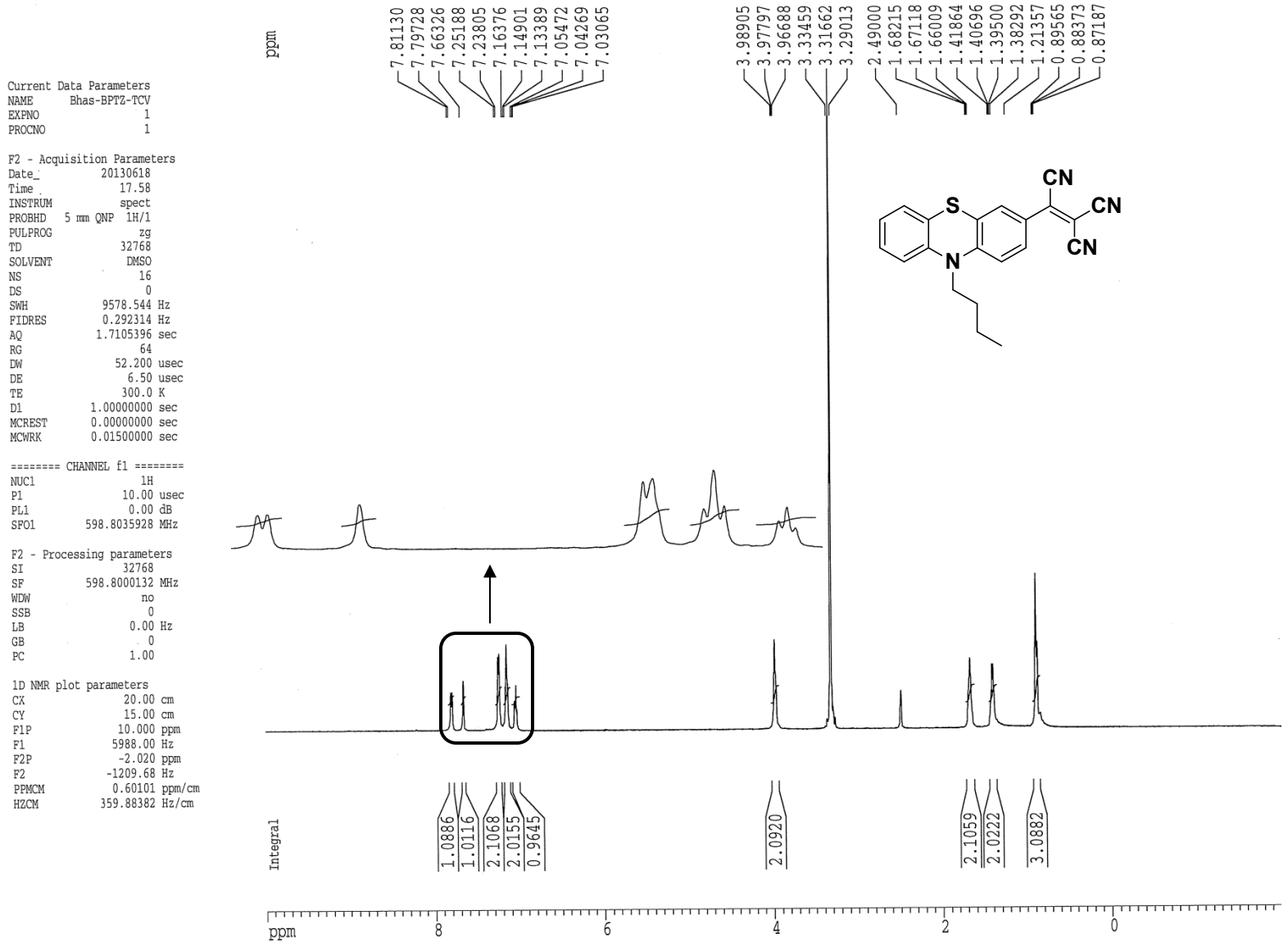

Figure S3 ^{1}H NMR spectrum of **PCP 1** in $(CD_3)_2SO$

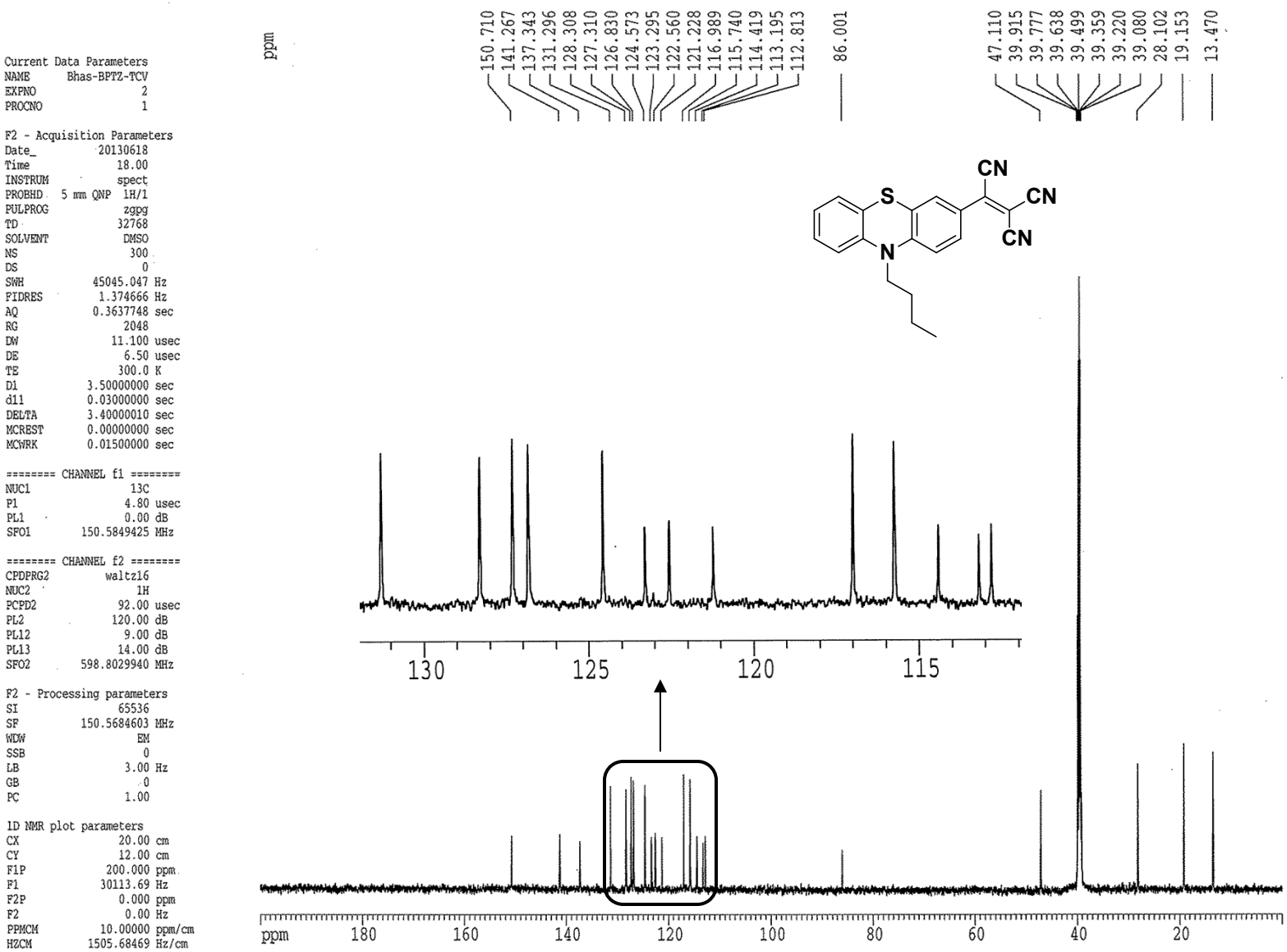

Figure S4 ^{13}C NMR spectrum of compound **PCP 1** in $(CD_3)_2SO$

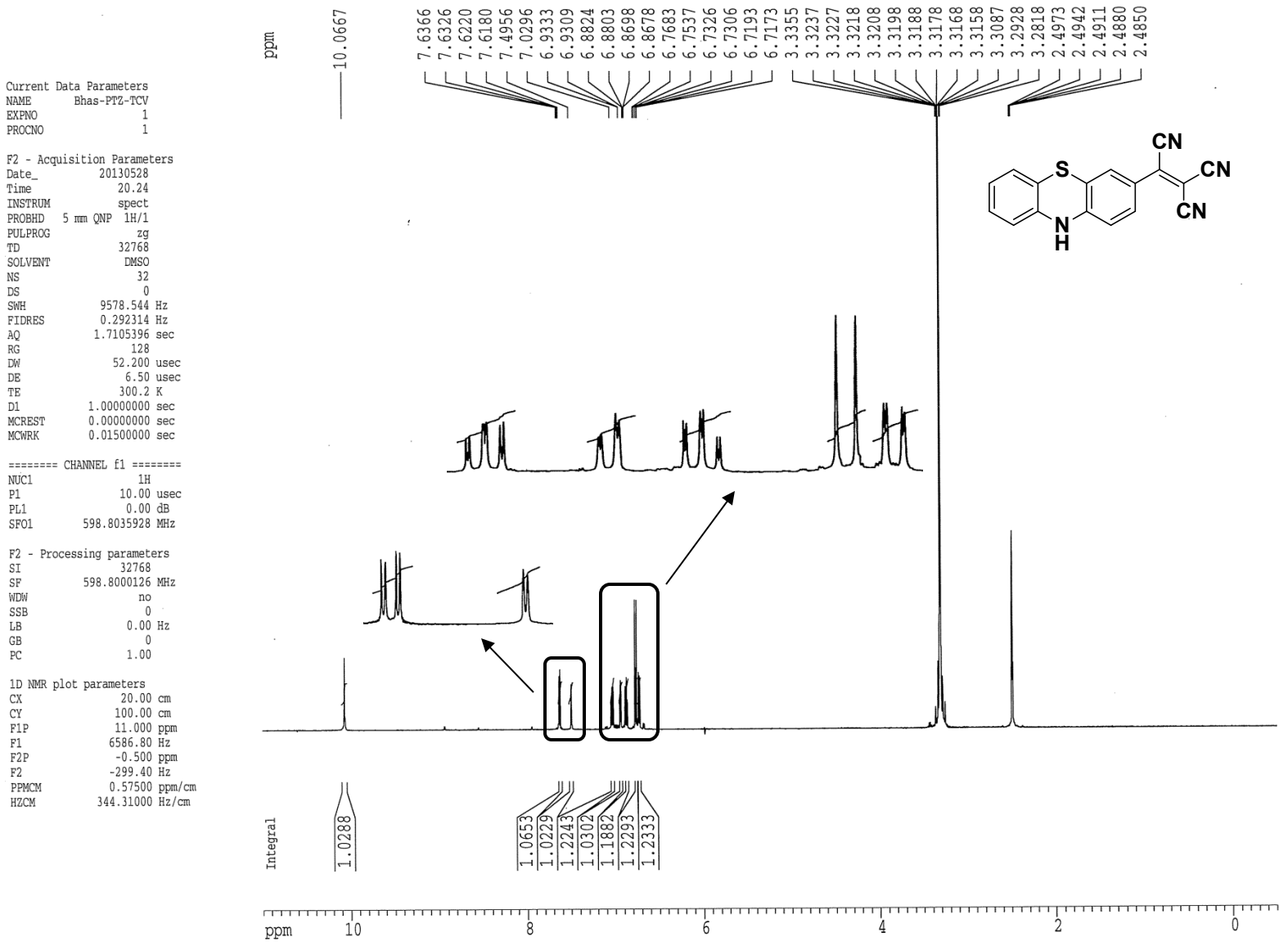

Figure S5. ^{1}H NMR spectrum of compound **4** in $(CD_3)_2SO$

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PROCNO                1

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AQ            0.3637748 sec
RG                2048
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DE                6.50 usec
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PL12               9.00 dB
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PC                 1.00

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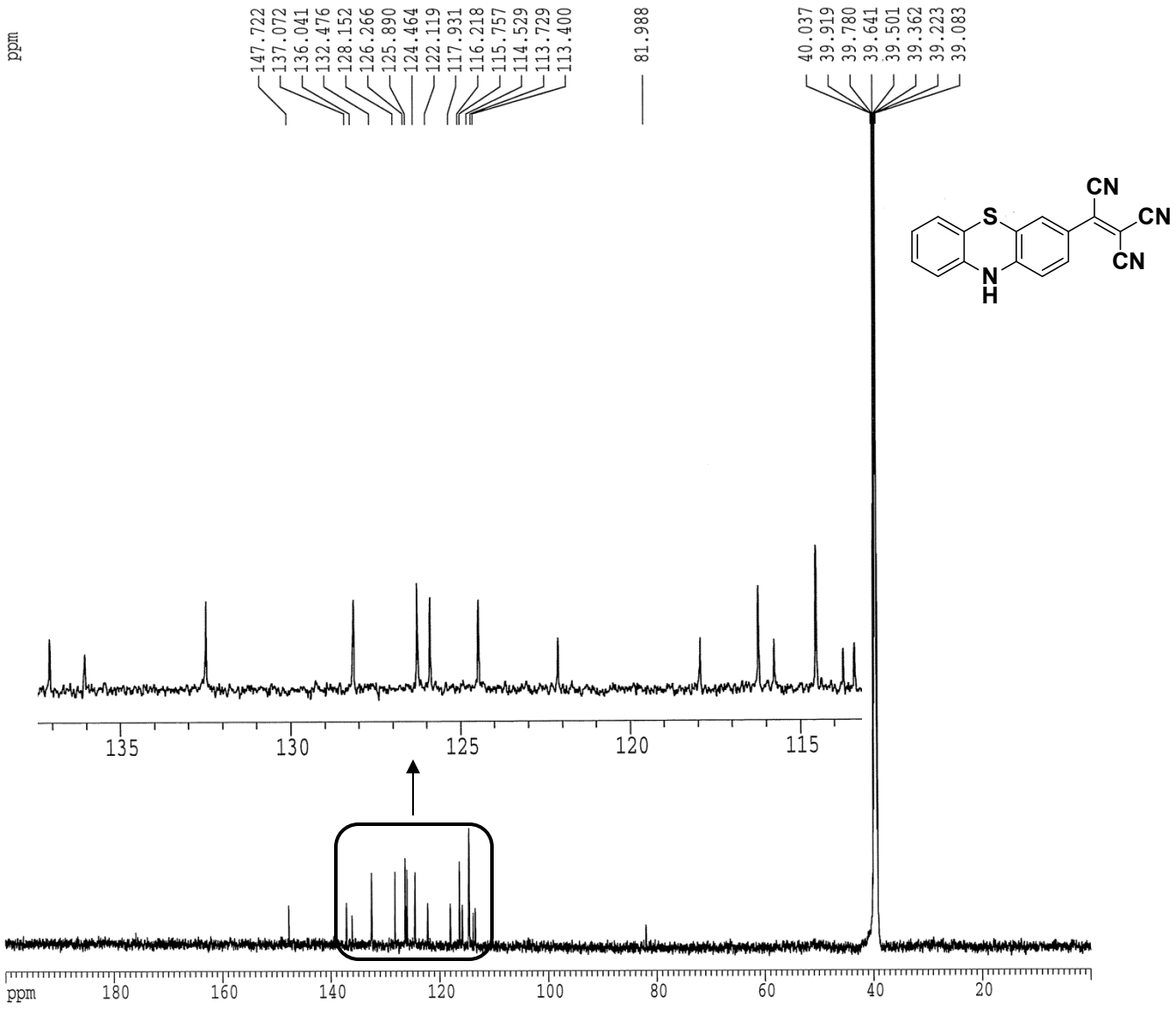


Figure S6. ^{13}C NMR spectrum of compound **4** in $(CD_3)_2SO$

Figure S7 Color changes of comp **4** (5 x 10^{-5} M) in DCM solution upon the addition of different anions (5 x 10^{-4} M); **A** = 4, **B** = F^-, **C** = Cl^-, **D** = Br^-, **E** = I^-, **F** = NO_3^-, **G** = AcO^-, **H** = $H_2PO_4^-$, **I** = HSO_4^-, and **J** = CN^-.

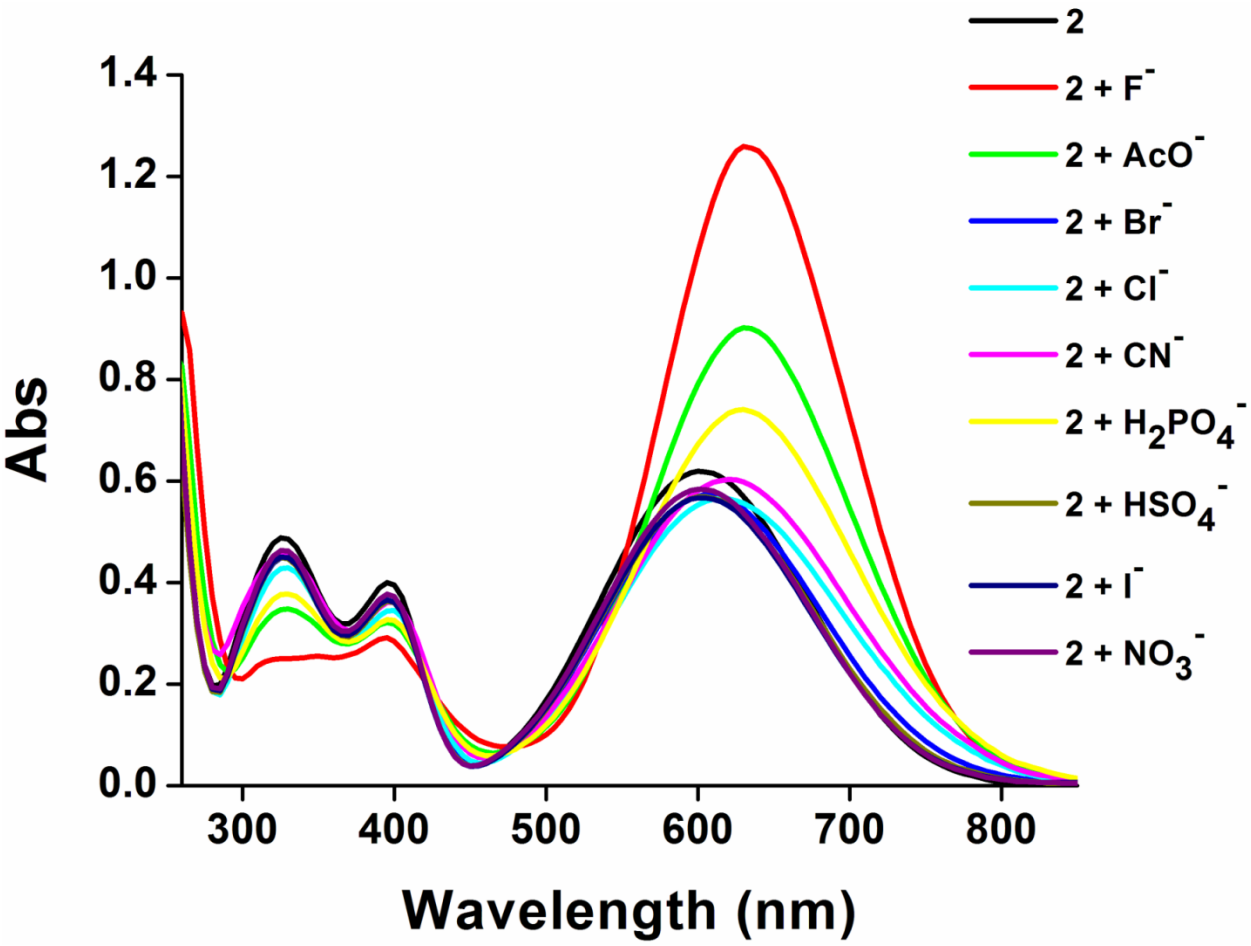
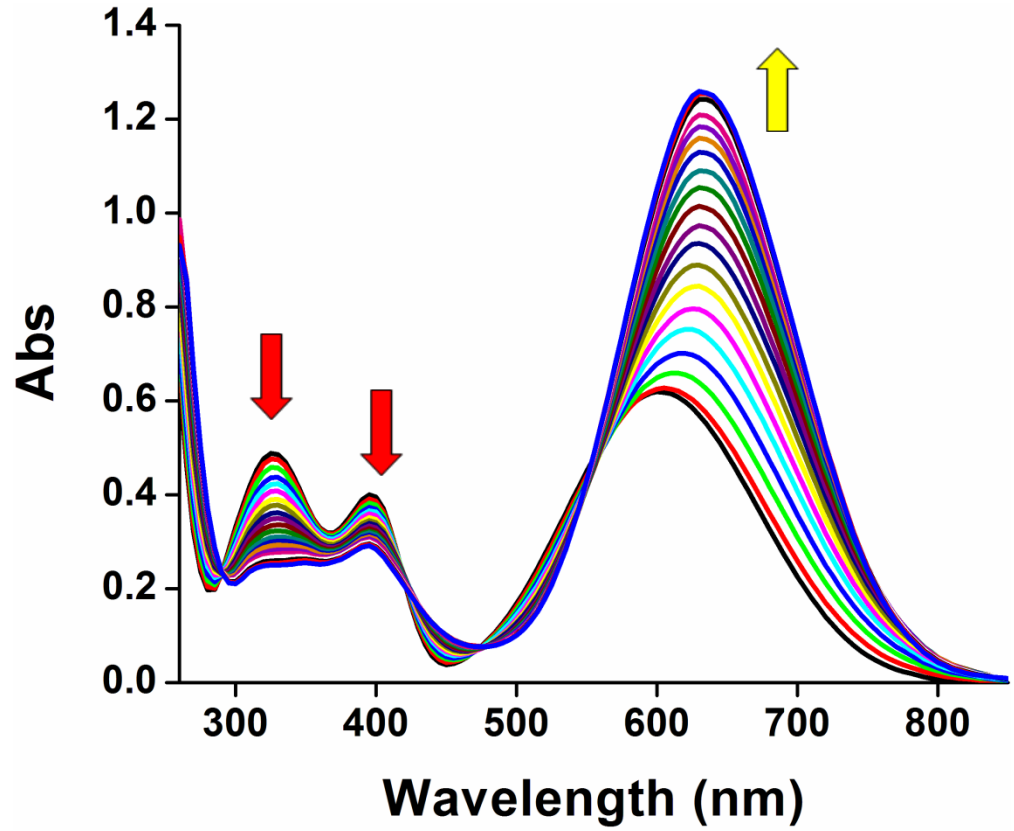


Figure S8 UV-vis absorption spectra of **4** (5.0 × 10^{-5} M) in DCM solution in the presence of different anions (5.0 × 10^{-4} M) as their TBA salts



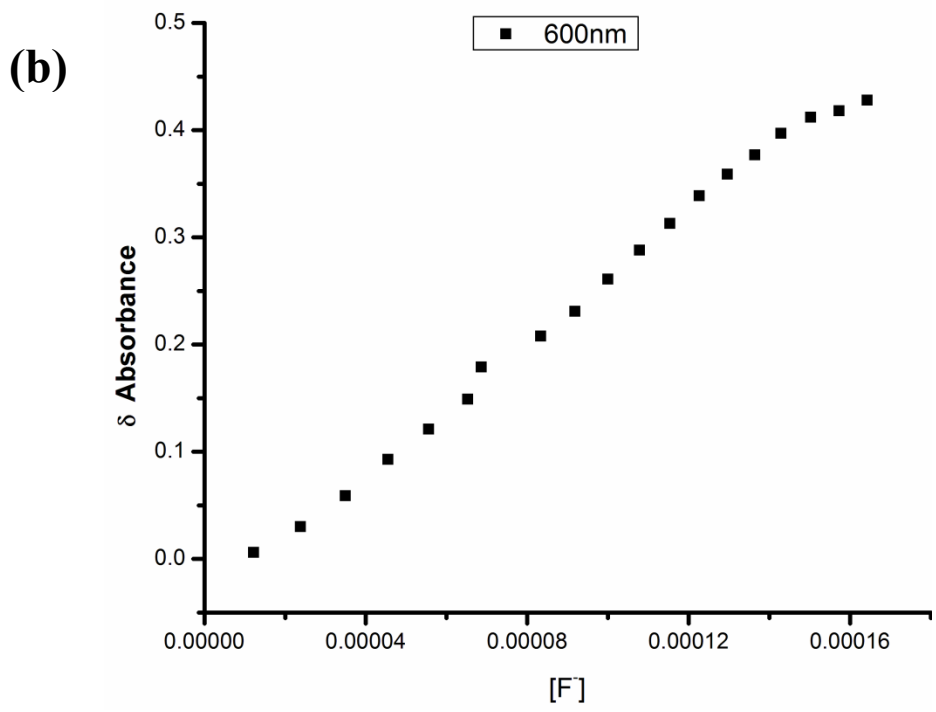
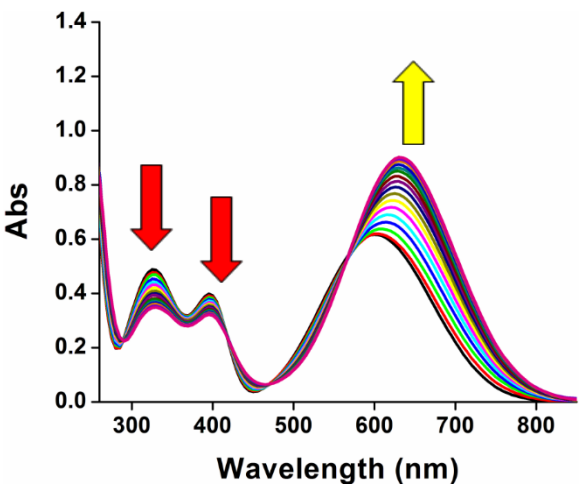
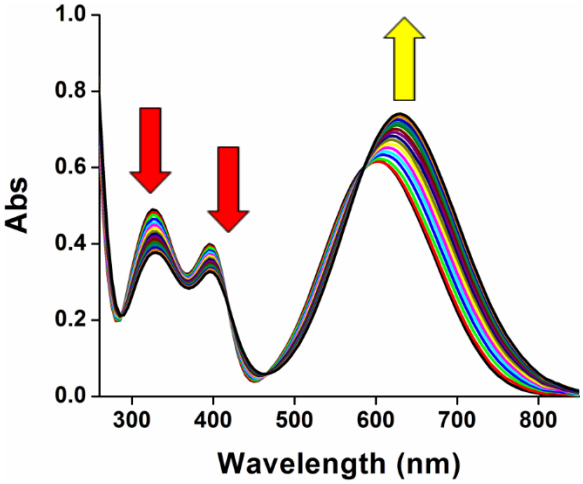


Figure S9 (a**)** Absorption spectroscopic titrations of compound **4** (5 x 10^{-5} M) in DCM solution with TBAF (5 x 10^{-4} M); (b) Titration profile of the observed changes at λ = 600 nm.

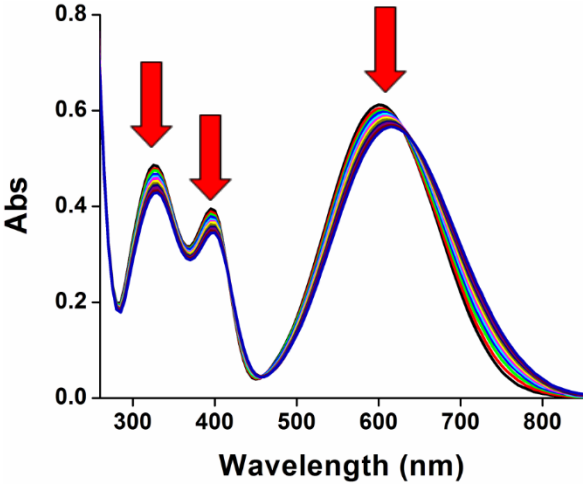
1) **4** / AcO^-



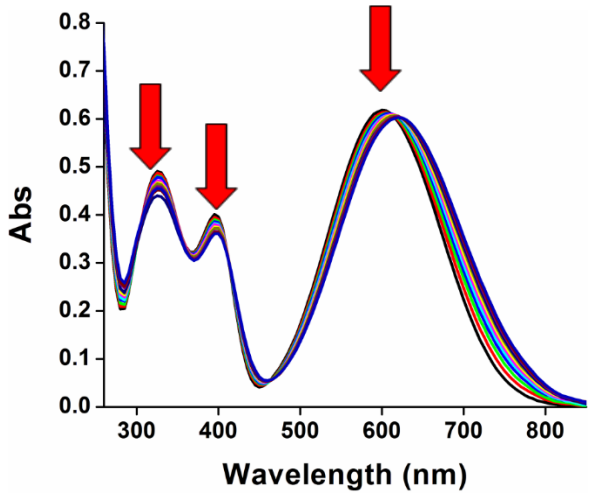
2) **4**/ $H_2PO_4^-$



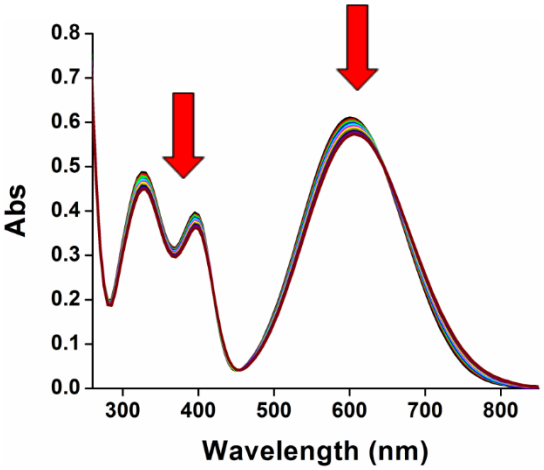
3) **4** / Cl^-



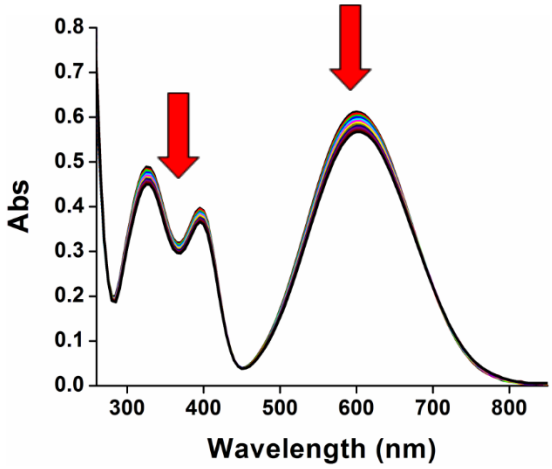
4) **4** / CN^-



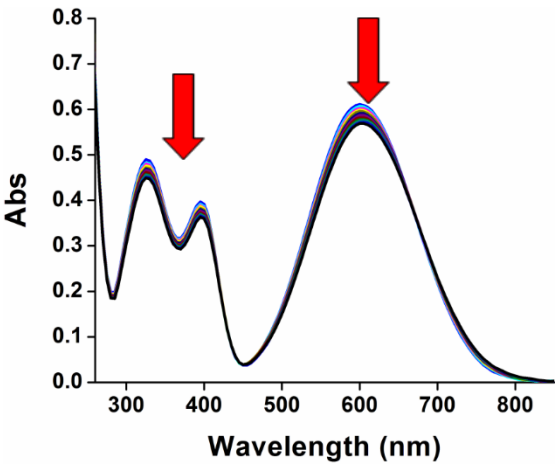
5) **4** / Br^-



6) **4** / I^-



7) **4** / HSO_4^-



8) **4** / NO_3^-

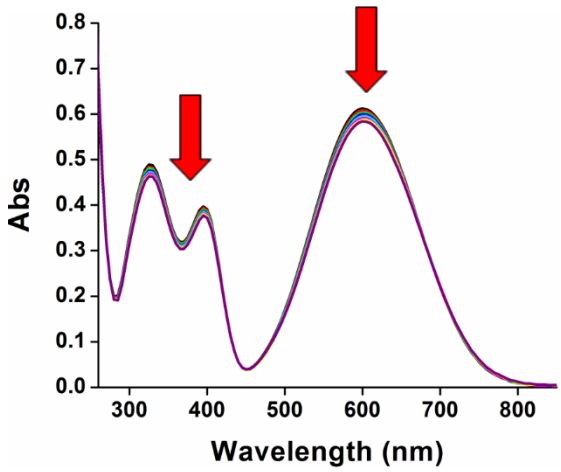


Figure S10 Absorption spectroscopic titrations of compound **4** (5 x 10^{-5} M) in DCM solution with different anions (5 x 10^{-4} M).

Computational Results:

Method: B3LYP (The default grid size for B3LYP method in Gaussian 09 is used)

Basis set: 6-311++G(d,p)

Program: Gaussian 09, Revision D.01;

The default parameters for geometry optimization and NBO analysis are used in all the calculation.[2,3]

Optimized structure of PCP 1

The optimized structure of **PCP 1** is shown in Figure S11. In particular, the PTZ-skeleton takes a butterfly-like conformation between the two benzene rings with an angle of 139.28°.

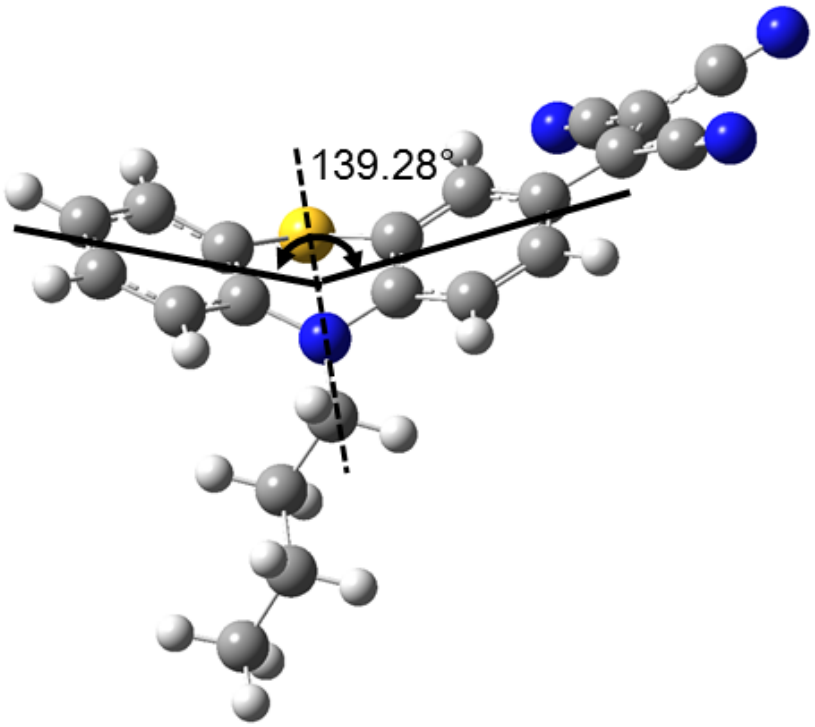


Figure S11 The optimized structure of **PCP 1**

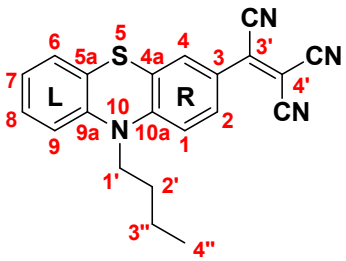
Charge distribution calculations

The calculated natural atomic charge distribution on **PCP 1** is shown in Table S1, Table S2 and Figure S12. In general, the electron density on the benzene rings is strongly affected by the adjacent functional groups. –CN groups and –N– are common electron-withdrawing groups while –S– is the electron-donating group. From the table S1, one can compare the charge distribution at the carbon and hydrogen atoms on the left and right benzene ring of **PCP 1**. We could find that:

- The Right benzene ring has one H atom less than the Left one.
- The charge distribution on each H atom is more or less the same (around 0.21~0.22). Therefore, C atoms contribute most to the difference.
- The Left ring has one positively charged carbon atom (C9a, charge = + 0.142).
- Even though atoms (C6, C7, C8) at left are a bit negative than atoms (C4, C3, C2) at right, the carbon atoms at left (C5a, C9, C9a) are significantly less negative than carbon atoms at right (C4a, C1, C10a). As a result, the benzene ring at the left side contains more positive charge than that of the right side.

Table S1 Rational charge distribution at left and right benzene rings in **PCP 1**

Left	C	H
5a	-0.199	–
6	-0.195	0.218
7	-0.202	0.212
8	-0.189	0.210
9	-0.229	0.210
9a	**0.142**	–
Sum	-0.872	0.850



Right	C	H
4a	-0.342	–
4	-0.184	0.232
3	-0.177	–
2	-0.150	0.224
1	-0.416	0.195
10a	-0.285	–
Sum	-1.554	0.419

Table S2 Charge distribution on vinyl and N-containing butyl chain in **PCP 1**

Carbon Number	Charge density
C3'	**-0.011**
C4'	-0.249
C1'	-0.178
C2'	-0.392
C3''	-0.381
C4''	-0.569

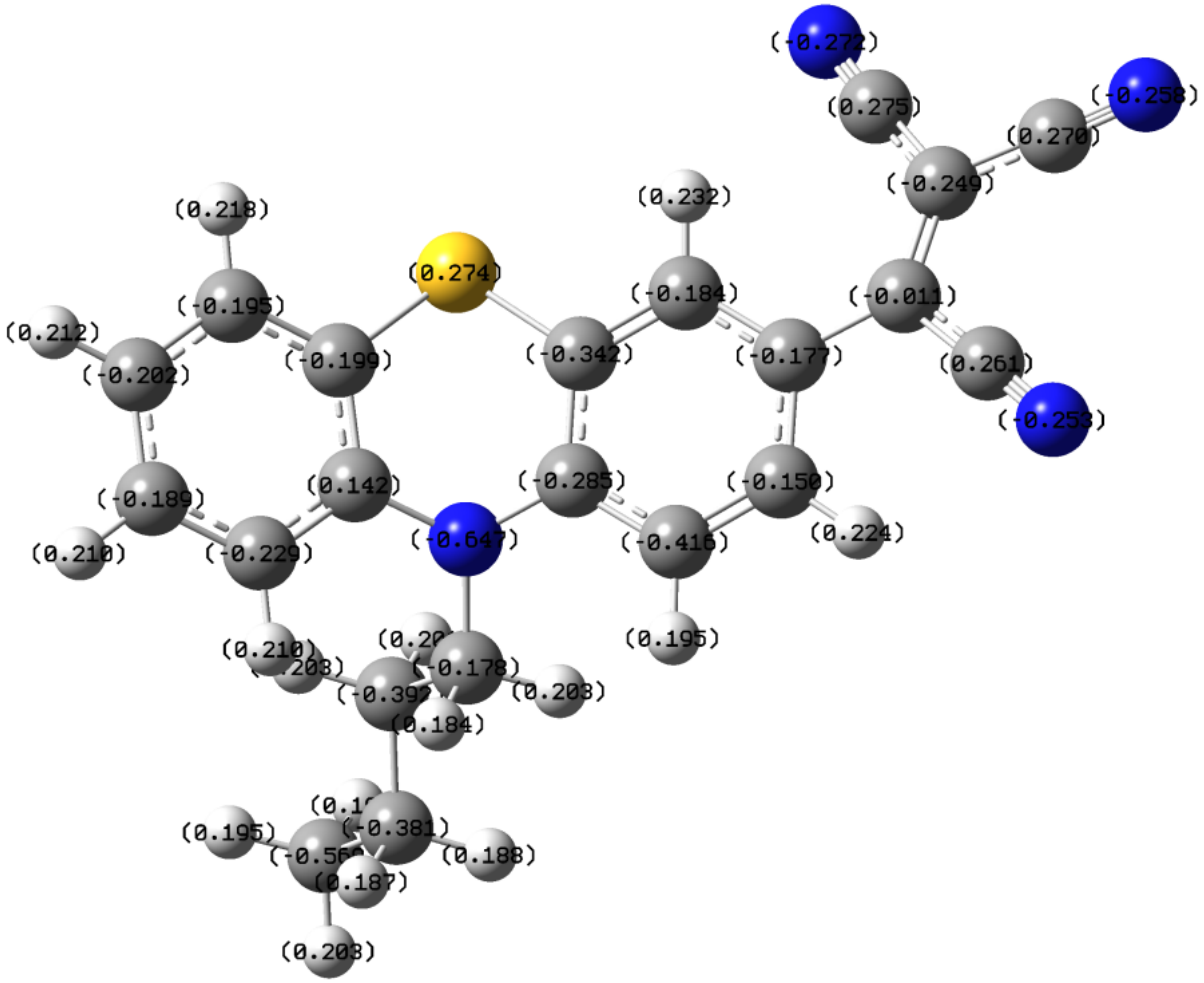


Figure S12 The calculated natural atomic charge distribution on **PCP 1**

The electronic potential (EP) distribution on the molecule surface contours the nucleophilic and the electrophilic parts of **REA.** The red and yellow regions of the molecular surface are rich in electron density, while the blue and cyan regions are electron deficient. As shown in the Figure S13, the electron density mainly focuses on the three –CN groups while the hydrogen atoms carry positive charge. It's also noticeable that the region close to the benzene π orbital is nucleophilic, which means abundant distribution of electrons. However, for the benzene ring conjugated to the electron-withdrawing –CN groups, the electron density near the π orbital is greatly reduced. Of the conjugate structure of the three –CN groups, vinyl group and the phenyl group, only the vinyl group provides evident electrophilic region.

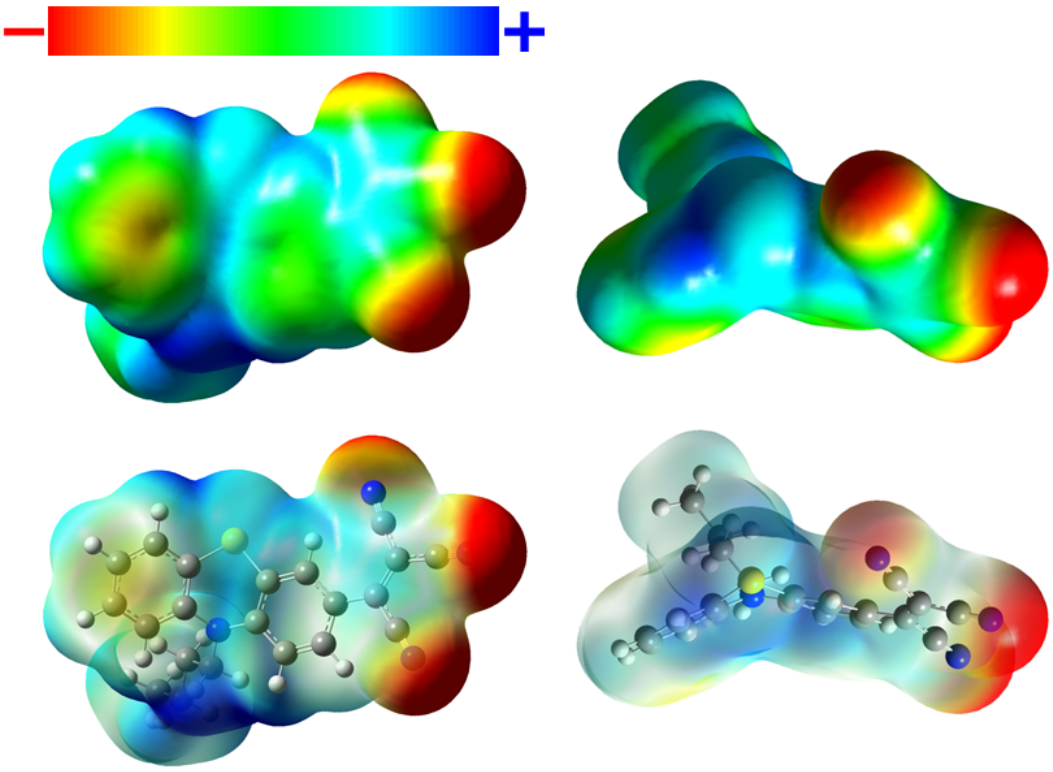


Figure S13 The opaque surface shows the regions with different charge, while the transparent surface shows the groups inside.

Total energy of **PCP 1**: **-1427.28480399 a.u.**

Cartesian coordinates for PCP 1

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.352366	2.056064	-1.549902
2	6	0	3.711407	0.844834	-1.300358
3	6	0	2.544218	0.799959	-0.528298
4	6	0	2.021027	2.006554	-0.038891
5	6	0	2.647365	3.219684	-0.317214
6	6	0	3.825773	3.247013	-1.058634
7	6	0	-0.268278	0.618320	0.205224
8	6	0	0.487043	-0.470232	-0.294971
9	6	0	-0.223504	-1.563191	-0.825683
10	1	0	0.307879	-2.396569	-1.263610
11	6	0	-1.605756	-1.584387	-0.830594
12	6	0	-2.359753	-0.513402	-0.311232
13	6	0	-1.651166	0.602179	0.182483
14	1	0	5.260662	2.063224	-2.140997
15	1	0	4.128232	-0.065900	-1.708860
16	1	0	2.212390	4.138729	0.058026
17	1	0	4.319228	4.190906	-1.256298
18	1	0	-2.110236	-2.443242	-1.255253
19	1	0	-2.173648	1.470630	0.556110
20	6	0	2.654756	-1.679356	-0.287289
21	1	0	3.070623	-1.864798	-1.285789
22	1	0	1.960459	-2.492220	-0.083030
23	6	0	3.755619	-1.720045	0.780093
24	1	0	4.450094	-0.886105	0.646746
25	1	0	3.289186	-1.582150	1.761451
26	6	0	4.531746	-3.042233	0.750130
27	1	0	4.992900	-3.172363	-0.236528
28	1	0	3.833733	-3.879286	0.873363
29	6	0	5.612886	-3.120066	1.831735
30	1	0	6.150108	-4.070779	1.786175
31	1	0	6.347099	-2.316930	1.716950
32	1	0	5.178304	-3.031013	2.831815
33	6	0	-3.816962	-0.589657	-0.329348
34	6	0	-4.721375	0.135926	0.422093
35	6	0	-4.382616	-1.548481	-1.236234
36	7	0	-4.807464	-2.328944	-1.973905
37	6	0	-6.128661	-0.024639	0.246813
38	7	0	-7.273587	-0.130973	0.128756
39	6	0	-4.357018	1.058189	1.444780
40	7	0	-4.109136	1.806995	2.290410
41	16	0	0.574090	1.969518	0.998149
42	7	0	1.879163	-0.428883	-0.259384

Table S3

Total energy of **PCP 1-**CN^- adduct: **-1520.23240702 a.u.**

Cartesian coordinates for PCP 1-CN^- adduct

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.642304	-2.353709	0.927722
2	6	0	3.972725	-1.132397	0.988598
3	6	0	2.789026	-0.924457	0.266816
4	6	0	2.281703	-1.990884	-0.500916
5	6	0	2.936152	-3.220271	-0.528212
6	6	0	4.128789	-3.402847	0.170778
7	6	0	-0.052135	-0.659875	-0.362424
8	6	0	0.679675	0.260844	0.407939
9	6	0	-0.029150	1.095421	1.273864
10	1	0	0.495572	1.791763	1.914939
11	6	0	-1.422791	1.052492	1.331935
12	6	0	-2.136831	0.153066	0.551095
13	6	0	-1.436042	-0.719690	-0.284853
14	1	0	5.561946	-2.483258	1.487827
15	1	0	4.377973	-0.337426	1.601135
16	1	0	2.511173	-4.030065	-1.110542
17	1	0	4.641813	-4.356699	0.128815
18	1	0	-1.942551	1.729666	1.997987
19	1	0	-1.978475	-1.428916	-0.898759
20	6	0	2.804516	1.528459	0.652512
21	1	0	3.200550	1.480358	1.678598
22	1	0	2.071478	2.334219	0.642485
23	6	0	3.919840	1.892984	-0.336466
24	1	0	4.642678	1.075641	-0.416095
25	1	0	3.470900	2.008763	-1.328562
26	6	0	4.646894	3.181739	0.063170
27	1	0	5.087576	3.058735	1.060591
28	1	0	3.920295	3.998759	0.150120
29	6	0	5.742339	3.581584	-0.929938
30	1	0	6.244729	4.502748	-0.620737
31	1	0	6.502979	2.799008	-1.015672
32	1	0	5.326566	3.748057	-1.928335
33	6	0	-4.075341	-1.296216	0.908874
34	7	0	-4.343646	-2.380942	1.193154
35	16	0	0.831278	-1.717531	-1.497748
36	7	0	2.094107	0.303873	0.284513
37	6	0	-3.684043	0.089963	0.549722
38	6	0	-4.232018	0.975993	1.617188
39	7	0	-4.676270	1.695271	2.403678
40	6	0	-4.253475	0.467728	-0.824103
41	6	0	-3.587445	1.439848	-1.577882
42	7	0	-3.013675	2.237974	-2.207997
43	6	0	-5.549661	0.070733	-1.172567
44	7	0	-6.624207	-0.278164	-1.464340

Table S4

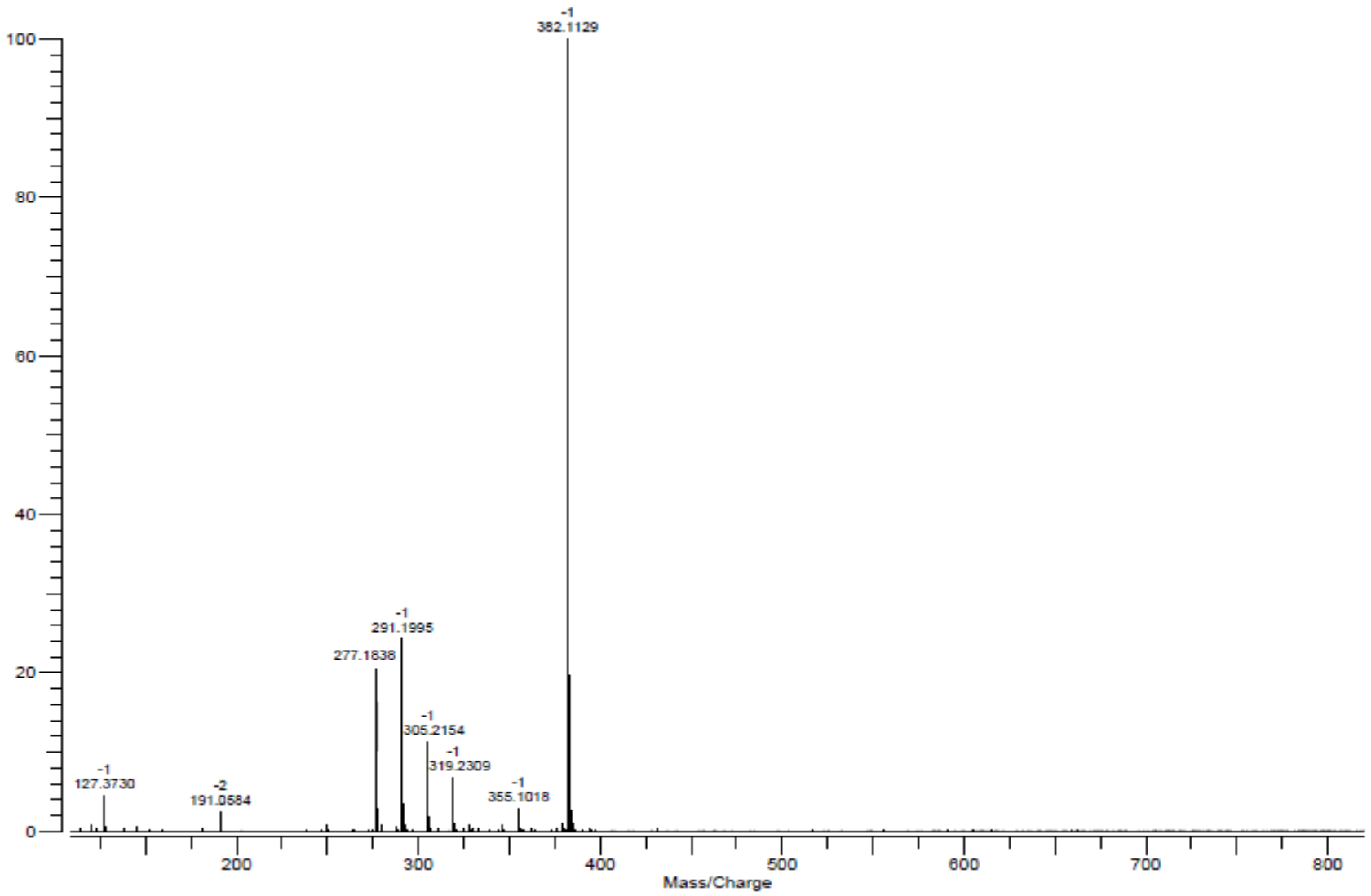
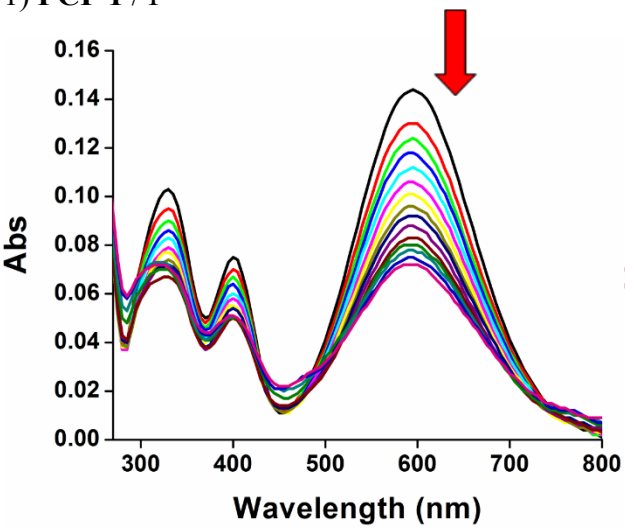
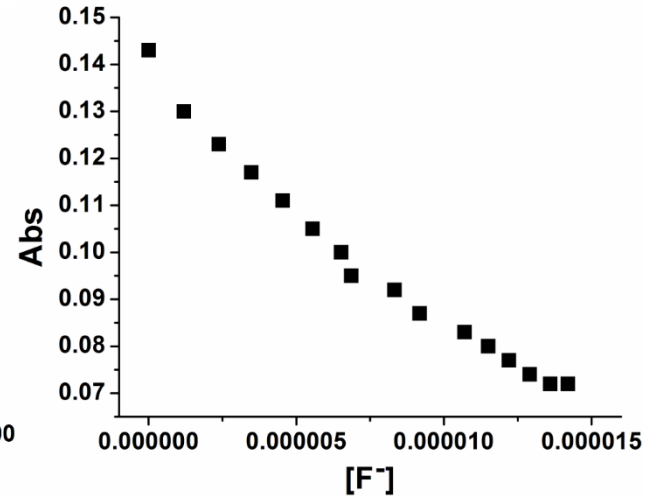


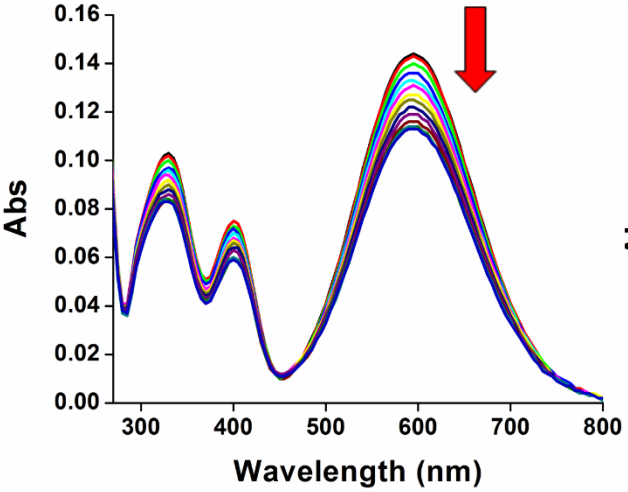
Figure S14 The high resolution negative ion ESI-MS spectrum of product obtained by mixing acetonitrile solution of **PCP 1** and TBACN (1×10^{-5} M each) after 5 min of incubation at room temperature.

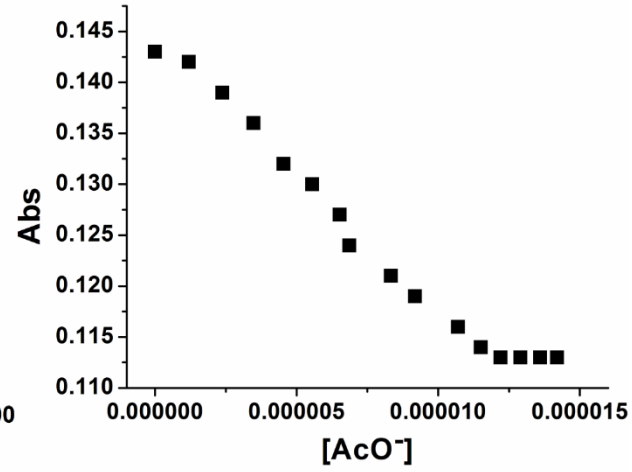
1) **PCP 1** / F^-



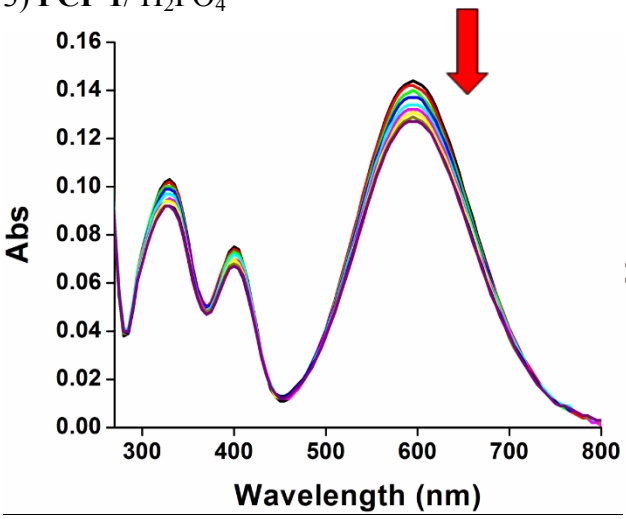


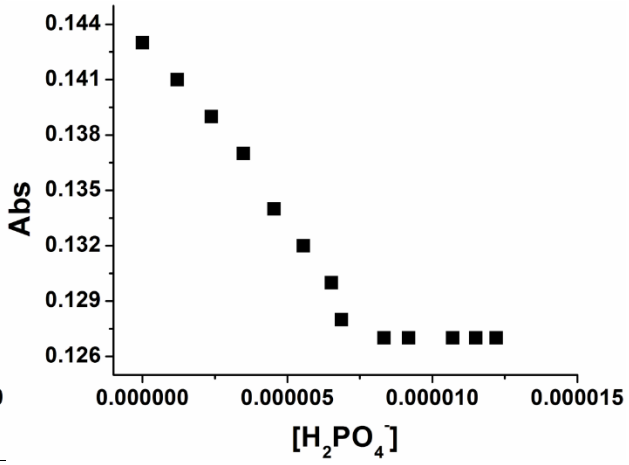
2) **PCP 1**/ AcO^-



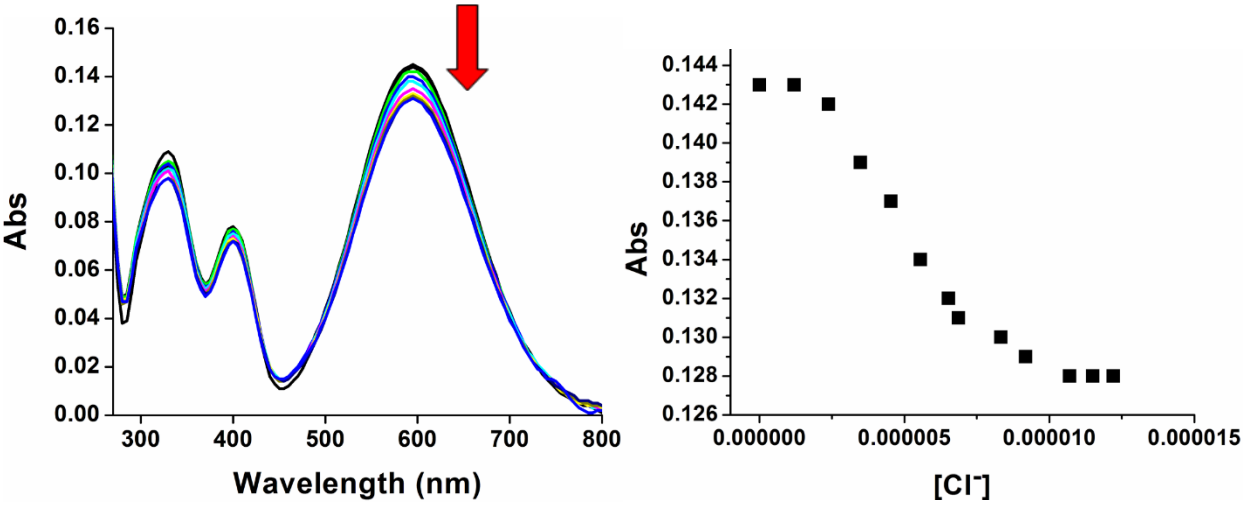


3) **PCP 1**/ $H_2PO_4^-$

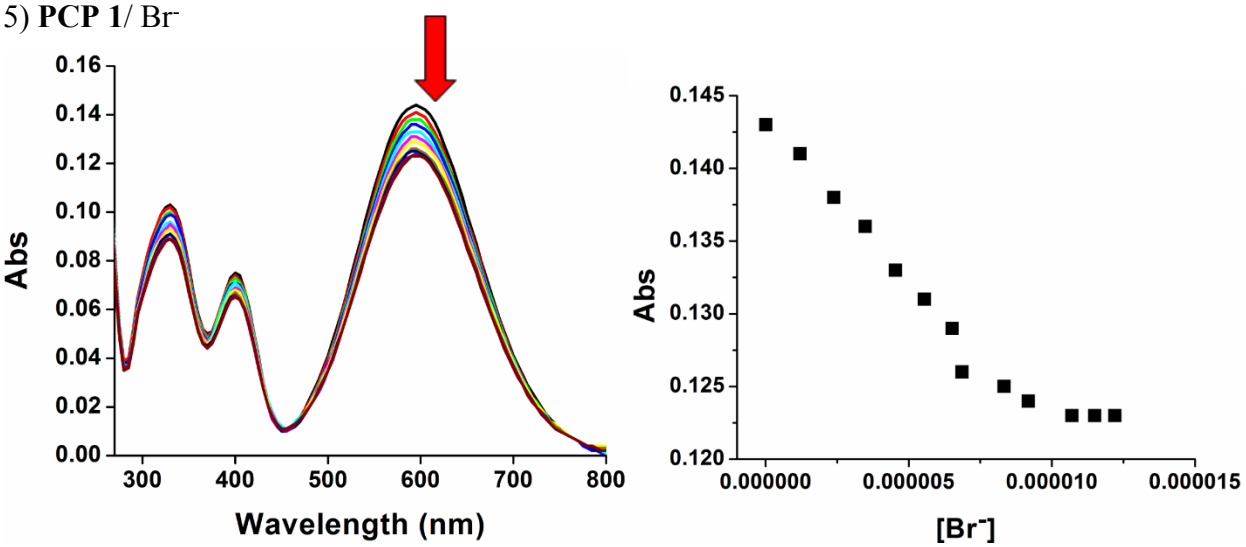




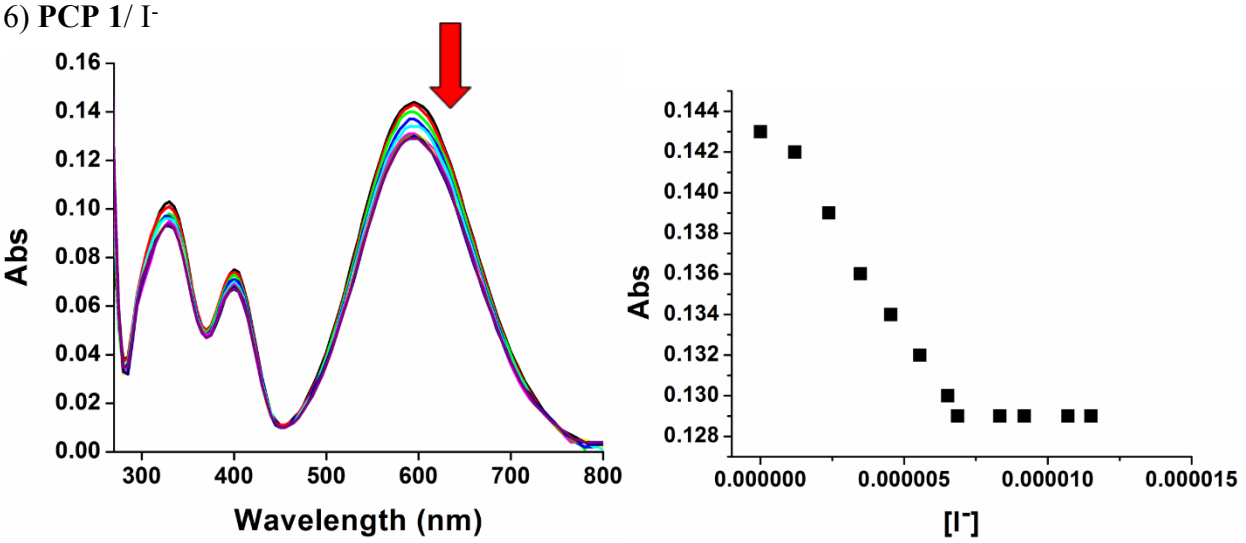
4) **PCP 1**/ Cl^-



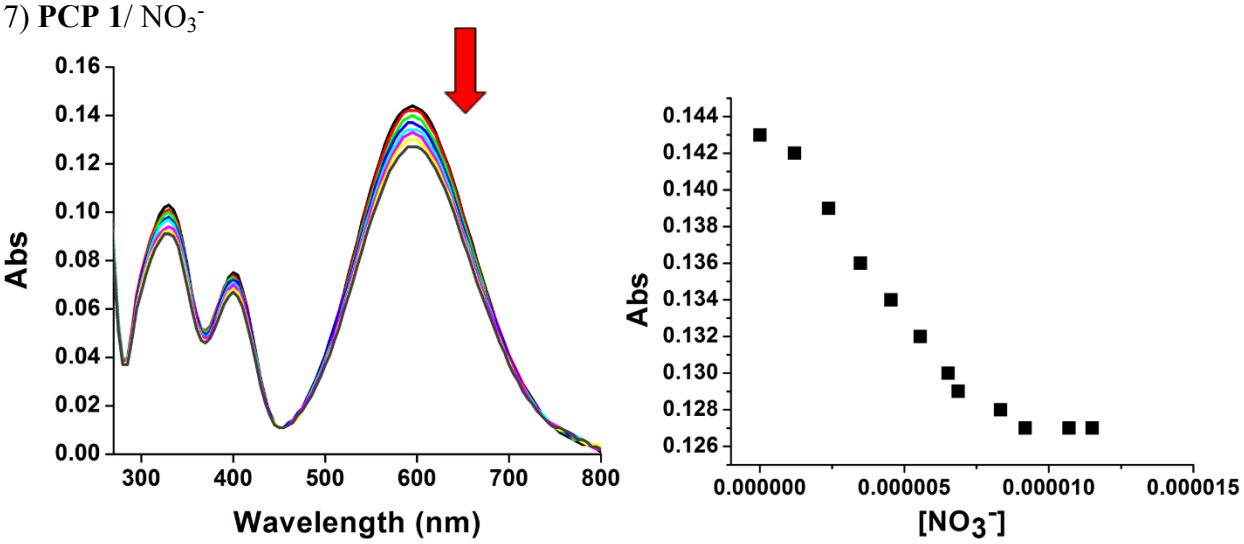
5) **PCP 1**/ Br^-



6) **PCP 1**/ I^-



7) **PCP 1**/ NO_3^-



8) **PCP 1**/ HSO_4^-

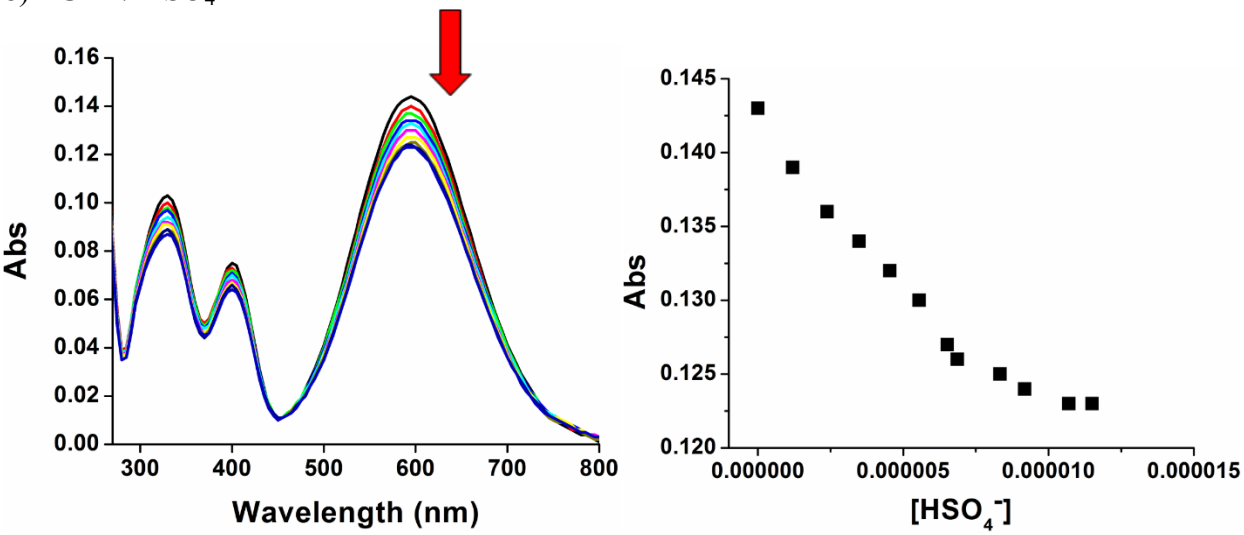


Figure S15 Absorption spectroscopic titrations of **PCP 1** (5 x 10^{-6} M) in DCM solution with different anions (5 x 10^{-5} M) and titrations profile of the observed changes at (λ = 600 nm)

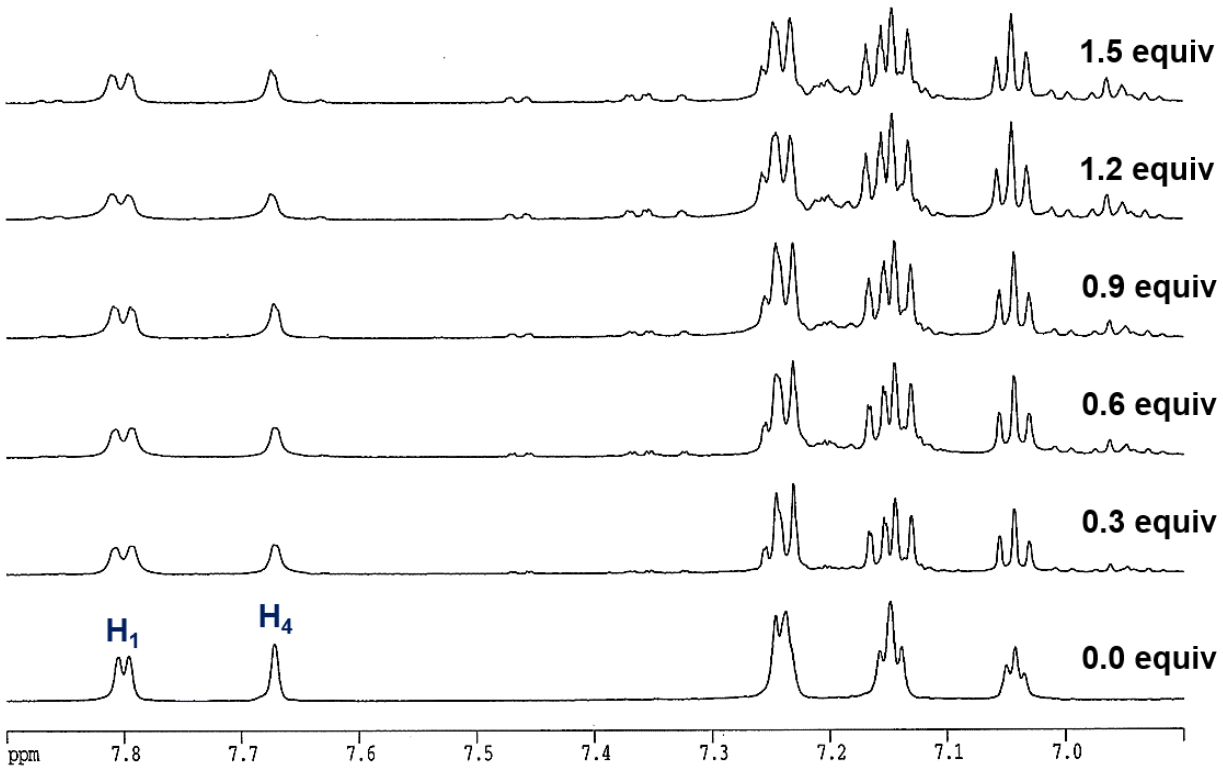


Figure S16 Partial ^{1}H NMR (600 MHz, $(CD_3)_2SO$) spectral changes seen upon the addition of 0-1.5 equiv of F^- (as tetrabutalammonium salt) to **PCP 1** (10.0 mM).

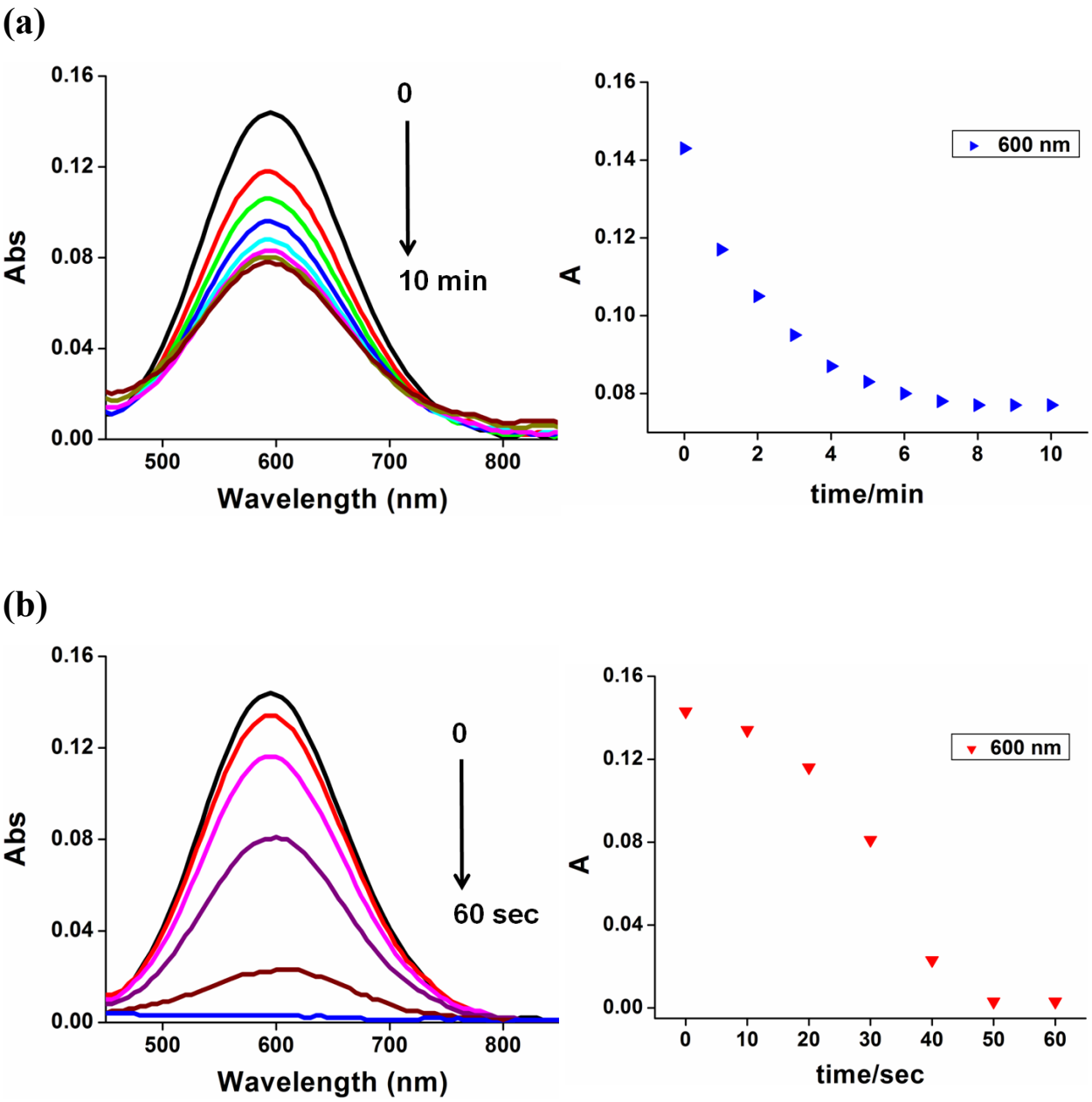


Figure S17 Time-dependent absorption spectral changes (top) and time-dependent absorption intensity changes at λ = 600 nm (bottom) of **PCP 1** (5.0×10^{-6} M) in the absence or presence of 5 equiv (a) TBAF (5.0×10^{-5} M) and (b) TBACN (5.0×10^{-5} M) in DCM solution.

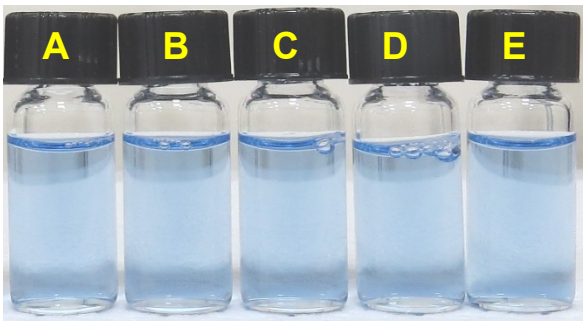


Figure S18 Colour responses of **PCP 1** (A; 1 μM) in Triton X-100-water solution in the presence of 1 μM (B), 1.5 μM (C), 2.5 μM (D), and 5 μM (E) of NaF after 10 min of incubation.

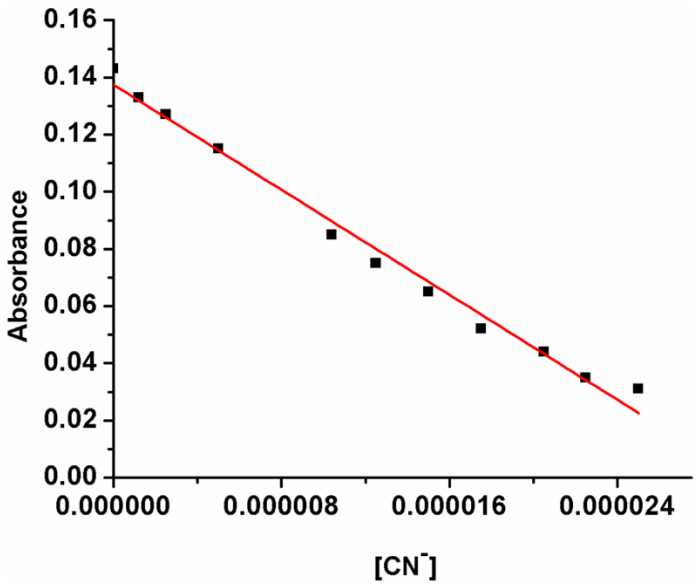


Figure S19 Changes in the absorbance at 600 nm in micellar solutions of **PCP 1** (2×10^{-5} M) *versus* increasing quantities of CN^-.

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