Electronic Supplementary Material (ESI) for Polymer Chemistry

Colorimetric sensing of cations and anions by clicked polystyrenes bearing side chain donor-acceptor chromophores

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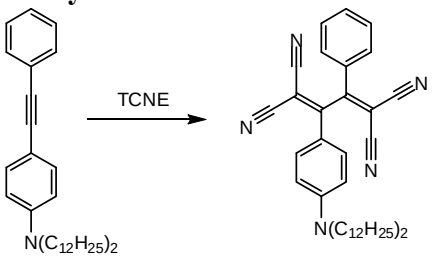
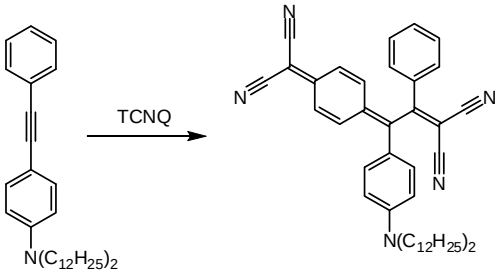
1. Synthesis and characterization



7 3

2-[4-(Didodecylamino)phenyl]-3-phenylbuta-1,3-diene-1,1,4,4-tetracarbonitrile (3). To a solution of *N*,*N*-didodecyl-4-(phenylethynyl)aniline (55 mg, 0.104 mmol) in CH_2Cl_2, TCNE (13.3 mg, 0.104 mmol) was added under nitrogen, and the mixture was stirred at 20 °C for 18 h. Removal of the solvent in vacuo and column chromatography (SiO_2, CH_2Cl_2) yielded the desired compound **3** (65.7 mg, 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.88 (*t*, *J* = 6.6 Hz, 6 H), 1.24-1.33 (*m*, 36 H), 1.63 (*br s*, 4 H), 3.37 (*t*, *J* = 7 Hz, 4 H), 6.65 (*d*, *J* = 9 Hz, 2 H), 7.53 (*t*, *J* = 9 Hz, 2 H), 7.61 (*t*, *J* = 7 Hz, 1 H), 7.74 (*d*, *J* = 9 Hz, 2 H), 7.78 ppm (*d*, *J* = 9 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.13, 22.63, 26.93, 27.28, 29.33, 29.50, 29.52, 29.55, 29.64, 29.69, 31.84, 51.42, 72.61, 86.96, 111.31, 112.04, 112.13, 114.57, 117.24, 129.45, 129.66, 131.87, 132.74, 134.20, 150.19, 152.99, 162.38, 162.49 ppm. IR (neat): ν = 2923, 2852, 2215, 1602, 1485, 1416, 1345, 1210, 1181 cm^{-1}. MALDI-TOF MS (dithranol): *m/z*: calcd for $C_{44}H_{59}N_5^+$: 657.48 g mol^{-1}; found: 657.35 g mol^{-1} $[M]^+$.



7 4

(4-{3,3-Dicyano-1-[4-(didodecylamino)phenyl]-2-phenylprop-2-en-1-ylidene}cyclohexa-2,5-dien-1-ylidene)propanedinitrile (4). To a solution of *N*,*N*-didodecyl-4-(phenylethynyl)aniline **7** (55 mg, 0.104 mmol) in 1,2-dichlorobenzene, TCNQ (21.2 mg, 0.104 mmol) was added under nitrogen, and the mixture was heated to 160 °C for 18 h. Removal of the solvent in vacuo and column chromatography (SiO_2, CH_2Cl_2) yielded the desired compound **4** (78.7 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.85 (*t*, *J* = 8.4 Hz, 6 H), 1.25-1.33 (*m*, 36 H), 1.62 (*br s*, 4 H), 3.34 (*t*, *J* = 7 Hz, 4 H), 6.64 (*d*, *J* = 9 Hz, 2 H), 6.92 (*dd*, *J* = 9.2 Hz, 1 H), 7.12 (*dd*, *J* = 9, 2 Hz, 1 H), 7.26 (*d*, *J* = 9 Hz, 2 H), 7.46-7.65 (*m*, 5 H), 7.67 ppm (*d*, *J* = 9 Hz, 2 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 14.06, 22.62, 26.97, 27.33, 29.26, 29.34, 29.50, 29.55, 29.56, 29.64, 31.90, 51.36, 70.23, 87.43, 112.16, 112.44, 112.90, 115.04, 123.00, 124.55, 124.91, 129.54, 129.58, 130.93, 133.53, 134.23, 134.72, 134.82, 135.77, 151.52, 151.79, 154.04, 172.90 ppm. IR (KBr): ν = 2922, 2851, 2202, 1576, 1395, 1344, 1167 cm^{-1}. MALDI-TOF MS (dithranol): *m/z*: calcd for $C_{50}H_{63}N_5^+$: 734.07 g mol^{-1}; found: 733.9 g mol^{-1} $[M]^+$.

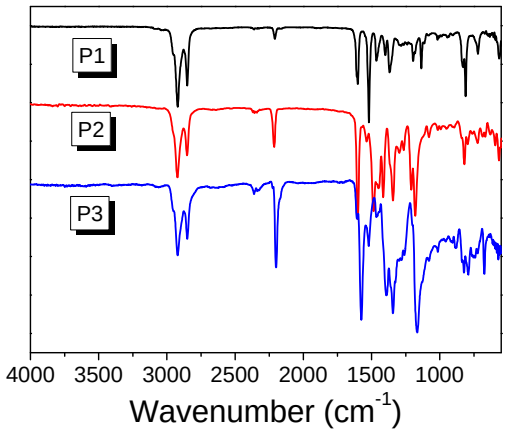


Fig. S1 IR spectra of **P1**, **P2** and **P3**.

2. Thermogravimetric analysis

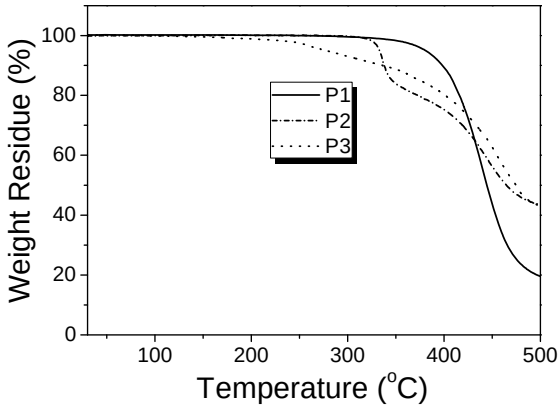


Fig. S2 TGA curves of polymers **P1**, **P2**, and **P3** at the heating rate of 10 ^{o}C min^{-1} under flowing nitrogen.

3. Electrochemistry

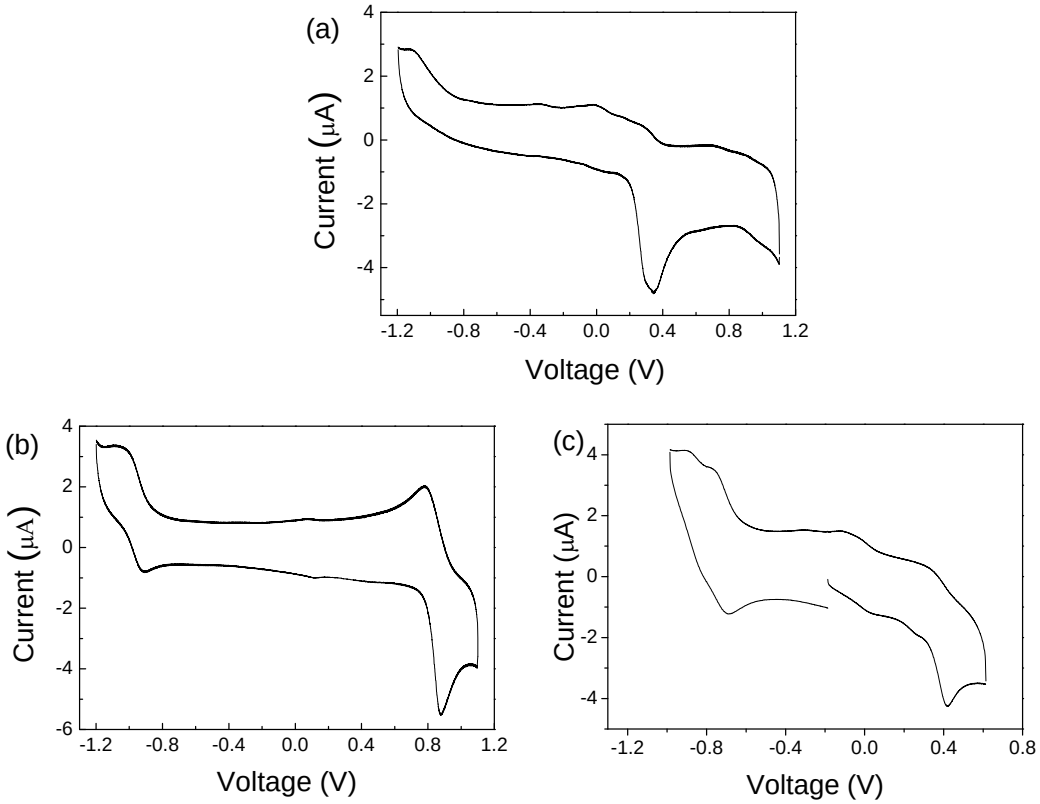


Fig. S3 Cyclic voltammograms of (a) **P1**, (b) **P2**, and (c) **P3** in CH_2Cl_2 (+0.1 M $(nC_4H_9)_4NClO_4$) at 20 °C.

Table S1 Summary of the electrochemistry data of the polystyrenes in CH_2Cl_2 (+ 0.1 M $(nC_4H_9)_4NClO_4$).[a]

polymer	$E_{ox,1}$ (V)	$E_{red,1}$ (V)	$\Delta(E_{ox,1}\text{-}E_{red,1})$ (V)	λ_{end} (nm [eV])
P1	0.34	-	-	-
P2	0.83	-1.00	1.83	750 [1.65]
P3	0.43	-0.72	1.15	1130 [1.09]

[a] Potentials vs. Fc/Fc^+. Working electrode: glassy carbon electrode; counter electrode: Pt; reference electrode: Ag/AgCl.

4. UV-vis-near IR spectra

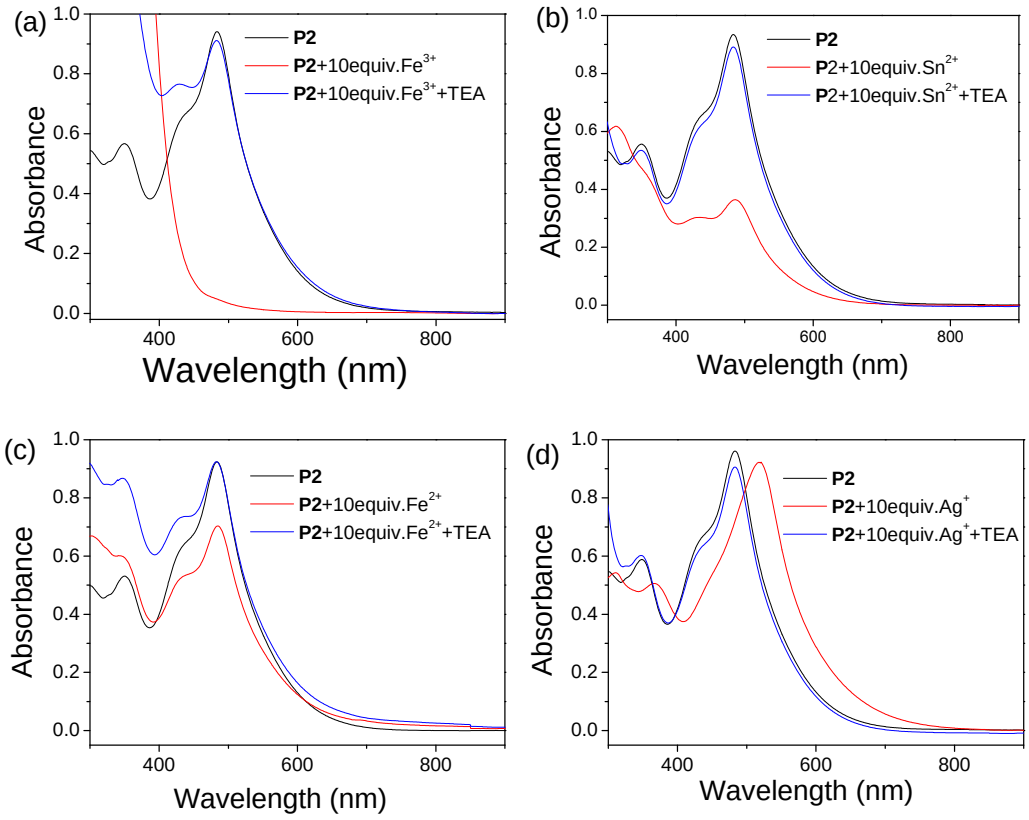


Fig. S4 UV-vis spectral changes of **P2** in $CHCl_3$ upon the addition of (a) Fe^{3+}, (b) Sn^{2+}, (c) Fe^{2+}, and (d) Ag^{+} ions, followed by triethylamine (TEA) at 20 ^{o}C.

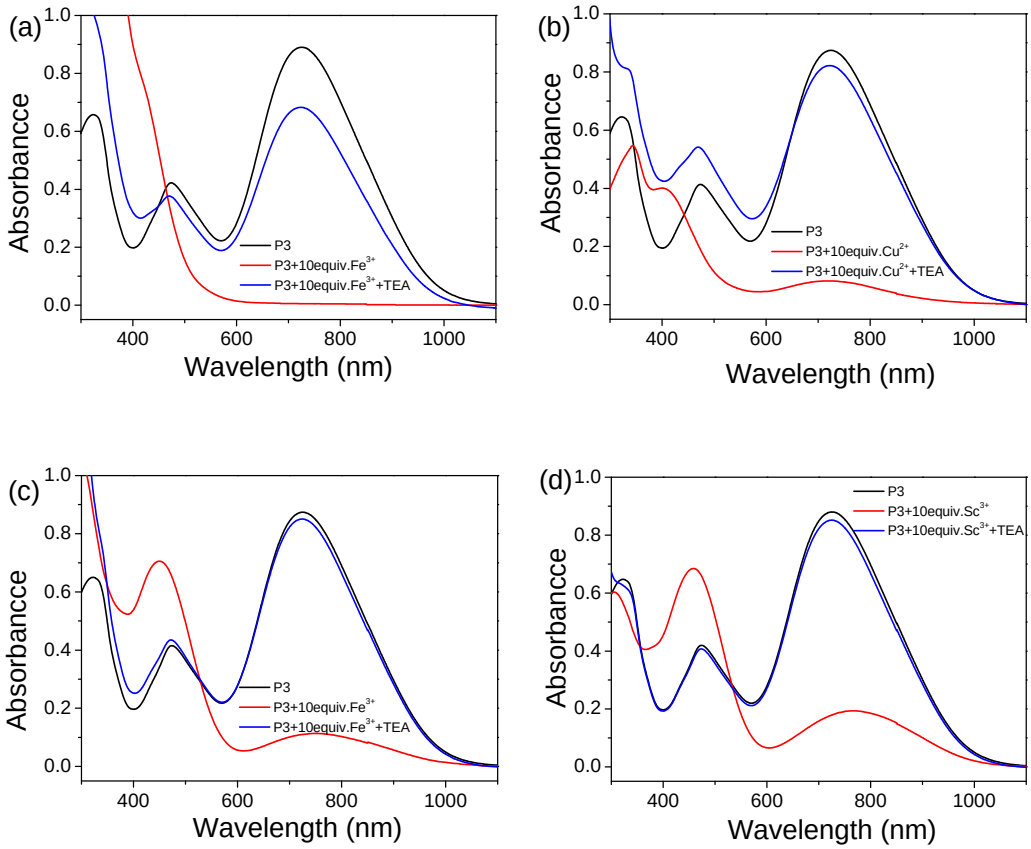


Fig. S5 UV-vis-near IR spectral changes of **P3** in $CHCl_3$ upon the addition of (a) Fe^{3+}, (b) Cu^{2+}, (c) Ti^{4+}, and (d) Sc^{3+} ions, followed by triethylamine (TEA) at 20 ^{o}C.

5. X-ray crystallography

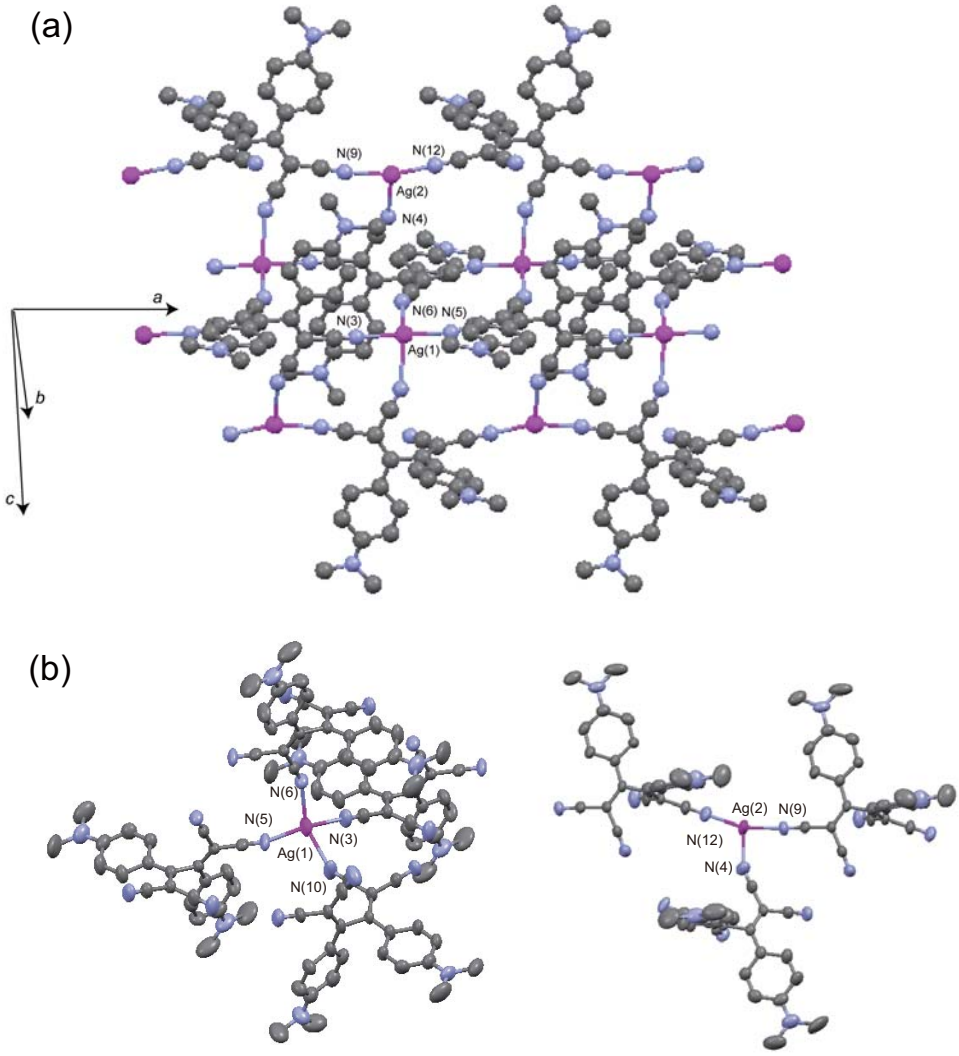


Fig. S6 (a) Crystal structure of the Ag^+ complex with **5** and (b) magnified coordination structures of Ag(1) and Ag(2) to the cyano groups of **5**. Hydrogen atoms and counter anions (OTf) are omitted for clarity.

6. Spectroscopic titration experiments of metal ions

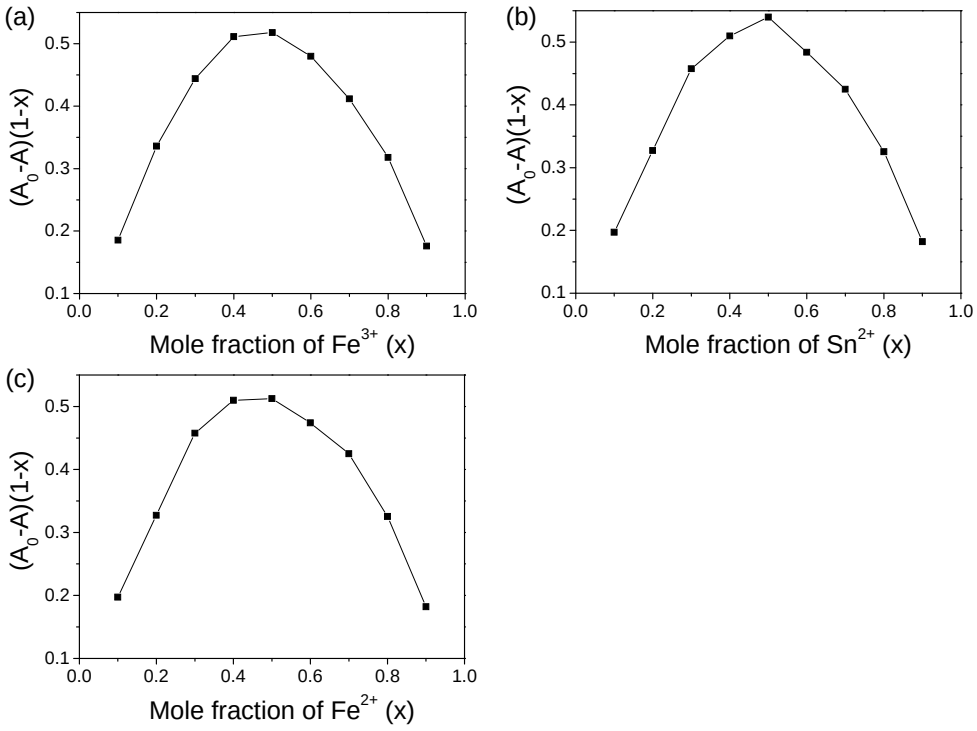


Fig. S7 Job plot analysis of **1** with (a) Fe^{3+}, (b) Sn^{2+}, and (c) Fe^{2+} ions in $CHCl_3$. The total concentration of **1** and metal ions is 60 μM.

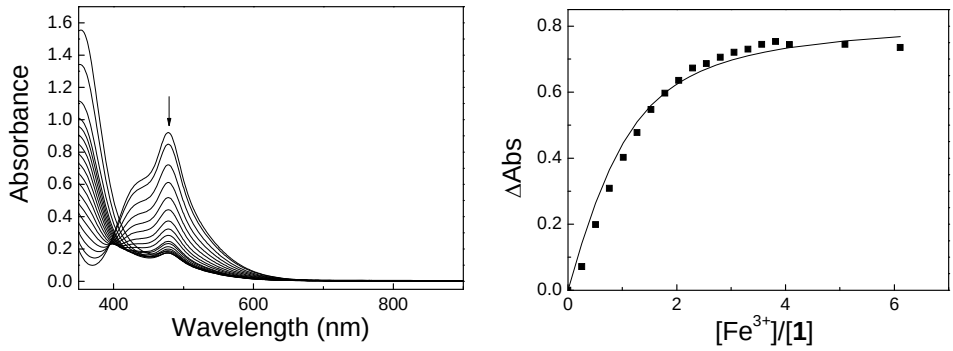


Fig. S8 UV-vis spectral changes of **1** (40.5 μM) in $CHCl_3$ upon the addition of Fe^{3+} ion (0-6 equiv.). A cuvette with a light-path length of 1 cm was used. ΔAbs was monitored at 469 nm.

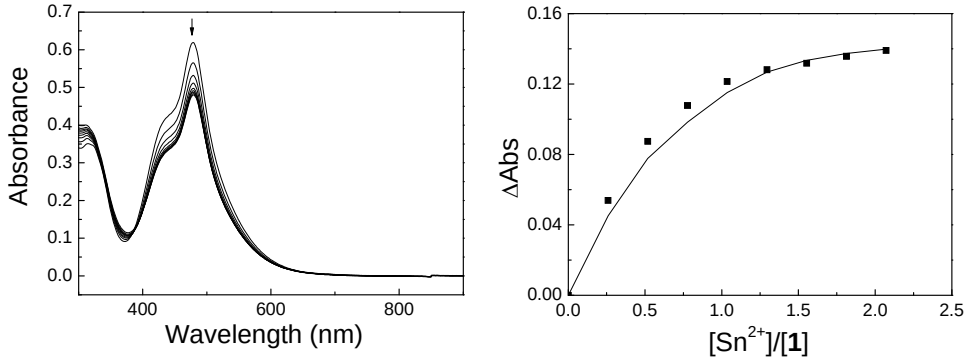


Fig. S9 UV-vis spectral changes of **1** (40.5 μM) in $CHCl_3$ upon the addition of Sn^{2+} ion (0-2 equiv.). A cuvette with a light-path length of 1 cm was used. ΔAbs was monitored at 469 nm.

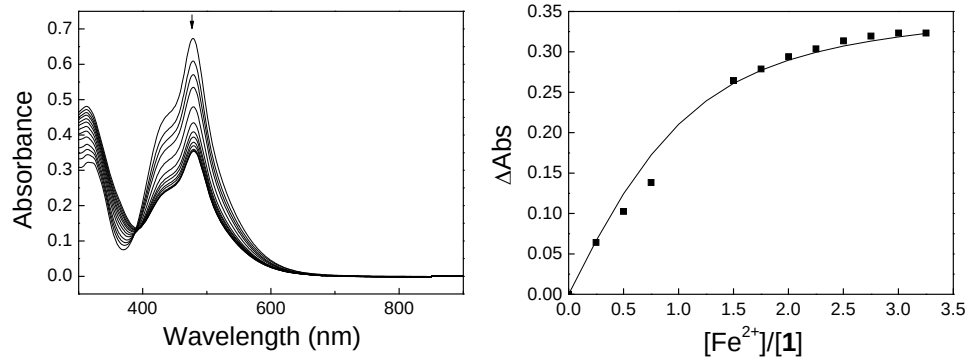


Fig. S10 UV-vis spectral changes of **1** (314 μM) in $CHCl_3$ upon the addition of Fe^{2+} ion (0-3 equiv.). A cuvette with a light-path length of 1 mm was used. ΔAbs was monitored at 469 nm.

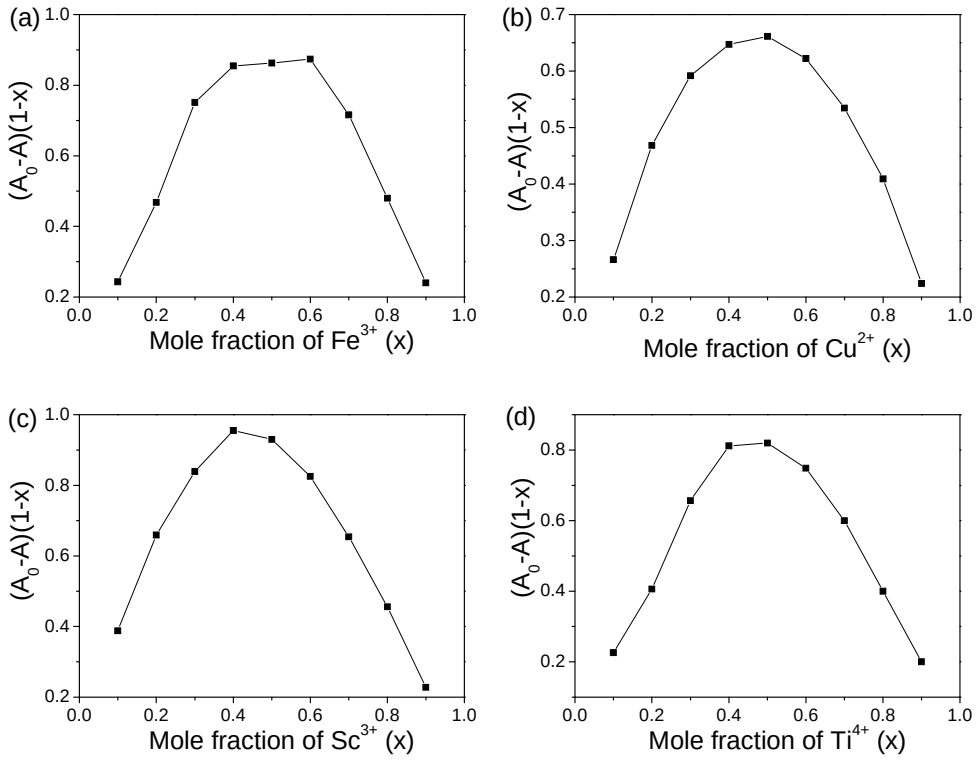


Fig. S11 Job plot analysis of **2** with (a) Fe^{3+}, (b) Cu^{2+}, (c) Sc^{3+}, (d) and Ti^{4+} ions in $CHCl_3$. The total concentration of **2** and metal ions is 60 μM.

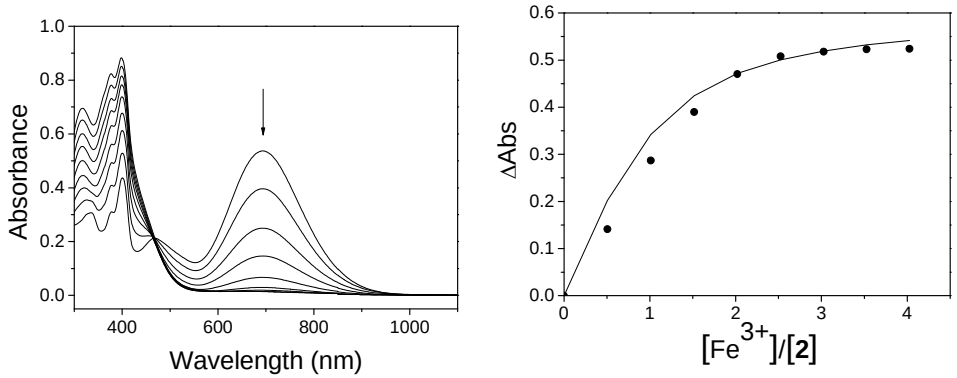


Fig. S12 UV-vis-near IR spectral changes of **2** (30.0 μM) in $CHCl_3$ upon the addition of Fe^{3+} ion (0-4 equiv.). A cuvette with a light-path length of 1 cm was used. ΔAbs was monitored at 698 nm.

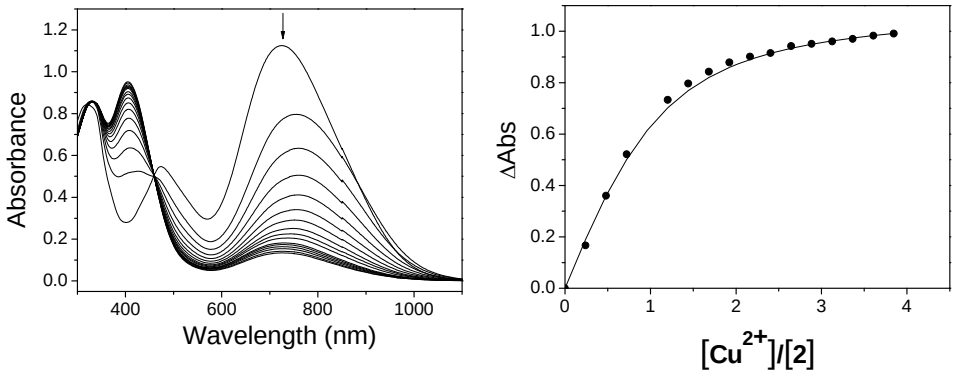


Fig. S13 UV-vis-near IR spectral changes of **2** (35.0 μM) in $CHCl_3$ upon the addition of Cu^{2+} ion (0-4 equiv.). A cuvette with a light-path length of 1 mm was used. ΔAbs was monitored at 698 nm.

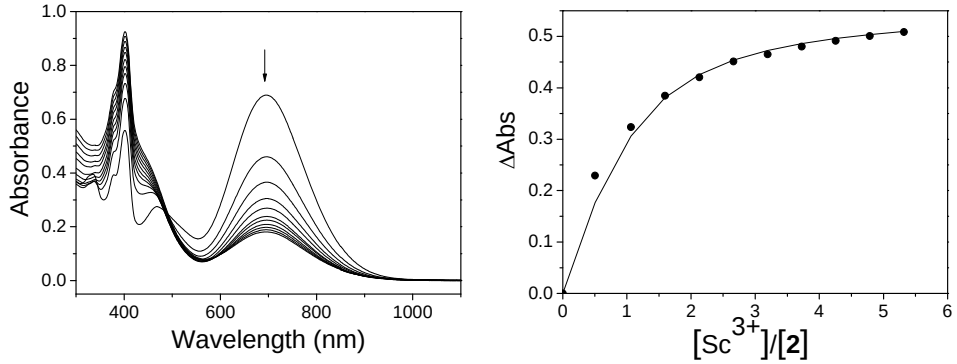


Fig. S14 UV-vis-near IR spectral changes of **2** (33.3 μM) in $CHCl_3$ upon the addition of Sc^{3+} ion (0-5 equiv.). A cuvette with a light-path length of 1 cm was used. ΔAbs was monitored at 698 nm.

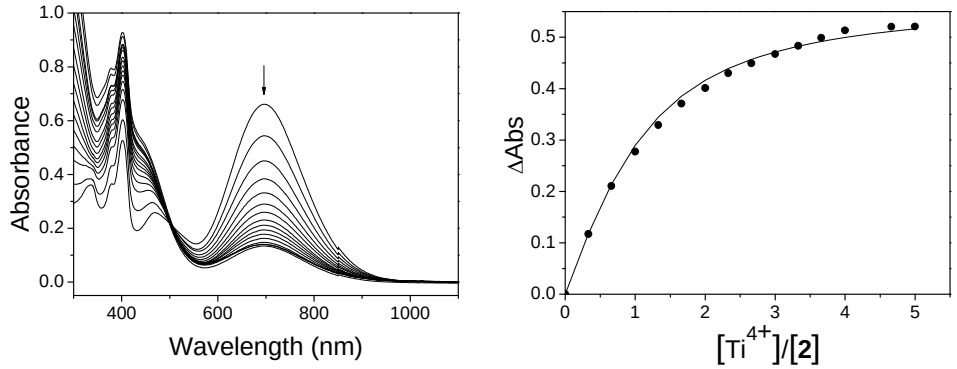


Fig. S15 UV-vis-near IR spectral changes of **2** (33.3 μM) in $CHCl_3$ upon the addition of Ti^{4+} ion (0-5 equiv.). A cuvette with a light-path length of 1 cm was used. ΔAbs was monitored at 698 nm.

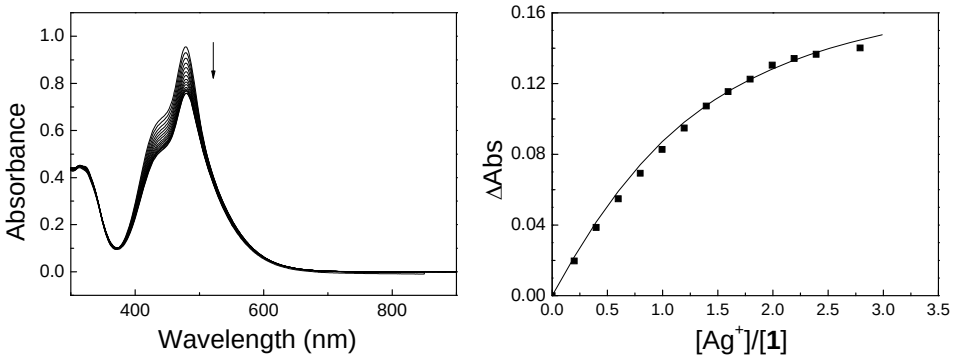


Fig. S16 UV-vis spectral changes of **1** (314 μM) in $CHCl_3$ upon the addition of Ag^+ ion (0-2 equiv.). A cuvette with a light-path length of 1 mm was used. ΔAbs was monitored at 469 nm.

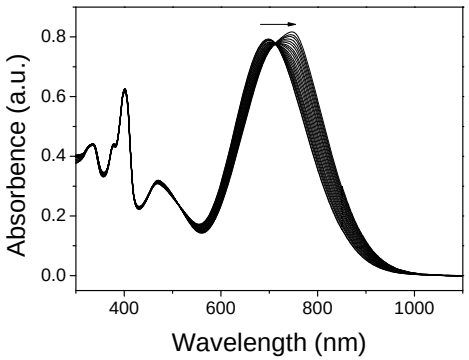


Fig. S17 UV-vis-near IR spectral changes of **2** (33.3 μM) in $CHCl_3$ upon the addition of Ag^+ ion (0-10 equiv.). A cuvette with a light-path length of 1 mm was used.

7. Spectroscopic titration experiments of anions

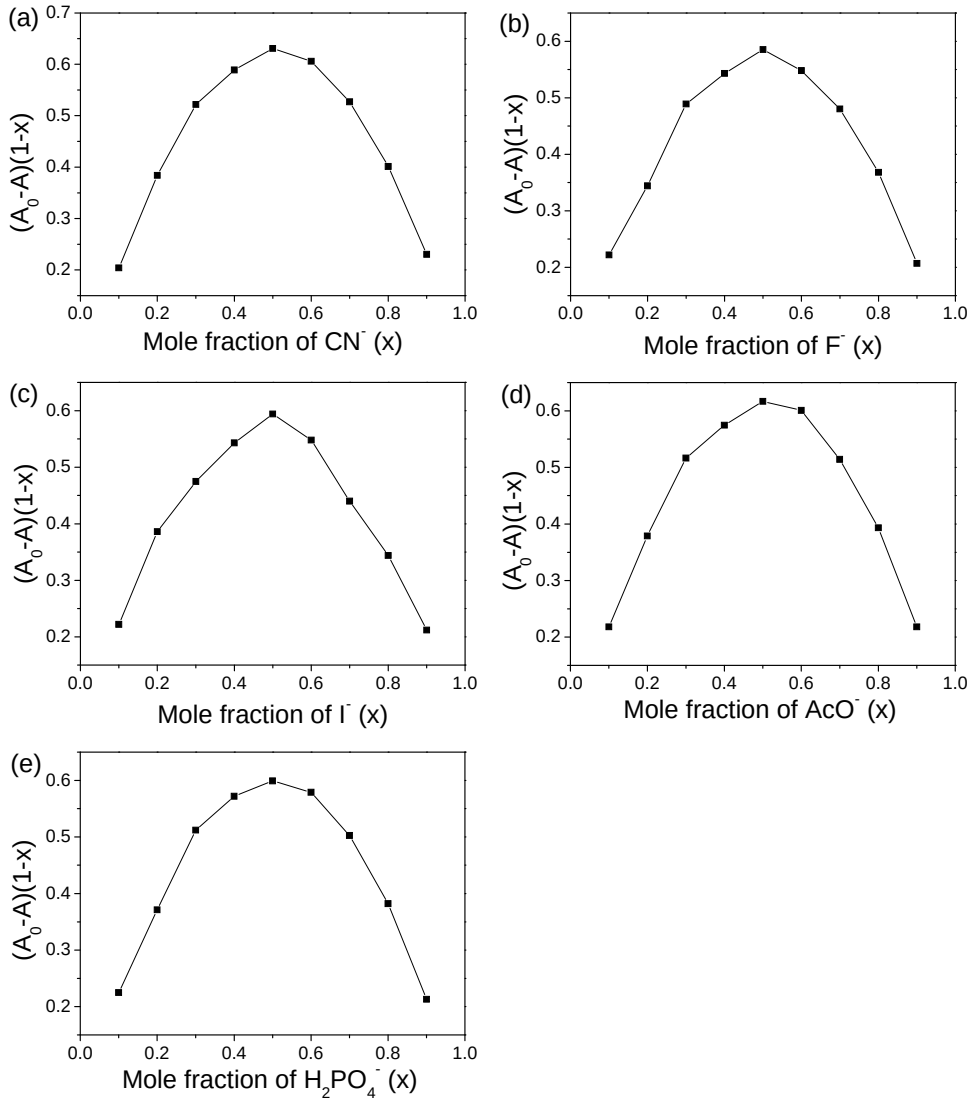


Fig. S18 Job plot analysis of **3** with (a) CN^-, (b) F^-, (c) I^-, (d) AcO^-, and (e) $H_2PO_4^-$ ions in THF. The total concentration of **3** and anions is 40 μM.

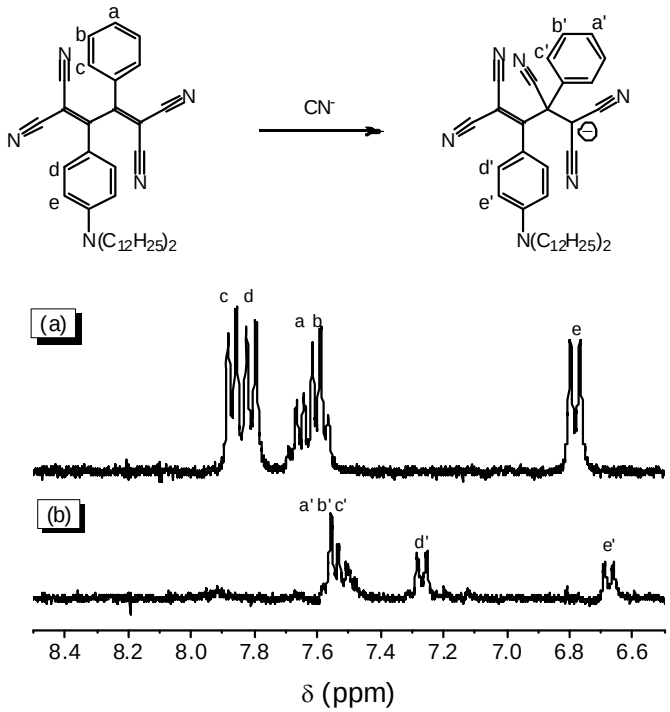


Fig. S19 ^{1}H NMR spectra of (a) **3** and (b) **3** upon the addition of a slight excess CN^- ion (2 equiv.) in DMSO-d_6 at 20 ^{o}C.

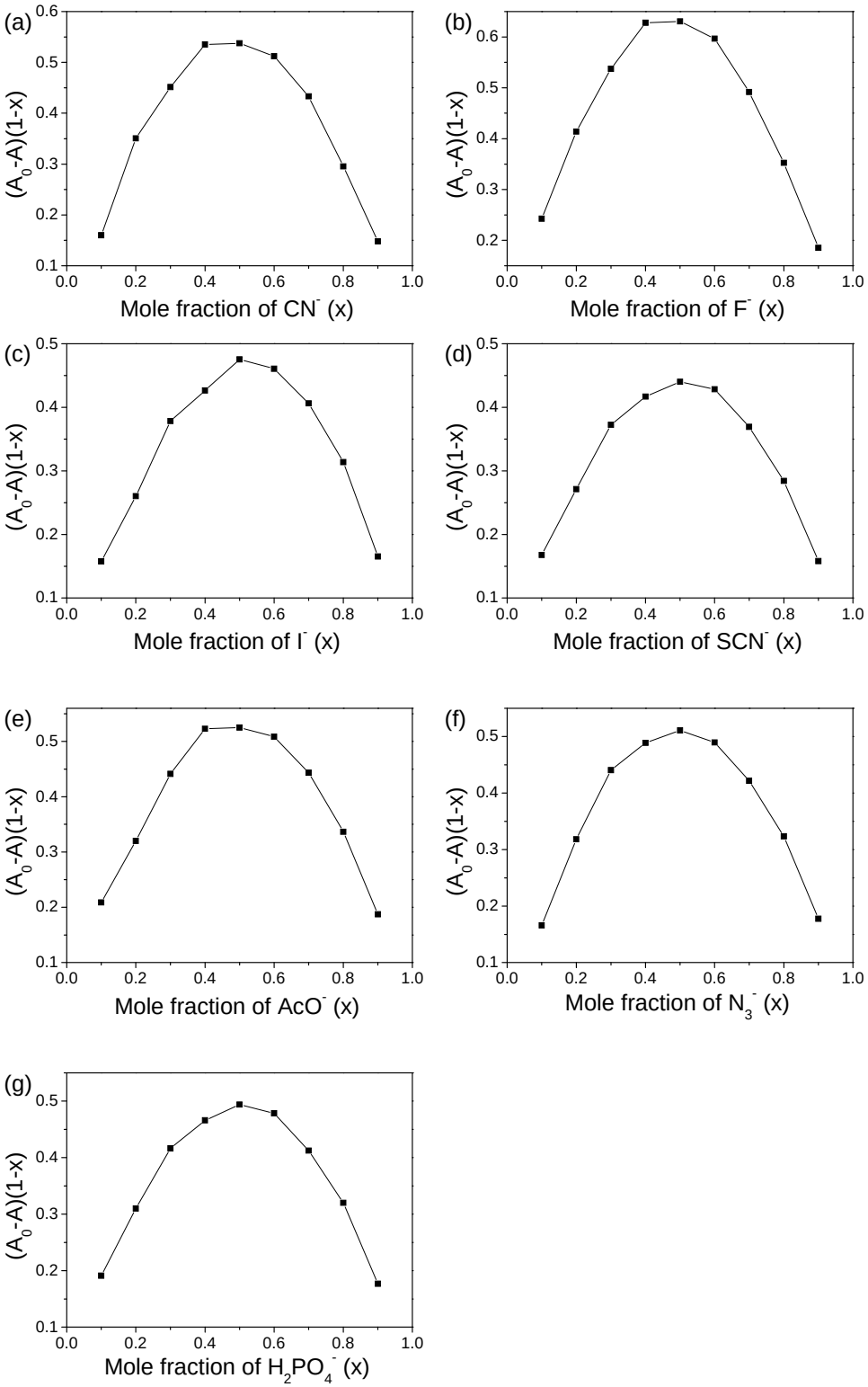


Fig. S20 Job plot analysis of **4** with (a) CN^-, (b) F^-, (c) I^-, (d) SCN^-, (e) AcO^-, (f) N_3^-, and (g) $H_2PO_4^-$ ions in THF. The total concentration of **4** and anions is 40 μM.

8. Competitive experiments

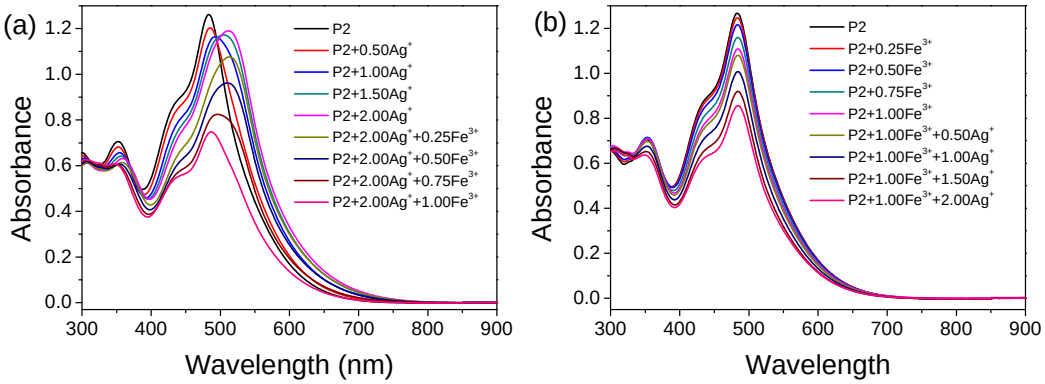


Fig. S21 UV-vis spectral change of **P2** in $CHCl_3$ (a) upon the addition of Ag^+ ion (0-2 equiv.) followed by addition of Fe^{3+} ion (0-1 equiv.) and (b) upon the addition of Fe^{3+} ion (0-1 equiv.) followed by the addition of Ag^+ ion (0-2 equiv.).

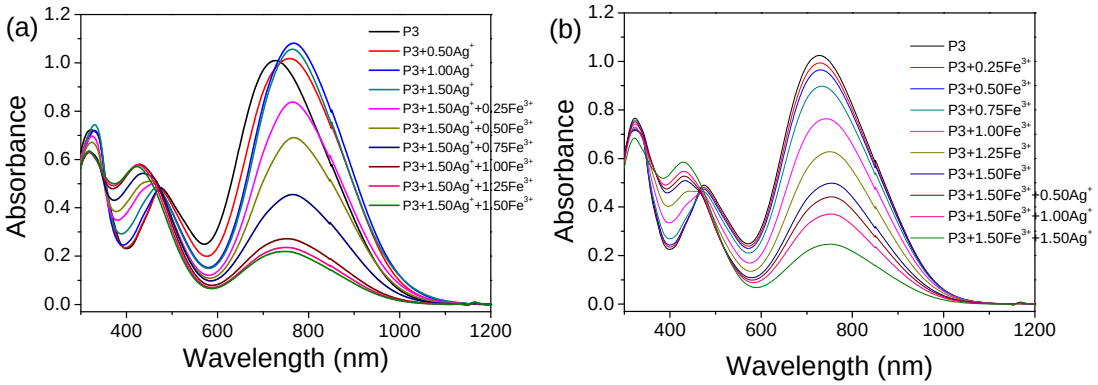


Fig. S22 UV-vis spectral change of **P3** in $CHCl_3$ (a) upon the addition of Ag^+ ion (0-1.5 equiv.) followed by the addition of Fe^{3+} ion (0-1.5 equiv.) and (b) upon the addition of Fe^{3+} ion (0-1.5 equiv.) followed by the addition of Ag^+ ion (0-1.5 equiv.).