Electronic Supplementary Information (ESI) for:

Colorimetric "Naked eye" detection of CN⁻, F⁻, CH₃COO⁻ and H₂PO₄⁻ ions by highly nonplanar electron deficient perhaloporphyrins

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Fig. S19. DPV traces of **1-4** in absence and presence of excess [F⁻] in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ at 298K.

Fig. S20. DPV titrations of **2-4** while increasing the concentration of F⁻ ion in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$ at 298K.

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Fig. S22. Overlayed UV-Visible Spectra of **1-4** with excess of *p*-toluene sulphonic acid, piperidine and fluoride ion in toluene at 298 K.

Fig. S23. (a) UV-Vis spectral titrations of **3** with TBACl (0.008 M) in toluene at 298 K. Inset shows the change in Soret region from 460-495 nm; (b) Hill plot log(A$_i$-A$_0$/A$_f$-A$_i$) *Vs* log [Cl⁻] showing 1:1 stoichiometry indicated by slope 1.

Fig. S24. (a) Treatment of **1**•2CN⁻ complex with aliquots of 1 mM solution TFA at 298 K. (b) Reusability test of regenerated **1** with aliquots of 8 mM solution of CN⁻ ions in toluene at 298 K.

Fig. S25. (a) Treatment of **2**•2CN⁻ complex with sufficient amount of TFA and (b) the colorimetric response for reversibility and reusability test.

Fig. S26. (a) Treatment of **3**•2CN⁻ complex with sufficient amount of TFA and (b) the colorimetric response for reversibility and reusability test.

Fig. S27. (a) Treatment of **4**•2CN⁻ complex with sufficient amount of TFA and (b) the colorimetric response for the reversibility and reusability test.

Table 1. UV-Vis absorption spectra data of **1** and **3** and fluorescence spectra of **1-4** in toluene at 298 K.

Table 2. Crystal structure data of 2,3,7,8,12,13,17,18-Octachloro-*meso*-tetraphenylporphyrin (**2**).
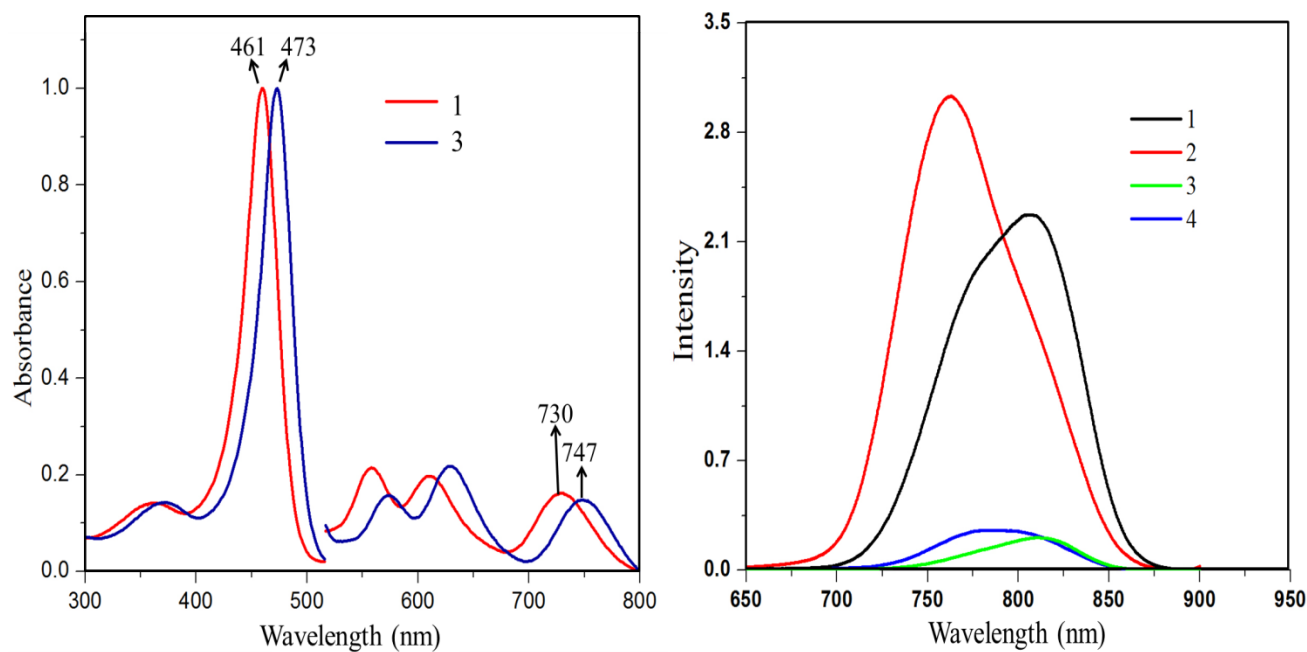
Table 3. Selected average bond lengths and bond angles of 2,3,7,8,12,13,17,18-Octachloro-*meso*-tetraphenylporphyrin (**2**).

Table 4. Selected average bond lengths and bond angles of 2-nitro-3,7,8,12,13,17,18-heptachloro-*meso*-tetraphenylporphyrin (**1**).

Table 5. Electrochemical redox potentials of **1-4** in CH$_2$Cl$_2$ at 298 K.

Table 6. Electronic absorption spectral data of **1-4** in presence of excess TFA, TBAOH and various anions in CH₂Cl₂ at 298 K.

Table 7. The detection limits (LOD) and quantification limits (LOQ) of anions by **1-4** in toluene.
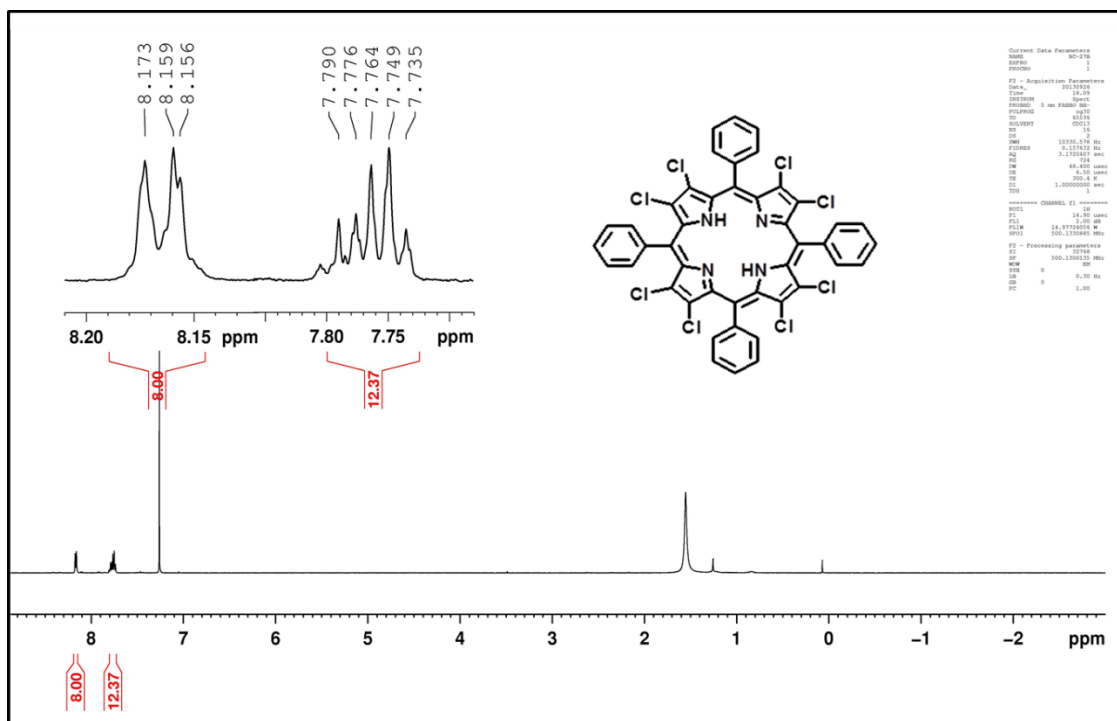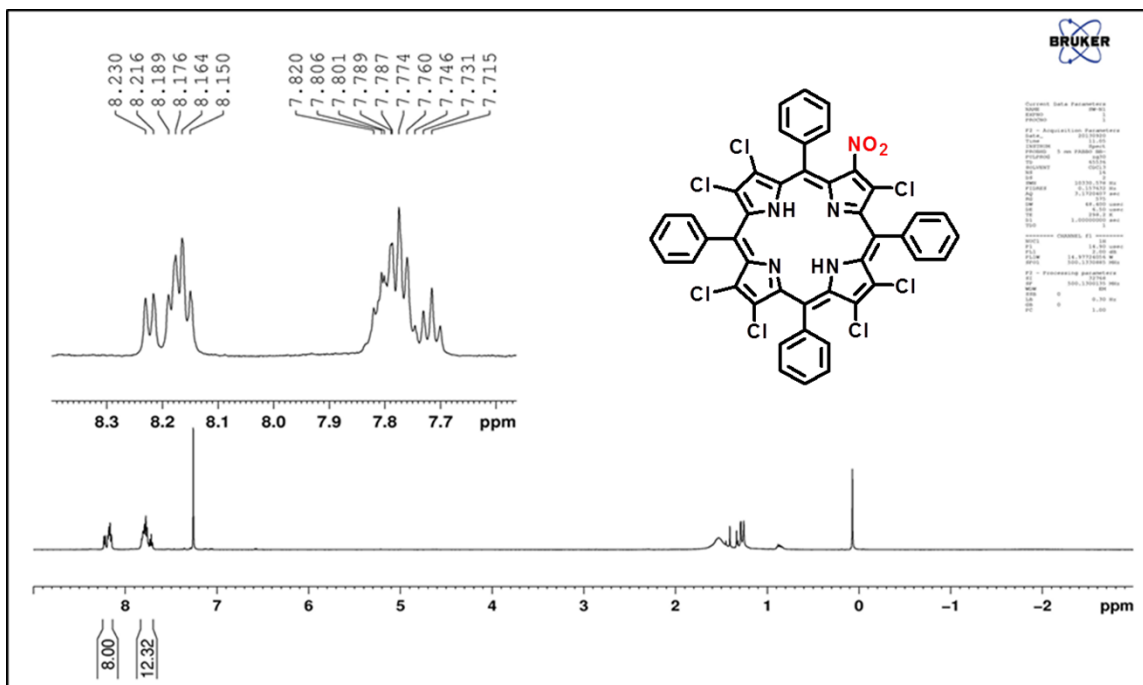

Figure S1. UV-Vis absorption spectra of **1** and **3** and fluorescence spectra of **1-4** in toluene at 298 K.
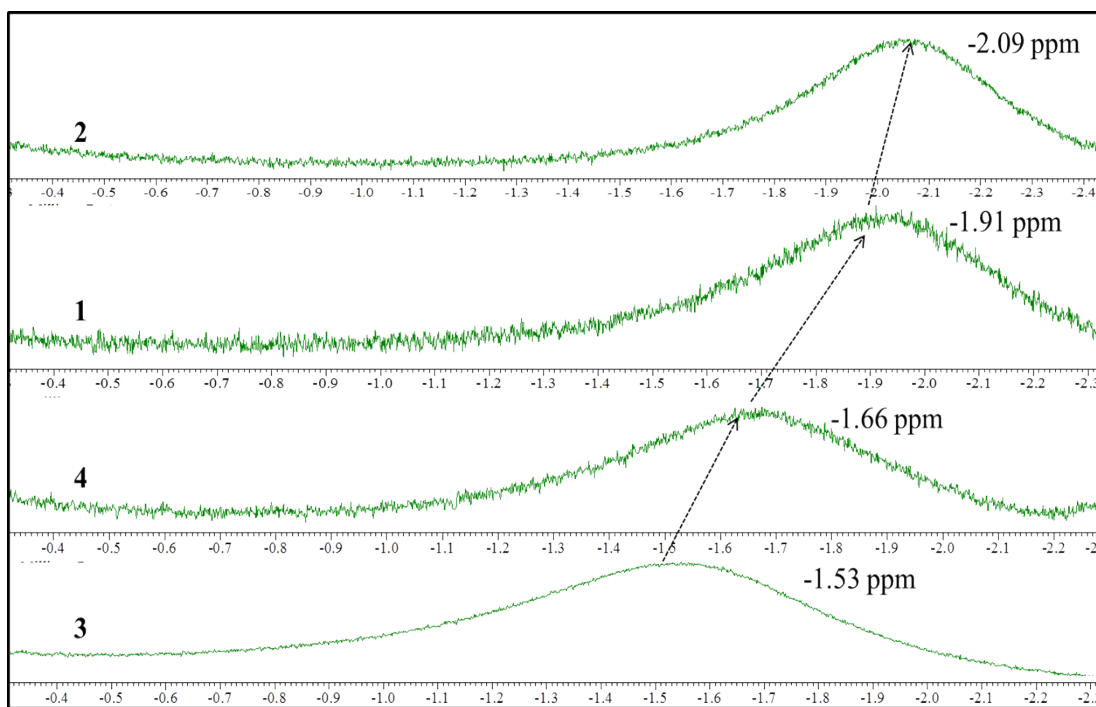
Table S1. UV-Visible and fluorescence spectral data of **1-4** in toluene at 298 K.

Porphyrin	B (Bands)	Q (Bands)	λ_{em}, nm
1	363(26.91), 461(190.5)	559(10.23), 612(9.54), 730(7.58)	809
2	356(24.54), 455(204.1)	552(11.48), 601(11.75), 718(6.17)	762
3	371(33.85), 473(239.9)	574(9.55), 628(13.49), 747(9.12)	816
4	364(31.62), 469(257.0)	570(11.48), 623(16.98), 739(8.70)	789

The values in parentheses refer to $\varepsilon \times 10^{-3} L\ mol^{-1}\ cm^{-1}$

Figure S2. ^{1}H NMR spectra of **1** (top) and **2** (bottom) in CDCl$_3$ at 298K.

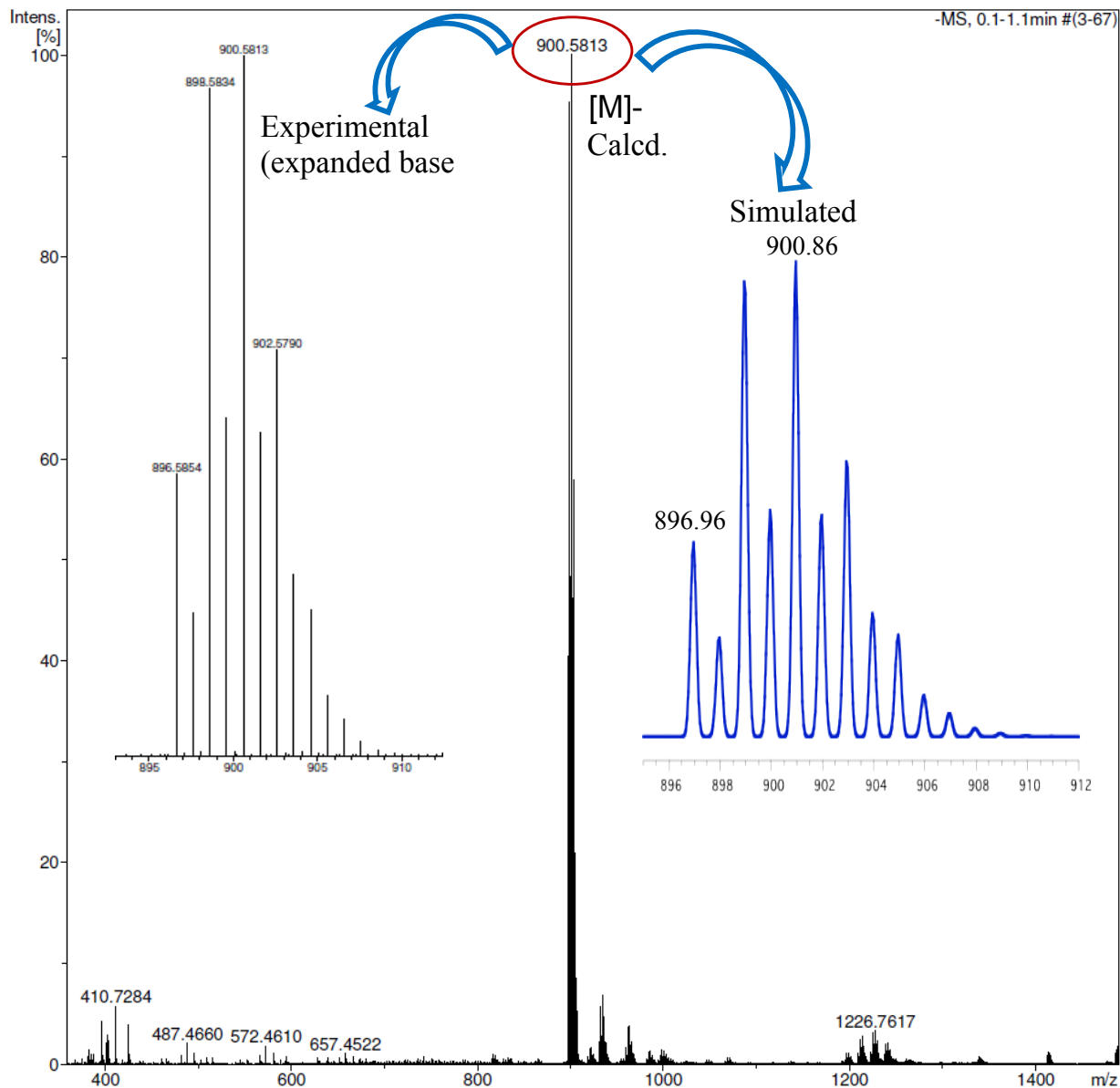**Figure S3.** Imino protons region of **1-4** in CDCl$_3$ at 298K

Display Report

Intens. [%]

-MS, 0.1-1.1min #(3-67)

900.5813
898.5834
902.5790
896.5854

Experimental (expanded base

[M]-
Calcd.

Simulated
900.86

896.96

410.7284
487.4660 572.4610 657.4522
1226.7617

Bruker Compass DataAnalysis 4.0   printed: 11/18/2014 6:44:00 PM   Page 1 of 1

Figure S4. Negative ion mode ESI Mass spectrum of $H_2TPPNO_2Cl_7$ (**1**) in CH_3CN.

Table S2. Crystal structure data of 2,3,7,8,12,13,17,18-Octachloro-*meso*-tetraphenylporphyrin (**2**).

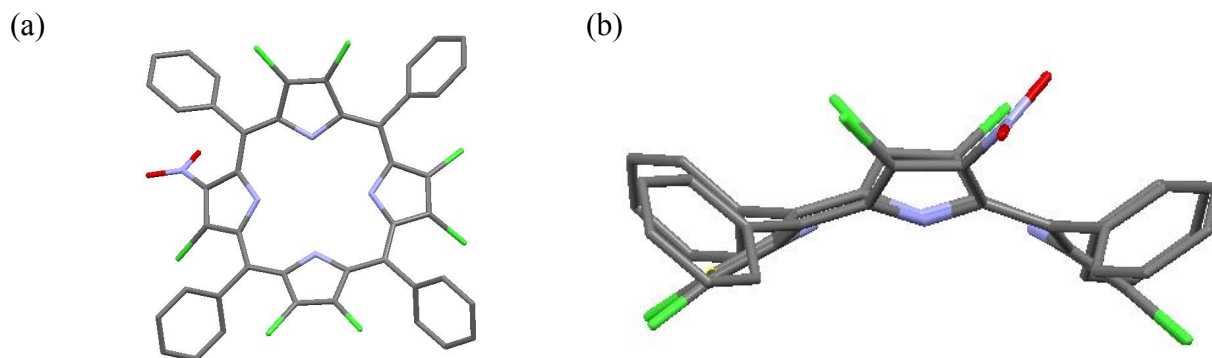|	**2**
Empirical formula	$C_{48}H_{30}N_6Cl_8O_2$
Formula wt.	1006.38
Crystal system	Tetragonal
Space group	I 4_1/a
a (Å)	19.880(3)
b (Å)	19.880(4)
c (Å)	13.1460(15)
$\alpha = \beta = \gamma$ (°)	90
Volume (Å^3)	5195.5(13)
Z	4
D_{cald} (mg/m^3)	1.287
λ (Å)	0.71073
T (°C)	293 K
No. of total reflns.	1781
No. of indepnt. reflns.	1483
R	0.0113
R_w	0.3293
CCDC	1033576

(a)

(b)

Figure S5. The ORTEP diagrams showing top (a) and side (b) views of 2,3,7,8,12,13,17,18-Octachloro-*meso*-tetraphenylporphyrin (**2**).

Table S3. Selected average bond lengths and bond angles of 2,3,7,8,12,13,17,18-Octachloro-*meso*-tetraphenylporphyrin (**2**).

Bond length (Å)		Bond angle (°)	
N-H	0.822(8)	$N-C_\alpha-C_m$	123.9(7)
$N-C_\alpha$	1.355(10)	$N-C_\alpha-C_\beta$	107.2(6)
$C_\alpha-C_\beta$	1.432(10)	$C_\alpha-C_\beta-C_\beta$	107.5(6)
$C_\beta-C_\beta$	1.345(11)	$C_\beta-C_\alpha-C_m$	128.5(7)
$C_\alpha-C_m$	1.411(10)	$C_\alpha-C_m-C_\alpha$	120.6(6)
ΔC_β(Å)	**1.2095**	$C_\alpha-N-C_\alpha$	110.0(6)
$\Delta 24$(Å)	**0.5695**		

[a]ΔC_β refers mean plane deviation of β-carbon atoms, [b]$\Delta 24$ refers mean plane deviation of 24 core atoms
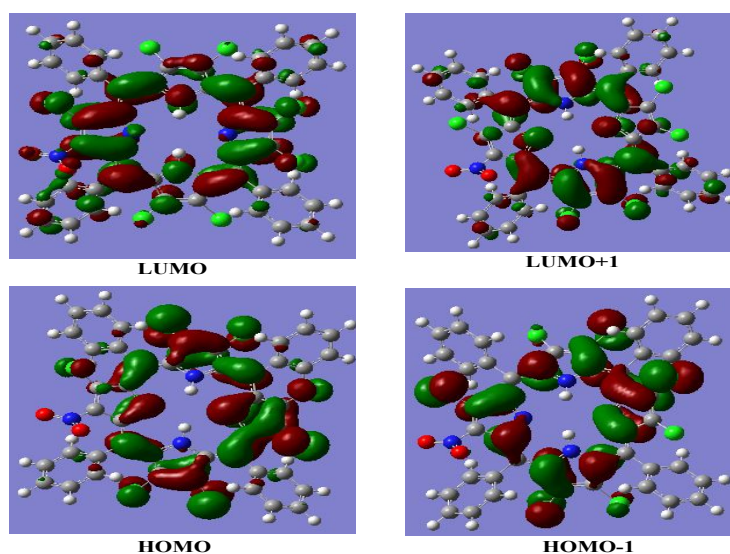
(a)   (b)

Figure S6. B3LYP/6-311G(d,p) optimised geometries showing top (a) as well as side (b) views of **1.**

Table S4. Selected average bond lengths and bond angles of 2-nitro-3,7,8,12,13,17,18-heptachloro-*meso*-tetraphenylporphyrin (**1**).
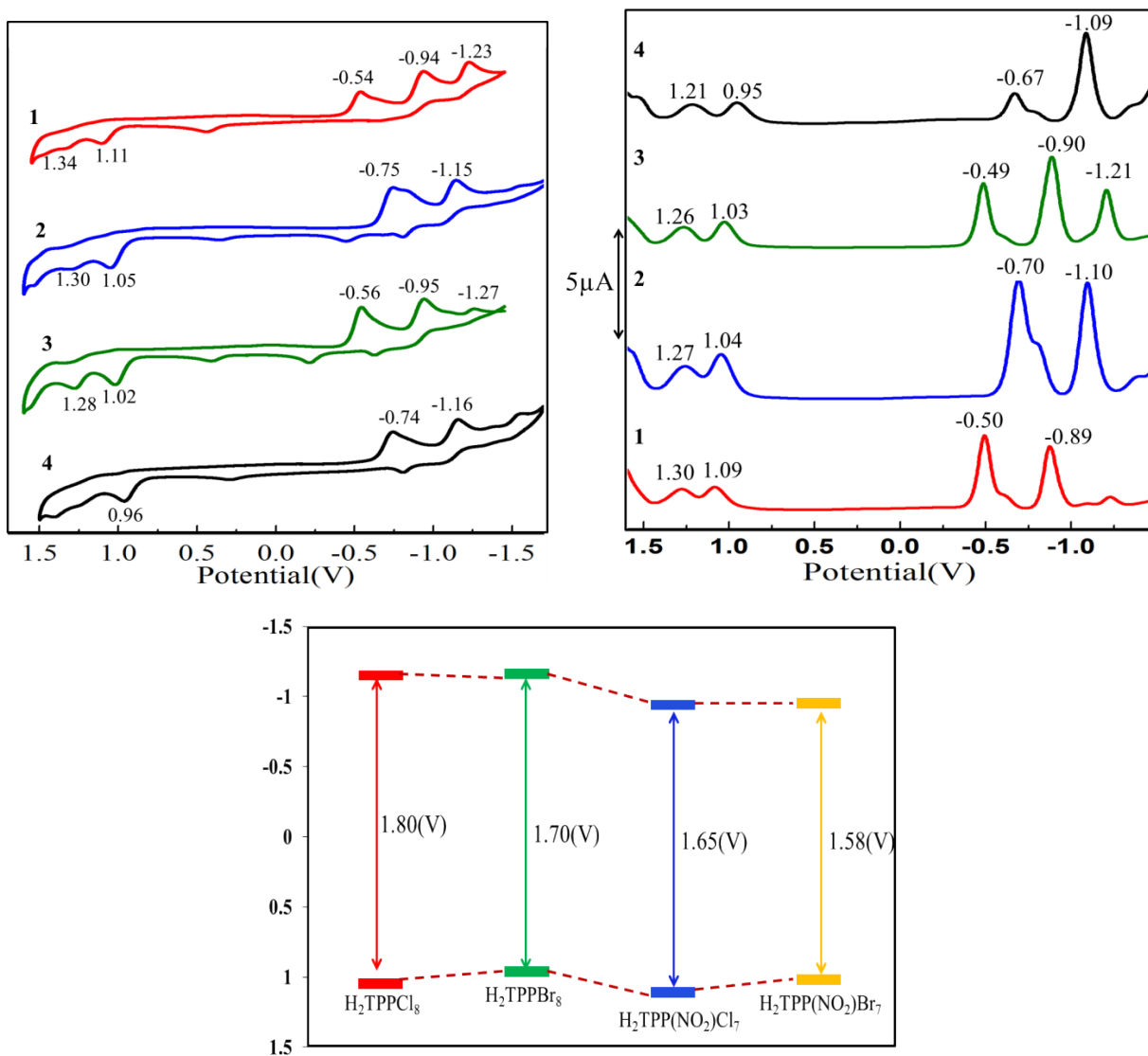

Bond length (Å)		Bond angle (º)	
N′- H	1.011	N- C_α-C_m	124.025
N-C_α	1.360	N-C_α′-C_m	124.623
N′-$C_{\alpha'}$	1.374	N-C_α-C_β	109.335
C_α-C_β	1.462	N-C_α′-C_β′	105.068
C_α′-C_β′	1.440	C_β-C_α-C_m	126.323
C_β-C_β	1.360	C_β′-C_α′-C_m	130.183
C_β′-C_β′	1.376	C_α-C_m-C_α′	122.755
C_α-C_m	1.416	C_α-C_β-C_β	106.635
C_α′-C_m	1.407	C_α-C_β′-C_β′	108.440
ΔC_β(Å)^a	**1.212**	C_α-N-C_α	107.725
$\Delta 24$(Å)^b	**0.515**	C_α′-N-C_α′	112.685

^{a}ΔC_β refers mean plane deviation of *β*-carbon atoms, ^{b}$\Delta 24$ refers mean plane deviation of 24 core atoms.

Figure S7. Pictorial representation of frontier orbitals of 2-nitro-3,7,8,12,13,17,18-heptachloro-*meso*-tetraphenylporphyrin (**1**).
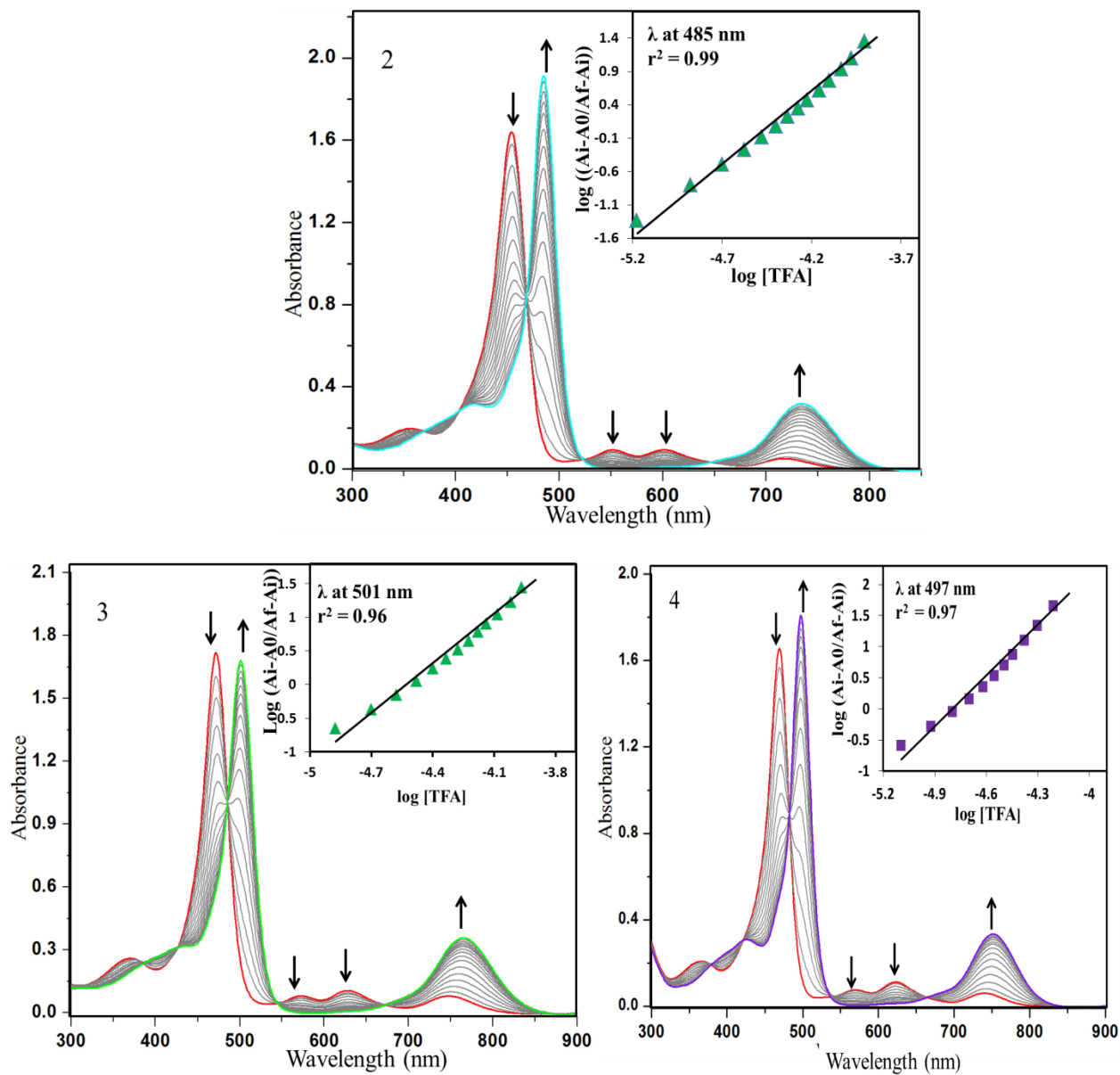
Figure S8. CVs and DPVs of **1-4** in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at 298 K (top). Representation of HOMO-LUMO gap of **1-4** obtained from electrochemical studies (bottom).

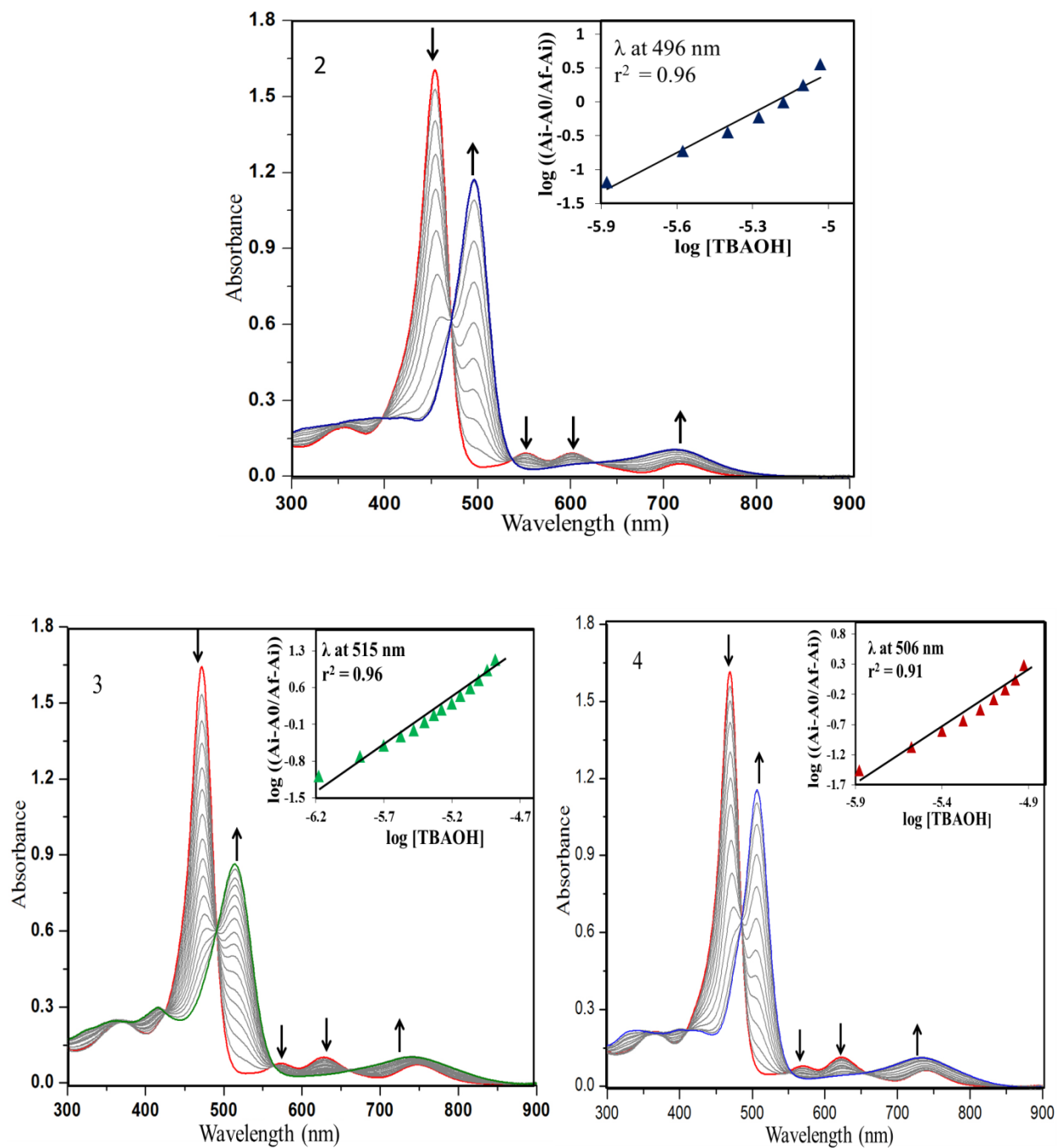**Table S5.** Electrochemical redox potentials[a] of **1-4** in CH_2Cl_2 at 298K.

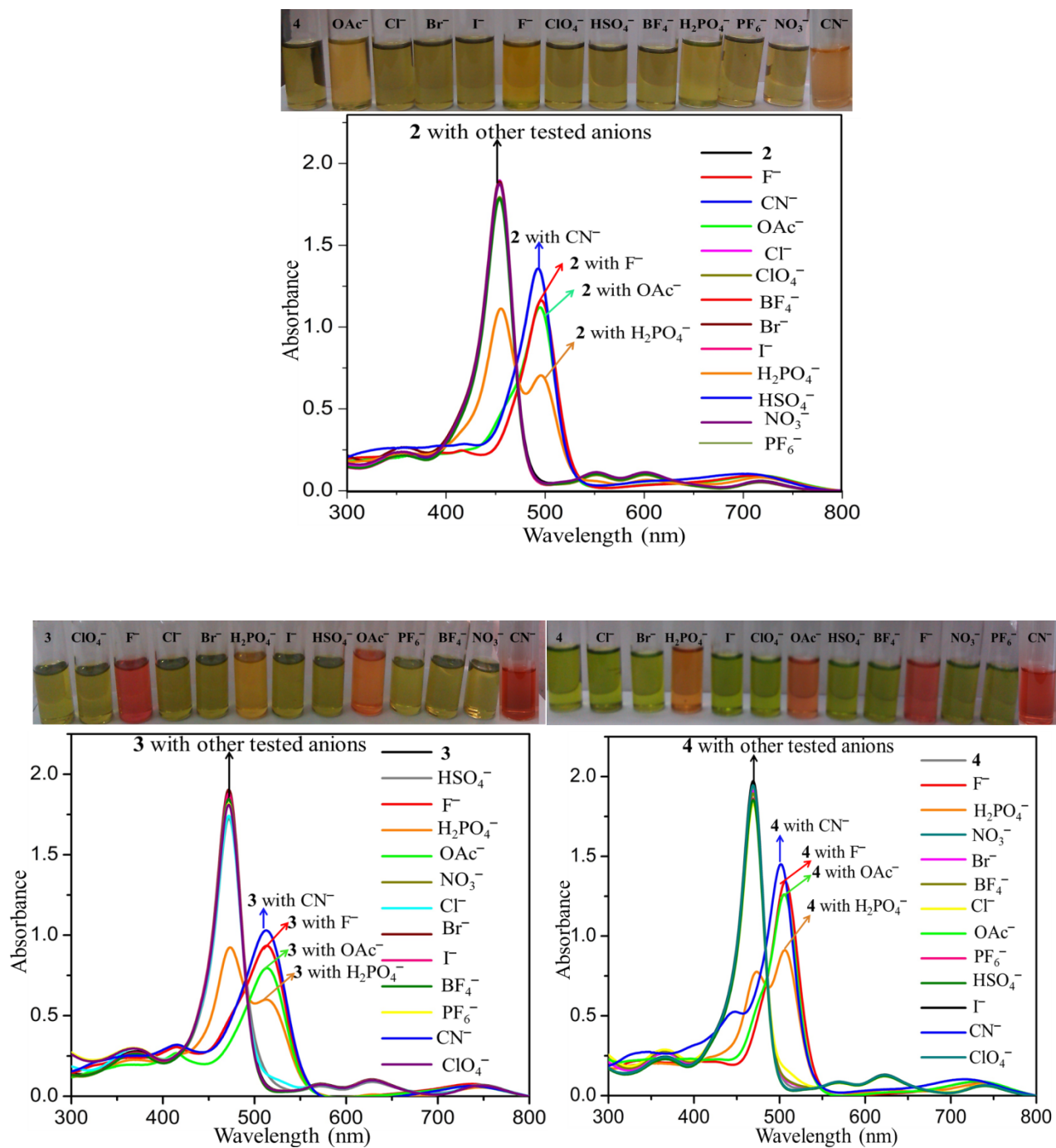| Porphyrin	Oxidation (Volts)		Reduction(Volts)			$\Delta E_{1/2}$ (I_{ox}-I_{red}) (Volts)
	I	II	I	II	III	
1	1.11	1.34	-0.54	-0.94	-1.23	1.65
2	1.05	1.30	-0.75	-1.15	–	1.80
3	1.02	1.28	-0.56	-0.95	-1.27	1.58
4	0.96	1.21[*]	-0.74	-1.16	–	1.70

[a]*vs* Ag/AgCl, [*]data obtained from DPV, all are irreversible potentials.

Figure S9. UV-Vis spectral titrations of **2-4** with TFA (protonation studies) in toluene at 298 K.

Figure S10. UV-Vis spectral titrations of **2-4** with TBAOH (deprotonation studies) in toluene at 298 K.
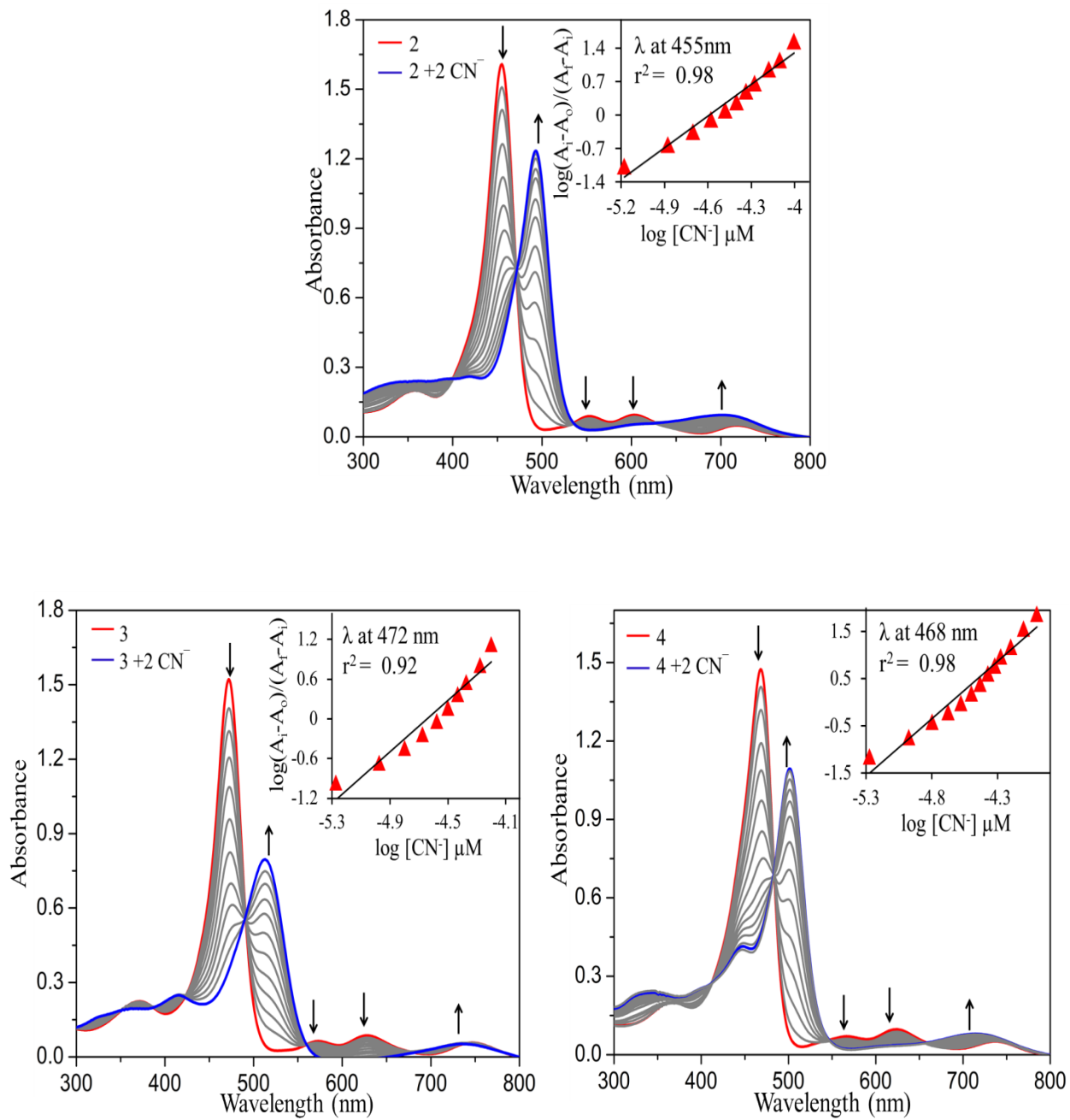
Figure S11. Colorimetric responses of **2-4** while adding of excess of anions in toluene at 298 K.
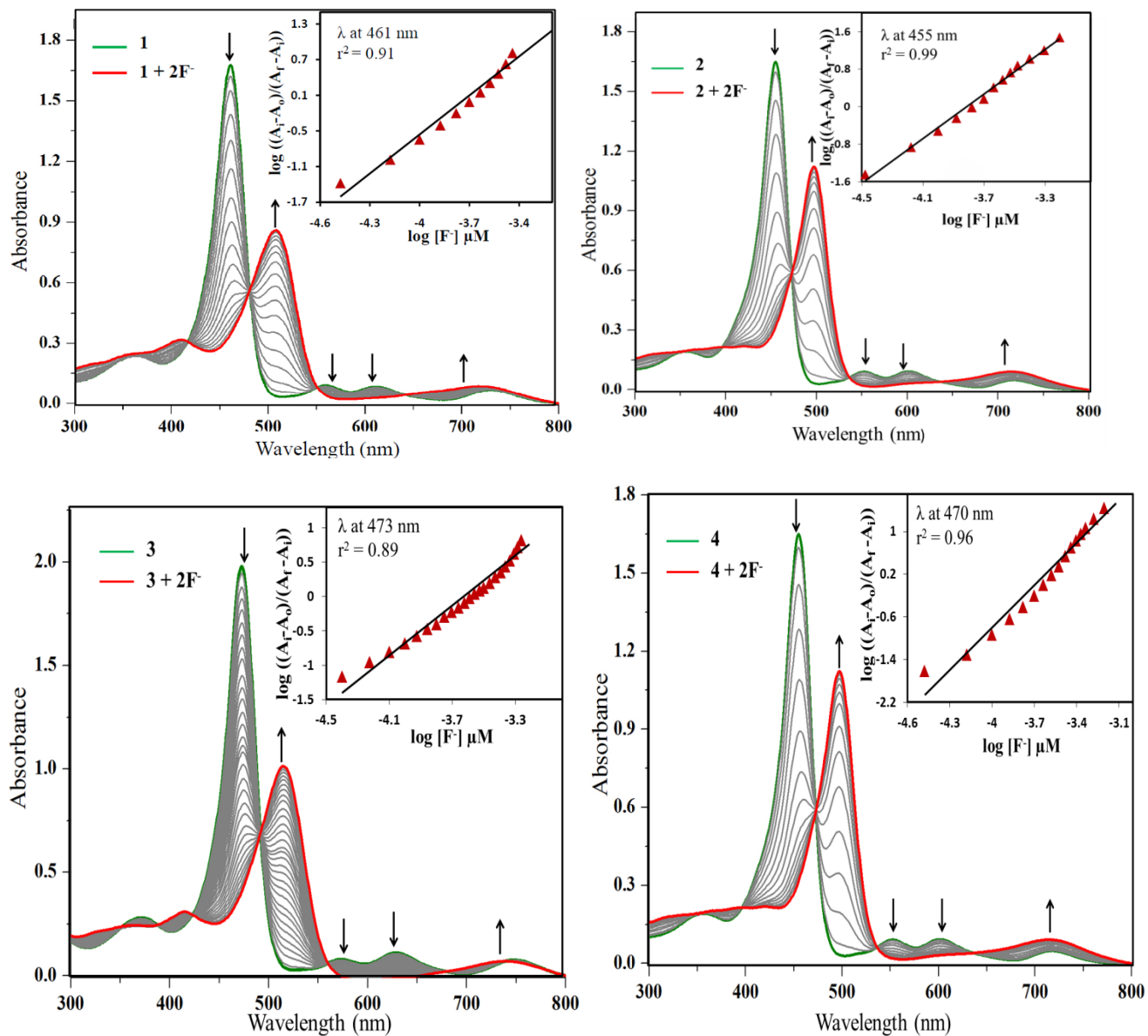
Table S6. Electronic absorption spectral data of **1-4** in presence of excess TFA, TBAOH and various anions in CH_2Cl_2 at 298K.

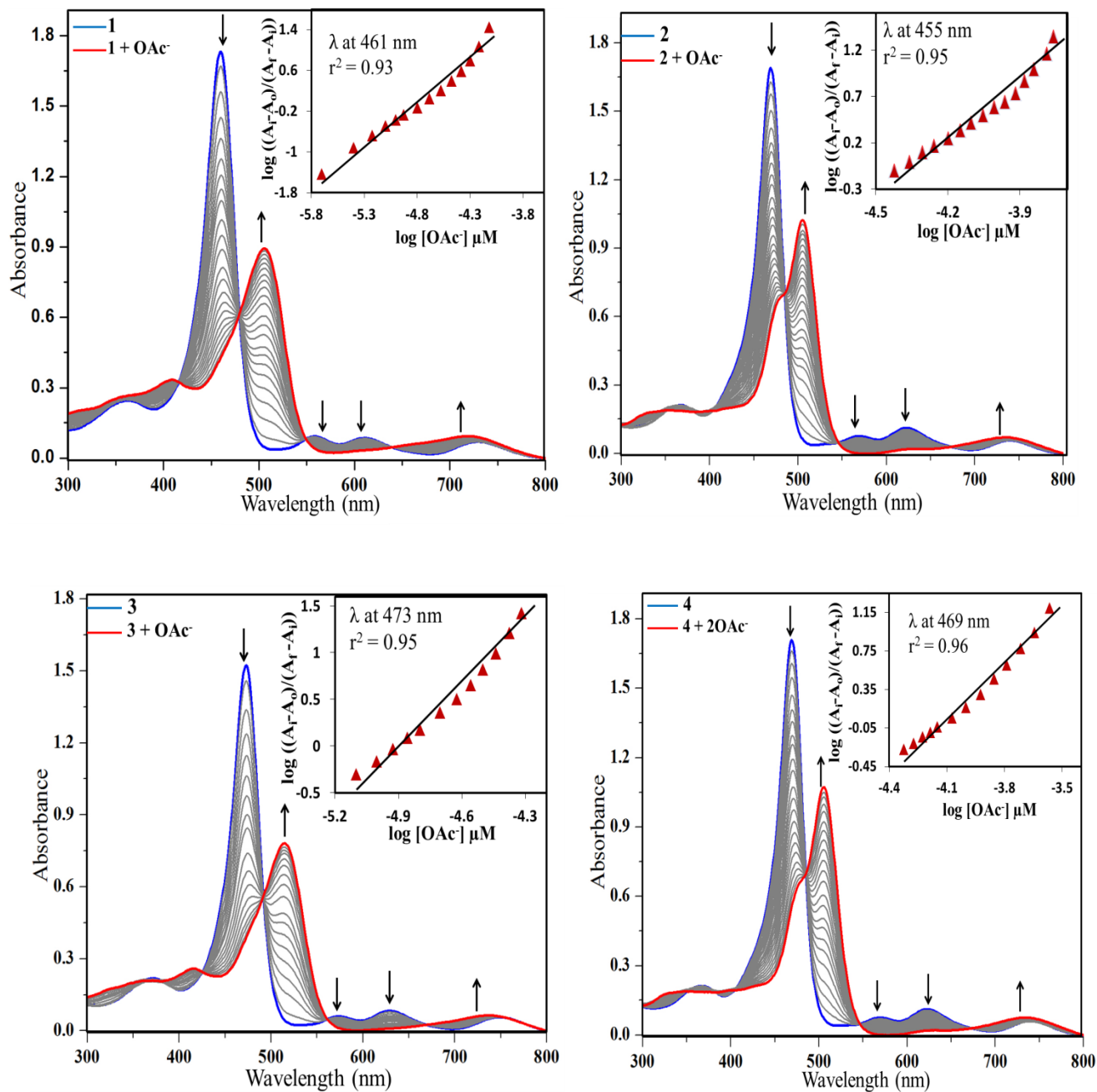| Porphyrin	B band(s)	Q band
$[1 \cdot 2H]^{2+}$	491 (94.16)	754 (11.95)
$[2 \cdot 2H]^{2+}$	415(22.14), 483 (151.99)	734 (24.90)
$[3 \cdot 2H]^{2+}$	501 (93.75)	768 (7.99)
$[4 \cdot 2H]^{2+}$	425(18.95), 495 (149.03)	750 (22.03)
Deprotonation		
$[1-2H]^{2-}$	409(17.69), 506 (47.81)	726 (4.01)
$[2-2H]^{2-}$	492 (87.13)	713(7.25)
$[3-2H]^{2-}$	414(15.94), 516 (50.21)	743(2.92)
$[4-2H]^{2-}$	401(15.55), 505 (88.66)	735 (6.11)
Cyanide		
$[1+2CN^-]$	412(19.24), 506 (52.04)	720 (4.26)
$[2+2CN^-]$	414(22.17), 492 (109.75)	713 (8.84)
$[3+2CN^-]$	414(17.19), 514 (53.06)	740 (3.41)
$[4+2CN^-]$	444(31.98), 503 (94.52)	723 (6.79)
Fluoride		
$[1+2F^-]$	490(20.57), 506 (55.65)	721 (4.91)
$[2+2F^-]$	492 (104.11)	710 (8.59)
$[3+2F^-]$	414(1.35), 516 (56.87)	739 (3.75)
$[4+2F^-]$	398(17.56), 504 (98.41)	731 (7.34)
Acetate		
$[1+2CH_3COO^-]$	410(22.07), 506 (58.50)	719 (5.22)
$[2+2CH_3COO^-]$	492 (77.95)	714 (7.04)
$[3+2CH_3COO^-]$	414(18.35), 516 (59.79)	737 (3.90)
$[4+2CH_3COO^-]$	472(53.79), 504 (88.60)	734 (6.76)
Dihydrogenphosphate		
$[1+2H_2PO_4^-]$	411(22.98), 506 (59.51)	721 (5.38)
$[2+2H_2PO_4^-]$	358(19.97), 456(73.95),492 (80.46)	716 (8.01)
$[3+2H_2PO_4^-]$	416(19.93), 516 (60.79)	741 (4.03)
$[4+2H_2PO_4^-]$	471(57.90), 504 (90.30)	734 (7.22)

Values in parentheses represent $\varepsilon \times 10^{-3} L\ mol^{-1}\ cm^{-1}$

Figure S12. UV-Vis spectral titrations of **2-4** while increasing [CN⁻] in toluene at 298K. Insets show the corresponding Hill plots.
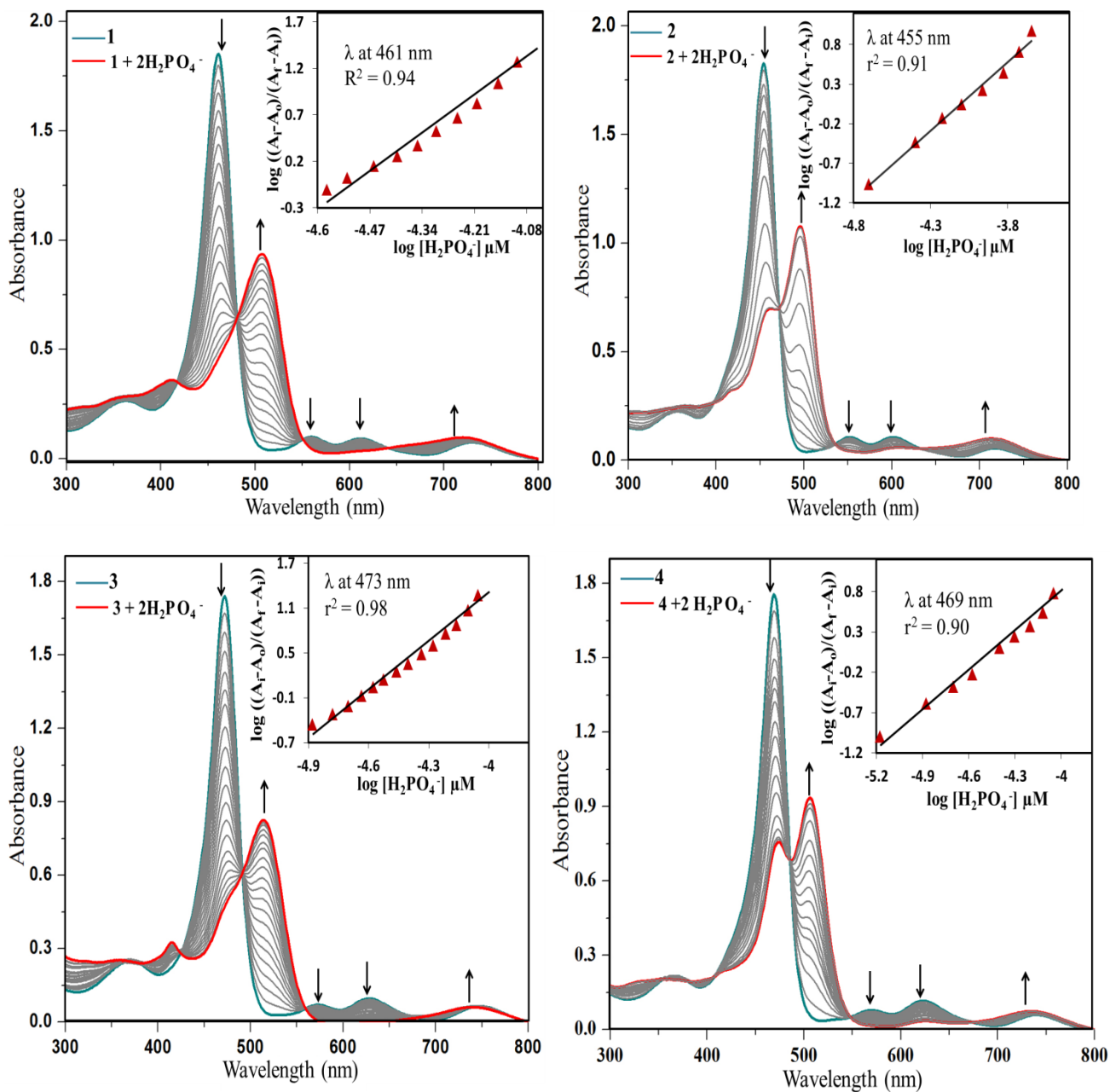
Figure S13. UV-Vis spectral titrations of **1-4** while increasing [F⁻] in toluene at 298K. Insets show the corresponding Hill plots.
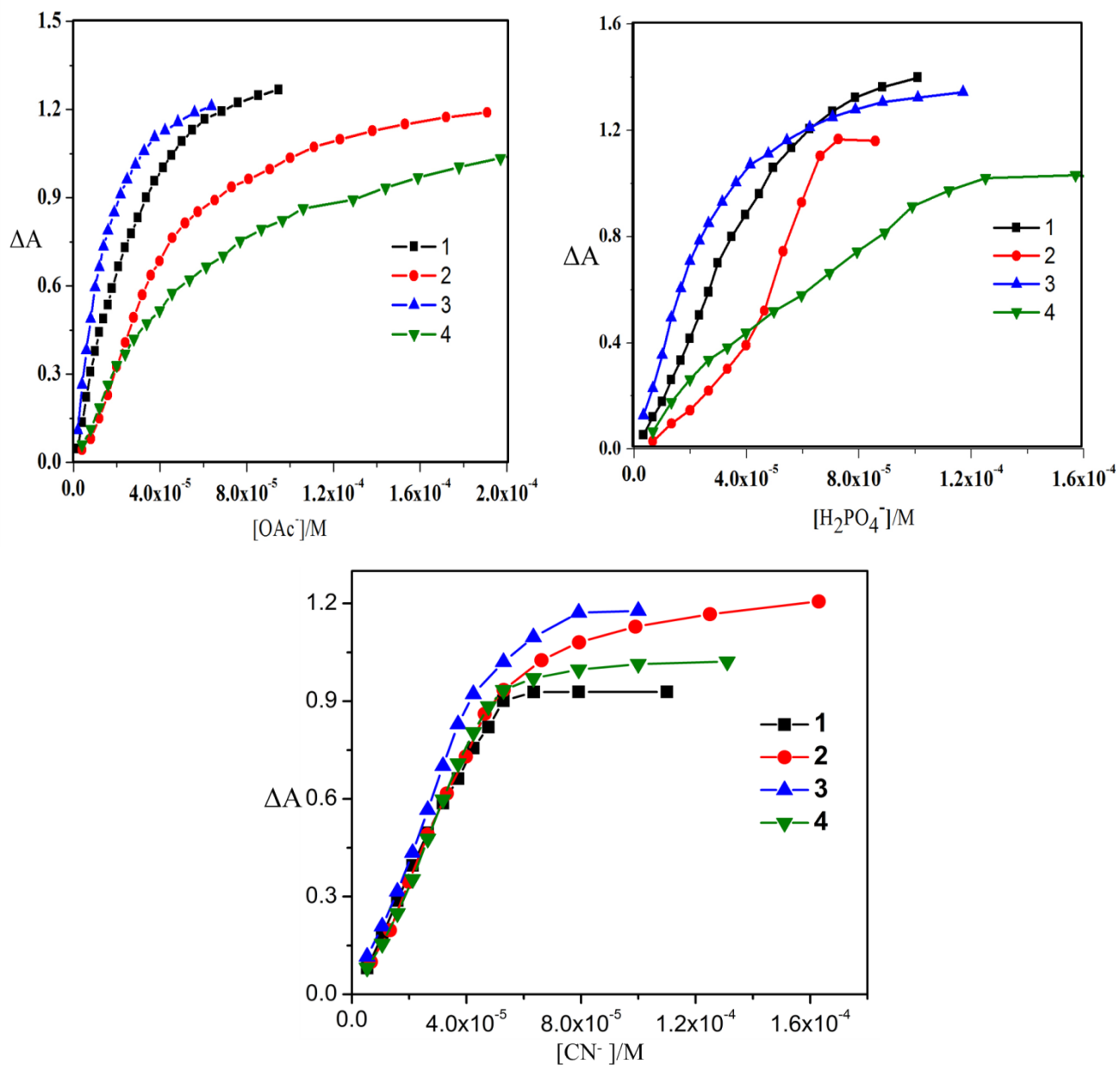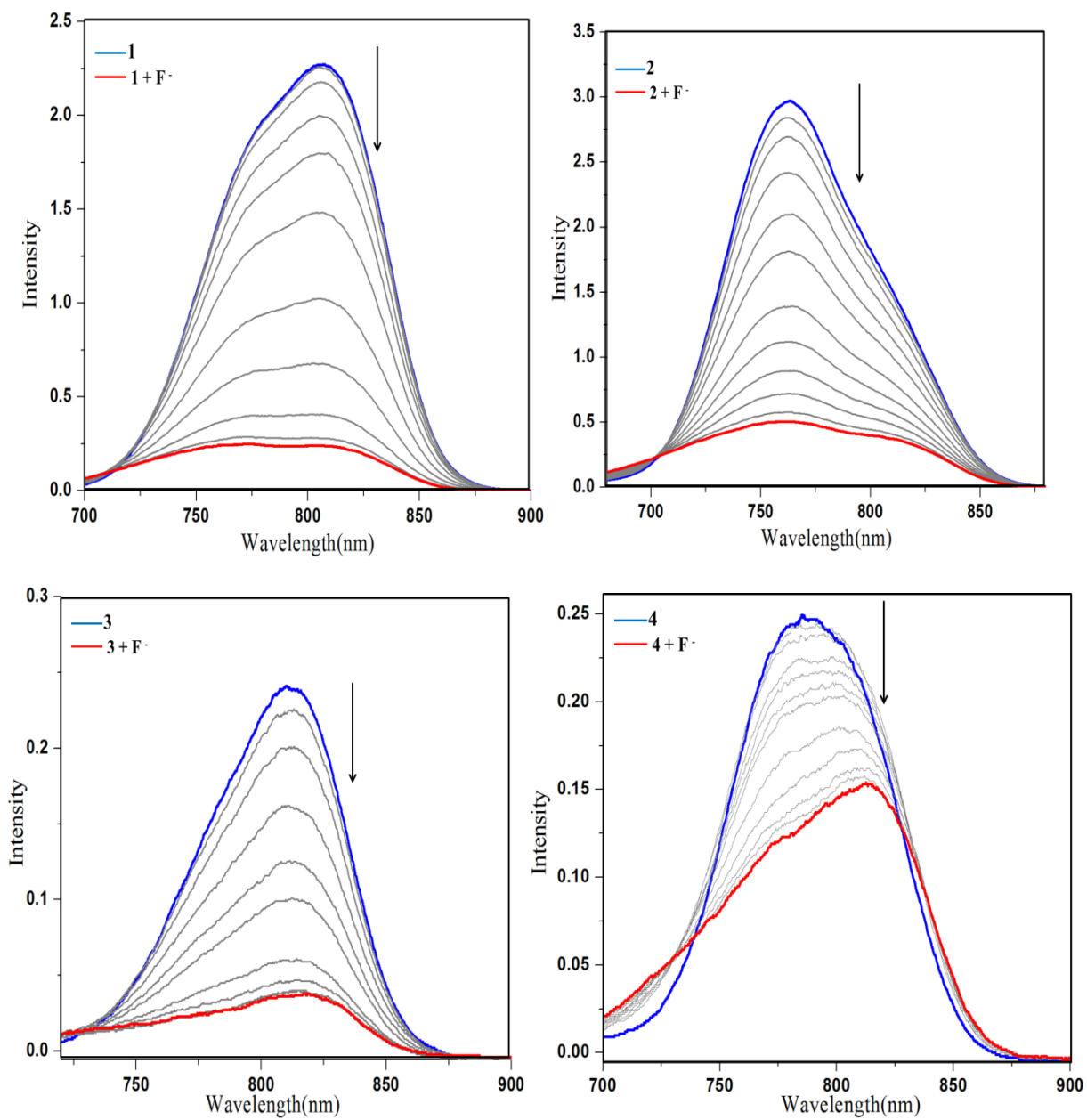
Figurre S14. UV-Vis spectral titrations of **1-4** while increasing [OAc⁻] in toluene at 298K. Insets show the corresponding Hill plots.

Figure S15. UV-Vis spectral titrations of **1-4** while increasing $[H_2PO_4^-]$ in toluene at 298K. Insets show the corresponding Hill plots.

Figure S16. Plots of ΔA at λ_{max} *vs* [OAc$^-$] or [H$_2$PO$_4^-$] or [CN$^-$] for **1-4** showing sigmoidal curve indicating the positive cooperative behavior.
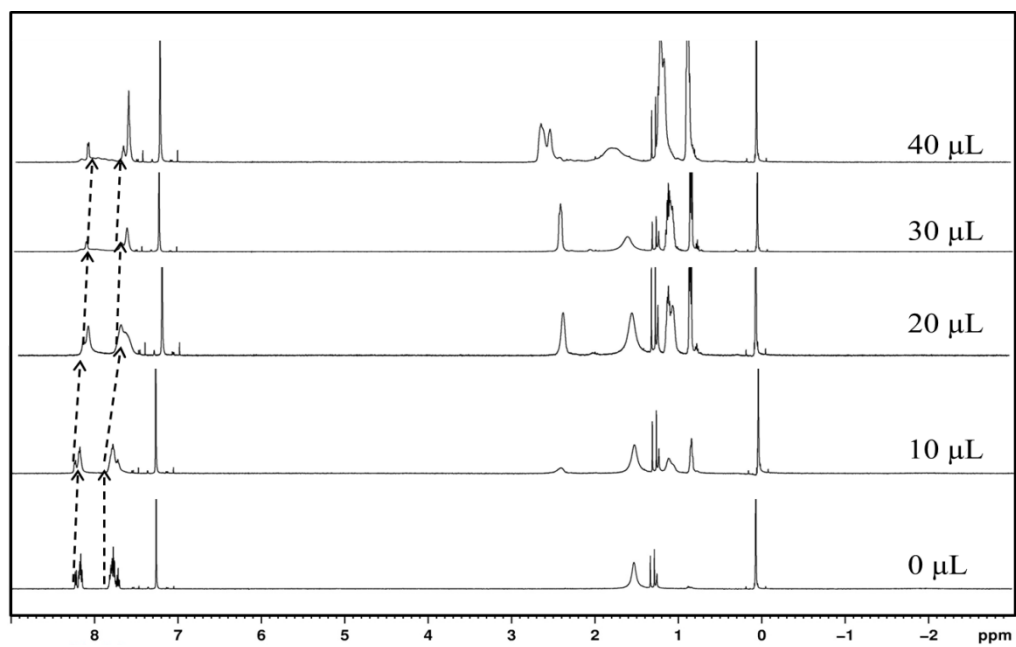
Table S7. The detection limits (LOD) and quantification limits (LOQ) of anions by **1-4** in toluene at 298K.

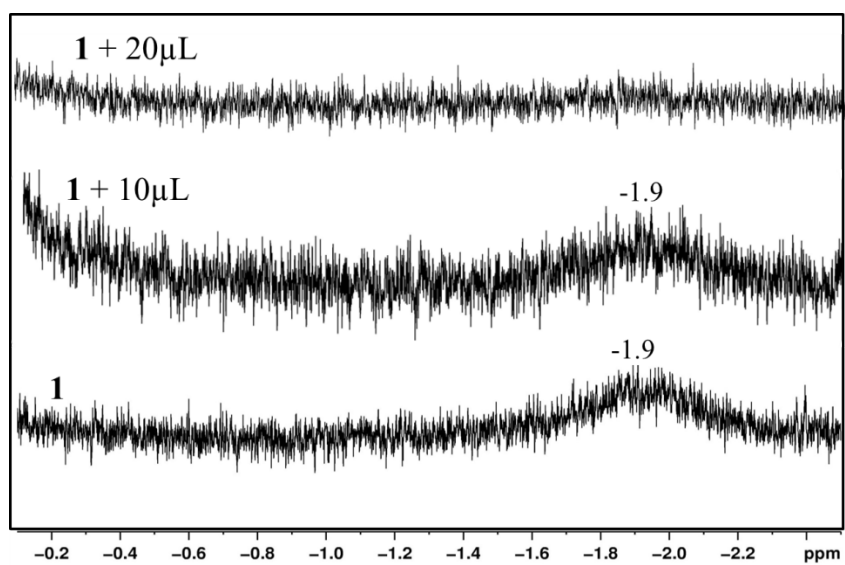| Por	CN⁻		F⁻		CH₃COO⁻		H₂PO₄⁻	
	LOD nM (ppb)	LOQ nM (ppb)	LOD nM (ppb)	LOQ nM (ppb)	LOD nM ppb)	LOQ nM (ppb)	LOD nM (ppb)	LOQ nM (ppb)
1	7.3(0.19)	22.3(0.87)	6.0(0.11)	18.2(0.34)	8.2(0.48)	24.7(1.45)	7.7(0.75)	23.4(2.26)
2	9.5(0.24)	28.7(0.75)	8.4(0.16)	25.4(0.48)	9.7(0.57)	29.4(1.73)	9.6(0.93)	29.2(2.83)
3	8.6(0.22)	26.1(0.68)	7.4(0.14)	22.3(0.42)	10.0(0.59)	30.3(1.78)	10.3(1.00)	31.3(3.04)
4	8.3(0.21)	25.3(0.66)	8.4(0.16)	25.3(0.48)	8.7(0.51)	26.2(1.55)	8.6(0.83)	26.0(2.52)

nM and ppb represent nanomolar and parts per billion respectively

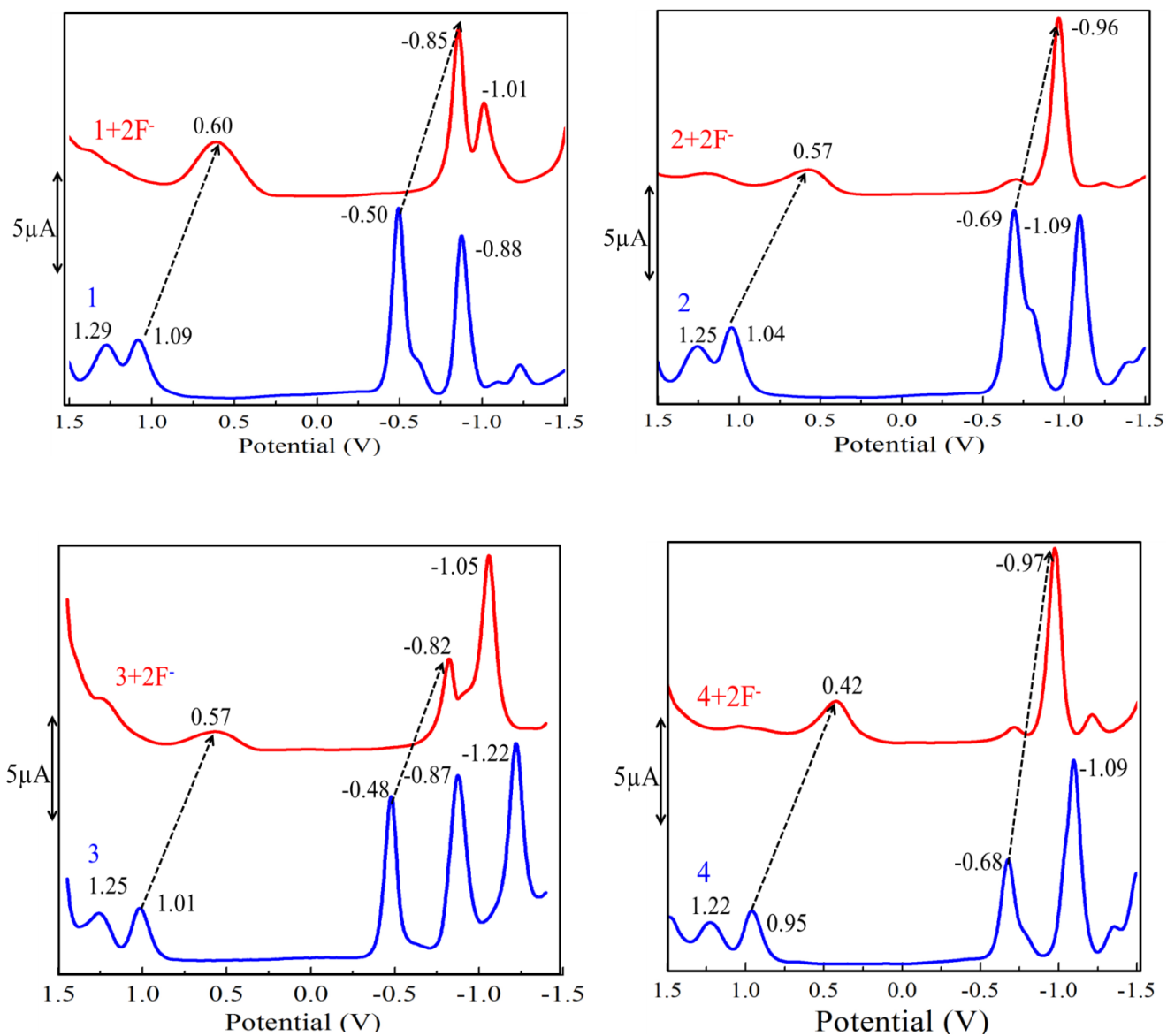**Figure S17.** Fluorescence spectral titrations (FL quenching) of **1-4** while increasing [F⁻] in toluene at 298K.
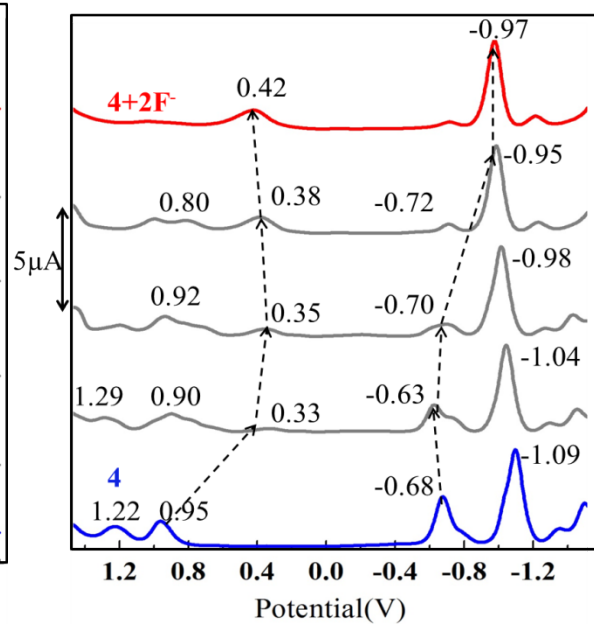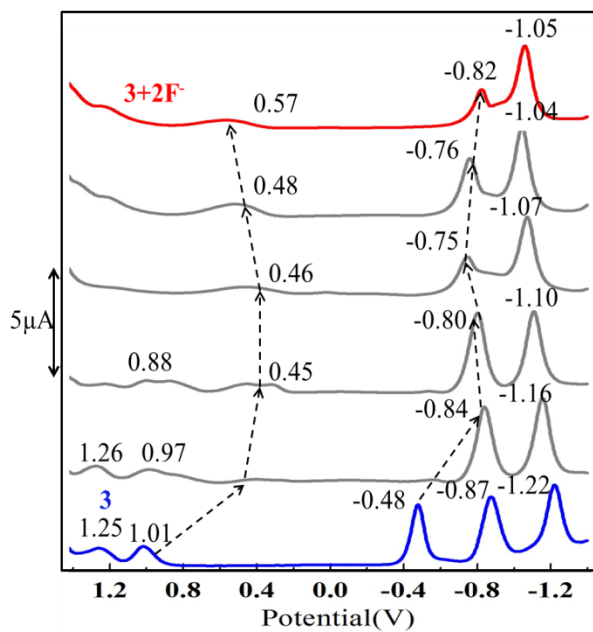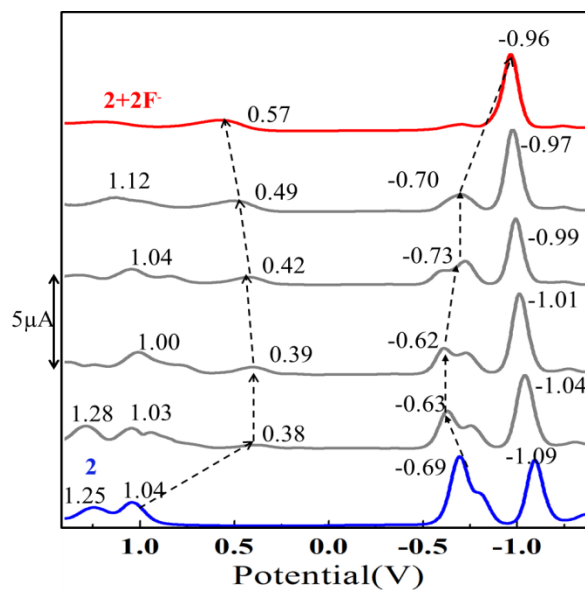
(a)

(b)
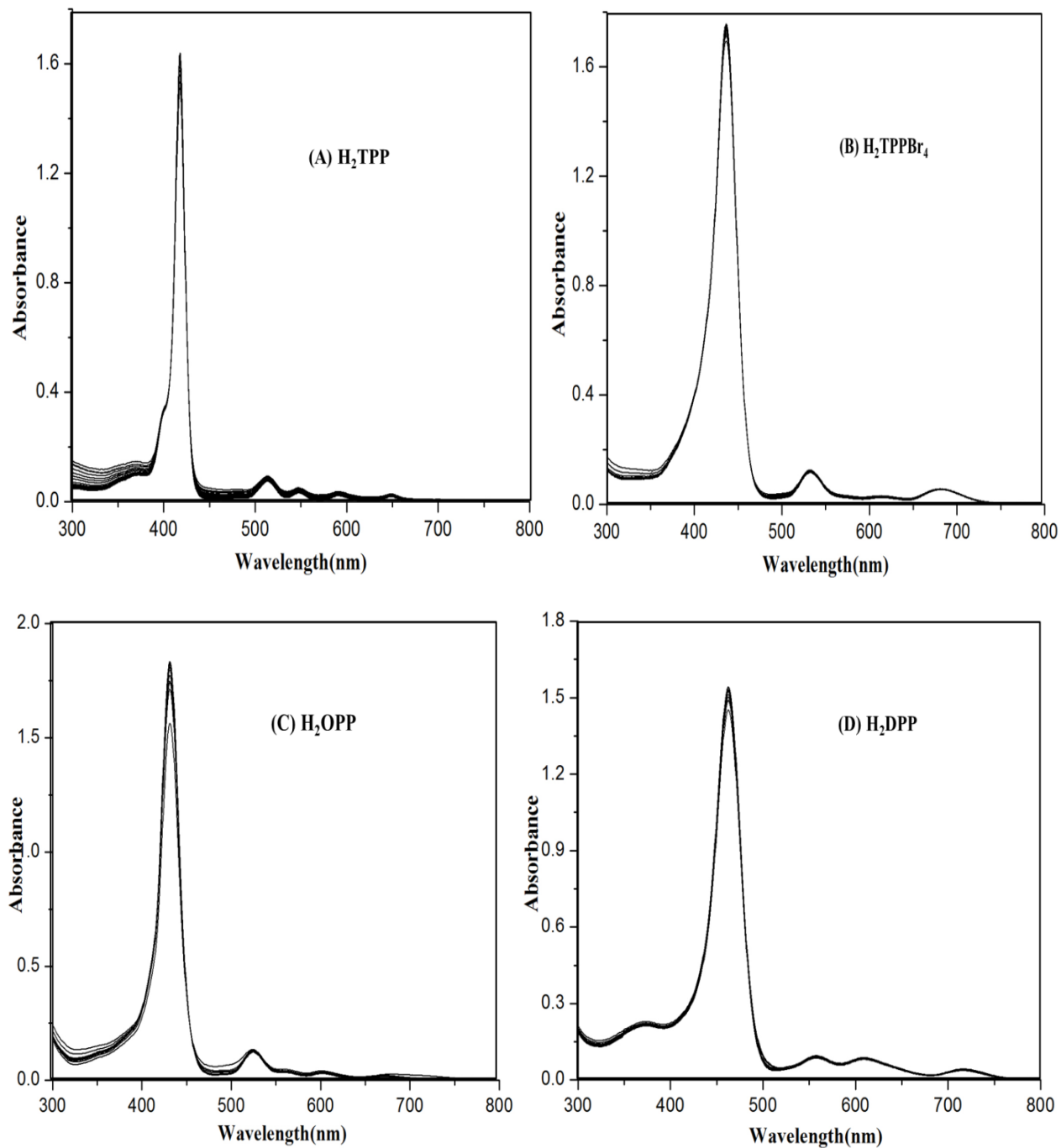
Figure 18. (a) ^1H NMR spectral changes of **1** while [F$^-$] in CDCl$_3$ at 298K. (b) Disappearance of NH protons of **1** upon increasing the aliquots of 0.05 M fluoride ion solution in CDCl$_3$ at 298K.

Figure S19. DPV traces of **1-4** in absence and presence of excess [F⁻] in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at 298K.
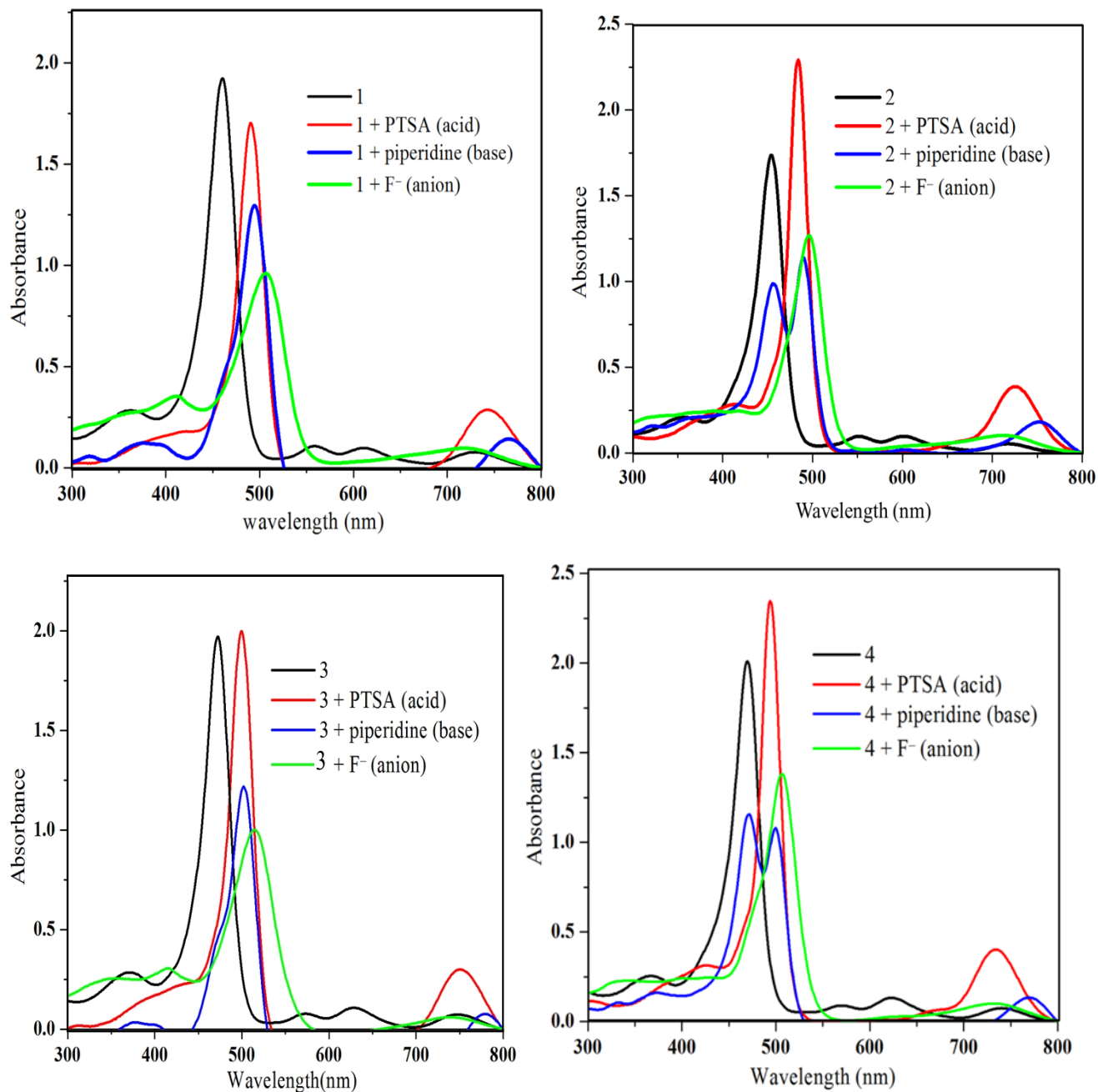
Figure S20. DPV titrations of **2-4** while increasing the concentration of F⁻ ion in CH_2Cl_2 containing 0.1 M $TBAPF_6$ at 298K.
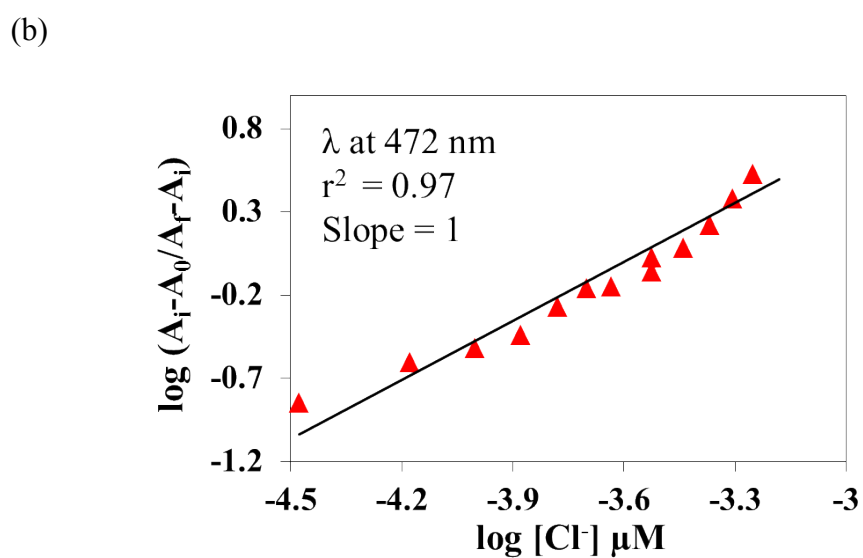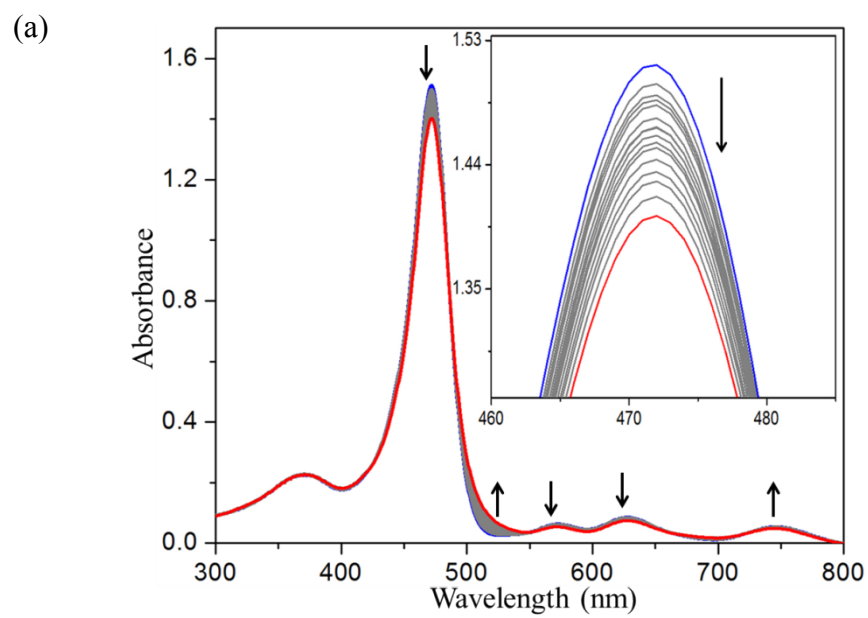
Figure S21: UV-Visible spectral titrations of planar porphyrins (*meso*-tetraphenylporphyrin (H$_2$TPP) and 2,3,5,10,15,17,18,20-octaphenylporphyrin (H$_2$TPP(Ph)$_4$) and nonplanar porphyrins (2,3,12,13-tetrabromo-*meso*-tetraphenylporphyrin (H$_2$TPPBr$_4$) and 2,3,5,7,8,10,12,13,15,17,18,20-dodecaphenyl-porphyrin (H$_2$TPP(Ph)$_8$)) while increasing [F$^-$] in toluene at 298 K.
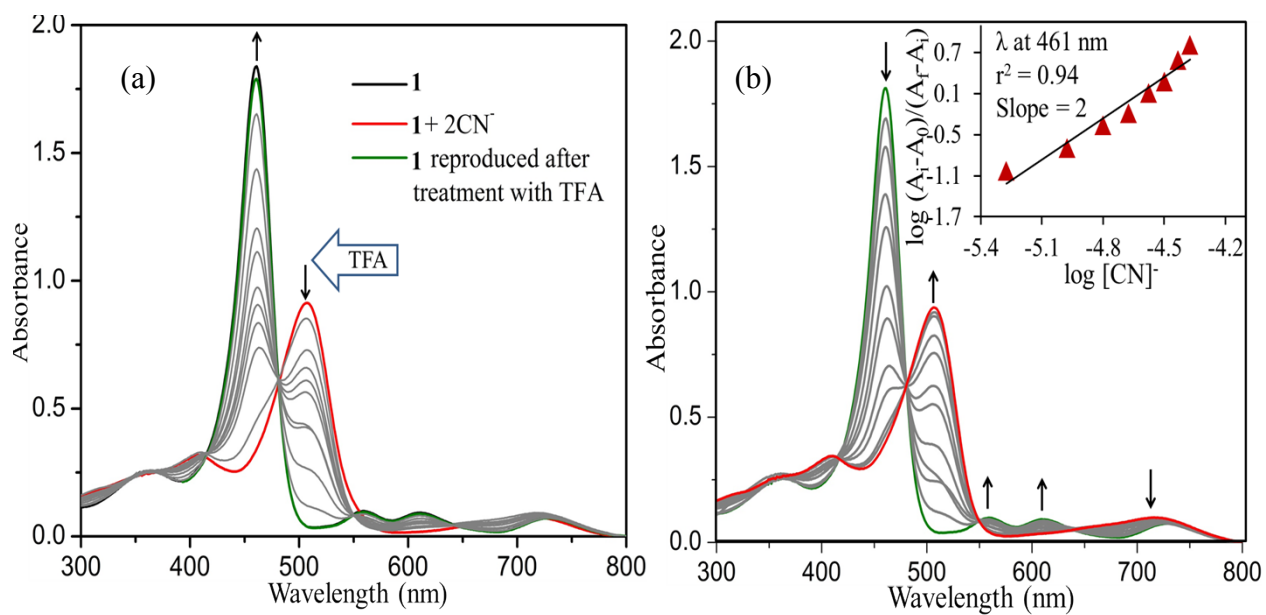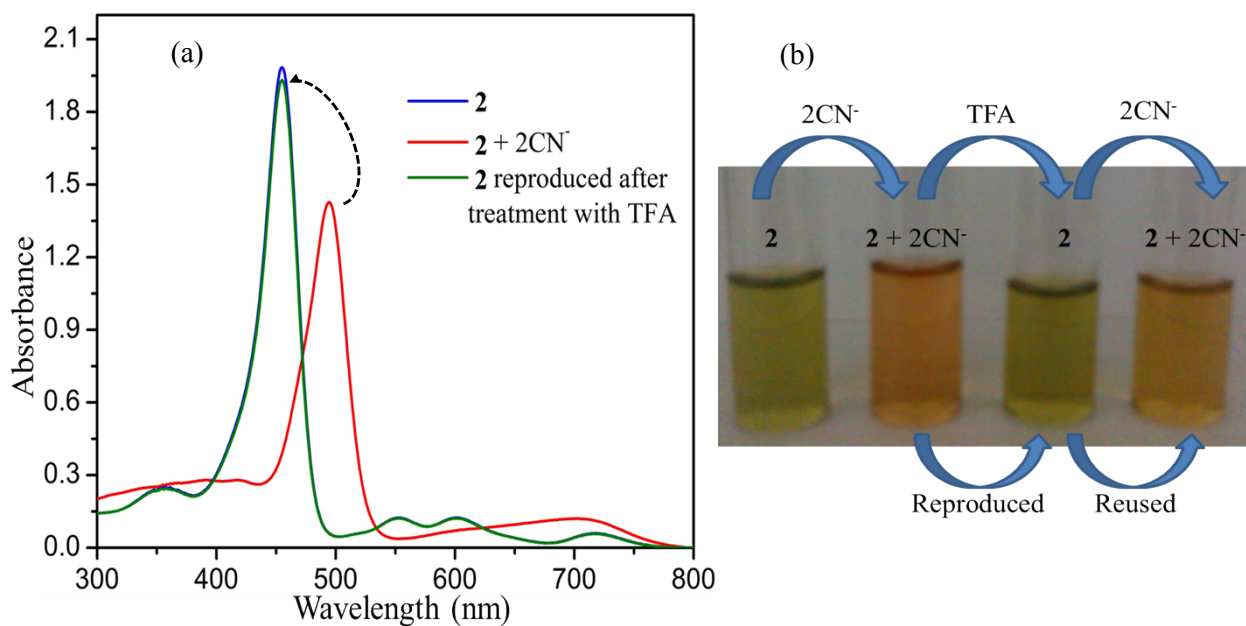
Figure S22. Overlayed UV-Visible Spectra of **1-4** with excess of *p*-toluenesulphonic acid (PTSA), piperidine and fluoride ions in toluene 298 K. Herein, piperidine forms 1:1 host:guest complex with **1-4** in 1,2-dichloroethane as reported in literature (Ref. P. Bhyrappa and P. Bhavana, *Chem. Phys. Lett.* 2002, **357**, 108).
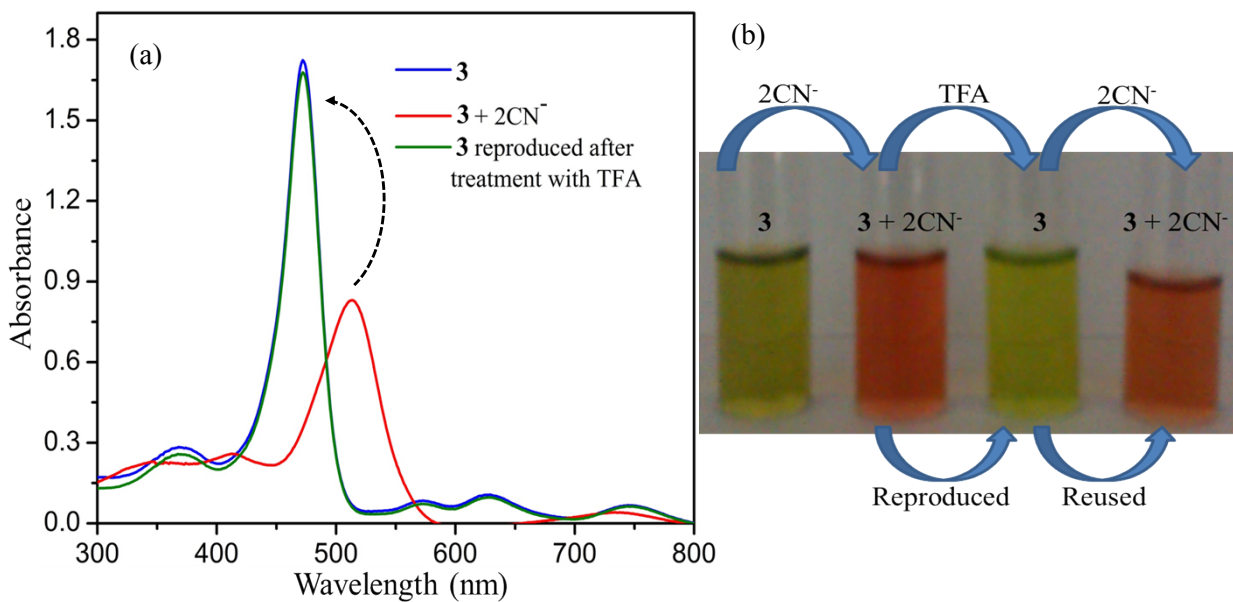
Figure S23. (a) UV-Vis spectral titrations of **3** with TBACl (0.008 M) in toluene at 298 K. Inset shows the absorbance changes in the Soret region; (b) Hill plot $\log(A_i-A_0/A_f-A_i)$ *vs.* log [Cl$^-$] showing 1:1 stoichiometry indicated by slope 1.
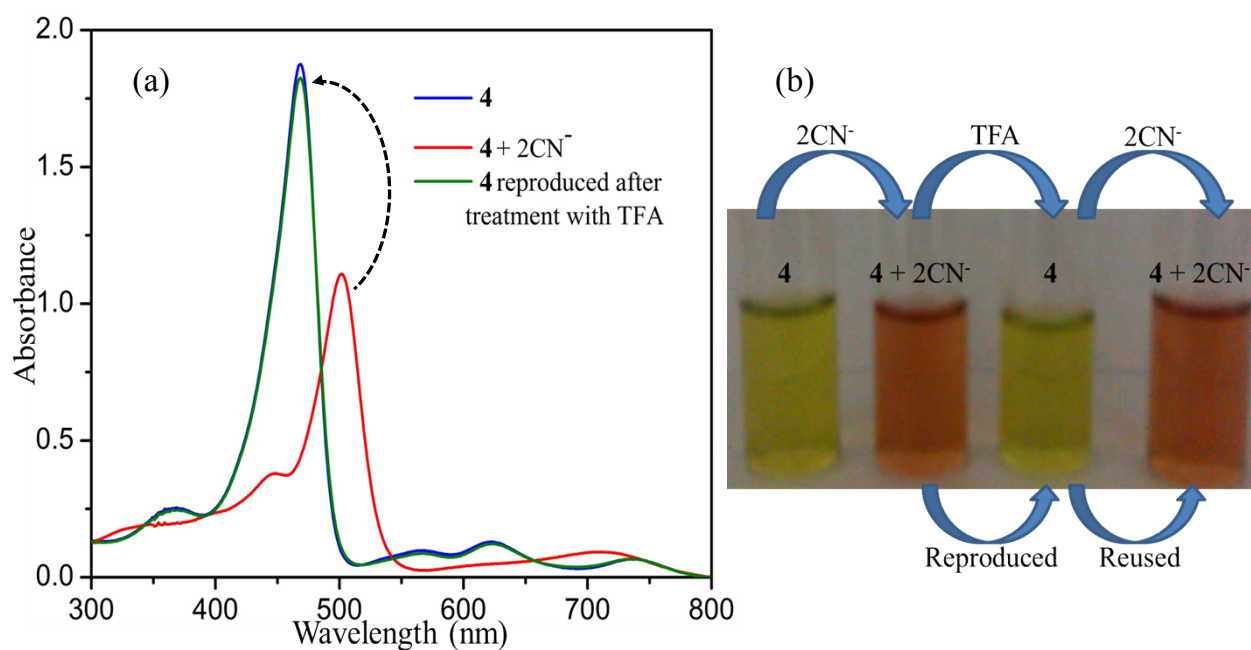
Figure S24. (a) Treatment of **1**•2CN⁻ complex with aliquots of 1 mM solution TFA at 298 K. (b) Reusability test of regenerated **1** with aliquots of 8 mM solution of CN⁻ ions in toluene at 298 K.

Figure S25. (a) Treatment of **2**•2CN⁻ complex with sufficient amount of TFA and (b) the colorimetric response for reversibility and reusability test.

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