

Supporting Information

High Sensitivity Viologen for Facile and Versatile Sensor of Base and Solvent Polarity in Solution and Solid State in Air Atmosphere

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Calculation of binding constants and base sensitivity

Figure S1. ^1H NMR, ^{13}C NMR and mass spectra of synthesized Compound $\mathbf{1}^{2+}\cdot 2\text{Cl}^-$ in D_2O

Figure S2. ^1H NMR, ^{13}C NMR and mass spectra of synthesized Compound $\mathbf{2}^{2+}\cdot 2\text{Cl}^-$ in deuterated TFA

Figure S3. ^1H NMR, ^{13}C NMR and mass spectra of synthesized Compound $\mathbf{3}^{2+}\cdot 2\text{Cl}^-$ in deuterated DMSO

Figure S4. ^1H NMR, ^{13}C NMR (in D-DMSO) and Mass spectra (TOF, in H_2O) of $(\mathbf{1})_3\cdot(\text{BiCl}_6)_2$

Figure S5. IR spectra of $(\mathbf{1})_3\cdot(\text{BiCl}_6)_2$ before (pale-yellow) and after (purple-blue) exposure to diethylamine (KBr disc).

Figure S6. UV-vis spectra of compound $\mathbf{1}$ in aqueous solution in the presence of different base

Figure S7. UV-vis spectra of compound $\mathbf{2}$ in aqueous solution in the presence of different base

Figure S8. UV-vis spectra of compound $\mathbf{3}$ in aqueous solution in the presence of different base

Figure S9. Uv-vis absorbance at different equivalence of base.

Figure S10 Regression of equilibrium constants of $\mathbf{1}\sim\mathbf{3}$ in different amount NaOH

Figure S11. Time dependence of UV-vis spectra of $\mathbf{1}\sim\mathbf{3}$ in the presence of NaOH.

Figure S12. UV-vis spectra of compound $\mathbf{4}$ in the absence and presence of NaOH.

Figure S13 UV-vis spectra of $\mathbf{1}$ in different solvents at different concentration.

Figure S14 UV-vis spectra of $\mathbf{2}$ in different solvents at different concentration.

Figure S15 UV-vis spectra of $\mathbf{3}$ in different solvents at different concentration.

Figure S16 Concentration dependence of absorption maximum in different organic solvents.

Figure S17 EPR spectra of compound $\mathbf{1}$, $\mathbf{2}$ and $\mathbf{3}$ in the presence of NaOH.

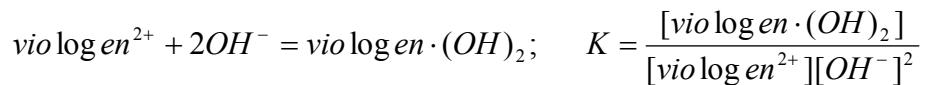
Figure S18 UV-vis spectra of $\mathbf{1}\sim\mathbf{4}$ in the presence of sodium hyposulfite

Figure S19. Reflectance spectra of $\mathbf{1}\cdot\text{Cl}_2$, $\mathbf{1}\cdot\text{BiCl}_6$ before and after expose to diethylamine vapor.

Table S1 Crystal structure data of colorless(pale yellow) and colored $(\mathbf{1})_3\cdot(\text{BiCl}_6)_2$

Calculation detail

(1) Binding constants



All three viologen in the absence of base are colorless. Upon adding enough base, the absorption reached plateau. Due to concentration of NaOH is much high than viologen, the total volume keep constant. From the maximum absorbance (A_∞) and the viologen concentration C_0 ,

At any NaOH concentration, the absorbance is A:

$$[\text{prod}] = A \times C_0 / A_\infty$$

$$[\text{Vio}^{2+}] = C_0 - [\text{prod}]$$

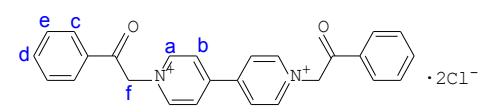
$$[\text{OH}^-] = [\text{OH}^- \text{ added}] - 2[\text{prod}]$$

Plot of $[\text{prod}]$ vs $[\text{Vio}^{2+}][\text{OH}^-]^2$, the slope is the K. Other binding stoichimic will not give straight line.

(2) Base sensitivity

Plot of A (at absorption maximum) vs [added base], gives a straight line (obey lambert-beer law in low base concentration (5 eq or less)). Read the base concentration at $\Delta_{\text{Abs.}} = 0.01$ or 0.05

$$\text{Sensitivity (ppm)} = \text{MW} \times [\text{base conc}] \times 1000$$



Compound 1

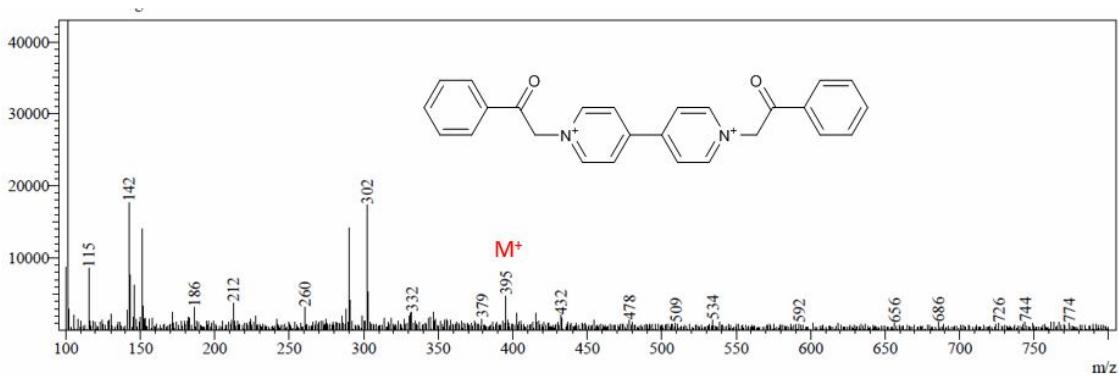
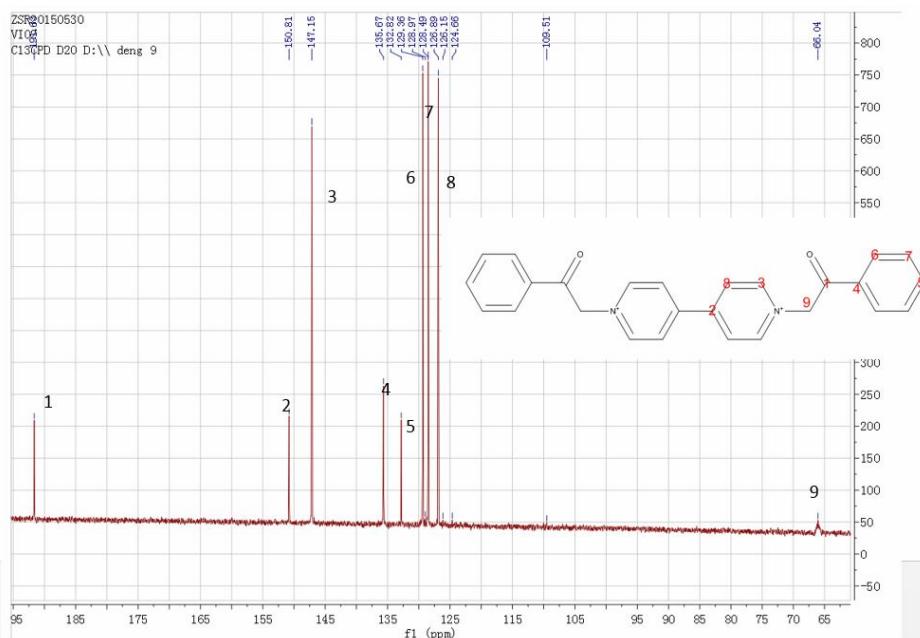
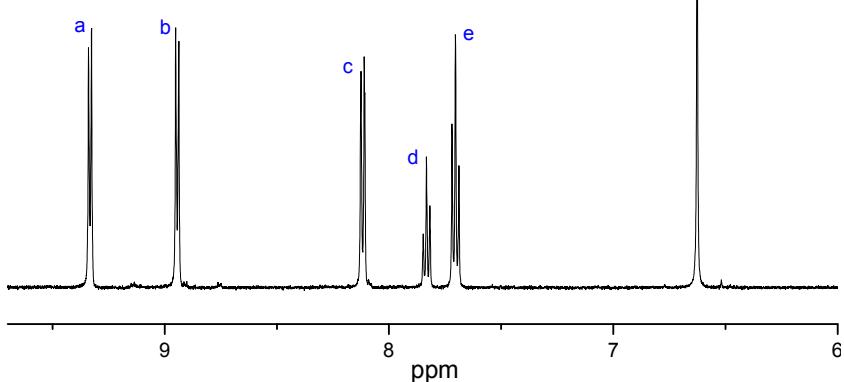


Figure S1. ¹H, ¹³C NMR in D₂O and Mass spectra (ESI, in CH₃OH) of Compound 1²⁺.2Cl⁻

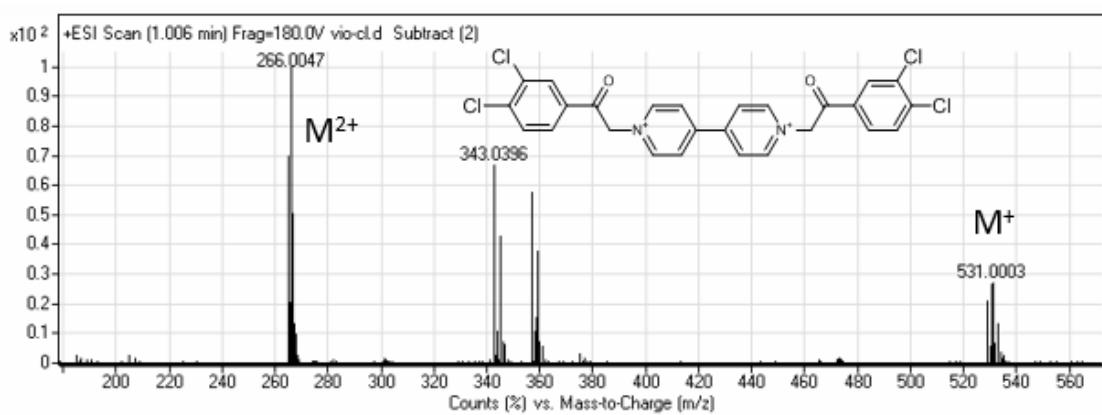
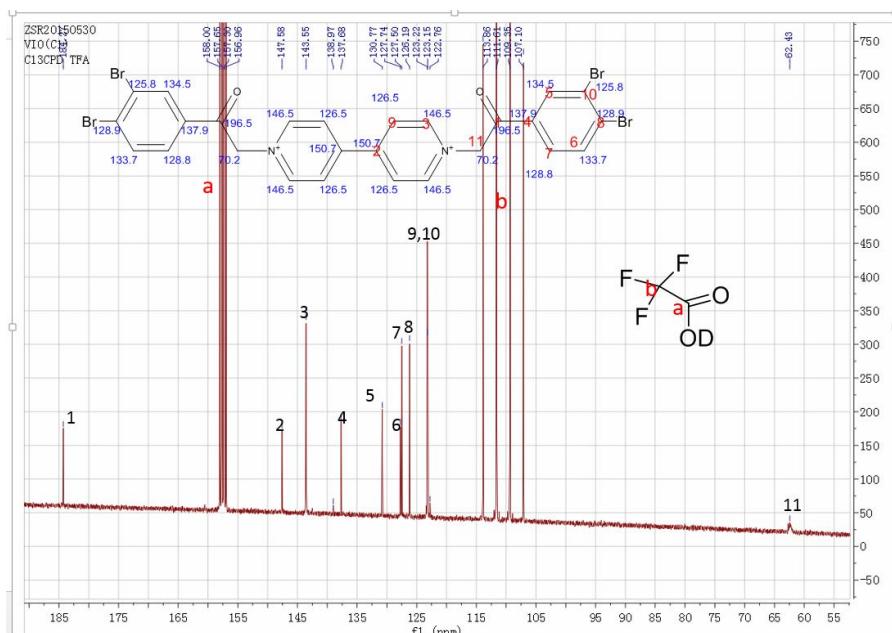
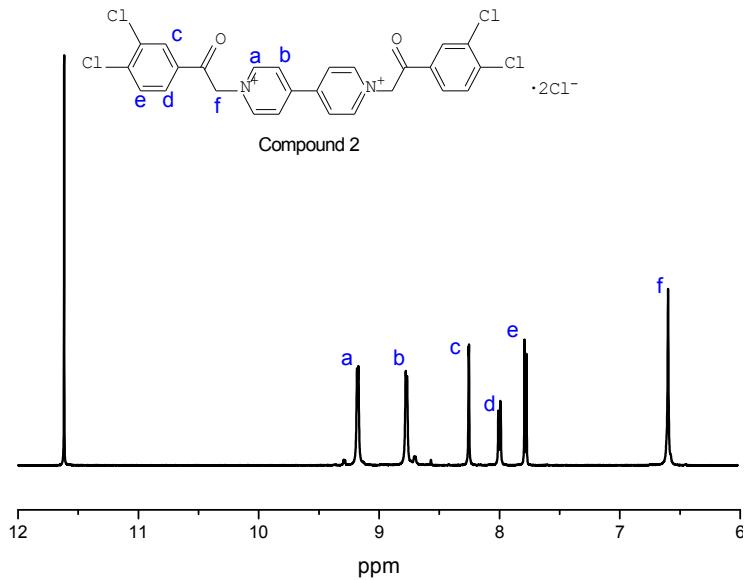


Figure S2. ^1H , ^{13}C NMR in TFA and Mass spectra (TOF, in H_2O) of Compound $2^{2+} \cdot 2\text{Cl}^-$ (chemical shifts in blue color are estimated by Chemdraw)

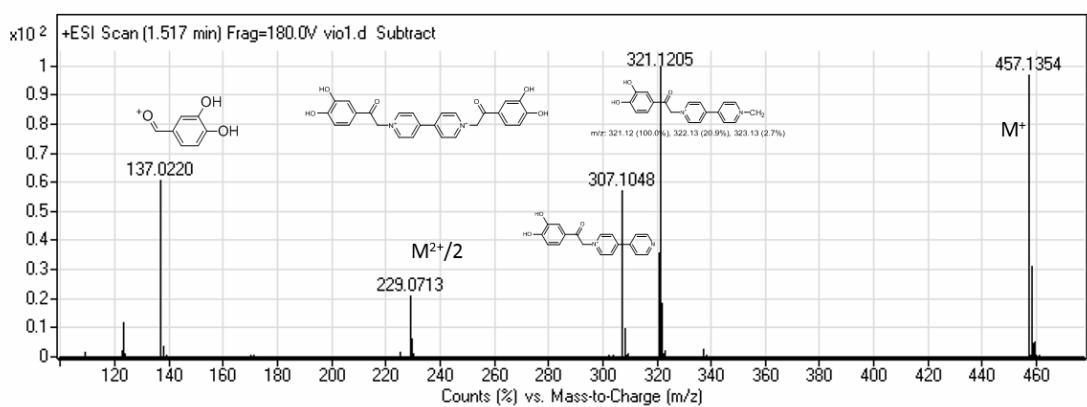
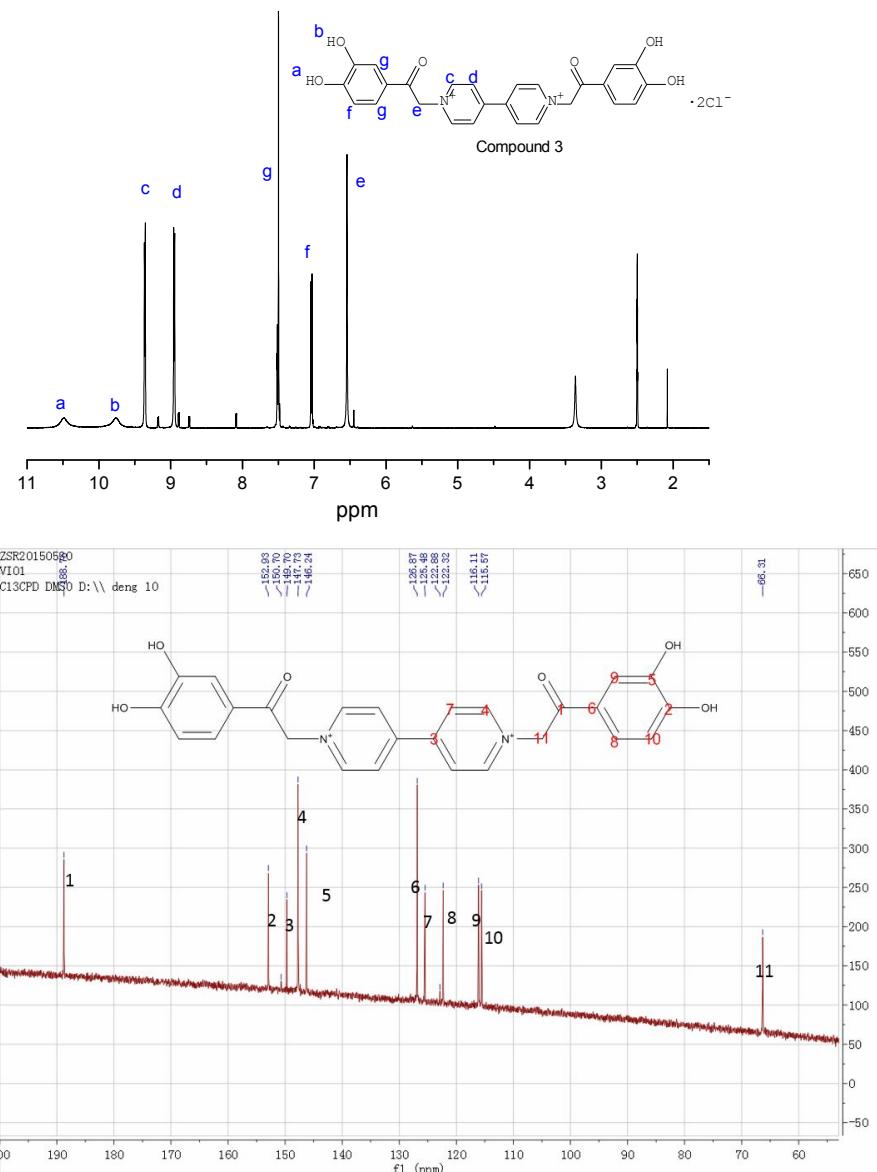


Figure S3. ¹H NMR, ¹³C NMR (in D-DMSO) and Mass spectra (TOF, in H₂O) of Compound **3²⁺·2Cl⁻**

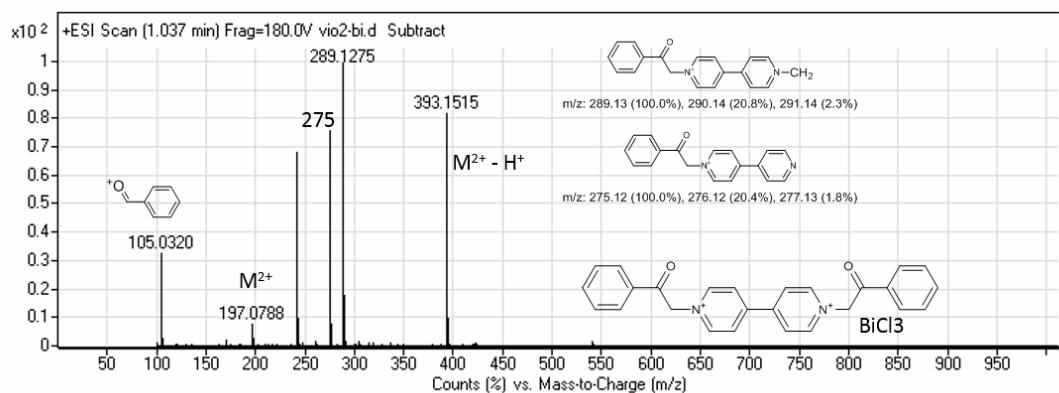
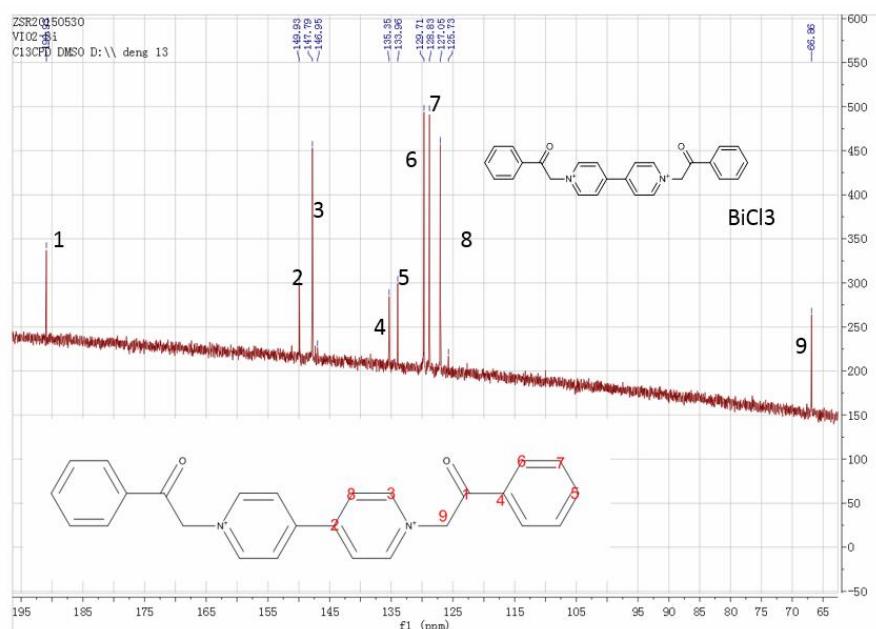
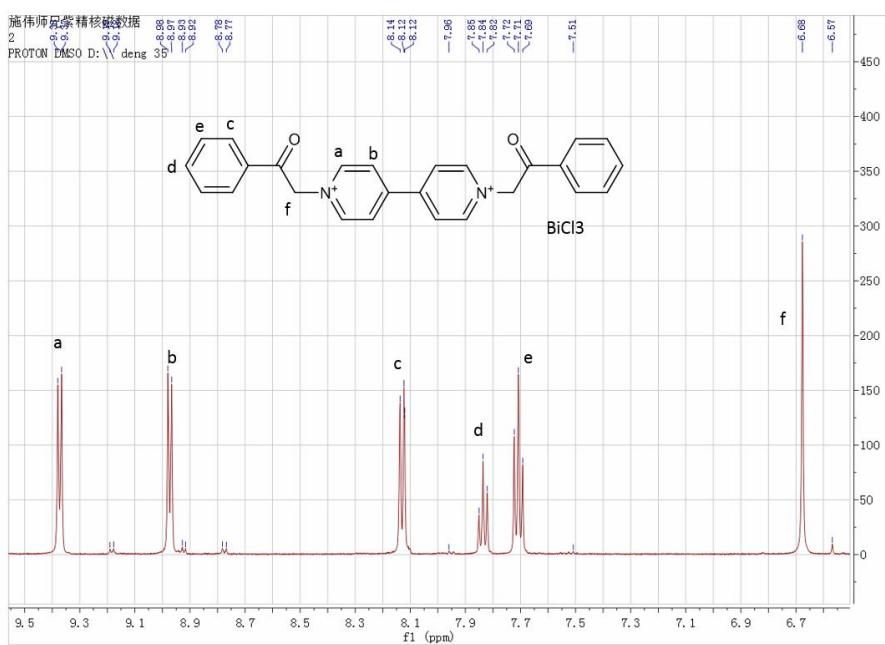


Figure S4. ¹H NMR, ¹³C NMR (in D-DMSO) and Mass spectra (TOF, in H₂O) of (1)₃·(BiCl₃)₂

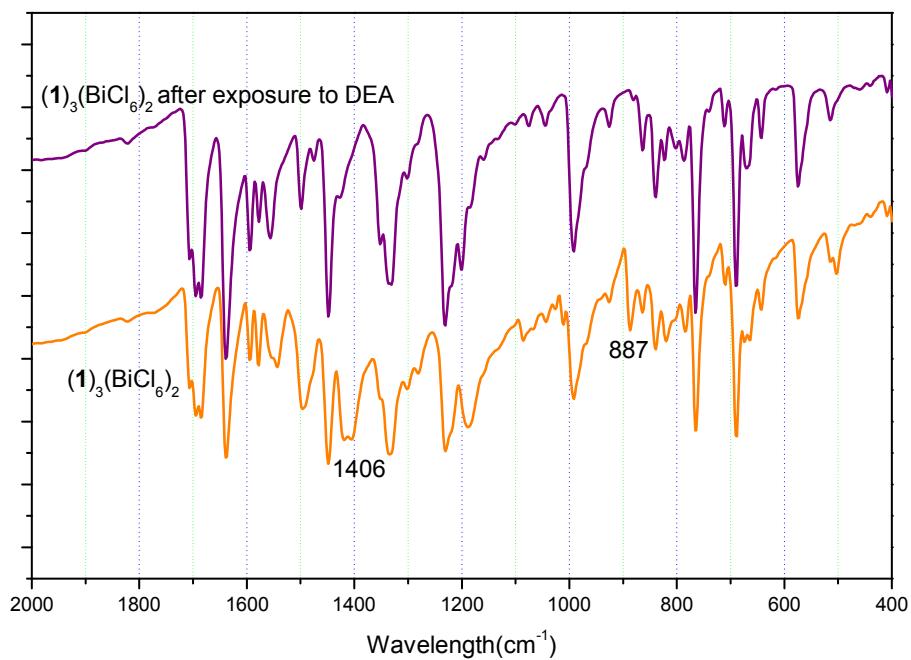
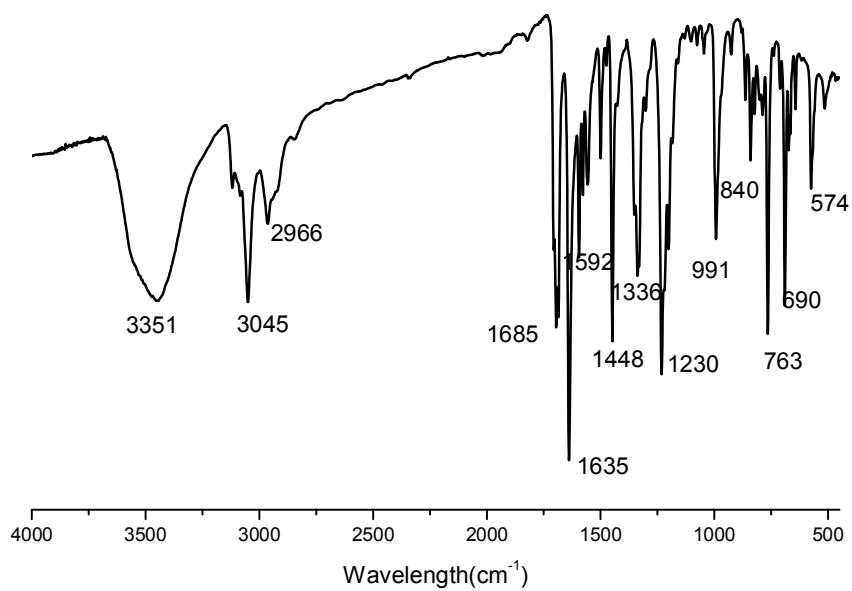


Figure S5. IR spectra of $(\mathbf{1})_3 \cdot (\text{BiCl}_6)_2$ before (pale-yellow, top) and after (purple-blue) exposure to diethylamine (KBr disc).

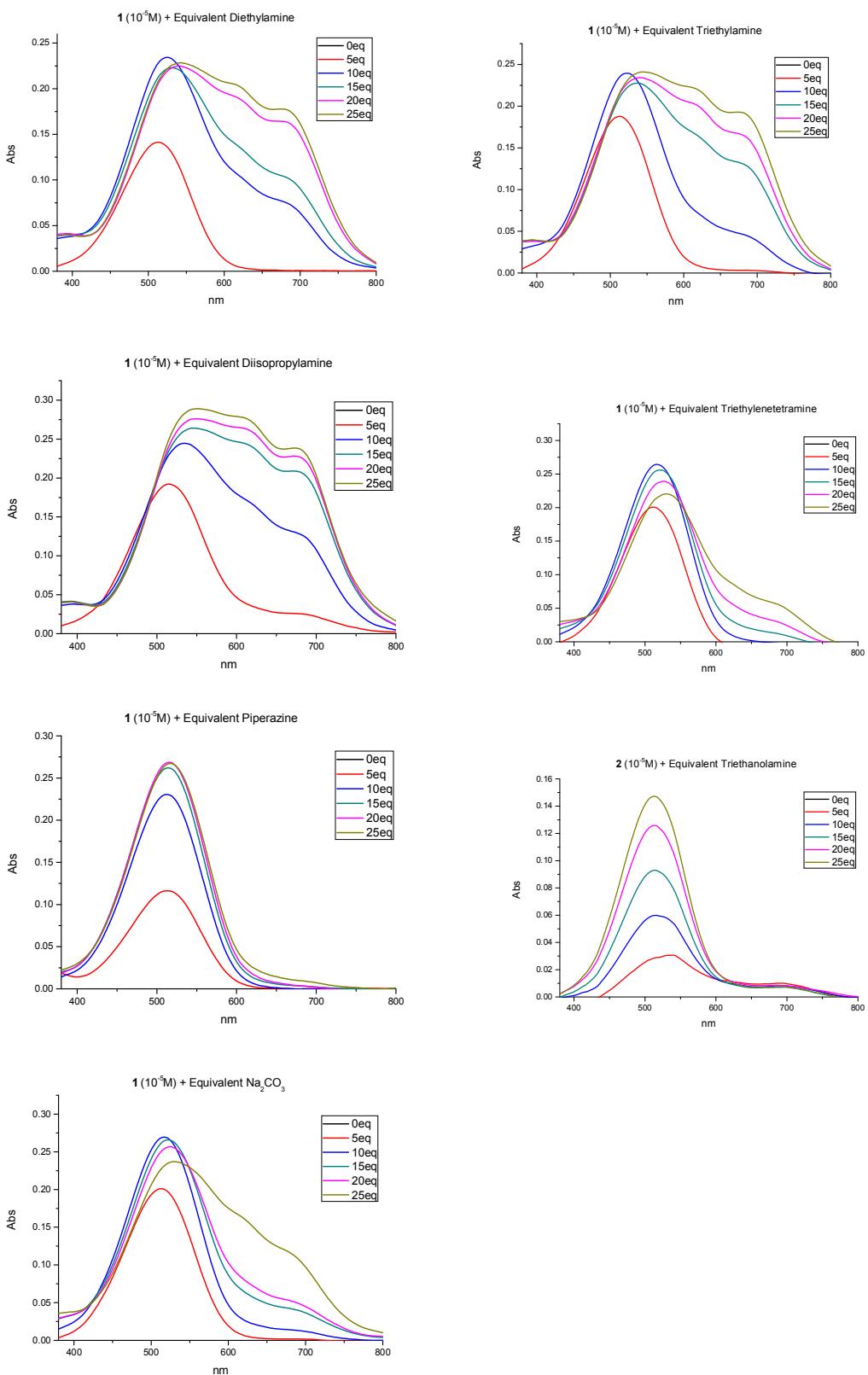


Figure S6. UV-vis spectra of 1.0×10^{-5} M compound **1** aqueous solution in the presence of different base at different concentrations. Base concentrations varies from 5 eq to 25 eq of **1**, with a color change from colorless to pink, and then to purple.

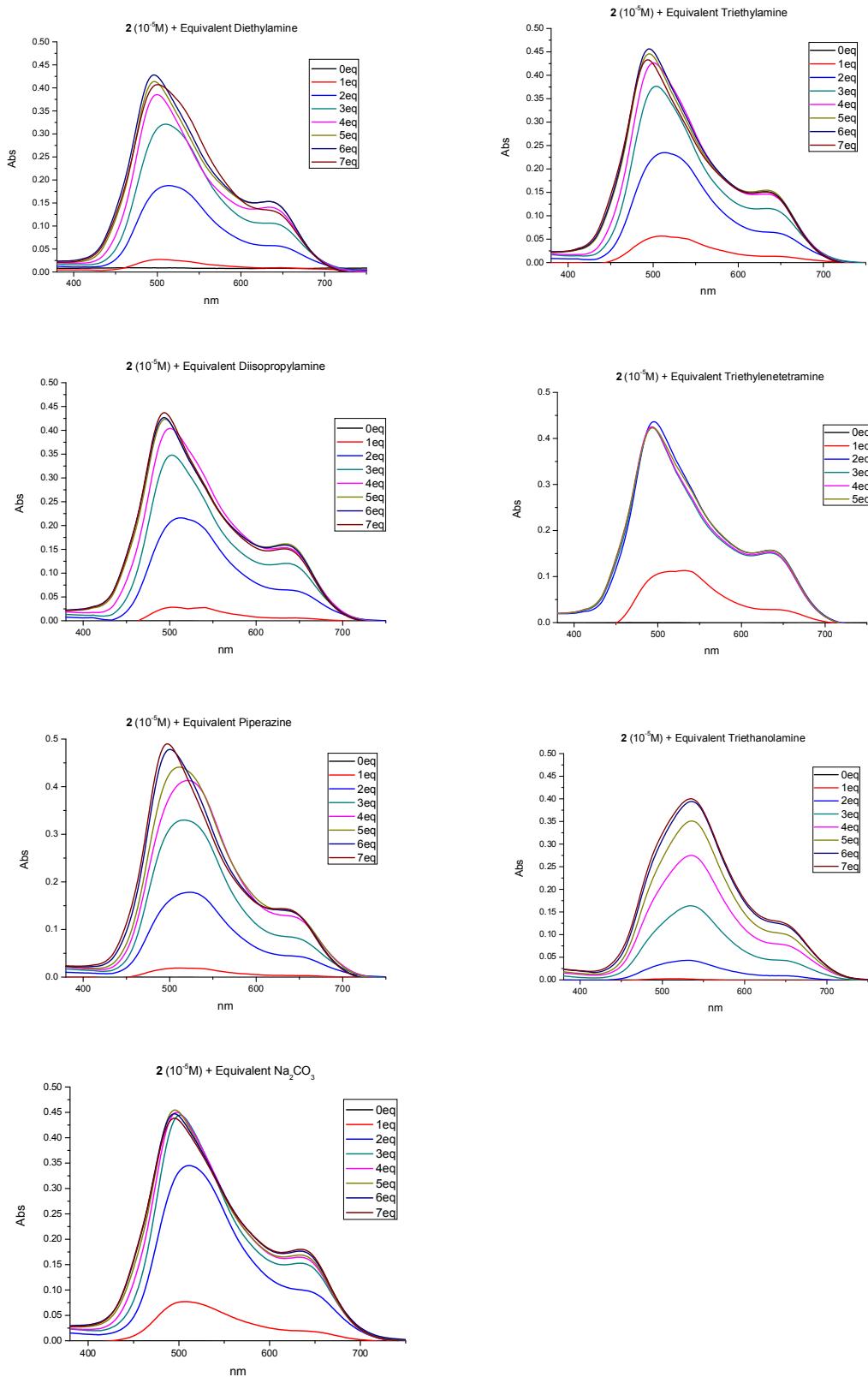


Figure S7. UV-vis spectra of 1.0×10^{-5} M compound **2** aqueous solution in the presence of different base at different concentrations. Base concentrations varies from 1eq to 7 eq of **2**, with a color change from colorless to purple.

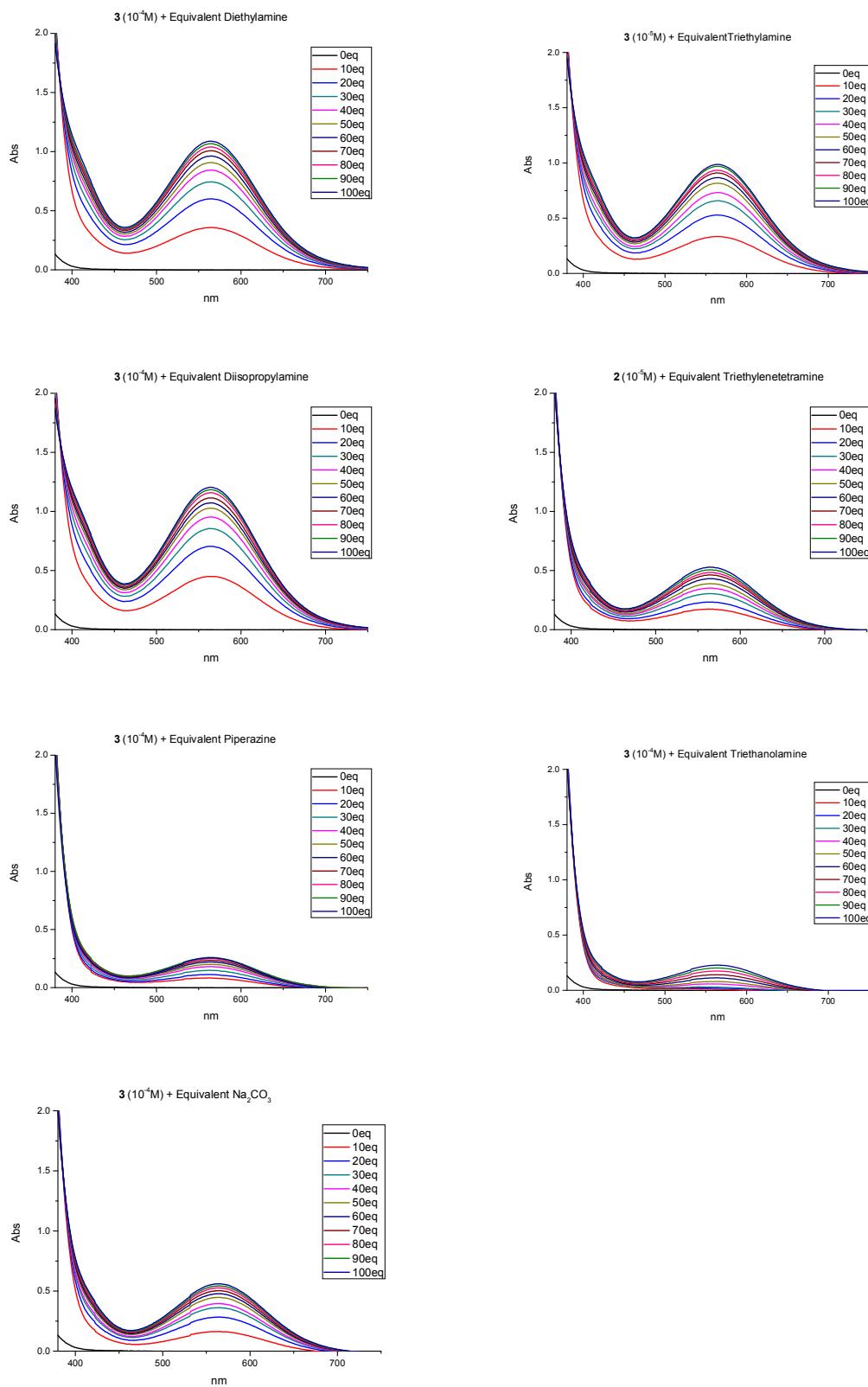


Figure S8. UV-vis spectra of 1.0×10^{-4} M compound **3** aqueous solution in the presence of different base at different concentrations. Base concentrations varies from 10eq to 100eq, with a color change from colorless to pale yellow then purple-blue. Note the concentrations of **3** as well as that of bases are much higher than in Figure S6 and Figure S7.

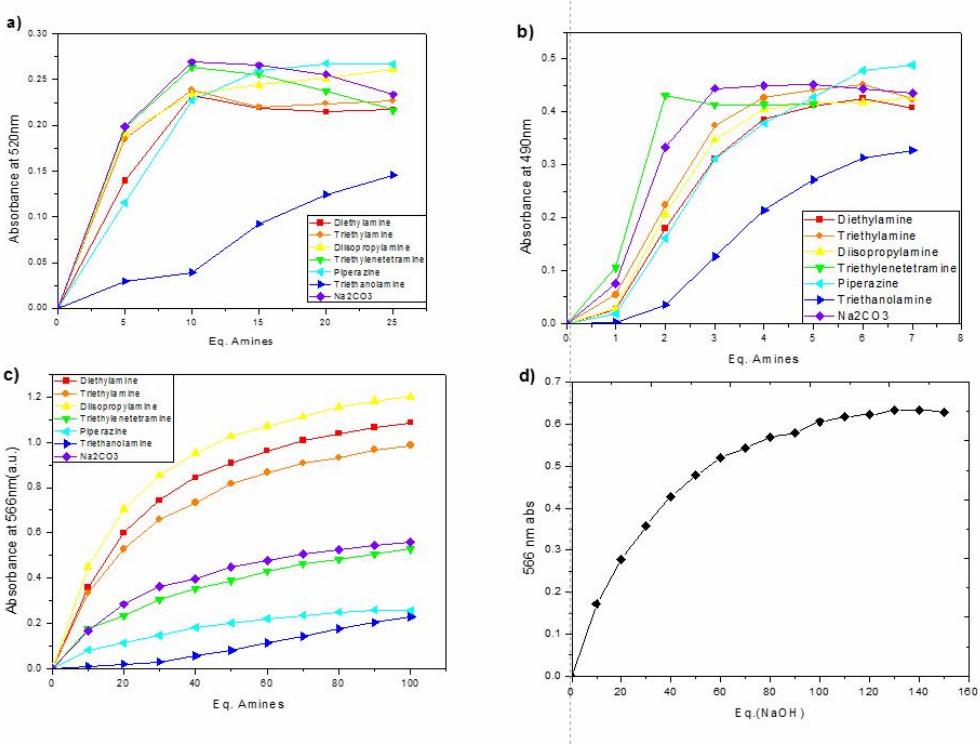


Figure S9. Uv-vis absorbance at different equivalence of base. The **1** (a) and **2** (b) are both 1.0×10^{-5} M, while **3** is 1.0×10^{-4} M (c) and 5.0×10^{-5} M (d).

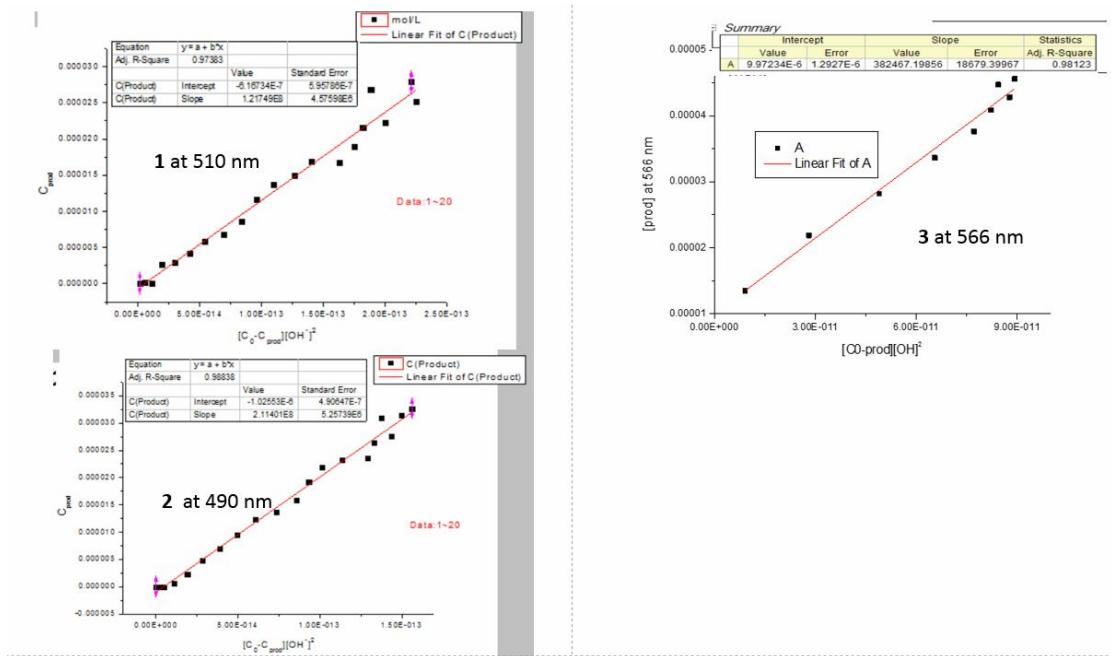


Figure S10 Regression of equilibrium constants of **1~3** in different amount of NaOH

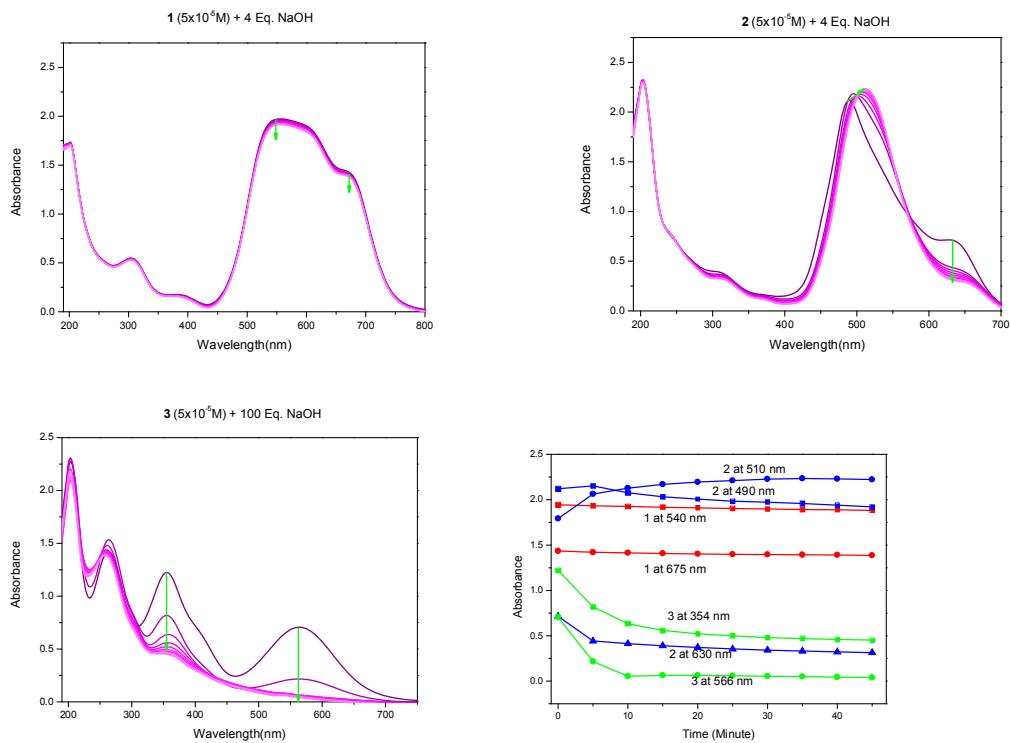


Figure S11 UV-vis spectra of (a) **1** (5.0×10^{-5} M, H₂O) with 4eq NaOH; (b) **2** (5.0×10^{-5} M, H₂O) with 4eq NaOH. (c) **3** (5.0×10^{-5} M, H₂O) with 100eq NaOH tested from 0 min to 45 min (5min each). (d) Absorption change with time from 0 to 45 minutes. Red line: **1** (5.0×10^{-5} M + 4eq NaOH); Blue line: **2** (5.0×10^{-5} M + 4eq NaOH); Green line: **3** (5.0×10^{-5} M+ 100eq NaOH). Different equivalents of NaOH were added in order to produce the maximum amount of radical cations

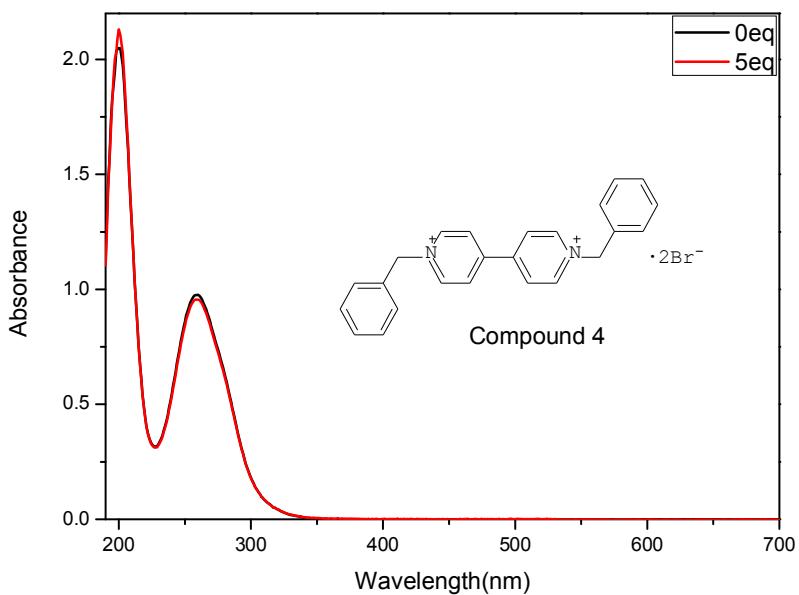


Figure S12 The UV-vis spectra of compound **4** (5.0×10^{-5} M, H₂O) without and with 5 eq NaOH.

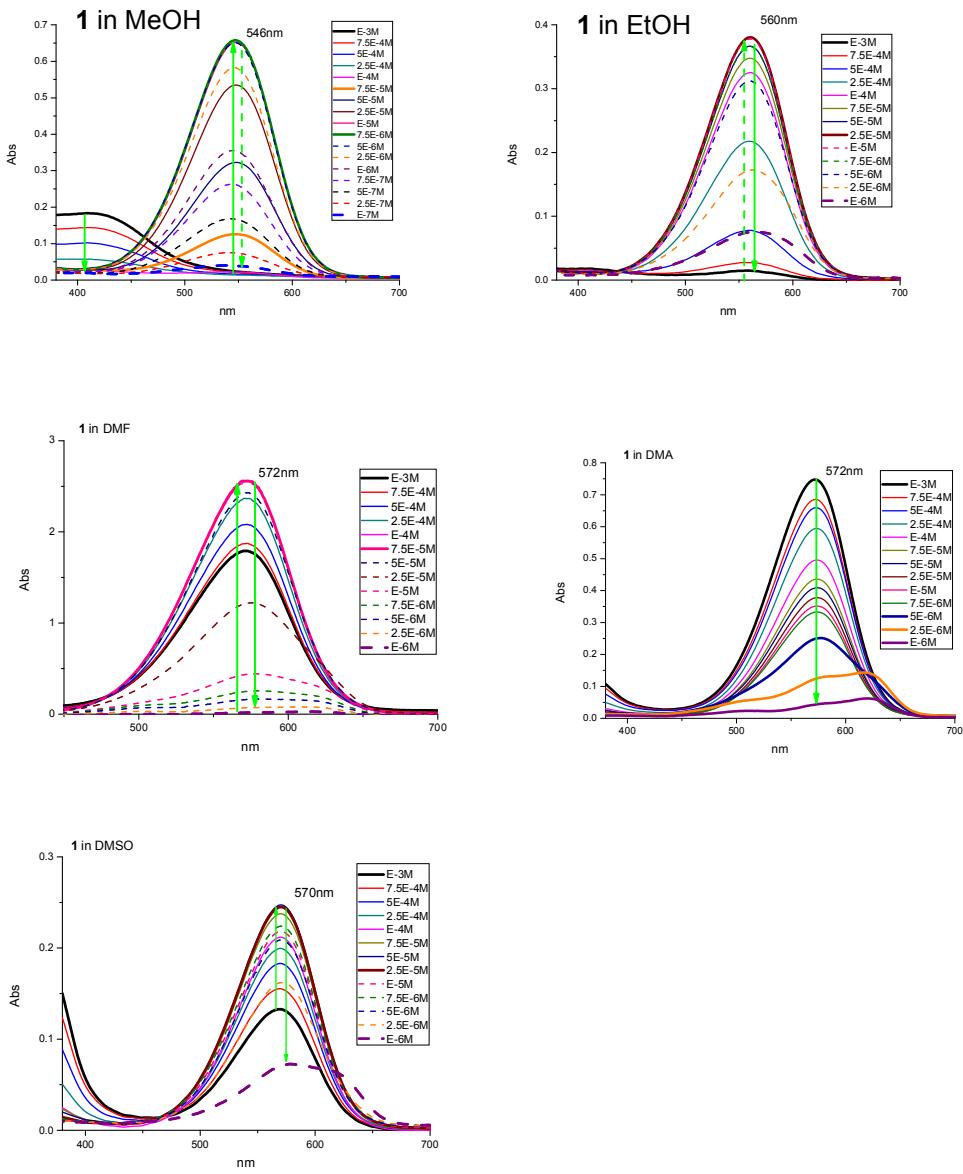


Figure S13 UV-vis spectra of **1** in different solvents at different concentration.

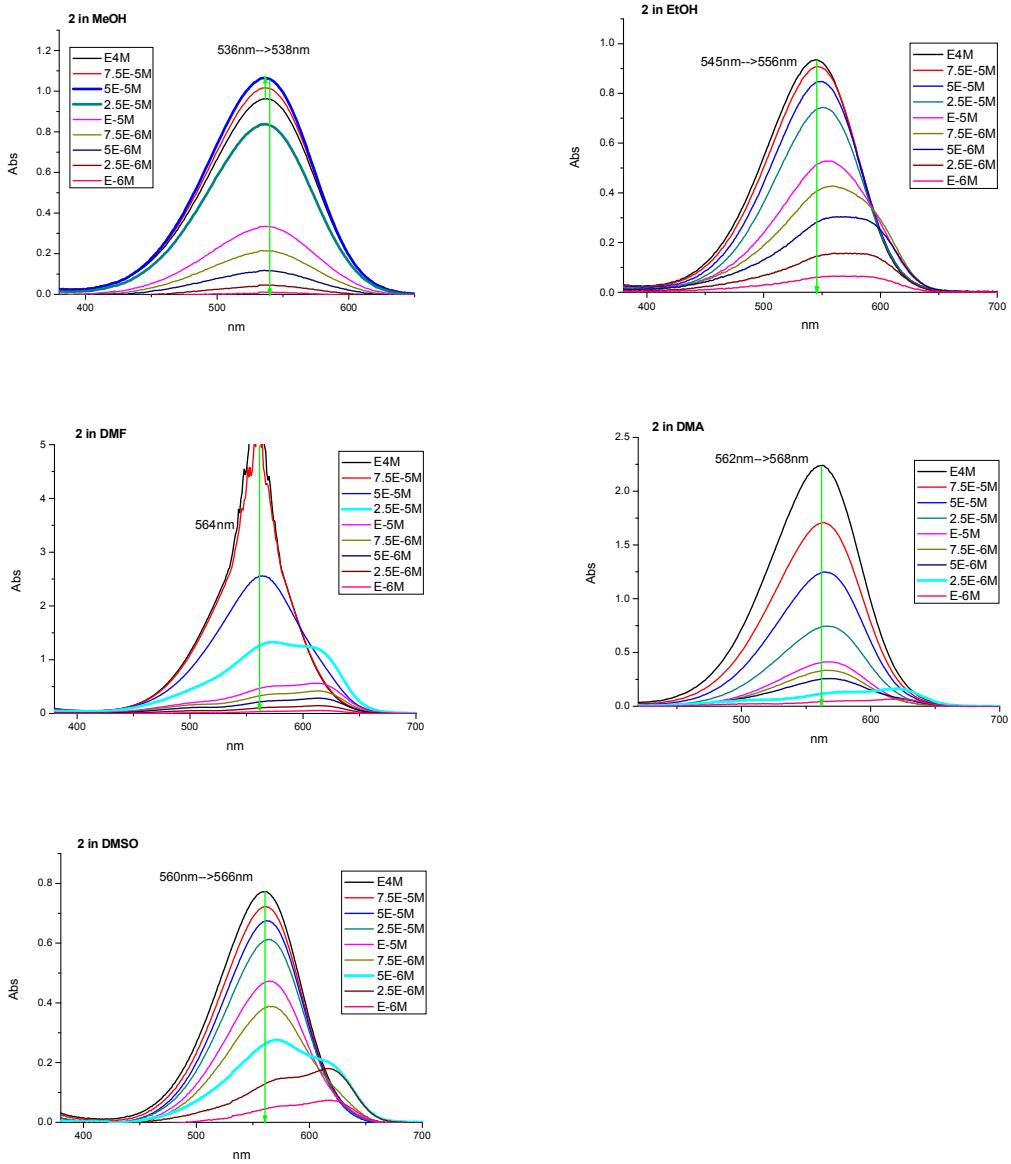


Figure S14 UV-vis spectra of **2** in different solvents at different concentration.

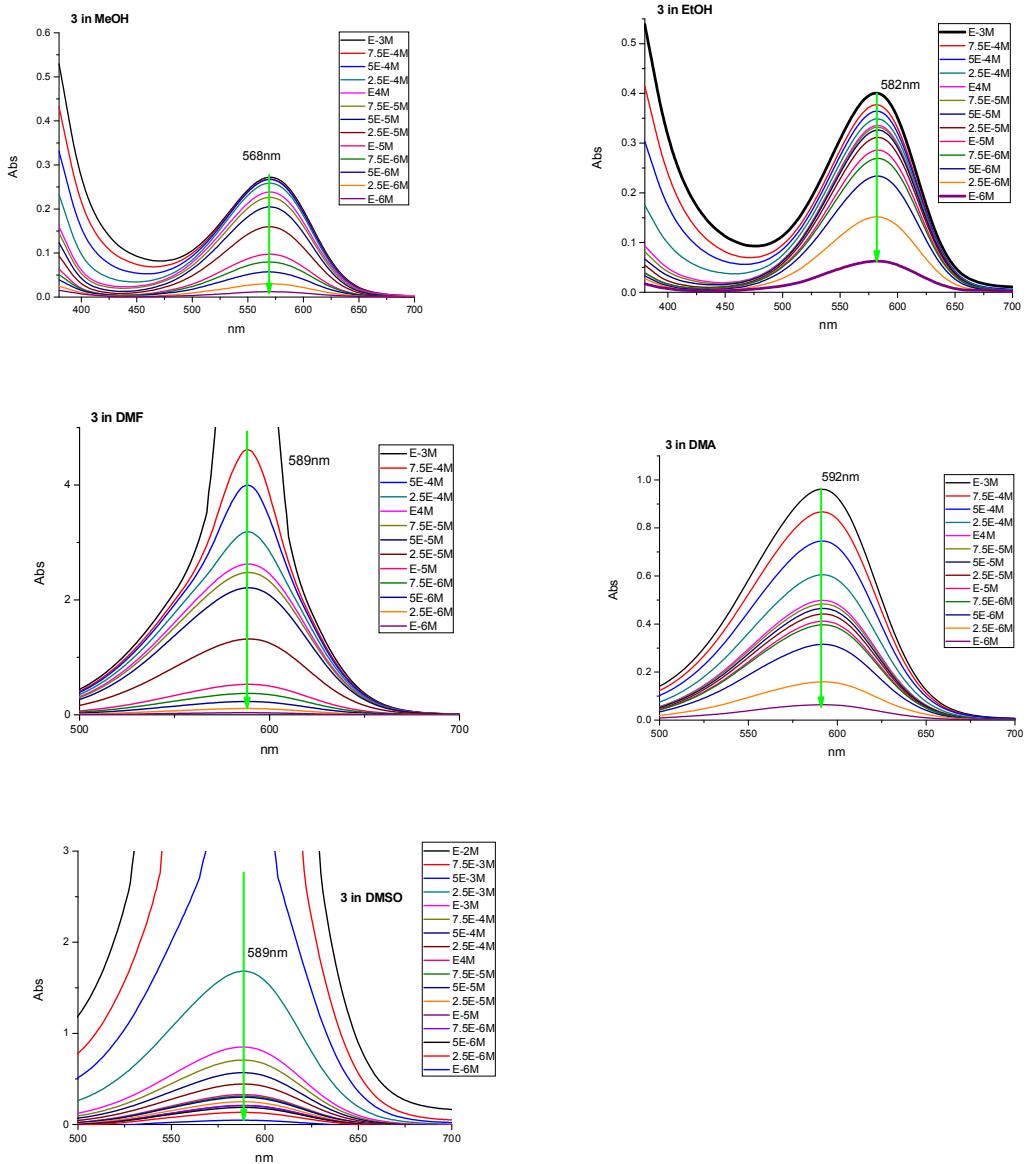


Figure S15 UV-vis spectra of **3** in different solvents at different concentration.

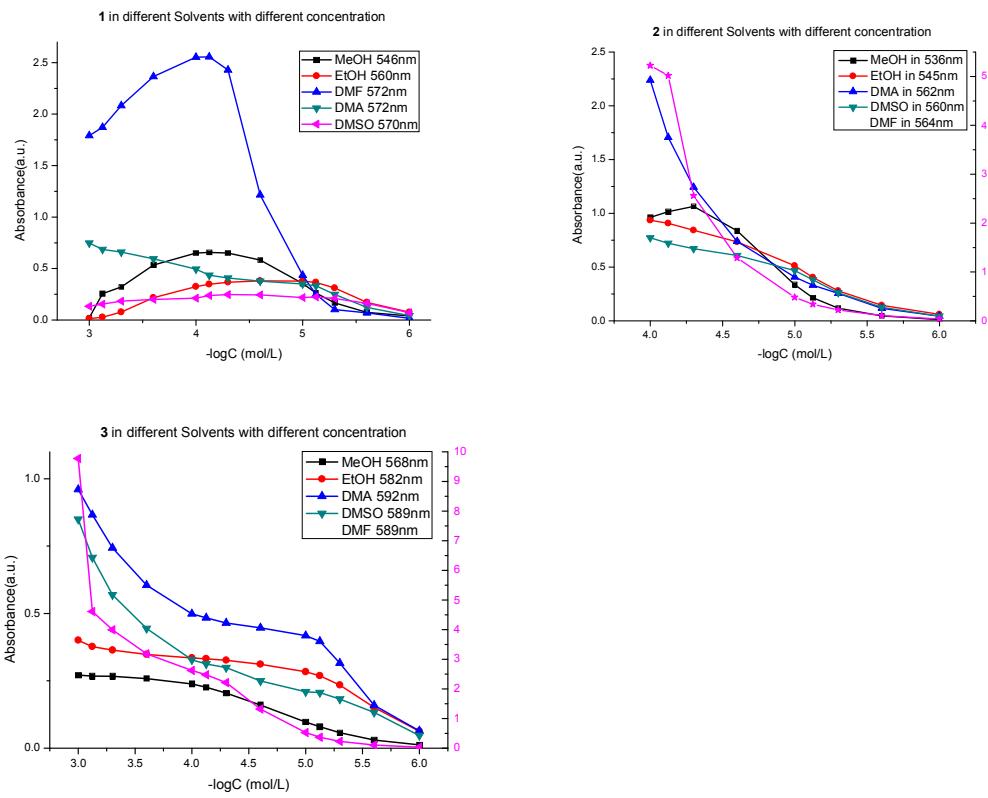


Figure S16 Maximum absorbance of (a) **1**; (b) **2**; (c) **3** in different solvents at different concentration. (**2** and **3** have limited solubility). Note that DMF solution is the deepest color, its absorbance is labeled in the right Y axis.

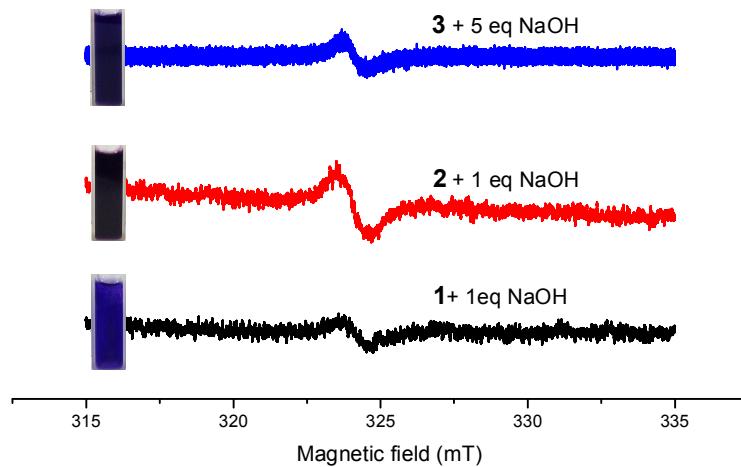


Figure S17 Comparison of X-band EPR spectra of (1.0×10^{-3} M, H₂O) of **1**, **2** and **3** in the presence of NaOH: 1+ 1eq NaOH (bottom); 2+ 1eq NaOH (middle); 3+ 5eq NaOH (top) at 243.15K. Microwave power was 0.99800mW

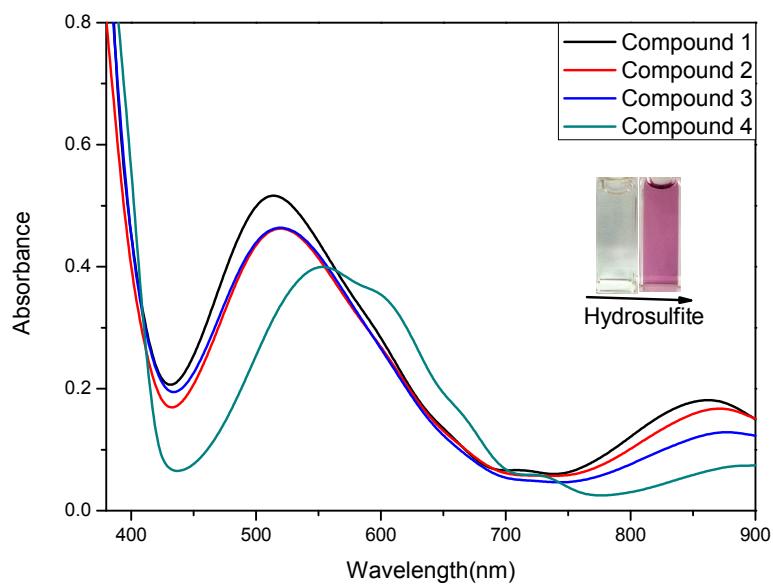


Figure S18 UV-vis spectra of **1~4** (5.0×10^{-5} M, H₂O, 3.0 mL) added ~5 mg sodium hyposulfite. Photographic images of compound **4** was shown.

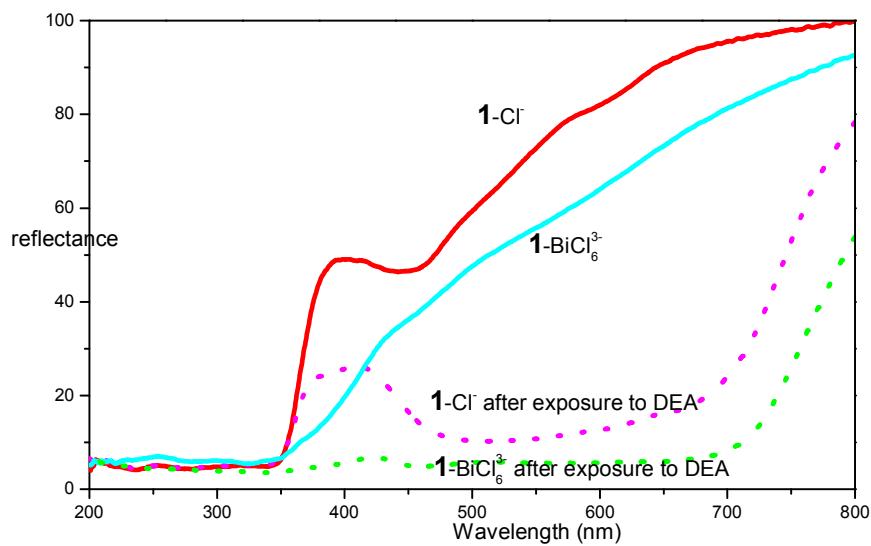


Figure S19. Reflectance spectra of $\mathbf{1}\cdot\text{Cl}_2$, $\mathbf{1}\cdot\text{BiCl}_6$ before and after expose to diethylamine vapor.

Table S1 Crystal structure data of colorless(pale yellow) and colored **(1)₃.(BiCl₆)₂**

compound	pale yellow	Blue-purple
formula	C ₇₈ H ₆₆ Bi ₂ Cl ₁₂ N ₆ O ₆	C ₇₈ H ₆₆ Bi ₂ Cl ₁₂ N ₆ O ₆
Fw	2026.73	2026.73
cryst syst	Triclinic	Triclinic
space group	<i>P-1</i>	<i>P-1</i>
<i>a</i> (Å)	11.585(3)	11.582(10)
<i>b</i> (Å)	13.311(3)	13.318(12)
<i>c</i> (Å)	14.923(4)	14.951(13)
α (°)	106.874(3)	106.738(10)
β (°)	107.017(3)	106.793(10)
γ (°)	99.008(3)	99.103(10)
<i>V</i> [Å ³]	2031.1(9)	2040(3)
<i>Z</i>	1	1
<i>D_c</i> (g cm ⁻³)	1.657	1.650
<i>F</i> (000)	994	994
μ (mm ⁻¹)	4.775	4.755
Reflections/ unique	10605 / 7024	10605 / 7066
<i>R</i> _{int}	0.0262	0.0173
Data /restraints/param	7024 / 0/469	7066 / 0/469
GOF on <i>F</i> ²	0.850	1.038
<i>R</i> ₁ , <i>wR</i> ₂ (I>2σ(I))	0.0360, 0.0844	0.0256, 0.0579
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0485, 0.0899	0.0317, 0.0594
Largest diff. peak and hole(e Å ⁻³)	0.491 and -0.715	0.710 and -0.974