Supporting Information

For

Phenolacetyl Viologen as Mutifunctional Chromic Material for Fast and Reversible Sensor of Solvents, Base, Temperature, Metal Ions, NH₃ Vapor and Grind in Solution and Solid State

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I. Experimental Section

1.1 Chemicals.
4,4'-Bipyridine (Sinopharm Chemical Reagent), 2-bromo-2'-hydroxyacetophenone (ENERGY Reagent). All other chemicals were used as received without further purification. Solutions were prepared with sub-boiled water distilled water in an all-quartz apparatus.

1.2. Instrumentation.
$^1$H and $^{13}$C NMR spectra were measured on a Bruker AV 500 MHz spectrometer. TOF mass spectra were collected on an Agilent 6510Q. ESI mass spectra were performed on a Shimadzu LCMS-2020. The elemental analyses (C, H, and N) were obtained on a Vario EL III analyzer. UV–vis absorption spectra were performed with a Puxi TU-1900 spectrometer with a 1.0 cm and 0.1cm quartz cell equipped with a temperature-controlled water bath (25 °C). Pure solvents were used as references. Electron paramagnetic resonance (EPR) spectra were recorded by a JES-FA 200 spectrometer fitted with the DICE ENDOR accessory, EN801 resonator, and an ENI A-500 rf power amplifier.

NH$_3$ and HCl vapor sensor were performed in air at room temperature. NH$_3$ vapor (on top of 25% NH$_3$ aqueous solution) were withdrawn with a syringe, the vapor in syringe were inject on surface of sample or paper from ~5 cm. HCl vapor were taken from 36% HCl aqueous solution. Other experimental procedure were identical to those reported in literature.\(^1\)

1.3. Synthesis of Compound H$_4$pav·Br$_2$.
4,4'-Bipyridine (314mg, 2 mmol) and 2-bromo-4'-phenylacetophenone (1.08g, 5 mmol) were dissolved in anhydrous DMF (8 mL). The solution was refluxed in a Schlenk flask with a magnetic stir bar for 24 h at 120 °C, then a pale yellow precipitate appeared. The residue was collected through centrifugation, washed with DMF and acetone several times, and dried under vacuum. Yield: 81% (0.95g, 1.62 mmol). $^1$H NMR (500MHz, DMSO, 25 °C): 11.36 (s, 2 H), δ 9.36 (d, J = 7.0, 4 H, ArH), 8.96 (d, J = 7.0, 4 H, ArH), 7.87 (dd, J$_1$ = 2.0, J$_2$ = 13.0, 4 H, ArH), 7.63-7.59 (m, 2 H, ArH), 7.19 (d, J = 3.0, 2 H, ArH), 7.05 – 7.02 (m, 2 H, ArH), 6.40 (s, 4 H). $^{13}$C NMR (DMSO): δ 190.7, 160.0, 149.7, 147.7, 136.9, 130.6, 126.7, 121.1, 120.0,119.1, 70.2. MS (ESI, in H$_2$O) m/z: 425.15[H$_4$pav$^+$, M$^+$], 213.08 [H$_4$pav$^{2+}$, M$^{2+}$]. Anal. Calcd for C$_{36}$H$_{22}$O$_4$N$_2$Br$_2$: C, 64.66; H, 4.64; N, 4.21. Found: C, 64.60; H, 4.28; N, 3.97.
II. Supplementary Physical and Chemical Characterizations
Figure S1. $^1$H NMR, $^{13}$C NMR (in D-DMSO), IR spectra and Mass spectra of H$_4$paBr$_2$. 
Base Titration in Aqueous Solution

UV–Vis spectra of $5.0 \times 10^{-5}$ M cation $\text{H}_4\text{pav}^{2+}$ in aqueous solution shows peaks at 265 (absorbance coefficient $\varepsilon = 5.16 \times 10^4$) and 324 nm ($\varepsilon = 1.04 \times 10^4$), which is colorless (Figure S2). The strong peak at 265 nm is almost identical to other acetyl viologen compounds without phenol hydroxyl. Phenol chalcone also has this 265 nm peak but obviously smaller absorbance coefficient. The 324 nm absorbance is thus attributed to the phenol moiety, which is similar to our catechol compounds (283, 312 nm with $\varepsilon = 1.0 \times 10^4$ and 8460 respectively). When a small amount of NaOH was added to an aqueous solution of $\text{H}_4\text{pav}^{2+}$, the 374 nm peak increased gradually. The isosbestic at 243 and 347 nm clearly indicate the equilibrium between $\text{H}_4\text{pav}^{2+}$ and $\text{H}_3\text{pav}^+$ in the presence of 1 eq NaOH or less. The 264 and 364 nm peaks decrease with the increase of NaOH and reach a plateau in the presence of 3 eq NaOH as shown in Figure 1 (inset). The pH at 3 eq NaOH is roughly neutral (7.8) indicate the $\text{H}_4\text{pav}^-$ species. At 0.5, 1.5, 2.5 and 3.5 eq NaOH, the pHs are 6.46, 6.58, 7.14 and 8.61 respectively, indicate the four pKa. In aqueous solution, the $\text{H}_4\text{pav}^2+$ (265, 374 nm), and $\text{H}_4\text{pav}^-$ peaked at 374 nm. While $\text{H}_3\text{pav}^+$, $\text{H}_2\text{pav}$ in the between. It should mention that the solution is very pale blue with absorbance <0.05 in ~550nm in the presence of ~2eq NaOH.

![Figure S2](image.png)

**Figure S2.** UV–vis spectral changes of $5.0 \times 10^{-5}$ M $\text{H}_4\text{pav}^{2+}$ upon gradually adding NaOH in aqueous solution. Color change from colorless to purple, and then colorless. The inset graph is the absorbance changes with equivs of NaOH.

Base Titration in non-Aqueous Solution

The UV–Vis spectra of $1.0 \times 10^{-5}$ M $\text{H}_4\text{pav}^{2+}$ in the presence of different amount NaOH in DMSO were shown in Figure S3. The viologen concentration is obviously lower than in Figure S2. Different from the colorless of $5.0 \times 10^{-5}$ M $\text{H}_4\text{pav}^{2+}$ in aqueous solution, $1.0 \times 10^{-5}$ M $\text{H}_4\text{pav}^{2+}$ in DMSO is clearly pink with absorbance maximum at 558 nm (Figure S3, black line). Gradually adding NaOH aqueous solution ($\text{H}_2\text{O}$ is less than 1% in the whole process), the 558 nm peak increases its intensity (red and blue lines corresponding to 0.25 and 0.5 eq, Figure S3). This peak reaches its maximum at 0.5 eq NaOH. Further adding NaOH, the 558 peak (purple color) shifted to 610 nm in the presence of 1.0 eq NaOH (orange line). The 610 nm peak reach to its maximum in the presence of 1.25
 eq NaOH (thick purple line). The 610 nm peak decreases upon further adding NaOH. With the decrease of 610 nm peak, a new peak at 490 nm appeared. The 490, 558 and 610 nm peak intensities with different NaOH eqs are illustrated in the inset figure. Clearly, the 558 (purple), 610 (blue) and 490 nm (orange) peaks, maximum at 0.5, 1.25 and 3 eq NaOH respectively, belongs to three different species. The 610 nm species is H₃Pav⁺, while the 490 nm species should be H₄Pav⁻ (Figure S3 inset). The color differs so great that indicate solvent plays key role in molecule orbital energy. ¹H NMR of H₄Pav²⁺ shows quite clean spectra (Figure S5). Upon adding 0.5 eq NaOD (purple color), the CH₂ group split into two signal with 2:1 ratio (Figure S5). This may indicate that one ketone is tautomerized into enolic structure. The enolic OH has signal at 8.3 ppm. The purple-blue color peaked at 610 nm (in 1~2 eq NaOD) obviously lost CH₂ and phenol hydroxyl signal due to the proton exchange with solvents.

The UV−vis of H₄Pav²⁺ in DMSO also varies with concentrations (Figure S4). In < 2.0× 10⁻⁶ M, it has 558 and 610 nm peaks. Further increase concentration will decreases the 610 nm peak. 610 nm peak disappeared at 1.0× 10⁻⁵ M. This can be explained by the weak pKa of H₄Pav²⁺. Lower the concentration will increase the proton dissociation. The concentration dependence spectra in other methanol, ethanol, DMA and DMF are shown in Figure S5. In methanol/ethanol solution (protic solvent), H₄Pav²⁺ has only one peak at ~556 nm. This peak increases with the concentration increase (0~10⁻⁴ M) in methanol. However, the ~556 nm peak increase in 0~1.0× 10⁻⁴ M, and then decrease with the concentration increase. This phenomenon is similar to previously reported¹. In aprotic solvent DMF/DMA, there are two peaks at 562 and 610(DMF), 619 (DMA). This is similar to the above mentioned DMSO solvent. The 619 nm peak maximize at 2.0 × 10⁻⁶ (DMA), which is similar to that in DMSO. The 610 nm peak maximized at 2.0× 10⁻⁵ (DMF). The ~562nm peak reaches maximum at ~3 × 10⁻⁵ and 4.0 × 10⁻⁵ in DMA and DMF respectively. The UV−Vis spectra of H₄PavBr²⁺ at different NaOH concentrations in DMF solution are similar to that in DMSO, which is showed figure in the S5. The coloration is multiple and interesting, in which we observed more colors and changes. A new longer wavelength peak at 661nm is appeared which is may attributed to viologen radical cation dimer.

The visible absorption in 5.0 × 10⁻⁵ M aqueous solution is far less than that of 1.0 × 10⁻⁷ M in DMSO solution. The absorption is not only stronger on organic solvents, but also much rich-color depends on base and concentrations (in organic solvents). ¹

EPR spectra were investigated to elucidate possible species. Adding bases can deepen the color of the viologen, and the pale blue samples have an EPR signal of free radical at g = 2.00 (Figure s6). To further prove that the deep colored species is a viologen radical (~550 nm in aqueous solution), we used the reducing agent sodium hyposulfite. In the presence of a small amount of sodium hyposulfite (~2 mg), the viologen shows a deeper color with a very strong EPR signal (Figure S6). All of these data indicate that radical cations formed once adding enough base (electron donor) or reducing hyposulfite in aqueous solution, which are consistent with the previous studies.¹ ³ However, the deep colored species in DMSO is EPR silent. Based on the pH titration in aqueous solution (Figure s2) and Figure s3, the reaction mechanism in DMSO is proposed in Scheme 1.

It is well known that viologen radicals aren’t stable. With easy synthesis and high sensitivity, H₄Pav²⁺ shows rich colors at different NaOH concentrations in air. It is a convenient visual sensor to monitor bases in DMSO and other organic solvents.
Figure S3. UV–vis spectral changes of $1.0 \times 10^{-5}$ M Hapav$^{2+}$ upon gradually adding NaOH in DMSO (top) and $1.0 \times 10^{-4}$ M Hapav$^{2+}$ in DMF (bottom) solution. Color change from pink to purple, blue, green and then yellow. The inset graph is the absorbance changes with equivs. of NaOH.
**H₄pavBr₂ in MeOH**

Absorbance vs Wavelength in MeOH.

- **556 nm**
- **1.0E⁻⁶**
- **1.5E⁻⁶**
- **2.0E⁻⁶**
- **2.5E⁻⁶**
- **3.0E⁻⁶**
- **3.5E⁻⁶**
- **4.0E⁻⁶**
- **4.5E⁻⁶**
- **5.0E⁻⁶**
- **5.5E⁻⁶**
- **6.0E⁻⁶**
- **6.5E⁻⁶**
- **7.0E⁻⁶**
- **7.5E⁻⁶**
- **8.0E⁻⁶**

**H₄pavBr₂ in DMA**

Absorbance vs Wavelength in DMA.

- **562 nm**
- **619 nm**
- **1.0E⁻⁶**
- **1.5E⁻⁶**
- **2.0E⁻⁶**
- **2.5E⁻⁶**
- **3.0E⁻⁶**
- **3.5E⁻⁶**
- **4.0E⁻⁶**
- **4.5E⁻⁶**
- **5.0E⁻⁶**
- **5.5E⁻⁶**
- **6.0E⁻⁶**
- **6.5E⁻⁶**
- **7.0E⁻⁶**
- **7.5E⁻⁶**
- **8.0E⁻⁶**
Figure S4. UV-vis spectra of H₄pavBr₂ in different solvents at different concentration.
Figure S5. $^1$H NMR of H₄pavBr₂ in the presence of different equiv. NaOD (top) in DMSO. The 8.32 ppm peak is CHCl₃. C-H COSY spectra of H₄pavBr₂ in the presence of 0.5 equiv. NaOD (bottom).
Figure S6. Comparison of X-band EPR spectra of H₄pavBr₂ (1.0 × 10⁻³ M) in the presence of NaOH and hyposulfite at 243.15K freezed aqueous solution. Microwave power = 0.99800 mW.

Figure S7. UV–vis spectral changes of 1.0 × 10⁻³ M H₄pavBr₂ upon adding 4 eq. metal ions in DMF solution.
Figure S8. IR spectra of H₄pavBr₂ and its Fe(NO₃)₃ and Cu(NO₃)₂ complexes precipitated from pH ~7 aqueous solution.

Figure S9. Temperature-depend NMR spectra of H₄pavBr₂ in DMSO (top) and the chemical shift of phenolic hydroxy hydrogen (bottom left) and methylene hydrogen (bottom right).
Figure S10. $^1$H NMR of $\text{H}_4\text{pavBr}_2$ before (red line) and after (blue line) grinding in DMSO.

Figure S11. Solid state X-band EPR spectra of $\text{NH}_3$ vapor response. $\text{H}_4\text{pavBr}_2$ before (bottom).
and after (top) grinding at room temperature. Microwave power = 0.99800 mW.

**Figure S12.** XRD patterns of H₄pavBr₂ in different solid states

**Figure S13** TG and DSC of H₄pavBr₂ before (red line) and after (black line) grinding.
Figure S14. UV-vis spectra of 5.00 mM H$_4$Pav$^{2+}$ with different amount Fe(NO$_3$)$_3$ (top) and Cu(NO$_3$)$_2$ (bottom) in aqueous solution. The 497 nm absorbance varies with Fe(III)/H$_4$Pav$^{2+}$ and is illustrated in the inset.
Scheme S1. Proposed Reaction Mechanism (main species) for $1.0 \times 10^{-5}$ M H$_4$paBr$_2$ with NaOH in DMSO. The wavelengths and NaOH equivs. are from Figure s3. Please note that the equivs are varies with concentrations. The first two protons deprotonate in very weak acidic and neutral solution, while the last two protons deprotonate in basic solution. Free radical may exist in solution, but not predominant species as weak and silent EPR in H$_2$O and DMSO.

Table S1. Maximum Absorption Wavelength ($\lambda_{\text{max}}$) (nm) of H$_4$paBr$_2$ in different solvents.

| Solvent | H$_2$O | MeOH | EtOH | DMSO | DMF | DMA |
|---------|--------|------|------|------|-----|-----|
| E'$_T$  | 1.000  | 0.762| 0.654| 0.444| 0.386| 0.377|
| $\lambda_{\text{max}}$ | ~529(weak) | 556 | 567 | 558 | 562 | 562 |

Table S2: Some important IR bands in H$_4$paBr$_2$ and its metal complexes (cm$^{-1}$)

| Compound | $\nu$OH | $\nu$CH(Aromatic) | $\nu$C=O | $\nu$Ph-C=C | Ph-C-C(in plane) | $\delta$OH(phenol) | $\nu$C-O(phenol) | $\nu$M-O |
|----------|---------|----------------|---------|-------------|-----------------|----------------|----------------|---------|
| H$_4$paBr$_2$ | ~3393 | ~3057 | ~1647 | ~1557 | ~1458 | ~1355 | ~1318 | / |
|          | (1604)$'$ | (1498)$'$ | | | | | (1288)$'$ | | |
| Fe$^{3+}$-complex | / | ~3048 | ~1630 | ~1557 | ~1470 | / | ~1272 | ~595 |
|          | (1593)$'$ | | | | | | (1118)$'$ | | |
| Cu$^{2+}$-complex | ~3415 | ~3048 | ~1603 | ~1568 | ~1461 | / | ~1249 | ~581 |
|          | | | | | | | (1147)$'$ | | |
References:

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2. M. Y. Fosso, H. LeVine, III, K. D. Green, O. V. Tsodikov and S. Garneau-Tsodikova, *Org. Biomol. Chem.*, 2015, 13, 9418-9426.

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