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

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Ⓢ *Supporting Information*

ABSTRACT: Viologen cations are excellent electro- and photo-chromic materials. They generally have no response or very low sensitivity to bases. In this paper, three compounds, 1,1′-bis(2-oxo-2-phenylethyl)-4,4′-bipyridinium (viologen) with different substituents, including H (**1**), Cl (**2**), and OH (**3**), were synthesized. All three, especially **1** and **2**, have very high sensitivity to base in both solution and solid state in air atmosphere. These viologens are responsive not only to bases but also to solvent polarity. NMR shows **1** became enolic and then a radical, whereas **3** is colored only in the radical form. These results are in agreement with EPR spectra. Crystal structures show that the C−C that links two pyridinium and N−C distances in coplanar pyridinium in the colored (radical) form is clearly longer than that of the pale-yellow form, indicating that the color is due to the viologen radical. Viologens containing an electron-withdrawing phenacetyl group are the most sensitive compounds for fast, naked eye detection of base and solvent polarity.
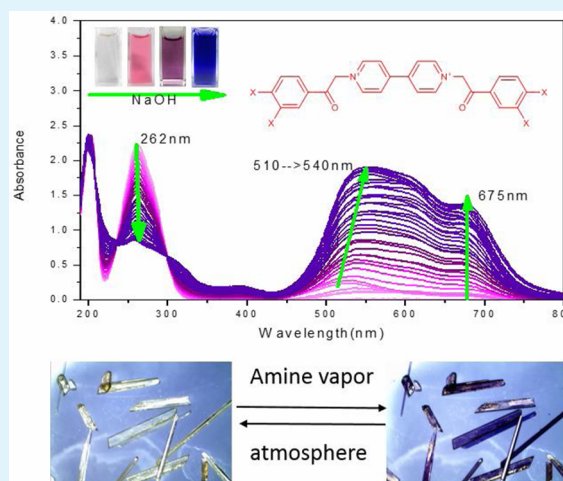
KEYWORDS: viologen, visual base sensor, electronic effect, solvatochromic, air-stable

■ INTRODUCTION

1,1′-Disubstituted-4,4′-bipyridinium salts, namely viologen, were first reported by Weidel and Russo for their prototype, methyl viologen, in 1882 and have a long history as important herbicides in the 20th century.[1] The real breakthrough for viologen materials came about when it was discovered that their particularly electron-deficient nature makes them great electron acceptors and, in a fast and reversible two step redox process, capable of forming three states: dication (V^{2+}), radical cation ($V^{+\bullet}$), and neutral (V^0).[2] The viologen radical cation is intensely colored due to the optical charge transfer between the N^{1+} and N^0 (Scheme 1).[3] Furthermore, the low-energy LUMO allows viologen derivatives to conduct CT (charge transfer) behavior with electron donors ranging from inorganic ions to organic moieties, which always causes a discernible conversion of color.[4,5] Thus, viologen has become one of the most important electrochromic and photochromic materials that can reversibly change their colors in response to electro- or photochemical switching.[6−9] Since then, viologen has been widely investigated in a variety of fields, including electrochromic devices[10−12] and solar energy conversion.[13,14]

In recent years, researchers have started to use viologen as colorimetric electron acceptors to recognize and sense anions, such as dicarboxylate and amines.[15−20] Because of their significant color switch between V^{2+} and $V^{+\bullet}$, the sensing process can be easily examined by UV−vis spectra and even visual inspection. However, most viologen research is still based on methyl or other alkyl viologen derivatives, focusing on the technical or modification methods to optimize their electrochromic characteristics.[21−26] Although there are many chromic studies,[27,28] the relationship between viologen structure, the electronic effect of substituents in particular, and sensibility and viability of viologens is still rare. Another disadvantage is that, although the deep-colored viologen radical cation is comparatively stable, it still faces a fading problem that makes the color change unsteady.[29,30] In most reports, anaerobic and non-H_2O environments are used to avoid the strong radical-quenching effect of H_2O and O_2.[15−20,31] Meanwhile, the sensitivity needs to be improved in order to produce a colorimetric sensor of guest molecules. In fact, due to wide application, guest molecule sensors have been a hot topic for a long time, and many systems have found very stable and high sensitivity.[32−35] However, viologen compounds still have the advantage due to their easy synthesis.

Most reactions are performed in solution. Solvent can strongly influence the reaction course, rate, and equilibrium position.[36] The position and intensity of the bands in the absorption spectra for many chemical systems are also dependent on the medium.[37] Significant changes in reactivity commonly accompany subtle changes in the composition

## Scheme 1. Chromic Process of Viologen

colorless V^{2+} deep colored $V^{\bullet+}$ light colored V
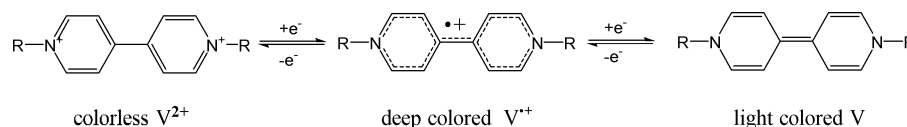
(polarity) of the medium used. Therefore, characterization of solvent polarity is of great importance. The solvent polarity is estimated by solvatochromic compound pyridinium N-phenolate betaine dyes.[37] The color (spectra) of this compound is highly dependent on solvent polarity (water content in organic solvent as well). However, its synthesis is tedious and expensive.[38] Viologens are pyridinium salts with well-studied photo-, thermo-, and electrochromic properties, but their solvatochromic property have yet to be studied. Developing sensors of bases that are pollutants in industry and the environment in solution and the gaseous phase is also of great importance. Wang et al. pioneered a visual sensor of organic bases through benzyl-substituted viologens. They found that 1×10^{-4} M viologens can act as visual sensor to monitor 1000 equiv bases (0.1 M) in degassed CH_3CN solution.[16] Visual sensors of guest molecules in solid state are still rare. A possible reason is that the reported viologens are alkyl substituted such that alkyl group cannot stabilize the colored viologen radical by delocalized electrons.

The development of a viologen derivative that can form its radical cation stably enough in aqueous solution and aerobic atmosphere to increase guest molecule sensitivity is in high demand and is a challenging task. Considering that electron-withdrawing substituents will increase electron-deficiency and thus may help in the formation of a colored monocationic radical ($V^{+\bullet}$), and a larger conjugation system will help to stabilize the radical cation ($V^{+\bullet}$), we design an α-phenacetyl-substituted 4,4'-dipyridinium (viologen), aiming to improve chromic sensitivity and stability even in aerobic aqueous solution. Furthermore, H-, Cl-, and OH-substituted α-phenacetyl were used to study the electronic effect on their sensitivity and stability (Scheme 2). The results indicate that

Scheme 2. Structure and Synthesis of Compounds 1−3

1: R=H; 2: R=Cl; 3: R=OH
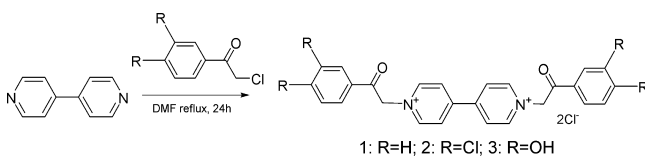
electron-withdrawing substituents will greatly increase viologens' sensitivity to guest molecules (Lewis bases). These new viologens not only respond to a Lewis base and/or electron donor but also respond to solvent polarity.

■ EXPERIMENTAL SECTION

Chemicals. 4,4-Bipyridine (Sinopharm Chemical Reagent), 2-chloroacetophenone (Xiya Reagent), 3,4-dichlorophenacyl chloride (TCI), 4-(chloroacetyl)-1,2-dihydroxybenzene (TCI), and benzyl bromide (Alfa Aesar) were used as received. All other chemicals were used as received without further purification. Solutions were prepared with sub-boiled water distilled in an all-quartz apparatus.

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 quartz cell equipped with a temperature-controlled water bath (25 °C). Pure solvents were used as references. If not mentioned, all spectral data were collected immediately after mixing. In titration experiments, fresh solutions were used in every single test. 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.

Synthesis of Compound 1. 4,4'-Bipyridine (1.56g, 10 mmol) and 2-chloroacetophenone (3.82g, 25 mmol) were dissolved in anhydrous DMF (20 mL). The solution was refluxed for 24 h at 120 °C, during which a pale yellow precipitate formed. The residue was collected through filtration, washed with DMF and acetone, and dried under vacuum. The crude product was dissolved in a minimal amount of room temperature deionized water (~0.5 mL). When large amounts of acetone were added to the solution, a pale yellow powder precipitated, giving a final product of 3.31 g (68.34%). ^{1}H NMR (D_2O, 25 °C, Figure S1 in the Supporting Information (SI)): δ 9.38 (d, J = 6.0, 2 H, ArH), 8.94 (d, J = 6.0, 2 H, ArH), 8.11 (d, J = 8.0, 2 H, ArH), 7.82 (m, 1 H, ArH), 7.70 (m, 2H), 6.62 (s, 2H). ^{13}C NMR (D_2O): δ 191, 151, 147, 136,133, 129, 128, 126, 66. MS (ESI, in CH_3OH) m/z: 395 [M^+]. Anal. Calcd for $C_{26}H_{22}O_2N_2Cl_2\cdot H_2O$: C, 64.60; H, 5.00; N, 5.79. Found: C, 64.49; H, 5.14; N, 5.57.

Synthesis of Compound 2. The procedure was identical to that of **1** except dichlorophenacyl chloride (5.58 g, 25 mmol) was used instead of 2-chloroacetophenone. The final product had a mass of 3.83 g (63.47%).^{1}H NMR (TFA, 25 °C, Figure S2 in the SI): δ 9.76 (d, 2 H, ArH), 8.77 (d, 2 H, ArH), 8.26 (d, 2 H, ArH), 7.99 (m, 1 H, ArH), 7.78 (m, 2 H), 6.59(s, 2H). ^{13}C NMR (TFA): δ 184, 148, 144, 138, 131, 127.7, 127.5, 126,123.2, 123.1, 62; MS (TOF, H_2O) m/z: 531 [M^+], 266 [M^{2+}]. Anal. Calcd for $C_{26}H_{18}O_2N_2Cl_6$: C, 51.78; H, 3.01; N, 4.64. Found: C, 51.81; H, 3.06; N, 4.58.

Synthesis of Compound 3. The procedure is similar to that of **1**. As 4-(chloroacetyl)-1,2-dihydroxybenzene is susceptible to oxidation, the reaction was carried out under a nitrogen atmosphere. The crude product (3.56 g) was dissolved in a minimal amount of hot deionized water (~2.5 g in 50 mL of H_2O). The solution was filtered while hot and then cooled with an ice-water bath until yellow powder precipitated, giving the final product of 1.83 g (52.3%). ^{1}H NMR (DMSO, 25 °C, Figure S3 in the SI): δ 10.48 (s, 1H), 9.77(s, 1H), 9.37 (d, 2 H, ArH), 8.94 (d, 2 H, ArH), 7.49 (d, 2 H, ArH), 7.02 (m, 2 H, ArH), 6.53 (s, 2H, CH_2). ^{13}C NMR (DMSO): δ 189, 153, 150, 148, 146, 127, 125, 122, 116, 115.6, 66. MS (TOF, H_2O) m/z: 457 [M^+], 229 [M^{2+}]. Anal. Calcd for $C_{26}H_{22}O_6N_2Cl_2$: C, 58.99; H, 4.19; N, 5.29. Found: C, 59.17; H, 4.25; N, 5.17.

Synthesis of Crystals. A (**1**)$_3$·(BiCl$_6$)$_2$ (pale yellow) crystal was obtained by the solvothermal reaction. BiCl$_3$ (5.36 mg, 0.017 mmol) and **1** (11.63 mg, 0.025 mmol) were placed in a 25 mL Teflon-lined autoclave, and 8 mL of H_2O and 10 drops of concentrated HCl (36−38%) were added. After being sealed, the autoclave was then heated to 120 °C, kept at that temperature for 3 days, and then slowly cooled to room temperature at 5 °C/h. Pale-yellow single crystals (68% yield based on **1**) were obtained and washed with acetone. ^{1}H NMR (DMSO, 25 °C, Figure S4 in the SI): δ 9.38 (d, J = 6.0, 2 H, ArH), 8.98 (d, J = 6.0, 2 H, ArH), 8.12 (d, J = 8.0, 2 H, ArH), 7.84 (t, 1 H, ArH), 7.71 (t, 2H) and 6.68 (s, 2H). ^{13}C NMR (DMSO): δ 191, 150, 148, 146, 135, 134, 130, 129, 127, 67. MS (TOF, H_2O) m/z: 393 [M^+], 197 [M^{2+}]. IR (KBr disc, Figure S5 in the SI): 3351, 3045, 2966, 1685,1635, 1592, 1448, 1406, 1336, 1230, 991, 887, 840, 763, 690, 574 cm^{-1}. Anal. Calcd for $C_{78}H_{66}Bi_2Cl_{12}N_6O_6$: C, 46.24; H, 3.28; N, 4.15%. Found: C, 46.13; H, 3.25; N, 4.17%.

Several $(1)_3 \cdot (BiCl_6)_2{}^{\bullet}$ (colored form, blue-purple, radical) crystals were placed in a 50 mL flask. A 2 mL syringe was used to extract the upper vapor of diethylamine liquid, which was then injected into the flask. The pale-yellow crystals turned purple immediately. After standing for 1 h in the amine atmosphere, the crystals were removed and wrapped in Vaseline for X-ray structural determination.

X-ray Crystallography. Well-shaped single crystals were selected for X-ray diffraction studies. Data were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo Kα radiation (λ = 0.71703 Å) using the φ and ω scan method at 293(2) K. The structures were solved by direct methods with the SHELXS-97 program[39] and refined by full-matrix least-squares on F^2 with the SHELXL-97 program. All non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located and included at their calculated positions. The crystallographic data and structure refinement results are listed in Table S1 in the SI.

■ RESULTS AND DISCUSSION

Visual Base Sensors in Aqueous Solution. Amine response abilities of **1**, **2**, and **3** were tested in aqueous solution without being degassed. As shown in Figure 1, all three

Figure 1. Photographic images of **1** (1.0×10^{-5} M) in the presence of 10 equiv of base (top), **2** (1.0×10^{-5} M) in the presence of 2 equiv of base (middle), and **3** (1.0×10^{-4} M) in the presence of 50 equiv of base (bottom). From left to right: (a) blank, (b) diethylamine, (c) triethylamine, (d) diisopropylamine, (e) triethylenetetramine, (f) piperazine, (g) triethynolamine, and (h) Na_2CO_3 (photos were taken within 30 s upon addition of the amines).

viologen compounds are colorless in aqueous solution. They become colored upon the addition of amine/base. **1** and **2** can both act as fast detectors of amines to the naked eye. The sensitivity is at least two orders higher than those reported for the 1×10^{-4} M viologen compound in the presence of 1000 equiv of base in solvents.[16,40] **1** and **2** are not only very sensitive but also very convenient for visual detection of different amines since degassing is not needed in our system.

UV−Vis Spectra. UV−vis spectra at different NaOH concentrations are shown in Figure 2. The changes of the UV−vis spectra of these three compounds in the presence of other amines are quite similar to NaOH and are shown in Figures S6−S8 in the SI for **1**, **2**, and **3**, respectively.

When a small amount of NaOH was added to an aqueous solution of **1** and **2**, they showed peaks at 510 and 490 nm, respectively (Figure 2). Increasing the NaOH concentration, both **1** and **2** shifted to longer wavelengths by 20−30 nm. New absorption peaks at 675 and 640 nm appeared for **1** and **2**, which can be assigned to viologen radical cations.[41] The color of the solution changed from colorless in the absence of base to purple and royal blue for **1** upon gradually adding 4 equiv of
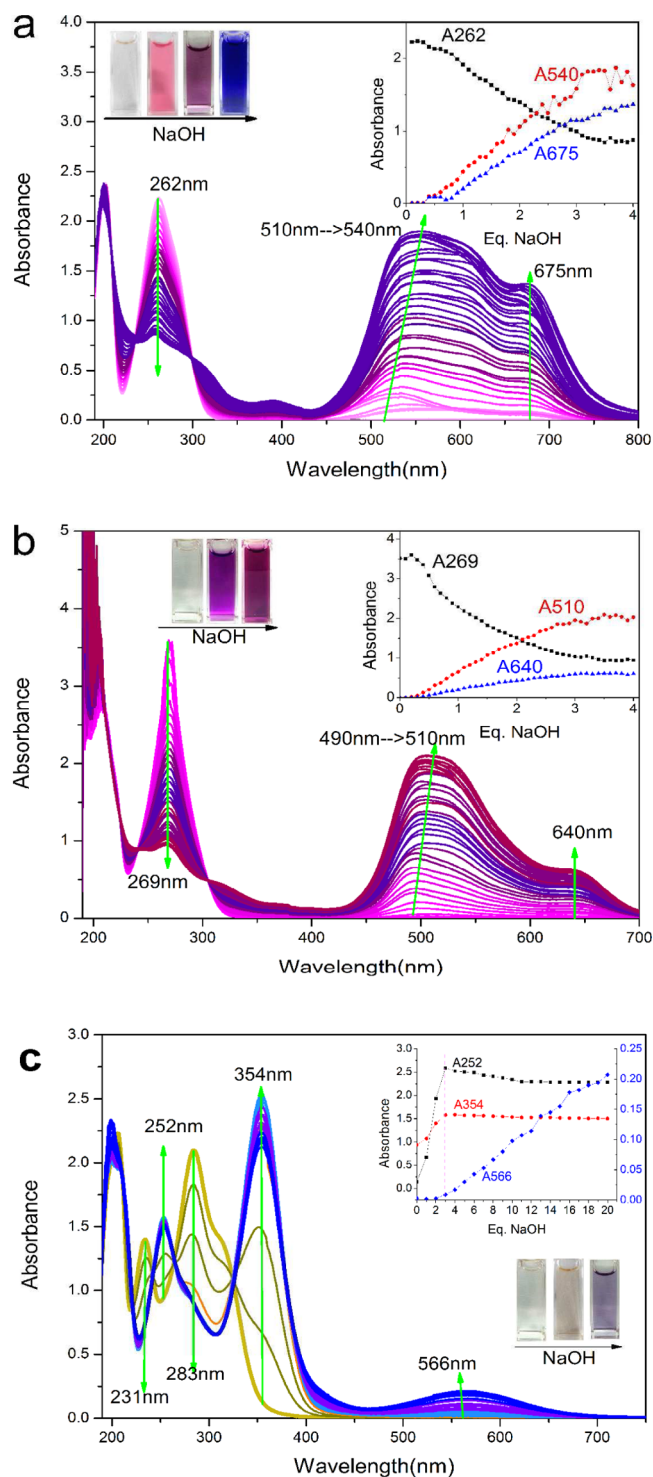

Figure 2. UV−vis spectral changes of 5.0×10^{-5} M viologen compounds upon gradually adding NaOH in aqueous solution. (a) **1**, color change from colorless to pink, purple, and then royal blue; (b) **2**, color change from colorless to red-purple; and (c) **3**, color change from colorless to light blue. The inset graph is the absorbance changes with equivs of NaOH.

NaOH. **2** also deepens its color when adding NaOH. Gradually adding NaOH to **3** results in an absorption peak at 354 nm increasing quickly to give a yellow color. After a further increase of NaOH (3 equiv or higher), a 566 nm peak appeared, whereas the absorption at 354 and 252 nm remained effectively

Table 1. Base Sensitivity at $\Delta_{Abs} = 0.01$ ($\Delta_{Abs} = 0.05$) of a 5.0 × 10⁻⁵ M Aqueous Solution of 1−3[a]

viologen	DEA	TEA	DPA	TETA	PIP	TEO	Na₂CO₃
1	0.26 (1.29)	0.24 (1.38)	0.24 (1.29)	0.41 (1.75)	0.44 (1.86)	2.73 (16.6)	0.25 (1.34)
2	0.27 (0.84)	0.18 (0.92)	0.37 (1.13)	0.13 (0.69)	0.49 (1.06)	1.88 (3.24)	0.14 (0.70)
3	2.63 (12.8)	3.04 (17.9)	3.64 (16.4)	12.7 (44.3)	14.99 (52.3)	223 (558)	9.22 (32.1)

[a]Reported in ppm. Abbreviations: DEA (diethylamine), TEA (triethylamine), DPA (diisopropylamine), TETA (triethylenetetraamine), PIP (piperazine), and TEO (triethanolamine).

constant (Figure 2c). The UV absorption at 231, 252, 283, and 354 nm can be attributed to the protonated and deprotonated state of the catechol substituent and has no relation to the viologen or radical.[42] The absorption in 252 and 354 nm increases drastically until three equivs of NaOH were added, suggesting monodeprotonated catechol was formed.[42] Three equiv of NaOH is enough to change 1 and 2 to the deepest color, whereas for 3, 3 equiv of NaOH is only a start for the colored species formation. The absorbance at 566 nm reaches a plateau at ~120 equiv of NaOH for 5.0 × 10⁻⁵ M compound 3, corresponding to 6.0 × 10⁻³ M NaOH (Figure S9d, SI)

The absorbance plateau (maximum) is a complete formation of viologen (OH)₂ (5.0 × 10⁻⁵ M). The different absorbances at different NaOH concentrations can be simulated according to reaction

$$viologen^{2+} + 2OH^- \overset{K}{\leftrightarrow} viologen(OH)_2$$
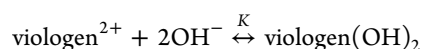
The binding constant $K = (1.22 \pm 0.05) \times 10^8$, $(2.11 \pm 0.05) \times 10^8$, and $(3.82 \pm 0.18) \times 10^5$ M⁻² for 1, 2, and 3, respectively (Figure S10, SI). Different from viologen-Cucurbit[7]uril 1:1 complexes with a binding constant of 10^2–10^6 M⁻¹,[43−47] viologen can form a 1:2 complex with OH⁻, whose stability is on the order of 10^5–10^8 M⁻², depending on the substituents. Electron-withdrawing substituent Cl tends to increase the binding constant as compound 2 has the highest constant among these three viologens.

Figure 2 as well as Figures S6−S8 in the SI indicate that these viologens are good visual sensors of bases. Table 1 lists the sensitivity of 1−3 to different bases, according to Δ_{Abs} 0.01 and 0.05 difference in the presence of bases. From Table 1, compound 2 showed the best sensibility toward all amines followed by compounds 1 and 3. Remarkably, 1 and 2 can both act as versatile high sensitivity visual sensors, their sensitivities are on the ppm level or less. Compound 3 is the least sensitive among the three viologens and is one order lower than 1 and 2. To our knowledge, these results, whether qualitatively or quantitatively, suggest that these viologens are the most sensitive base sensors.[16,18,20]

Also worth mentioning is that all of the results are achieved in aqueous solution in air atmosphere, which has no precedence to the best of our knowledge. With easy synthesis and high sensitivity, 1 and 2 are the best visual sensors to monitor bases in aqueous solution in air atmosphere.

As mentioned in the introduction, one of the biggest challenges for the practical use of viologen derivatives is the quick fade of its radical cations. Colored viologen radicals still react quickly with other components in the solution because most radicals are quite active.[3] Thus, O₂ in the air and even the solvent could cause the disappearance of the viologen's characteristic color.[48] In this respect, the stability of 1−3 in the presence of base were investigated (Figure S11, SI). 1 showed a 0.06 decrease of its absorbance at 540 nm and 0.05 at 675 nm within 45 min, which can be considered negligible. 2 is labile over the first 5 min, especially the 630 nm absorbance

that experienced an ~50% decrease, but the most strong peak at ~510 nm is quite stable without discernible fading. 3 shows the greatest decrease in both 566 and 354 nm absorbance, possibly due to a very high (6.0 × 10⁻³ M) NaOH concentration. Compared to other studies, radical cations of 1 and 2 have a much longer lifetime of hours which makes them more convenient as practical sensors.

To further prove the function of the ketone substituent, we synthesized benzyl substituent compound 4, which is similar to that of 1 but without the ketone moiety, for comparision and found that it cannot form an enolic form[9] (Figure S12, SI). There was no color change with 5.0 × 10⁻⁵ M of 4 upon adding up to 5 equiv of NaOH, which is more than enough for 1−3 to be fully colored. This phenomenon indicates that the ketone substitutent plays very important role in the formation of colored viologen radical forms. We believe that the ketone moiety can delocalize/stabilize the radical form. It is the electronic withdrawal/delocalization effect of the ketone group in 1 and 2 that greatly increases their chromic sensitivity.

Solvatochromism. It is well-known that solvent polarity dominates a chemical reaction. Characterization of solvent polarity is of great importance. Interestingly, besides the great sensitivity toward amine/base, 1, 2, and 3 are all solvent sensitive as well (Figure 3). Their spectra in different organic
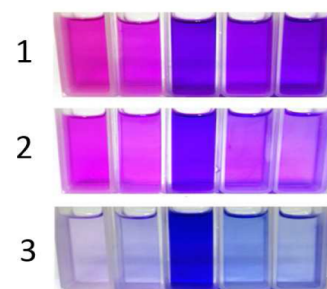

Figure 3. Photographic images of 1−3 (1.0 × 10⁻⁴ M) in different solvents. From left to right: methanol, ethanol, DMF, DMA, and DMSO.

solvents (without any amines) at different concentrations are shown in Figures S13−S15 in the SI. Concentration dependence at the absorption maximum is illustrated in Figure S16 in the SI. The spectrometric data in different solvents are summarized in Table 2.

The maximum absorbance wavelength in different solvents is related to the polarity of the solvent, which shows a blue-shift in higher polarity solvents. The different color in different solvents indicates that all three of these viologens are possible solvatochromic materials.[49] Empirical parameters of normalized solvent polarity (E_T^N) were taken from reported data.[50] Regression of maximum absorption wavelength λ with solvent (i.e., $\lambda = aE_T^N + b$), we have

Table 2. Maximum Absorption Wavelength (λ_{max}) (nm) of 1−3 in Different Solvents[a]

solvent	MeOH	EtOH	DMSO	DMF	DMA	H$_2$O
E_T^N	0.762	0.654	0.444	0.386	0.377	1.00
1	546	560	570	572	572	510
2	536	545	560	564	562	490
3	568	582	589	589	592	566

[a]Reported in nm. E_T^N is the empirical parameter of normalized solvent polarity taken from ref 37.

a, b = −93.7 ± 13.3, 611.6 ± 8.6 for **1**; −108.8 ± 15.5, 608.5 ± 10.0 for **2**; −43.6 ± 6.8, 607.3 ± 4.3 for **3**; respectively

Compound **2** has the largest negative solvatochromic effect as it has a more negative a. Although our viologens are less solvatosensitive than widely used negatively solvatochromic pyridinium N-phenolate betaine dyes,[37] our viologen derivatives have the advantage of easy synthesis and good viability. It should be mentioned that although it is difficult to explain why, compound **1** has the deepest color at ∼7.5 × 10^{-5} M, and a higher or lower concentration will lighten the color in some solvents (Figure S13, SI). Similar to betaine dyes, solvatochromism of the these viologen compounds is possible due to the solvation change in the LUMO and HOMO orbital energy.[50]

NMR and EPR. ^{1}H NMR (Figure 4) and EPR spectra (Figure 5) were investigated to elucidate possible species. Free **1** has five different aromatic protons in the 7.6−9.1 ppm ranges and one set of a methylene proton at 6.55 ppm as shown in Figure 4. Upon adding diethylamine (0.1 equiv), the solution becomes purple, methylene protons adjacent to the α-carbonyl at 6.55 ppm disappear. This indicates that an enolic form has formed. **3** in DMSO is pale-blue, and upon adding excess diethylamine, it changes to a deep-blue color. ^{1}H NMR becomes much broader and weaker. Differing from that of **1**, methylene protons still exist in **3**. All protons shifted to higher field except benzene protons. Interestingly, viologen protons in colored **3** were split into two sets, indicating that one pyridinum cation becomes radical, and the two pyridyl protons are unequal. This indicates that the blue color originates from the viologen radical.

Adding bases can greatly deepen the color of the **1**, **2** and **3** viologens. The colored samples have an EPR signal of free radical at g = 2.00 (Figure 5). Trisodium citrate is a very weak base; it can change 1.0 × 10^{-3} M aqueous solution of **1** from colorless to pink. The pink sample is essentially EPR silent. Upon further standing at room temperature, the color
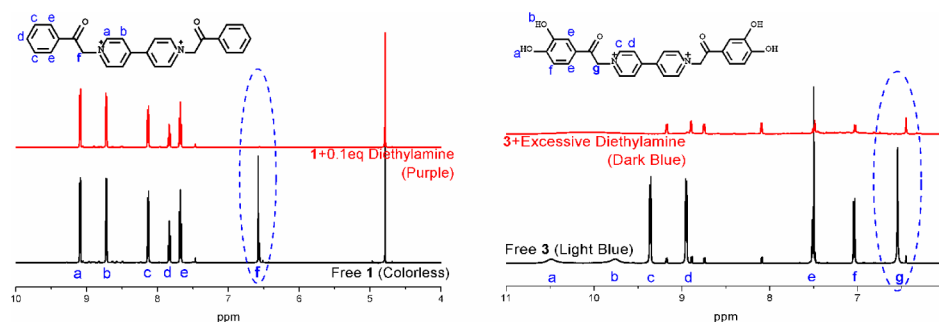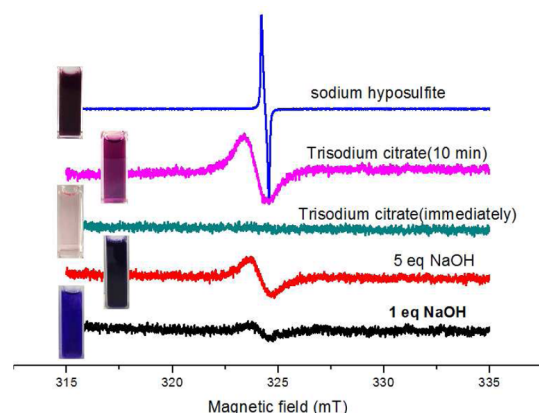

Figure 5. Comparison of X-band EPR spectra of **1** (1.0 × 10^{-3} M) in the presence of different bases and hyposulfite at 243.15K. Microwave power = 0.99800 mW.

deepened with the appearance of an EPR signal at g = 2.00. To further prove that the deep colored species is a viologen radical, we employed the reducing agent sodium hyposulfite. In the presence of a small amount of sodium hyposulfite (∼5 mg), **1** shows a very deep color with a very strong EPR signal (Figure 5). All of these data indicate that radical cations formed upon adding enough base (electron donor) or reducing hyposulfite.[51,52] From Figure S17 in the SI, radical formation ability is in the order **2 > 1 > 3**, which is the same as their sensitivity to base.

No response to base is seen, however, for 5.0 × 10^{-5} M benzyl viologen **4** without ketone group, but it can still be reduced by strong electron-donor hyposulfite to produce a deep colored viologen radical as shown in Figure S18 in the SI.

The reaction processes of the three compounds are illustrated in Scheme 3. The high stability of the radical form is due to better delocalization of the charge compared to those without a phenylacetyl group. The 850 nm peak in the presence of the phenylacetyl group may account for dimerization of the radical, but it is insignificant in the presence of base.

Crystal Structure. For a practical application as chromic materials (sensors), it would be preferably if the compound can show its reversible colorimetric changes not only in solution but also in the solid state. (**1**)$_3$·(BiCl$_6$)$_2$ was synthesized, and we examined its sensitivity toward amine vapor. Pale yellow (**1**)$_3$·(BiCl$_6$)$_2$ responds to amine vapor immediately and becomes dark blue-violet upon exposing the crystal to dimethylamine vapor (DEA). Figure S19 in the SI shows their reflectance spectra before and after exposure to amine vapor. Before

Figure 4. (left) ^{1}H NMR spectra of **1** in D$_2$O in the absence or presence of 0.1 equiv of diethylamine. (right) **3** in DMSO-d_6 in the absence (light blue) and presence (dark blue) of diethylamine.

Scheme 3. Proposed Reaction Mechanism for 1−3

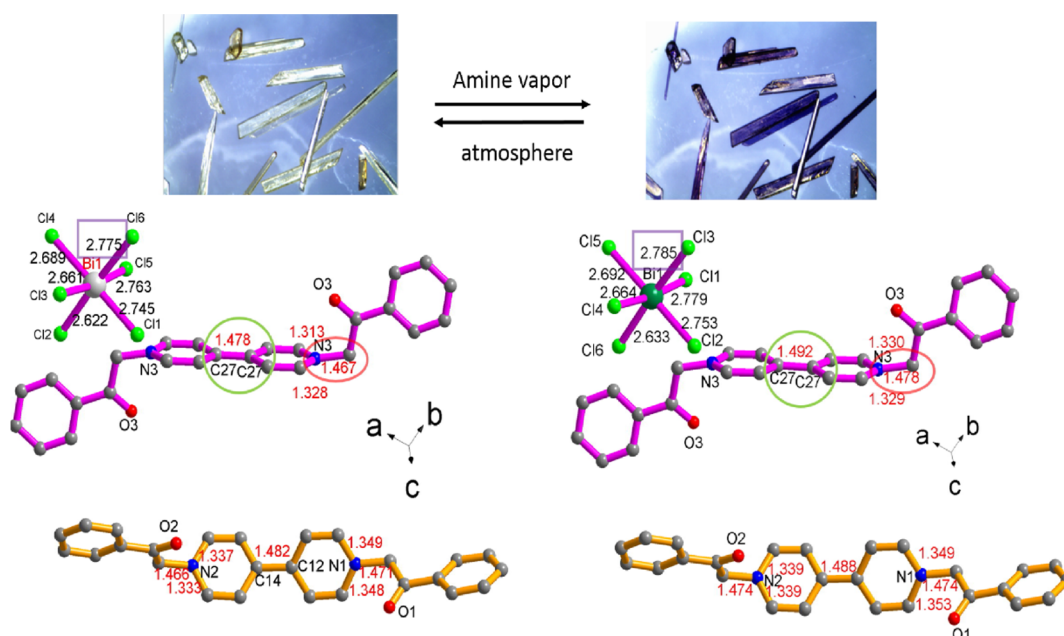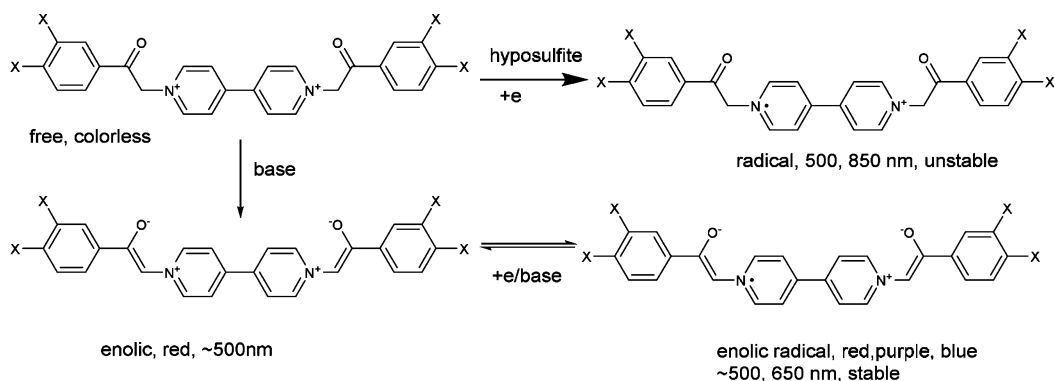**Figure 6.** Crystal structure of $(1)_3 \cdot (BiCl_6)_2$ before (left, pale yellow) and after (right, blue-purple) exposure to diethylamine vapor.

exposure to DEA vapor, both $(1)_3 \cdot (BiCl_6)_2$ and $1 \cdot Cl_2$ are high reflectance in the >400 nm region. Upon exposure to DEA vapor, the reflectance in the visible region is much lower.

The crystal structures of $(1)_3 \cdot (BiCl_6)_2$ before and after exposure to DEA vapor are shown in Figure 6. Although DEA cannot be identified in the crystal, there are obvious bond-length differences before and after exposure to DEA in addition to change in their color. The most obvious change is C27−C27 that links two pyridinium moieties in the coplanar viologen (Figure 6, purple bonds), which increased 0.014 Å after exposure to diethylamine vapor. N⁺−C distances in the central symmetric viologen in blue form (1.477(6) Å) were also obviously longer than those in the colorless form (1.465(8) Å). Some Bi−Cl distances also increased, which is similar to previously reported data.[8] Whereas other distances are essentially the same with a variation of <0.01 Å, generally <0.005 Å, difference, especially in the nonsymmetrical structure (Figure 6, orange color). Considering that only one pyridinium partially reduced to a radical form, the bond-distance effect is much more obvious than in the crystal structure. This bond distance further proves that it is the pyridinium nitrogen that reduced to neutral, which makes the N⁺−C distance longer.

These compounds respond to the electron donor in both solids and liquids; thus, chromic selectivity has not yet been found.

CONCLUSIONS

1,1′-Diphenacetyl-4,4′-dipyridinium with different benzene substituents, H (1), Cl (2) and OH (3), were synthesized. Electronic-withdrawing phenacetyls 1 and 2 have much more sensitivity to weak electronic donors (bases) in both solution and solid state in air atmosphere. The viologen forms 1:2 species with OH⁻ with a binding constant of $10^5 - 10^8$, depending on the substituent. These viologens are responsive not only to bases but also to solvent polarity. Both 1 and 2 can be good solvatochromic materials to colormetrically measure solvent polarity. Crystal structures prove radical formation is in solid state. Electron-withdrawing substituents greatly enhanced viologen sensitivity to electron donors. 1 and 2 are the most sensitive chromic materials reported to date.

ASSOCIATED CONTENT

Ⓢ Supporting Information

^{1}H NMR, ^{13}C NMR, mass spectra of all the compounds, UV−vis spectra of 1, 2, and 3 in the presence of different bases in

aqueous solution, UV−vis spectra of **1**, **2**, and **3** in different solvents at different concentrations, X-band EPR spectra of **1**, **2**, and **3** in the presence of NaOH, reflectance spectra of **1**·Cl$_2$ and (**1**)$_3$·(BiCl$_6$)$_2$ before and after exposure to diethylamine vapor, and crystal structure data (CCDC 1052816 and 1052817). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b03932.

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Notes

The authors declare no competing financial interest.

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