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Improved Photochromic Properties on Viologen-Based Inorganic–Organic Hybrids by Using π-Conjugated Substituents as Electron Donors and Stabilizers

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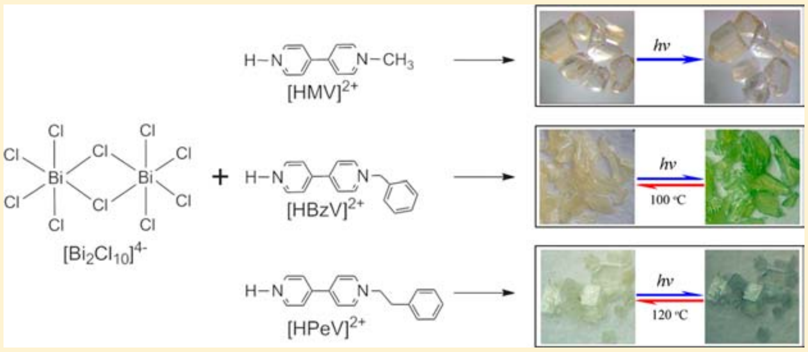
Supporting Information



ABSTRACT: A series of inorganic–organic hybrid compounds $L_2(Bi_2Cl_{10})$ (L = HMV^{2+} = *N*-proton-*N*′-methyl-4,4′-bipyridinium for **1**, L = $HBzV^{2+}$ = *N*-proton-*N*′-benzyl-4,4′-bipyridinium for **2**, and L = $HPeV^{2+}$ = *N*-proton-*N*′-phenethyl-4,4′-bipyridinium for **3**) have been successfully synthesized by an in situ solvothermal reaction. Compounds **1**–**3**, with the same metal halide as anions but different asymmetric viologen molecules as cations, are ideal model compounds for investigating the detailed effect of different photochromically active molecules on the photochromic properties of the hybrids. Compound **1** shows no photochromic behavior, but compounds **2** and **3** possess photochromism and show a faster photoresponse rate than other reported viologen metal halide hybrids. Studies on the relationship between the structure and photochromic behavior clearly reveal that π-conjugated substituents could be used to improve the photoresponsibility and enrich the developed color efficiently and that the $\pi\cdots\pi$ interaction among organic components may not only be a powerful factor to stabilize the viologen monocation radical but also act as the second path of electron transfer from the π-conjugated substituent to the viologen cation for the photochromic process, which significantly influences the photochromic properties.

■ INTRODUCTION

Photochromic materials are attractive and promising for applications in many fields such as protection, decoration, optical switching, memory, filters, displays, and modulators.[1] The research on this domain is mainly concentrated on pure organic or/and inorganic photochromic compounds, while recently more and more attention has been drawn to the development of photochromic inorganic–organic hybrids not only because of the opportunity to combine the distinctive properties of both inorganic and organic components in one material[2] but also because of the possibility of producing novel properties by the synergetic interactions between two counter-components.[3]

Since the discovery of its reductive property by Michaelis in 1932, viologen (N,N′-disubstituted 4,4′-bipyridinium), possessing excellent photoelectrochromic properties and electron-accepting nature, has been widely applied to electron mediation in photosynthesis and herbicides,[4] electrochromic display devices,[5] organic electrical conductors,[6] chemically modified electrodes,[7] solar energy storage,[8] and the photocatalytic reduction of water to hydrogen.[9] One of the most interesting properties of viologen is its photochromism, which usually derives from photocatalyzed electron transfer to the viologen dication from the counteranion. This photoinduced color change has been found in liquid crystals, solution, or film systems but seldom in crystalline states.[5b,10]

One of the critical issues of a viologen-based photochromic hybrid material needing to be solved before practical application is how to obtain a material with a fast photoresponsibility and reversibility by rational design and synthesis. Until now, all reported compounds in this field show very slow

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photoresponse rate: the process of color change needs several hours under UV irradiation and the fading of color consumes from several days to months.[11] To solve this problem, a detailed study on the relationship between the structure and photoresponsibility of the material is very necessary. For example, by studying the structure variation of viologen cations before and after UV irradiation on the same single crystal for the first time, we found that the short distance for N(viologen)···Cl(metal halides) seems to be necessary for the observation of photochromism,[11a] while Mercier et al. found that the anionic oligomer size, iodide doping, and chloride/viologen ratio can influence the photochromic properties in the other viologen halobismuthate hybrids.[11c,12] However, up to now, the researchers have put most of their efforts into investigating the influence of the surroundings of MV^{2+} (methyl viologen = *N*,*N*′-dimethyl-4,4′-bipyridinium) on the photochromism, such as different counterions and different coexisting guest species, but not the influence of the viologen molecule itself. Actually, we feel the effect of the different photochromically active viologen molecules should be an equally or even more important factor to the photochromic properties of the hybrid. Meanwhile, to the best of our knowledge, only symmetrical viologens with the same substituent at nitrogen have been widely studied, while the asymmetric viologen and its corresponding metal−halide hybrid have not been explored.

In order to investigate the detailed effect of different active molecules on the photochromism, a series of inorganic−organic hybrid compounds $L_2(Bi_2Cl_{10})$ (L = HMV^{2+} = *N*-proton-*N*′-methyl-4,4′-bipyridinium for **1**, L = $HBzV^{2+}$ = *N*-proton-*N*′-benzyl-4,4′-bipyridinium for **2**, and L = $HPeV^{2+}$ = *N*-proton-*N*′-phenethyl-4,4′-bipyridinium for **3**) have been successfully synthesized. These compounds with the same metal halide counterions but different asymmetric viologen molecules are ideal model compounds for investigating the detailed effect of different active molecules on the photochromism. In this paper, we report the syntheses, crystal structures, improved photoresponsibility, tunable color, and detailed analyses of the relationship between the structure and photochromic properties of these compounds.

EXPERIMENTAL SECTION

Materials and Methods. $BiCl_3$, 4,4′-bipyridine, methanol, benzyl alcohol, 2-phenylethanol, and concentrated HCl were purchased and used without further purification. FT-IR spectra were obtained on a Nicolet Magna 750 spectrometer using KBr disks in the range 4000−400 cm^{-1}. Powder X-ray diffraction (PXRD) patterns were collected with a Rigaku MiniFlex2 diffractometer at 30 kV and 15 mA for Cu Kα (λ = 1.5406 Å), with a scan rate of 5 °C/min at room temperature. Simulated patterns were produced using the *Mercury* program and single-crystal reflection diffraction data. Electron-spin resonance (ESR) spectra were recorded on a Bruker A300 spectrometer with a 100 kHz magnetic field in X band at room temperature. UV−vis spectra were recorded at room temperature on a computer-controlled PE Lambda 900 UV−vis spectrometer equipped with an integrating sphere in the wavelength range of 190−820 nm. A $BaSO_4$ plate was used as a reference (100% reflectance), on which the finely ground powders of the samples were coated.

Syntheses of 1−3. Compounds **1**−**3** were obtained in a solvothermal reaction of $BiCl_3$, concentrated HCl, 4,4′-bipyridine, and relevant alcohols. Their viologen cations are obtained by a one-step in situ N-alkylated reaction of 4,4′-bipyridine under acidic conditions,[11a,b,13] which provides a less toxic, more convenient, and effective route for the new inorganic−organic hybrids in comparison with the traditional methods.

Compound **1**: $BiCl_3$ (200 mg, 0.63 mmol) and 4,4′-bipyridine (60 mg, 0.38 mmol) were placed in a 25 mL Teflon-lined autoclave and covered with 2 mL of concentrated HCl (36−38%), 8 mL of 2-phenylethanol, and 1 mL of methanol. After being sealed, the autoclave was then heated at 2 °C/min to 130 °C, kept at that temperature for 3 days, and then slowly cooled to room temperature at 4 °C/h. Colorless single crystals of **1** (61% yield based on 4,4′-bipyridine) were obtained and washed with ethanol. The IR spectrum is shown in Figure S1a in the Supporting Information. Its phase purity was checked by PXRD (Figure S2a in the Supporting Information).

Compound **2**: $BiCl_3$ (200 mg, 0.63 mmol) and 4,4′-bipyridine (60 mg, 0.38 mmol) were placed in a 25 mL Teflon-lined autoclave and covered with 2 mL of concentrated HCl (36−38%). Benzyl alcohol (8 mL) was added to this mixture, and the autoclave was subsequently sealed. The autoclave was then heated at 2 °C/min to 140 °C and held at that temperature for 2 days. At the end of this period, the autoclave was cooled to 70 °C at 2 °C/h and held at this temperature for 6 h before cooling to room temperature at the same cooling rate. Yellow single crystals of **2** (67% yield based on 4,4′-bipyridine) were obtained and washed with ethanol. The IR spectrum is shown in Figure S1b in the Supporting Information. The phase purity was checked by PXRD (Figure S2b in the Supporting Information).

Compound **3**: $BiCl_3$ (100 mg, 0.32 mmol) and 4,4′-bipyridine (192 mg, 1.22 mmol) were placed in a 25 mL Teflon-lined autoclave and covered with 1 mL of concentrated HCl (36−38%) and 9 mL of 2-phenylethanol. After being sealed, the autoclave was then heated at 2 °C/min to 130 °C, kept at that temperature for 3 days, and then slowly cooled to room temperature at 3 °C/h. Pale-yellow single crystals of **3** (12% yield based on $BiCl_3$) were obtained and washed with ethanol. The IR spectrum is shown in Figure S1c in the Supporting Information. The phase purity was checked by PXRD (Figure S2c in the Supporting Information).

X-ray Crystallographic Study. X-ray diffraction measurements of **1**−**3** were performed on a Rigaku SATURN70 CCD diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Intensity data sets were collected using an ω-scan technique and corrected for Lorentz and polarization effects. The structures were solved by direct methods using the Siemens *SHELXTL*, version 5, package of crystallographic software.[14] Difference Fourier maps based on these atomic positions yield other non-hydrogen atoms. The final structure was refined using a full-matrix least-squares refinement on F^2. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were allowed to ride on their respective parent atoms and included in the structure factor calculations with assigned isotropic thermal parameters. Pertinent crystal data and structure refinement results for the compounds are summarized in Table 1, and the selected bond lengths and bond angles are given in Table S1 (Supporting Information). The significant hydrogen-bond and C−H···π interaction parameters can be found in Tables S2 and S3, respectively (Supporting Information).

RESULTS AND DISCUSSION

Description of the Crystal Structures. Compounds **1**−**3** contain the same metal halide $(Bi_2Cl_{10})^{4-}$ as anions but different viologens as cations: *N*-proton-*N*′-methyl-4,4′-bipyridinium (HMV^{2+}) for **1**, *N*-proton-*N*′-benzyl-4,4′-bipyridinium ($HBzV^{2+}$) for **2**, and *N*-proton-*N*′-phenethyl-4,4′-bipyridinium ($HPeV^{2+}$) for **3**, respectively (Figure 1).

Compound **1** crystallizes in the orthorhombic space group *Pbca*, and compounds **2** and **3** crystallize in the triclinic space group $P\bar{1}$. As shown in Figure 2, the same metal halide $(Bi_2Cl_{10})^{4-}$ anion in **1**−**3** is built of two edge-shared $BiCl_6$ octahedra, and the Bi−Cl bonds in this moiety could be divided into terminal bonds and bridging ones with the following bond distances: 2.564(2)−2.698(2) and 2.946(2)−2.993(2) Å in **1**; 2.5490(10)−2.8151(10) and 2.8454(9)−2.9446(9) Å in **2**; 2.576(2)−2.790(2) and 2.825(2)−2.870(2) Å in **3**. Both asymmetric units of **1** and **3** are constituted by one

Table 1. Crystal Data and Structure Refinements for 1−3

	1	2	3
empirical formula	$C_{22}H_{24}Bi_2Cl_{10}N_4$	$C_{34}H_{32}Bi_2Cl_{10}N_4$	$C_{18}H_{18}BiCl_5N_2$
fw	1116.91	1269.1	648.57
color and habit	colorless block	colorless block	colorless block
cryst size (mm^3)	0.42 × 0.20 × 0.16	0.14 × 0.08 × 0.05	0.11 × 0.06 × 0.04
cryst syst	orthorhombic	triclinic	triclinic
space group	*Pbca*	$P\bar{1}$	$P\bar{1}$
a (Å)	13.049(3)	10.5078(19)	9.958(7)
b (Å)	13.957(3)	10.9976(19)	10.917(7)
c (Å)	18.266(4)	18.979(4)	11.074(8)
α (deg)	90	76.743(6)	70.96(3)
β (deg)	90	87.521(7)	67.43(3)
γ (deg)	90	72.980(5)	74.46(4)
V (Å^3)	3326.7(12)	2040.6(6)	1036.7(12)
Z	4	2	2
D_{calcd} (g/cm^3)	2.230	2.065	2.078
μ (mm^{-1})	11.390	9.298	9.153
F(000)	2080	1200	616
θ (deg)	2.92−25.35	2.04−25.50	2.24−25.50
GOF on F^2	1.374	1.066	1.032
reflns measd	22528	15388	7764
indep reflns (R_{int})	3030 (0.0564)	7316 (0.0208)	3720 (0.0235)
obsd reflns [$I > 2\sigma(I)$]	2999	6683	3536
final R1, wR2 indices (obsd)	0.0432, 0.0889	0.0203, 0.0477	0.0204, 0.0470
R1, wR2 indices (all)	0.0441, 0.0893	0.0234, 0.0489	0.0220, 0.0476
$(\Delta/\sigma)_{max}$	0.002	0.001	0.001
$(\Delta\rho)_{max/min}{}^{-3}$	0.638, −0.882	1.481, −0.996	0.996, −1.509

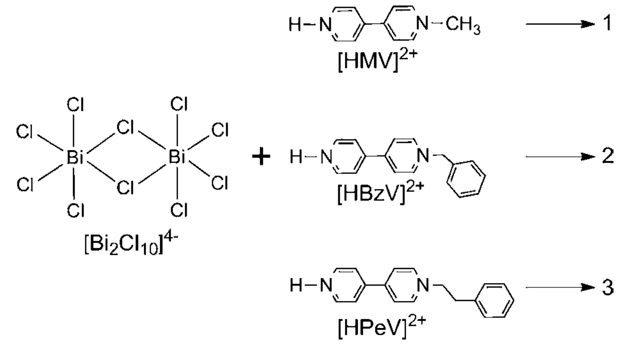

Figure 1. View of the $[Bi_2Cl_{10}]^{4-}$ anion and three types of viologen cations in **1**−**3**.

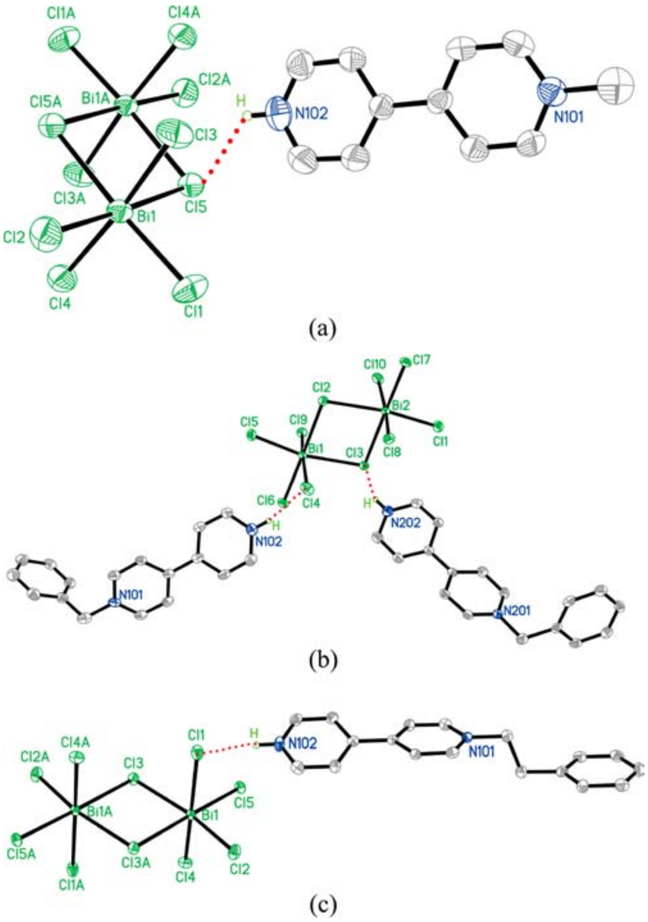

Figure 2. ORTEP[16] drawing at 50% probability level of the crystallographically asymmetric units of **1** (a; symmetry code: A, −*x*, −*y*, −*z* + 1), **2** (b), and **3** (c; symmetry code: A, −*x* + 1, −*y* + 2, −*z* + 1). N−H···Cl hydrogen-bond contacts are displayed by dotted lines. Only the hydrogen atoms involved in the hydrogen bonds are shown for clarity. All carbon atoms are not labeled.

independent viologen cation (HMV^{2+} for **1** and $HPeV^{2+}$ for **3**) and half of the $(Bi_2Cl_{10})^{4-}$ anion, while that of **2** is composed of two $HBzV^{2+}$ cations and one $(Bi_2Cl_{10})^{4-}$ anion. In **1**, the $(Bi_2Cl_{10})^{4-}$ anions and HMV^{2+} cations are connected by N−H···Cl hydrogen bonds, with a N102···Cl5 distance of 3.248 Å (Figure 2a). The angle between the N102···Cl5 direction and the normal to the pyridinium ring is about 9.042°, and the angle of Bi1−Cl5···N102 is about 101.310°. In **2**, the nitrogen protons H10A−N102 and H20A−N202 from two $HBzV^{2+}$ cations are involved in bifurcated hydrogen-bond interactions with the terminal chlorine Cl4 and the bridging chlorine Cl3 of the same $(Bi_2Cl_{10})^{4-}$ anions, and the distances above N−H···Cl are 3.106 and 3.110 Å (Figure 2b), respectively. The angle between the N202···Cl3 direction and the normal to the pyridinium ring is about 13.634°, and the angle of Bi2−Cl3···N202 is about 98.212°. On the other hand, each $HBzV^{2+}$ cation connects with three neighboring $HBzV^{2+}$ cations by C−H···π interactions to form edge-to-face π···π interactions.[15] The distances of C−H···C_g (π ring) are 3.204, 2.873, and 2.742 Å, and their angles are 122.04, 115.35, and 137.73°, respectively (Figure 3). In **3**, the $(Bi_2Cl_{10})^{4-}$ anions and $HPeV^{2+}$ cations are linked together by N−H···Cl hydrogen bonds (N···Cl, 3.086 Å; Figure 2c). The angle between the N102···Cl1 direction and the normal to the pyridinium ring is about 7.712°, and the angle of Bi1−Cl1···N102 is about 95.622°. Among the $HPeV^{2+}$ cations, the short distances of C−H···C_g with values of 3.205, 3.395, and 3.022 Å and the angles of C−H···C_g of 121.55, 109.90, and 98.02°, respectively, afford $HPeV^{2+}$ cations; edge-to-face π···π interactions further stabilize the crystal structure of **3** (Figure 4). The main difference between the packing of **1** and the ones of **2** and **3** is that in **1** the cation is segregated in a nest of chloride neighbors, while in the others, some cation···cation contacts are present (Figure S3 in the Supporting Information).

Photochromic Properties. Upon irradiation by sunlight, a 13 W compact fluorescent lamp, or 365 nm UV light at room temperature in air, the color change of crystals **2** and **3** could be clearly observed. Differently, crystal **1** constantly remains silent even after exposure to UV light for a long time (Figure 5a).

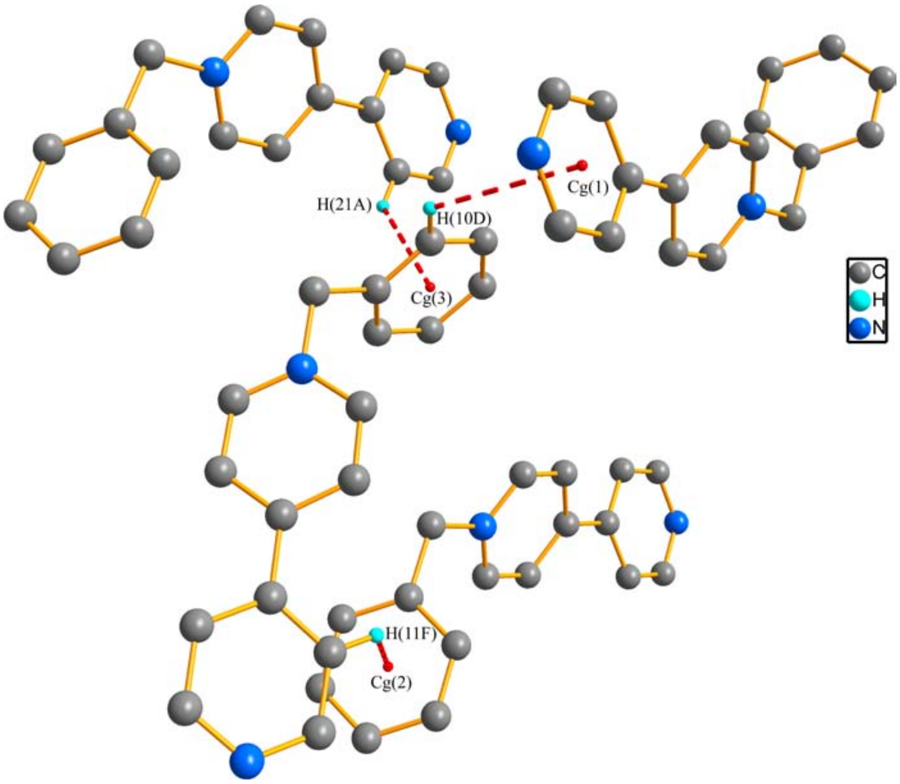

Figure 3. Each HBzV^{2+} cation in **2** interacting with three neighboring HBzV^{2+} cations by three C−H···π interactions. C−H(10D)···Cg(1) = 3.2038 Å; C−H(11F)···Cg(2) = 2.8729 Å; C−H(21A)···Cg(3) = 2.7416 Å. Only the hydrogen atoms involved in supramolecular interactions are shown for clarity.

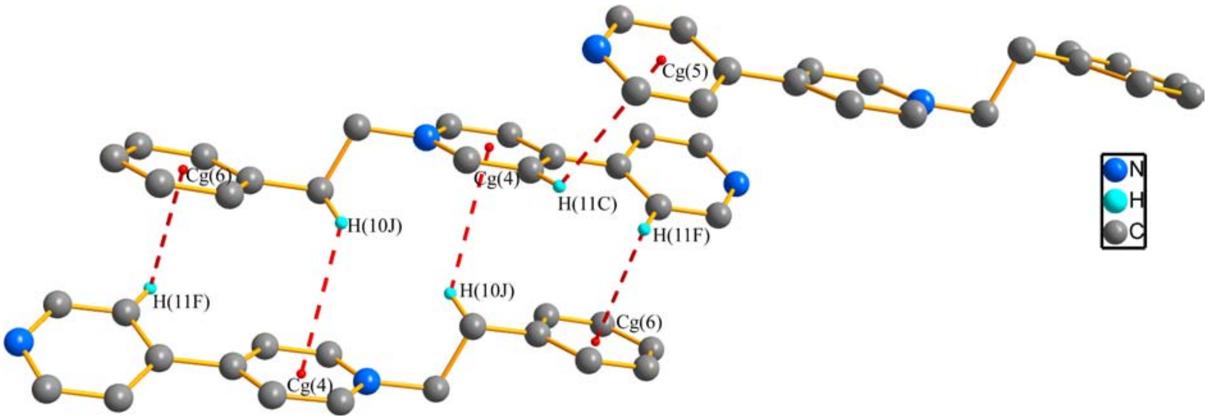

Figure 4. Each HPeV^{2+} cation in **3** interacting with two neighboring HPeV^{2+} cations by three C−H···π interactions. C−H(10J)···Cg(4) = 3.2051 Å; C−H(11C)···Cg(5) = 3.3947 Å; C−H(11F)···Cg(6) = 3.0216 Å. Only the hydrogen atoms involved in supramolecular interactions are shown for clarity.

Compound **2** is rather photosensitive: it gives an eye-detectable change from yellow to green upon exposure to UV light under air within 30 s and gives a new clear absorption band centered at 620 nm. The coloration of **2** tends to be saturated after illumination for 10 min (Figure 5b). Compound **3** changes from pale yellow to pale blue after illumination for 1 min, and it generates a new absorption band centered at 610 nm and achieves saturation after irradiation for 1 h, but its absorption intension is smaller than that of **2** (Figure 5c). The photoproduct of **2** can be completely decolored in 1 day in the dark (Figure S4 in the Supporting Information) or in 30 min by heating at 100 °C in air, while decoloration of the photoproducts of **3** took 3 days in the dark or 1 h by heating at 120 °C for completion. So, compounds **2** and **3** showed faster photoresponse rates than the other viologen halobismuthate hybrids.[11] Meanwhile, the circular color changes of **2** and **3** can be repeated by UV irradiation and heating, respectively, which indicates their typical photochromic behavior.

Similar to our previous study in this field, compounds **2** and **3** show single resonances at $g = 2.0015$ and 1.9973, respectively, after UV irradiation (Figures 6b,c) but remain ESR-silent before irradiation and/or after heating, which is similar to those found in MV^{2+} and other viologen compounds.[11a,b,17,18] Therefore, the photochromism of these two compounds can be primarily ascribed to the reversible interconversion between the monocation radical $[V]^{\bullet+}$ and the dication $[V]^{2+}$. This

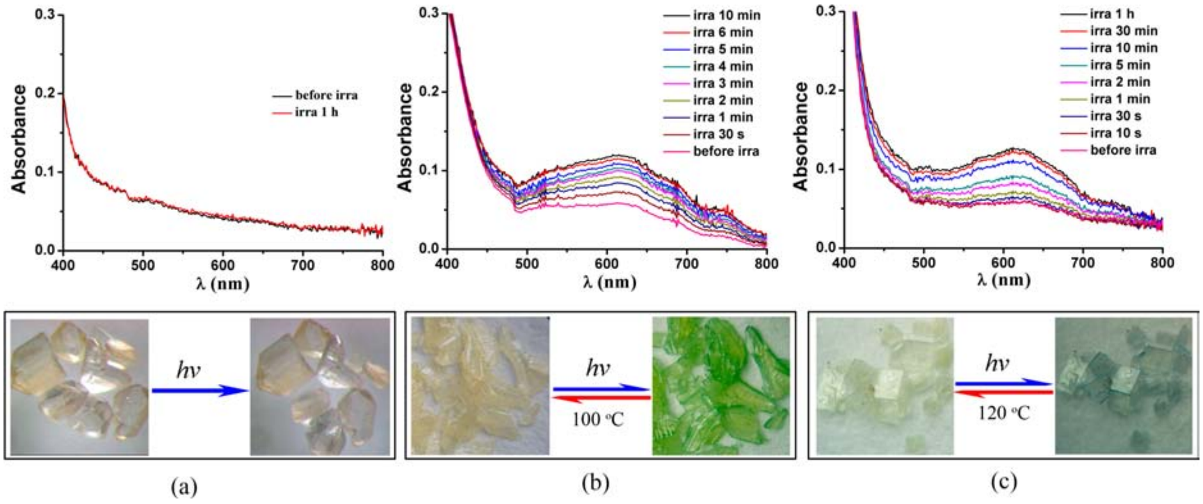

Figure 5. UV−vis diffuse-reflectance spectra and photographs showing the photochromic behavior of (a) **1**, (b) **2**, and (c) **3**.

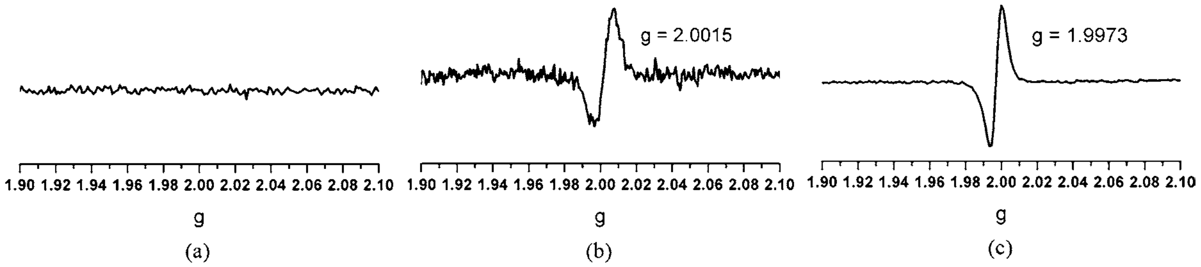

Figure 6. ESR spectra of **1**−**3** upon irradiation in the solid state at room temperature: (a) **1**; (b) **2**; (c) **3**.

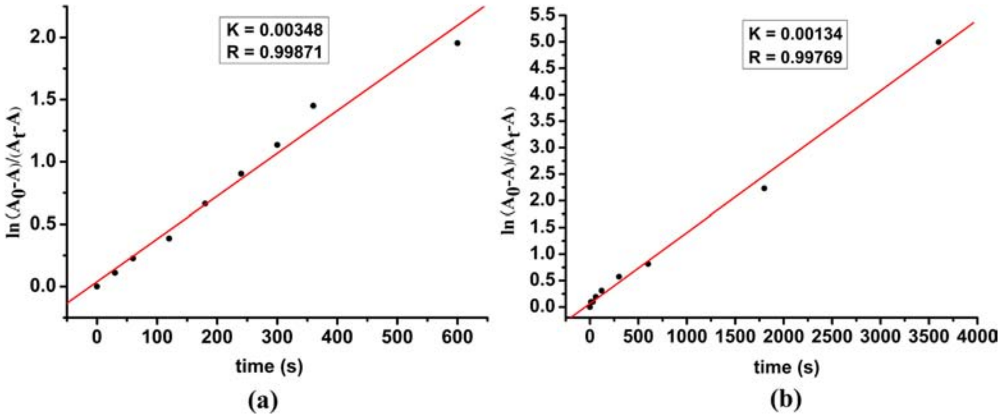

Figure 7. Photoinduced electron-transfer process kinetics of **2** (a) and **3** (b).

could also be supported by the UV−vis diffuse-reflectance spectra of **2** and **3**. Upon irradiation with UV light, new and broad peaks around 620 nm for **2** and 610 nm for **3** gradually appear in their UV−vis diffuse-reflectance spectra. Such a change is similar to those observed in other photochromic viologen compounds and can be attributed to the production of the monocation radical in viologen.[17] Compound **1** does not show ESR (Figure 6a) and UV−vis absorption activity during UV irradiation, which evidences again its absence of photochromism not only in the visible region but also in the UV-light region.

The kinetics of the above photochemical reactions could be analyzed with eq 1:

$$\ln \frac{A_0 - A_\infty}{A_t - A_\infty} = kt \tag{1}$$

where k is the first-order rate constant and A_0, A_t, and A_∞ are the absorbance at 620 nm for **2** and 610 nm for **3** at times 0 and t and the photostationary stage, respectively.[19] The linear fit of the data shown in Figure 7 indicates that the photoinduced electron-transfer process follows first-order reaction kinetics, with the rate constants being 3.48×10^{-3} s^{-1} for **2** and 1.34×10^{-3} s^{-1} for **3**, respectively. It is clear that the photoresponse rate of **2** is faster than that of **3** and consistent with the experimental result.

It has been reported by us and others that methylviologen bismuthate halides can show photochromism,[11] and these compounds could be taken as a family with the common formula $(MV)_{(2n+2)/2}(Bi_{2n}Cl_{8n+2})$ (n = 1, 2, 3, and ∞). The photochromic behavior of this family arises from electron transfer from bismuth halides to viologen molecules through the N···Cl pathway and highly depends on the size of the bismuthated halide oligomer.[11c] The photoresponsibility of the related compound would diminish with a decrease of the size of the inorganic oligomer, because a smaller inorganic oligomer has worse ability of stabilizing the monocation radical viologen in air possibly. It has been reported that the photochromic properties disappear compeletely when $n \leq 2$. Compounds **1**–**3** contain the same inorganic anionic species $(Bi_2Cl_{10})^{2-}$ (n = 1). We cannot observe the photochromic behavior in **1**, but interestingly compounds **2** and **3** show obvious photoinduced color change.

Compounds **2** and **3** show relatively faster rates of color change by light irradiation than the other reported compounds in this domain, which can be ascribed to the shorter pathway of electron transfer from the inorganic component to the organic component. The N···Cl distances of 3.106 Å in **2** and 3.086 Å in **3** are about 0.2 Å shorter than that of $(MV)_4[Bi_6Cl_{26}]$ [3.366(3) Å].[11c] However, it is worth noting that the photoresponse rate of **2** is about 3 times faster than that of **3**, although the N···Cl distance in **2** is a little longer than that in **3**. Therefore, it is reasonable that there should be other factors causing this phenomenon.

In the structure, the biggest difference of **1**–**3** is possessing different viologen molecules as the organic parts: HMV^{2+} in **1**, $HBzV^{2+}$ in **2**, and $HPeV^{2+}$ in **3** (as shown in Figure 1). Therefore, their different photochromic behaviors should mainly originate from different organic components. In the known photochromic halobismuthate hybrids with viologen molecules, the $\pi\cdots\pi$ interactions among viologens are only observed in **2** and **3** but not in **1**. The N-substituent groups of viologens in **2** and **3** contain benzene rings uniquely, which makes them easier to form face-to-face or edge-to-face $\pi\cdots\pi$ interactions. The shortest $H\cdots C_g$ separation in C(217)–H(21A)···$C_g(3)$ of ~2.742 Å in **2** and C(115)–H(11F)···$C_g(6)$ of ~3.022 Å in **3** can be utilized to build a significant edge-to-face $\pi\cdots\pi$ interaction. For the ability to stabilize radical species, $\pi\cdots\pi$ interactions that are powerful enough to stabilize the viologen monocation radical have been reported.[20] Therefore, the $\pi\cdots\pi$ interactions among viologen cations existing in both **2** and **3** may be powerful enough to stabilize the viologen monocation radical $[V]^{\bullet+}$, resulting in compounds **2** and **3** showing photochromic behavior, while compound **1** does not have $\pi\cdots\pi$ interactions and this results in compound **1** being photochromic-silent.

Although the fact that $\pi\cdots\pi$ interactions can be beneficial in stabilizing the viologen monocation radical has been well documented, it is uncertain whether they can be regarded as another possible way for charge transfer in photochromic compounds.[17c,21] Generally, the factors related to the photoresponse rate of photochromism include the distance of the channel of charge transfer, the electron-accepting ability of $[V]^{2+}$, and the electron-donating ability of the counterion. Compounds **2** and **3** contain the same electron-donating species $(Bi_2Cl_{10})^{2-}$, while the electron-accepting ability of $[V]^{2+}$ (Figure S5 in the Supporting Information) in **2** is worse than that in **3**, and the N···Cl distance in **2** is a little longer than that in **3**, which means that the photoresponse rate of **3** should be faster than that of **2**, in conflict with the results of the experiment mentioned above. The edge-to-face $\pi\cdots\pi$ distance in **2** is 0.28 Å shorter than that in **3**, suggesting that intermolecular edge-to-face $\pi\cdots\pi$ interactions in **2** are stronger than those in **3**. Therefore, we can rationally propose that these intermolecular edge-to-face $\pi\cdots\pi$ interactions may act as the second path of electron transfer from a π-conjugated substituent to a viologen cation for the photochromic process, resulting in a faster photoresponse rate for **2**.

Up to now, the developed color of the photochromic compounds based on viologen chlorobismuthate is uniquely black. Different developed colors of materials could supply more selection to the design of memory devices in the future.[1,22] In this study, we found that the developed color of viologen hybrids could be tuned by designing different substituents on the viologen molecule. When the substituent on the viologen changed from benzyl in **2** to phenethyl in **3**, the developed color of $L_2(Bi_2Cl_{10})$ varies from green to blue (Figure 5). The difference of the developed color between **2** and **3** can be monitored from their UV–vis diffuse-reflectance spectra, where the new emerged peak after UV irradiation in **2** red-shifts about 10 nm in comparison with that in **3**. Much more modification on the developed color in this series of compounds could be achieved by an organic strategy, for example, introducing a bigger aromatic system instead of a benzene group or employing an electron pull–push system in the viologen molecule.[18]

■ CONCLUSIONS

In conclusion, a series of viologen metal halide hybrid compounds with the common formula $L_2(Bi_2Cl_{10})$ (L = HMV^{2+} for **1**, $HBzV^{2+}$ for **2**, and $HPeV^{2+}$ for **3**), have been synthesized by an in situ solvothermal reaction. They contain the same inorganic anionic species $(Bi_2Cl_{10})^{2-}$ but different organic cations, which enables us to study the effect of the different photochromically active molecules on the photochromic properties of the hybrids. Different from the viologen-based photochromic compounds, where electron transfer to the viologen molecule is coming from and stabilized by inorganic counterions, the electron in this study may arise from both inorganic and organic components and be stabilized by the π-conjugated groups in the substituent of an in situ generated viologen group and the distance between the benzene ring and the viologen aromatic ring has a significant influence on the photochromic properties. Therefore, our research provides a new way to design and synthesize new photochromic hybrids with excellent properties. This work also shows the possibility of tuning the color of the hybrids after UV irradiation by changing the substituent groups on the viologen molecule. Meanwhile, our research is the first report on using asymmetric viologen molecules as cations to construct hybrid compounds and studying their photochromic properties in this field.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data for complexes **1**–**3** in CIF format, FT-IR spectra, PXRD patterns, single-crystal results, selected bond lengths and bond angles, hydrogen-bond parameters for **1**–**3**, C–H···π interactions of the bond donor/acceptor schemes of **2** and **3**, packing diagrams of complexes **1**–**3**, absorption spectra of **2**, density functional theory calculations, and Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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