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Iodine-Induced Solvothermal Formation of Viologen Iodobismuthates

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Reactions of BiI_3, KI, 4,4′-bipyridine (4,4′-bipy) and alcohols (methanol, benzyl alcohol, 2-propanol or propanol) in the presence of I_2 and a small amount of water afforded four iodobismuthate complexes of *N*,*N*′-dialkyl-4,4′-bipyridinium (viologen, V^{2+}), $[MV][BiI_5]$ (**1**, MV^{2+} = *N*,*N*′-dimethyl-4,4′-bipyridinium), $[BzV]_2[Bi_2I_8(\mu\text{-}I)_2]$ (**2**, BzV^{2+} = *N*,*N*′-dibenzyl-4,4′-bipyridinium), $[iPV]_2[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$ (**3**, iPV^{2+} = *N*,*N*′-diisopropyl-4,4′-bipyridinium) and $[PV]_2[Bi_4I_8(\mu\text{-}I)_8]$ (**4**, PV^{2+} = *N*,*N*′-dipropyl-4,4′-bipyridinium) under solvothermal conditions. The V^{2+} dications were formed from iodine-induced C–O bond cleavage of alcohols followed by alkylation of 4,4′-bipy. The Bi centre of the $[BiI_5]^{2-}$ anion of **1** adopts a square-pyramidal coordination geometry, whereas the $[Bi_2I_{10}]^{4-}$ anion of **2** consists of a dimeric structure comprising two edge-sharing BiI_6 octahedra. The tetranuclear $[Bi_4I_{16}]^{4-}$ anion of **3** has an incomplete double cubane structure in which two incomplete $[Bi_3(\mu\text{-}I)_2(\mu_3\text{-}I)_2]$ cubane-like fragments are fused by sharing two Bi and two μ_3-I atoms, whereas that of **4** contains a bent Bi_4 chain in which the $[Bi_2I_{10}]^{4-}$ anion of **2** is fused with two BiI_6 units through six shared μ-I atoms. The optical, electrical conductivity and dielectric properties of **1**–**4** were also investigated.

Introduction

Viologens, namely, *N*,*N*′-dialkyl-4,4′-dipyridinium compounds, are a class of organic cations of interest because of their wide applications in solar energy storage,[1] electron mediation in photosynthesis and herbicides,[2] electrochromic display devices,[3] chemically modified electrodes,[4] organic electrical conductors,[5] probes in DNA and zeolites,[6] photocatalytic reduction of water to hydrogen[7] and construction of supramolecular systems.[8] The traditional method of preparation of V^{2+} is the alkylation of 4,4′-bipyridine (4,4′-bipy) with halohydrocarbons, although alcohols have been reported to be alkylation reagents in the presence of metal salts and strong acids.[9] The pyridinium cations such as V^{2+} are known as counterions and have been used as templates to form various pyridinium metal/halide hybrids.[10] One of these hybrids, pyridinium iodobismuthate, is of importance due to its intriguing architectures and potential applications in optics and electronics.[11] The common synthetic route is to mix BiI_3 with the preformed pyridinium iodide in an organic solvent. In some cases, NaI, KI or even toxic HI is appended to increase the solubility of the products and ease their crystallization.[11a–11i] However, only a few viologen iodobismuthates have been prepared by this method because few viologen iodides are available.

We have employed a new method to prepare viologen iodobismuthate complexes through iodine-induced solvothermal reactions of 4,4′-bipy with alcohols in the presence of BiI_3, KI, I_2 and a small amount of water in MeCN. Four viologen iodobismuthate complexes, $[MV][BiI_5]$ (**1**, MV^{2+} = *N*,*N*′-dimethyl-4,4′-bipyridinium), $[BzV]_2[Bi_2I_8(\mu\text{-}I)_2]$ (**2**, BzV^{2+} = *N*,*N*′-dibenzyl-4,4′-bipyridinium), $[iPV]_2[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$ (**3**, iPV^{2+} = *N*,*N*′-diisopropyl-4,4′-bipyridinium) and $[PV]_2[Bi_4I_8(\mu\text{-}I)_8]$ (**4**, PV^{2+} = *N*,*N*′-dipropyl-4,4′-bipyridinium), were isolated (Scheme 1). Herein we describe the structural chemistry and the optical, electrical conductivity and dielectric properties of **1**–**4**.

Results and Discussion

Synthesis and Spectral Aspects

Complexes **1**–**4** were formed under solvothermal conditions, in which the V^{2+} cations were formed in situ from iodine-induced alcohol C–O bond cleavage followed by the addition of alkyl groups on to the nitrogen atoms of 4,4′-bipy. A possible mechanism is shown in Scheme 2. Firstly, iodine reacts with water to form HI, which reacts with alcohols to produce iodohydrocarbons. Secondly, the iodohydrocarbons further react with 4,4′-bipy to form the V^{2+} cations (Figure 1). The V^{2+} cations act as templates to

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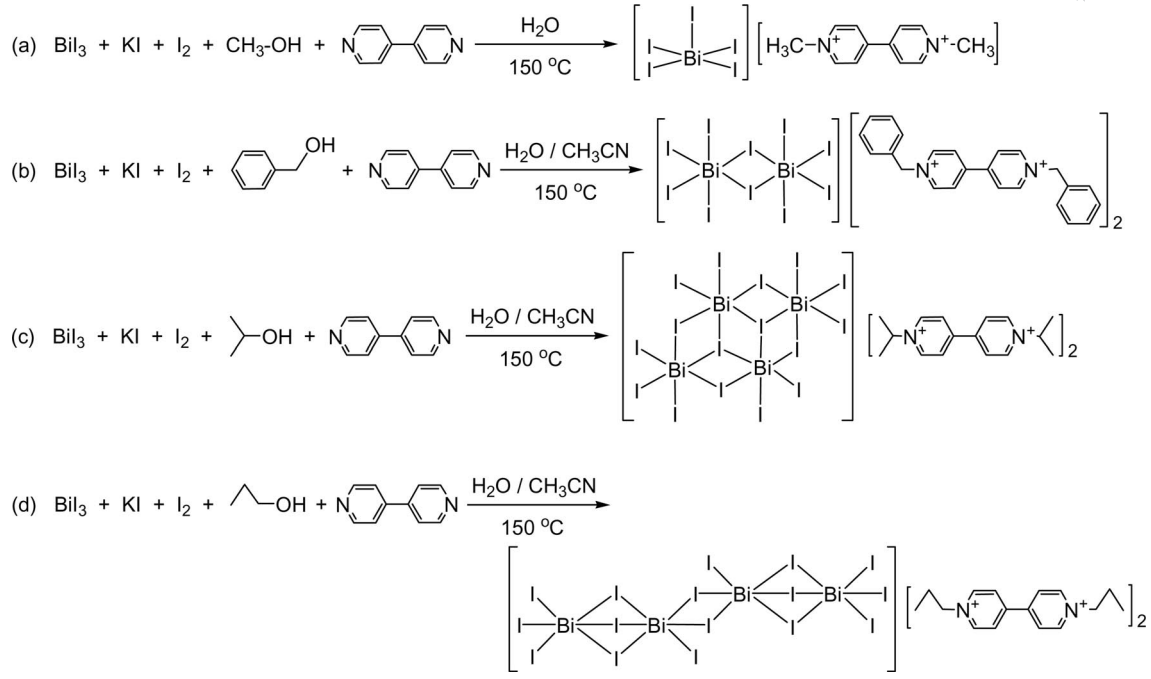
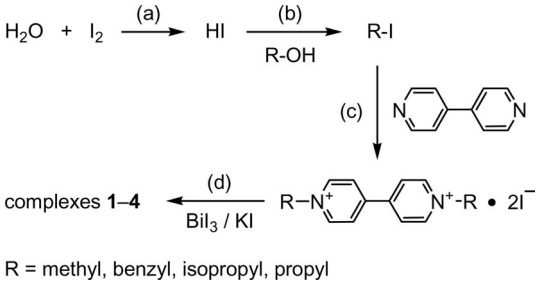


Scheme 1. Synthesis of complexes **1**–**4**.

provoke Bi^{3+} and I^- to self-aggregate into a mononuclear $[BiI_5]^{2-}$ anion (**1**), a binuclear $[Bi_2I_8(\mu\text{-}I)_2]^{4-}$ anion (**2**) and two tetranuclear $[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]^{4-}$ (**3**) and $[Bi_4I_8(\mu\text{-}I)_8]^{4-}$ anions (**4**) (Figure 2). If iodine is not added the viologen complexes are not generated and yellow crystals of 4,4′-bipyridine·$2I_2$ are generated in 30% yield.[12a]



Scheme 2. Possible mechanism for the formation of complexes **1**–**4**.

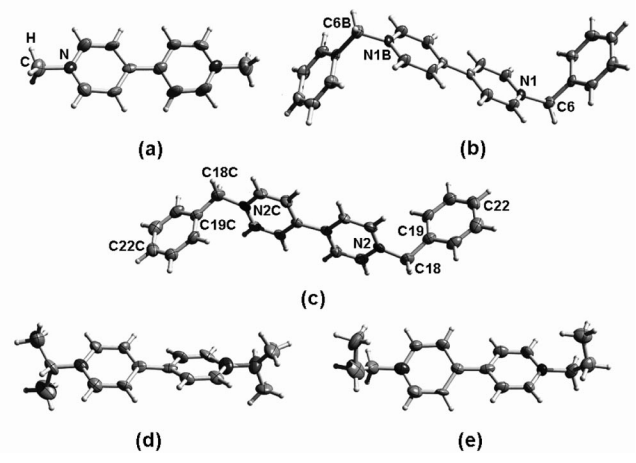


Figure 1. View of the V^{2+} cations in **1**–**4** with 50% thermal ellipsoids for C and N atoms.

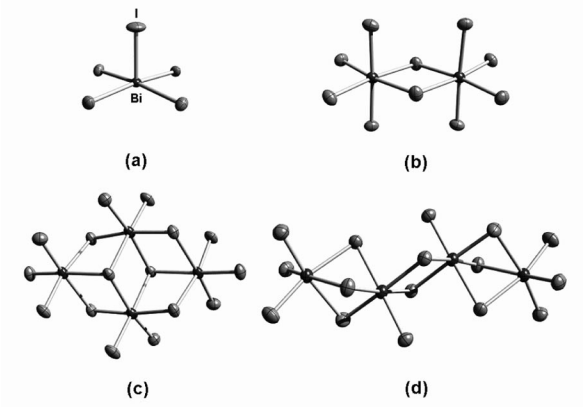


Figure 2. View of the four types of iodobismuthate anions in **1**–**4** with 50% thermal ellipsoids.

Complexes **1**–**4** are air and moisture stable, insoluble in common solvents such as methanol, acetone, acetonitrile, toluene and THF and soluble in DMF and DMSO. Their elemental analyses were consistent with their chemical formulae. The IR spectra show medium strength peaks at ca. 3050 cm^{-1} and strong or medium peaks in the range of 1650–1450 cm^{-1} indicating the existence of pyridyl groups. Medium-strength peaks in the range of 3000–2800 cm^{-1} indicate the existence of alkyl groups in **1**–**4**.[12b] The ^1H NMR spectra in $[D_6]$DMSO at room temperature showed the correct pyridyl/alkyl proton ratios of V^{2+} cations for **1**–**4**. The identities of **1**–**4** were further confirmed by single-crystal diffraction analysis.

Crystal Structure of [MV][BiI_5] (1)

Complex **1** crystallizes in the monoclinic space group $P2_1$ and its asymmetric unit contains one MV^{2+} cation (Figure 1a) and one discrete $[BiI_5]^{2-}$ anion (Figure 2a). The Bi centre in the $[BiI_5]^{2-}$ anion has an unusual square-pyramidal coordination geometry. The mean apical and bottom Bi–I bond lengths [2.8715(11) and 3.0631(14) Å, respectively] in **1** are slightly shorter than those of other complexes containing a tetragonal pyramidal BiI_5 unit, e.g. α-$((CH_3)_2S(CH_2)_2NH_3)BiI_5$ [2.9298(7) and 3.1109(9) Å].[11i] Each $[BiI_5]^{2-}$ anion is weakly interconnected with adjacent units through Bi···I secondary interactions [3.6566(13) Å], forming a linear $[BiI_5]_n^{2n-}$ chain extending along the *a* axis (Figure 3a). In the family of iodobismuthates, 1D zigzag $[BiI_5]_n^{2n-}$ chains consisting of corner-sharing BiI_6 octahedra have been reported previously,[11g–11i] but the linear $[BiI_5]_n^{2n-}$ chain seen in **1** is rare. However, a similar structure was observed in the bromide analogue.[10c] The MV^{2+} cations stack along the *a* axis to form 1D rhombic channels where the $[BiI_5]_n^{2n-}$ chains are included (Figure 3b).

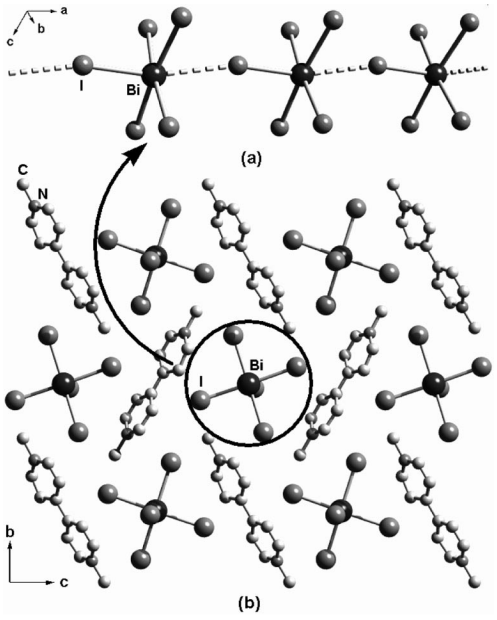


Figure 3. (a) View of the linear $[BiI_5]_n^{2n-}$ chain in **1** extending along the *a* axis. The dashed line represents the Bi···I secondary interaction between two adjacent $[BiI_5]^{2-}$ anions. (b) View of the $[BiI_5]_n^{2n-}$ chains enclosed into rhombic channels assembled by MV^{2+} cations in **1** (looking along the *a* axis). H atoms are omitted for clarity.

Crystal Structure of [$BzV]_2[Bi_2I_8(\mu\text{-}I)_2]$ (2)

Complex **2** crystallizes in the triclinic space group $P\bar{1}$ and its asymmetric unit comprises two halves of a BzV^{2+} cation (Figure 1b,c) and half a $[Bi_2I_8(\mu\text{-}I)_2]^{4-}$ anion (Figure 2b). The $[Bi_2I_{10}]^{4-}$ anion may be viewed as being built of two BiI_6 edge-sharing octahedra. The mean terminal Bi–I bond length [3.0232(12) Å] in **2** is almost the same as that of [2,2′-bipyridinium]$_4[Bi_2I_8(\mu\text{-}I)_2]$ [3.0215(55) Å], whereas the mean Bi–μ-I bond length [3.2719(13) Å] is slightly longer than that of [2,2′-bipyridinium]$_4[Bi_2I_8(\mu\text{-}I)_2]$ [3.2086(58) Å].[11p] The Bi···Bi contact in this dimeric anion (4.787 Å) is too long to include any metal-metal interaction. The two BzV^{2+} cations have somewhat different *trans-trans* configurations. In one BzV^{2+} bearing N1 and N1B (Figure 1b), each phenyl group swings along the C6–N1–N1B–C6B line from 90° to 110.18° while each phenyl group in another BzV^{2+} bearing N2 and N2C not only swings along the corresponding C18–N2–N2C–C18C line from 90° to 114.34°, but also rotates along the C18–C19–C22 line by ca. 56.03° (Figure 1c). Pairs of BzV^{2+} cations surround each inorganic anion through static forces and stack along the *c* axis to form an rhombic channel where the $[Bi_2I_8(\mu\text{-}I)_2]^{4-}$ anion is encapsulated (Figure 4).

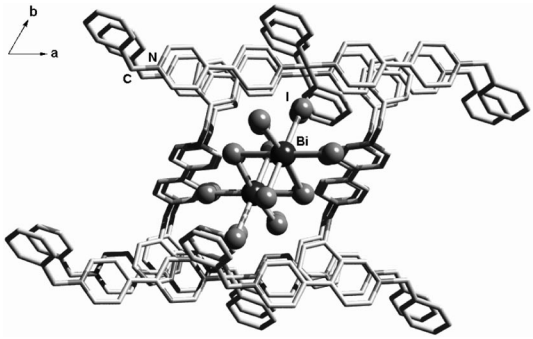


Figure 4. View of the 1D channel (along the *c* axis) constructed by one list of discrete $[Bi_2I_{10}]^{4-}$ anions and six lists of BzV^{2+} cations. H atoms are omitted for clarity.

Crystal Structure of [$iPV]_2[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$ (3)

Complex **3** crystallizes in the monoclinic space group $P2_1/c$ and its asymmetric unit consists of three discrete iPV^{2+} cations (Figure 1d) and one and a half tetranuclear $[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]^{4-}$ anions (Figure 2c). The $[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]^{4-}$ anion may be considered as having a double incomplete cubane structure in which two incomplete $[Bi_3(\mu\text{-}I)_2(\mu_3\text{-}I)_2]$ cubane fragments fuse by sharing two Bi and two μ_3-I atoms. This structure closely resembles those of [1,2-diethyl-3,4,5-trimethylpyrazolium]$_4[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$, [Ru-(2,2′-bipyridine)$_3]_2[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$ and [(phthalocyaninato)Bi]$_4[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$.[11l,11n,11o] The mean terminal Bi–I bond length [2.9041(17) Å] and the mean Bi–μ-I bond length [3.2158(17) Å] in **3** are slightly shorter than those of **2**. The average Bi–μ_3-I bond length [3.3399(17) Å] in **3** is slightly longer than that found in [1,2-diethyl-3,4,5-trimethylpyrazolium]$_4[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$ [3.2966(6) Å],[11l] is comparable to that in [Ru-(2,2′-bipyridine)$_3]_2[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$ [3.3379(11) Å][11n] and is somewhat shorter than that of [(phthalocyaninato)Bi]$_4[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]$ [3.3414(15) Å].[11o] In **3**, fours pairs of iPV^{2+} cations lying in the (1 0 3) plane are arranged in a manner that creates a rectangular cavity, which is occupied by one $[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]^{4-}$ anion (Figure 5, Figure S1 in the Supporting Information).

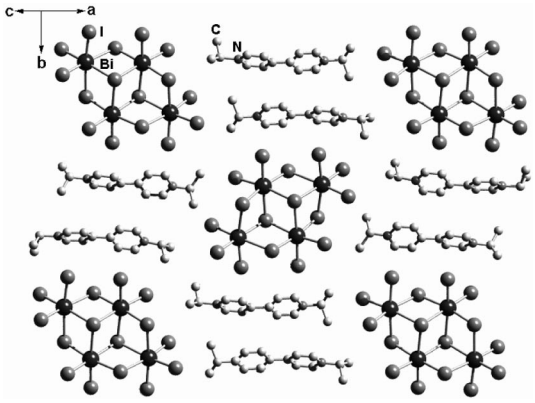


Figure 5. View of the $[Bi_4I_{10}(\mu\text{-}I)_4(\mu_3\text{-}I)_2]^{4-}$ anion enclosed into a rectangular cavity assembled by six iPV^{2+} cations in the crystal of **3** (looking along the (1 0 3) plane). H atoms are omitted for clarity.

Crystal Structure of $[PV]_2[Bi_4I_8(\mu\text{-}I)_8]$ (4)

Complex **4** crystallizes in the monoclinic space group $P2_1/c$, and its asymmetric unit contains one PV^{2+} cation (Figure 1e) and half a $[Bi_4I_8(\mu\text{-}I)_8]^{4-}$ tetraanion (Figure 2d). The $[Bi_4I_8(\mu\text{-}I)_8]^{4-}$ anion may be viewed as having a bent Bi_4 chain in which the $[Bi_2I_{10}]^{4-}$ anion of **2** is fused with two BiI_6 units via sharing six μ-I atoms. Such a bent Bi_4 chain structure is unprecedented in iodobismuthate chemistry. The average terminal Bi–I bond length [2.9070(13) Å] is shorter than that of **2** and is nearly equal to that of **3** [2.9041(17) Å], whereas the mean Bi–μ-I bond length [3.2126(14) Å] is slightly shorter than that of **2**, and is comparable to that of **3**. The two propyl groups of the PV^{2+} in **4** are located on the same side of the 4,4′-bipy plane, forming a rare staple-shaped configuration. The inorganic anions and the organic cations in **4** are not arranged in one layer, but stack alternatively layer by layer (Figure 6a, Figure S2). Intriguingly, a group of six PV^{2+} cations forms a chair-like cyclohexane cavity that encapsulates a $[Bi_4I_8(\mu\text{-}I)_8]^{4-}$ anion (Figure 6b).

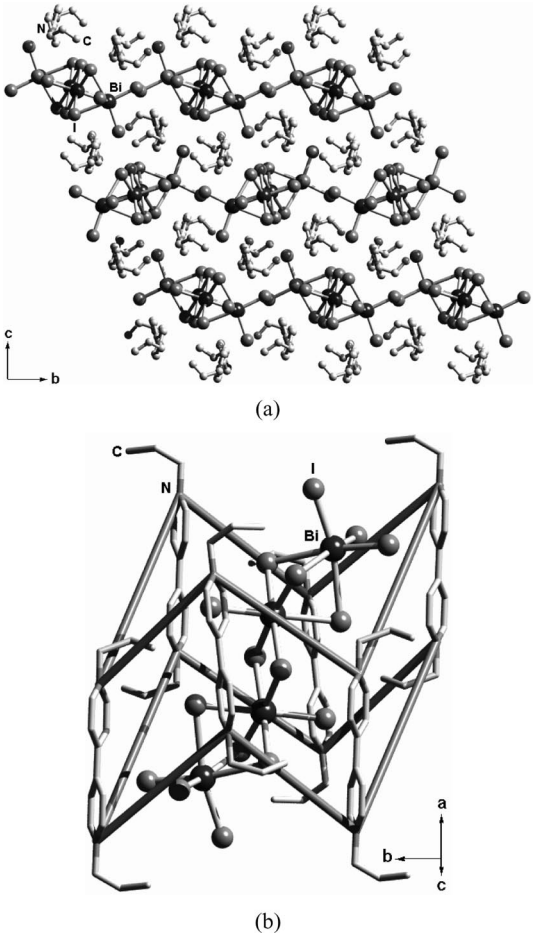


Figure 6. (a) 3D packing diagram of **4** looking down along *a* axis. (b) View of the $[Bi_4I_8(\mu\text{-}I)_8]^{4-}$ clusters enclosed by a chair-like cyclohexane cavity constructed through a group of six PV^{2+} in **4**. H atoms are omitted for clarity.

Optical, Electrical Conductive and Dielectric Properties

The optical diffuse-reflection spectra of crystalline solids **1**–**4** were measured at room temperature. The absorption (*α*/*S*) data were calculated from the reflectance using the Kubelka–Munk function.[13] The energy band gaps (Eonset) obtained by extrapolation of the linear portion of the absorption edges were estimated to be 1.70 (**1**), 1.86 (**2**), 1.82 (**3**) and 1.90 eV (**4**) (Figure 7), indicating a semiconductor nature. The values of energy band gaps of **1**–**4** are all blueshifted with respect to that of the layered semiconductor BiI_3 (1.68 eV),[14a,14b] which suggests that breaking the layered structure of BiI_3 into small polynuclear Bi/I species may decrease the activities of electrons due to the quantum confinement effect.[14c,14d] Compared with that of the quasi-1D complex **1**, the energy band gaps of **2**–**4** are somewhat blueshifted, which may be due to the quantum confinement effect.[14c,14d]

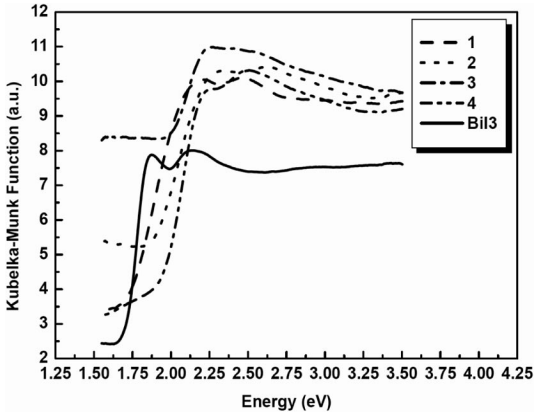


Figure 7. Solid state optical diffuse-reflection spectra of **1**–**4** and BiI_3 derived from diffuse reflectance data at room temperature.

In order to further explore the semiconducting properties of **1**–**4**, we measured the electrical conductivities of crystalline powder samples at variable frequencies at 298 K.[15] Shown in Figure 8, the electrical conductivities of **1**–**4** and BiI_3, increased linearly from 1 Hz to 10^6 Hz with the magnitude ranging from ca. 10^{-11} S cm^{-1} to ca. 10^{-5} S cm^{-1}. Signif-

icantly, the conductivity behaviour of bulk BiI_3 is better than those of **1**–**4**, which is in accord with results derived from the optical diffuse-reflection measurements.

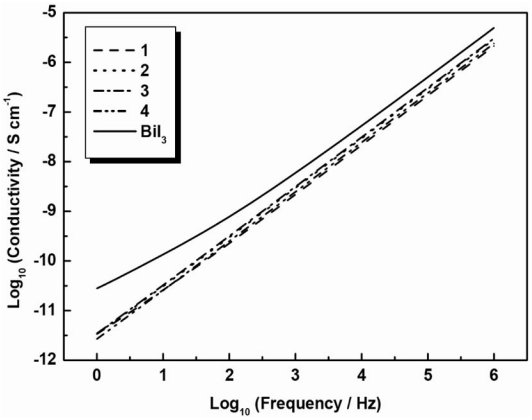


Figure 8. Frequency dependence of electric conductivity of crystalline powders of **1**–**4** and BiI_3 at 298 K.

Low dielectric constant materials (low-*k* materials) are useful for the modern semiconductor industry,[16] and most low-*k* materials are based on inorganosilica[17] and organosilica[18] complexes, aromatic polymers,[19] fluorinated polymers,[20] polyimides,[21] low-dimensional nanomaterials[22] and copper and aluminum composites.[23] Few studies have explored the dielectric properties of pyridinium iodobismuthates. To this end, we measured the dielectric behaviours of **1**–**4** based on the continuous variation of frequency at 298 K. As shown in Figure 9a, the dielectric constants of **1**–**4** in the range of 1 Hz to 10^6 Hz were nearly independent of frequency with values estimated to be 4.93 (**1**), 6.34 (**2**), 6.63 (**3**) and 5.46 (**4**), which were all smaller than that observed value for BiI_3 (10.20, 10^3 Hz–10^6 Hz). These values were slightly larger than that of the traditional low-*k* material SiO_2 (4.3).[16] In addition, the dielectric losses of **1**–**4** are obviously lower than that of BiI_3, especially in the low frequency range. The dielectric losses of **3** and **4** are nearly independent of frequency with magnitudes of ca. 10^{-3} (Figure 9b). The results showed that the incorporation of viologens in the structural framework of a metal halide may provide an effective way to decrease the dielectric constants of metal halides.

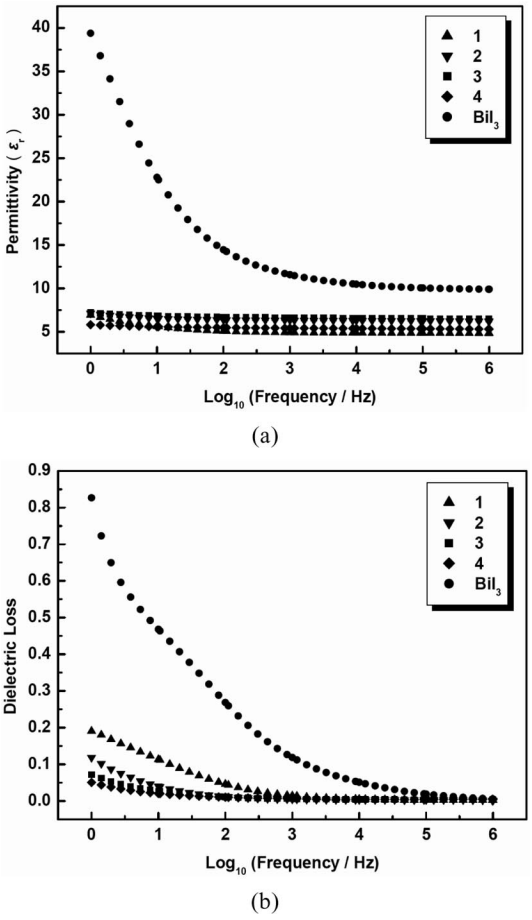


Figure 9. (a) Frequency dependence of permittivity (ε_r) of **1**–**4** and BiI_3 at 298 K. (b) Frequency dependence of dielectric loss ($\varepsilon_i/\varepsilon_r$) of **1**–**4** and BiI_3 at 298 K. The ε_r and ε_i are the real and imaginary parts of permittivity, respectively.

Conclusions

In summary, we have demonstrated an efficient approach to the preparation of a family of viologen iodobismuthates **1**–**4** by solvothermal reactions of alcohols with 4,4′-bipy, BiI_3, KI, I_2 and a small amount of water in MeCN. The resulting viologen cations were generated in situ from the cleavage of the alcohol C–O bond followed by alkylation of 4,4′-bipy. The optical, electrical conductivity and dielectric properties of **1**–**4** were explored. It was found that the introduction of viologen cations into bulk BiI_3 degrades the framework dimensions, increases the energy band gaps, decreases the electrical conductivity and significantly reduces the dielectric constant of the material. It is anticipated that the as-synthesized complexes may have potential applications in semiconductors and low-*k* materials as they possess frequency-independent behaviour in microelectronic fields. Our synthetic methodology may be applied to the preparation of other low-dimensional viologen iodometalates with new structures, better optical and electrical conductive performances as well as low dielectric constant characteristics.

Experimental Section

Materials and Physical Measurements: Starting materials were purchased from commercial sources and used without further purification. Solvents were purchased as reagent grade and distilled prior to use. The elemental analyses for C, H and N were performed with a Carlo–Erba CHNO–S microanalyzer. The IR spectra were recorded with a Varian 1000 FTIR spectrometer as KBr disks (4000–400 cm^{-1}). ^1H NMR spectra were recorded at room temperature with a Varian UNITY-400 spectrometer, and the chemical shifts were referenced to the deuterated dimethyl sulfoxide ([D_6]-DMSO) signal. Solid-state UV/Vis/NIR spectra were measured with a Shimadzu UV-3150 spectrometer at room temperature in the range 200–2000 nm. The frequency-dependent electrical conductivity measurements and the permittivity measurements were per-

formed with a Novocontrol Concept 80 broadband dielectric spectrometer at 298 K.

[MV][BiI$_5$] (1): To a Pyrex glass tube (length: 15 cm, inner diameter: 7 mm) was introduced BiI_3 (30 mg, 0.05 mmol), KI (8 mg, 0.05 mmol), I_2 (13 mg, 0.05 mmol), 4,4′-bipy (8 mg, 0.05 mmol), water (3 μL) and methanol (2 mL). The tube was sealed and heated in an oven at 150 °C for 35 h and then cooled to room temperature at a rate of 5 °C/100 min to form dark red plates of **1**, which were collected by filtration, washed with ethyl acetate and dried in air; yield 16 mg (31% based on 4,4′-bipy). $C_{12}H_{14}BiI_5N_2$ (1029.73): calcd. C 14.00, H 1.37, N 2.72; found C 13.65, H 1.59, N 2.41. FTIR (KBr): $\tilde{\nu}$ = 3102 (w), 3080 (w), 3040 (m), 2930 (w), 1654 (w), 1634 (s), 1560 (m), 1494 (w), 1425 (m), 1405 (m), 1385 (m), 1331 (m), 1268 (m), 1210 (m), 1182 (m), 1107 (w), 1074 (w), 1043 (w), 814 (s), 792 (w), 700 (w), 671 (w), 533 (w), 470 (m) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, TMS): δ = 9.26 (d, 4 H, Py-H), 8.74 (d, 4 H, Py-H), 4.46 (s, 6 H, -CH$_3$) ppm.

[BzV]$_2$[Bi$_2$I$_8$(μ-I)$_2$] (2): Red plates of **2** were prepared by a similar method as described for the synthesis of **1** except that methanol was replaced by benzyl alcohol (0.5 mL) and acetonitrile (1.5 mL); yield 28 mg (47% based on 4,4′-bipy). $C_{24}H_{22}BiI_5N_2$ (1181.92): calcd. C 24.39, H 1.88, N 2.37; found C 23.96, H 1.61, N 2.04. FTIR (KBr): $\tilde{\nu}$ = 3107 (w), 3072 (w), 3039 (m), 2980 (w), 2938 (w), 1632 (s), 1552 (m), 1494 (m), 1440 (s), 1384 (m), 1363 (w), 1342 (w), 1283 (w), 1212 (w), 1161 (m), 1078 (w), 1041 (w), 836 (w), 805 (m), 749 (s), 718 (m), 697 (m), 615 (w), 552 (w), 460 (w) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, TMS): δ = 9.51 (d, 4 H, Py-H), 8.74 (d, 4 H, Py-H), 7.50 (m, 10 H, Ph-H), 5.95 (s, 4 H, -CH$_2$-) ppm.

[iPV]$_2$[Bi$_4$I$_{10}$(μ-I)$_4$(μ$_3$-I)$_2$] (3): Red sheets of **3** were prepared by a similar method as described for the synthesis of **1** except that benzyl alcohol was replaced by 2-propanol (0.5 mL); yield 16 mg (39% based on BiI_3). $C_{48}H_{66}Bi_6I_{24}N_6$ (5026.68): calcd. C 11.47, H 1.32, N 1.67; found C 11.52, H 1.37, N 1.55. FTIR (KBr): $\tilde{\nu}$ = 3167 (w), 3110 (w), 3080 (m), 3057 (m), 2969 (w), 2928 (w), 1633 (m), 1596 (s), 1509 (w), 1486 (m), 1443 (w), 1408 (m), 1384 (m), 1259 (w), 1203 (w), 1138 (w), 1059 (m), 1002 (m), 980 (w), 938 (w), 795 (s), 755 (m), 626 (m), 486 (w) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]-DMSO, 298 K, TMS): δ = 9.47 (d, 4 H, Py-H), 8.79 (d, 4 H, Py-H), 5.12 (m, 2 H, -CH-), 1.68 (d, 12 H, -CH$_3$) ppm.

[PV]$_2$[Bi$_4$I$_8$(μ-I)$_8$] (4): Red sheets of **4** were prepared by a similar method as described for the synthesis of **2** except that benzyl alcohol was replaced by propanol (0.5 mL); yield 19 mg (46% based on BiI_3). $C_{16}H_{22}Bi_2I_8N_2$ (1675.52): calcd. C 11.47, H 1.32, N 1.67; found C 11.33, H 1.29, N 1.61. FTIR (KBr): $\tilde{\nu}$ = 3106 (w), 3073 (w), 3047 (m), 2958 (w), 2926 (w), 2869 (w), 1631 (s), 1554 (w), 1499 (w), 1438 (m), 1385 (s), 1341 (w), 1267 (w), 1215 (w), 1165 (m), 1093 (w), 820 (m), 711 (w), 669 (w), 528 (w) cm^{-1}. ^{1}H NMR (400 MHz, [D$_6$]DMSO, 298 K, TMS): δ = 9.39 (d, 4 H, Py-H), 8.80 (d, 4 H, Py-H), 4.67 (t, 4 H, -CH$_2$-), 2.02 (m, 4 H, -CH$_2$-), 0.93 (t, 6 H, -CH$_3$) ppm.

Crystallographic Data Collection and Refinement: Crystals of **1**–**4** suitable for X-ray analysis were obtained directly from the above preparations. Measurements were made with a Rigaku Mercury CCD X-ray diffractometer using graphite monochromated Mo-K_α (λ = 0.71073 Å). Single crystals of **1**–**4** were mounted on glass fibres and cooled to 223 K (for **1**, **2** and **4**) and 123 K (for **3**) in a liquid nitrogen stream. Cell parameters were refined on all observed reflections by using the program *CrystalClear* (Rigaku and MSc, ver. 1.3, 2001). The collected data were reduced by the program *CrystalClear*, and an absorption correction (multiscan) was applied. The reflection data were also corrected for Lorentz and polarization effects. The crystal structures of **1**–**4** were solved by direct method and refined on F^2 by full-matrix least-squares methods with the SHELXL-97 program.[24] For **3**, one isopropyl group bearing C43, C44 and C45 atoms was disordered over two positions on the two methyl groups with occupancy factors of 0.52/0.48 for C43/C43′ and C45/C45′. For **4**, one propyl group bearing C14, C15 and C16

Table 1. Crystal data and details of data collections and refinement for **1**–**4**.

Complexes	**1**	**2**	**3**	**4**
Empirical formula	$C_{12}H_{14}N_2BiI_5$	$C_{24}H_{22}N_2BiI_5$	$C_{32}H_{44}N_4Bi_4I_{16}$	$C_{16}H_{22}N_2Bi_2I_8$
Formula weight	1029.73	1181.92	3351.03	1675.52
Crystal system	monoclinic	triclinic	monoclinic	monoclinic
Space group	$P2_1$	$P\bar{1}$	$P2_1/c$	$P2_1/c$
Flack parameter	0.090(8)			
a [Å]	6.4772(13)	10.511(2)	15.369(3)	14.531(3)
b [Å]	15.276(3)	12.660(3)	20.136(4)	11.797(2)
c [Å]	11.250(2)	12.738(3)	34.038(9)	19.569(4)
α [°]		88.57(3)		
β [°]	101.62(3)	66.00(3)	111.58(3)	103.63(3)
γ [°]		71.40(3)		
V [Å^3]	1090.3(4)	1456.8(7)	9795(4)	3260.1(12)
Z	2	2	6	4
T [K]	223(2)	223(2)	123(2)	223(2)
D_c [g cm^{-3}]	3.137	2.694	3.409	3.414
F(000)	896	1056	8664	2888
μ(Mo-K_α) [mm^{-1}]	15.158	11.364	18.337	18.365
Total reflections	9915	14082	48249	16850
Unique reflections	4461	6554	17171	7290
Number of parameters	185	289	664	266
R[a]	0.0380	0.0367	0.0763	0.0747
R_w[b]	0.0739	0.0580	0.1401	0.2132
GOF[c]	0.851	0.876	1.118	1.071
$\Delta\rho_{max}/\Delta\rho_{min}$ [e Å^{-3}]	2.397/–1.681	1.825/–1.661	2.018/–1.836	4.921/–3.385

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR = \{\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] $GOF = [\Sigma w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$, where n = number of reflections and p = total numbers of parameters refined.

atoms was disordered over two positions on the terminal methyl atom with occupancy factors of 0.52/0.48 for C16/C16′. All the non-hydrogen atoms in **1**–**4** were refined anisotropically. All hydrogen atoms were placed in geometrically idealized positions and constrained to ride on their parent atoms. A summary of key crystallographic information for **1**–**4** was given in Table 1. The selected bond lengths and angles for **1**–**4** are listed in Table S1.

CCDC-782101 (for **1**), -782102 (for **2**), -782103 (for **3**), -782104 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/datarequest/cif.

Supporting Information (see also the footnote on the first page of this article): Selected bond lengths [Å] and angles [°] for **1**–**4**, additional figures for **2**–**4** and frequency dependence of permittivity of **1**–**4** at 298 K.

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