

Three inorganic–organic hybrids of bismuth(III) iodide complexes containing substituted 1,2,4-triazole organic components with characterizations of diffuse reflectance spectra

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Abstract

The reactions of two kinds of substituted 1,2,4-triazoles with BiI_3 yielded three inorganic–organic hybrids: $[\text{HL}1]_4[\text{Bi}_6\text{I}_{22}] \cdot [\text{L}1]_4 \cdot 4\text{H}_2\text{O}$ (**1**) ($\text{L}1 = 3-(1,2,4\text{-triazole-4-yl})-1\text{H-}1,2,4\text{-triazole}$); $[\text{HL}2]_4[\text{Bi}_6\text{I}_{22}] \cdot 6\text{H}_2\text{O}$ (**2**); $[\text{HL}2]_2[\text{Bi}_2\text{I}_8] \cdot [\text{L}2]_2$ (**3**) ($\text{L}2 = (m\text{-phenol})\text{-}1,2,4\text{-triazole}$). Both **1** and **2** have polynuclear anions of $[\text{Bi}_6\text{I}_{22}]^{4-}$ to build up the inorganic layers and substituted 1,2,4-triazoles as the organic layers. Hybrid **3** consists of two BiI_5 square pyramids as inorganic layers. There exist hydrogen bondings and $\text{I} \cdots \text{I}$ interactions in the structures of **1**, **2** and **3**. Optical absorption spectra of **1**, **2** and **3** reveal the presence of sharp optical gaps of 1.77, 1.77 and 2.07 eV, respectively, suggesting that these materials behave as semiconductors.

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1. Introduction

Research on intramolecular charge-transfer (CT) interactions has obtained much important information about conformational effects in CT phenomena [1]. Aromatics as π -donor can form π -donor–acceptor systems with organic and inorganic π -electron acceptors, whose ionizations depend on the degree of the CT in the ground state. The bismuth– π -aromatics donor–acceptor systems have had various stoichiometries and in unusual structural motifs [2]. Metal iodides based on components like SnI_2 , AuI or HgI_2 often show interesting electrical or optical properties [3]. The bismuth iodide-based hybrids are interesting because of the potentially semiconducting character of the inorganic framework, as well as the rich structural diversity of these frameworks [4]. There exist many types of polynuclear anions formulated as $[\text{Bi}_3\text{I}_{12}]^{3-}$, $[\text{Bi}_4\text{I}_{16}]^{4-}$, $[\text{Bi}_5\text{I}_{19}]^{4-}$, $[\text{Bi}_6\text{I}_{22}]^{4-}$ and $[\text{Bi}_8\text{I}_{28}]^{4-}$. These units are built from

distorted BiI_6 -octahedra, which are joined by common corners, edges or faces through bridging I atoms. The organic parts such as $[\text{N}(\text{C}_4\text{H}_9)_4]^+$, $[\text{K}(18\text{-crown-}6)]^+$, $[\text{P}(\text{C}_2\text{H}_5)_4]^+$, $[\text{Li}(\text{thf})_4]^+$, as weakly interacting individual large organic cations, were applied to form isolated polynuclear anions [5]. The nature of the cations, such as the factors of size, shape and localization of charge, determines the degree of polymerization of the BiI_6 -units. The solvent and concentration of the reactants might also be important in determination of the type of anions [4]. Substituted 1,2,4-triazoles contain six electrons in their triazole five-membered rings thus forming π -electron-rich aromatic heterogeneous conjugate systems. In view of the π -electron character of substituted 1,2,4-triazoles, with the aim of extending the chemistry of bismuth– π -aromatics donor–acceptor systems and obtain further information about the influencing factors on the degree of polymerization, we have investigated the reactions of substituted 1,2,4-triazoles with BiI_3 . Herein, three BiI_3 complexes are presented in this paper with the determination of crystallographic structures and character of diffuse reflectance UV–vis spectra.

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2. Experimental

2.1. General

All reagents and solvents were used directly as supplied commercially, without further purification; except that 3-(1,2,4-triazole-4-yl)-1H-1,2,4-triazole (L1), (*m*-phenol)-1,2,4-triazole (L2) were prepared by literature methods [6–8], with some modifications of prolonging the reaction time to three days at 170 °C to enhance the yield. The IR spectra were recorded on a Nicolet Magna 750 FT-IR spectrometer with KBr pellets in the range of 4000–400 cm⁻¹, and elemental analyses of C, H and N were carried out on a Vario EL III elemental analyzer. Optical diffuse reflectance spectra were measured at room temperature with a Lambda 35 UV–vis spectrophotometer. The samples were ground into fine powder with corresponding crystals and pressed onto a thin glass slide holder. The BaSO₄ plate was used as reference. The absorption spectra were calculated from reflection spectra by the Kubelka–Munk function: $\alpha/S = (1 - R)^2/2R$ (α is the absorption coefficient, S is the scattering coefficient, which is practically wavelength-independent when the particle size is larger than 5 μm , and R is the reflectance).

2.2. Synthesis

2.2.1. Synthesis of $[HL1]_4[Bi_6I_{22}] \cdot [L1]_4 \cdot 4H_2O$ (1)

In a typical synthesis, BiI₃ (59 mg, 0.1 mmol) and L1 (27 mg, 0.2 mmol) were placed in a 20 mL Teflon-lined stainless-steel autoclave with mixed solvents of 4 mL ethanol and 4 mL water in a furnace at 170 °C for 3 days, and then naturally cooled to room temperature. The reaction solution was filtered to obtain a red solution. Evaporation of the red solution at room temperature for several weeks yielded red prismatic crystals suitable for X-ray diffraction. Yield on L1: 24 mg, 19%. Elemental analysis (%), found (calcd): C, 7.35(7.38); H, 0.88(0.85); N, 12.86(12.90). IR data (in KBr, cm⁻¹): 3411 (br, vs), 2975 (s), 2900 (m), 1634 (s), 1446 (w), 1382 (w), 1362 (w), 1274 (w), 1089 (s), 1050 (s), 881 (s), 801 (m), 665 (w), 437 (w).

2.2.2. Synthesis of $[HL2]_4[Bi_6I_{22}] \cdot 6H_2O \cdot (2)$

BiI₃ (59 mg, 0.1 mmol) and L2 (32 mg, 0.2 mmol) were placed in a 20 mL Teflon-lined stainless-steel autoclave with mixed solvents of 4 mL ethanol and 4 mL water in a furnace at 170 °C for 3 days, and then naturally cooled to room temperature. The reaction solution was filtered to obtain a deep red solution. Evaporation of the solution at room temperature for several weeks yielded red prismatic crystals suitable for X-ray diffraction. Yield on L2: 55 mg, 23%. Elemental analysis (%), found (calcd): C, 8.06 (8.01); H, 0.78 (0.80); N, 3.52 (3.50). IR data (in KBr, cm⁻¹): 3435 (br, s), 2974 (m), 2919 (m), 1630 (m), 1455 (m), 1378 (w), 1270 (w), 1088 (s), 1051 (s), 880 (s), 805 (w), 678 (w), 651 (w).

2.2.3. Synthesis of $[HL2]_2[Bi_2I_8] \cdot [L2]_2$ (3)

A measure of 10 mL of ethanol solution of BiI₃ (59 mg, 0.1 mmol) was added dropwise to 20 mL hot aqueous solution of L2 (32 mg, 0.2 mmol). The reaction mixture was stirred at room temperature for 6 h, producing a clear deep red solution. Evaporation of the solution yielded red block crystals suitable for X-ray diffraction. Yield on L2: 21 mg, 21%. Elemental analysis (%), found (calcd): C, 18.49(18.47); H, 1.42(1.45); N, 8.11(8.08). IR data (in KBr, cm⁻¹): 3414 (br, s), 2975 (m), 2928 (m), 1630 (m), 1456 (m), 1380 (w), 1271 (w), 1090 (s), 1050 (s), 881 (s), 804 (w), 676 (w), 649 (w).

2.3. Structure determinations and refinements of 1–3

X-ray crystallographic experiments were carried out on a Rigaku Mercury CCD diffractometer equipped with a graphite-monochromated MoK α radiation ($\lambda = 0.71073 \text{ \AA}$). Single crystals were mounted on the diffractometer under a stream of cold N₂ at –120 °C. The intensity data were collected by the ω scan technique. Accurate cell parameters were obtained with refined collections of intensities and were corrected in the usual way. The intensity data were reduced using CrystalClear program [9]. The structures were solved by direct methods using SHELXTLTM package of crystallographic software [10] and refined by full-matrix least-square technique on F^2 . All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included in the final stage of the refinement on calculated positions bonded to their carrier atoms. But no H atoms were included for water molecules. A summary of the crystal data and data collection and refinement parameters for the complexes 1–3 was listed in Table 1.

3. Results and discussion

3.1. Structural descriptions of compounds 1–3

3.1.1. $[HL1]_4[Bi_6I_{22}] \cdot [L1]_4 \cdot 4H_2O$ (1) and $[HL2]_4[Bi_6I_{22}] \cdot 6H_2O$ (2)

1 crystallizes in the $P\bar{1}$ space group and consists of one isolated polynuclear $[Bi_6I_{22}]^{4-}$ anion (Fig. 1), four protonated 3-(1,2,4-triazole-4-yl)-1H-1,2,4-triazole (L1) molecules as the cationic building units and four neutral L1, and four water molecules. The compound is charge-neutral so that the four negative charges on the $[Bi_6I_{22}]^{4-}$ anion are balanced by four protonated L1. The centrosymmetric $[Bi_6I_{22}]^{4-}$ anion is established by six bismuth atoms, each of them coordinated by six iodine atoms to form distorted octahedra. The two octahedra of Bi1 and its symmetry-related Bi1A are linked by edge-sharing to four adjacent octahedra, the octahedra of Bi2 and Bi2A linked to three adjacent octahedra and the two residual octahedra connected to only two octahedra (Table 2).

The $[Bi_6I_{22}]^{4-}$ anion has already been described previously [5c,5d,11], and here displays the expected range of bond lengths and angles. There exist three kinds of iodine

Table 1
Crystallographic data for 1–3

	1	2	3
Empirical formula	C ₁₆ H ₂₂ Bi ₃ I ₁₁ N ₂₄ O ₂	C ₃₂ H ₃₈ Bi ₆ I ₂₂ N ₁₂ O ₁₀	C ₁₆ H ₁₅ Bi ₄ N ₆ O ₂
Color and habit	Red prism	Red prism	Red block
Crystal size (mm)	0.12 × 0.1 × 0.1	0.4 × 0.3 × 0.1	0.4 × 0.35 × 0.3
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$
<i>a</i> (Å)	10.662(3)	34.975(11)	8.921(3)
<i>b</i> (Å)	13.850(4)	10.638(3)	11.984(4)
<i>c</i> (Å)	19.150(5)	24.347(8)	13.411(4)
α (°)	70.973(4)	90	63.482(9)
β (°)	88.229(8)	94.831(4)	76.004(10)
γ (°)	82.421(8)	90	84.675(13)
<i>V</i> /Å ³	2649.8(12)	9026(5)	1244.6(7)
<i>Z</i>	2	4	2
<i>F</i> _w	2605.42	4796.42	1039.92
<i>D</i> _{calcd} (Mg m ⁻³)	3.265	3.530	2.775
μ (mm ⁻¹)	16.391	19.225	12.068
<i>F</i> (000)	2268	8232	928
θ (°)	3.10 to 25.03	3.01 to 25.03	3.05 to 25.03
Reflections measured	16749	28032	7772
Independent reflections	9258 (<i>R</i> _{int} = 0.0462)	7958 (<i>R</i> _{int} = 0.0886)	4326 (<i>R</i> _{int} = 0.0307)
Observed reflections	6451	6675	3786
Final <i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0495, 0.1067	0.0598, 0.1617	0.0346, 0.0810
<i>GOF</i> on <i>F</i> ²	1.015	1.073	1.009
(Δ/σ) _{max/min}	0.001, 0.000	0.002, 0.000	0.003, 0.000
Largest difference peak/eÅ ⁻³	2.765, -3.252	1.495, -2.376	1.684, -1.922

$$R_1 = (\sum ||F_o| - |F_c|| / \sum |F_o|), wR_2 = [\sum (w(F_o^2 - F_c^2)^2) / \sum w(F_o^2)]^{1/2}.$$

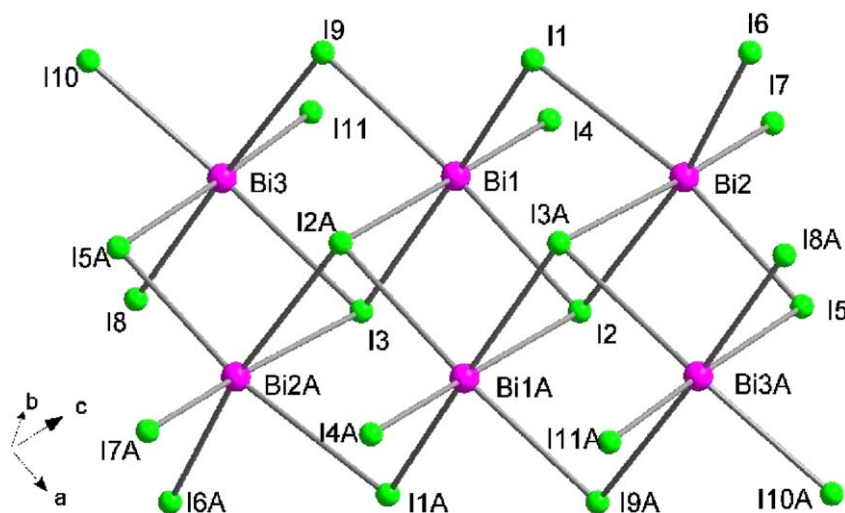


Fig. 1. View of the polynuclear $[\text{Bi}_6\text{I}_{22}]^{4-}$ anion in 1.

atoms with coordination modes of 12 terminal iodine atoms, six μ_2 - and four μ_3 -iodine atoms. The Bi–I_{terminal} distances (average value of 2.8858(12) Å) are significantly shorter than the Bi–I_{bridging} distances (average value of 3.2111(13) Å). The μ_2 –(Bi–I) distances (average value of 3.1796(13) Å) are also very similar to the situation in BiI₃ [12], shorter than average value of 3.2426(12) Å of the μ_3 –(Bi–I) distances. Atoms μ_2 -I and μ_3 -I bridge Bi(III) centers with unequal Bi–I bond distances: for example, Bi2–I1 distance of 3.2614(12) Å is 0.237 Å longer than the other

Bi1–I1 distance of 3.0244(11) Å. The variation of the I–Bi–I angles (82.37(3) to 177.02(3)°) is attributed to the different connectivities of iodine. The I_{terminal}–Bi–I_{terminal} angles in octahedra range from 93.66(3) to 96.05(4) (average value of 94.77(3)°), deviating from the ideal 90°. And the I2–Bi–I3 angle of 88.93(3)° in the case of μ_3 -bridging modes, comparable to similar polynuclear anions [13], is the largest deviation to the ideal octahedra. The distortion in the angles could be interpreted as the beginning of localization of the lone pair trans to the Bi–Bi vector and

the geometric arrangement [4]. In the inorganic layers, the I⋯I interactions of I5⋯I10A ($A = 1-x, -y, 1-z$), I8⋯I8B ($B = 1-x, -y, z$), I7⋯I11C and I4⋯I4C ($C = 1-x, 1-y, 1-z$) in the range of 3.755 and 4.214 Å are slightly shorter than twice the iodine atom van der Waals (2.15 Å), indicating there are I⋯I interactions between the polynuclear anions. The shortest distance of the groups of L1 larger than 5.08 Å shows no $\pi\cdots\pi$ interactions in the structure.

Table 2
Selected bond distances (Å) for 1–3

	1		2		3	
I_{terminal}	Bi1–I4	2.8383(11)	Bi1–I5	2.8914(7)	Bi1–I4	2.8664(7)
	Bi2–I7	2.8695(11)	Bi2–I6	2.8507(8)	Bi1–I1	2.9347(9)
	Bi2–I6	2.9054(12)	Bi2–I7	2.8689(8)	Bi1–I2	2.9891(9)
	Bi3–I11	2.8627(12)	Bi3–I10	2.8840(8)		
	Bi3–I8	2.8972(12)	Bi3–I11	2.8908(9)		
	Bi3–I10	2.9416(12)	Bi3–I9	2.9213(8)		
$I_{\mu 2}$	Bi1–I1	3.0244(11)	Bi1–I2	3.0005(8)	Bi1–I3	3.1607(9)
	Bi1–I9	3.0496(11)	Bi1–I4	3.0968(8)	Bi1–I3A	3.2280(9)
	Bi2–I5	2.9661(12)	Bi2–I8	3.0302(8)		
	Bi2–I1	3.2614(12)	Bi2–I4A	3.1692(7)		
	Bi3–I9	3.3667(13)	Bi3–I8	3.3086(8)		
	Bi3–I5A	3.4093(12)	Bi3–I2	3.3590(9)		
$I_{\mu 3}$	Bi1–I2	3.1479(11)	Bi1–I3	3.1042(8)		
	Bi1–I3	3.1934(12)	Bi1–I1A	3.1545(8)		
	Bi2–I2	3.3342(12)	Bi1–I1	3.2995(8)		
	Bi3–I3	3.2947(11)	Bi2–I1	3.3934(9)		
	Bi3–I5A	3.4093(12)	Bi3–I3	3.3534(8)		

Symmetry code, (1): $A = -x + 1, -y, -z + 1$; (2): $A = -x + 0.5, -y + 0.5, -z + 1$; (3): $A = -x + 3, -y + 2, -z + 1$.

The layered structure is built up from regular organic layers separated by the inorganic sheets of $[\text{Bi}_6\text{I}_{22}]^{4-}$ units of edge-sharing octahedra as shown in Fig. 2. There exist hydrogen bondings ($\text{N11-H}\cdots\text{N61A} = 2.874(15)$ Å, 176.4° , $A = 1 + x, y, z$; $\text{N71-H}\cdots\text{O2WB} = 2.830(16)$ Å, 158.9° , $B = x - 1, 1 + y, z - 1$) in the organic layers.

The conformation of **2** is similar to **1**, consisting of one isolated polynuclear $[\text{Bi}_6\text{I}_{22}]^{4-}$ anion, four protonated L2 and six lattice water molecules, indicating the bulky polynuclear $[\text{Bi}_6\text{I}_{22}]^{4-}$ anion needs multi-protonated organic components or bulky cations to balance the negative charges. This situation can be found in similar complexes containing $[\text{Bi}_6\text{I}_{22}]^{4-}$ anion, such as containing $(\text{Et}_4\text{P}^+)_4$ [5d] $[(\text{CH}_3)_2\text{PhEtN}^+]_4$ [11], and $(\text{THF})_6\text{Na}^+$ [13]. The polyhedra of the polynuclear $[\text{Bi}_6\text{I}_{22}]^{4-}$ anion in **2** is the same as that of **1**. The Bi–I distances are in agreement with those in **1**, and the Bi–I distances are decreasing with the order of $\mu_3\text{-(Bi-I)}$, $\mu_2\text{-(Bi-I)}$, $\text{Bi-I}_{\text{terminal}}$, with the average values of 3.2610(9), 3.1607(9) and 2.8845(9) Å, respectively. The structure of **2** consists of inorganic–organic layers (Fig. 3), in which there exist I⋯I interactions and hydrogen bondings: the I⋯I interactions in the inorganic layers are in the range of 3.911 and 4.273 Å; the lattice water molecules are involved in hydrogen bondings from 2.761 to 2.895 Å with the N and O atoms of the triazoles, as well as the lattice water molecules.

3.1.2. $[\text{HL}_2]_2[\text{Bi}_2\text{I}_8] \cdot [\text{L}_2]_2 \cdot (3)$

The asymmetric unit of **3** contains one protonated L2 and a $[\text{Bi}_4\text{I}_4]^-$ anion and a neutral L2. The anion is completed by the symmetry operations of an inversion center. The structure is characterized by the dimeric anion

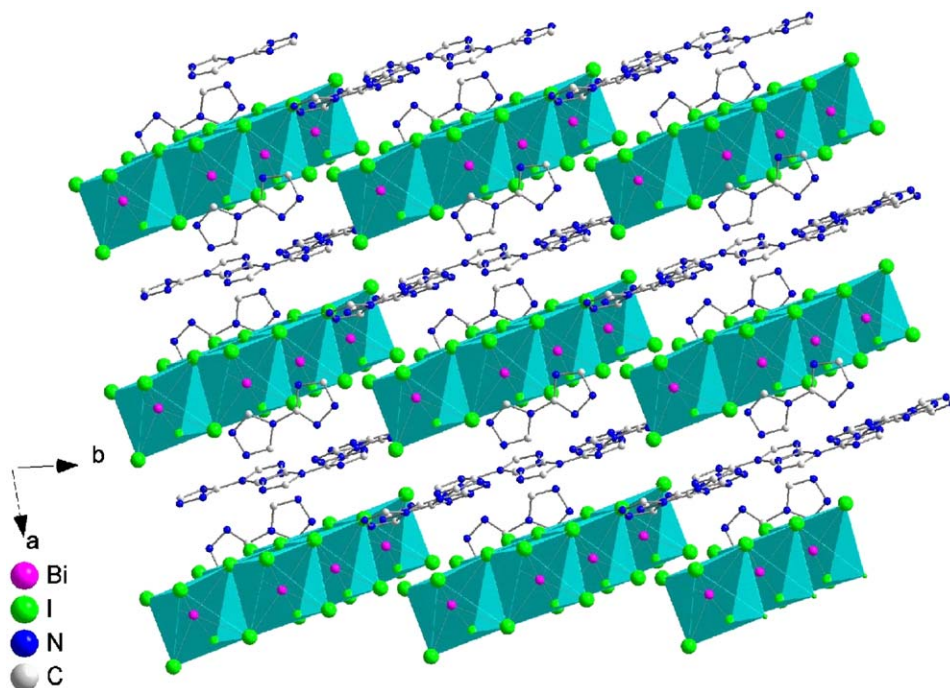


Fig. 2. The layered structure built up from organic layers separated by the inorganic sheets of $[\text{Bi}_6\text{I}_{22}]^{4-}$ units described as edge-sharing octahedral.

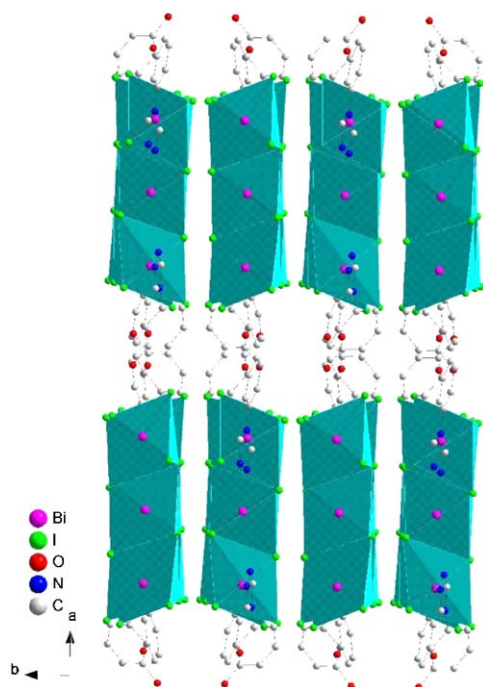


Fig. 3. The layered crystal structure as $-ABAB-$ stacking of **2**. $[Bi_6I_{22}]^{4-}$ units described as edge-sharing octahedral.

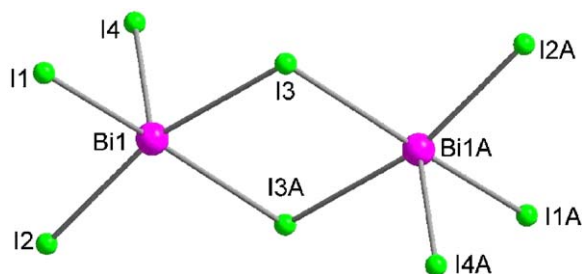


Fig. 4. View of the polynuclear $[Bi_2I_8]^{2-}$ anion in **3**.

$[Bi_2I_8]^{2-}$, a distorted bi-square pyramid, which is formed from two oppositely oriented edge-sharing BiI_5 square pyramids as shown in Fig. 4. The average terminal Bi–I distances of 2.9301(9) Å and the bridging Bi–I distances of 3.1607(9) and 3.2280(9) Å are in the range observed in previous [14]. It is noteworthy that the geometry of BiI_5 square pyramid is not common, there being only two examples [14i, 14h]. The Bi(III) centers display slightly distorted BiI_5 square pyramids with $\tau = 0.053$ (τ defined as $(\beta - \alpha)/60$, α and β being the bigger bond angles around bismuth; $\tau = 0$ for an ideal square pyramid with $\alpha = \beta = 180^\circ$) [15].

The layer structure of **3** stacking as $-ABAB-$, is also built up from organic layers separated by inorganic–organic layers of $[Bi_2I_8]^{2-}$ dimeric units of edge-sharing square pyramids (Fig. 5). In the structure, there exist $I \cdots I$ interactions: $I2 \cdots I3A$, $I2 \cdots I2B$ ($B = 3 - x, 3 - y, -z$) and interactions are 4.2838(12) and 4.1061(15) Å, respectively. The hydrogen bondings of $O1-H \cdots N22C$ (2.796(7) Å, 163.7° , $C = x, -1 + y, z$) and $O2-H \cdots O2D$ (2.909(11) Å,

172.7° , $D = 3 - x, 2 - y, -z$) are formed in the organic layers to stabilize the structure.

When compared with the synthetic conditions of **2** and **3**, some experimental factors affecting the degree of polymerization can be possibly inferred, such as temperature. The molar ratio of BiI_3 and L2 (1:2) and solvents of **2** and **3** are same, except the temperature: **2** in hydrothermal reaction of $170^\circ C$ and **3** in room temperature, which indicates the factor of temperature partly determine the degree of polymerization of the BiI_6 -units; the higher temperature perhaps vails to form higher nucleus of the polynuclear.

3.2. Properties of diffuse reflectance UV–vis spectra

The bismuth iodine inorganic frameworks raise much interest because of the potentially semiconducting character. The optical properties of the title compounds were assessed by its optical diffuse reflectance data [16]. The Kubelka–Munk (or remission, F) functions converted from the diffuse reflectance data were plotted according to the diffuse reflectance data as shown in Fig. 6. Optical absorption spectra of compounds **1**, **2** and **3** reveal the presence of sharp optical gaps of 1.77, 1.77 and 2.07 eV, respectively, which suggests that these materials behave as semiconductors and are consistent with the dark red color of the crystals (black red for **3**).

The present compounds of **1** and **2** with the same polynuclear anions and different organic components give same energy band gaps; **2** and **3** with different polynuclear anions and the same organic components give different energy band gaps. The energy band gaps of the three reported compounds are also compared to that of BiI_3 itself (1.73 eV) [17]. The results show that the energy band gaps mainly derive from the CT of the inorganic components [18]. Some energy band gaps of different degrees of polymerization of the BiI-units are listed in Table 3. The same rule can be found in $(H_2DAH)BiI_5$, [19] $(H_2AETH)BiI_5$, $(H_2DDDA)BiI_5$ [18] and $(C_6H_5C_2H_4NH_3)_4BiI_7 \cdot H_2O$ [20], whose energy band gaps are in a narrow range from 2.24 to 2.62 eV, and in $(CH_3NH_3)_3BiI_9$ [21] and $(AESBT)_3BiI_9$ [14k], whose energy band gaps are 2.51 and 2.49 eV, respectively. The small difference may come from the minor effect of the balance organic components on the optical spectra for the three compounds. In **1–3**, the organic layers in the stacks are almost parallel and equidistant: the interplanar distances are 3.408, 4.860 and 4.732 Å, indicating short intermolecular contacts between the organic layers. Furthermore, another cursory tendency can be found when compared the energy band gaps with different degrees of polymerization: it seems that the higher degree of polymerization of the BiI-units results in lower energy band gaps.

4. Conclusion

It is the first time that substituted 1,2,4-triazoles have been used in place of amines as the organic component of

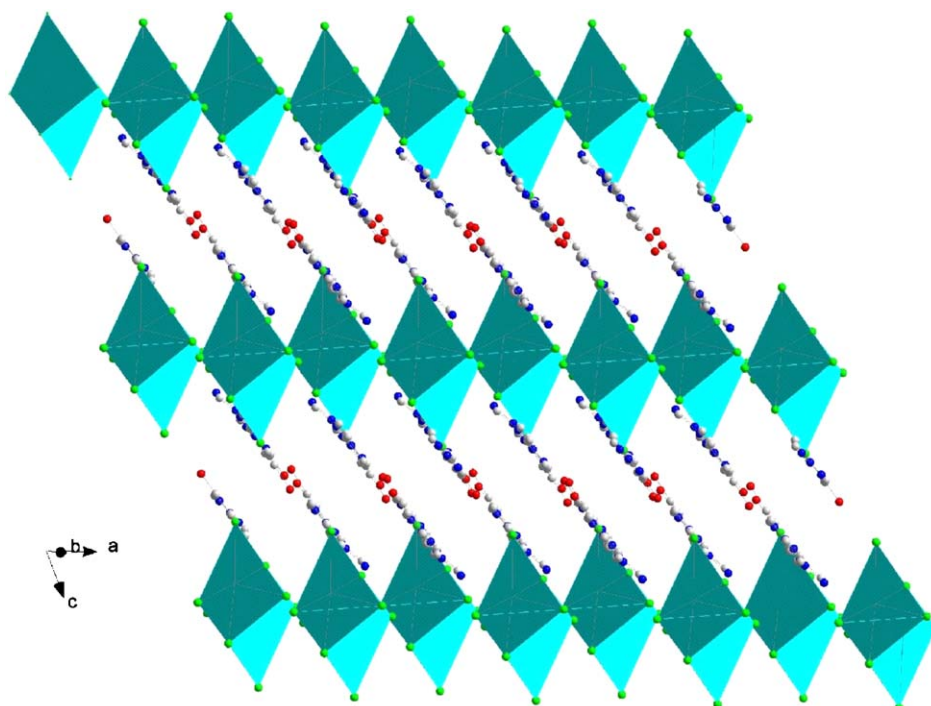


Fig. 5. The layered structure as –ABAB– stacking of **3** built up from organic layers separated by the inorganic sheets of $[\text{Bi}_2\text{I}_8]^{2-}$ units described as edge-sharing octahedral.

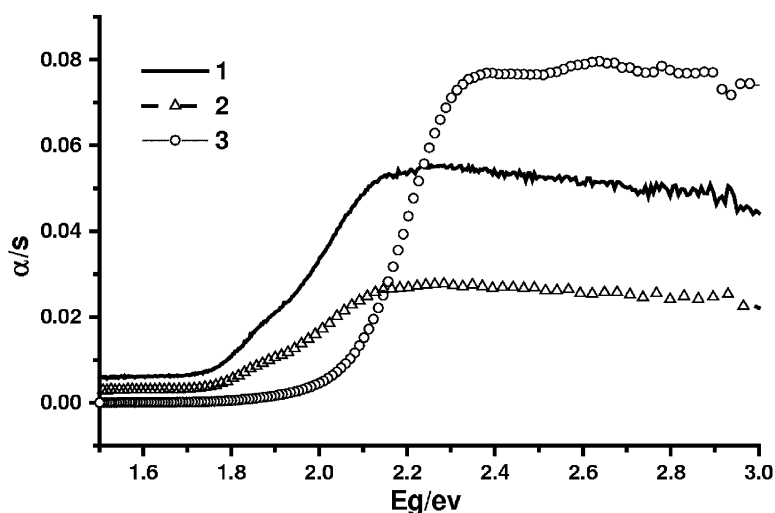


Fig. 6. The band gaps of **1**, **2** and **3** estimated to be 1.77, 1.77 and 2.07 eV were assessed by the optical diffuse reflectance data.

the organic–inorganic hybrids. The introduction of a metal at the +III oxidation state (Bi^{III}) in the iodometalate inorganic part has been considered in the case of the protonated positive substituted 1,2,4-triazole. The energy band gaps of **1–3** as compared with that of BiI_3 and other bismuth iodine complexes indicate that introduction of BiI_3 can obtain some inorganic–organic hybrid materials with low-energy band gaps. The degree of polymerization of the BiI -units has important effect on the energy band gaps.

5. Supplementary material

Crystallographic data for **1–3** have been deposited at the Cambridge Crystallographic Data Center as supplementary publications [CCDC-267905 (**1**), 267906 (**2**) and 267907 (**3**)]. The data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the CCDC, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk).

Table 3
Some energy band gaps of different degree of polymerization of the BiI_n units

Compound	Bi _x I _y ⁿ⁻	λ (nm)	E _g (eV)	Ref.
(H ₂ AETH)BiI ₅	BiI ₅ ²⁻	491	2.53	[18]
(H ₂ DDDA)BiI ₅	BiI ₅ ²⁻	515	2.41	[18]
(H ₂ DAH)BiI ₅	BiI ₅ ²⁻	554	2.24	[19]
(C ₆ H ₅ C ₂ H ₄ NH ₃) ₄ BiI ₇ ·H ₂ O	BiI ₆ ³⁻	474	2.62	[20]
(CH ₃ NH ₃) ₃ Bi ₂ I ₉	Bi ₂ I ₉ ³⁻	494	2.51	[21]
(AESBT) ₃ Bi ₂ I ₉	Bi ₂ I ₉ ³⁻	498	2.49	[14k]
[Ru(2,2'-bipy) ₃] ₂ [Bi ₄ I ₁₆]	Bi ₄ I ₁₆ ²⁻	600	2.1	[17]
[HL2] ₂ [Bi ₂ I ₈]·[L2] ₂ (3)	Bi ₂ I ₈ ²⁻	600	2.07	This work
[HL1] ₄ [Bi ₆ I ₂₂]·[L1] ₄ ·4H ₂ O (1)	Bi ₆ I ₂₂ ⁴⁻	702	1.77	This work
[HL2] ₄ [Bi ₆ I ₂₂]·6H ₂ O (2)	Bi ₆ I ₂₂ ⁴⁻	702	1.77	This work

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Appendix A. Supplementary analysis tools

A collection of macros that can be applied to sequence batches of up to 5000 sequences can be obtained from our web site (<http://igm.ccc.uab.edu/~schroeder/publications/>).

Appendix B. Supplementary data

Supplementary data associated with this article can be found in the online version at [doi:10.1016/j.jssc.2006.02.011](https://doi.org/10.1016/j.jssc.2006.02.011).

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