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Reversibly Thermochromic Bismuth–Organic Materials with Tunable Optical Gaps

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ABSTRACT: Five reversibly thermochromic bismuth-based inorganic-organic hybrid materials were synthesized via facile one-step condensation reactions between triphenylbismuth and four arenedithiols and a diselenol. The materials were characterized by UV-vis and FT-IR spectroscopy, powder X-ray diffraction (PXRD), energy dispersive X-ray spectroscopy (EDS), scanning electron microscopy (SEM), elemental analysis (EA), and thermogravimetric analysis (TGA). The bismuth-organic materials (Bi-OMs) are colored materials with optical HOMO-LUMO gaps that were readily tuned by systematic modification of the steric and electronic character of the π -conjugated organic linkers. All five Bi-OMs exhibit completely reversible thermochromism in the solid-state, and possess excellent thermal stability in air up to nearly 300 °C. This combination of physical properties, coupled with the ease of synthesis and the inexpensive, non-toxic nature of bismuth, make this class of inorganic-organic hybrid materials potentially promising for reversible smart window applications, camouflage coatings, temperature sensing, photocatalysis, color filters and displays.

INTRODUCTION

Purely inorganic materials that contain bismuth have been widely studied and used as optoelectronic materials,¹⁻⁹ thermoelectrics,¹⁰⁻¹³ photocatalysts,¹⁴⁻¹⁷ scintillators,¹⁸ lanthanide host materials,^{19, 20} and biomedical X-ray contrast agents.²¹⁻²⁴ This myriad of applications attests to the versatility and technological importance of bismuth in advanced functional materials. In contrast, hybrid organic-inorganic materials containing bismuth, such as Bi-based metal-organic frameworks (BiMOFs), are still relatively unexplored, with the vast majority of reported MOFs being based on transition metals. Nevertheless, interest in bismuth-organic materials (Bi-OMs) has been gaining momentum lately, with several systems having been published in recent years.²⁵⁻³³ Considering its high abundance, low cost, rich chemistry, nontoxic and non-radioactive nature (unusual for such a heavy element), bismuth makes for an attractive choice of metal for designing novel hybrid materials with wide-ranging technological applications. Incorporating bismuth into inorganic-organic systems would open the door to many new and interesting materials due to the element's flexible coordination geometry, stereoactive 6s lone pair, and relativistic spin-orbit coupling effects. Of the Bi-OMs reported so far, essentially all of them have been synthesized through Bi–O and Bi–N bond formations between Bi(III) ions and coordinating carboxylate or multidentate N-heterocycle-based π -linker ligands. With the idea of promoting enhanced metalligand interaction, we envisaged that the use of larger coordinating atoms (e.g., S, Se) on the ligands would mitigate the atomic size mismatch and foster better orbital overlap between Bi and the π -linker. To the best of our knowledge, Bi-OMs made by iterative Bi-S bond formations has not yet been explored, in contrast to the recent surge in metal-dithiolene frameworks³⁴⁻³⁶ synthesized from transition metals and aromatic polythiols. Heightened interest in transition-metal dithiolene networks has been primarily motivated by the unique optoelectronic properties of these two-dimensional π -d conjugated organometallic materials, in which π -conjugated organic linkers

were connected to the transition metals by strong metal-sulfur covalent bonds. In the case of bismuth compounds, Bi-S bonds are generally regarded as thermodynamically stable (favorable soft-soft interactions) and less labile than Bi-O bonds.^{37,38} Thus, synthesizing organobismuth networks via iterative Bi-S bond formations presented a viable strategy for the construction of novel and robust Bi-OM materials. Based on documented ligand-to-metal charge transfer ($S \rightarrow Bi$) effects observed in bismuth-thiolate complexes,³⁹⁻⁴³ it was anticipated that the use of electron-rich aromatic dithiols⁴⁴ as π -linkers would give rise to interesting $\pi \rightarrow \sigma^*$ interactions between the organic components and the bismuth centers. Our interest in such systems was inspired in part by the optoelectronic properties of bismuth chalcogenides⁴⁵⁻⁴⁸, thermochromic properties of select organobismuth molecules,⁴⁹ and recent advances in the tuning of bandgaps in metal-organic frameworks.⁵⁰⁻⁵⁴ By using an organic-inorganic hybrid system, we hoped to obtain materials with interesting optical and chromic properties that can be fine-tuned by rational functionalization of the organic linkers.^{55, 56} Herein we report the synthesis and characterization of five Bi-OMs (Figure 1). These materials were prepared from triphenylbismuth and various arenedithiols (and a diselenol) through a polycondensation reaction that afforded volatile benzene as the only byproduct. We demonstrate that the optical HOMO-LUMO gaps of the Bi-OMs can be fine-tuned through systematic functionalization of the π -conjugated organic linkers that connect the metal atoms. In addition to color tunability, all five Bi-OMs also exhibited intriguing reversible solidstate thermochromism and excellent thermal stability in air. Where suitably stable, such thermochromic materials⁵⁷⁻⁶⁰ show great promise for utilization in technologies such as reversible smart windows, camouflage coatings, photocatalysts, and nanothermometers.









Bi-OM-2









Bi-OM-5

Figure 1. Schematic representation of the synthesis of Bi-OM-1 through Bi-OM-5, and their molecular structures.

EXPERIMENTAL SECTION

Materials and methods. All synthetic procedures were performed in oven-dried glassware under anhydrous nitrogen atmosphere using standard Schlenk techniques. All reagents and chemicals were purchased from Sigma-Aldrich, Alfa Aesar, TCI America and Fisher Scientific, and used without further purification. Reaction solvents were dried over activated 3Å molecular sieves and rigorously degassed by sparging with nitrogen prior to use. Intermediates were purified by flash column chromatography on silica gel (60–230 mesh). The NMR spectra of Bi-OM precursors were recorded on a Bruker AVANCE II 400 MHz NMR spectrometer. Solid-state UV-vis diffuse reflectance spectra (DRS) were obtained on a Varian Cary® 100 UV-vis spectrophotometer, equipped with a diffuse reflectance accessory consisting of a 73-mm diameter integrating sphere. Infrared spectra were recorded on a Varian 640 FTIR spectrometer equipped with an ATR in the 500–4000 cm⁻¹ range. Powder X-ray diffraction studies were carried out on a Rigaku Ultima IV Diffractometer. Scanning electron microscopy and energy dispersive X-ray spectroscopy was done on a JSM-7500 FESEM (JEOL) instrument. Elemental analysis (EA) was performed at the Analytical and Instrumentation Laboratory at the University of Alberta. Thermogravimetric analysis (TGA) data were recorded on a Q5000 IR instrument (TA Instruments; New Castle, DE, USA), and the samples were heated from 25 °C to 500 °C in air with a temperature rise of 10 °C/min. TGA data were analyzed using TA Instruments Universal Analysis 2000 Version 4.5 A.

Synthesis of triphenylbismuth (1). Triphenylbismuth was readily prepared using literature protocols.⁶¹ To a cooled (-78 °C) solution of bromobenzene (3.3 mL, 31 mmol) in THF was added 1.6 M *n*-butyllithium (19.4 mL, 31.0 mmol) and the mixture was stirred for 1 h before being warmed up to 0 °C. Next, bismuth(III) bromide (4.49 g, 10.0 mmol) dissolved in THF was added via syringe to the re-cooled (-78 °C) solution of phenyllithium. The stirred reaction mixture was allowed to gradually warm up to room temperature overnight (16 h) before being quenched with

methanol. The resulting mixture was partitioned between water and dichloromethane within a separatory funnel, after which the triphenylbismuth was extracted (3 x 50 mL) into the organic layer. After drying over anhydrous Na₂SO₄, the organic solution was rotary evaporated to dryness and the crude product was recrystallized from ethanol to afford pure triphenylbismuth as white crystals. Yield: 2.95 g, 67 %. (Note: Triphenylbismuth is not commercially available in certain locations, and cannot be shipped internationally due to export regulations.)

Synthesis of Bi-OM-1. A solution of triphenylbismuth (0.409 g, 0.920 mmol) and benzene-1,4dithiol (0.192 g, 1.33 mmol) in anhydrous degassed toluene (70 mL) was refluxed with vigorous stirring over 72 h. A reddish-orange precipitate developed over the course of three days. At the end of the reaction, the mixture was cooled to room temperature, during which the reddish **Bi-OM-1** precipitate was observed to gradually turn yellow-orange in color. The product was isolated by suction filtration, washed thoroughly with hot acetone, and then dried under high vacuum at 120 °C for 24 h to remove solvent traces. Yield: 0.293 g, 76.1 %. Anal. Calcd. for $C_{12}H_9BiS_2$ (formula of one repeat unit): C, 33.81; H, 2.13; S, 15.04. Found: C, 33.96; H, 2.12; S, 15.18.

Synthesis of Bi-OM-2. This inorganic-organic hybrid material was synthesized in the same way as **Bi-OM-1**, but using benzene-1,3-dithiol instead of the *para* isomer. The **Bi-OM-2** product was isolated as a yellow solid. Yield: 0.220 g, 56.1 %. Anal. Calcd. for C₁₂H₉BiS₂ (formula of repeat unit): C, 33.81; H, 2.13; S, 15.04. Found: C, 33.35; H, 2.18; S, 14.46.

Synthesis of Bi-OM-3. This material was synthesized in the same manner as **Bi-OM-1**, but using biphenyl-4,4'-dithiol in place of benzene-1,4-dithiol. **Bi-OM-3** was isolated as a yellow solid. Yield: 0.271 g, 73.8 %. Anal. Calcd. for C₁₈H₁₃BiS₂ (formula of repeat unit): C, 43.03; H, 2.61; S, 12.76. Found: C, 44.91; H, 2.65; S, 14.08.

Synthesis of 2,3,5,6-tetrafluorobenzene-1,4-dithiol (2). The two-step synthesis of 2 was performed according to a published procedure,⁶² starting from hexafluorobenzene (1.86 g, 10.0 mmol). Yield over two steps: 0.700 g, 32.7 %.

Synthesis of Bi-OM-4. This material was synthesized in the same manner as Bi-OM-1, but using the perfluorinated dithiol 2 instead of benzene-1,4-dithiol. Bi-OM-4 was isolated as a yellow solid (which turns yellow-orange at elevated temperatures). Yield: 0.268 g, 84.8 %. Anal. Calcd. for $C_{12}H_5BiF_4S_2$ (formula of repeat unit): C, 28.93; H, 1.01; S, 12.87. Found: C, 29.02; H, 1.07; S, 12.91.

Synthesis of benzene-1,4-diselenol (3). The synthesis of 3 starting from 1,4-dibromobenzene was adapted from a literature procedure,⁶³ with several key modifications to work around the airsensitive nature of the diselenol. First, 1,4-dibromobenzene (1.65 g, 7.00 mmol) was first dissolved in THF (60 mL) and cooled to -78 °C. A solution of 1.7 M tert-butyllithium in pentane (17.3 mL, 29.4 mmol) was then added via syringe to the cooled dibromide solution. The solution was stirred for 2 h at -78 °C and then warmed to 0 °C for 30 min. Black selenium powder (1.10 g, 14.0 mmol) was then added over 30 min, before re-cooling the stirred reaction mixture down to -78 °C. At this point, acetyl chloride (1.10 mL, 16.1 mmol) was introduced via syringe. The resulting solution was allowed to warm to room temperature and stirred for 14 h. This was partially purified by extraction (3 x 50 mL dichloromethane), evaporated to dryness to yield crude product, which was purified by column chromatography on silica with hexane/dichloromethane (2:1 v/v) as the eluent followed by recrystallization from hexane to give pure bis-selenoester as pink crystals (yield: 1.21 g, 54.0 %). Next, a two-neck round-bottom flask was charged with the bis-selenoester (0.096 g, 0.30 mmol) and p-toluenesulfonic acid monohydrate (0.006 g, 0.03 mmol), thoroughly purged of air, and placed under nitrogen atmosphere. Rigorously degassed toluene (25 mL) and absolute ethanol (0.040 mL, 0.72 mmol) were added, and the mixture was

heated at 80 °C for 8 h. During this time, a yellow solution containing benzene-1,4-diselenol was produced. The diselenol was not isolated, but used directly in the next step for the synthesis of **Bi-OM-5**.

Synthesis of Bi-OM-5. Bi-OM-5 was synthesized from triphenylbismuth and benzene-1,4diselenol in a similar manner as **Bi-OM-1**, but using a lower reaction temperature (i.e. 25 °C). The abovementioned yellow solution containing the in situ generated benzene-1,4-diselenol was first cooled to room temperature, after which a solution of triphenylbismuth (0.088 g, 0.20 mmol) in degassed toluene (10 mL) was introduced. The reaction mixture was then allowed to stir for 72 h at room temperature. A red precipitate of **Bi-OM-5** was formed over the three days of reaction. The brick-red **Bi-OM-5** was filtered off, washed thoroughly with hot acetone, and dried under high vacuum at 120 °C for 24 h. Yield: 0.072 g, 64 %. Anal. Calcd. for $C_{12}H_9BiSe_2$ (formula of repeat unit): C, 27.71; H, 1.74. Found: C, 27.90; H, 1.78.

RESULTS AND DISCUSSION

The Bi-OMs in the present study feature Bi(III) nodes connected by rigid aromatic dithiolate π -linkers to form a network structure. Aromatic dithiols were selected as the organic linkers with the idea of creating a structure based on strong Bi–S bonds and also in view of the favorable π -conjugation and electronic delocalization between the sulfur lone pairs and benzene rings.⁴⁴ Owing to the affinity of sulfur for soft metals, such dithiols have been used as molecular contacts in single-molecule conductance studies^{44, 64} and as π -conjugated linkers between inorganic semiconductor nanocrystals.⁶⁵ These dithiol building blocks are available commercially or via straightforward syntheses. The bismuth source for the synthesis of our Bi-OMs was triphenylbismuth, which can be inexpensively purchased or conveniently synthesized in one step from a bismuth(III) halide and phenyllithium. Employing triphenylbismuth as the metal source has

the advantage of generating a volatile by-product (i.e. benzene) that is easily removed from the Bi-OMs. Our chosen protocol involving the reaction of aromatic dithiols with triphenylbismuth was adapted from the preparation of bismuth(III) thiolates by Norman et al.^{66, 67} and Gilman.^{68, 69} As pointed out, this method allowed for the construction of the target materials while producing benzene as the sole by-product. This facilitates subsequent workup and purification as the precipitated Bi-OMs can be separated from the organic-soluble precursors and by-products by simple filtration. Remaining traces of benzene and toluene (reaction solvent) were completely removed by first washing the Bi-OMs in hot acetone, followed by drying at 120 °C under high vacuum for at least 24 h. The elemental ratios of **Bi-OMs 1–5** were characterized by microanalysis, and their compositions were further confirmed by energy dispersive X-ray spectroscopy (EDS) (Figure S12–S16).

Powder X-ray diffraction (PXRD) experiments revealed that all five Bi-OMs possessed bulk crystallinity (Figure 2). For example, **Bi-OM-1** showed a well-defined diffraction pattern with a large peak observed at 2θ (Cu_{ka} radiation) of ~10.2°, medium-intensity peaks at ~12.5°, ~15.0°, ~21.0°, and ~24.5°, along with several other lower-intensity peaks (Figure 2a). The experimental PXRD pattern was in good agreement with the simulated pattern (Figure S17). Similarly, well-defined patterns were also observed with Bi-OMs **3** and **4**. In general, better crystallinity and long-range order was obtained when linear arenedithiol linkers were employed (i.e. in Bi-OMs **1**, **3**, and **4**) instead of the bent *meta*-arenedithiols of **Bi-OM-2** or the diselenolates of **Bi-OM-5**. Scanning electron microscopy (SEM) studies were also carried out on **Bi-OMs 1** – **5**. The SEM images of **Bi-OMs 1**, **3**, and **4** (Figures 2c, i, and l) revealed morphologies resembling rigid, linear rod-like crystallites. Among the more salient features of the high-magnification SEM image of **Bi-OM-1** (Figure 2b) were the micrometer-scale rectangular rods with sharp faces, edges, and corners. **Bi-OM-2**, which bears a structure isomeric to **Bi-OM-1** but featuring bent

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meta-disubstituted linkers rather than linear *para* connectors, displayed a morphology that was instead more reminiscent of flexible bent-fibers. Finally, the SEM images of diselenolate-derived **Bi-OM-5** (Figure 2n, o) showed plate-like morphologies with relatively smooth surfaces, as opposed to the rod/belt-like appearance of the sulfur-based analogs.





Figure 2. PXRD diffraction patterns and SEM images of Bi-OMs 1 through 5.

The spectroscopic properties of the five Bi-OMs were characterized by attenuated total reflectance (ATR) FTIR spectroscopy and solid-state UV-vis spectroscopy. The absence of signals arising from S-H stretches (~2500-2600 cm⁻¹) in the FTIR spectra of **Bi-OMs 1** through **4** indicated the absence of dithiol starting materials in the products (Figure 3). Absorption signals around 3050 cm⁻¹ due to aromatic C–H stretches were prominent in all the Bi-OMs except **Bi-OM-4**, where the peaks were less pronounced due to the high percentage of perfluorinated aromatic rings. With **Bi-OM-4**, strong absorption peaks around ~1400 cm⁻¹ arising from the aromatic C–F bonds were observed instead. In all five samples, the absence of signals around 2900 cm⁻¹ due to aliphatic C–H groups indicated the complete removal of residual toluene.



Figure 3. ATR FTIR spectra of Bi-OMs 1 through 5.

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The Bi-OMs are colored materials ranging from yellow-orange to brick-red, with optical HOMO-LUMO gaps measuring between 1.9 to 2.5 eV depending on the functionalization of their organic π -linkers. All five materials also exhibited reversible thermochromism in the solid-state. **Bi-OM-1** is a yellow-orange solid at room temperature, and its UV-vis diffuse reflectance spectrum revealed an absorption edge of about 530 nm, which corresponds to an estimated optical gap of about 2.28 eV (Figure 4).





The measured optical properties and observed colors of Bi-OMs 1–4 were consistent with charge transfer (CT) behavior from electron-rich sulfur atoms to the bismuth centers (i.e., $S\rightarrow Bi$).³⁹⁻⁴³ In particular, the absorptions between 350-450 nm are characteristic of S–Bi ligandto-metal charge-transfer (LMCT) bands. When the benzene-1,4-dithiolate linkers of **Bi-OM-1** were replaced with the isomeric and cross-conjugated *meta* analogs, the resulting **Bi-OM-2** showed a slight widening of its HOMO-LUMO gap to 2.4 eV due to the disruption in π -

conjugation. Attenuation of its absorption coefficient relative to **Bi-OM-1** was also consistent with the diminished oscillator strengths of cross-conjugated π -systems versus fully conjugated ones.⁷⁰ Published on 14 September 2017. Downloaded by University of Cambridge on 15/09/2017 15:39:55.

The optical gap of the bismuth-organic system could also be widened in alternative ways without incurring the same large decrease in absorption coefficient. This was demonstrated in two ways, the first employing a steric approach (i.e. with **Bi-OM-3**) and the second using an electronic induction strategy (i.e. **Bi-OM-4**). In both cases, the linear, fully π -conjugated connectivity was maintained. In the case of **Bi-OM-3**, employing the longer ditopic biphenyl-4,4'-dithiolate π -linker widened the HOMO-LUMO gap to 2.5 eV. The larger energy gap of Bi-OM-3 compared to Bi-**OM-1** can be attributed to diminished π -conjugation resulting from sterically-induced interannular twisting between the two rings of the biphenyl linker.⁴⁴ The optical HOMO-LUMO gap could also be widened using an inductive approach as in the case of **Bi-OM-4**. When electron-deficient perfluorinated benzene-1,4-dithiolate linkers were used in place of the non-fluorinated versions, a lemon yellow-colored **Bi-OM-4** with a HOMO-LUMO gap of 2.5 eV was obtained. Here, the strong inductive effect of the electronegative fluorines lowers the electron density on the connector S atoms and reduces the degree of charge-transfer from sulfur to bismuth. Finally, we investigated the possibility of narrowing the optical gap of the Bi-OM by substituting the sulfur atoms of **Bi-OM-1** with selenium. An analogous trend is known from the bismuth(III) chalcogenide series (i.e. Bi_2X_3 where X = S, Se, Te), where heavy atom substitution results in narrowing of the HOMO-LUMO energy gap. Our as-synthesized selenium-based Bi-OM-5 showed a pronounced bathochromic shift in its solid-state UV-vis absorption compared with the sulfur analogs. This was a red material with an optical gap measuring around 1.94 eV, the smallest of the five Bi-OMs. Comparing Bi-OM-5 and Bi-OM-1, one observes that replacing the sulfurs with heavier chalcogens results in optical gap reduction. Modulating the optical and/or electronic properties of functional materials by chalcogen replacement is a strategy that has also been

successfully implemented with transition metal dichalcogenides, covalent-organic frameworks, and linear π -conjugated polymers.^{71, 72}

Interestingly, all five Bi-OMs displayed stable and reversible solid-state thermochromism, becoming more intensely colored at elevated temperatures (i.e. above 90 °C) and reverting to their original appearance upon cooling to 25 °C (Figure 5). Starting off as a yellow-orange solid at room temperature, **Bi-OM-1** gradually turned red on heating to 100 °C, before reverting to its original state when cooled. The other four Bi-OMs also exhibited similar chromic phenomena when heated: **Bi-OM-2** (yellow to pale orange), **Bi-OM-3** (yellow to orange), **Bi-OM-4** (yellow to orange), **Bi-OM-5** (brick-red to dark/intense red). Reversible thermochromism was also observed when the materials were cooled instead of heated. When the external temperature of the Bi-OMs was lowered to -78 °C in a dry-ice/acetone bath, they gradually adopted lighter colorations. Upon returning to 25 °C, their original colors were subsequently restored.



Figure 5. Reversible solid-state thermochromism as exhibited by Bi-OMs 1–5.

To rule out thermochromic behavior based on a dehydration-rehydration mechanism,^{73, 74} we performed thermogravimetric analyses (TGA) on the five Bi-OMs (Figures S7–S11). When heated in air, the TGA curves showed zero mass loss for any of the Bi-OMs at temperatures below 260 °C. In particular, there was no weight decrease between 90-110 °C corresponding to water loss. This was further supported by the complete absence of O–H stretches in the IR spectra of the

Bi-OMs (Figure 3). Therefore, a thermochromic mechanism based on heat-induced loss of bound H₂O and subsequent rehydration on cooling was not operative in these Bi-OMs. The gradual rather than abrupt heat-induced color changes suggested that enhanced intramolecular CT at the expense of intermolecular CT was taking place as a result of increasing separation between molecular layers/chains. Such mechanisms involving the disruption of supramolecular environments have been responsible for the gradual thermochromic transitions in some π conjugated organic systems⁷⁵ as well as metal complexes.⁷⁶ Common intermolecular interactions in organobismuth compounds include S. Bi secondary bonding and/or arene-bismuth ($\pi \rightarrow \sigma^*$) interactions.⁷⁷ The former type of bonding has been frequently characterized in bismuth(III) thiolates, where dimers are held together by weak intermolecular secondary bonding between S lone pairs and Bi–S σ^* -orbitals (Figure 6a).⁶⁶ It is likely that the thiolate-based **Bi-OMs 1–4** also possess similar soft-soft interactions in the solid-state (Figure 6b). The tendency of bismuth to form secondary bonding interactions, coupled with its flexible coordination geometry and high coordination number, often result in dense or layered nonporous Bi-OMs.²⁵ Through porosimetry measurements, we ascertained that our system did indeed have low surface areas and small pore sizes (Figure S23), which would be expected given the multitude of possible S...Bi secondary bonding modes. It is plausible that the thermally-induced disruption of weak interchain S...Bi interactions in these Bi-OMs strengthens intrachain CT at the expense of interchain CT, leading to the intensification of observed colors. Such competing CT interactions at the molecular level have often been the basis of reversible thermochromic behavior in π -conjugated organic systems.⁷³⁻⁷⁵ Compared to chromic materials that are purely organic or inorganic, chromic organic-inorganic hybrid materials with separate organic/inorganic components can generally be more readily finetuned to provide a set of tailor-made properties.⁷⁸



Figure 6. (a) Loosely-bound centrosymmetric bismuth(III) thiolate dimer featuring long S...Bi contacts.⁶² (b) Proposed structure of **Bi-OM-1** featuring analogous secondary bonding interactions.

In terms of stability, the Bi-OMs appeared to have good aqueous stability at neutral pH. Sonicating and suspending the materials in water at pH 7 (~2 mg/10 mL) over 24 hours did not induce any decomposition. The materials were however, found to be unstable to mineral acids. Exposing the Bi-OMs to strong acids led to rapid decolorization of the materials due to hydrolysis of their bismuth–chalcogen bonds. Finally, in regard to the thermal stability of the five Bi-OMs, the TGA studies described previously showed them to be very thermally resilient. Heating the Bi-OMs up to 280 °C in air resulted in a mere 5% weight loss (Figure S7–S10), in contrast to the air and moisture sensitivity of many simple bismuth(III) thiolate complexes. Overall, the optical properties and ambient stability of these Bi-OMs make them amenable to further studies that will focus on the exploration of potential practical applications.

CONCLUDING REMARKS

In summary, we have developed a series of bismuth-containing inorganic-organic hybrid materials via facile one-step reactions between triphenylbismuth and various arenedithiols (and a diselenol). By varying the structural and electronic nature of the π -conjugated organic linkers, the optical HOMO-LUMO gaps and chromic phenomena associated with the Bi-OMs could be tuned in a reliable manner. All five Bi-OMs reported in this study exhibited completely reversible solid-state thermochromism, and were found to possess excellent thermal stability in air. Taken together, the combination of physical properties makes these stimuli-responsive materials potentially useful for a diverse range of applications that include reversible smart windows, camouflage coatings, photocatalysts, optoelectronics, and temperature sensors.

ACKNOWLEDGEMENTS

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This work was financially supported by the Natural Sciences and Engineering Research Council (NSERC Discovery Grant; RGPIN-2016-04614), the Canada Foundation for Innovation (CFI) John R. Evans Leaders Fund (CFI-JELF project no. 34474), the Ministry of Research and Innovation (MRI), and the University of Ottawa. We also thank Janire Matas for the videography work on our thermochromic materials (Electronic Supporting Information).

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Table of Contents Entry:



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