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# Aerobic Solid State Red Phosphorescence from Benzobismole Monomers and Patternable Self-Assembled Block Copolymers

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**Abstract:** The synthesis of the first bismuth-containing macromolecules that exhibit phosphorescence in the solid state and in the presence of oxygen is reported. These red emissive high molecular weight polymers (> 300 kDa) feature benzobismoles appended to a hydrocarbon scaffold, and were built via an efficient ring-opening metathesis (ROMP) protocol. Moreover, our general procedure readily allows for the formation of cross-linked networks and block copolymers. Attaining stable red phosphorescence with non-toxic elements remains a challenge and thus our new class of soluble (processable) polymeric phosphor is of great interest. Furthermore the formation of bismuth-rich cores within organic-inorganic block copolymer spherical micelles is possible, leading to patterned arrays of bismuth in the film state.

 $\pi$ -Conjugated materials containing p-block elements have found applications as integral components of solar cells, transistors, OLEDs, and, more recently, as luminescent dyes for bioimaging.<sup>[1]</sup> To date, the vast majority of these materials contain lighter p-block elements (e.g. B, Si, S, and P).<sup>[2]</sup> Encouraging recent synthetic advances have enabled the incorporation of heavier main group elements into cyclic mframeworks leading to novel properties<sup>[1b,3]</sup> such as room temperature phosphorescence (RTP).<sup>[4]</sup> Achieving efficient and stable phosphorescence in the condensed phase remains a cornerstone of OLEDs,<sup>[5]</sup> wherein expensive, and potentially toxic, transition metal-containing complexes are generally used to promote population of emissive excited triplet states via the "heavy element effect" [6] Despite a promising early report by Ohshita and coworkers<sup>[7]</sup> on the detection of dual fluorescence and phosphorescence from dithienylbismoles, heterocyclic bismuth compounds have been scarcely explored as potential emitters of low toxicity,<sup>[8]</sup> largely due to a lack of suitable synthetic methods for their preparation. Furthermore,

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phosphorescent polymers are of particular interest for optoelectronic devices due to the simplification of device fabrication via solution processing,<sup>[9]</sup> while block copolymers allow the formation of higher-order (including metallized) structures of controllable composition.<sup>[10]</sup>

It is challenging to prepare red emitting phosphorescent materials that operate in the presence of O2, a well-known quencher of phosphorescence. Red emission is highly sought for bioimaging applications, wherein interfering background fluorescence (of short wavelength blue and green light) can be readily filtered away from the red emission of the dye.[1c,1d,11] However, in general, one sees a dramatic reduction of quantum yield as longer wavelengths of light are emitted due to an increase in non-radiative decay rate (Energy Gap Law).<sup>[12]</sup> To combat oxygen quenching, one can slow down O<sub>2</sub> diffusion by promoting molecular aggregation,<sup>[4,13]</sup> or by-pass non-radiative processes through establishing photoinduced metal-metal bonding in the solid state.<sup>[14]</sup> However, a general drawback is the need for tailored intermolecular interactions (such as Br---H bonding)<sup>[15]</sup> which cannot always be designed a priori. In this Communication we report the modular synthesis of bismuthcontaining orange and red phosphorescent molecules and polymers with negligible oxygen quenching in the solid state (Figure 1). We also show that block copolymers of controllable bismuth content can be made, and that assembly of these copolymers into spherical micelles with bismuth-rich (metallized) cores is possible. The synthetic tools outlined provide a general route to a wide swath of new long-lifetime emitters for possible bioimaging and OLED applications, while the ability to organize bismuth into localized arrays via block copolymer assembly opens the door for the production of Bi nanodot seeds for patterned semi-conductor nanowire growth.[16]



**Figure 1.** [Left] Generic benzobismole structure showing the sites of easy modification due to our modular synthesis; [Right] Perfluorinated benzobismole (R = Ph;  $R' = C_6F_5$ ) **6** used as an ink to draw on filter paper and crystals of the phenylated benzobismole **3** (R and R' = Ph), both illuminated with 365 nm light in air at room temperature.

Following a modified Fagan-Nugent protocol,<sup>[17a]</sup> the arylated benzozirconacycles **1** and **2** were combined with the bismuth(III) dihalides  $ArBiCl_2$  (Ar = Ph or  $Ar^{ROMP}$ ; Scheme 1) leading to the formation of the desired benzobismoles **3–6**. To facilitate Zr/Bi exchange, 10 % CuCl was added, as reported previously by Takahashi and coworkers to form stannoles.<sup>[17b]</sup> The ArBiCl<sub>2</sub> reactants were generated *in situ* by the ligand scrambling of triarylbismuthine and 2 equiv. of BiCl<sub>3</sub>.<sup>[7b]</sup>

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### COMMUNICATION



Scheme 1. Synthesis of the benzobismoles  $\mathbf{3} - \mathbf{6}$ .

the molecular structures of perphenylated The benzobismole 3 and its fluorinated counterpart 4 are depicted in Figure 2.<sup>[18]</sup> In each structure the peripheral aryl rings fan out from the central bismole ring in a propeller-like fashion and prevent close packing of the central bismole rings [closest Bi---Bi contacts > 5.0 Å]. However each of the canted aryl rings forms close interactions with the rings of neighboring molecules that presumably limit intramolecular rotations in the crystalline state. The sum of the bond angles at the Bi centers  $[270.3(2)^{\circ}$  in 3; 264.4(2)° in 4] indicate high s-character of the lone pair, and partially explains the air-stability of these compounds.<sup>[7b]</sup> A racemic sample of 3 could be separated into its constituent isomers by chiral HPLC, while no signs of racemization in 10% 2-propanol in hexane was noted for either purified enantiomer (Figure S36).<sup>[18]</sup>



**Figure 2.** Molecular structures of **3** (left) and **4** (right) with ORTEPs at the 30 % probability level. Selected bond lengths [Å] and angles [°]: **3**: Bi-C1 2.256(3), Bi-C4 2.221(3), Bi-C11 2.260(4), C2-C3 1.482(5); C1-Bi-C4 78.6(2), C11-Bi-C1 96.8(2), C11-Bi-C4 95.0(2). **4**: Bi-C1 2.238(3), Bi-C8 2.265(3), Bi-C31 2.272(3), C6-C7 1.476(4); C1-Bi-C8 77.7(2), C31-Bi-C1 93.6(2), C31-Bi-C8 93.1(2).

The perphenylated benzobismole **3** shows red emission in the crystalline state in air [ $\lambda_{em} = 610$  nm; Figure 3a], and the introduction of electron-withdrawing C<sub>6</sub>F<sub>5</sub> groups in **4** shifts the emission color to orange-red [ $\lambda_{em} = 596$  nm; Figures 1 and 3b].<sup>[18]</sup> Moreover, in THF/water mixtures (40:60 wt. %) these Bi heterocycles show aggregation induced emission (AIE) (Figure S24).<sup>[18,19]</sup> Time-dependent luminescence measurements on drop-cast films (from hexanes) of **3** and **4**, as well as their norbornene-substituted analogues **5** and **6** (Scheme 1), yield similar emission lifetimes ( $\tau$ ) in the narrow range of 6.6 to 7.5 µs, in line with phosphorescence.<sup>[4]</sup> Absolute quantum yields ( $\Phi$ ) of bismole samples prepared by drop-casting from hexanes suspensions were measured and it was found that the  $\Phi$  of the phenyl-substituted benzobismoles **3** (0.8%) and **5** (0.7%) were

slightly lower than in the respective fluorinated benzobismoles **4** (2.5%) and **6** (1.6%); the possible increased quantum yield in **4** and **6** may arise from added restriction in molecular motion imposed by the perfluorinated aryl groups. In accordance with this postulate, the <sup>19</sup>F{<sup>1</sup>H} NMR spectra of **4** and **6** indicate that one of the C<sub>6</sub>F<sub>5</sub> rings exhibits restricted rotation in solution (see Figures S44 and S56).<sup>[18]</sup> There was no significant increase in quantum yield upon measurement under an Ar atmosphere (Figure S26). The observed resistance to oxygen quenching may be due to limited oxygen diffusion through the aggregates.



**Figure 3.** Solid state emission and excitation spectra of films made from dropcasting hexanes suspensions of benzobismoles **3** (a) and **4** (b); all data recorded in air at room temperature. For related spectra for the aryl norbornene-capped benzobismoles **5** and **6** see the ESI (Figure S28).<sup>[18]</sup>

When the benzobismoles 3 and 4 are drop-cast from THF, CH<sub>2</sub>Cl<sub>2</sub> or toluene, transparent films are formed which do not show discernable emission [Figures 4 (inset; right) and S25].<sup>[18]</sup> However the opaque films of 3 and 4, prepared from fine suspensions in hexanes, yield significantly brighter phosphorescence [Figures 4 (inset; left) and S25].<sup>[18]</sup> Thus, phosphorescence is highly dependent on the morphology of the solids, an effect previously noted for tellurophenes.<sup>[20]</sup> Accordingly, a drop-cast film of 3 from a hexanes suspension gave rise to a powder XRD pattern that showed high crystallinity, and matched that predicted from the single-crystal XRD data (Figures 4 and S5).<sup>[18]</sup> Alternatively, the non-emissive film made from drop-casting a solution of 3 in CH<sub>2</sub>Cl<sub>2</sub> gave rise to a powder pattern indicative of amorphous packing. These data show that 3 and 4 exhibit not only AIE, but more specifically, crystallization induced emission (CIE) in which there is a strong correlation between the crystallinity and the intensity of emission for the materials.<sup>[21, 22]</sup>

Time-dependent density functional theory (TD-DFT) computations were carried out for the Ph and  $C_6F_5$ -substituted benzobismoles **3** and **4**. The predicted absorption maxima at the

(CAM-)B3LYP/cc-pVTZ(-PP) level(s) of theory are in agreement with experimental UV-vis data.<sup>[18]</sup> The most intense component of the absorptions arises from a HOMO-LUMO transition of predominantly C-C  $\pi$ - $\pi^*$  character, while HOMO-1 to LUMO transitions of substantial oscillator strength and significant orbital character from Bi were also computed (Figure 5). Previously we have found that orbital participation from a heavy main group element during excitation is a pre-requisite for efficient phosphorescence,<sup>[7b,23]</sup> and thus we have achieved the same goal in the newly prepared benzobismoles 3 and 4. Moreover, the computed differences of the zero-point corrected adiabatic energies  $(E_{0-0})$  of the S<sub>0</sub> and T<sub>1</sub> states, at their corresponding optimized geometries, match well with the experimentally observed phosphorescence energies; similar results were noted when relativistic effects and spin-orbit coupling were included in the computations.[18]



**Figure 4**. Powder XRD patterns of films of **3** drop-cast from  $CH_2Cl_2$  and hexanes; inset: drop-cast films from hexanes (left) and  $CH_2Cl_2$  (right) under ambient light (top) and 365 nm irradiation (bottom).



**Figure 5.** TD-DFT [B3LYP/cc-pVTZ(-PP)] computed main transitions including excitation wavelengths and oscillator strengths (*f*) to low-lying singlet states for **3** (left) and **4** (right) and the associated molecular orbitals; *iso*-surface values of +0.02/–0.02 (blue/red).

Ring-opening metathesis polymerization (ROMP) of the norbornene-substituted benzobismoles **5** and **6** with 1 mol% of Grubbs' 2<sup>nd</sup>-generation catalyst<sup>[24]</sup> successfully afforded the airand moisture-stable homopolymers **P1** and **P2** (Scheme 2). The polymerization reactions were found to be rapid with complete monomer conversion in < 6 min. Though weaker than for

monomers 5 and 6, polymers P1 and P2 display observable red luminescence that is bathochromically-shifted by ca. 60 nm from their respective monomers (Figure S29).<sup>[18]</sup> It is hypothesized that an increase in the free volume about the bismole units in the polymeric materials allows for increased vibrational and rotational motions (which decrease emission intensity) as well as possible geometric stabilization of singlet and triplet excited states, yielding the bathochromic shift in emission. <sup>1</sup>H and <sup>19</sup>F{<sup>1</sup>H} NMR data for P1 and P2 gave expectedly broad resonances, while gel permeation chromatography (GPC) in THF afforded very high molecular weights ( $M_n = 2.1$  MDa and PDI = 1.5 for P1;  $M_n = ca. 600$  kDa and PDI = 1.6 for P2). However, characterization of these polymers was made more difficult by their limited solubility. Powder XRD analysis of P1 revealed amorphous character and heat annealing films of P1 did not help to increase the crystallinity of the samples (Figure S6).<sup>[18]</sup> To improve the solubility of the phosphorescent polybenzobismoles, the new alkvlated aryInorbornene monomers 7 and 8 (Scheme 2) were prepared. The corresponding bismuth-free homopolymers P3 and P4 along with various random copolymers derived from benzobismole (5 and 6) and alkylarene (7 and 8) units in differing ratios were also synthesized (P5-P9),<sup>[18]</sup> with a maximum benzobismole content of 38 mol% (as judged by <sup>1</sup>H NMR spectroscopy). Each copolymer was soluble in THF and CHCl<sub>3</sub> with Mn values all exceeding 150 kDa. TGA analysis indicates thermal stability up to 250 °C (Figures S13 and S14)<sup>[18]</sup> for each copolymer. Red luminescence ( $\lambda_{max}$  = 660 nm) is maintained within the mixed benzobismole/arylalkyl copolymers (Figures S29);<sup>[18]</sup> however as in the benzobismole homopolymers P1 and P2, the emission is less intense than for the monomeric benzobismoles 5 and 6, thus precluding the determination of reliable absolute quantum yields and emission lifetime data.



Scheme 2. Synthesis of homopolymers P1 - P4, and the cross-linking agent  $BiAr^{ROMP}_{3}$ .

To increase the rigidity of the benzobismole polymer matrix, and possibly enhance phosphorescence, cross-linked polymers were synthesized. Benzobismole **5** was cross-linked with the trifunctional bismuthine  $Bi(Ar^{ROMP}_{3})$  (Scheme 2) using 1 mol% Grubbs' 2<sup>nd</sup> generation catalyst in THF, with ratios that varied from 25 mol% crosslinker (P10) to 80 mol% (P11). Both P10 and

**P11** were completely insoluble in common organic solvents, indicating successful cross-linking. Despite the possible decrease in intramolecular motion in **P10** and **P11**, similarly weak red emission was noted as in the non-crosslinked polymers; enhanced emission was observed upon cooling the sample to 77 K. These findings suggest that even within the cross-linked polymer network, the amorphous packing (as indicated by PXRD analysis; Figure S9)<sup>[18]</sup> of the benzobismole side groups allows enough room for internal molecular motions<sup>[25]</sup> to contribute to increased rates of non-radiative decay.

With the goal of obtaining well-defined block copolymers that self-assemble into ordered micelles,<sup>[10]</sup> living ROMP was instigated using Grubbs' 3rd generation catalyst. As shown in Scheme 3, benzobismole 5 and the arylated norbornene monomer 8 were sequentially copolymerized to yield the THFsoluble block-copolymer P12; this block copolymer shows red emission at  $\lambda_{em}$  = 684 nm (Figure S31) in the film state.<sup>[18]</sup> A combination of GPC and <sup>1</sup>H NMR analysis indicated a benzobismole/arylalkyl block ratio of ca. 1:6 [Mn = 51 kDa]. As the arylalkyl block has significantly higher solubility in hexanes than the benzobismole segment, a combination of hexanes and THF was used to promote the formation of spherical micelles containing benzobismole blocks cores surrounded by an arylalkyl corona. P12 was incubated in 5 % THF in hexanes at a concentration of 1 mg/mL at 50 °C for 1 hour and then allowed to cool to room temperature, after which samples were taken for analysis by TEM and dynamic light scattering (DLS).<sup>[18]</sup> DLS indicated the presence of a species with an average diameter of 35 nm while TEM shows discrete spherical regions of high contrast Bi in the film state (Scheme 3c). Future work will involve pyrolytic conversion of these organized films to possibly yield patterned Bi nanodots<sup>[16]</sup> or bismuth films with potential antibacterial<sup>[26]</sup> and topological insulating properties.<sup>[27]</sup>



Scheme 3. Synthesis of block copolymer P12 (a), Tyndall scattering observed upon shining a laser pointer through a 1 mg/mL solution of P12 in 5 % THF in hexanes (b), a TEM image of P12 deposited from a 1 mg/mL solution in 5 % THF in hexanes onto a glassy carbon grid (c).

In summary, a series of phosphorescent bismuthcontaining polymers and block copolymers have been synthesized. We introduce a general synthetic strategy to rapidly generate high molecular weight organic and bismuth-containing polymers with red phosphorescence, good solubility, and ordered self-assembly properties. Going forward, we will prepare new main group element (E)-based block copolymers for the controlled self-assembly of strongly emissive structures (by increasing molecular rigidity and via related Zr/E exchange chemistry), along with optimization of the patterning of nanodimensional Bi for semi-conductor nanowire growth.<sup>[16]</sup>

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**Turning on Bismuth**: The synthesis of red and orange emitting bismuthbased phosphors is reported. Our modular synthetic approach allows for rapid ring-opening metathesis polymerization to yield block copolymer spherical micelles that assemble into organized films with bismuth-rich, metallized, domains.



Sarah M. Parke, Emanuel Hupf, Gunwant K. Matharu, Inara de Aguiar, Letiang Xu, Haoyang Yu, Michael P. Boone, Gabriel L. C. de Souza, Robert McDonald, Michael J. Ferguson, Gang He,\* Alex Brown,\* and Eric Rivard\*

[Page No. – Page No.] Aerobic Solid State Red Phosphorescence from Benzobismole Monomers and Patternable Self-Assembled Block Copolymers