

Supplementary Material (ESI) for Dalton Transactions  
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## Design, Synthesis and Characterization of Self-Assembled As<sub>2</sub>L<sub>3</sub> and Sb<sub>2</sub>L<sub>3</sub> Cryptands

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### Supporting Information

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#### Experimental Section

<sup>1</sup>H NMR spectra were measured using a Varian INOVA-300 spectrometer operating at 299.935 MHz. *J* values are given in Hz. Commercially available reagents were used as received unless otherwise noted. *Warning: Arsenic and its complexes are highly toxic! Use appropriate safety precautions.*

#### As<sub>2</sub>4<sub>3</sub> cryptand

2,3-dimethyl-1,4-bis(mercaptomethyl)-benzene<sup>S1</sup> (H<sub>2</sub>4, 0.160 g, 0.807 mmol) was dissolved in CHCl<sub>3</sub> (100 mL) under N<sub>2</sub>. 0.1 M KOH in MeOH (20 μL) was added. The reaction mixture was stirred at 55 °C and AsCl<sub>3</sub> (45.8 μL, 0.537 mmol) was added, causing precipitation of a white solid. After 2 h the suspension was cooled to room temperature and filtered through glass wool to yield a white powder. The powder was dissolved in DCM which was washed with H<sub>2</sub>O (50 mL), brine (3 × 50 mL), and concentrated under vacuum, yielding a white solid, As<sub>2</sub>2<sub>3</sub>. Crystals suitable for X-ray analysis were grown by the slow diffusion of hexanes into a CHCl<sub>3</sub> solution of As<sub>2</sub>4<sub>3</sub>.

#### 2,5,4'-Trimethylbenzophenone (5a)

AlCl<sub>3</sub> (100 g, 750 mmol) was added to a 1 L round bottom flask and covered with CS<sub>2</sub> (150 mL). *p*-Xylene (69 g, 650 mmol) and *p*-toluoyl chloride (100 g, 646 mmol) were dissolved in CS<sub>2</sub> (75 mL) and added slowly to the stirring suspension of AlCl<sub>3</sub> in CS<sub>2</sub>. After the addition was complete and the reaction mixture reached room temperature, the suspension was stirred at reflux for 2 h. The reaction mixture was cooled in an ice bath and 200 mL of H<sub>2</sub>O was added slowly while stirring. The resulting mixture was extracted with 500 mL of diethyl ether. The organic phase was washed with H<sub>2</sub>O (3 × 200 mL), 10% NaOH (2 × 250 mL), and again with H<sub>2</sub>O (2 × 200 mL). The organic phase was dried with sodium sulfate and concentrated under vacuum

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yielding a white solid. Vacuum distillation (110-120 °C, 0.05 mmHg) provided 2,5,4'-trimethylbenzophenone (**5a**) as a blue powder. (117.5 g, 81% yield). <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) δ 7.70 (d, 2 H, CH, J 8.1), 7.19 (m, 5 H, CH), 2.423 (s, 3 H, CH<sub>3</sub>), 2.325 (s, 3 H, CH<sub>3</sub>), 2.248 (s, 3 H, CH<sub>3</sub>).

#### **Anthraquinone-2,6-dicarboxylic acid (5d)**

2,5,4'-trimethylbenzophenone (**5a**, 555 g, 245 mmol) was heated at reflux under air for 6 h with vigorous stirring. The reaction mixture was then cooled to room temperature to give an orange solid. The solid was triturated with ether (10 mL) and the insoluble portion was collected by vacuum filtration and washed with cold ether. The solvent from the combined filtrate and ether washings was removed under reduced pressure and triturated again as described above. After repeating this process four times, 35 g of ether-insoluble material was collected. Recrystallization from CS<sub>2</sub> gave a 3:2 mixture of 2,6-dimethyl-9(10H)-anthracenone (**5b**) and 2,6-dimethylantracene (**5c**) as a yellow solid (15 g, 28% yield). The crude mixture was used without further purification.

CrO<sub>3</sub> (59.4 g, 594 mmol) was added to a well-stirred solution of sulfuric acid (2 mL), acetic anhydride (15 mL, 160 mmol), and acetic acid (350 mL) and cooled to 20 °C in an ice bath. Maintaining a reaction temperature below 35 °C, the mixture of **5b** and **5c** (11.6 g, <54.0 mmol) was added in small portions and then stirred for 2 h. *Warning: This reaction is highly exothermic. Chromium trioxide is a strong oxidizing agent and chromium byproducts of this reaction are toxic. This procedure should be conducted with care, especially at this scale.* It was then heated to 120 °C for 3 h, cooled to room temperature, and poured into H<sub>2</sub>O (2 L). The resultant precipitate was removed by vacuum filtration, washed with H<sub>2</sub>O, and dried in a vacuum oven to afford 2,6-anthraquinonedicarboxylic acid (**5d**) as a yellow solid (15.4 g, 96.2% yield). <sup>1</sup>H NMR (300 MHz; DMSO) δ 8.70 (s, 2 H, CH), δ 8.44 (d, 2 H, CH J 7.8), δ 8.36 (d, 2 H, CH J 8.1).

#### **Dimethyl 2,6-anthracenedicarboxylate (5h)**

CuSO<sub>4</sub> (0.8 g, 5 mmol), metallic Zn (94.2 g, 1.44 mol), and concentrated NH<sub>4</sub>OH (715 mL) were stirred in a 2 L round bottom flask in an ice bath as 2,6-anthraquinonedicarboxylic acid (**5d**, 30.2 g, 102 mmol) was added slowly. After complete addition the reaction was heated to 100 °C and additional concentrated NH<sub>4</sub>OH (715 mL) was added over 4 h. The reaction was complete when the red color dissipated and the mixture became clear (if after 4 h the reaction remained red, additional CuSO<sub>4</sub> (2.4 g, 15 mmol) was added in portions to drive the reaction to completion). Upon completion the mixture was cooled and filtered. The filtrate was acidified with 12 M HCl to give a bright yellow precipitate which was collected by vacuum filtration and dried in a vacuum oven to yield a 1:2 mixture of anthracene-2,6-dicarboxylic acid (**5e**) and 9,10-dihydroanthracene-2,6-dicarboxylic acid (**5f**) as a bright yellow solid (27.14 g, 99% yield) which was used without further purification.

A suspension of the mixture of **5e** and **5f** (27 g, <0.10 mol), iodomethane (142 g, 1.00 mol), and lithium carbonate (74 g, 1.0 mol) in DMF (1300 mL) was stirred for 24 h and then added to 1 M HCl (5 L). The resulting yellow precipitate was collected by vacuum filtration and dried in a vacuum oven to give a 2:1 mixture of dimethyl 9,10-dihydro-2,6-anthracenedicarboxylate (**5g**) and dimethyl 2,6-anthracenedicarboxylate (**5h**) (20.9 g, 70% yield).

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2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 7.5 g, 30 mmol) was added to the mixture of **5g** and **5h** (6.8 g, 23 mmol) in benzene (278 mL) and the suspension was stirred at reflux for 1 h. After cooling to room temperature the solid was collected by vacuum filtration. The solid was washed with methanol and dried in a vacuum oven to give dimethyl 2,6-anthracenedicarboxylate (**5h**) as a bright yellow solid (6.061 g, 90% yield). <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) δ 8.83 (s, 2 H, CH), 8.59 (s, 2 H, CH), 8.06 (m, 4 H, CH), 4.02 (s, 6 H, CH<sub>3</sub>).

### 2,6-Bis(bromomethyl)anthracene (**5j**)

Dimethyl 2,6-anthracenedicarboxylate (**5h**, 2.13 g, 7.23 mmol) was suspended in freshly distilled THF (225 mL) and stirred in an ice bath. LiAlH<sub>4</sub> (0.415 g, 11 mmol) was added slowly to the yellow suspension and the reaction mixture was stirred for an additional 40 min on ice and then heated to reflux for 1 h. The mixture was cooled to room temperature and EtOAc (100 mL) was added to quench any remaining LiAlH<sub>4</sub>. The solvents were removed under reduced pressure to afford a pale yellow solid. 6 M HCl (400 mL) was added and the suspension was stirred briefly, filtered, washed with 6 M HCl (125 mL), and dried under vacuum to give 2,6-bis(hydroxymethyl)anthracene (**5i**) as a pale yellow solid (1.72 g, 98.5%).

2,6-Bis(hydroxymethyl)anthracene (**5i**, 1.0 g, 4.2 mmol) was suspended in freshly distilled DCM (160 mL) and stirred in an ice bath under N<sub>2</sub>. A solution of PBr<sub>3</sub> (0.5 g, 1.8 mmol) in 17 mL DCM was slowly added to the yellow suspension. After 15 min. the reaction mixture was allowed to warm to room temperature and was stirred overnight (~17 h). The resulting green suspension was washed with 2 M NaOH (1 × 250 mL) and extracted with DCM (3 × 200 mL). The combined organics were washed with 2 M HCl (1 × 250 mL). The HCl wash was extracted with DCM (2 × 150 mL) which was added to the combined organics. The combined organics were washed with H<sub>2</sub>O (1 × 250 mL), dried with brine (1 × 250 mL), Na<sub>2</sub>SO<sub>4</sub>, and evaporated under reduced pressure to afford 2,6-bis(bromomethyl)anthracene (**5j**) as a bright yellow solid (1.32 g, 86%). <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) δ 8.37 (s, 2 H, CH), 7.98 (m, 4 H, CH), 7.51 (dd, 2 H, CH), 4.70 (s, 4 H, CH<sub>2</sub>).

### 2,6-Bis(mercaptomethyl)anthracene (**H<sub>2</sub>5**)

2,6-Bis(bromomethyl)anthracene (**5j**, 1.7 g, 467 mmol) and thiourea (1.07 g, 14 mmol) were suspended in acetone (60 mL) and stirred at reflux overnight (~15 h.). The mixture was cooled and filtered and the solid was washed with acetone to give 2,6-bis(thiuroniummethyl)anthracene bromide(**5k**) as a pale yellow solid. This salt was placed under N<sub>2</sub> and 2 M NaOH (~50 mL) was added via a pressure equalizing addition funnel. The reaction was stirred at reflux for 2 h. The pale yellow solution was cooled in an ice bath and 6 M HCl (~15 mL) was added which caused a pale yellow precipitate to form. The precipitate was collected by vacuum filtration and dried under reduced pressure overnight in a desiccator to afford 2,6-bis(mercaptomethyl)anthracene (**H<sub>2</sub>5**) as a pale yellow solid (1.10 g, 88%). <sup>1</sup>H NMR (300 MHz; CDCl<sub>3</sub>; Me<sub>4</sub>Si) δ 8.26 (s, 2 H, CH), 7.90 (d, 4 H, CH, J 8.7), 7.39 (dd, 2 H, CH), 3.87 (d, 4 H, CH<sub>2</sub>, J 7.5), 1.76 (t, 1 H, SH, J 7.6).

### As<sub>2</sub>S<sub>3</sub> cryptand

2,6-bis(mercaptomethyl)anthracene (**H<sub>2</sub>5**, 0.060 g, 0.222 mmol) was placed under N<sub>2</sub> and a solution of freshly distilled THF (60 mL), MeOH (20 mL), and KOH (0.025 g, 0.444 mmol) was added *via* cannula. The reaction mixture was stirred at 55 °C and AsCl<sub>3</sub> (0.027 g, 0.148 mmol) was added, causing precipitation of a white solid. After 2 h the suspension was cooled to room

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temperature, filtered through glass wool, and concentrated under vacuum to afford crude  $\text{As}_2\text{S}_3$  as a white powder (0.071 g, 54% yield). The powder was dissolved in benzene which was allowed to slowly evaporate, yielding X-ray quality crystals.

#### 4,4'-bis(bromomethyl)dibenzyl (6a)

Dibenzyl (3.2 g, 17 mmol), paraformaldehyde (1.6g), and ZnBr (6g, 26 mmol) were added to 33% HBr/HOAc (30 mL) and stirred at 80 °C for 18 h. After cooling, the reaction mixture was poured into 200 mL  $\text{H}_2\text{O}$  and extracted with DCM. The organic extract was washed with saturated sodium bicarbonate solution and evaporated to dryness. Pure product (0.675g, 10%) was obtained by recrystallization from benzene.  $^1\text{H}$  NMR (500 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  7.31 (d, 4H, CH,  $J$  8.0), 7.15 (d, 4H, CH,  $J$  8.0), 4.49 (s, 4H,  $\text{CH}_2$ ), 2.90 (s, 4H,  $\text{CH}_2$ ).

#### 4,4'-bis(mercaptomethyl)dibenzyl ( $\text{H}_2\text{6}$ )

**6a** (0.675 g, 1.8 mmol) and thiorea (0.334 g, 4.4 mmol) were dissolved in 15 mL ethanol and stirred at 70 °C for 16 h. After cooling, diethyl ether was added causing precipitation of a white solid. This salt was removed, washed with diethyl ether, and dried in a vacuum desiccator. The salt was dissolved in degassed 2M NaOH under  $\text{N}_2$ , and heated at reflux for 2 h. After cooling, degassed 4M HCl was added *via* cannula until an acidic pH was achieved, causing a white precipitate to form. This precipitate was removed by filtration, washed with acetone and  $\text{H}_2\text{O}$ , and dried in a vacuum desiccator (0.205g, 67%).  $^1\text{H}$  NMR (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  7.24 (d, 4 H, CH,  $J$  8.3), 7.14 (d, 4 H, CH,  $J$  8.1), 3.73 (d, 4H,  $\text{CH}_2$   $J$  7.4), 2.88 (s, 4H,  $\text{CH}_2$ )  $\delta$  1.75 (t, 2H, SH,  $J$  7.5).

#### $\text{As}_2\text{S}_3$ cryptand

$\text{H}_2\text{6}$  (0.131 g, 0.47 mmol) was added to a flamed-dried 3-neck flask and placed under  $\text{N}_2$ . 0.102 M KOH in methanol (14.9 mL) was diluted with 50 mL dry THF, degassed, and added to  $\text{H}_2\text{7}$  *via* cannula. The mixture was heated to 55 °C and 30  $\mu\text{L}$   $\text{AsCl}_3$  was slowly added. After stirring at 55 °C for 2.5 h the solution was cooled, filtered through glass wool, and concentrated under vacuum. Slow evaporation yielded crystals suitable for X-ray diffraction analysis.

#### 4,4'-dimethyltolan (7a)

A 500 ml Schlenk flask was charged with a stir bar, 4-iodotoluene (11 g, 51 mmol),  $\text{PdCl}_2(\text{PPh}_3)_2$  (2.14 g, 3.05 mmol), and copper iodide (1 g, 5.2 mmol) and placed under  $\text{N}_2$ . In a separate flask DBU (41 ml, 270 mmol) was dissolved in acetonitrile (11 ml), degassed, and transferred to the reaction vessel *via* cannula. Trimethylsilylacetylene (TMSA) (3.6 ml, 25 mmol) was added via syringe. The reaction mixture was stirred at room temperature for 24 h. The solvent was evaporated to near-dryness and the remaining mixture poured into DCM which was washed with 1 M HCl and  $\text{H}_2\text{O}$ . The extract was dried over sodium sulfate and evaporated to dryness leaving a brown oily solid. The crude product was purified *via* a celite/silica/celite plug (10:1 hexanes:ethyl acetate) yielding a crystalline, colorless solid (60% isolated yield).  $^1\text{H}$  NMR (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  7.42 (d, 4H, CH,  $J$  8.1), 7.16 (d, 4H, CH,  $J$  7.8), 2.37 (s, 6H,  $\text{CH}_3$ ).

#### 4,4'-bis(bromomethyl)tolan (7b)

A flame dried 3-neck 250 mL round bottom flask was equipped with a condenser and charged with a stir bar, 4,4'-dimethyltolan (0.5 g, 2.4 mmol), and *N*-bromosuccinimide (1.07 g, 6.06 mmol) and placed under  $\text{N}_2$ . Benzoyl peroxide (58 mg, 0.24 mmol) was dissolved in 130 ml of

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freshly distilled, degassed  $\text{CCl}_4$ . This benzoyl peroxide solution was transferred *via* cannula into the reaction vessel. The solution was heated to 60 °C for 23 hours. The reaction mixture was washed with 1 M HCl, 1 M NaOH, and deionized  $\text{H}_2\text{O}$ , dried over sodium sulfate and evaporated. The crude product (34% isolated yield) was washed repeatedly with diethyl ether, dried, and used without further purification.  $^1\text{H}$  NMR (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  7.53 (d, 4H, CH,  $J$  8.7), 7.37 (d, 4H, CH,  $J$  8.7),  $\delta$  4.49 (s, 4H,  $\text{CH}_3$ ).

#### 4,4'-bis(mercaptomethyl)tolan (**H27**)

4,4'-bis(bromomethyl)tolan (**7b**, 1.5 g, 4.1 mmol) and thiourea (1 g, 13 mmol) were dissolved in ethanol (120 mL) and 2 mL acetone was added to the mixture. The reaction was heated to reflux for 3 h. The precipitate was filtered and the white solid was rinsed with acetone and dried in a vacuum desiccator. The dried precipitate was dissolved in degassed 2 M NaOH (120 mL), placed under  $\text{N}_2$ , and stirred at reflux for 3.5 h. After cooling, 4 M HCl (degassed) was added *via* cannula until an acidic pH was achieved and the solution was extracted with DCM ( $3 \times 100$  mL). The extract was dried over sodium sulfate and evaporated to dryness, yielding a white solid (55% isolated yield).  $^1\text{H}$  NMR (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  7.48 (d, 4H, CH,  $J$  8.1), 7.31 (d, 4H, CH,  $J$  8.1), 3.75 (s, 4H,  $\text{CH}_2$ ,  $J$  7.8), 1.77 (t, 2H, SH,  $J$  7.7).

#### As<sub>2</sub>7<sub>3</sub> cryptand

**H27** (22 mg, 0.06 mmol) was dissolved in 8 ml of dried, degassed, DCM and  $\text{AsCl}_3$  (7  $\mu\text{L}$ , 0.027 mmol) was added slowly. X-ray quality crystals were obtained when pentane was slowly diffused (via vapor diffusion) into the solution.

#### As<sub>2</sub>8<sub>3</sub> cryptand

2,6-bis(mercaptomethyl)naphthalene<sup>S2</sup> (**H28**, 90.8 mg, 0.411 mmol) and  $\text{AsCl}_3$  (23.4  $\mu\text{L}$ , 0.274 mmol) were dissolved in  $\text{CHCl}_3$  (125 mL) and stirred at 50 °C under  $\text{N}_2$ . The reaction vessel was exposed to high vacuum for 5-10 seconds every 0.5-1.5 hours for two working days (left under  $\text{N}_2$  overnight). The volume of the solution was reduced to 8 mL under a stream of  $\text{N}_2$  and layered with hexanes to give clear, colorless crystals (35.6 mg, 0.0422 mmol, 31%).  $^1\text{H}$  NMR (300 MHz;  $\text{CDCl}_3$ ;  $\text{Me}_4\text{Si}$ )  $\delta$  7.50 (m, 4H, CH), 7.13 (s, 2H, CH), 3.95 (ABq, 4H,  $\text{CH}_2$ ,  $J$  12.3).

#### Sb<sub>2</sub>8<sub>3</sub> cryptand

2,6-bis(mercaptomethyl)naphthalene<sup>S2</sup> (**H28**, 67.5 mg, 0.305 mmol) and  $\text{SbCl}_3$  (49.1 mg, 0.215 mmol) were dissolved in  $\text{CHCl}_3$  (125 mL) and stirred at 50 °C under  $\text{N}_2$ . The reaction vessel was exposed to high vacuum for 5-10 seconds several times a day for 10 days. The volume of the solution was reduced to 10 mL by vacuum and layered with  $\text{CH}_3\text{CN}$  to give < 10 mg of clear, colorless crystals suitable for single crystal x-ray diffraction studies.

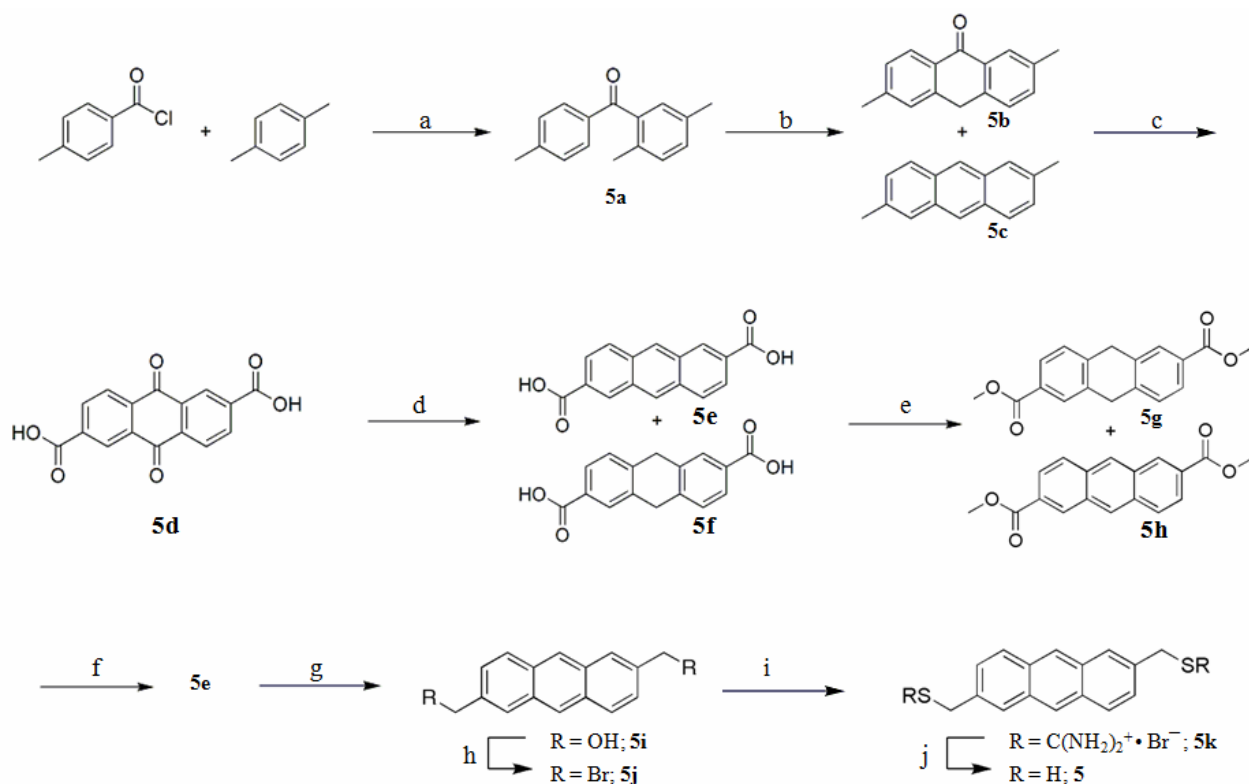
#### X-ray Crystallography

Diffraction intensities were collected at 173(2) K on a Bruker Apex CCD diffractometer using  $\text{MoK}\alpha$  radiation  $\lambda = 0.71073$  Å. Absorption corrections were applied by SADABS.<sup>S7</sup> Structures were solved by direct methods and Fourier techniques and refined on  $F^2$  using full matrix least-squares procedures. All non-H atoms were refined with anisotropic thermal parameters. H atoms were refined in calculated positions in a rigid group model. Solvent molecules,  $\text{CHCl}_3$  in **As<sub>2</sub>8<sub>3</sub>** and  $\text{CH}_3\text{CN}$  in **Sb<sub>2</sub>8<sub>3</sub>**, are disordered around -3 axis and were treated by SQUEEZE.<sup>S8</sup> Corrections of the X-ray data by SQUEEZE (343 and 23 electron/cell, respectively for **As<sub>2</sub>8<sub>3</sub>**, **Sb<sub>2</sub>8<sub>3</sub>**) are close to the required values of 348 and 22 electron/cell for six and one molecules,

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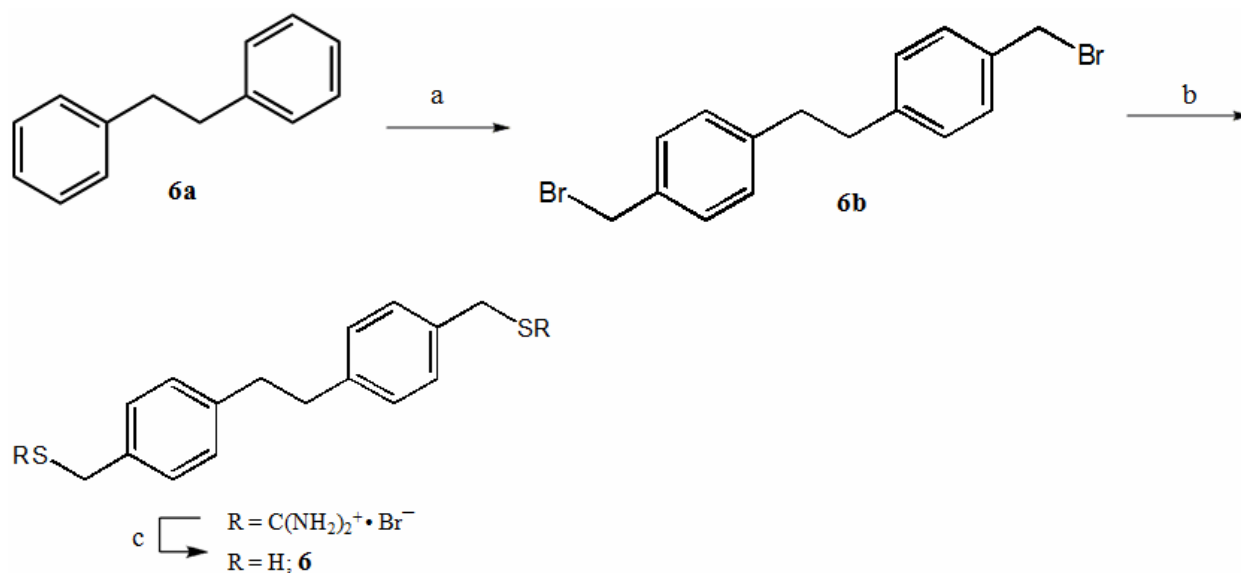
respectively, in the full unit cells. In  $\text{As}_2\mathbf{6}_3$  elongations of thermal ellipsoids for some carbon atoms in ligands perpendicular to C-C bonds were found. Such elongations seem to be related to a disorder for these carbon atoms. Some structural features in  $\text{Sb}_2\mathbf{8}_3$  also indicate that the molecules in this structure are flexible or could be disordered as well. As results some of C-C bond distances in  $\text{Sb}_2\mathbf{8}_3$ ,  $\text{As}_2\mathbf{5}_3$  and  $\text{As}_2\mathbf{6}_3$  were not able to be measured precisely. All calculations were performed by the Bruker SHELXTL (v. 6.10) package.<sup>S9</sup>

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**Scheme S1** – Synthesis of H<sub>2</sub>5. Reagents and Conditions for H<sub>2</sub>5 synthesis.<sup>S3-S5</sup> (a) CS<sub>2</sub>, AlCl<sub>3</sub>, rt, 3 h, (b) 360 °C, 4 h, air, (c) CrO<sub>3</sub>, acetic acid, 120 °C, 3 h, (d) CuSO<sub>4</sub>, Zn<sup>0</sup>, NH<sub>4</sub>OH, 90 °C, 4 h, (e) CH<sub>3</sub>I, Li<sub>2</sub>CO<sub>3</sub>, DMF, RT, 24 h, (f) DDQ, PhH, 90 °C, 1h, (g) LAH, THF, 70 °C, 1 h, (h) DCM, PBr<sub>3</sub>, rt, N<sub>2</sub>, 24 h, (i) NH<sub>2</sub>CSNH<sub>2</sub>, acetone, 70 °C, (j) NaOH, 110 °C, 2 h.

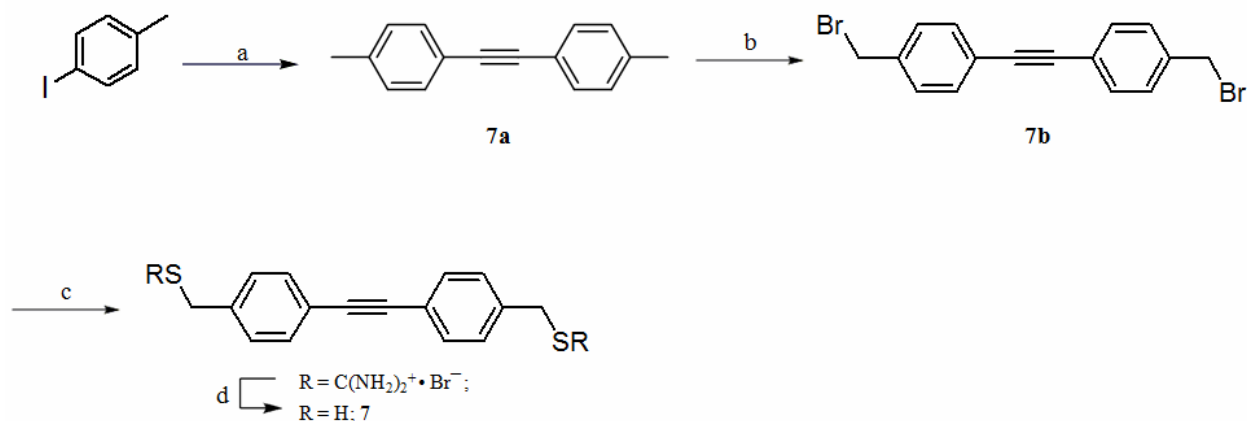
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**Scheme S2** – Synthesis of H<sub>2</sub>6. Reagents and Conditions: (a) (CH<sub>2</sub>O)<sub>n</sub>, ZnBr, 30% HBr/HOAc, 80 °C, 18 h, (b) NH<sub>2</sub>CSNH<sub>2</sub>, ethanol, 60 °C, 16 h, (c) NaOH, 100 °C, 2 h.



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**Scheme S3** – Synthesis of H<sub>2</sub>7. Reagents and Conditions:<sup>S6</sup> (a) TMSA, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, CuI, DBU, CH<sub>3</sub>CN, RT, 24 h, (b) NBS, benzoyl peroxide, CCl<sub>4</sub>, 60 °C, 23 h, (c) NH<sub>2</sub>CSNH<sub>2</sub>, EtOH, 60 °C, 3 h, (d) NaOH, 110 °C, 2 h.

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