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Synthetic Methods

Non-Pyrolytic, Large-Scale Synthesis of Trichalcogenasumanene: A Two-Step Approach**

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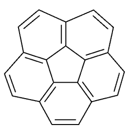
Abstract: *Trichalcogenasumanenes were synthesized on a multigram scale through a two-step approach that takes advantage of non-pyrolytic cyclization and solventless ring contraction. Solid-state structure and photophysical investigations demonstrate that these compounds are promising candidates for electronic materials.*

The discovery of fullerene has stimulated much interest in polycyclic aromatic hydrogencarbons (PAHs) with a curved surface, namely, buckybowls.[1] These bowl-shaped PAHs can serve as synthetic intermediates for fullerenes,[2] end caps for carbon nanotubes,[3] and warped nanographene.[4] The curved PAHs also exhibit unique physicochemical properties related to their concave and convex surfaces.[5] There are two representative subunits for buckybowls: the C_{5v} symmetric corannulene (**1**) and the C_{3v} symmetric sumanene (**2**). Corannulene was firstly synthesized in 17 steps by Lawton and Barth in 1966,[6] and a practical synthetic route was established by the Scott group using flash vacuum pyrolysis (FVP) as key step.[7] The latter sparked many others to join in this field and finally lead to the non-pyrolytic synthesis of **1** by the Siegel[8] and Rabideau[9] groups. Compared with **1**, sumanene **2** is a more strained buckybowl,[10] and its chemical synthesis is thus more challenging owing to higher strain energy for the ring cyclization. Several approaches to **2** have been attempted since 1993,[11] but the first successful synthesis was accomplished by Sakurai et al. in 2003.[12] Subsequent investigation indicated that this new buckybowl system shows interesting features for coordination chemistry[13] and as electronic materials.[14]



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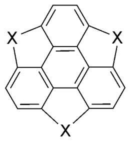
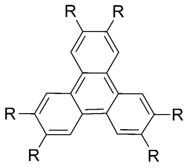
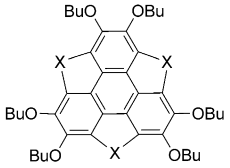


X = CH_2, **2**
S, **3**



R = H, **4**
OBu, **5**



X = Se, **6**
S, **7**

The heterasumanenes, in most cases derived from **2** by substituting the benzylic positions with heteroatoms, are promising buckybowls because the aromaticity of the five-membered rings differs from each other with regards to the heteroatoms.[15] To date, there have been a handful of reports about heterasumanene.[16] Very recently, the Sakurai group has reported the synthesis of a different type of heterasumanene, one having pyridine skeletons in the molecule.[16h] The key issues in this field are mainly 1) the development of a practical synthetic route and 2) large scale production. In 1999, the Otsubo group reported a four-step synthesis of trithiasumanene (**3**) from benzotrithiophene,[16a] but this approach suffers from harsh reaction conditions (FVP at 1000 °C and 0.005 Torr), low-efficiency (total yield $<5\%$), and small-scale (milligrams) production. On the other hand, triphenylene (**4**) has the fundamental skeleton of **2**, and its derivatives are less expensive than benzotrithiophene and can be conveniently functionalized at the outer edges. Thus, one promising option for the synthesis of **3** is the insertion of sulfur bridges in the “bay” regions of **4**. However, early reports indicate that it is difficult to introduce three sulfur bridges into **4** simultaneously, and only the mono- and di-bridged species are formed at 500–550 °C.[17] Subsequent theoretical calculations suggest that it would be challenging to synthesize **3** from **4**.[18] It is thus highly desirable, and also of practical importance, to explore a new synthetic strategy toward heterasumanenes from the triphenylene framework. Several heterasumanenes have been synthesized from triphenylene derivatives through relatively long synthetic routes.[16b–f] Herein, we disclose a non-pyrolytic two-step synthesis of triselenasumanene (**6**) and trithiasumanene (**7**) from triphenylene derivatives, as shown in Scheme 1. The present synthesis can be easily conducted and the desired products can be obtained in multigram quantities. The photophysical

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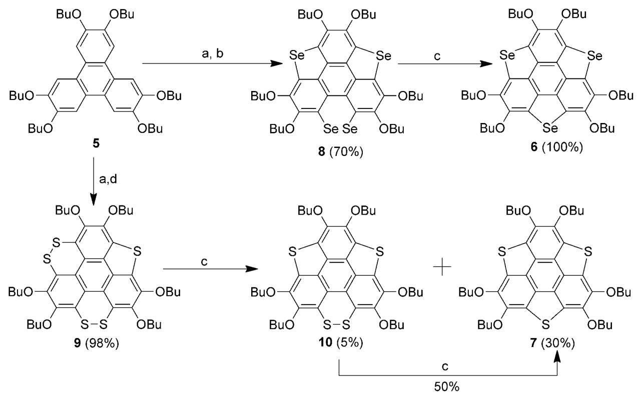

Scheme 1. Synthetic approach toward triselenasumanene (**6**) and trithiasumanene (**7**). Yields of isolated products are shown in parentheses. Reaction conditions: a) **5** (6.6 g, 0.01 mol), TMEDA (15 mL), *n*BuLi (2.4 M in hexane, 41.6 mL, 0.1 mol), 60 °C, 3 h; b) Se powder (7.9 g, 0.1 mol), −78 °C to room temperature (RT); c) Cu powder (80–100 nm, 10 equiv), 200 °C, 2 h; d) S powder (4.8 g, 0.15 mol), −78 °C to RT.

properties and crystal structures of **6**, **7**, and their precursors are elucidated.

Our strategy for synthesis lies in 1) ring cyclization, fusion of multiple chalcogenole and 1,2-dichalcogenin rings at the bay regions of the triphenlyene skeleton, and 2) ring contraction, dechalcogenation of 1,2-dichalcogenin to form the desired trichalcogenasumanene. The fusion of 1,2-dichalcogenin at the bay region of triphenylene can be achieved by a one-pot reaction,[19] and the dechalcogenation of 1,2-dichalcogenin with copper has been widely employed in the synthesis of chalcogenoles.[20] Thus, we conducted the synthesis of trichalcogenasumanenes **6** and **7** from 2,3,6,7,10,11-hexa(1-butoxy)triphenylene (**5**).

As a typical example, the two-step synthesis of **6** is as follows: In the first step, triphenylene derivative **5** was lithiated with *n*BuLi (10 equiv) in tetramethylethylenediamine (TMEDA) at 60 °C to form the hexanionic intermediate;[21] the resulting solution was then cooled down to −78 °C, followed by the addition of selenium powder in one portion and slowly warming up to room temperature (RT). This one-pot reaction constructs two selenophene rings and one 1,2-diselenin ring (**8**) at the bay regions of **5** in a yield of 70 %. In the second step, the deselenation of **8** was conducted by simply heating a mixture of powdered **8** and nanopowdered copper (80–100 nm grain size) in the solid state at 200 °C for two hours, and the desired product **6** was quantitatively obtained. This is the first synthesis of triselenasumanene, and all of the reactions can be performed on a multigram scale. As for the synthesis of **7** under the same reaction conditions, the ring cyclization constructs one thiophene and two 1,2-dithiin rings (**9**) almost quantitatively; the desulfurization of **9** affords **7** in 30 %, along with 5 % of **10**, which can be further transformed into **7** by desulfurization. The synthetic discrepancy for the ring cyclization/contraction between **6** and **7** is ascribable to the difference in the bond lengths of C−Se (ca. 1.92 Å) and C−S (ca. 1.80 Å), as shown in the following section, which give rise to the different strain energies for the formation of selenophene and thiophene rings. The present method distinguishes itself from the early one[16a] by its less expensive starting materials, shorter synthetic route, absence of high-temperature FVP, and large-scale production. Thermogravimetric analysis (TGA) indicates that **6** and **7** decompose at around 320 °C (Supporting Information, Figure S1), thus the FVP method at a temperature higher than 320 °C would not be suitable for the synthesis of **6** and **7**. This further demonstrates the superiority of our synthetic route.

Single crystals of **6** (brown hexagonal crystals) and **8** (orange platelet) suitable for X-ray diffraction analysis were obtained by slow evaporation of their CH_2Cl_2 solutions at RT. Unfortunately, compound **7** only formed tiny needle-like crystals with a crystal length of more than 3 cm, whereas compounds **9** and **10** provided thin platelet crystals; these crystals were not suitable for X-ray diffraction. Thus, we were only able to determine the crystal structures of **6** and **8**;[22] the selected crystallographic data are supplied in the Supporting Information.

In the crystal structure of **6** (Figure 1), there are three different molecules (**A**, **B**, and **C**) with their centers located on the crystallographic 3-fold axes. The π-conjugated skeletons for these three molecules are almost identical, and the top view of molecule **A** is shown in Figure 1 a. In this molecule, the hub six-membered ring shows bond alternation to give r_1 and r_5 bond lengths of 1.38 Å and 1.42 Å, respectively. On the other hand, the bond lengths (r_1–r_4, 1.38–1.40 Å) in the flanking six-membered ring are very close to each other. Thus, the configuration of the triphenylene framework in **6** is similar to that in **3**,[16a] but slightly different

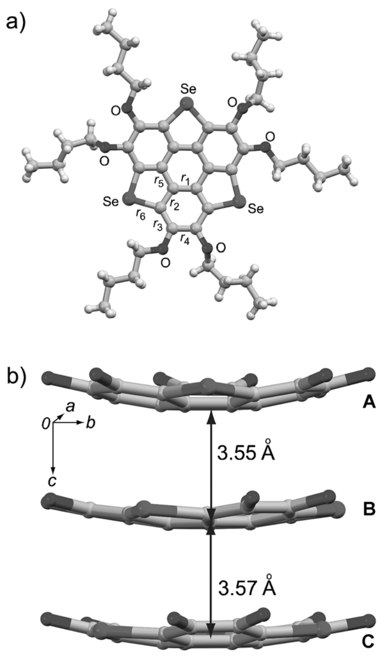

Figure 1. Crystal structure of **6**. a) Top view of **A**; bond lengths (Å): $r_1 = 1.38(1)$; $r_2 = 1.38(1)$; $r_3 = 1.40(1)$; $r_4 = 1.40(1)$; $r_5 = 1.42(1)$; $r_6 = 1.92(1)$. b) Molecular packing with the bowl-to-bowl distances shown; butyl groups omitted for clarity.

from that in **2**, in which r_4 has a bond length of 1.44 Å, which is clearly longer than the others (r_1–r_3, 1.39–1.40 Å).[10] The C–Se bond length (r_6, 1.93(1) Å) of the selenophene ring in **6** is significantly longer than the corresponding ones in **3** (C–S, 1.80 Å) and **2** (C–C, 1.55 Å). Consequently, although **6** possesses a bowl-shaped structure (Figure 1 b), its bowl depth (0.47 Å) is shallower than those of **3** (0.65 Å) and **2** (1.11 Å). Trisilasumanene possesses the planar shape,[16b,g] although the bond length of C–Si (1.89 Å) in its silole ring is slightly shorter than that of C–Se in **6**. Molecules **A**, **B**, and **C** stack in a concave–convex manner along the 3-fold crystallographic axis, with interplanar distances of 3.55–3.57 Å (Figure 1 b). These distances are much shorter than that observed in **2** (ca. 3.86 Å),[10] which suggests that **6** has better π-orbital overlap than **2** in the solid state. Although we could not solve the crystal structure of **7**, theoretical calculations suggest that **7** also shows a bowl-shaped structure with a bowl depth of 0.70 Å, which is close to that of **3**, but slightly deeper than that of **6**.[16a] The long, tiny needle-like crystal shape, which shows no alteration upon exchanging the terminal alkyl chain, implies that **7** most likely forms concave–convex columnar stacks in the crystal.

In the crystal structure of **8**, the two molecules **A** and **B** are crystallographically unique (Figure 2), but their geometries are almost identical. The triphenylene skeleton and two selenophene rings are nearly coplanar, whereas the 1,2-diselenin ring deviates significantly from the planar structure with a C-Se-Se-C dihedral angle of 42° (Figure 2 a). The C–Se bond lengths of selenophenes are 1.92(1) Å, which is close to that in **6**. The hub benzene ring shows bond alternation to give an r_1 (1.48 Å) much larger and an r_4 (1.38 Å) shorter than the others (ca. 1.41 Å). This molecule forms zig-zag chain-like stacks of the form -**A**-**B**-**A**-**B**-, as shown in Figure 2 b, where the core separation distance between the neighboring molecules is more than 3.9 Å. Although we could not get single crystals of **9** that were suitable for X-ray diffraction, the crystal structure for its hexa(1-propoxy) analogue (**11**) has been solved.[22] This compound exhibits a so-called "flying-squirrel-like" molecular structure[23] and forms the columnar stack (Figure S4).

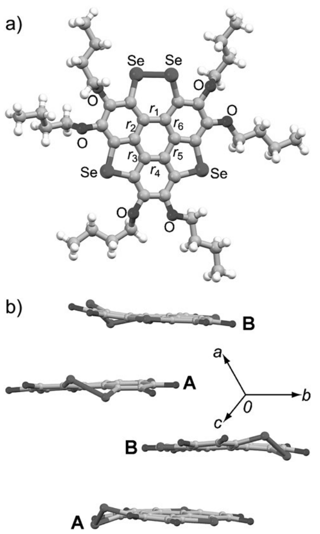

Figure 2. Crystal structure of **8**. a) Top view of **A**. b) Molecular packing; butyl groups omitted for clarity.

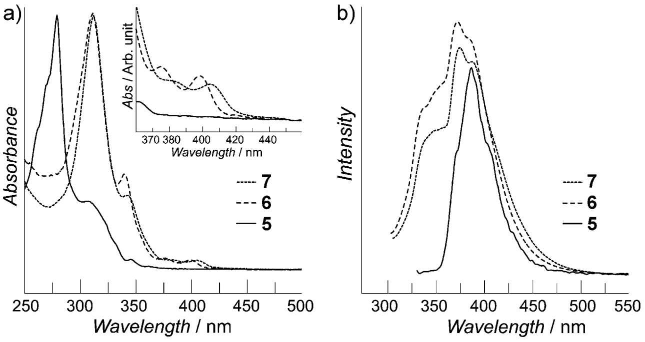

Figure 3. UV/Vis absorption (a) and emission spectra (b) of **6** and **7** measured in dichloromethane ($c = 10^{-5}$ mol L^{-1}) at 20 °C, along with those of **5** for comparison. The insert in (a) shows an expansion of absorption spectra in the long-wavelength region.

To elucidate the electronic structure, the UV/Vis absorption spectra of **5**–**10** were measured in dichloromethane (CH_2Cl_2) at RT. Figure 3 a depicts the absorption spectra of **5**, **6**, and **7**, whereas those of **8**, **9**, and **10** are provided in the Supporting Information (Figures S5a and S6a). The absorption spectra of **6** and **7** are almost identical, both show an intense absorption band at 312 nm ($\log\varepsilon = 4.93$) with a shoulder ($\lambda_{max} = 339$ nm, $\log\varepsilon = 4.50$) that is clearly red-shifted from that of **5** ($\lambda_{max} = 278$ nm, $\log\varepsilon = 5.14$) and **2** ($\lambda_{max} = 278$ nm). Moreover, a weak absorption band in the longer-wavelength region (370–420 nm) is observed in **6** and **7**. According to theoretical calculations (Table S5 and Figures S8 and S10), this long-wavelength absorption is mainly attributed to the HOMO–LUMO transition of **6** and **7**, which suggests the existence of n–π conjugation between the lone pair electrons on the selenium/sulfur atoms and the π-conjugated triphenylene framework. Theoretical calculations also indicate that the lone pairs of the oxygen atoms of *n*-butoxy groups show a strong contribution on the HOMO level of **6** and **7**, and the HOMO–LUMO gaps are narrower than those of the corresponding trichalcogenasumanenes without butoxy groups. In fact, the lowest energy absorption band of **3** in CH_2Cl_2 is at 368 nm,[16a] which is distinctly blue-shifted from **7**. Thus, the terminal butoxy groups have a strong perturbation effect on the electronic nature of **6** and **7**, as has also been reported for trisilasumanene derivatives.[16b–e] In comparison with **6**, the lowest energy absorption band of compound **8**, which has one 1,2-diselenin ring, is significantly red-shifted to 390–470 nm, with enhanced absorption intensity. This band is assignable to the transition from the HOMO (mainly consisting of n–π conjugation) to the LUMO (mainly consisting of the Se–Se σ* orbital; Figure S12). The same tendency is also observed in **7, 9**, and **10**. The red-shift of absorption band caused by transition between n–π conjugation and Se–Se/S–S σ* orbital has been reported in the other systems containing both chalcogenole and 1,2-dichalcogenin rings.[20,23]

The emission spectra of **6** and **7** are almost identical, both show blue fluorescence at 374 nm with a shoulder at 387 nm (Figure 3b). In comparison with pristine triphenylene **5**, the emission bands of **6** and **7** are broadened, whereas the centers of emission bands are slightly blue-shifted by about 20 nm. The emission spectra of **8** and **10** are similar to those of **6** and **7**, respectively, whereas that of **9** shows a distinct red-shift to 420 nm (Figure S6b). At the present stage, it is difficult to elucidate the origin of the red-shift emission in **9** and the blue-shift emission in the others, because compounds **6**–**10** possess narrower HOMO–LUMO gaps than **5**.

In conclusion, we have developed a high-yielding and multigram-scale synthesis of trichalcogenasumanene from triphenylene that takes advantages of non-pyrolytic cyclization and solventless ring contraction. Crystallographic investigation indicates that triselenasumanene **6** assumes a bowl-shaped conformation and stacks in a concave–convex manner, with shorter intermolecular distances than pristine sumanene. Photophysical and theoretic studies demonstrate that **6** and **7**, as well as their precursors (**8**, **9**, and **10**) possess a narrower HOMO–LUMO gap than sumanene. Moreover, the terminal butoxy chains largely increase their solubility, which is beneficial to solution-processed molecular devices.[24] These results suggest that the present trichalcogenasumanenes and their synthetic precursors are promising candidates for electronic materials. The elucidation of their electronic-transport properties is in progress.

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Keywords: crystal structure · cyclization reaction · photophysical properties · ring contraction · trichalcogenasumanenes

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[22] CCDC 955536 (**6**), 955537 (**8**), and 955538 (**11**) contains 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/data_request/cif.

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