

Ring Reconstruction on a Trichalcogenasumanene Buckybowl: A Facile Approach to Donor–Acceptor-Type [5-6-7] Fused Planar Polyheterocycles**

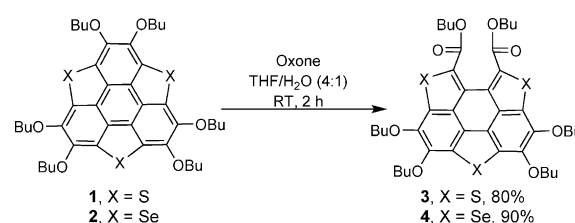
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Abstract: The transformation of trichalcogenasumanene buckybowl into donor–acceptor-type [5-6-7] fused polyheterocycles is disclosed. The strategy involves a highly efficient ring-opening of the flanking benzene upon oxidation at room temperature, and facile ring closure by functional-group transformation. Crystallographic studies indicate that the resulting [5-6-7] fused polyheterocycles possess a planar conformation owing to the release of ring strain by expansion of one of the six-membered flanking rings to the seven-membered one. Additionally, the [5-6-7] fused polyheterocycles bear electron-withdrawing groups, which reduce the HOMO–LUMO energy gap, and display broad absorption bands extending to $\lambda = 590$ nm. Consequently, these compounds show strong red emission with fluorescence quantum yields of up to 38 %.

The π -conjugated polycycles have attracted widespread interest as they possess excellent optical and/or electrical properties which can be applied in the organic electronics. While most of the attention has been on polycycles possessing a planar π -conjugated system, those with a curved π surface are of interest because of their unique physicochemical features.^[1] As typical polycycles with a curved π surface, buckybowl (or π bowl) are of growing interest,^[2] and the chemistry of buckybowl leads to the synthesis of C_{60} ,^[3] end-caps of carbon nanotubes,^[4] warped nanographene,^[5] nitrogen-doped graphitic carbons,^[6] and chrysaoroles.^[7] Sumanene, a C_{3v} -symmetric buckybowl with high ring strain, was firstly synthesized by the group of Hirao.^[8] The last decade has witnessed the rich chemistry of the sumanene families,^[9]

including bowl-to-bowl inversion dynamics,^[8,10] coordination chemistry,^[11] and material science.^[9b,12]

Except for the introduction of functional groups at the benzylic positions and flanking benzene rings,^[9] the modification of sumanene can also be performed by either substitution of the benzylic positions with heteroatoms^[13] or replacing the flanking benzene with pyridine,^[14] thus resulting in the heterasumanenes. To date, most of effort has been devoted to the synthesis of heterasumanenes by varying heteroatoms,^[2e,13–15] whereas the chemical reactivities and modifications of them are less explored. Very recently, we reported the facile syntheses of trichalcogenasumanenes bearing six *n*-butoxy groups on their flanking benzene rings (**1** and **2**; Scheme 1).^[16] Moreover, **1** and **2** can be produced on multigram scale, thus facilitating the study of their chemical activities and the successive transformations to create new types of polyheterocycles.



Scheme 1. Oxidation of trichalcogenasumanenes. Experimental details are provided in the Supporting Information.

Crystallographic studies show that **1** and **2** possess a bowl-shaped conformation, and the theoretical investigations illustrate that the *n*-butoxy groups and chalcogen bridges show large contributions to their frontier orbitals.^[16] The intrinsic ring strain and electron-rich nature of **1** and **2** suggest they would display unique chemical activities. In fact, we have found that **1** and **2** can afford different products by varying the reaction conditions. Herein, we report the oxidation of **1** and **2** by a stable and convenient oxidant, Oxone (potassium peroxymonosulfate), thus resulting in the highly efficient ring-cleavage of the flanking benzene at room temperature (Scheme 1). On the basis of this ring-opening reaction, a “molecular-surgery-type”^[17] functionalization of **1** and **2** leads to the creation of a series of unprecedented donor–acceptor-type [5-6-7] fused polyheterocycles. Crystallographic, theoretical, and photophysical studies reveal that these [5-6-7] fused polyheterocycles are promising candidates for optoelectronic materials.

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The oxidation of **1** was performed by reaction with Oxone (2 equiv) in a mixed solvent system of THF/H₂O (4:1, v/v) at room temperature (Scheme 1). Thin-layer chromatography indicated that only one product was formed, along with the unreacted **1**. High-resolution mass spectrometry revealed that the resulting product contained two additional oxygen atoms as compared with **1**. Meanwhile, ¹³C NMR and IR spectra demonstrated that the product contained C=O groups (see the Supporting Information). Thus, the oxygen atoms are not bonded to the sulfur atoms of **1**, although Oxone can oxidize thiophene into the corresponding thiophene *S,S*-dioxide.^[18] The structure of this product was finally determined by single-crystal X-ray structure analysis (Figure 1).^[19] Surprisingly, one

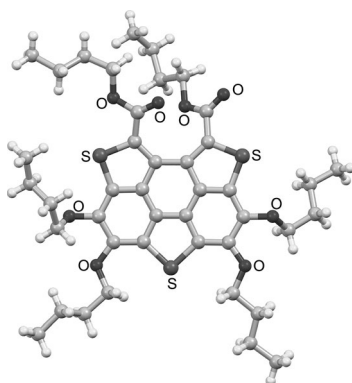


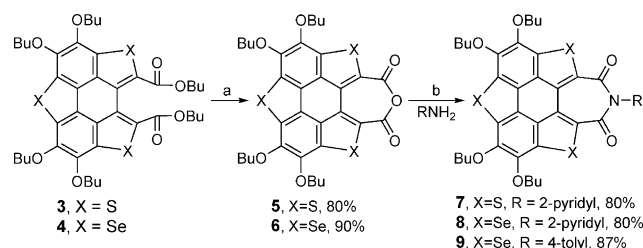
Figure 1. Molecular structure of **3** in the crystal. The main framework is slightly deviated from the plane owing to the distortion of the central six-membered ring. The unsymmetrical alignment of butoxycarbonyl groups is ascribed to the intramolecular dipole–dipole interaction between them.

of the flanking benzene rings of **1** is opened upon oxidation to give the compound **3**, which possesses two butoxycarbonyl groups. The oxidation of **1** with excess Oxone (> 4 equiv) afforded **3** as the single product, with some unreacted **1**. The optimized conversion rate of **1** is 46% in the presence of 2 equivalents of Oxone, and the yield of **3** is 80% based on conversion rate. However, **2** was almost completely converted into **4** (90%) under the same reaction conditions, thus suggesting that the chalcogen atoms play an important role in this reaction. Noteworthy is that the ring-opening of **1** and **2** can also be achieved by oxidation with *tert*-butyl hydroperoxide (TBHP), but the conversion rate for both **1** and **2** is reduced (< 40%).

The cleavage of the aromatic ring is of great interest,^[20] and the oxidative degradation of an aromatic ring usually needs harsh reaction conditions.^[21] In general, oxidation of a C=C bond by Oxone results in epoxidation without cleavage of C–C bond.^[22] However, **1** and **2** show highly efficient ring-opening of the flanking benzene at room temperature upon oxidation with Oxone, and is attributed to their unique feature in both structural and electronic aspects. To gain insight into the chemical reactivity of **1** and **2**, the following should be considered. Firstly, we have performed the oxidation of HBT (2,3,6,7,10,11-hexabutoxytriphenylene), an electron-rich but nonstrained polyaromatic hydrocarbon,

with both Oxone and TBHP under the same reaction conditions. However, the cleavage of aromatic ring on HBT did not occur, and only HBT was recovered. Secondly, sumanene is a more strained buckybowl than either **1** or **2**, but does not contain electron-rich substituents. The oxidation of sumanene with TBHP resulted in trioxosumanene, that is, the benzylic positions were converted into ketals, as reported by Hirao group.^[23] These results illustrate that the electron-rich nature and ring strain of **1** and **2** show a synergetic effect on the cleavage of the flanking benzene. The reaction could involve two main steps, that is, the oxidation of the outer C=C bond on the flanking benzene by Oxone and the successive ring-opening. The driving force for the oxidation is mainly attributed to the electron-rich nature of **1** and **2** since both butoxy groups and chalcogen bridges are electron-donating units. The ring strain would also need to be taken into account as the curved π system decreases the aromaticity. The ring cleavage should be very quick owing to the ring strain derived from the bowl shape of the framework. This fast ring cleavage is also evidenced by the oxidation of **1** (or **2**) with 1 equivalent of Oxone; no intermediates could be isolated in this case.

On the basis of the ring-opened products **3** and **4**, a series of unprecedented polyheterocycles (**5–9**) were created by facile chemical transformations as shown in Scheme 2. Thus, **3**



Scheme 2. Synthesis of **5–9**. Reaction conditions: a) 1. NaOH, EtOH/H₂O (10:1, v/v), reflux, 2 h; 2. HCl aqueous (3 N); 3. Ac₂O, reflux; b) DCC, THF, reflux. Experimental details are provided in the Supporting Information. DCC = dicyclohexylcarbodiimide, THF = tetrahydrofuran.

and **4** were converted into the corresponding anhydrides **5** and **6** with yields of 80 and 90%, respectively. The successive transformation of **5** and **6** led to the synthesis of **7**, **8**, and **9**. There may be other synthetic approaches to **5–9**; however, the present ring-opening and ring-closure strategy is much practical because the starting materials (**1** and **2**) can be readily prepared on a multigram scale.^[16] Besides, the present approach shows the advantages of easy handling, mild reaction conditions, and high production yields.

The compounds **5–9** possess a new skeleton having the following features: 1) multiple different ring systems condensed together, that is the [5-6-7] fused polyheterocycles; 2) contain both electron-withdrawing (anhydride/imide) and electron-donating units (1,2-dibutoxyphenyl, chalcogenole). These features result in distinct effects on their structural and photophysical nature, as reported in the following sections.

The red needle-like single crystals of **7** and **9**, suitable for single-crystal X-ray diffraction analyses,^[19] were obtained by

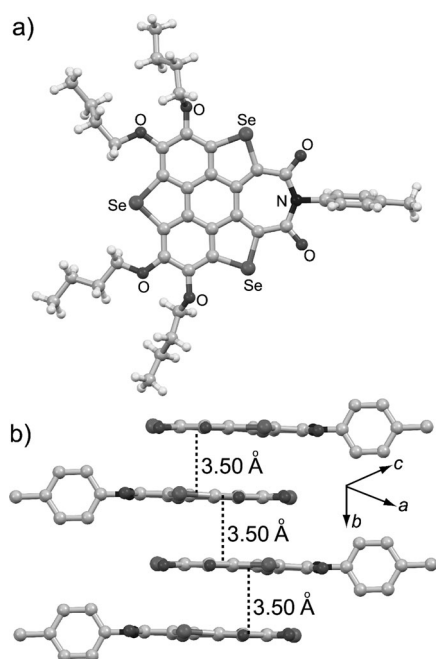


Figure 2. Crystal structure of **9**. a) Top view. b) Molecular packing viewed along the side direction of the [5-6-7] fused central core with the interplanar distances shown (butyl groups and hydrogen omitted for clarity).

slow evaporation of their dichloromethane solution at room temperature. The compound **9** crystallizes in the monoclinic $C2/c$ space group with one molecule crystallographically unique (Figure 2a). The central [5-6-7] fused framework of **9** is nearly planar, and the tolyl plane is almost perpendicular to the central framework. The planar conformation of **9** is ascribed to the ring expansion, that is, one of the six-membered rings is expanded to the seven-membered one. The compound **9** forms head-to-tail type columnar arrays in the solid state (Figure 2b). The interplanar distance (3.50 Å) between the neighboring [5-6-7] fused frameworks is shorter than the bowl-to-bowl distance (3.57 Å) in **2**, thus suggesting that **9** forms better π -orbital overlap than **2** in solid state.

The compound **7** crystallizes in the monoclinic $P2_1/c$ space group with three crystallographically unique molecules (**A**, **B**, and **C**; see Figure S7 in the Supporting Information). These three molecules show almost identical conformation, and Figure 3 depicts the structure of molecule **A** in the crystal. Similar to that of **9**, the central [5-6-7] fused conjugated framework of **A** is nearly planar with the pyridyl plane perpendicular to it. The compound **7** forms the columnar stacks in the sequence of **-A-B-C-** as shown in Figure S7. Within a packing column, the mean planes of the [5-6-7] fused framework of **B** and **C** are almost parallel to each other with the interplanar distance of 3.44 Å. The mean plane of the central framework of **A** is slightly tilted compared to those of the other two molecules. Noteworthy is that **8** also afforded red needle-like single crystals, but the structure refinement of it was not satisfactorily performed because of the low quality of the crystals. The preliminary structure analysis indicates that **8** possesses the similar molecular geometry and packing motif to those of **7** and **9** (see Figures S9 and S10).

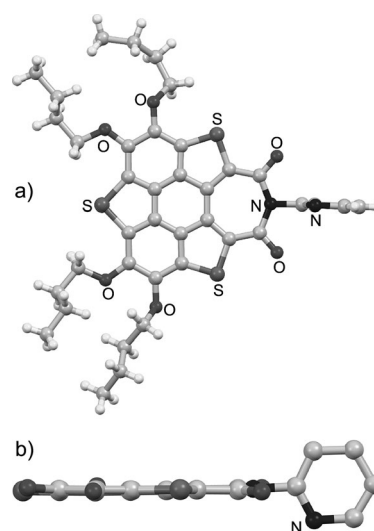


Figure 3. Crystal structure of **7**. a) Top view. b) Side view. The butyl groups and hydrogen atoms in (b) are omitted for clarity.

The electronic structures of **3–9** were elucidated by UV/Vis absorption spectra and theoretical calculations. Figure 4a depicts the UV/Vis absorption spectra of compounds derived from **1**, and those derived from **2** are shown in Figure S11. The compound **1** displays a sharp maximum absorption band at $\lambda = 311$ nm ($\log \epsilon = 4.93$), thus corresponding to the typical absorption of the HBT core and a weak broad band at $\lambda = 370$ – 420 nm corresponding to the n - π transition.^[16] Com-

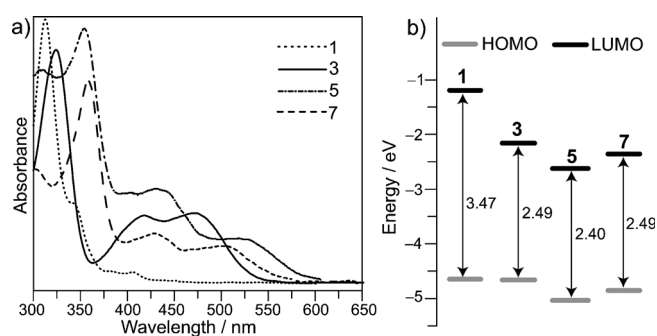


Figure 4. a) UV/Vis absorption spectra in CH_2Cl_2 ($c = 10^{-5} \text{ mol L}^{-1}$). b) Calculated HOMO and LUMO energy levels of **1**, **3**, **5**, and **7** at the B3LYP/6-31G(d,p) level of theory.

pared with **1**, the maximum absorption bands of **3**, **5**, and **7** are red-shifted to $\lambda = 324$ nm ($\log \epsilon = 4.39$), $\lambda = 354$ nm ($\log \epsilon = 4.40$), and $\lambda = 358$ nm ($\log \epsilon = 4.32$), respectively. Besides, **3**, **5**, and **7** display strong absorbances ($\log \epsilon \approx 3.50$) at $\lambda = 360$ – 550 nm, $\lambda = 380$ – 570 nm, and $\lambda = 390$ – 590 nm, respectively. Theoretical studies indicate that the HOMO orbitals of **3**, **5**, and **7** are mainly located on the [5-6] fused framework, similar to that of **1**. Meanwhile, the butoxycarbonyl groups on **3**, anhydride group on **5**, and imide group on **7** show an important contribution to their LUMO orbitals (see Figures S23, S25, and S27). Hence the LUMO levels of **3**, **5**, and **7** are distinctly lowered (Figure 4b), whereas the HOMO levels show a slight negative-shift as compared with those of **1**.

Consequently, the HOMO–LUMO energy gap of **3** (2.49 eV), **5** (2.40 eV), and **7** (2.49 eV) is much narrower than that of **1** (3.47 eV), and consistent with their absorption spectra. These results also suggest that the HOMO–LUMO transitions of **3**, **5**, and **7** feature intramolecular electron transfer, that is, from the electron-rich [5-6] fused framework to the corresponding electron-withdrawing units. Compared with the ring-opening product **3**, both the HOMO and LUMO levels of [5-6-7] fused heterocycles (**5** and **7**) are lowered, and ascribed to the non-negligible contributions of the seven-membered rings on their frontier orbitals (see Figures S25 and S27). Electrochemical studies prove that **5** and **7** possess two oxidation waves (see Figure S30). The onset of the first oxidation wave, which reflects the HOMO energy level, of **5** and **7** is 1.01 V and 0.94 V, respectively, and consistent with theoretical estimations (**5** has a lower HOMO level than **7**). The compounds derived from triselenasumanene (**2**, **4**, **6**, **8**, and **9**) display similar tendencies as the trithiasumanene series with regard to absorption spectra, molecular orbitals, and electrochemical behavior as shown in the Supporting Information.

The fluorescent emission of **1**, **3**, **5**, and **7** are measured in their dichloromethane solutions at room temperature as shown in Figure 5a, and those of compounds derived from **2**

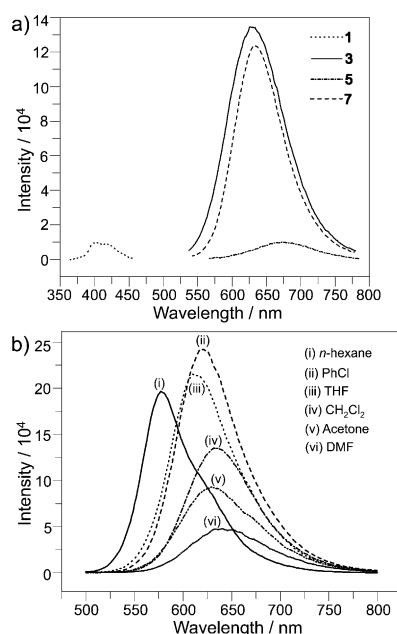


Figure 5. a) Emission spectra of **1**, **3**, **5**, and **7** in CH_2Cl_2 ($c = 10^{-5} \text{ mol L}^{-1}$) at 20°C. b) Emission spectra of **7** in different solvents ($c = 10^{-5} \text{ mol L}^{-1}$).

show similar emission phenomena (see Figure S12). The compound **1** displays the blue emission at $\lambda = 404 \text{ nm}$ with a fluorescence quantum yield (Φ_F) of 6.9%, whereas the maximum emission of **3** ($\lambda = 638 \text{ nm}$), **5** ($\lambda = 683 \text{ nm}$), and **7** ($\lambda = 635 \text{ nm}$) are distinctly red-shifted, and consistent with their narrower HOMO–LUMO energy gaps. Moreover, the fluorescence quantum yields of **3** ($\Phi_F = 40\%$) and **7** ($\Phi_F = 38\%$) are obviously improved, and consequently they display

much stronger fluorescence than either **1** or **5** ($\Phi_F = 6.7\%$). As mentioned above, the main conjugated framework of **3** and **7** is almost planar, whereas **1** possesses the curved surface. Therefore, in the excited state the nonradiative transition of **1**, most plausibly the bowl-to-bowl inversion, would result in the low fluorescence quantum yield as compared with that of **3** and **7**.

Regarding the electron-transfer transition feature on the excited states of **3–9**, the emission properties were studied in the different solvents. The compounds **3–9** exhibited the solvatochromic fluorescence behaviors as expected.^[24] Figure 5b depicts the emission spectra of **7** in varying solvents, and those of the others are shown in Figures S13–S18. In general, the wavelength of maximum emission (λ_{em}) of **7** is gradually red-shifted as the solvent polarity increases. The λ_{em} of **7** is $\lambda = 579 \text{ nm}$ ($\Phi_F = 35.6\%$) in the nonpolar solvent *n*-hexane, and is finally red-shifted to $\lambda = 640 \text{ nm}$ ($\Phi_F = 12.5\%$) in the polar solvent *N,N*-dimethylformamide.

In summary, we have disclosed a highly efficient ring-opening reaction of electron-rich and bowl-shaped trichalcogenasumanenes by oxidation with Oxone, and it leads to a molecular-surgery-like functionalization on trichalcogenasumanenes. By employing the ring-opening and ring-closure strategy, a series of unprecedented [5-6-7] fused polyheterocycles have been created. The release of ring strain by enlarging one of the flanking rings makes [5-6-7] fused compounds take on planar conformations, thus forming tight stacks in the solid state. Photophysical and theoretical studies suggest that these [5-6-7] fused polyheterocycles would be promising candidates for optoelectronic applications, as they have low-lying HOMO and LUMO levels, narrow HOMO–LUMO gaps, and long wavelength emissions with high quantum yields. Moreover, the ring-opening products (**3** and **4**) as well as [5-6-7] fused ones (**5** and **6**) can be employed to synthesize other types of conjugated polyheterocycles, and such work is underway in our laboratory.

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