Diselenolodiselenole: a selenium containing fused heterocycle for conjugated systems†‡

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The synthesis of new conjugated building blocks, diselenolodiselenole (C₄Se₄) derivatives, is described for the first time. The structural and optoelectronic properties of C₄Se₄-derivatives are tuned by varying end-capping aromatic substituents. In cyclic voltammetry, all C₄Se₄-derivatives show two reversible oxidation peaks.

Organoselenium compounds have attracted considerable interest due to their wide range of applications in many fields. Chalcogenophene containing building blocks are being given great importance to synthesize new conjugated organic materials. Their applications in the state-of-the-art technologies including field-effect transistors, flexible light emitting diodes and organic photovoltaics are being extensively studied. Though the development in this field has grown rapidly in the last two decades, the conjugated electroactive building blocks with promising properties are limited. Conjugated chalcogenophene based materials with reversible redox activity have found applications in organic electronic devices.

Though the applications of thiophene based electroactive small molecules or polymers in organic electronics have attracted considerable research attention, their selenium counterparts are sparsely reported. Partly, it can be ascribed to the difficulties in the synthesis of selenophene derivatives and their instabilities in the charged states. The advantages of replacement of sulfur by selenium in conjugated systems are manifold: (a) intermolecular Se···Se interactions lead to a wide bandwidth in organic conductors, which should facilitate intermolecular charge transfer, (b) selenium containing organoheteroles have lower oxidation and reduction potentials than that of sulfur containing heterocycles, (c) due to higher polarizability of Se than that of S, compounds with the selenium atom attached to the conjugated backbone possess more polarizability than their sulfur analogues, (d) selenium containing compounds should have a lower band gap than their sulfur counterparts and, consequently, their optoelectronic properties also differ.

Blum and co-workers reported the synthesis of the first example of dithiolodithiole (C₄S₄) derivatives in 26% yield from 1,4-diphenyldiyn butadiyne and elemental sulfur at 150 °C for 52 h. The growing interest in the C₄S₄ systems led to the development of a more facile synthetic strategy and a systematic study reported by Swager et al focusing on their interesting structural and optoelectronic properties. According to Hückel’s rule, the C₄S₄ system is formally aromatic in the ground state and non-aromatic in the excited state; thus these molecules can lead to interesting electronic properties. The structural and electronic properties of these systems can be further tuned by an atomistic approach by replacing S with Se, which may lead to a more interesting and important fused conjugated system (C₄Se₄). Here, we present for the first time the synthesis of diselenolodiselenole (C₄Se₄) derivatives, bicyclic heterocycles, as a new class of conjugated building blocks.

We have synthesized a series of compounds containing C₄Se₄ as the central conjugated system. The precursor diyne compounds 1a, 1b, 1c and 1d were prepared by a previously reported procedure. Diynes 1b and 1d were synthesized by new synthetic methods (see ESI†). The conversion of diynes to C₄Se₄ derivatives could proceed through the radical mechanism similar to the formation of C₄S₄ derivatives. However, the reaction of 1a with Se powder in the presence of solvent (1,2-dichloroethane (DCE)-o-dichlorobenzene (o-DCB)) and the radical initiator (azobisisobutyronitrile (AIBN)-2,2,6,6-tetramethylpiperidinyloxy (TEMPO)) at 190 °C in a pressure vessel with and without microwaves resulted in very low yields (Scheme 1, conditions I and II).

Moreover, heating of elemental selenium with 1a nearly at the melting point of selenium without any solvents afforded the best yield of 23% for 2a (Scheme 1, condition III). Therefore, condition III was considered as a general procedure to prepare C₄Se₄ derivatives 2a–2e from diyne precursors (Scheme 2). The yields were obtained in the range of 10–30%. Though the strongly electron donating substituents on the phenyl ring were reasoned to cause a
complex mixture of the product and low yield in the case of C₄S₄ derivatives,⁹ the reaction of di(phenylhexyloxyphenyl) diacetylene (1c) afforded the highest yield (30%) in this series.

Crystals of 2a–2c were obtained by the slow evaporation method from their solution in dichloromethane (DCM). In the crystal structure of 2a, capped phenyl rings are twisted from the C₄Se₄ core by a dihedral angle of 53° (C₈–C₇–C₆–C₅ = 126.8(4)) (Fig. 1a and b), which is significantly higher (by 28°) than that of sulfur analogue 3a.⁹ Molecules of 2a form end-to-end dimers via intermolecular π–π interactions (C₄–C₅ = 3.91 Å and C₄–C₄ = 3.37 Å). Selenium atoms of the Se–Se bond of 2a form Se/C/C/C/Se interactions (Se1/C/C/C/Se2 = 3.64 Å) with the neighboring two molecules. This leads to the formation of a virtual (Se–Se/C/C/C/Se–Se)ₙ polymeric chain along the c-axis, from which the phenyl rings are hanged like pendants (Fig. 1c), whereas in the crystal packing of 3a, face-to-face dimer formation was observed via S/C/C/C/S interactions.⁹

Interestingly, in the case of thiophene capped C₄Se₄ (2b) the torsional angle between the outer thiophene ring and the central C₄Se₄ unit is found to be only 10° (C₁–C₂–C₃–C₄ = 169.3(7)) (Fig. 2a and b). The nearly planar conjugated backbone of 2b exhibited resolute intermolecular interactions through heteroatoms.

In the crystal structure of 2b, a pair of Se atoms of each diselenole unit forms two perpendicular dimers by three different Se/C/C/C/Se interactions (Se1–Se1 = 3.648(1) and Se2–Se1 = 3.525(1), Se2–Se2 = 3.726(1)) with the diselenole unit of neighboring molecules (Fig. 2c). Thus four molecules connected by Se/C/C/C/Se and π–H–C interactions (C₆–H₆ = 2.81 Å) form a 2D brick-like structure in bulk. This 2D crystal packing with several nonbonding interactions could facilitate the intermolecular charge transport. In 2c the dihedral angle between the hexyloxy substituted phenyl ring and the central C₄Se₄ unit is ~58° (C₈–C₃–C₂–C₁ = −122.4(5)) (Fig. S1, ESI†).

DFT optimized structures (at B3LYP/6-31G(d)) of 2a and 2b showed dihedral angles of 47° and 0°, respectively, between the central C₄Se₄ unit and end-capping substituents. Corresponding values for C₄S₄ derivatives are 39° and 0°, respectively.

Compounds 2a–2e exhibited two sets of absorption peaks with λ_max ranging from 236 to 277 nm and 427 to 484 nm, respectively (Fig. 3 and Table 1). Compound 2a showed λ_max at 440 nm in solution, which was blue shifted compared to its C₄S₄ analogues. This may be ascribed to the large dihedral angle between the outer phenyl rings and the central C₄Se₄ unit that reduces the effective overlap between these two conjugated
parts. A similar trend was observed in the absorption spectra of $\text{C}_4\text{Se}_4$ and $\text{C}_4\text{S}_4$. The absorption spectrum of $\text{C}_4\text{S}_4$ is red-shifted compared to that of $\text{C}_4\text{Se}_4$, $\text{C}_4\text{Se}_4$ and $\text{C}_4\text{S}_4$. The red shift due to better electron donating properties of $\text{C}_4\text{Se}_4$ than that of $\text{C}_4\text{S}_4$ in the presence of the stronger electron accepting carboxylate substituted capped phenyl rings. The highest value of $\lambda_{\text{max}}$ for $\text{C}_4\text{Se}_4$ among all $\text{C}_4\text{Se}_4$ derivatives is due to its nearly planar structures, which allow the effective end-to-end conjugation and enhance donor-acceptor properties.

All $\text{C}_4\text{Se}_4$ derivatives $\text{a}–\text{e}$ exhibited two reversible oxidation potentials in the range of 0.30–0.54 V and 0.90–1.10 V, respectively, in cyclic voltammetry (CV) experiments (Fig. 4) similar to that of $\text{C}_4\text{S}_4$ derivatives. The variation in the oxidation potentials of $\text{a}–\text{e}$ could be understood on the basis of substituents on capped phenyl rings. Though thiophene is electron rich compared to benzene, $\text{b}$ has higher oxidation potentials than those of $\text{a}$, and it is comparable with those of $\text{d}$ and $\text{e}$. The planar structure of $\text{b}$ could result in improved delocalization of the electrons of the $\text{C}_4\text{Se}_4$ unit throughout the conjugated backbone, which could decrease the electron density on the $\text{C}_4\text{Se}_4$ unit. The planarity of the conjugated core in $\text{b}$ assisted the selenium atoms to exert the effect of its larger polarizability and less electronegativity on the extended conjugation. The first oxidation potential of $\text{C}_4\text{Se}_4$ derivatives is nearly in the same range as that of $\text{C}_4\text{S}_4$ derivatives, however, the difference between the first and second oxidation potentials is ~0.1 V less than that of $\text{C}_4\text{S}_4$ derivatives.9

Discussion of DFT calculated absorption spectra, HOMO–LUMO energy values, HOMO–LUMO gaps of $\text{a}$ and $\text{b}$ and comparison with $\text{C}_4\text{S}_4$ derivatives and experimental results is given in ESI† (Table S2, Fig. S2 and S3).

In summary, a new class of conjugated compounds, diselenolodiselenoles, was successfully synthesized simply by heating diaryl diselenides with elemental selenium. The structural and optoelectronic properties of diselenolodiselenole derivatives can be tuned by the judicious choice of the capped aryl groups. The thiophene capped $\text{C}_4\text{Se}_4$ displayed a nearly planar structure with its absorption at the highest wavelength among the compounds in the present series. Therefore, it is a promising candidate to be exploited for application in organic electronics. Due to the presence of Se···Se interactions, diselenolodiselenole derivatives can arrange into interesting crystalline motifs. Thus, we have shown that the structural engineering and atomistic approach could be beneficial to synthesize meaningful building blocks for conjugated systems.

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Notes and references


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**Table 1** Yields, absorption and electrochemical properties of $\text{a}–\text{e}$

<table>
<thead>
<tr>
<th>Compound</th>
<th>Yield (%)</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$E_{1/2}$ vs. Ag/Ag$^+$ (V) $\text{Ag}$ $\text{Ag}^+$</th>
<th>$E_{\text{opt}}$ (eV)</th>
<th>HOMO$^b$ (eV)</th>
<th>LUMO$^b$ (eV)</th>
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<tr>
<td>$\text{a}$</td>
<td>23</td>
<td>240, 440</td>
<td>0.35, 0.86</td>
<td>2.39</td>
<td>--7.9</td>
<td>--5.4</td>
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<tr>
<td>$\text{b}$</td>
<td>12</td>
<td>275, 484</td>
<td>0.47, 0.98</td>
<td>2.21</td>
<td>--5.0</td>
<td>--5.0</td>
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<tr>
<td>$\text{c}$</td>
<td>30</td>
<td>277, 428</td>
<td>0.25, 0.77</td>
<td>2.46</td>
<td>--6.9</td>
<td>--5.2</td>
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<tr>
<td>$\text{d}$</td>
<td>15</td>
<td>253, 427</td>
<td>0.49, 1.03</td>
<td>2.43</td>
<td>--5.0</td>
<td>--5.0</td>
</tr>
<tr>
<td>$\text{e}$</td>
<td>19</td>
<td>236, 475</td>
<td>0.50, 1.04</td>
<td>2.15</td>
<td>--7.9</td>
<td>--7.9</td>
</tr>
</tbody>
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**Fig. 3** UV-vis spectra of $\text{a}–\text{e}$ in DCM.

**Fig. 4** Electrochemical properties of compounds $\text{a}–\text{e}$ in 0.1 M TBAPF$_6$ in dry DCM as solvent using a Pt-disk working electrode, a Pt-wire counter electrode and a Ag/AgCl reference electrode.