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Graphical abstract:

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ABSTRACT

The synthesis and characterization of indacenediselenophene (IDS) and diindenoselenophene (DIS), the selenophene-containing analogues of indacenedithiophene (IDT) and diindenothiophene (DIT), respectively, are described. Cyclic voltammetry reveals that IDS and DIS both undergo a two-electron reduction and a one-electron oxidation and have narrower HOMO/LUMO energy gaps when compared to their thiophene-containing counterparts. The UV-Vis spectrum of IDS exhibits a red-shifted absorbance maximum with respect to the S-containing IDT, and single crystal XRD shows close C–Se contacts of 3.407 Å (IDS) and close C–C contacts of 3.358 Å (DIS).

Keywords: Selenophene, indenofluorene, quinodimethane, polycyclic aromatics, organic electronics

Introduction

The study of highly conjugated polycyclic hydrocarbons has attracted great interest in the last two decades due to their interesting photophysical and electronic properties, as well as the practical applicability of these compounds.[1-9] Polycyclic aromatic hydrocarbons (PAHs) such as pentacene (**1**) and related polycyclic aromatics (PAs) such as anthradithiophene (**2**) have been used with great success in device applications from field effect transistors to light emitting diodes (Fig. 1).[5-7,10-13] Unfortunately, acenes are often susceptible to oxidative and photolytic degradation, and as a result, heteroatom inclusion has been explored both to increase stability and to tune the physical and electronic properties of the resultant PAs.[13-19] Thieno-fusion has been a particularly attractive option due to increased stability, processability and modified electronic properties.[20-24] In addition to its inclusion within small molecules, thiophene has long been an important building block of oligomers and polymers because of the resultant polymer's low oxidation potential, high conductivity, and highly tunable electronic properties.[14,25-27]

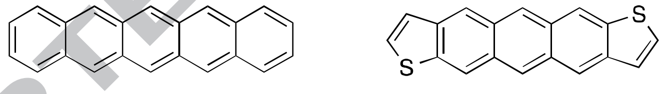


Figure 1. Pentacene (**1**) and anthradithiophene (**2**).

In the past five years, selenium has emerged as a promising heteroatom for use in electronic organics.[11,28-37] Typically Se incorporation results in a narrower HOMO/LUMO energy gap as well as stronger intermolecular interactions due to selenium's easily polarized nature, larger van der Waals radius, and typically lower oxidation and reduction potentials than sulfur.[31,34] Indeed, one of the best performing thin-film transistors to date is a selenophene-containing polymer with an average hole mobility of 9.8 $cm^2 V^{-1} s^{-1}$.[38]

Since 2010 our lab has been studying an underexplored class of highly conjugated pentacyclic hydrocarbons called indenofluorenes (IFs).[39] Structurally similar to pentacene, the inclusion of the two five-membered rings in indenofluorenes such as **3**[40-42] and **4**[43] (Figure 2) imparts an intrinsic ability of this motif to readily accept electrons.[44] In addition to purely hydrocarbon structures, we recently disclosed the synthesis and characterization of two thiophene-containing IFs variants based on indacenedithiophene (IDT, **5**)[45] and diindenothiophene (DIT **6**).[46] Given the promising attributes observed in other Se-containing compounds, we were interested in exploring the effects of selenophene substitution into our previously reported thiophene-containing indenofluorene analogues. We report herein the synthesis of indacenediselenophene (IDS, **7**) and diindenoselenophene (DIS, **8**) and describe their respective optical, electrochemical and structural data.

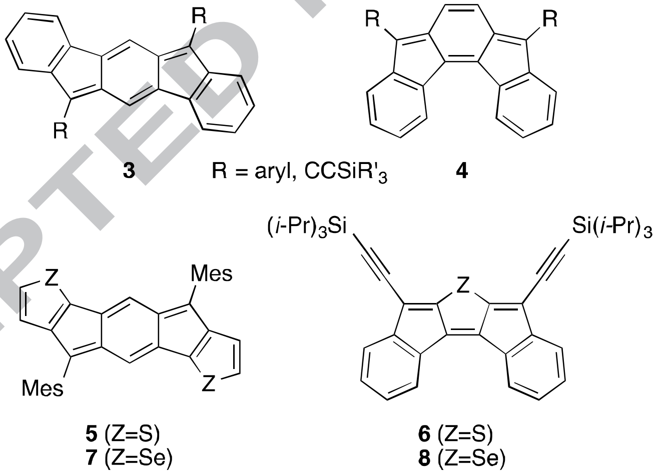
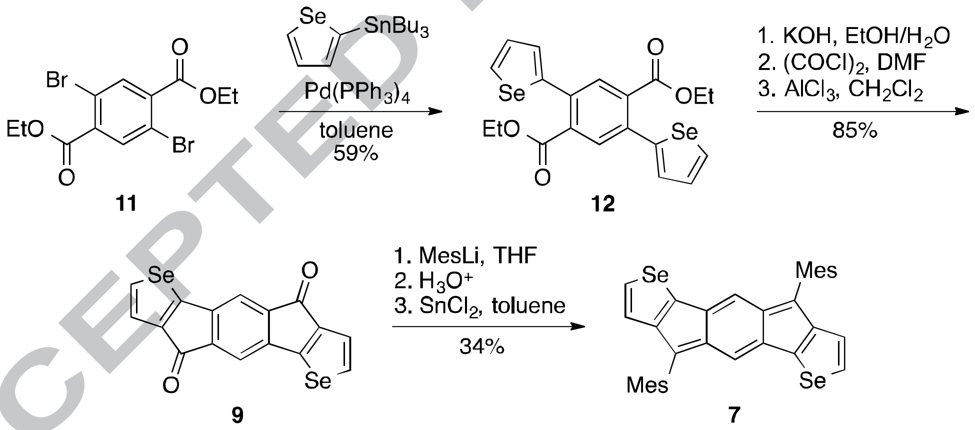


Figure 2. Indenofluorenes **3** and **4** with their thiophene- and selenophene-containing counterparts IDT **5**, DIT **6**, IDS **7** and DIS **8**.

Results and discussion

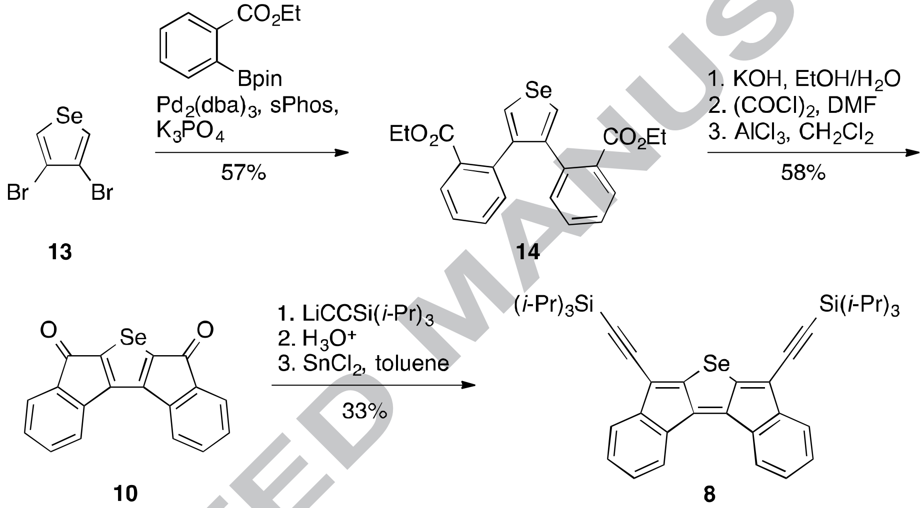
The syntheses of IDS **7** (Scheme 1) and DIS **8** (Scheme 2) follow the typical pathway utilized to generate IFs, IDTs and DITs—addition of a nucleophile to the corresponding dione (**9** or **10**, respectively) followed by a $SnCl_2$-mediated reductive dearomatization reaction. Although neither dione has been reported in the literature, the preparation of both IDS-dione **9** and DIS-dione **10** proved relatively simple and followed a similar methodology to the synthesis employed for the respective diones of **5** and **6**.[45,46]

Our previous investigation of IDTs indicated that the steric bulk of a mesityl group was necessary to kinetically stabilize the indacene core; thus, we elected to use mesityl lithium for the preparation of **7**. A Stille cross-coupling of dibromide **11**[47] with tri-*n*-butyl(selenophen-2-yl)tin[48] provided key diester **12**. Ester saponification followed by Friedel-Crafts acylation provided gram quantities of IDS-dione **9** in excellent yield.[49] Addition of mesityllithium gave the crude diol, which in turn was reacted with $SnCl_2$ to afford stable, deep purple crystals of IDS **7** in moderate yield after recrystallization.



Scheme 1. Synthesis of indacenediselenophene **7** via IDS-dione **9**.

Conversely, our studies into the DITs revealed no need for kinetic stabilization with a bulky group immediately next to the fully conjugated core. Typically, as substitution with silyl-protected acetylenes leads to more favorable packing in the solid state (important to device performance), we elected to use lithium tri(isopropylsilyl)acetylide ($LiCCSi(i\text{-}Pr)_3$) as the nucleophile (Scheme 2). Suzuki cross-coupling of 3,4-dibromoselenophene (**13**)[36] with 2-ethoxycarbonylbenzeneboronic acid yielded **14**. Saponification of the diester followed by Friedel-Crafts acylation of the resultant diacid furnished selene-dione **10** in good yield. Treatment of **10** with LiCCSi(*i*-Pr)$_3$ provided the crude diol which, when subjected to the $SnCl_2$-mediated reductive dearomatization, gratifyingly furnished DIS **8** as stable dark green crystals in modest overall yield.



Scheme 2. Synthesis of diindenoselenophene **8** via DIS-dione **10**.

Figure 3 shows the electronic absorption spectra for IDT **5** and IDS **7** (left) and DIT **6** and DIS **8** (right). These data, along with the experimentally determined E^{redox} values, HOMO and LUMO energies and energy gaps are summarized in Table 1. The spectrum of **7** displays a maximum absorbance from 310 to 380 nm along with a lower energy absorption with a $_{max}$ of 577 nm. This value is 21 nm red-shifted from the $_{max}$ of **5** and is expected due to the typically smaller band gap observed in selenophene-containing compounds compared to their thiophene counterparts.[31,34] The spectrum of **8** displays acene-like vibronic features in the 350-500 nm region and a low energy absorption reaching into the NIR (520-825 nm). DIT **6** and DIS **8** show almost identical absorbance profiles with **6** and **8** having ${}_{max}$ of 676 and 675 nm, respectively. Similar to the IDTs and DITs, both **7** and **8** are non-emissive, a trait inherent to all indenofluorenes and related structures.[50]

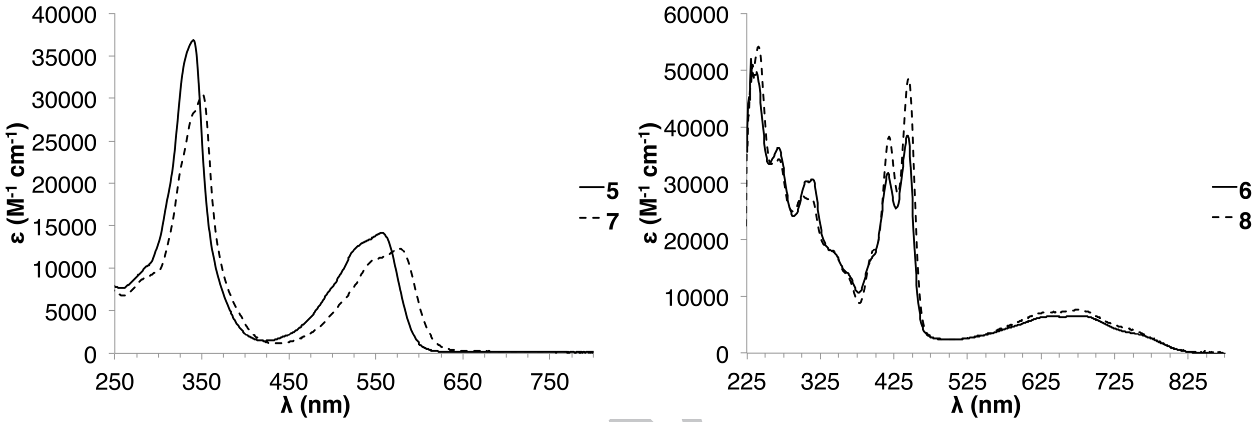


Figure 3. Electronic absorption spectra of IDT **5** and IDS **7** (left) and DIT **6** and DIS **8** (right) in CH_2Cl_2.

Table 1. Electrochemical and optical data for compounds **5**–**8**

compd	Electrochemical^a						Optical^b	
	E_{red}^1 (V)	E_{red}^2 (V)	E_{ox}^1 (V)	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)	${}_{max}$ (nm)	E_{gap} (eV)
5	–0.92	–1.69^c	0.93	–5.57	–3.72	1.85	556	2.06
6	–0.80	–1.22^c	0.99	–5.63	–3.84	1.93	676	1.52
7	–0.95	–1.74^c	0.74	–5.38	–3.69	1.69	577	2.02
8	–0.76	–1.17^c	1.07	–5.71	–3.89	1.82	675	1.52

[a] CVs were recorded using 1-5 mM of analyte in 0.1 M Bu_4NBF_4/CH_2Cl_2 at a scan rate of 50 mV s^{-1} with a glassy carbon working electrode, a Pt coil counter electrode, and a Ag wire pseudo-reference. Values reported as the half-wave potential (*vs.* SCE) using the Fc/Fc^+ couple (0.46 V) as an internal standard. HOMO and LUMO energy levels in eV were approximated using SCE = –4.68 eV *vs.* vacuum (see ref. 51) and $E_{1/2}$ values for reversible processes or E_p values for irreversible processes. [b] Spectra were obtained in CH_2Cl_2. The optical HOMO/LUMO energy gap was determined as the intersection of the *x*-axis and a tangent line passing through the inflection point of the lowest energy absorption. [c] Reported as *V* at peak current, not half-wave potential.

Cyclic voltammetry reveals that IDS **7** undergoes one partially reversible reduction in solution with a second irreversible reduction, while DIS **8** undergoes two reversible reductions in the solution state (Fig. 4).[51] The oxidation of both **7** and **8** is irreversible. In both **7** and **8**, a smaller E_{gap} (0.16 eV for **7** *vs.* **5** and 0.11 eV for **8** *vs.* **6**) is observed, which is consistent with the substitution of Se for S.[28,29] Although there are some seemingly large variances between the experimentally determined optical and electrochemical energy gaps (Table 1), such differences are not uncommon.[52]

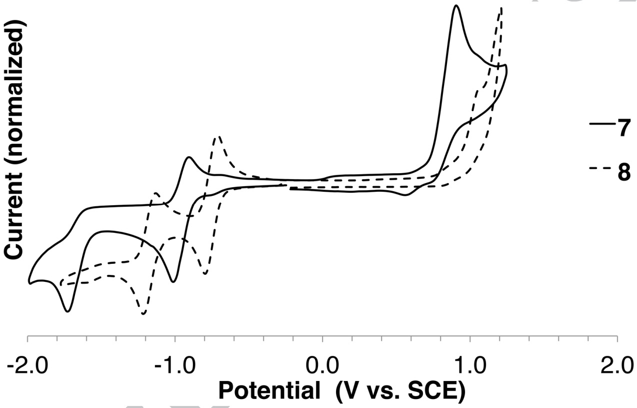


Figure 4. Cyclic voltammetry of IDS **7** and DIS **8**.

Crystals suitable for x-ray diffraction were grown by slow diffusion of CH_3CN into CH_2Cl_2 (**7**) or by slow evaporation of CH_2Cl_2 (**8**). The structures of both molecules are shown in Figure 5; select bond lengths for **7** and **8** as well as for thiophene counterparts **5** and **6** are given in Table 2. Both **7** and **8** exhibit bond length alteration consistent with the proposed quinoidal structure of the core. IDS **7** packs in a herringbone-like motif with the Se atoms pointing towards the center of the five membered ring of an adjacent molecule (3.493 Å from the Se atom to the centroid of the five membered ring). The Se atom participates in the closest intermolecular interaction (van der Waals radius for C–Se is 3.60 Å) with two short contacts of 3.407 and 3.460 Å. The C4-Se1-C8 angle is 86.8° while the dihedral angle between average planes of the mesityl

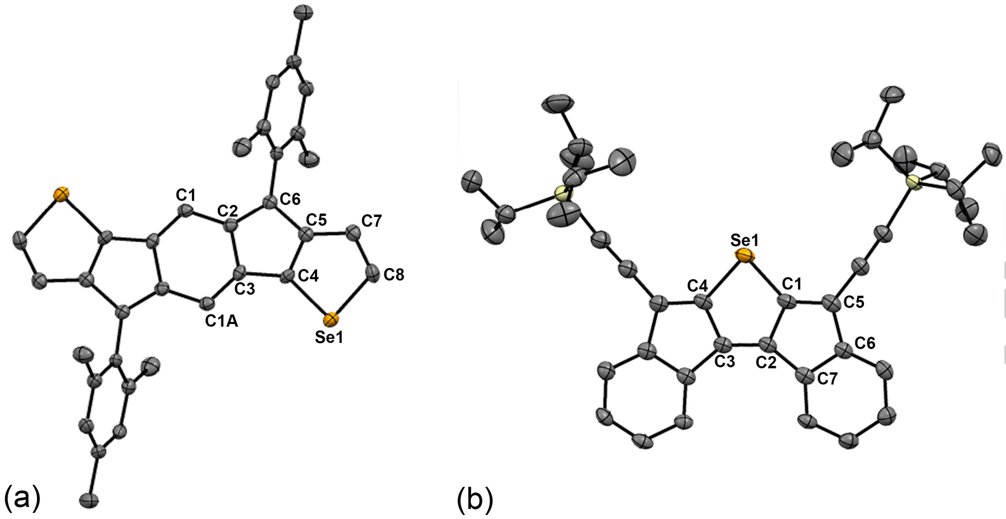


Figure 5. Molecular structures of IDS **7** (a) and DIS **8** (b). Hydrogen atoms omitted for clarity. Ellipsoids drawn at 50% probability level.

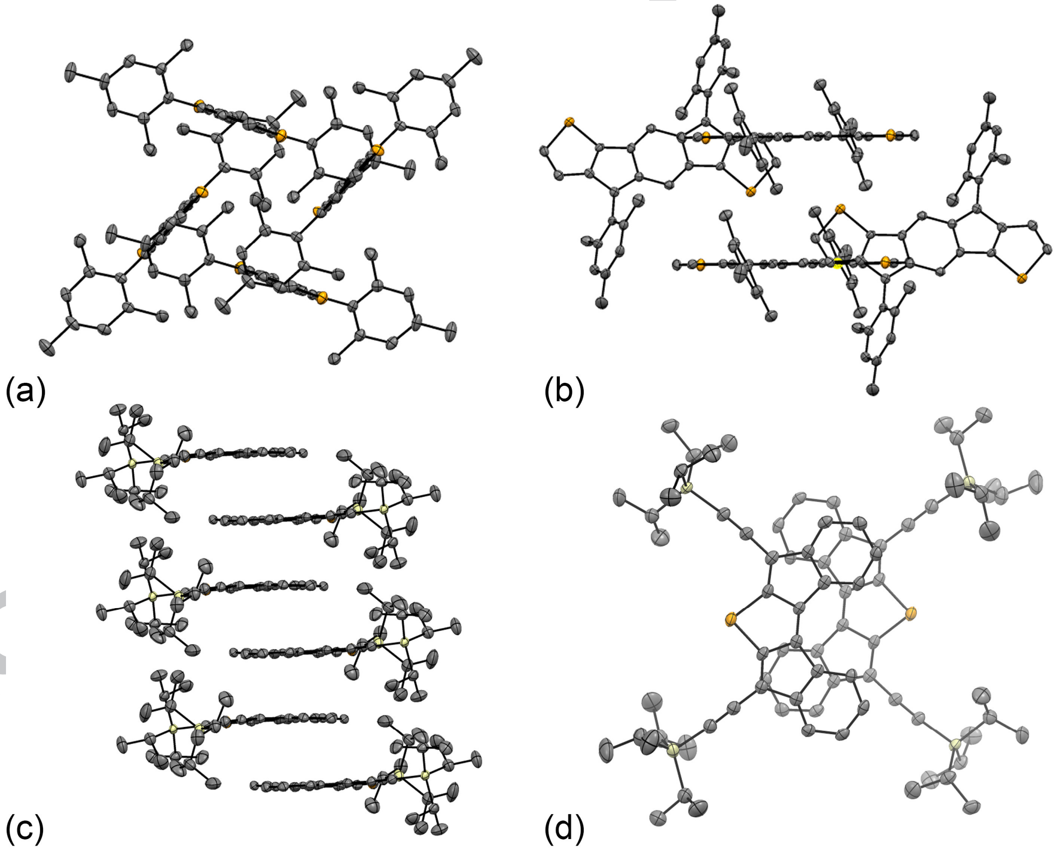


Figure 6. Solid-state packing of IDS **1** (a and b) and DIS **2** (c and d); H atoms omitted for clarity; ellipsoids draws at 50% probability level.

Table 2. Selected bond lengths (Å) for compounds **5**–**8**

	IDT/IDS		DIT/DIS	
bond[a]	**5**	**7**	**6**	**8**
C1–C2	1.432(2)	1.432(5)	1.453(2)	1.449(5)
C1A–C3	1.360(2)	1.356(5)	—	—
C1–C5	—	—	1.365(3)	1.356(5)
C2–C3	1.469(2)	1.460(5)	1.359(3)	1.367(5)
C2–C6	1.388(2)	1.386(5)	—	—
C2–C7	—	—	1.463(2)	1.470(5)
C3–C4	1.452(2)	1.443(5)	1.456(2)	1.453(5)
C4–C5	1.389(2)	1.383(5)	—	—
C5–C6	1.460(2)	1.461(5)	1.482(2)	1.493(5)
C5–C7	1.417(2)	1.424(5)	—	—
C6–C7	—	—	1.416(3)	1.418(5)
C7–C8	1.355(3)	1.354(6)	—	—
C1–S/Se1	—	—	1.750(2)	1.898(3)
C4–S/Se1	1.706(2)	1.865(4)	1.747(2)	1.893(4)
C8–S/Se1	1.736(2)	1.884(4)	—	—

[a] Number scheme shown in Fig. 5.

group and the IDS core is 66.3°, a slightly smaller angle than for IDT **5** (68.2°). As with DIT **6**, DIS **8** arranges into pairwise slipped stacks in the solid state with an average distance between planes of 3.357 Å within the close pairs and an average distance of 3.391 Å between planes of far pairs. Lateral (short axis) slip of the cores is 1.004 Å for the close pairs and 5.877 Å for the far pairs. The closest intermolecular interaction for DIS **8** is a C–C contact of 3.358 Å between close pairs and 3.397 Å between far pairs. The C1-Se1-C4 angle for DIS **8** is 84.5°. Aside from the longer C–Se bonds within the selenophene moiety, the core units within compounds **7** and **8** are essentially isostructural with their thieno-analogues **5** and **6**.

Conclusion

In summary, we have developed the synthesis of two Se-containing indenofluorene analogues, indacenediselenophene **7** and diindenoselenophene **8**. Optical and electrochemical characterization reveal that selenophene substitution results in a decrease in the HOMO/LUMO energy gap compared to thiophene incorporation (1.69 *vs.* 1.85 eV for **7** *vs.* **5**, and 1.82 *vs.* 1.93 for **8** *vs.* **6**), while structural characterization shows shorter relative intermolecular contacts. These data suggest that much like previously described indenofluorenes and related thiophene-containing compounds, selenophene-containing IF conjoiners could make excellent candidates as organic semiconductors for electronic applications.

Acknowledgments

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Supplementary data

Supplementary data (experimental procedures, characterization data and copies of ^{1}H and ^{13}C NMR spectra of all new compounds, UV-Vis spectra of diones **9** and **10**, X-ray crystallographic data) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tetlet.201x.xxxx.

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