

## Charge Transfer Complexes of New Sulfur- and Selenium-Rich Aromatic Donors

Qian Qin,\* André J. Hebert, Ricardo L. Cruz, and Joel T. Mague

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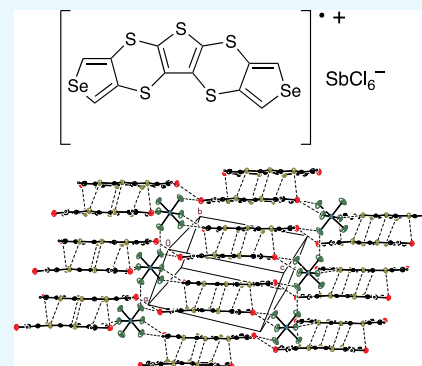
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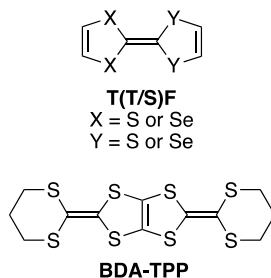
Supporting Information

**ABSTRACT:** Two new sulfur- and selenium-rich pentacyclic aromatic compounds were prepared by short chemical syntheses. The two donors readily formed charge transfer (CT) complexes upon reaction with antimony pentachloride or tris(4-bromophenyl)-ammonium hexachloroantimonate. The X-ray structures of the heterocyclic donors and their CT complexes were determined. The donors flattened considerably upon CT complex formation.



## INTRODUCTION

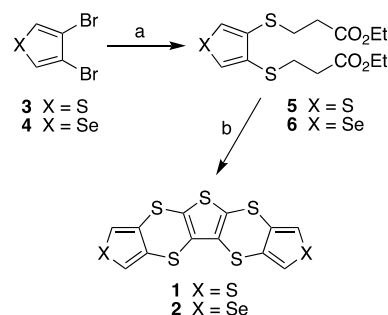
Saito and Yoshida's 2011 review<sup>1</sup> of organic superconductors lists 23 organic electron donors whose cations, in conjunction with various inorganic anions, form approximately 75 charge transfer (CT) complexes that display superconductivity under some conditions. Of these 23 donor molecules, 22 are based on the fulvalene core T(T/S)F, illustrated below. The sole exception is the closely related BDA-TPP. The dominance of tetrathiafulvalene (TTF)-like structures in organic superconductors persists to this day, but surely there must be other heterocycles that would serve as donors for organic superconductors.



To this end, we have prepared and studied CT complexes of other sulfur-rich aromatic compounds,<sup>2</sup> as have many other groups.<sup>3a,c</sup> Such donor molecules have several desirable features. First, the numerous sulfur atoms and extensive conjugation will stabilize their radical cations and lower their oxidation potentials. Second, the planar polycyclic structures of the cations facilitate  $\pi$ - $\pi$  stacking of the molecules in the solid state, which is desirable for conductivity.<sup>3</sup> Finally, the presence of many peripheral sulfur atoms facilitates the orbital overlap of

adjacent molecules via sulfur-sulfur interactions, which is observed to favor the onset of superconductivity in the bulk solids.<sup>3c,4</sup> With these features in mind, we designed the pentacyclic donors 1 and 2 (Scheme 1). These new compounds are sulfur-rich (or selenium-rich) and highly conjugated, with multiple heteroatoms on the perimeter of the polycycles. We now report the short syntheses of these

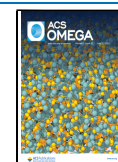
**Scheme 1. Conditions:** (a) Ethyl 2-Mercaptopropionate, Pd<sub>2</sub>dba<sub>3</sub>, DPEphos, K<sub>2</sub>CO<sub>3</sub>, Toluene, Reflux, 78% for 5, 64% for 6 and (b) Tetrachlorothiophene, tBuOK, DMF, Reflux, 38% for 1, 14% for 2

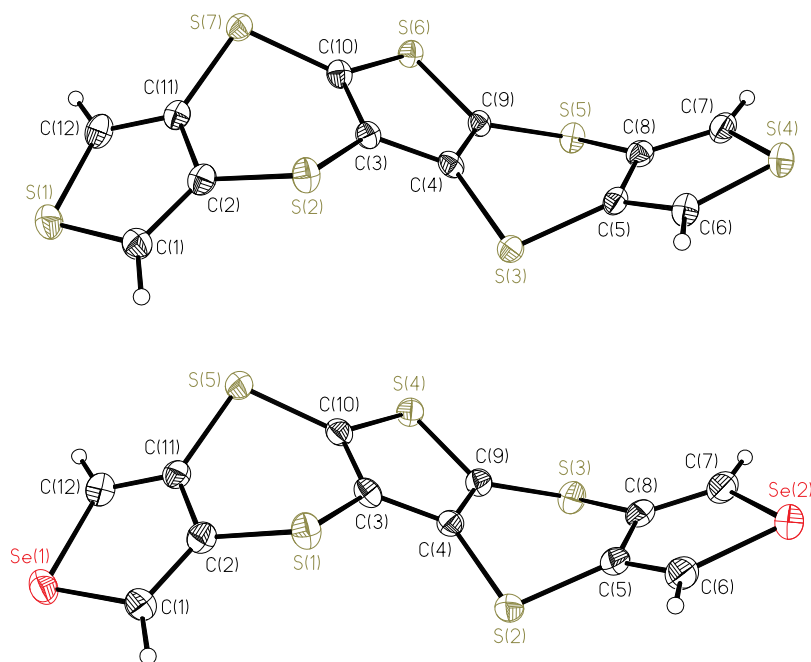


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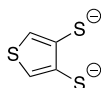


**Figure 1.** Molecular structures of compounds **1** (top) and **2** (bottom). Thermal ellipsoids have been drawn at the 50% probability level.

compounds from simple halogenated thiophenes and selenophenes and the crystal structures of three CT complexes of these donors.

## RESULTS AND DISCUSSION

**Synthesis of Compounds 1 and 2.** Thioliates are powerful nucleophiles that perform nucleophilic aromatic substitution reactions even on unactivated aromatic rings.<sup>5</sup> If one could generate, for example, thiophene-3,4-dithiolate shown below, or its equivalent, then its reaction with tetrachlorothiophene would yield compound **1** (see Scheme 1).



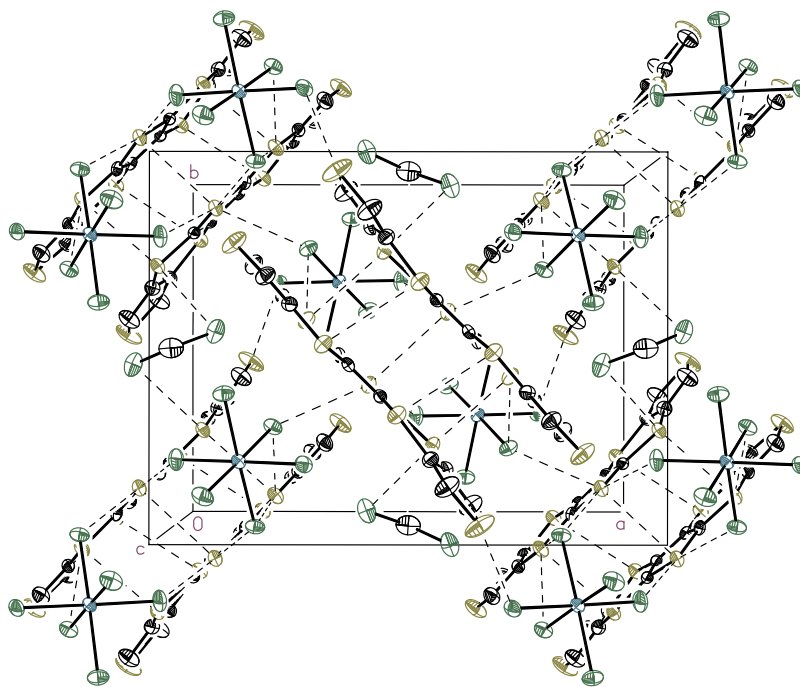
The desired dithiolate proved very difficult to prepare, but a recent paper by Jepsen et al.<sup>6</sup> indicated that ethoxycarbonylthio groups can serve as thiolate equivalents, and this report led to the simple syntheses of compounds **1** and **2** shown in Scheme 1. The palladium-catalyzed Hartwig cross-coupling<sup>7</sup> of ethyl 2-mercaptopropionate and 3,4-dibromothiophene (**3**), both commercial products, gave diester **5** in 78% yield. The subsequent elimination of ethyl acrylate promoted by potassium *tert*-butoxide gave the desired thiolate which reacted in situ with tetrachlorothiophene to give pentacycle **1** in 38% yield.

A similar cross-coupling of ethyl 2-mercaptopropionate and 3,4-dibromoselenophene<sup>8</sup> (**4**) gave diester **6** in 64% yield, and the subsequent base-promoted reaction of diester **6** with tetrachlorothiophene gave pentacycle **2** in a modest 14% yield. The yields of both **1** and **2** are lower than might be hoped, but the starting materials are relatively inexpensive. Fortunately, the neutral pentacycles are not planar (as will be seen below), and they have sufficient solubility for easy chromatographic purification.

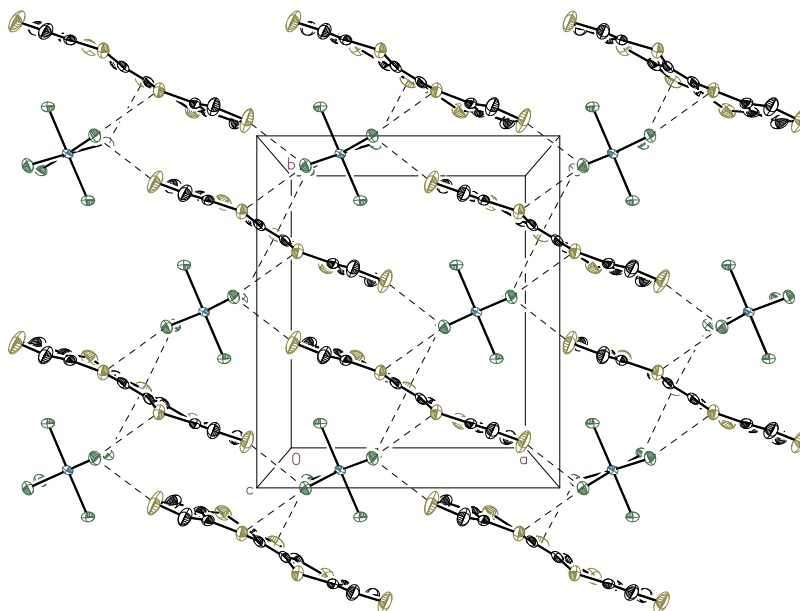
**Structures of Compounds 1 and 2.** The pentacyclic donors **1** and **2** crystallize in the space group *P1*, and the

molecules lie on general positions in the crystal. The molecules have an approximate  $C_2$  symmetry, and their molecular structures are illustrated in Figure 1. Both molecules are nonplanar and strongly folded. The mean planes of the terminal thiophene rings in compound **1** [containing S(1) and S(4)] make dihedral angles of 45.3 and 46.2°, respectively, with the mean plane of the central thiophene ring. Similarly, in compound **2**, the mean planes of the terminal selenophene rings make dihedral angles of 46.8 and 45.7° with the mean plane of the central thiophene.

**Attempted Preparation of CT Complexes with Organic Acceptors.** Although TTF- tetracyanoquinodimethane (TCNQ) is not a superconductor, TCNQ is the gold standard organic acceptor for CT complex formation. Surprisingly, neither compound **1** nor **2** formed CT complexes with TCNQ or chloranil. The B3LYP/6-31G(d)-calculated highest occupied molecular orbital (HOMO) levels of compounds **1** and **2** (−5.61 and −5.59 eV) are comparable to that of  $C_3$  benzotrithiophene (−5.69 eV), which readily forms CT complexes with TCNQ.<sup>2a</sup> Cyclic voltammetry (CV) was carried out to estimate the HOMO energies of compounds **1** and **2**. Both compounds show reversible first oxidations, and their HOMO potentials are estimated from the oxidation onset to be very similar, −5.45 eV (see the Supporting Information).<sup>9</sup> This value is higher than both the experimental HOMO potentials of  $C_3$  and  $D_{2h}$  benzotrithiophenes (−6.19 and −5.55 eV).<sup>10,11</sup> In addition, UV–vis spectra of compound **1**, compound **2**, and their 1:1 mixtures with TCNQ in chloroform were measured. The donors have similar spectra [compound **1**:  $\lambda_{\max}$  (log  $\epsilon$ ), 269 (4.3), 298 (4.1), 338 (sh, 3.8); compound **2**: 274 (4.4), 308 (4.3), 340 (sh, 4.0)]. Furthermore, there are minimal changes in the absorption peaks in mixtures with TCNQ (see the Supporting Information). This again indicates little or no CT between the two donors and TCNQ. Although CV and UV–vis measurements probe the electronic properties, they are imperfect predictors for CT complex formation in the solid state. While donor abilities can be estimated by a variety of



**Figure 2.** Crystal structure of  $1 \cdot \text{SbCl}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$ . Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

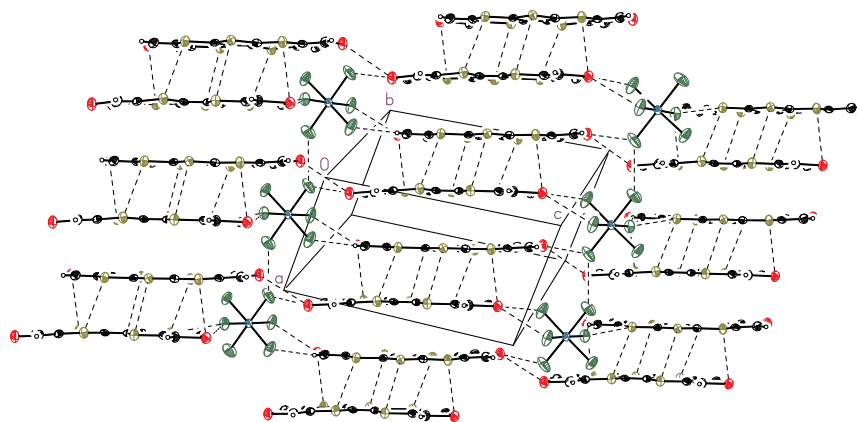


**Figure 3.** Crystal structure of  $1 \cdot \text{SbCl}_6$ . Thermal ellipsoids have been drawn at the 50% probability level, and hydrogen atoms have been omitted for clarity.

experimental and computation methods, again there might be opposing effects at work. For example, while the electron donors are strengthened by more conjugation, larger molecules often have lower solubility.<sup>12</sup> It is also conceivable that the bent shapes of neutral compounds **1** and **2** lessen the  $\pi$ – $\pi$  interaction with TCNQ and chloranil, which may be necessary for effective CT.

**Preparation of CT Complexes with  $\text{SbCl}_5$ .** Most existing superconducting CT complexes consist of planar donor radical cations with nonplanar counter anions.  $\text{SbCl}_5$  is a strong electron acceptor with a spherical shape. Its commercial availability and solubility in common organic solvents also

make it an attractive acceptor for CT complex formation. Crystals of the hexachloroantimonate salts of the radical cation of **1** were prepared by layering a less dense pure solvent over a solution of  $\text{SbCl}_5$  in  $\text{CCl}_4$ , followed by a layer of a solution of donor **1** in toluene. Dark crystals formed overnight. When the intermediate solvent included dichloromethane, crystals of hemisolvate  $1 \cdot \text{SbCl}_6 \cdot 0.5\text{CH}_2\text{Cl}_2$  were formed. When the intermediate solvent was 1,2-dichloroethane or acetonitrile, solvent-free crystals of  $1 \cdot \text{SbCl}_6$  were formed. The crystals of **2**· $\text{SbCl}_6$  were prepared in a similar manner. In addition, when tris(4-bromophenyl)ammonium hexachloroantimonate (magic



**Figure 4.** Crystal structure of  $2 \cdot \text{SbCl}_6 \cdot 0.5\text{C}_7\text{H}_8$ . Thermal ellipsoids have been drawn at the 50% probability level. Hydrogen atoms and the disordered molecule of toluene have been omitted for clarity.

blue) was used in place of  $\text{SbCl}_5$  with compound **1**, the same crystal forms were observed.

**Structure of  $1 \cdot \text{SbCl}_6 \cdot 0.5 \text{CH}_2\text{Cl}_2$ .** The structure of the methylene chloride hemisolvate CT complex of compound **1** is shown in Figure 2. The complex crystallizes in the chiral space group  $P2_12_12$  (no. 18). Both **1** and hexachloroantimonate occupy general positions, and methylene chloride lies on a crystallographic  $C_2$  axis.

Most obvious is the flattening of donor **1** in the complex. Such flattening is also observed in the radical cations of thianthrenes.<sup>13</sup> Instead of the ca.  $45^\circ$  dihedral angles between the thiophene rings in neutral **1**, the presumably cationic **1** in the complex exhibits dihedral angles of only  $3.6$  and  $8.6^\circ$  between the mean planes of the central and terminal thiophene rings, respectively. A second striking feature is the dimerization of the donors in the crystal. Each sulfur atom in one donor makes a close contact with a sulfur atom in its partner, with an average S–S distance of  $3.60 \text{ \AA}$ . The closest of such a contact distance is  $3.36$ ,  $0.24 \text{ \AA}$  less than the sum of the van der Waals radii.<sup>14</sup> In contrast, the donor molecules have no close contacts with donors outside the pair. All such contact distances are greater than  $4.0 \text{ \AA}$ . Although there are some close contacts between the donors and hexachloroantimonates, such a structure is unlikely to have the orbital overlap necessary for superconductivity under any conditions.

**Structure of  $1 \cdot \text{SbCl}_6$ .** The structure of the solvent-free CT complex of compound **1** is shown in Figure 3. The complex crystallizes in the space group  $Ccca$  (no. 68), and both **1** and hexachloroantimonate lie on special positions possessing a crystallographic  $C_2$  symmetry.

Once again, cation **1** is flattened, with (symmetry-related) dihedral angles between the central and peripheral thiophenes of  $12.2^\circ$ . This structure consists of mixed stacks of the donor and acceptor, but because of the much greater width of the donor compared with the roughly spherical acceptor, there exists overlap of the terminal thiophenes in adjacent stacks. This gives rise to staircase-like stacks of the donors in the crystal. However, the overlapping thiophenes are not particularly close, with the shortest interatomic contact distance being  $3.82 \text{ \AA}$ .

**Structure of  $2 \cdot \text{SbCl}_6$ .**  $1 \cdot \text{SbCl}_6$  crystallized with the same structure from two different solvent systems, and we expected the solvent-free complex  $2 \cdot \text{SbCl}_6$  crystallized in the same way, to be isomorphous, but this was not the case. Crystallization under the same conditions as those used for  $1 \cdot \text{SbCl}_6$  gave

instead the toluene hemisolvate,  $2 \cdot \text{SbCl}_6 \cdot 0.5\text{C}_7\text{H}_8$ . The structure of this complex is shown in Figure 4. The space group is  $P\bar{1}$ , and the molecules lie on general positions in the crystal.

The donor cations are very flat, with dihedral angles of  $4.8$  and  $1.6^\circ$  between the mean planes of the terminal selenophene rings and the central thiophene ring, respectively. The donors and acceptors form segregated stacks, a desirable feature for conductivity and superconductivity.<sup>3a,b</sup> However, there is a substantial degree of dimerization in the stacks, as may be seen from the distribution of dotted lines, representing close contacts, in Figure 4. The close pairs of molecules have a short Se–S contact distance of  $3.53$ ,  $0.17 \text{ \AA}$  shorter than the sum of the van der Waals radii, as well as several close S–S contacts. In contrast, the more highly separated pairs of donors have no short interatomic contacts. However, there are short interstack Se–Se contacts of  $3.74 \text{ \AA}$ , a desirable feature for possible superconductivity.<sup>3c,4</sup>

## CONCLUSIONS

The search for an organic superconductor with a new structural motif is a worthy pursuit. As noted in the Introduction, the vast majority of known organic superconductors have been prepared from the same core structure. A successful donor from a new structural class would be extremely exciting and possibly lead to an improved understanding of the mechanism of superconductivity in organic materials.<sup>15</sup>

Thiophene and its derivatives are favorite structural elements in organic electronic materials and form the basis for a variety of semiconducting and conducting materials.<sup>16</sup> Its selenium analogue, being more electron-rich and having larger orbitals on the heteroatom, might yield superior electronic properties. Here, we have developed a speedy synthesis of two new electron-rich heteroaromatic donor molecules based on sulfur-substituted thiophenes and selenophenes. We have demonstrated that these new donors successfully form CT complexes upon reaction with  $\text{SbCl}_5$ . The crystal structures of the CT complexes are quite variable and dependent on the crystallizing solvents. One crystal form in particular,  $2 \cdot \text{SbCl}_6 \cdot 0.5\text{C}_7\text{H}_8$ , showed a highly desirable, multidimensional long-range order of the donor molecules. Preliminary measurements at atmospheric pressure showed no evidence of superconductivity (data not shown), but efforts to prepare larger

crystals of these CT complexes for conductivity measurements under high pressure are ongoing.

## EXPERIMENTAL SECTION

3,4-Dibromoselenophene was prepared by the method in the study of Patra et al.<sup>8</sup> All other reagents and starting materials were commercial products and used without further purifications.

**3,4-Bis(ethoxycarbonylthio)thiophene (5).** Anhydrous toluene (5 mL), 3,4-dibromothiophene (3, 0.242 g, 1.00 mmol), bis[(2-diphenylphosphino)phenyl]ether (DPEphos; 53.9 mg, 0.100 mmol), and K<sub>2</sub>CO<sub>3</sub> (0.346 g, 2.50 mmol) were placed in an oven-dried round bottom flask. The mixture was purged with N<sub>2</sub> for 10 min. Ethyl 3-mercaptopropionate (0.317 mL, 2.50 mmol) was added, followed by tris(dibenzylideneacetone)dipalladium(0) [Pd<sub>2</sub>(dba)<sub>3</sub>; 45.8 mg, 0.050 mmol], and the dark suspension was heated at reflux for 17 h. After cooling to room temperature, saturated aqueous NH<sub>4</sub>Cl was added to quench the reaction. The organic layer was taken, and the aqueous portion was extracted three times with ethyl acetate. The combined organics were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give a dark brown oil. Purification by column chromatography (silica gel, 4:1 hexanes–ethyl acetate) gave compound 5 as a light-yellow oil (0.270 g, 0.776 mmol, 78%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.28 (t, *J* = 7.2 Hz, 6 H), 2.64 (t, *J* = 7.4 Hz, 4 H), 3.13 (t, *J* = 7.4 Hz, 4 H), 4.16 (q, *J* = 7.2 Hz, 4 H), 7.28 (s, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 14.3, 29.5, 34.4, 60.9, 125.9, 132.9, 171.8; HRMS (ESI-TOF) *m/z*: 349.0580 (M + H)<sup>+</sup>, calcd for C<sub>14</sub>H<sub>20</sub>O<sub>4</sub>S<sub>3</sub>, 349.0602.

**4,5,6,10,11-Pentathia-4,6,10,11-tetrahydrodithieno[3,4-*b*:3',4'-*h*]fluorene (1).** Diester 5 (2.53 g, 7.27 mmol), tetrachlorothiophene (808 mg, 3.64 mmol), and anhydrous dimethylformamide (DMF; 80 mL) were placed in an oven-dried Pyrex screw-capped tube. The solution was purged with N<sub>2</sub> for 10 min, and anhydrous KOtBu (2.45 g, 21.8 mmol) was added. The mixture was heated at reflux for 20 h. After cooling to room temperature, the reaction was quenched with sat. NH<sub>4</sub>Cl. The organic layer was taken, and the aqueous portion was extracted three times with toluene. The combined organics were washed with water five times, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give a black semisolid. Purification by column chromatography (silica gel, eluting gradient of hexane to 4:1 hexane–toluene) gave compound 1 as an off-white solid (520 mg, 1.40 mmol, 38%). <sup>1</sup>H NMR (300 MHz, C<sub>6</sub>D<sub>6</sub>): δ 6.29 (d, *J* = 3.1 Hz, 2 H), 6.32 (d, *J* = 3.1 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, C<sub>6</sub>D<sub>6</sub>): δ 120.2, 120.5, 129.2, 131.5, 131.7, 131.9; HRMS (ESI-TOF) *m/z*: 371.8345 (M + H)<sup>+</sup>, calcd for C<sub>12</sub>H<sub>4</sub>S<sub>7</sub>, 371.8358. Single crystals for X-ray analysis were obtained from hexane–toluene.

**3,4-Bis(ethoxycarbonylthio)selenophene (6).** Anhydrous toluene (20 mL), 3,4-dibromoselenophene (4, 1.29 g, 4.47 mmol), DPEphos (242 mg, 0.449 mmol), and K<sub>2</sub>CO<sub>3</sub> (1.56 g, 11.3 mmol) were placed in an oven-dried round bottom flask. The mixture was purged with N<sub>2</sub> for 10 min. Ethyl 3-mercaptopropionate (1.37 mL, 10.8 mmol) was added, followed by Pd<sub>2</sub>(dba)<sub>3</sub> (205.7 mg, 0.225 mmol). This dark suspension was heated at reflux for 17 h. After cooling to room temperature, sat. NH<sub>4</sub>Cl was added to quench the reaction. The organic layer was taken, and the aqueous portion was extracted three times with ethyl acetate. The combined organics were washed with brine, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give a dark-brown oil. Purification by column

chromatography (silica gel, 4:1 hexane–ethyl acetate) gave compound 6 as an orange oil (1.13 g, 2.86 mmol, 64%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 1.26 (t, *J* = 7.2 Hz, 6 H), 2.63 (t, *J* = 7.4 Hz, 4 H), 3.11 (t, *J* = 7.4 Hz, 4 H), 4.15 (q, *J* = 7.2 Hz, 4 H), 7.28 (s, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 14.3, 29.4, 34.3, 60.9, 129.2, 134.1, 171.8; IR (ATR)  $\bar{\nu}_{\text{max}}$  (cm<sup>-1</sup>): 3091, 2923, 1476, 1400, 1323, 1302, 1259, 1159, 1049; UV (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  (log  $\epsilon$ ), 269 (4.3), 298 (4.1), 338 (sh, 3.8); HRMS (ESI-TOF) *m/z*: 397.0043 (M + H)<sup>+</sup>, calcd for C<sub>14</sub>H<sub>20</sub>O<sub>4</sub>S<sub>2</sub>Se, 397.0046.

**4,5,6,10,11-Pentathia-4,6,10,11-tetrahydrodiselenopheno[3,4-*b*:3',4'-*h*]fluorene (2).** Diester 6 (0.240 g, 0.607 mmol), tetrachlorothiophene (67.4 mg, 0.303 mmol), and anhydrous DMF (10 mL) were placed in an oven-dried Pyrex screw-capped tube. This solution was purged with N<sub>2</sub> for 5 min, and anhydrous KOtBu (1.52 g, 2.5 mmol) was added. The mixture was heated at reflux for 20 h. After cooling to room temperature, the reaction was quenched with sat. NH<sub>4</sub>Cl. The organic layer was taken, and the aqueous portion was extracted three times with toluene. The combined organics were washed with water five times, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated to give a black semisolid. Purification by column chromatography (silica gel, eluting gradient of hexanes to 4:1 hexane–toluene) gave compound 2 as a yellow-orange solid (20 mg, 0.043 mmol, 14%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.77 (d, *J* = 2.6 Hz, 2 H), 7.81 (d, *J* = 2.6 Hz, 2 H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 124.3, 124.4, 131.7, 133.4; IR (ATR)  $\bar{\nu}_{\text{max}}$  (cm<sup>-1</sup>): 3089, 2969, 2926, 1475, 1416, 1397, 1306, 1291, 1260, 1142, 1131, 1085, 1080, 1019; UV (CHCl<sub>3</sub>)  $\lambda_{\text{max}}$  (log  $\epsilon$ ), 274 (4.4), 308 (4.3), 340 (sh, 4.0); HRMS (ESI-TOF) *m/z*: 467.7250 (M + H)<sup>+</sup>, calcd for C<sub>12</sub>H<sub>4</sub>S<sub>5</sub>Se<sub>2</sub>, 467.7243. Single crystals for X-ray analysis were obtained from hexane–toluene–CHCl<sub>3</sub>.

**Crystallization of CT Complexes.** Single crystals of the CT complexes were grown in capped 13 mm × 100 mm test tubes by carefully layering less dense pure solvents over a solution of the acceptor, followed by a still less dense solution of the donor. Thus, to prepare crystals of 1·SbCl<sub>5</sub>·0.5CH<sub>2</sub>Cl<sub>2</sub>, pure CH<sub>2</sub>Cl<sub>2</sub> (~0.5 mL) was layered on top of a solution of SbCl<sub>5</sub> (5  $\mu$ L, 40  $\mu$ mol) in CCl<sub>4</sub> (~1 mL), followed by a layer of 1:1 CH<sub>2</sub>Cl<sub>2</sub>–toluene (~0.5 mL), and finally followed by a solution of 1 (5–8 mg, 13–21  $\mu$ mol) in toluene (1–1.5 mL). This we designate as “SbCl<sub>5</sub>–CCl<sub>4</sub>/CH<sub>2</sub>Cl<sub>2</sub>/CH<sub>2</sub>Cl<sub>2</sub>–toluene/1-toluene”. In a similar manner, crystals of 1·SbCl<sub>6</sub> were grown from both SbCl<sub>5</sub>–CCl<sub>4</sub>/1,2-dichloroethane (DCE)/DCE–toluene/1-toluene and from SbCl<sub>5</sub>–CCl<sub>4</sub>/CH<sub>3</sub>CN/1-toluene. Crystals of 2·SbCl<sub>6</sub>·0.5C<sub>7</sub>H<sub>8</sub> were grown from SbCl<sub>5</sub>–CCl<sub>4</sub>/–DCE/DCE–toluene/2-toluene.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre (CCDC) with supplementary publication numbers CCDC 2154499–2154503. Copies of the data can be obtained, free of charge, on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK [fax: +44(0)-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk].

**Cyclic Voltammetry.** Cyclic voltammograms were obtained in aerated methylene chloride solution saturated with tetraethylammonium hexafluorophosphate. The cell consisted of a glassy carbon working electrode (Pine Instruments, 3 mm planar disk), a Pt wire counter electrode, and a Ag wire coated with AgCl as a pseudo reference electrode. Potentials were measured relative to the ferrocenium/ferrocene (Fc<sup>+</sup>/Fc)

internal reference potential. Scan rates were 0.1 V/s for survey scans in the absence of ferrocene and 0.025 V/s in the presence of ferrocene.

**Computational Studies.** All density functional theory calculations were performed with the Spartan 18 program at the B3LYP/6-31G(d) level of theory. The built-in default thresholds for the wavefunction and gradient convergence were employed.

## ■ ASSOCIATED CONTENT

### SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsomega.2c01549>.

NMR spectra of compounds **1**, **2**, **5**, and **6** and IR spectra, UV–vis spectra, and cyclic voltammograms of compounds **1** and **2** (PDF)

Crystallographic data of RAP170\_0m\_a, RAP171\_0ma\_a, RAP172\_a, rap190\_5, and rap191\_4\_a (CIF)

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### Notes

The authors declare no competing financial interest.

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