

CrystEngComm

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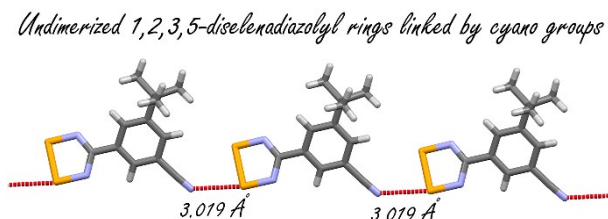
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High Z' structures of 1,2,3,5-dithiadiazolyls and of 1,2,3,5-diselenadiazolyls containing the first structurally characterized monomeric diselenadiazolyls†

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TOC Graphic and brief text



The β -form of 4-(3-cyano-5-*tert*butyl-phenyl)-3H-1,2,3,5-diselenadiazol-3-yl contains chains of monomeric radicals with $\text{-C}\equiv\text{N}\cdots\text{Se}$ as the shortest contacts, in addition to double chains of dimers in a $Z' = 5$ structure. Two other structures with high Z' (3 and 6) are also reported and discussed.

Abstract

Crystals of 4-[3-(trifluoromethyl)phenyl]-3H-1,2,3,5-dithiadiazol-3-yl grown by slow sublimation in a three-zone furnace form in $P\bar{1}$ with $Z = 12$. The six independent molecules combine into two *cis*-oid and one twisted dimer, which arrange in a layer structure as two elegant clusters, with non-crystallographic four-fold and two-fold symmetry, respectively. Crystals of 4-(3-cyano-5-*tert*butyl-phenyl)-3H-1,2,3,5-diselenadiazol-3-yl, formed from decomposition of a *bis*-diselenadiazolyl, grow in two forms under different sublimation conditions using the same furnace. The α form crystallizes in $P\bar{1}$ with $Z = 6$ and the β in $P2_1/c$ with $Z = 20$. The α polymorph consists of a distorted *cis*-oid dimer linked electrostatically to a monomer in the asymmetric unit. These cluster with a second unit to a centrosymmetric aggregate of six heterocycles. The β polymorph consists of clusters of four *cis*-oid dimers that link into chains along the b axis, whereas the fifth molecule links via $\text{-C}\equiv\text{N}\cdots\text{Se}$ supramolecular synthons into an infinite chain of monomers also along the b axis but out-of-register with the dimer chain. A carefully curated compilation of all 83 distinct 1,2,3,5-dithiadiazolyl and of all 24 distinct 1,2,3,5-diselenadiazolyl crystal structures reveals an extraordinarily large number of structures with $Z' > 1$ (72%) and also those with $Z' \geq 3$ (24%), compared to the average for organic molecules over the whole collection in the Cambridge Structure Database. This high incidence is analyzed and attributed to competing intermolecular synthons.

Keywords: dithiadiazolyl; diselenadiazolyl; radical dimer; high Z' ; monomeric free radicals; sublimation; crystallography

† Electronic supplementary information (ESI) available: CIF for all X-ray structures have been deposited. CCDC 1512475-1512478. For ESI and crystallographic data in electronic format see DOI: 10.1039/xxxx.

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Introduction

There is currently strong interest in high Z' crystal structures (having more than one *equivalent* chemical entity in the asymmetric unit) induced in part by the tremendous improvements in single-molecule crystallography with the development of ever better area detectors and more common access to high intensity sources.¹ A database for structures of this type has been established,² which includes several 1,2,3,5-dithiadiazolys (hereafter: DTDA) and 1,2,3,5-diselenadiazolys (hereafter: DSDA). Although the majority of interactions – the *intermolecular synthons* – considered in high Z' structures involve only the common organic functional groups,³ DTDA and DSDA are explicitly considered in a magisterial treatment by Brock on organizing principles behind crystal structures with $Z' > 4$.^{4,5} Recently we published a detailed analysis of a $Z' = 8$ crystal structure of a phenyl DTDA radical bearing a 4-trifluoromethyl group, **1** (Chart 1).⁶ In molecules of this type, the individual radicals have a high tendency towards dimerization as a result of ‘pancake bonding’ interactions,^{7,8} a specific quantum-mechanically defined form of $e^-—e^-$ pairing. Indeed, the eight individual heterocyclic radicals in the structure we reported for **1** are found to dimerize in the familiar *cis*-oid co-facial arrangement thought to maximize pancake bonding, despite the considerable steric crowding of the bulky trifluoromethyl groups on the two proximate aryl rings of the dimer. In the supramolecular structure, four such [DTDA]₂ dimers cluster into pin-wheel arrays with non-crystallographic four-fold symmetry.⁶

In DTDA/DSDA chemistry, the Z' adopted in the crystals is not merely a curiosity but is directly related to crystal engineering attempts to frustrate $e^-—e^-$ pairing in order to stabilize *radical monomers* which have interesting electronic and magnetic properties.^{9–18} A number of intermolecular synthons have been employed to achieve these goals, amongst which aryl cyano groups are the most common. The crystal engineering of the DTDA family was comprehensively reviewed by Haynes in 2011.¹⁹

Here we report on three additional structures of related systems with bulky aryl substituents, all *meta*-derivatives (3- and 3,5-substitution patterns). For the 3-trifluoromethyl isomer of **2**, a structure has been obtained which has $Z' = 6$. Structures with $Z' = 3$, **4a**, and $Z' = 5$, **4b**, have been determined for the α - and β -polymorphs of 3-cyano-5-*tert*butylphenyl-1,2,3,5-diselenadiazolyl (Chart 1), both of which contain both *cis*-oid DSDA dimers and unprecedented monomers. A recent publication, which was part of the stimulus for this article, has breathed new life into DSDA chemistry by reporting seven different structures which, however, all crystallize as dimers (four *cis*-oid, one antarafacial, two in a new orthogonal interaction mode).²⁰

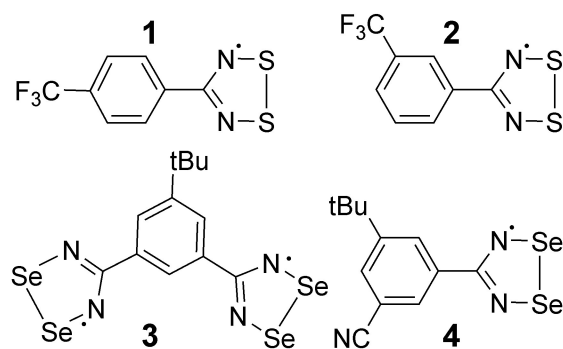


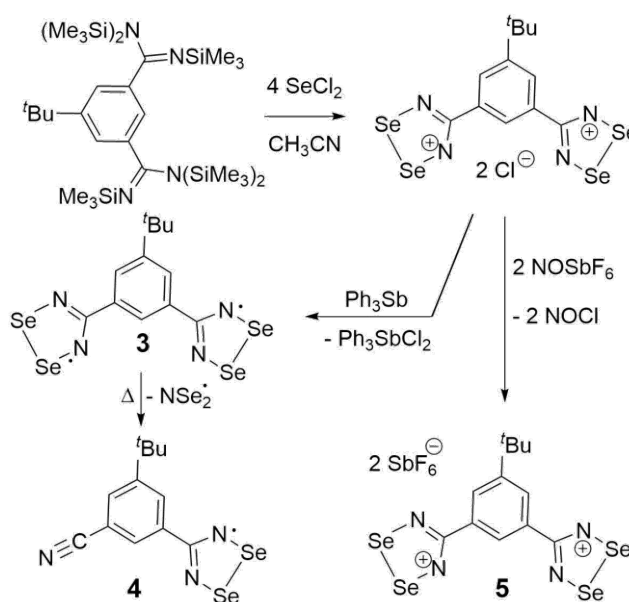
Chart 1

Results and discussion

Sample Preparation

DTDA **2** was prepared by Ph_3Sb reduction of the corresponding chloro-salt as previously reported.²¹ The precipitated radical dimer was first purified by sublimation onto a water-cooled cold finger under dynamic vacuum at 60–70 °C; the resulting crystalline material melts cleanly at 142–145 °C. Crystals suitable for X-ray diffraction were grown by vacuum sublimation within a sealed Pyrex glass tube using a three-zone tube furnace under 'static' vacuum. The temperature was adjusted in 5 °C steps in each of the three zones until dark crystals were deposited in the tube at a sufficient distance from that of the crude material and from the light-coloured crystals formed from impurities and/or from thermal decomposition of the radicals.

The bifunctional DSDA **3** is prepared by the same method as the corresponding DTDA analogue (Scheme 1).¹⁶ The reaction proceeds through an insoluble chloro-salt which was reduced with Ph_3Sb to the crude neutral diradical **3**, filtered, dried and subjected to sublimation. The chloro-salt was also reacted with NOSbF_6 and converted cleanly to crystalline SbF_6^- salt **5**, which confirms formation of the *bis*-diselenadiazolium salt in the first step.



Scheme 1

Attempts to purify diradical **3** by high-vacuum sublimation were unsuccessful due to thermal decomposition. Although the raw product sublimes under conditions of dynamic vacuum ($>160^\circ\text{C}$, 10^{-1} Torr), green/brown clumps of plates harvested from the sublimation were later identified by crystallography as the α -phase of 4-(3-cyano-5-tertbutyl-phenyl)-3H-1,2,3,5-diselenadiazol-3-yl, **4a**. In one experiment where the furnace zones were set to Z1 = 200°C / Z2 = 170°C / Z3 = 150°C , in addition to **4a**, clumps of extremely fine needles were found at the Z2/Z3 interface. These black needles have a high melting point and were shown by single-crystal X-ray diffraction to be "hexagonal" or "grey" selenium (see below).²² Se_∞ is probably formed from the unstable radical $\text{NSeSe}^\bullet$ (or $\text{SeNSe}^\bullet$) initially formed from decomposition of the DSDA ring.^{23–25} The majority of the first sublimation product was further purified by repeated sublimations. Attempts to grow better crystals in sealed tubes failed when the material melted and decomposed at 200°C . Under dynamic vacuum, sublimation was

successful with $Z1 = 190^\circ\text{C}$ / $Z2 = 170^\circ\text{C}$ / $Z3 = 65^\circ\text{C}$, producing small brown clumps at the $Z2/Z3$ interface. These were later identified by crystallography as the β -phase of 4-(3-cyano-5-*tert*butyl-phenyl)-3H-1,2,3,5-diselenadiazol-3-yl, **4b**.

Single-crystal X-ray diffraction of **2**: a new high Z' DTDA structure

The crystal structure of **2** in $P\bar{1}$ with $Z = 12$ ($\therefore Z' = 6$; see Figure 1 and Table 1) is an interesting contrast to that observed for **1** ($Z' = 8$)⁶ because the significant steric crowding between the 4- CF_3 groups on adjacent rings of the *cis*-oid dimers in **1** can be relieved by an opposite orientation of 3- CF_3 groups. This conformation occurs in the two *cis*-oid dimers S1-S4 and S9-S12 (Figure 1a,b). Surprisingly, this apparently favourable arrangement appears to be unique in DTDA chemistry as none of the other 15 *meta*-substituted structures that dimerize *cis*-oid adopt it; rather they have their substituents on the same side, resulting in significant skewing of the rings to minimize steric conflicts. Interestingly, the fifth and sixth monomers in the lattice adopted by **2** have a less-common DTDA dimer orientation known in the literature as “twisted”,¹⁹ where the two CN_2S_2 heterocycles are oriented at approximately right angles (Figure 1c). This twisted geometry was previously reported in ten of the ~ 110 DTDA crystal structures compiled in the Cambridge Structural Database (CSD Version 5.38 updated to February 2017).²⁶ [CSD refcodes: BOZMEJ, DENDAB, HEMZAA, IFULUQ, IFULUQ03, IFULUQ04, JARNAR, JATNEX, NIGZUY, WASHEE; see Table S1 in the ESI].

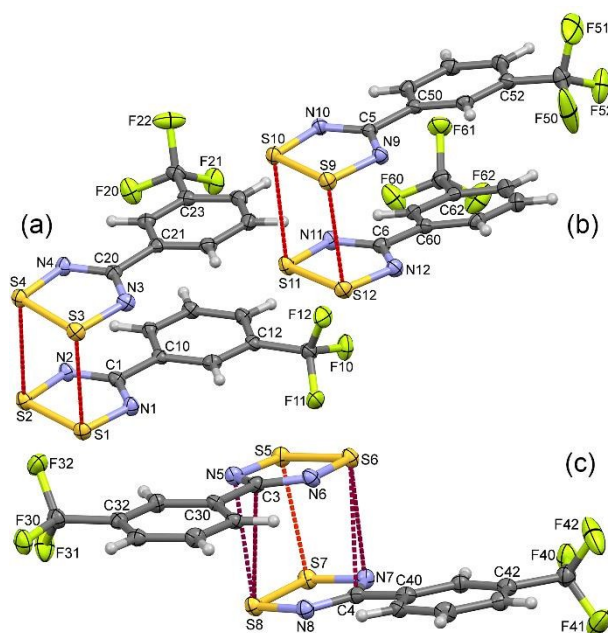


Figure 1. Displacement ellipsoids plot (40% probability) of the three DTDA dimers in the solid-state lattice of **2**. (a) The *cis*-oid S1-S4 dimer with *trans*-displaced 3- CF_3 aryl rings. (b) The similar *cis*-oid S9-S12 dimer. (c) The twisted S5-S8 dimer with *exo*-oriented 3- CF_3 aryl rings. Inter-dimer contacts are shown as dashed lines. The dimers have been oriented to enhance viewing; for views of their actual positions in the lattice see Figures 2 and S1 (in the ESI).

There is nevertheless an appealing similarity in the overall arrangements in the lattices of isomers **1** and **2** (Figures 2 and S1). Whereas the former has *two* independent but almost identical pin-wheel clusters (previously described as a frustration of an ideal tetragonal symmetry, possibly due to the disorder created by CF_3 group repulsions),⁶ the latter shows two *different* kinds of 'molecular squares' of different sizes. One is a pinwheel that is remarkably similar (see Figures S3 – S4 in the ESI) to those in **1**; the other, shown to the right

of the pinwheel in Figure 2, a sort of 'inverted square' resulting from two adjacent twisted dimers linked by π -stacking of the phenyl rings (strictly, this second cluster only has two-fold symmetry). The volume occupied by the structural motifs in **1** and **2** must be almost identical since the normalized cell volumes of the structures of the two isomers differ by only 0.2%. A detailed analysis of intermolecular contacts less than the sums of the van der Waals radii (Σr_{vdw}) in the structure of **2** has been undertaken and is presented in Table S7 in the ESI. They compare closely to similar parameters observed in **1** and other DTDA structures with high Z' values.

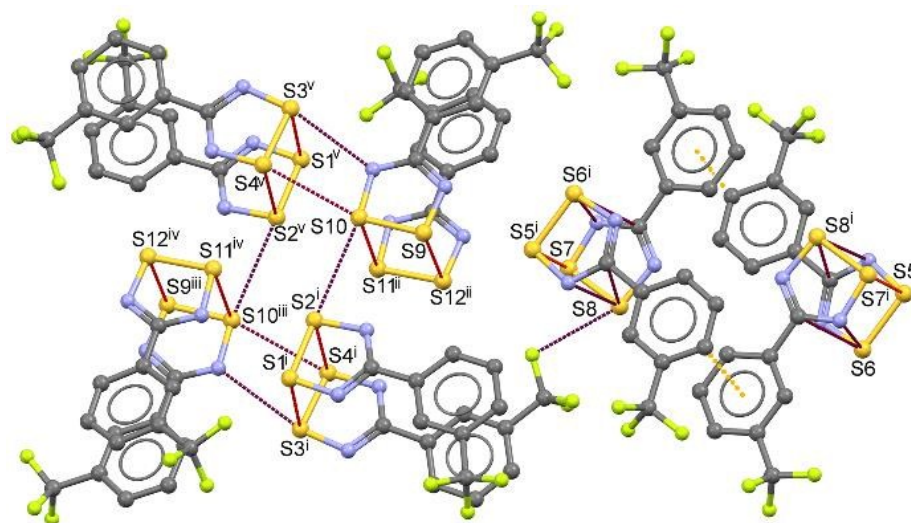


Figure 2. View of the centrosymmetric, pin-wheel clusters found in the lattice of **2** as well as the two rings that dimerize 'twisted' (shown here at the right only) along with a second twisted dimer linked to the former by π -stacking (3.406(7) Å ring centroid to C33). Intermolecular contacts shorter than ($\Sigma r_{vdw} - 0.2$ Å) are indicated with dashed lines and H atoms have been removed to enhance visibility. [Symmetry codes: (i) 1-x,-y,1-z; (ii) 1-x,1-y,1-z, (iii) -x,-y,-z, (iv) -1+x,-1+y,-1+z, (v) -1+x,y,-1+z.]

Identification of 'hexagonal' or 'grey' selenium

During attempts to purify *bis*DSDA **3** by vacuum sublimation, clumps of very small needles were repeatedly observed in the sublimation tubes from which, eventually, crystals of the partly decomposed DSDA rings **4** were also obtained. The identity of the small crystals as elemental selenium was inferred by the absence of infra-red bands and a melting point of $\sim 230^\circ\text{C}$. Recently, by making use of a micro-focus copper source on a powerful new SuperNova diffractometer, the identity of these tiny needles could be determined by crystallography and confirmed to be the hexagonal or "grey" form of elemental selenium (see ESI and Figure S5).²⁷

Table 1. Selected interatomic distances (Å) and angles (°) in the crystal structures of **2**, **4a**, **4b**.

Parameter ^a	2 -i ^b	2 -ii ^c	2 -iii ^d	2 -iv ^e	2 -v ^f	2 -vi ^g
S1–S2	2.0918(15)	2.0933(15)	2.1017(15)	2.0977(14)	2.0870(14)	2.0855(15)
S1–N1	1.621(4)	1.625(4)	1.623(4)	1.626(4)	1.633(4)	1.631(4)
S2–N2	1.650(4)	1.634(4)	1.640(4)	1.629(4)	1.642(4)	1.635(4)
N1–C1	1.322(5)	1.335(6)	1.348(5)	1.356(5)	1.332(5)	1.343(5)
N2–C1	1.341(5)	1.340(5)	1.328(5)	1.324(6)	1.341(5)	1.335(5)
N1–S1–S2	94.05(14)	94.36(14)	94.79(13)	94.55(14)	94.45(14)	94.72(13)
N2–S2–S1	94.62(14)	94.47(14)	94.09(14)	94.25(14)	94.70(14)	94.48(14)
C1–N1–S1	115.4(3)	114.6(3)	113.8(3)	114.0(3)	114.4(3)	114.1(3)
C1–N2–S2	113.0(3)	114.0(3)	114.0(3)	114.9(3)	113.5(3)	114.2(3)
N2–C1–N1	122.9(4)	122.5(4)	123.3(4)	122.3(4)	122.9(4)	122.5(4)
Parameter ^h	4a -i ⁱ	4a -ii ^j	4a -iii ^k	average		average ↓ ^r
Se1–Se2	2.3096(10)	2.3096(9)	2.3183(12)	2.313(4)		2.093(6)
Se1–N1	1.782(4)	1.793(4)	1.779(5)	1.785(6)		1.627(4)
Se2–N2	1.789(4)	1.805(4)	1.767(5)	1.787(16)		1.638(7)
N1–C1	1.328(6)	1.313(6)	1.323(7)	1.321(6)		1.339(11)
N2–C1	1.326(6)	1.335(6)	1.298(7)	1.320(16)		1.335(7)
N1–Se1–Se2	90.56(13)	90.24(13)	90.65(17)	90.48(18)		94.5(2)
N2–Se2–Se1	91.79(14)	91.91(13)	90.03(16)	91.2(8)		94.4(2)
C1–N1–Se1	115.7(3)	116.3(3)	115.6(4)	115.9(3)		114.4(5)
C1–N2–Se2	114.2(4)	113.7(4)	117.3(4)	115.1(16)		113.9(6)
N2–C1–N1	127.7(5)	127.8(5)	126.4(5)	127.3(6)		122.7(3)
Parameter ^l	4b -i ^m	4b -ii ⁿ	4b -iii ^o	4b -iv ^p	4b -v ^q	average
Se1–Se2	2.3347(6)	2.3337(5)	2.3274(5)	2.3360(5)	2.3299(5)	2.332(3)
Se1–N1	1.783(3)	1.781(3)	1.786(3)	1.797(3)	1.792(3)	1.788(6)
Se2–N2	1.760(4)	1.797(3)	1.790(3)	1.797(3)1	1.791(3)	1.787(14)
N1–C1	1.335(5)	1.342(4)	1.341(4)	1.338(4)	1.339(4)	1.339(2)
N2–C1	1.309(5)	1.326(4)	1.338(4)	1.333(4)	1.334(4)	1.328(10)
N1–Se1–Se2	90.50(11)	90.54(9)	90.76(9)	90.09(9)	90.56(9)	90.5(2)
N2–Se2–Se1	89.93(11)	91.49(10)	91.71(9)	92.23(9)	91.85(9)	91.4(8)
C1–N1–Se1	115.9(3)	115.6(2)	115.5(2)	115.4(2)	115.2(2)	115.5(2)
C1–N2–Se2	118.1(3)	114.3(2)	114.4(2)	113.4(2)	114.1(2)	114.9(17)
N2–C1–N1	125.4(4)	128.0(3)	127.7(3)	128.9(3)	128.3(3)	127.7(12)

^a Atom numbering scheme is that of the first DTDA in Figure 1. ^b DTDA i: S1,2. ^c DTDA ii: S3,4. ^d DTDA iii: S5,6. ^e DTDA iv: S7,8. ^f DTDA v: S9,10. ^g DTDA vi: S11,12. ^h Atom numbering scheme is the first DSDA in Figure 4. ⁱ DSDA i: Se1,2. ^j DSDA ii: Se3,4. ^k DSDA iii: Se5,6. ^l Atom numbering scheme is the first DSDA in Figure 5. ^m DSDA i: Se1,2. ⁿ DSDA ii: Se3,4. ^o DSDA iii: Se5,6. ^p DSDA iv: Se7,8. ^q DSDA v: Se9,10. ^r Column 7 reports the average values for the structure of **2** from the first section of the Table.

Single-crystal X-ray diffraction: two high Z' polymorphic forms of a new diselenadiazolyl

The structure of **4a** in $P\bar{1}$ with $Z = 6$ has three DSDA monomers in the asymmetric unit (Figure 3, left). Two of these are combined as a common *cis*-oid face-to-face dimer (Se1–Se4).^{20,28} The ^tBu groups for both of these rings are disordered and were modelled as a two-part rotation in 71:29 (C9) and 60:40 (C21) refined occupancies. Surprisingly and quite unlike what is observed in the case of **2**, the two aryl rings are in a *cis*-orientation which results in severe twisting of the aryl rings of the dimers with respect to the heterocyclic rings,

caused by the proximate ^tBu groups. Nevertheless, the $[-\text{CN}_2\text{Se}_2]_2$ moieties have quite normal structures ($d(\text{Se1}\cdots\text{Se3}) = 3.147(1)$; $d(\text{Se2}\cdots\text{Se4}) = 3.275(1)$ Å). The structure evidently adopts the strongly twisted conformations of the phenyl rings to accommodate the N11 and N12 cyano group contacts to four selenium atoms Se1' – Se4' at distances of 2.963(6) to 3.320(5) Å (see Table S8 in the ESI). Most of these contacts are shorter than those reported recently for 4-NC-C₆F₄CN₂Se₂ (3.04(1) – 3.14(1) Å).²⁰ This behaviour accords with the efficacy of cyano group supramolecular synthons in thiazyl and selenazyl chemistry.^{10,14,15,17,18,20,29-39} There are further surprises in store in this geometrically challenged structure, because the third DSDA ring (Se5,6) is *not* dimerized, the first reported example of this kind for selenium. In DTDA chemistry there are several well-documented examples of monomerized structures, often associated with interesting magnetic properties.^{10,14,15,17,18,37,38} The Se5,6 ring makes short contacts from the two selenium atoms to N4 of the dimeric ring (3.093(5) and 3.175(4) Å); whilst such *orthogonal* interactions are known in DSDA chemistry and can lead to magnetic coupling, the odd-electron count associated with **4a** should prevent adoption of a diamagnetic ground state. Notably, the cyano group of the monomeric DSDA is involved in a short intermolecular contact (through N13) to the cluster of dimers. Nevertheless, in the extended lattice, the grouping of three DSDA rings is doubled centrosymmetrically by sideways $\text{Se}^{\delta+}\cdots\text{N}^{\delta-}$ contacts that link two of the Se1-Se4 dimers together with relatively short contact distances (Figure 4, right). Atom Se5 of the monomer makes an additional contact $d(\text{Se5}\cdots\text{Se3}') = 3.566(1)$ Å to a DSDA dimer in the next unit cell (Figure S6). In all, there are nine different Se $\cdots$ Se and Se $\cdots$ N contacts over the cluster of six DSDA rings that are shorter than ($\Sigma r_{\text{vdW}} - 0.1$ Å) and hence magnetic coupling over the whole lattice may be expected (see Table S8 in the ESI). Within the triclinic unit cells, there are columns containing all the Se,N atoms, surrounded by an insulating zone of aromatic and ^tBu groups (Figure S7 in the ESI).

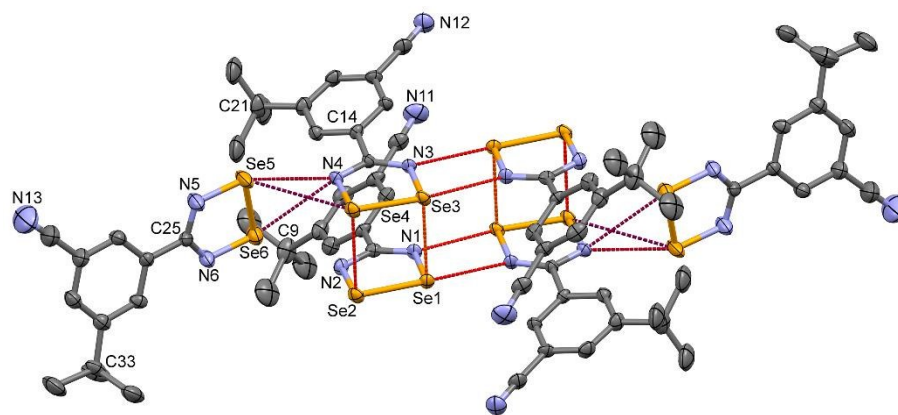


Figure 3. Displacement ellipsoids plot (40% probability) showing the unit cell contents of the solid-state lattice of **4a**. The asymmetric unit, shown at left, has key atoms labeled. H atoms on C and minor components of disordered C9 and C21 ^tBu groups in the *cis*-oid dimers are omitted.

The importance of electrostatic forces in the observed intramolecular interactions in DSDAs has been well-recognized in other reports.²⁰ In order to substantiate the situation in **4a**, we have calculated UB3LYP/6-311+G(2d,p) hybrid DFT NPA atomic charges on the asymmetric unit (a cluster of 3 DSDA rings with a doublet electronic ground state, see Figure S8 and Table S9 in the ESI). There are indeed high partial charges (+0.40) on the Se atoms of the *monomer* and on the N atoms (−0.22, −0.23) of the *dimeric* DSDA rings. By contrast, the cyano group N atoms are considerably less negatively charged in this cluster (−0.15 to −0.16). A more

sophisticated analysis using molecular electrostatic potential maps may provide a deeper insight into these properties.⁴⁰

The asymmetric unit of the $P2_1/c$ polymorph **4b** with $Z = 20$ is shown in Figure 4. The *cis*-oid Se3-Se6 and Se7-Se10 dimers each have the sterically demanding *cis*-orientation of the aryl rings similar to what obtains in **4a** for the Se1-Se4 dimer. Here too, the *cis*-orientation facilitates strong interactions of cyano groups with selenium atoms of neighbouring dimers (N12 to Se3',Se4'; N13 to Se5',Se6'; N14 to Se7',Se8'; N15 to Se9',Se10'; see Table S10 in the ESI). Since the two dimers are also centrosymmetrically paired by sideways electrostatic interactions (Figure 5), the sum of the $\text{Se}^{\delta+} \cdots \delta^- \text{N}$ and $\text{Se}_2^{\delta+} \cdots \delta^- \text{N} \equiv \text{C}-\text{R}$ contacts results in a double-stranded chain along the crystallographic b axis of the lattice (Figures 6 and S8 in the ESI). Interestingly, in both **4a** and **4b**, the intradimer Se $\cdots$ Se are all significantly shorter on the side *away* from the *cis*-disposed *t*Bu groups (so that the heterocycles are not entirely parallel). This may simply be a result of the twisting distortions of the large substituents but, alternatively, the resulting strong intra- and inter-dimer Se and N contacts conceivably could be a driving force for the adoption of these conformations in the crystalline lattice.

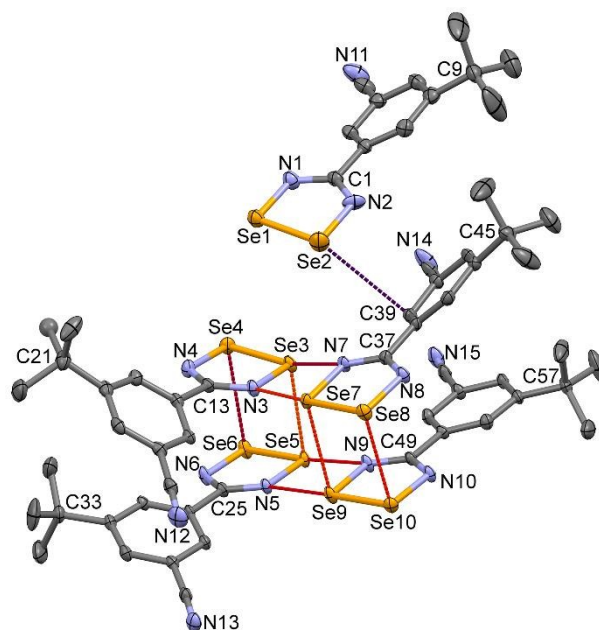


Figure 4. Displacement ellipsoids plot (40% probability) of the two DSDA dimers and the monomer in the asymmetric unit in **4b**, showing important atom labels. H atoms on C and minor components of the C21 *t*Bu group disorder have been omitted. Intermolecular contacts are indicated which are shorter than ($\Sigma r_{\text{vdW}} - 0.35$ Å) except for the weak Se2 $\cdots$ C39 contact at $\Sigma r_{\text{vdW}} - 0.15$ Å.

Most significantly, **4b** also contains the *monomeric* Se1,2 DSDA. This monomer is unaffected by any internal strain and forms relatively unimpeded chains linked, also along the b axis, by nitrile N11 $\cdots$ Se1' contacts, a known motif in a cyano-substituted undimerised DTDA crystal structure [YOMXUT, YOMXUT01-10].^{10,14,15,17,18,37,38} To the best of our knowledge, such a motif has never been observed previously in DSDA structures but is important for possible ferromagnetic coupling. This chain is found in the overall packing of the unit cell to be located above and below two layers of the double-stranded dimer chain (Figure 5 and Figures S9,10 in the ESI). These monomeric chains interact only weakly with the dimer double ribbons because they are out of register and thus the shortest contacts at 3.448(4) Å are between Se2 and aromatic carbon atom C39 (Figure 4). As can

be seen from the partial packing diagram depicted in Figure 5, the structure of **4b** consists of columns of CN_2Se_2 chains linked *via* cyano groups in both types of parallel chains along the *b* axis, with the consequence that the aryl rings and *t*Bu groups are concentrated into layers in the *ab* plane centred on *c* = 0.25, 0.75. The selenazyl-rich zones are therefore found at *c* = 0, 0.5. There is significant similarity in the geometries of the side-by-side dimer-of-dimer moieties found in both structures **4a** and **4b**; however, the positioning and interaction of the monomeric DSDA ring differs in the two structures. In **4a**, where the ratio of monomer to dimer is 1:2, the monomers interact in an end-on fashion with the dimeric pairs (and aggregate into the aforementioned 6-mers). By contrast, in **4b** where the ratio is 1:4, the monomeric DSDA forms these interesting autonomous chains.

A UB3LYP/6-311+G(2d,p) hybrid DFT calculations including NPA charges on a three molecule chain of just the monomeric Se1,2 rings was performed using a quartet ground state. The selenium atoms all develop large partial positive charges (+0.38 to +0.44) and the nitrile N atoms are negative (−0.16 to −0.18, see Figure S12 and Table S11 in the ESI). That these nitrogen charges are again lower than for the ring atoms (−0.21 to −0.24) suggests that dispersion also plays a significant role in strong intermolecular interactions from cyano groups to the selenium atoms of a DSDA moiety.

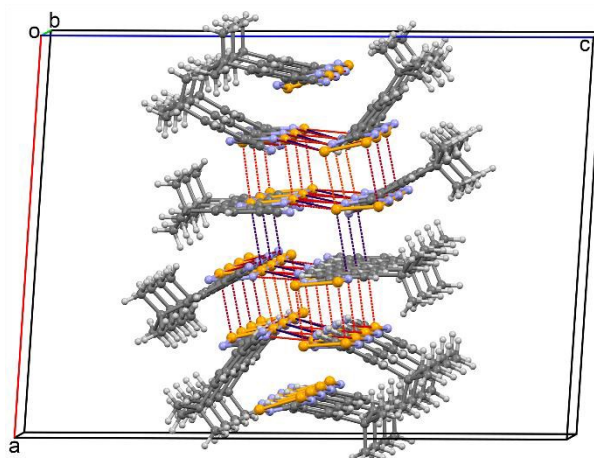


Figure 5. A view down the unit cell *b* axis in an expanded chain representation of the crystal structure of **4b**. In the middle are located two double-layer ribbons of dimers, while at the top and bottom are the out-of-register monomer chains that have no short contacts to Se or N atoms in the double-layer ribbons.

The structures of **4** in the α and β polymorphs (**4a** and **4b**) contrast strongly to that of its sulfur analogue (refcode: SEKDU1) which crystallizes with $Z' = 1$ but with the DTDA rings in the rare *trans*-cofacial orientation which *inter alia* facilitates the cyano group $\text{S}^{\delta+} \cdots \text{N}^{\delta-}$ cross contacts.^{35,36} This leads to a much more benign overall geometry, with little of the severe straining of the *cis*-oid arrangement of the heavily substituted aromatic rings observed in the structures of **4a** and **4b**. This structure also segregates into lipophilic and chalcogen-nitrogen rich regions in the crystal lattice as do both polymorphs of **4**.

A survey of Z' in DTDA and DSDA crystal structures

As mentioned in the Introduction, the occurrence of DTDA and DSDA with very high Z' structures has been recognized but, apparently, the overall incidence of $Z' > 1$ has not been evaluated for this class of compound.^{1,4} This prompted us to undertake a review of Z' values for known DTDA and DSDA crystal structures, recognizing

that, taken together, their number is now quite large (> 100) and perhaps of statistical significance. We have reviewed all structures known to us or reported in the CSD and produced carefully curated lists which are provided in Tables S1 and S2 of the ESI. First, the very definition of Z' is likely to be controversial for DTDA/DSDA species and the CSD is not entirely consistent. For the vast majority of entries, the CSD considers the *monomeric radical* as the chemical entity defining Z , which we consider the correct viewpoint, but exceptions exist where the diamagnetic dimers are taken as the chemical entity. For consistency, our compilation has treated *all* entries based on counting the monomer and the contradictory Z values in the CSD are overruled. This is the viewpoint adopted by Brock in a recent comprehensive examination of all known crystal structures with $Z' > 4$ and is defended on the basis that the dimerization energy⁴¹ of a typical DTDA of $\sim 35 \text{ kJ mol}^{-1}$ is comparable to that of carboxylic acid dimers, for which monomers are taken as the chemical entity.⁴ The variable patterns of DTDA/DSDA dimerization was also cited as a reason to base the compilation on monomers.⁴ Five major modes of dimerization have been recognized in DTDAs (*cis*-oid, *trans*-cofacial, *trans*-antarafacial, twisted and orthogonal)¹⁹ and a second kind of orthogonal interaction, rotated by 90° from the geometry for sulfur, was recently recognized in DSDAs.²⁰

It was necessary to review the CSD entries cautiously, since a given six-character refcode is most commonly assigned to one chemical species and multiple *reports* on those species are numerically incremented as REFCOD01, REFCOD02, etc. The increments may refer to a second publication of the *same* dataset, to repeated measurements on the same polymorph, to different polymorphs of the same structures, or to corrections to an erroneous structure report. The latter are particularly important to this analysis as the corrections may alter the value of Z' .¹ Two corrections of this type due to missed superlattices are included in our review set: MEJZIL vs. MEJZIL01⁴² and NIBAH vs NIBAH01.^{43,44} It is certainly possible that some other entries in our compilation suffer from such mistakes but the intense scrutiny that DTDA/DSDA structures receive from the focus on crystal engineering helps to keep unrecognized mistakes rare.

Table 2. Frequency of Z' values for DTDA and DSDA neutral radical crystal structures^a

Z'	No. DTDA	% DTDA	No. DSDA	% DSDA	No. combined	% combined
0.5	5	6.0	0	0.0	5	4.7
1	23	27.7	3	12.5	26	24.3
2	34	41.0	16	66.7	50	47.7
3	0	0.0	2	8.3	2	1.9
4	13	15.7	1	4.2	14	13.1
5	0	0.0	1	4.2	1	0.9
6	3	3.6	0	0.0	3	2.8
8	4	4.8	1	4.2	5	4.7
12	1	1.2	0	0.0	1	0.9
totals:	83	100	24	100	107	100

^a Data taken from this work and the CSD (release 5.38 updated to Feb 2017). A full listing is provided in Tables S1 and S2, ESI, showing the methodology used and providing details of the structural types and full literature citations.

The data in Tables S1 and S2 have further been scrutinized to remove oxidized species (i.e. those that form salts with coordinating (e.g. Cl^-) or weakly-coordinating (e.g. SbF_6^-) anions) as well as numerous examples of *partial* oxidation in "charge-transfer" complexes, of which there are many examples from the work on molecular conductors.⁴⁵⁻⁴⁷ Finally, there is an emerging small group of DTDA co-crystal structures where the

hosts can be aromatic rings⁶ or small molecules.^{47,48} Since these are small in number and also since the guest molecules are sometimes overlooked, they have been included in Table S1 *but are not counted in the Z' statistics*. The modes of dimerization (see above) are noted in the descriptions of the asymmetric units in Tables S1 and S2. A further complexity in this discussion is that a single molecule can have one (radical), two (biradical) or three (triradical) DTDA/DSDA moieties (indicated by "No. of rings per monomer" in Tables S1/S2). Beyond noting this feature, no further distinction has been made for the purpose of Z' analysis.

A summary of the Z' data compiled from the curated lists is reported in Table 2 and the results are dramatic. The vast majority have Z' > 1 (66% of DTDA and 88% of DSDAs) against an average across the CSD of ~7% in 1965 increasing to ~10% in 2014, and also much higher than the 2014 frequency for organic molecules with Z' > 1 of ~16%.¹ Even if the potentially controversial choice of monomers as the counting unit is set aside, which directly accounts for the 42% of DTDA and 67% of DSDAs with Z' = 2, the incidence of Z' ≥ 3 (25% and 21%, respectively) is off the scale against the CSD average for organic structures of 1.24%.¹

Origins of high Z' structural tendencies in DTDA and DSDA species

It is becoming well-recognized that there are many contributing factors for the adoption of structures with high Z' and specifically that these are not necessarily cases of frustrated crystallization or metastable states.⁵ A number of contributing factors have been examined and are carefully described in the reviews and compilations of Steed and Steed¹ and Brock.⁴ How do these explanations fit for the DSDA/DTDA family?

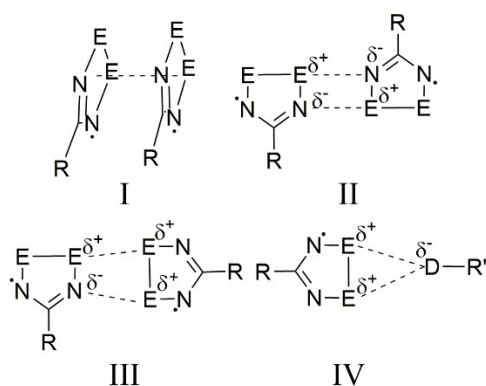
First of all, many DTDA/DSDAs are small, symmetrical molecules and thus there *are* cases where Z' < 1 although far fewer than might be expected from their molecular shapes. Interestingly, the five known examples (refcodes: CUQBUN, HAKYOI, ILUKU, POYXAC and YOMXUT) are all found as monomeric radicals in the lattice, the rare and extremely sought-after targets in this field of research (The overall structure of CUQBUN is a stack of dimers but evenly spaced;¹¹ it may be compared to the behaviour observed in POYXAC¹⁶). Of the 23 DSDA/DTDA in the lists for which Z' = 1, only three are monomeric in the lattice and the remaining twenty are (diamagnetic) dimers, showing that the e⁻—e⁻ pairing driving force does not *require* the asymmetric unit to be a dimer. Thus, many of the *vast majority* of DSDA/DTDA with Z' > 1 probably fit the category of having 'wasted' molecular symmetry opportunities in their solid-state lattices.¹ In other words, their intrinsic shapes are compatible with crystallizing either as monomers in the asymmetric unit or even with higher site symmetry (mirrors or two-fold rotation.) Efforts to overcome this tendency may help crystal engineers realize more of the desired structures that retain monomeric radicals in the lattice.

Of the factors that are often used to explain high Z', the following appeared to us most likely to apply to DTDA/DSDAs: (i) the presence of strong directional inter-molecular bonding, especially where there are competing demands of more than one intermolecular synthon, (ii) awkwardness of molecule shape, (iii) a tendency to have smaller-than-average sizes, and (iv) crystallization methods. Considering these factors in reverse order, Nangia *et al.* have reviewed the contribution of sublimation to structures with Z' ≥ 3 for 334 organic molecules prepared by sublimation and found the frequency to be 3.89% (compared to the CSD average of 1.24%).⁴⁹ This may be very significant since a very large number of the crystals for structures included in Tables S1/S2 are reported to have been grown by sublimation. Interestingly, Nangia *et al.* attributed the high incidence of Z' ≥ 3 to the *rapid cooling* that sublimates face when impinged on a cold-finger.⁴⁹ DSDA/DTDA crystals, however, are most often formed by very slow, controlled gradient sublimation processes

pioneered by Oakley²⁹ and widely adopted by workers in the field, so if sublimation plays a role the cause is not likely to be rapid cooling.

Awkward shape is no doubt a contributing factor, as seen *inter alia* in the distortions of the molecular shapes caused by bulky 4-CF₃ groups in the structure of **1**,⁶ as well as in the extraordinarily distorted aryl ring conformations encountered in **4a** and **4b** (see above). However, a polymorph of **1** is known with $Z' = 2$ and the sulfur analogue to **4** crystallizes (refcode: SEKDUI) with $Z' = 1$, as previously mentioned.^{35,36} Could it therefore be that DSDAs have a stronger 'pancake bonding' driving force for *cis*-oid dimerization than DTDAs, given that SEKDUI forms a *trans*-cofacial dimer? Exactly such a claim has been made in a recent paper.²⁰ Thus awkward shapes likely play a role but are probably not a dominant factor.

It has been noted that organic structures with $Z' > 1$ have slightly smaller unit cell volumes (by 50 Å³) than those with $Z' = 1$.¹ Firstly, of the 97 *different compounds* compiled in Tables S1/S2, only eight have polymorphic forms, and of these only two DTDAs have polymorphs including both $Z' = 1$ and higher variants. In one case, PAHRIZ ($Z' = 2$) has a cell that is 1.4% *larger* than PAHRIZ01 ($Z' = 1$) – both datasets taken at 295 K.³² In the IFOLUQ series, three of the four low-temperature $Z' > 1$ structure determinations have larger volumes than the sole exemplar with $Z' = 1$.⁵⁰⁻⁵² These are obviously too few to draw statistically meaningful conclusions, but the available examples suggest that molecular volume does not play the role for these compounds that it does for general organic structures.



Scheme 2. Limiting Intermolecular Synthons (LIMS) in DTDA/DSDAs

Competing intermolecular synthons are likely to be a very strong factor for the DTSA/DSDA series.^{19,20} The role of the $e^- - e^-$ pairing driving force in dimerization is well-recognized, and has been quantitatively assessed computationally and described by 'pancake bonding';^{7,8} these investigations show that the interaction is maximized in *cis*-oid dimerization. We consider this mode to be the *limiting* (or idealized) inter-molecular synthon I (LIMS-I) for pancake bonding (Scheme 2). Significantly, $e^- - e^-$ pairing can operate even when pancake bonding is frustrated as in the case of *trans*-antarafacial dimerization, which we therefore consider to be a general, or non-ideal, variant of the same synthon.¹⁹ In addition, most thiazyl and selenazyl compounds show propensity for electrostatic interactions due to the significant E—N bond polarity. Across chalcogen-nitrogen structural chemistry, the most common interaction between such bonds is a side-by-side orientation that is more in-plane than orthogonal, which we thus designate as LIMS-II. Previously, Bond and Haynes have considered *polymorphism* in DTDA structures and, in addition to the various modes of pancake bonding, introduced an additional classification of electrostatic contacts; LIMS-II here corresponds closely to the "SN-II", i.e. sulfur to nitrogen type II, interaction in their scheme for DTDAs.^{19,49} We suggest that Scheme 2 may be

helpful as an alternative, simpler, approach for considering all the different intermolecular synthons that affect DTDA/DSDA lattices, and the competition between them. The LIMS-II interaction, thought to be dominated by electrostatic effects, is so common that it must always be considered.^{40,53} In the 'twisted' and *trans*-cofacial dimerizations of DTDA/DSDA radicals, $e^-—e^-$ pairing and dipolar effects are co-mixed, which can either be considered as additional synthons, or as admixtures of LIMS-I with LIMS-II. Also commonly observed are sideways interactions between an S—N and an S—S bond, here designated as LIMS-III ("SN-IV" in the Bond/Haynes analysis).^{19,49} Such an interaction occurs in the pinwheel clusters in **1** and **2** (Figure 2). Since these do not optimize electrostatic interactions, we can surmise considerable contributions from dispersion. Indeed, dispersion is likely to contribute significantly to all intermolecular interactions of DTDA/DSDAs, in view of the polarizability of the chalcogen atoms and the electron-richness of the radical monomers. Additionally, many of the structures listed in Tables S1/S2 in the ESI contain additional, remote, donor groups which interact with chalcogen atoms, designated here as LIMS-IV for the 'ideal' interaction with both chalcogen atoms. This synthon is often introduced *intentionally* in crystal engineering for desired solid-state properties; it may also occur accidentally, as reported in this work by the thermolytic formation of cyano groups leading to crystals of **4a** and **4b** from precursor **3**. Most commonly, donor D is attached in some way to the principal R group (thereby intensifying the competition between synthons) but R' can also describe independent adducts, e.g. in emerging co-crystal structures. Note also that LIMS-IV includes the possibility that the donor atom D is the nitrogen of another DTDA/DSDA ring, which is an observed chain-forming mode in DTDA (this synthon is designated as "SN-I" in the Bond/Haynes classification scheme).^{19,50}

To illustrate the roles of these competing intermolecular synthons, consider the two known polymorphs of 4-[4-(trifluoromethyl)phenyl]-3H-1,2,3,5-dithiadiazol-3-yl, **1** (refcodes: LIXGAB01 and LIXGAB02).^{6,54} In the former, the $Z' = 8$ structure contains two independent, complex, pinwheel structures supported by LIMS-I, -II and -III (Figure S4), whereas the latter $Z' = 2$ structure forms straight chains of *cis*-oid dimers along the [1 0 1] lattice vector with fluorine-to-sulfur as the sole *interdimer* short contacts (Figure S11 in the ESI). In other words, the β -polymorph is supported exclusively by LIMS-I plus LIMS-IV. This results in a 3% higher-density structure for LIXGAB02 compared to LIXGAB01 ($D_c = 1.841$ and 1.783 g cm^{-3} , respectively).

In the extended lattice of **2**, LIMS-I link four of the six rings into *cis*-oid dimers while a (non-ideal) twisted $e^-—e^-$ pairing interaction forms the third dimer. The dimers which form pin-wheel clusters are linked via LIMS-III. LIMS-IV operates between the DTDA sulfur atoms and fluorine atoms of CF_3 groups on neighbouring molecules. However, the common LIMS-II mode is not observed here. By contrast, in **4a** *cis*-oid dimers (LIMS-I) pair up sideways through strong LIMS-II interactions. LIMS-IV links occurs by cyano nitrogen to selenium contacts, as well as in the link between the monomeric Se5,6 ring with the N4 atom belonging to one ring of the *cis*-oid dimer. The very similar central cluster in the lattice of **4b** is similarly a pair of LIMS-I *cis*-oid dimers side-ways linked *via* LIMS-II. LIMS-IV contacts link all the cyano groups to selenium atoms of neighbouring molecules, which occurs both for the double-strand of dimers as well as for the non-dimerized Se1,2 DSDA.

Experimental Details

Full experimental details for the work reported here are provided in the ESI. Crystal and experimental parameters are compiled in Table S3, selected (Table 1) and full (Tables S4 – S6) interatomic parameters are available in the text and the ESI. Full archival structural data have been deposited. Structure depositions: CCDC 1512475-1512478, contain the supplementary crystallographic data for this paper. These data can be obtained,

free of charge, via <http://www.ccdc.cam.ac.uk/products/csd/request/> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

Conclusions

High Z' crystal structures are extremely common for the well-known DTDA radicals and we have added an interesting example of this phenomenon in the case of the *meta*-CF₃ substituted aryl compound **2**. For DSDAs, markedly more difficult to prepare and purify than DTDA, there are far fewer structurally characterized examples. Here we have reported new α and β polymorphs of 3-cyano-5-*tert*butylphenyl DSDA, **4a** and **4b**, which doubles the number of known $Z' \geq 3$ DSDA structures. Both **4a** and **4b** contain heretofore unknown monomeric (i.e. non-dimerized) DSDAs, which may dispel some of the pessimism about discovering true monomers expressed in a recent paper which reported seven new DSDAs that all crystallize as dimers.²⁰ Work in our laboratory is underway that aims to prepare radical **4** by direct synthesis rather than fortuitous thermolysis of **3**. We hope thereby to be able to produce this compound in bulk in order to investigate its transport properties.

Crystallographers may be surprised to learn of the exceptionally high frequency of $Z' > 1$ and especially of $Z' \geq 3$ structures amongst DTDA and DSDAs. We have attempted to classify the different inter-molecular synthons to provide tools for evaluating competing interactions and here propose four *ideal* interaction categories (LIMS) for DTDA/DSDAs, each of which have non-ideal variants. In doing so, we recognize that this is little more than providing names for interaction types that have already been recognized by others but perhaps the competition between them has not been fully appreciated before. All three structures described here have such multiple LIMS and a survey of our curated lists suggests this is also the case for most or all DTDA and DSDA crystal structures. Further research into the role of competing LIMS contributing to the unusual structural diversity in this class of compounds may increase understanding of the general phenomenon of high Z' crystal structures.

Acknowledgements

The Natural Sciences and Engineering Research Council of Canada (NSERC) is gratefully acknowledged for generous support through the Discovery Grants program. The diffractometers were purchased with the help of NSERC (APEX II) and especially the University of Lethbridge (APEX II and SuperNova). The contributions of Richard Beekman and Judy Yip to the synthesis and purification of the compounds described here is gratefully acknowledged.

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High Z' structures of 1,2,3,5-dithiadiazolyls and of 1,2,3,5-diselenadiazolyls containing the first structurally characterized monomeric diselenadiazolyls

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Table S1. Table of Z' in reported DTDA crystal structures (CSD Release 5.38 to Feb 2017)

Refcode	Polymorphic? or comment	No. of rings /mon.	Space Gp. Symbol	Z Value	Z Prime	Assym. Unit (see paper for details)	Year	Ref.
ASODET		1	P21	4	2	cis-oid dimer	2016	1
ASODIX		2	P-1	4	2	monomer $\times 2^1$	2016	1
ASODUJ		1	P21	4	2	cis-oid dimer	2016	1
ASOFAR		1	P-1	4	2	cis-oid dimer	2016	1
ASOFEV		1	P21/n	4	1	monomer 2	2016	1
BOZMEJ		1	C2/c	8	1	monomer 3	2009	2
CIQXUV		2	P21/n	4	1	monomer 4	1999	3
COHJOZ		1	P-1	2	1	monomer 4	2008	4
CUQBUN CUQCAU, 01	Polymorph1 (HT) (repeats at dif. T)..	2	Fdd2	8	0.5	half monomer molec. 6	2015	68
CUQCAU02-08	Polymorph2 (LT) (repeats at dif. T).	2	P21	8	4	cis-oid dimer	2015	68
DENDAB		1	P-1	8	4	twisted dimer $\times 2$	1985	4
DIXMII		1	P21/n	8	2	cis-oid dimer	2014	6
DIXMOO		1	P-1	8	4	cis-oid dimer $\times 2$	2014	6
DIXNAB		1	P21/c	8	2	cis-oid dimer	2014	6
DIXNEF		1	P-1	24	12	cis-oid dimer $\times 6$	2014	6
DOQYUD		1	P21/n	4	1	monomer 4	2000	7
EXIQUY		1	P21	4	2	cis-oid dimer	2011	8
FUWRIZ		1	P21/n	16	4	cis-oid dimer $\times 2$	2010	9
GOTQEL		1	Aba2	8	1	monomer 5	1999	10
HAKYOI		1	C2/c	4	0.5	half monomer molec. 5	2004	11
HAWRAZ	Polymorph 1	1	P-1	8	4	monomer $\times 4^{2,5}$	2005	12
HAWRAZ01	Polymorph 2	1	Pna21	8	2	monomer $\times 2^5$	2005	12
HEMZAA		1	C2	4	1	monomer 3	1994	13
IFULUQ	Polymorph 1	1	P21/c	16	4	monomer $\times 2$ + dimer 3	2002	14
IFULUQ01	Polymorph 2	1	P21/n	8	2	cis-oid dimer	2002	14
IFULUQ02	Polymorph 3	1	P21/c	32	8	cis-oid dimer $\times 4$	2002	14
IFULUQ03	Polymorph 4	1	P-1	8	4	twisted dimer $\times 2$	2004	15
IFULUQ04	Polymorph 5	1	C2/c	8	1	monomer 3	2005	16
ILUKIJ		1	P41212	4	0.5	half monomer molec. 5	2003	17
JARNAR		1	P-1	4	2	twisted dimer	1989	18
JATNEX		1	P-1	16	8	twisted dimer $\times 4$	1989	19
JEFRIW		1	P21/c	4	1	monomer 6	2006	20
KUFDUK		3	P21/c	8	2	cis-oid dimer	1992	21
KUNXEW		2	Pna21	8	2	cis-oid dimer	1992	22
KUNXIA		1	P21/n	8	2	cis-oid dimer	1992	22
LAJRET		3	C2/c	8	1	monomer 1	1993	23
LEJDUZ	Co-crystal	(omitted)	P-1	12	6	(cis-oid dimer $\times 3$ + N $_2$)	1994	24
LELPOJ		1	C2/c	16	2	cis-oid dimer	2013	25
LELPUP		1	P21	4	2	cis-oid dimer	2013	25
LELQAW		1	P21/c	32	8	cis-oid dimer $\times 4$	2013	25
LIXGAB LIXGAB01	Polymorph 1 (same)	1	P-1	16	8	dimer $\times 2$ + monomer $\times 4^1$	2008 2016	26 27
LIXGAB02	Polymorph 2	1	P21/c	8	2	cis-oid dimer	2016	1
MEJZIL MEJZIL01 MEJZIL02	Missed supercell. Correct lattice (same as 01)	1	P-1	8	4	cis-oid dimer $\times 2$	2003 2011 2014	28 29 6
NIGZUY		1	P-1	4	2	twisted dimer	1997	30
NIHBAH NIHBAH01	Wrong SG Correct SG	1	P42/n I41/a	8 32	2	cis-oid dimer	1997 2000	31 30
OLOFOL		1	Pc	8	4	dimer + monomer $\times 2^6$	2011	29
PAHRAR		1	P-1	4	2	cis-oid dimer	1992	32
PAHRIZ	Polymorph 1	1	P21/n	8	2	cis-oid dimer	1992	32
PAHRIZ01	Polymorph 2	1	P21/n	4	1	monomer 2	1992	32

PESGOJ		1	P21/n	24	6	<i>cis</i> -oid dimer × 12	1993	33
PHTHAZ	(repeat) (repeat) ⁷	1	P212121	16	4	<i>cis</i> -oid dimer × 2	1980	34
PHTHAZ01							2009	35
PHTHAZ02							2014	36
PIZDOR	S.O.R ⁷ Misreported ⁸	2	P21/c	4	1	monomer ¹	1994	37
PIZDOR10			P21/c	2			1994	38
POYXAC		2	I-42m	8	0.5	half monomer molec. ⁶	1998	39
QEFGIT		1	P21/n	8	2	<i>cis</i> -oid dimer	2012	40
QEFGOZ		1	P21/c	16	4	<i>cis</i> -oid dimer × 2	2012	40
QUNQOG	(repeat) (repeat)	1	C2/c	8	1	monomer ¹	2009	35
QUNQOG01							2014	36
QUNQOG02							2016	41
QUNQUM	Mixed dimer (same)	1	P21/c	4	1	<i>cis</i> -oid dimer	2009	35
QUNQUM01							2014	36
RELKUO		2	P21/n	4	1	monomer ¹	1996	42
RELLAV		2	P21/n	4	1	monomer ¹	1996	42
ROSKEP		1	P21/n	8	2	<i>cis</i> -oid dimer	1999	43
SAGMOD		1	P-4	8	2	<i>cis</i> -oid dimer	2004	44
SEKDUI	(same)	1	Pbca	8	1	monomer ⁴	2006	45
SEKDUI01							2007	46
SOBSOR		2	I41/a	32	2	<i>cis</i> -oid dimer	1991	47
UJETAG	Co-crystal	(omitted)	P-1	2	2	(<i>cis</i> -oid dimer+Ph ₃ Sb)	2016	27
UMAROP		1	P-1	8	4	<i>cis</i> -oid dimer × 4	2003	48
UMARUV	Co-crystal	(omitted)	Pbcn	16	2	(<i>cis</i> -oid dimer+N ₂)	2003	48
UMASAC	Co-crystal	(omitted)	Pbcn	16	2	(<i>cis</i> -oid dimer+CO ₂)	2003	48
UMASEG	Co-crystal	(omitted)	Pbcn	16	2	(<i>cis</i> -oid dimer+Ar)	2003	48
UMASIK	Co-crystal	(omitted)	Pbcn	16	2	(<i>cis</i> -oid dimer+SO ₂)	2003	48
VINJIL		2	P21/n	4	1	monomer ¹	1991	49
VUQGIY		1	P21/n	8	2	<i>cis</i> -oid dimer	2010	50
VUQGOE		1	P-1	8	4	<i>cis</i> -oid dimer × 2	2010	50
VUQGUK		1	I41/a	32	2	<i>cis</i> -oid dimer	2010	50
VUQHAR		1	P21/c	24	6	<i>cis</i> -oid dimer × 3	2010	50
VUQHEV		1	P-1	4	2	<i>cis</i> -oid dimer	2010	50
VUXZEU	Polymorph 1	1	P21/c	8	2	monomer × 2 ^{2,5}	2010	51
VUXZEU01	Polymorph 2	1	P21/c	8	2	<i>cis</i> -oid dimer	2010	50
VUXZEU02	Polymorph 3	1	I41/a	32	2	<i>cis</i> -oid dimer	2010	50
WALCOC	Mixed dimer (same)	2	P21/n	4	1	monomer ⁶	2005	52
WALCOC01							2007	53
WASHAA		1	P21/n	8	2	<i>cis</i> -oid dimer	2005	16
WASHEE		1	C2/c	8	1	monomer ³	2005	16
WIMNAH	(same)	1	C2/c	16	2	<i>cis</i> -oid dimer	1994	54
WIMNAH01							2016	55
WUXPAG		1	C2/c	8	1	monomer ¹	2002	56
YAXVUO		2	P21/c	8	2	<i>cis</i> -oid dimer	1993	57
YIMNIT	Mixed dimer	1	Pcab	16	2	<i>cis</i> -oid dimer	2013	58
YOMXUT	Polymorph 1 (same)	1	P-1	2	1	monomer ⁵	1995	59
YOMXUT08-10							2016	60
YOMXUT01	Polymorph 2 (repeats) (pressure study)	1	Fdd2	8	0.5	half monomer molec. ⁵	1996	61
YOMXUT02							2010	62
YOMXUT03-07							2012	63
ZADVAB	(same)		I2/a				1995	64
ZADVAB01	Better SG	1	C2/c	8	1	monomer ⁵	2016	41
2 1512475		1	P-1	12	6	dimer + monomer × 4 ^{1,3}	2017	65

Total			Analysis					
Z' =	No.	% of total	Z' =	No.	% of total	Z' =	No.	% of total
0.5	5	6.0 %	1	23	27.7 %	2	34	41.0 %
4	13	15.7 %	6	3	3.6 %	8	4	4.8 %
12	1	1.2 %	> 1	55	66.3 %	> 4	8	9.6 %

¹ Combine to *cis*-oid dimer in lattice. ² Combine to *trans*-antiarafacial dimer. ³ Combine to twisted dimer. ⁴ Combine to *trans*-cofacial dimer. ⁵ Monomeric in lattice. ⁶ Complex, see original data. ⁷ S.O.R. = Structure of Record. ⁸ A correction has been entered in the CSD (S. Holgate, Private Communication.)

Explanation of the Method Used in Tables S1 and S2

There is considerable ambiguity in the selection of the data. First of all, the majority of the Z' data is taken directly from the CSD, which treats the majority of these systems by the *number of monomeric DTDA/DSDA molecules in the asymmetric unit*. This is also the approach taken by C. P. Brock, who has treated the DTDA/DSDA examples with $Z' > 4$ known to her at the time (there are several more now) in her ground-breaking analysis.⁶⁶ Brock argues that a DTDA dimer is energetically similar to a hydrogen-bonded carboxylic acid dimer, and *those* are considered to have $Z' = 2$. This was applied also to the few examples where the CSD treats DTDA/DSDA molecules as *dimers*, and here we have re-interpreted these as monomers like all the rest (JARNAR, LEJDUZ, PESGOJ, JEFBIF, YAGLIB, ZEXVON). That this is somewhat arbitrary is evident from the *mixed dimers* QUNQUM, WALCOC and YIMNIT, where two different DTDAs join in the lattice in a dimer. These exceptional cases have been treated here as dimeric entities and thus have a lower Z' but they *do* form by combination of monomers during crystallization.

Also, unlike studies focused merely on the Z' number, in our collection all examples that are (i) co-crystals with a guest molecule, (ii) partially- or (iii) entirely oxidized to salt-like molecules have been excluded, since the focus here is on the neutral DTDA and DSDA molecules which are sought after for their solid-state electronic properties in cases where they *do not* dimerize in the solid state, leading to odd-electron states. The salt-like species have not been listed at all whereas the co-crystals, which seem to interact only weakly with adducts, have been listed but have been omitted from the counting and from the statistics.

Compared to the overall frequency of $Z' > 1$ structures ($\sim 7\%$ in 1965 increasing to $\sim 10\%$ in 2014),² it is clear that pure neutral DTDA and DSDA crystals *vastly* exceed the averages: 66.7 % and 85.7 %, respectively, exceeding by a huge margin even the higher Z' frequency for organic molecules of $\sim 16\%$. Even if the 'dimer' phenomenon is discounted, the values for $Z' > 4$ for our samples (9.6 % and 8.4 %, respectively) is off the scale against the CSD average of 0.07 %!⁶⁷

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Table S2. Table of Z' in reported DSDA crystal structures (CSD Release 5.38 to Feb 2017)

Refcode	Polymorphic? or comment	No. of rings /mon.	Space Gp. Symbol	Z Value	Z Prime	Assym. Unit	Year	Ref.
BARWUO		1	P21/c	4	1	monomer ¹	2012	1
JEFBIF		1	Pbca	16	2	cis-oid dimer	1989	2
PAHREV		1	P-1	4	2	cis-oid dimer	1992	3
PAHROF		1	P21/n	8	2	cis-oid dimer	1992	3
PAHRUL		1	P21	4	2	cis-oid dimer	1992	3
SOBSUX	Polymorph 1	2	I41/a	32	2	cis-oid dimer	1991	4
SOBSUX01	Polymorph 2	2	P21/n	8	2	cis-oid dimer	1992	5
VINJOR		2	P21/n	4	1	monomer ²	1991	6
WAJGUJ		1	P-1	4	2	cis-oid dimer	1993	7
WERQEP		1	P21	4	2	cis-oid dimer	2000	8
WIMNEL	(same)						1994	9
WIMNEL10	S.O.R. ⁵		P21/n	8	2	cis-oid dimer	1995	10
XEHTIN		1	P21/c	8	2	dimer (orthog)	2000	11
XEHTOT	(repeated)						2000	11
XEHTOT01	S.O.R. ⁵	1	Pca21	8	2	dimer (orthog)	2016	12
YAGLIB		1	P-1	4	2	cis-oid dimer	1992	13
YAXWAV		2	P21/c	8	2	cis-oid dimer	1993	14
YIFHUQ		1	P21	16	8	cis-oid dimer × 4	2001	15
ZEXVON		1	P-1	8	4	twisted dimer × 2	1995	16
UBOHOL		1	I2/a	8	1	monomer ²	2016	12
UBOHUR		1	P-1	4	2	cis-oid dimer	2016	12
UBOJED		1	P-1	4	2	cis-oid dimer	2016	12
UBOJIH		1	P-1	4	2	cis-oid dimer	2016	12
UBOJON		1	P-1	6	3	monomer × 3 ³	2016	12
4a 1512476		1	P-1	6	3	cis-oid dimer + mon. ⁴	2017	17
4b 1512477		1	P21/c	20	5	cis-oid dimer × 2 + mon. ⁴	2017	17

Total	24		Analysis					
Z' =	No.	% of total	Z' =	No.	% of total	Z' =	No.	% of total
0.5	0	0 %	1	3	12.5 %	2	16	66.7 %
3	2	8.3 %	4	1	4.2 %	5	1	4.2 %
8	1	4.2 %	> 1	21	87.6 %	> 4	2	8.4 %

¹ Combine to form *trans*-cofacial dimer in the lattice. ² Combine to form *cis*-oid dimer. ³ Combine to *trans*-antarafacial dimers. ⁴ Monomeric in lattice. ⁵ Structure of record.

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Full Experimental Details

General

5-*tert*-Butylisophthalic acid, selenium powder, 1,1,1,3,3,3-hexamethyl disilazane, *n*-butyllithium, selenium powder, ammonium hydroxide, chlorotrimethylsilane, nitrosonium hexafluoroantimonate, and triphenylantimony were all obtained commercially (Aldrich). Lithium bis(trimethylsilyl)amide diethyl etherate. was prepared as described previously.¹ Acetonitrile (Fisher HPLC grade) was distilled over phosphorous pentoxide before use, toluene over sodium metal. 4-[3-(Trifluoromethyl)phenyl]-3H-1,2,3,5-dithiadiazol-3-yl, **2**, was prepared as previously reported,² [CJC1993] as was 5-*t*Bu-1,3-DIBADS.³ All reactions were performed under an atmosphere of dry nitrogen using modified Schlenk techniques or a nitrogen-filled glove box. NMR spectra were acquired at 250.13 (¹H) and 62.90 (¹³C) MHz on a Bruker AC250-F spectrometer and referenced to CHCl₃ at 7.25 (¹H) or CDCl₃ at 77 ppm (¹³C). Infrared spectra (KBr pellets 4000-450 cm⁻¹, nujol mulls CsI optics 4000-200 cm⁻¹) were obtained on a Bomen MB102 instrument. Elemental analyses were performed by MHW laboratories, Phoenix, AZ.

Preparation of SeCl₂

Chlorine gas (excess) was first flushed through a 250-mL side arm flask equipped with a magnetic stirring bar and selenium powder (2.00 g, 25.3 mmol), then the stopper was placed and the Cl₂ was condensed by cooling the flask with dry ice / ethanol. The stir bar was activated for approximately one minute to complete reaction, coolant removed, and excess Cl₂ flushed out with an N₂ stream. Acetonitrile (125 mL) was added after which additional Se (2.00 g, 25.3 mmol) was added to the stirred suspension, resulting in immediate change from light yellow (SeCl₄) to deep brown. Care was taken to insure that all the SeCl₄ had been converted into SeCl₂ before use. The crude product was used without purification in the next steps; yield 7.59 g, approximating 100%.

Preparation of 5-*t*Bu-1,3-(Se₂N₂C)₂-C₆H₃, **3**

To a solution of SeCl₂ (7.59 g, 50.7 mmol) in 125 mL of acetonitrile was added 5-*t*Bu-1,3-DIBADS (8.25 g, 12.7 mmol) after which the solution was refluxed for 2 hours. A brick red precipitate in a dark solution indicated that crude 5-*t*Bu-1,3-[(Se₂N₂C)C₆H₃(CN₂Se₂)]₂⁺2Cl⁻ had formed. This suspension was reacted with triphenylantimony (4.47 g, 12.7 mmol) and refluxed, with stirring, overnight. The cooled mixture was filtered and dried *in vacuo*, yield 7.0 g, 13.3 mmol, 105 %, mp 225-231°C. IR (KBr pellet): 2959 (m), 2365 (w), 2344 (w),

1674 (s), 1593 (m), 1364 (s), 1300 (vs), 1256 (vs), 1154 (w) 959 (w), 895 (m), 824 (m), 735 (vs), 700 (s), 419 (sh) cm^{-1} . All attempts to purify **3** by oil-vacuum sublimation employing a sophisticated three-zone tube furnace so far have resulted in partial thermal decomposition to afford Se_∞ , α - and β -3-NC-5- t Bu-C₆H₃-(CN₂Se₂)₂, **4a** and **4b**, all of which have been characterized by single-crystal X-ray diffraction (see below).

Preparation of [5- t Bu-1,3-(Se₂N₂C)₂-C₆H₃][SbF₆]₂, **5**

NOSbF₆ (0.89 g, 3.34 mmol) and 5- t Bu-1,3-[(Se₂N₂C)C₆H₃(CN₂Se₂)]₂+2Cl⁻ were added to a 250-mL side-arm flask in the glovebox to avoid hydrolysis. Acetonitrile (5 mL) was added under a counter flow of N₂ and the mixture refluxed using an air-condenser with an N₂ stream over the opening connected to an oil-bubbler to assist in driving off NOCl(g). After cooling and settling, the solvent was removed to a clean flask, layered with 60 mL of CH₂Cl₂ and cooled to -30°C to afford dark red crystals. Analysis for C₁₂H₁₂F₁₂N₄Sb₂Se₄: Calc. C, 14.42; H, 1.21; N, 5.61 %. Found C 14.40; H, 1.23 %; N 5.82%. MP 295-298°C, but dec. > 260°C. IR (nujol, CsI): 2319 (w), 2263 (w), 1688 (w), 1591 (w), 1460 (s), 1377 (s), 1327 (s), 1223 (m), 1022 (w), 926 (w), 903 (w), 839 (w), 804 (m), 760 (m), 720 (m), 662 (vs), 463 (w), 287 (vs) cm^{-1} . The infrared spectrum has dominant bands at 662 (vs) and 287 (vs) cm^{-1} , which fit very well with literature reports for e.g. KSbF₆ (ν_3 = 665; ν_5 = 288 cm^{-1}).⁴ The vibrational spectroscopy is therefore consistent with a successful introduction of the SbF₆⁻ counterions.

X-ray Crystallography

An extremely thin, violet-brown, plate corresponding to **2** was selected, coated in Paratone™ oil, mounted on a MiTeGen loop and cooled to 100(1) K on the goniometer of a Rigaku-Oxford Diffraction SuperNova/Pilatus200K diffractometer. Data was collected using Cu K α radiation (λ = 1.54184 Å) from a micro-focus sealed tube. The images were integrated and the data processed using CrysAlisPro 1.171.38.43, corrected for absorption, solved with SHELXT, and refined using SHELXL-2014 within the Olex2 suite of programs without any complications and no obvious disorder for any of the F atoms of the CF₃ groups. (This is a significant contrast to the experience with the structure of **1**, which is multiply disordered.)⁵ In the same way, the structure of Se_∞ was determined from a tiny black needle. Although the absorption coefficient for Cu radiation is high (39.3 mm⁻¹), sufficient diffraction intensity could not be obtained with Mo radiation. The resulting structure is of excellent quality and provided the first confirmation of the identity of the "mystery" crystals as grey selenium. Unlike rhombic and monoclinic sulfur, selenium is not currently in the CSD and hence it was not identified using CellCheckCSD during initial screening of the crystals. A very thin brown plate of **4a** was mounted on the end of a thin glass capillary and cooled on the goniometer head to 173(2) K with the Bruker low-temperature accessory. A full hemisphere of data was collected on a Bruker APEX-II diffractometer using Mo K α radiation (λ = 0.71073 Å) controlled by APEX2 software.⁶ A multi-scan absorption correction (SADABS)⁵ was applied to the data, scaled and corrected for polarization (SAINT-Plus),⁶ whereafter the structure was solved with SHELXT⁷ and refined using SHELXL-2014.⁸ H atoms attached to carbon were observed in a fine-focused Fourier map and were treated as riding on their attached aromatic carbon atoms with C-H = 0.95 Å and $U_{\text{iso}} = 1.2U_{\text{eq}}(\text{C})$ for the purpose of model refinement. Typical rotational disorder was encountered for the t Bu groups on two of the three independent molecules in the asymmetric unit. A two-part disorder model was applied. Isotropic refinement converged to occupancies of 0.71:0.29 for the major and minor components of carbons attached to C9, and to 0.60:0.40 for those on C21. These occupancies were then frozen and anisotropic refinement was undertaken using EADP to afford a stable model. A small green-brown block corresponding to **4b** was broken off a cluster of crystals and data was collected as for **4a** using Mo radiation and the structure determined in like manner. There are five independent molecules in the asymmetric unit and *one* of these is found to have a severely disordered t Bu group, for the carbons attached to C21. A two-part rotational disorder model was

developed. Isotropic refinements led to close to 50:50 occupancy, which were then frozen at this level. Despite using EADP and ISOR restraints, the C22/C22A component went highly oblate and therefore these two atoms alone were refined isotropically. Crystal and experimental parameters are compiled in Table S3, and selected interatomic distances are available in Table 1. Comprehensive distances and angle data are provided for the structures of **2**, **4a** and **4b** in Tables S4 – S6, respectively. The simplicity of the Se_∞ geometry does not require a distances/angle table and the geometry is presented in full in the main article. Structures were visualized and the lattice geometrical properties were analyzed with the use of Mercury v3.9.⁹ Full archival structural data in electronic format have been deposited. CCDC 1512475-1512478, contain the supplementary crystallographic data for this paper. These data can be obtained, free of charge, via <http://www.ccdc.cam.ac.uk/products/csd/request/> (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K. (Fax: 44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk)).

Computation

Hybrid density functional theory (DFT) calculations were undertaken on static geometries taken from the crystal structures at the PBE/PBE/6-311+G(2df,2p) level of theory in Gaussian W03 on a personal computer under Windows 7.¹⁰ The Normal Population Analysis atomic charges and the calculated dipole moment were visualized in GaussView (Figures S7, S11).

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Table S3. Crystal, structure determination and refinement parameters

Parameter	2	Se	4a	4b
Formula	C ₈ H ₄ F ₃ N ₂ S ₂	Se	C ₁₂ H ₁₂ N ₃ Se ₂	C ₁₂ H ₁₂ N ₃ Se ₂
FW (amu)	249.25	78.96	356.17	356.17
Temperature (K)	100.0(1)	100(1)	173(2)	173(2)
Radiation, λ (Å)	Cu, 1.54184	Cu, 1.54184	Mo, 0.71073	Mo, 0.71073
Crystal system	Triclinic	Trigonal	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P3_121$	$P\bar{1}$	$P2_1/c$
a (Å)	7.12511(16)	4.3125(3)	9.379(3)	21.1972(16)
b (Å)	16.8803(4)	4.3125(3))	10.667(4)	10.6954(8)
c (Å)	24.7194(5)	4.9711(4)	20.458(7)	28.994(2)
α (°)	108.455(2)	90	80.562(4)	90
β (°)	91.6884(17)	90	84.783(4)	93.6610(10)
γ (°)	98.597(2)	120	81.218(4)	90
Volume (Å ³)	2779.16(12)	80.064(11)	1990.9(12)	6559.9(9)
Z	12	3	6	20
D_{calc} (g/cm ³)	1.787	4.913	1.782	1.803
μ (mm ⁻¹)	5.398	39.344	5.553	5.617
$F(000)$	1500	102	1038.0	3460.0
Habit, colour	Plate, brown	Needle, black	Plate, brown	Block, brown
Crystal size (mm ³)	0.24 x 0.18 x 0.06	0.12 x 0.02 x 0.02	0.25 x 0.23 x 0.04	0.18 x 0.17 x 0.10
θ range (°)	7.566 to 155.252	23.826 to 151.336	3.91 to 54.86	3.308 to 57.604
Index ranges:	-7 $\leq h \leq$ 9 -21 $\leq k \leq$ 21 -31 $\leq l \leq$ 31	-5 $\leq h \leq$ 4 -5 $\leq k \leq$ 5 -6 $\leq l \leq$ 6	-12 $\leq h \leq$ 12 -13 $\leq k \leq$ 13 -26 $\leq l \leq$ 26	-27 $\leq h \leq$ 27 -13 $\leq k \leq$ 13 -39 $\leq l \leq$ 39
Total rfl.	51041	1066	21974	74801
Indep. rfl.	11371	120	8884	15899
R_{int}	0.0622	0.0315	0.0828	0.0447
Compl. (%), $\theta = 25.5^\circ$	99.0	100.0	99.5	99.8
Abs. corr.	Gaussian		Semi-empirical from equivalents	
Max., min. transmission	0.857 0.652	1.000 0.210	0.7456 0.3586	0.8995 0.5755
Data / restr. / param. ^a	11371 / 0 / 811	120 / 0 / 7	8884 / 0 / 454	15899 / 0 / 800
GOF, F^2	1.059	1.381	0.918	1.036
Final R_1 [$>2\sigma$]	0.0650	0.0409	0.0532	0.0379
wR_2 (all data)	0.1678	0.1090	0.1170	0.0817
Larg. pk (e/Å ⁻³)	0.93	1.42	1.19	0.99
Larg. hole (e/Å ⁻³)	-0.67	-1.18	-0.90	-0.92
CCDC depositions	1512475	1512478	1512477	1512476

^a Full-matrix least-squares on F^2 .

Table S4 Comprehensive table of bond lengths [Å] and angles [°] for the crystal structure of **2**

S(1)-S(2)	2.0918(15)	C(43)-C(44)	1.384(7)
S(1)-N(1)	1.621(4)	C(44)-H(44)	0.9300
S(2)-N(2)	1.650(4)	C(44)-C(45)	1.383(6)
F(10)-C(16)	1.336(5)	C(45)-H(45)	0.9300
F(11)-C(16)	1.345(5)	S(3)-S(4)	2.0933(15)
F(12)-C(16)	1.334(5)	S(3)-N(3)	1.625(4)
N(1)-C(1)	1.322(5)	S(4)-N(4)	1.634(4)
N(2)-C(1)	1.341(5)	F(20)-C(027)	1.348(5)
C(1)-C(10)	1.488(6)	F(21)-C(027)	1.332(5)
C(10)-C(11)	1.392(6)	F(22)-C(027)	1.341(6)
C(10)-C(15)	1.390(6)	N(3)-C(20)	1.335(6)
C(11)-H(11)	0.9300	N(4)-C(20)	1.340(5)
C(11)-C(12)	1.387(6)	C(20)-C(21)	1.482(6)
C(12)-C(13)	1.388(6)	C(21)-C(22)	1.386(6)
C(12)-C(16)	1.504(6)	C(21)-C(26)	1.394(6)
C(13)-H(13)	0.9300	C(22)-H(22)	0.9300
C(13)-C(14)	1.395(6)	C(22)-C(23)	1.377(6)
C(14)-H(14)	0.9300	C(23)-C(24)	1.399(6)
C(14)-C(15)	1.390(6)	C(23)-C(027)	1.485(6)
C(15)-H(15)	0.9300	C(24)-H(24)	0.9300
S(9)-S(10)	2.0870(14)	C(24)-C(25)	1.389(6)
S(9)-N(9)	1.633(4)	C(25)-H(25)	0.9300
S(10)-N(10)	1.642(4)	C(25)-C(26)	1.387(6)
F(50)-C(56)	1.301(6)	C(26)-H(26)	0.9300
F(51)-C(56)	1.337(7)	S(11)-S(12)	2.0855(15)
F(52)-C(56)	1.318(6)	S(11)-N(11)	1.631(4)
N(9)-C(5)	1.332(5)	S(12)-N(12)	1.635(4)
N(10)-C(5)	1.341(5)	F(60)-C(66)	1.337(6)
C(5)-C(50)	1.482(6)	F(61)-C(66)	1.336(6)
C(50)-C(51)	1.391(6)	F(62)-C(66)	1.345(6)
C(50)-C(55)	1.401(6)	N(11)-C(6)	1.343(5)
C(51)-H(51)	0.9300	N(12)-C(6)	1.335(5)
C(51)-C(52)	1.389(6)	C(6)-C(60)	1.483(6)
C(52)-C(53)	1.393(6)	C(60)-C(61)	1.394(6)
C(52)-C(56)	1.493(6)	C(60)-C(65)	1.402(6)
C(53)-H(53)	0.9300	C(61)-H(61)	0.9300
C(53)-C(54)	1.384(6)	C(61)-C(62)	1.388(6)
C(54)-H(54)	0.9300	C(62)-C(63)	1.392(6)
C(54)-C(55)	1.388(6)	C(62)-C(66)	1.491(6)
C(55)-H(55)	0.9300	C(63)-H(63)	0.9300
S(7)-S(8)	2.0977(14)	C(63)-C(64)	1.377(7)
S(7)-N(7)	1.626(4)	C(64)-H(64)	0.9300
S(8)-N(8)	1.629(4)	C(64)-C(65)	1.382(7)
F(00S)-C(46)	1.330(6)	C(65)-H(65)	0.9300
F(40)-C(46)	1.327(6)	S(5)-S(6)	2.1017(15)
F(41)-C(46)	1.328(6)	S(5)-N(5)	1.623(4)
N(7)-C(4)	1.356(5)	S(6)-N(6)	1.640(4)
N(8)-C(4)	1.324(6)	F(30)-C(36)	1.332(5)
C(4)-C(40)	1.480(6)	F(31)-C(36)	1.348(6)
C(40)-C(41)	1.383(6)	F(32)-C(36)	1.354(6)
C(40)-C(45)	1.405(6)	N(5)-C(3)	1.348(5)
C(41)-H(41)	0.9300	N(6)-C(3)	1.328(5)
C(41)-C(42)	1.388(6)	C(3)-C(30)	1.489(6)
C(42)-C(43)	1.395(6)	C(30)-C(31)	1.395(6)
C(42)-C(46)	1.499(6)	C(30)-C(35)	1.398(6)
C(43)-H(43)	0.9300	C(31)-H(31)	0.9300

C(31)-C(32)	1.387(6)	C(54)-C(53)-H(53)	120.1
C(32)-C(33)	1.388(6)	C(53)-C(54)-H(54)	120.0
C(32)-C(36)	1.487(6)	C(53)-C(54)-C(55)	120.0(4)
C(33)-H(33)	0.9300	C(55)-C(54)-H(54)	120.0
C(33)-C(34)	1.389(6)	C(50)-C(55)-H(55)	119.9
C(34)-H(34)	0.9300	C(54)-C(55)-C(50)	120.2(4)
C(34)-C(35)	1.382(6)	C(54)-C(55)-H(55)	119.9
C(35)-H(35)	0.9300	F(50)-C(56)-F(51)	106.3(5)
		F(50)-C(56)-F(52)	108.5(5)
N(1)-S(1)-S(2)	94.05(14)	F(50)-C(56)-C(52)	113.4(4)
N(2)-S(2)-S(1)	94.62(14)	F(51)-C(56)-C(52)	112.0(4)
C(1)-N(1)-S(1)	115.4(3)	F(52)-C(56)-F(51)	103.2(4)
C(1)-N(2)-S(2)	113.0(3)	F(52)-C(56)-C(52)	112.7(4)
N(1)-C(1)-N(2)	122.9(4)	N(7)-S(7)-S(8)	94.55(14)
N(1)-C(1)-C(10)	117.7(4)	N(8)-S(8)-S(7)	94.25(14)
N(2)-C(1)-C(10)	119.4(4)	C(4)-N(7)-S(7)	114.0(3)
C(11)-C(10)-C(1)	118.7(4)	C(4)-N(8)-S(8)	114.9(3)
C(15)-C(10)-C(1)	122.2(4)	N(7)-C(4)-C(40)	118.0(4)
C(15)-C(10)-C(11)	119.1(4)	N(8)-C(4)-N(7)	122.3(4)
C(10)-C(11)-H(11)	120.0	N(8)-C(4)-C(40)	119.8(4)
C(12)-C(11)-C(10)	120.1(4)	C(41)-C(40)-C(4)	120.4(4)
C(12)-C(11)-H(11)	120.0	C(41)-C(40)-C(45)	119.8(4)
C(11)-C(12)-C(13)	121.0(4)	C(45)-C(40)-C(4)	119.8(4)
C(11)-C(12)-C(16)	118.2(4)	C(40)-C(41)-H(41)	120.1
C(13)-C(12)-C(16)	120.8(4)	C(40)-C(41)-C(42)	119.8(4)
C(12)-C(13)-H(13)	120.5	C(42)-C(41)-H(41)	120.1
C(12)-C(13)-C(14)	119.0(4)	C(41)-C(42)-C(43)	120.5(4)
C(14)-C(13)-H(13)	120.5	C(41)-C(42)-C(46)	120.5(4)
C(13)-C(14)-H(14)	120.0	C(43)-C(42)-C(46)	119.0(4)
C(15)-C(14)-C(13)	120.1(4)	C(42)-C(43)-H(43)	120.3
C(15)-C(14)-H(14)	120.0	C(44)-C(43)-C(42)	119.4(4)
C(10)-C(15)-C(14)	120.8(4)	C(44)-C(43)-H(43)	120.3
C(10)-C(15)-H(15)	119.6	C(43)-C(44)-H(44)	119.7
C(14)-C(15)-H(15)	119.6	C(45)-C(44)-C(43)	120.5(4)
F(10)-C(16)-F(11)	106.3(4)	C(45)-C(44)-H(44)	119.7
F(10)-C(16)-C(12)	113.2(4)	C(40)-C(45)-H(45)	120.1
F(11)-C(16)-C(12)	111.5(4)	C(44)-C(45)-C(40)	119.8(4)
F(12)-C(16)-F(10)	106.8(4)	C(44)-C(45)-H(45)	120.1
F(12)-C(16)-F(11)	106.1(4)	F(00S)-C(46)-C(42)	112.9(4)
F(12)-C(16)-C(12)	112.4(4)	F(40)-C(46)-F(00S)	105.5(4)
N(9)-S(9)-S(10)	94.45(14)	F(40)-C(46)-F(41)	105.5(4)
N(10)-S(10)-S(9)	94.70(14)	F(40)-C(46)-C(42)	113.7(4)
C(5)-N(9)-S(9)	114.4(3)	F(41)-C(46)-F(00S)	106.5(4)
C(5)-N(10)-S(10)	113.5(3)	F(41)-C(46)-C(42)	112.1(4)
N(9)-C(5)-N(10)	122.9(4)	N(3)-S(3)-S(4)	94.36(14)
N(9)-C(5)-C(50)	117.7(4)	N(4)-S(4)-S(3)	94.47(14)
N(10)-C(5)-C(50)	119.4(4)	C(20)-N(3)-S(3)	114.6(3)
C(51)-C(50)-C(5)	120.1(4)	C(20)-N(4)-S(4)	114.0(3)
C(51)-C(50)-C(55)	119.6(4)	N(3)-C(20)-N(4)	122.5(4)
C(55)-C(50)-C(5)	120.2(4)	N(3)-C(20)-C(21)	118.4(4)
C(50)-C(51)-H(51)	120.2	N(4)-C(20)-C(21)	119.0(4)
C(52)-C(51)-C(50)	119.7(4)	C(22)-C(21)-C(20)	119.5(4)
C(52)-C(51)-H(51)	120.2	C(22)-C(21)-C(26)	120.1(4)
C(51)-C(52)-C(53)	120.6(4)	C(26)-C(21)-C(20)	120.4(4)
C(51)-C(52)-C(56)	120.4(4)	C(21)-C(22)-H(22)	120.0
C(53)-C(52)-C(56)	119.1(4)	C(23)-C(22)-C(21)	120.1(4)
C(52)-C(53)-H(53)	120.1	C(23)-C(22)-H(22)	120.0
C(54)-C(53)-C(52)	119.9(4)	C(22)-C(23)-C(24)	120.3(4)

C(22)-C(23)-C(027)	120.3(4)	C(64)-C(65)-C(60)	120.0(4)
C(24)-C(23)-C(027)	119.4(4)	C(64)-C(65)-H(65)	120.0
C(23)-C(24)-H(24)	120.3	F(60)-C(66)-F(62)	106.5(4)
C(25)-C(24)-C(23)	119.5(4)	F(60)-C(66)-C(62)	113.3(4)
C(25)-C(24)-H(24)	120.3	F(61)-C(66)-F(60)	106.2(4)
C(24)-C(25)-H(25)	119.9	F(61)-C(66)-F(62)	106.0(4)
C(26)-C(25)-C(24)	120.2(4)	F(61)-C(66)-C(62)	112.7(4)
C(26)-C(25)-H(25)	119.9	F(62)-C(66)-C(62)	111.7(4)
C(21)-C(26)-H(26)	120.1	N(5)-S(5)-S(6)	94.79(13)
C(25)-C(26)-C(21)	119.8(4)	N(6)-S(6)-S(5)	94.09(14)
C(25)-C(26)-H(26)	120.1	C(3)-N(5)-S(5)	113.8(3)
F(20)-C(027)-C(23)	112.5(4)	C(3)-N(6)-S(6)	114.0(3)
F(21)-C(027)-F(20)	106.0(4)	N(5)-C(3)-C(30)	116.9(4)
F(21)-C(027)-F(22)	106.6(4)	N(6)-C(3)-N(5)	123.3(4)
F(21)-C(027)-C(23)	113.8(4)	N(6)-C(3)-C(30)	119.8(4)
F(22)-C(027)-F(20)	104.5(4)	C(31)-C(30)-C(3)	118.8(4)
F(22)-C(027)-C(23)	112.7(4)	C(31)-C(30)-C(35)	119.5(4)
N(11)-S(11)-S(12)	94.72(13)	C(35)-C(30)-C(3)	121.7(4)
N(12)-S(12)-S(11)	94.48(14)	C(30)-C(31)-H(31)	120.1
C(6)-N(11)-S(11)	114.1(3)	C(32)-C(31)-C(30)	119.8(4)
C(6)-N(12)-S(12)	114.2(3)	C(32)-C(31)-H(31)	120.1
N(11)-C(6)-C(60)	118.5(4)	C(31)-C(32)-C(33)	121.0(4)
N(12)-C(6)-N(11)	122.5(4)	C(31)-C(32)-C(36)	118.0(4)
N(12)-C(6)-C(60)	119.0(4)	C(33)-C(32)-C(36)	121.0(4)
C(61)-C(60)-C(6)	120.2(4)	C(32)-C(33)-H(33)	120.6
C(61)-C(60)-C(65)	119.1(4)	C(32)-C(33)-C(34)	118.9(4)
C(65)-C(60)-C(6)	120.7(4)	C(34)-C(33)-H(33)	120.6
C(60)-C(61)-H(61)	119.9	C(33)-C(34)-H(34)	119.5
C(62)-C(61)-C(60)	120.2(4)	C(35)-C(34)-C(33)	121.0(4)
C(62)-C(61)-H(61)	119.9	C(35)-C(34)-H(34)	119.5
C(61)-C(62)-C(63)	120.1(4)	C(30)-C(35)-H(35)	120.0
C(61)-C(62)-C(66)	119.9(4)	C(34)-C(35)-C(30)	119.9(4)
C(63)-C(62)-C(66)	119.9(4)	C(34)-C(35)-H(35)	120.0
C(62)-C(63)-H(63)	120.1	F(30)-C(36)-F(31)	106.4(4)
C(64)-C(63)-C(62)	119.8(4)	F(30)-C(36)-F(32)	106.3(4)
C(64)-C(63)-H(63)	120.1	F(30)-C(36)-C(32)	114.0(4)
C(63)-C(64)-H(64)	119.6	F(31)-C(36)-F(32)	105.0(4)
C(63)-C(64)-C(65)	120.8(4)	F(31)-C(36)-C(32)	112.2(4)
C(65)-C(64)-H(64)	119.6	F(32)-C(36)-C(32)	112.4(4)
C(60)-C(65)-H(65)	120.0		

Table S5 Comprehensive table of bond lengths [Å] and angles [°] for the crystal structure of **5a**

Se(1)-Se(2)	2.3096(10)	C(5)-C(6)	1.381(8)
Se(1)-N(1)	1.782(4)	C(6)-C(7)	1.385(7)
Se(2)-N(2)	1.789(4)	C(6)-C(8)	1.451(8)
N(1)-C(1)	1.328(6)	C(7)-H(7)	0.9500
N(2)-C(1)	1.326(6)	C(9)-C(10)	1.521(13)
N(11)-C(8)	1.125(7)	C(9)-C(11)	1.518(12)
C(1)-C(2)	1.475(6)	C(9)-C(12)	1.591(13)
C(2)-C(3)	1.376(7)	C(9)-C(10A)	1.44(3)
C(2)-C(7)	1.382(7)	C(9)-C(11A)	1.42(3)
C(3)-H(3)	0.9500	C(9)-C(12A)	1.59(3)
C(3)-C(4)	1.400(7)	C(10)-H(10A)	0.9800
C(4)-C(5)	1.375(8)	C(10)-H(10B)	0.9800
C(4)-C(9)	1.514(9)	C(10)-H(10C)	0.9800
C(5)-H(5)	0.9500	C(11)-H(11A)	0.9800

C(11)-H(11B)	0.9800	Se(6)-N(6)	1.767(5)
C(11)-H(11C)	0.9800	N(5)-C(25)	1.323(7)
C(12)-H(12A)	0.9800	N(6)-C(25)	1.298(7)
C(12)-H(12B)	0.9800	N(13)-C(32)	1.132(9)
C(12)-H(12C)	0.9800	C(25)-C(26)	1.481(7)
C(10A)-H(10D)	0.9800	C(26)-C(27)	1.376(7)
C(10A)-H(10E)	0.9800	C(26)-C(31)	1.384(7)
C(10A)-H(10F)	0.9800	C(27)-H(27)	0.9500
C(11A)-H(11D)	0.9800	C(27)-C(28)	1.382(8)
C(11A)-H(11E)	0.9800	C(28)-C(29)	1.388(8)
C(11A)-H(11F)	0.9800	C(28)-C(32)	1.428(9)
C(12A)-H(12D)	0.9800	C(29)-H(29)	0.9500
C(12A)-H(12E)	0.9800	C(29)-C(30)	1.371(8)
C(12A)-H(12F)	0.9800	C(30)-C(31)	1.384(8)
Se(3)-Se(4)	2.3096(9)	C(30)-C(33)	1.514(8)
Se(3)-N(3)	1.793(4)	C(31)-H(31)	0.9500
Se(4)-N(4)	1.805(4)	C(33)-C(34)	1.533(9)
N(3)-C(13)	1.313(6)	C(33)-C(35)	1.521(9)
N(4)-C(13)	1.335(6)	C(33)-C(36)	1.507(9)
N(12)-C(20)	1.133(7)	C(34)-H(34A)	0.9800
C(13)-C(14)	1.487(6)	C(34)-H(34B)	0.9800
C(14)-C(15)	1.368(7)	C(34)-H(34C)	0.9800
C(14)-C(19)	1.391(7)	C(35)-H(35A)	0.9800
C(15)-H(15)	0.9500	C(35)-H(35B)	0.9800
C(15)-C(16)	1.398(7)	C(35)-H(35C)	0.9800
C(16)-C(17)	1.370(7)	C(36)-H(36A)	0.9800
C(16)-C(20)	1.438(8)	C(36)-H(36B)	0.9800
C(17)-H(17)	0.9500	C(36)-H(36C)	0.9800
C(17)-C(18)	1.381(8)		
C(18)-C(19)	1.386(7)	N(1)-Se(1)-Se(2)	90.56(13)
C(18)-C(21)	1.527(8)	N(2)-Se(2)-Se(1)	91.79(14)
C(19)-H(19)	0.9500	C(1)-N(1)-Se(1)	115.7(3)
C(21)-C(22)	1.47(2)	C(1)-N(2)-Se(2)	114.2(4)
C(21)-C(23)	1.56(2)	N(1)-C(1)-C(2)	116.2(4)
C(21)-C(24)	1.553(18)	N(2)-C(1)-N(1)	127.7(5)
C(21)-C(22A)	1.60(3)	N(2)-C(1)-C(2)	116.0(5)
C(21)-C(23A)	1.39(4)	C(3)-C(2)-C(1)	119.5(5)
C(21)-C(24A)	1.47(3)	C(3)-C(2)-C(7)	119.4(5)
C(22)-H(22A)	0.9800	C(7)-C(2)-C(1)	121.1(5)
C(22)-H(22B)	0.9800	C(2)-C(3)-H(3)	118.5
C(22)-H(22C)	0.9800	C(2)-C(3)-C(4)	123.1(6)
C(23)-H(23A)	0.9800	C(4)-C(3)-H(3)	118.5
C(23)-H(23B)	0.9800	C(3)-C(4)-C(9)	121.2(6)
C(23)-H(23C)	0.9800	C(5)-C(4)-C(3)	116.2(6)
C(24)-H(24A)	0.9800	C(5)-C(4)-C(9)	122.6(6)
C(24)-H(24B)	0.9800	C(4)-C(5)-H(5)	119.2
C(24)-H(24C)	0.9800	C(4)-C(5)-C(6)	121.7(6)
C(22A)-H(22D)	0.9800	C(6)-C(5)-H(5)	119.2
C(22A)-H(22E)	0.9800	C(5)-C(6)-C(7)	121.1(6)
C(22A)-H(22F)	0.9800	C(5)-C(6)-C(8)	119.4(5)
C(23A)-H(23D)	0.9800	C(7)-C(6)-C(8)	119.5(6)
C(23A)-H(23E)	0.9800	C(2)-C(7)-C(6)	118.5(5)
C(23A)-H(23F)	0.9800	C(2)-C(7)-H(7)	120.8
C(24A)-H(24D)	0.9800	C(6)-C(7)-H(7)	120.8
C(24A)-H(24E)	0.9800	N(11)-C(8)-C(6)	179.8(7)
C(24A)-H(24F)	0.9800	C(4)-C(9)-C(10)	111.0(6)
Se(5)-Se(6)	2.3183(12)	C(4)-C(9)-C(11)	111.8(7)
Se(5)-N(5)	1.779(5)	C(4)-C(9)-C(12)	113.8(6)

C(4)-C(9)-C(12A)	107.6(11)	C(15)-C(16)-C(20)	121.3(5)
C(10)-C(9)-C(12)	104.6(8)	C(17)-C(16)-C(15)	120.7(5)
C(11)-C(9)-C(10)	110.1(8)	C(17)-C(16)-C(20)	118.0(5)
C(11)-C(9)-C(12)	105.2(8)	C(16)-C(17)-H(17)	119.2
C(10A)-C(9)-C(4)	104.9(11)	C(16)-C(17)-C(18)	121.6(5)
C(10A)-C(9)-C(12A)	107.5(17)	C(18)-C(17)-H(17)	119.2
C(11A)-C(9)-C(4)	107.2(12)	C(17)-C(18)-C(19)	116.9(5)
C(11A)-C(9)-C(10A)	121.5(19)	C(17)-C(18)-C(21)	120.0(5)
C(11A)-C(9)-C(12A)	107.5(17)	C(19)-C(18)-C(21)	123.1(5)
C(9)-C(10)-H(10A)	109.5	C(14)-C(19)-H(19)	118.8
C(9)-C(10)-H(10B)	109.5	C(18)-C(19)-C(14)	122.4(5)
C(9)-C(10)-H(10C)	109.5	C(18)-C(19)-H(19)	118.8
H(10A)-C(10)-H(10B)	109.5	N(12)-C(20)-C(16)	175.9(7)
H(10A)-C(10)-H(10C)	109.5	C(18)-C(21)-C(23)	105.5(7)
H(10B)-C(10)-H(10C)	109.5	C(18)-C(21)-C(24)	109.0(7)
C(9)-C(11)-H(11A)	109.5	C(18)-C(21)-C(22A)	104.1(9)
C(9)-C(11)-H(11B)	109.5	C(22)-C(21)-C(18)	111.0(8)
C(9)-C(11)-H(11C)	109.5	C(22)-C(21)-C(23)	121.4(11)
H(11A)-C(11)-H(11B)	109.5	C(22)-C(21)-C(24)	110.3(8)
H(11A)-C(11)-H(11C)	109.5	C(24)-C(21)-C(23)	98.6(11)
H(11B)-C(11)-H(11C)	109.5	C(23A)-C(21)-C(18)	119.0(11)
C(9)-C(12)-H(12A)	109.5	C(23A)-C(21)-C(22A)	90.1(15)
C(9)-C(12)-H(12B)	109.5	C(23A)-C(21)-C(24A)	115.5(17)
C(9)-C(12)-H(12C)	109.5	C(24A)-C(21)-C(18)	115.9(10)
H(12A)-C(12)-H(12B)	109.5	C(24A)-C(21)-C(22A)	107.1(12)
H(12A)-C(12)-H(12C)	109.5	C(21)-C(22)-H(22A)	109.5
H(12B)-C(12)-H(12C)	109.5	C(21)-C(22)-H(22B)	109.5
C(9)-C(10A)-H(10D)	109.5	C(21)-C(22)-H(22C)	109.5
C(9)-C(10A)-H(10E)	109.5	H(22A)-C(22)-H(22B)	109.5
C(9)-C(10A)-H(10F)	109.5	H(22A)-C(22)-H(22C)	109.5
H(10D)-C(10A)-H(10E)	109.5	H(22B)-C(22)-H(22C)	109.5
H(10D)-C(10A)-H(10F)	109.5	C(21)-C(23)-H(23A)	109.5
H(10E)-C(10A)-H(10F)	109.5	C(21)-C(23)-H(23B)	109.5
C(9)-C(11A)-H(11D)	109.5	C(21)-C(23)-H(23C)	109.5
C(9)-C(11A)-H(11E)	109.5	H(23A)-C(23)-H(23B)	109.5
C(9)-C(11A)-H(11F)	109.5	H(23A)-C(23)-H(23C)	109.5
H(11D)-C(11A)-H(11E)	109.5	H(23B)-C(23)-H(23C)	109.5
H(11D)-C(11A)-H(11F)	109.5	C(21)-C(24)-H(24A)	109.5
H(11E)-C(11A)-H(11F)	109.5	C(21)-C(24)-H(24B)	109.5
C(9)-C(12A)-H(12D)	109.5	C(21)-C(24)-H(24C)	109.5
C(9)-C(12A)-H(12E)	109.5	H(24A)-C(24)-H(24B)	109.5
C(9)-C(12A)-H(12F)	109.5	H(24A)-C(24)-H(24C)	109.5
H(12D)-C(12A)-H(12E)	109.5	H(24B)-C(24)-H(24C)	109.5
H(12D)-C(12A)-H(12F)	109.5	C(21)-C(22A)-H(22D)	109.5
H(12E)-C(12A)-H(12F)	109.5	C(21)-C(22A)-H(22E)	109.5
N(3)-Se(3)-Se(4)	90.24(13)	C(21)-C(22A)-H(22F)	109.5
N(4)-Se(4)-Se(3)	91.91(13)	H(22D)-C(22A)-H(22E)	109.5
C(13)-N(3)-Se(3)	116.3(3)	H(22D)-C(22A)-H(22F)	109.5
C(13)-N(4)-Se(4)	113.7(4)	H(22E)-C(22A)-H(22F)	109.5
N(3)-C(13)-N(4)	127.8(5)	C(21)-C(23A)-H(23D)	109.5
N(3)-C(13)-C(14)	116.4(4)	C(21)-C(23A)-H(23E)	109.5
N(4)-C(13)-C(14)	115.8(4)	C(21)-C(23A)-H(23F)	109.5
C(15)-C(14)-C(13)	120.5(5)	H(23D)-C(23A)-H(23E)	109.5
C(15)-C(14)-C(19)	119.5(5)	H(23D)-C(23A)-H(23F)	109.5
C(19)-C(14)-C(13)	120.0(5)	H(23E)-C(23A)-H(23F)	109.5
C(14)-C(15)-H(15)	120.6	C(21)-C(24A)-H(24D)	109.5
C(14)-C(15)-C(16)	118.9(5)	C(21)-C(24A)-H(24E)	109.5
C(16)-C(15)-H(15)	120.6	C(21)-C(24A)-H(24F)	109.5

H(24D)-C(24A)-H(24E)	109.5	C(30)-C(31)-H(31)	118.4
H(24D)-C(24A)-H(24F)	109.5	N(13)-C(32)-C(28)	178.3(9)
H(24E)-C(24A)-H(24F)	109.5	C(30)-C(33)-C(34)	108.7(5)
N(5)-Se(5)-Se(6)	90.65(17)	C(30)-C(33)-C(35)	109.6(5)
N(6)-Se(6)-Se(5)	90.03(16)	C(35)-C(33)-C(34)	108.1(6)
C(25)-N(5)-Se(5)	115.6(4)	C(36)-C(33)-C(30)	113.3(6)
C(25)-N(6)-Se(6)	117.3(4)	C(36)-C(33)-C(34)	110.0(5)
N(5)-C(25)-C(26)	117.2(5)	C(36)-C(33)-C(35)	106.9(6)
N(6)-C(25)-N(5)	126.4(5)	C(33)-C(34)-H(34A)	109.5
N(6)-C(25)-C(26)	116.4(5)	C(33)-C(34)-H(34B)	109.5
C(27)-C(26)-C(25)	121.0(5)	C(33)-C(34)-H(34C)	109.5
C(27)-C(26)-C(31)	119.1(5)	H(34A)-C(34)-H(34B)	109.5
C(31)-C(26)-C(25)	119.8(5)	H(34A)-C(34)-H(34C)	109.5
C(26)-C(27)-H(27)	120.7	H(34B)-C(34)-H(34C)	109.5
C(26)-C(27)-C(28)	118.6(6)	C(33)-C(35)-H(35A)	109.5
C(28)-C(27)-H(27)	120.7	C(33)-C(35)-H(35B)	109.5
C(27)-C(28)-C(29)	121.1(6)	C(33)-C(35)-H(35C)	109.5
C(27)-C(28)-C(32)	119.8(6)	H(35A)-C(35)-H(35B)	109.5
C(29)-C(28)-C(32)	119.0(6)	H(35A)-C(35)-H(35C)	109.5
C(28)-C(29)-H(29)	119.5	H(35B)-C(35)-H(35C)	109.5
C(30)-C(29)-C(28)	121.1(6)	C(33)-C(36)-H(36A)	109.5
C(30)-C(29)-H(29)	119.5	C(33)-C(36)-H(36B)	109.5
C(29)-C(30)-C(31)	116.8(6)	C(33)-C(36)-H(36C)	109.5
C(29)-C(30)-C(33)	123.2(6)	H(36A)-C(36)-H(36B)	109.5
C(31)-C(30)-C(33)	120.0(6)	H(36A)-C(36)-H(36C)	109.5
C(26)-C(31)-C(30)	123.1(6)	H(36B)-C(36)-H(36C)	109.5
C(26)-C(31)-H(31)	118.4		

Table S6 Comprehensive table of bond lengths [Å] and angles [°] for the crystal structure of **4b**

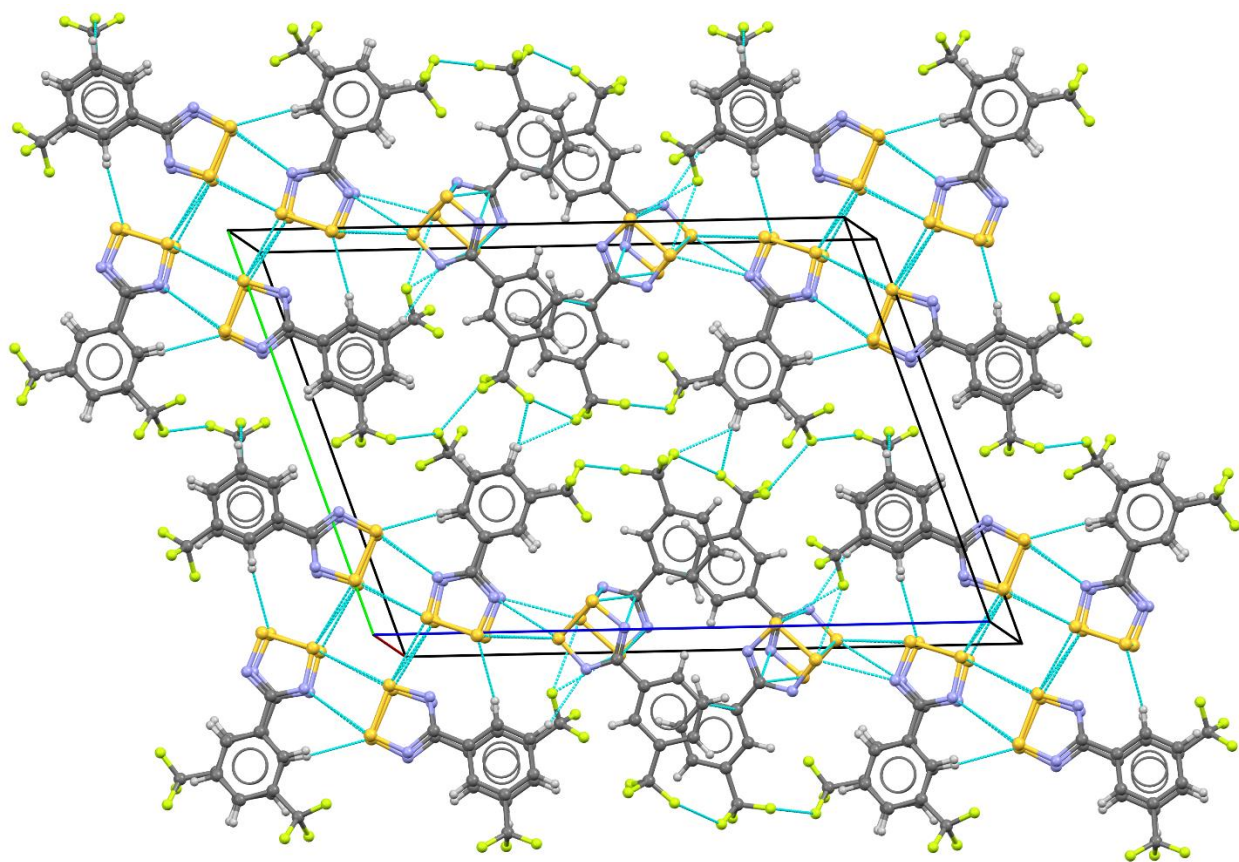
Se(1)-Se(2)	2.3347(6)	C(12)-H(12A)	0.9800
Se(1)-N(1)	1.783(3)	C(12)-H(12B)	0.9800
Se(2)-N(2)	1.760(4)	C(12)-H(12C)	0.9800
N(1)-C(1)	1.335(5)	Se(9)-Se(10)	2.3299(5)
N(2)-C(1)	1.309(5)	Se(9)-N(9)	1.792(3)
N(11)-C(8)	1.164(5)	Se(10)-N(10)	1.791(3)
C(1)-C(2)	1.502(5)	N(9)-C(49)	1.339(4)
C(2)-C(3)	1.384(5)	N(10)-C(49)	1.334(4)
C(2)-C(7)	1.399(5)	N(15)-C(56)	1.142(5)
C(3)-H(3)	0.9500	C(49)-C(50)	1.506(4)
C(3)-C(4)	1.406(5)	C(50)-C(51)	1.402(5)
C(4)-C(5)	1.395(6)	C(50)-C(55)	1.391(5)
C(4)-C(8)	1.432(6)	C(51)-H(51)	0.9500
C(5)-H(5)	0.9500	C(51)-C(52)	1.383(5)
C(5)-C(6)	1.392(6)	C(52)-C(53)	1.401(5)
C(6)-C(7)	1.392(6)	C(52)-C(56)	1.454(5)
C(6)-C(9)	1.547(6)	C(53)-H(53)	0.9500
C(7)-H(7)	0.9500	C(53)-C(54)	1.389(5)
C(9)-C(10)	1.528(7)	C(54)-C(55)	1.398(5)
C(9)-C(11)	1.514(7)	C(54)-C(57)	1.540(5)
C(9)-C(12)	1.509(7)	C(55)-H(55)	0.9500
C(10)-H(10A)	0.9800	C(57)-C(58)	1.524(6)
C(10)-H(10B)	0.9800	C(57)-C(59)	1.520(6)
C(10)-H(10C)	0.9800	C(57)-C(60)	1.525(6)
C(11)-H(11A)	0.9800	C(58)-H(58A)	0.9800
C(11)-H(11B)	0.9800	C(58)-H(58B)	0.9800
C(11)-H(11C)	0.9800	C(58)-H(58C)	0.9800

C(59)-H(59A)	0.9800	C(21)-C(23A)	1.558(12)
C(59)-H(59B)	0.9800	C(21)-C(24A)	1.58(3)
C(59)-H(59C)	0.9800	C(22)-H(22A)	0.9800
C(60)-H(60A)	0.9800	C(22)-H(22B)	0.9800
C(60)-H(60B)	0.9800	C(22)-H(22C)	0.9800
C(60)-H(60C)	0.9800	C(23)-H(23A)	0.9800
Se(7)-Se(8)	2.3360(5)	C(23)-H(23B)	0.9800
Se(7)-N(7)	1.797(3)	C(23)-H(23C)	0.9800
Se(8)-N(8)	1.797(3)	C(24)-H(24A)	0.9800
N(7)-C(37)	1.338(4)	C(24)-H(24B)	0.9800
N(8)-C(37)	1.333(4)	C(24)-H(24C)	0.9800
N(14)-C(44)	1.137(5)	C(22A)-H(22D)	0.9800
C(37)-C(38)	1.506(5)	C(22A)-H(22E)	0.9800
C(38)-C(39)	1.381(5)	C(22A)-H(22F)	0.9800
C(38)-C(43)	1.399(5)	C(23A)-H(23D)	0.9800
C(39)-H(39)	0.9500	C(23A)-H(23E)	0.9800
C(39)-C(40)	1.396(5)	C(23A)-H(23F)	0.9800
C(40)-C(41)	1.402(5)	C(24A)-H(24D)	0.9800
C(40)-C(44)	1.449(5)	C(24A)-H(24E)	0.9800
C(41)-H(41)	0.9500	C(24A)-H(24F)	0.9800
C(41)-C(42)	1.390(5)	Se(5)-Se(6)	2.3274(5)
C(42)-C(43)	1.400(5)	Se(5)-N(5)	1.786(3)
C(42)-C(45)	1.540(5)	Se(6)-N(6)	1.790(3)
C(43)-H(43)	0.9500	N(5)-C(25)	1.341(4)
C(45)-C(46)	1.495(6)	N(6)-C(25)	1.338(4)
C(45)-C(47)	1.492(6)	N(13)-C(32)	1.136(5)
C(45)-C(48)	1.567(6)	C(25)-C(26)	1.489(4)
C(46)-H(46A)	0.9800	C(26)-C(27)	1.395(5)
C(46)-H(46B)	0.9800	C(26)-C(31)	1.389(4)
C(46)-H(46C)	0.9800	C(27)-H(27)	0.9500
C(47)-H(47A)	0.9800	C(27)-C(28)	1.392(5)
C(47)-H(47B)	0.9800	C(28)-C(29)	1.390(5)
C(47)-H(47C)	0.9800	C(28)-C(32)	1.448(5)
C(48)-H(48A)	0.9800	C(29)-H(29)	0.9500
C(48)-H(48B)	0.9800	C(29)-C(30)	1.405(5)
C(48)-H(48C)	0.9800	C(30)-C(31)	1.393(5)
Se(3)-Se(4)	2.3337(5)	C(30)-C(33)	1.527(5)
Se(3)-N(3)	1.781(3)	C(31)-H(31)	0.9500
Se(4)-N(4)	1.797(3)	C(33)-C(34)	1.521(6)
N(3)-C(13)	1.342(4)	C(33)-C(35)	1.529(6)
N(4)-C(13)	1.326(4)	C(33)-C(36)	1.523(6)
N(12)-C(20)	1.141(5)	C(34)-H(34A)	0.9800
C(13)-C(14)	1.493(5)	C(34)-H(34B)	0.9800
C(14)-C(15)	1.398(5)	C(34)-H(34C)	0.9800
C(14)-C(19)	1.394(5)	C(35)-H(35A)	0.9800
C(15)-H(15)	0.9500	C(35)-H(35B)	0.9800
C(15)-C(16)	1.383(5)	C(35)-H(35C)	0.9800
C(16)-C(17)	1.395(5)	C(36)-H(36A)	0.9800
C(16)-C(20)	1.443(5)	C(36)-H(36B)	0.9800
C(17)-H(17)	0.9500	C(36)-H(36C)	0.9800
C(17)-C(18)	1.401(5)		
C(18)-C(19)	1.388(5)	N(1)-Se(1)-Se(2)	90.50(11)
C(18)-C(21)	1.537(5)	N(2)-Se(2)-Se(1)	89.93(11)
C(19)-H(19)	0.9500	C(1)-N(1)-Se(1)	115.9(3)
C(21)-C(22)	1.638(10)	C(1)-N(2)-Se(2)	118.1(3)
C(21)-C(23)	1.564(11)	N(1)-C(1)-C(2)	115.7(3)
C(21)-C(24)	1.49(2)	N(2)-C(1)-N(1)	125.4(4)
C(21)-C(22A)	1.424(10)	N(2)-C(1)-C(2)	118.8(4)

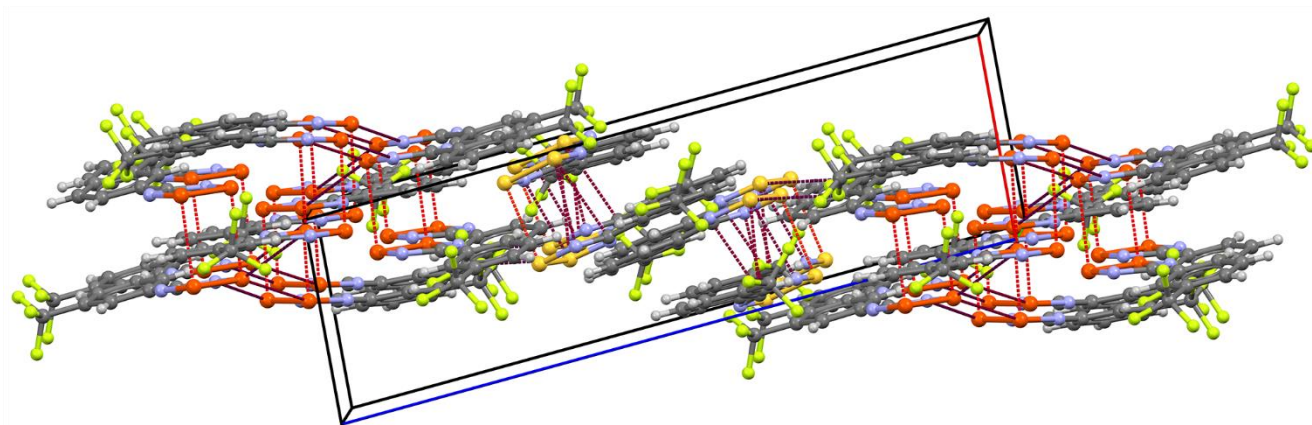
C(3)-C(2)-C(1)	119.1(3)	C(53)-C(52)-C(56)	117.7(3)
C(3)-C(2)-C(7)	119.9(4)	C(52)-C(53)-H(53)	119.7
C(7)-C(2)-C(1)	120.9(3)	C(54)-C(53)-C(52)	120.6(3)
C(2)-C(3)-H(3)	120.9	C(54)-C(53)-H(53)	119.7
C(2)-C(3)-C(4)	118.2(4)	C(53)-C(54)-C(55)	117.5(3)
C(4)-C(3)-H(3)	120.9	C(53)-C(54)-C(57)	122.4(3)
C(3)-C(4)-C(8)	120.3(4)	C(55)-C(54)-C(57)	120.1(3)
C(5)-C(4)-C(3)	121.3(4)	C(50)-C(55)-C(54)	122.4(3)
C(5)-C(4)-C(8)	118.4(4)	C(50)-C(55)-H(55)	118.8
C(4)-C(5)-H(5)	119.7	C(54)-C(55)-H(55)	118.8
C(6)-C(5)-C(4)	120.6(4)	N(15)-C(56)-C(52)	176.0(4)
C(6)-C(5)-H(5)	119.7	C(58)-C(57)-C(54)	111.9(3)
C(5)-C(6)-C(9)	119.5(4)	C(58)-C(57)-C(60)	107.3(4)
C(7)-C(6)-C(5)	117.5(4)	C(59)-C(57)-C(54)	108.8(3)
C(7)-C(6)-C(9)	122.9(4)	C(59)-C(57)-C(58)	109.2(4)
C(2)-C(7)-H(7)	118.8	C(59)-C(57)-C(60)	109.8(4)
C(6)-C(7)-C(2)	122.4(4)	C(60)-C(57)-C(54)	109.8(3)
C(6)-C(7)-H(7)	118.8	C(57)-C(58)-H(58A)	109.5
N(11)-C(8)-C(4)	177.2(5)	C(57)-C(58)-H(58B)	109.5
C(10)-C(9)-C(6)	107.3(4)	C(57)-C(58)-H(58C)	109.5
C(11)-C(9)-C(6)	111.4(4)	H(58A)-C(58)-H(58B)	109.5
C(11)-C(9)-C(10)	108.6(5)	H(58A)-C(58)-H(58C)	109.5
C(12)-C(9)-C(6)	109.9(4)	H(58B)-C(58)-H(58C)	109.5
C(12)-C(9)-C(10)	112.2(5)	C(57)-C(59)-H(59A)	109.5
C(12)-C(9)-C(11)	107.6(5)	C(57)-C(59)-H(59B)	109.5
C(9)-C(10)-H(10A)	109.5	C(57)-C(59)-H(59C)	109.5
C(9)-C(10)-H(10B)	109.5	H(59A)-C(59)-H(59B)	109.5
C(9)-C(10)-H(10C)	109.5	H(59A)-C(59)-H(59C)	109.5
H(10A)-C(10)-H(10B)	109.5	H(59B)-C(59)-H(59C)	109.5
H(10A)-C(10)-H(10C)	109.5	C(57)-C(60)-H(60A)	109.5
H(10B)-C(10)-H(10C)	109.5	C(57)-C(60)-H(60B)	109.5
C(9)-C(11)-H(11A)	109.5	C(57)-C(60)-H(60C)	109.5
C(9)-C(11)-H(11B)	109.5	H(60A)-C(60)-H(60B)	109.5
C(9)-C(11)-H(11C)	109.5	H(60A)-C(60)-H(60C)	109.5
H(11A)-C(11)-H(11B)	109.5	H(60B)-C(60)-H(60C)	109.5
H(11A)-C(11)-H(11C)	109.5	N(7)-Se(7)-Se(8)	90.09(9)
H(11B)-C(11)-H(11C)	109.5	N(8)-Se(8)-Se(7)	92.23(9)
C(9)-C(12)-H(12A)	109.5	C(37)-N(7)-Se(7)	115.4(2)
C(9)-C(12)-H(12B)	109.5	C(37)-N(8)-Se(8)	113.4(2)
C(9)-C(12)-H(12C)	109.5	N(7)-C(37)-C(38)	115.8(3)
H(12A)-C(12)-H(12B)	109.5	N(8)-C(37)-N(7)	128.9(3)
H(12A)-C(12)-H(12C)	109.5	N(8)-C(37)-C(38)	115.3(3)
H(12B)-C(12)-H(12C)	109.5	C(39)-C(38)-C(37)	120.6(3)
N(9)-Se(9)-Se(10)	90.56(9)	C(39)-C(38)-C(43)	119.7(3)
N(10)-Se(10)-Se(9)	91.85(9)	C(43)-C(38)-C(37)	119.7(3)
C(49)-N(9)-Se(9)	115.2(2)	C(38)-C(39)-H(39)	120.6
C(49)-N(10)-Se(10)	114.1(2)	C(38)-C(39)-C(40)	118.8(3)
N(9)-C(49)-C(50)	116.7(3)	C(40)-C(39)-H(39)	120.6
N(10)-C(49)-N(9)	128.3(3)	C(39)-C(40)-C(41)	121.0(3)
N(10)-C(49)-C(50)	115.1(3)	C(39)-C(40)-C(44)	120.7(3)
C(51)-C(50)-C(49)	121.0(3)	C(41)-C(40)-C(44)	118.3(3)
C(55)-C(50)-C(49)	119.4(3)	C(40)-C(41)-H(41)	119.4
C(55)-C(50)-C(51)	119.5(3)	C(42)-C(41)-C(40)	121.1(3)
C(50)-C(51)-H(51)	120.8	C(42)-C(41)-H(41)	119.4
C(52)-C(51)-C(50)	118.5(3)	C(41)-C(42)-C(43)	116.7(3)
C(52)-C(51)-H(51)	120.8	C(41)-C(42)-C(45)	121.0(3)
C(51)-C(52)-C(53)	121.5(3)	C(43)-C(42)-C(45)	122.1(3)
C(51)-C(52)-C(56)	120.8(3)	C(38)-C(43)-C(42)	122.7(3)

C(38)-C(43)-H(43)	118.6	C(24)-C(21)-C(18)	111.1(9)
C(42)-C(43)-H(43)	118.6	C(24)-C(21)-C(22)	106.3(8)
N(14)-C(44)-C(40)	177.8(5)	C(24)-C(21)-C(23)	111.7(9)
C(42)-C(45)-C(48)	110.1(4)	C(22A)-C(21)-C(18)	110.3(5)
C(46)-C(45)-C(42)	112.3(3)	C(22A)-C(21)-C(23A)	114.9(7)
C(46)-C(45)-C(48)	104.5(4)	C(22A)-C(21)-C(24A)	111.3(9)
C(47)-C(45)-C(42)	108.2(4)	C(23A)-C(21)-C(24A)	103.6(8)
C(47)-C(45)-C(46)	114.7(5)	C(21)-C(22)-H(22A)	109.5
C(47)-C(45)-C(48)	106.8(4)	C(21)-C(22)-H(22B)	109.5
C(45)-C(46)-H(46A)	109.5	C(21)-C(22)-H(22C)	109.5
C(45)-C(46)-H(46B)	109.5	H(22A)-C(22)-H(22B)	109.5
C(45)-C(46)-H(46C)	109.5	H(22A)-C(22)-H(22C)	109.5
H(46A)-C(46)-H(46B)	109.5	H(22B)-C(22)-H(22C)	109.5
H(46A)-C(46)-H(46C)	109.5	C(21)-C(23)-H(23A)	109.5
H(46B)-C(46)-H(46C)	109.5	C(21)-C(23)-H(23B)	109.5
C(45)-C(47)-H(47A)	109.5	C(21)-C(23)-H(23C)	109.5
C(45)-C(47)-H(47B)	109.5	H(23A)-C(23)-H(23B)	109.5
C(45)-C(47)-H(47C)	109.5	H(23A)-C(23)-H(23C)	109.5
H(47A)-C(47)-H(47B)	109.5	H(23B)-C(23)-H(23C)	109.5
H(47A)-C(47)-H(47C)	109.5	C(21)-C(24)-H(24A)	109.5
H(47B)-C(47)-H(47C)	109.5	C(21)-C(24)-H(24B)	109.5
C(45)-C(48)-H(48A)	109.5	C(21)-C(24)-H(24C)	109.5
C(45)-C(48)-H(48B)	109.5	H(24A)-C(24)-H(24B)	109.5
C(45)-C(48)-H(48C)	109.5	H(24A)-C(24)-H(24C)	109.5
H(48A)-C(48)-H(48B)	109.5	H(24B)-C(24)-H(24C)	109.5
H(48A)-C(48)-H(48C)	109.5	C(21)-C(22A)-H(22D)	109.5
H(48B)-C(48)-H(48C)	109.5	C(21)-C(22A)-H(22E)	109.5
N(3)-Se(3)-Se(4)	90.54(9)	C(21)-C(22A)-H(22F)	109.5
N(4)-Se(4)-Se(3)	91.49(10)	H(22D)-C(22A)-H(22E)	109.5
C(13)-N(3)-Se(3)	115.6(2)	H(22D)-C(22A)-H(22F)	109.5
C(13)-N(4)-Se(4)	114.3(2)	H(22E)-C(22A)-H(22F)	109.5
N(3)-C(13)-C(14)	115.5(3)	C(21)-C(23A)-H(23D)	109.5
N(4)-C(13)-N(3)	128.0(3)	C(21)-C(23A)-H(23E)	109.5
N(4)-C(13)-C(14)	116.4(3)	C(21)-C(23A)-H(23F)	109.5
C(15)-C(14)-C(13)	120.8(3)	H(23D)-C(23A)-H(23E)	109.5
C(19)-C(14)-C(13)	119.8(3)	H(23D)-C(23A)-H(23F)	109.5
C(19)-C(14)-C(15)	119.3(3)	H(23E)-C(23A)-H(23F)	109.5
C(14)-C(15)-H(15)	120.6	C(21)-C(24A)-H(24D)	109.5
C(16)-C(15)-C(14)	118.7(3)	C(21)-C(24A)-H(24E)	109.5
C(16)-C(15)-H(15)	120.6	C(21)-C(24A)-H(24F)	109.5
C(15)-C(16)-C(17)	121.4(3)	H(24D)-C(24A)-H(24E)	109.5
C(15)-C(16)-C(20)	120.3(3)	H(24D)-C(24A)-H(24F)	109.5
C(17)-C(16)-C(20)	118.3(3)	H(24E)-C(24A)-H(24F)	109.5
C(16)-C(17)-H(17)	119.7	N(5)-Se(5)-Se(6)	90.76(9)
C(16)-C(17)-C(18)	120.7(3)	N(6)-Se(6)-Se(5)	91.71(9)
C(18)-C(17)-H(17)	119.7	C(25)-N(5)-Se(5)	115.5(2)
C(17)-C(18)-C(21)	121.1(3)	C(25)-N(6)-Se(6)	114.4(2)
C(19)-C(18)-C(17)	117.1(3)	N(5)-C(25)-C(26)	117.0(3)
C(19)-C(18)-C(21)	121.6(4)	N(6)-C(25)-N(5)	127.7(3)
C(14)-C(19)-H(19)	118.6	N(6)-C(25)-C(26)	115.3(3)
C(18)-C(19)-C(14)	122.7(4)	C(27)-C(26)-C(25)	120.8(3)
C(18)-C(19)-H(19)	118.6	C(31)-C(26)-C(25)	119.4(3)
N(12)-C(20)-C(16)	177.6(4)	C(31)-C(26)-C(27)	119.8(3)
C(18)-C(21)-C(22)	112.2(4)	C(26)-C(27)-H(27)	121.0
C(18)-C(21)-C(23)	112.1(5)	C(28)-C(27)-C(26)	118.1(3)
C(18)-C(21)-C(23A)	110.2(5)	C(28)-C(27)-H(27)	121.0
C(18)-C(21)-C(24A)	106.0(9)	C(27)-C(28)-C(32)	121.0(3)
C(23)-C(21)-C(22)	103.1(6)	C(29)-C(28)-C(27)	121.7(3)

C(29)-C(28)-C(32)	117.2(3)	C(33)-C(34)-H(34B)	109.5
C(28)-C(29)-H(29)	119.6	C(33)-C(34)-H(34C)	109.5
C(28)-C(29)-C(30)	120.8(3)	H(34A)-C(34)-H(34B)	109.5
C(30)-C(29)-H(29)	119.6	H(34A)-C(34)-H(34C)	109.5
C(29)-C(30)-C(33)	121.2(3)	H(34B)-C(34)-H(34C)	109.5
C(31)-C(30)-C(29)	116.7(3)	C(33)-C(35)-H(35A)	109.5
C(31)-C(30)-C(33)	122.0(3)	C(33)-C(35)-H(35B)	109.5
C(26)-C(31)-C(30)	122.9(3)	C(33)-C(35)-H(35C)	109.5
C(26)-C(31)-H(31)	118.5	H(35A)-C(35)-H(35B)	109.5
C(30)-C(31)-H(31)	118.5	H(35A)-C(35)-H(35C)	109.5
N(13)-C(32)-C(28)	176.5(4)	H(35B)-C(35)-H(35C)	109.5
C(30)-C(33)-C(35)	110.7(3)	C(33)-C(36)-H(36A)	109.5
C(34)-C(33)-C(30)	111.4(3)	C(33)-C(36)-H(36B)	109.5
C(34)-C(33)-C(35)	106.5(4)	C(33)-C(36)-H(36C)	109.5
C(34)-C(33)-C(36)	109.7(4)	H(36A)-C(36)-H(36B)	109.5
C(36)-C(33)-C(30)	108.7(3)	H(36A)-C(36)-H(36C)	109.5
C(36)-C(33)-C(35)	109.8(4)	H(36B)-C(36)-H(36C)	109.5
C(33)-C(34)-H(34A)	109.5		



(a)



(b)

Figure S1. Two views of the layer structure in the crystal lattice of **2**. The layer is ~ 6.7 Å thick and approximately parallel to the (1 0 1) Miller plane. Both the pin-wheel tetramers (sulfur atoms false-orange) and two-fold clusters (sulfur yellow) lie within the plane which is seen (a) from a top view and (b) a side view. The unit cell boundaries are included. These views may be contrasted with Figure S3 in the ESI of R.T. Boéré, *CrystEngComm*, 18, 2748, 2016.

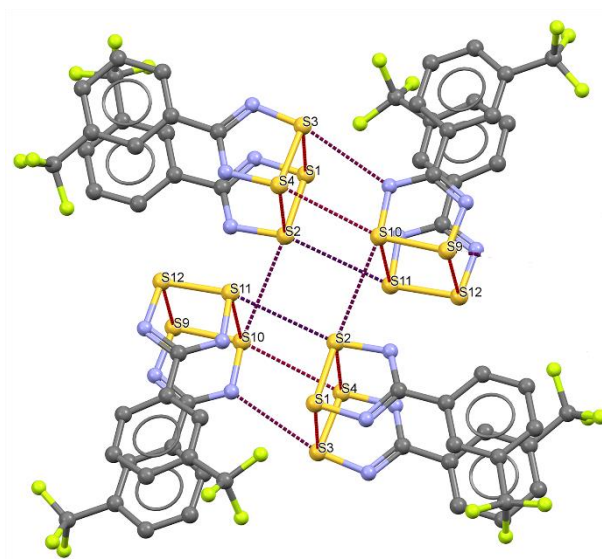


Figure S2. View of the centrosymmetric, pin-wheel clusters in the asymmetric unit of **2** showing intermolecular contacts shorter than ($\Sigma r_{vdW} - 0.2 \text{ \AA}$). H atoms have been removed to enhance visibility.

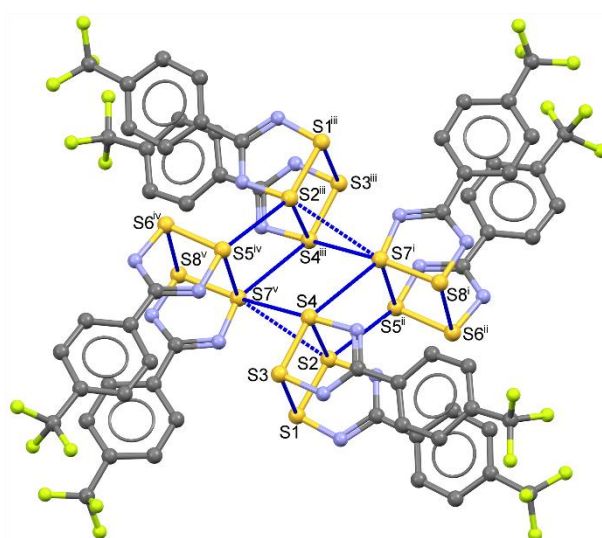
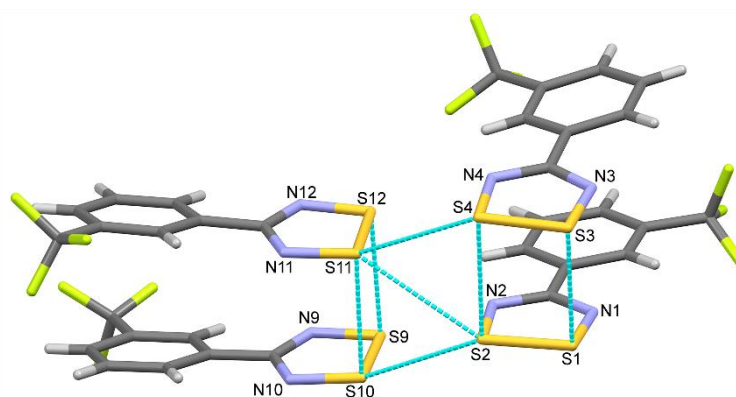


Figure S3. One of two symmetry-independent, centrosymmetric, pin-wheel clusters in the asymmetric unit of **1** showing intermolecular contacts shorter than ($\Sigma r_{vdW} - 0.2 \text{ \AA}$). H atoms have been removed to enhance visibility. [Symmetry codes: (i) $x, -1+y, z$; (ii) $1+x, -1+y, z$, (iii) $1+x, -1+y, z$, (iv) $-x, 1-y, 1-z$, (v) $1-x, 1-y, 1-z$.] The similarity in pin-wheel arrangement to that observed for the single pin-wheel found in **2** (Figure S3) is striking.

Table S7. Intermolecular Contacts in **2** less than ($\Sigma r_{vdW} - 0.1$ Å) (except for inter-slice distances)

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length < Σr_{vdW}
<i>Cis-oid Dimer</i>					
S1	S3	x,y,z	x,y,z	3.089(2)	-0.511
S9	S12	x,y,z	1-x,1-y,1-z	3.115(2)	-0.485
S10	S11	x,y,z	1-x,1-y,1-z	3.119(2)	-0.481
S2	S4	x,y,z	x,y,z	3.149(2)	-0.451
<i>Mean(s.u.)</i>				3.12(2)	-0.48(2)
<i>Twisted Dimer</i>					
S7	S5	x,y,z	1-x,-y,1-z	3.009(2)	-0.591
N7	S6	x,y,z	1-x,-y,1-z	3.066(4)	-0.284
S8	N5	x,y,z	1-x,-y,1-z	3.094(4)	-0.256
<i>S,N Mean(s.u.)</i>				3.08(1)	-0.38(15)
<i>Dimer-to-neighbour – Cis-oid Pinwheel</i>					
N10	S3	x,y,z	-1+x,y,-1+z	3.119(4)	-0.231
S10	S4	x,y,z	-1+x,y,-1+z	3.317(2)	-0.283
S2	S10	x,y,z	1-x,-y,1-z	3.387(1)	-0.213
S2	S11	x,y,z	x,-1+y,z	3.461(1)	-0.139
S4	S11	-1+x,y,z	x,-1+y,z	3.495(1)	-0.105
<i>S,S Mean(s.u.)</i>				3.42(7)	-0.19(7)
<i>Dimer-to-neighbour – Cis-oid to Twisted</i>					
S9	S5	x,y,z	1-x,-y,1-z	3.404(2)	-0.196
S12	S5	x,y,z	x,1+y,z	3.489(2)	-0.111
<i>Mean(s.u.)</i>				3.35(8)	-0.25(7)
<i>Inter-slice</i>					
C25	C11	x,y,z	-1+x,y,z	3.315(6)	-0.085
C25	C12	x,y,z	-1+x,y,z	3.458(6)	+0.058
S4	S11	x,y,z	1-x,1-y,2-z	3.601(2)	+0.001

**Figure S4.** Detailed view of the end-to-side contacts of one DTDA dimer with another in the same layer in the structure of **2**. This group is the left-hand side of the pin-wheel cluster shown in Figure S2.

Single-crystal X-ray diffraction: 'hexagonal' or 'grey' selenium

During attempts to purify *bis*DSDA **3** by vacuum sublimation, clumps of very small needles were repeatedly observed in the sublimation tubes from which, eventually, crystals of the partly decomposed DSDA rings **4** were also obtained. The structure was solved and refined in $P3_121$ with $Z = 3$ and displays three-fold helical chains of Se atoms along all the c unit cell edges. The repeat distance along the cell edge is 1.657 Å (one third) whilst the Se-Se bond length is 2.3801(15) Å and the Se-Se-Se angles are 103.12(5)° (lit. 2.373 Å, 103.1°).²⁷ The Se-Se-Se-Se torsion angle is 100.7(1)°. These data are in good agreement with the literature: N. N. Greenwood and A. Earnshaw, *Chemistry of the Elements*, 2nd Ed. (Oxford: Butterworth-Heinemann, 1997), p. 751.

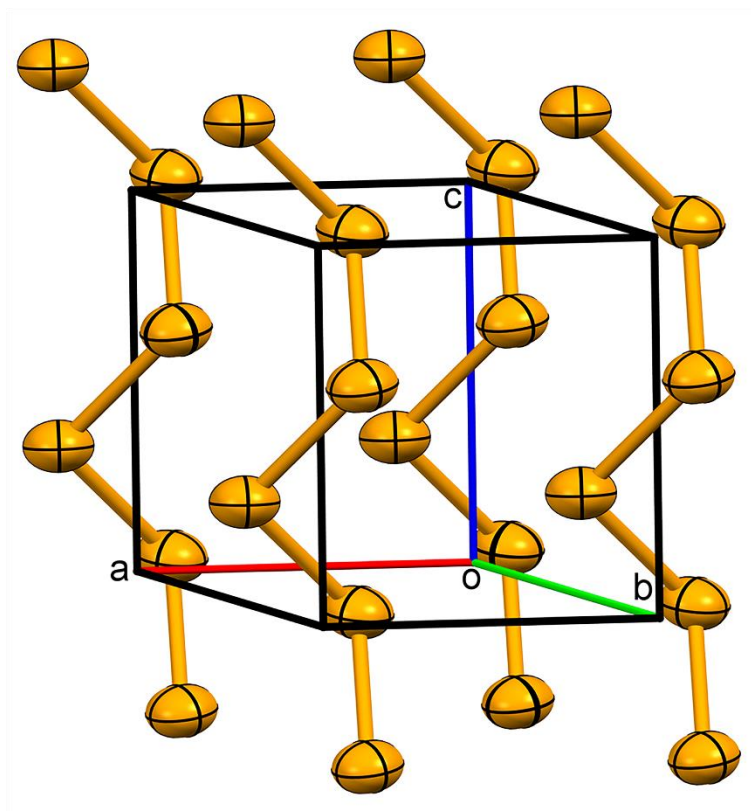


Figure S5. Displacement ellipsoids plot (40% probability) of grey selenium showing the three-fold helices of Se_∞ along the edges of the trigonal primitive cell in the c direction.

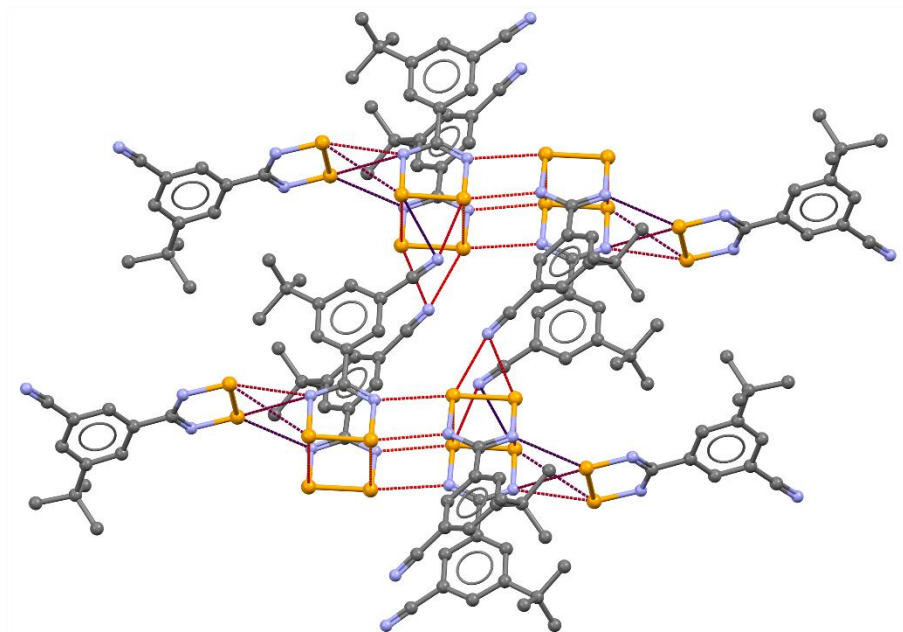


Figure S6. A close-up view of the packing in the lattice of **4a**, showing four asymmetric units linked *via* $\text{Se}_2 \cdots \text{N} \equiv \text{C}-$ contacts, a classic intermolecular synthon in DTDA/DSDA chemistry.

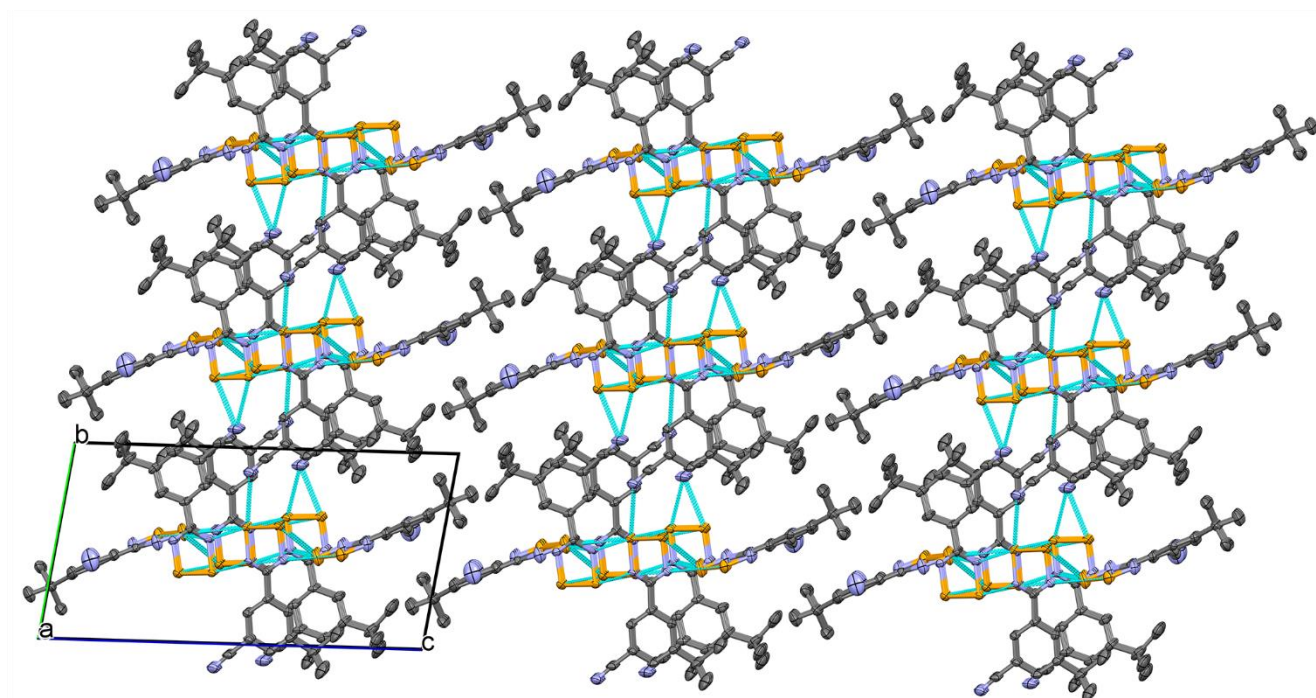


Figure S7. Packing diagram viewed approximately down the b axis for the crystal structure of **4a**. The 6-DSDA ring clusters described in the main text (Figure 4) are linked *via* $\text{Se}_2 \cdots \text{N} \equiv \text{C}-$ contacts. The structure consists of columns of CN_2Se_2 heteroatoms surrounded on all sides by a hydrocarbon sheath.

Table S8. Intermolecular Contacts in **4a** less than ($\Sigma r_{\text{vdW}} - 0.1 \text{ \AA}$)

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length- Σr_{vdW}
Intra-Dimer					
Se1	Se3	x,y,z	x,y,z	3.147(1)	-0.653
Se2	Se4	x,y,z	x,y,z	3.275(1)	-0.526
			<i>Mean(s.u.)</i>	3.211(2)	-0.59
Dimer to side neighbour					
Se1	N3	x,y,z	-x,1-y,1-z	2.968(5)	-0.482
N1	Se3	x,y,z	-x,1-y,1-z	2.921(5)	-0.529
			<i>Mean(s.u.)</i>	2.944(5)	-0.51(2)
Dimer to monomer					
N1	Se5	x,y,z	-x,1-y,1-z	3.208(5)	-0.242
N2	Se6	x,y,z	1-x,1-y,1-z	3.284(5)	-0.166
N4	Se5	x,y,z	1-x,1-y,1-z	3.093(5)	-0.357
N4	Se6	x,y,z	1-x,1-y,1-z	3.175(4)	-0.275
			<i>Mean(s.u.)</i>	3.19(7)	-0.26(7)
Se3	Se5	x,y,z	x,y,z	3.566(1)	-0.234
Se4	Se5	x,y,z	1-x,1-y,1-z	3.563(1)	-0.237
Se4	Se6	x,y,z	1-x,1-y,1-z	3.668(1)	-0.132
			<i>Mean(s.u.)</i>	3.60(5)	-0.20(5)
Dimer to N≡C– (cyano group)					
Se1	N11	x,y,z	x,1+y,z	2.963(6)	-0.487
Se2	N11	x,y,z	x,1+y,z	3.030(5)	-0.42
Se3	N12	x,y,z	x,1+y,z	3.040(6)	-0.41
Se4	N12	x,y,z	x,1+y,z	3.320(5)	-0.13
			<i>Mean(s.u.)</i>	3.09(14)	-0.36(14)

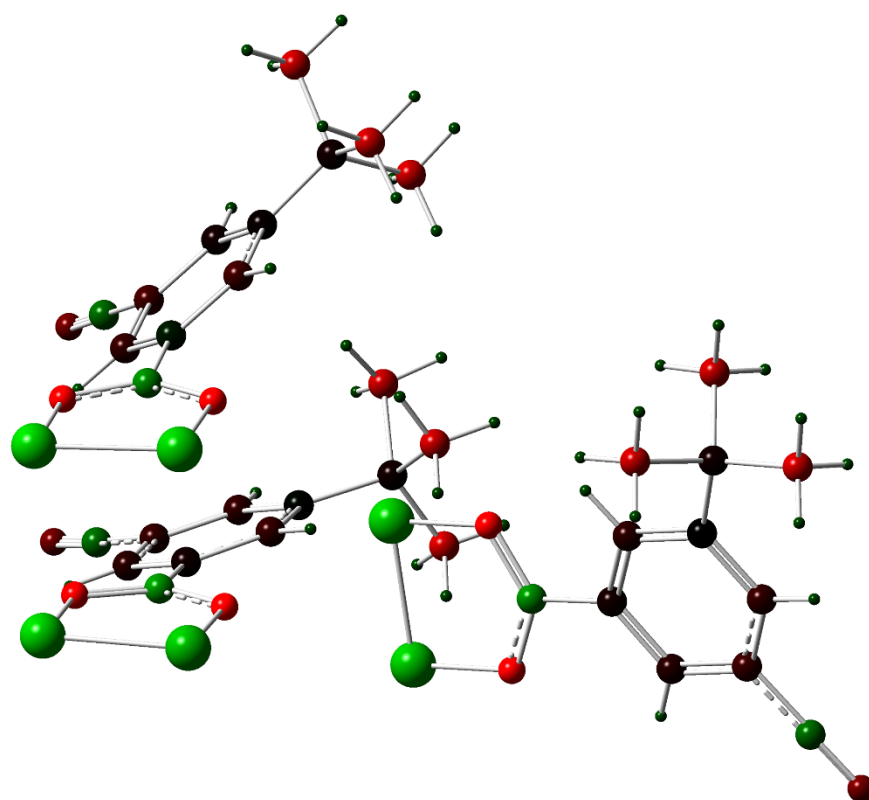


Figure S8. Computed NPA atomic charges from a UB3LYP/6-311+G(2d,p) hybrid DFT calculation on one asymmetric unit of three *dsda* radicals in the crystal structure of **4a**. A doublet electronic state was used which places most of the spin density on the Se1/Se2 *dsda* ring. Bright green represents the most positive and bright red the most negative charges and darker colours are the gradient between these limits. The atom numbers below can be used to read off specific charge values using Table S3, which follows.

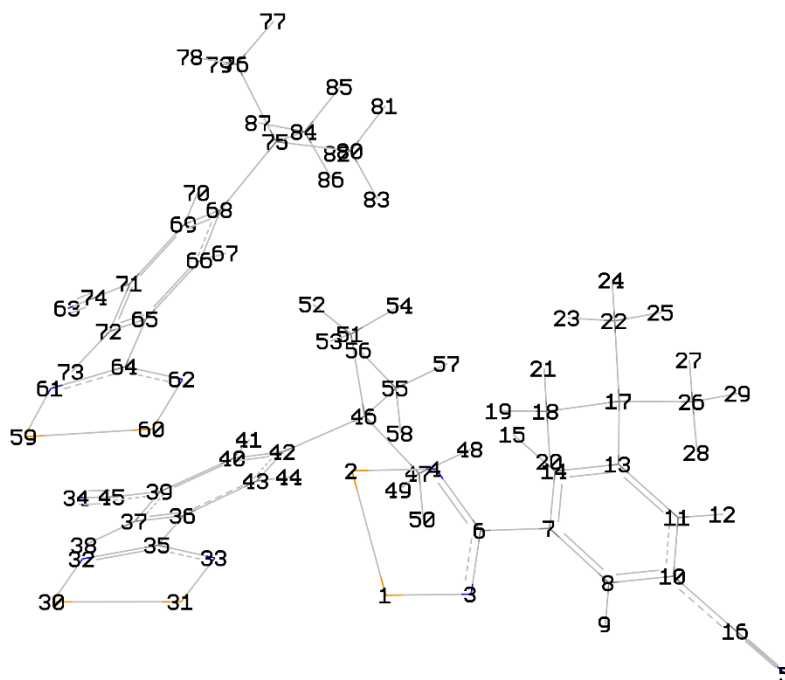


Table S9. Summary of Natural Population Analysis from a DFT Calculation on the Asymmetric Unit in **4a**.

Atom	No	Charge	Core	Valence	Rydberg	Total
Se	1	0.40474	13.99889	2.57707	0.01929	16.59526
Se	2	0.40746	13.99886	2.56987	0.02381	16.59254
N	3	-0.22371	0.9997	2.70545	0.01856	3.72371
N	4	-0.23168	0.99966	2.71379	0.01823	3.73168
N	5	-0.15759	0.99978	2.64407	0.01374	3.65759
C	6	0.14234	0.99942	1.84237	0.01588	2.85766
C	7	-0.02517	0.99951	2.01315	0.01251	3.02517
C	8	-0.05901	0.99942	2.05007	0.00952	3.05901
H	9	0.10205	0	0.39721	0.00074	0.39795
C	10	-0.07689	0.99947	2.06734	0.01008	3.07689
C	11	-0.07633	0.99947	2.06933	0.00754	3.07633
H	12	0.09499	0	0.40441	0.0006	0.40501
C	13	0.00455	0.99951	1.9848	0.01114	2.99545
C	14	-0.071	0.99944	2.06251	0.00906	3.071
H	15	0.09587	0	0.40335	0.00079	0.40413
C	16	0.14335	0.9996	1.83996	0.01709	2.85665
C	17	-0.02821	0.99962	2.02099	0.00761	3.02821
C	18	-0.26239	0.99957	2.25683	0.00599	3.26239
H	19	0.09289	0	0.40662	0.00049	0.40711
H	20	0.09465	0	0.40486	0.00049	0.40535
H	21	0.09352	0	0.40594	0.00054	0.40648
C	22	-0.26313	0.99957	2.25748	0.00607	3.26313
H	23	0.09302	0	0.40649	0.00049	0.40698
H	24	0.09321	0	0.40623	0.00056	0.40679
H	25	0.09434	0	0.40516	0.0005	0.40566
C	26	-0.27194	0.99958	2.26604	0.00632	3.27194
H	27	0.09679	0	0.40271	0.0005	0.40321
H	28	0.09431	0	0.40513	0.00057	0.40569
H	29	0.09447	0	0.40497	0.00056	0.40553
Se	30	0.27144	13.99893	2.70942	0.02021	16.72856
Se	31	0.25348	13.99897	2.72802	0.01953	16.74652
N	32	-0.37214	0.99968	2.85319	0.01927	3.87214
N	33	-0.39543	0.99971	2.87719	0.01853	3.89543
N	34	-0.14964	0.99978	2.63666	0.01321	3.64964
C	35	0.20016	0.99954	1.78427	0.01603	2.79984
C	36	-0.0292	0.99946	2.01687	0.01287	3.0292
C	37	-0.05888	0.99947	2.04983	0.00958	3.05888
H	38	0.10156	0	0.3977	0.00074	0.39844
C	39	-0.0699	0.99946	2.06026	0.01018	3.0699
C	40	-0.06722	0.99947	2.05856	0.00919	3.06722
H	41	0.09463	0	0.40479	0.00058	0.40537
C	42	0.00935	0.99951	1.97882	0.01232	2.99065
C	43	-0.07307	0.99945	2.06356	0.01007	3.07307
H	44	0.0942	0	0.40453	0.00127	0.4058

C	45	0.14342	0.9996	1.84001	0.01697	2.85658
C	46	-0.02658	0.99961	2.01804	0.00893	3.02658
C	47	-0.27236	0.99955	2.26664	0.00617	3.27236
H	48	0.09655	0	0.40287	0.00057	0.40345
H	49	0.09642	0	0.40307	0.00051	0.40358
H	50	0.09815	0	0.40135	0.00051	0.40185
C	51	-0.26066	0.99955	2.25476	0.00634	3.26066
H	52	0.09451	0	0.40455	0.00095	0.40549
H	53	0.09115	0	0.40831	0.00053	0.40885
H	54	0.09303	0	0.40639	0.00058	0.40697
C	55	-0.26501	0.99957	2.25915	0.00629	3.26501
H	56	0.0931	0	0.40628	0.00063	0.4069
H	57	0.09386	0	0.40562	0.00052	0.40614
H	58	0.09015	0	0.40914	0.00072	0.40985
Se	59	0.28164	13.99889	2.69871	0.02077	16.71836
Se	60	0.26964	13.99892	2.71168	0.01976	16.73036
N	61	-0.36595	0.9997	2.84628	0.01998	3.86595
N	62	-0.37171	0.9997	2.85185	0.02016	3.87171
N	63	-0.15133	0.99978	2.63737	0.01417	3.65133
C	64	0.17959	0.99959	1.80105	0.01976	2.82041
C	65	0.03532	0.99946	1.95194	0.01329	2.96468
C	66	-0.08693	0.99953	2.07159	0.0158	3.08693
H	67	0.09619	0	0.40307	0.00074	0.40381
C	68	-0.01442	0.99954	1.99771	0.01717	3.01442
C	69	-0.02859	0.99948	2.01773	0.01138	3.02859
H	70	0.08842	0	0.41048	0.00111	0.41158
C	71	-0.09057	0.99949	2.0744	0.01668	3.09057
C	72	-0.07242	0.99953	2.05684	0.01604	3.07242
H	73	0.10161	0	0.39721	0.00117	0.39839
C	74	0.14064	0.99958	1.84219	0.01759	2.85936
C	75	-0.02979	0.99962	2.02179	0.00837	3.02979
C	76	-0.26427	0.99957	2.25851	0.0062	3.26427
H	77	0.09414	0	0.40529	0.00057	0.40586
H	78	0.09528	0	0.40414	0.00057	0.40472
H	79	0.09239	0	0.40705	0.00056	0.40761
C	80	-0.2653	0.99956	2.25962	0.00612	3.2653
H	81	0.09443	0	0.40496	0.00061	0.40557
H	82	0.09246	0	0.40698	0.00056	0.40754
H	83	0.09446	0	0.40493	0.00061	0.40554
C	84	-0.26251	0.99956	2.25702	0.00593	3.26251
H	85	0.09433	0	0.40516	0.00051	0.40567
H	86	0.09206	0	0.40729	0.00065	0.40794
H	87	0.09291	0	0.40654	0.00054	0.40709
Total		0.50228	128.9739	129.3234	0.70043	258.9977

Determined by a UB3LYP/6-311+G(2d,p) hybrid DFT calculation in Gaussian W03 for the asymmetric unit defined as an electronic doublet state. The numbering scheme for the DFT calculation is shown above.

Table S10. Intermolecular Contacts in **4b** less than ($\Sigma r_{\text{vdW}} - 0.1 \text{ \AA}$)

Atom1	Atom2	Symm. op. 1	Symm. op. 2	Length	Length- Σr_{vdW}
Intra-Dimer					
Se3	Se5	x,y,z	x,y,z	3.1402(6)	-0.66
Se4	Se6	x,y,z	x,y,z	3.4435(6)	-0.356
Se7	Se9	x,y,z	x,y,z	3.2209(6)	-0.579
Se8	Se10	x,y,z	x,y,z	3.2528(6)	-0.547
			<i>Mean(s.u.)</i>	<i>3.26(11)</i>	<i>-0.54(11)</i>
Dimer to side neighbour					
Se7	N3	x,y,z	x,y,z	2.877(3)	-0.573
N7	Se3	x,y,z	x,y,z	3.098(3)	-0.352
Se9	N5	x,y,z	x,y,z	2.994(3)	-0.456
N9	Se5	x,y,z	x,y,z	2.994(3)	-0.456
			<i>Mean(s.u.)</i>	<i>2.99(8)</i>	<i>-0.46(8)</i>
Dimer to monomer					
C39	Se2	x,y,z	x, ½-y, - ½+z	3.448(4)	-0.152
Monomer to N≡C– (cyano group)					
Se1	N11	x,y,z	x,1+y,z	3.019(4)	-0.431
Dimer to N≡C– (cyano group)					
Se7	N14	x,y,z	x,1+y,z	3.001(3)	-0.449
Se8	N14	x,y,z	x,1+y,z	3.007(4)	-0.443
Se9	N15	x,y,z	x,1+y,z	2.972(3)	-0.478
N12	Se3	x,y,z	x,1+y,z	2.915(3)	-0.535
N12	Se4	x,y,z	x,1+y,z	3.158(4)	-0.292
N13	Se5	x,y,z	x,1+y,z	2.945(3)	-0.505
N13	Se6	x,y,z	x,1+y,z	3.091(3)	-0.359
			<i>Mean(s.u.)</i>	<i>3.01(8)</i>	<i>-0.44(8)</i>

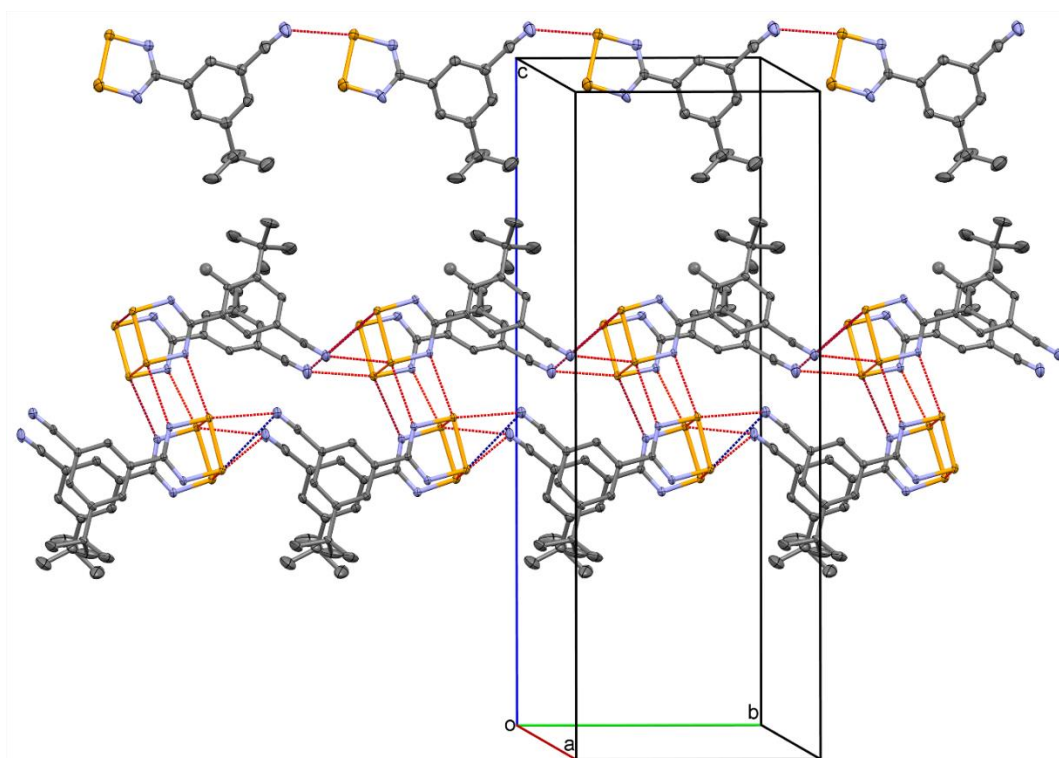


Figure S9. Another view of the lattice structure of **4b**, showing the double-layer strand of the *cis*-oid dimers catenated through $\text{-C}\equiv\text{N}$: to Se contacts and, at the top, the chain of monomeric Se1,Se2 radicals also catenated via $\text{-C}\equiv\text{N}$: to Se contacts.

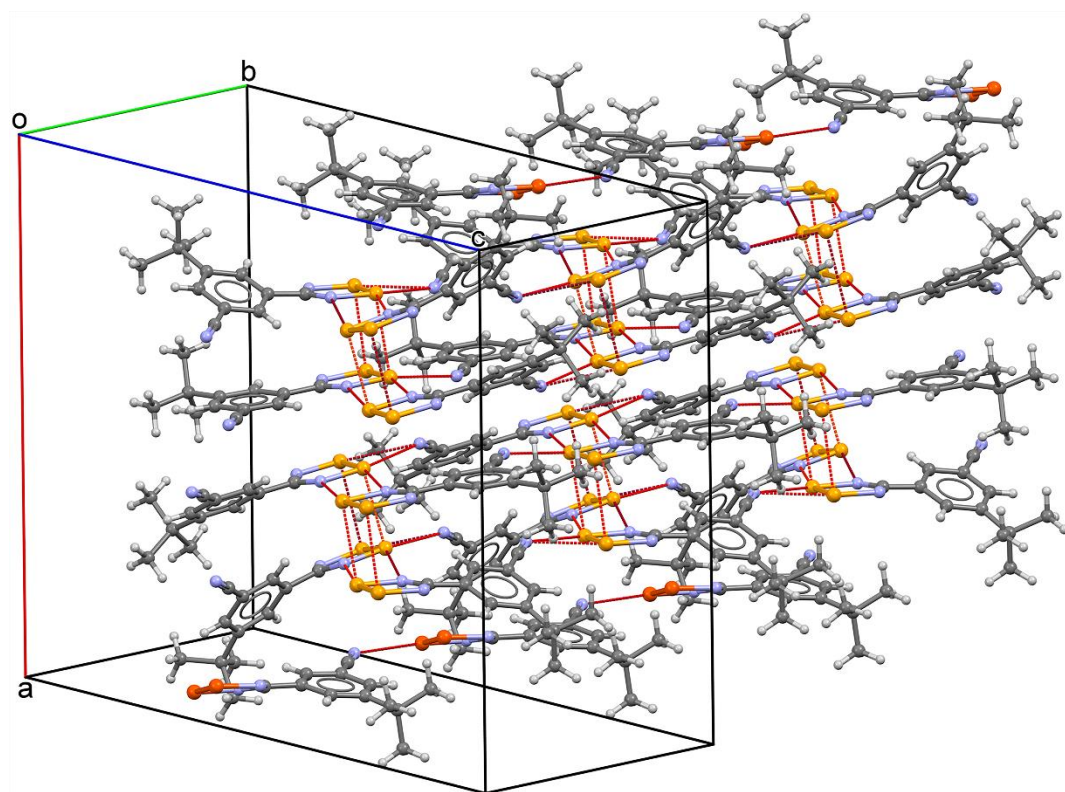


Figure S10. Alternate packing diagram for the structure of **4b**.

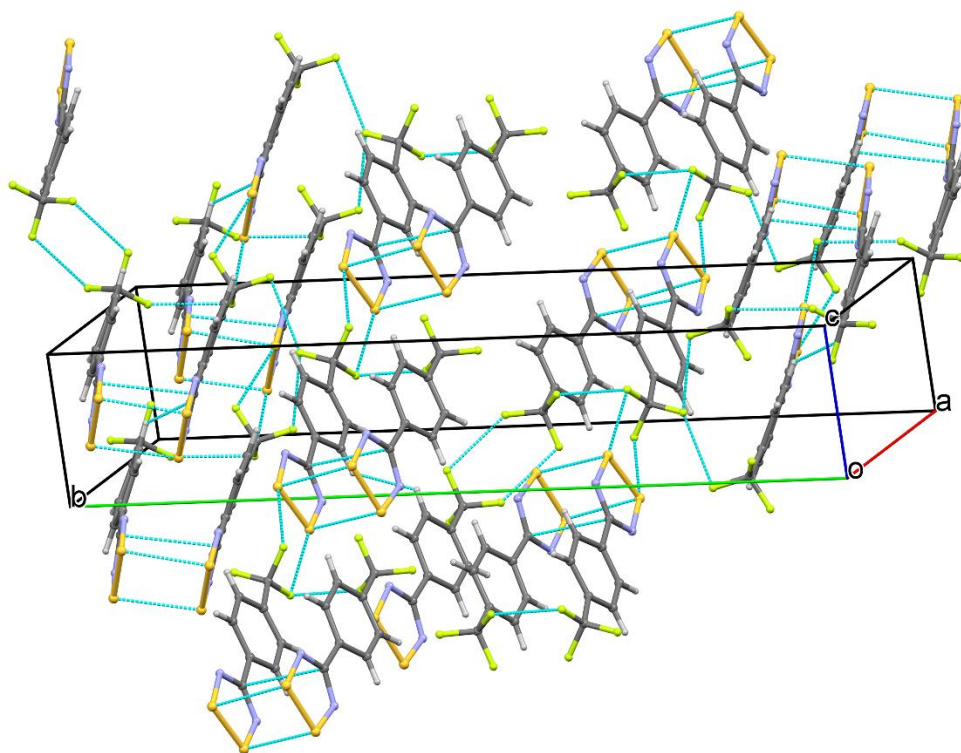


Figure S11. The extended structure of lixgab02 showing the LIMS-I and LIMS-IV short-contacts.

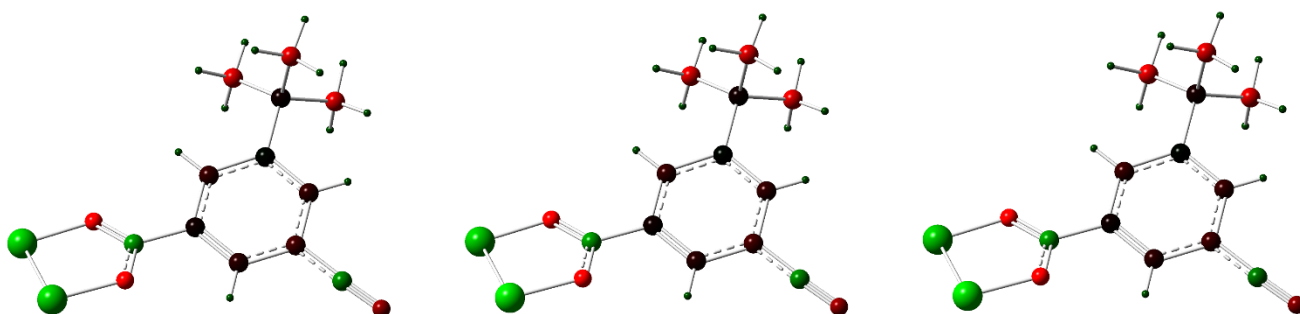


Figure S12. Computed NPA atomic charges from a UB3LYP/6-311+G(2d,p) hybrid DFT calculation on a chain of three of the undimerized Se1,Se2 DSDA radicals in the crystal structure of **4b**. A quartet electronic state was used to simulate a chain of Se1,Se2 DSDA radicals. The atom numbers below can be used to read off specific charge values using Table S4, which follows.

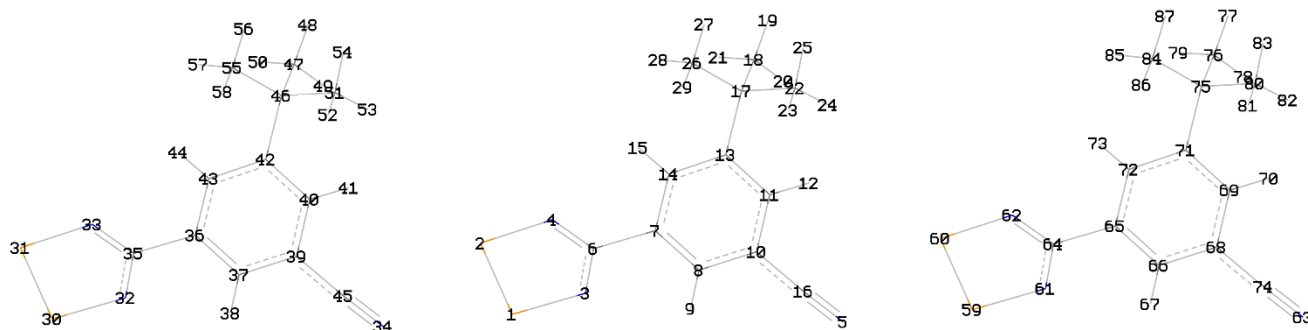


Table S11. Summary of Natural Population Analysis from a DFT calculation on a chain of radicals in **5b**.

Atom	No	Charge	Core	Valence	Rydberg	Total
Se	1	0.43624	13.99893	2.54461	0.02022	16.56376
Se	2	0.38003	13.99883	2.6005	0.02064	16.61997
N	3	-0.22176	0.99971	2.7051	0.01695	3.72176
N	4	-0.24073	0.99967	2.72353	0.01753	3.74073
N	5	-0.18494	0.99976	2.67199	0.01319	3.68494
C	6	0.14076	0.99955	1.84599	0.01371	2.85924
C	7	-0.017	0.9995	2.00607	0.01143	3.017
C	8	-0.05511	0.99943	2.04651	0.00917	3.05511
H	9	0.10144	0	0.39783	0.00073	0.39856
C	10	-0.08317	0.99948	2.07382	0.00987	3.08317
C	11	-0.06898	0.99944	2.06159	0.00795	3.06898
H	12	0.09265	0	0.40657	0.00078	0.40735
C	13	0.00995	0.99953	1.97921	0.0113	2.99005
C	14	-0.07276	0.99944	2.06454	0.00878	3.07276
H	15	0.09634	0	0.4028	0.00085	0.40366
C	16	0.16431	0.99963	1.81978	0.01629	2.83569
C	17	-0.02394	0.99962	2.01674	0.00758	3.02394
C	18	-0.26317	0.99956	2.2577	0.00591	3.26317
H	19	0.09363	0	0.40581	0.00056	0.40637
H	20	0.09452	0	0.405	0.00049	0.40548
H	21	0.09432	0	0.40519	0.00049	0.40568
C	22	-0.26845	0.99957	2.2625	0.00638	3.26845
H	23	0.09549	0	0.40399	0.00051	0.40451
H	24	0.09169	0	0.4077	0.00061	0.40831
H	25	0.09529	0	0.40417	0.00054	0.40471
C	26	-0.27145	0.99957	2.26555	0.00633	3.27145
H	27	0.09563	0	0.40385	0.00052	0.40437
H	28	0.09285	0	0.40662	0.00053	0.40715
H	29	0.09631	0	0.40318	0.00051	0.40369
Se	30	0.39939	13.99891	2.58249	0.01921	16.60061
Se	31	0.40026	13.99884	2.58129	0.0196	16.59974
N	32	-0.21244	0.9997	2.69443	0.01831	3.71244
N	33	-0.23428	0.99967	2.71532	0.0193	3.73428
N	34	-0.18407	0.99976	2.67102	0.01328	3.68407
C	35	0.14163	0.99955	1.84466	0.01415	2.85837
C	36	-0.01638	0.99949	2.00555	0.01133	3.01638
C	37	-0.05925	0.99949	2.05156	0.0082	3.05925
H	38	0.10184	0	0.39741	0.00075	0.39816
C	39	-0.08061	0.99947	2.07114	0.01	3.08061
C	40	-0.06757	0.99944	2.06004	0.0081	3.06757
H	41	0.09294	0	0.40628	0.00078	0.40706
C	42	0.01138	0.99953	1.97773	0.01136	2.98862
C	43	-0.07261	0.99943	2.06427	0.0089	3.07261
H	44	0.09683	0	0.40234	0.00083	0.40317

C	45	0.16445	0.99963	1.8197	0.01623	2.83555
C	46	-0.02385	0.99962	2.01666	0.00757	3.02385
C	47	-0.26304	0.99956	2.25754	0.00594	3.26304
H	48	0.09418	0	0.40526	0.00055	0.40582
H	49	0.09434	0	0.40517	0.00049	0.40566
H	50	0.0945	0	0.40501	0.00049	0.4055
C	51	-0.26839	0.99957	2.26243	0.00639	3.26839
H	52	0.09552	0	0.40397	0.00051	0.40448
H	53	0.09143	0	0.40795	0.00061	0.40857
H	54	0.0958	0	0.40367	0.00053	0.4042
C	55	-0.27137	0.99957	2.26543	0.00636	3.27137
H	56	0.09623	0	0.40325	0.00051	0.40377
H	57	0.09297	0	0.40649	0.00053	0.40703
H	58	0.09624	0	0.40325	0.00051	0.40376
Se	59	0.4336	13.99893	2.54717	0.02031	16.5664
Se	60	0.37795	13.99883	2.60253	0.02068	16.62205
N	61	-0.22005	0.99971	2.70331	0.01703	3.72005
N	62	-0.23916	0.99967	2.72186	0.01764	3.73916
N	63	-0.16142	0.9998	2.64869	0.01294	3.66142
C	64	0.13999	0.99955	1.8466	0.01386	2.86001
C	65	-0.01562	0.99949	2.00502	0.01111	3.01562
C	66	-0.06103	0.99949	2.05313	0.00841	3.06103
H	67	0.10181	0	0.39742	0.00077	0.39819
C	68	-0.07541	0.99948	2.066	0.00993	3.07541
C	69	-0.073	0.99948	2.06581	0.00772	3.073
H	70	0.09297	0	0.40639	0.00064	0.40703
C	71	0.00984	0.99953	1.97936	0.01127	2.99016
C	72	-0.07635	0.99944	2.06796	0.00896	3.07635
H	73	0.09614	0	0.40299	0.00087	0.40386
C	74	0.14476	0.99963	1.83932	0.01628	2.85524
C	75	-0.03083	0.99961	2.0235	0.00773	3.03083
C	76	-0.26322	0.99956	2.25766	0.006	3.26322
H	77	0.0932	0	0.40622	0.00057	0.4068
H	78	0.09487	0	0.40465	0.00048	0.40513
H	79	0.09451	0	0.40498	0.0005	0.40549
C	80	-0.26815	0.99957	2.26217	0.00641	3.26815
H	81	0.09588	0	0.40361	0.00051	0.40412
H	82	0.092	0	0.4075	0.0005	0.408
H	83	0.09476	0	0.40468	0.00056	0.40524
C	84	-0.28229	0.99963	2.27578	0.00688	3.28229
H	85	0.09707	0	0.40234	0.0006	0.40293
H	86	0.10142	0	0.39801	0.00057	0.39858
H	87	0.0997	0	0.39974	0.00057	0.4003
Total		1.5	128.9739	128.3942	0.63197	258

Determined by a UB3LYP/6-311+G(2d,p) hybrid DFT calculation in Gaussian W03 for a three-radical chain defined as an electronic quartet state. The numbering scheme for the DFT calculation is shown below.