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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Electronic Supplementary Information

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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 × 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 × 2	1985	4
DIXMII		1	P21/n	8	2	*cis*-oid dimer	2014	6
DIXMOO		1	P-1	8	4	*cis*-oid dimer × 2	2014	6
DIXNAB		1	P21/c	8	2	*cis*-oid dimer	2014	6
DIXNEF		1	P-1	24	12	*cis*-oid dimer × 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 × 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 × 4 [2,5]	2005	12
HAWRAZ01	Polymorph 2	1	Pna21	8	2	monomer × 2 [5]	2005	12
HEMZAA		1	C2	4	1	monomer [3]	1994	13
IFULUQ	Polymorph 1	1	P21/c	16	4	monomer × 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 × 4	2002	14
IFULUQ03	Polymorph 4	1	P-1	8	4	twisted dimer × 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 × 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×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 × 4	2013	25
LIXGAB LIXGAB01	Polymorph 1 *(same)*	1	P-1	16	8	dimer×2 + monomer×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 × 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 × 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	*cis*-oid dimer × 12	1993	33
PHTHAZ PHTHAZ01 PHTHAZ02	 *(repeat)* *(repeat)* [7]	1	P212121	16	4	*cis*-oid dimer × 2	1980 2009 2014	34 35 36
PIZDOR PIZDOR10	S.O.R [7] Misreported [8]	2	P21/c P21/c	4 2	1	monomer [1]	1994 1994	37 38
POYXAC		2	I-42m	8	0.5	half monomer molec. [6]	1998	39
QEFGIT		1	P21/n	8	2	*cis*-oid dimer	2012	40
QEFGOZ		1	P21/c	16	4	*cis*-oid dimer × 2	2012	40
QUNQOG QUNQOG01 QUNQOG02	 *(repeat)* *(repeat)*	1	C2/c	8	1	monomer [1]	2009 2014 2016	35 36 41
QUNQUM QUNQUM01	Mixed dimer *(same)*	1	P21/c	4	1	*cis*-oid dimer	2009 2014	35 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	*cis*-oid dimer	1999	43
SAGMOD		1	P-4	8	2	*cis*-oid dimer	2004	44
SEKDUI SEKDUI01	 *(same)*	1	Pbca	8	1	monomer [4]	2006 2007	45 46
SOBSOR		2	I41/a	32	2	*cis*-oid dimer	1991	47
UJETAG	*Co-crystal*	(omitted)	P-1	2	2	(*cis*-oid dimer+Ph_3Sb)	2016	27
UMAROP		1	P-1	8	4	*cis*-oid dimer × 4	2003	48
UMARUV	*Co-crystal*	(omitted)	Pbcn	16	2	(*cis*-oid dimer+N_2)	2003	48
UMASAC	*Co-crystal*	(omitted)	Pbcn	16	2	(*cis*-oid dimer+CO_2)	2003	48
UMASEG	*Co-crystal*	(omitted)	Pbcn	16	2	(*cis*-oid dimer+Ar)	2003	48
UMASIK	*Co-crystal*	(omitted)	Pbcn	16	2	(*cis*-oid dimer+SO_2)	2003	48
VINJIL		2	P21/n	4	1	monomer [1]	1991	49
VUQGIY		1	P21/n	8	2	*cis*-oid dimer	2010	50
VUQGOE		1	P-1	8	4	*cis*-oid dimer × 2	2010	50
VUQGUK		1	I41/a	32	2	*cis*-oid dimer	2010	50
VUQHAR		1	P21/c	24	6	*cis*-oid dimer × 3	2010	50
VUQHEV		1	P-1	4	2	*cis*-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	*cis*-oid dimer	2010	50
VUXZEU02	Polymorph 3	1	I41/a	32	2	*cis*-oid dimer	2010	50
WALCOC WALCOC01	Mixed dimer *(same)*	2	P21/n	4	1	monomer [6]	2005 2007	52 53
WASHAA		1	P21/n	8	2	*cis*-oid dimer	2005	16
WASHEE		1	C2/c	8	1	monomer [3]	2005	16
WIMNAH WIMNAH01	 (same)	1	C2/c	16	2	*cis*-oid dimer	1994 2016	54 55
WUXPAG		1	C2/c	8	1	monomer [1]	2002	56
YAXVUO		2	P21/c	8	2	*cis*-oid dimer	1993	57
YIMNIT	Mixed dimer	1	Pcab	16	2	*cis*-oid dimer	2013	58
YOMXUT YOMXUT08-10	Polymorph 1 *(same)*	1	P-1	2	1	monomer [5]	1995 2016	59 60
YOMXUT01 YOMXUT02 YOMXUT03-07	Polymorph 2 *(repeats)* *(pressure study)*	1	Fdd2	8	0.5	half monomer molec. [5]	1996 2010 2012	61 62 63
ZADVAB ZADVAB01	*(same)* *Better SG*	1	I2/a C2/c	8	1	monomer [5]	1995 2016	64 41
2 1512475		1	P-1	12	6	dimer + monomer × 4 [1,3]	2017	65

Total 83

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*-antarafacial 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 (~7% in 1965 increasing to ~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 ~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]

References for Table S1 and Explanation Section

1. W. Clegg, M. R. J. Elsegood, CSD Communication (Private Communication), 2016.
2. N. G. R. Hearns, R. Clerac, M. Jennings and K. E. Preuss, *Dalton Trans.*, 2009, 3193.
3. T. M. Barclay, A. W. Cordes, N. A. George, R. C. Haddon, M. E. Itkis and R. T. Oakley, *Chem.Commun.*, 1999, 2269.
4. K. V. Shuvaev, A. Decken, F. Grein, T. S. M. Abedin, L. K. Thompson and J. Passmore, *Dalton Trans.*, 2008, 4029.
5. H.-U. Hofs, J. W. Bats, R. Gleiter, G. Hartmann, R. Mews, M. Eckert-Maksic, H. Oberhammer and G. M. Sheldrick, *Chem. Ber.,* 1985, **118**, 3781.
6. C. P. Constantinides, D. J. Eisler, A. Alberola, E. Carter, D. M. Murphy and J. M. Rawson, *CrystEngComm*, 2014, **16**, 7298.
7. N. Bricklebank, S. Hargreaves and S. E. Spey, *Polyhedron*, 2014, **19**, 7298.
8. J. M. Cole, C. M. Aherne, J. A. K. Howard, A. J. Banister and P. G. Waddell, *Acta Crystallogr., Sect. E: Struct. Rep. Online*, 2011, **67**, o2514.
9. E. M. Fatila, J. Goodreid, R. Clerac, M. Jennings, J. Assoud and K. E. Preus, *Chem. Commun*., 2010, **46**, 6569.
10. G. Antorrena, J. E. Davies, M. Hartley, F. Palacio, J. M. Rawson, J. N. B. Smith and A. Steiner, *Chem. Commun.*, 1999, 1393.
11. A. Alberola, R. J. Lees, F. Palacio, C. M. Pask and J. M. Rawson, *Molecules*, 2004, **9**, 771.

12. A. Alberola, C. S. Clarke, D. A. Haynes, S. I. Pascu and J. M. Rawson, *Chem. Commun*., 2005, 4726.
13. J. N. Bridson, S. B. Copp, M. J. Schriver, S. Zhu and M. J. Zaworotko, *Can. J. Chem.*, 1994, **72**, 1143.
14. A. D. Bond, D. A. Haynes, C. M. Pask and J. M. Rawson, *J. Chem. Soc., Dalton Trans*., 2002, 2522.
15. C. S. Clarke, S. I. Pascu and J. M. Rawson, *CrystEngComm*, 2004, **6**, 79.
16. C. Knapp, E. Lork, K. Gupta and R. Mews, *Z. Anorg. Allg. Chem.*, 2005, **631**, 1640.
17. A. Alberola, R. J. Less, C. M. Pask, J. M. Rawson, F. Palacio, P. Oliete, C. Paulsen, A. Yamaguchi, R. D. Farley and D. M. Murphy, *Angew. Chem., Int. Ed*., 2003, **42**, 4782.
18. A. W. Cordes, J. D. Goddard, R. T. Oakley and N. P. C. Westwood, *J. Am. Chem. Soc*., 1989, 111, 6147.
19. A. J. Banister, M. I. Hansford, Z. V. Hauptman, S. T. Wait and W. Clegg, *J. Chem. Soc., Dalton Trans.*, 1989, 1705.
20. M. Jennings, K. E. Preuss and J. Wu, *Chem. Commun*., 2006, 341.
21. A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer and J. V. Waszczak, *J. Am. Chem. Soc*., 1992, **114**, 5000.
22. A. W. Cordes, C. M. Chamchoumis, R. G. Hicks, R. T. Oakley, K. M. Young and R. C. Haddon, *Can. J. Chem*., 1992, **70**, 919.
23. A. W. Cordes, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, L. F. Schneemeyer and J. V. Waszczak, *Inorg. Chem*., 1993, **32**, 1554.
24. C. D. Bryan, A. W. Cordes, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, C. D. MacKinnon, R. T. Oakley, T. T. M. Palstra, A. S. Perel, S. R. Scott, L. F. Schneemeyer and J. V. Waszczak, *J. Am. Chem. Soc*., 1994, **116**, 1205.
25. Y. Beldjoudi, D. A. Haynes, J. J. Hayward, W. J. Manning, D. R. Pratt and J. M. Rawson, *CrystEngComm*, 2013, **15**, 1107.
26. H. F. Lau, P. C. Y. Ang, V. W. L. Ng, S. L. Kuan, L. Y. Goh, A. S. Borisov, P. Hazendonk, T. L. Roemmele, R. T. Boeré and R. D. Webster, *Inorg. Chem*., 2008, **47**, 632.
27. R. T. Boeré, *CrystEngComm*, 2016, **18**, 2748.
28. M. B. Hursthouse, S. J. Coles and N. Bricklebank, CSD Communication (Private Communication), 2003.
29. A. Alberola, E. Carter, C. P. Constantinides, D. J. Eisler, D. M. Murphy and J. M. Rawson, *Chem. Commun*., 2011, **47**, 2532.
30. A. J. Banister, A. S. Batsanov, O. G. Dawe, P. L. Herbertson, J. A. K. Howard, S. Lynn, I. May, J. N. B. Smith, J. M. Rawson, T. E. Rogers, B. K. Tanner, G. Antorrena and F. Palacio, *J. Chem. Soc., Dalton Trans*., 1997, 2539.
31. L. Beer, A. W. Cordes, D. J. T. Myles, R. T. Oakley and N. J. Taylor, *CrystEngComm*, 2000, **2**, 109.
32. A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley and T. T. M. Palstra, *Inorg. Chem*., 1992, **31**, 1802.
33. A. W. Cordes, C. D. Bryan, W. M. Davis, R. H. de Laat, S. H. Glarum, J. D. Goddard, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, S. R. Scott and N. P. C. Westwood*, J. Am. Chem. Soc*., 1993, **115**, 7232.
34. A. Vegas, A. Perez-Salazar, A. J. Banister and R. G. Hey, *J. Chem. Soc., Dalton Trans*., 1980, 1812.
35. C. Alan, D. A. Haynes, C. M. Pask and J. M. Rawson, *CrystEngComm*, 2009, **11**, 2048.
36. S. Domagala, K. Kosc, S. W. Robinson, D. A. Haynes and K. Wozniak, *Cryst. Growth Des.*, 2014, **14**, 4834.
37. C. D. Bryan, A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra and A. J. Perel, *Chem. Commun.*, 1994, 1447.
38. R. G. Hicks, C. D. Mackinnon, R. T. Oakley, C. D. Bryan, A. W. Cordes and R. C. Haddon, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, 1994, **93**, 439.
39. R. A. Beekman, R. T. Boeré, K. H. Moock and M. Parvez, *Can. J. Chem*., 1998, **76**, 85.

40. J. M. Cole, C. M. Aherne, P. G. Waddell, A. J. Banister, A. S. Batsanov and J. A. K. Howard, *Polyhedron*, 2012, **45**, 61.
41. S. Domagala and D. A. Haynes, *CrystEngComm*, 2016, **18**, 7116.
42. A. W. Cordes, R. C. Haddon, C. D. MacKinnon, R. T. Oakley, G. W. Patenaude, R. W. Reed, T. Rietveld and K. E. Vajda, *Inorg. Chem*., 1996, **35**, 7626.
43. A. M. T. Bell, J. N. B. Smith, J. P. Attfield, J. M. Rawson, K. Shankland and W. I. F. David, *New J. Chem.*, 1999, **23**, 565.
44. N. G. R. Hearns, K. E. Preuss, J. F. Richardson and S. Bin-Salamon, *J. Am. Chem. Soc.*, 2004, **126**, 9942.
45. H. F. Lau, V. W. L. Ng, L. L. Koh, G. K. Tan, L. Y. Goh, T. L. Roemmele, S. D. Seagrave and R. T. Boeré, *Angew. Chem., Int. Ed*., 2006, **45**, 4498.
46. R. T. Boeré, L.-Y. Goh, C. Y. Ang, S. L. Kuan, H. F. Lau, V. W. L. Ng, T. L. Roemmele and S. D. Seagrave, *J. Organomet. Chem*., 2007, **692**, 2697.
47. M. P. Andrews, A. W. Cordes, D. C. Douglass, R. M. Fleming, S. H. Glarum, R. C. Haddon, P. Marsh, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, G. W. Trucks, R. Tycko, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc.*, 1991, **113**, 3559.
48. C. S. Clarke, D. A. Haynes, J. M. Rawson and A. D. Bond, *Chem. Commun.*, 2003, 2774.
49. A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman*, J. Am. Chem. Soc*., 1991, **113**, 582.
50. C. S. Clarke, D. A. Haynes, J. N. B. Smith, A. S. Batsanov, J. A. K. Howard, S. I. Pascu and J. M. Rawson, *CrystEngComm*, 2010, **12**, 172.
51. E. M. Fatila, M. C. Jennings, J. Goodreid and K. E. Preuss, *Acta Crystallogr., Sect.* C, 2010, **66**, o260.
52. T. S. Cameron, M. T. Lemaire, J. Passmore, J. M. Rawson, K. V. Shuvaev and L. K. Thompson, *Inorg. Chem.*, 2005, **44**, 2576.
53. A. Decken, T. S. Cameron, J. Passmore, J. M. Rautiainen, R. W. Reed, K. V. Shuvaev and L. K. Thompson, *Inorg. Chem*., 2007, **46**, 7436.
54. R. T. Boeré, K. H. Moock and M. Parvez, *Z. Anorg. Allg. Chem*., 1994, **620**, 1589.
55. W. Clegg, CSD Communication (Private Communication), 2016.
56. G. Antorrena, S. Brownridge, T. S. Cameron, F. Palacio, S. Parsons, J. Passmore, L. K. Thompson and F. Zarlaida, *Can. J. Chem*., 2002, **80**, 1568.
57. A. W. Cordes, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, S. R. Scott and J. V. Waszczak, *Chem. Mater*., 1993, **5**, 820.
58. S. W. Robinson, D. A. Haynes and J. M. Rawson, *CrystEngComm*, 2013, **15**, 10205.
59. A. J. Banister, N. Bricklebank, W. Clegg, M. R. J. Elsegood, C. I. Gregory, I. Lavender, J. M. Rawson and B. K. Tanner, *Chem. Commun*., 1995, 679.
60. Y. Beldjoudi, A. Arauzo, F. Palacio, M. Pilkington and J. M. Rawson, *J. Am. Chem. Soc*., 2016, **138**, 16779.
61. A. J. Banister, N. Bricklebank, I. Lavender, J. M. Rawson, C. I. Gregory, B. K. Tanner, W. Clegg, M. R. J. Elsegood and F. Palacio, *Angew. Chem., Int. Ed.*, 1996, **35**, 2533.
62. M. Deumal, J. M. Rawson, A. E. Goeta, J. A. K. Howard, R. C. B. Copley, M. A. Robb and J. J. Novoa, *Chem.-Eur. J*., 2010, **16**, 2741.
63. R. I. Thomson, C. M. Pask, G. O. Lloyd, M. Mito and J. M. Rawson, *Chem.-Eur. J*., 2012, **18**, 8629.
64. A. J. Banister, N. Bricklebank, W. Clegg, M. R .J. Elsegood, C. I. Gregory, I. Lavender, J. M .Rawson and B. K. Tanner, CSD Communication (Private Communication), 1995.
65. This work

66. C. P. Brock, *Acta Cryst. B: Structure Science, Crystal Engineering, Materials*, 2016, B**72**, 807.
67. K. M. Steed and J. W. Steed, *Chem. Rev.*, 115, 2015, 2895.
68. R. Suiza, A. Iwasaki, Y. Shuku and K. Awaga, *J. Mater. Chem. C*., 2015, **3**, 7968.

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 WIMNEL10	*(same)* S.O.R. [5]		P21/n	8	2	*cis*-oid dimer	1994 1995	9 10
XEHTIN		1	P21/c	8	2	dimer (orthog)	2000	11
XEHTOT XEHTOT01	*(repeated)* S.O.R. [5]	1	Pca21	8	2	dimer (orthog)	2000 2016	11 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.

References for Table S2

1. J. Wu, D. J. MacDonald, R. Clerac, I.-R. Jeon, M. Jennings, A. J. Lough, J. Britten, C. Robertson, P. A. Dube and K. E. Preuss, *Inorg. Chem*., 2012, **51**, 3827.
2. P. Del Bel Belluz, A. W. Cordes, E. M. Kristof, P. V. Kristof, S. W. Liblong and R. T. Oakley, *J. Am. Chem. Soc*. 1989, **111**, 9276.
3. A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley and T. T. M. Palstra, *Inorg. Chem*., 1992, **31**, 1802.
4. M. P. Andrews, A. W. Cordes, D. C. Douglass, R. M. Fleming, S. H. Glarum, R. C. Haddon, P. Marsh, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, G. W. Trucks, R. Tycko, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc*., 1991, **113**, 3559.
5. A. W. Cordes, R. C. Haddon, R. G. Hicks, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer and J. V. Waszczak, *J. Am. Chem. Soc*., 1992, **114**, 1729.
6. A. W. Cordes, R. C. Haddon, R. T. Oakley, L. F. Schneemeyer, J. V. Waszczak, K. M. Young and N. M. Zimmerman, *J. Am. Chem. Soc*., 1991, **113**, 582.

7. W. M. Davis, R. G. Hicks, R. T. Oakley, B. Zhao and N. J. Taylor, *Can. J. Chem*., 1993, **71**, 180.
8. L. Beer, A. W. Cordes, D. J. T. Myles, R. T. Oakley and N. J. Taylor, *CrystEngComm*, 2000, **2**, 109.
9. R. T. Boeré, K. H. Moock and M. Parvez, *Z. Anorg. Allg. Chem.*, 1994, **620**, 1589.
10. M. Parvez, R. T. Boeré and K. H. Moock, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1995, **51**, 2118.
11. N. Feeder, R. J. Less, J. M. Rawson, P. Oliete and F. Palacio, *Chem. Commun*., 2000, 2449.
12. R. L. Melen, R. J. Less, C. M. Pask and J. M. Rawson, *Inorg. Chem*., 2016, **55**, 11747.
13. A. W. Cordes, S. H. Glarum, R. C. Haddon, R. Hallford, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, T. T. M. Palstra and S. R. Scott, *Chem. Commun.,* 1992, 1265.
14. A. W. Cordes, R. C. Haddon, R. G. Hicks, D. K. Kennepohl, R. T. Oakley, T. T. M. Palstra, L. F. Schneemeyer, S. R. Scott and J. V. Waszczak, *Chem. Mater*., 1993, **5**, 820.
15. J. F. Britten, O. P. Clements, A. W. Cordes, R. C. Haddon, R. T. Oakley and J. F. Richardson, *Inorg. Chem.,* 2001, **40**, 6820.
16. C. D. Bryan, A. W. Cordes, R. T. Oakley and R. E. von H. Spence, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.,* 1995, **51**, 2402.
17. This work.

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 (^{1}H) and 62.90 (^{13}C) MHz on a Bruker AC250-F spectrometer and referenced to $CHCl_3$ at 7.25 (^{1}H) or $CDCl_3$ at 77 ppm (^{13}C). 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 $SeCl_2$

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 Cl_2 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 Cl_2 flushed out with an N_2 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 ($SeCl_4$) to deep brown. Care was taken to insure that all the $SeCl_4$ had been converted into $SeCl_2$ 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-$(Se_2N_2C)_2$-C_6H_3, 3

To a solution of $SeCl_2$ (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-$[(Se_2N_2C)C_6H_3(CN_2Se_2)]_2^{+}2Cl^{-}$ 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-C_6H_3-$(CN_2Se_2)_2$, **4a** and **4b**, all of which have been characterized by single-crystal X-ray diffraction (see below).

Preparation of [5-^{t}Bu-1,3-$(Se_2N_2C)_2$-C_6H_3][SbF_6]$_2$, 5

$NOSbF_6$ (0.89 g, 3.34 mmol) and 5-^{t}Bu-1,3-$[(Se_2N_2C)C_6H_3(CN_2Se_2)]_2^+2Cl^-$ 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 N_2 and the mixture refluxed using an air-condenser with an N_2 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 CH_2Cl_2 and cooled to −30°C to afford dark red crystals. Analysis for $C_{12}H_{12}F_{12}N_4Sb_2Se_4$: 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. $KSbF_6$ (ν_3 = 665; ν_5 = 288 cm^{-1}).[4] The vibrational spectroscopy is therefore consistent with a successful introduction of the SbF_6^- 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 Kα 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 CF_3 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 Kα 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 SHELXT [7] 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_{iso} = 1.2U_{eq}(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 off 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 where then frozen at this level. Despite using EADP and ISOR restraints, the C22/C22A component went highly oblate ad 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 PBEPBE/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).

References for the Experimental Section

1. R. T. Boeré, R. G. Hicks and R. T. Oakley. *Inorg. Synth*., 1997, **21**, 94-98.
2. R. T. Boeré, K. H. Moock, S. Derrick, W. Hoogerdijk, K. Preuss and J. Yip, *Can. J. Chem.*, 1993, 473-486.
3. R. A. Beekman, R. T. Boeré, K. H. Moock and M. Parvez, *Can. J. Chem.*, 1998, **76**, 85-93.
4. G. Davidson, *Spectroscopic Properties of inorganic and organometallic compounds*, RSC Specialist Periodical Reports, 1991, vol 34.
5. R. T. Boeré, *CrystEngComm*, 2016, **18**, 2748-2756.
6. Bruker (2008). *APEX2*, *SAINT-Plus* and *SADABS*. Bruker AXS Inc., Madison Wisconsin, USA.
7. G. M. Sheldrick, *Acta Crystallogr. Sect. A, Found. Crystalog.,* 2008, **64**, 112–122.
8. G. M. Sheldrick, *Acta Crystalogr. Sect. C,. Struct. Chem.,* 2015, **71**, 3–8.
9. D. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Cryst.,* 2006, **39**, 453–457.
10. Gaussian 03, Revision C.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, and J. A. Pople, Gaussian, Inc., Wallingford CT, 2004.

Table S3. Crystal, structure determination and refinement parameters

Parameter	**2**	**Se**	**4a**	**4b**
Formula	$C_8H_4F_3N_2S_2$	Se	$C_{12}H_{12}N_3Se_2$	$C_{12}H_{12}N_3Se_2$
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	Monoclinc
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:	$-7 \le h \le 9$	$-5 \le h \le 4$	$-12 \le h \le 12$	$-27 \le h \le 27$
	$-21 \le k \le 21$	$-5 \le k \le 5$	$-13 \le k \le 13$	$-13 \le k \le 13$
	$-31 \le l \le 31$	$-6 \le l \le 6$	$-26 \le l \le 26$	$-39 \le l \le 39$
Total rfl.	51041	1066	21974	74801
Indep. rfl.	11371	120	8884	15899
R_{int}	0.0622	0.0315	0.0828	0.0447
Compl. (%), θ = 25.5°	99.0	100.0	99.5	99.8
Abs. corr.	Gaussian	Semi-empirical from equivalents		
Max., min. transmission	0.857	1.000	0.7456	0.8995
	0.652	0.210	0.3586	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 [$I>2\sigma$]	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(32)-C(33)	1.388(6)
C(32)-C(36)	1.487(6)
C(33)-H(33)	0.9300
C(33)-C(34)	1.389(6)
C(34)-H(34)	0.9300
C(34)-C(35)	1.382(6)
C(35)-H(35)	0.9300
N(1)-S(1)-S(2)	94.05(14)
N(2)-S(2)-S(1)	94.62(14)
C(1)-N(1)-S(1)	115.4(3)
C(1)-N(2)-S(2)	113.0(3)
N(1)-C(1)-N(2)	122.9(4)
N(1)-C(1)-C(10)	117.7(4)
N(2)-C(1)-C(10)	119.4(4)
C(11)-C(10)-C(1)	118.7(4)
C(15)-C(10)-C(1)	122.2(4)
C(15)-C(10)-C(11)	119.1(4)
C(10)-C(11)-H(11)	120.0
C(12)-C(11)-C(10)	120.1(4)
C(12)-C(11)-H(11)	120.0
C(11)-C(12)-C(13)	121.0(4)
C(11)-C(12)-C(16)	118.2(4)
C(13)-C(12)-C(16)	120.8(4)
C(12)-C(13)-H(13)	120.5
C(12)-C(13)-C(14)	119.0(4)
C(14)-C(13)-H(13)	120.5
C(13)-C(14)-H(14)	120.0
C(15)-C(14)-C(13)	120.1(4)
C(15)-C(14)-H(14)	120.0
C(10)-C(15)-C(14)	120.8(4)
C(10)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
F(10)-C(16)-F(11)	106.3(4)
F(10)-C(16)-C(12)	113.2(4)
F(11)-C(16)-C(12)	111.5(4)
F(12)-C(16)-F(10)	106.8(4)
F(12)-C(16)-F(11)	106.1(4)
F(12)-C(16)-C(12)	112.4(4)
N(9)-S(9)-S(10)	94.45(14)
N(10)-S(10)-S(9)	94.70(14)
C(5)-N(9)-S(9)	114.4(3)
C(5)-N(10)-S(10)	113.5(3)
N(9)-C(5)-N(10)	122.9(4)
N(9)-C(5)-C(50)	117.7(4)
N(10)-C(5)-C(50)	119.4(4)
C(51)-C(50)-C(5)	120.1(4)
C(51)-C(50)-C(55)	119.6(4)
C(55)-C(50)-C(5)	120.2(4)
C(50)-C(51)-H(51)	120.2
C(52)-C(51)-C(50)	119.7(4)
C(52)-C(51)-H(51)	120.2
C(51)-C(52)-C(53)	120.6(4)
C(51)-C(52)-C(56)	120.4(4)
C(53)-C(52)-C(56)	119.1(4)
C(52)-C(53)-H(53)	120.1
C(54)-C(53)-C(52)	119.9(4)
C(54)-C(53)-H(53)	120.1
C(53)-C(54)-H(54)	120.0
C(53)-C(54)-C(55)	120.0(4)
C(55)-C(54)-H(54)	120.0
C(50)-C(55)-H(55)	119.9
C(54)-C(55)-C(50)	120.2(4)
C(54)-C(55)-H(55)	119.9
F(50)-C(56)-F(51)	106.3(5)
F(50)-C(56)-F(52)	108.5(5)
F(50)-C(56)-C(52)	113.4(4)
F(51)-C(56)-C(52)	112.0(4)
F(52)-C(56)-F(51)	103.2(4)
F(52)-C(56)-C(52)	112.7(4)
N(7)-S(7)-S(8)	94.55(14)
N(8)-S(8)-S(7)	94.25(14)
C(4)-N(7)-S(7)	114.0(3)
C(4)-N(8)-S(8)	114.9(3)
N(7)-C(4)-C(40)	118.0(4)
N(8)-C(4)-N(7)	122.3(4)
N(8)-C(4)-C(40)	119.8(4)
C(41)-C(40)-C(4)	120.4(4)
C(41)-C(40)-C(45)	119.8(4)
C(45)-C(40)-C(4)	119.8(4)
C(40)-C(41)-H(41)	120.1
C(40)-C(41)-C(42)	119.8(4)
C(42)-C(41)-H(41)	120.1
C(41)-C(42)-C(43)	120.5(4)
C(41)-C(42)-C(46)	120.5(4)
C(43)-C(42)-C(46)	119.0(4)
C(42)-C(43)-H(43)	120.3
C(44)-C(43)-C(42)	119.4(4)
C(44)-C(43)-H(43)	120.3
C(43)-C(44)-H(44)	119.7
C(45)-C(44)-C(43)	120.5(4)
C(45)-C(44)-H(44)	119.7
C(40)-C(45)-H(45)	120.1
C(44)-C(45)-C(40)	119.8(4)
C(44)-C(45)-H(45)	120.1
F(00S)-C(46)-C(42)	112.9(4)
F(40)-C(46)-F(00S)	105.5(4)
F(40)-C(46)-F(41)	105.5(4)
F(40)-C(46)-C(42)	113.7(4)
F(41)-C(46)-F(00S)	106.5(4)
F(41)-C(46)-C(42)	112.1(4)
N(3)-S(3)-S(4)	94.36(14)
N(4)-S(4)-S(3)	94.47(14)
C(20)-N(3)-S(3)	114.6(3)
C(20)-N(4)-S(4)	114.0(3)
N(3)-C(20)-N(4)	122.5(4)
N(3)-C(20)-C(21)	118.4(4)
N(4)-C(20)-C(21)	119.0(4)
C(22)-C(21)-C(20)	119.5(4)
C(22)-C(21)-C(26)	120.1(4)
C(26)-C(21)-C(20)	120.4(4)
C(21)-C(22)-H(22)	120.0
C(23)-C(22)-C(21)	120.1(4)
C(23)-C(22)-H(22)	120.0
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
C(11)-H(11C)	0.9800
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(10A)-H(10D)	0.9800
C(10A)-H(10E)	0.9800
C(10A)-H(10F)	0.9800
C(11A)-H(11D)	0.9800
C(11A)-H(11E)	0.9800
C(11A)-H(11F)	0.9800
C(12A)-H(12D)	0.9800
C(12A)-H(12E)	0.9800
C(12A)-H(12F)	0.9800
Se(3)-Se(4)	2.3096(9)
Se(3)-N(3)	1.793(4)
Se(4)-N(4)	1.805(4)
N(3)-C(13)	1.313(6)
N(4)-C(13)	1.335(6)
N(12)-C(20)	1.133(7)
C(13)-C(14)	1.487(6)
C(14)-C(15)	1.368(7)
C(14)-C(19)	1.391(7)
C(15)-H(15)	0.9500
C(15)-C(16)	1.398(7)
C(16)-C(17)	1.370(7)
C(16)-C(20)	1.438(8)
C(17)-H(17)	0.9500
C(17)-C(18)	1.381(8)
C(18)-C(19)	1.386(7)
C(18)-C(21)	1.527(8)
C(19)-H(19)	0.9500
C(21)-C(22)	1.47(2)
C(21)-C(23)	1.56(2)
C(21)-C(24)	1.553(18)
C(21)-C(22A)	1.60(3)
C(21)-C(23A)	1.39(4)
C(21)-C(24A)	1.47(3)
C(22)-H(22A)	0.9800
C(22)-H(22B)	0.9800
C(22)-H(22C)	0.9800
C(23)-H(23A)	0.9800
C(23)-H(23B)	0.9800
C(23)-H(23C)	0.9800
C(24)-H(24A)	0.9800
C(24)-H(24B)	0.9800
C(24)-H(24C)	0.9800
C(22A)-H(22D)	0.9800
C(22A)-H(22E)	0.9800
C(22A)-H(22F)	0.9800
C(23A)-H(23D)	0.9800
C(23A)-H(23E)	0.9800
C(23A)-H(23F)	0.9800
C(24A)-H(24D)	0.9800
C(24A)-H(24E)	0.9800
C(24A)-H(24F)	0.9800
Se(5)-Se(6)	2.3183(12)
Se(5)-N(5)	1.779(5)
Se(6)-N(6)	1.767(5)
N(5)-C(25)	1.323(7)
N(6)-C(25)	1.298(7)
N(13)-C(32)	1.132(9)
C(25)-C(26)	1.481(7)
C(26)-C(27)	1.376(7)
C(26)-C(31)	1.384(7)
C(27)-H(27)	0.9500
C(27)-C(28)	1.382(8)
C(28)-C(29)	1.388(8)
C(28)-C(32)	1.428(9)
C(29)-H(29)	0.9500
C(29)-C(30)	1.371(8)
C(30)-C(31)	1.384(8)
C(30)-C(33)	1.514(8)
C(31)-H(31)	0.9500
C(33)-C(34)	1.533(9)
C(33)-C(35)	1.521(9)
C(33)-C(36)	1.507(9)
C(34)-H(34A)	0.9800
C(34)-H(34B)	0.9800
C(34)-H(34C)	0.9800
C(35)-H(35A)	0.9800
C(35)-H(35B)	0.9800
C(35)-H(35C)	0.9800
C(36)-H(36A)	0.9800
C(36)-H(36B)	0.9800
C(36)-H(36C)	0.9800

N(1)-Se(1)-Se(2)	90.56(13)
N(2)-Se(2)-Se(1)	91.79(14)
C(1)-N(1)-Se(1)	115.7(3)
C(1)-N(2)-Se(2)	114.2(4)
N(1)-C(1)-C(2)	116.2(4)
N(2)-C(1)-N(1)	127.7(5)
N(2)-C(1)-C(2)	116.0(5)
C(3)-C(2)-C(1)	119.5(5)
C(3)-C(2)-C(7)	119.4(5)
C(7)-C(2)-C(1)	121.1(5)
C(2)-C(3)-H(3)	118.5
C(2)-C(3)-C(4)	123.1(6)
C(4)-C(3)-H(3)	118.5
C(3)-C(4)-C(9)	121.2(6)
C(5)-C(4)-C(3)	116.2(6)
C(5)-C(4)-C(9)	122.6(6)
C(4)-C(5)-H(5)	119.2
C(4)-C(5)-C(6)	121.7(6)
C(6)-C(5)-H(5)	119.2
C(5)-C(6)-C(7)	121.1(6)
C(5)-C(6)-C(8)	119.4(5)
C(7)-C(6)-C(8)	119.5(6)
C(2)-C(7)-C(6)	118.5(5)
C(2)-C(7)-H(7)	120.8
C(6)-C(7)-H(7)	120.8
N(11)-C(8)-C(6)	179.8(7)
C(4)-C(9)-C(10)	111.0(6)
C(4)-C(9)-C(11)	111.8(7)
C(4)-C(9)-C(12)	113.8(6)

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

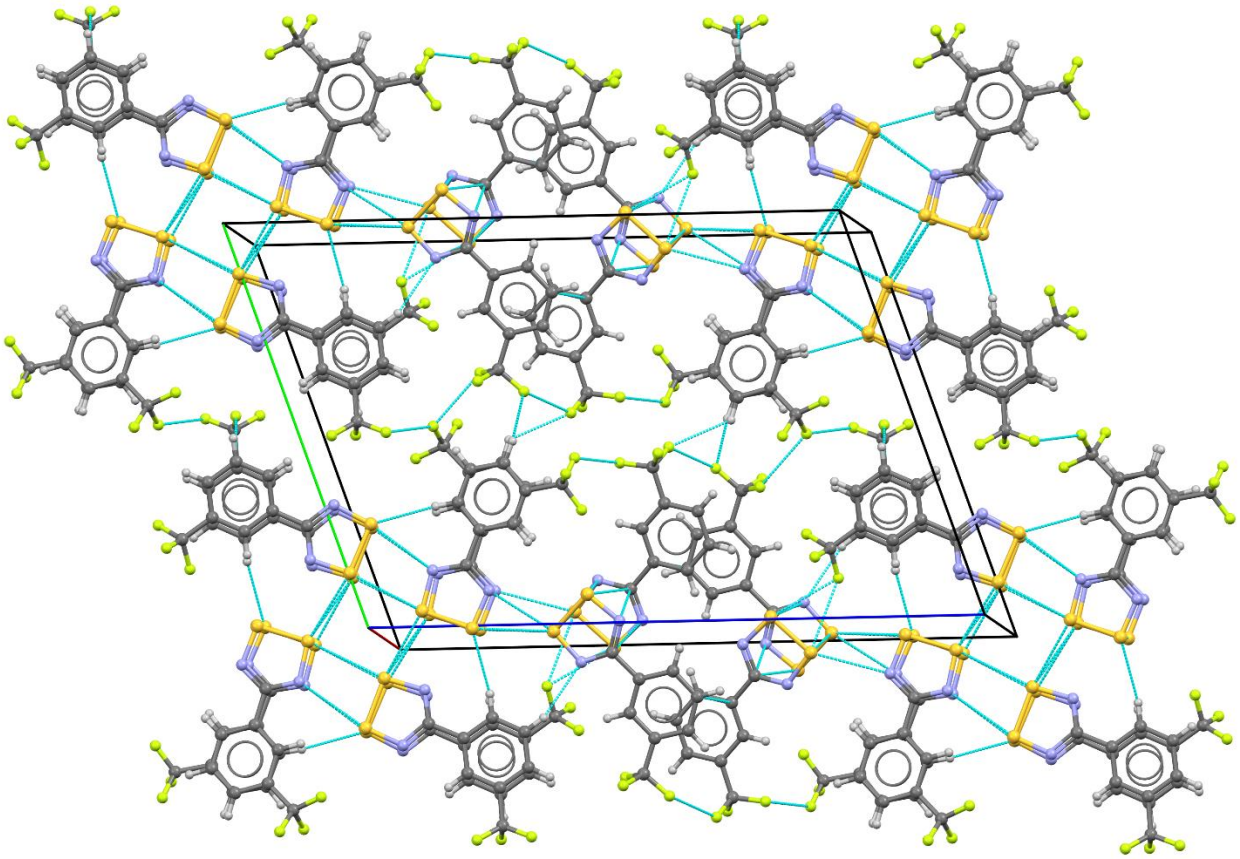
Se(1)-Se(2)	2.3347(6)	C(12)-H(12A)	0.9800
Se(1)-N(1)	1.783(3)	C(12)-H(12B)	0.9800
Se(2)-N(2)	1.760(4)	C(12)-H(12C)	0.9800
N(1)-C(1)	1.335(5)	Se(9)-Se(10)	2.3299(5)
N(2)-C(1)	1.309(5)	Se(9)-N(9)	1.792(3)
N(11)-C(8)	1.164(5)	Se(10)-N(10)	1.791(3)
C(1)-C(2)	1.502(5)	N(9)-C(49)	1.339(4)
C(2)-C(3)	1.384(5)	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)

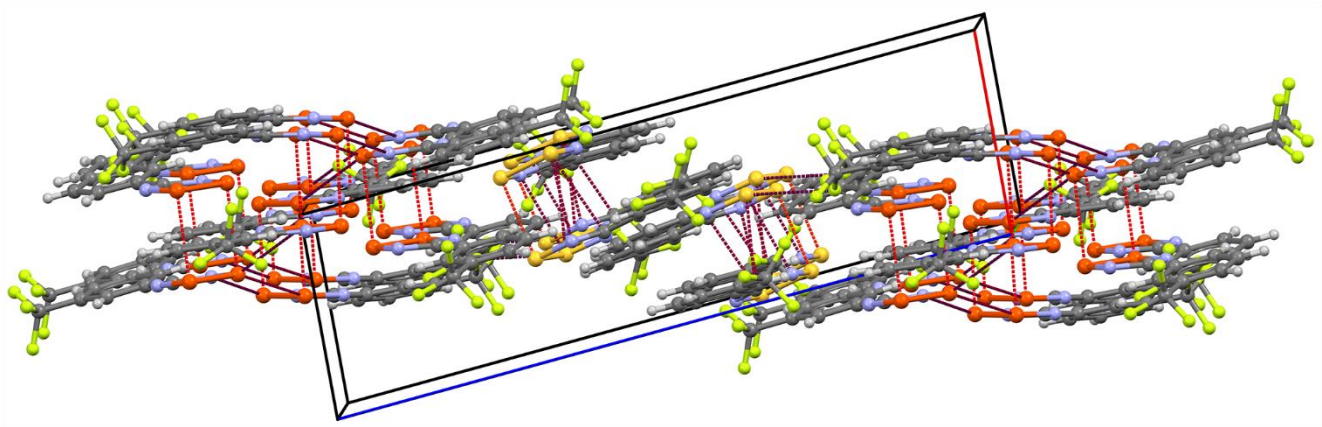
C(3)-C(2)-C(1)	119.1(3)
C(3)-C(2)-C(7)	119.9(4)
C(7)-C(2)-C(1)	120.9(3)
C(2)-C(3)-H(3)	120.9
C(2)-C(3)-C(4)	118.2(4)
C(4)-C(3)-H(3)	120.9
C(3)-C(4)-C(8)	120.3(4)
C(5)-C(4)-C(3)	121.3(4)
C(5)-C(4)-C(8)	118.4(4)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-C(4)	120.6(4)
C(6)-C(5)-H(5)	119.7
C(5)-C(6)-C(9)	119.5(4)
C(7)-C(6)-C(5)	117.5(4)
C(7)-C(6)-C(9)	122.9(4)
C(2)-C(7)-H(7)	118.8
C(6)-C(7)-C(2)	122.4(4)
C(6)-C(7)-H(7)	118.8
N(11)-C(8)-C(4)	177.2(5)
C(10)-C(9)-C(6)	107.3(4)
C(11)-C(9)-C(6)	111.4(4)
C(11)-C(9)-C(10)	108.6(5)
C(12)-C(9)-C(6)	109.9(4)
C(12)-C(9)-C(10)	112.2(5)
C(12)-C(9)-C(11)	107.6(5)
C(9)-C(10)-H(10A)	109.5
C(9)-C(10)-H(10B)	109.5
C(9)-C(10)-H(10C)	109.5
H(10A)-C(10)-H(10B)	109.5
H(10A)-C(10)-H(10C)	109.5
H(10B)-C(10)-H(10C)	109.5
C(9)-C(11)-H(11A)	109.5
C(9)-C(11)-H(11B)	109.5
C(9)-C(11)-H(11C)	109.5
H(11A)-C(11)-H(11B)	109.5
H(11A)-C(11)-H(11C)	109.5
H(11B)-C(11)-H(11C)	109.5
C(9)-C(12)-H(12A)	109.5
C(9)-C(12)-H(12B)	109.5
C(9)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
N(9)-Se(9)-Se(10)	90.56(9)
N(10)-Se(10)-Se(9)	91.85(9)
C(49)-N(9)-Se(9)	115.2(2)
C(49)-N(10)-Se(10)	114.1(2)
N(9)-C(49)-C(50)	116.7(3)
N(10)-C(49)-N(9)	128.3(3)
N(10)-C(49)-C(50)	115.1(3)
C(51)-C(50)-C(49)	121.0(3)
C(55)-C(50)-C(49)	119.4(3)
C(55)-C(50)-C(51)	119.5(3)
C(50)-C(51)-H(51)	120.8
C(52)-C(51)-C(50)	118.5(3)
C(52)-C(51)-H(51)	120.8
C(51)-C(52)-C(53)	121.5(3)
C(51)-C(52)-C(56)	120.8(3)
C(53)-C(52)-C(56)	117.7(3)
C(52)-C(53)-H(53)	119.7
C(54)-C(53)-C(52)	120.6(3)
C(54)-C(53)-H(53)	119.7
C(53)-C(54)-C(55)	117.5(3)
C(53)-C(54)-C(57)	122.4(3)
C(55)-C(54)-C(57)	120.1(3)
C(50)-C(55)-C(54)	122.4(3)
C(50)-C(55)-H(55)	118.8
C(54)-C(55)-H(55)	118.8
N(15)-C(56)-C(52)	176.0(4)
C(58)-C(57)-C(54)	111.9(3)
C(58)-C(57)-C(60)	107.3(4)
C(59)-C(57)-C(54)	108.8(3)
C(59)-C(57)-C(58)	109.2(4)
C(59)-C(57)-C(60)	109.8(4)
C(60)-C(57)-C(54)	109.8(3)
C(57)-C(58)-H(58A)	109.5
C(57)-C(58)-H(58B)	109.5
C(57)-C(58)-H(58C)	109.5
H(58A)-C(58)-H(58B)	109.5
H(58A)-C(58)-H(58C)	109.5
H(58B)-C(58)-H(58C)	109.5
C(57)-C(59)-H(59A)	109.5
C(57)-C(59)-H(59B)	109.5
C(57)-C(59)-H(59C)	109.5
H(59A)-C(59)-H(59B)	109.5
H(59A)-C(59)-H(59C)	109.5
H(59B)-C(59)-H(59C)	109.5
C(57)-C(60)-H(60A)	109.5
C(57)-C(60)-H(60B)	109.5
C(57)-C(60)-H(60C)	109.5
H(60A)-C(60)-H(60B)	109.5
H(60A)-C(60)-H(60C)	109.5
H(60B)-C(60)-H(60C)	109.5
N(7)-Se(7)-Se(8)	90.09(9)
N(8)-Se(8)-Se(7)	92.23(9)
C(37)-N(7)-Se(7)	115.4(2)
C(37)-N(8)-Se(8)	113.4(2)
N(7)-C(37)-C(38)	115.8(3)
N(8)-C(37)-N(7)	128.9(3)
N(8)-C(37)-C(38)	115.3(3)
C(39)-C(38)-C(37)	120.6(3)
C(39)-C(38)-C(43)	119.7(3)
C(43)-C(38)-C(37)	119.7(3)
C(38)-C(39)-H(39)	120.6
C(38)-C(39)-C(40)	118.8(3)
C(40)-C(39)-H(39)	120.6
C(39)-C(40)-C(41)	121.0(3)
C(39)-C(40)-C(44)	120.7(3)
C(41)-C(40)-C(44)	118.3(3)
C(40)-C(41)-H(41)	119.4
C(42)-C(41)-C(40)	121.1(3)
C(42)-C(41)-H(41)	119.4
C(41)-C(42)-C(43)	116.7(3)
C(41)-C(42)-C(45)	121.0(3)
C(43)-C(42)-C(45)	122.1(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. Boeré, *CrystEngComm*, 18, 2748, **2016**.

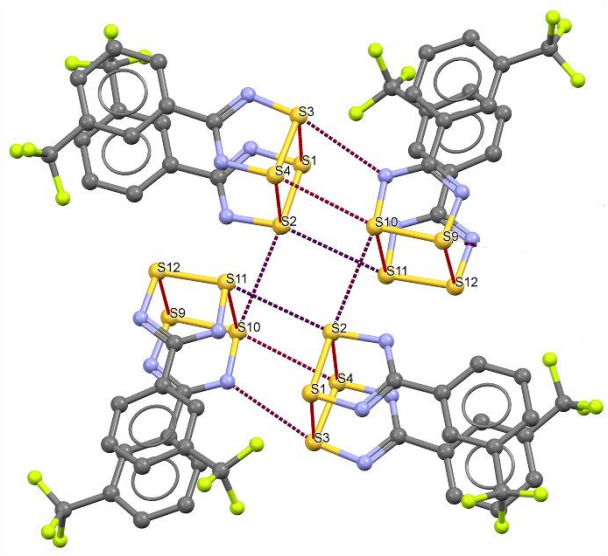


Figure S2. View of the centrosymmetric, pin-wheel clusters in the asymmetric unit of **2** showing intermolecular contacts shorter than (Σr_{vdW} – 0.2 Å). H atoms have been removed to enhance visibility.

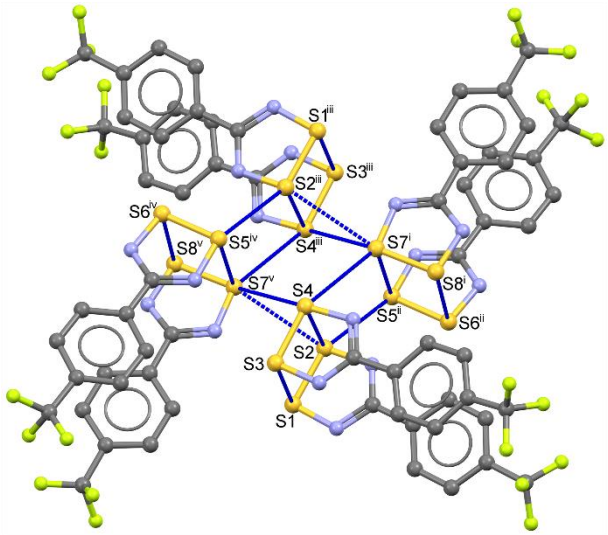


Figure S3. One of two symmetry-independent, centrosymmetric, pin-wheel clusters in the asymmetric unit of **1** showing intermolecular contacts shorter than (Σr_{vdW} – 0.2 Å). H atoms have been removed to enhance visibility. [Symmetry codes: (i) x,-1+y,z; (ii) 1+x,-1+y,z, (iii) 1+x,-1+y,z, (iv) -x,1-y,1-z, (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 (Σr_{vdW} – 0.1 Å) (except for inter-slice distances)

Atom1	**Atom2**	**Symm. op. 1**	**Symm. op. 2**	**Length**	**Length < Σr_{vdW}**
Cis-oid Dimer					
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
			Mean(s.u.)	*3.12(2)*	*-0.48(2)*
Twisted Dimer					
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
			S,N Mean(s.u.)	*3.08(1)*	*-0.38(15)*
Dimer-to-neighbour – *Cis*-oid Pinwheel					
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
			S,S Mean(s.u.)	*3.42(7)*	*-0.19(7)*
Dimer-to-neighbour – *Cis*-oid to Twisted					
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
			Mean(s.u.)	3.35(8)	-0.25(7)
Inter-slice					
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

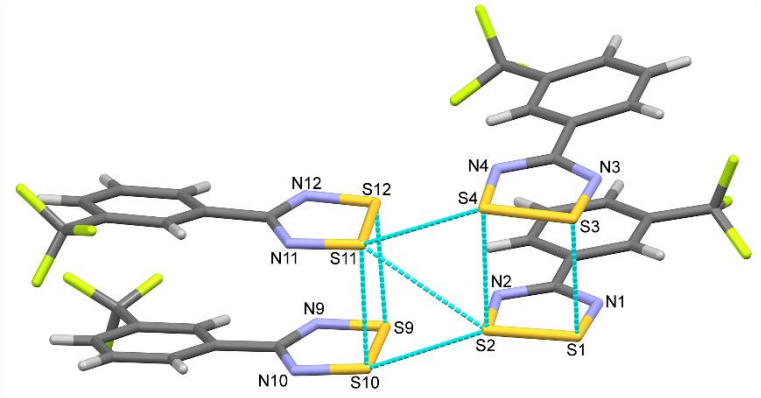


Figure S4. Detailed view of the end-to-side contacts of one DTDA dimer with another in the same layer in the structure of **2**. This group is the left-hand side of the pin-wheel cluster shown in Figure S2.

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.

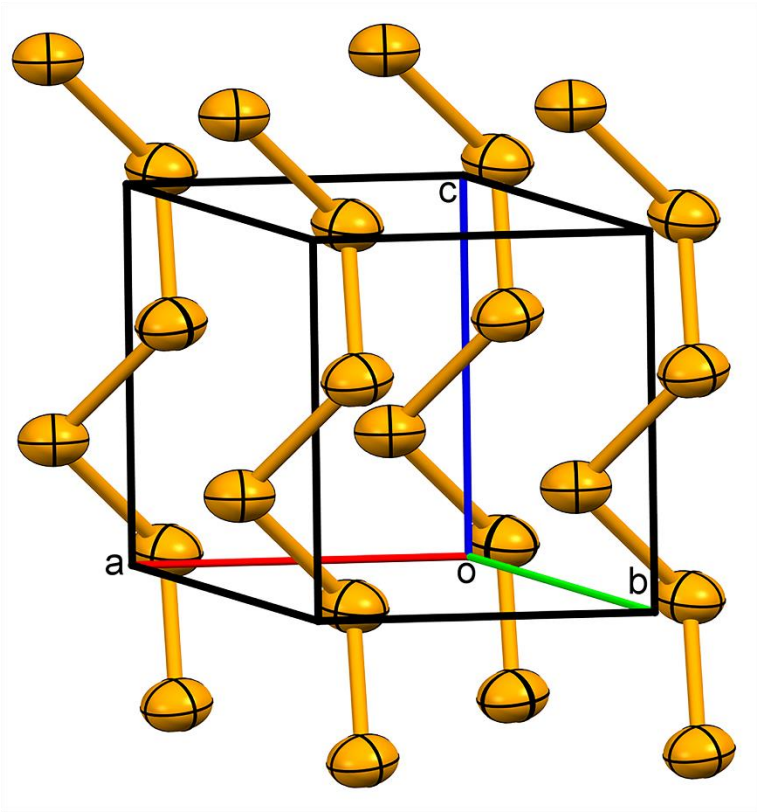


Figure S5. Displacement ellipsoids plot (40% probability) of grey selenium showing the three-fold helices of Se_∞ along the edges of the trigonal primitive cell in the *c* direction.

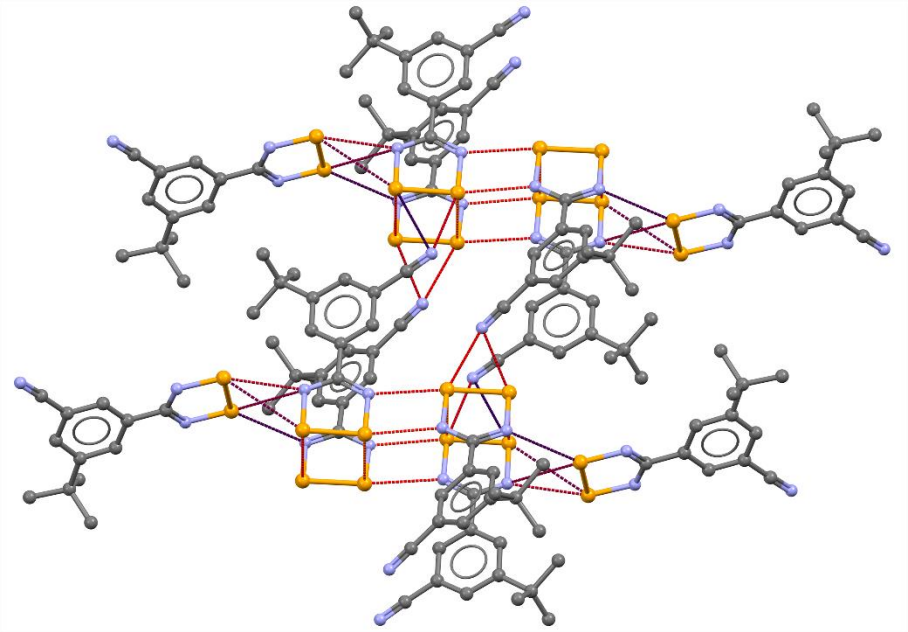


Figure S6. A close-up view of the packing in the lattice of **4a**, showing four asymmetric units linked *via* $Se_2\cdots N{\equiv}C$- contacts, a classic intermolecular synthon in DTDA/DSDA chemistry.

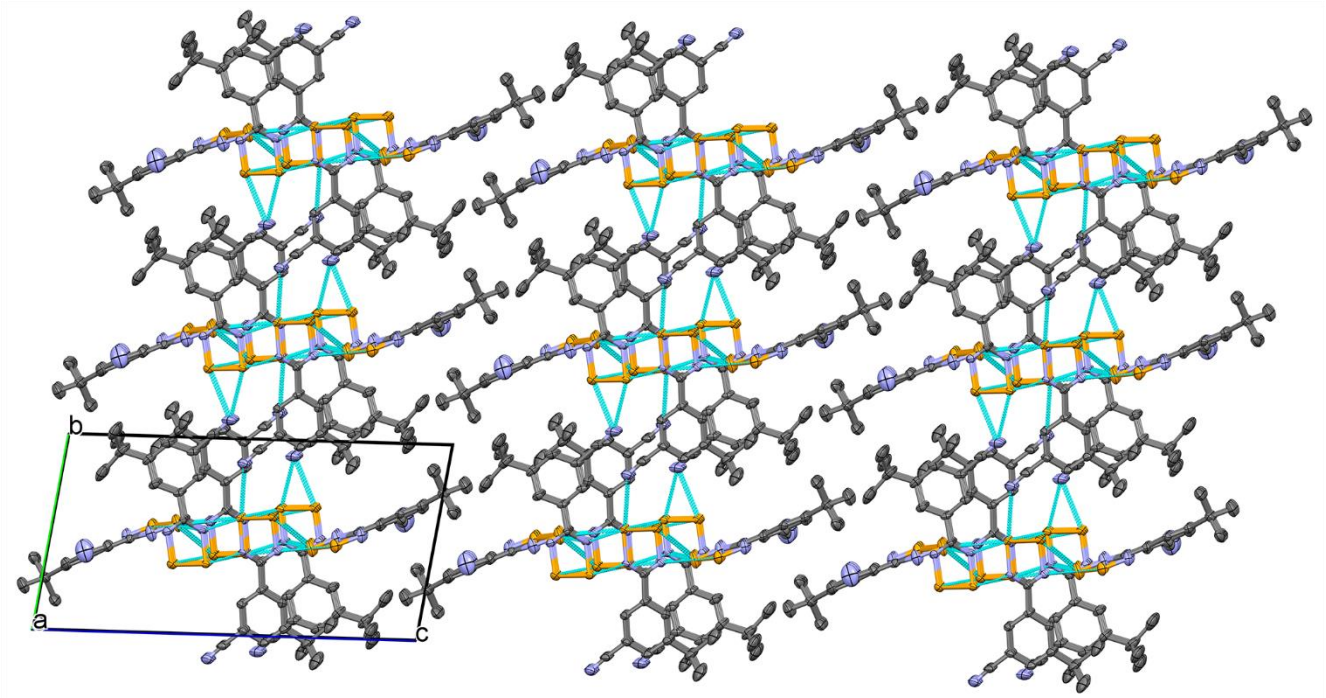


Figure S7. Packing diagram viewed approximately down the *b* axis for the crystal structure of **4a**. The 6-DSDA ring clusters described in the main text (Figure 4) are linked via $Se_2\cdots N{\equiv}C$- contacts. The structure consists of columns of CN_2Se_2 heteroatoms surrounded on all sides by a hydrocarbon sheath.

Table S8. Intermolecular Contacts in **4a** less than (Σr_{vdW} – 0.1 Å)

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
			Mean(s.u.)	*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
			Mean(s.u.)	*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
			Mean(s.u.)	*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
			Mean(s.u.)	*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
			Mean(s.u.)	*3.09(14)*	*-0.36(14)*

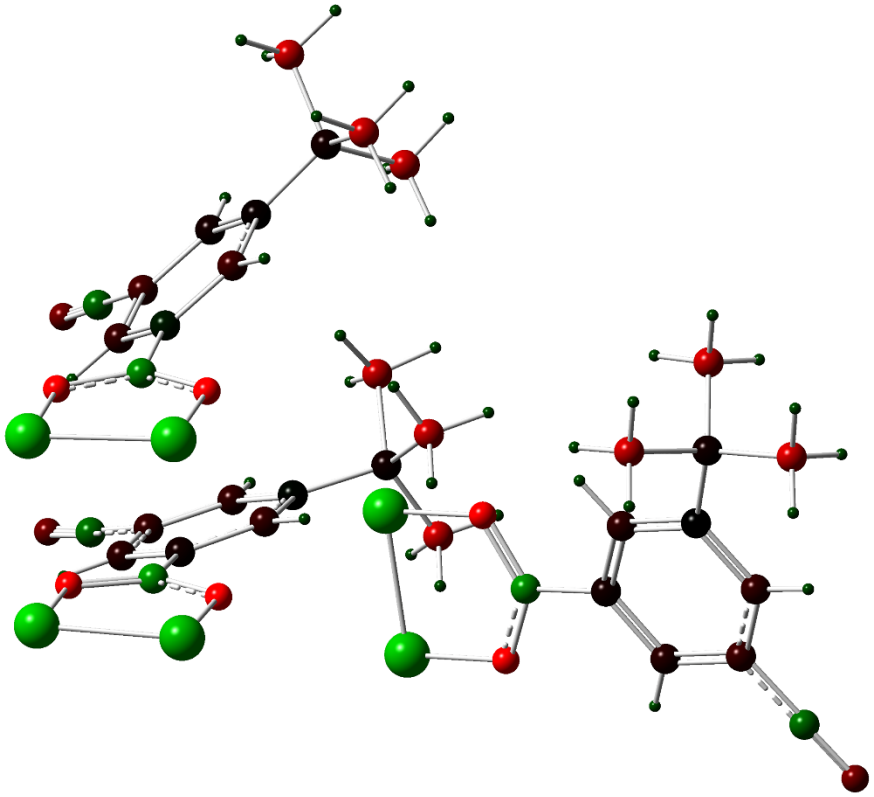


Figure S8. Computed NPA atomic charges from a UB3LYP/6-311+G(2d,p) hybrid DFT calculation on one asymmetric unit of three *dsda* radicals in the crystal structure of **4a**. A doublet electronic state was used which places most of the spin density on the Se1/Se2 *dsda* ring. Bright green represents the 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.

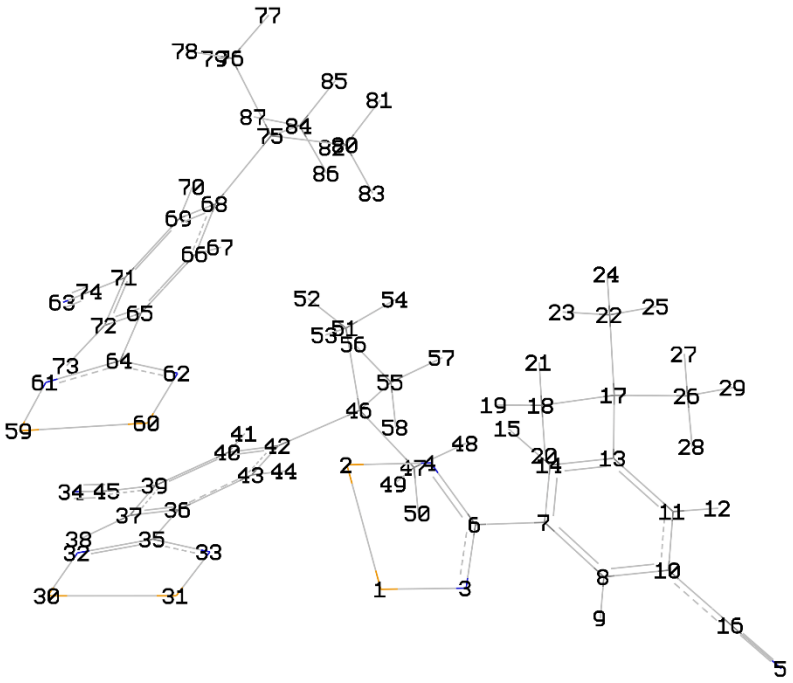


Table S9. Summary of Natural Population Analysis from a DFT Calculation on the Asymmetric Unit in **4a.**

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 (Σr_{vdW} – 0.1 Å)

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
			Mean(s.u.)	*3.26(11)*	*-0.54(11)*
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
			Mean(s.u.)	*2.99(8)*	*-0.46(8)*
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
			Mean(s.u.)	*3.01(8)*	*-0.44(8)*

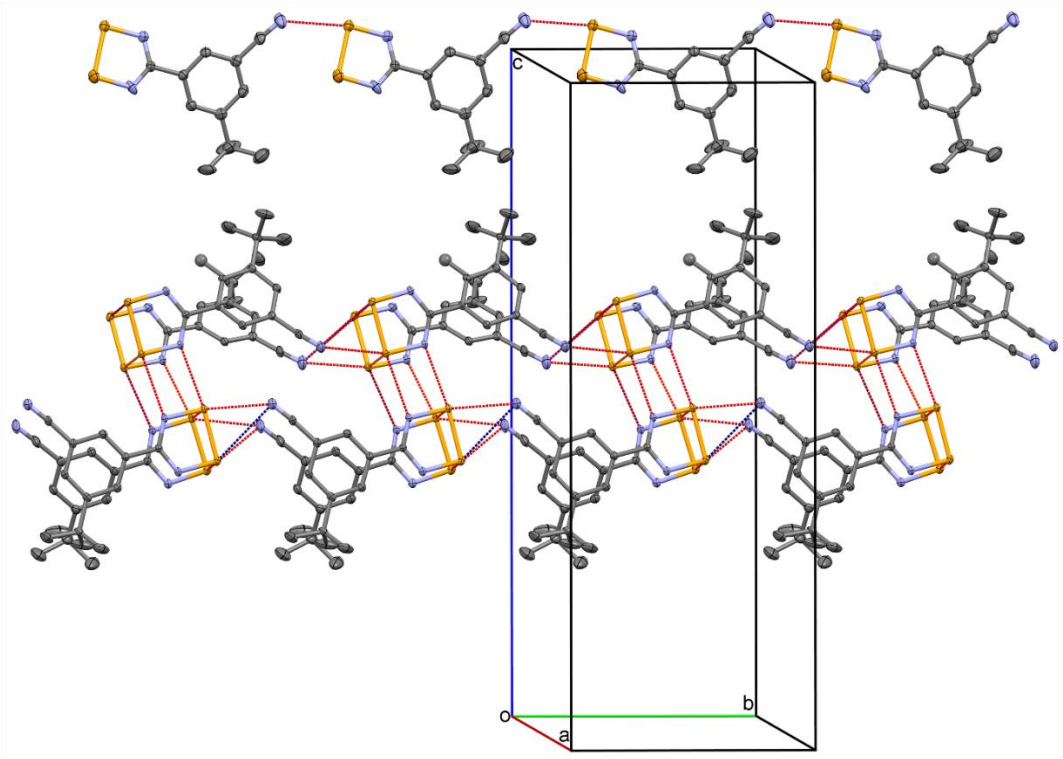


Figure S9. Another view of the lattice structure of **4b**, showing the double-layer strand of the *cis*-oid dimers catenated through -C≡N: to Se contacts and, at the top, the chain of monomeric Se1,Se2 radicals also catenated via -C≡N: to Se contacts.

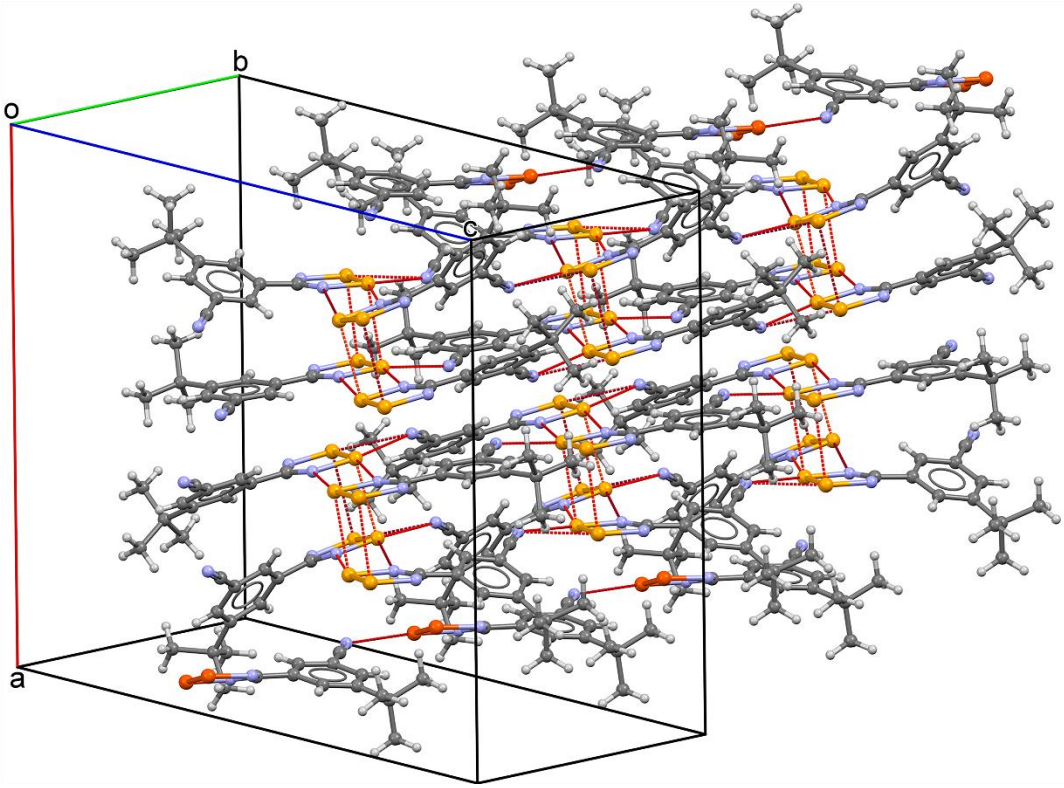


Figure S10. Alternate packing diagram for the structure of **4b**.

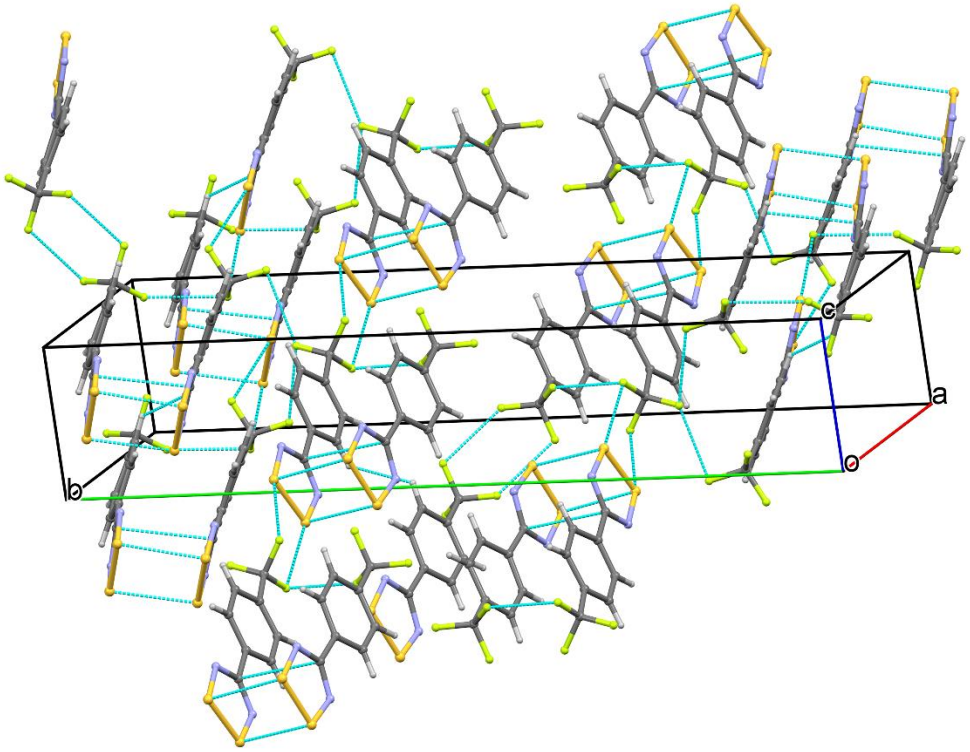


Figure S11. The extended structure of lixgab02 showing the LIMS-I and LIMS-IV short-contacts.

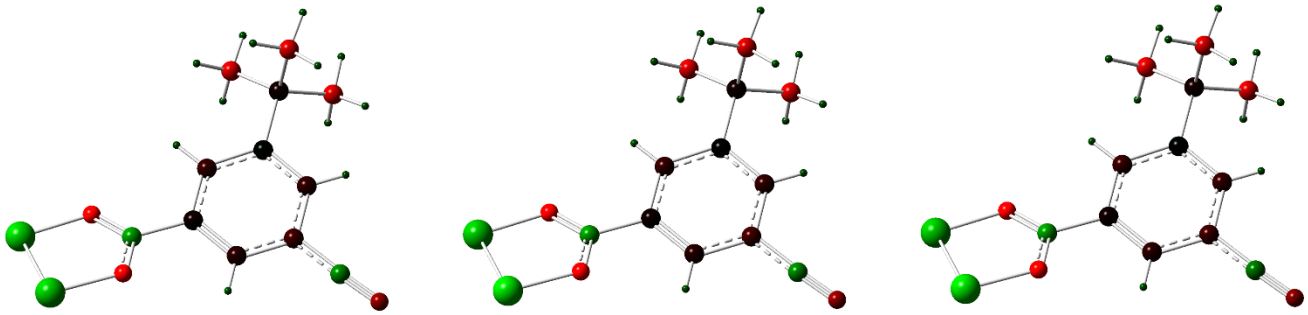


Figure S12. Computed NPA atomic charges from a UB3LYP/6-311+G(2d,p) hybrid DFT calculation on a chain of three of the undimerized Se1,Se2 DSDA radicals in the crystal structure of **4b**. A quartet electronic state was used to simulate a chain of Se1,Se2 DSDA radicals. The atom numbers below can be used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

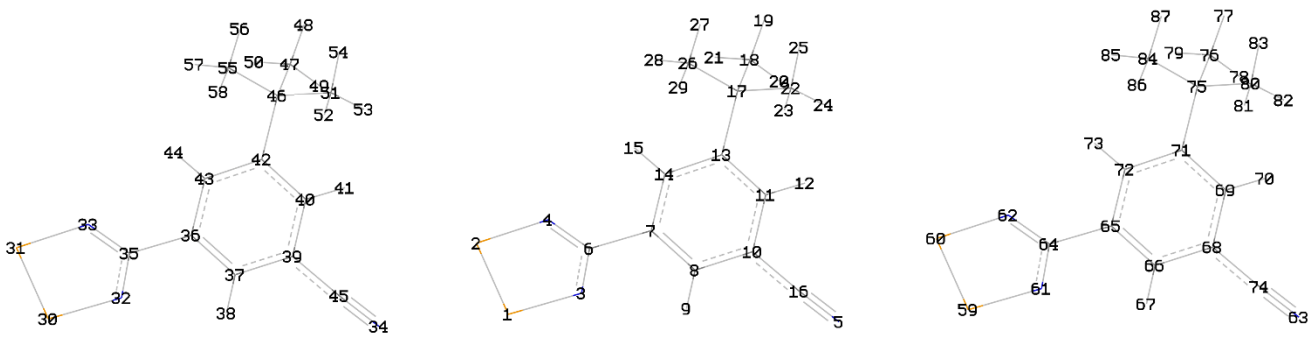


Table S11. Summary of Natural Population Analysis from a DFT calculation on a chain of radicals in **5b.**

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.