Chalcogen Bonding in Co-Crystals: Activation through 1,4-Perfluorophenylene vs. 4,4′-Perfluorobiphenylene Cores

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Abstract: The ability of alkylseleno/alkyltelluroacetylenes such as bis(selenomethylethynyl)-perfluorobenzene (4F-Se) to act as a ditopic chalcogen bond (ChB) donor in co-crystals with ditopic Lewis bases such as 4,4′-bipyridine is extended here to the octafluorobiphenylene analog, 4,4′-bis(selenomethylethynyl)-perfluorobiphenyl (8F-Se), with the more electron-rich 4,4′-biprydylethylene (bpe), showing in the 1:1 (8F-Se)•••bpe co-crystal a shorter and more linear C−Se•••N ChB interaction than in (4F-Se)•••bpe, with Se•••N distances down to 2.958(2) Å at 150 K, i.e., a reduction ratio of 0.85 vs. the van der Waals contact distance.

Keywords: chalcogen bonding; sigma-hole activation; crystal engineering; Lewis-base

1. Introduction

Crystal engineering strategies are manifested by the choice of intermolecular interactions owing to their strength, directionality and predictability that allow one to transfer the packing instructions in a molecule [1]. In this context, halogen bond (XB) [2,3], a subset of sigma-hole interactions, has emerged as an indispensable tool due to its significant linear directionality and tuneable sigma-hole activation that opens the door for a wide range of applications [4–6]. Similarly, chalcogen bond (ChB) [7] is an interaction between an electron-depleted site of an activated chalcogen atom and an electron-rich site of a Lewis-base [8,9]. Chalcogen bond, being a sister non-covalent interaction to halogen bond [10,11], has been mostly targeted to follow the trails of halogen bond in the field of crystal engineering but it is often limited by the presence of two sigma holes on chalcogen atoms. At variance with mono-valent halogen atoms, one extra valency of Se/Te can indeed invite additional changes in crystal packing that consequently dilutes the predictability of ChB interaction. Furthermore, organic selenides/tellurides are more reactive and are synthetically far less investigated compared to organic halides. Despite that, over the years, interesting ChB donors have been developed and some earlier examples include S(CN)2 [12], Se(CN)2 [13], 1,2,5-chalcogenadiazoles [14,15], 1,2-chalcogenazole N-oxides [16,17], or alkyltelluroalkynyl derivatives [18,19] that self-associate into discrete solid-state structures. To recover the linear directionality characteristic of halogen bonding interactions, chalcogen atoms are typically disymmetricized with only one strongly electron-withdrawing substituent to force a diger electron depletion along one favored single direction, as recently observed in organic selenocyanates, such as 1,4-bis(selenocyanatomethyl)-benzene that forms 1-D chains with 4,4′-bipyridine through short and directional Se•••N contacts [20–23]. The interaction strength parallels the degree of activation in both donor and acceptor molecules, an aspect often used in crystal engineering to quantify the robustness of a supramolecular motif.

In this regard, hydrogen and halogen bonding interactions have been extensively utilized to selectively tune the strength of intermolecular interactions in co-crystals by systematically treating either a donor with various acceptors of different Lewis-base character.
or an acceptor with various donors exhibiting different modes of activation. However, chalcogen bonding still remains less explored in this direction and one such example includes a recent study by Bryce et al. on investigations of Ch•••N strength in a series of co-crystals between 3,4-dicyano-1,2,5-seleno/telluro-diazole acting as Ch•••N donor and various N-oxide and pyridyl derivatives acting as Ch•••N acceptors [24,25]. Rigid Ch•••N donors such as alkylseleno/alkyltelluroacetylenes were recently demonstrated to exhibit a strong sigma-hole activation and remarkable control of directionality in co-crystal formation with bipyridyl derivatives, allowing for a fine tuning of Ch•••N interaction strength within the chalcogen-bonded 1-D chain motif [26]. In addition, a recent investigation of the U-shaped Ch•••N donor 1,8-bis(telluromethylethynyl)-anthracene (BTMEA) with a series of (strong to weak) bipyridyl derivatives suggested that the strongest Te•••N interaction was indeed associated with the strongest Lewis-base used in this study [27]. Such fundamental studies become very crucial to understanding the limitations of chalcogen bond formed under different chemical and electronic environments. Surprisingly, the reverse situation where Ch•••N strength can be tuned in a supramolecular motif through structural modification of the chalcogen bond donor itself is much less explored. In this context, an interesting example based on XB (Scheme 1b) showed that sigma-hole on iodine atom is rather enhanced when moving from 1,4-diiodotetrafluorobenzene (DITF) to 4,4′-diiodoctafluorobiphenyl (DOB) that incorporates a stronger activating core. This was also evident from VS,max values of +38.28 and +40.16 kcal mol\(^{-1}\) (mapped on the electron density surface cut at the 0.002 e/Å\(^3\) level) observed for DITF and DOB respectively [28]. Additionally, their co-crystals with nicotine (A1), formed through halogen bonds, reveal that the strongest N•••I interaction was present in the structure of DOB•A1 with distance 2.808 Å (RR = 0.79) vs. 2.869 Å (RR = 0.81) found in DITF•A1 [28]. On contrary, a study by Aakeroy et al. on a series of co-crystals between these XB donors and heteroaryl-2-imidazoles (A2), driven through XB and HB, revealed that the strongest N•••I interaction was always associated with DITF•A2 structures in contrast to DOB•A2 co-crystals [29]. Hence, although the electrostatic surface potential suggests a stronger sigma-hole activation in DOB over DITF, this information is not explicitly reflected in their ability to form co-crystals with Lewis-base. Another element of comparison is brought by the pKa1 values of their analogous dicarboxylic acid derivatives (Scheme 1a) which were estimated to be approximately the same, indicating a negligible effect of the core on hydrogen bonding behavior [30].

Inspired by these results, we present herein a case study on the modulation of chalcogen bond with respect to the activation core in two Ch•••N donors, namely 1,4-bis(selenomethy
lithethyl)-perfluorobenzene (4F-Se) vs. 4,4′-bis(selenomethylthylethynyl)-perfluorobiphenyl (8F-Se) (Scheme 1c).

2. Results and Discussions

The tendency of a molecule to engage in different types of intermolecular non-covalent interactions where electrostatics, besides dispersion, play a significant role can primarily be anticipated by mapping the electrostatic potential (ESP) on molecular surfaces. ESP calculations for our two ChB donors revealed the presence of a significant σ-hole on the Se atoms along the (C≡C)−Se bond with V_{S,max} values of +35.7 kcal mol\(^{-1}\) and +37.4 kcal mol\(^{-1}\) for donors 4F-Se and 8F-Se respectively (Figure 1). These values clearly indicate a comparatively larger activation of the σ-hole in 8F-Se, demonstrating that the perfluorobiphenyl core plays an additional activating effect with respect to the perfluorophenyl one incorporated in 4F-Se. A less significant second σ-hole is also present along the CH\(_3\)−Se bonds in both 4F-Se and 8F-Se donors, with V_{S,max} values of respectively +18.45 kcal mol\(^{-1}\) and +20.2 kcal mol\(^{-1}\) establishing potentially a secondary directional preference of these donors toward molecular assembly.

![Electrostatic potential](image.png)

**Figure 1.** Electrostatic potential map of BTMEA in an optimized geometry showing the deep electron-depleted area (blue regions) in the prolongation of (C≡C)−Se bonds and a less significant one in the prolongation of the (CH\(_3\))−Se bonds. Color range from 0.0 (red) to 37.7 kcal/mol (blue) and isosurfaces of electron density at $\rho = 0.002$ a.u.

The synthesis of the new ChB donor 8F-Se is outlined in Scheme 2 and starts with commercially available 4,4′-dibromoperfluorobiphenyl to first obtain compound 2 through Sonogashira coupling reaction. Subsequently, silyl deprotection followed by lithiation with Se metal and alkylation with MeI furnished the desired donor 8F-Se in good yield. The same strategy starting with 1,4-diodotetrafluorobenzene is then followed to obtain 4F-Se as described in our previous report [26].

![Synthesis route](image2.png)

**Scheme 2.** Synthesis route to the ChB donor 8F-Se.

Molecule 8F-Se crystallizes in the triclinic system (SG P\(\overline{1}\)) into 1-D chains driven through Se•••Se contacts with the shortest intermolecular distance at 3.429 Å, which
corresponds to a reduction ratio (RR) of 0.90 relative to the sum of van der Waals radii (2 × 1.90(Se) = 3.80 Å). The C−Se⋯Se bond angle values of 164.3° and 158.1° suggest these Se⋯Se interactions to be of type-I (Figure 2). The molecule is in general position with a torsion angle of 57.54° between both aromatic rings. Concerning the crystal structure of donor 4F-Se, two different polymorphs in monoclinic (SG P2₁/c) and tetragonal (SG I4₁/a) systems were reported in our previous paper [26].

![Figure 2](image_url)

**Figure 2.** Crystal packing of 8F-Se showing type-I Se⋯Se interactions. Hydrogens are omitted for clarity.

To further evaluate this difference in sigma-hole activation, we decided to co-crystallize both donors with various ditopic Lewis-bases to assess their ability to form chalcogen bonded 1D chains. We could obtain co-crystals from both ChB donors 4F-Se and 8F-Se with the 1,2-bis(4-pyridyl)ethane (bpe) as Lewis-base. Data were collected for both co-crystals at room temperature and at 150 K, in order to evaluate also the evolution of the ChB interaction with temperature.

4F-Se•bpe crystallizes in the monoclinic system, SG P2₁/n, with both molecules located on inversion centers, while 8F-Se•bpe crystallizes in the monoclinic system, SG C2/c, with the bpe molecule located on an inversion center and the 8F-Se Ch donor on a 2-fold axis. The torsion angle between the two aromatic rings in 8F-Se amounts to 57.5(1)° at RT and to 55.4(1)° at 150 K, i.e., very close to that found in the crystal structure of 8F-Se. Both co-crystallizations with bpe resulted in the formation of 1:1 cocrystals 4F-Se•bpe and 8F-Se•bpe. In both systems, the 1D chains assembled by ChB motifs develop through short Se⋯N contacts (Table 1) with intermolecular distances at RT of 3.052(2) Å in 4F-Se•bpe and a shorter 3.029(4) Å distance in case of 8F-Se•bpe, suggesting a stronger activation of the σ-hole in Se-atoms in the latter (Figure 3). This slight strengthening with the 8F-Se ChB donor is enhanced at low temperatures (150 K) with the Se⋯N distances decreasing to 3.005(2) and 2.958(2) Å in 4F-Se•bpe and 8F-Se•bpe, respectively.

| Co-Crystal | T (K) | Se⋯N dist. (Å) | RR  | C−(Se)⋯N Angle (°) |
|------------|-------|----------------|-----|-------------------|
| 4F-Se•bpe  | 296   | 3.052 (2)      | 0.88| 172.1 (1)         |
| 8F-Se•bpe  | 296   | 3.029 (4)      | 0.87| 176.7 (1)         |
| 4F-Se•bpe  | 150   | 3.005 (2)      | 0.87| 172.7 (1)         |
| 8F-Se•bpe  | 150   | 2.958 (2)      | 0.85| 177.3 (1)         |

The strength of the Se⋯N interactions in these 1D motifs is also manifested by their almost linear directionality, as the (C≡C−Se⋯N angles are very close to 180° with 4F-Se, and even closer with 8F-Se (Table 1).
In conclusion, it appears that replacement of the p-tetrafluorophenylene core in 4F-Se by the extended p-octafluorobiphenylene one in 8F-Se not only preserves the robustness of the 1D chalcogen-bonded motif in cocrystals with ditopic Lewis bases such as bpe, but also strengthens it, albeit to a limited extend. This strengthening provides, however, an incentive to prepare even longer ChB donors based on these (chalcogenoalkyl)alkynyl derivatives, toward the elaboration of more complex, eventually porous, systems stabilized by such non-bonding σ-hole-based intermolecular interactions.

![Figure 3. Details of the solid-state structures of 1:1 co-crystals of bpe with 4F-Se and 8F-Se at RT. Hydrogens atoms are omitted for clarity.](image)

3. Materials and Methods

General Information. Oxygen- and moisture-sensitive experiments were carried out under a dry oxygen-free nitrogen atmosphere using standard Schlenk techniques. THF was dried using a commercial solvent purification system from Inert Technologies. NMR spectra were recorded on Bruker spectrometers (300 MHz, Bruker, Mannheim, Germany) referenced to residual solvent signals as internal standards. Elemental analyses were performed at BioCIS (Elementar Vario/Perkin Elmer 2400 series, PerkinElmer, Wathen, MA, USA). Commercially available compounds 4,4'-dibromoperfluorobiphenyl, 1,2-bis(4-pyridyl)ethane (bpe) and anhydrous triethylamine were purchased and used as received.

4,4'-Bis(trimethylsilylthynyl)-perfluorobiphenylene 2. 4,4'-dibromoperfluorobiphenyl (1.5 g, 3.3 mmol) was placed in an oven-dried 100 mL round bottom flask. Anhydrous trimethylamine (50 mL) was added under argon followed by TMS-acetylene (1.4 mL, 9.86 mmol, 3 eq.). PdCl₂(PPh₃)₂ (230 mg, 0.32 mmol, 0.1 eq.) and Cul (62 mg, 0.32 mmol, 0.1 eq.) were then added to the reaction mixture under argon and the mixture was refluxed overnight. The reaction mixture was cooled down to room temperature and the precipitate formed was filtered off. Trimethylamine was evaporated using rotary evaporator under reduced pressure and the crude solid residue was subjected to flash column chromatography on silica gel for purification (eluent: petroleum ether) to afford 2 (1.1 g, 70%) as a white solid. Rf = 0.5 (petroleum ether); ¹H NMR (300 MHz, CDCl₃): δ 0.33 (s, 18H); ¹⁹F NMR (300 MHz, CDCl₃): δ −135.5, −138.5.

4,4'-Diethynylperfluorobiphenylene 3. Compound 2 (150 mg, 0.30 mmol) was dissolved in tert-butanol (20 mL) under argon, and potassium carbonate (400 mg, 2.9 mol, 9.6 eq.) was added at 30°C. Reaction was monitored by TLC and 0.1 mL of MeOH was added in an interval of one hour until all the starting material was consumed. Caution: Use of methanol in excess results in the formation of the methoxynitrene derivative. Reaction mixture was filtered over Celite® and the solution was evaporated using rotary evaporator under reduced pressure. The residue was subjected to flash column chromatography on silica gel (eluent: petroleum ether) for purification to afford 3 (94 mg, 89%) as white solid. Rf = 0.4 (petroleum ether); ¹H NMR (300 MHz, CDCl₃): δ 3.78 (s, 2H); ¹⁹F NMR (300 MHz, CDCl₃): δ −135.1, −137.8.
4,4′-Bis(selenomethylethynyl)-perfluorobiphenylene 8F-Se. Compound 3 (240 mg, 0.69 mmol) was placed in an oven-dried 100 mL round bottom flask under inert atmosphere. Dry THF (20 mL) was added under argon flow and the solution was cooled to −78 °C. A solution of nBuLi (2.5 M in hexane, 0.624 mL, 1.52 mmol, 2.2 eq.) was added and the reaction mixture was stirred for half an hour. A finely ground dry Se powder (120 mg, 1.52 mmol, 2.2 eq.) was added under argon flow at −78 °C and the reaction mixture was gradually allowed to warm to RT. After 5 h, MeI (0.094 mL, 1.52 mmol, 2.2 eq.) was added dropwise to the dark red solution and stirring was continued overnight. Reaction was quenched with saturated aqueous ammonium chloride solution (5 mL for 1 mmol of alkyne). The mixture was extracted with diethyl ether (2 × 30 mL). The combined organic layers were dried over Na2SO4, filtered and concentrated under reduced pressure. The obtained crude product was subjected to column chromatography (eluent: petroleum-ether) to afford 8F-Se (120 mg, 52%) as light-yellow solid. Rf = 0.3 (petroleum ether). Mp: 142–144 °C; 1H NMR (300 MHz, CDCl3): δ 2.49 (s, 6H); 19F NMR (300 MHz, CDCl3): δ −136.6, −138.5. 13C NMR (300 MHz, CDCl3): δ 10.2, 83.2, 89.2, 106.9, 142.2, 145.4, 148.6. Anal. Calcd. for C18H6F8Se2: C, 40.62; H, 1.14; found: C, 41.73; H, 1.31. The slightly too large C content can be attributed to some partial decomposition.

4,4′-Bis(selenomethylethynyl)-perfluorobenzene 4F-Se. This was synthesized following the same strategy starting with 1,4-diiodotetrafluorobenzene, as also described in the previous report [26].

Co-crystal Preparation

4F-Se•bpe. To a solution of 4F-Se (7 mg) in EtOAc (0.5 mL) was layered with 1,2-bis(4-pyridyl)ethane (3.3 mg, 1 equiv.) dissolved in EtOAc (0.5 mL). Slow evaporation of solvent resulted in the formation of yellow plate-shaped crystals. Mp: 103 °C; Anal. Calcd. for C24H19F4N2Se2: C, 50.72; H, 3.19; N, 4.93; found: C, 49.40; H, 3.49; N, 4.47.

8F-Se•bpe. To a solution of 8F-Se (9 mg) in EtOAc (0.5 mL) was layered with 1,2-bis(4-pyridyl)ethane (3.1 mg, 1 equiv.) dissolved in EtOAc (0.5 mL). An overnight slow evaporation of solvent resulted in the formation of yellow plate-shaped crystals. Mp: 125–127 °C. Anal. Calcd. for C30H18F8N2Se2: C, 50.52; H, 2.62; N, 3.86.

Crystallography

Data collections at RT were performed on an APEX II Bruker-AXS diffractometer (Mannheim, Germany) equipped with a CCD camera and data collections at 150 K on a D8 VENTURE Bruker AXS diffractometer. Structures were solved by direct methods using the SIR97 program and then refined with full-matrix least-square methods based on F2 (SHELX-97) [31] with the aid of the WINGX program [32]. All non-H atoms of the molecules were refined anisotropically, and hydrogen atoms were introduced at calculated positions (riding model), included in the structure factor calculations but not refined. Details about data collection and solution refinement are given in Table 2. CCDC No. 2090416-2090420. contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

Theoretical Calculations

Molecular structures of 4F-Se and 8F-Se have been optimized in gas phase (vacuum) with Gaussian 09 software using density functional theory [33]. B3LYP functional was used, completed with D3 dispersion Grimme dispersion correction [34]. The def2-TZVPP basis set was employed for all atoms. Frequency calculations were performed in order to check that true energy minima were obtained. Isosurfaces of electron density (ρ = 0.002 a.u.) mapped with the corresponding total electrostatic potential were calculated and drawn with AIMAll software [35].
Table 2. Summary of crystal data.

| Title 1          | 8F-Se | 4F-Se•bpe (RT) | 4F-Se•bpe (150 K) | 8F-Se•bpe (RT) | 8F-Se•bpe (150 K) |
|------------------|-------|---------------|------------------|---------------|------------------|
| CCDC number      | 2090416 | 2090417       | 2090418          | 2090419       | 2090420          |
| Formula          | C18H6F8Se2 | C24H18F4N2Se2 | C24H18F4N2Se2    | C30H18F8N2Se2 | C30H18F8N2Se2    |
| Space group      | P1     | P21/n         | P21/n            | C2/c          | C2/c             |
| a/Å              | 8.4551 (6) | 12.6631 (8)   | 12.6624 (16)     | 22.529 (2)    | 21.575 (2)       |
| b/Å              | 8.6842 (5) | 5.7143 (4)    | 5.6541 (8)       | 6.2237 (6)    | 6.1938 (5)       |
| c/Å              | 12.4001 (9) | 16.6845 (13)  | 16.341 (2)       | 21.539 (3)    | 21.412 (2)       |
| α/°              | 91.956 (2) | 90.00         | 90.00            | 90.00         | 90.00            |
| β/°              | 108.704 (2) | 105.503 (4)   | 105.367 (4)      | 105.862 (7)   | 105.762 (3)      |
| γ/°              | 94.837 (2) | 90.00         | 90.00            | 90.00         | 90.00            |
| V/Å³             | 3857.52 (10) | 1163.38 (14)  | 1128.1 (3)       | 2905.1 (6)    | 2753.7 (4)       |
| Z                | 2      | 2             | 2                | 4             | 4                |
| Dc/g cm⁻³        | 2.061  | 1.622         | 1.673            | 1.638         | 1.728            |
| T/K              | 150 (2) | 296 (2)       | 296 (2)          | 150 (2)       | 150 (2)          |
| μ/ mm⁻¹          | 4.395  | 3.224         | 3.325            | 2.620         | 2.764            |
| F(000)           | 508    | 560           | 560              | 1408          | 1408             |
| Refl. collected  | 4049   | 7490          | 7242             | 13879         | 18466            |
| Refl. indep. (R(int)) | 3944 (0.0583) | 2635 (0.0489) | 2570 (0.0409)  | 3295 (0.0439) | 3152 (0.0426)    |
| Refl. Obs. [I > 2σ(I)] | 3449 | 1779          | 1985             | 2005          | 2568             |
| GOF on F²        | 1.076  | 1.018         | 1.046            | 1.126         |                  |
| R₁ [I > 2σ(I)] (all) | 0.0264 (0.0332) | 0.0453 (0.080)  | 0.0373 (0.0559) | 0.0419 (0.0842) | 0.0333 (0.0452)  |
| wR₂ [I > 2σ(I)] (all) | 0.0609 (0.0651) | 0.0966 (0.107)  | 0.0795 (0.0853) | 0.1031 (0.1224) | 0.0680 (0.0725)  |
| Δρmax/min/e Å⁻³ | +0.508, -0.933 | +0.899, -0.606 | +0.561, -0.514  | 0.546, -0.297  | +0.573, -0.461   |

Author Contributions: A.D. and M.F. conceived the project; A.D. designed and performed the syntheses and crystal growth experiments, he analyzed the solid-state organizations; O.J. carried out the crystallographic studies; E.A. and E.E. carried out and analyzed the ESP calculations; A.D. and M.F. wrote the manuscript, with contributions from all the authors. All authors have read and agreed to the published version of the manuscript.

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