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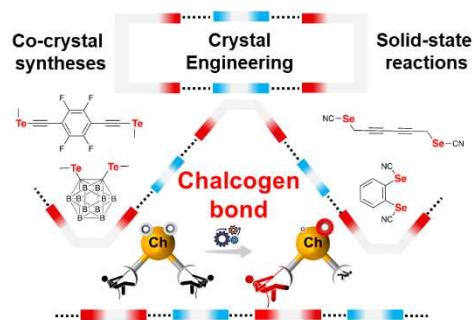
# **Selective Activation of Chalcogen Bonding: An Efficient Structuring Tool Towards Crystal Engineering Strategies**

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**CONSPECTUS:** Among the noncovalent interactions available in the toolbox of crystal engineering, *chalcogen bonding* (ChB) has recently entered the growing family of  $\sigma$ -hole interactions, following the strong developments based on the halogen bonding (XB) interaction over the last 30 years. The monovalent



character of halogens provides halogen bonding directionality and strength. Combined with the extensive organic chemistry of Br and I derivatives, it has led to many applications of XB, in solution (organo-catalysis, anion recognition and transport), in the solid state (co-crystals, conducting materials, fluorescent materials, topochemical reactions, ...), in soft matter (liquid crystals, gels, ...) and in biochemistry. The recognition of the presence of two  $\sigma$ -holes on divalent chalcogens and the ability to activate them, as in XB, with electron-withdrawing groups (EWG) has fueled a more recent interest on chalcogen bonding. However, despite being identified for many years, ChB still struggles to make a mark due to: (i) the underdeveloped synthetic chemistry of heavier Se and Te, (ii) the limited stability of organic chalcogenides, especially tellurides, (iii) the poor predictability of ChB associated with the presence of two  $\sigma$ -holes. It therefore, invites a great deal of attention of molecular chemists to design and develop selected ChB donors, for the scrutiny of fundamentals of ChB and their successful use in different applications. This Account aims to summarize our own contributions in this direction that extends from fundamental studies focused on addressing the lack of directionality/predictability in ChB to a systematic demonstration of its potential, specifically in *crystal engineering*, and particularly toward anionic networks on the one hand, topochemical reactions on the other hand.

In this Account, we share our recent results aimed at recovering with ChB the same degree of strength and predictability found with XB, by focusing on divalent Se and Te systems with two different substituents, only one of them with an EWG, to strongly unbalance both  $\sigma$ -holes. For that purpose, we explored this dissymmetrization concept within three chemical families, selenocyanates R–SeCN, alkynyl derivatives R–C $\equiv$ C–(Se/Te)Me, and *o*-carborane derivatives. Such compounds were systematically engaged in co-crystals with either halide salts, or neutral bipyridines as ChB acceptors, revealing their strong potential to chelate halides, as well as their ability to organize reactive molecules such as alkenes and butadiynes toward [2+2] cycloadditions and polydiacetylene formation respectively. This selective activation concept is not limited to ChB but can be effectively used on all other  $\sigma$ -hole interactions

(pnictogen bond, tetrel bond, ...) where one needs to control the directionality of the interaction.

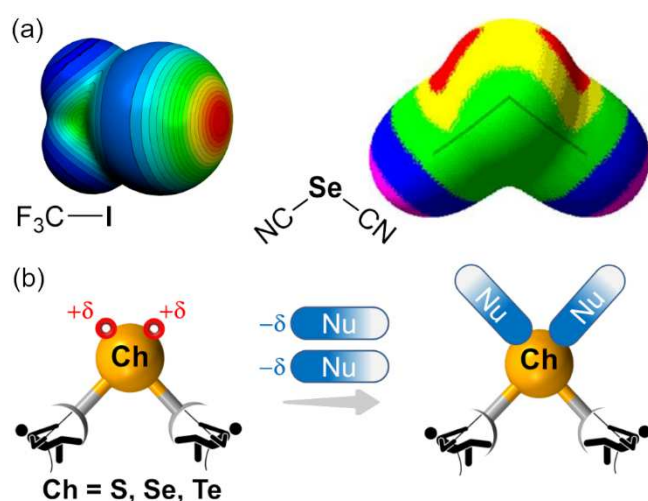
## KEY REFERENCES

- Huynh, H.-T.; Jeannin, O.; Fourmigué, M. Organic selenocyanates as strong and directional chalcogen bond donors for crystal engineering, *Chem. Commun.* **2017**, 53, 8467–8469.<sup>1</sup> *In this paper, we demonstrated, for the first time, the ability of organic selenocyanates to act as ChB donors, toward the controlled formation of 1D motifs upon interaction with 4,4'-bipyridine and analogs.*
- Dhaka, A.; Jeannin, O.; Jeon, I.-R.; Aubert, E.; Espinosa, E.; Fourmigué, M. Activating Chalcogen Bonding (ChB) in Alkylseleno/Alkyltelluroacetylenes toward Chalcogen Bonding Directionality Control. *Angew. Chem. Int. Ed.* **2020**, 132, 23789–23793.<sup>2</sup> *Here, we showed that alkynyl substituents are efficient at activating Se and Te toward the formation of (i) self-assembled helical systems through Se•••Se or Te•••Te ChB and, (ii) 1D robust chalcogen-bonded co-crystals with pyridines.*
- Beau, M.; Lee, S.; Kim, S.; Han, W.-S.; Jeannin, O.; Fourmigué, M.; Aubert, E.; Espinosa, E.; Jeon, I.-R. Strong  $\sigma$ -hole Activation on Icosahedral Carborane Derivatives for a Directional Halide Recognition. *Angew. Chem. Int. Ed.* **2021**, 60, 366–370.<sup>3</sup> *In this Communication, the strong activating power of carboranes, anticipated from earlier theoretical studies, is experimentally demonstrated in the crystal structures of halide networks.*
- Alfuth, J.; Jeannin, O.; Fourmigué, M. Topochemical, Single-Crystal-to-Single-Crystal [2+2] Photocycloadditions Driven by Chalcogen-Bonding Interactions. *Angew. Chem. Int. Ed.* **2022**, 61, e202206249.<sup>4</sup> *Application of ChB in topochemical reactions is demonstrated here by using aromatic selenocyanates for parallel ChB interactions to favor the proper face-to-face organization of bipyridylethylenes toward formation of cyclobutane derivatives through [2+2] photocycloadditions.*

## 1. INTRODUCTION

Crystal engineering<sup>5</sup> has proven highly effective in creating chemical or physical properties in molecular crystalline assemblies, properties not present in the individual building blocks, by using non-covalent interactions such as hydrogen bond or  $\pi$ - $\pi$  stacking. These approaches play now a crucial role in the formation, design, and implementation of active pharmaceutical ingredients, production of energetic materials, catalysis, recognition processes, etc.

The involvement of p-block elements in supramolecular strategies is rooted in the anisotropic electronic distribution present in their covalently bonded form. These elements exhibit indeed regions of positive electrostatic potential, known as  $\sigma$ -holes (Figure 1a), along their covalent bonds when substituted with electron-withdrawing groups (EWG). These  $\sigma$ -holes can interact with regions of opposite polarity in their surroundings (Figure 1b), as in hydrogen-bonded systems.



**Figure 1.** (a) Electrostatic potential (ESP) surfaces of  $\text{CF}_3-\text{I}$  (left) and  $(\text{NC})_2\text{Se}$  (right) computed on the 0.001 electrons/bohr<sup>3</sup> contour of the electronic density, illustrating the charge-depleted area (in red) in the prolongation of the bond to an electron-withdrawing group (EWG). Data from refs. 6 and 14. (b) Schematic representation of chalcogen bond (ChB) formation, with EWG activating two  $\sigma$ -holes (in red) on the chalcogen atoms, to interact with nucleophilic species.

Such non-covalent interactions, based on the  $\sigma$ -hole concept, involve electrophilic and nucleophilic sites and are named according to the respective groups of the electrophilic atoms in the periodic table. Examples include halogen bond (group 17, XB),<sup>6,7</sup> chalcogen bond (group 16, ChB),<sup>8</sup> pnictogen bond (group 15, PnB),<sup>9</sup> etc. The features of strong directionality and

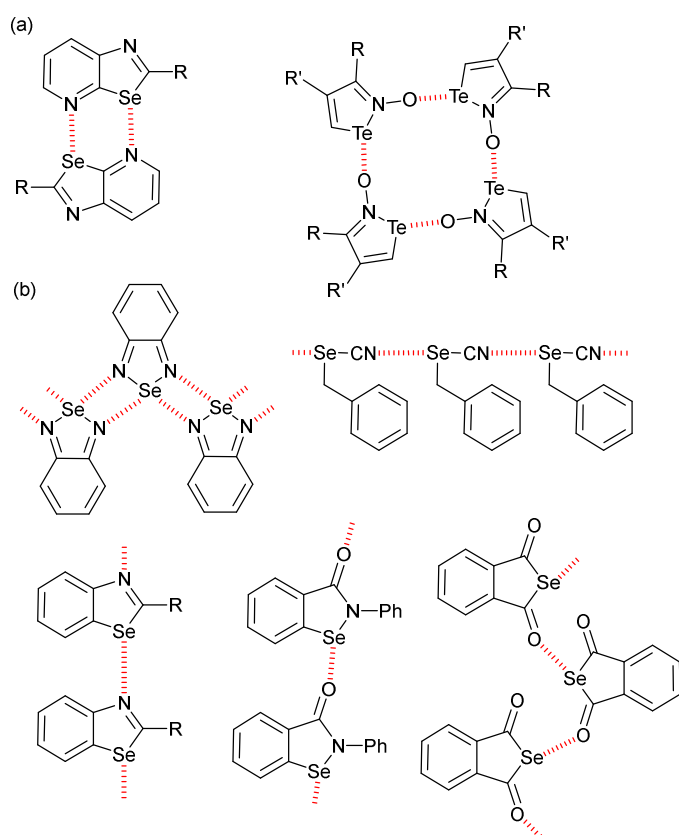
predictability in halogen bond (XB), i.e. two key aspects of a crystal engineering strategy, allowed its extensive use in supramolecular synthesis of designed 1D, 2D and 3D solid-state structures. Other potential applications have been demonstrated in the field of anion recognition, catalysis, soft-materials, *etc.* Such  $\sigma$ -hole interactions have been the subject of many review papers, most of them collected in a recent article.<sup>10</sup>

The early chemistry of chalcogens in relation to non-covalent interactions involved only sulfur, when, back in 1977, Parthasarathy showed that nucleophiles approach a divalent sulfur in R–S–R' system roughly along the covalent bonds (R–S or R'–S) whereas electrophiles do so roughly perpendicular to the R-S-R molecular plane, toward the sulfur lone pairs.<sup>11</sup> Theoretical investigations of model systems based on selenocyanate and alkynyl derivatives were reported in 2006 by Gleiter *et al.* who investigated the nature of the interactions of HC≡C–ChMe and N≡C–ChMe (Ch = O, S, Se, Te) with the corresponding ethers Me<sub>2</sub>Ch as ChB acceptors. It was shown that the ChB interaction strength increases with the (static as well as dynamic) polarizability of the chalcogen, with an added charge-transfer component in the most activated seleno(telluro)cyanate model systems,<sup>12</sup> illustrating the important contribution of such n→ $\sigma^*$  orbital delocalization between a lone pair (n) of the ChB donor and the antibonding  $\sigma^*$  orbital of the ChB acceptor.<sup>13</sup> While the  $\sigma$ -hole concept was first defined in the frame of halogen bond, Politzer extended this concept to the group 16 elements in 2007,<sup>14</sup> establishing the presence of  $\sigma$ -holes also on chalcogen atoms. For example, the electrostatic potential (ESP) surface of Se(CN)<sub>2</sub> (Figure 1a) demonstrated the ability of chalcogens to develop positive potential in the prolongation of covalent bonds when attached to electron withdrawing substituents.<sup>8</sup>

Despite the similarities between ChB and XB, chalcogen bonding poses significant challenges in terms of its use in supramolecular strategies. In contrast to the halogens with only one sigma-hole, the binary valence of chalcogens leads to two  $\sigma$ -holes roughly in the prolongation of each covalent bond that typically strengthen in the order of increasing polarizability O << S < Se < Te. It has been shown that the local positive potential extrema,  $V_{s,max}$ , associated with the  $\sigma$ -hole of chalcogens can significantly deviate from their expected position (C–Ch bond axis) as a consequence of the increasing contributions from the surroundings.<sup>15</sup> This effect is essentially absent in XB as the single R substituent in R–X causes minimal deviation and therefore retains the directionality. Chalcogen atoms, with two  $\sigma$ -holes and less linearity, raise therefore questions on directionality and more importantly predictability of a ChB interaction in the solid state. Nevertheless, following the trails of XB,

ChBs have been successfully implemented, particularly in *solution-studies* such as anion recognition and catalysis.<sup>8a,b</sup> In the field of *crystal engineering*,<sup>8c</sup> ChB was first investigated successfully in amphoteric molecules bearing simultaneously ChB donor sites and at least a ChB acceptor site, providing supramolecular assemblies as illustrated in Scheme 1, allowing the formation of 0D (dimers,<sup>16</sup> tetramers, pentamers)<sup>17</sup> and 1D structures.<sup>18</sup> The extension to *co-crystal formation* was considered in a second step, and is the main topic of this Account.

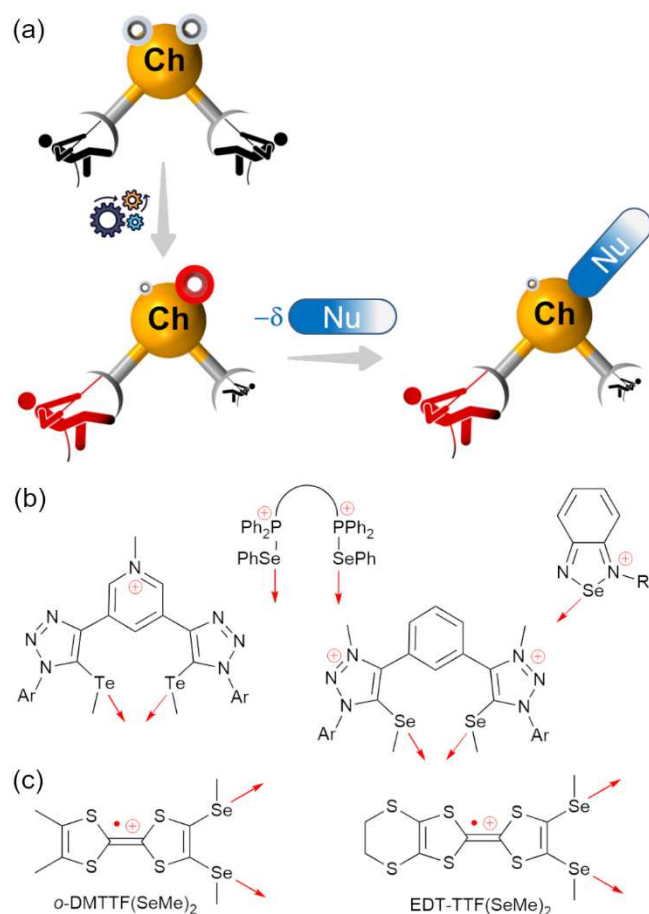
**Scheme 1. Examples of Recently Reported 0D and 1D Chalcogen-Bonded Motifs with Molecules Bearing both ChB-Donor and ChB-Acceptor sites.**



**2. DIRECTIONALITY CONTROL THROUGH CHALCOGEN DISSYMMETRIZATION**

The success of halogen bonding in crystal engineering strategies, particularly in the conception and elaboration of co-crystals is essentially due to: (i) the strength of the interaction, and (ii) its strong directionality and hence predictability. In order to recover with ChB the same degree of predictability, we concentrated our efforts toward chalcogenated molecules with two *different* substituents on the chalcogen atom, and only one of them with a strong electron-

withdrawing character (Figure 2a).<sup>19</sup> Under these circumstances, we expect a differentiation of the two  $\sigma$ -holes up to a point where the strongest one will essentially control the supramolecular organization of co-crystals, in a way similar to that observed with XB. As illustrated in Figure 2b, this approach has been already used in cationic ChB donors aimed at interacting with different neutral or anionic Lewis bases toward anion recognition effects or organo-catalysis applications.<sup>20,21,22</sup>

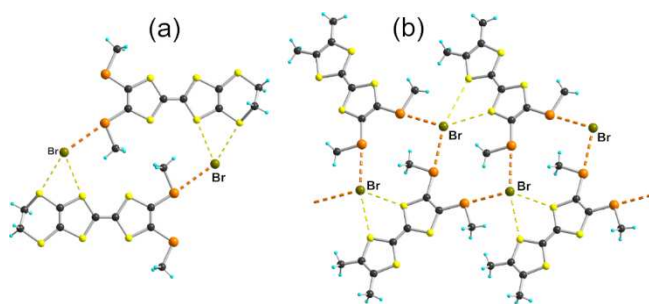


**Figure 2.** (a) Schematic representation of chalcogen bond (ChB) dissymmetrization through  $\sigma$ -hole (in red) differentiation toward directional ChB interaction with nucleophilic species. (b) Examples of cationic ChB donors with a such a strong differentiation. (c) Charge activation of one  $\sigma$ -hole on each Se atom upon  $1e^-$  oxidation of TTF derivatives.

In this direction, our own efforts have been focused to redox-active tetrathiafulvalene (TTF) derivatives. Indeed, an iodine atom of iodo-TTF derivatives develops, upon oxidation to the cation radical, a charge-depleted area on the iodine atom in the prolongation of  $C_{TTF}-I$  bond. This concept of charge-induced activation of XB in iodo-TTF is well demonstrated in solid state<sup>23</sup> as well as in solution.<sup>24</sup> To further extend this strategy in ChB, we investigated the



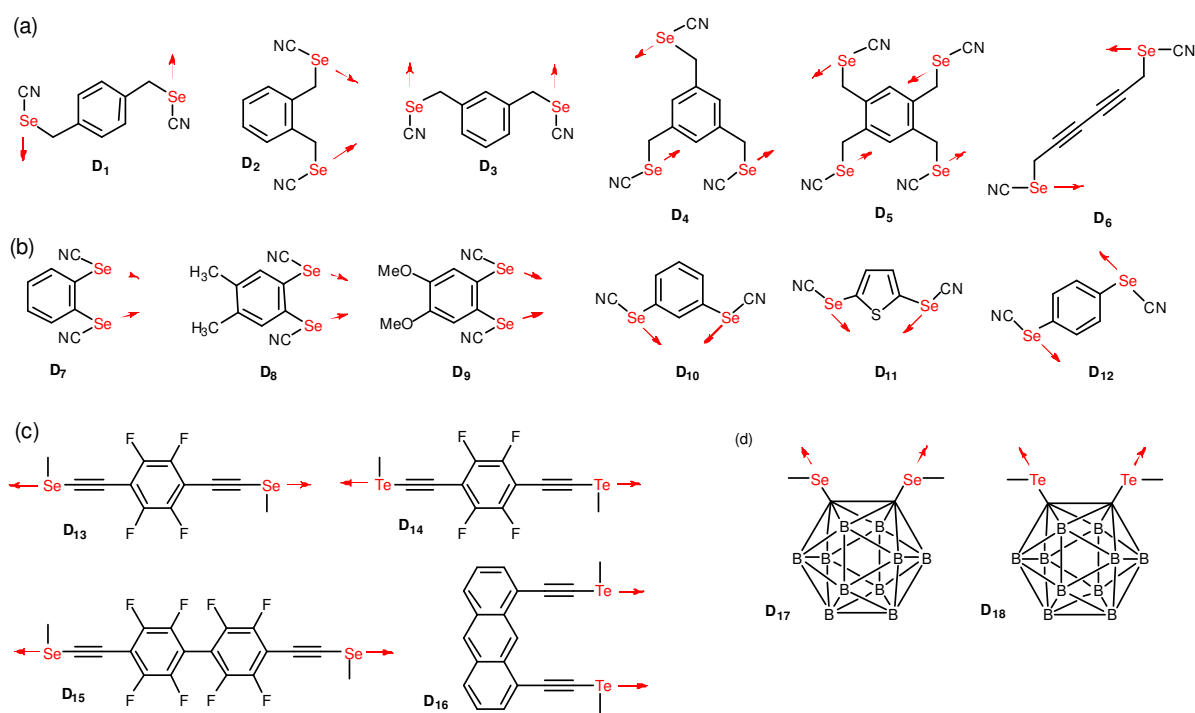
radical salts of two bis(selenomethyl)-TTF derivatives (Figure 2c).<sup>25</sup> The calculated ESP value on Se atoms, upon oxidation, increases from +20 to +85 kcal mol<sup>-1</sup>, comparable to that reported on iodine in oxidized iodo-TTFs. The galvanostatic oxidation of a MeCN solution containing these neutral TTF derivatives and PPh<sub>4</sub>Br or Et<sub>4</sub>NBr afforded the 1:1 cation radical salts. Both reveal the apparition of short and highly linear ChB interactions between Se and bromide anions ( $C_{\text{TTF}}\text{-Se}\cdots\text{Br}^-$ : 174.3 – 177.1°), demonstrating the efficient  $\sigma$ -hole activation (Figure 3). Weaker, secondary interactions involving the sulfur atoms of the TTF<sup>+</sup> moiety, complete the coordination sphere of the bromide. These TTF derivatives have been also recently engaged in charge transfer salts with electron acceptors such as TCNQ or TCNQF<sub>2</sub> (TCNQ: tetracyanoquinodimethane), providing mixed-valence salts with metallic conductivity, stabilized by  $\text{Se}\cdots\text{N}\equiv\text{C}_{\text{TCNQ}}$  ChB interactions.<sup>26</sup>



**Figure 3.** Details of the ChB motifs between the cation radical salts (a) [EDT-TTF(SeMe)<sub>2</sub>]<sup>+</sup>•, Br<sup>-</sup> and (b) [*o*-DMTTF(SeMe)<sub>2</sub>]<sup>+</sup>•, Br<sup>-</sup>. Yellow dotted lines indicate the weaker S<sup>•••</sup>Br<sup>-</sup> interactions, orange dotted lines the strongest and directional Se<sup>•••</sup>Br<sup>-</sup> ChB, with in (a) Se<sup>•••</sup>Br<sup>-</sup>: 3.502(3) Å and C<sub>TTF</sub>-Se<sup>•••</sup>Br<sup>-</sup>: 174.3(1)°; and in (b) Se<sup>•••</sup>Br<sup>-</sup>: 3.367(2) Å and C<sub>TTF</sub>-Se<sup>•••</sup>Br<sup>-</sup>: 177.1(3)°, Se<sup>•••</sup>Br<sup>-</sup>: 3.442(2) Å and C<sub>TTF</sub>-Se<sup>•••</sup>Br<sup>-</sup>: 176.4(3)°.

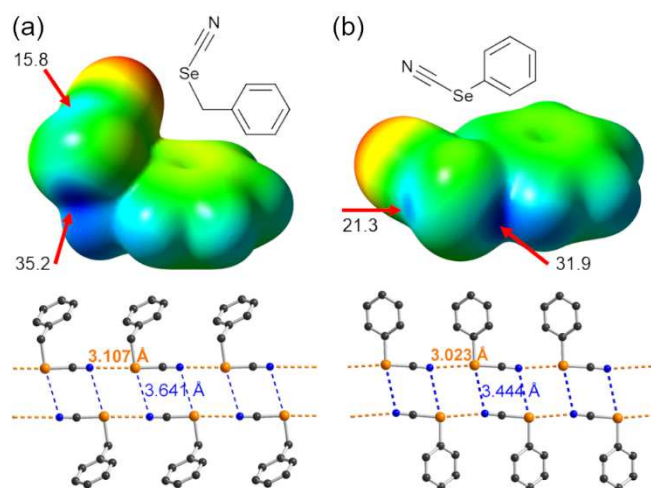
We wanted to extend this dissymmetrization concept to *neutral* ChB donors and developed this approach along three main families respectively, selenocyanates R-SeCN, alkynyl derivatives R-C≡C-(Se/Te)Me, and *o*-carborane derivatives B<sub>10</sub>H<sub>10</sub>[C-(Se/Te)Me]<sub>2</sub>, as gathered in Scheme 2.

**Scheme 2. Different Neutral ChB Donors with Specific Activation of one  $\sigma$ -Hole, as Illustrated by the Red Arrows.**



## 2.1 Activation through CN Moieties in Organic Selenocyanates

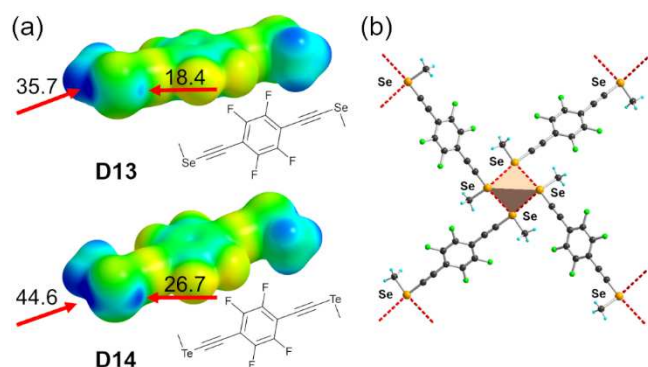
With one strongly EWG cyanide substituent and one other alkyl, benzyl, propargyl or aryl substituent, organic selenocyanates appear as promising ChB donors with a strong differentiation of their two  $\sigma$ -holes, as already demonstrated from theoretical investigations on NC–SeMe as ChB donor model system.<sup>12</sup> A CSD analysis of the reported structures of organic selenocyanates showed indeed the recurrent formation of self-complementary chain-like motifs where the  $\sigma$ -hole in the prolongation of the Se–CN bond interacts through ChB with the nitrogen lone pair of a neighboring molecule (Scheme 1b).<sup>27,28</sup> We extended these series to benzylic bis-, tris- or tetrakis-substituted derivatives **D1–D5**,<sup>29</sup> the propargyl derivative **D6** (Scheme 2a)<sup>30</sup> as well as the aromatic bis(selenocyanate) compounds **D7–D12** (Scheme 2b).<sup>4,31</sup> As illustrated in Figure 4 for benzylselenocyanate BzSeCN and phenylselenocyanate PhSeCN, electrostatic potential calculations confirmed the presence of a stronger electron depletion along the N≡C–Se bond. The secondary  $\sigma$ -hole is stronger in aromatic selenocyanates than in benzylic ones.<sup>31</sup> This effect has an influence on the antiparallel solid-state arrangement of the ChB-bonded  $\bullet\bullet\bullet\text{NC}(\text{R})\text{Se}\bullet\bullet\bullet\text{NC}(\text{R})\text{Se}\bullet\bullet\bullet$  chains through this weak secondary ChB (in blue dotted lines in Fig. 3), shorter in PhSeCN (3.444 Å, RR = 0.99) than in BzSeCN (3.641 Å, RR = 1.05) where it exceeds the van der Waals contact distance (the reduction ratio RR is defined as the experimental distance divided by the van der Waals contact distance).



**Figure 4.** Computed electrostatic potential on the 0.001 electron/bohr<sup>3</sup> isodensity surface with the local maxima indicated in kcal mol<sup>-1</sup> (top) and illustration of the antiparallel organization of ChB-bonded chains (bottom) in: (a) benzylselenocyanate BzSeCN and (b) phenylselenocyanate.

## 2.2. Activation through Alkynyl Substituents

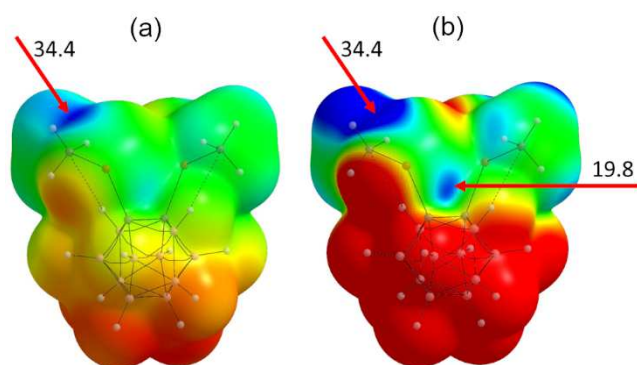
Looking toward more rigid ChB donors, we turned our attention to known XB donors such as diiodoacetylene where iodine atom is strongly activated by alkynyl (C≡C) substitution.<sup>32</sup> Cyclic and acyclic oligoalkynes capped with SeMe/TeMe moieties have been previously described,<sup>33</sup> organizing in the solid state into tubular structures with short Ch•••Ch interactions. These findings opened a route toward the exploration of such alkynyl derivatives as efficient strong ChB donors.<sup>12,34</sup> However, their potential to form co-crystals through ChB interactions was not explored. Replacing the two iodine atoms in acetylene-based ditopic 1,4-bis(iodoethynyl)-perfluorobenzene XB donor<sup>35</sup> by SeMe/TeMe moieties resulted in the ChB donors **D13** and **D14** (Scheme 2c).<sup>2</sup> ESP calculations confirmed the presence of a strong electron depletion along the C≡C–Ch bond (Ch = Se:  $V_{s,max} = +35.6$  kcal/mol ; Te:  $V_{s,max} = +44.6$  kcal/mol), to be compared also with the  $V_{s,max}$  value of the iodine analog (+51.0 kcal/mol). In the solid state, these molecules organize into tetrahedral motifs through short, Se•••Se or Te•••Te ChB interactions (Figure 5b) leading to the formation of helical systems.<sup>2</sup>



**Figure 5.** (a) Computed electrostatic potential on the 0.002 electron/bohr<sup>3</sup> isodensity surface with the local maxima indicated in kcal mol<sup>-1</sup> for **D13** and **D14**. Potential scale ranges from –31.4 (red) to +31.4 kcal/mol (blue). (b) One tetrahedral motif formed by directional Se•••Se ChB in the crystal structure of **D13**. Se•••Se distances and (CC)–Se•••Se angles among the seven crystallographically independent motifs are in the range 3.633–3.668 Å, 166.4–168.4°.

### 2.3 Activation by Carboranes

We also directed our attention to *ortho*-carboranes as excellent activating candidates. Appending a chalcogen atom on the electronegative carbon vertices can potentially render strongly activated ChB donor sites. Theoretical studies on the diiodo *o*-carborane derivative B<sub>10</sub>H<sub>10</sub>[C–I]<sub>2</sub> recently highlighted the presence of a sizeable  $\sigma$ -hole on both iodine atoms in the prolongation of the C–I bonds,<sup>36</sup> while other chalcogenated derivatives were also theoretically investigated.<sup>37</sup> We therefore considered functionalizing both carbon atoms of *o*-carborane with SeMe/TeMe substituents and designed ditopic ChB donors **D17** and **D18** (Scheme 2d).<sup>3</sup> Indeed, strong electron deficient region is generated for each chalcogen atom in the prolongation of the C<sub>carborane</sub>–Ch bond, with a contribution of the hydrogen atom of the methyl substituent (Fig. 6).



**Figure 6.** Computed electrostatic potential of **D18** (Te) on the 0.001 electron/bohr<sup>3</sup> contour of the electronic density with the local maxima indicated in kcal mol<sup>-1</sup>, shown at two different

potential scale ranges to visualize both  $\sigma$ -holes, (a) from  $-15.7$  (red) to  $+34.5$  (blue) kcal mol $^{-1}$ , (b) from 0 (red) to  $+21.3$  (blue) kcal mol $^{-1}$ .

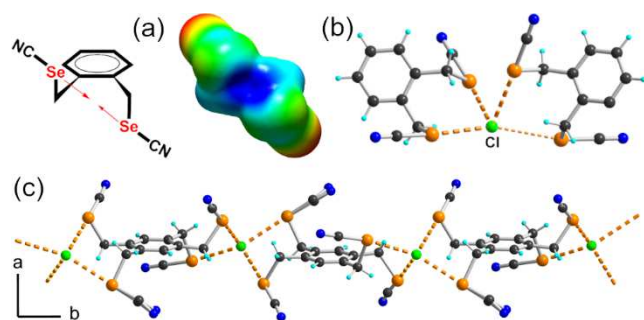
With these extended series of ChB donor molecules **D1–D18** at hand, we describe in the following their involvement in the formation of extended networks upon ChB interaction with first anionic halides (Part 3), then with neutral pyridine-based Lewis bases (Part 4), and finally with applications in topochemical reactions (Part 5).

### 3. ChB ANIONIC NETWORKS

Anion recognition through XB interactions have been intensively investigated owing to the strong interaction reinforced by charge assistance.<sup>38</sup> With halides in particular, a charge-inverted coordination chemistry has even been defined,<sup>39</sup> with coordination numbers up to eight.<sup>40</sup> In the solid state, using di-, tri- or tetratopic XB donors, such interactions lead to the formation of 1D to 3D halogen-bonded anion organic networks.<sup>41,42</sup> A similar coordination chemistry of halides through ChB is still in its infancy,<sup>43</sup> with some recent investigations in solution by spectroscopic methods<sup>44</sup> or toward anion transport across lipid bilayers,<sup>45</sup> together with theoretical studies.<sup>46</sup> Our contribution along this direction, particularly in the solid state, is detailed in the following sections.

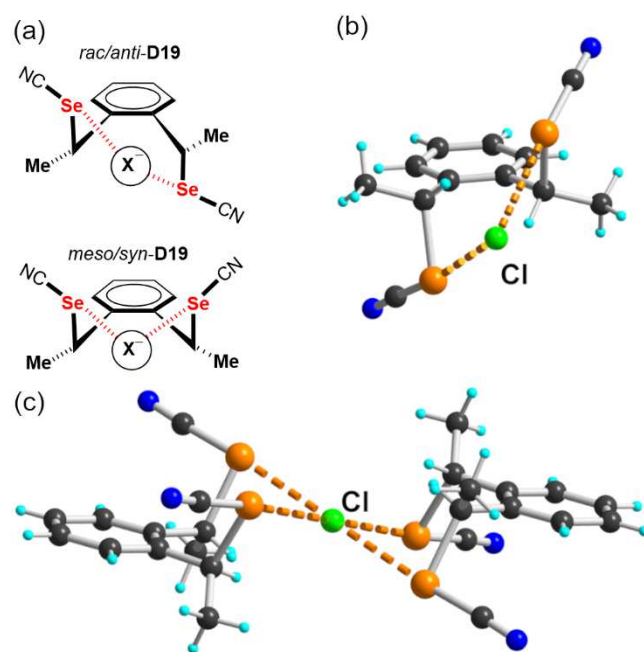
#### 3.1. Organic Selenocyanates as a Chelating Halide Receptors

In the *ortho*-substituted benzylic derivatives **D2** and **D5** (Scheme 2a), two neighboring SeCN moieties can act as a pincer, either in *syn* or *anti* conformation, to chelate halides ( $\text{Cl}^-$  and  $\text{Br}^-$ ) through a broad electron-deficient region characterized by large  $V_{s,\text{max}}$  values of 48–52 kcal/mol (Figure 7).<sup>47,48</sup> The observed ChB interactions with halides feature recurrent  $\mu_2$ - and  $\mu_4$ -motifs. The  $\mu_4$ -halide ChB motifs adopt the so-called seesaw geometry with  $\text{Br}^-$  and close-to-tetrahedral geometry with  $\text{Cl}^-$ . The  $^1\text{H}$  shift of solution NMR signals of **D2** as a function of chloride quantity confirmed the sizable interaction with an association constant of  $148 \text{ M}^{-1}$ ,<sup>47</sup> while changes in the  $^{13}\text{C}$  and  $^{77}\text{Se}$  chemical shifts were also reported with **D1** and **D5**.<sup>48</sup>



**Figure 7.** (a) Computed electrostatic potential of **D2** on the 0.001 electron/bohr<sup>3</sup> isodensity surface, in its *anti* conformation. Potential scale ranges from  $-25$  to  $+38$  kcal mol<sup>-1</sup>. (b) Detail of  $\mu_4$ -Cl<sup>-</sup> coordination in the crystal structures of (**D2**)<sub>2</sub>•PPh<sub>4</sub>Cl•Et<sub>2</sub>O. The three shortest ChB are found with (C)Se•••Cl<sup>-</sup> distances and angles at 3.166(3) Å/174.9(2)°, 3.188(2) Å/172.6(3)°, 3.220(3) Å/179.2(3)°. (c) Detail of the chains incorporating the  $\mu_4$ -Cl<sup>-</sup> motif in (**D6**)•Bu<sub>4</sub>NCl, with Se•••Cl<sup>-</sup> distances and angles at 3.092(5) Å/173.0(3)° and 3.244(7)Å/169.7(3)°.

The control of the *syn* vs. *trans* conformation of the chelating bis(selenocyanate) **D2** was realized with a *chiral* ChB donor, 1,2-bis(1-selenocyanoethyl)benzene **D19** (Figure 8a), obtained by introducing methyl substituents on both benzylic arms of the achiral **D2**.<sup>49</sup> The racemic derivative adopts the *trans* configuration in its  $\mu_2$ -Cl<sup>-</sup> co-crystal (Figure 8b) while the *meso* form crystallizes in the *syn* configuration in its  $\mu_4$ -Cl<sup>-</sup> co-crystal (Figure 8c). Altogether these results demonstrate the efficiency of such benzylic selenocyanates to interact with halides and the flexibility brought by the two possible *syn* and *anti* conformations.

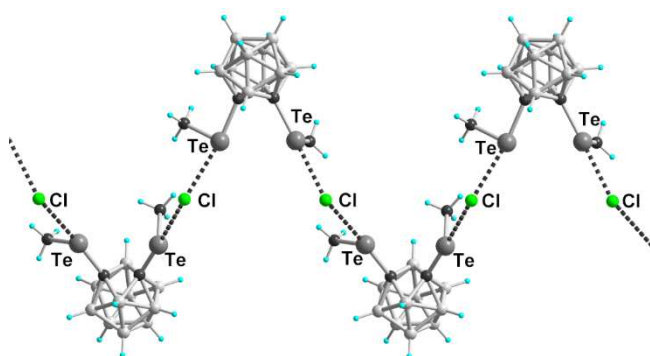


**Figure 8.** (a) *Anti* vs. *syn* conformation of the chiral ChB donors *rac*-**D19** and *meso*-**D19**. (b) Detail of  $\mu_2$ -Cl<sup>-</sup> coordination of the [(*rac*-**D19**)Cl<sup>-</sup>] anionic motif in the crystal structure of [(*rac*-**D19**)Cl<sup>-</sup>]. (c) Detail of the chains incorporating the  $\mu_4$ -Cl<sup>-</sup> motif in the crystal structure of [(*meso*-**D19**)Cl<sup>-</sup>].

(*rac*-**D19**)•Ph<sub>4</sub>PCl•(Et<sub>2</sub>O)<sub>0.5</sub> with Se•••Cl<sup>-</sup> ChB distances and angles at 3.262(6) Å/173.7(1)° and 3.330(7) Å/173.7(1)°. (c) Detail of the μ<sub>4</sub>-Cl<sup>-</sup> coordination in the [(*meso*-**D19**)<sub>2</sub>Cl<sup>-</sup>] anionic motif in (*meso*-**D19**)<sub>2</sub>•Bu<sub>4</sub>NCl with Se•••Cl<sup>-</sup> ChB distances and angles at 3.108(3) Å/176.2(2)° and 3.160(1) Å/176.0(3)°.

### 3.2. Halide Recognition by *o*-Bis(chalcogenomethyl)carboranes

As shown in the section 2.3, the carborane derivatives **D17** (Se) and **D18** (Te) show a strongly electron deficient region in the prolongation of C–Ch bonds, indicating good ChB donor ability. Their co-crystallization with *n*-tetrabutylammonium halides (X = Cl<sup>-</sup> or Br<sup>-</sup>) afforded single crystals of (Bu<sub>4</sub>N)[(**D17**)Br] and (Bu<sub>4</sub>N)[(**D18**)Cl]. With **D17**, only one of the two Se atoms interacts with the bromide to form a μ<sub>1</sub>-motif with the modest RR value (0.95), which is coherent with the less pronounced *V*<sub>s,max</sub> value. In contrast, both tellurium atoms in **D18** are engaged in ChB interactions with the chloride ions in a μ<sub>2</sub>-motif (Figure 9). The observed ChB interactions are remarkably short with RR values down to 0.79, and highly linear. At variance with the selenocyanates derivatives **D2**, **D6**, or **D19**, the carboranes **D17** and **D18** cannot chelate one single chloride anion because the activated σ-hole is located on the prolongation of the two diverging C<sub>carborane</sub>–Te bonds. Consequently, one-dimensional zig-zag chains are formed.



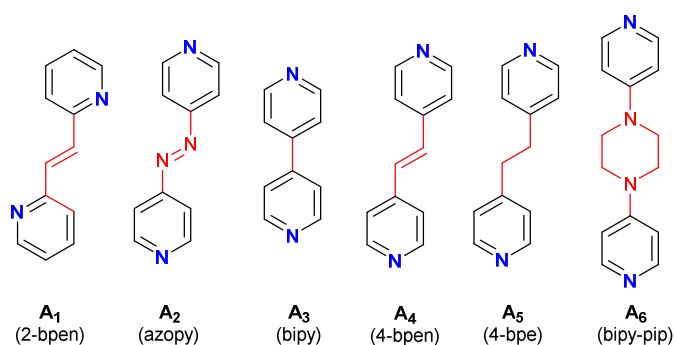
**Figure 9.** Detail of the chalcogen-bonded [(**D18**)Cl<sup>-</sup>] anionic chain in **D18**•Bu<sub>4</sub>NCl with Te•••Cl<sup>-</sup> ChB distances and angles at 3.064(8) Å/170.9(5)° and 3.154(8) Å/177.3(6)°.

## 4. ChB CO-CRYSTALS WITH NEUTRAL LEWIS BASES

Accessing ChBs to engineer hetero-molecular, discrete supramolecular architectures continues to present significant challenges.<sup>50</sup> These difficulties arise from the difficult integration of appropriate ChB donor sites in a molecule while maintaining its desired orientation. While

negatively charged halides make efficient ChB acceptors (see above Part 3), their spherical shape hinders any predictability for the outcome of the co-crystal structures. Therefore, use of neutral Lewis bases with one single available lone pair as potential ChB acceptor may provide a better control over formation of discrete supramolecular architectures, as demonstrated in the following with linear ditopic bis(pyridine) derivatives shown in Scheme 3.

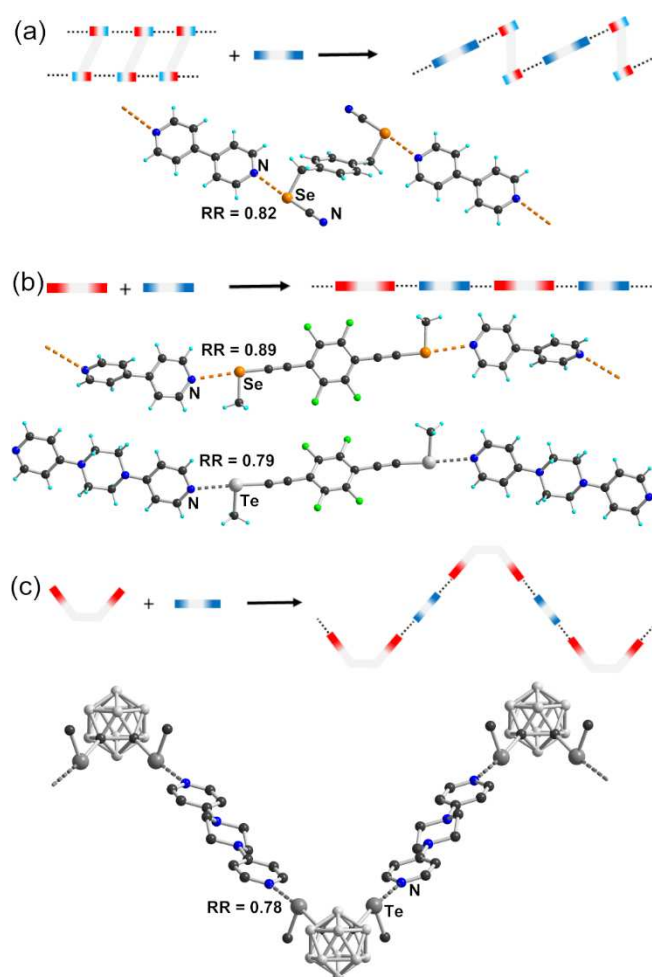
**Scheme 3. Bis(pyridine)-Based ChB Acceptors, Organized from Left to Right According to Their Increasing Lewis-Base Character.**



#### 4.1. 1D ChB Motifs in Co-Crystals

To create solid-state structures using intermolecular interactions, it is crucial to incorporate highly directional and strongly interacting sites on the partners involved. For example, a ChB supramolecular chain can be formed by combining a linear ditopic ChB donor with a linear ditopic ChB acceptor. Our early focus on benzylselenocyanates as ChB donors for co-crystal formation was stemmed from their proven capability to self-associate through  $\text{Se}\cdots\text{N}\equiv\text{C}$  ChBs (section 2.1).<sup>27,31</sup> The *para*-substituted 1,4-bis(selenocyanatomethyl)benzene **D1** with two activated ChB sites meet the structural requirements for chain formation. Its co-crystallization with **A3** (4,4'-bipy) successfully resulted in the anticipated **D1•A3** 1:1 composition, which adopts a 1D chain motif (Figure 10a), stabilized by very short ( $\text{RR} = 0.82$ ) and directional [ $\text{C}-\text{Se}\cdots\text{N}_{\text{bipy}}: 177.2(1)^\circ$ ] chalcogen bonds.<sup>1</sup> This marked the first reported co-crystal between a ditopic ChB donor and a ditopic ChB acceptor, showing that selenocyanates exhibit excellent  $\sigma$ -hole donor ability toward neutral ChB acceptors.





**Figure 10.** One-dimensional chalcogen bonded motifs in neutral co-crystals with (a) a selenocyanate-based ChB donor in **D1•A3** with Se•••N ChB distance and angle at 2.897(4) Å/176.7(1)°, (b) alkynyl derivatives as ChB donors in **D13•A3** and **D14•A6** with Se•••N ChB distance and angle at 3.055(4) Å/176.1(1)° in **D13•A3** and Te•••N ChB distance and angle at 2.855(4) Å/171.8(1)° in **D14•A6**, (c) a carborane-based ChB donor in **D18•A6** with ChB distance and angle at 2.834(9) Å/171.3(2)°.

The molecular flexibility of benzyl selenocyanates makes the ChB sites easily accessible but limits, to some extent, the construction of more rigid supramolecular systems. This led us to design the neutral, linear and rigid bis(alkynyl) ChB donors **D13** and **D14** (Cf. Scheme 2). Accordingly, their co-crystallization with **A3** also produced the desired chain motif (Figure 10b), driven by short and directional Ch•••N<sub>bipy</sub> ChBs, engaging the  $\sigma$ -hole present in the prolongation of the (C≡C)–Ch bond with RR values of 0.89 and 0.82 for Ch = Se and Te, respectively.<sup>2</sup> The robustness of these ChB-based one-dimensional motifs was further tested by employing **A6**, a ditopic analog of the strong Lewis base 4-dimethylaminopyridine (Scheme 3). Its co-crystallization with **D13** and **D14** provided similar chain motifs with even shorter Ch•••N<sub>bipy-pip</sub> contacts, with RR values down to 0.87 and 0.79 respectively for Ch = Se and Te.

It should be stressed here that the RR value in **D14•A6** compares with that found in the iodine analog (0.77),<sup>2</sup> demonstrating that alkynyl-tellurium derivatives can be as efficient as prototypical alkynyl-iodine ones to engage into strong and directional  $\sigma$ -hole interactions.

The excellent  $\sigma$ -hole donor ability of bis(telluromethyl)carborane **D18** demonstrated in its co-crystals with halides (Part 3.2), together with its ditopic character led us to engage it also into co-crystallizations with the neutral ditopic ChB acceptors **A5** and **A6**. The structure of the co-crystals **D18•A5** and **D18•A6** (Figure 10c) revealed indeed the formation of the desired ChB-bonded chains driven by very short Te $\cdots$ N contacts, with RR values of 0.79 and 0.78 in **D18•A5** and **D18•A6** respectively.<sup>51</sup>

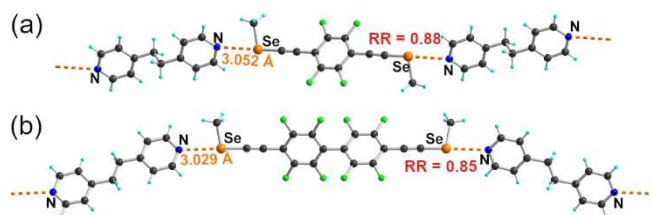
In conclusion, the success of these three approaches based on cyanate, alkynyl and *o*-carborane substitution toward co-crystal formation provides the crystal engineering community with efficient, and neutral, ChB donors for the elaboration of supramolecular 1D (and potentially 2D or 3D) architectures, with a degree of strength and predictability comparable to that of halogen bonding.

## 4.2. Tunability

With the assumption that the sigma-hole interactions (XB and ChB) investigated here are primarily electrostatic in nature, the ESP values at interacting sites can be used in crystal engineering to predict their robustness.<sup>52,53</sup> Also, the ESP values associated to the  $\sigma$ -hole in isolated molecules are useful in establishing a ranking among different donors, thereby introducing parameter of selectivity and predictability in multicomponent supramolecular synthesis.<sup>54</sup> Such fundamental studies become crucial to understand the limitations of  $\sigma$ -hole interactions formed under different chemical and electronic environments, and studies in this direction exploring specifically chalcogen bonds still remain scarce.

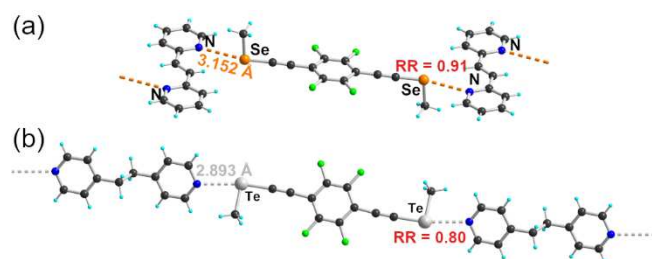
Our first attempt to investigate the tunability of ChB involve modifications of the activation power of the electron withdrawing part in the ChB donor molecule. For example, we considered replacing the *p*-tetrafluorophenylene core in **D13** by the extended *p*-octafluorobiphenylene core (**D15** in Scheme 2). In the co-crystal of **D13** with **A5** (4-bipyridylethane), the typical 1D motif was observed with RR = 0.88 for the Se $\cdots$ N<sub>A5</sub> ChB. The co-crystallization of the extended **D15** ChB donor with the same ChB acceptor **A5** not only preserved the 1D chalcogen-bonded motif (Figure 11) but slightly strengthened it (RR= 0.85).<sup>55</sup> Albeit limited, this strengthening provides an incentive to prepare even longer ChB donors

based on these alkynyl derivatives, toward the elaboration of more complex, eventually porous, systems.



**Figure 11.** Details of the ChB interactions in (a) **D13•A5** with Se•••N ChB distance and angle at 3.052(6) Å/172.1(1)° and, (b) **D15•A5** with Se•••N ChB distance and angle at 3.029(9)/176.7(1)°.

To further study the tunability of these ChBs, we considered varying the Lewis base character of the ChB acceptor molecules in our co-crystals. Having already the co-crystals of **D13** and **D14** with **A3** and **A6** in our hands (4 structures),<sup>2</sup> we wanted to extend this library to two other ChB acceptors, namely **A1** and **A5**. While **D13•A5** was already reported by us,<sup>55</sup> the three other co-crystals **D13•A1**, **D14•A1** and **D14•A5** were prepared and structurally characterized here (See SI). In all of them, the recurrent chalcogen-bonded 1D motif is systematically observed (Figure 12), with RR values varying from 0.91 down to 0.79, depending on the nature of the ChB acceptor (see below).



**Figure 12.** Detail of the ChB chains within the co-crystals (a) **D13•A1** with Se•••N ChB distance and angle at 3/152(6) Å/165.6(1)° and, (b) **D14•A5** with Te•••N ChB distance and angle at 2.893(9) Å/169.8(5)°.

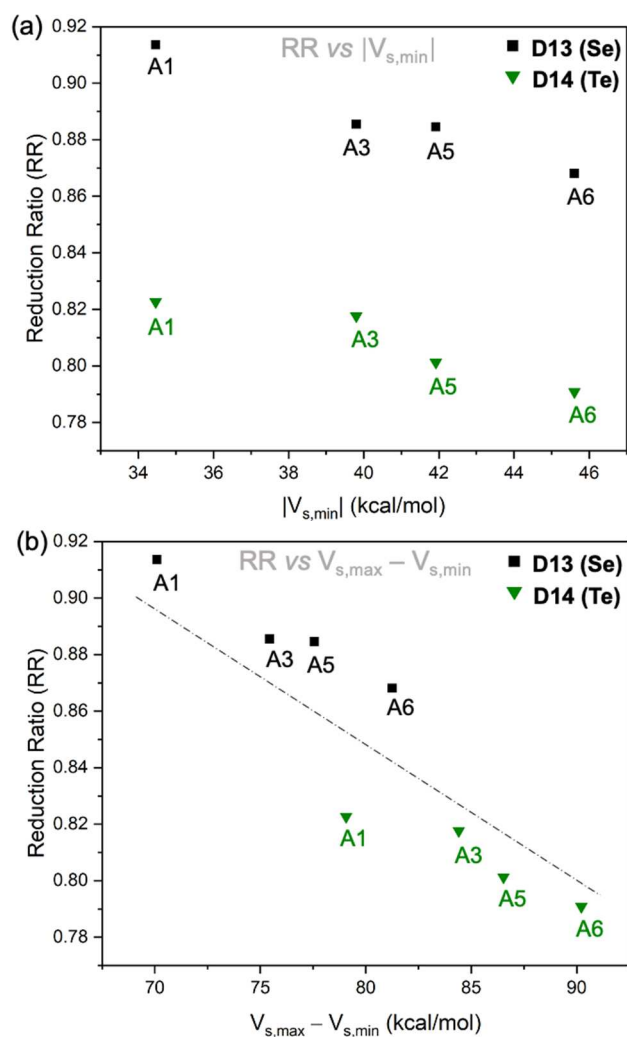
This extended library of eight co-crystals allows us now to study the evolution of Ch•••N distances (Table 1). The increasing order of nucleophilicity of the ChB acceptor follows the trend **A1** < **A3** < **A5** < **A6**, as demonstrated by the increasing  $V_{s,min}$  (negative potential at the ChB acceptor site) values (Table 1). As shown in Figure 13a, a correlation is

observed between RR and  $V_{s,\min}$  values within each series of co-crystals with respectively **D13** (Ch = Se) and **D14** (Ch = Te), *i.e.*, the shortest ChB with the strongest acceptor (**A6**), the longest ChB with the weakest acceptor (**A1**). We also note that, with every acceptor, not only the RR value but the Te•••N distance itself is systematically shorter than the Se•••N distance, a signature of ChB in these systems. Altogether this analysis demonstrates that a systematic tuning of the ChB strength over a wide range is possible within such 1D motifs by modulating the electronic properties of both donor and acceptor molecules.

**Table 1.** Negative potential at the ChB acceptor site  $V_{s,\min}$  (kcal mol<sup>-1</sup>) and experimental ChB distances (Å) for each pair of donor/acceptor (with the corresponding RR value in parentheses). The  $V_{s,\max}$  values for the two ChB donors are +35.6 kcal mol<sup>-1</sup> for **D13** (Se) and +44.6 kcal mol<sup>-1</sup> for **D14** (Te).

	<b>A1</b>	<b>A3</b>	<b>A5</b>	<b>A6</b>
$V_{s,\min}$ (kcal mol <sup>-1</sup> )	- 34.4	- 39.8	- 41.9	- 45.6
Se•••N (Å) with <b>D13</b>	3.152 (0.91)	3.055 (0.88)	3.052 (0.88)	2.995 (0.86)
Te•••N (Å) with <b>D14</b>	2.970 (0.82)	2.952 (0.81)	2.893 (0.80)	2.855 (0.79)

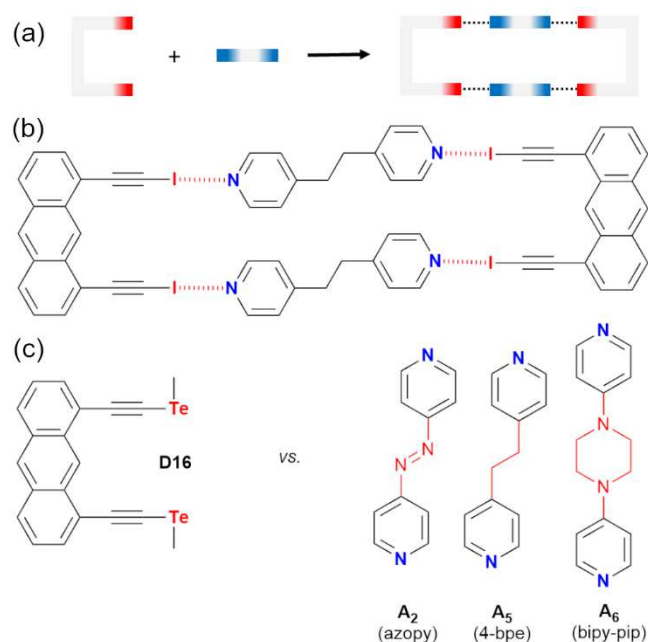
Finally, to comment on the electrostatic nature of these Ch•••N ChBs, we introduce here a descriptor ( $V_{s,\max} - V_{s,\min}$ ) that integrates permanent electrostatics in both interacting partners.<sup>53,56</sup> In principle, for an electrostatic interaction, a higher  $V_{s,\max} - V_{s,\min}$  value should result into a stronger interaction (and associated smaller RR value), neglecting the polarization effects which appears upon ChB formation. As shown in Figure 13b, this general trend is indeed observed for the eight co-crystals. The weakest interaction (RR = 0.91) is associated with the smallest ( $V_{s,\max} - V_{s,\min}$ ) value (+70.0 kcal mol<sup>-1</sup>) in co-crystal **D13•A1** whereas the strongest interaction (RR = 0.79) in **D14•A6** with largest ( $V_{s,\max} - V_{s,\min}$ ) value (+90.2 kcal mol<sup>-1</sup>).



**Figure 13.** Evolutions of the RR values in the eight crystals involving **D13** and **D14** as ChB donors, **A1**, **A3**, **A5** and **A6** as ChB acceptors vs. (a)  $V_{s,min}$ , (b)  $(V_{s,max} - V_{s,min})$ . Correlation coefficients for linear fits amount to 0.98 for both Se and Te compounds in Fig. 13a, to 0.92 for Fig. 13b.

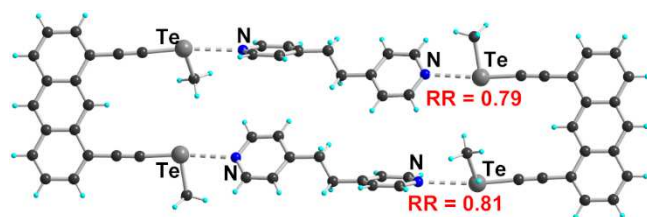
### 4.3. Chalcogen-Bonded Rectangles

Supramolecular rectangles can be synthesized by combining a U-shaped ditopic donor molecule and a linear ditopic Lewis-base or vice-versa (Figure 14a). Such a XB bonded supramolecular motif has been reported by Aakerøy from the co-crystallization of the U-shaped ditopic halogen-bond donor, 1,8-diiodoethynylantracene, and ditopic XB acceptors such as **A5** (Figure 14b).<sup>57</sup> Drawing inspiration from this work, we considered replacing both iodine atoms with telluromethyl moieties and designed the ChB donor **D16** (Figure 14c).<sup>58</sup>



**Figure 14.** (a) Supramolecular assembly toward rectangle motifs, (b) Example of an XB association, (c) Proposed ChB systems.

ESP calculations confirmed the favorable directionality and sigma-hole donor ability of **D16**. Its co-crystallization with ditopic acceptors such as **A2**, **A5** and **A6** resulted into the desired rectangular motifs, held together with very short and directional Te...N ChBs, as illustrated in Figure 15 for the tetramolecular system (**D16**)<sub>2</sub>(**A5**)<sub>2</sub>, with very short and linear Te...N<sub>bpe</sub> interactions and RR values in the range 0.79-0.81.



**Figure 15.** Detail of the rectangular motif in the 2:2 co-crystal **D16•A5** with Te...N ChB distances and angles at 2.854(6) Å/174.7(2)° and 2.943(5) Å/172.1(2)°.

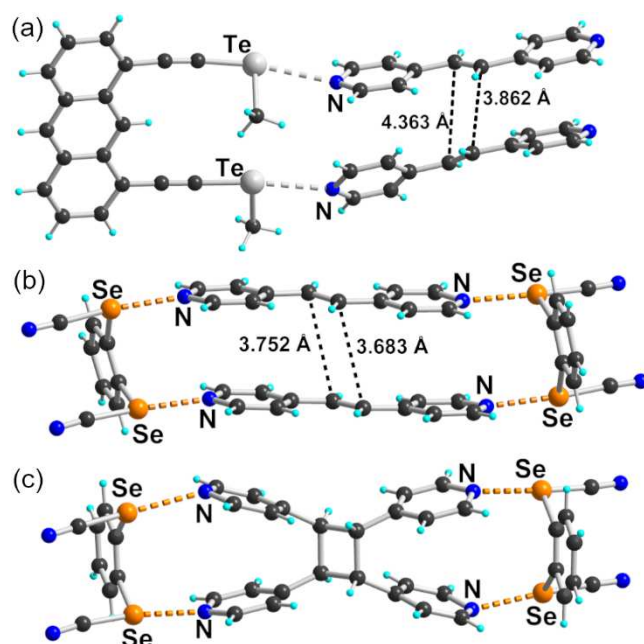
## 5. TOPOCHEMICAL REACTIONS IN CHALCOGEN-BONDED SYSTEMS

Topochemical reactions refer to chemical transformations that take place within a crystalline environment when subjected to external stimuli such as light, heat, or pressure.<sup>59</sup> These reactions involve specific reactive motifs, such as alkene, alkyne, azide, diacetylene, etc., arranged within the crystal with precise distances and angles. Hydrogen bonds and  $\pi$ - $\pi$  stacking are typically used to achieve the required molecular arrangement within the crystal. The

potential applications of ChB in topochemical reactions remained unexplored until recently when our research group successfully unraveled the first instances of topochemical reactions in supramolecular assemblies under ChB control, as described in the following sections.

### 5.1. [2+2] Cycloadditions

Our process to explore ChBs in solid-state reactions originated from the studies focusing on ChB bonded rectangular motifs (Cf Part 4.3.) wherein ChB acceptor molecules are ordered face-to-face at relatively short distances, as for example the ethylene moieties of bipyridylethylene (bpen, **A4**) in the co-crystal **D16**•(**A4**)<sub>2</sub> (Figure 16a). Note that the complete rectangular motif could not be isolated here but rather a trimeric motif. This system offers a possibility for photochemical [2+2] cycloaddition of the two bpen molecules. Such cycloadditions under UV irradiation are known to be possible when the C=C...C=C distance lies below 4.0-4.2 Å.<sup>60</sup> However, UV irradiation of **D16**•(**A4**)<sub>2</sub> crystals did not show any reactivity, which might find its origin in the unfavorable orientation and large distances (3.86, 4.36 Å) between ethylenic moieties of the two bpen molecules facing each other.



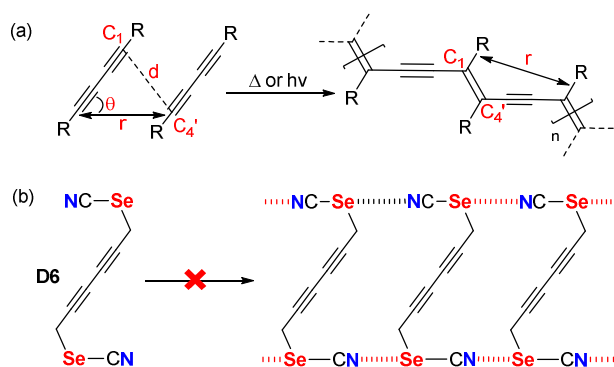
**Figure 16.** (a) Detail of the trimeric assembly between the ChB donor **D16** and bipyridylethylene **A4** in **D16**•(**A4**)<sub>2</sub> with Te...N ChB distances and angles at 3.003(12) Å/168.7(2)° and 2.910(11) Å/173.0(2)°. (b) One rectangular motif identified in the crystal structure of (**D7**)<sub>2</sub>•(**A4**)<sub>2</sub>. (c) The [2+2] cycloaddition product obtained under UV light irradiation of (**D7**)<sub>2</sub>•(**A4**)<sub>2</sub> in a single-crystal-to-single crystal transformation.

Therefore, we designed a series of aromatic *ortho*-substituted bis(selenocyanate) ChB donors **D7**, **D8** and **D9** (Scheme 2) as possible alternative linkers, which upon co-crystallization, possibly promote a similar face-to-face association of bpen (**A4**) molecules with C=C...C=C intermolecular distances under the required limit i.e., < 4.2 Å. Co-crystallization of these ChB donors, specifically **D7** and **D9**, with **A4** resulted into the formation of the anticipated rectangular motifs with C=C...C=C distances now in the favorable range 3.6–3.8 Å (Figure 16b). UV-irradiation of these crystals proceeded with [2+2] photo-chemical cycloaddition and formed desired cyclobutane in a single-crystal-to-single-crystal fashion (Figure 16c).<sup>4</sup> The centrosymmetric nature of the ChB motifs before irradiation leads to similar centrosymmetric racemic cyclobutane motifs in the crystal after irradiation.

## 5.2. Diacetylene Polymerization

Diacetylenes undergo 1,4-topochemical polymerization to form polydiacetylene (PDA), a conjugated polymer with alternating C=C and C≡C bonds (Scheme 4a). PDAs exhibit multi-photon absorption, making them suitable for nonlinear optical properties, drug delivery, and semiconductor materials.<sup>61</sup>

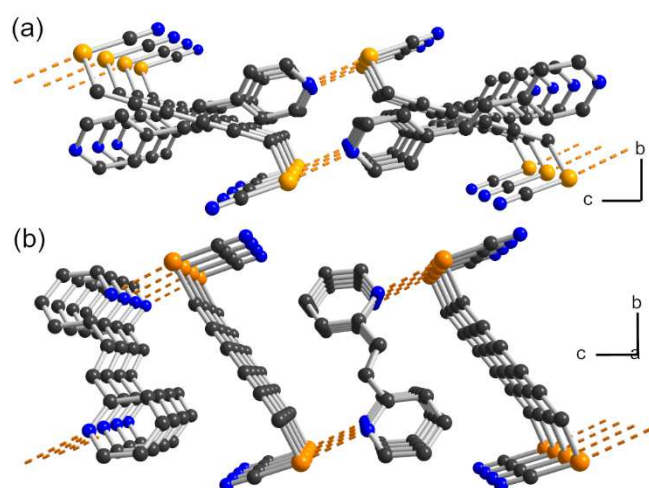
**Scheme 4. (a) Favorable Alignment of Acetylenes for 1,4-Polymerization with Values  $r = 4.9\text{-}5.0$  Å,  $\theta = 45^\circ$  and  $d = 3.5$  Å. (b) Thought-After Structural Organization of the Butadiyne **D6**.**



One supramolecular chemistry strategy to align diacetylenes into such a reactive orientation is based on co-crystal formation, with a host structure held together by strong hydrogen bonding (HB) synthons such as diamides,<sup>62</sup> interacting through secondary interactions (HB, XB)<sup>63</sup> with the diacetylene. In order to meet the structural requirements for diacetylene polymerization through ChBs, we designed the ChB donor **D6**,<sup>30</sup> anticipating that self-association ability of



selenocyanates through  $\cdots\text{NC(R)Se}\cdots\text{NC(R)Se}\cdots$  interactions<sup>27,28,31</sup> (Cf Part 2.1.) could align the diacetylenes in a reactive conformation (Scheme 4b). However, we were unsuccessful in obtaining suitable single crystals of **D6**. Therefore, we considered co-crystallizing **D6** with ChB acceptors such as **A1** and **A4** to promote the desired diacetylene arrangement. Co-crystal **D6•A4** revealed formation of chalcogen-bonded 1D chains through  $\text{Se}\cdots\text{N}$  contacts with  $\text{RR} = 0.79$  but the diacetylene molecules alternate with the ChB acceptor molecules **A4** along  $a$  (Figure 17a), preventing any possible short contacts between the butadiyne moieties. On the other hand, in co-crystal **D6•A1**, diacetylenes are stacked along  $a$  (Figure 17b) with a repeat distance  $r = 4.417 \text{ \AA}$ , a tilt angle  $\theta$  of  $53^\circ$ , and a  $\text{C1}\cdots\text{C4}'$  distance of  $3.71 \text{ \AA}$ , fully compatible for 1,4-topochemical polymerization.



**Figure 17.** (a) Detail of the structure of the **D6•A4** co-crystal showing the alternation of **D6** and **A4** molecules along the  $a$  axis with  $\text{Se}\cdots\text{N}$  ChB distance and angle at  $2.737(5) \text{ \AA}/174.4(1)^\circ$  (b) Detail of the structure of the **D6•A1** co-crystal with  $\text{Se}\cdots\text{N}$  ChB distance and angle at  $2.792(6) \text{ \AA}/172.4(2)^\circ$ , showing the segregated stacks of **D6** and **A1** molecules favoring the thermally-induced polymerization of **D6** along the  $a$  axis.

Successful thermally-induced ( $100^\circ\text{C}$ ) topochemical polymerization of **D6•A1** led to the formation of the desired PDA backbone, which was confirmed by time-dependent IR and DSC measurements.<sup>30</sup> Moreover, an increase in conductivity by 8 orders of magnitude upon iodine doping further proved the formation of the PDA polymer. Strikingly, the course of thermal polymerization is accompanied here with sublimation of the ChB acceptor molecules **A1**, providing the polymer in a pure form with full recovery of the co-former, at variance with the usual hydrogen-bonded co-crystal strategies where the coformer always remains embedded in the polymer.

## 6. SUMMARY AND PERSPECTIVES

Along these lines, we aimed at recovering with ChB the same degree of strength and predictability found with XB, by focusing on neutral, divalent Se and Te systems with two different substituents, one of them only with an EWG, to strongly unbalance the two  $\sigma$ -holes. We explored this dissymmetrization concept within three chemical families, selenocyanates R–SeCN, alkynyl derivatives R–C $\equiv$ C–(Se/Te)Me, and *o*-carborane derivatives. Such compounds were systematically engaged in co-crystals with ChB acceptors, either halide salts, or neutral bipyridines.

Interactions with halides proved very strong, while providing (i) *efficient chelating* systems, otherwise much more difficult to conceive with XB interactions, and potentially useful for anion transport, (ii) *chiral halide complexes*, both opening perspectives toward enantioselective organo-catalysis through ChB interactions.<sup>64</sup>

Co-crystals with ditopic bis(pyridinyl) derivatives **A1-A6** led to *recurrent 1D chain-like neutral* systems, with very strong ChB characterized and RR values down to 0.79. The extension to 2D or 3D chalcogen-bonded co-crystals, well known in the field of XB systems, still remains a challenge. Additionally, a systematic tuning of the ChB strength over a wide range was demonstrated by playing with the activation power of employed donor and/or acceptor molecules.

This recovered predictability allowed to stabilize *rectangular objects*, favoring the face-to-face-organization of photoreactive 1,2-bis(4-pyridyl)ethylene (dpen, **A4**) for further [2+2] photocyclization under UV irradiation in a single-crystal-to-single-crystal transformation to the corresponding cyclobutanes, while preserving the ChB interactions despite the crystal re-organization. Similarly, the solid-state organization of butadiyne **D6** in its co-crystal with 2-bpen (**A1**) allowed for the isolation of **D6•A1** where the side-by-side alignment of butadiyne molecules presents the requested geometrical features for transformation under heating to the pure polydiacetylene. Indeed, the **A1** cofomer molecules were shown to quantitatively sublime out of the material during the polymerization process. These two examples demonstrate the robustness and efficiency of ChB in materials science applications, as also illustrated in the conducting charge transfer salts based on selenomethyl substituted tetrathiafulvalene derivatives (Cf Figure 3).<sup>25,26</sup>

Finally, it should be stressed here that this dissymmetrization approach offers the advantage of being systematic and not strictly limited to ChB. It will indeed find applications with all other interactions where several  $\sigma$ -holes compete for a specific acceptor, as illustrated recently in pnictogen bonding,<sup>65</sup> or tetrel bonding.<sup>66</sup> We strongly believe that its generalization will provide many opportunities, particularly in crystal engineering, as illustrated here with ChB.

## ASSOCIATED CONTENT

### Supporting Information

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

Preparation and X-ray crystal data of **D13•A1**, **D14•A1** and **D14•A5** co-crystals.

### Accession Codes

CCDC 2302240-2302242 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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## Notes

The authors declare no competing financial interest.

## Biographies

**Arun Dhaka** received his PhD from Université de Rennes, France in 2022. He is currently a post-doctoral researcher at Politecnico di Milano, Italy. His research interests are in the field of crystal engineering and materials science with a particular focus to sigma-hole interactions, namely halogen and chalcogen bonds.

**Ie-Rang Jeon** received a PhD from the University of Bordeaux in 2012. After completing a post-doctoral position at Northwestern University, she joined the CNRS in 2017 at the Institut des Sciences Chimiques de Rennes (ISCR). Her research interest is applying synthetic organic/inorganic chemistry and crystal engineering strategies to develop multifunctional molecular materials by controlling geometric and electronic structures.

**Marc Fourmigué** received a PhD (prepared in part at H. C. Ørsted Institut in Copenhagen) from Paris XI University in 1988. He joined the CNRS in 1990, first at LPS (Orsay), before moving to IMN (Nantes) in 1995 and then to MOLTECH-Anjou (Angers) in 2002. He joined the Institut des Sciences Chimiques de Rennes (ISCR) in 2006 and is acting as director of the Institute since 2017. His research interests are in the field of electroactive organic, organometallic and coordination systems, toward crystalline molecular conductors and metals, with a focus on noncovalent interactions, crystallography and phase transitions.

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