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Activating chalcogen bonding (ChB) in alkylseleno/ alkyltelluroacetylenes toward ChB directionality control

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ABSTRACT

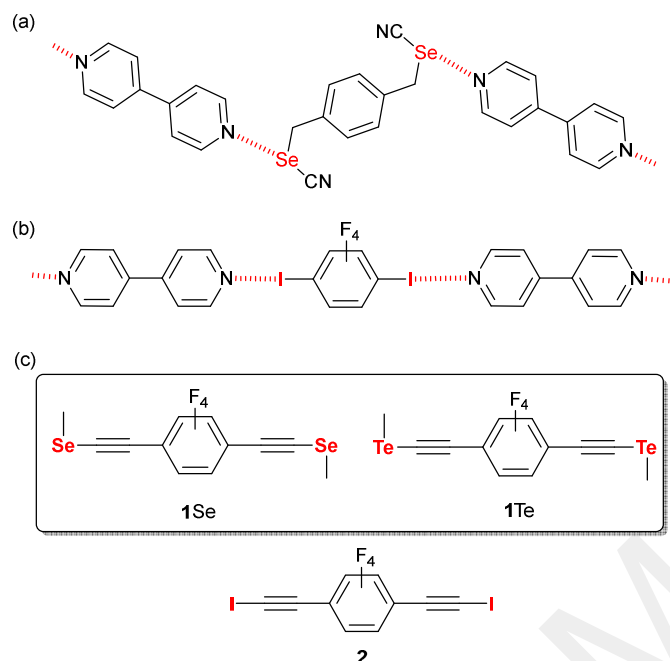
Activation of a deep electron-deficient area on chalcogen atoms (Ch = Se, Te) is demonstrated here in alkynyl chalcogen derivatives, in the prolongation of the (C \equiv)C–Ch bond. The solid-state structures of 1,4-bis(methylselenoethynyl)perfluorobenzene (**1Se**) show the formation of recurrent chalcogen-bonded (ChB) motifs. Association of **1Se** and the tellurium analog **1Te** with 4,4'-bipyridine and with the stronger Lewis base 1,4-di(4-pyridyl)piperazine gives 1:1 co-crystals with 1D extended structures linked by short and directional ChB interactions, comparable to those observed with the corresponding halogen bond (XB) donor, 1,4-bis(iodoethynyl)-perfluorobenzene. This “alkynyl” approach for chalcogen activation 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 in iodoacetylene derivatives.

Introduction

Crystal engineering strategies are rooted in our ability to manipulate intermolecular interactions with a high degree of prediction about the expected outcome of the attempted intermolecular associations.^[1] This predictability is not only a direct consequence of the strength of the interaction, but also of its directionality.^[2,3] Besides hydrogen bonding,^[4,5] the so-called sigma-hole interactions have raised in the last 20 years a very strong interest. For example, the success of halogen bonding^[6] and its applications in a wide variety of domains,^[7,8,9] is essentially based not only on its strength, but also on its strong directionality as the charge-depleted area which develops in the prolongation of a C–X bond is concentrated within a limited area.

Besides halogen bonding, chalcogen bonding also enters in this category of sigma-hole interactions.^[10] First investigated by theoretical methods,^[11,12,13] and on the basis of high-resolution diffraction studies,^[14,15] ChB has been known and identified for decades in the crystal structures of many chalcogenated derivatives,^[16,17] but its involvement in crystal engineering strategies still struggles to make a strong mark as its XB analog, due mainly to a lack of control of directionality. Indeed, at variance with halogens, the presence of two σ -bonds on the divalent chalcogen atom generates two σ -holes. Different strategies have been reported recently however, aiming at controlling in some way the ChB interactions for a specific goal. We can mention first the *association on the same molecule of strong ChB donor and acceptor sites*, as in 1,2,5-telluradiazoles,^[18] 1,2-chalcogenazole N-oxide,^[19,20] benzo-1,3-chalcogenazole,^[21] favoring the formation of infinite ribbons^[18,22] or discrete supramolecular assemblies.^[23] The use of ChB donors in organocatalysis^[24,25] or anion recognition^[26,27] processes involves the preparation of *bidentate chelating molecules bearing two activated chalcogen atoms*, able to interact with one single Lewis base, neutral or anionic, as found in molecules linking two tellurophenes,^[28] two 5-(methylchalcogeno)-1,2,3-triazole moieties,^[29] two thiophene units bearing Electron Withdrawing Groups (EWG),^[30] or two selenocyanate groups.^[31] In several examples, one of the two substituents linked to the chalcogen atom has a strong EWG character, favoring the formation of a stronger σ -hole in the prolongation of this EWG–Ch bond. This strategy to recover part of the directionality characteristic of XB has been explored with *para*-bis(selenocyanatomethyl)benzene (Scheme 1a), which co-crystallizes with 4,4'-bipyridine to form a ChB chain motif through very short and directional Se•••N \equiv C contacts.^[32] This 1D structure mimics those obtained with ditopic XB donors such as 1,4-diiodoperfluorobenzene (Scheme 1b), or diiodoacetylene. Looking for more rigid ditopic ChB donors than these selenocyanate derivatives, we considered the possibility to replace the two iodine atoms in rigid

ditopic XB donors by selenoalkyl or telluroalkyl moieties (Scheme 1c) and we specifically concentrated here on the **1Se** and **1Te** derivatives, as analogs of 1,4-bis(iodoethynyl)perfluorobenzene **2**, with the idea that an alkynyl group could activate a strong σ -hole on the chalcogen atom as it does on iodine.



Scheme 1.

Several linear oligoalkynes, α,ω -substituted with chalcogenomethyl groups, $\text{MeCh}-(\text{C}\equiv\text{C})_n-\text{ChMe}$ ($\text{Ch} = \text{Se}, \text{Te}; n = 2-4$), were described in 2002.^[33,34] Among them, one ($\text{Ch} = \text{Te}, n = 2$) was shown to organize into tubular nanostructure stabilized by $\text{Ch}\cdots\text{Ch}$ intermolecular interactions slightly below the van der Waals contact distance,^[35] but their potential to form co-crystals with Lewis bases through ChB interactions had not been addressed. To answer this question, we investigated the ability of **1Se** or **1Te** to co-crystallize with linear, ditopic Lewis bases such as the prototypical 4,4'-bipyridine. The success of this approach, as shown below, provides us with extremely efficient and directional ChB donors for the elaboration of supramolecular architectures, with a degree of strength and predictability comparable to that of halogen bonding.

The ChB donor ability of **1Se** and **1Te** has been first evaluated from the calculated values of the extrema of the electrostatic potential surfaces (ESP), the largest the positive ESP value, the more important the σ -hole at the chalcogen atom and therefore the ChB donor ability.

As shown in Fig. 1 (see calculation details in ESI), both Se and Te derivatives exhibit a notable σ -hole in the prolongation of the (C \equiv)C–Ch bond, much stronger than that in the prolongation of the other H₃C–Ch bond (Fig. S1 in ESI). This points already for a potential good directionality of ChB interactions involving these atoms. Comparison with the analogous iodo derivative **2** shows that, albeit slightly smaller (–12%), **1Te** exhibits a comparable σ -hole extremum.

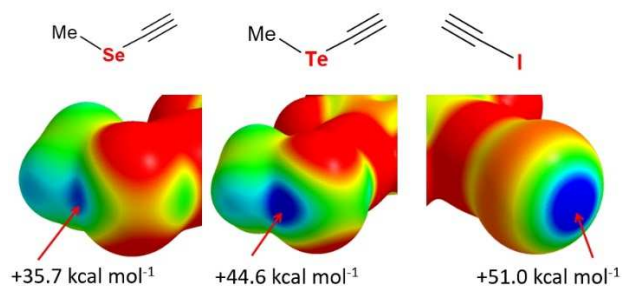
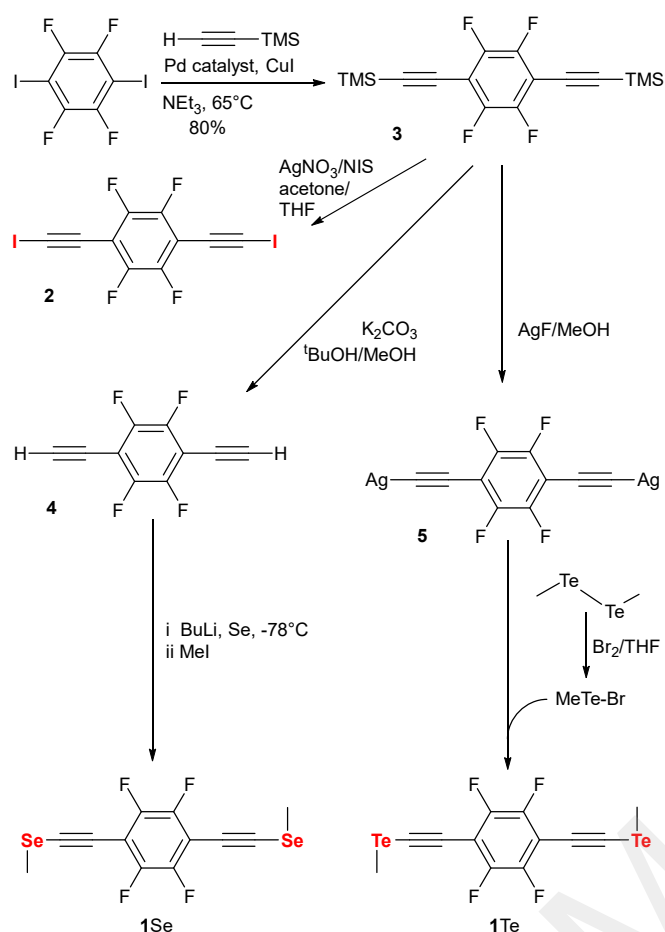


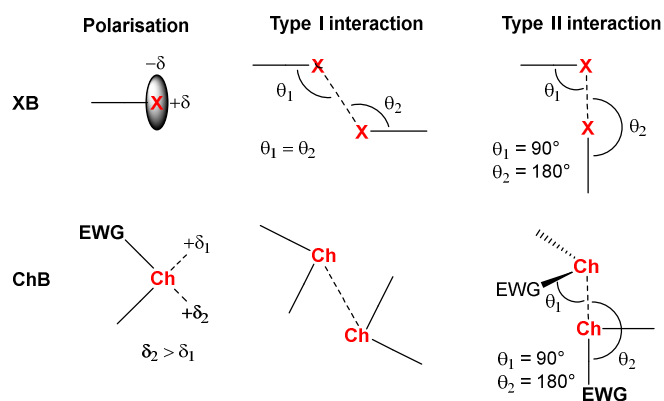
Fig. 1. Details of the ESP maps of (from left to right) **1Se**, **1Te** and **2** at optimized geometries, plotted on the 0.002 electron/bohr³ isosurface of the electronic density. The extrema values $V_{s,max}$ of the electropositive (blue) area are indicated. Potential scale ranges from 0 (red) to 37.7 (blue) kcal/mol.

The preparation of **1Se** (Scheme 2) is based on the metalation of the bis(alkynyl) derivative **4** with BuLi, followed by reaction with grey selenium and alkylation with MeI. This procedure failed in our hands with tellurium. An alternative route to **1Te** involves the reaction of the bis(alkynylsilver) derivative **5** with methyltelluroniumbromide MeTe–Br.^[29c] The diiodo derivative **2** was prepared as reported earlier from the reaction of the bis(trimethylsilylalkynyl) compound **3**, through reaction with NIS and AgNO₃.^[36]



Scheme 2. Synthetic paths to the **1Se**, **1Te** and **2**.

Compound **2** crystallizes in the monoclinic system (SG $P2_1/c$) into layers driven by π - π interactions (Fig. S2) with the shortest $\text{I}\cdots\text{I}$ contacts above 4.05 Å, excluding the presence of XB interactions. Two polymorphs of **1Se** were isolated under different crystallization conditions (see ESI). Phase A (monoclinic, SG $P2_1/c$) shows inversion-centered $\text{Se}\cdots\text{Se}$ contacts (Fig S3) at 3.59 and 3.62 Å i.e. a reduction ratio RR (defined as the actual interatomic distance over the sum of the van der Waals radii) around 0.95. They correspond to Type I $\text{Ch}\cdots\text{Ch}$ interactions, by analogy with the Type I/Type II terminology adopted for halogen \cdots halogen interactions (See Scheme 3).^[37] Phase B (tetragonal, SG $I4_1/a$) is characterized by 10 independent **1Se** molecules, including two **1Se** molecules inserted inside channels (see below) with a refined 2/3 occupancy. Molecules are organized through highly directional Type II $\text{Se}\cdots\text{Se}$ contacts (Fig. 2) with facing electrophilic \cdots nucleophilic regions to generate tetrahedral motifs, with $\text{Se}\cdots\text{Se}$ distances in a 3.63-3.66 Å range (RR = 0.96) (see also Fig. S4 and Table S2).



Scheme 3. Comparison of $X\cdots X$ and $Ch\cdots Ch$ interaction motifs. Type II interactions refer to the so-called halogen bonding (XB) or chalcogen bonding (ChB).

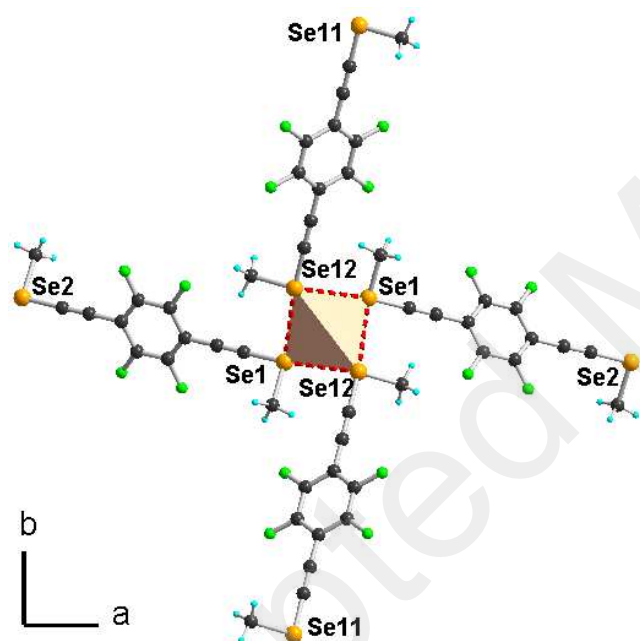


Fig. 2. One tetrahedral motif formed by directional, Type II $(C\equiv C)C-Se\cdots Se$ ChB in **1Se** (phase B) (See Table S2 and Fig. S4).

These motifs stack along the c -axis to delineate a tubular square-lattice network (Fig. 3a, Fig. S5) organized into helical chains running along c (Fig. 3b). At the center of these helical stacks, a large volume is occupied by two other molecules (in red and black in Fig. 3) interacting with each other within the channels into a double helix through Type I, slightly shorter ($RR = 0.92$) $Se\cdots Se$ interactions (Fig. 3b, Fig. S7, Table S2).

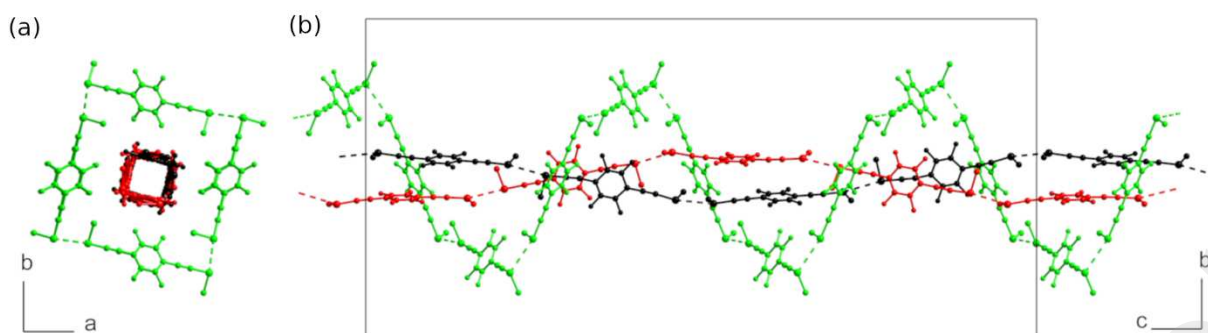


Fig. 3. Detail of the solid-state arrangement in **1Se** (Phase B) showing the helical organization of molecules (only one helix out of six is shown in green, see Fig. S7 for all helices), and two other molecules inserted inside channels (in red and black).

With these two new **1Se** and **1Te** derivatives at hand, we can now evaluate their ability to act as ChB donors in supramolecular assemblies as well-known iodoacetylene derivatives (as **2**) do with halogen bonding. As shown in Figure 5a, we found that cocrystallization of **2** with bipy leads indeed to the formation of chains with a short and directional **I**•••**N** contact ($RR = 0.79$). Using the ditopic ChB donors **1Se** and **1Te** leads to a very similar 1D motif, with the formation of **1Se**•bipy and **1Te**•bipy co-crystals which exhibit the sought-after, short and directional ChB interactions (Table 1), demonstrating the efficiency of the alkynyl substituent to activate chalcogen atoms toward ChB interactions, with a strength almost comparable to that of the iodinated analog **2**. In both co-crystals, the ChB interaction involves the σ -hole in the prolongation of the alkynyl–chalcogen bond and the reduction ratio is almost comparable between iodine (0.79) and tellurium (0.82). In other words, alkynyl-tellurium derivatives can be as efficient as prototypical alkynyl-iodine derivatives to enter into strong and directional σ -hole interactions toward Lewis bases.

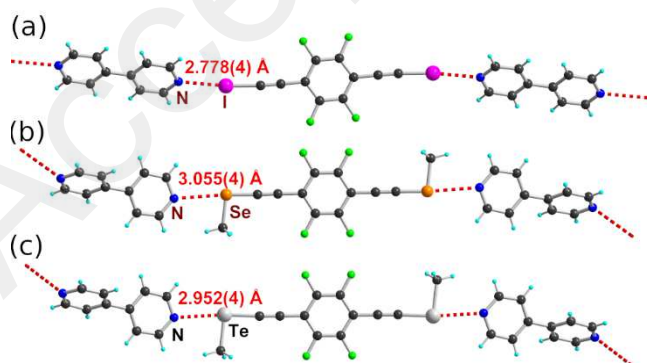
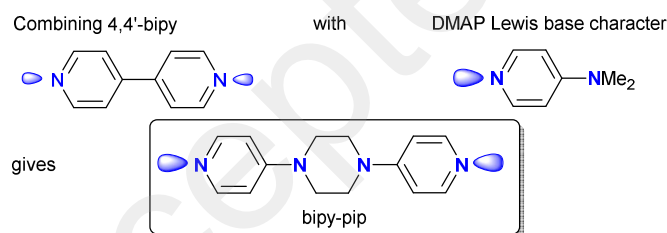


Figure 5. Details of the solid-state structures of the 1:1 co-crystals of bipy with **2** (a), **1Se** (b) and **1Te** (c) (see also Fig. S8).

Table 1. Pertinent structural characteristics of the ChB (XB) interactions in co-crystals (Ch = Se, Te; X = I).

Co-crystal	Ch/X...N dist. (Å)	RR	C–(Ch/X)...N angle (°)
2 •bipy	2.778(4)	0.79	173.5(1)
1Se •bipy	3.055(4)	0.89	176.1(1)
1Te •bipy	2.952(4)	0.82	173.9(1)
2 •bipy-pip	2.718(9)	0.77	176.9(1)
	2.700(8)	0.76	178.9(1)
1Se •bipy-pip	2.995(11)	0.87	171.6(1)
1Te •bipy-pip	2.855(4)	0.79	171.8(1)

In order to further strengthen these ChB interactions, we considered bipyridine analogs which could exhibit a stronger Lewis base character, as for example observed when one replaces pyridine with the more electro-rich 4-dimethylaminopyridine (DMAP). To reach this goal, we envisioned the piperazine derivative^[38] hereafter abbreviated as bipy-pip (Scheme 3) which combines the ditopic character of 4,4'-bipyridine with the stronger Lewis-base character of DMAP. To our surprise, this interesting molecule has never been used as XB (nor ChB) acceptor.^[39]



Scheme 3. Combining the electron donating effect of –NMe₂ with the ditopic character of bipyridine.

Its co-crystallization with **1Se** and **1Te** (and **2**) was as successful as with bipy and the three 1:1 co-crystals were isolated and structurally characterized. They all exhibit short and directional σ -hole interactions, in the prolongation of the alkynyl–chalcogen bond, notably shorter than with bipy itself (see Table 1), with RR value down to 0.79 in **1Te**•bipy-pip, and leading to the recurrent formation of 1D structures (Fig. 6).

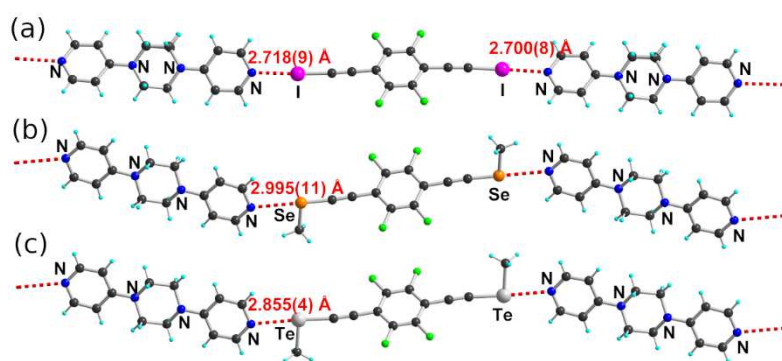


Figure 6. Details of the solid-state structures of the 1:1 co-crystals of bipy-pip with **2** (a), **1Se** (b) and **1Te** (c).

In conclusion, we have demonstrated here that an alkynyl moiety can activate a deep electron-deficient area on chalcogen atoms (Se, Te) in the prolongation of the $(C\equiv C)-Ch$ bond. The solid-state structures of **1Se** itself highlight the formation of either Type I $Ch\cdots Ch$ or type II ChB interactions, with tetrahedral Se_4 motifs leading to a helical structure, which accommodates extra **1Se** molecules within the pores. Association of **1Se** and **1Te** with ditopic Lewis bases such as bipy and bipy-pip gives 1:1 co-crystals with 1D structures linked by short and directional ChB interactions, comparable to those observed in iodoacetylene derivatives. The success of this “alkynyl” approach 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.

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Keywords: Alkynes • Chalcogens • Crystal Engineering • Lewis bases

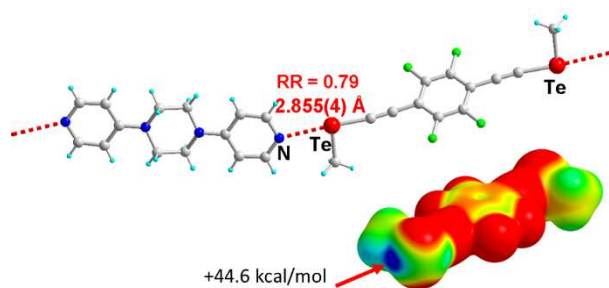
References

- [1] a) J. -M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*. VCH: Weinheim, 1995; b) J. W. Steed, J. L. Atwood, *Supramolecular Chemistry*, 2nd ed.; J. Wiley & Sons: Chichester, 2009.
- [2] a) G. R. Desiraju, G. R. *Angew. Chem. Int. Ed.* **1995**, *34*, 2311–2327; *Angew. Chem.*, **1995**, *Angew. Chem.* **1995**, *107*, 2541–2558; b) V. R. Thalladi, B. S. Goud, V. J. Hoy, F. H. Allen, J. A. K. Howard, G. R. Desiraju, *Chem. Commun.* **1996**, 401–402.
- [3] a) C. B. Aakeröy, N. R. Champness, C. Janiak, *CrystEngComm* **2010**, *12*, 22–43; b) C. B. Aakeroy, K. R. Seddon, *Chem. Soc. Rev.* **1993**, *22*, 397–407.
- [4] A. Mukherjee, S. Tothadi, G. R. Desiraju, *Acc. Chem. Res.* **2014**, *47*, 2514–2524.
- [5] T. Steiner, T. *Angew. Chem. Int. Ed.* **2002**, *41*, 48–76; *Angew. Chem.* **2002**, *114*, 50–80.
- [6] P. Scilabra, G. Terraneo, G. Resnati, *Acc. Chem. Res.* **2019**, *52*, 1313–1324.
- [7] a) G. Cavallo, P. Metrangolo, R. Milani, T. Pilati, A. Priimagi, G. Resnati, G. Terraneo, *Chem. Rev.* **2016**, *116*, 2478–2601; b) L. C. Gilday, S. W. Robinson, T. A. Barendt, M. J. Langton, B. R. Mullaney, P. D. Beer, *Chem. Rev.* **2015**, *115*, 7118–7195.
- [8] P. Metrangolo, F. Meyer, T. Pilati, G. Resnati, G. Terraneo, *Angew. Chem. Int. Ed.* **2008**, *47*, 6114 – 6127; *Angew. Chem. Int. Ed.* **2008**, *120*, 6206–6220; b) A. Priimagi, G. Cavallo, P. Metrangolo, G. Resnati, *Acc. Chem. Res.* **2013**, *46*, 2686–2695.
- [9] C. B. Aakeroy, N. R. Champness, C. Janiak, *CrystEngComm* **2010**, *12*, 22–43.
- [10] a) C. B. Aakeroy, D. L. Bryce, G. R. Desiraju, A. Frontera, A. C. Legon, F. Nicotra, K. Rissanen, S. Scheiner, G. Terraneo, P. Metrangolo, G. Resnati, *Pure Appl. Chem.* **2019**, *91*, 1889–1892; b) L. Vogel, P. Wonner, S. M. Huber. *Angew. Chem. Int. Ed.* **2018**, *57*, 1880–1891; *Angew. Chem.* **2018**, *131*, 1896–1907; c) K. T. Mahmudov, M. N. Kopylovich, M. F. C. Guedes da Silva, A. J. L. Pombeiro, *Dalton Trans.* **2017**, *46*, 10121–10138.
- [11] S. Scheiner, *Chem. Eur. J.* **2016**, *22*, 18850–18858 and references therein.
- [12] P. Politzer, J. S. Murray, *Crystals* **2017**, *7*, 212.
- [13] a) C. Bleiholder, D. B. Werz, H. Köppel, R. Gleiter, *J. Am. Chem. Soc.* **2006**, *128*, 2666–2674; b) C. Bleiholder, R. Gleiter, D. B. Werz, H. Köppel, *Chem. Rev.* **2018**, *118*, 2010–2041.
- [14] a) M. Pyziak, J. Pyziak, M. Hoffmann, M. Kubicki, *Cryst. Growth Des.* **2015**, *15*, 5223–5232; b) R. Shukla, D. Chopra, *Cryst. Growth Des.* **2016**, *16*, 6734–6742; c) M.

- Brezgunova, J. Lieffrig, E. Aubert, S. Dahaoui, P. Fertey, S. Lebègue, J. Angyan, M. Fourmigué, E. Espinosa, *Cryst. Growth Design* **2013**, *13*, 3283–3289.
- [15] S. P. Thomas, S. P. K. P. Veccham, L. J. Farrugia, T. N. Guru Row, *Cryst. Growth Des.* **2015**, *15*, 2110–2118.
- [16] P. Scilabra, G.; Terraneo, G.; Resnati, *Acc. Chem. Res.* **2019**, *52*, 1313–1324.
- [17] M. Fourmigué, A. Dhaka, *Coord. Chem. Rev.* **2020**, *403*, 213084
- [18] a) A. F. Cozzolino, J. F. Britten, I. Vargas-Baca, *Cryst. Growth Des.* **2006**, *6*, 181–186; b) A. F. Cozzolino, I. Vargas-Baca, S. Mansour, A. H. Mahmoudkhani, *J. Am. Chem. Soc.* **2005**, *127*, 3184–3190; c) G. E. Garrett, G. L. Gibson, R. N. Straus, D. S. Seferos, M. S. Taylor, *J. Am. Chem. Soc.* **2015**, *137*, 4126–4133.
- [19] P.C. Ho, P. Szydłowski, J. Sinclair, P.J.W. Elder, J. Kubel, C. Gendy, L.M. Lee, H. Jenkins, J.F. Britten, D.R. Morim, I. Vargas-Baca, *Nat. Commun.* **2016**, *7*, 11299.
- [20] P.C. Ho, J. Rafique, J. Lee, L.M. Lee, H.A. Jenkins, J.F. Britten, A.L. Braga, I. Vargas-Baca, *Dalton Trans.* **2017**, *46*, 6570–6579.
- [21] A. Kremer, A. Fermi, N. Biot, J. Wouters, D. Bonifazi, *Chem. Eur. J.* **2016**, *22*, 5665–5675.
- [22] A.F. Cozzolino, Q. Yang, I. Vargas-Baca, *Cryst. Growth Des.* **2010**, *10*, 4959–4964.
- [23] L.-J. Riwar, N. Trapp, K. Root, R. Zenobi, F. Diederich, *Angew. Chem. Int. Ed.* **2018**, *57*, 17259–17264; *Angew. Chem.* **2018**, *130*, 17506–17512.
- [24] a) P. Wonner, L. Vogel, M. Düser, L. Gomes, F. Kniep, B. Mallick, D.B. Werz, S. M. Huber, *Angew. Chem. Int. Ed.* **2017**, *56*, 12009–12011; *Angew. Chem.* **2017**, *129*, 12172–12176 ; b) P. Wonner, L. Vogel, F. Kniep, S. M. Huber, *Chem. Eur. J.* **2017**, *23*, 16972–16975; c) P. Wonner, A. Dreger, L. Vogel, E. Engelage, S.M. Huber, *Angew. Chem. Int. Ed.* **2019**, *58*, 16923–16927; *Angew. Chem.* **2019**, *131*, 17079–17083; d) P. Wonner, T. Steinke, L. Vogel, S.M. Huber, *Chem. Eur. J.* **2020**, *26*, 1258–1262.
- [25] S. Benz, A.I. Poblador-Bahamonde, N. Low-Ders, S. Matile, *Angew. Chem. Int. Ed.* **2018**, *57*, 5408–5412; *Angew. Chem.* **2018**, *130*, 5506–5510.
- [26] M. S. Taylor, *Coord. Chem. Rev.* **2020**, *413*, 213270.
- [27] N. A. Semenov, D. E. Gorbunov, M. V. Shakhova, G. E. Salnikov, I. Y. Bagryanskaya, V. V. Korolev, J. Beckmann, N. P. Gritsan, A. V. Zibarev, *Chem. Eur. J.* **2018**, *24*, 12983 – 12991
- [28] G. E. Garrett, E. I. Carrera, D. S. Seferos, M. S. Taylor, *Chem. Commun.* **2016**, *52*, 9881–9884.

- [29] a) J. Y. C. Lim, I. Marques, A. L. Thompson, K. E. Christensen, V. Félix, P. D. Beer, *J. Am. Chem. Soc.* **2017**, *139*, 3122–3133; b) J. Y. C. Lim, J. Y. Liew, P. D. Beer, *Chem. Eur. J.* **2018**, *24*, 14560–14566; c) A. Borissov, I. Marques, J. Y. C. Lim, V. Félix, M. D. Smith, P. D. Beer, *J. Am. Chem. Soc.* **2019**, *141*, 4119–4129; d) J. Y. C. Lim, I. Marques, V. Félix, P. D. Beer, *Chem. Commun.* **2018**, *54*, 10851–10854.
- [30] a) S. Benz, M. Macchione, Q. Verolet, J. Mareda, N. Sakai, S. Matile, *J. Am. Chem. Soc.* **2016**, *138*, 9093–9096; b) K. Strakova, L. Assies, A. Goujon, F. Piazzolla, H.V. Humeniuk, S. Matile, *Chem. Rev.* **2019**, *119*, 10977–11005; c) L. M. Lee, M. Tsemperouli, A. I. Poblador-Bahamonde, S. Benz, N. Sakai, K. Sugihara, S. Matile, *J. Am. Chem. Soc.* **2019**, *141*, 810–814.
- [31] A. M. S. Riel, H.-T. Huynh, O. Jeannin, O. Berryman, M. Fourmigué, *Cryst. Growth Des.* **2019**, *19*, 1418–1425
- [32] H.-T. Huynh, O. Jeannin, M. Fourmigué, *Chem. Commun.* **2017**, *53*, 8467–8469
- [33] a) D. B. Werz, R. Gleiter, F. Rominger, *J. Am. Chem. Soc.* **2002**, *124*, 10638–10639; b) D. B. Werz, R. Gleiter, *J. Org. Chem.* **2003**, *68*, 9400–9405; c) D. B. Werz, R. Gleiter, F. Rominger, *Organometallics* **2003**, *22*, 843–849.
- [34] R. Gleiter, G. Haberhauer, D.B. Werz, F. Rominger, C. Bleiholder, *Chem. Rev.* **2018**, *118*, 2010–2041.
- [35] A. Bondi, *J. Phys. Chem.* **1964**, *68*, 441–451.
- [36] H. M. Yamamoto, R. Maeda, J.-I. Yamaura, R. Kato, *J. Mater. Chem.* **2001**, *11*, 1034–1041.
- [37] G. R. Desiraju, R. Parthasarathy, *J. Am. Chem. Soc.* **1989**, *111*, 8725–8726.
- [38] F. Louerat, P. C. Gros, Y. Fort, *Synlett* **2006**, 1379–1383.
- [39] Only one reported example of hydrogen-bonded structure with carboxylic acids: L. M. Henling, R. E. Marsh, *Acta Cryst.* **2014**, *C70*, 834–836.

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Chalcogen bond activation by alkynyl substitution is realized in bis(selenomethyl-alkynyl) and bis(telluromethyl-alkynyl) derivatives, as evidenced in co-crystals with ditopic Lewis bases such as 4,4'-bipyridine and 1,4-di(pyridin-4-yl)piperazine, with Te...N interactions as short as I...N halogen bonds with analogous iodo-alkynyl derivatives.