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COMMUNICATION

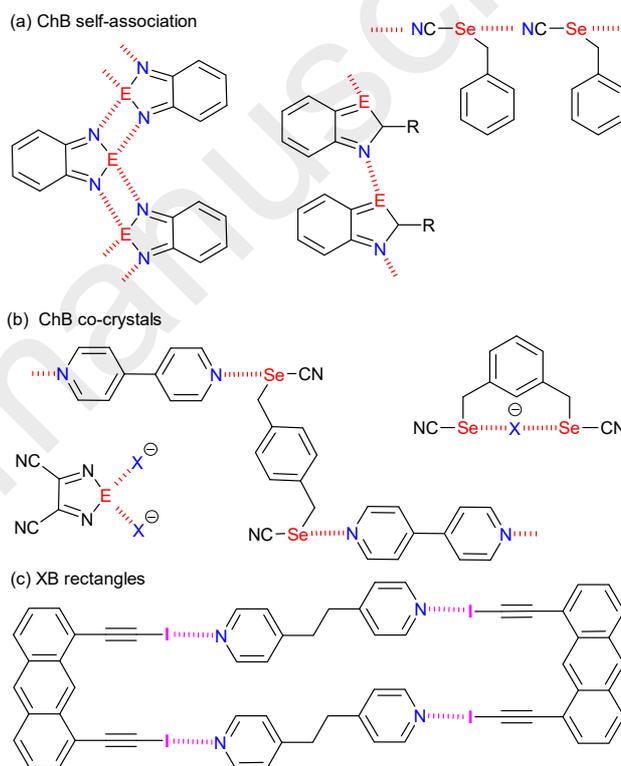
Supramolecular rectangles through directional chalcogen bonding†

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Supramolecular rectangles are built from the 2+2 chalcogen bonding-based (ChB) association of 1,8-bis(telluromethylethynyl)-anthracene (BTMEA) and ditopic Lewis bases such as 4,4'-bipyridyl-ethane and analogs, demonstrating the strength and directionality of the ChB interaction in such alkynyl-telluroalkyl derivatives.

The field of crystal engineering, originally evolving in the frame of hydrogen bonding,¹ concerns the control of solid-state molecular organization with the understanding of intermolecular interactions to eventually achieve desired functional outcome.² Coordination complexes also offer a simple way to build desired solid-state structures through metal coordination with their predictable geometrical fate³ but over the time this focus rapidly shifted toward supramolecular synthesis^{4,5} involving non-covalent interactions. In this context, halogen bonding (XB)^{6,7} has emerged in the category of sigma-hole interactions as an effective tool in supramolecular synthesis of 1D, 2D or 3D solid-state structures.^{8–10} Similarly, chalcogen bonding (ChB) has been defined as an attractive interaction between an electron depleted area of a chalcogen atom and a Lewis-base.^{11–14} At variance with monovalent halogens, a divalent chalcogen atom bears two sigma-holes roughly in the prolongation of each covalent bond that strongly limits the predictability of chalcogen bonding interactions. In this context, use of ChB donors toward supramolecular architectures still remains very limited. Earlier examples include alkyltelluroalkynyl derivatives reported by Gleiter, with in one instance a supramolecular nanotube supported by Te•••Te interactions.^{15–17} Some notable examples of amphoteric ChB donors/acceptors include S(CN)₂,¹⁸ Se(CN)₂,¹⁹ 1,2,5-chalcogenadiazoles,^{20,21} benzo-1,3-chalcogenazoles²² or benzo-1,2-chalcogenazole N-oxides^{23,24} that self-associate into discrete or extended solid-state structures through ChB (Scheme 1a). More rarely, chalcogen bond donors have been employed into cocrystals



Scheme 1 Examples of ChB or XB supramolecular structures. E and X stand for Se/Te and halide anion respectively.

with neutral Lewis bases or with halide anions (Scheme 1b).^{25,26}

The design and construction of *discrete* supramolecular architectures through intermolecular interactions require installation of highly directional and strongly interacting sites at specific positions on both donor and acceptor molecules. For instance, XB triangular motifs, formerly observed in the hexachlorobenzene and hexabromobenzene crystal structures where halogen atoms bear at the time anchoring electrophilic and nucleophilic sites leading to 180°/120° geometries,²⁷ were then engineered by directing self-complementary donor and acceptor sites at an angle of 60° along the sides of an equilateral triangle using triiodoimidazolium²⁸ or iodoethynylpyridine²⁹ XB donors. Similarly,

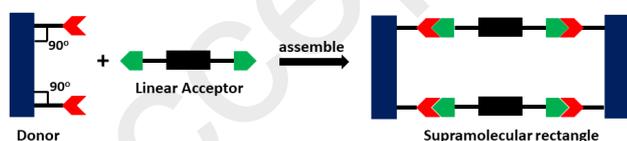
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based on ChB, benzo-2,1,3-chalcogenodiazole-based cavitands were shown to form a homo-molecular dimeric capsule through multiple $\text{Ch}\cdots\text{N}$ interactions.³⁰ The targeted formation of discrete, but *heteromolecular* halogen-bonded assemblies is illustrated for example by rectangular motifs formed upon co-crystallization of complementary ditopic XB donors such as 1,8-diidoethynylantracene and ditopic XB acceptors such as 1,2-bis(4-pyridyl)ethane (bpe) (Scheme 1c).³¹ The reverse situation is also reported, from a U-shaped anthracene-based ditopic Lewis base with linear ditopic halogen bond donors.³² To the best of our knowledge, chalcogen-bonded, discrete, *heteromolecular* supramolecular architectures have not been reported so far and still remain challenging. The only examples of such heteromolecular species involve solvates of 2,1,3-telluradiazole dimers with DMSO or pyridine as ChB acceptors.^{33,34} This fact can be attributed to the weaker linearity/predictability of chalcogen bonding compared to that of halogen bonding and more difficult integration of ChB donor sites in a molecule with a controlled orientation.

One strategy to circumvent the predictability of ChB in crystal engineering relies on a disymmetrisation of the chalcogen atom, with only one strongly electron-withdrawing substituent. For example, organic selenocyanates such as bis(selenocyanatomethyl)-benzene derivatives were shown to form chalcogen bonded 1D chains with 4,4'-bipyridine through short and directional $\text{Se}\cdots\text{N}_{\text{py}}$ contacts (Scheme 1b).^{35,36} Also, activation of a strong sigma-hole on chalcogen atom has been recently demonstrated in alkylseleno/alkyltelluroacetylenes as rigid ditopic ChB donors and a remarkable control of directionality to engineer 1D chalcogen-bonded chain motifs engaging ditopic Lewis-bases.³⁷ We envisioned this alkynyl approach to be a potential route to design and engineer supramolecular heteromolecular macrocycles under ChB control. Inspired from the work on 1,8-diidoethynylantracene XB donor (Scheme 1c),³¹ we considered replacing both iodine atoms with telluroalkyl moieties, anticipating that the strong activation of a sigma-hole on the tellurium atom in the prolongation of the $(\text{C}\equiv\text{C})\text{-Te}$ bond could similarly favor supramolecular assembly into discrete rectangles upon co-crystallization with a ditopic Lewis-base, as shown in Scheme 2.



Scheme 2 Design principle and structural requirements in donor and acceptor molecules to build a supramolecular rectangle.

Herein, we report the synthesis of 1,8-bis(telluromethylethynyl)-anthracene (**BTMEA**), a new U-shaped ditopic ChB donor and its co-crystallization with various linear ditopic Lewis bases, resulting into the sought-after heteromolecular rectangles. Calculations of electrostatic potential surface of **BTMEA** (Fig. 1) revealed the presence of a deep electron depletion area in the prolongation of the $(\text{C}\equiv\text{C})\text{-Te}$ bonds with V_{max} values of $+38.8 \text{ kcal mol}^{-1}$, comparable to those found in similar iodoalkynyl derivatives.³⁷ This feature already

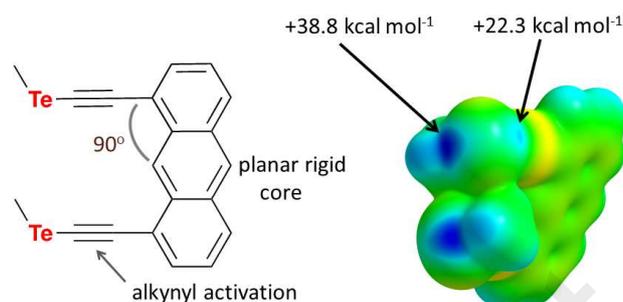
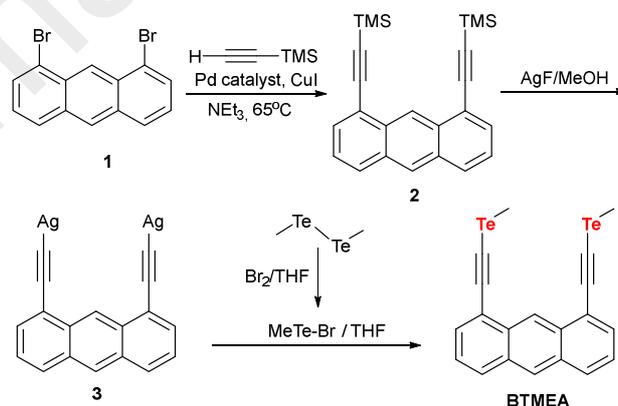


Fig. 1 Electrostatic potential map (plotted on the 0.002 e/bohr^3 isosurface of the electronic density) of **BTMEA** in optimized geometry showing the two σ -holes in the prolongation of the $(\text{C}\equiv\text{C})\text{-Te}$ and Me-Te bonds.

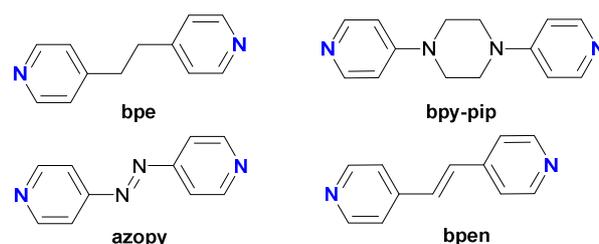
establishes the ability and the linear disposition of the σ -hole in the chalcogen bond donor of **BTMEA**, as anticipated (Scheme 2). Note also the second, weaker σ -hole along the Me-Te bond which will contribute to the overall structural organization (See ESI for details).

Synthesis of **BTMEA** ChB donor starts with 1,8-dibromoanthracene **1** to first obtain compound **2** through Sonogashira coupling followed by reaction of the corresponding silver salt **3** (*caution, alkynyl silver salts might be explosive*) with methyltelluronium bromide MeTe-Br (Scheme 3). 1,8-Dibromoanthracene **1** was prepared following reported procedures from 1,8-dichloroanthraquinone (see ESI).



Scheme 3 Synthetic route to **BTMEA**.

The formation of heteromolecular supramolecular boxes was investigated through co-crystallization experiments of this new U-shaped ChB donor and several linear ditopic Lewis-bases (Scheme 4).



Scheme 4 Ditopic linear ChB acceptors employed in this study.

Co-crystallization with **bpe** resulted indeed into the formation of the predicted rectangular motif, held together by four short Te•••N ChB contacts in the range 2.85–2.94 Å, which correspond to a reduction ratio relative to the sum of van der Waals radii [$2.06(\text{Te}) + 1.55(\text{N}) = 3.61$ Å] down to 0.79 (Fig. 2). The ChB directionality in this motif is manifested by the presence of highly linear Te•••N contacts with (C≡)C–Te•••N angles in the range 172–175° (Fig. 2). These structural features demonstrate thus the excellent efficiency of the alkynyl substitution for the elaboration of ChB supramolecular architectures.

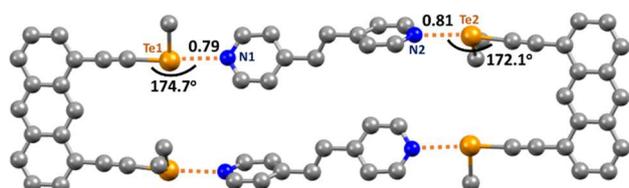


Fig. 2 Detail of the rectangular motif in the 2:2 co-crystal **BTMEA•bpe**. Hydrogens are omitted for clarity. The methyl group on Te2 is disordered over two positions with 65:35

To further prove the efficiency of this approach, we considered employing the bipyridylpiperazine derivative (**bpy-pip**) which is slightly longer and has the advantage of a stronger Lewis-base character, comparable to that of dimethylaminopyridine derivatives.³⁷ In this case, we similarly observed the formation of 2:2 complex with two independent donor and acceptor molecules in the asymmetric unit, leading to two crystallographically independent rectangles with equally short Te•••N contacts (Fig. 3).

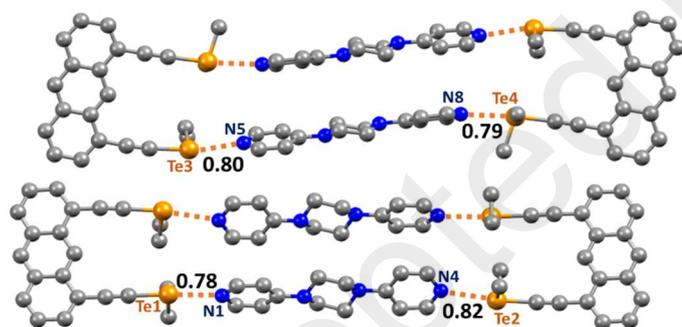


Fig. 3 The two rectangular motifs found in the 2:2 co-crystal **BTMEA•bpy-pip**. Hydrogens are omitted for clarity. The methyl groups are disordered over two positions with 45:55 distribution on Te1, 49:51 on Te2, 53:47 on Te3, and 23:77 on Te4.

An analogous ditopic Lewis base, namely 4,4'-azopyridine (**azopy**), a chemo- and photo-responsive candidate,³⁶ has been extensively used in metal organic frameworks, supramolecular chemistry, and crystal engineering with XB,^{37,38} but to our surprise this molecule has never been used as ChB acceptor. This further motivated us to use **azopy** in our co-crystallization experiments and consequently we observed again a 2:2 complex with **BTMEA** (Fig. 4), isostructural with the **BTMEA•bpe** co-crystal, and characterized by slightly weaker Te•••N ChB contacts, in accordance with the decreased Lewis base character of **azopy**. Note that the analogous

1,8-diiodoethynylanthracene XB donor (Scheme 1c) does not form a rectangular motif with **azopy** but instead favours a 1:2 (donor:acceptor) complex giving rise to a trimeric structure.³¹

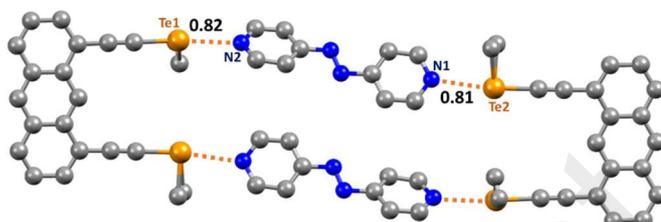


Fig. 4 X-ray crystal structure of 2:2 co-crystal between **BTMEA** and **azopy**. Hydrogens are omitted for clarity. The methyl groups on tellurium atoms are disordered over two positions with 27:73 distribution on Te1, 65:35 on Te2.

Actually, a similar 1:2 trimeric structure was also isolated in our co-crystallization experiments between **BMTEA** and the closely related **bpen** Lewis base (Fig. 5). Our attempts to favour the rectangle formation by working with a default of **bpen** was unsuccessful. Such **bpen** derivatives, when organized into a face-to-face arrangement at relatively short distances (< 4.2 Å) are prone to exhibit a [2+2] cycloaddition under UV irradiation.⁴¹ Templates acting as hydrogen bond⁴² or halogen⁴³ bond donors have been reported to organize **bpen** molecules in this expected face-to-face organization. The templating effect of the **BTMEA** molecule, even if restricted here to the open box, might also favour such a topochemical reaction. Accordingly, we irradiated our crystals within a UV reactor equipped with a Hg lamp (254 nm) but did not observe any change. This behaviour might find its origin either in the somehow large distances between the ethylenic moieties of the **bpen** molecules (3.862 and 4.363 Å) in the (**BTMEA**)(**bpen**)₂ co-crystal, or the light absorption properties of the crystals.

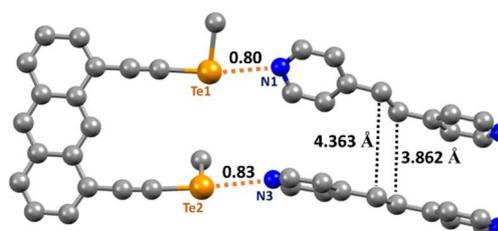


Fig. 5 X-ray crystal structure of 1:2 co-crystal between **BTMEA** and **bpen**. Hydrogens are omitted for clarity.

The four ChB structures reported here also offer the opportunity to evaluate the correlation between the Te•••N distance and the Lewis-base character of the ChB acceptors. The latter has been evaluated from the extremum value $V_{s,\min}$ of the ESP on the nitrogen atom of the four bipyridine derivatives (see Figs S1–S4 in ESI). As shown in Table 1, the ranking of V_{\min} magnitudes parallels that of the shortest Te•••N distance (in bold in Table 1) observed for each acceptor, indicating that stronger electrostatic interactions correspond indeed to the most electron-rich pyridines along the series **bpy-pip** > **bpe** > **bpen** > **azopy**.

Table 1 Evolution of Te•••N distances with $V_{s,\min}$ on the N atom.

| Compound | $V_{s,\min}$ (kcal/mol) | Te•••N (Å) | $\langle \text{Te}•••\text{N} \rangle$ (Å) |
|----------|----------------------------|---------------------------------------|---|
| bpy-pip | -45.61 | 2.824 , 2.885, 2.914, 2.976 | 2.900 |
| bpe | -41.92 | 2.854 , 2.943 | 2.899 |
| bpen | -40.90 | 2.910 , 3.003 | 2.957 |
| azopy | -38.34 | 2.927 , 2.961 | 2.944 |

In conclusion, we have demonstrated here that the combination of tellurium activation through alkynyl substitution, with a proper orientation of the two alkynyltelluromethyl moieties on the anthracene core, provides an efficient template for the successful construction of robust molecular rectangles, stabilized by very short and highly linear (C≡)C–Te•••N chalcogen bonding interactions. These results open perspectives toward the elaboration of higher complexity polygons through a control of the relative orientation and number of the telluroalkynyl linkers. Also, the possibility for three-component structures involving a third molecular entity stabilized within such a cage is also a future attractive target, made possible by the robustness of these rectangular motifs.

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