

Activating chalcogen bonding in alkylseleno/alkyltelluro acetylenes: Helical arrangements and crystal engineering strategies

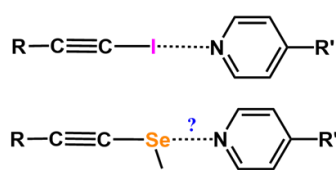
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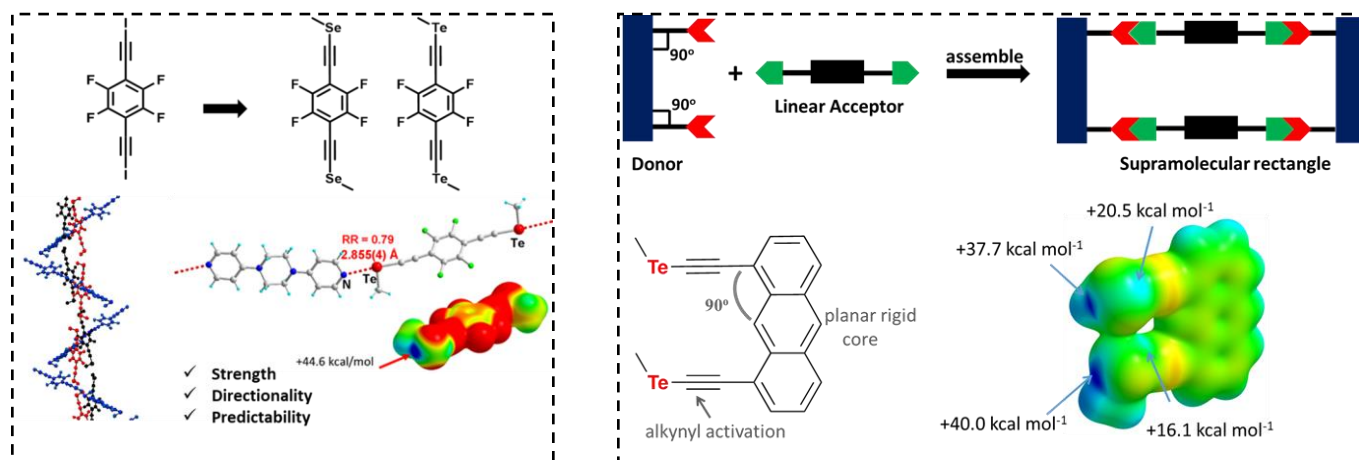
In the category of sigma-hole interaction, halogen bonds (XBs) have been extensively exploited in the field of supramolecular chemistry and crystal engineering owing to the great strength of the interaction, tunability, strong directionality and most importantly predictability.^[1] A sister non-covalent interaction, chalcogen bonding (ChB),^[2] is an interaction between the electropositive surface of a chalcogen atom acting as chalcogen bond donor and a Lewis-base acting as chalcogen bond acceptor.^[1-2] Chalcogen bonds, despite being known for decades, still struggle to make a mark in crystal engineering, owing mainly to the lack of predictability and also underdeveloped synthetic chemistry of chalcogens. The figure 1 demonstrates activation of a strong sigma-hole on iodine through an alkynyl substitution which helps this XB donor to interact efficiently with a Lewis-base. Looking for such analogous rigid and directional ChB donors, we considered the possibility of replacing the iodine with alkylseleno/alkyltelluro moiety by asking ourselves the questions if an alkynyl substitution can similarly generate a sigma-hole on Se/Te and eventually help this ChB donor to interact with a Lewis-base (Fig 1).



(Figure. 1)

Herein, we describe the synthesis and solid-state assembly of 1,4-bis(methylseleno/telluroethynyl) perfluorobenzene derivatives acting as directional chalcogen bond donors in crystal engineering. Both type-I and type-II ChB•••Ch contacts in this series of derivatives, allow for a unique helical arrangement in the solid-state assembly of donor molecule alone. Co-crystallization with various ditopic Lewis-bases fabricate chain motifs with short chalcogen bonds, with a degree of strength, directionality and predictability, quite comparable to that of halogen bonds with the analogous iodo derivatives (fig. left). We further demonstrated utility of this alkynyl approach by first designing a new U-shaped ChB donor which upon co-crystallization with linear di-topic acceptors yield

discrete supramolecular rectangular motifs held together by very short Te•••N contacts (fig. right). In summary, we provide crystal-engineering community with an efficient tool that can potentially be used to engineer 2D/3D chalcogen bonded architectures and also synthesis of multi-component crystals is an interesting future target.



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[2] a). Aakeroy, C. B., Bryce, D. L., Desiraju, G. R., Frontera, A., Legon, A. C., Nicotra, F., Rissanen, K., Scheiner, S., Terraneo, G., Metrangolo, P., Resnati, G. Definition of the chalcogen bond (IUPAC Recommendation 2019). (2019). *Pure Appl. Chem.*, **91**, 1889-1892. b). Vogel, L., Wonner, P., Huber, S. M. (2019). *Angew. Chem. Int. Ed.*, **58**, 1880-1891.

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