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Carborane-based heteromolecular extended networks driven by directional C–Te···N chalcogen bonding interactions†

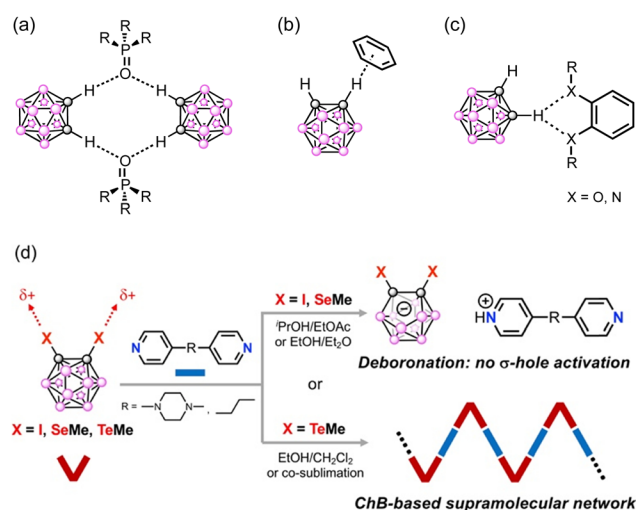
Maxime Beau,^a Olivier Jeannin,^a Marc Fourmigué,^a Emmanuel Aubert,^b Enrique Espinosa,^b Sunhee Lee,^c Won-Sik Han^c and le-Rang Jeon^c*

We demonstrate that *o*-closo-(TeMe)₂carborane directs, in the presence of linear ditopic neutral Lewis bases, the formation of co-crystals with 1D extended supramolecular networks. Specifically, the network formation is systematically stabilized by short and quasi-linear C–Te···N chalcogen-bonding (ChB) interactions. In sum, we report efficient carborane-based tectons to rationally design high-dimensional neutral heteromolecular networks.

Icosahedral carboranes (dicarba-*closo*-dodecaboranes) are well-known for their rich boron content, versatile chemistry, aromaticity, and chemical and thermal stability.^{1–3} Owing to such intriguing properties, these molecules have been considered as an ideal building block in the field of medicinal chemistry and material science, with their uses in applications such as boron neutron capture therapy,⁴ biomedicine,⁵ molecular motors,⁶ gas sorption,⁷ and luminescent devices.⁸ While these materials are often conceived exploiting synthetic organic chemistry and coordination chemistry, the crystal engineering approach to build a supramolecular extended architecture has yet to be explored, regarding the proven ability of crystal engineering in materials science to finely tune the properties and even to engender new functionalities.⁹

Carboranes feature acidic protons on carbon atoms, acting as hydrogen bond (HB) donors as proven by structural investigations of the molecule itself or of their solvated phases.¹⁰ It is also proven that periodination of the carborane increases the

acidity of the CH protons, which then act as a stronger hydrogen bond donor.¹¹ Despite these features, their employment for crystal engineering has been largely limited to discrete assemblies. The first reported examples are 1:1 co-crystals of *o*-, *m*-, and *p*-carboranes with hexamethylphosphoramide (Scheme 1a), showing varied structures in the solid state owing to the distinctive arrangement of CH sites.¹² Later, *o*-carboranes were also investigated for host-guest systems with aza crown ethers as a flexible host molecule¹³ or with cavitand molecules, such as cyclotrimeratrylene¹⁴ and calixarenes.¹⁵ In the latter, the guest inclusion was stabilized mainly through the C–H···π hydrogen bonding (HB) interaction (Scheme 1b).¹⁶ In some cases, the CH proton of carborane is engaged in bifurcated C–H···O or C–H···N HB interactions with a chelating 1,2-dimethoxybenzene moiety or 1,10-phenanthroline (Scheme 1c).¹⁷ Of the small number of reported examples, the co-crystal of the *o*-carborane moiety is essentially limited to the discrete supramolecular assemblies, with



Scheme 1 Examples of hydrogen bonding interactions involving *o*-carborane (a)–(c) and chalcogen bonding (ChB)-based crystal engineering involving *o*-carborane (d, this work).

^a Univ Rennes, CNRS, ISCR (Institut des Sciences Chimiques de Rennes), Campus de Beaulieu, Rennes 35000, France

E-mail: marc.fourmigue@univ-rennes.fr, ie-rang.jeon@univ-rennes.fr

^b CRM2, Université de Lorraine, CNRS, Nancy, F-54500, France

^c Department of Chemistry, Seoul Women's University, Seoul 01797, Republic of Korea

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only one exception of an extended network mediated by bifurcated hydrogen bonds, whose final structure is almost impossible to predict in advance.^{16c} This fact might be attributed to the weaker directionality and predictability of the CH proton of the carborane as well as the inadequate geometrical shape of the acceptor.

In targeting carborane-based supramolecular networks, the choice of carborane-based tecton is crucial to provide more than one directional interaction with a rigid multidentate acceptor molecule. In this context, the incorporation of more robust and directional supramolecular interactions would be ideal. Recently, halogen bonding (XB)¹⁸ and chalcogen bonding (ChB)^{19,20} interactions have emerged as reliable and effective supramolecular interactions in the field of crystal engineering. In contrast to directional XB,²¹ the use of ChB in crystal engineering is challenging due to the weaker directionality related to the divalent character of a chalcogen atom. Nevertheless, design strategies of using one electron withdrawing substituent to lift the degeneracy of two σ -holes on a chalcogen atom have been proven successful to recover predictability as in XB.²²

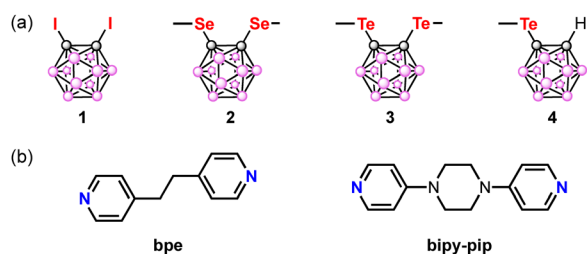
Along this line, we have recently designed *o*-carboranes involving an iodo- or a chalcogenomethyl substituent on each skeletal carbon vertice, *o-closo*-X₂C₂B₁₀H₁₀ (X = I (1), SeMe (2), and TeMe (3); Scheme 2a), and have shown their efficient XB and ChB interactions with halide anions.²³ The electrostatic potential surface (ESP) calculation showed a highly activated σ -hole in the prolongation of the C_{carborane}-X bond, owing to the strong electron withdrawing effect by the carborane unit. However, while the negative charge of a halide leads to strong XB or ChB interactions, their spherical shape hinders any predictability for the outcome of the co-crystal structures. By introducing a linear ditopic Lewis base, one can therefore expect two highly directional σ -holes diverging from the carborane unit to allow the formation of a controlled supramolecular 1D zig-zag chain network (Scheme 1d). Herein, we investigate the ability of *o-closo*-X₂C₂B₁₀H₁₀, 1-3,²³ to act as XB and ChB donors in heteromolecular network assemblies through co-crystallization with such linear, neutral ditopic Lewis bases, 1,2-di(4-pyridyl)ethane and 1,4-di(4-pyridyl)piperazine (bpe and bipy-pip, respectively, Scheme 2b).

Slow evaporation of ¹PrOH/EtOAc solution containing an equimolar amount of 1 and bpe provided colourless prism-shaped crystals. Surprisingly, structural analyses show the deboronation of 1 to afford an anionic *nido*-7,8-I₂C₂B₉H₁₀

species, and consequently the protonation of bpe to a Hbpe⁺ cation, to yield [*nido*-7,8-I₂C₂B₉H₁₀][−](Hbpe)⁺ (Scheme 1d, Fig. 1a). Indeed, such nucleophilic attack on the electron-poor boron has been reported to occur quite commonly under strongly basic conditions (KOH/EtOH or organic amines) or in the presence of F[−].²⁴ The presence of the electron-withdrawing halogen substituents on the C-carbon vertices is known to accelerate the deboronation reaction even under mild conditions such as DMSO, MeOH, or Et₂O.²⁵

To avoid electron-withdrawing iodine substituents that facilitate the deboronation, we moved to the selenomethyl-substituted carborane, 2. Slow evaporation of EtOH/Et₂O solution containing 2 and 1,4-di(4-pyridyl)piperazine (bipy-pip) provided colourless needle-shaped single crystals. Structural analyses again indicate the deboronation to obtain a salt, [*nido*-7,8-(SeMe)₂C₂B₉H₁₀][−](Hbipy-pip)⁺ (Scheme 1d, Fig. 1b).

None of the obtained *nido*-carborane salts feature any σ -hole interaction. Instead, the anionic *nido*-carboranes likely engage in cage[−]⋯cage[−] and cage[−]⋯ π interactions (Fig. S1 and S2, ESI[†]).²⁶ In addition, the protonated cations, Hbpe⁺ and Hbipy-pip⁺, are self-assembled to form a 1D chain through N-H⋯N hydrogen bonding (Fig. S3, ESI[†]). To build a supramolecular network driven by efficient XB or ChB interaction, the key requirements are strongly activated σ -holes on the carborane-substituted halogen/chalcogen atoms and strong ditopic Lewis bases. In carborane-based systems, however, the presence of a strong Lewis base favours the deboronation reaction and the resulting anionic *nido*-carborane will not activate anymore the σ -hole. The loss of strongly charge-depleted region on the I and Se atoms upon deboronation is indeed confirmed by the ESP calculations, showing negative potential values of $V_{s,max} = -44.5$ and -39.07 kcal mol^{−1} for *nido*-7,8-I₂C₂B₉H₁₀ and *nido*-7,8-(SeMe)₂C₂B₉H₁₀, respectively (Fig. 1c and d). This is



Scheme 2 Carborane tectons used in this work.

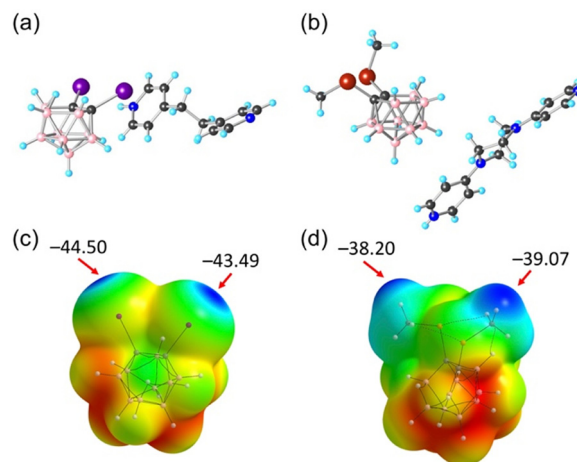


Fig. 1 Structure of [*nido*-7,8-I₂C₂B₉H₁₀][−](Hbpe)⁺ (a) and [*nido*-7,8-(SeMe)₂C₂B₉H₁₀][−](Hbipy-pip)⁺ (b). Purple, brick, blue, black, pink, and cyan spheres represent I, Se, N, C, B, and H atoms, respectively. Solvents in (a) were removed for clarity. ESP mapped on the 0.001 a.u. isodensity surface of *nido*-7,8-I₂C₂B₉H₁₀ (c) and *nido*-7,8-(SeMe)₂C₂B₉H₁₀ (d) with the ESP range of -89.7 (red) and -43.3 kcal mol^{−1} (blue). The $V_{s,max}$ values are indicated in kcal mol^{−1}.



in stark contrast to $V_{S,max} = +36.4$ and $+27.5$ kcal mol⁻¹, observed for **1** and **2**, respectively. It therefore turned out to be challenging to perform XB- or ChB-based crystal engineering with the carborane substituent, which is otherwise an excellent σ -hole activating group.

Given difficulties to obtain co-crystals with **1** and **2** despite different trials, we moved our attention to the TeMe-derivative, **3**. Slow evaporation of EtOH/CH₂Cl₂ solution containing an equimolar amount of **3** and bipy-pip provided colourless plate-shaped single crystals of **3**·(bipy-pip). It crystallizes in the monoclinic system, space group $P2_1/m$, with **3** located on a mirror plane and the bipy-pip on an inversion centre, affording a 1:1 stoichiometry. As shown in Fig. 2, the pyridine nitrogen atom engages in a ChB with the activated σ -hole of the Te atom. The Te...N contact distance of 2.834(9) Å is notably shorter than the sum of van der Waals radii, leading to a very small reduction ratio (RR) = 0.79. Moreover, the C-Te...N angle amounts to 171.3°, highlighting the short and almost linear ChB interaction. This gives rise to the formation of the sought-after supramolecular zig-zag chain structure where carborane units are bridged by bipy-pip molecules without deboronation.

To further probe the efficiency of **3** as a tecton favouring the formation of a carborane-based network, we tried co-crystallization with the bpe linker featuring a decreased Lewis base character. Despite our efforts, a similar solution co-crystallization technique did not afford a single crystal suitable for an X-ray diffraction study. To avoid the use of the polar solvents, which could favour the deboronation reaction and could hinder the co-crystallization, we used a solvent-free co-sublimation technique,²⁷ where **3** and bpe are placed in a two-zone furnace under static vacuum. The co-sublimation successfully afforded pale-yellow prism-shaped crystals of **3**·(bpe). It crystallizes in the monoclinic system, space group $P2_1/n$, with the asymmetric unit containing one molecule of **3** and two halves of bpe located on an inversion centre, giving a 1:1 stoichiometry. As shown in Fig. S4 (ESI†), ChB between the ditopic carborane donor and linear acceptor again favours the formation of a 1D structure, similar to **3**·(bipy-pip). Due to the less basic character of bpe, the observed Te...N contacts (2.855(9), 2.88(1),

and 2.883(8) Å for Te1A...N1, Te1B...N1, and Te2...N2, respectively) are slightly longer than those in **3**·bipy-pip (RR = 0.79 and 0.80). Nevertheless, the ChB interaction is again highly linear (\angle C-Te...N = 169.4–178.1°).

Upon co-sublimation of **3** and bpe, a few colourless prism-shaped crystals of by-product have also been observed, which turned out to be mono-substituted TeMe-carborane **4**, that was co-crystallized with bpe, forming **4**·bpe (Fig. 3). Given the insignificant quantity of **4**·bpe found in the co-crystallization tube, **4** is likely a minor by-product in the synthesis of **3** or thermally decomposed product in the vapor medium of the co-sublimation process. **4**·bpe crystallizes in the triclinic system, space group $P\bar{1}$, with the asymmetric unit involving one molecule of **4** and two halves of bpe located on an inversion centre, giving a 1:1 co-crystal. As expected, the pyridine nitrogen is engaged in directional interaction with the Te atom, affording a very short Te...N contact (2.819(3) Å) with RR down to 0.78. The Te...N contact observed in **4**·bpe, shorter than that observed in **3**·bpe (2.883 vs. 2.819 Å), is also coherent with the optimized structures of **3** and **4** by periodic DFT calculations without considering temperature effects (2.646 vs. 2.629 Å; Fig. S5, ESI†). Indeed, ESP calculation on **4** shows $V_{S,max} = +36.5$ kcal mol⁻¹ (Fig. S6, ESI†), which is slightly deeper than the one previously found in **3** (34.4 kcal mol⁻¹).²³ The shorter Te...N contacts in **4**·bpe can therefore be attributed convincingly to the deeper charge depletion of Te on the mono-substituted one.

To our surprise, the remaining CH proton in **4** is also engaged in a highly directional and non-bifurcated hydrogen bond with the pyridine nitrogen, which was reported to be unsuccessful with non-substituted *o*-carborane and ditopic Lewis bases.¹⁷ The observed C...N distance of 3.160(4) Å (H...N 2.087 Å), with the C-H...N angle of 164.0°, is indeed very short for a CH...X hydrogen bond, which is typically weak compared to normal hydrogen bonds involving OH or NH groups.²⁸ Indeed the $V_{S,max}$ value estimated on the CH proton (32.5 kcal mol⁻¹, Fig. S6, ESI†) is as strong as the one on the Te. Such CH hydrogen bonds are now generally recognized as an important complementary interaction to ultimately direct specific structural patterns.²⁹ In **4**·bpe, the concerted manifestation of the

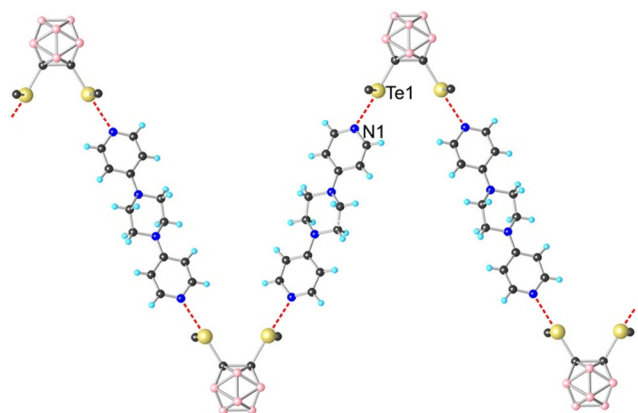


Fig. 2 Structure of **3**·bipy-pip with ChB interactions in red dotted lines. Gold, blue, black, pink, and cyan spheres represent Te, N, C, B, and H atoms, respectively; H atoms on **3** are omitted for clarity.

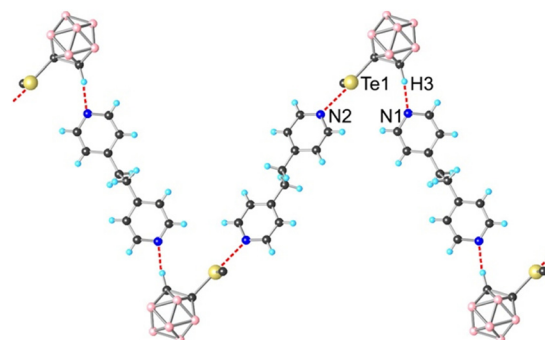


Fig. 3 Structure of **4**·bpe with ChB and HB interactions in red dotted lines. Gold, blue, black, pink, and cyan spheres represent Te, N, C, B, and H atoms, respectively; H atoms on –BH and –CH₃ are omitted for clarity.



chalcogen- and CH hydrogen-bonds indeed favours the formation of the extended chain structure, as observed in the co-crystals with ditopic ChB donor tecton 3.

In conclusion, we have demonstrated here that a supramolecular synthetic approach successfully provides carborane-based extended networks based on ChB. Harnessing carborane-based tectons in such a supramolecular synthesis appeared to be very challenging due to the deboronation side reaction in the presence of strong Lewis bases, which serve as ChB acceptors. In order to circumvent the nucleophilic attack, the choice of a carborane-based ChB donor with a less electron withdrawing –TeMe group was essential. In conjunction with that, the elimination of the solvent was found to be another key parameter to consider. Owing to the strong Te activation through carborane-substitution, the observed C–Te···N ChB interaction is extremely short and highly linear. These results open perspectives toward the elaboration of carborane-based supramolecular materials, which could find their place in numerous applications where carboranes play an important role.

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Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ The –Te1Me group is disordered over two positions with 52:48 occupancy.

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