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*Functional properties ensue from cooperation of different interactions*

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According to the definition recommended by IUPAC [1], a halogen bond (XB) occurs when there is evidence of a net attractive interaction between an electrophilic region in a halogen atom and a nucleophilic region in another atom. The halogen bond has many similarities with the hydrogen bond (HB) and here we discuss the specific profile of the two interactions. We also show how the cooperation between the two interactions afford crystalline systems possessing unique and useful properties. For instance, the diiodide, dibromide, and dichloride salts of the 1,6-bis(trimethylammonium)hexane cation (hexamethonium, HMET2+, cation) react with two equivalents of diiodine in a solid-gas reaction and the corresponding bis-trihalides (halogen bonded adducts) are formed [2]. No cavities are present in the starting dihalides and the observed behavior reveals the dynamically porous character of bis(trimethylammonium)alkane dihalides. In the obtained bis-trihalides a net of  $X^- \cdots H-C$  HBs ( $X=Cl, Br, I$ ) plays a decisive role in controlling the crystal packing: Four cationic columns embrace an anionic twin column formed by stacking of trihalide dimers. When heated, these bis-trihalides lose one diiodine molecule and the virtually unknown tetrahalide dianions  $[I_4]^{2-}$ ,  $[I_2Br_2]^{2-}$ , and  $[I_2Cl_2]^{2-}$  are formed. These dianions are the product of the double pinning of a diiodine molecule by two halide anions via strong XBs. The last two tetrahalides were never obtained in solution. The confined environment of dynamically porous materials clearly confers useful synthetic opportunities relative to solution-state processes. Other cases are described wherein XB and HB cooperate in driving self-assembly processes which afford solid materials endowed with useful properties. For instance, we will discuss the formation of two-component supramolecular gels [3] wherein a bis-urea and a diiodoarene self-assemble via cooperative XB and HB.

[1] G. R. Desiraju, P. S. Ho, L. Kloo, A. C. Legon, R. Marquardt, P. Metrangolo, P. Politzer, G. Resnati, K. Rissanen, *Pure Appl. Chem.*, 2013, 85, 1711–1713, [2] J. Marti-Rujas, L. Meazza, G. K. Lim, G. Terraneo, T. Pilati, K. D. M. Harris, P. Metrangolo, G. Resnati, *Angew. Chem. Int. Ed.*, 2013, 52, 13444–13448, [3] L. Meazza, J. A. Foster, K. Fucke, P. Metrangolo, G. Resnati, J. W. Steed, *Nature Chem.*, 2013, 3, 42–47.

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