Supporting Information

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Hybrid Networks Formation via Halogen Bonding of the Neutral Bromo-Substituted Organic Molecules with Anionic Metal-Bromide Complexes

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IR spectra of components and co-crystals (Figure S1), elementary cage of the network in the $(NBu_4)_2[ZnBr_4]\cdot CBr_4$ co-crystals (Figure S2), halogen-bonded hybrid networks (Figure S3) ESP and LUMO of halogen-bond donors (Figures S4 and S5), UV-Vis spectra of the $C_3Br_2F_6/Br^-$ solutions (Figure S6).

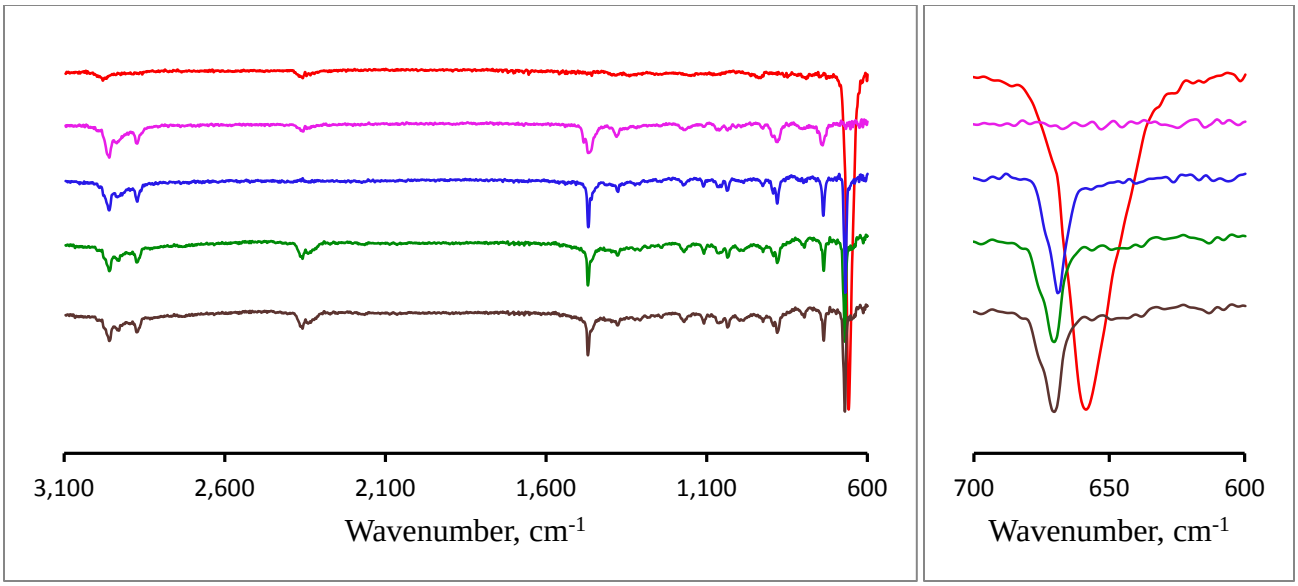


Figure S1. A) FT-IR spectra of individual CBr_4(red) and $(Bu_4N)_2[ZnBr_4]$ (magenta) as well as $(Bu_4N)_2[ZnBr_4]\cdot CBr_4$ (blue) $(Bu_4N)_2[CoBr_4]\cdot CBr_4\cdot$(green) and) $(Bu_4N)_2[CdBr_4]\cdot CBr_4\cdot$(brown) co-crystals. B) Fragments of the IR spectra showing consistent shift of C-Br vibrations of CBr_4 in its associates with metal-bromide complexes.

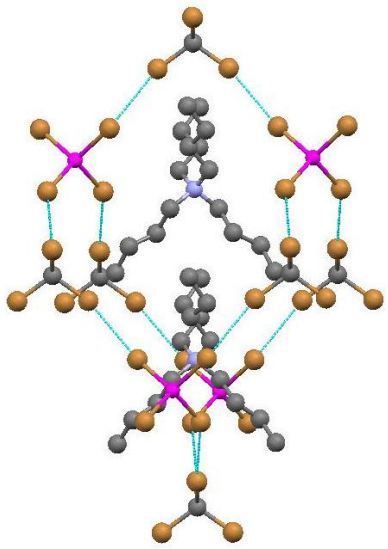
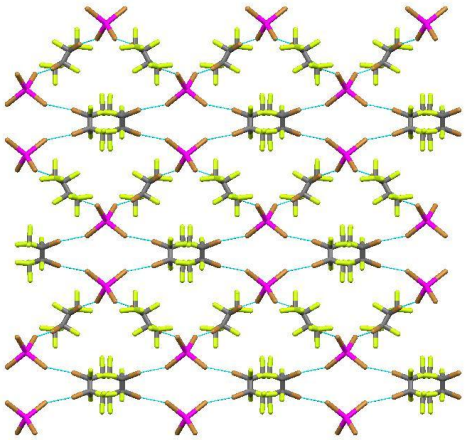
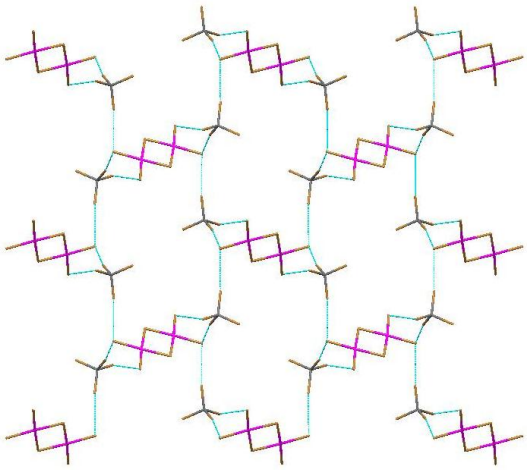


Figure S2. Elementary cage of the diamandoid network formed via halogen bonds between tetrahedral CBr_4 and ZnBr4 counterparts in the structure of $(NBu_4)_2[ZnBr_4]\cdot CBr_4$ co-crystals. Colors as follows: C, grey; N, blue; Br, brown; Zn, magenta; halogen bonds are shown as light blue lines (for clarity, tetrabutylammonium hydrogen atoms are not shown).

A)



B)



C)

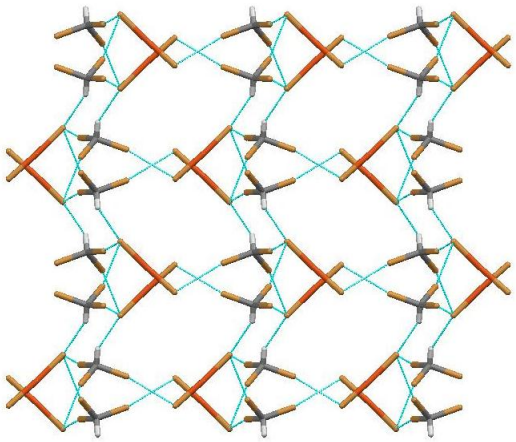


Figure S3. Halogen-bonded hybrid networks: A) in the $(NBu_4)_2[ZnBr_4]\cdot 2C_3Br_2F_6$ salt (view along axis a); B) in the $(NBu_4)_2\ [Pt_2Br_6]\cdot 2CBr_4$ co-crystals (view along axis a) C) in the $(NPr_4)[CuBr_2]\cdot 2CHBr_3$ co-crystals (view along axis c).

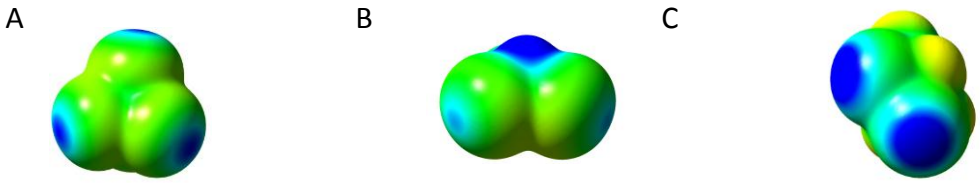


Figure S4. Electrostatic potential on the molecular surfaces of (A) CBr_4, (B) $CHBr_3$ and (C) $C_2F_6Br_2$ (bromines are in forefront and left). Blue, green and red colors depict positive, neutral and negative potentials, respectively, on the 0.0004 electrons $bohr^{-3}$ molecular surfaces.

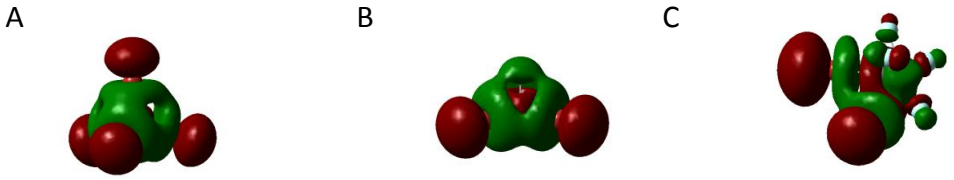


Figure S5. Lowest unoccupied molecular orbital (LUMO) of (A) CBr_4 (B) $CHBr_3$ and (C) $C_2F_6Br_2$ (bromines are in forefront and left) showing segments along C-Br axes.

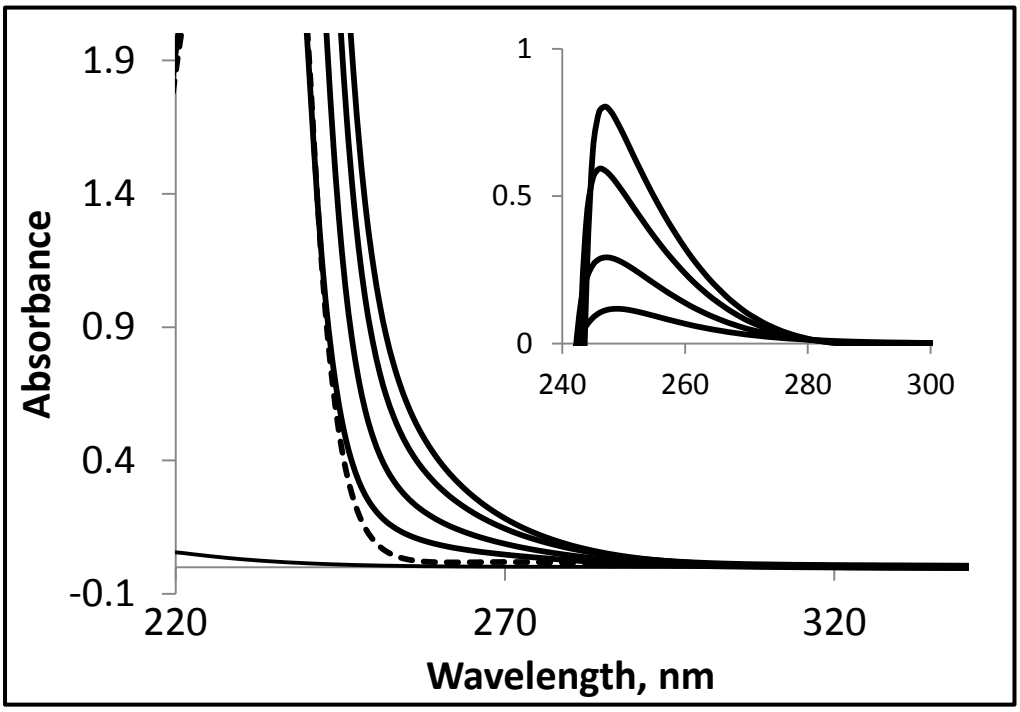


Figure S6. Spectral changes attendant upon the addition of Bu_4NBr to 2.5 mM solution of $C_3Br_2F_6$ (in CH_2Cl_2, 22◦C). Concentration of Bu_4NBr (mM, solid lines from bottom to top): 0, 150,309, 464, 620. Dashed line corresponds to separate 150 mM solution of Bu_4NBr. Inset: UV-Vis spectra of the $C_3Br_2F_6$ / Bu_4NBr mixtures after subtraction of the components' absorption.