

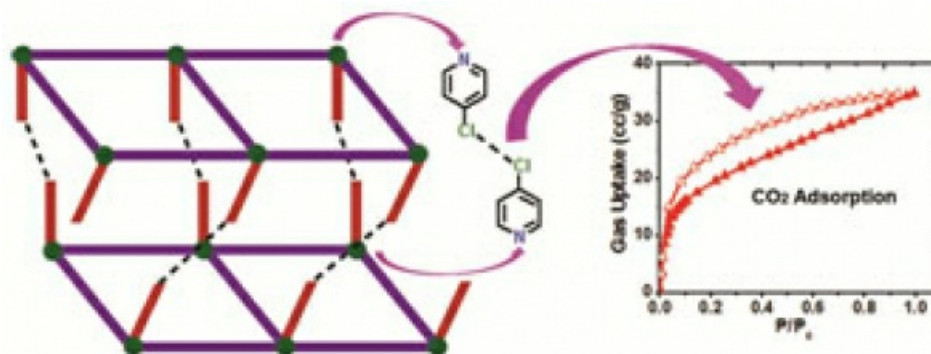
*Halogen...Halogen interactions in 2D coordination polymers impact the Sorption behavior*Mohammad Hedayetullah Mir¹¹Department Of Chemistry, Aliah University, Kolkata, India

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Halogen-halogen interactions have become an increasingly popular field of research over the past decades for the construction of intriguing structures and prominent applications from catalysis to medicinal chemistry. Desiraju and coworkers have used this type of interaction for the design and crystal engineering of organic polymers. However, the utility of halogen-halogen interactions in the construction of high dimensional porous coordination polymers (PCPs) for the sorption studies is still rare. Herein, we report four two-dimensional coordination polymers (2D CPs) [Cu₂(muco)₂(4-clpy)₂] (1), [Cu₂(muco)₂(4-brpy)₂] (2), [Zn₂(bdc)₂(4-clpy)₂] (3) and [Zn₂(bdc)₂(4-brpy)₂] (4) (H₂muco = trans, trans-muconic acid or 1,3-butadiene-1,4-dicarboxylic acid; H₂bdc = 1,4-benzene dicarboxylic acid; 4-clpy = 4-chloro pyridine and 4-brpy = 4-bromo pyridine) assembled through weak interactions to form three-dimensional (3D) aggregates. Of these 1 and 2 are isotypical and form 3D supramolecular aggregation based on type I halogen-halogen interactions (Cl...Cl or Br...Br) and have impact on CO₂ sorption properties. For the first time, halogen-halogen interactions have been used as tool in the construction of high dimensional CPs for sorption studies. Compound 1 shows little high adsorption capacity may be due to better interactions in the confined space of pillared layer structure generated by strong chlorine-chlorine interaction. This work affords an efficient method for sorption of greenhouse gas CO₂ from industrial emission. However, analogous compounds 3 and 4 are expanded to 3D supramolecular structures based on n...n interactions. These compounds have no halogen-halogen interactions and hence become non-porous towards CO₂ sorption. It appears that the retention of 3D structure by halogen...halogen interaction is related to the sorption behavior. Furthermore, this work provides us further insights for the construction of a series of 2D PCPs involving supramolecular interactions by the replacement of pyridine based ligands.

1) Desiraju, G. R. et al. Acc. Chem. Res. 2014, 47, 2514–2524.

2) Mir, M. H. et al. Cryst. Growth Des. 2016, 16, 5514–5519.

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