

An Alkyne-Bridged Covalent-Organic Framework Featuring Interactive Pockets for Cooperative Bromine Capture

Ankita De

Sattwick Haldar,¹ Johannes Schmidt,² Saeed Amirjalayer,³ Fanny Reichmayr,¹ Nikolaj Lopatik,¹ Leonid Shupletsov,¹ Eike Brunner,¹ Inez Weidinger,¹ Andreas Schneemann¹

¹TU Dresden, Dresden, Germany ²TU Berlin, Berlin, Germany ³University of Münster, Münster, Germany
Ankita.de@tu-dresden.de

Halogens like bromine and iodine pose a serious threat to the environment as they cause ozone layer depletion.^[1] Although iodine is beneficial to human health in small amounts, bromine is highly corrosive and volatile, thus making it toxic.^[2] Bromine emissions are mainly due to its use in aerosols, flame retardants, pharmaceuticals or fine chemical production, reduction of mercury vapor emissions, and agriculture.^[3] Moreover, bromine can coexist with iodine in an equilibrium product of IBr.^[4] These problems connected to bromine call for a search for suitable materials to capture bromine^[5] selectively over iodine. Here, we propose a new Covalent Organic Framework (COF) featuring electron-rich sites to capture Bromine effectively (amongst the highest in porous reticular materials) and have conducted an in-detail study of the capture mechanism.

The backbone of the COF featured in this study consists of triple bonds, an electron-rich pyrene unit, and heteroatoms (N sites). These sites enhance the capture of Br₂ versus I₂ in static conditions with vapor as well as solution phase. Moreover, when the COF is exposed to a mixture of I₂ and Br₂, the λ_{\max} shifts to that of I₂ in solution. As monitored by solution Raman spectroscopy, we observe the disappearance of the band corresponding to Br₂ and IBr from the solution after equilibration. To give some mechanistic insights into the capture, we see the disappearance of the Raman band corresponding to the triple bond after Br₂ capture. From XPS as well as computational studies, the participation of the electron-rich triple bond is evident for bromine capture. The participation of the triple bond forms a major difference owing to the higher orbital overlap due to the lower atomic size of Br₂ compared to I₂, thus leading to higher and selective bromine capture. This involvement of the triple bond can be classified as a cooperative physisorption as well as a chemisorption process, giving rise to a unique method for the capture of Br₂. The captured halogens can also be reversibly released and the material can be recycled with minimum loss in the overall capture capacity. This study thus gives material chemists a guide to targeted material design for the capture of environmentally benign chemical species.

References

- [1] Pratt, K. A.; Custard, K. D.; et al. *Nature Geoscience* (2013), 6 (5), 351–356.
- [2] Pang, J.; Yuan, S.; et al. *Angew. Chem. Int. Ed.* (2017), 56 (46), 14622–14626.
- [3] John. Kirk-Othmer Encyclopedia of Chemical Technology (2004) 4th ed [27 vols] Vol 5
- [4] Troy, R. C.; Kelley, M. D.; et al. *Inorg. Chem.* (1991), 30 (25), 4838–4845.
- [5] Tulchinsky, Y.; Hendon, C. H.; et al. *J. Am. Chem. Soc.* (2017), 139 (16), 5992–5997.

Figure

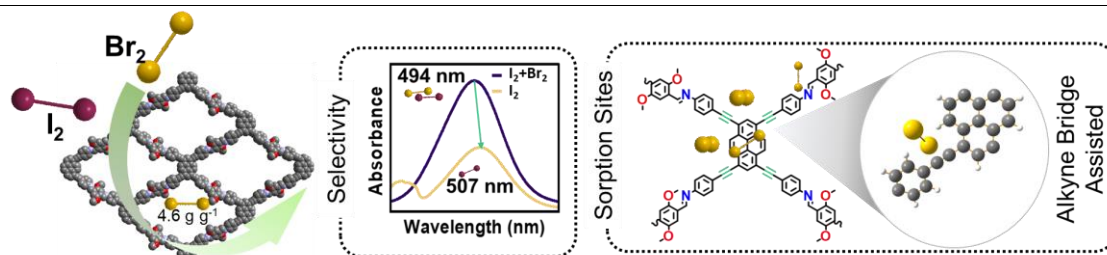


Figure 1: Scheme showing the selective capture of bromine in a strategically designed COF