

A Porous Organic Framework Captures Greenhouse Gases

This report features the work of Ognjen Š. Miljanić and his co-workers published in Nat. Commun. 5, 5131 (2014).

Since 1995 the chemistry of porous materials has become revolutionized with the development of crystallographically ordered hybrid frameworks.¹ Noncovalent organic frameworks (nCOF), constructed through the self-assembly of discrete organic molecules via noncovalent interactions (e.g. hydrogen bonding, $[\pi \cdots \pi]$, or $[C-H \cdots \pi]$ interactions), have attracted much attention because of their modularity and processability in solution, but it is still challenging to synthesize a nCOF that possesses great thermal and hydrolytic stability, and a permanent porosity.

Based on the reported syntheses of extensively fluorinated ligands,² a lightweight porous material with microscopic pores that captures several potent greenhouse gases in large proportions has been developed through the self-assembly of extensively fluorinated molecules.³ A collaborative team including researchers from the NSRRC, University of Houston, and Advanced Photon Source at Argonne National Laboratory performed this research.

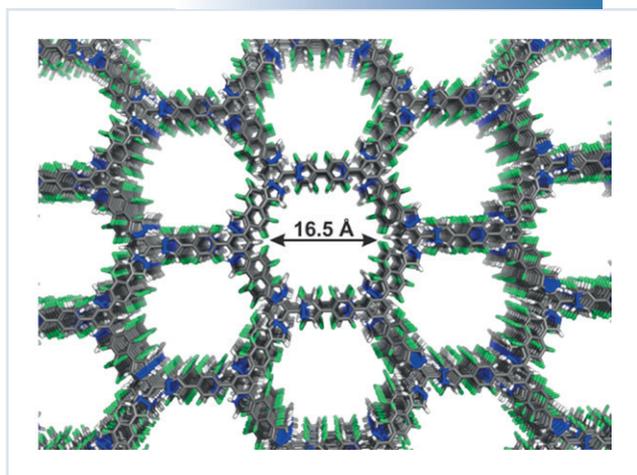


Fig. 1: Crystal structure of the porous organic framework, which has infinite fluorine-lined hexagonal channels protruding throughout the structure along the crystallographic *c* axis. Element colors: C-gray, N-blue, F-lime, and H-white. (Reproduced from Ref. 3)

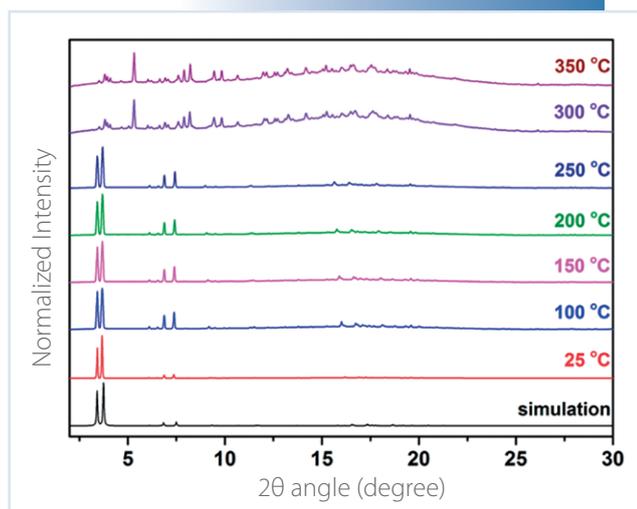


Fig. 2: Variable temperature PXRD revealed no alteration of structure until at least 250 °C. (Reproduced from Ref. 3)

Greenhouse gases such as carbon dioxide have received much attention because of their potential to affect greatly the terrestrial climate. Although carbon dioxide presents the largest problem, several other compounds are hundreds or thousands of times as potent in their global warming potential per unit mass. These include chlorofluorocarbons (CFC) and fluorocarbons (common refrigerants or propellants), which are highly stable organic compounds in which one or more hydrogen atoms have been replaced with fluorine. Because these chemicals cause the depletion of ozone in the upper atmosphere, the manufacture of such compounds

has been banned under the *Montreal Protocol*; they are being replaced with other products such as hydrofluorocarbons, hydrocarbons and CO₂, but even these replacements present potent greenhouse gases.

A collaborative team led by Ognjen Miljanić from University of Houston (USA) has developed a molecule that self-assembles into a structure that can capture these greenhouse vapors to the extent 75% by mass. In their paper, they report that a small molecule based on an extensively fluorinated backbone forms a structure with minuscule one-dimensional honeycomb channels of diameter about 1.6 nm. These pores are lined with fluorine atoms, which endow them with a great affinity for other molecules containing fluorine, including fluorocarbons and CFC.

Previous authors have developed other porous materials with similar pore sizes, but those were generally heavy (because of the presence of metals), sensitive to water, and difficult to process and recycle. The advantage of the current material is that it is stable to water and composed of individual molecules held together by only weak interactions—hydrogen bonding and $[\pi \cdots \pi]$ stacking. The latter feature makes this material light weight, because there is no metal connector. The weak interactions between the molecules can be broken when needed; the molecule can thus be recycled or deposited on a surface.

The molecule is thermally stable to at least 250 °C (Fig. 2), proved by synchrotron powder X-ray diffraction (PXRD) data collected at BL01C2 at the TLS. This is a rare instance of an organic crystal that retains permanent porosity after the removal of guest solvents from its voids. The crystal is stable in acidic and basic solutions, and most organic solvents. Also, the material does not adsorb H₂O even at 90% humidity.

The University of Houston researchers investigated the uptake of greenhouse gases carried by nitrogen onto this porous material. Of these, some were adsorbed

Table 1: Sorption capacities and other characteristics of guest adsorbed within the pores of nCOF. (Reproduced from Ref. 3)

Guest species	Boiling point (°C)	20-year greenhouse gas potential (vs. CO ₂)	Adsorption in nCOF		
			Mass (%) ^a	Mol/ Mol nCOF ^b	Desorption temperature (°C)
Toluene	110	—	30.6 (29.7)	2.39	62
Hexane	68	—	27.7 (27.4)	2.31	52
Cyclohexane	81	—	25.7 (25.6)	2.20	61
Chloroform	61	—	52.5 (53.4)	3.17	62
Dichloromethane	40	31	49.8 (49.6)	4.22	45
Perfluorohexane	56	6,600	74.0 (73.6)	1.58	62
CFC-113 (Cl ₂ FC–CClF ₂)	48	6,540	65.6 (64.9)	2.52	62
HCFC-225ca (CF ₃ CHF ₂ CHCl ₂)	51	429	58.0 (58.0)	2.06	63

^a Values in parentheses indicate mass adsorption capacities observed in the second attempt.

^b Molar values were calculated with mass adsorption data from the first attempt.

to up to 75% by mass in the prepared material (Table 1). The reversibility of this process was confirmed on performing adsorption and desorption in over 20 cycles; no loss of capacity was observed. The uptake is rapid: the material becomes saturated with molecules of greenhouse gases in less than 20 s. Near 23 °C, all examined guests can be removed completely from the pores of material within minutes on evacuation, but, if evacuation is not applied, fluorinated guests remain in the pores of material even after the flow of guest-enriched nitrogen is stopped; this behavior, along with the rapid uptake, indicates a great fluorophilicity of the material.

In summary, a thermally stable, porous, hydrophobic and fluorophilic nCOF has been synthesized. Its great affinity toward fluorocarbons and CFC is promising for the capture and recycling of greenhouse gases, some of which also cause ozone depletion.

References

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2. T.-H. Chen, I. Popov, O. Zenasni, O. Daugulis, and O. Š. Miljanić, *Chem. Commun.* **49**, 6846 (2013).
3. T.-H. Chen, I. Popov, W. Kaveevivitchai, Y.-C. Chuang, Y.-S. Chen, O. Daugulis, A. J. Jacobson, and O. Š. Miljanić, *Nat. Commun.* **5**, 5131 (2014).