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- Authors: Guanfei Gong, Siheng Lv, Jixin Han, Fei Xie, Qian Li, Ning Xia, Wei Zeng, Yi Chen, Lu Wang, Jike Wang, and Shigui Chen

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# Halogen-Bonded Organic Framework (XOF) Based on Iodonium-Bridged N…I<sup>+</sup>…N Interactions: A Type of Diphase Periodic Organic Network

Guanfei Gong,<sup>[a], +</sup> Siheng Lv,<sup>[a], +</sup> Jixin Han,<sup>[a]</sup> Fei Xie,<sup>[b]</sup> Qian Li,<sup>[a]</sup> Ning Xia,<sup>[a]</sup> Wei Zeng,<sup>[a]</sup> Yi Chen,<sup>[a]</sup> Lu Wang,<sup>[a]</sup> Jike Wang,<sup>[a]\*</sup> and Shigui Chen,<sup>[a]\*</sup>

Dedicated to the 100th Anniversary of Chemistry at Nankai University.

[a]	G. F. Gong, S. H. Lv, J. X. Han, Q. Li, N. Xia, W. Zeng, Y, Chen, Dr. L. Wang, Prof. Dr. J. K. Wang, Prof. Dr. S. G. Chen
	The Center for Precision Synthesis, Institute for Advanced Studies, Wuhan University
	299 Bayi Road, Wuhan, Hubei 430072, P. R. China
	E-mail: sgchen@whu.edu.cn; jike.Wang@whu.edu.cn.
[b]	F. Xie
	National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei 230029, China.
[+]	These authors contributed equally to this work.

Abstract: Due to the fascinating structures and wide applications, porous materials with open frameworks have attracted more and more attentions. Herein, a novel two-dimensional (2D) halogen-bonded organic framework (XOF-TPPE) was successfully designed and fabricated by iodonium-bridged N···I+···N interactions between pyridyl groups and I<sup>+</sup> for the first time. The formation of XOF-TPPE and its linear analogue was monitored by <sup>1</sup>H NMR, UV-Vis, X-ray photoelectron spectroscopy (XPS), IR, SEM, TEM, HRTEM and selected-area electron diffraction (SAED). The structural model of XOF-TPPE was established based on powder X-ray diffraction (PXRD) data and theoretical simulations. Significantly, synchrotron small-angle X-ray scattering (SAXS), DLS and UV-vis spectroscopy experiments suggested that XOF-TPPE still maintains a stable 2D framework structure in solutions. This research opens up a novel avenue for the development of organic frameworks materials, and may bring new promising applications for the field of porous materials.

Great attentions have been paid to the exploration of crystalline porous materials for their fascinating structures and wide applications in the past decades.<sup>[1]</sup> Both covalent and noncovalent interactions have been employed to build crystalline porous materials with open frameworks, giving diversity of structures and functions. Due to the high stability of covalent bonds, covalent organic frameworks (COFs) are usually stable, even under harsh conditions.<sup>[2]</sup> Formed by coordination bonds between metal ions and organic ligands, metal organic frameworks (MOFs) are of inherent crystallinity and fragility.<sup>[3]</sup> Metal ions are not only connection nodes, but also the effective functional sites.<sup>[4]</sup> Hydrogen-bonded organic frameworks (HOFs), constructed with building blocks connected by hydrogen bonds, are another type of crystalline porous organic frameworks.<sup>[5]</sup> Due to the weakness of hydrogen bonds, HOFs are usually less stable than COFs and MOFs, but facile to process and rebuild.<sup>[6]</sup> Particularly, built based on strong host-guest interactions, soluble supramolecular organic frameworks (SOFs) represent a unique class porous materials, which exist stably in solution phase while still maintaining periodic structures.[7] The properties and functions for porous frameworks depend on not only the organic building units, but also the connection knots.<sup>[8]</sup> Thus, the development of new connection motifs is still of importance for expanding the family of porous architectures with unexploited properties and functions.

Halogen bond (XB) interactions have more stringent directionality than hydrogen bond (HB) interactions,<sup>[9]</sup> which offer a robust tool for the construction of distinctive supramolecular architectures,<sup>[10]</sup> showing wide applications in crystal engineering,<sup>[11]</sup> molecular recognition,<sup>[12]</sup> catalysis,<sup>[13]</sup> drug design,<sup>[14]</sup> etc. A halogen bond occurs when there is evidence of a net attractive interaction between an electrophilic region associated with a halogen atom in a molecular entity and a nucleophilic region in another, or the same, molecular entity.<sup>[15]</sup> When multivalent halogen-bond donors and accepters were introduced, a few examples of halogen-bonded frameworks have been investigated in cocrystal states.<sup>[16]</sup> Nevertheless, organic frameworks with inherent nanopore structures based on halogen bonds are still unexplored. It is known that halonium ions (X<sup>+</sup>) feature positive *p*-holes due to the empty *p*-orbital, which interact with two Lewis bases in both lobes,<sup>[17]</sup> and they tend to form robust, three-center-four-electron [D...X+...D] halogen bonds in a straight arrangement, making halonium ions ideal building knots in supramolecular assembly.<sup>[18]</sup> It is worth noting that discrete supramolecular structures have been well fabricated based on D····X<sup>+</sup>····D halogen bonds, such as capsules,<sup>[19]</sup> cages,<sup>[20]</sup> helices<sup>[21]</sup> due to the predicable characteristics. Herein, we reported the construction of a two-dimensional (2D) halogenbonded organic framework (XOF-TPPE) by the three-center-fourelectron halogen bond interactions for the first time. In this method, pyridyl units were firstly coordinated with Ag<sup>+</sup> to generate corresponding [N-Ag-N]<sup>+</sup> MOF structure. Then, the XOF structure was prepared via in situ replacing Ag<sup>+</sup> cations of the [N-Ag-N]<sup>+</sup> linkers in the MOF with I<sup>+</sup> to form [N-I-N]<sup>+</sup> linkers (Scheme 1). Meaningfully, XOF-TPPE not only is of crystallinity in solid state but also still maintains a stable 2D periodic structure in solution state.



Scheme 1. The construction of  $[N \cdots l^+ \cdots N]$ -bridged XOF-TPPE and the linear analogue XOF-BPy.



Figure 1. (a) XPS spectrum of I 3d for XOF-BPy; (b) Partial <sup>1</sup>H NMR spectra of BPy, MOF-BPy and XOF-BPy in CDCl<sub>3</sub>/MeOH-d<sub>4</sub> (4:1, v/v, 600 MHz, 298 K); (c) IR spectra of BPy, MOF-BPy, XOF-BPy; (d) Single crystal structure of MOF-BPy with different views.

To demonstrate the validity of this design, 4,4'-bipyridine (BPy), the simplest pyridyl linker, was firstly selected as a model to fabricate linear MOF-BPy and XOF-BPy (see the Supporting Information for details). The structures of MOF-BPy and XOF-BPy were investigated via UV-Vis, X-ray photoelectron spectroscopy (XPS), <sup>1</sup>H NMR, IR spectroscopy, X-ray crystallographic analysis, and scanning electron microscopy (SEM). XPS has been used to analyze the surface properties of XOF-BPy (Figure 1a). The peaks of I 3d<sub>3/2</sub> at 618.6 eV and I 3d<sub>5/2</sub> at 630.1 eV could be attributed to Agl species, while the other peaks at 620.1 (I 3d<sub>3/2</sub>) and 631.6 (I 3d<sub>5/2</sub>) eV should be attributed to I<sup>+</sup> by referring to National Institute of Standards and Technology (NIST) XPS database<sup>[22]</sup> and pertinent literature.<sup>[23]</sup> In addition, this result is consistent with I 3d spectrum of Barluenga's reagent (Figure S3),<sup>[24]</sup> which further proves the existence of I<sup>+</sup>. Meanwhile, the UV spectrum of XOF-BPy shows a significant broad absorption around 463 nm, which is consistent with the absorption of iodonium ions (see the Supporting Information for details, Figure S4-S5).

In the <sup>1</sup>H-NMR spectra (Figure 1b), the signals of H<sub>a</sub> and H<sub>b</sub> of pyridyl groups of **MOF-BPy** and **XOF-BPy** display deshielded effect compared to those of **BPy** monomer due to the coordination interactions of the pyridyl units to  $Ag^+/I^+$ .<sup>[25]</sup> Moreover, in the corresponding IR spectra (Figure 1c), upon the addition of Ag<sup>+</sup> (1.0 equiv.) into the **BPy**, the =C-H, C=N stretching vibrations shift from 3027, 1586 to 3109, 1601 cm<sup>-1</sup>, respectively. The signals of =C-H and C=N move back slightly with the addition of iodine (1.0 equiv.) to **MOF-BPy**. These shifts further support  $Ag^+/I^+$  binding with pyridyl groups of **BPy** by coordination interactions to form **MOF-BPy** and **XOF-BPy**, respectively.

Notably, high quality crystal of MOF-BPy was successfully obtained in acetonitrile by solvent diffusion method and analyzed via X-ray crystallography (Figure 1d). The crystal structure reveals that MOF-BPy consists of 1D linear structure of alternating arrangement of Ag<sup>+</sup> and BPy. The the N-Ag distance of 2.16 ~ 2.17 Å in **MOF-Bpy** is shorter than the coordination distance (2.23 ~ 2.56 Å) between the nitrogen atom in unconjugated aromatic system and silver ion, which could be attributed to charge delocalization into the conjugated aromatic system during the coordination with Ag<sup>+</sup>.<sup>[26]</sup> The N···Ag···N angle is 177.140°, nearly linear. Unfortunately, all attempts to obtain single crystal of XOF-BPy were unsuccessful. What's more, the morphologies for BPy, MOF-BPy and XOF-BPy were investigated by SEM (Figure S6). The images show that BPy exists in irregular powder structures, while MOF-BPy and XOF-BPy exhibit fibrous-like morphologies, confirming that Ag<sup>+</sup>/I<sup>+</sup> could induce obvious aggregation of **BPy**.

The pyridyl functionalized tetraphenyl ethylene (**TPPE**) was introduced to fabricate 2D halogen-bonded organic framework (**XOF-TPPE**) following the similar procedure for **XOF-BPy**. XPS, UV-Vis, <sup>1</sup>H NMR, IR spectroscopy, powder X-ray diffraction (PXRD), SEM, TEM and HRTEM experiments were performed to investigate the formation of **MOF-TPPE** and **XOF-TPPE**. In the XPS experiment of **XOF-TPPE** (Figure S7), the signal peaks of I3d at 620.1 (I 3d<sub>3/2</sub>) and 631.6 (I 3d<sub>5/2</sub>) eV indicate the existence of I<sup>+</sup>. Meanwhile, **TPPE** exhibits two N1s peaks at 398.9 and 401.0 eV (Figure S8), while the N1s peaks of **MOF-TPPE** and **XOF-TPPE** shift to higher binding energies because of coordination interactions between pyridyl groups and Ag<sup>+</sup>/I<sup>+</sup>, respectively. In addition, UV-vis spectrum of **XOF-TPPE** shows a similar broad

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absorption centered at 479 nm, which further confirms the presence of I<sup>+</sup> (Figure S9). In their <sup>1</sup>H-NMR spectra (Figure 2a), the aromatic proton signals ( $H_a \sim H_d$ ) of **MOF-TPPE** and **XOF-TPPE** display a large deshielded effect compared with the free **TPPE** ligand, which could be attributed to the electron density decrease of pyridyl groups during the coordination with Ag<sup>+</sup>/I<sup>+</sup>. Furthermore, as revealed by their IR spectra (Figure S10), the =C-H and C=N signals of **MOF-TPPE** and **XOF-TPPE** show significant blue shifts compared with those of **TPPE** monomer. These results also indicate the formation of **MOF-TPPE** and **XOF-TPPE**.

The morphologies of **TPPE**, **MOF-TPPE** and **XOF-TPPE** were further investigated by SEM and TEM. The SEM image of **TPPE** shows spherical particles (Figure S11a), while **MOF-TPPE** and **XOF-TPPE** exhibit similar block structures (Figure S12a and Figure S11b). Interestingly, the TEM images of **MOF-TPPE** and **XOF-TPPE** show crossnetworking structures (Figure S12b and Figure 2b). In addition, the clear lattice fringes and the typical diffraction pattern related to single crystal were observed by HRTEM and SAED, respectively (Figure S12c and Figure 2c), indicating that **MOF-TPPE** and **XOF-TPPE** have high crystallinity. <sup>[27]</sup>



Figure 2. (a) Partial <sup>1</sup>H NMR spectra of TPPE, MOF-TPPE, XOF-TPPE in CDCl<sub>3</sub>/MeOH- $d_4$  (4:1, v/v) at 298 K; (b) TEM, and (c) HRTEM and SAED (inset) images of XOF-TPPE.

To elucidate the crystal structures of **MOF/XOF-TPPE**, PXRD studies were performed and the possible 2D structures with different stacking models were built and optimized by the Materials Studio with Forcite molecular dynamics module method. The experimental PXRD patterns of **MOF-TPPE** match well with the simulated pattern of eclipsed AA stacking model (Figure 3a and Figure S13a). As revealed by the experimentally observed PXRD pattern, the first intense peak at a low angle of 4.68° (2 $\theta$ ) corresponds to the (110) Bragg reflection. The other two peaks at 9.59° and 14.08° are attributed to (220) and (330) reflections, respectively. Pawley refinement was performed to give the unit cell parameters of *a* = 36.97 Å, *b* = 22.07 Å, *c* = 5.67 Å, *a* =  $\beta = \gamma = 90^\circ$ , with  $R_{wp} = 4.60$ %, and  $R_p = 3.65$ %. For **XOF-TPPE**, the simulated PXRD patterns of the eclipsed AA stacking model

match better with the experimental results (Figure 3b and Figure S13b), suggesting the practical structure of eclipsed AA stacking model. In addition, Pawley refinement was implemented to give the unit cell parameters of *a* = 38.13 Å, *b* = 26.15 Å, *c* = 5.56 Å, *a* =  $\beta = \gamma = 90^{\circ}$ , with  $R_{wp} = 6.82$  % and  $R_p = 3.84$  %). The difference plot suggests that the refined PXRD patterns match well with the experimental result. When exposed to air for 50 days, the unaltered PXRD pattern of **XOF-TPPE** indicates its good stability (Figure S15). In addition, nitrogen adsorption-desorption measurements were performed to give the Brunaner-Emmett-Teller (BET) surface areas for **TPPE**, **MOF-TPPE** and **XOF-TPPE** as 0.08, 34.74 and 13.13 m<sup>2</sup>/g, respectively (Figure S14). The relatively low surface areas of **MOF/XOF-TPPE** should be attributed to the large size of tetrafluoroborate anions filled in the pores (Figure S13c).<sup>[28]</sup>



Figure 3. Experimented (balck) and refined (red) PXRD, the difference plots between the experimental and refined PXRD patterns, simulated PXRD patterns for eclipsed AA stacking and staggered AB stacking mode for **MOF-TPPE** (a) and **XOF-TPPE** (b), and respectively. Inset: Top views of structural representations of **MOF-TPPE** (a) and **XOF-TPPE** (b) in eclipsed AA stacking model.

Since **MOF-TPPE** and **XOF-TPPE** are slightly soluble in MeOH, DMF and DMSO, the assembly structures of **MOF-TPPE** and **XOF-TPPE** in solution state were further investigated by smallangle X-ray scattering (SAXS, Figure 4 and Figure S16), which is a powerful technique to characterize the assembly architectures with periodic structures in solutions.<sup>[29]</sup> The one-dimensional

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scattering curves of MOF-TPPE and XOF-TPPE show clear bumps (Figure 4c and Figure S17a), implying the existence of periodic structures inside the samples. Fourier transformation was further performed for the scattering curves, and the second order derivative was calculated to provide the chord length distribution (CLD) function (Figure 4d and Figure S17b, see the Supporting Information for SAXS experiment details). According to the theory of the CLD function,<sup>[30]</sup> the first extreme value in the curve is interpreted as the length of the minimum period while the second extreme value corresponds to the length of the second minimum period at the orthogonal direction. The extreme values between 5 and 10 nm reflect chords penetrating multiple interfaces. The CLD function curves indicate that MOF-TPPE and XOF-TPPE maintain regular 2D frameworks in solutions while the lengths of the minimum periods at orthogonal directions are 2.38 nm and 4.46 nm, respectively, which are consistent with the result of Pawley refinement results (~2.27 nm and ~3.85 nm). The oscillation mode of the CLD curves further demonstrate the periodicity of MOF-TPPE and XOF-TPPE. From dynamic light scattering (DLS) experiments, the hydrodynamic diameters  $(D_{\rm H})$ of MOF/XOF-TPPE in polar solvents (MeOH, DMF, and DMSO) were determined to be around 710 nm, which was significantly larger than that of the monomer TPPE (about 100 nm) (Figure S18). The much large sizes of MOF/XOF-TPPE is consistent with the proposed 2D framework structures. The unchanged absorption coefficients of MOF/XOF-TPPE, based on UV-vis spectroscopy experiments, indicated that the frameworks do not dissociate upon dissolution and they are of high stability in solutions (Figure S19-S20).





In summary, we have demonstrated a supramolecular approach to successfully construct a novel 2D halogen-bonded organic framework (**XOF-TPPE**) formed from pyridyl modified organic ligand with iodonium ions via three-center-four-electron

halogen-bonding interactions. Significantly, **XOF-TPPE** not only has high crystallinity in solid state, but also still maintains stable 2D framework structures in solutions. To the best of our knowledge, it is the first 2D XOF with a stable structure in both solid and solution state via three-center-four-electron halogen bonds. As a new member to the family of organic frameworks, XOFs distinguish themselves from COFs, MOFs, HOFs and SOFs by connecting building blocks through less common but intriguing halogen bonds, which should endow them with exotic properties. In this context, the development of XOFs extends the boundary of crystalline porous organic materials, and may bring attracting properties as well as bright perspective for this emerging field.

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[2]

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Construction of Novel Halogen-Bonded Organic Frameworks (XOFs) Based on Iodonium-Bridged N····I<sup>+</sup>····N Interaction