Electronic Supplementary Information

Crystalline covalent organic frameworks embedded with crystalline supramolecular organic framework for efficient iodine capture

Yao Zhu, [‡a] Yue Qi, [‡b] Xinhua Guo, [b] Meicheng Zhang, [b] Zhimin Jia, [b] Chuanqin Xia, [b] Ning Liu, [d] Chiyao Bai, *[c] Lijian Ma,*[b] Qin Wang*[a]

[a] Key Laboratory of Medical Electrophysiology, Ministry of Education, School of Pharmacy, Southwest Medical University, Luzhou 646000, China. E-mail: wq_ring@hotmail.com
[b] College of Chemistry, Sichuan University, Key Laboratory of Radiation Physics & Technology, Ministry of Education, No. 29 Wangjiang Road, Chengdu, 610064, P. R. China. E-mail: ma.lj@hotmail.com
[c] Chengdu New Radiomedicine Technology CO. LTD., Chengdu, 610064, P. R. China. E-mail: baichiyao@outlook.com
[d] Institute of Nuclear Science and Technology, Sichuan University, Key Laboratory of Radiation Physics & Technology, Ministry of Education, No. 29 Wangjiang Road, Chengdu, 610064, P. R. China
‡ (Y. Zhu, Y. Qi) These authors contributed equally to this work.

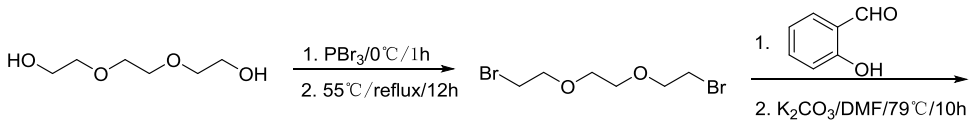
Content

Section S1. Regents.....- 2 -
Section S2. Synthesis and characterization of BBI-3:.....- 2 -
Section S3. General procedures for volatile iodine uptake and release.....- 4 -
Table S1. Single crystal diffraction conditions and cell data of BBI-3•$CHCl_3$.....- 6 -
Fig. S1 Experimental and simulated PXRD patterns of Bm-SOF.....- 7 -
Fig. S2 TG analysis of Bm-SOF, BTM and TPT-DHBD COF.....- 7 -
Fig. S4 XPS survey spectra of Bm-SOF and BTM.....- 8 -
Fig. S7 ^{1}H NMR of **b.**.....- 9 -
Fig. S8 ^{1}H NMR of BBI-3.....- 10 -
Fig. S9 ^{13}C NMR of BBI-3.....- 10 -
Fig. S10 PXRD spectra of BTM, TPT-DHBD COF and BTM.....- 11 -
Table S2. Fractional Atomic Coordinates ($\times10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2\times10^3$) for BBI-3•$CHCl_3$.....- 12 -
Table S3. Anisotropic Displacement Parameters ($Å^2\times10^3$) for BBI-3•$CHCl_3$.....- 13 -
Table S4. Bond Lengths for BBI-3•$CHCl_3$.....- 14 -
Table S5. Bond Angles for BBI-3•CHCl3.....- 15 -
Table S6. Hydrogen Atom Coordinates ($Å\times10^4$) and Isotropic Displacement Parameters ($Å^2\times10^3$) for BBI-3•$CHCl_3$.....- 16 -
Table S7. Summary of the reported adsorption capacity of iodine adsorbents.....- 17 -
References:.....- 17 -

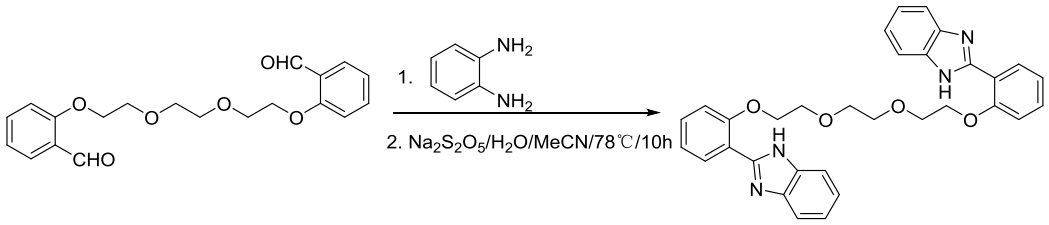
Section S1. Regents

Salicylaldehyde, Cyanuric chloride, *p*-hydroxy benzaldehyde, 3, 3 '- dihydroxy benzidine and ice acetic acid, mesitylene, dioxane, acetone, tetrahydrofuran, N, N - dimethyl formamide, ethanol, phosphorus tribromide, *o*-phenylendiamine, ethyl acetate, petroleum ether, chloroform, sodium bicarbonate, anhydrous potassium carbonate, anhydrous sodium sulfate, sodium hydroxide, deuterium dimethyl sulfoxide, acetonitrile, etc., are purchased by business and can be used without further purification.

Section S2. Synthesis and characterization of BBI-3:

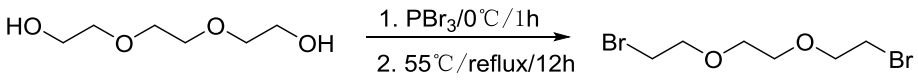


a



b **c**

1. Synthesis of **a**:

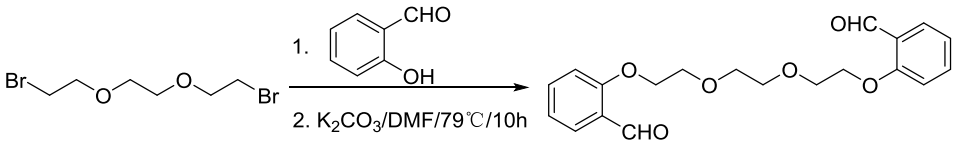


a

To a solution of triethylene glycol (24.02 g, 226.20 mmol) in $CHCl_3$ (90 mL) was added PBr_3 (40.82 g, 150.80 mmol) in 20 mL $CHCl_3$ dropwise at 0°C for 1 h and then refluxed at 55□ for 12 h. After the complete consumption of the starting material, the mixture was left to cool to room temperature and a orange paste liquid was obtained.

The reaction mixture was quenched with 40 mL of water, extracted with $CHCl_3$ (20 mL × 3). The combined organic phase was washed with saturated $NaHCO_3$ solution (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography of the residue through silica gel (petroleum ether: ethyl acetate = 10:1) gave **a** as a white solid (yield: 53.17%).

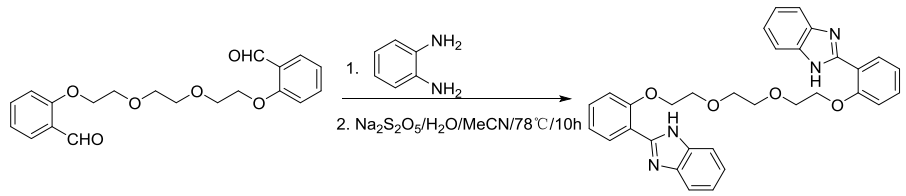
2. Synthesis of **b**:



a **b**

To a solution of K_2CO_3 (8.33 g, 60.20 mmol) and **a** (9.30 g, 40.20 mmol) in DMF (90 mL) was added salicylaldehyde (9.44 mL, 90.45 mL) in 20 mL DMF dropwise at 79℃ for 10 h. After the complete consumption of the starting material, the mixture was left to cool to room temperature and a turgid orange liquid was obtained. The turgid orange liquid was quenched with 40 mL of 10% NaOH aqueous solution, extracted with $CHCl_3$ (20 mL × 3). The combined organic phase was washed with brine (20 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography of the residue through silica gel (petroleum ether: ethyl acetate = 10:1, 3:1, 1:1) gave **b** as a white solid (yield: 87.30%). ^1H NMR (400 MHz, $CDCl_3$) δ 10.47 (dd, J = 1.6, 0.9 Hz, 1H), 7.80 – 7.72 (m, 1H), 7.52 – 7.43 (m, 1H), 7.00 – 6.91 (m, 1H), 4.19 (dt, J = 16.9, 8.6 Hz, 1H), 3.87 (dd, J = 3.2, 1.3 Hz, 1H), 3.71 (s, J = 2.2 Hz, 1H).

3. Synthesis of **c (**BBI-3):



b **c**

To a solution of $Na_2S_2O_5$ (3.39 g, 17.85 mmol) in 5 mL H_2O was added *o*-phenylenediamine (3.72 g, 34.39 mmol) in MeCN (10 mL) dropwise at 55□ for stirring 30 min. Then a solution of **b** (3.75 g, 11.90 mmol) in MeCN (30 mL) was added within 1 h, allowed the reaction mixture stirred and refluxed at 78□ for 10 h. After the complete consumption of the starting material, the mixture was left to cool to room temperature and a orange yellow liquid was obtained. The reaction mixture was quenched with 40 mL of water, extracted with $CHCl_3$ (10 mL × 3). The combined organic phase was washed with saturated $NaHCO_3$ solution (10 mL), dried over Na_2SO_4, filtered and concentrated under reduced pressure. Flash chromatography of the residue through silica gel (petroleum ether: ethyl acetate = 3:1, 1:1, 1:3) gave **c** as a light yellow solid (yield: 27.23%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (*s*, 1H), 8.39 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.87 – 7.31 (m, 2H), 7.25 (dd, *J* = 7.7, 6.2 Hz, 1H), 7.21 (*s*, 2H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.78 – 6.54 (m, 1H), 4.06 (d, *J* = 2.1 Hz, 2H), 3.96 (t, *J* = 6.9 Hz, 2H), 3.93 (dd, *J* = 3.9, 1.9 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.63 (s), 149.82 (s), 130.94 (s), 130.09 (s), 122.17 (s, J = 19.2 Hz), 118.51 (s), 112.72 (s), 77.53 – 76.99 (m), 76.99 – 76.85 (m), 76.70 (s), 70.57 (s), 69.42 (s), 67.12 (s).

Section S3. General procedures for volatile iodine uptake and release

3.1. Iodine uptake: iodine uptake experiments based on gravimetric measurements

were performed in the following procedure. 10 mg of adsorbent in an open glass Pyrex Beaker (2 mL) and 500 mg of iodine solids were place in a sealed glass vial (50 mL) and heated at 75□ and 1.0 bar using an oven. After adsorption of the iodine vapor for a while (0-48 h), the adsorbed polymer powders were cooled down to room temperature and weighted. The iodine uptake capacities for adsorbent was calculated by weight gains:

$$Cu = (W_2 - W_1) / W_1 \times 100\ wt\%,$$

Cu is the iodine uptake capacity and W_1, W_2 are the mass weight of TPT-DHBDX COFs before and after adsorbed iodine vapor.

3.2. Iodine release：Iodine release and adsorbent recycle upon heating were conducted as follows: Iodine-equilibrium absorbent was charged in anopen glass Pyrex Beaker (2 mL) in an open glass vial (50 mL) and heated at 125 □ and 1.0 bar in an oil bath. The iodine release efficiency was calculated by weight gains:

$$Er = (W_x – W_t) / W_x \times 100\ wt\%$$

Er is the iodine release efficiency and W_t is the mass weight of iodine-equilibrium absorbent after heating release (0-420 min). W_x is the iodinemass weight of absorbent.

Table S1. Single crystal diffraction conditions and cell data of BBI-3•$CHCl_3$

Empirical formula	$C_{17}H_{16}Cl_3N_2O_2$
Formula weight	386.67
Temperature/K	135.00(10)
Crystal system	cubic
Space group	Ia-3d
a/Å	35.7725(6)
b/Å	35.7725(6)
c/Å	35.7725(6)
α/°	90.00
β/°	90.00
γ/°	90.00
Volume/$Å^3$	45776.9(13)
Z	96
$\rho_{calc}mg/mm^3$	1.347
m/mm^{-1}	0.492
F(000)	19104.0
Crystal size/mm^3	0.32 × 0.29 × 0.25
2θ range for data collection	5.8 to 49.98 °
Index ranges	$-39 \leq h \leq 13$, $-31 \leq k \leq 26$, $-20 \leq l \leq 42$
Reflections collected	18217
Independent reflections	3357[R(int) = 0.0796]
Data/restraints/parameters	3357/0/225
Goodness-of-fit on F^2	1.032
Final R indexes [I>=2σ (I)]	R_1 = 0.0847, wR_2 = 0.2180
Final R indexes [all data]	R_1 = 0.1618, wR_2 = 0.2635
Largest diff. peak/hole / e $Å^{-3}$	0.48/-0.29

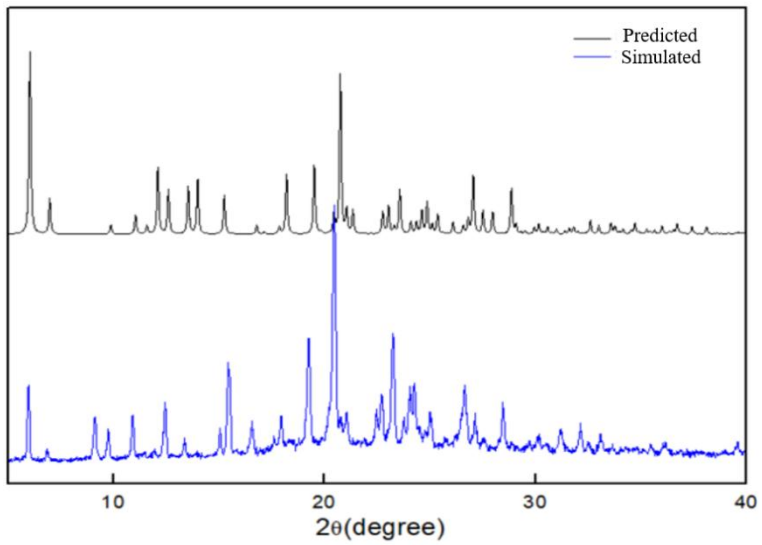


Fig. S1 Experimental and simulated PXRD patterns of Bm-SOF.

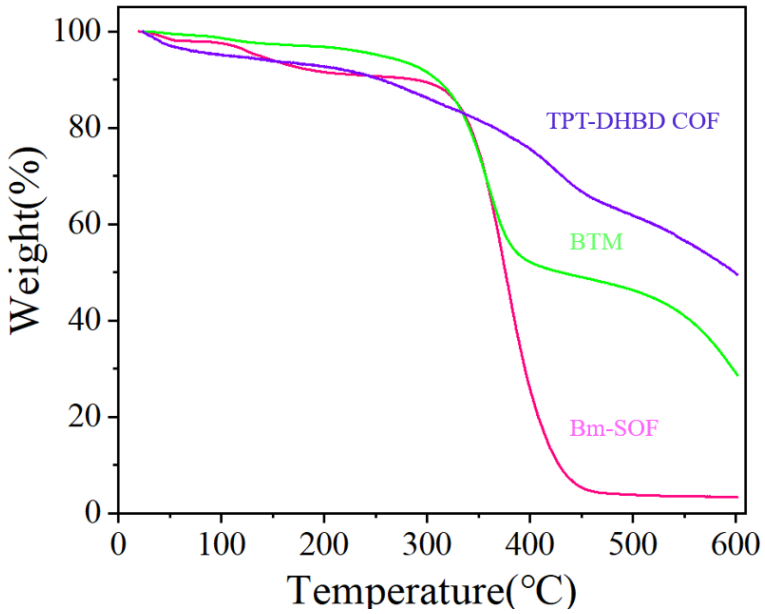


Fig. S2 TG analysis of Bm-SOF, BTM and TPT-DHBD COF.

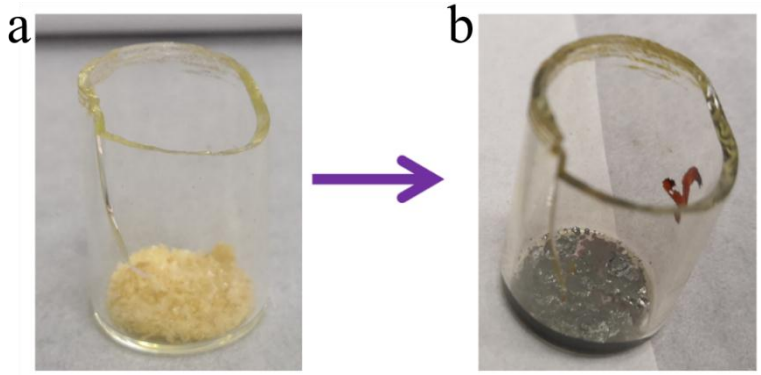


Fig. S3 Picture of Bm-SOF (a) and Bm-SOF@I_2 (b).

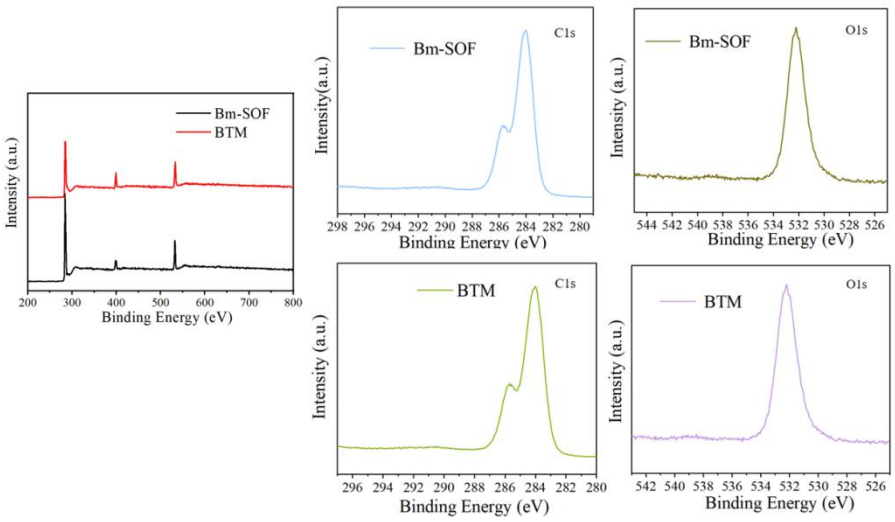


Fig. S4 XPS survey spectra of Bm-SOF and BTM.

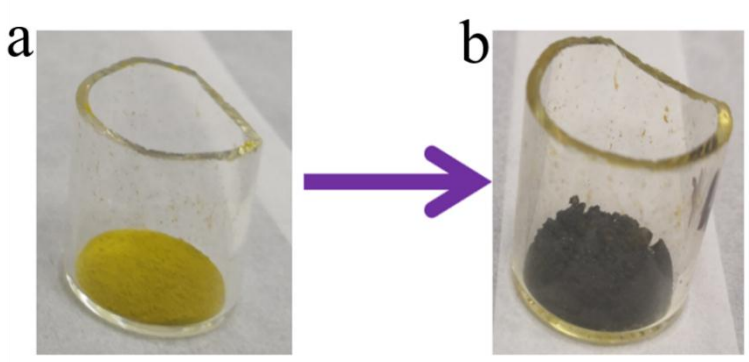


Fig. S5 Picture of BTM (a) and BTM@I_2 (b).

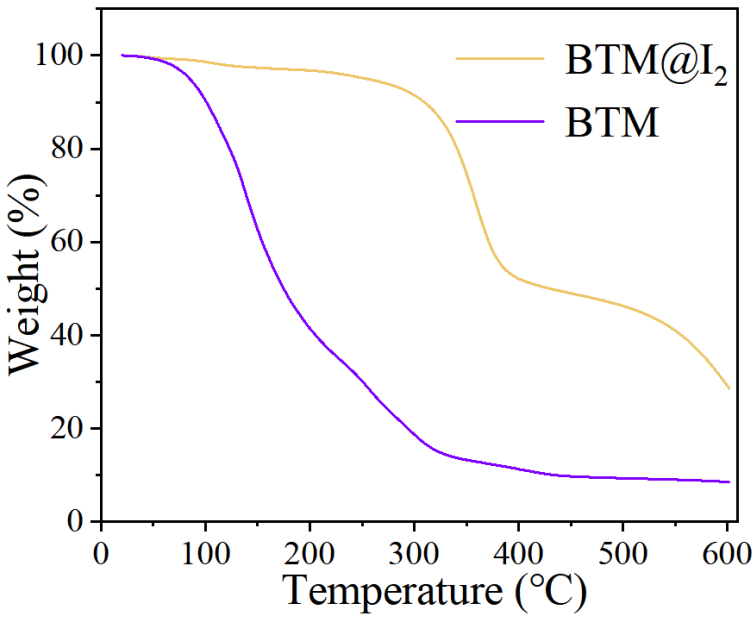


Fig. S6 TG analysis of BTM and BTM@I_2.

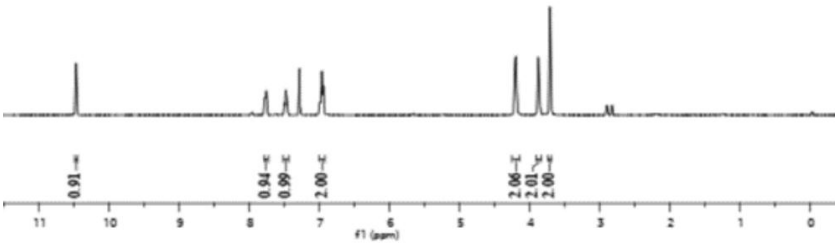


Fig. S7 ^{1}H NMR of **b.**

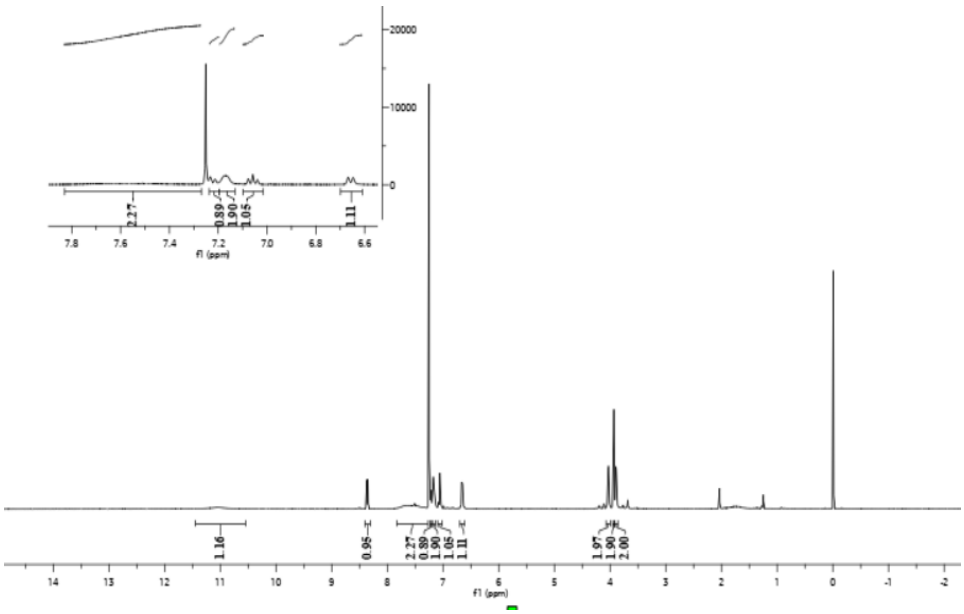


Fig. S8 ^{1}H NMR of BBI-3.

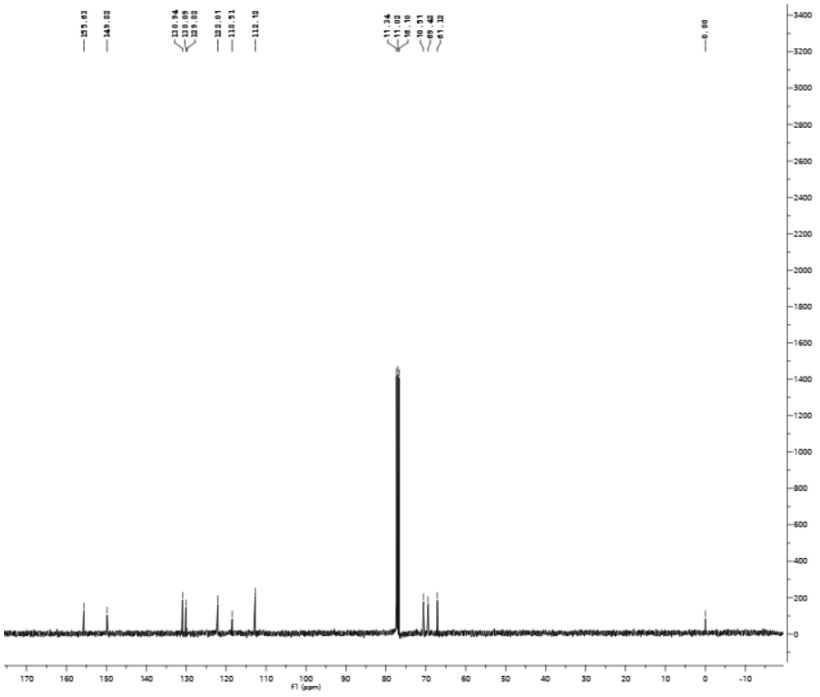


Fig. S9 ^{13}C NMR of BBI-3.

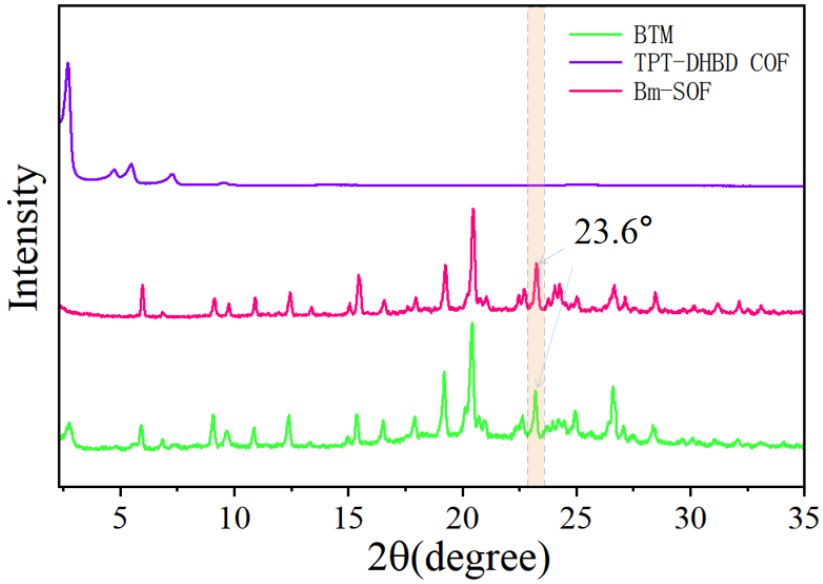


Fig. S10 PXRD spectra of BTM, TPT-DHBD COF and BTM.

Table S2. Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for BBI-3•$CHCl_3$.

Atom	*x*	*y*	*z*	U(eq)
Cl1	8688.0(5)	5105.1(5)	353.0(5)	73.1(6)
Cl2	8919.3(6)	4346.4(6)	212.4(5)	87.4(7)
Cl3	8139.3(5)	4514.3(5)	346.2(5)	76.3(6)
O1	6619.4(13)	6431.7(15)	-540.2(15)	94.5(18)
O2	7257(2)	6744(2)	-265(3)	73(2)
N1	6293.5(13)	6800.2(13)	-9.4(13)	50.6(12)
N2	5725.8(13)	6604.4(14)	160.5(14)	56.1(13)
C1	6195.7(16)	7020.9(17)	288.1(16)	52.6(15)
C2	5842.5(17)	6899.3(17)	390.5(17)	56.9(16)
C3	5653.5(19)	7066(2)	691.4(19)	71.0(19)
C4	5839.5(17)	7351(2)	881.2(19)	67.6(19)
C5	6189.2(19)	7469.8(19)	765.6(19)	68.0(19)
C6	6373.2(17)	7312.3(19)	475.1(19)	65.2(18)
C7	6003.6(17)	6554.7(17)	-73.5(18)	54.5(16)
C8	6012.5(17)	6273.2(16)	-369.9(16)	51.1(15)
C9	6319.7(18)	6204.0(17)	-606.1(18)	56.8(16)
C10	6298(2)	5943.9(19)	-886.3(19)	68.1(19)
C11	5984(3)	5748.6(19)	-951(2)	81(2)
C12	5679(2)	5804(2)	-731(2)	95(2)
C13	5692(2)	6063(2)	-429(2)	76(2)
C14	6967(2)	6364(2)	-723(2)	80(2)
C15	7215(3)	6710(3)	-660(3)	62(3)
C16	7460(3)	7081(2)	-194(2)	100(3)
C17	8562.7(19)	4683.5(18)	146.2(17)	65.0(18)
O2A	7113(6)	6881(5)	-387(6)	73(2)
C15A	7246(6)	6538(7)	-487(7)	62(3)

Table S3. Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for BBI-3•$CHCl_3$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	88.8(13)	71.8(12)	58.9(10)	-8.2(9)	-3.6(9)	4.9(9)
Cl2	94.9(14)	89.4(14)	77.8(13)	-13.3(10)	0.1(10)	32.9(11)
Cl3	95.0(14)	69.3(12)	64.7(11)	-2.8(9)	13.3(10)	4.2(10)
O1	52(3)	115(4)	116(4)	-51(3)	18(3)	6(3)
O2	76(6)	47(5)	96(6)	21(4)	9(4)	0(4)
N1	45(3)	59(3)	48(3)	2(2)	0(2)	5(2)
N2	46(3)	64(3)	58(3)	-9(3)	5(3)	-5(3)
C1	41(3)	66(4)	51(4)	5(3)	-11(3)	-3(3)
C2	51(4)	60(4)	60(4)	-2(3)	-5(3)	-8(3)
C3	58(4)	78(5)	77(5)	-17(4)	23(4)	-13(4)
C4	52(4)	87(5)	64(4)	-29(4)	9(3)	-6(4)
C5	63(4)	77(5)	64(4)	-13(4)	-6(4)	2(4)
C6	43(4)	79(5)	74(5)	-12(4)	-9(3)	-8(3)
C7	47(4)	58(4)	59(4)	6(3)	-9(3)	2(3)
C8	59(4)	54(4)	41(3)	3(3)	1(3)	-4(3)
C9	57(4)	57(4)	56(4)	2(3)	-1(3)	2(3)
C10	82(5)	64(4)	58(4)	5(4)	16(4)	20(4)
C11	114(7)	55(4)	74(5)	-6(4)	25(5)	-14(4)
C12	95(6)	91(6)	98(6)	-14(5)	14(5)	-35(5)
C13	72(5)	86(5)	71(5)	-20(4)	7(4)	-20(4)
C14	62(4)	80(5)	100(6)	3(4)	20(4)	23(4)
C15	59(5)	54(6)	72(7)	29(5)	14(5)	9(5)
C16	105(6)	92(6)	103(6)	9(4)	24(6)	-25(5)
C17	80(5)	70(4)	44(3)	5(3)	3(3)	9(4)
O2A	76(6)	47(5)	96(6)	21(4)	9(4)	0(4)
C15A	59(5)	54(6)	72(7)	29(5)	14(5)	9(5)

Table S4. Bond Lengths for BBI-3•$CHCl_3$

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C17	1.739(7)	C4	C5	1.384(9)
Cl2	C17	1.771(7)	C5	C6	1.353(9)
Cl3	C17	1.781(7)	C7	C8	1.463(8)
O1	C9	1.367(8)	C8	C9	1.408(8)
O1	C14	1.426(8)	C8	C13	1.389(8)
O2	C15	1.427(15)	C9	C10	1.370(9)
O2	C16	1.430(11)	C10	C11	1.345(10)
N1	C1	1.370(7)	C11	C12	1.360(10)
N1	C7	1.378(7)	C12	C13	1.421(10)
N2	C2	1.402(7)	C14	C15	1.539(13)
N2	C7	1.311(7)	C14	C15A	1.45(3)
C1	C2	1.386(8)	C16	$C16^{1}$	1.416(16)
C1	C6	1.392(8)	C16	O2A	1.59(2)
C2	C3	1.404(8)	O2A	C15A	1.36(3)
C3	C4	1.394(9)			

Table S5. Bond Angles for BBI-3•CHCl3

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	O1	C14	120.3(6)	O1	C9	C8	113.8(5)
C15	O2	C16	107.4(7)	O1	C9	C10	125.1(6)
C1	N1	C7	107.7(5)	C10	C9	C8	121.0(6)
C7	N2	C2	104.5(5)	C11	C10	C9	121.8(7)
N1	C1	C2	104.9(5)	C10	C11	C12	119.6(7)
N1	C1	C6	133.5(6)	C11	C12	C13	120.6(8)
C2	C1	C6	121.6(6)	C8	C13	C12	119.7(7)
N2	C2	C3	128.8(6)	O1	C14	C15	107.4(7)
C1	C2	N2	110.7(5)	O1	C14	C15A	105.1(10)
C1	C2	C3	120.6(6)	C15A	C14	C15	34.1(8)
C4	C3	C2	117.0(6)	O2	C15	C14	105.8(8)
C5	C4	C3	120.7(6)	O2	C16	O2A	31.6(6)
C6	C5	C4	122.8(6)	C16[1]	C16	O2	106.0(6)
C5	C6	C1	117.3(6)	C16[1]	C16	O2A	125.7(10)
N1	C7	C8	122.9(6)	Cl1	C17	Cl2	110.4(4)
N2	C7	N1	112.2(6)	Cl1	C17	Cl3	110.1(3)
N2	C7	C8	124.9(6)	Cl2	C17	Cl3	109.1(3)
C9	C8	C7	125.0(6)	C15A	O2A	C16	104.2(18)
C13	C8	C7	117.8(6)	O2A	C15A	C14	107.4(17)
C13	C8	C9	117.2(6)				

Table S6. Hydrogen Atom Coordinates ($Å \times 10^4$) and Isotropic Displacement Parameters ($Å^2 \times 10^3$) for BBI-3•$CHCl_3$.

Atom	*x*	*y*	*z*	U(eq)
H1	6499	6813	-134	61
H3	5415	6989	761	85
H4	5727	7462	1088	81
H5	6302	7666	893	82
H6	6609	7395	403	78
H10	6507	5901	-1036	82
H11	5974	5577	-1146	97
H12	5460	5672	-777	114
H13	5486	6091	-273	91
H14A	6927	6324	-988	96
H14B	7086	6143	-620	96
H14C	6969	6475	-971	96
H14D	7013	6098	-746	96
H15A	7457	6677	-779	74
H15B	7098	6932	-763	74
H16A	7689	7085	-338	120
H16B	7311	7297	-260	120
H16C	7681	6980	-315	120
H16D	7446	7341	-267	120
H17	8525	4723	-122	78
H15C	7289	6387	-266	74
H15D	7480	6563	-621	74

Table S7. Summary of the reported adsorption capacity of iodine adsorbents

Porous materials	Temperature (□)	Iodine uptake (g/g)	References
BisImi-POP@2	75	10.30	S1
BisImi-POP@1	75	9.50	S1
BisImi POP@4	75	6.45	S1
QTD-COF-V	75	6.29	S2
QTD-COF-3	75	5.16	S2
QTD-COF-4	75	4.85	S2
BisImi-POP@3	75	4.83	S1
QTD-COF-1	75	4.67	S2
BTM	75	4.46	This Work
BisImi-POP@6	75	3.93	S1
COP_1^0	60	3.80	S3
KOH-AC	77	3.76	S4
HCMP-3	85	3.36	S5
HCMP-2	85	3.16	S5
AzoPPN	77	2.90	S6
PAF-24	75	2.76	S7
PAF-23	75	2.71	S7
PAF-25	75	2.60	S7
Azo-Trip	77	2.38	S8
MOF-808	80	2.18	S9
NOP-54		2.02	S10
Cu-BTC	75	1.75	S11
ZIF-8	75	1.20	S12
ThSINAP-8	80	0.473	S13
JLUE-BM-SOF-3-DMSO	25	0.207	S14

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