Supporting Information

Thiol grafted Imine-Based Covalent Organic Framework for Water Remediation Through Selective Removal of Hg(II)

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- General methods. All reactions with air sensitive materials were carried out under Ar using standard Schlenk techniques. Thin-layer chromatography (TLC) was performed using pre-coated silica gel 60 F254 and developed in the indicated solvent system. Compounds were visualized under UV light ($\lambda = 254$ nm). Merck 60 (230–400 Mesh) silica gel was used for column chromatography.

¹H NMR and ¹³C NMR spectra were recorded on a 300 MHz spectrometer. Chemical shifts are reported in ppm and referenced to the residual non-deuterated solvent frequencies (CDCl₃: δ 7.26 ppm for ¹H, 77 .0 ppm for ¹³C). ¹³C cross-polarized magic angle spinning solid-state NMR (¹³C CP/MAS NMR) were recorded on a 400 MHz spectrometer Wide Bore (probe: Hv /X BB de 4 mm). The sample rotation frequency was 12 kHz and a 2.5 mm ZrO₂ rotor was used. Mass spectra were recorded by means of Matrix-Assisted Laser Desorption/Ionization-Time Of Flight (MALDI-TOF) and fast atom bombardment/electron ionization (FAB/EI) techniques. UV-vis spectra were recorded in a spectrometer for solid samples, using teflon to register the base line. Infrared spectra are reported in wavenumbers (cm⁻¹). Solids were analyzed by attenuated total reflectance (ATR) on a diamond plate or as films on sodium chloride. Elemental Analysis (EA) were obtained using LECO CHNS-932 elemental analyser.

Powder X-ray diffraction (PXRD)

Powder X-ray diffraction measurement were carried out with a PANalytical X'Pert PRO Powder system using K α ($\lambda = 1.5406$ Å) for values of 2 θ from 1° to 10° range and/or X'PERT MPD with conventional Bragg-Brentano geometry for values of 2 θ from 5° to 90°.

Thermogravimetric analysis (TGA)

Thermogravimetric analysis was performed on a TGA-Q-50 instrument on a platinum plate, heating the samples under nitrogen atmosphere at a heating rate of 10°C/min.

Scanning electron microscopy (SEM)

Scanning electron microscopy was carried out using a JOEL JSM 6335F scanning electron microscope. The sample was dispersed over a slice of conductive adhesive (graphite) adhered to a flat copper platform sample holder and then coated with gold using a sputter coater before being submitted to SEM characterization.

High Resolution Transmission Electron Microscopy (HRTEM)

High Resolution Transmission Electron Microscopy (HRTEM) images were obtained in a JEOL-JEM GRAND ARM 300cF microscope equipped with a Cs Corrector (ETA-JEOL). A precise measurement of the aberrations and an optimized correction has been done using the corrector control software JEOL COSMO. The accelerating voltage was set to 60 kV in order to minimize the sample damage. The HRTEM images were acquired by a slow-scan CCD camera (4096 x 4096 pixels, Gatan OneView Camera). Sample preparation: 1 mg of RT-COF-1AcB was sonicated in 3 mL of isopropanol: water 8:2 at 320 W and 37 kHz in a sonication bath (Elma Sonic P300H) for 30 minutes. The resulting suspension centrifuged at 1500 rpm for 5 minutes. Several drops of the suspension were casted on the TEM grids (200 mesh, copper-based holey carbon film, EMS). It should be noticed the low sample stability even when working at 60 kV.

X-ray photoelectron spectroscopy (XPS)

XPS analysis of COFs were performed on ground powders using a SPECS (Berlin, Germany) equipped with a Phoibos analyzer 150 1D-DLD and a monochromatic Al K α X-ray source (1486.6 eV). An initial analysis of all the elements present was carried (wide scan: step energy 1 eV, dwell time 0.1 s, pass energy 80 eV), then a detailed analysis was performed (detail scan: step energy 0.1 eV, dwell time 0.1 s, pass energy 30 eV) with an angle of 90° for the electrons exit. The spectra were processed by Casa XPS 2.3.16 software. Prior to the XPS measurements, the crystalline powders were pressed on copper foil, mounted on stubs, and successively put into the entry-load chamber to pump.

Analytical equipment

Analysis was carried out with a Direct Mercury Analyser (DMA-80, Milestone Srl, Italy) and/or cold vapour atomic fluorescence spectroscopy (CV-AFS). For DMA measurements controlled heating stages are implemented to first dry and then thermally decompose the sample introduced into a quartz tube. A continuous flow of air carries the decomposition products through a catalyst bed where interferences, like halogens or nitrogen/sulfur oxides, are trapped. All mercury species are reduced to elemental Hg and are then carried along to a gold amalgamator where the mercury is selectively trapped. The system is purged and the amalgamator is subsequently heated to release all mercury vapors to the single beam, fixed wavelength atomic absorption spectrophotometer. Here, absorbance measured at 253.7 nm is

proportional to mercury content in the sample (www.milestonesrl.com). A Thermo X Series 300 ICP-MS (Thermo Electron Corporation, USA) and Agilent 720 ICP-OES have been employed for multielemental analysis for polymer cross-reactivity and breakthrough experiments.

Materials

The following reagents were commercially available and were used as received: 2,5dimethoxyterephtaldehyde (**DMTA**), CuI, *o*-DCB, *n*-butanol, dithiotreitol (Clealand reagent), bis(2-dihydroxyethanol)disulfide, NaN₃ and DIPEA.

2,5-dihydroxyterephtaldehyde (**DHTA**),¹ 2,5-bis(prop-2-in-1-yloxy)terephtaldehyde (**BPTA**),² 1,3,5-Tris-(4-aminophenyl)benzene (**TAPB**),³ $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF**², bisazide 1⁴, 1-azidopropane⁵ were prepared according to reported procedures.

Hg uptake experiments

The Hg(II) uptake was performed mixing the solid sorbent with the solutions for a certain time. Filtration was then performed, and the ion concentrations in the filtrated solutions were determined using a DMA-80. The adsorptive capacity was evaluated from the difference in Hg(II) concentrations in mother and filtrated solutions. The Hg content in the sorbent was also calculated using DMA-80 for selected samples.

Selectivity test experiments

The ion uptakes from aqueous solutions with various metal ions concentrations were studied using the batch method. The metal ions involved, are used as their chloride salts. After mixing the solid sorbents with the solutions for certain time, filtration was performed, and the ion concentrations in the filtrated solutions were determined using ICP-MS HP-7700 Plus (Agilent Technologies, Analytical System, Tokyo, Japan) and Agilent 720 ICP-OES. The adsorptive capacity was evaluated from the difference encounter of ion concentrations in initial and filtrated solutions.

- Synthesis of COFs and characterization

- Synthesis of $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF:¹



Scheme S1. Synthesis of $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF.

Following the procedure previously described,¹ from **DMTA** (11.9 mg, 0.06 mmol), **BPTA** (14.5 mg, 0.06 mmol), **TAPB**² (29.1 mg, 0.08 mmol) and *o*-DCB/*n*-Butanol (2 mL/2 mL) and acetic acid (6 M, 0.4 mL) in a Pyrex vessel ($\phi = 18$ mm, h = 10 cm) were obtained, after Soxhlet extraction in THF, 27.3 mg (53%) of a yellow-greenish solid. FTIR (KBr) (cm⁻¹): 2924, 2856, 2119, 1902, 1741, 1589, 1494, 1458, 1408, 1284, 1203, 1143, 1031, 829.



Figure S1. Comparative FTIR spectra of **DMTA** (green), **BPTA** (red), **TAPB** (orange), $[HC \equiv C]_{0.5}$ -**TPB-DMT-COF** (purple).

- Larger scale synthesis of $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF:

 $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF fold x1.5: Reagents: DMTA (17.6 mg, 0.09 mmol), BPTA (21.9 mg, 0.09 mmol), TAPB (42.2 mg, 0.12 mmol), *o*-DCB/*n*-Butanol (2 mL/2 mL) and acetic acid (6 M, 0.4 mL). 50.2 mg (66% yield)

 $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF fold x4: DMTA** (46.6 mg, 0.24 mmol), **BPTA** (58.1 mg, 0.24 mmol), **TAPB** (112.5 mg, 0.32 mmol), *o*-DCB/*n*-Butanol (2 mL/2 mL), and acetic acid (6 M, 0.4 mL). 150 mg (75% yield)

 $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF fold x20** (Pyrex vessel: $\phi = 32 \text{ mm}$, h = 10 cm): **DMTA** (236 mg, 1.22 mmol), **BPTA** (297 mg, 1.23 mmol), **TAPB** (589 mg, 1.68 mmol), *o*-DCB/*n*-Butanol (10.1 mL/10.1 mL), and acetic acid (6 M, 2.1 mL) seven days at 130 °C. 795 mg (77% yield). FTIR (ATR) (cm⁻¹): 3286, 2919, 1677, 1589, 1498, 1451, 1407, 1368, 1204, 1181, 1143, 1033, 973, 923, 876, 824, 729, 691, 668, 628.



Figure S2. PXRD patterns at small-angle ranges of $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF**.

Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	FWHM (°2θ)
2.7835	31.741	100	0.1771
4.7910	18.445	4.30	0.1771
5.5694	15.868	9.75	0.1771

Table S1. PXRD at small-angle ranges of $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF**.

7.3718	11.992	3.55	0.1476
9.6841	9.133	0.53	0.1476

Table S2. PXRD of $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF**.

COF fold x20		COF fold x4			COF initial				
	Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	Роз. (°2θ)	d-spacing (Å)	Rel. Int. (%)	Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)
	5.67	15.599	100	5.66	15.606	100	5.53	15.974	100
	7.48	11.822	49.58	7.49	11.803	52.92	7.36	12.007	53.65
	9.74	9.085	13.70	9.79	9.035	14.50	9.60	9.215	18.99
	25.2	3.532	11.59	25.4	3.507	8.78	25.31	3.519	6.38

- UV-vis data of $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF and TPB-DMTP-COF-SH



Figure S3. UV-vis spectra of $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF (black) and TPB-DMTP-COF-SH (red).

- Synthesis of COFs: TPB-DMTP-COF-N₃ and TPB-DMTP-COF-SH



Scheme S2. Synthesis of TPB-DMTP-COF-SH.

- TPB-DMTP-COF-N₃:



1 g of CuI and 0.5 g of **TPB-DMTP-COF** were suspended in a mixture of THF/H₂O (26/17 mL). The suspension was purged with Argon for 5 min and then *N*,*N*-diisopropylethylamine (DIPEA) was added (0.1 mL). The mixture was purged with Argon for 5 min and toluene (5 mL) and 1.5 g of the azide **1** were added. The suspension was stirred overnight at room temperature under argon. The solid was centrifuged with 30 mL of THF. Then, it was washed with THF and acetonitrile thoroughly and dried, yielding a clear brown solid. (690 mg). FTIR (KBr) (cm⁻¹): 3031, 2925, 2860, 2363, 2102, 1592, 1498, 1460, 1410, 1286, 1208, 1147, 1038, 833. FTIR (ATR) (cm-1): 2102, 1739, 1590, 1504, 1410, 1288, 1210, 1148, 1040, 976, 877, 828, 695.

- TPB-DMTP-COF-SH:



0.5 g of **TPB-DMTP-COF-N₃** was suspended in 10 mL of THF under argon. Then, 230 mg of DTT (Dithiothreitol, Clealand reagent) and 0.5 mL of TEA (triethyl amine) were added. The mixture was stirred overnight under argon. The solid was collected by centrifugation, washed with THF and acetonitrile and dried yielding 0.34 g of a dark brown solid.

FTIR (KBr) (cm⁻¹): 3030, 2929, 1594, 1505, 1460, 1410, 1286, 1208, 1150, 1037, 831. FTIR (ATR) (cm⁻¹): 1742, 1590, 1506, 1444, 1411, 1288, 1210, 1149, 1039, 878, 828,696, 667, 632.

- Characterization of TPB-DMTP-COF-N₃ and TPB-DMTP-COF-SH



Figure S4. Comparative FTIR (ATR) spectra of $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF, TPB-DMTP-COF-N₃, TPB-DMTP-COF-SH.



Figure S5. PXRD patterns at small-angle ranges of $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF** (A), **TPB-DMTP-COF-N₃** (B) and **TPB -DMTP-COF-SH** (C).

TPB-DMTP-COF-N₃			Tł	PB-DMTP-COI	F-SH
Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)
2.7498	32.130	100	2.7714	31.879	100
4.7523	18.595	2.85	4.7694	18.528	3.07
5.5264	15.992	12.96	5.5619	15.890	11.09

Table S3. PXRD at small-angle ranges of TPB-DMTP-COF-N₃ and TPB-DMTP-COF-SH.

Table S4. PXRD of TPB-DMTP-COF-N₃ and TPB-DMTP-COF-SH.

TPB-DMTP-COF-N₃			TPB-DMTP-COF-SH			
Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	
5.6109	15.751	100	5.6107	15.752	100	
7.6053	11.624	36.19	6.5897	13.414	43.79	
8.0209	11.023	28.99	7.4170	11.920	48.32	
9.7438	9.078	28.74	9.7438	9.078	33.40	
12.2003	7.255	21.76	12.1833	7.265	27.05	
14.1865	6.243	21.21	13.2486	6.683	19.43	
18.1532	4.887	25.26	13.9450	6.351	20.19	
20.8628	4.258	18.59	18.0338	4.919	29.45	
25.2953	3.521	25.61	25.3714	3.511	21.86	



Figure S6. Comparative PXRD: (A) $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF initial (green), $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF fold x4 (red), $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF fold x20 (black); (B) $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF (black), TPB-DMTP-COF-SH (red), TPB-DMTP-COF-N₃(green), TPB-DMTP-COF-SH fold x4 (blue).

- Nitrogen Isotherm Data (Figure 2)

	BET surface area (m² g⁻¹)	Pore volume (cm ³ g ⁻¹)	Pore size (nm)
[HC≡C] _{0.5} -TPB-DMTP-COF	1510	0.94	2.53
TPB-DMTP-COF-SH	291	0.41	2.14

Table S5. BET surface area, pore volume and pore size distribution of $[HC \equiv C]_{0.5}$ - TPB -
DMTP-COF and TPB-DMTP-COF-SH



Figure S7. (1). Pore size distribution of $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF** (black) and **TPB-DMTP-COF-SH** (red).





Figure S8. UV-vis spectra of **TPB-DMTP-COF-SH** (left) and **TPB-DMTP-COF-TAZ** (right) before (red) and after Hg(II) uptake (blue).



Figure S9. Comparative UV-vis spectra of **TPB-DMTP-COF-SH** and **TPB-DMTP-COF-TAZ** before and after Hg(II) uptake.

- TGA of TPB -DMTP-COF-SH



Figure S10. TGA profile of TPB-DMTP-COF-SH.

Synthesis of TPB-DMTP-COF-TAZ



Scheme S3. Synthesis of TPB-DMTP-COF-TAZ.

34.4 mg (0.18 mmol) of CuI and 129.2 mg of $[HC \equiv C]_{0.5}$ -**TPB -DMTP-COF** were suspended in a mixture of THF/H₂O (3.9/1.7 mL). The suspension was purged with Argon for 5 min and then *N*,*N*-diisopropylethylamine (DIPEA) was added (92.7 μ L). The mixture was purged with Argon for 5 min and toluene (0.2 mL) and 60 mg of 1-azidopropane³ were added. The suspension was stirred overnight at room temperature under argon. The solid was centrifuged with 5 mL of THF. Then, it was washed thoroughly with water, THF and dried, yielding a yellow solid (166 mg). FTIR (KBr) (cm⁻¹): 2965, 2971, 1769, 1591, 1503, 1463, 1414, 1380, 1290, 1146, 1042, 877, 829, 733, 696, 607.



Figure S11. Comparative FTIR spectra of $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF**, of **TPB-DMTP-COF-N**₃, of **TPB-DMTP-COF-SH**, **TPB- DMTP-COF-TAZ**.



Figure S12. PXRD patterns of TPB-DMTP-COF-TAZ.

Small-angle range			•	Wide-angle range			
	Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	
	2.6829	32.931	100	5.6783	15.564	100	
	5.6243	15.714	9.23	7.4671	11.829	45.80	
				25.4213	3.504	18.83	

Table S6. PXRD of TPB-DMTP-COF-TAZ.

- TGA of TPB-DMTP-COF-TAZ



- Figure S13. TGA profile of TPB-DMTP-COF-TAZ.

- Kinetic Investigations

- Table S7. Kinetics investigation data of TPB-DMTP-COF-SH Hg(II) sorption under the Hg(II) initial concentration of 7.4 mg L⁻¹, V = 50 mL, m_{COF} = 25.3 mg, T = 24°C.

t (min)	[Hg] (ng)	% retention
0	7400.00	-
1.3	1186.94	83.96
2.3	976.14	86.81
4	513.47	93.06
5.3	440.90	94.04
7	385.20	94.79
10	204.76	97.23
16	71.43	99.03
30	18.91	99.74
60	9.38	99.87
120	0.04	99.99

- **Table S8.** Data for plot Kinetics of **TPB-DMTP-COF-SH** Hg(II) sorption under the Hg(II) initial concentration of 7.4 mg L⁻¹, V = 50 mL, m_{COF} = 25.3 mg, T = 24°C.

ng ads / g COF	t (min)	qt (mg ads / g COF)	t/qt (min mg g ⁻¹)	
245575.34	1.3	0.246	5.29	
253907.67	2.3	0.254	9.06	
272194.78	4.0	0.272	14.70	
275063.40	5.3	0.275	19.27	
277264.74	7.0	0.277	25.25	
284396.76	10	0.284	35.16	
289666.88	16	0.290	55.24	
291742.69	30	0.292	102.83	
292119.53	60	0.292	205.40	
292488.38	120	0.292	410.27	



Figure S14. Kinetics investigation of **TPB-DMTP-COF-SH**. Left: Hg(II) sorption under the Hg(II) initial concentration of 10 ppm / V = 1 mL / m_{COF} = 19.3 mg. Right: The pseudo-second-order kinetic plot for the adsorption (Hg(II) concentration) in **TPB-DMTP-COF-SH**.



Figure S15. PXRD pattern at small-angle ranges of TPB-DMTP-COF-SHg ([Hg(II)] = 10 mg L⁻¹).

Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	FWHM (°2θ)
2.7554	32.065	100	0.1181
4.7857	18.465	3.02	0.1476
5.5545	15.911	8.70	0.1476
7.3534	12.022	1.45	0.2362

Table S9. PXRD at small-angle ranges of TPB-DMTP-COF-SHg.

Pos. (°2θ)	d-spacing (Å)	Rel. Int. (%)	FWHM (°2θ)
5.6033	15.773	100	0.1968
7.4996	11.788	37.60	0.1574
9.7666	9.056	26.33	0.2362
12.1948	7.258	19.73	0.3149
12.9405	6.841	12.55	0.0787
14.5679	6.080	17.69	0.9446
15.0304	5.894	23.89	0.1181
18.0418	4.917	19.84	0.1574
19.4492	4.564	17.62	0.1968
25.6505	3.473	20.38	0.4723

Table S10. PXRD of TPB-DMTP-COF-SHg.



Figure S16. Comparative PXRD patterns of $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF** initial (black), **TPB-DMTP-COF-N₃** (red), **TPB-DMTP-COF-SH** (green); **TPB-DMTP-COF-SHg** (blue).

- Hg uptake capacity of TPB-DMTP-COF-SH. Langmuir and Freundlich isotherms

ng Hg loaded	[Hg] (M)	ng adsorbed	mol ads / g COF	% retention
500	2.49E-06	497	1.26E-07	99.34
1500	7.48E-06	1493	3.78E-07	99.54
6500	3.24E-05	6492	1.64E-06	99.87
16500	8.23E-05	16490	4.17E-06	99.94
53500	2.67E-04	53429	1.35E-05	99.87
127500	6.36E-04	127113	3.22E-05	99.70
312500	1.56E-03	309258	7.83E-05	98.96
682500	3.40E-03	672568	1.70E-04	98.54
1237500	6.17E-03	1208006	3.06E-04	97.62
1977500	9.86E-03	1886330	4.77E-04	95.39
7157500	3.57E-02	5634796	1.43E-03	78.73
14557500	7.26E-02	9050500	2.29E-03	62.17
51557500	2.57E-01	29077600	7.36E-03	56.40
88557500	4.41E-01	38693000	9.79E-03	43.69

Table S11. Data obtained for the adsorption isotherms of TPB-DMTP-COF-SH at rt

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(24°C).<sup>a,b</sup>
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^a V = 1 mL; m = 0.019 g of COF; Contact time: 10 min, $pH_{initial} = 5.6$, $pH_{final} = 2.5$.

^bThe ng of Hg(II) loaded are the sum of the quantity of Hg(II) adsorbed by the COF. These values are calculated in base of the Hg(II) present in the extracts after filtering off the pristine. Addition of increasing concentrated solutions of Hg(II) samples (HgCl₂) were loaded progressively into the COF until saturation of the sample.



Figure S17. Inset of the adsorbed amount of Hg(II) by TPB-DMTP-COF-SH.

- Comparative Data for the Hg(II) uptake of TPB-DMTP-COF-SH at different pHs

Table S12. Hg(II) uptake of **TPB-DMTP-COF-SH** (25 mg, V = 50 mL, 10 min, 24° C).

[Hg (II)]	рН	% Hg(II) adsorbed	% Hg(II) expelled
10 ppm/50mL	2.2	90	
	Washed (35 mL H ₂ O)/pressure)		100
10 ppm/50mL	5.5	96	
	Washed (35 mL H ₂ O/pressure)		0.4
10 ppm/50mL	12	99.99	
	Washed (35 mL H ₂ O/pressure)		0.2



Figure S18. Comparative PXRD of TPB-DMTP-COF-SHg at different pHs.

- Evaluation of the adsorbent dose of TPB-DMTP-COF-SH for Hg(II) uptake

Similar batch experiments were carried out by mixing a solution of 1 mL of a highly concentrated sample of Hg(II) (10 mg L⁻¹) with different quantities of **TPB-DMTP-COF-SH**, (2.5, 5, 7,5, 10, 12.5, 15, 20 mg). The mixture, in each case, was shaken for 10 min, the pristine was filtered off, washed with water (20 mL) and the Hg(II) concentration was measured in the extracts as usual. (Table S13)

Table S13. Hg(II) uptake as a function of the sorbent dose. Time: 10 min, [Hg(II)] = 10 mg L^{-1} .

Sorbent dose (mg)	2.5	5	7.5	10	12.5	15	20
[Hg(II)] (ppb)	602	91	70	58	25	11	1
Retention (%)	40	80	93	94	97	98.8	99.9

- Comparative Data for the Hg(II) uptake of TPB-DMTP-COF,¹ TPB-DMTP-COF-SH and TPB-DMTP-COF-TAZ



Figure S19. Structure of TPB-DMTP-COF.

ng Hg loaded	ng non retained	% retained
50	45	14

Table S15. Hg(II) uptake of TPB-DMTP-COF-SH (19.3 mg, V = 1 mL, 10 min).

ng Hg loaded	ng retained	% retained
50	48	96

Table S16. Hg(II) uptake of TPB-DMTP-COF-SH (19.3 mg, V = 50 mL, 10 min).

ng Hg loaded	% retained
10	96

Table S17. Hg(II) uptake of TPB-DMTP-COF-TAZ (19.3 mg, V = 50 mL, 10 min).

ng Hg loaded	% retained
10	50.4

- Energy Dispersive X-ray Spectroscopy (EDS) Data



Figure S20. EDS of TPB-DMTP-COF-SH before (A) and after treatment with Hg(II) (B).

- Mapping of TPB-DMTP-COF-SH



Figure S21. SEM image of the mapping zone of TPB-DMTP-COF-SH.



Figure S22. Mapping of TPB-DMTP-COF-SH; S, green, O, red, N, blue.

- Elemental Analysis

• $[HC \equiv C]_{0.5}$ -**TPB-DMTP-COF**

Calculated - C: 80.75 %, H: 4.84 %, N: 6.73 % Experimental - C: 78.33 %, H: 4.98 %, N: 6.36 % Experimental - C: 78.29 %, H: 4.97 %, N: 6.37 %

• TPB-DMTP-COF-SH

Calculated - C: 68.62 %, H: 4.96 %, N: 13.80 %, S: 6.32 % Experimental - C: 54.83 %, H: 4.48 %, N: 9.29 %, S: 5.41 % Experimental - C: 54.48 %, H: 4.47 %, N: 9.22 %, S: 5.47 %

• TPB-DMTP-COF-TAZ

Calculated - C: 73.60 %, H: 5.56 %, N: 14.31 % Experimental - C: 64.14 %, H: 4.99 %, N: 10.24 % Experimental - C: 64.58 %, H: 5.00 %, N: 10.27 % Experimental - C: 64.10 %, H: 4.91 %, N: 10.13 % - SEM images of TPB-DMTP-COF-SH and TPB-DMTP-COF-SHg



Figure S23. SEM of TPB-DMTP-COF-SH before (left) and after treatment with Hg(II) (right).



Figure S24. SEM images of TPB-DMTP-COF-SHg. ((B) image obtained by retrodispersion).

- Mappings of TPB-DMTP-COF-SHg



Figure S25. SEM image of the mapping zone of TPB-DMTP-COF-SHg.



Figure S26. Mapping of TPB-DMTP-COF-SH; S, green, Hg, orange.

- HRTEM images of TPB-DMTP-COF-SH



- TEM images of TPB-DMTP-COF-SH

Figure S27. Representative TEM-images of **TPB-DMTP-COF-SH** (a) Low magnification image confirming the laminar structure and (b) HRTEM image showing fringes of 1.6 nm periodicity, characteristic of the (200) planes in agreement to the XRD data. The corresponding FFT (Fast Fourier Transform), displayed in the inset, also confirms this description.

A sample of 25 mg of **TPB-DMTP-COF-SH** was treated with a solution of 5 mg L⁻¹ of Hg(II) (2 mL) at rt. After stirring for 10 min, the solid was filtered, washed with 10 mL of water and the extracted samples were evaluated by CV-AF. Then, the COF was treated with 2 mL of HCl (6M) for 10 min, washed with 10 mL of water and the extract contents evaluated. The same procedure was repeated for 4 cycles. The pristine was then analyzed by PXRD and the BET nitrogen isotherm calculated.

	ng Hg loaded	% Hg(II) (retained)	% removed
Cycle I	50	99.99	77
Cycle II	50	99.99	68
Cycle III	50	99.99	64
Cycle IV	50	99.99	60

Table S18. Recyclability Data. Time: 10 min.



Figure S28. PXRD pattern of TPB-DMTP-COF-SH after recycling tests



Table S19. BET surface area, pore volume and pore size distribution of TPB-DMTP-COF-
SH after the recycling tests.

Figure S29. A) N_2 adsorption isotherms: left, TPB-DMTP-COF-SH recycled; right, comparative isotherms before and after recycling. B) pore size distribution of TPB-DMTP-COF-SH after the recycling tests.

Selectivity test. Cross reactivity. TPB-DMTP-COF-SH (19.7 mg) was treated with a solution (1 mL) of 1 mg L⁻¹ of As(III), Cd(II), Pb(II), Sn(II) and Hg(II). After stirring for 10 min, the solid was filtered and the extract was evaluated by ICP-MS. The same sorbent was further treated with a solution of 100 mg L⁻¹ (1 mL) of Ca(II), Cu(II), Mg(II), Na(I) and Zn(II) and 1 mg L⁻¹ of Hg(II). Then, following the same procedure the extract content was analyzed by ICP-OES (three replicates).

Metal	⁷⁵ As	¹¹¹ Cd	¹¹⁸ Sn	²⁰² Hg	²⁰⁸ Pb
[ppb initial]	1000	1000	1000	1000	1000
[ppb] extract	806	790	30	14	508
% retention	19%	21%	97%	99%	49%
$K_d (mL/g)$	12.3	13.6	1649.7	3593.3	49.4

Table	S20.	Cross	reactivity
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Metal	λ	Concentration
	(nm)	(mg L ⁻¹)
Ca	317.933	97.921
	393.366	97.156
	396.847	97.515
	422.673	97.387
Mg	279.553	81.558
	289.800	80.996
	383.829	76.561
Na	568.821	96.122
	588.995	108.894
	589.592	103.078
Zn	206.200	92.424
	213.857	91.034
	328.233	87.160
	334 502	87 636

Table S21. Cross reactivity DATA by ICP-OES.

- Breakthrough experiments

Breakthrough experiments were performed on a real matrix, using seawater (obtained from the Mediterranean Sea, Benidorm, Spain, pH = 7.8). Thus, two similar experiments were performed. Firstly, with a solution containing an equimolar mixture (1 mg L⁻¹) of Cu(II), Zn(II), As(III), Cd(II), Pb(II), Sn(II) and Hg(II) (Figure S30A). Then, using a high concentrated sample (100 mg L⁻¹) of the same metals (with the exception of Zn(II)) and 1 mg L⁻¹ of Hg(II). (Figure S30B).



Figure S30. Adsorption selectivity test of **TPB-DMTP-COF-SH** in seawater in the presence of ions: A) Cu(II), Zn(II), As(III), Cd(II), Pb(II), Sn(II) Hg(II) (equimolar concentration, 1 mg L⁻¹). B) Zn(II), As(III), Cd(II), Pb(II), Sn(II) (equimolar concentration, 100 mg L⁻¹) *vs* Hg(II) (1 mg L⁻¹).

- XPS spectra



Figure S31. XPS of Hg for TPB-DMTP-COF-SHg.



Figure S32. XPS of N 1s and O 1s for TPB-DMTP-COF-SH, TPB-DMTP-COF-SHg and TPB-DMTP-COF-TAZHg.



Figure S33. ¹³C CP/MAS NMR of $[HC \equiv C]_{0.5}$ -TPB-DMTP-COF.



Figure S34. ¹³C CP/MAS NMR of TPB-DMTP-COF-SH.



Figure S35. Comparative ¹³C CP/MAS NMR of TPB-DMTP-COF-SH (red) and TPB-DMTP-COF-SH (red) and TPB-DMTP-COF-SHg (blue).



Figure S36. Comparative FTIR TPB-DMTP-COF-SH (blue) and TPB-DMTP-COF-SHg (red).



Figure S37. ¹³C CP/MAS NMR TPB-DMTP-COF-TAZ (a) and TPB-DMTP-COF-TAZHg (b).

- ¹H NMR, ¹³C NMR and FTIR spectra of starting materials



FTIR **DHTA**



1 H NMR **BPTA**





- 4.85

¹³C NMR **BPTA**





FTIR 1,3,5-Tris-(4-nitrophenyl)benzene:





FTIR TAPB





FTIR Bisazide 1



FTIR (ATR) of **TPB-DMTP-COF**



FTIR (ATR) of TPB-DMTP-COF-N₃



FTIR (ATR) of **TPB-DMTP-COF-SH**



FTIR (ATR) of **TPB-DMTP-COF-TAZ**



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