Supporting Information

Chemical Warfare Agents Detoxification Properties of Zirconium Metal-Organic Frameworks by Synergistic Incorporation of Nucleophilic and Basic Sites

Rodrigo Gil-San-Millan[a], Elena López-Maya[a], Morgan Hall[b], Natalia M. Padial[c], Gregory W. Peterson[b], Jared B. DeCoste[b], L. Marleny Rodríguez-Albelo[a], J. Enrique Oltra[c], Elisa Barea[a] and Jorge A. R. Navarro[a*]

[a] *Departamento de Química Inorgánica, Universidad de Granada*
Av. Fuentenueva S/N, 18071, Granada, Spain
**e-mail: jarn@ugr.es*

[b] *Edgewood Chemical Biological Center*
Aberdeen Proving Ground, MD 21010, United States

[c] *Departamento de Química Orgánica, Universidad de Granada*
Av. Fuentenueva S/N, 18071, Granada, Spain

General methods

All the general reagents and solvents were commercially available and used as received. XRPD data were obtained on a D2 PHASER Bruker diffractometer using CuKα radiation (λ = 1.5418 Å) by means of a scan in the 5-35° 2θ range with 0.05° steps. The compounds were manually grounded in an agate mortar and then deposited in the hollow of a zero-background silicon sample holder. N_2 adsorption isotherms were measured at 77 K on a Micromeritics Tristar 3000 volumetric instrument. Prior to measurement, powder samples were heated 7 h at 423 K and outgassed to 10^{-1} Pa. In order to determine the amount of organic material of the MOF materials, CHN Elemental and Thermogravimetric Analysis were carried out, by a FLASH 2000 CHNS/O Analyzer and a METTLER-TOLEDO mod. TGA/DSC1 system, respectively.

Synthesis of the materials

A. UiO-66 Materials

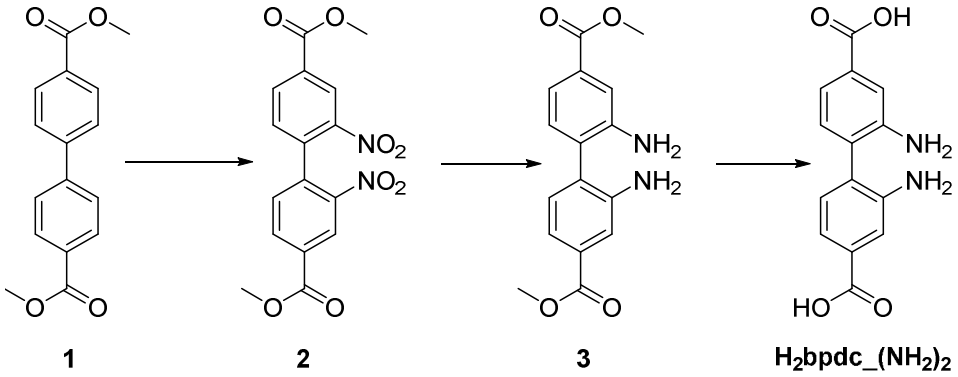
Synthesis of UiO-66. $[Zr_6O_4(OH)_4(bdc)_6]$ (bdc = benzene-1,4-dicarboxylate) named as **UiO-66** sample was prepared according to a method reported in literature.[1]

Synthesis of UiO-66 materials with H_2bdc_NH_2 ligands UiO-66-xNH_2 (x= 0.25, 0.5, 0.75, 1): UiO-66-xNH_2. Different mixtures of H_2bdc_NH_2 and H_2bdc ligands (1.33 mmol), with variable molar ratio (0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0, respectively), and $ZrCl_4$ (318 mg, 1.33 mmol) were dissolved in 60 mL of DMF. Then 0.6 mL of HCl and 0.6 mL of TFA were added. The reactions were carried out under solvothermal conditions (393K, 24h), where a microcrystalline powder was obtained. In order to calculate the amount of H_2bdc_NH_2 and H_2bdc ligands in these materials, 10 mg of MOF were suspended in 1 mL of NaOH 2M (D_2O) overnight; then the suspension was filtered and ^{1}H NMR spectrum of liquid phase was recorded in D_2O. (*Note: we consider equal solubility of H_2bdc_NH_2 and H_2bdc ligands).*

Incorporation of LiO^tBu in UiO-66-xNH_2: UiO-66-xNH_2@LiO^tBu. The samples **UiO-66-xNH_2@LiO^tBu** were prepared following a method inspired in the one reported by our group,[2] in order to obtain certain degree of crystallinity on every modified MOF. 100 mg of UiO-66-xNH_2 precursor were suspended in 5 mL of LiO^tBu/THF 1M, and stirred at ambient temperature for 30 minutes, under Ar atmosphere. The obtained product was washed three times with THF and stored under Ar atmosphere.

B. UiO-67 Materials

B.1 Synthesis of $H_2bpdc\_(NH_2)_2$



Scheme S1. Synthesis of 2,2'-diamino-[1,1'-biphenyl]-4,4'-dicarboxylic acid.

Synthesis of dimethyl-2,2'-dinitro-[1,1'-biphenyl]-4,4'-dicarboxylate (2):

To a solution of commercial dimethyl-biphenyl-4,4´-dicarboxylate (10 g, 37 mmol) in 100 mL of concentrated H_2SO_4 at 288-293 K, a mixture of nitric acid (56%, 12 mL, 74 mmol) in 15 mL of concentrated sulfuric acid was added dropwise. The reaction mixture was stirred vigorously for 2 h at 288-293 K and then was carefully poured on ice (300 g). The pale yellow precipitated was filtered, washed with abundant cold water until neutral pH and air-dried to obtain 10.5 g of **2** (yield: 85.7 %). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.90 (s, 2H), 8.37 (dd, J = 7.9, 1.7 Hz, 2H), 7.41 (d, J = 7.9 Hz, 2H), 4.03 (s, 6H). ^{13}C NMR (125MHz, $CDCl_3$, DEPT) δ: 164.5 (C), 146.9 (C), 137.6 (C), 134.2 (CH), 131.9 (C), 130.9 (CH), 126.1 (CH), 52.9 (CH_3). HRMS (TOF MS ES$^+$) Calc. for $C_{16}H_{13}N_2O_8$: 361.0671, found 361.0667.

Synthesis of dimethyl 2,2'-diamino-[1,1'-biphenyl]-4,4'-dicarboxylate (3):

A 250-mL three-necked round-bottomed flask was charged with 3.2 g of 5% Pd/C, 5 g of **2** (13.8 mmol) and 165 mL of THF. Then, hydrogen was bubbled and the mixture was stirred overnight at room temperature under hydrogen atmosphere. After filtration over Celite, the solvent was removed in vacuo affording 3.7g.

5 g (90.6 %) of product **3** isolated as a light yellow solid. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.52 – 7.045 (m, 4H), 7.17 (d, J = 7.8 Hz, 2H), 3.92 (s, 6H).^{13}C NMR (125 MHz, $CDCl_3$, DEPT) δ: 167.0 (C), 144.0 (C), 130.9 (C), 130.8 (CH), 128.0 (C), 119.8 (CH), 116.6 (CH), 52.1 (CH_3). HRMS (TOF MS ES$^+$) Calc. for $C_{16}H_{17}N_2O_4$: 301.1188, found 301.1184.

Synthesis of 2,2'-diamino-[1,1'-biphenyl]-4,4'-dicarboxylic acid ($H_2bpdc\_(NH_2)_2$):

Compound **3** (3.75 g, 12.5 mmol) was dissolved in a mixture of 50:50 v/v THF/5% KOH (total volume 200 mL). The mixture was stirred overnight at 353 K. The aqueous layer was separated,

then concentrated HCl was added until acid pH to give a yellowish solid. The solid was filtered, washed with abundant cold water and air-dried to obtain the desired product (3.33 g, 12.25 mmol, 98%). ^{1}H NMR (400 MHz, DMSO-d_6) δ: 7.46 (d, J = 1.3 Hz, 2H), 7.27 (dd, J = 7.8, 1.3 Hz, 2H), 7.08 (d, J = 7.8 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6, DEPT) δ: 167.9 (C), 144.6 (C), 131.4 (CH), 131.2 (C), 128.5 (C), 118.9 (CH), 117.3 (CH). HRMS (TOF MS ES$^+$) Calc. for $C_{14}H_{13}N_2O_4$: 273.0875, found 273.0879.

B.2 UiO-67 Materials

Synthesis of UiO-67. [$Zr_6O_4(OH)_4$(bpdc_$NH_2)_6$] (bpdc = 4,4-biphenyl-dicarboxilylate) named as **UiO-67** sample was prepared according to a method reported in literature.[1]

Synthesis of UiO-67 materials with H_2bpdc_$(NH_2)_2$ ligands UiO-67- x$(NH_2)_2$ (x = 0.25, 0.5, 0.75, 1): UiO-67- x$(NH_2)_2$. Different mixtures of H_2bpdc_$(NH_2)_2$ and H_2bpdc ligands (1.33 mmol), with variable molar ratio (0.25:0.75, 0.5:0.5, 0.75:0.25 and 1:0, respectively), and $ZrCl_4$ (318 mg, 1.33 mmol) were dissolved in 60 mL of DMF. Then 0.6 mL of TFA and 0.6 mL of HCl were added. The reactions were carried out under solvothermal conditions (393 K, 24h), where a microcrystalline powder was obtained. In order to calculate the amount of H_2bpdc_NH_2 and H_2bpdc ligands in these materials, 10 mg of MOF were suspended in 1 mL of NaOH 2M (D_2O) overnight; then the suspension was filtered and ^{1}H NMR spectrum of liquid phase was recorded in D_2O. (*Note: we considered equal solubility of H_2bpdc_NH_2 and H_2bpdc ligands).*

Incorporation of LiO^tBu in UiO-67-x$(NH_2)_2$: UiO-67-x$(NH_2)_2$@LiO^tBu. The samples **UiO-67-x$(NH_2)_2$@LiO^tBu** were prepared following a method inspired in the one reported by our group[2], in order to obtain certain degree of crystallinity on every modified MOF. 100 mg of UiO-67-x$(NH_2)_2$ precursor were suspended in 5 mL of LiO^tBu/THF 1M, and stirred at ambient temperature for 30 minutes, under Ar atmosphere. The obtained product was washed three times with THF and stored under Ar atmosphere.

Thermogravimetrical Analysis

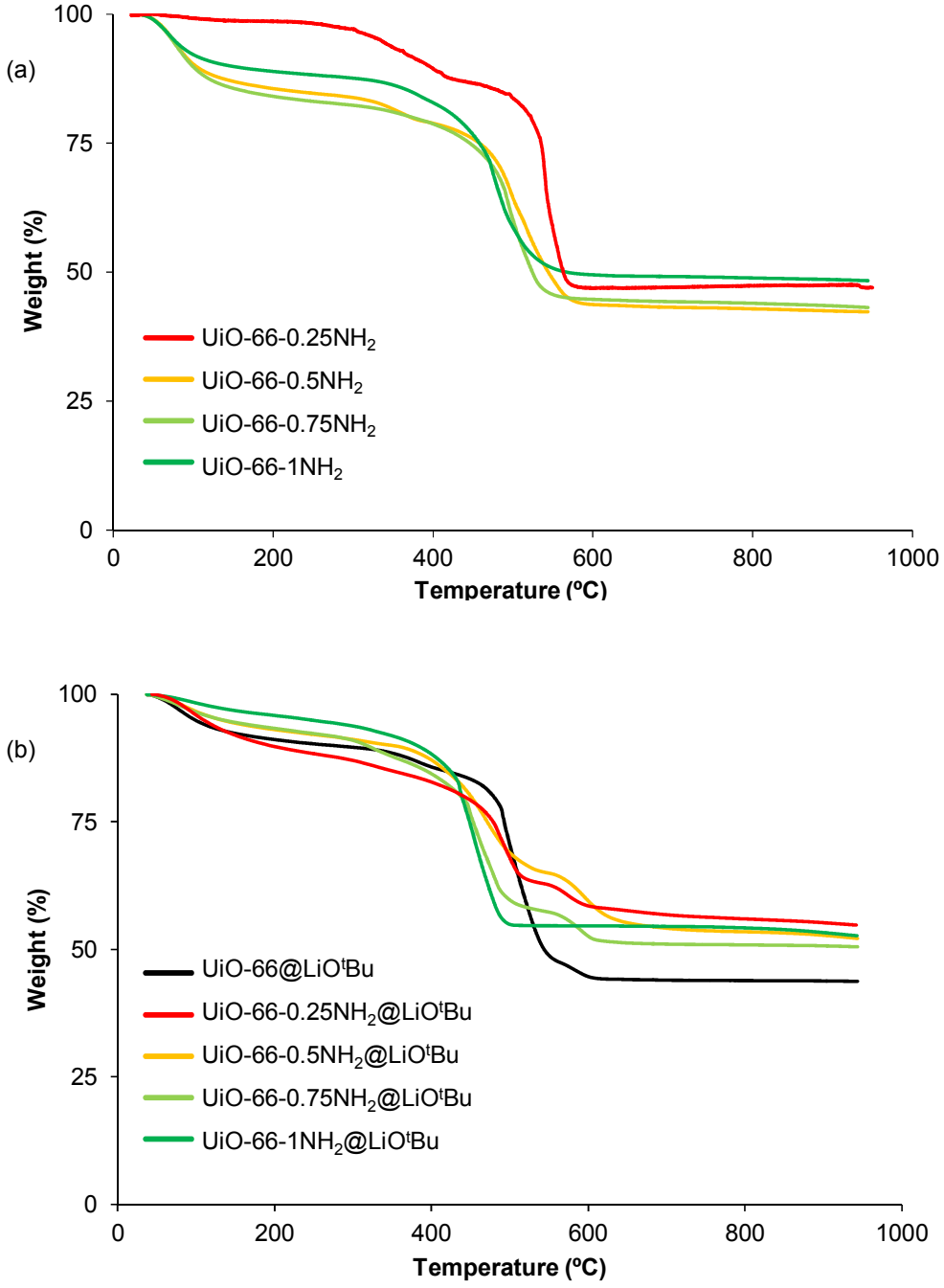


Figure S1. TGA plots of (a) **UiO-66-xNH$_2$** and (b) **UiO-66-xNH$_2$@LiO^{t}Bu** materials

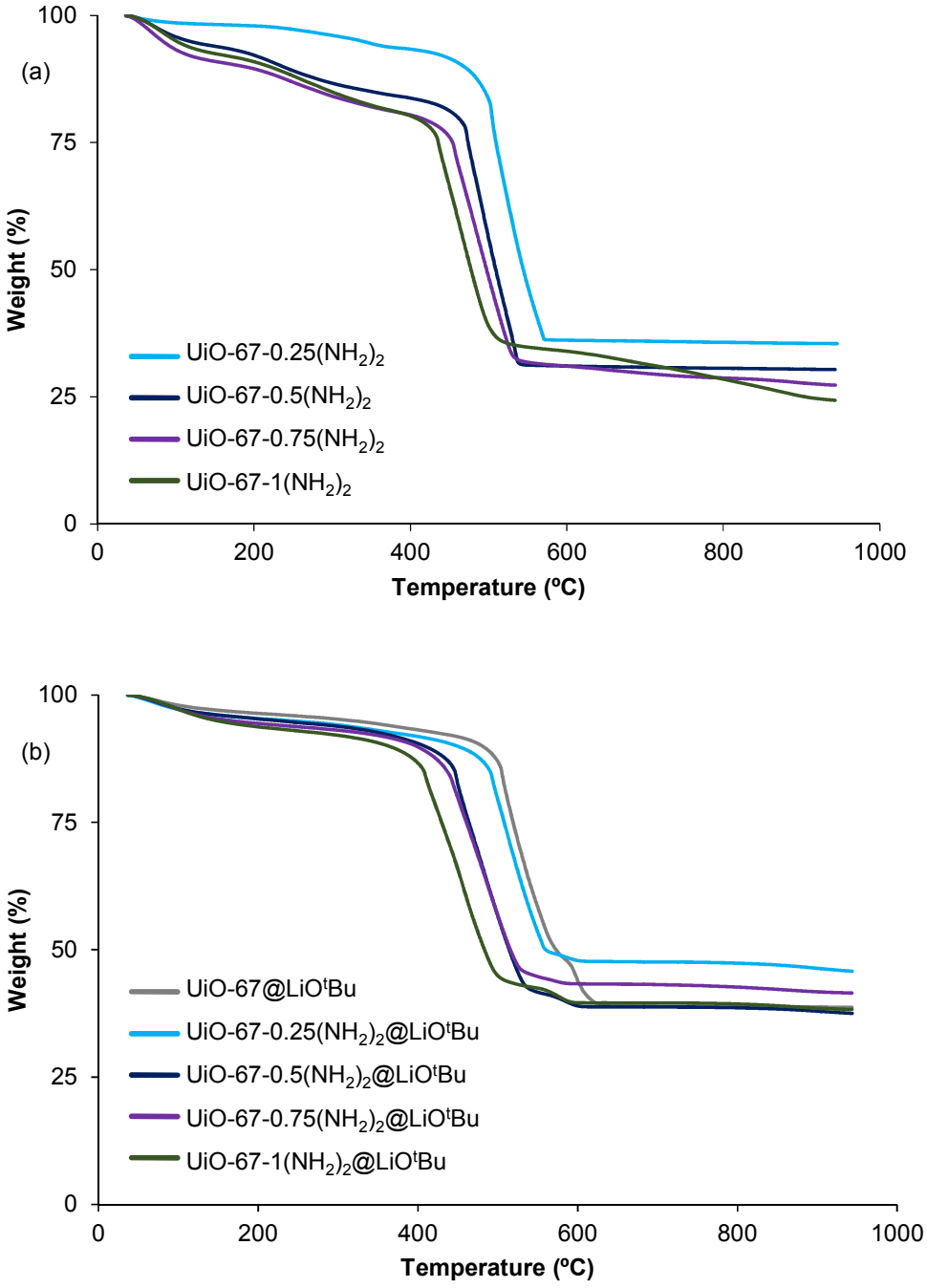


Figure S2. TGA plots of (a) **UiO-67-x(NH_2)$_2$** and (b) **UiO-67-x(NH_2)$_2$@LiO^{t}Bu** materials

Elemental Analysis

A. UiO-66 materials

A.1 UiO-66-xNH_2 materials

A.1 UiO-66-xNH_2 materials

Elemental Analysis calc. for **UiO-66-0.25NH_2**:

Calculated for **[$Zr_6O_4(OH)_4(C_2O_2F_3)_2(C_8H_4O_4)_{3.75}(C_8H_5NO_4)_{1.25}(H_2O)_{12}$]**

(MW = 1960.9 g mol^{-1}): %C: 26.95; H: 2.53; N: 0.89; Found: C, 26.79; H, 2.13; N, 1.00.

^{1}H NMR (300 MHz, D_2O): 22% H_2bdc-NH_2, 78% H_2bdc.

Elemental Analysis calc. for **UiO-66-0.5NH_2:**

[$Zr_6O_4(OH)_4(C_2O_2F_3)_4(C_8H_4O_4)_{1.8}(C_8H_5NO_4)_{2.2}(H_2O)_{17}$]

(MW = 2127.17 g mol^{-1}): %C, 22.58; H, 2.66; N, 1.44; Found: C, 22.00; H, 2.23; N, 1.64.

^{1}H NMR (300 MHz, D_2O): 56% H_2bdc-NH_2, 44% H_2bdc.

Elemental Analysis calc. for **UiO-66-0.75NH_2:**

[$Zr_6O_4(OH)_4(C_2O_2F_3)_5(C_8H_4O_4)_{0.5}(C_8H_5NO_4)_3(H_2O)_{13}$]

(MW = 2098.09 g mol^{-1}): %C: 21.75; H: 2.25; N: 2.00; Found: C, 21.32; H, 2.14; N, 2.58

^{1}H NMR (300 MHz, D_2O): 80% H_2bdc-NH_2, 20% H_2bdc.

Elemental Analysis calc. for **UiO-66-1NH_2:**

[$Zr_6O_4(OH)_4(C_2O_2F_3)_{5.5}(C_8H_5NO_4)_{3.25}(H_2O)_9$]

(MW = 2045 g mol^{-1}): %C: 21.72; H: 1.89; N: 2.23; Found: C, 21.22 ; H, 1.81; N, 3.05.

A.2 UiO-66-xNH_2@LiO^tBu materials

Elemental Analysis calc. for **UiO-66@LiO^tBu:**

[$Zr_6O_4(OH)_8(C_8H_4O_4)_4(LiOC_4H_9)_{0.35}(C_3H_7NO)_{0.2}(H_2O)_3$]

(MW = 1500,54 g mol^{-1}): % C, 27.24; H, 2.32; N, 0.18; Found: C, 27.46; H, 2.65; N, 0.21.

Elemental Analysis calc. for **UiO-66-0.25NH_2@LiO^tBu:**

[$Zr_6O_6(OH)(C_2O_2F_3)_2(C_8H_4O_4)_{1.7}(C_8H_5NO_4)_{0.8}(LiOC_4H_9)_{0.25}(H_2O)_5$]

(MW = 1294.78 g mol^{-1}): %C, 19.48; H, 2,34; N, 0.87; Found: C, 19.01; H, 1.84; N, 0.90.

Elemental Analysis calc. for **UiO-66-0.5NH_2@LiO^tBu:**

[$Zr_6O_6(OH)_6(C_8H_4O_4)_{1.5}(C_8H_5NO_4)_{1.5}(LiOC_4H_9)_{0.3}(H_2O)_5$

(MW = 1374,34 g mol^{-1}): %C, 21.36; H, 2.04; N, 1.61; Found: C, 21.57; H, 1.95; N, 1.55.
Calculated residual oxides $(ZrO_2)_{8.5}(Li_2O)_{0.25}$ 55.69%; from TGA: 54.28%

Elemental Analysis calc. for **UiO-66-0.75NH$_2$@LiO^{t}Bu:**
$[Zr_6O_6(OH)_6(C_8H_4O_4)_{0.75}(C_8H_5NO_4)_{2.25}(LiOC_4H_9)_{0.3}(H_2O)_3]$
(MW = 1349.57 g mol^{-1}): %C, 22.42; H, 2.16; N, 2.33; Found: C, 22.91; H, 2.33; N, 2.38.
Elemental Analysis calc. for **UiO-66-1NH$_2$@LiO^{t}Bu:**
$[Zr_6O_6(OH)_5(C_8H_5NO_4)_{3.5}(LiOC_4H_9)_{0.3}(H_2O)_7$
(MW = 1505,45 g mol^{-1}): %C, 23.29; H, 2.62; N, 3.26; Found: C, 23.09; H, 2.55; N, 3.41.

B. UiO-67 materials

B.1 UiO-67-x(NH$_2$)$_2$ materials

Elemental Analysis calc. for **UiO-67:**
$[Zr_6O_4(OH)_4(C_2F_3O_2)_{0.4}(C_{14}H_8O_4)_{5.8}](H_2O)_6(C_4H_8O)_2$
(MW = 2370.1g mol^{-1}): %C, 45.6; H, 3.33; Found: C, 45.65; H, 3.17.
Calculated residual oxides $(ZrO_2)_6$: 31.19%

Elemental Analysis calc. for **UiO-67-0.25(NH$_2$)$_2$:**
$[Zr_6O_4(OH)_4(C_2F_3O_2)_2Cl(C_{14}H_8O_4)_{3.5}(C_{14}H_{10}N_2O_4)_1](H_2O)_8(C_3H_7NO)_{0.5}(ZrO_2)_{0.2}$
(MW = 2257.14 g mol^{-1}): % C: 36.45; H: 2.74 ; N: 1.55; Found: C, 36.7; H, 2.92; N, 1.57.
Calculated residual oxides $(ZrO_2)_{6.2}$: 33.84%; from TGA: 35.45%
^{1}H NMR (300 MHz, D_2O): 78% H_2bpdc, 22% H_2bpdc-$(NH_2)_2$.

Elemental Analysis calc. for **UiO-67-0.5(NH$_2$)$_2$:**
$[Zr_6O_4(OH)_4(C_2F_3O_2)Cl(C_{14}H_8O_4)_{3.5}(C_{14}H_{10}N_2O_4)_2](H_2O)_{10}(C_3H_7NO)$
(MW = 2462.3g mol^{-1}): %C: 40; H: 3.23; N: 2.85; Found: C, 40.40; H, 3.35; N, 3.09.
Calculated residual oxides $(ZrO_2)_{6.2}$: 30.02%; from TGA: 30.41%
^{1}H NMR (300 MHz, D_2O): 62% H_2bpdc, 38% H_2bpdc-$(NH_2)_2$.

Elemental Analysis calc. for **UiO-67-0.75(NH$_2$)$_2$:**
$[Zr_6O_4(OH)_4(C_2F_3O_2)_{0.6}(C_{14}H_8O_4)_{1.2}(C_{14}H_{10}N_2O_4)_{4.5}](H_2O)_{18}$
(MW = 2575.79 g mol^{-1}): %C: 37.76; H: 3.70; N: 4.89; Found: C, 37.63; H, 3.67; N, 4.63.
Calculated residual oxides $(ZrO_2)_6$: 28.7%; from TGA: 27.8%
^{1}H NMR (300 MHz, D_2O): 17% H_2bpdc, 83% H_2bpdc-$(NH_2)_2$.

Elemental Analysis calc. for **UiO-67-1(NH$_2$)$_2$:**

$[Zr_6O_4(OH)_4(C_2F_3O_2)_{1.2}(C_{14}H_{10}N_2O_4)_{5.4}](H_2O)_{18}$

(MW = 2598.56 g mol^{-1}): %C: 36.05; H: 3.64; N: 5.82; Found: C, 36.01; H, 3.88; N, 6.02.

Calculated residual oxides $(ZrO_2)_6$: 28.45%; from TGA: 28.8%

B.2 UiO-67-x$(NH_2)_2$@LiO^{t}Bu materials

Elemental Analysis calc. for **UiO-67@LiO^{t}Bu:**

$[Zr_6O_6(OH)(C_{14}H_8O_4)_{5.5}(LiOC_4H_9)_{0.5}](H_2O)_6(C_4H_8O)_{0.5}(ZrO_2)_2$

(MW = 2412.12 g mol^{-1}): %C, 40.33; H, 2.74; Found: C, 39.97; H, 2.93.

Calculated residual oxides $(ZrO_2)_8(Li_2O)_{0.25}$: 41.17%; from TGA: 39.22%

Elemental Analysis calc. for **UiO-67-0.25$(NH_2)_2$@LiO^{t}Bu:**

$[Zr_6O_6(OH)_{2.6}Cl(C_{14}H_8O_4)_{3.5}(C_{14}H_{10}N_2O_4)_{0.7}(LiOC_4H_9)_{0.5}](H_2O)_{5.4}(ZrO_2)_3$

(MW = 2259.5 g mol^{-1}): %C, 32.31; H, 2.36; N, 0.86; Found: C, 32.71; H, 2.36; N, 0.71.

Calculated residual oxides $(ZrO_2)_9(Li_2O)_{0.25}$: 49.41%; from TGA: 47.83%

Elemental Analysis calc. for **UiO-67-0.5$(NH_2)_2$@LiO^{t}Bu:**

$[Zr_6O_6Cl(C_{14}H_8O_4)_{3.5}(C_{14}H_{10}N_2O_4)_2(LiOC_4H_9)_{0.3}](H_2O)_8(ZrO_2)_{2.2}$

(MW = 2499.24 g mol^{-1}): %C, 37.58; H, 2.69; N, 2.24; Found: C, 37.23; H, 2.61; N, 2.33.

Calculated residual oxides $(ZrO_2)_{8.2}(Li_2O)_{0.15}$: 40.6%; from TGA: 41.2%

Elemental Analysis calc. for **UiO-67-0.75$(NH_2)_2$@LiO^{t}Bu:**

$[Zr_6O_6(OH)_3(C_{14}H_8O_4)_{1.2}(C_{14}H_{10}N_2O_4)_{3.3}(LiOC_4H_9)_{0.5}](H_2O)_5(C_4H_8O)_{0.5}(ZrO_2)_4$

(MW = 2533.45 g mol^{-1}): %C, 31.76; H, 2.55; N, 3.64; Found: C, 31.76; H, 2.29; N, 3.45.

Calculated residual oxides $(ZrO_2)_{10}(Li_2O)_{0.25}$: 48.93%; from TGA: 46.85%

Elemental Analysis calc. for **UiO-67-1$(NH_2)_2$@LiO^{t}Bu:**

$[Zr_6O_6(OH)_{2.4}(C_{14}H_{10}N_2O_4)_{4.8}(LiOC_4H_9)_{0.5}](H_2O)_2(ZrO_2)_{3.5}$

(MW = 2488.64g mol^{-1}): %C, 33.40; H, 2.38; N, 5.40; Found: C, 33.75; H, 2.31; N, 5.26.

Calculated residual oxides $(ZrO_2)_{9.5}(Li_2O)_{0.25}$: 47.33%; from TGA: 47.08%

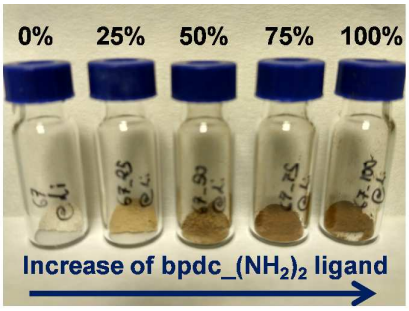


Figure S3. Picture of **UiO-67-x(NH_2)$_2$@LiO^{t}Bu** materials prepared in this work, showing the variation of brownish color with increasing amounts of amino-ligand.

Powder X-Ray Diffraction

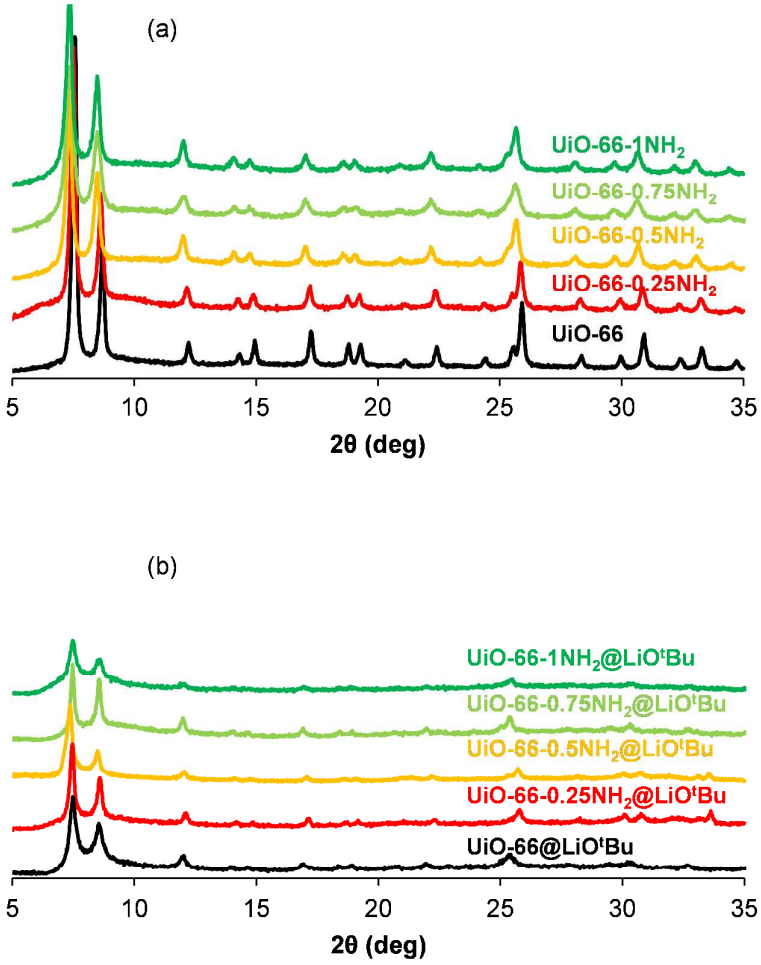


Figure S4. XRPDs for (a) **UiO-66-xNH$_2$** materials, and (b) **UiO-66-xNH$_2$@LiO^{t}Bu** materials.

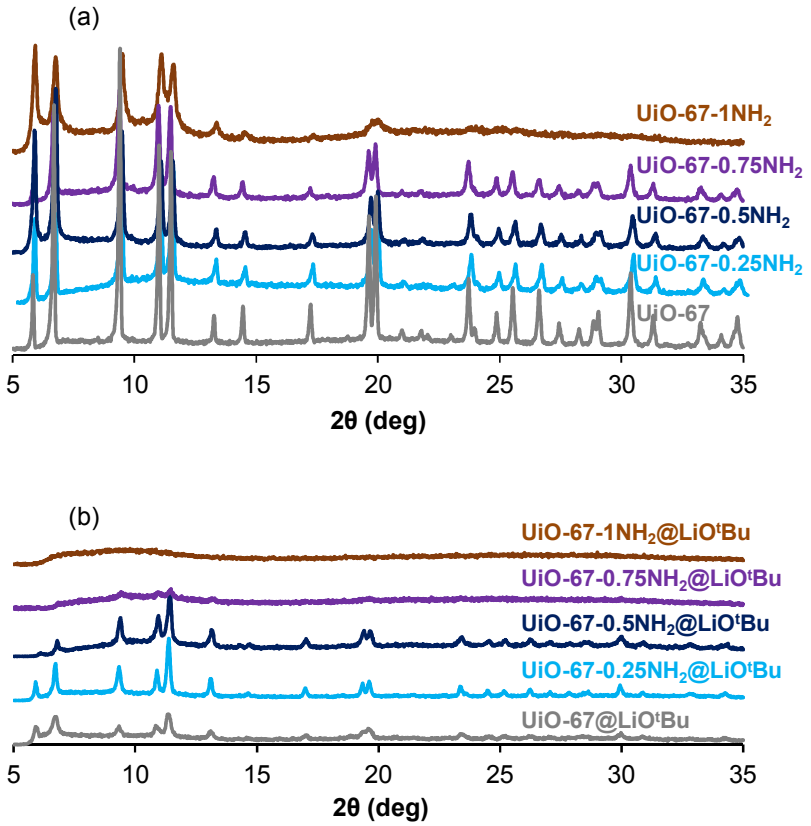
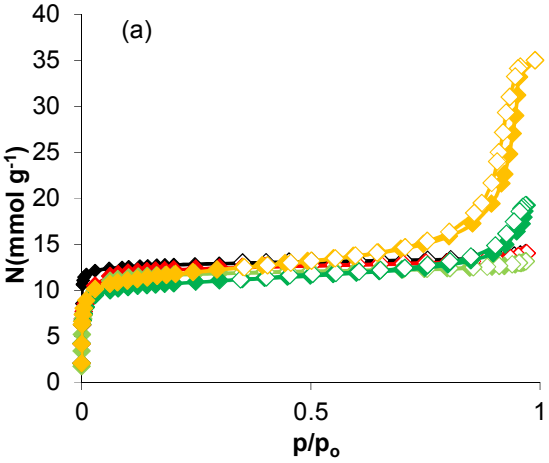
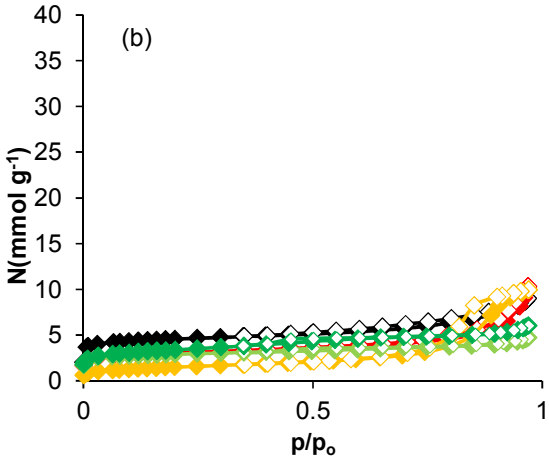


Figure S5. XRPDs for (a) **UiO-67-x(NH_2)$_2$** materials, and (b) **UiO-67-x(NH_2)$_2$@LiO^tBu** materials.

Gas adsorption measurements

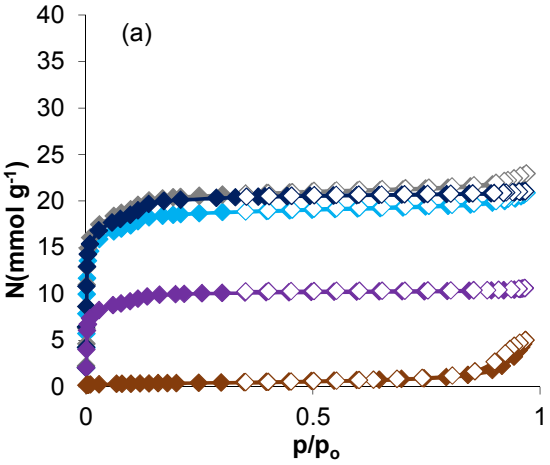


MOF	S_{BET} (m^2 g^{-1})
UiO-66	990
UiO-66-0.25NH_2	940
UiO-66-0.5NH_2	900
UiO-66-0.75NH_2	880
UiO-66-1NH_2	820

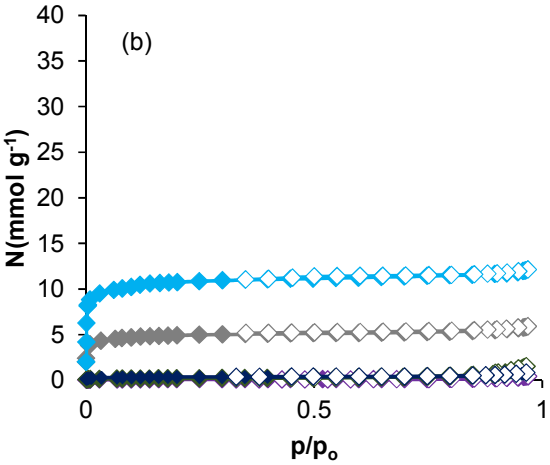


MOF	S_{BET} (m^2 g^{-1})
UiO-66@LiO^{t}Bu	347
UiO-66-0.25NH_2@LiO^{t}Bu	236
UiO-66-0.5NH_2@LiO^{t}Bu	119
UiO-66-0.75NH_2@LiO^{t}Bu	225
UiO-66-1NH_2@LiO^{t}Bu	263

Figure S6. N_2 adsorption isotherms at 77 K and S_{BET} superficial areas for (a) **UiO-66-xNH_2,** and (b) **UiO-66-xNH_2@LiO^{t}Bu** materials



MOF	S_{BET} (m^2 g^{-1})
UiO-67	1950
UiO-67-0.25$(NH_2)_2$	1820
UiO-67-0.5$(NH_2)_2$	1472
UiO-67-0.75$(NH_2)_2$	755
UiO-67-1$(NH_2)_2$	323



MOF	S_{BET} (m^2 g^{-1})
UiO-67@LiO^{t}Bu	373
UiO-67-0.25$(NH_2)_2$@LiO^{t}Bu	823
UiO-67-0.5$(NH_2)_2$@LiO^{t}Bu	29
UiO-67-0.75$(NH_2)_2$@LiO^{t}Bu	7
UiO-67-1$(NH_2)_2$@LiO^{t}Bu	17

Figure S7. N_2 adsorption isotherms at 77 K and S_{BET} superficial areas for (a) **UiO-67-x$(NH_2)_2$**, and (b) **UiO-67-x$(NH_2)_2$@LiO^{t}Bu** materials

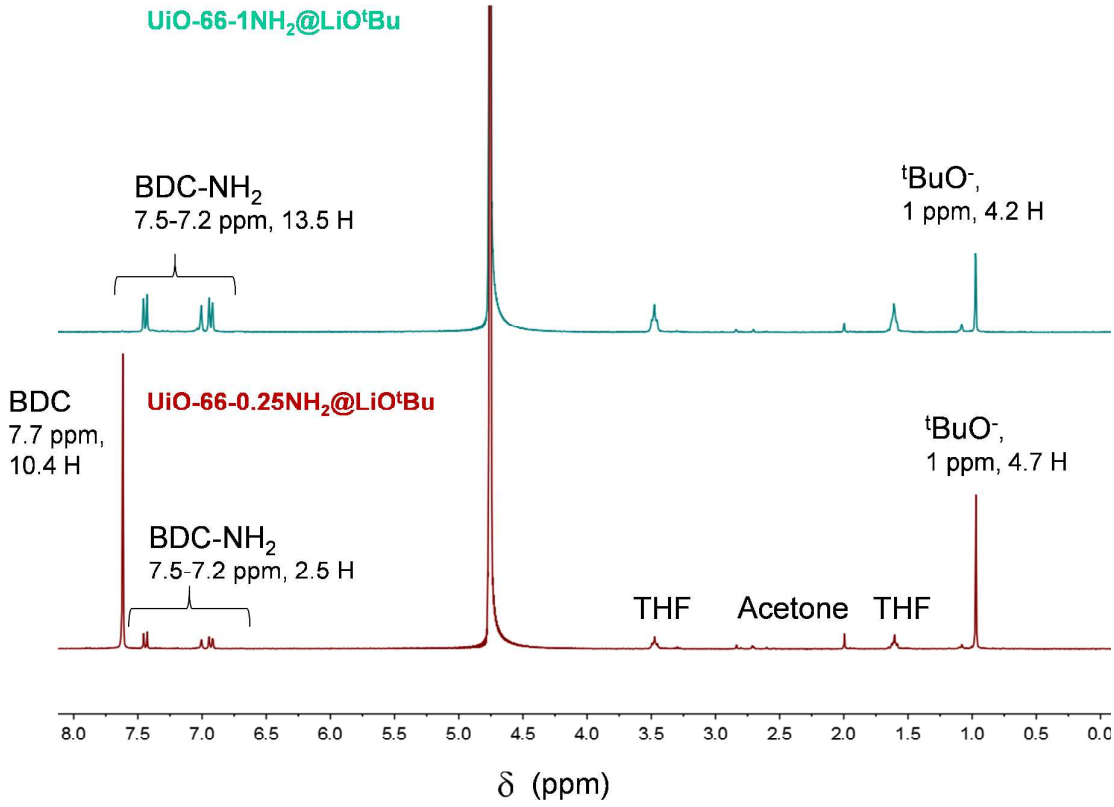


Figure S8. ^{1}H RMN spectra for NaOH digested **UiO-66-1NH$_2$@LiO^{t}Bu** and **UiO-66-0.25NH$_2$@LiO^{t}Bu** materials showing the presence of both terephthalate linkers and tertbutoxide.

Heterogeneous catalytic degradation of CWA analogues from aqueous phase.

In this study, we have proceeded to evaluate the catalytic degradation of diisopropylfluorophosphate (DIFP), and 2-chloroethylethylsulphide (CEES), as respective models of nerve and vesicant CWAs.

The degradation of DIFP, was studied employing 20 mg of each activated material suspended in 0.5 mL of H_2O. Afterwards, 2.5 μL of DMSO (used as internal reference) and 2.5 μL DIFP were added to the suspension.

The degradation of CEES, was studied employing 20 mg of each activated material suspended in 0.5 mL of a EtOH/H_2O mixture (1:1). Afterwards, 2.5 μL of DMF (used as internal reference) and 2.5 μL CEES were added to the suspension.

The concentration of DIFP and CEES was followed at room temperature by means of gas chromatography employing an Agilent 30 m-column (0.53 mm internal diameter) and taking 0.2 μL aliquots of the supernatant solution.

A. Diisopropylfluorophosphate (DIFP) hydrolytic degradation kinetics

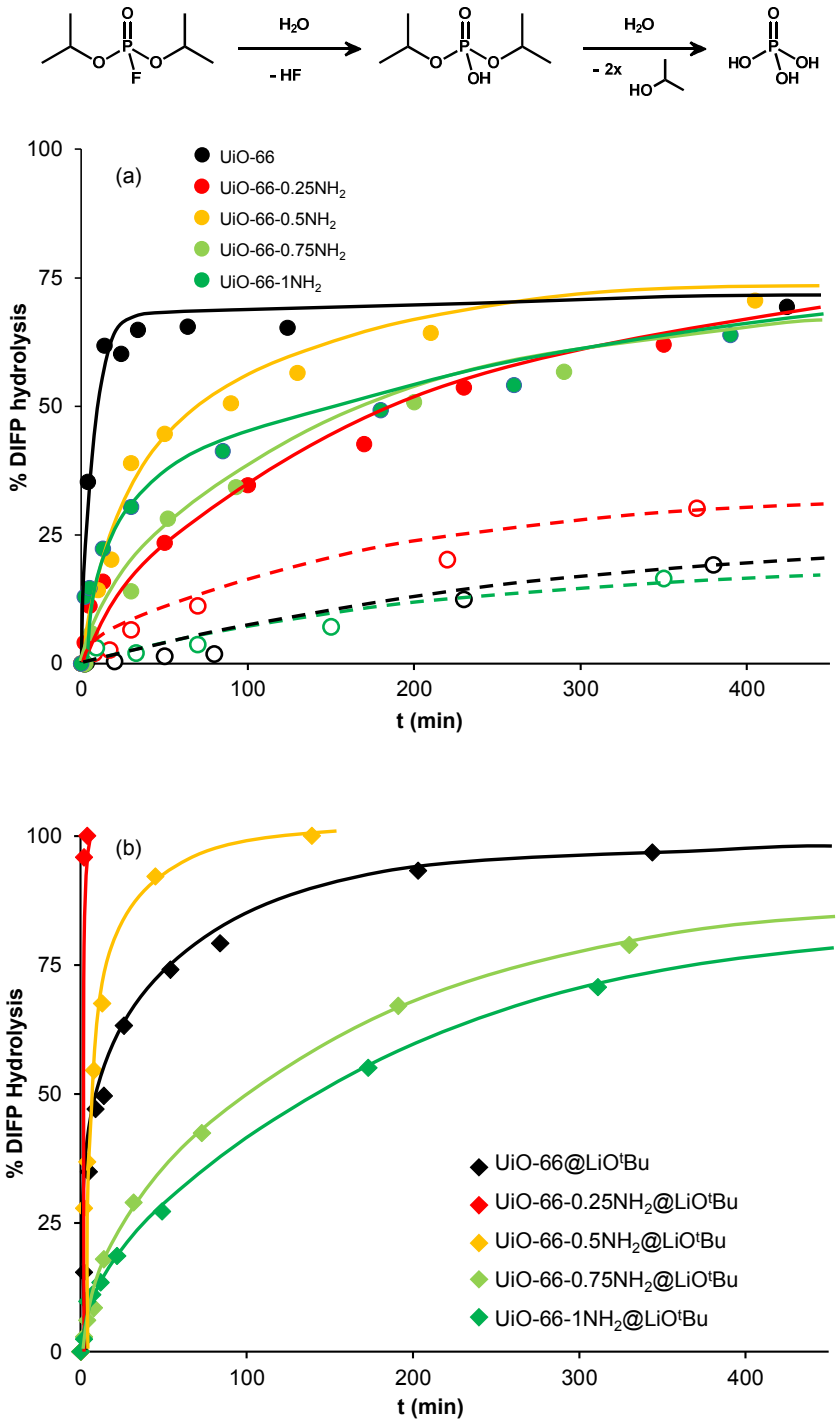


Figure S9. Profiles of catalytic hydrolytic degradation of DIFP upon exposure to the (a) **UiO-66-xNH$_2$** and (b) **UiO-66-xNH$_2$@LiO^{t}Bu** materials, at room temperature. Open symbols in (a) refer to inhibition effect of the addition of an equimolecular amount of the typical degradation product of nerve agents, namely methylphosphonic acid, on the reaction profile of UiO-66-xNH$_2$ systems where x = 0, 0.25, 1.

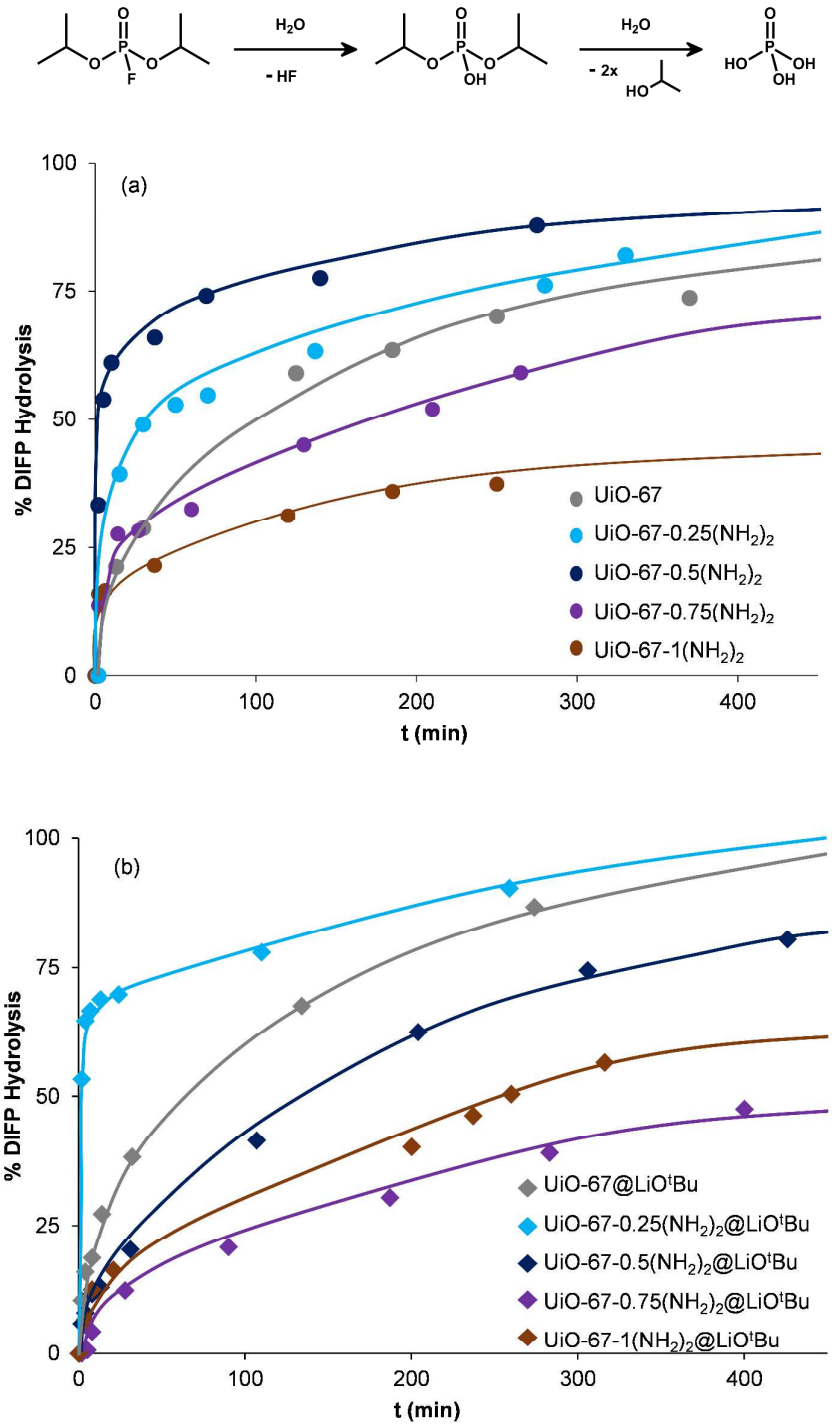
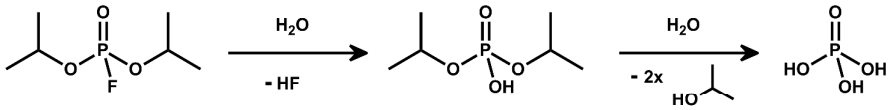
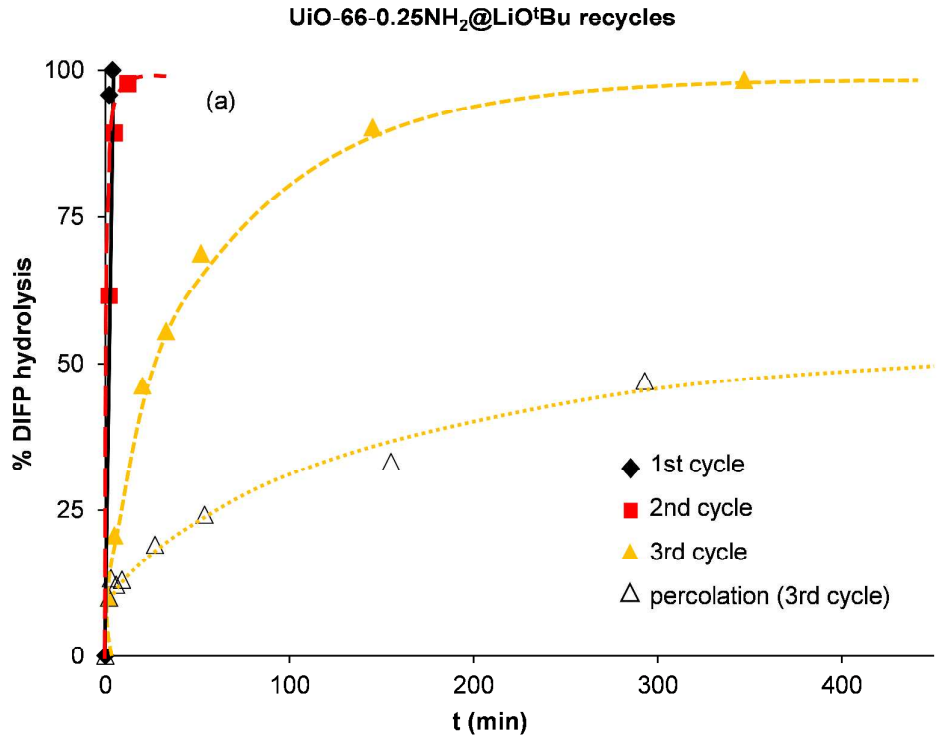


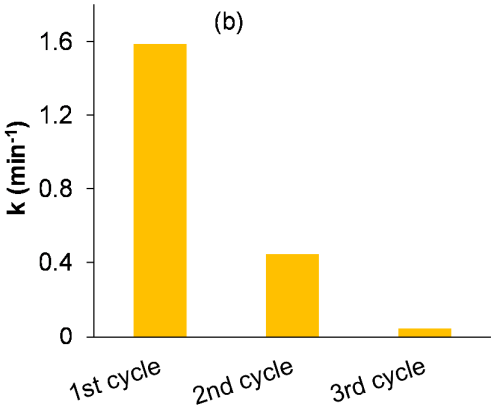
Figure S10. Profiles of catalytic hydrolytic degradation of DIFP upon exposure to the (a) **UiO-67-x(NH_2)$_2$** and (b) **UiO-67-x(NH_2)$_2$@LiO^{t}Bu** materials, at room temperature

Table S1. Summary of DIFP hydrolysis reaction rate constant (k) and half-life time ($t_{1/2}$) values for **UiO-66-xNH$_2$**, **UiO-66-xNH$_2$@LiO^{t}Bu**, **UiO-67-x(NH$_2$)$_2$** and **UiO-67-x(NH$_2$)$_2$@LiO^{t}Bu** materials, after adjusting to a first-order kinetic model. *Note: Reaction rate constant values of UiO-66-0.25NH$_2$@LiO^{t}Bu could not be precisely calculated because of almost instantaneous degradation of DIFP (0% DIFP after 3 minutes), the minimum estimated value of* $t_{1/2}$ *is 0.4 min.*

	UiO-66-xNH$_2$		**UiO-66-xNH$_2$@LiO^{t}Bu**		**UiO-67-x(NH$_2$)$_2$**		**UiO-67-x(NH$_2$)$_2$@LiO^{t}Bu**	
%NH$_2$	k(min^{-1})	$t_{1/2}$(min)	k(min^{-1})	$t_{1/2}$(min)	k(min^{-1})	$t_{1/2}$(min)	k(min^{-1})	$t_{1/2}$(min)
0	0.040	17	0.071	9.7	0.008	87	0.020	35
25	0.004	173	~1.6 (*)	~0.4(*)	0.015	46	0.147	4.7
50	0.017	41	0.094	7.4	0.070	10	0.009	77
75	0.005	139	0.014	51	0.003	230	0.005	140
100	0.004	173	0.012	57	0.0007	990	0.009	77







	k(min^{-1})	$t_{1/2}$ (min)
1st cycle	1.59	0.44
2nd cycle	0.45	1.56
3rd cycle	0.05	15.1

Figure S11. (a) Catalytic profiles of three succesive cycles on the hydrolytic degradation of DIFP upon exposure to **UiO-66-0.25NH$_2$@LiO^{t}Bu** at room temperature, and heterogeneity test of the catalytic process *via* percolation on the third cycle. (b) Reaction rate constant **(***k)* and half-life time ($t_{1/2}$) values after adjusting to a first-order kinetic model.

B. 2-chloroethylethylsulphide (CEES) hydrolytic degradation kinetics

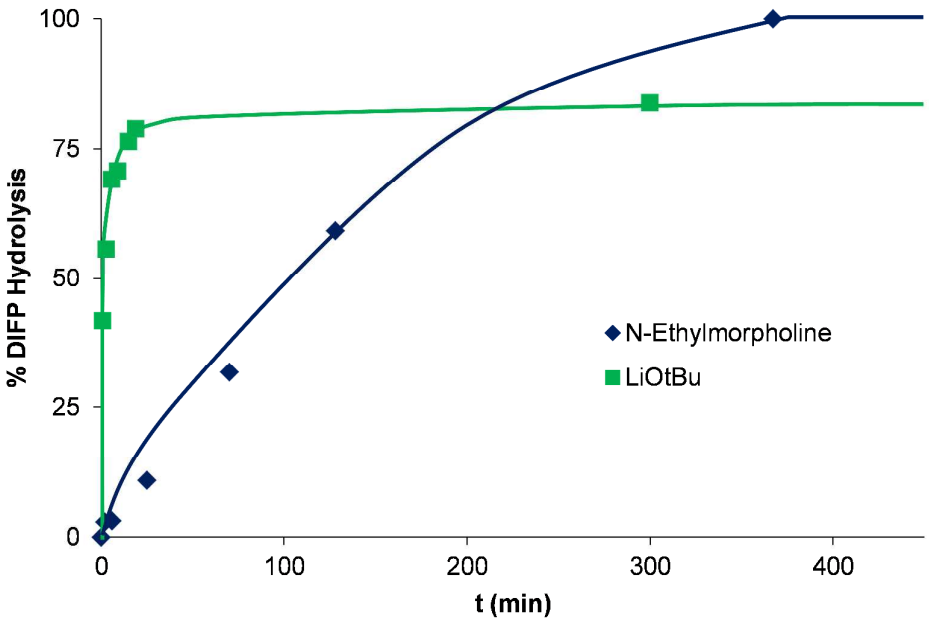
Table S2. Summary of CEES hydrolysis reaction rate constant (k) and half-life time ($t_{1/2}$) values for UiO-66-xNH_2, UiO-66-xNH_2@LiO^tBu, UiO-67-x$(NH_2)_2$ and UiO-67-x$(NH_2)_2$@LiO^tBu materials (x = 0, 0.25).

	k (min^{-1})	$t_{1/2}$ (min)
UiO-66	0.012	55.9
UiO-66-0.25NH_2	0.011	63.0
UiO-66@LiO^tBu	0.040	17.3
UiO-66-0.25NH_2@LiO^tBu	0.072	9.6
UiO-67	0.011	63.6
UiO-67-0.25$(NH_2)_2$	0.016	42.8
UiO-67@LiO^tBu	0.020	35.4
UiO-67-0.25$(NH_2)_2$@LiO^tBu	0.020	35.2

pH measurements

Table S3. pH values of reaction media for the catalysts prepared in this work. Measures were taken before DIFP addition (0 min) and after that at different times

	0 min (no DIFP)	*2 min*	*10 min*	*1 h*	*24 h*
Control	5.5	2.3	2.2	2.2	1.5
UiO-66	5.1	3.4	3.5	3.5	3.3
UiO-66-0.25NH_2	2.5	1.7	1.6	1.6	1.3
UiO-66-1NH_2	2.3	1.6	1.6	1.6	1.3
UiO-67	3.2	3.5	3.5	3.4	3.5
UiO-67-0.25$(NH_2)_2$	3.2	2.6	2.7	2.9	3.0
UiO-67-1$(NH_2)_2$	2.2	1.9	1.9	1.9	1.7
UiO-66@LiO^tBu	8.1	6.3	6.0	5.6	4.9
UiO-66-0.25NH_2@LiO^tBu	8.1	6.2	6.3	6.2	5.8
UiO-66-1NH_2@LiO^tBu	8.9	7.4	7.2	7.1	6.7
UiO-67@LiO^tBu	7.6	7.3	7.4	7.3	7.3
UiO-67-0.25$(NH_2)_2$@LiO^tBu	7.8	6.6	6.7	6.4	6.1
UiO-67-1$(NH_2)_2$@LiO^tBu	9.1	7.1	7.0	6.7	6.2



	$t_{1/2}$(min)
N-Ethylmorpholine 0.5M	160.8
LiO^{t}Bu 0.1M	2.76

Figure S12. Profiles of catalytic hydrolytic degradation of DIFP upon exposure to N-Ethylmorpholine 0.5 M and LiOtBu 0.1 M solutions, and its half life times.

Notes and References

[1] Cavka, J. H.,et al *J. Am. Chem. Soc.*, **2008**, *130*, 13850-13851.

[2] López-Maya, et al. *Angew. Chem. Int. Ed.ition*, **2015**, *54*, 6790-6794.