Supporting Information

Efficient Amines Oxidation Using Metal-Organic Framework Photocatalysts for Aminoalkyl Radicals-Mediated Halogen-Atom Transfer

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Table of Contents

1. Materials and Instrumentation

Chemicals without special descriptions were commercially available and used without further purification.

Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku SmartLab X-Ray diffractometer operated at 40 kV/30 mA with Cu Kα radiation (λ = 1.54178 Å) at room temperature. The data were collected at a 10 deg/min scanning speed in the 2θ range from 3° to 50°. The UV-vis DRS spectrum of solid sample was recorded on a Cary 7000 spectrophotometer equipped with an integrating sphere. The UV-vis spectrum of solution was collected on a SHIMADZU UV-2550 spectrophotometer. Photocurrent measurements, Mott-Schottky plots and cyclic voltammetry were conducted on electrochemical workstation CHI 660E (ChenHua Instrument, Shanghai). The morphologies of samples were characterized by a field emission scanning electron microscopy (SEM, HITACHI SU8000) with an acceleration voltage of 3.0 kV. Edinburgh FLS920 fluorescence spectrometer was used to measure the emission lifetime and fluorescence quenching. Gas chromatography (GC) analysis was performed on a Shimadzu GC-2010 equipment. A 300 W xenon lamp was used as light source for the irradiation of catalytic reaction where a cut-off filter at 420 nm has been used to remove UV light and reaction vial was set to be 10 cm. For mass spectrometry, gas chromatograph−mass spectrometry was obtained using GC-MS (Agilent 6890/5973) with the following conditions: oven temperature, 300 °C; injector temperature, 290 °C; constant carrier gas flow rate, 1.0 mL/min; column temperature program, 10 °C/min, from 80 to 280 °C holding for 10 min. The MS ionization source was 70 eV and the temperature of the ion source was 200 °C.

Chromatographic purification of products was accomplished by silica gel chromatography. Thin layer chromatography (TLC) was performed on silica gel 60 F_{254} plates. Visualization of the developed chromatogram was performed with either a compact UV-lamp (254/365 nm) and basic aqueous potassium permanganate ($KMnO_4$) stain solutions. ^{1}H NMR spectra were recorded on Varian 500 MHz spectrometers at 25 °C. Chemical shifts were reported in ppm from TMS with the solvent as the internal standard ($CDCl_3$ referenced at 7.27 ppm). Data for ^{1}H NMR were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, br. s = broad singlet, d = doublet, dd = doublet duplet, ddd = double triplet t = triplet, q = quartet, m = multiplet,) and coupling constants (Hz).

2. Figures S1-S15 and Tables S1-S2

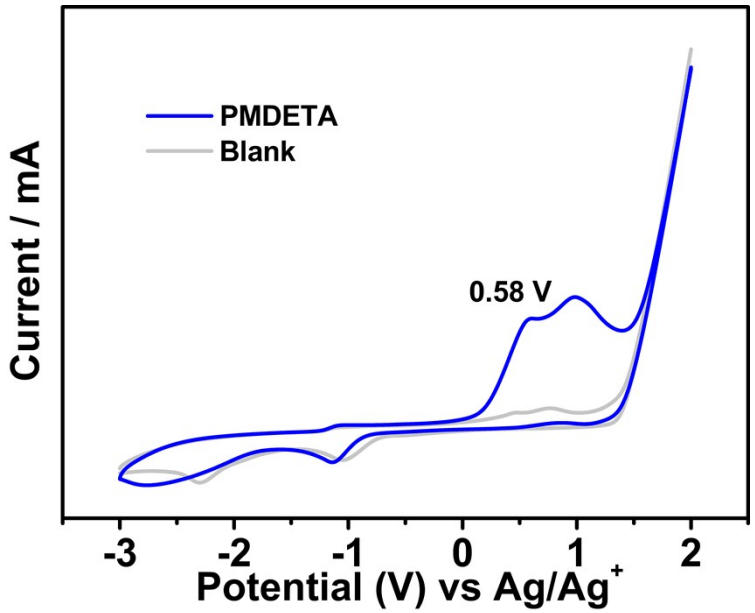


Figure S1. Cyclic voltammogram of PMDETA in DMF. E_{ox}= + 0.92 V vs. SCE.

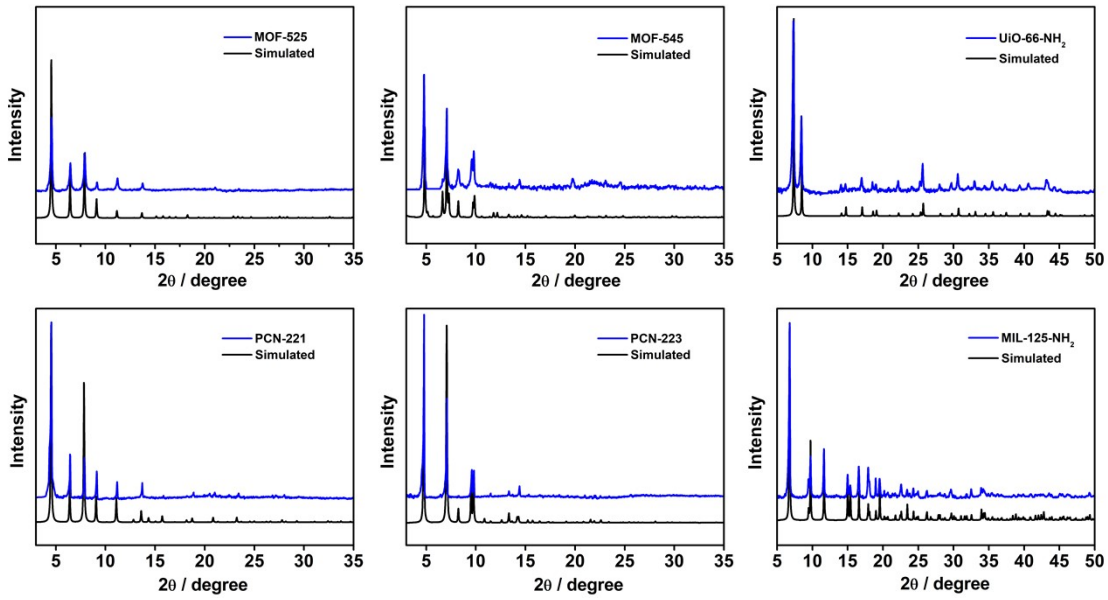


Figure S2. Experimental and simulated PXRD patterns of MOFs.

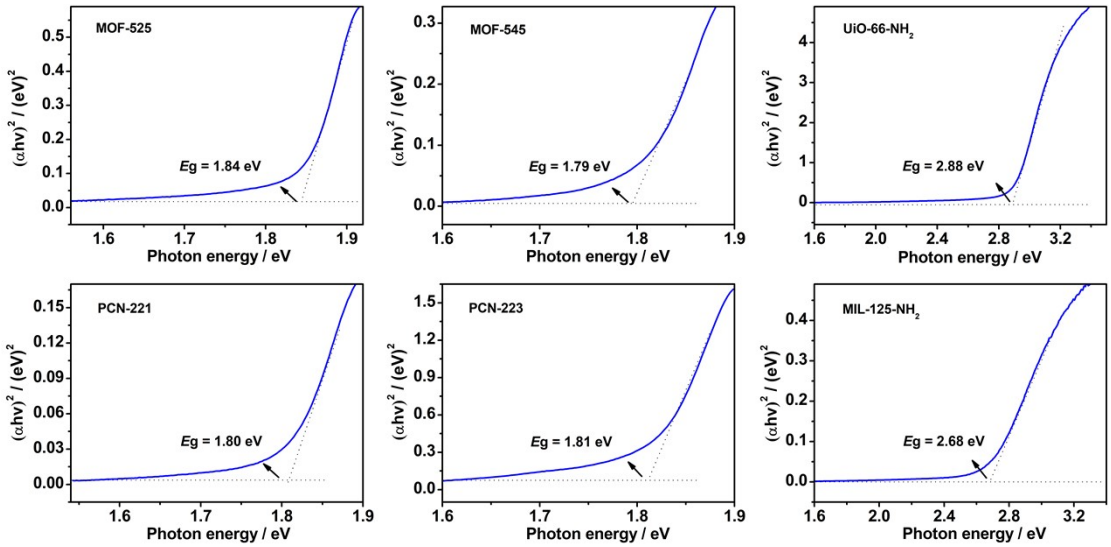


Figure S3. Tauc plots of MOFs.

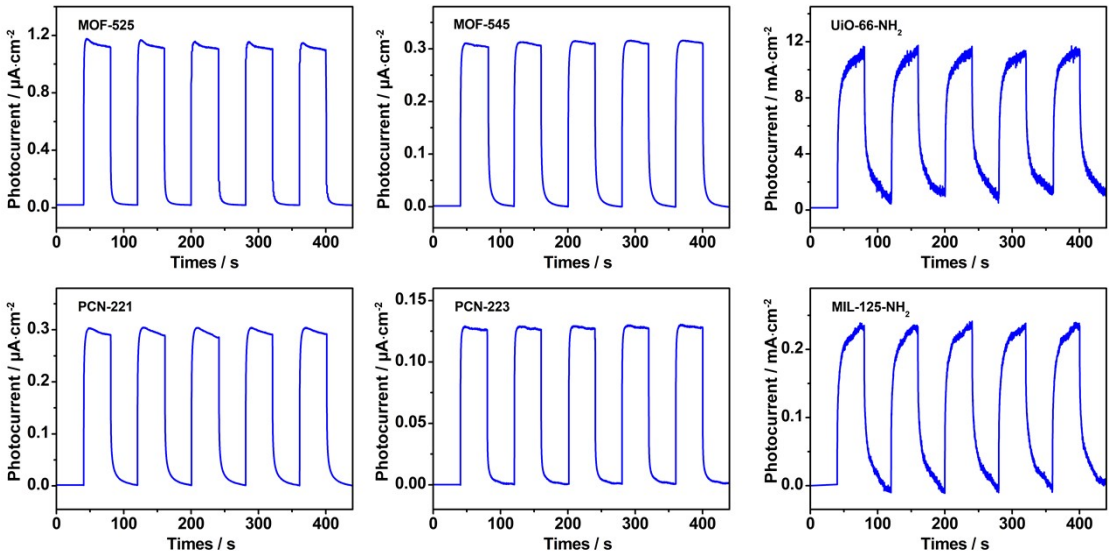


Figure S4. Transient photocurrent response of MOFs.

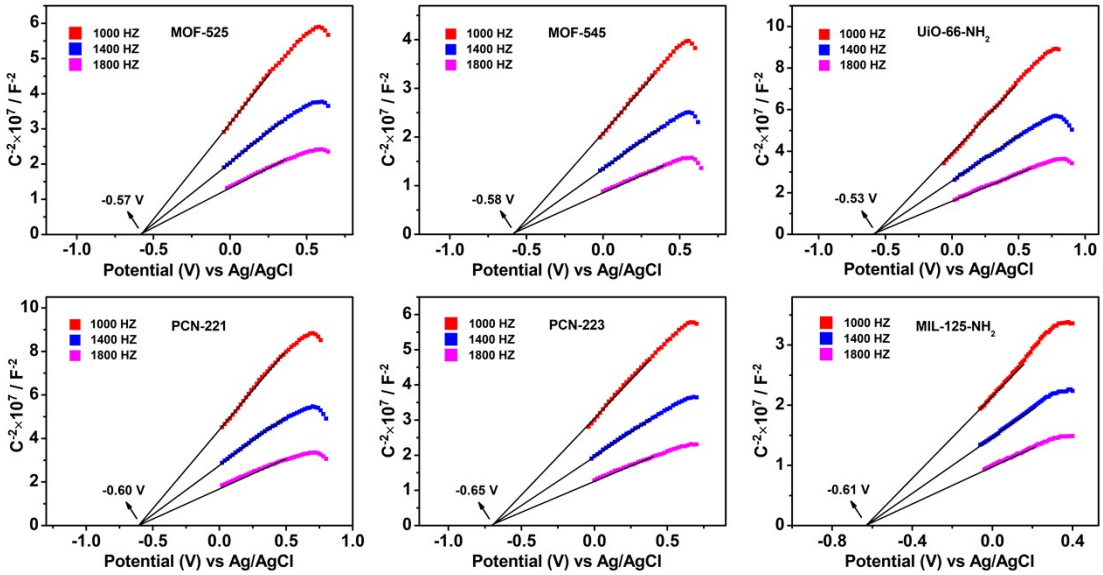


Figure S5. Mott-Schottky plots of MOFs.

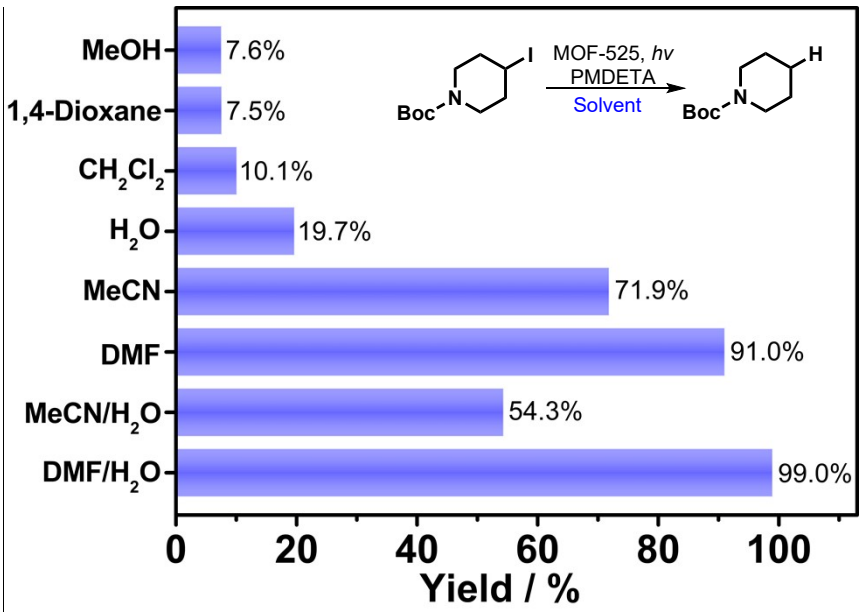


Figure S6. Solvent influence on photocatalytic dehalogenation using MOF-525.

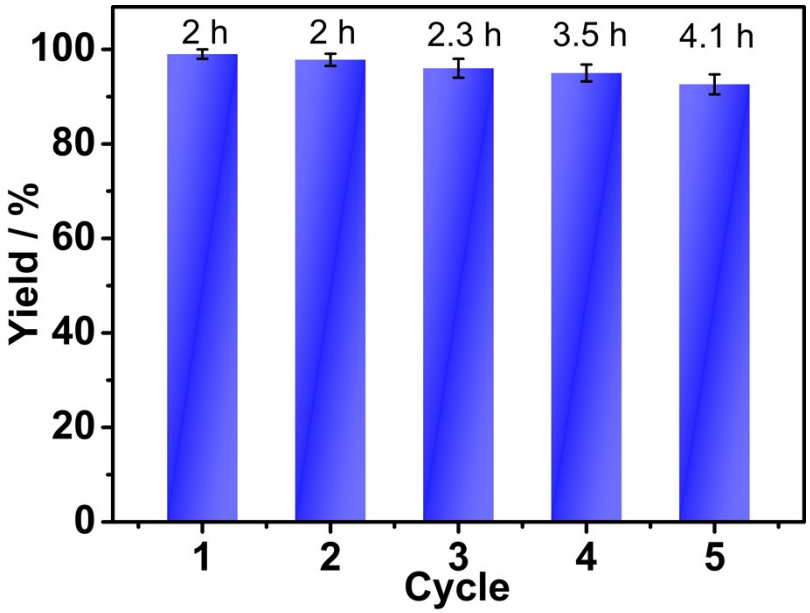


Figure S7. Cycling experiments of photocatalytic dehalogenation using MOF-525.

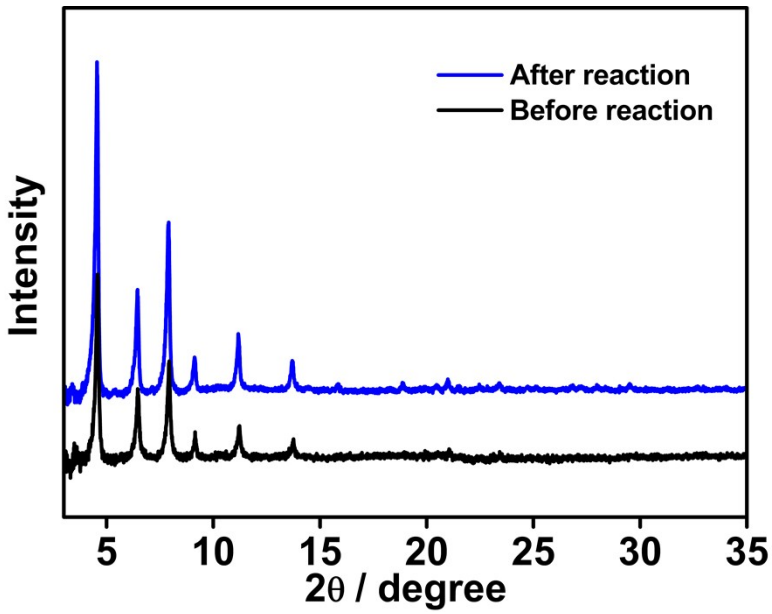


Figure S8. PXRD patterns of MOF-525 before and after cycling photocatalytic dehalogenation.

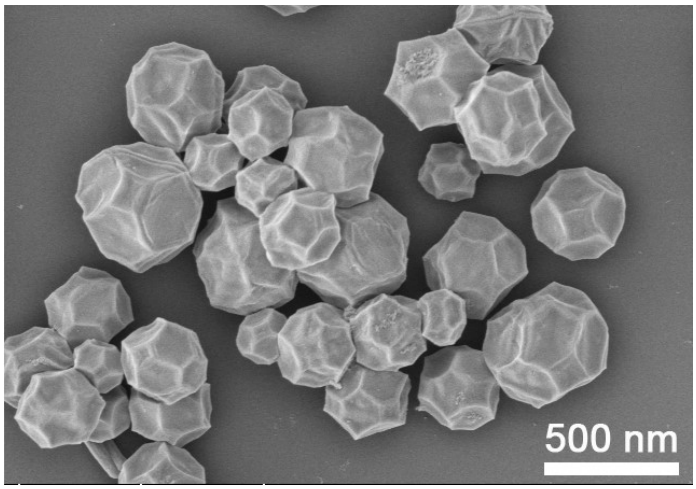


Figure S9. SEM of MOF-525 after cycling photocatalytic reaction.

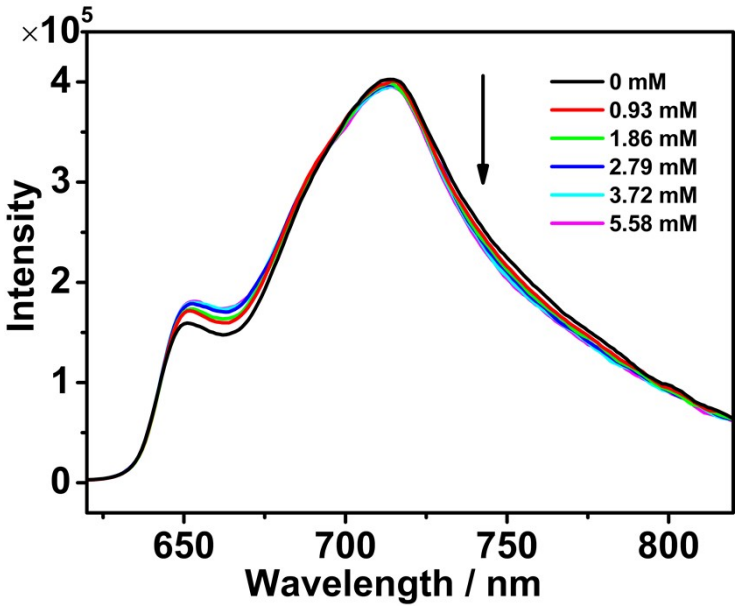


Figure S10. Fluorescence quenching of MOF-525 by **1** in DMF.

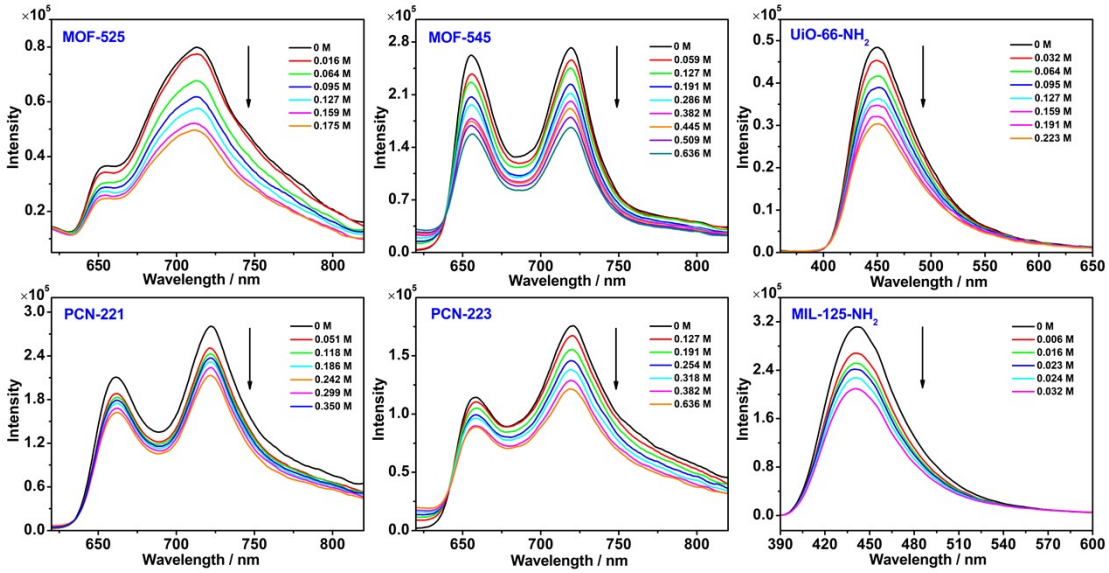


Figure S11. Fluorescence quenching of different MOFs using PMDETA. The excitation wavelength (λ_{ex}) of MOF-525, MOF-545, PCN-221 and PCN-223 is 420 nm, and λ_{ex} (UiO-66-NH_2 and MIL-125-NH_2) is 280 nm.

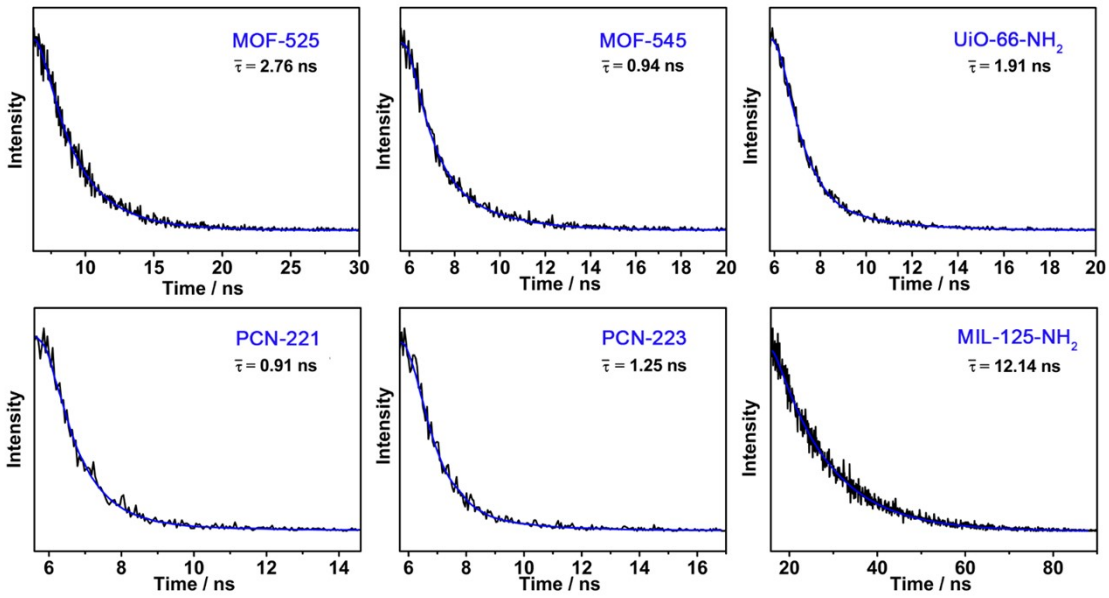


Figure S12. Fluorescence decay of MOFs.

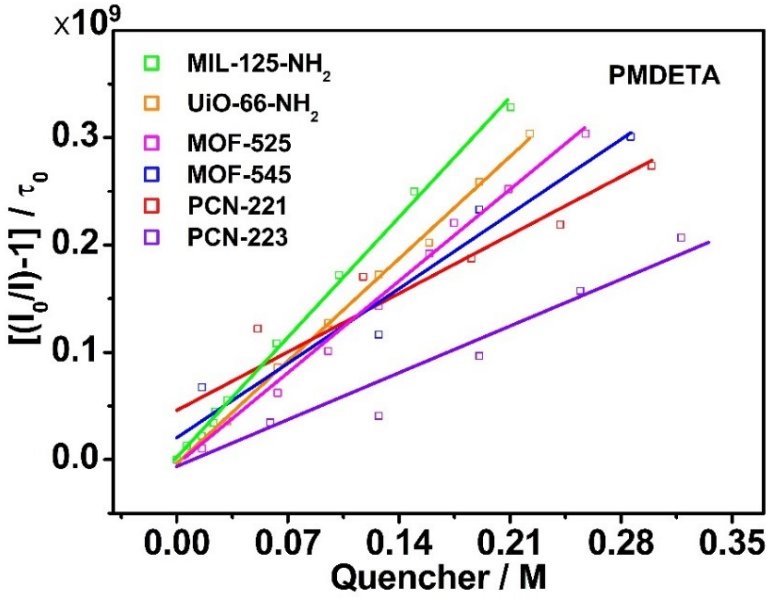


Figure S13. Quenching rate constants of various MOFs using PMDETA. Porphyrinic MOF-525, MOF-545, PCN-221 and PCN-223 were excited at 420 nm, UiO-66-NH_2 and MIL-125-NH_2 were excited at 280 nm.

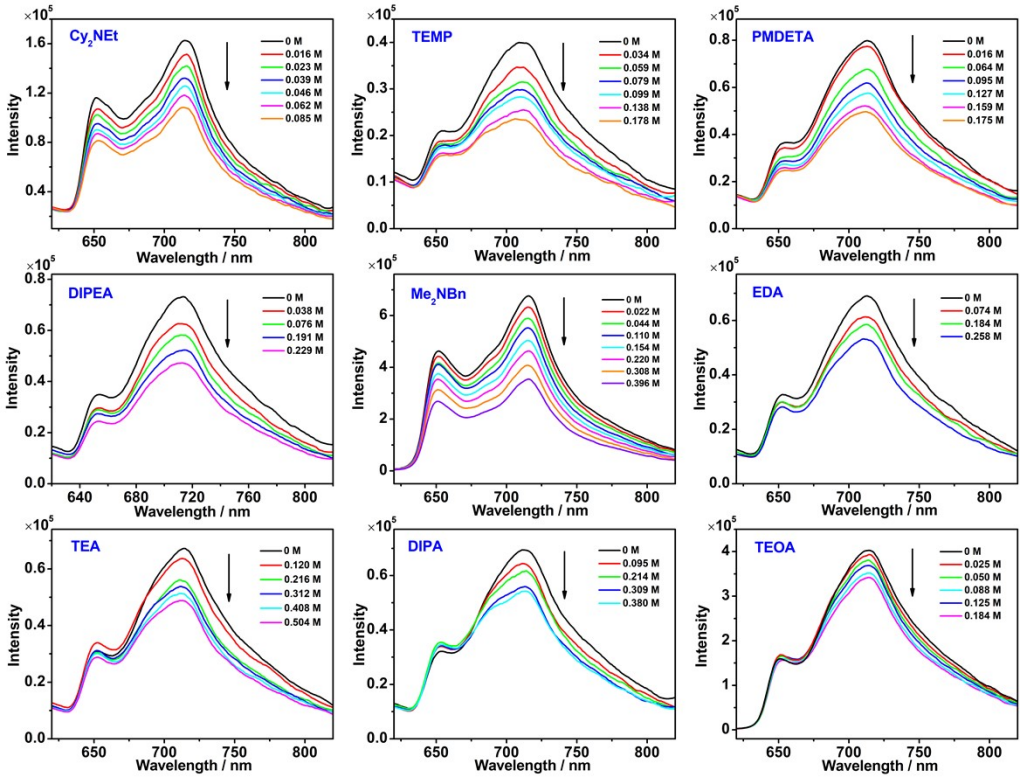


Figure S14. Fluorescence quenching of MOF-525 using different amines in DMF.

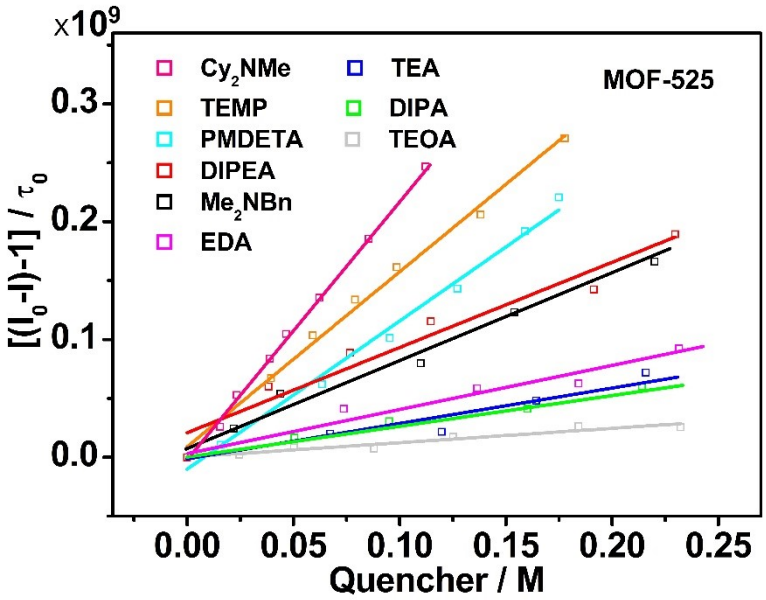
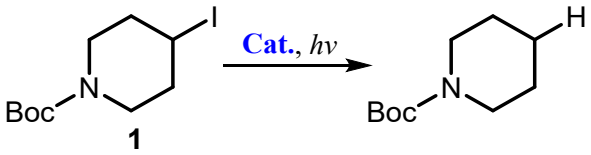


Figure S15. Quenching rate constants of MOF-525 using various amines.

Table S1. Visible-light-mediated dehalogenation under different conditions.



1

Entry	Catalyst	Yield (%)
1	Zr^{4+}	3.1
2	TCPP	3.0
3	Zr^{4+} + TCPP	7.3
4	BDC-NH_2	2.2
5	Zr^{4+} + BDC-NH_2	3.1
6	Ti^{4+}	2.6
7	Ti^{4+} + BDC-NH_2	2.9

Scale of reaction: Catalyst (1.0 mol%), **1** (0.1 mmol), DMF/H_2O (*v*/*v*=9/1, 1.0 mL), visible light, 2 hours.

Table S2. Information on experimental parameters of MOFs.

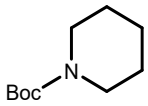
MOF	*E*g (ev)	CB (vs. SCE)	VB (vs. SCE)	τ (ns)	K_{SV} (M^{-1})	k_q ($\times 10^9$ M^{-1} s^{-1})	Yield[a] (%)
MOF-525	1.84	-0.71	1.13	2.76	3.47	1.26	99.0
MOF-545	1.79	-0.72	1.07	0.94	0.95	1.01	95.8
PCN-221	1.80	-0.74	1.06	0.91	0.86	0.95	90.7
PCN-223	1.81	-0.79	1.02	1.25	0.77	0.62	86.5
UiO-66-NH_2	2.88	-0.67	2.21	1.91	2.60	1.36	75.0
MIL-125-NH_2	2.68	-0.75	1.93	12.14	20.49	1.67	66.5

[a]Yield of photocatalytic dehalogenation using halide **1**.

3. General procedure.

3.1 Photocatalytic dehalogenation

tert-Butyl piperidine-1-carboxylate



A vial (4 mL) was charged with MOF-525 (1.0 mol%), *tert*-butyl 4-iodopiperidine-1-carboxylate **1** (31.1 mg, 0.1 mmol), PMDETA (63 μL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 2 h, gave compound (18.3 mg, 99%) as an oil. The same use of *tert*-butyl 4-bromo-1-piperidinecarboxylate **9** (26.4 mg, 0.1 mmol) and *tert*-butyl 4-chloropiperidine-1-carboxylate **12** (21.9 mg, 0.1 mmol) to react for 6-12 h, obtain the corresponding compounds (13.7 mg, 74% or 1.8 mg, 10%).

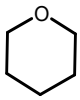
^{1}H NMR (500 MHz, $CDCl_3$)[1]: δ = 3.34 – 3.32 (m, 4H), 1.32 (s, 9H), 1.31 – 1.29 (m, 6H).

Cyclohexane

A vial (4 mL) was charged with using MOF-525 (1.0 mol%), 1-iodocyclohexane **2** (21.0 mg, 0.1 mmol), PMDETA (63 μL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 2 h, gave compound (6.7 mg, 80.0%) as an oil. The same use of 1-bromocyclohexane **11** (16.3 mg, 0.1 mmol) to react for 12 h, obtain the corresponding compounds (2.0 mg, 27%).

^{1}H NMR (500 MHz, $CDCl_3$)[2]: δ = 1.41 (m, 12H).

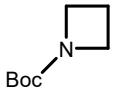
Oxane



A vial (4 mL) was charged with MOF-525 (1.0 mol%), 4-iodotetrahydropyran **3** (21.2 mg, 0.1 mmol), PMDETA (63 μL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 2 h, gave compound (5.2 mg, 60%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[3]: δ = 3.63 (t, *J* = 5.2 Hz, 4H), 1.63 – 1.58 (m, 2H), 1.57 – 1.53 (m, 4H).

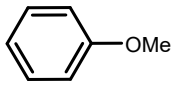
tert-Butyl azetidine-1-carboxylate



A vial (4 mL) was charged with using MOF-525 (1.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate **4** (28.3 mg, 0.1 mmol), PMDETA (63 µL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 12 h, gave compound (2.7 mg, 18%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[4]: δ = 3.92 – 3.85 (m, 4H), 2.11 (p, *J* = 7.6 Hz, 2H), 1.38 (s, 9H).

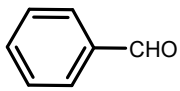
Methoxybenzene



A vial (4 mL) was charged with using MOF-525 (1.0 mol%), *para*-iodoanisole **5** (24.6 mg, 0.1 mmol), PMDETA (63 µL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 12 h, gave compound (4.5 mg, 42%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[5]: δ = 7.30 – 7.26 (m, 2H), 6.95 – 6.88 (m, 3H), 3.80 (s, 3H).

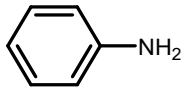
Benzaldehyde



A vial (4 mL) was charged with using MOF-525 (1.0 mol%), 4-Iodobenzaldehyde **6** (23.2 mg, 0.1 mmol), PMDETA (63 µL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 12 h, gave compound (4.2 mg, 40%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[6]: δ = 10.01 (s, 1H), 7.87 (d, *J* = 6.9 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.6 Hz, 2H).

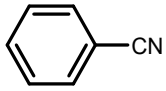
Aniline



A vial (4 mL) was charged with using MOF-525 (1.0 mol%), 4-iodobenzenamine **7** (22.0 mg, 0.1 mmol), PMDETA (63 µL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 12 h, gave compound (2.3 mg, 25%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[7]: δ = 7.21 – 7.28 (m, 2H), 6.80 – 6.87 (m, 1H), 6.71 – 6.83 (m, 2H), 3.60 (bs, 2H).

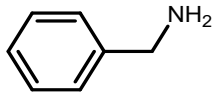
Benzonitrile



A vial (4 mL) was charged with using MOF-525 (1.0 mol%), 2-Iodobenzonitrile **8** (22.9 mg, 0.1 mmol), PMDETA (63 µL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 12 h, gave compound (1.0 mg, 10%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[8]: δ = 7.61 – 7.50 (m, 3H), 7.41 (t, *J* = 7.3 Hz, 2H).

Benzylamine

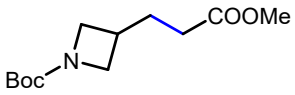


A vial (4 mL) was charged with using MOF-525 (1.0 mol%), 4-Bromobenzylamine **10** (12.6 µL, 0.1 mmol), PMDETA (63 µL, 0.3 mmol), DMF (0.9 mL) and H_2O (0.1 mL), 12 h, gave compound (3.2 mg, 30%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[9]: δ = 7.32 - 7.26 (m, 5H), 3.85 (s, 2H), 2.07 (s, active H).

3.2 Photocatalytic hydroalkylation

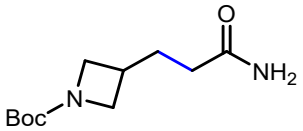
tert-Butyl 3-(3-Methoxy-3-oxopropyl)azetidine-1-carboxylate (13)



A vial (4 mL) was charged with MOF-525 (5.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (28.3 mg, 0.1 mmol), methyl acrylate (36 µL, 0.4 mmol), PMDETA (104 µL, 0.5 mmol), DMF (0.5 mL) and H_2O (0.5 mL), 48 h, gave compound (15.6 mg, 32%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[10]: δ = 3.98 – 3.90 (t, *J* = 8.4 Hz, 2H), 3.63 (s, 3H), 3.48 (dd, *J* = 8.6, 5.5 Hz, 2H), 2.41 – 2.51 (m, 1H), 2.23 (t, *J* = 7.5 Hz, 2H), 1.85 (q, *J* = 7.6 Hz, 2H), 1.39 (s, 9H).

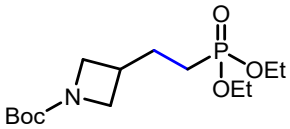
tert-Butyl 3-(3-Amino-3-oxopropyl)azetidine-1-carboxylate (14)



A vial (4 mL) was charged with using MOF-525 (5.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (28.3 mg, 0.1 mmol), acrylamide (29 mg, 0.4 mmol), PMDETA (104 µL, 0.5 mmol), DMF (0.5 mL) and H_2O (0.5 mL), 48 h, gave compound (19.9 mg, 43%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[10]: δ = 5.80 – 5.59 (m, 2H), 3.92 (t, *J* = 8.3 Hz, 2H), 3.47 (dd, *J* = 8.5, 5.4 Hz, 2H), 2.53 – 2.40 (m, 1H), 2.10 (t, *J* = 7.5 Hz, 2H), 1.85 (q, *J* = 7.6 Hz, 2H), 1.38 (s, 9H).

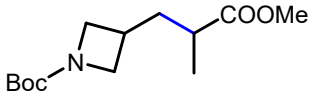
tert-Butyl 3-(2-(Diethoxyphosphoryl)ethyl)azetidine-1-carboxylate (15)



A vial (4 mL) was charged with using MOF-525 (5.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (28.3 mg, 0.1 mmol), diethyl vinylphosphonate (62 µL, 0.4 mmol), PMDETA (104 µL, 0.5 mmol), DMF (0.5 mL) and H_2O (0.5 mL), 48 h, gave compound (35.6 mg, 55%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[10]: δ = 4.10 – 3.95 (m, 4H), 3.90 (t, *J* = 8.3 Hz, 2H), 3.45 (dd, J = 8.6, 5.4 Hz, 2H), 2.50 – 2.41 (m, 1H), 1.85 – 1.70 (m, 2H), 1.63 – 1.50 (m, 2H), 1.32 (s, 9H), 1.22 (t, *J* = 7.1 Hz, 6H).

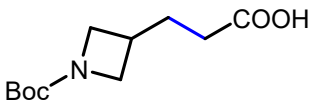
tert-Butyl 3-(3-Methoxy-2-methyl-3-oxopropyl)azetidine-1-carboxylate (16)



A vial (4 mL) was charged with MOF-525 (5.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (28.3 mg, 0.1 mmol), methyl methacrylate (43 µL, 0.4 mmol), PMDETA (104 µL, 0.5 mmol), DMF (0.5 mL) and H_2O (0.5 mL), 48 h, gave compound (22.2 mg, 43%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[10]: δ = 3.96 (t, *J* = 8.3 Hz,1H), 3.91 (t, *J* = 8.3 Hz, 1H), 3.60 (s, 3H), 3.46 (t, *J* = 6.0 Hz, 1H), 3.44 (t, *J* = 6.0 Hz, 1H), 2.52 – 2.40 (m, 1H), 2.39 – 2.29 (m, 1H), 1.91 (dt, J =13.8, 7.7 Hz, 1H), 1.63 (ddd, *J* =14.0, 8.2, 6.1 Hz, 1H), 1.37 (s, 9H), 1.08 (d, *J* = 7.0 Hz, 3H).

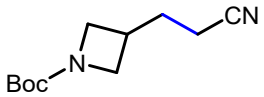
3-(1-(*tert*-Butoxycarbonyl)azetidin-3-yl)propanoic acid (17)



A vial (4 mL) was charged with MOF-525 (5.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (28.3 mg, 0.1 mmol), acrylic acid (28 µL, 0.4 mmol), PMDETA (104 µL, 0.5 mmol), DMF (0.5 mL) and H_2O (0.5 mL), 48 h, gave compound (6.9 mg, 23%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[10]: δ = 3.93 (t, *J* = 8.4 Hz, 2H), 3.46 (dd, *J* = 8.6, 5.5 Hz, 2H), 2.55 – 2.42 (m, 1H), 2.23 (t, *J* = 7.4 Hz, 2H), 1.86 (q, *J* = 7.6 Hz, 2H), 1.35 (s, 9H).

tert-Butyl 3-(2-Cyanoethyl)azetidine-1-carboxylate (18)

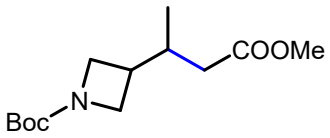


A vial (4 mL) was charged with MOF-525 (5.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (28.3 mg, 0.1 mmol), acrylonitrile (26 µL, 0.4

mmol), PMDETA (104 µL, 0.5 mmol), DMF (0.5 mL) and H_2O (0.5 mL), 48 h, gave compound (38.9 mg, 76%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[10]: δ = 4.01 (t, *J* = 8.4 Hz, 2H), 3.55 – 3.52 (dd, *J* = 8.7, 5.4 Hz, 2H), 2.62 – 2.56 (m, 1H), 2.29 (t, *J* = 7.1 Hz, 2H), 1.92 (q, *J* = 7.3 Hz, 2H), 1.37 (s, 9H);

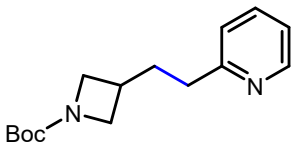
tert-Butyl 3-(4-Methoxy-4-oxobutan-2-yl)azetidine-1-carboxylate (19)



A vial (4 mL) was charged with MOF-525 (5.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (28.3 mg, 0.1 mmol), methyl crotonate (43 µL, 0.4 mmol), PMDETA (104 µL, 0.5 mmol), DMF (0.5 mL) and H_2O (0.5 mL), 48 h, gave compound (40.3 mg, 78%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[10]: δ = 3.86 (t, *J* = 8.4 Hz, 1H), 3.85 (t, *J* = 8.2 Hz, 1H), 3.62 (s, 3H), 3.57 – 3.53 (m, 2H), 2.36 – 2.25 (m, 1H), 2.25 – 2.18 (m, 1H), 2.14 – 2.04 (m, 1H), 2.04 – 1.98 (m, 1H), 1.37 (s, 9H), 0.85 (d, *J* = 6.3 Hz, 3H).

tert-Butyl 3-(2-(Pyridin-2-yl)ethyl)azetidine-1-carboxylate (20)

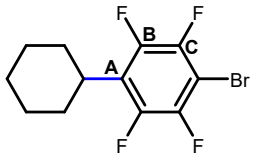


A vial (4 mL) was charged with MOF-525 (5.0 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (28.3 mg, 0.1 mmol), 2-vinylpyridine (43 µL, 0.4 mmol), PMDETA (104 µL, 0.5 mmol), DMF (0.5 mL) and H_2O (0.5 mL), 48 h, gave compound (18.6 mg, 35%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[10]: δ = 8.45 – 8.41 (m, 1H), 7.51 (td, *J* = 7.7, 1.8 Hz, 1H), 7.02 (m, 2H), 3.90 (t, *J* = 8.3 Hz, 2H), 3.46 (dd, *J* = 8.5, 5.6 Hz, 2H), 2.71 – 2.63 (m, 2H), 2.51 – 2.40 (m, 1H), 1.94 (q, *J* = 7.7 Hz, 2H), 1.36 (s, 9H).

3.3 Photocatalytic polyfluoarylation

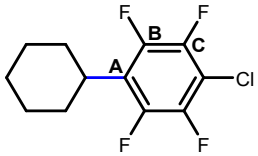
1-bromo-4-cyclohexyl-2,3,5,6-tetrafluorobenzene (21)



A vial (4 mL) was charged with MOF-525 (2.5 mol%), 1-iodocyclohexane (42.0 mg, 0.2 mmol), bromopentafluorobenzene (246.9 mg, 1.0 mmol), PMDETA (208 μL, 1.0 mmol), DMF (0.4 mL), 24 h, gave compound (42.4mg, 69%) as an oil.
A:B:C=30:26:7

^{1}H NMR (500 MHz, $CDCl_3$)[11]: δ = 2.41 – 2.24 (m, 1H), 1.66 – 1.36 (m, 6H), 1.24 – 0.93 (m, 4H).

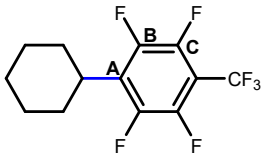
1-chloro-4-cyclohexyl-2,3,5,6-tetrafluorobenzene (22)



A vial (4 mL) was charged with using MOF-525 (2.5 mol%), 1-iodocyclohexane (42.0 mg, 0.2 mmol), chloropentafluorobenzene (202.5 mg, 1.0 mmol), PMDETA (208 μL, 1.0 mmol), DMF (0.4 mL), 24 h, gave compound (31.2 mg, 59%) as an oil.
A:B:C=30:24:5

^{1}H NMR (500 MHz, $CDCl_3$)[11]: δ = 3.04 – 2.70 (m, 1H), 1.56 – 1.23 (m, 7H), 0.98 (td, *J* = 13.5, 12.5, 7.3 Hz, 3H).

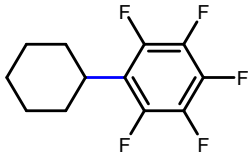
1-cyclohexyl-2,3,5,6-tetrafluoro-4-(trifluoromethyl)benzene (23)



A vial (4 mL) was charged with MOF-525 (2.5 mol%), 1-iodocyclohexane (42.0 mg, 0.2 mmol), octafluoroyoluene (230.1 mg, 1.0 mmol), PMDETA (208 μL, 1.0 mmol), DMF (0.4 mL), 24 h, gave compound (36.6 mg, 61%) as an oil.
A:B:C=29:23:9

^{1}H NMR (500 MHz, $CDCl_3$)[11]: δ = 2.74 (dtt, *J* = 28.1, 11.9, 4.3 Hz, 1H), 1.63 – 1.26 (m, 7H), 0.91 (ddt, *J* = 21.8, 13.0, 4.7 Hz, 3H).

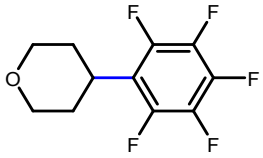
1-cyclohexyl-2,3,4,5,6-pentafluorobenzene (24)



A vial (4 mL) was charged with MOF-525 (2.5 mol%), 1-iodocyclohexane (42.0 mg, 0.2 mmol), hexafluorobenzene (186.0 mg, 1.0 mmol), PMDETA (208 μL, 1.0 mmol), DMF (0.4 mL), 24 h, gave compound (21.5 mg, 43%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[11]: δ = 2.38 (tt, *J* = 11.3, 4.7 Hz, 1H), 1.34 – 1.00 (m, 7H), 0.83 – 0.54 (m, 3H).

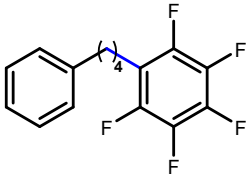
4-(perfluorophenyl)tetrahydro-2H-pyran (25)



A vial (4 mL) was charged with MOF-525 (2.5 mol%), 4-iodotetrahydropyran (42.4 mg, 0.2 mmol), hexafluorobenzene (186.0 mg, 1.0 mmol), PMDETA (208 μL, 1.0 mmol), DMF (0.4 mL), 24 h, gave compound (27.2 mg, 54%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[11]: δ = 3.43 (dd, *J* = 11.7, 4.5 Hz, 2H), 2.88 (td, *J* = 12.0, 2.0 Hz, 2H), 2.59 (tt, *J* = 12.5, 3.8 Hz, 1H), 1.67 (tddd, *J* = 12.3, 10.7, 4.6, 1.6 Hz, 2H), 1.03 – 0.95 (m, 2H).

1,2,3,4,5-pentafluoro-6-(4-phenylbutyl)benzene (26)

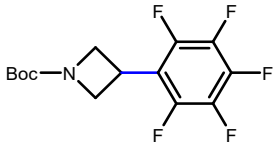


A vial (4 mL) was charged with MOF-525 (2.5 mol%), (4-iodobutyl)benzene (52.0 mg, 0.2 mmol), hexafluorobenzene (186.0 mg, 1.0 mmol), PMDETA

(208 µL, 1.0 mmol), DMF (0.4 mL), 24 h, gave compound (18 mg, 30%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[11]: δ = 6.66 – 6.53 (m, 2H), 6.52 – 6.43 (m, 3H), 5.84 – 5.66 (m, 2H), 5.42 (d, *J* = 9.7 Hz, 1H), 3.65 – 3.43 (m, 2H), 2.05 (t, *J* = 6.9 Hz, 2H), 1.16 (dq, *J* = 6.9, 2.3, 1.5 Hz, 4H).

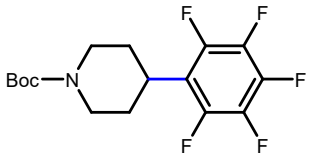
tert-butyl 3-(perfluorophenyl)azetidine-1-carboxylate (27)



A vial (4 mL) was charged with MOF-525 (2.5 mol%), *tert*-butyl-3-iodoazetidine-1-carboxylate (56.6 mg, 0.2 mmol), hexafluorobenzene (186.0 mg, 1.0 mmol), PMDETA (208 µL, 1.0 mmol), DMF (0.4 mL), 24 h, gave compound (28.8 mg, 45%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[11]: δ = 3.61 (t, *J* = 8.7 Hz, 2H), 3.43 (dd, *J* = 8.5, 7.0 Hz, 2H), 3.38 (tt, *J* = 8.9, 6.5 Hz, 1H), 0.77 (s, 9H).

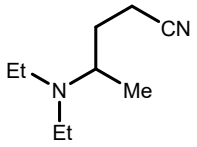
tert-butyl 4-(perfluorophenyl)piperidine-1-carboxylate (28)



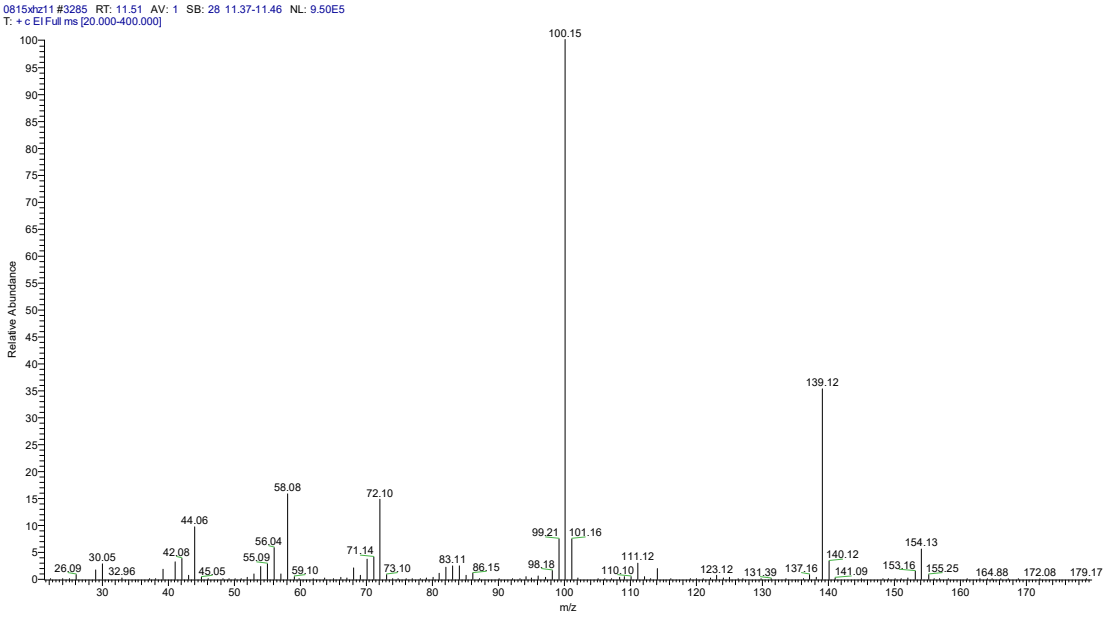
A vial (4 mL) was charged with MOF-525 (2.5 mol%), *tert*-butyl 4-iodopiperidine-1-carboxylate (62.2 mg, 0.2 mmol), hexafluorobenzene (186.0 mg, 1.0 mmol), PMDETA (208 µL, 1.0 mmol), DMF (0.4 mL), 24 h, gave compound (24.5 mg, 35%) as an oil.

^{1}H NMR (500 MHz, $CDCl_3$)[11]: δ = 3.55 (s, 2H), 2.40 (tt, *J* = 12.5, 3.7 Hz, 1H), 2.13 – 2.04 (m, 2H), 1.71 – 1.12 (m, 2H), 1.10 – 0.85 (m, 3H), 0.87 (s, 9H).

4. GC-MS spectrum for the trapping of α-aminoalkyl radical



Chemical Formula: $C_9H_{18}N_2$
Exact Mass: 154.15
Molecular Weight: 154.26
m/z: 154.15 (100.0%), 155.15 (9.7%)
Elemental Analysis: C, 70.08; H, 11.76; N, 18.16



5. Determination of the Quantum Yield

Determination of the photon flux at 435 nm:

The photon flux of the spectrophotometer was determined following the work of Yoon and coworkers,[12] utilizing standard ferrioxalate actinometry.[13,14] A 0.15 M solution of potassium ferrioxalate was prepared by dissolving 2.21 g of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux of the spectrophotometer, 2.0 mL of the potassium ferrioxalate solution was placed in the vial and irradiated for 90.0 s at 435 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the vial. The solution was allowed to rest for 1 h (complete coordination of ferrous ions to phenanthroline). The absorbances of irradiated and non-irradiated solutions at 510 nm were measured respectively. Conversion was calculated using eq 1:

$$Mol\ Fe^{2+} = \frac{V \times \Delta A}{1 \times \varepsilon} \qquad (1)$$

In this equation, V is the total volume of the solution after addition of the phenanthroline (0.00235 L), ΔA is the difference in the absorbance at 510 nm between the irradiated and the non-irradiated solutions, l is the path length (1.0 cm), and ε is the molar absorptivity at 510 nm (11100 L mol^{-1} cm^{-1}).[12-14] The mole of Fe^{2+} was calculated to be 3.667×10^{-4}.

The photon flux can be calculated using eq 2:

$$photon\ flux = \frac{Mol\ Fe^{2+}}{\Phi \times t \times f} \qquad (2)$$

In this equation, Φ is the quantum yield of the ferrioxalate actinometer (Φ = 1.01 for a 0.15 M solution),[13-15] t is the time of the irradiation (90.0 s), and f is the fraction of the light absorbed at 435 nm, which can be calculated using eq 3 based on the measured absorbance (A) (see Figure S16).

$$f = 1 - 10^{-A} \qquad (3)$$

Thus, the f value was determined to be 0.999 and the photon flux of the spectrophotometer was calculated (average of three experiments) to be 4.038×10^{-6} einstein s^{-1}.

Determination of the quantum yield:

For dehalogenation reaction, a 4 mL vial was charged with MOF-525 (1.0 mol%), **1** (0.1 mmol), PMDETA (0.3 mmol), DMF/H_2O (*v*/*v*=9/1, 1.0 mL). The sample was stirred and irradiated at 435 nm for 600 s (10 min).

For hydroalkylation reaction, MOF-525 (5.0 mol%), **4** (0.1 mmol), acrylonitrile (0.4 mmol), PMDETA (0.5 mmol), DMF/H_2O (*v*/*v*=1/1, 1.0 mL). The sample was stirred and irradiated at 435 nm for 3600 s (1 h).

For polyfluoroarylation reaction, MOF-525 (2.5 mol%), 1-iodocyclohexane (0.2 mmol), bromopentafluorobenzene (1.0 mmol), PMDETA (1.0 mmol), DMF (0.4 mL). The sample was stirred and irradiated at 435 nm for 3600 s (1 h).

The yield of the product was determined by gas chromatography, and the quantum yield was determined using the following eq 4. The experimental results were shown in Table S3.

$$\Phi = \frac{mol\ product}{flux \times t \times f} \tag{4}$$

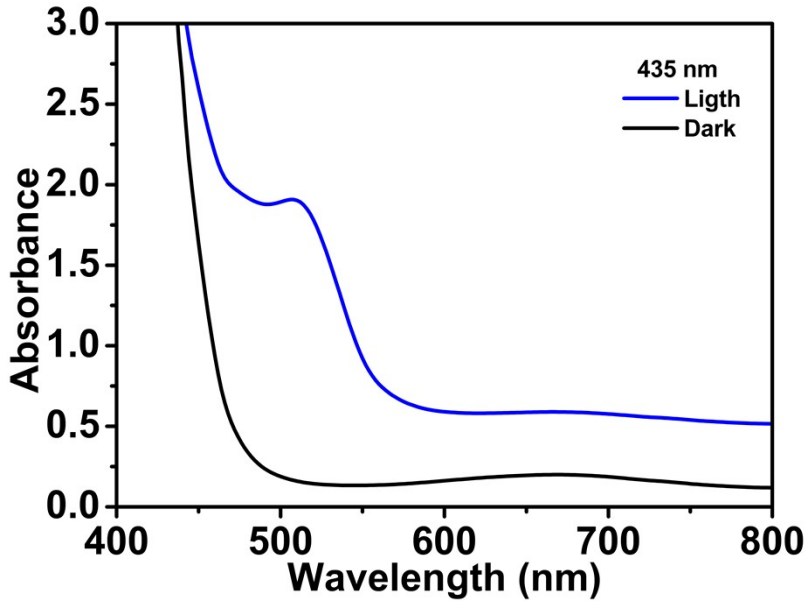


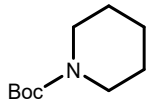
Figure S16. Absorbance of the ferrioxalate actinometer solution.

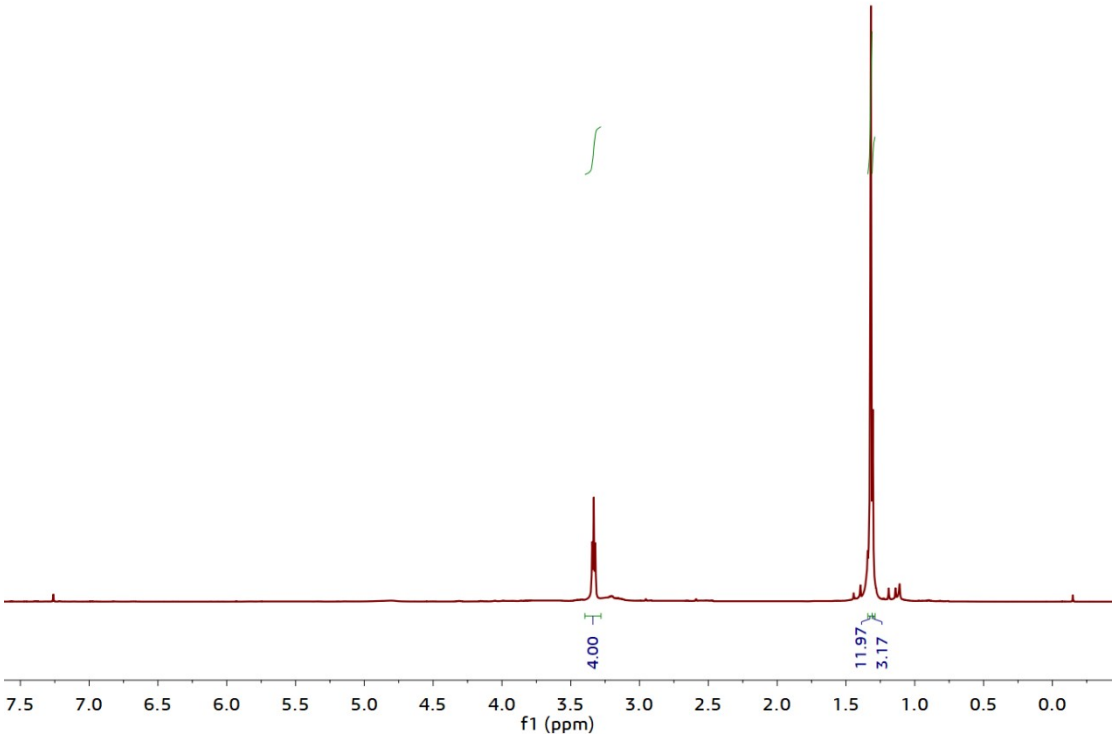
Table S3. Quantum yields of photocatalytic reactions at 435 nm.

Entry	Reaction	Time (s)	Yield (%)	Quantum yield
1	Dehalogenation	600	1.6	0.66
2	Hydroalkylation	3600	0.3	0.02
3	Polyfluoroarylation	3600	0.7	0.05

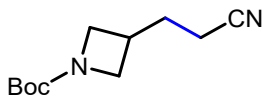
6. ^{1}H NMR Spectral Data

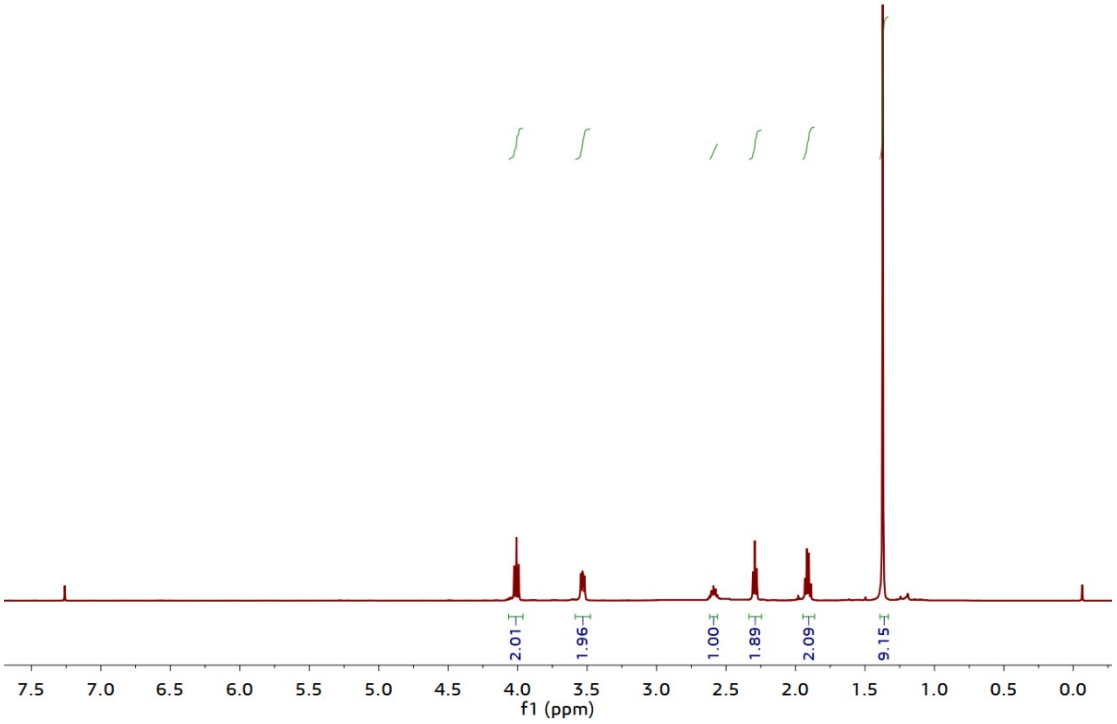
tert-Butyl piperidine-1-carboxylate



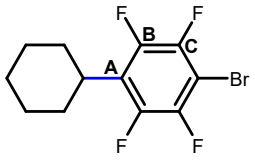


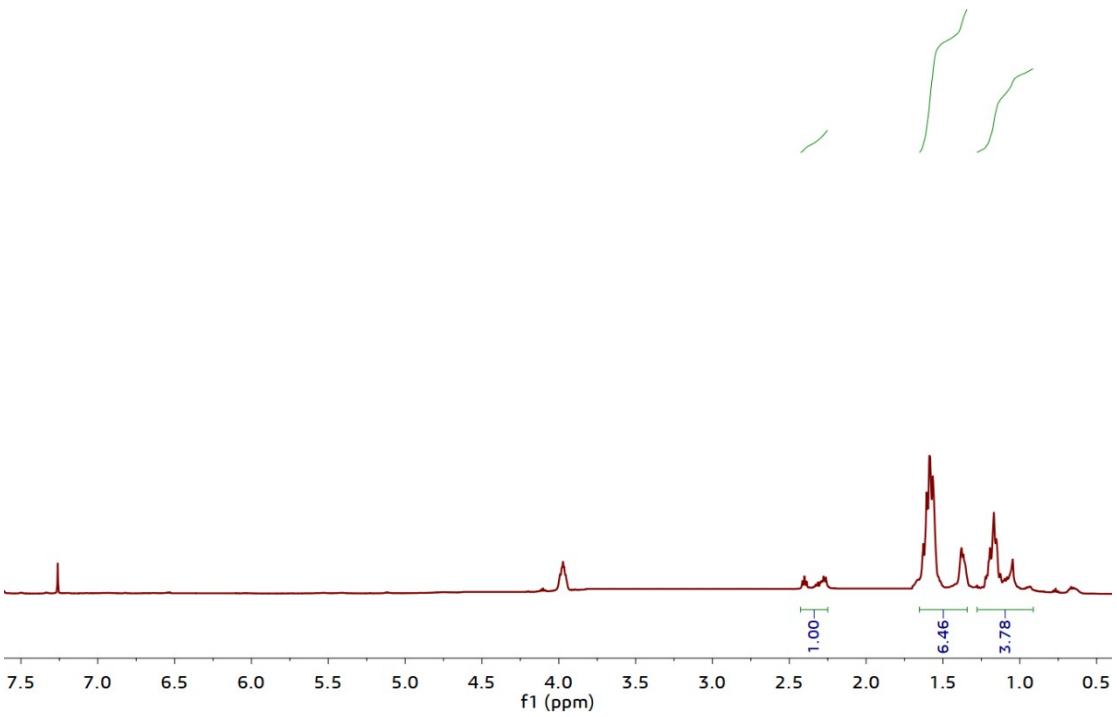
tert-Butyl 3-(2-Cyanoethyl)azetidine-1-carboxylate (18)





1-bromo-4-cyclohexyl-2,3,5,6-tetrafluorobenzene (21)





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