Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Carboxylate BODIPY integrated in MOF-5: easy preparation and solid state luminescence

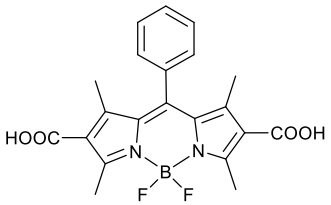
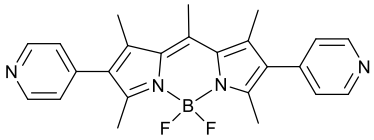
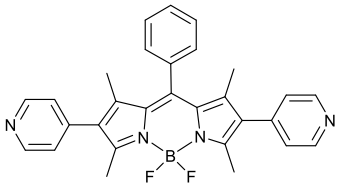
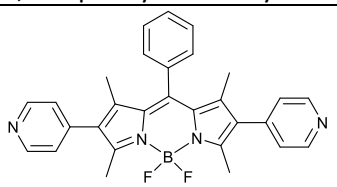
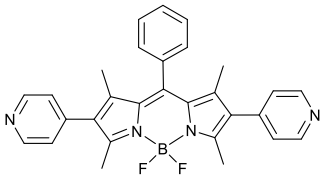
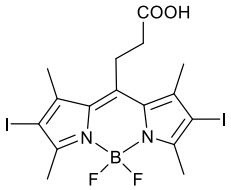
Alexis Tran[a], Marion Leroux[a], Clément Michelin[a], François Réveret[a], Damien Boyer[a], Federico Cisnetti[a]*

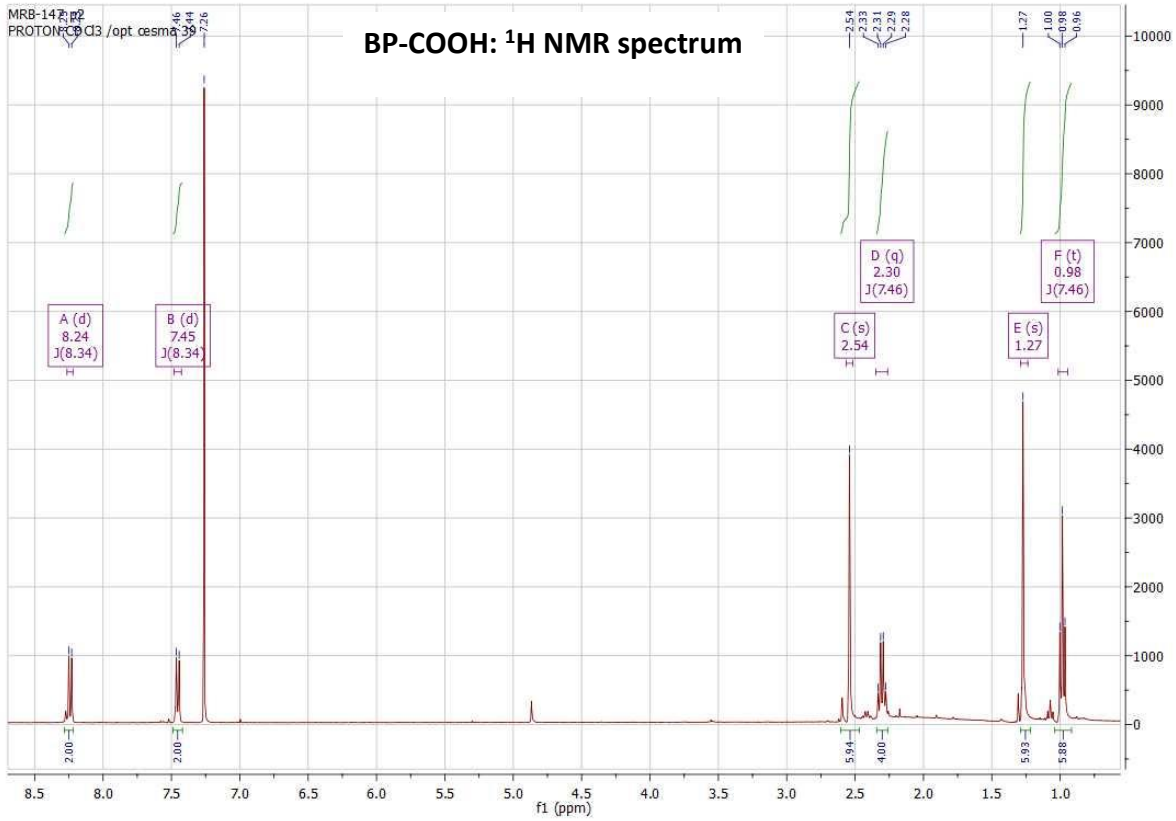
Université Clermont Auvergne, Clermont Auvergne INP, CNRS, ICCF, F-63000 Clermont-Ferrand. * federico.cisnetti@uca.fr

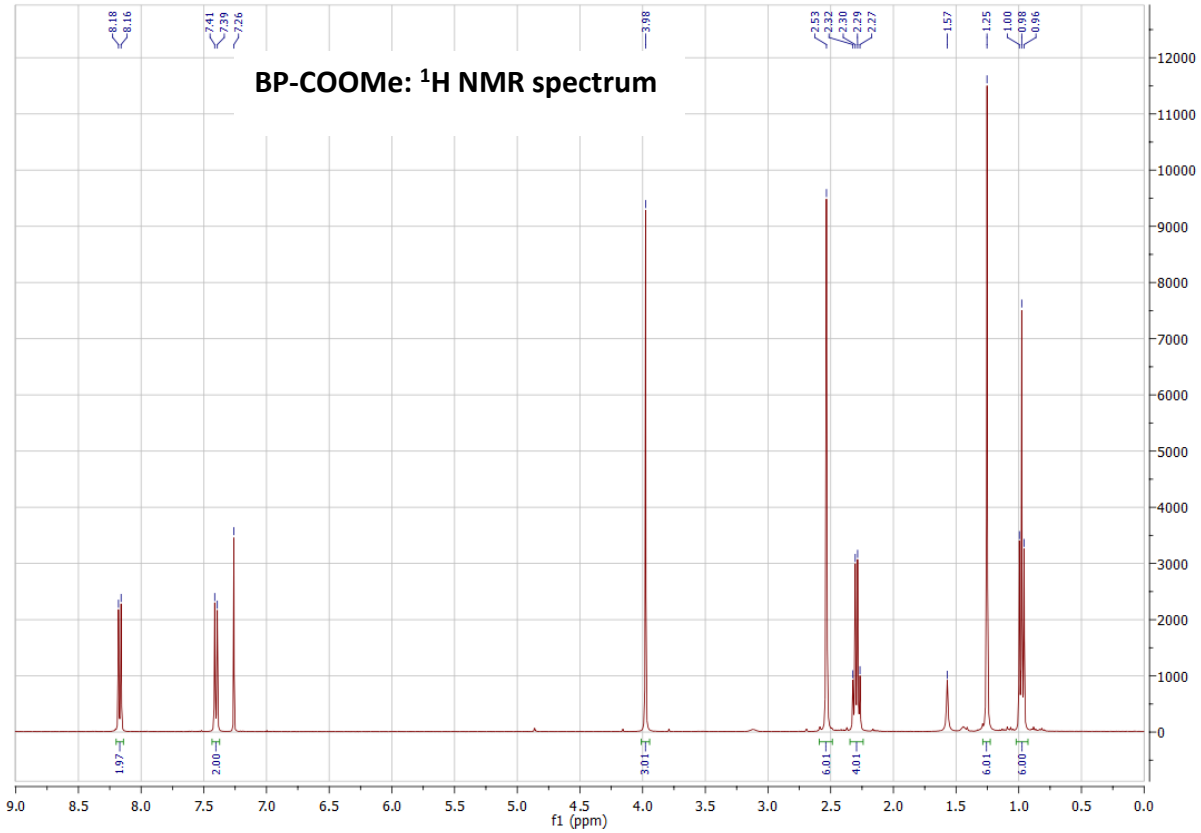
Supporting Information

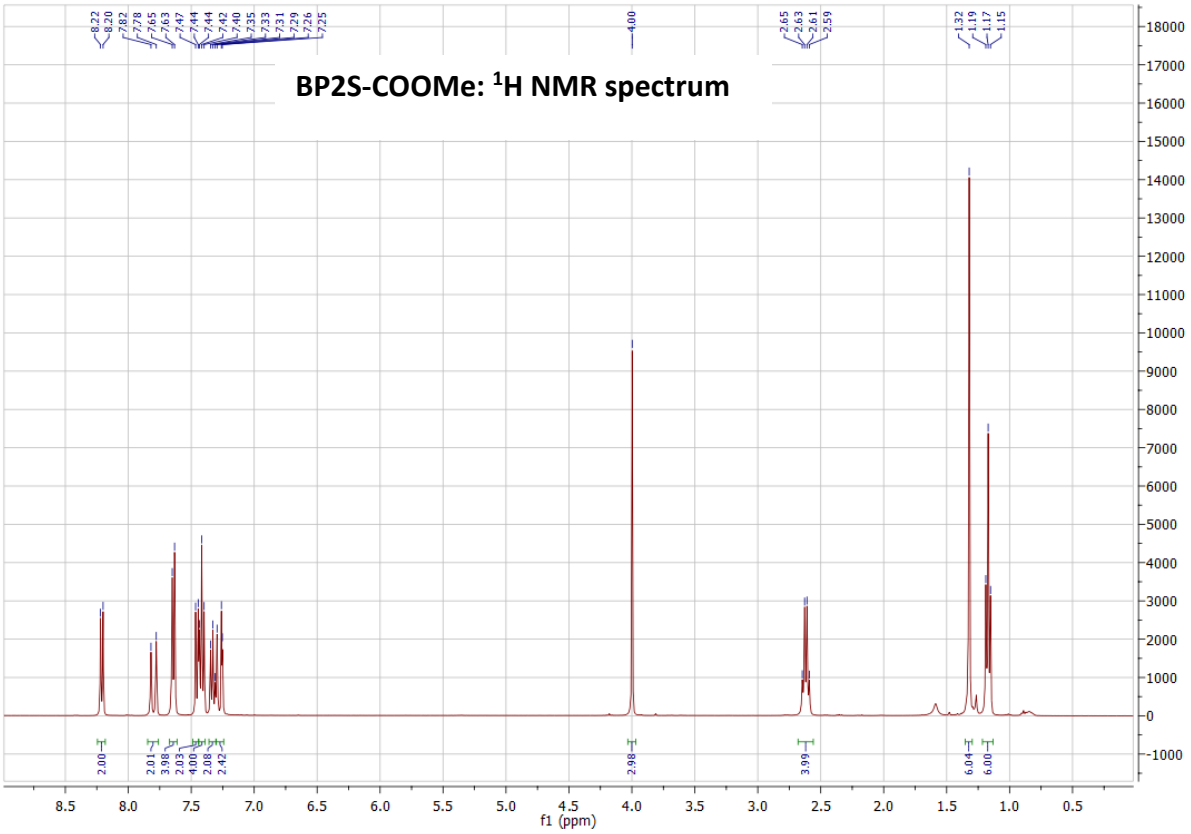
Contents

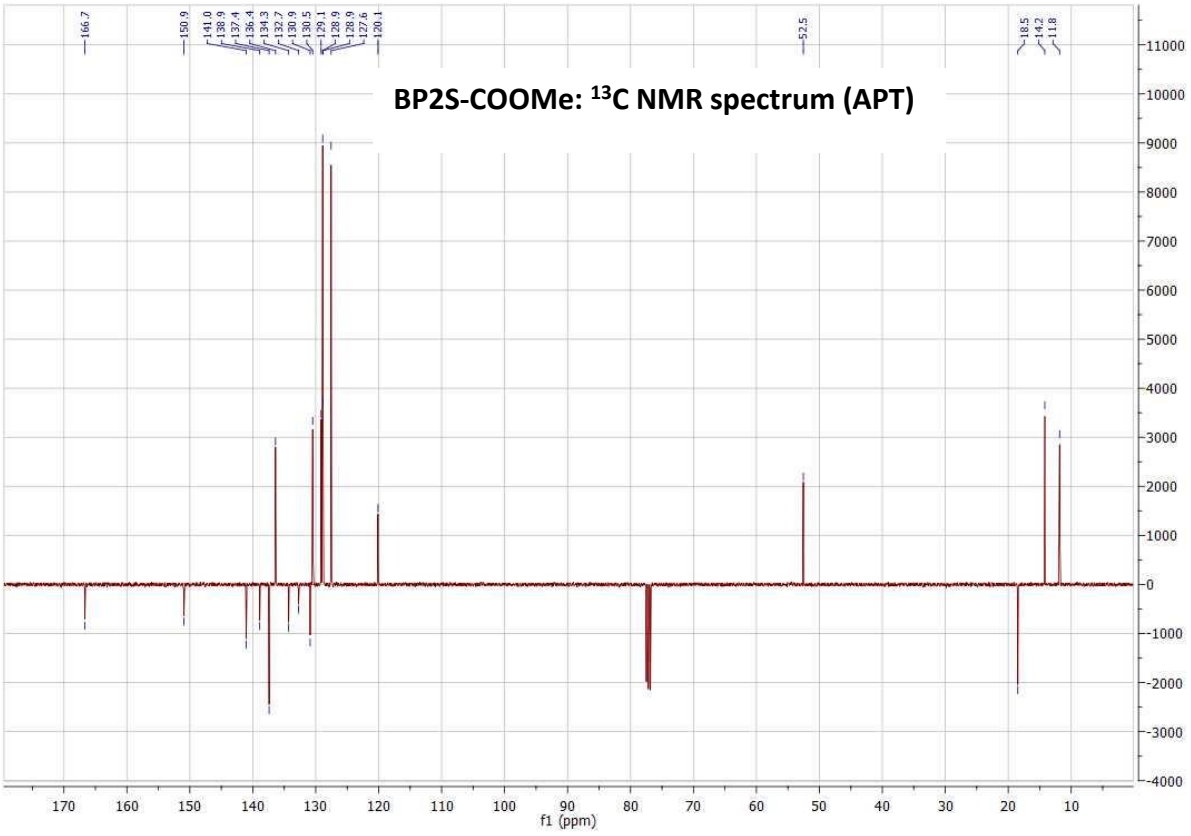
Table S1: Relevant literature comparisons

Reference	BODIPY (and other strut(s) if present)	Metal ion(s)	Synthetic method	PLQY or other luminescence property reported
Ref 17		Zn^{2+}, Cd^{2+}	Direct Solvothermal synthesis (presence of acid)	< 2% $PLQY_{int}$
Ref 18	 1,4-benzenedicarboxylic acid or 1,3,5-benzenetricarboxylic acid	Zn^{2+}, Cd^{2+}	Direct Solvothermal synthesis (presence of acid)	PLQY not reported ("strong photoluminescence")
Ref 19	 4,4'-biphenyldicarboxylic acid	Zn^{2+}	Direct solvothermal synthesis (presence of acid)	PLQY not reported (scope of ref. 19 is photocatalysis)
Ref 20	 anthracene dicarboxylic acid	Zn^{2+}	Direct solvothermal synthesis (presence of acid)	0.5% PLQY (upon excitation of the anthracene moiety, no other data reported)
Ref. 21	 ,4-dibromo-2,3,5,6-tetrakis(4-carboxyphenyl)benzene or tetraacid porphyrin)	Zn^{2+}	Direct solvothermal synthesis (presence of acid). Delayed addition of BODIPY in the case of porphyrin	PLQY not reported (energy transfer from BODIPY to porphyrin evidenced)
Ref 25	 terephthalic acid (preformed UiO-66)	Zr^{4+} (preformed UiO-66)	Ligand exchange	PLQY not reported (scope of ref 25 is X-ray tomography)
Ref. 26	BP-alkyne and azide-functionalized 1,3,5-benzenetribenzoic acid derivative (preformed PCN-262 derivative)	Fe^{3+} (preformed PCN-262 derivative)	Copper-catalysed azide alkyne cycloaddition on preformed MOF	PLQY not reported (fluorescence enhancement after reaction demonstrated)


BP-COOH: ^{1}H NMR spectrum
A (d)
8.24
J(8.34)
B (d)
7.45
J(8.34)
C (s)
2.54
D (q)
2.30
J(7.46)
E (s)
1.27
F (t)
0.98
J(7.46)
f1 (ppm)


BP-COOMe: ^{1}H NMR spectrum
f1 (ppm)


BP2S-COOMe: ^{1}H NMR spectrum
f1 (ppm)


BP2S-COOMe: ^{13}C NMR spectrum (APT)
f1 (ppm)

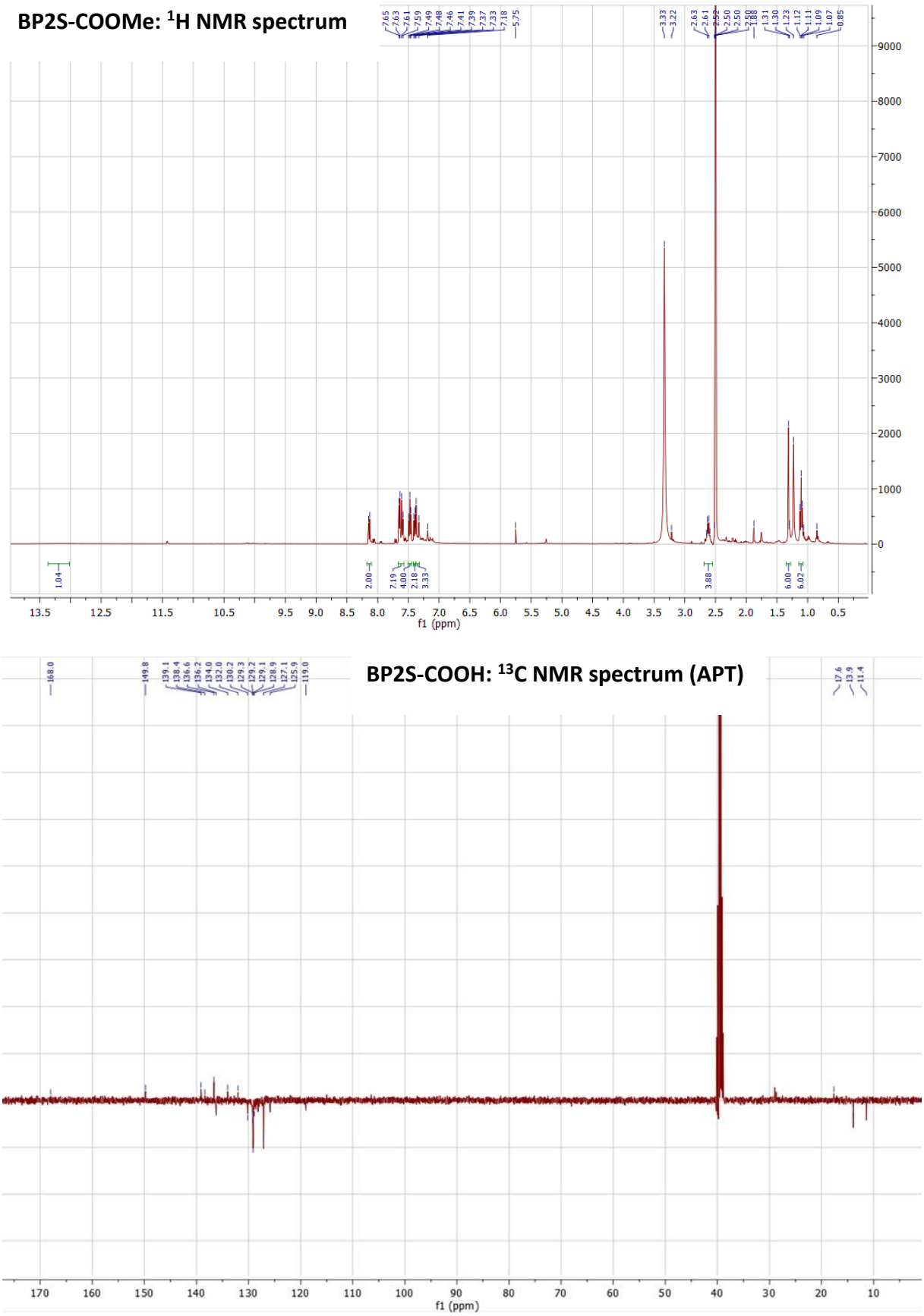


Fig. S1: ^{1}H and ^{13}C NMR spectra of organic compounds

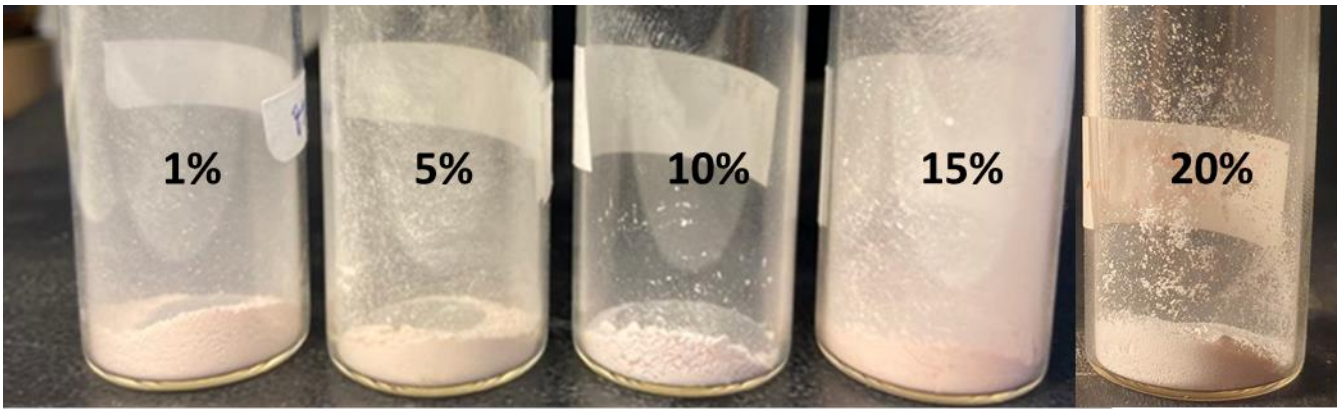


Fig. S2: MOF@BP-COO^- samples after synthesis and centrifugation under daylight.

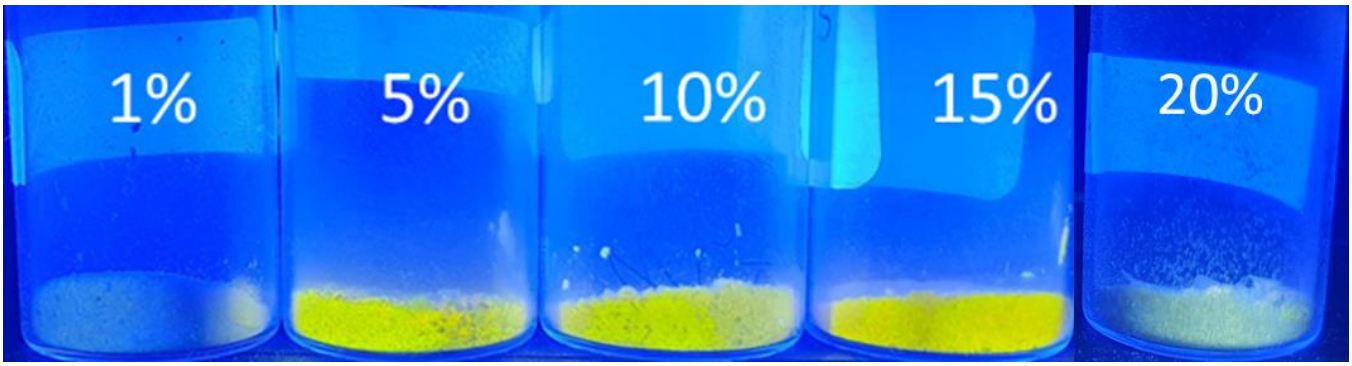


Fig. S3: MOF@BP-COO^- samples after synthesis and centrifugation under 365 nm UV lamp.

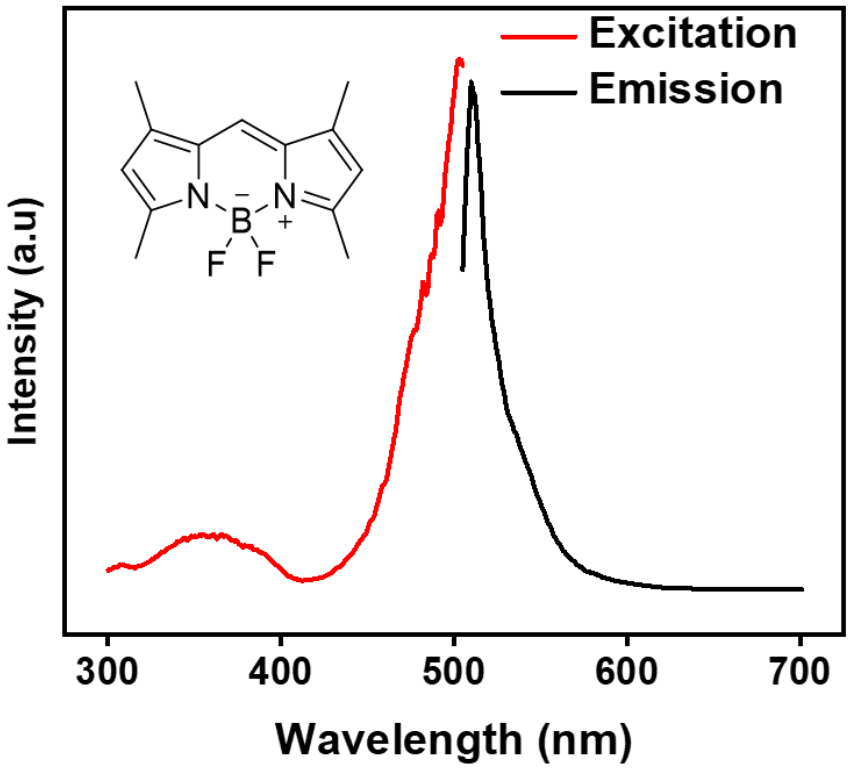


Fig. S4: Structure of BP2, its excitation (λ_{em} = 510 nm) and emission (λ_{exc} = 504 nm) spectra in EtOH at 1.10^{-5} mol.L^{-1}.

Fig. S5: From the right to the left: first and second supernatant for the attempted synthesis of MOF@BP2 under UV at 365 nm. MOF-5 after centrifugation in the centrifugation tube (not luminescent).

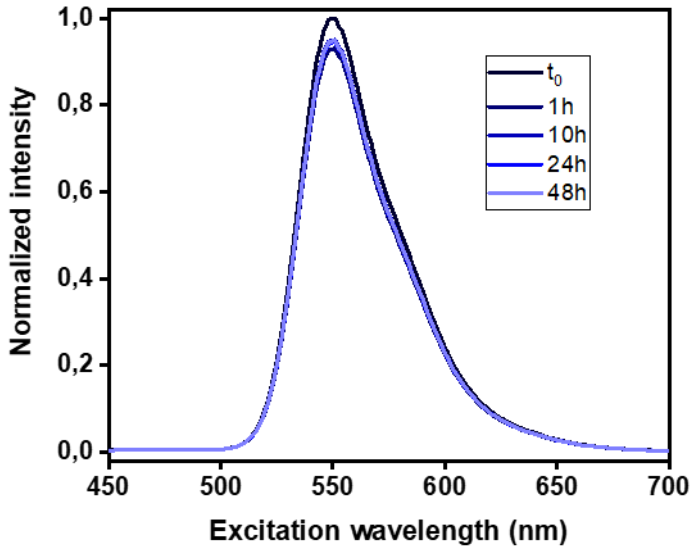


Fig. S6: Evolution of the emission spectra (λ_{ex} = 525 nm) of a MOF@BP-$COO^-_{10.6\%}$ sample after several hours in chloroform.

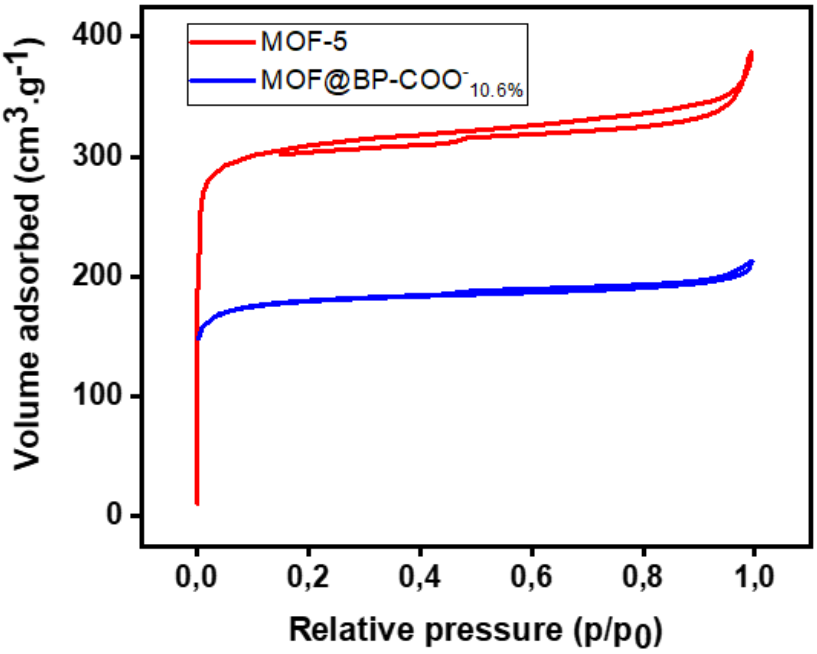


Fig. S7: Adsorption and desorption isotherms of the MOF-5 and the MOF@BP-$COO^-_{10.6\%}$ sample. The specific surface area for the MOF-5, measured by BET is 957 $m^2.g^{-1}$ and 560 $m^2.g^{-1}$ for the MOF@BP-$COO^-_{10.6}$%.

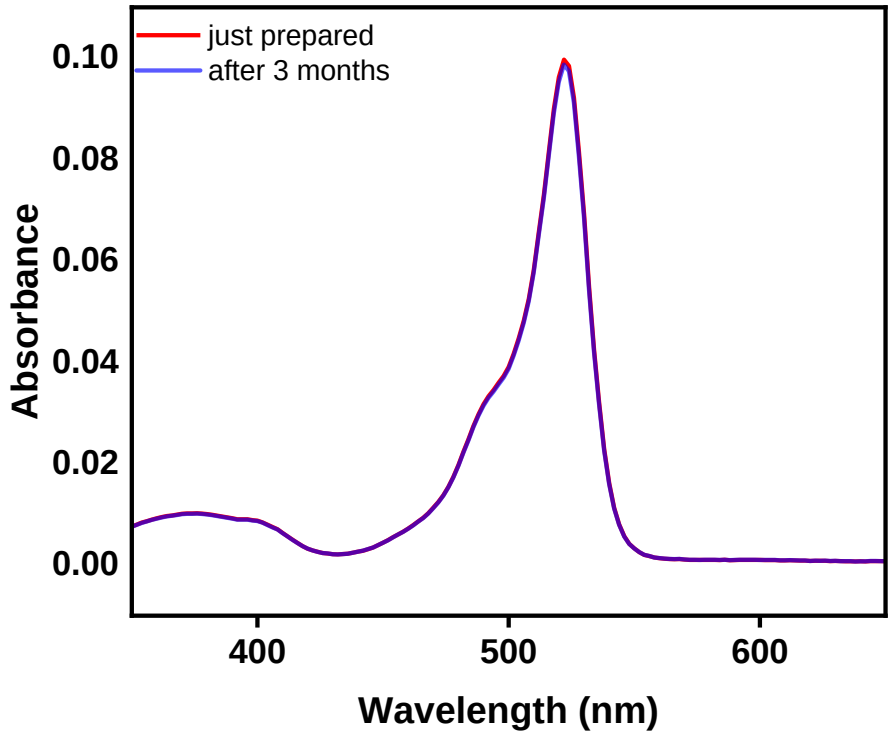


Fig. S8: Evolution of the absorption spectra of BP-COO⁻ in solution (DMF/Et_3N: 75/1; *v*/*v*) after 3 months (3.4 10^{-5} mol.L^{-1} stock solution diluted 100 times).

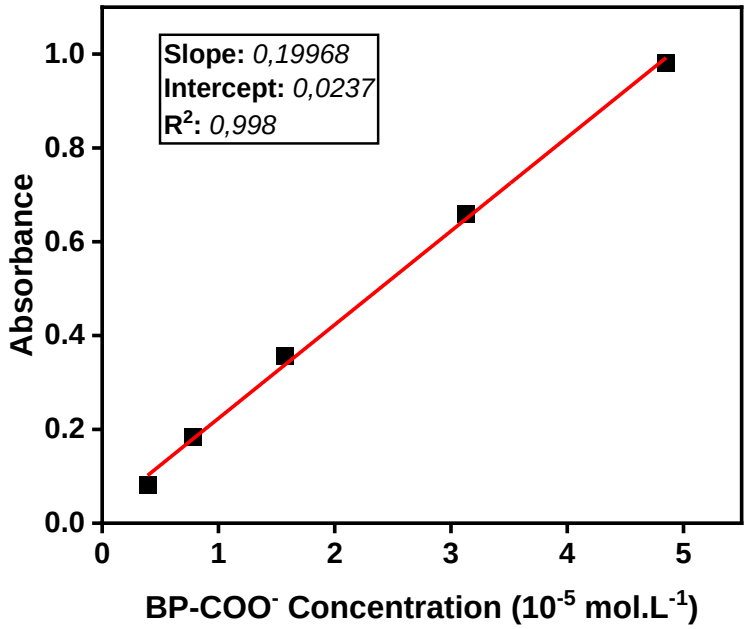


Fig. S9: Absorbance standard curve at λ_{max} for BP-COO⁻ in solution (DMF/Et_3N; 75/1; *v*/*v*) as a function of the concentration

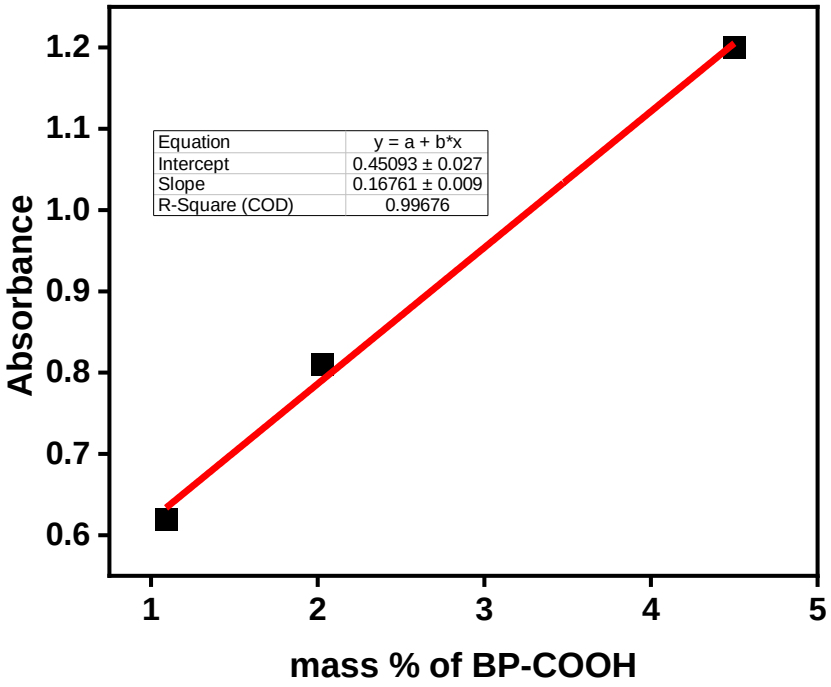
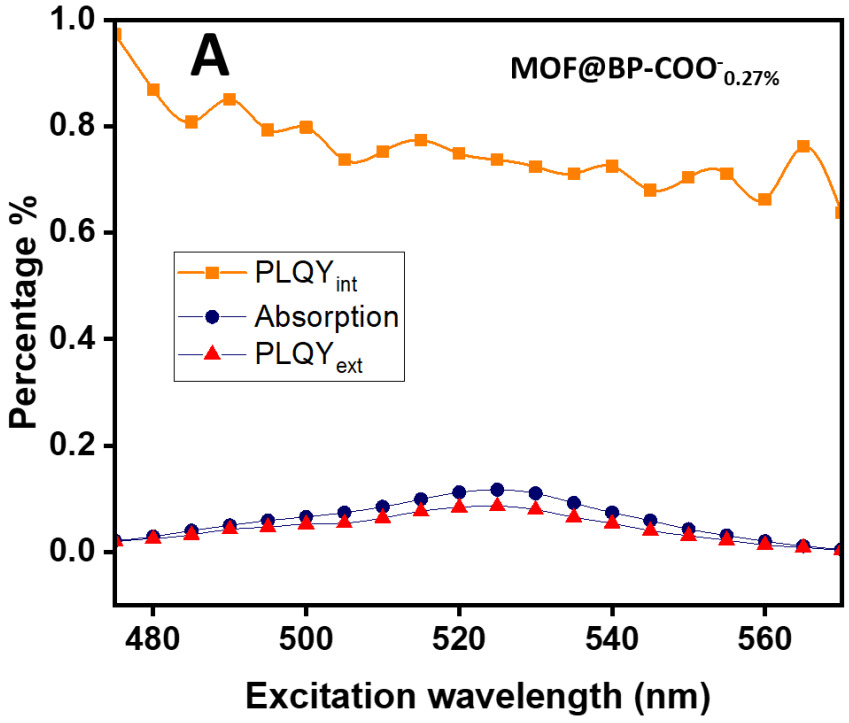
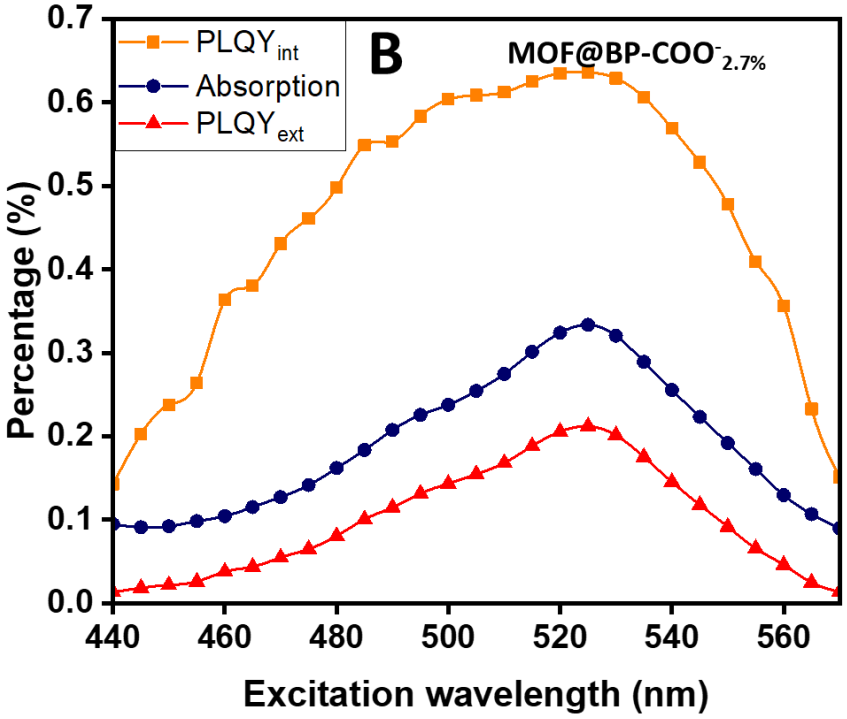
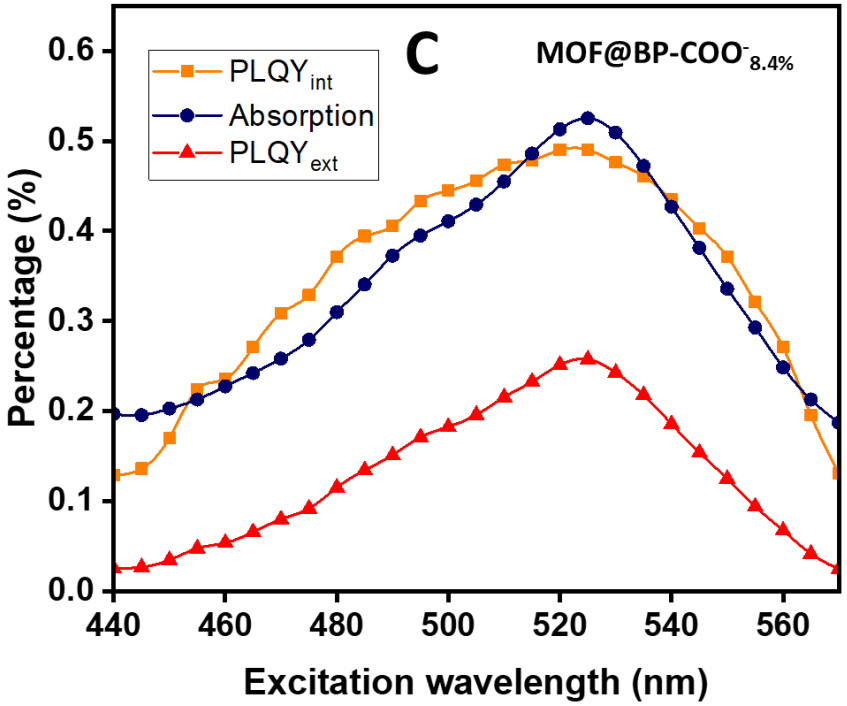


Fig. S10: Absorbance standard curve at λ_{max} for BP-COO^- in KBr pellets as a function of the mass % of BP-COOH in the pellets




B
MOF@BP-COO-2.7%
PLQYint
Absorption
PLQYext
Percentage (%)
Excitation wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
440
460
480
500
520
540
560


C
MOF@BP-COO-8.4%
PLQYint
Absorption
PLQYext
Percentage (%)
Excitation wavelength (nm)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
440
460
480
500
520
540
560

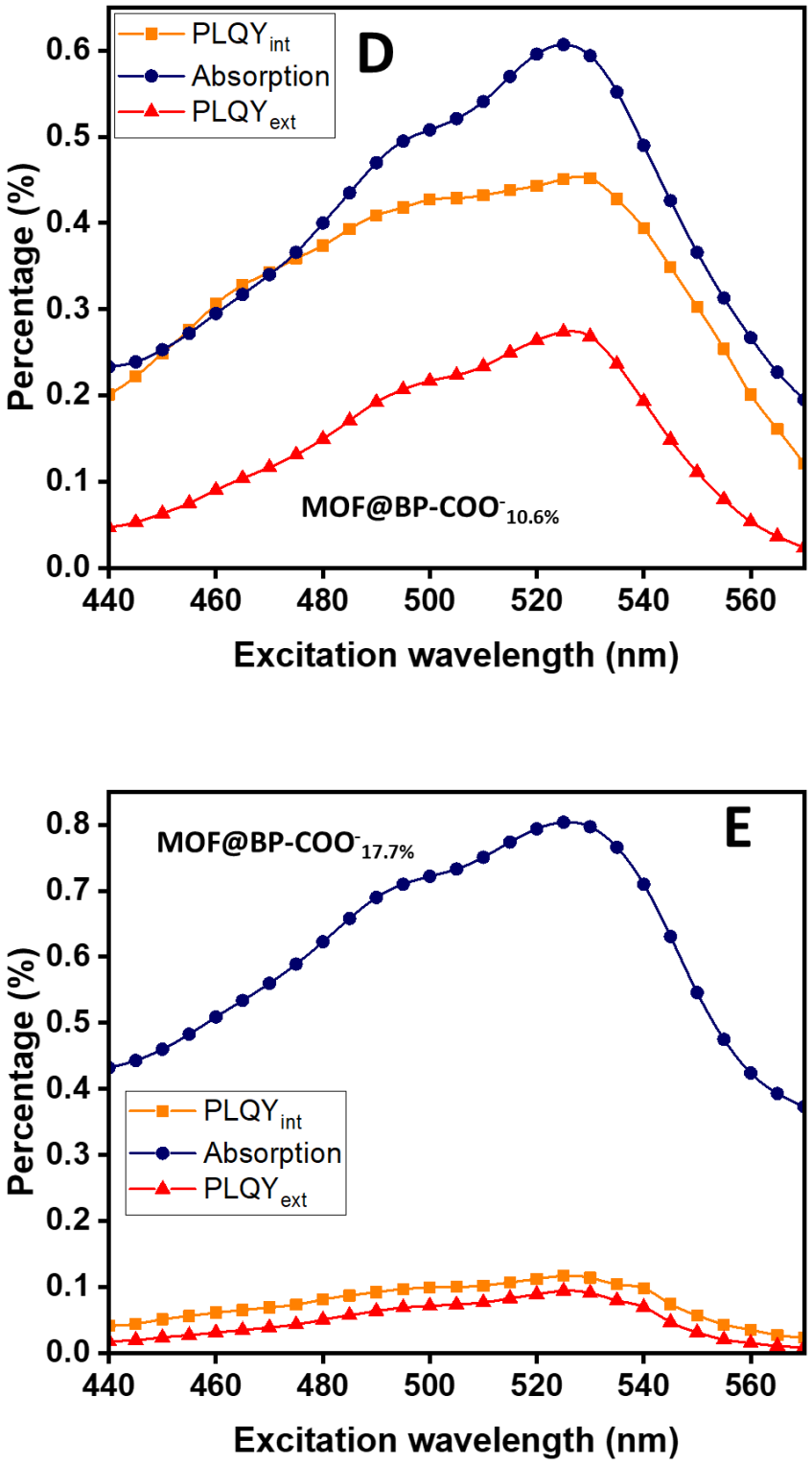


Fig. S11: Evolution of $PLQY_{int,}$ the absorption coefficient and $PLQY_{ext}$, as function of the excitation wavelength for the different MOF@BP-$COO^-_{x\%}$ samples (A: *x* = 0.27%, B: *x* = 2.7%, C: *x* = 8.4%, D: *x* = 10.6%, E: *x* = 17.7%).

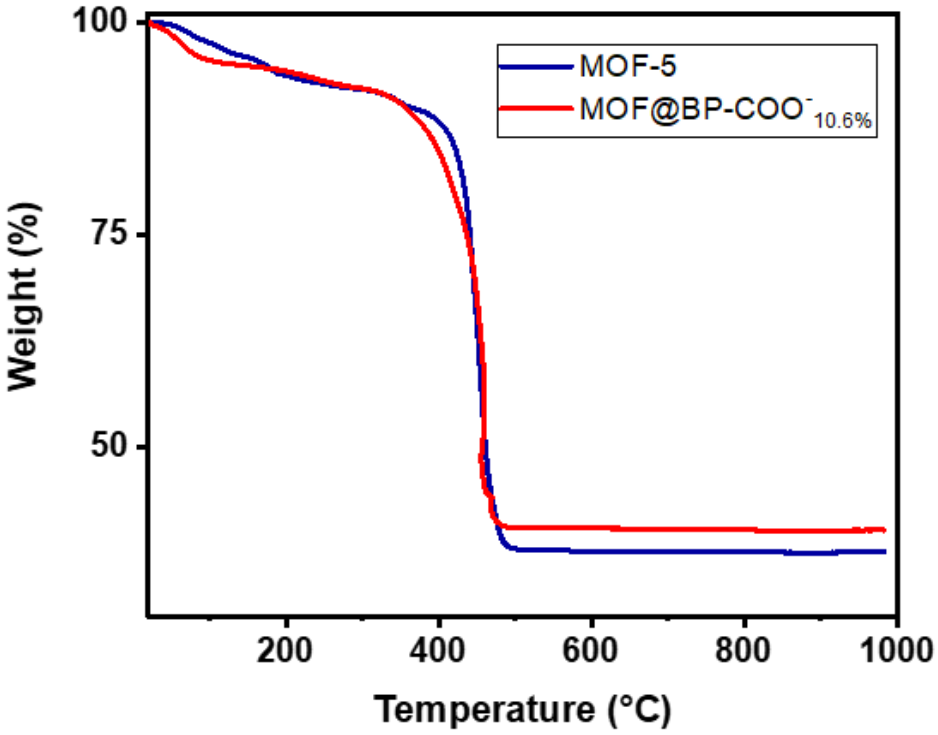


Fig. S12: TGA analysis of a MOF@BP-$COO^-_{10.6\%}$ compared with a MOF-5 sample prepared in the same conditions.

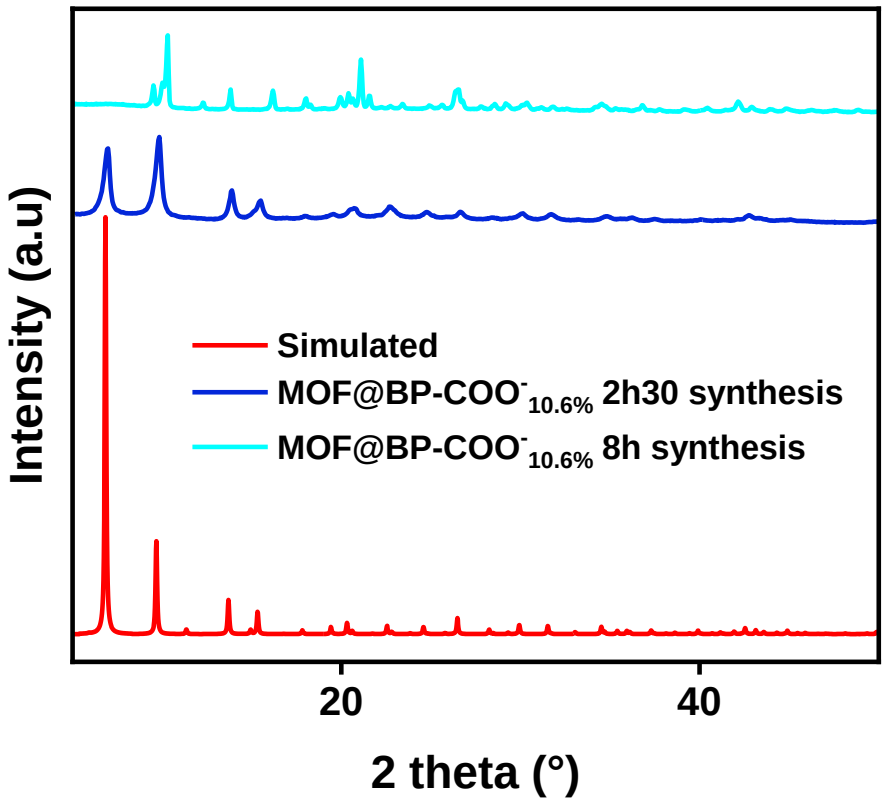


Fig. S13: Diffractogram of MOF@BP-$COO^-_{10.6\%}$ after 2h30 and 8h of synthesis.

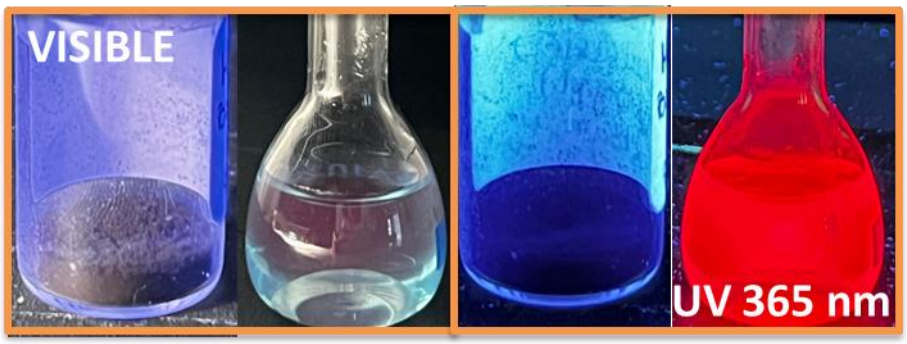


Fig. S14: Picture of BP2S-COOH in solid state and in solution (DMF/Et_3N; 75/1; *v*/*v*) under daylight and UV (365 nm).

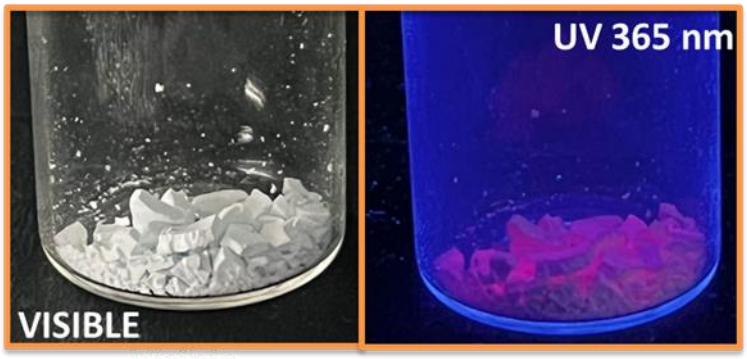


Fig. S15: Picture of the synthesized MOF@BP2S-COO^- under daylight and UV (365 nm).

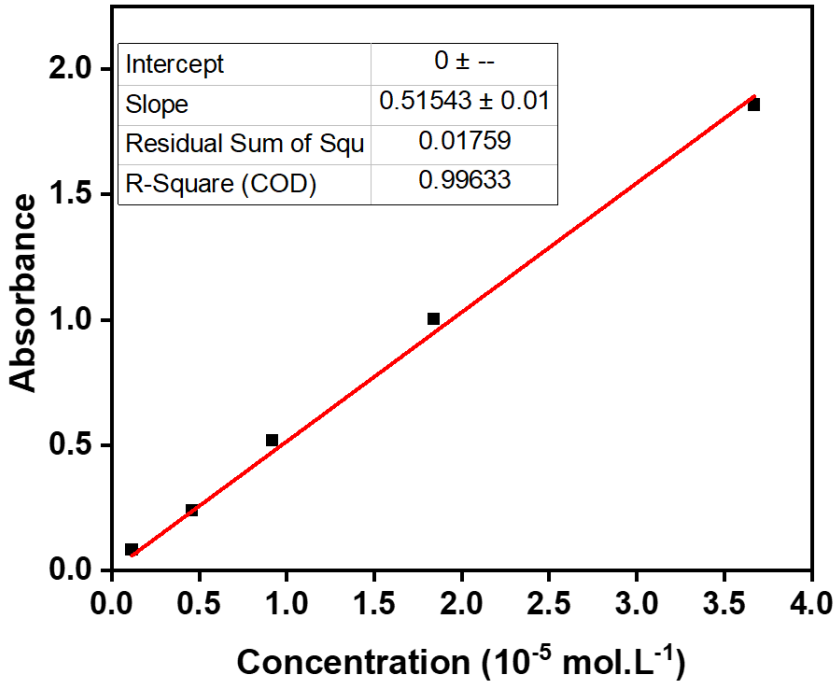


Fig. S16: Absorbance standard curve at λ_{max} for BP2S-COO^- in solution (DMF/Et_3N; 75/1; *v*/*v*) as a function of the concentration.

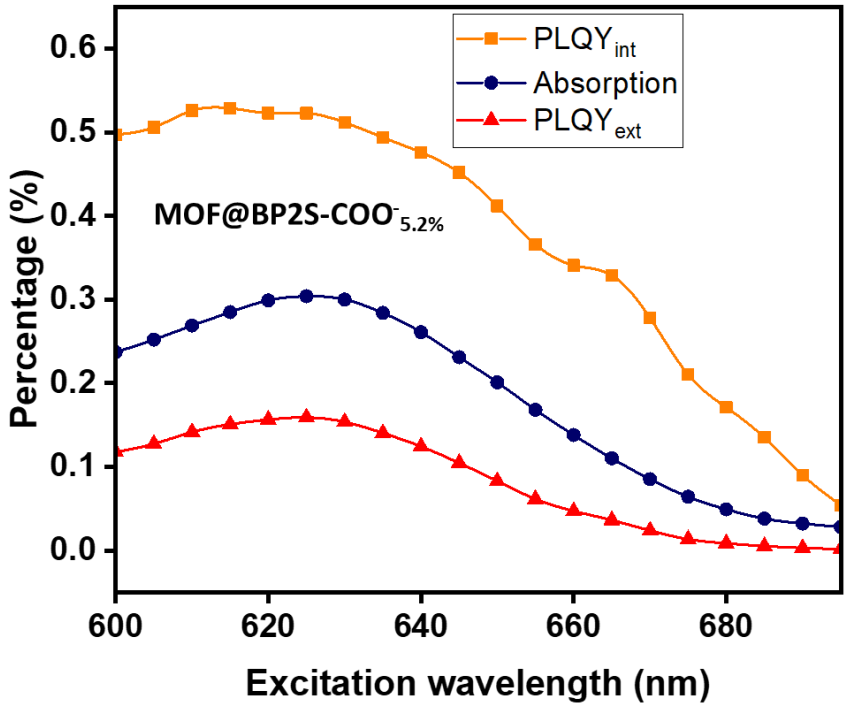


Fig. S17: Evolution of $PLQY_{int}$, the absorption coefficient and $PLQY_{ext}$, as function of the excitation wavelength for the MOF@BP2S-$COO^-_{5.2\%}$.