Supporting information

Supercritical CO_2 synthesis of porous metalloporphyrin frameworks: application in photodynamic therapy

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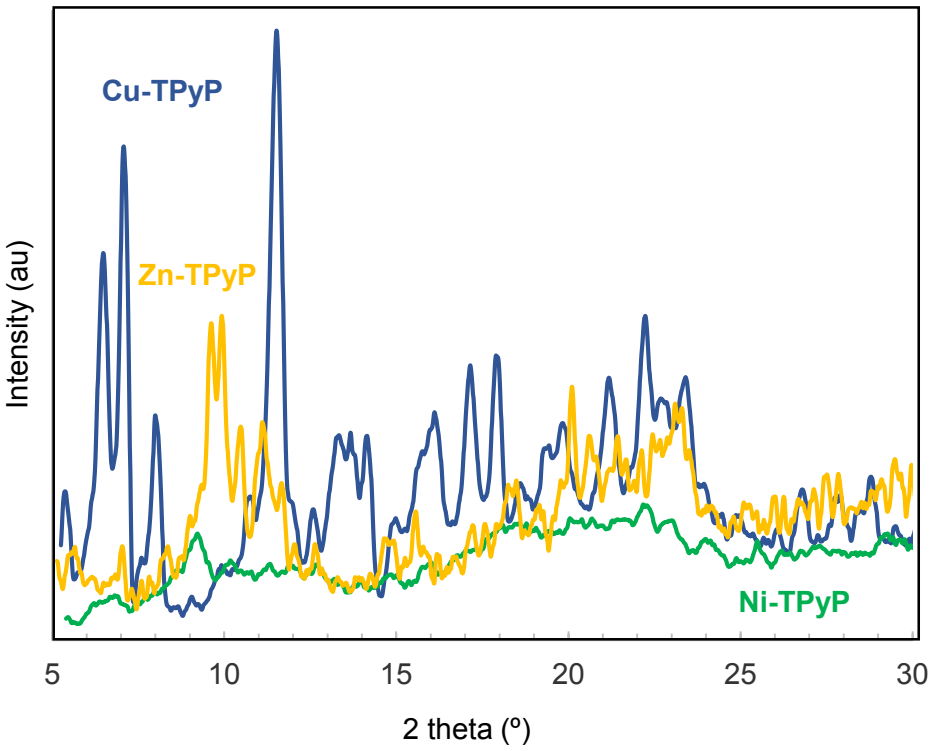

Figure S1. Capillary PXRD patterns of reaction products from the layering runs of Cu(II), Zn(II) an Ni (II) reacted with H_2TPyP.

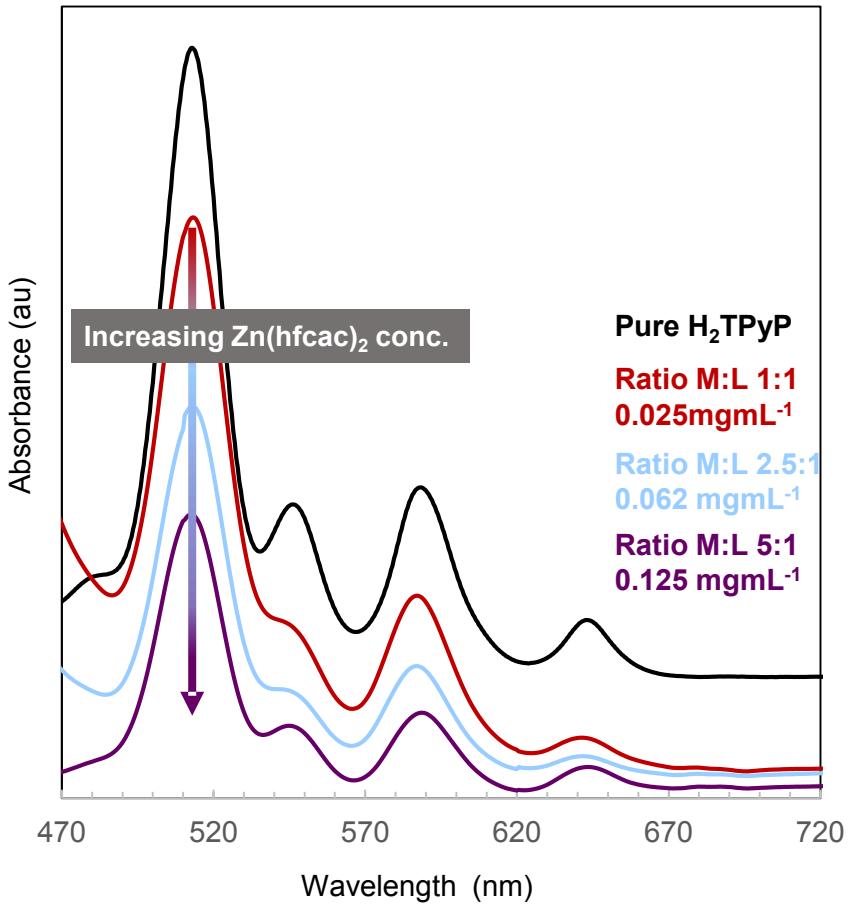

Figure S2. Titration experiments of H_2TPyP with $Zn(hfac)_2$. The porphyrin concentration was 0.025 $mgmL^{-1}$. The concentrations for the metal were 0.025 $mgmL^{-1}$ (red), 0.0625 $mgmL^{-1}$ (blue) and 0.125 $mgmL^{-1}$ (purple).

Table S1. Crystallographic data for compound $[\{Co(hfac)_2\}H_2TPyP]_n$ determined by single crystal diffraction.

Compound	**$[\{Co(hfac)_2\}H_2TPyP]_n$**
Empirical formula	$C_{15}H_{7.5}CoF_6N_2O_2$
Formula weight	391.19
Radiation	X-rays
T (K)	100(2)
Wavelength (Å)	0.72932
System, space group	Monoclinic, *C 2/m (12)*
a (Å)	22.913(10)
b (Å)	25.721(4)
c (Å)	6.524(1)
β (°)	105.60(2)
V (Å^3)	3703.25
Z	8
*D*calc (g cm^{-3})	1.403
μ (mm^{-1})	0.597
F(000)	1560
Crystal size (mm^3)	0.100x0.060x0.040
hkl ranges	-31≤h≤31, -35≤k≤35, -8≤l≤8
2θ range (°)	1.248 to 29.967
Reflections collected/unique/[R_{int}]	125748/5021/[R_{int} = 0.0546]
Completeness	98.6%
Refinement method	Full matrix least-squares on $\|F\|^2$
Data/restrains/parameters	5021/0/234
Goodness of fit (GOF) on $\|F\|^2$	1.134
Final *R* indices [$I>2\sigma(I)$]	R1 = 0.0483, wR2 = 0.1401
R indices (all data)	R1 = 0.0500, wR2 = 0.1416
Largest. Diff. peak and hole (e Å^{-3})	0.945 and -0.995

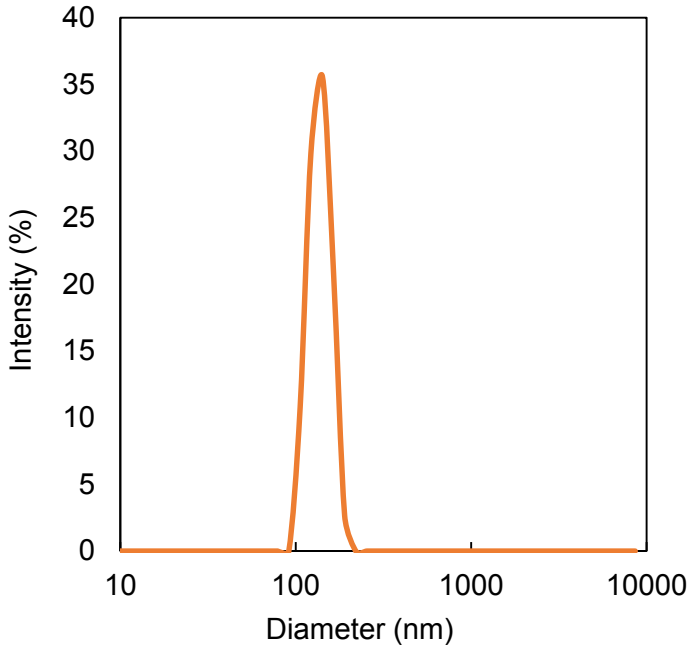

Figure S3. DLS measurement of $[Zn\text{-}TPyP]_n$ sample in water.

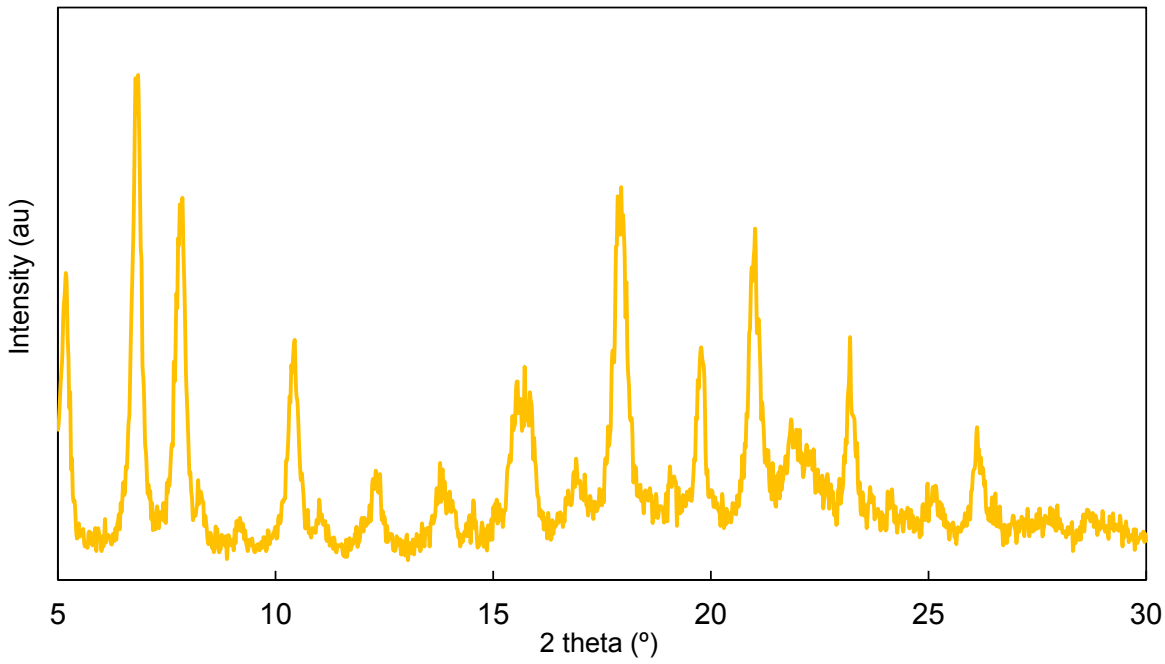

Figure S4. PXRD of the $[Zn\text{-}TPyP]_n$ sample after its dispersion in water achieved applying sonication.

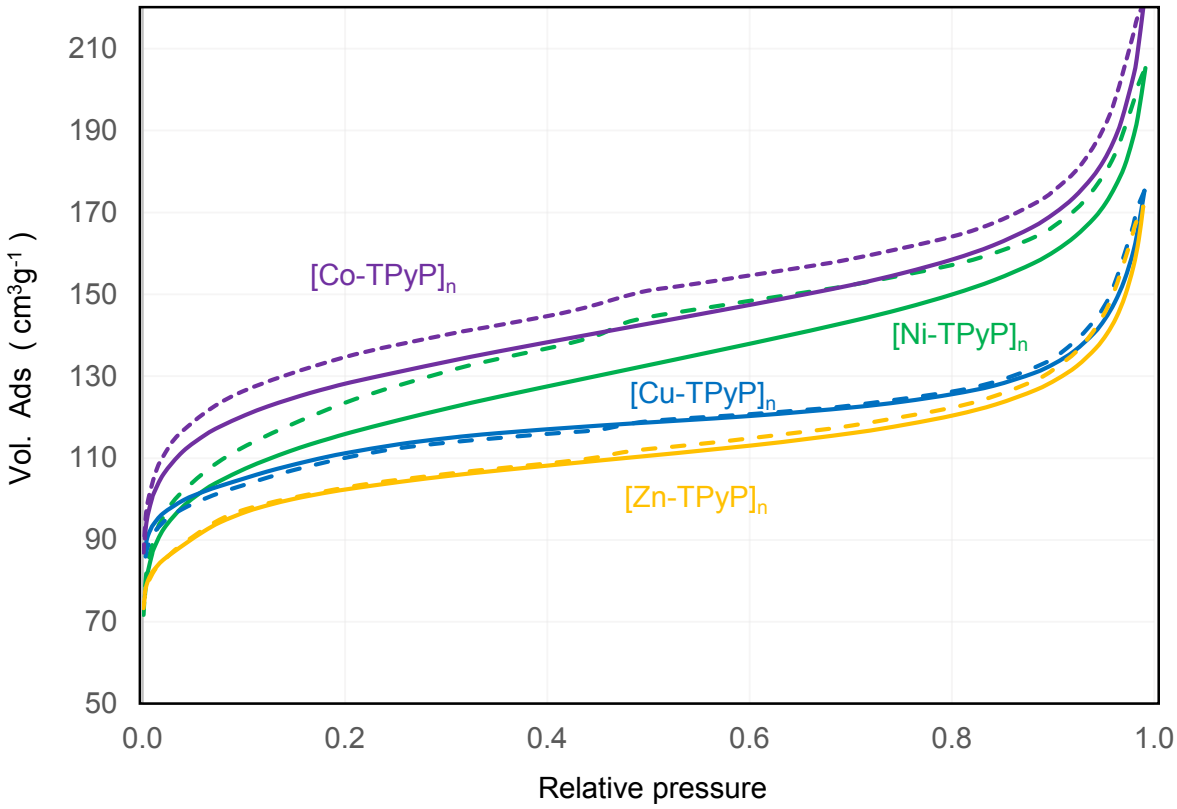

Figure S5. N_2 adsorption-desorption isotherms at -196 ºC for all samples.

Table S2. Experimentally measured C, H and N molar percentages obtained by elemental analysis, presented together with metal molar percentages by ICP for the samples precipitated in $scCO_2$.

Sample	Atom	Exp. data	Derived viable formula
$[Cu\text{-}TPyP]_n$	C	46.44	$[(Cu(hfac)_2)_2Cu_{0.32}\ (H_2)_{0.67}TPyP]_n$
	H	1.96	1.0 % H_2TpyP
	N	6.99	
	Cu	9.22	
$[Zn\text{-}TPyP]_n$	C	46.74	$[(Zn(hfac)_2)_2Zn_{0.30}(H_2)_{0.70}TPyP]_n$
	H	1.94	
	N	7.40	
	Zn	9.31	
$[Co\text{-}TPyP]_n$	C	44.45	$[(Co(hfac)_2)_2Co_{0.70}(H_2)_{0.30}TPyP]_n$
	H	2.00	
	N	6.40	
	Co	9.24	
$[Ni\text{-}TPyP]_n$	C	44.64	$[(Ni(hfac)_2)_2NiTPyP]_n$
	H	1.67	3.5 % $Ni(hfac)_2$
	N	6.63	
	Ni	14.31	