

Supporting Information

**Metalloporphyrin-based Metal-organic Frameworks for
Photocatalytic Carbon Dioxide Reduction: The Influence of
Metal Centers**

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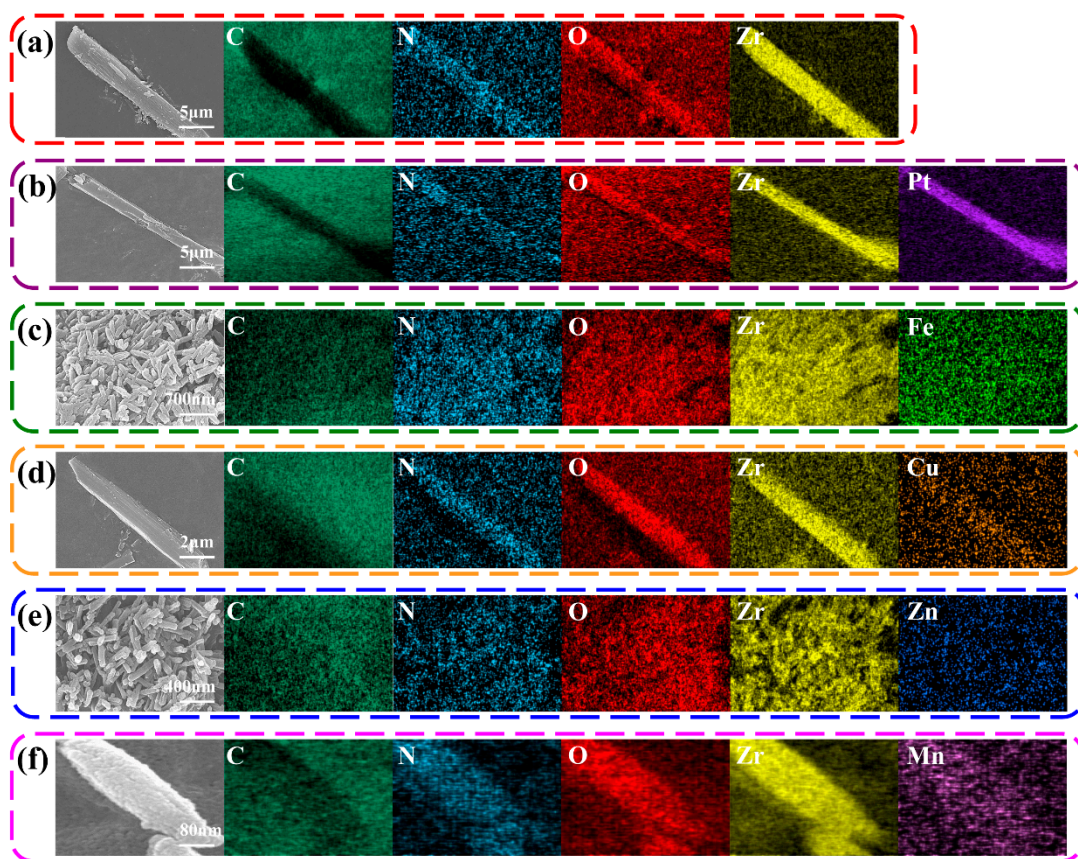


Figure S1. EDX-mapping images of (a) PCN-222(2H), (b) PCN-222(2H&Pt), (c) PCN-222(2H&Fe), (d) PCN-222(2H&Cu), (e) PCN-222(2H&Zn) and (f) PCN-222(2H&Mn), respectively.

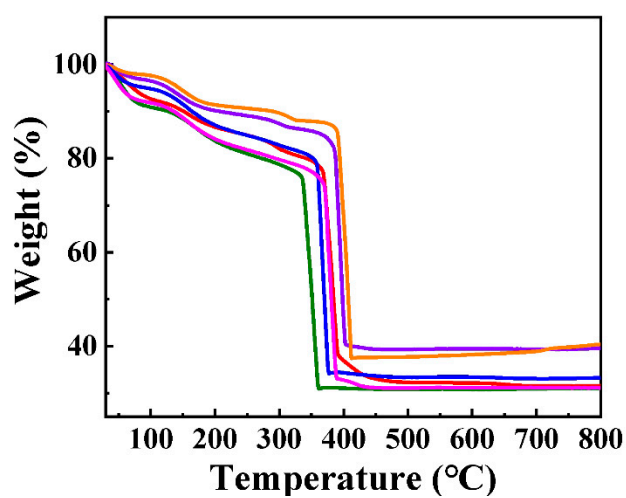


Figure S2. TGA curves of PCN-222(2H) and PCN-222(2H&M).

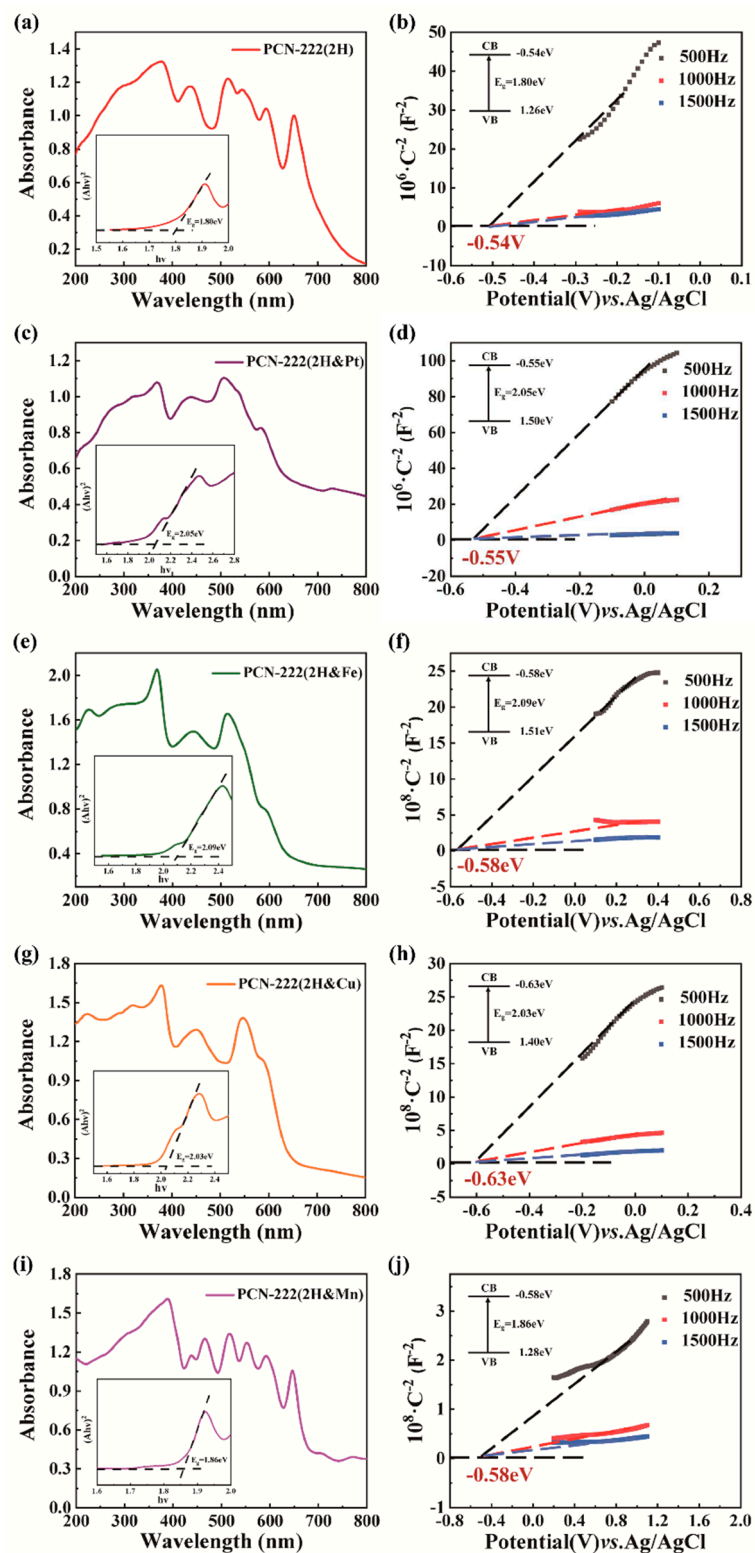


Figure S3. (a) UV-vis diffusion spectra and Tauc plot of PCN-222(2H), (b) Mott-Schottky plots of PCN-222(2H), (c) UV-vis diffusion spectra and Tauc plot of PCN-222(2H&Pt), (d) Mott-Schottky plots of PCN-222(2H&Pt), (e) UV-vis diffusion spectra and Tauc plot of PCN-222(2H&Fe), (f) Mott-Schottky plots of PCN-

222(2H&Fe), (g) UV-vis diffusion spectra and Tauc plot of PCN-222(2H&Cu), (h) Mott-Schottky plots of PCN-222(2H&Cu), (i) UV-vis diffusion spectra and Tauc plot of PCN-222(2H&Mn), and (j) Mott-Schottky plots of PCN-222(2H&Mn).

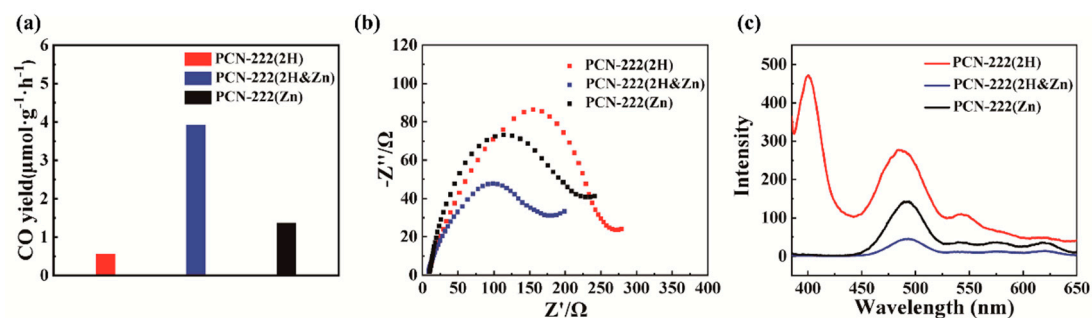


Figure S4. (a) The average CO yield, (b) EIS and (c) solid-state PL spectra excited at $\lambda = 350$ nm of PCN-222(2H), PCN-222(2H&Zn) and PCN-222(Zn).

Table S1. Structural characteristics of PCN-222 materials

	SSA/m ² ·g ⁻¹	$V_{\text{total}}/\text{cm}^3\text{ g}^{-1}$	V_{micro}	V_{meso}	$V_{\text{meso}}/V_{\text{micro}}$
2H	1553	1.09	0.33	0.72	2.15
Zn	1350	0.85	0.25	0.57	2.29
Cu	1249	0.75	0.22	0.49	2.19
Pt	1126	0.68	0.23	0.43	1.92
Fe	1124	0.69	0.20	0.45	2.29
Mn	1071	0.45	0.10	0.29	2.86

Table S2. Summary of photocatalytic CO₂ reduction performances of porphyrin-based MOFs materials in water or water vapor without the use of any organic solvent, photosensitizer, and sacrificial reagent.

Photocatalyst	Reaction condition	Products	References
PCN-224(Cu)	CO ₂ , H ₂ O	CO: 3.717 μmol/(g·h) CH ₄ : 1.357 μmol/(g·h)	<i>ACS Sustainable Chem. Eng.</i> 2019 , 7, 15660
15%PCN-224(Cu)/TiO ₂	CO ₂ , H ₂ O	CO: 37.21 μmol/(g·h) CH ₄ : 0.2113 μmol/(g·h)	
TiO ₂	CO ₂ , H ₂ O	CO: 0.8183 μmol/(g·h)	
PCN-601	CO ₂ , H ₂ O vapor	CO: 6.0 μmol/(g·h) CH ₄ : 10.1 μmol/(g·h)	<i>J. Am. Chem. Soc.</i> 2020 , 142, 12515
PCN-222	CO ₂ , H ₂ O vapor	CO: 5.5 μmol/(g·h) CH ₄ : 3.5 μmol/(g·h)	
Ni ₃ TCPP	CO ₂ , H ₂ O vapor	CO: 1.5 μmol/(g·h) CH ₄ : 0.6 μmol/(g·h)	
PCN-222(Cu)	CO ₂ , H ₂ O	CO: ~0.2 μmol/(g·h)	<i>Wuli Huaxue Xuebao.</i> 2020 , 36, 19050861-19050868
10%PCN-222(Cu)/TiO ₂	CO ₂ , H ₂ O	CO: 13.24 μmol/(g·h) CH ₄ : 1.73 μmol/(g·h)	