Supporting Information

Hierarchical Hybrid Metal–Organic Frameworks: Tuning the Visible/ Near Infrared Optical Properties by a Combination of Porphyrin and Its Isomer Units

Yufeng Yang,[†] Masatoshi Ishida,[*,†] Yuhsuke Yasutake,[‡] Susumu Fukatsu,[‡] Chihoko Fukakusa,[†] Masa-aki Morikawa,[†] Teppei Yamada,[†] Nobuo Kimizuka,[†] and Hiroyuki Furuta[*,†]

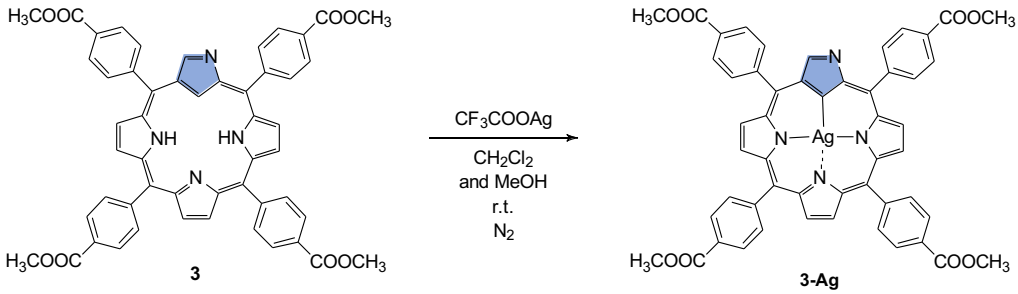
[†]*Department of Chemistry and Biochemistry, Graduate School of Engineering, and Center for Molecular Systems, Kyushu University, Fukuoka 819-0395, Japan*

[‡]*Graduate School of Arts and Sciences, The University of Tokyo, Tokyo 153-8902, Japan*

Content:

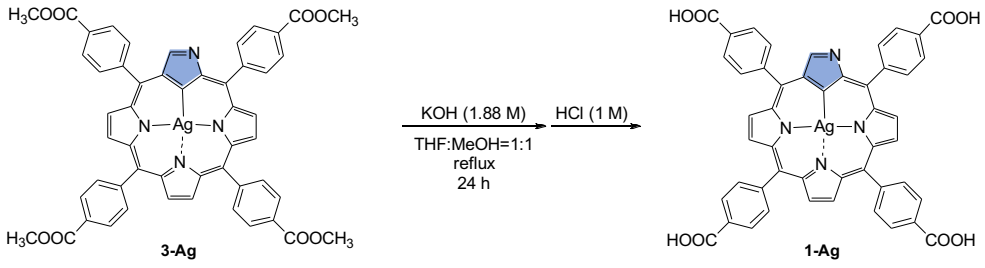
1. Synthesis

Synthesis of [2-aza-5,10,15,20-tetrakis(*p*-methoxycarbonylphenyl)-21-carbaporphyrinato]-Ag(III) (3-Ag) [s1]



To a 200 mL of 3-necked flask, 2-aza-5,10,15,20-tetrakis(*p*-methoxycarbonylphenyl)-21-carbaporphyrin **3** (150 mg, 0.18 mmol) was added and dissolved in 88 mL of dry dichloromethane (DCM) under nitrogen atmosphere. Then CF_3COOAg (156 mg, 0.71 mmol) dissolved in 1.6 mL of methanol was added to the mixture. The mixture was stirred at room temperature overnight and the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, the solvents were removed *in vacuo* and the residue was purified by a silica gel chromatography using an eluent of DCM/MeOH (99:1 (v/v)). The compound **3-Ag** was obtained as a brown solid by recrystallization. Yield: 140 mg, 0.15 mmol (82% yield). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.46 (s, 1H, α-H), 8.93 (d, J = 5.4 Hz, 1H, β-H), 8.80 (d, J = 4.7 Hz, 1H, β-H), 8.69 (d, J = 5.0 Hz, 1H, β-H), 8.64 (d, J = 5.0 Hz, 1H, β-H), 8.63 (d, J = 5.3 Hz, 1H, β-H), 8.59 (d, J = 5.1 Hz, 1H, β-H), 8.46 (d, J = 7.5 Hz, 4H, Ar-H), 8.43 (d, J = 5.1 Hz, 4H, Ar-H), 8.26 (d, J = 7.8 Hz, 2H, Ar-H), 8.23 (d, J = 7.9 Hz, 2H, Ar-H), 8.21 (dd, J = 7.9, 2.4 Hz, 4H, Ar-H), 4.11 (s, 6H, COOMe), 4.10 (s, 3H, COOMe), 4.00 (s, 3H, COOMe); MALDI-TOF-MASS: calcd for $C_{53}H_{35}N_4O_8Ag$ ($[M]^+$), 950.1506, found 950.845; UV/Vis (CH_2Cl_2, nm): λ_{max} = 383.5, 450, 522, 638.5.

Synthesis of [2-aza-5,10,15,20-tetrakis(*p*-carbonylphenyl)-21-carbaporphyrinato]-Ag(III) (1-Ag) [s2]



An aqueous solution (25 mL) of KOH (0.67 g, 12 mmol) was added to a mixture of **3-Ag** (200 mg, 0.21 mmol) in THF/MeOH (50 mL, 1:1 (v/v)). The mixture was stirred overnight at reflux. After cooling to room temperature, the resulting solution was concentrated *in vacuo*. Then water was added to the residue to dissolve completely. After solid impurity was removed be filtration, 1 M HCl solution was added to the filtrate up to pH of 3. The resulting dark brown solid was collected by filtration, washed with water, and dried *in vacuo*. Yield of **1-Ag**: 147 mg, 0.16 mmol (78% yield). ^{1}H NMR (500 MHz, DMSO-d_6): δ 13.27 (s, 4H, COOH), 9.35 (s, 1H, α-H), 8.95 (d, J =

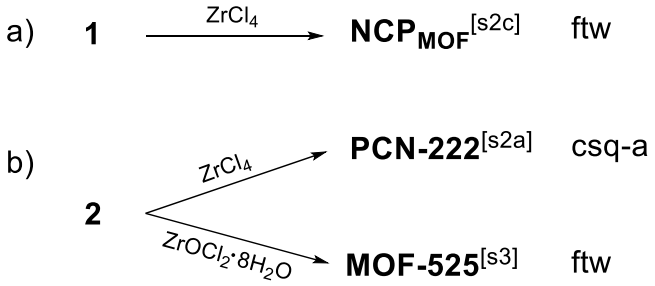
5.0 Hz, 1H, β-H), 8.85 (d, J = 4.7 Hz, 1H, β-H), 8.67 (d, J = 4.8 Hz, 1H, β-H), 8.6–8.62 (m, 2H, β-H), 8.59 (d, J = 5.0 Hz, 1H, β-H), 8.42–8.21 (m, 16H, Ar-H); HRMS (FAB): calcd for $C_{48}H_{28}N_4O_8Ag$ ($[M+1]^+$): 895.0953, found 895.0958; UV/Vis (*N*,*N*-dimethylformamide, nm): λ_{max} = 447.5, 586.5, 739.

Fabrication of Metal–Organic Frameworks

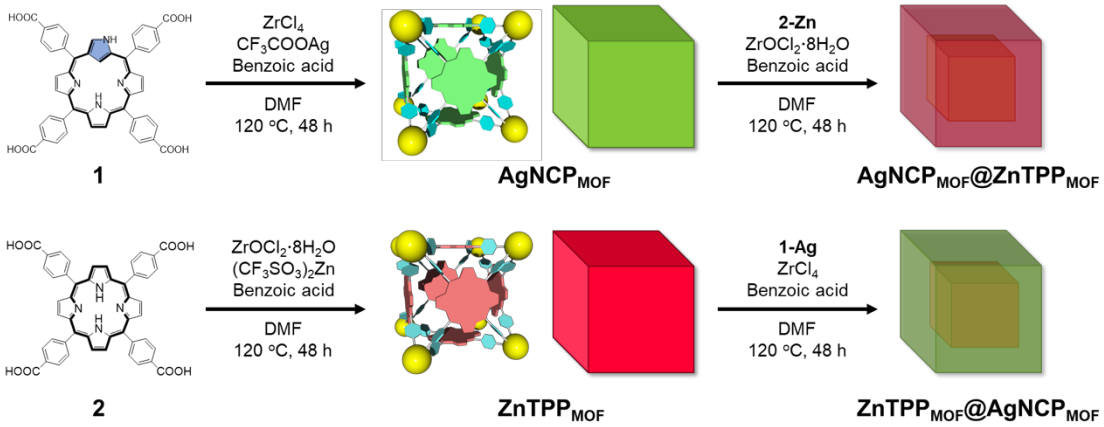
Synthesis of TPP$_{MOF}$. 103 mg of $ZrOCl_2 \cdot 8H_2O$, 50 mg of **2** and 2700 mg of benzoic acid were dissolved in 8 mL of DMF under the ultrasonic irradiation for over 1 h. The mixture was then stirred at 120 °C for 48 h. After cooling the solution to the room temperature gradually, the precipitated violet-colored solid was collected by filtration, followed by washing with DMF carefully (Scheme 1). The yield for **TPP$_{MOF}$**; 58.7 mg (38%). The detailed characterization is given below (e.g., SEM images and XRD patterns).

Synthesis of ***ZnTPP$_{MOF}$.*** 103 mg of $ZrOCl_2 \cdot 8H_2O$, 50 mg of **2**, 133 mg of $(CF_3SO_3)_2Zn$, and 2700 mg of benzoic acid were dissolved in 8 mL of DMF, and stirred in the ultrasonic mixer for over 1 h. The resulting mixture was then heated to 120 °C and stirred for 48 h. After cooling to room temperature gradually, the violet solid powder was collected by filtration, followed by washing with DMF (Scheme S2). Yield for **ZnTPP$_{MOF}$**; 65.8 mg (23%). The detailed characterization is given below (e.g., SEM images and XRD patterns).

Synthesis of ***AgNCP$_{MOF}$.*** 75 mg of $ZrCl_4$, 50 mg of **1**, 2700 mg of benzoic acid and 70 mg of CF_3COOAg were dissolved in 8 mL of DMF, and stirred in the ultrasonic mixer for over 1 h. The resulting mixture was then heated to 120 °C and stirred for 48 h. After cooling to room temperature slowly, the dark brownish solid was collected by filtration, followed by washing with DMF (Scheme S2). Yield for **AgNCP$_{MOF}$**; 45.6 mg (23%). The detailed characterization is given below (e.g., SEM images and XRD patterns).



Scheme S1. Metal-dependent syntheses of a) **NCP$_{MOF}$** using **1** and b) **PCN-222** and **MOF-525** using **2**.



Scheme S2. Schematic description for synthetic strategies of **AgNCP$_{MOF}$@ZnTPP$_{MOF}$** and **ZnTPP$_{MOF}$@AgNCP$_{MOF}$** through a seed-mediated ligand exchange reaction.[s4]

Table S1. Reaction conditions for hybrid MOF fabrication using seed-mediated synthesis

Entry	*Porphyrin linker* / mg*	*DMF / mL*	*Zr reagent** / mg*	*Seed*** / mg*	*Benzoic acid / mg*	*Results*
1	50 [a]	8	103 [f]	20 [g]	2700	Crystalline powder (76.5 mg)
2	50 [a]	8	75 [e]	20 [h]	2700	Crystalline powder (97.8 mg)
3	50 [b]	8	103 [f]	20 [g]	2700	Crystalline powder (100.4 mg)
4	10 [b]	2	20 [f]	40 [g]	2700	Crystalline powder (21.0 mg)
5	50 [d]	8	75 [e]	20 [i]	2700	Crystalline powder (63.1 mg)
6	10 [c]	2	20 [f]	40 [j]	540	Crystalline powder (22.6 mg)
7	25 [a] + 25 [b]	8	75 [e]	-	2700	Amorphous powder

*Linker: a) **1**, b) **2**, c) **2-Zn**, d) **1-Ag**

**Zr reagent: e) $ZrCl_4$, f) $ZrOCl_2 \cdot 8H_2O$

***Seed: g) **NCP$_{MOF}$**, h) **TPP$_{MOF}$**, i) **ZnTPP$_{MOF}$**, j) **AgNCP$_{MOF}$**

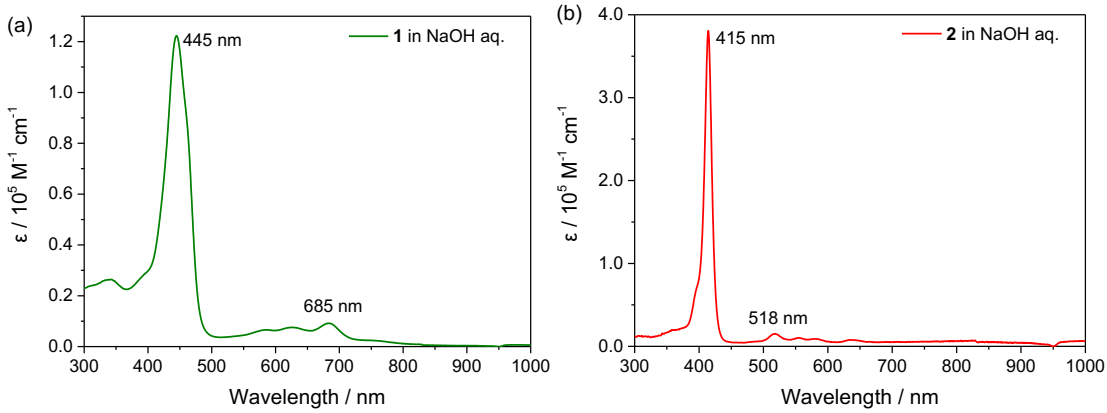
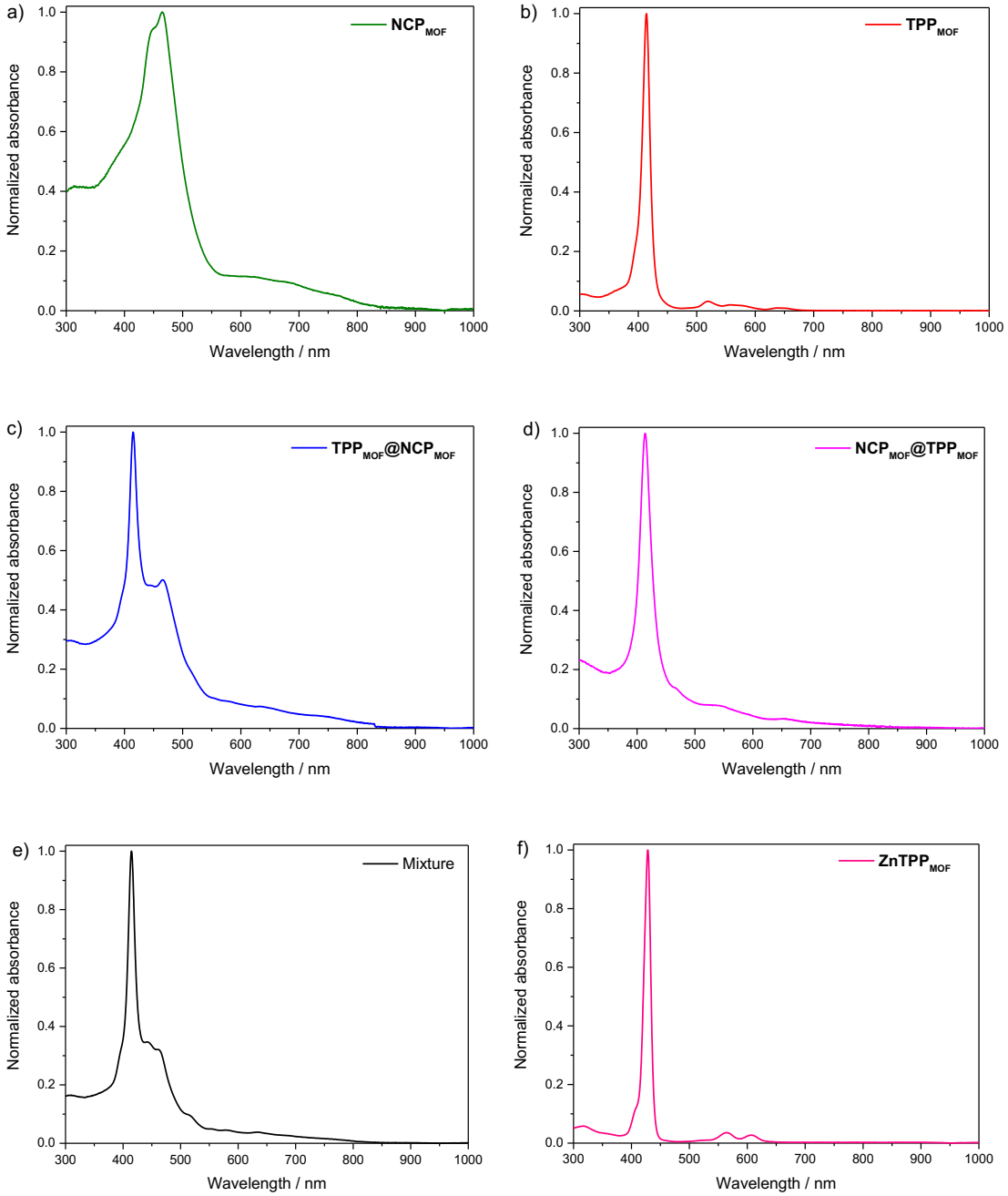


Figure S1. Absorption spectra of **1** (a, green line) and **2** (b, red line), dissolved in NaOH aq.



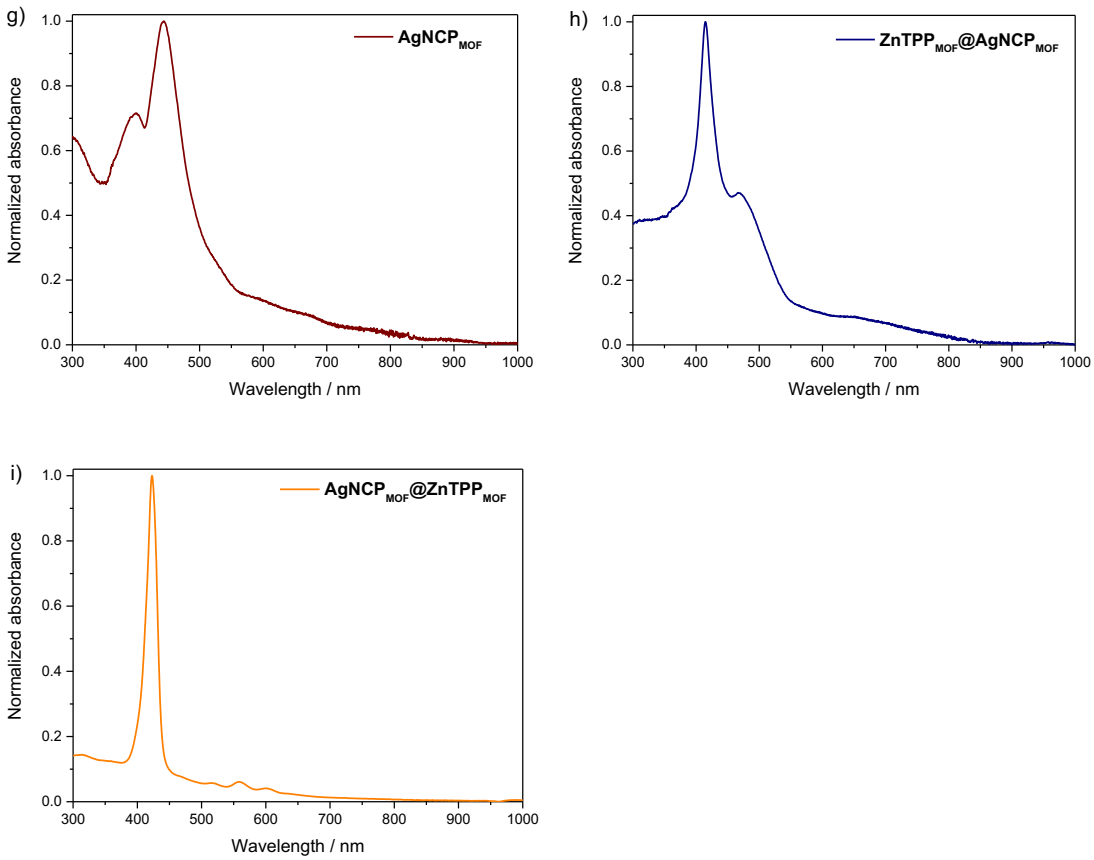


Figure S2. Absorption spectra of **NCP$_{MOF}$** (a, green line), **TPP$_{MOF}$** (b, red line), **NCP$_{MOF}$@TPP$_{MOF}$** (c, pink line), **TPP$_{MOF}$@NCP$_{MOF}$** (d, blue line), mixture (**NCP$_{MOF}$** : **TPP$_{MOF}$**=5:2) (e, black line), **ZnTPP$_{MOF}$** (f, purple line), **AgNCP$_{MOF}$** (g, brown line), **ZnTPP$_{MOF}$@AgNCP$_{MOF}$** (h, dark blue line), and **AgNCP$_{MOF}$@ZnTPP$_{MOF}$** (i, orange line), dissolved in 0.1 M NaOH aq.

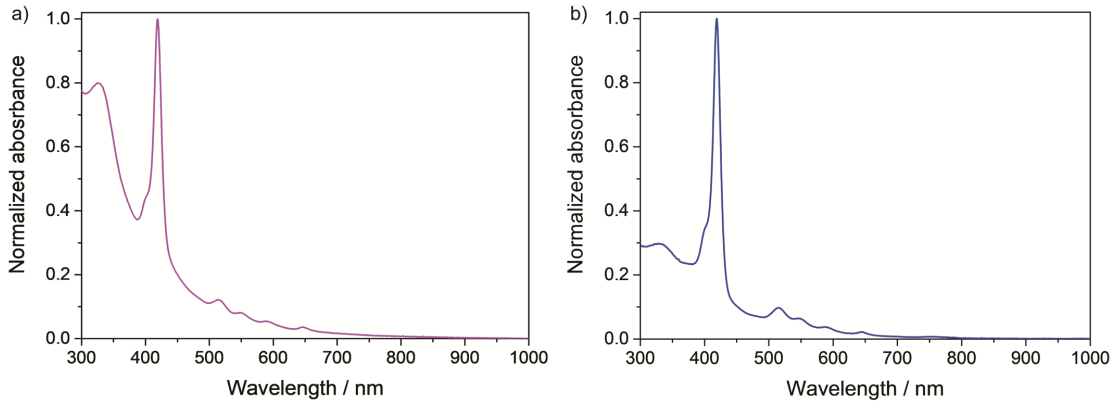


Figure S3. Absorption spectra of filtrates obtained in the synthesis of a) **NCP$_{MOF}$@TPP$_{MOF}$** (pink line) and b) **TPP$_{MOF}$@NCP$_{MOF}$** (blue line). The detailed reaction conditions are described in the experimental section.

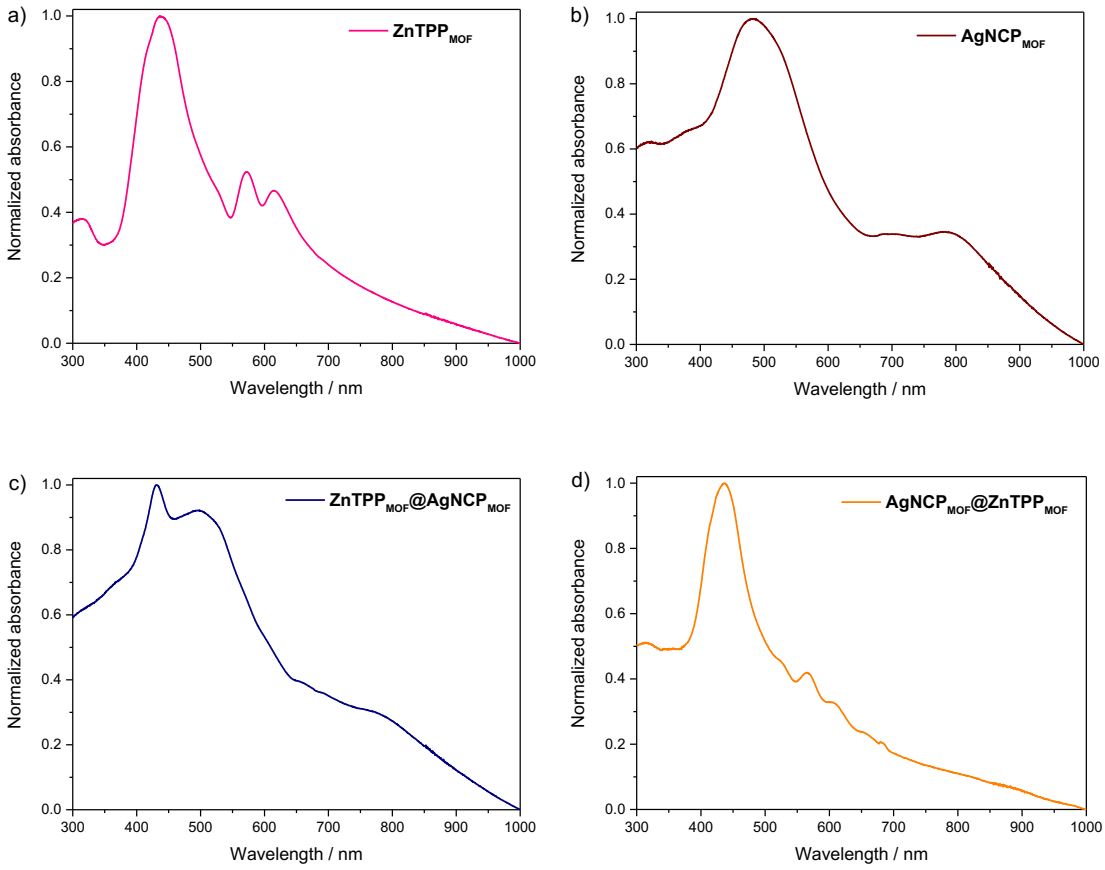


Figure S4. Absorption spectra of a) **ZnTPP$_{MOF}$** (purple line), b) **AgNCP$_{MOF}$** (brown line), c) **ZnTPP$_{MOF}$@AgNCP$_{MOF}$** (dark blue line), and d) **AgNCP$_{MOF}$@ZnTPP$_{MOF}$** (orange line), in the KBr pellet.

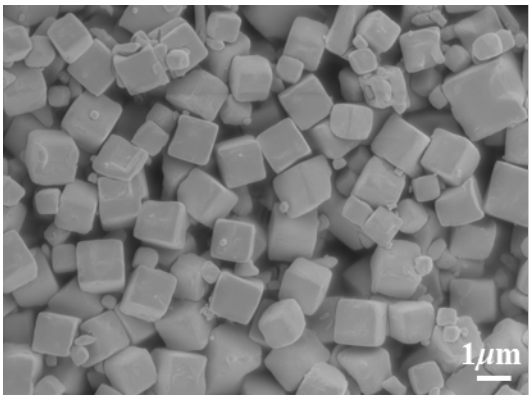


Figure S5. SEM image of **TPP$_{MOF}$** synthesized by the modified procedure. Scale bar is set to 1 μm.

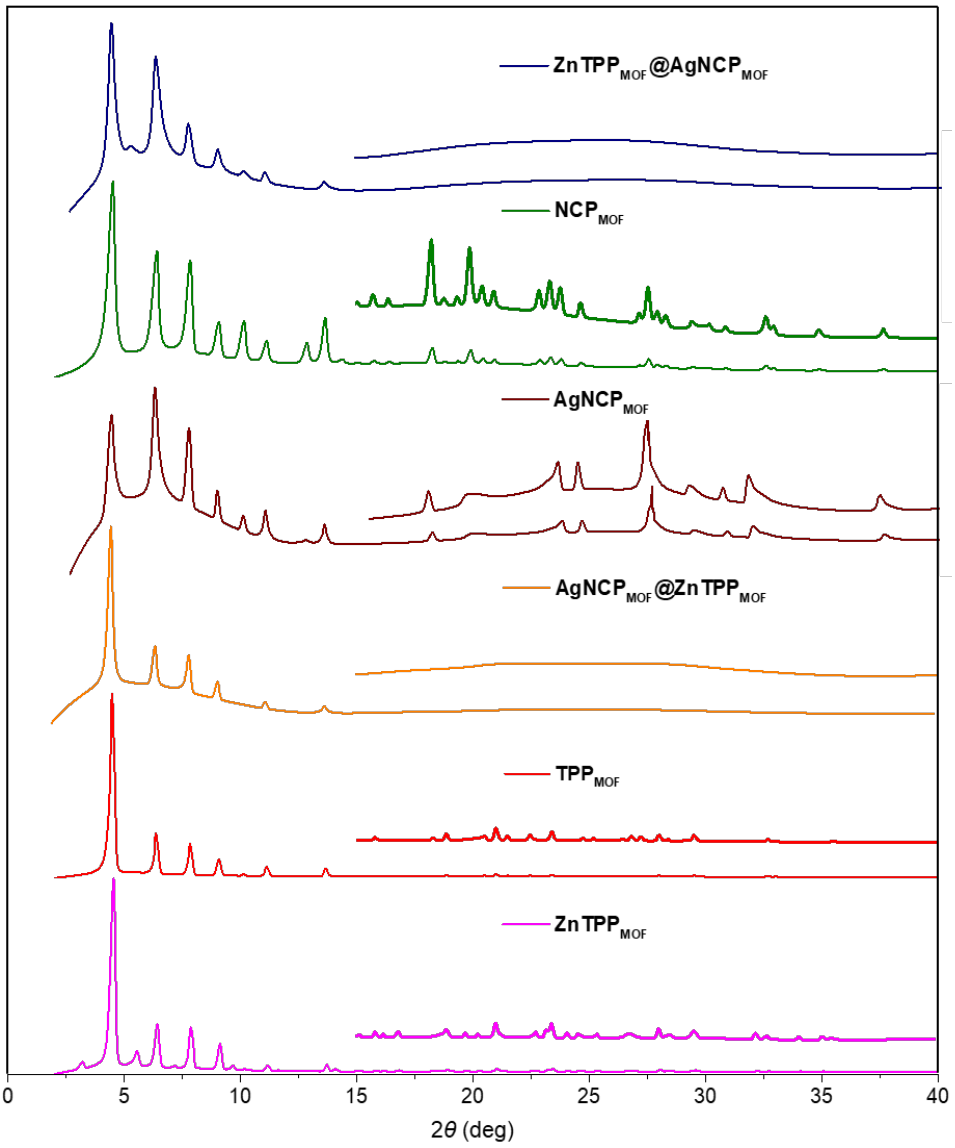


Figure S6. Wide-angle PXRD patterns of the metalloporphyrinic Zr-MOFs; **ZnTPP$_{MOF}$@AgNCP$_{MOF}$** (dark blue), **AgNCP$_{MOF}$** (brown), **AgNCP$_{MOF}$@ZnTPP$_{MOF}$** (orange), and **ZnTPP$_{MOF}$** (purple). The plots for **NCP$_{MOF}$** (green) and **TPP$_{MOF}$** (red) are shown for comparison.

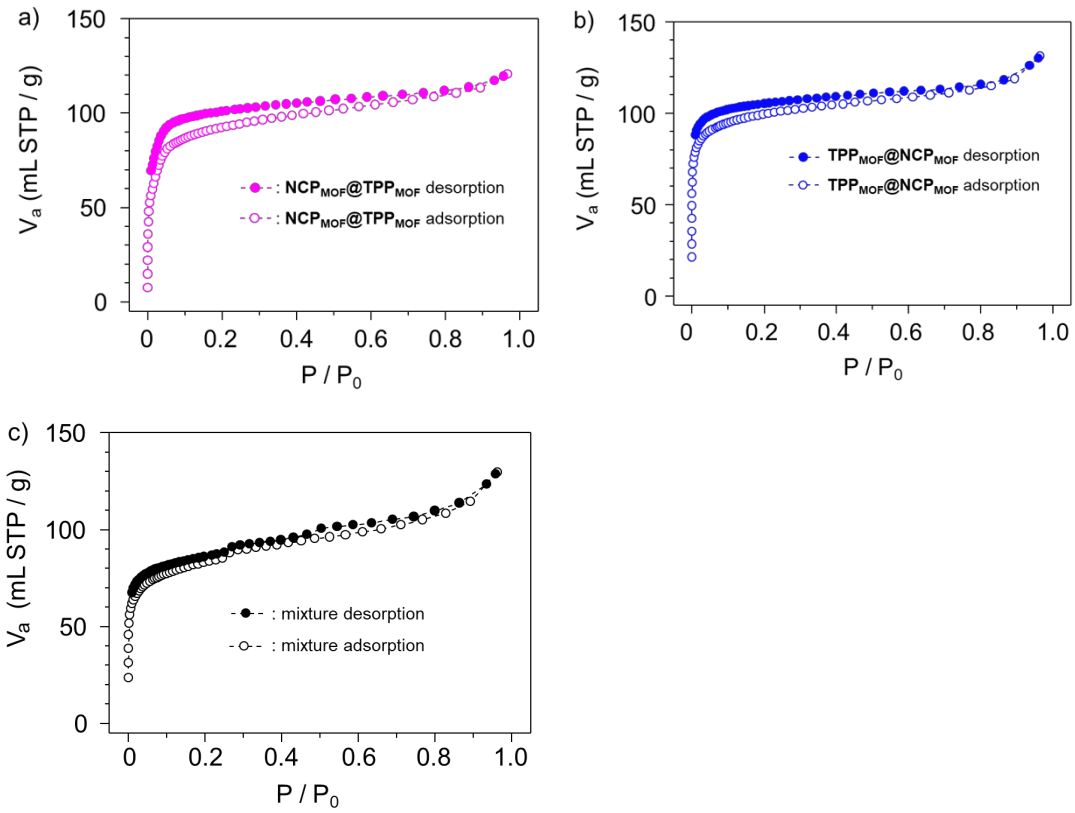


Figure S7. N_2 adsorption isotherms (hollow circle: adsorption, solid circle: desorption) of a) **NCP_{MOF}@TPP_{MOF}** (pink dotted line), b) **TPP_{MOF}@NCP_{MOF}** (blue dotted line), and c) a mixture (**NCP_{MOF}** : **TPP_{MOF}** = 5:2, black dotted line) at 77 K.

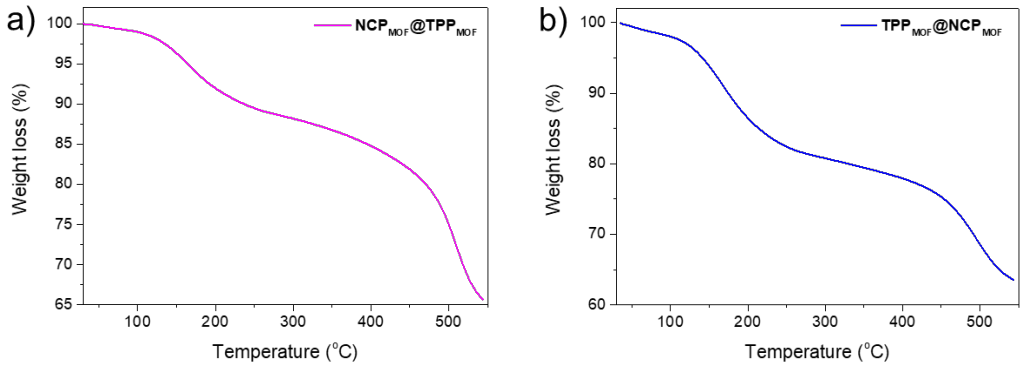


Figure S8. Thermogravimetric analyses of a) **NCP_{MOF}@TPP_{MOF}** (pink line) and b) **TPP_{MOF}@NCP_{MOF}** (blue line).

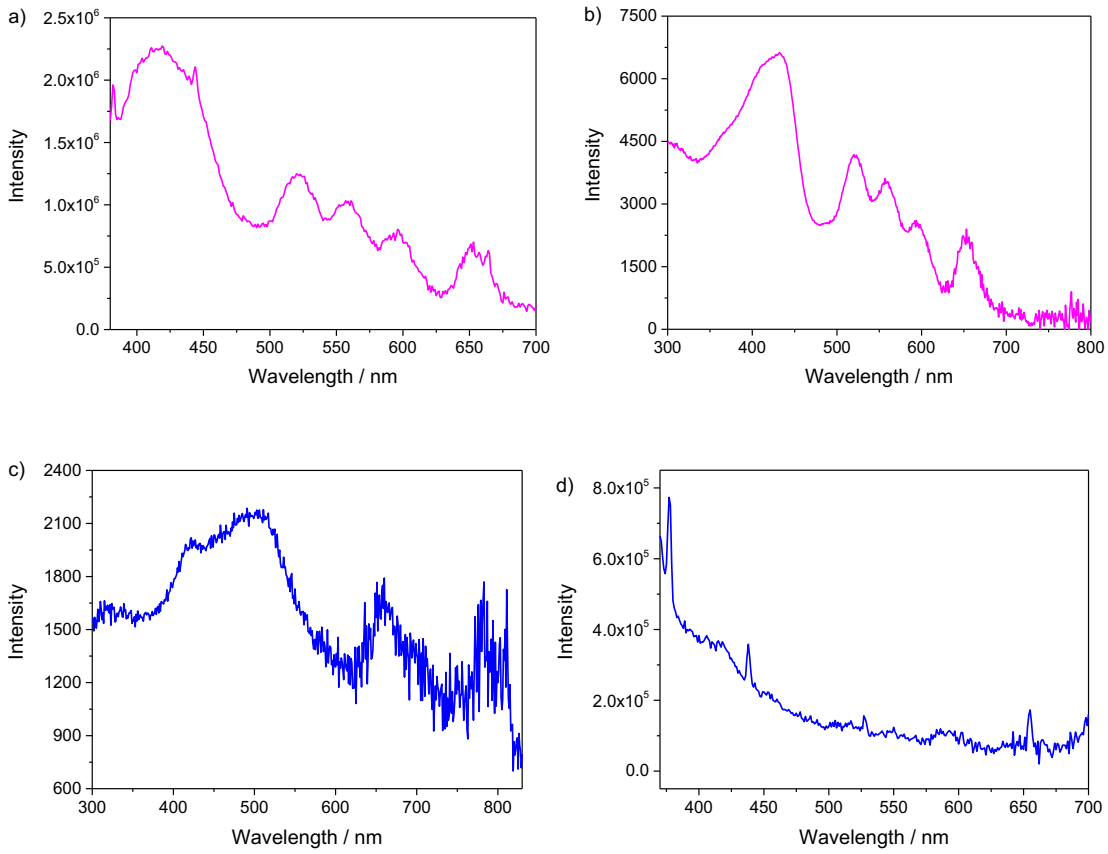


Figure S9. Excitation spectra of **NCP$_{MOF}$@TPP$_{MOF}$** (pink line) monitored at a) 730 nm and b) 910 nm, and **TPP$_{MOF}$@NCP$_{MOF}$** (blue line) monitored at c) 900 nm and d) 720 nm.

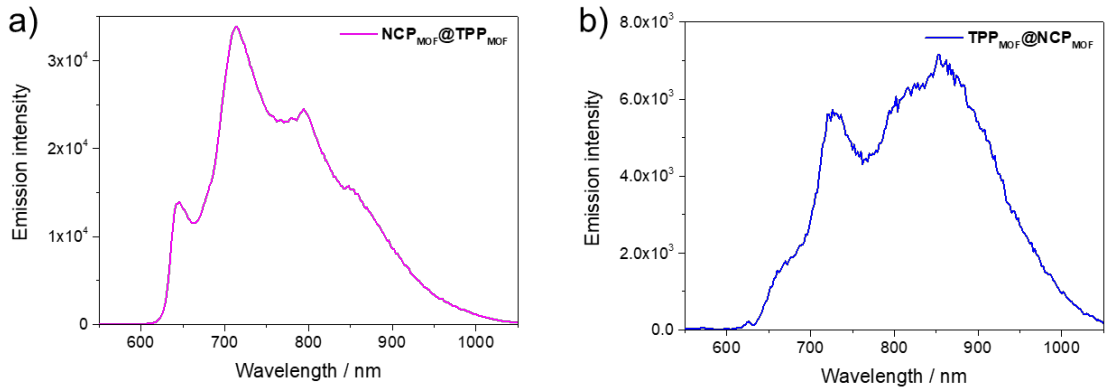


Figure S10. Emission spectra of a) **NCP$_{MOF}$@TPP$_{MOF}$** (pink line) and b) **TPP$_{MOF}$@NCP$_{MOF}$** (blue line) dispersed in DMF. (λ_{ex} = 455 nm)

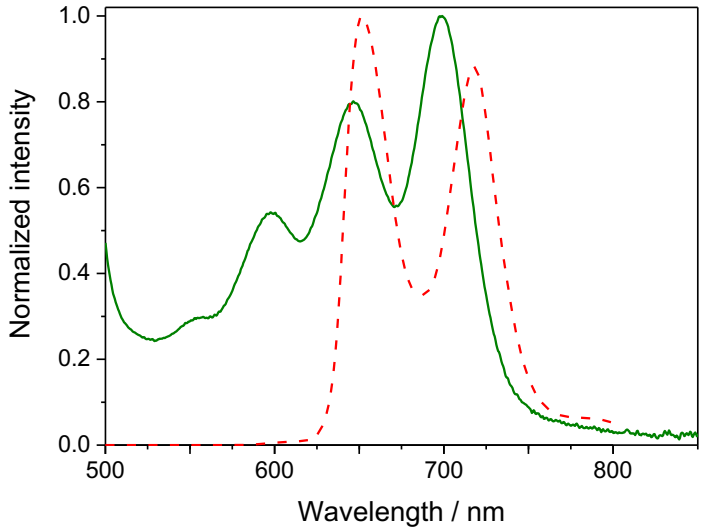


Figure S11. Absorption spectrum of **1** (green solid line) and emission spectrum of **2** (red dotted line) in DMF solution. (λ_{ex} = 420 nm)

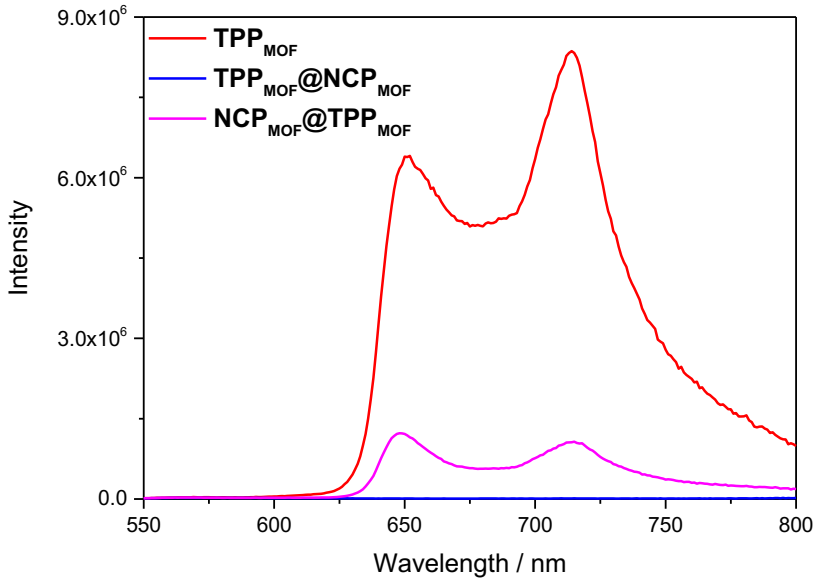


Figure S12. Emission spectra of **TPP$_{MOF}$** (red line), **TPP$_{MOF}$@NCP$_{MOF}$** (blue line), and **NCP$_{MOF}$@TPP$_{MOF}$** (purple line) dispersed in DMF with λ_{ex} = 455 nm.

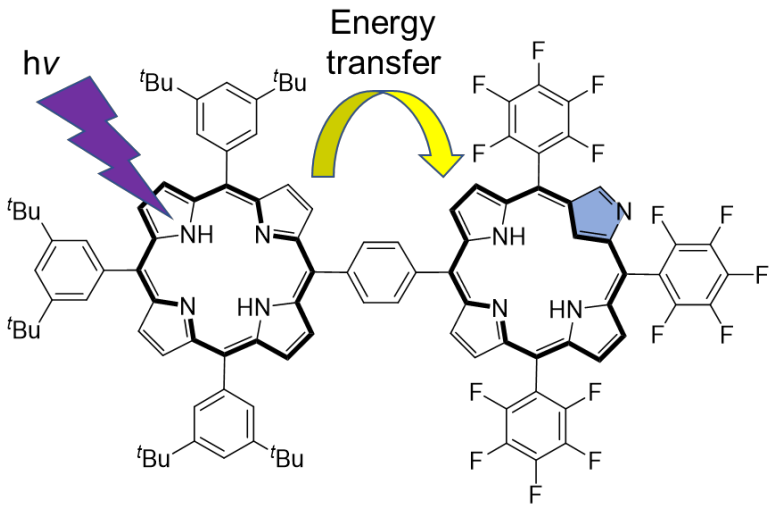


Figure S13. Chemical structure of the dyad molecule containing a tetraarylporphyrin and an N-confused isomer for the study of energy transfer phenomenon.[s5]

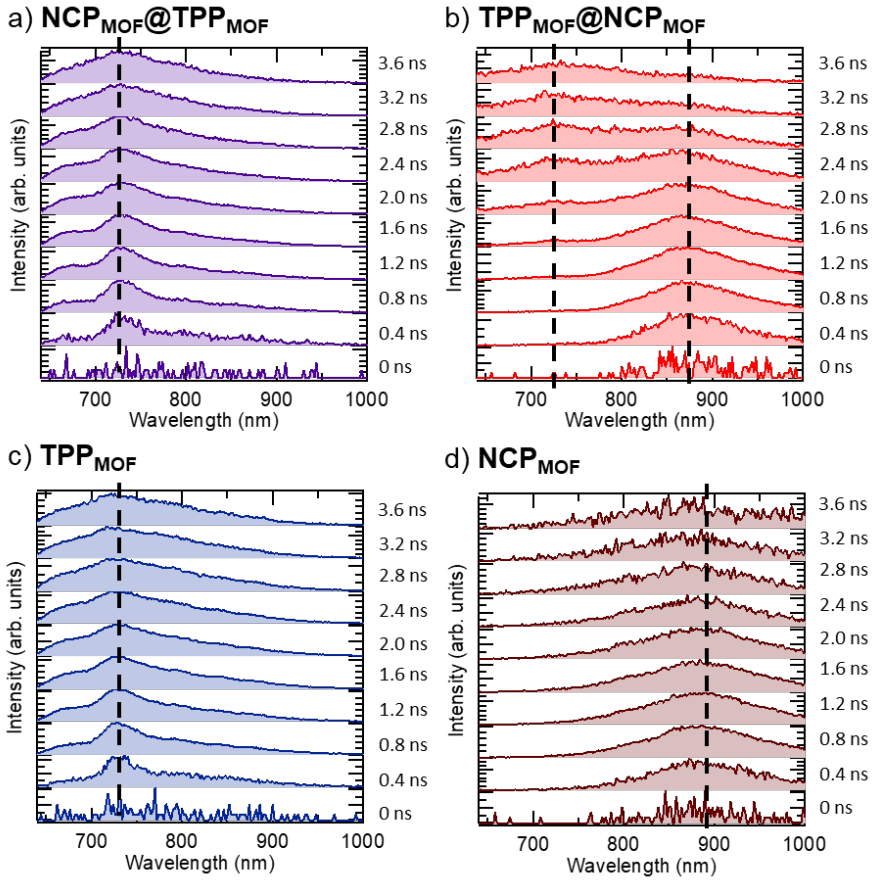


Figure S14. Time-resolved emission spectra of a) **NCP$_{MOF}$@TPP$_{MOF}$**, b) **TPP$_{MOF}$@NCP$_{MOF}$**, c) **TPP$_{MOF}$**, and d) **NCP$_{MOF}$** dispersed in DMF. The emission intensities are normalized. (λ_{ex} = 532 nm)

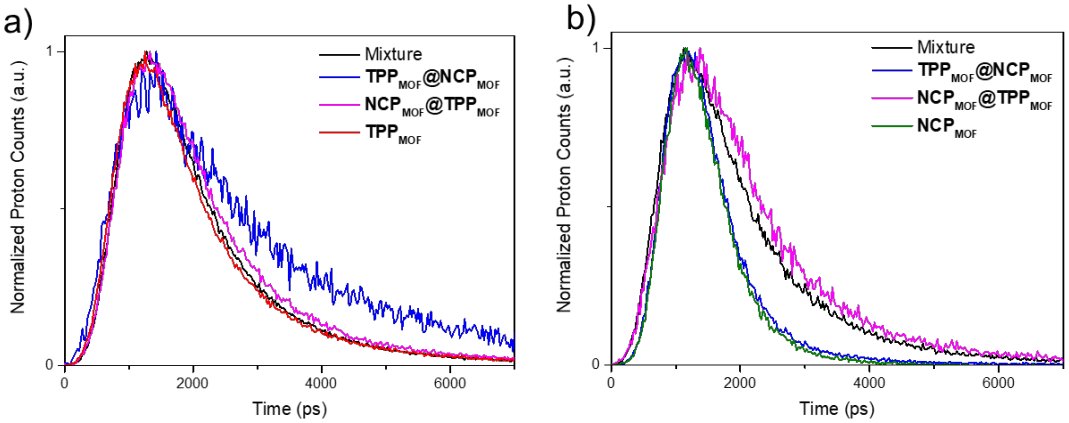


Figure S15. Emission decay curves of the hybrid MOFs, **NCP$_{MOF}$@TPP$_{MOF}$**, **TPP$_{MOF}$@NCP$_{MOF}$**, and a mixture of MOFs (**NCP$_{MOF}$** : **TPP$_{MOF}$** = 5 : 2) dispersed in DMF probed in the range of a) 720–730 nm and b) 850–880 nm. (λ_{ex} = 532 nm)

Table S2. Summary of emission lifetimes of the MOFs dispersed in DMF.

Sample	τ_{em} (ns) probed at 720–730 nm			τ_{em} (ns) probed at 850–880 nm		
	τ_1	τ_2	τ_{mean}	τ_1	τ_2	τ_{mean}
Mixture	1.16 (99.2%)	18.82 (0.8%)	1.30	1.18 (99.2%)	26.08 (0.8%)	1.38
NCP$_{MOF}$@TPP$_{MOF}$	1.24 (98.8%)	20.15 (1.2%)	1.46	1.33 (100%)		1.33
TPP$_{MOF}$@NCP$_{MOF}$	1.83 (86.5%)	6.07 (13.5%)	2.41	0.64 (100%)		0.64
TPP$_{MOF}$	1.14 (98.3%)	10.69 (1.7%)	1.30	-	-	-
NCP$_{MOF}$	-	-	-	0.62 (100%)		0.62

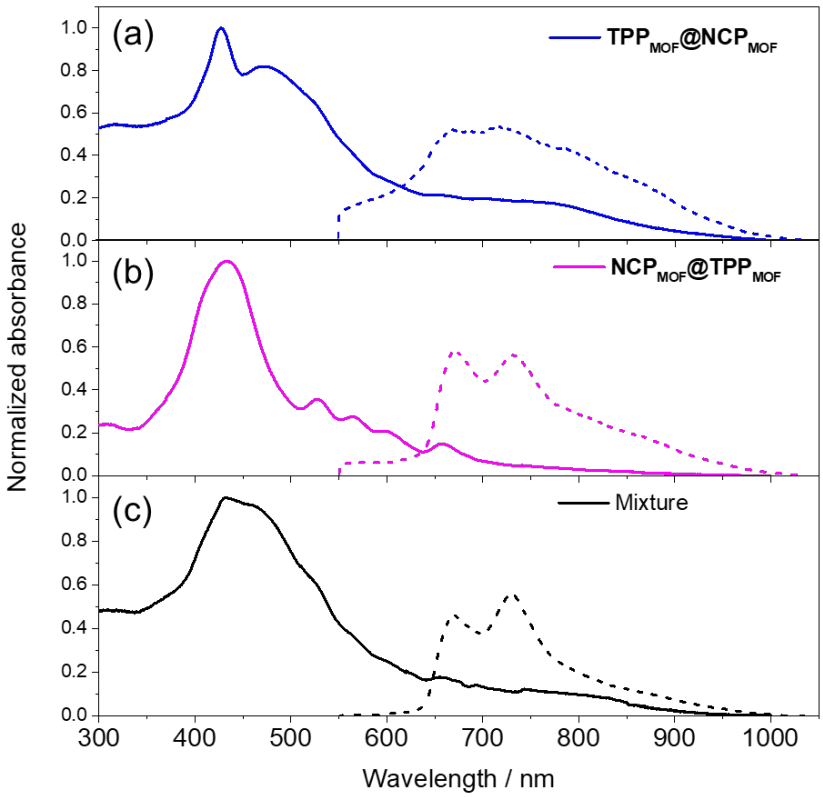


Figure S16. Absorption spectra (in KBr pellet, solid line) and solid state fluorescent spectra (broken line) of (a) **TPP$_{MOF}$@NCP$_{MOF}$** (blue color), (b) **NCP$_{MOF}$@TPP$_{MOF}$** (pink color), and (c) mixture of **NCP$_{MOF}$** and **TPP$_{MOF}$** (in 5:2 ratio, black color). The emission spectra were measured with the excitation wavelength at the maximum peak of the Soret band.

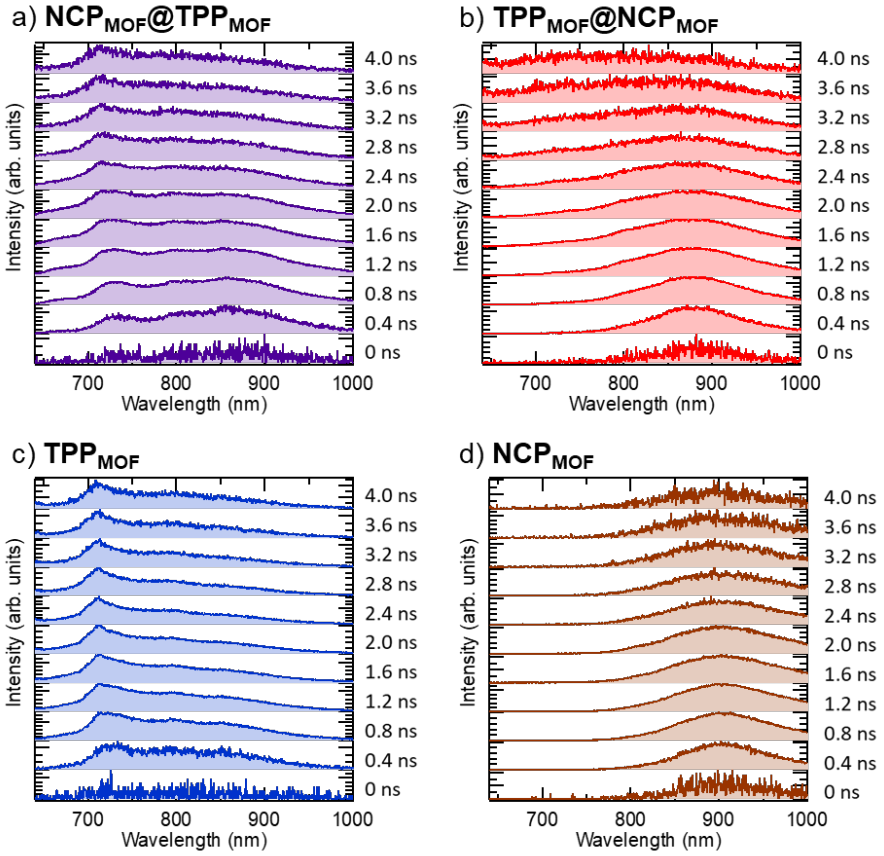


Figure S17. Time-resolved emission spectra of a) **NCP$_{MOF}$@TPP$_{MOF}$**, b) **TPP$_{MOF}$@NCP$_{MOF}$**, c) **TPP$_{MOF}$**, and d) **NCP$_{MOF}$** in solid state. The emission intensities are normalized. (λ_{ex} = 532 nm)

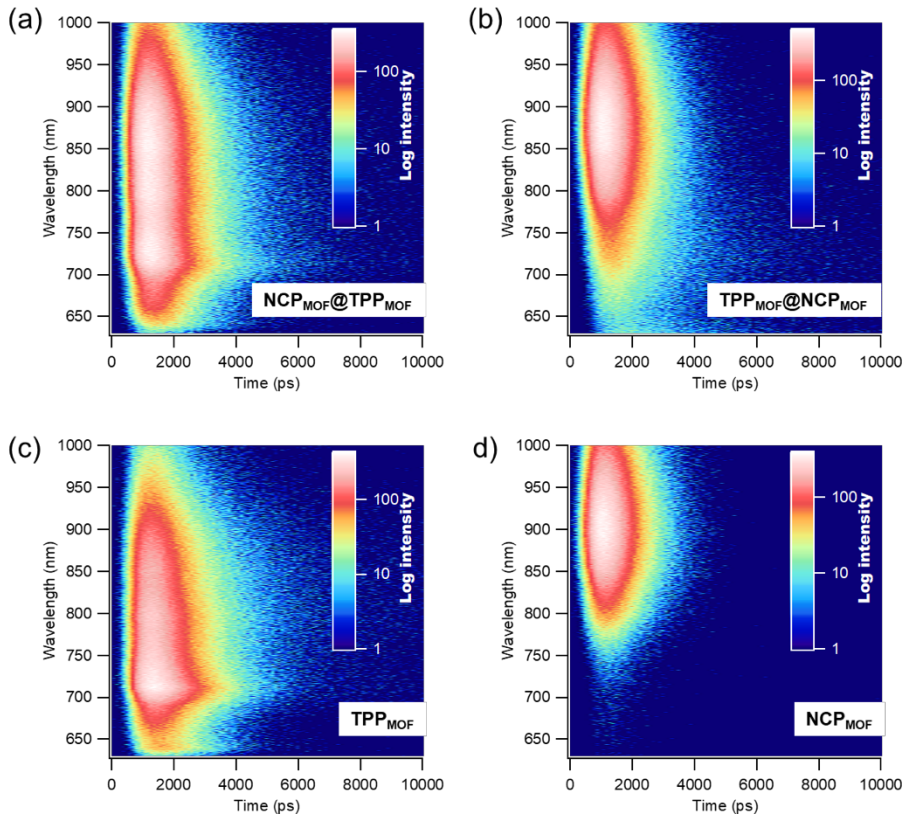


Figure S18. Time-resolved 2D fluorescence spectra of the MOFs in solid state; (a) **NCP$_{MOF}$@TPP$_{MOF}$**, (b) **TPP$_{MOF}$@NCP$_{MOF}$**, (c) **TPP$_{MOF}$**, and (d) **NCP$_{MOF}$**. (λ_{ex} = 532 nm)

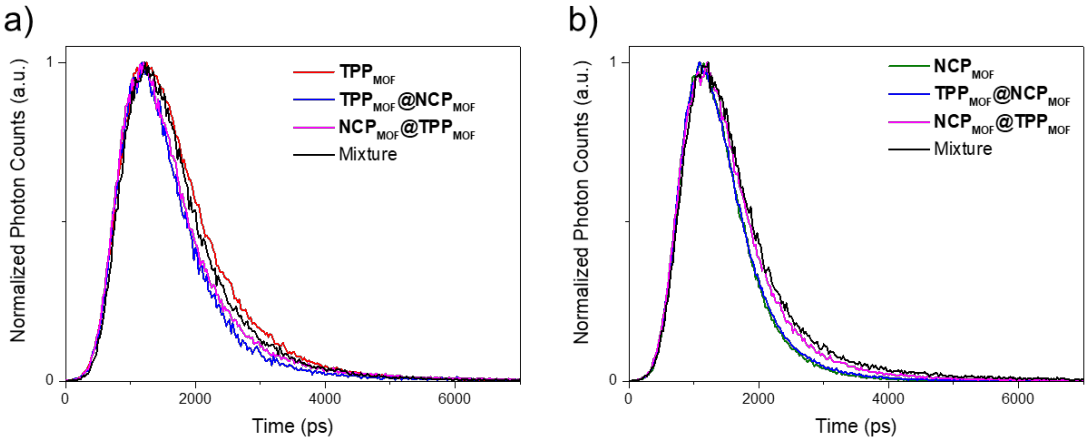


Figure S19. Emission decay curves of the hybrid MOFs, **NCP$_{MOF}$@TPP$_{MOF}$**, **TPP$_{MOF}$@NCP$_{MOF}$**, and a mixture of MOFs (**NCP$_{MOF}$** : **TPP$_{MOF}$** = 5 : 2) in solid state probed in the range of a) 720–730 nm and b) 850–880 nm. (λ_{ex} = 532 nm)

Table S3. Summary of emission lifetimes of the solid MOFs.

Sample	τ_{em} (ns) probed at 720–730 nm	τ_{em} (ns) probed at 850–880 nm
TPP_{MOF}@NCP_{MOF}	0.67	0.57
NCP_{MOF}@TPP_{MOF}	0.77	0.68
TPP_{MOF}	0.90	-
NCP_{MOF}	-	0.62
Mixture*	0.80	0.73

*Note that the mixed sample contains **NCP_{MOF}** and **TPP_{MOF}** in 5:2 ratio. The lifetimes for the major amplitudes are given.

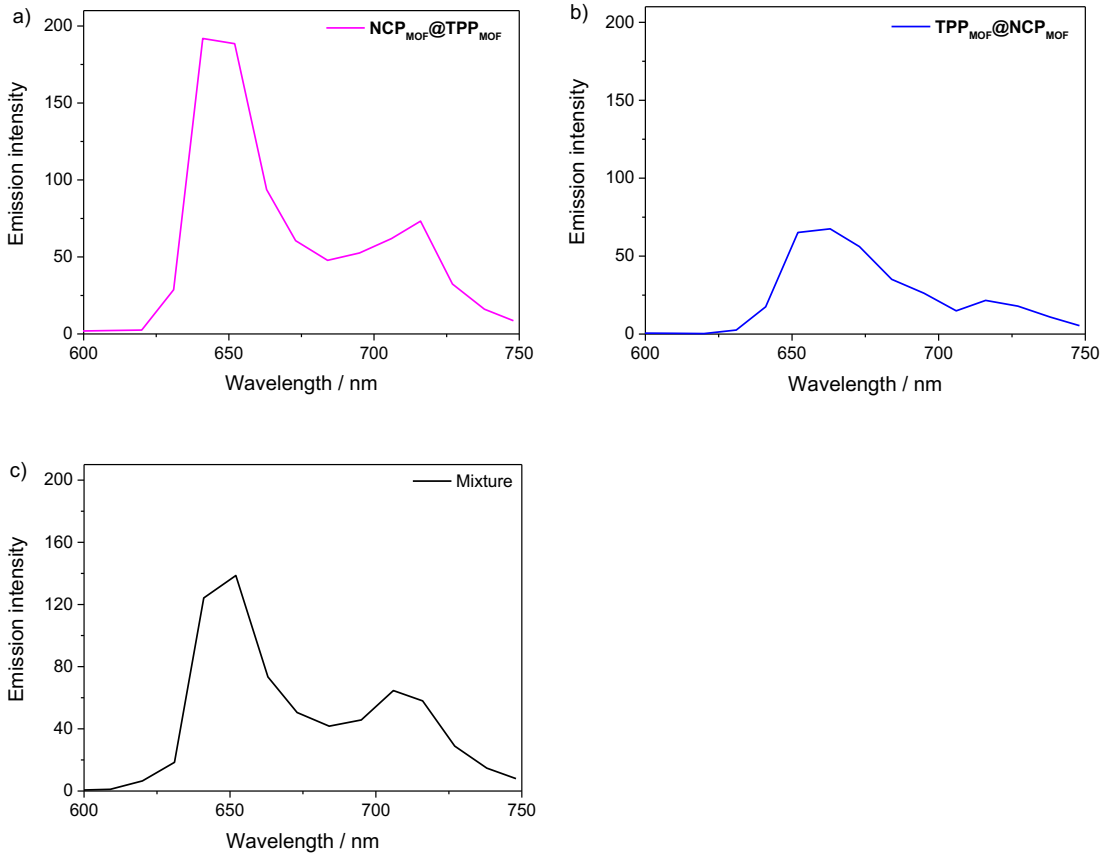


Figure S20. Emission spectra of selected particles for a) **NCP_{MOF}@TPP_{MOF}** (pink line), b) **TPP_{MOF}@NCP_{MOF}** (blue line), and c) a mixture of MOFs (**NCP_{MOF}** + **TPP_{MOF}**, black line), visualized by the confocal laser scanning microscopy. (λ_{ex} = 430 nm)

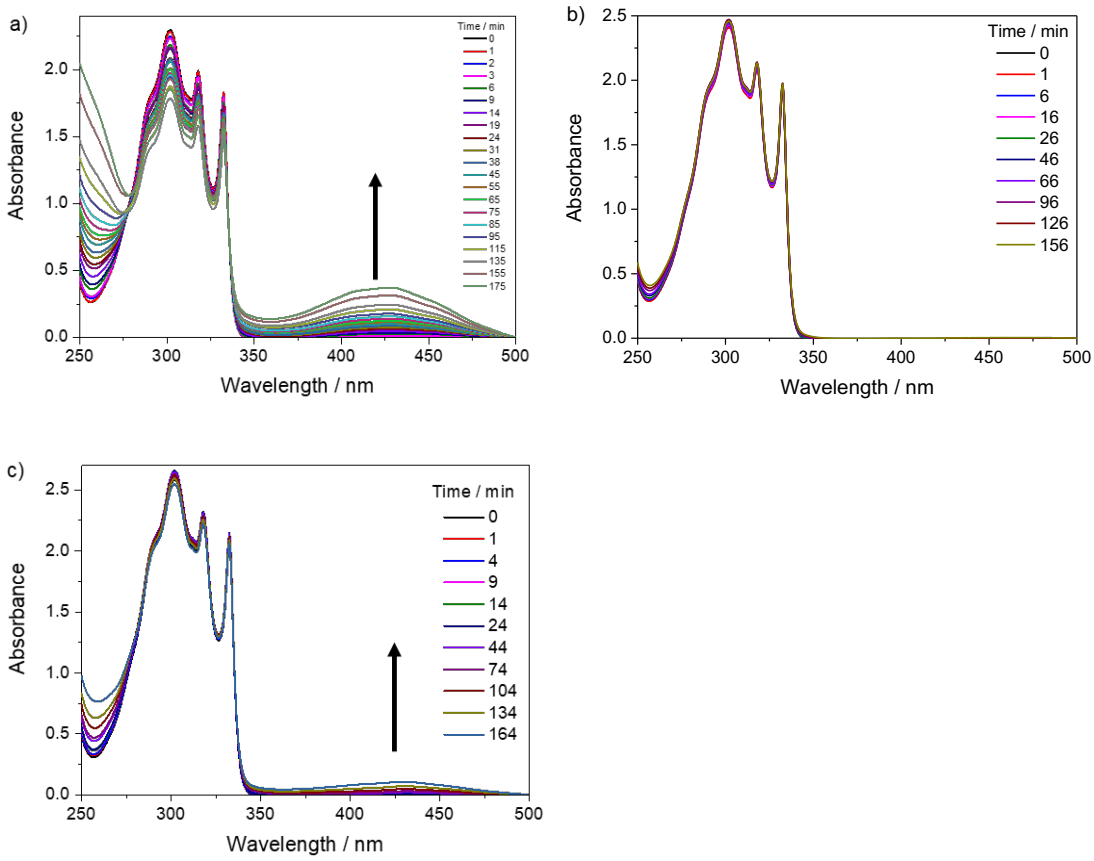


Figure S21. Absorption spectral changes of DHN in the presence of sensitizers, a) $\mathbf{TPP_{MOF}}$, b) $\mathbf{NCP_{MOF}}$, and c) $\mathbf{TPP_{MOF}@NCP_{MOF}}$, under photoirradiation (λ; 450–700 nm).

References

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