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Electronic Supplementary Information for

Porphyrin trap and release of microporous organic hollow spheres: Fluorescent alerting systems for organic solvent existence in water

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Experimental Sections

TEM (EDS mapping) and SEM images were obtained using a JEOL 2100F (200 kV) and a FE-SEM (JSM6700F), repectively. The N_2 sorption isotherms (77 K) were measured using a BELSORP II-mini equipment. For the pore size analysis, the DFT method was applied. PXRD patterns were obtained using a Rigaku MAX-2200 operating with filtered Cu-Ka radiation. The absorption and emission spectra were obtained with a JASCO V-630 and JASCO FP-6200 spectrofluorometers, respectively The solid phase ^{13}C-NMR spectrum was obtained on a Bruker 400 MHz Solid State DSX NMR spectrometer at the Korea Basic Science Institute (Daegu, South Korea).

Synthetic procedure of Por@MOH-A

The Por-1, Por-4, Por-8, Por-16, and their silica composites containing 19~28 w% porphyrins were prepared by following synthetic procedures in the literature.[1-2] To prepare Por-SiO_2@MON, the Por-SiO_2 composite (0.30 g) was dispersed in triethylamine (30 mL). After adding $(PPh_3)_2PdCl_2$ (8.4 mg, 0.50.012 mmol) and CuI (2.2 mg, 0.012 mmol), the solution was treated with sonication for 1 hour. After adding tetra(4-ethynylphenyl)methane (50 mg, 0.12 mmol) and 1,4-diiodobenzene (80 mg, 0.24 mmol), the reaction mixture was refluxed for 48 hours. The Por-SiO_2@MON powders were retrieved via centrifugation, washed with methanol, dichloromethane, and acetone, and dried under a vacuum. To prepare Por@MOH-A, the Por-SiO_2@MON was treated with a HF solution (48%, 10 mL) in a Falcon tube for 1 hour. The resultant Por@MOH-A powders were retrieved via centrifugation, washed with water and dried under a vacuum.

Synthetic procedure of Zn-Por@MOH-B

Silica spheres with a 130 nm diameter were prepared by following the Stöber method.[3] In a 500 mL round-bottomed flask, ethanol (200 mL), ammonia solution (28~30%, 4 mL), and water (2.7 mL) were stirred for 10 minutes. After adding tetrethylorthosilicate (TEOS, 4.4 mL), the mixture was stirred for 18 hours at room temperature. The silica spheres were retrieved via centrifugation, washed with ethanol, and dried under a vacuum. Microporous organic hollows (MOHs)[4] and Zn-porphyrins (Zn-Por-1, Zn-Por-4, Zn-Por-8) were prepared by following procedures in the literature.[5] To prepare Zn-Por@MOH-B, MOH (40 mg) was added to a methanol solution (20 mL) of Zn-Por (0.050 mmol). The reaction mixture was stirred for 12 hours at room temperature and then the solvent was evaporated. The powders were dried under a vacuum, washed with water until no color leaching was observed, and finally dried under a vacuum.

Release test procedure

The guest@MOH-B (10 mg) was loaded on a sintered glass filter and was packed with sea sand. The system was connected with a 2 mm silicone tube. A peristaltic pump made water flow at a 3 mL/min rate from the reservoir solution to the collector. The solution collected per 2 minutes was analyzed via UV/vis absorption and emission spectroscopy. For Zn-Por@MOH-B materials, the emission peak at 625 nm (with 426 excitation) was analyzed.

1. M. Magaraggia et al., *Photochem. Photobiol. Sci.* 2013, **12**, 2170
2. (a) I. B. Adilina et al., *J. Mol. Catal. A: Chem.* 2012, **361**, 72; (b) M. C. Gomes et al., *Photochem. Photobiol. Sci.* 2011, **10**, 1735; (c) A. G. Tovmasyan et al., *J. Porphyr. Phthalocya.* 2008, **12**, 1100; (d) A. Ghosh et al., *Thin Solid Films* 2011, **519**, 8066; (e) X. He et al., *Spectrochim. Acta A* 1999, **55**, 873.
3. W. Stöber, A. Fink and E. Bohn, *J. Colloid Inter. Sci.* 1968, **26**, 62.
4. N. Kang et al., *J. Am. Chem. Soc.* 2013, **135**, 19115.
5. (a) C. Pavani et al., *Photochem. Photobiol. Sci.* 2009, **8**, 233; (b) Y. Amao et al., *Inorg. Chim. Acta* 1998, **267**, 257.

Table S1. The amount of guests entrapped in MOHs.

Materials	M.W. of Guests	Entrapped Amount of Guests[a]		Size: L/L'[b]
	g/mol	w%	mmol/g	nm/nm
Por-1@MOH-A	1186.5	6.2	0.052	1.9/1.5
Por-4@MOH-A	1166.8	6.4	0.055	2.6/1.8
Por-8@MOH-A	1391.2	3.8	0.027	3.5/2.4
Por-16@MOH-A	1840.1	7.4	0.040	4.9/3.6
Por-1@MOH-B	1186.5	42	0.35	1.9/1.5
Por-4@MOH-B	1166.8	41	0.35	2.6/1.8
Por-8@MOH-B	1391.2	34	0.24	3.5/2.4
Zn-Por-1@MOH-B	1249.8	42	0.33	1.9/1.5
Zn-Por-4@MOH-B	1230.1	40	0.33	2.6/1.8
Zn-Por-8@MOH-B	1454.6	37	0.25	3.5/2.4

a The amount of guests entrapped in MOHs was obtained by weighing the guests which were extracted using methanol and dried under vacuum.

b L and L' correspond to the following lengths. (Spartan '08 software of Wavefunction Inc. was used.)

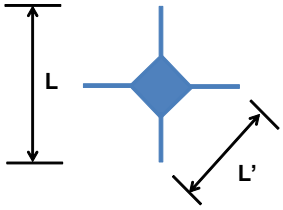

Fig. S1 SEM images of **Por-SiO$_2$** composites (**Por-1-SiO$_2$**, **Por-4-SiO$_2$**, **Por-8-SiO$_2$**, and **Por-16-SiO$_2$**)

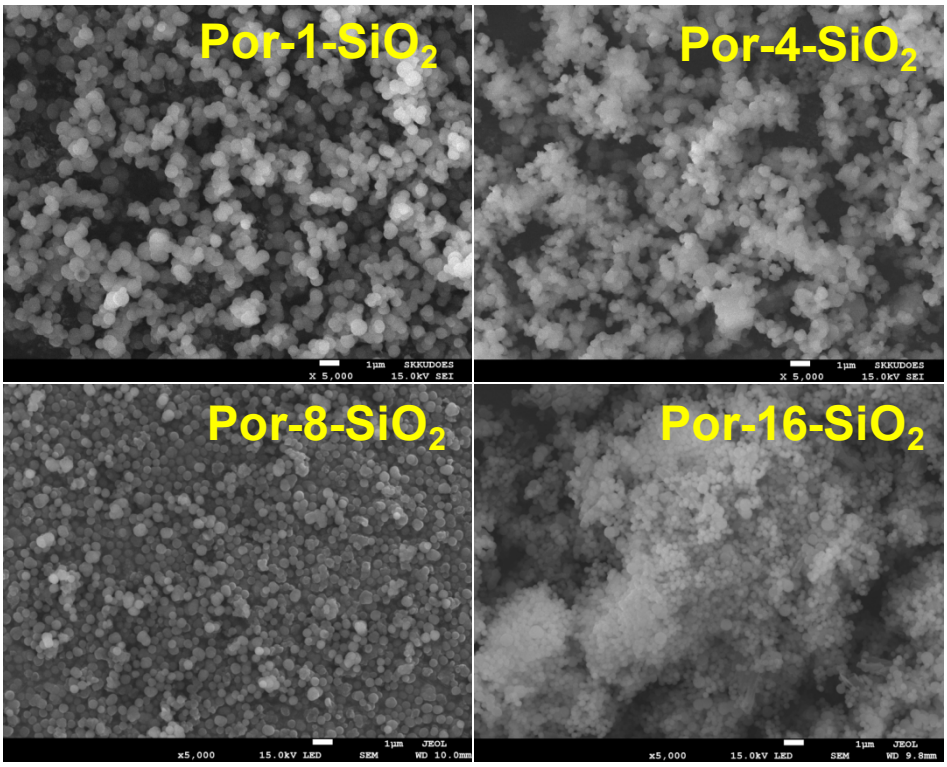

Fig. S2 N_2 adsorption and desorption isotherms of **Por-8-SiO$_2$** composites, **Por-8-SiO$_2$@MON**, and microporous organic hollows (MOH-A) obtained by release of **Por-8** guests in **Por-8@MOH-A** through MeOH treatment. (S.A.: surface area)

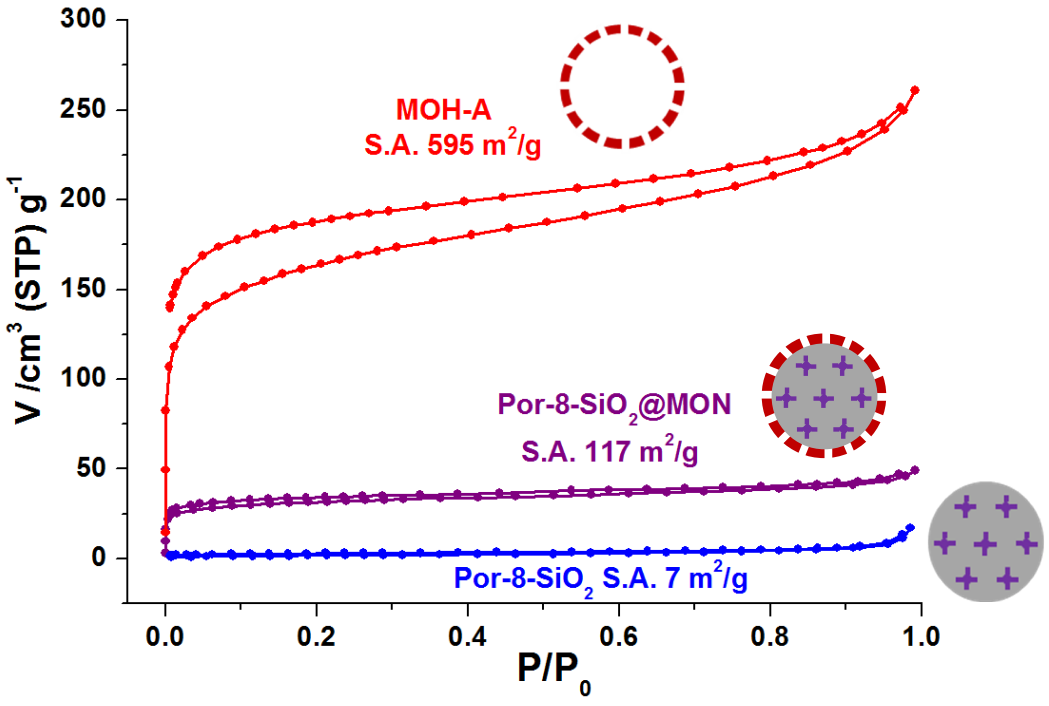

Fig. S3 PXRD patterns of MOH-A obtained by release of **Por-8** guests in **Por-8@MOH-A** through MeOH treatment, and MOH-B used for **Zn-Por-1@MOH-B** in route B.

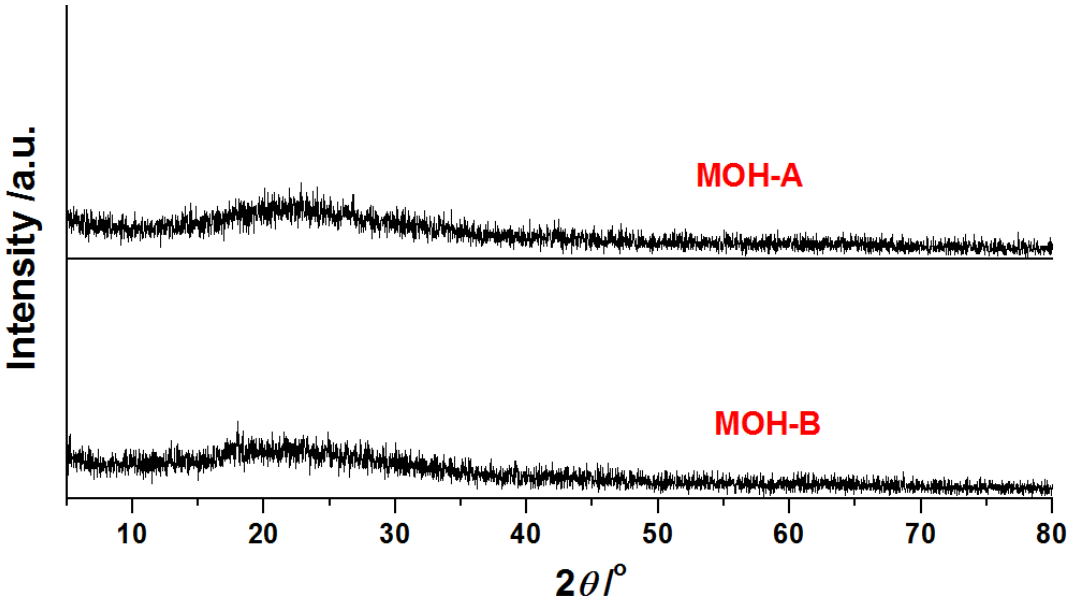

Fig. S4 ^{1}H NMR spectra of the original **Por-8** and the **Por-8** released from **Por-8@MOH-A**.

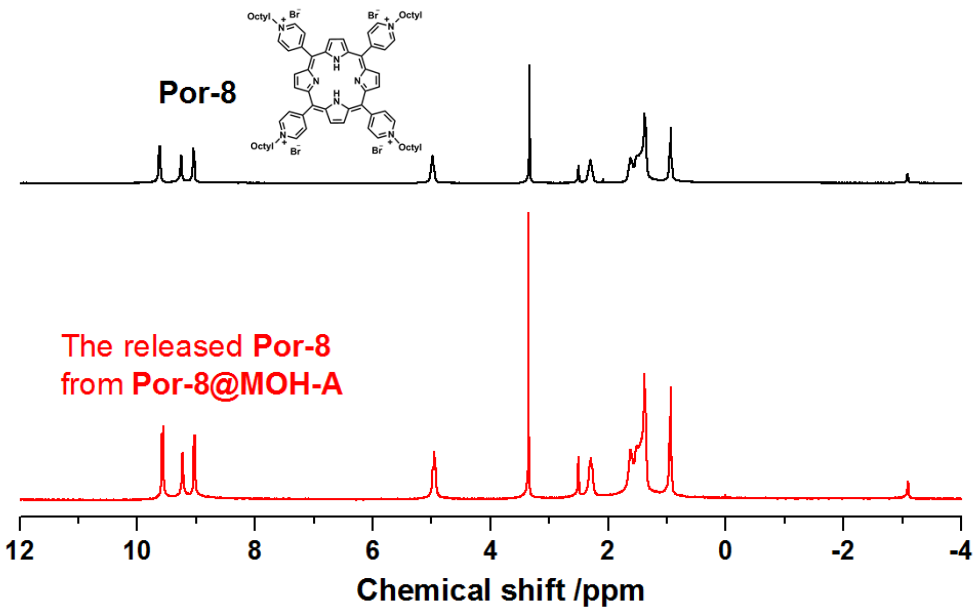

Fig. S5 Pore size distributions of (a) MOH-A obtained by release of **Por-8** guests in **Por-8@MOH-A** through MeOH treatment, (b) MOH-B used for **Zn-Por@MOH-B** in route B. The DFT method was applied for analysis of pore size distribution. The comparison of the size range of guests with pore size distribution (**orange region**, for the size values of guests, refer to table S1).

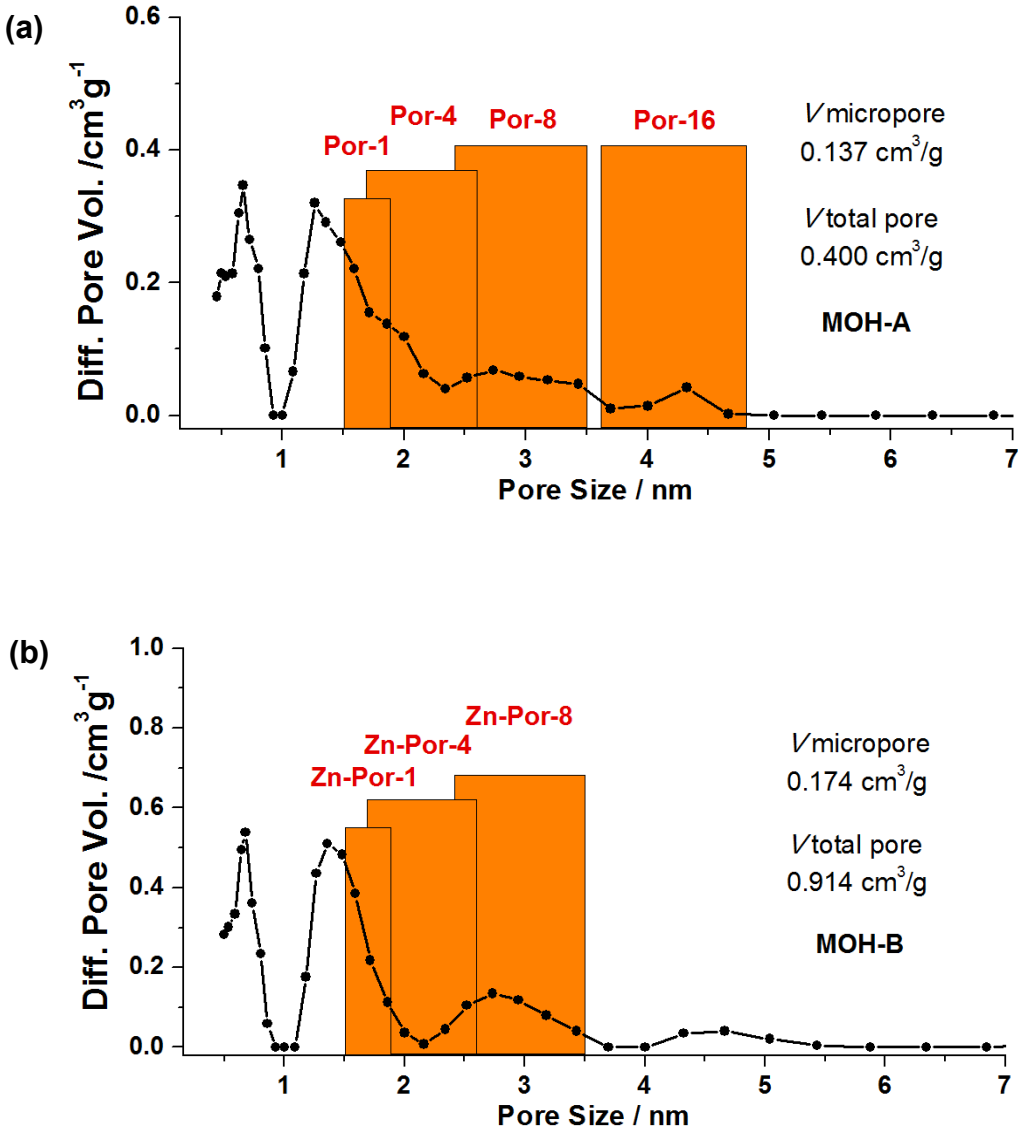

Fig. S6. (a) Comparison of pore size distributions of MOH-B with **Zn-Por-1@MOH-B**, (b) comparison of pore size distributions of MOH-B with MOH-B (calculated) in **Zn-Por-1@MOH-B** (We supposed that the **Zn-Por-1** (42w%) entrapped in MOH-B is non-porous. Thus, the volume values on Y-axis were divided by 0.58. As shown in Fig. S6b, the pore size diagrams of MOH-B and "calculated MOH-B" in **Zn-Por-1@MOH-B** were overlapped well, indicating that the pores of MOH-B in **Zn-Por-1@MOH-B** were completely retained after entrapment and the guests are located in the inner hollow spaces rather than in the microporous walls). The DFT method was applied for analysis of pore size distribution.

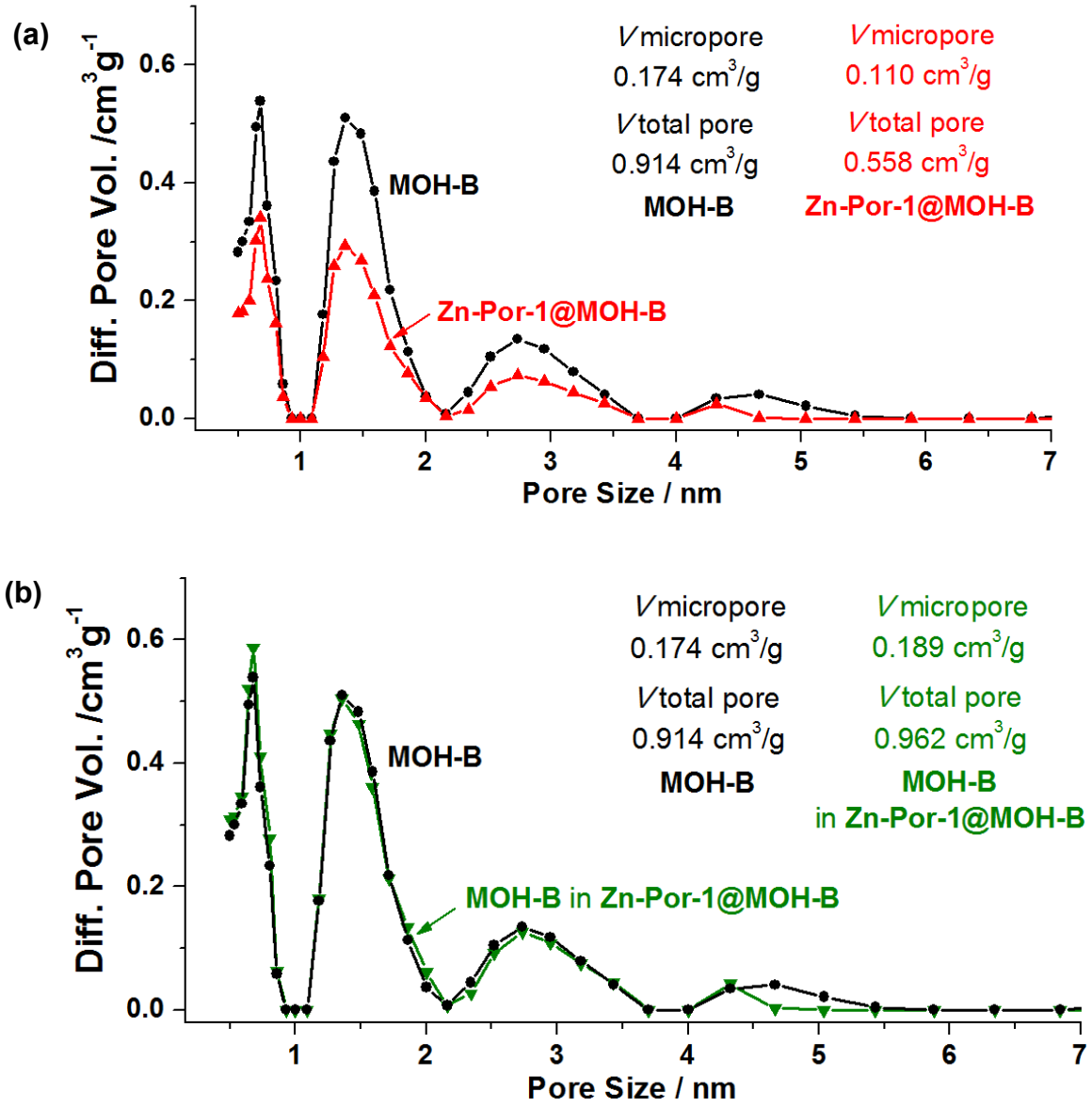

Fig. S7 N_2 adsorption and desorption isotherms of MOH-B and **Zn-Por-1**(42 w%)**@MOH-B**. (S.A.: surface area)

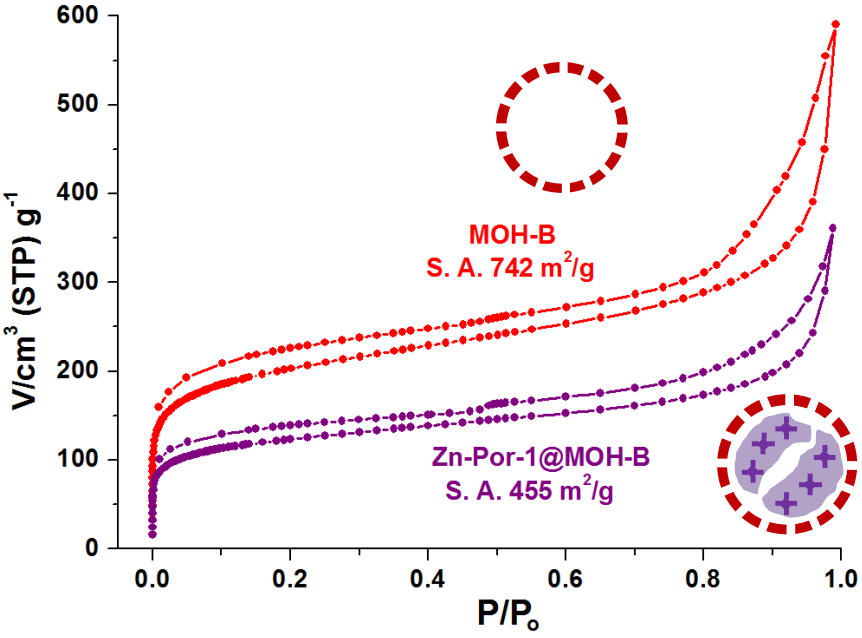

Fig. S8. Solid phase ^{13}C NMR spectra of MOH-A obtained by release of **Por-8** guests in **Por-8@MOH-A** through MeOH treatment, and MOH-B used for **Zn-Por-1@MOH-B** in route B.

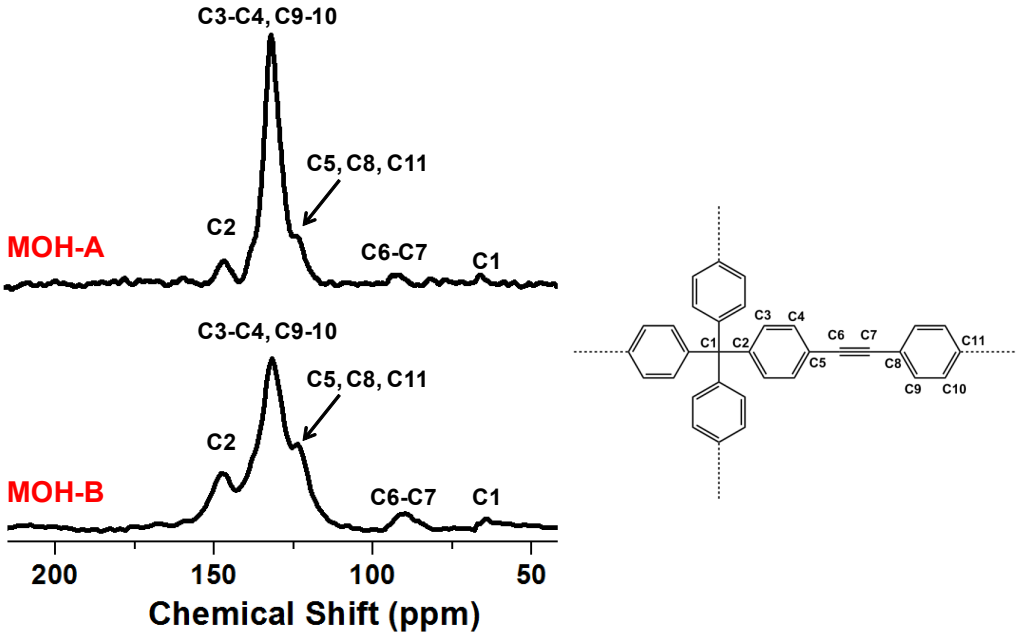

Fig. S9 TEM images of **Zn-Por-1@MOH-B**, **Zn-Por-4@MOH-B**, and **Zn-Por-8@MOH-B**.

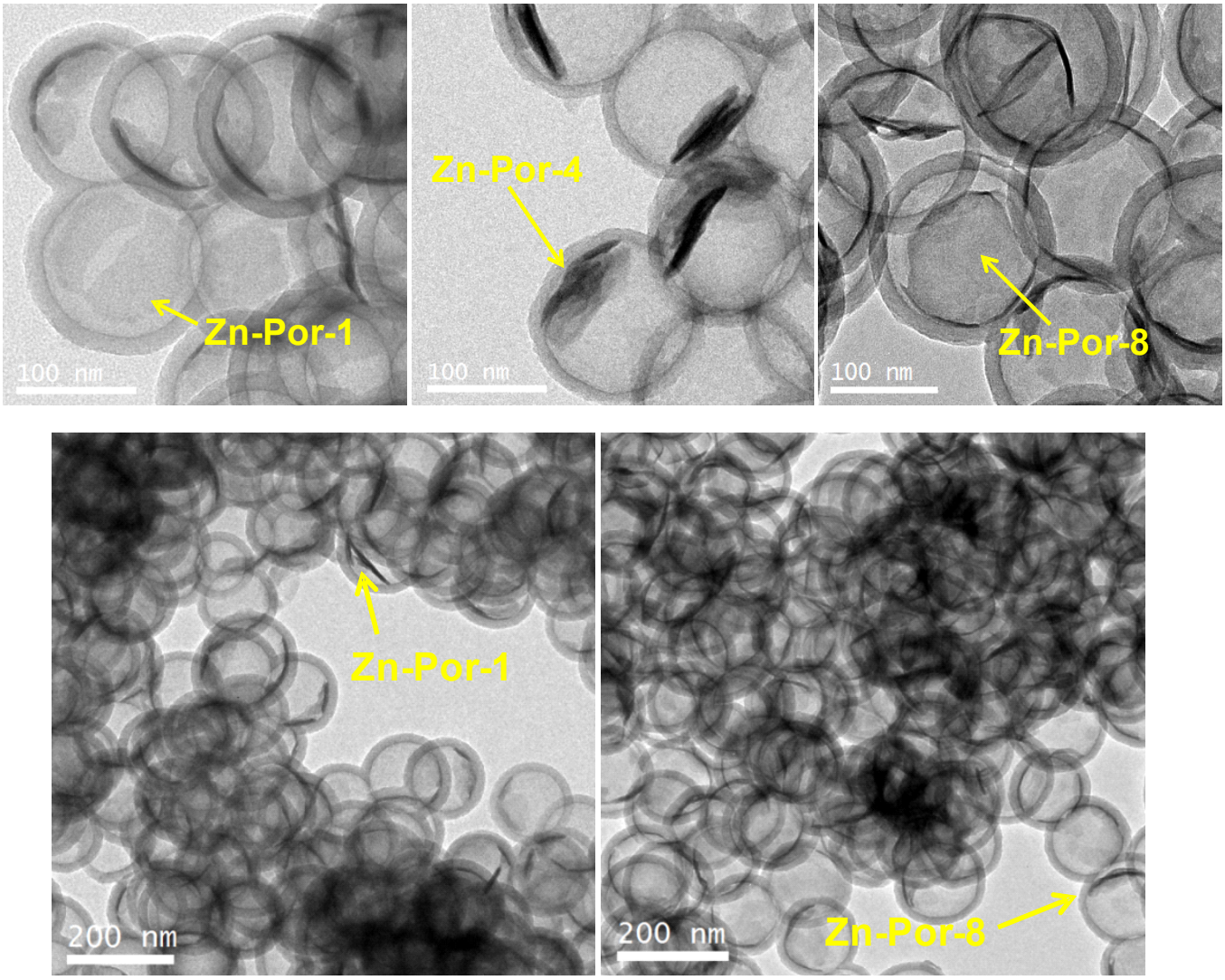

Fig. S10 Zn-EDS mapping images of **Zn-Por-1@MOH-B**.

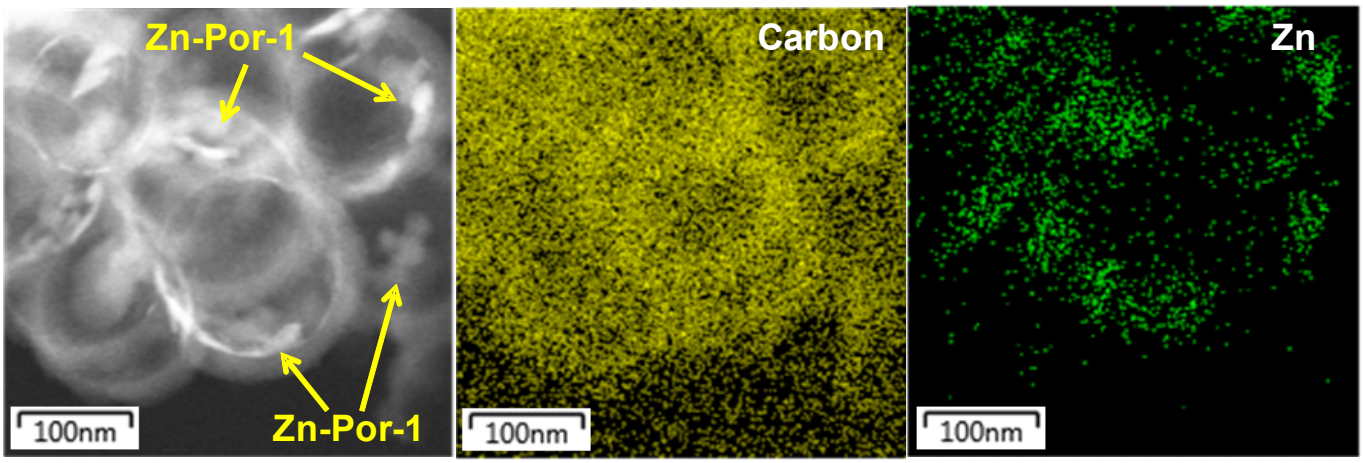

Fig. S11 ^{1}H NMR spectra of the original **Zn-Por-1** and the **Zn-Por-1** released from **Zn-Por-1@MOH-B**.

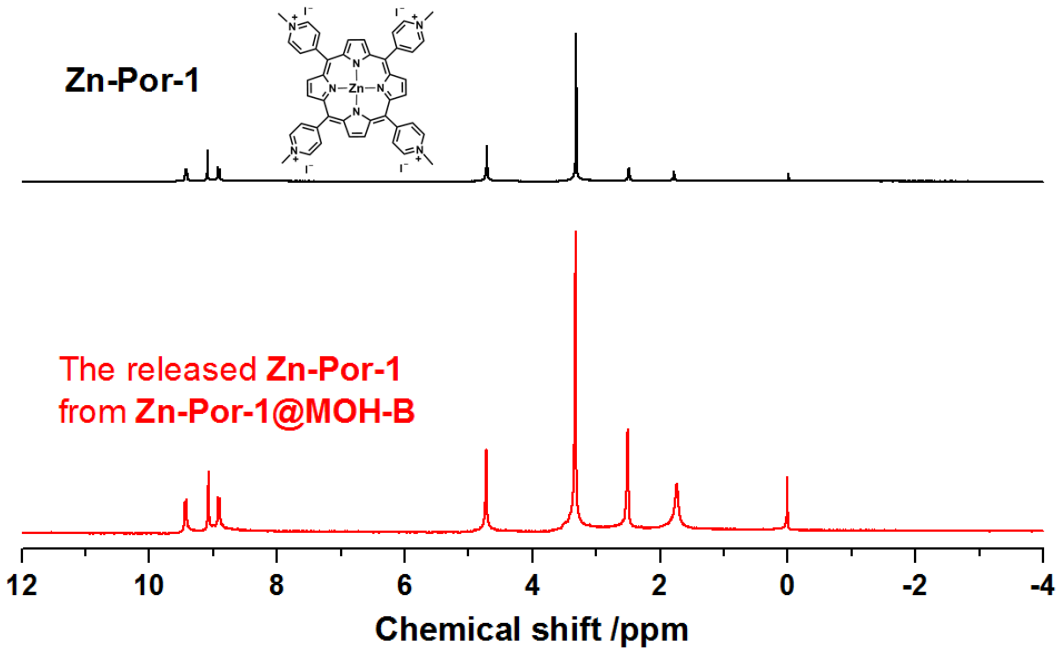

Fig. S12 UV/vis absorption and emission spectra of **Zn-Por-1**, **Zn-Por-4**, and **Zn-Por-8**. Emission spectra were obtained with 436 nm excitation. (The 5× 10^{-6} M compounds in water were used.)

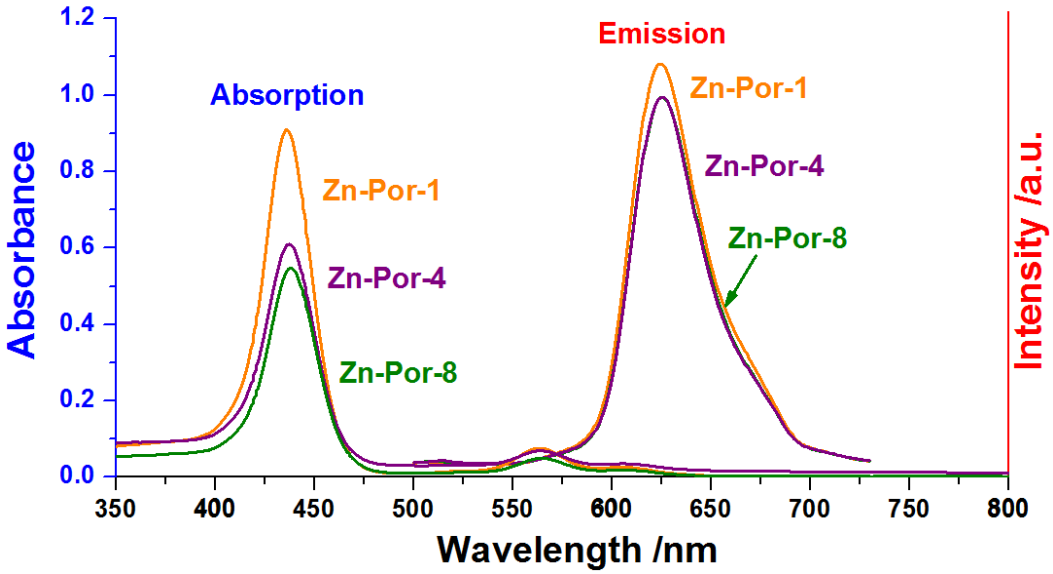

Fig. S13 Water contact angle of MOH-B (Pellet). The water contact angles of ACFs were measured using the Theta Optical Tensiometer model (KSV instruments, Ltd.) and lectrooptics comprising a CCTV camera connected to a computer (software Attension Theta).