

Electronic Supplementary Information for
Morphology engineering of Suzuki coupling-based microporous organic polymer (MOP) using Sonogashira coupling-based MOP for enhanced nitrophenol sensing in water

Sang Hyun Ryu,^a Doo Hun Lee,^a Sang Moon Lee,^b Hae Jin Kim,^b Yoon-Joo Ko,^c
Kyoung Chul Ko,^{*d} and Seung Uk Son^{*a}

^aDepartment of Chemistry, Sungkyunkwan University, Suwon 16419, Korea

^bKorea Basic Science Institute, Daejeon 34133, Korea

^cLaboratory of Nuclear Magnetic Resonance, National Center for Inter-University Research Facilities (NCIRF),
Seoul National University, Seoul 08826, Korea d.

^dDepartment of Chemistry Education, Chonnam National University, Gwangju 61186, Korea E-mail: kcko1982@jnu.ac.kr

Experimental Sections

Water contact angles were measured by a Theta Optical Tensiometer (KSV Instruments, Ltd.) and electrooptics that comprised a CCTV camera connected to a computer (software Attension Theta). The morphologies and sizes of materials were investigated through scanning and transmission electron microscopy by a JSM6700F and a JEOL 2100F. The surface areas were measured through the analysis of N₂ adsorption-desorption isotherm curves which were obtained at 77K by a Micromeritics ASAP2020 and a BELSORP II-mini analyzer. The pore size distributions were analyzed by the density functional theory method. Infrared absorption spectroscopy was conducted by a Bruker VERTEX 70 FT-IR spectrometer. Solid phase ¹³C nuclear magnetic resonance spectra (CP/TOSS mode) were obtained by a 500 MHz Bruker ADVANCE II NMR spectrometer at the National Center for Inter-University Research Facilities of Seoul National University. UV/vis absorption spectra were obtained through the conversion of the corresponding reflectance spectra which were obtained by a SHIMADZU UN-3600. The emission spectra were obtained using a JASCO FP-6200. Powder X-ray diffraction patterns were obtained by a Rigaku MAX-2200. Thermogravimetric curve was obtained by a Seiko Exstar 7300.

Synthesis of SUM-T, H-SOM, H-SOM@SUM-Ts

Tetra(4-bromophenyl)ethylene was prepared by the synthetic procedures reported in the literature.¹ For the preparation of SUM-T, (PPh₃)₄Pd (2.2 mg, 1.9 μmol), K₂CO₃ (1 mL, 2 M aqueous solution), and DMF (20 mL) were added to a flame-dried 50 mL Schlenk flask under argon. The mixture was treated by sonication for 5 min. After tetra(4-bromophenyl)ethylene (0.325 g, 0.502 mmol) and 1,4-phenylenedibromic acid (0.166 g, 1.0 mmol) were added, the reaction mixture was heated at 150 °C for 24 h. After being cooled to room temperature, the solid was separated by centrifugation, washed with water (40 mL, 7 times), acetone (40 mL, 3 times), methylene chloride (40 mL, 3 times), and ethanol (40 mL, 3 times), and dried under vacuum.

For the preparation of H-SOM@SUM-T, first, silica spheres with a diameter of 250 nm were prepared by the

Stöber method reported in the literature.² Ethanol (20 mL), distilled water (8 mL), and ammonia solution (5 mL, 28~30%) were added to a 250 mL round-bottomed flask. The mixture was stirred at room temperature for 30 min. After tetraethyl orthosilicate (14 mL) was added, the reaction mixture was stirred (800 rpm) at room temperature for 18 h. The solid was separated by centrifugation, washed with ethanol (40 mL, 4 times), and dried at room temperature. The silica spheres were treated at 500 °C for 5 h in a furnace under air and then, cooled. For the preparation of H-SOM, silica spheres (0.50 g), $(\text{PPh}_3)_2\text{PdCl}_2$ (14 mg, 20 μmol), CuI (4.0 mg, 21 μmol), triethylamine (40 mL), and toluene (20 mL) were added to a flame-dried 100 mL Schlenk flask. The reaction mixture was sonicated for 1 h at room temperature. After tetra(4-ethynylphenyl)methane (83 mg, 0.20 mmol) and 1,4-diodobenzene (132 mg, 0.400 mmol) were added, the reaction mixture was heated at 80 °C for 24 h. After being cooled to room temperature, the solid was separated by centrifugation, washed with methylene chloride (40 mL, 4 times), acetone (40 mL, 4 times), and ethanol (40 mL, 4 times), and dried under vacuum. The solid ($\text{SiO}_2@\text{SOM}$) was added to a mixture of HF (5 mL, 45% aqueous solution), water (15 mL), and methanol (10 mL) in a 50 mL Falcon tube. *Caution: The HF solution is very toxic and should be handled in a hood with specific gloves.* The mixture was stirred at room temperature for 2 h. The solid was separated by centrifugation, washed with a mixture of water (30 mL) and methanol (10 mL) 5 times, and methanol (40 mL) 3 times, and dried under vacuum. *Caution: The excess HF solution should be neutralized by adding NaOH solution.*

For the preparation of H-SOM@SUM-T1, H-SOM (10 mg), $(\text{PPh}_3)_4\text{Pd}$ (0.3 mg, 0.3 μmol), K_2CO_3 (0.1 mL, 2 M aqueous solution), and DMF (10 mL) were added to a flame-dried 50 mL Schlenk flask under argon. The mixture was sonicated for 5 min. After tetra(4-bromophenyl)ethylene (6.5 mg, 10 μmol) and 1,4-phenylenedibromic acid (3.3 mg, 20 μmol) were added, the reaction mixture was heated at 150 °C for 24 h. After being cooled to room temperature, the solid was separated by centrifugation, washed with water (40 mL, 7 times), acetone (40 mL, 3 times), methylene chloride (40 mL, 3 times), and ethanol (40 mL, 3 times), and dried under vacuum. For the preparation of H-SOM@SUM-T2, the same procedures were applied except using $(\text{PPh}_3)_4\text{Pd}$ (0.70 mg, 0.61 μmol), K_2CO_3 (0.3 mL, 2 M aqueous solution), tetra(4-bromophenyl)ethylene (19.5 mg, 30 μmol), and 1,4-phenylenedibromic acid (9.9 mg, 60 μmol). For the preparation of H-SOM@SUM-T3, the same procedures were applied except using $(\text{PPh}_3)_4\text{Pd}$ (1.1 mg, 1.0 μmol), K_2CO_3 (0.5 mL, 2 M aqueous solution), tetra(4-bromophenyl)ethylene (32.5 mg, 50.1 μmol), and 1,4-phenylenedibromic acid (16.5 mg, 100 μmol).

Procedures of sensing studies

Aqueous solutions of 2,4,6-trinitrophenol (TNP), 2,6-dinitrophenol (DNP), 4-nitrophenol (4NP), 2-nitrophenol (2NP), phenol, 4-chlorophenol, and 4-methylphenol with concentrations of 0, 0.00050, 0.010, 0.020, 0.030, 0.040, 0.10, 0.25, and 1.0 mM were prepared. H-SOM@SUM-T or SUM-T (5 mg) was dispersed in distilled water (30 mL). The substrate solution (1.5 mL) and the dispersion (1.5 mL) of H-SOM@SUM-T or SUM-T were mixed. After 30 min, the emission intensities at 517 nm for H-SOM@SUM-T1 and at 547 nm for H-SOM@SUM-T2 and H-SOM@SUM-T3 were measured with an excitation

wavelength of 410 nm. The measurement was repeated three times for each test. The K_{sv} values were obtained through the Stern-Volmer plots ($I_0/I = K_{sv}[M]+1$, I_0 : the original intensity of emission, I : the emission intensity in the presence of sensing targets, $R^2 > 0.99$ in the linear regressions.) The limit of detection was obtained from the $3\sigma/S$ value (σ : standard deviation, S : slope).

For the recyclability tests, the solution of TNP (1.5 mL, 1.0 mM) and the dispersion of H-SOM@SUM-T2 (1.5 mL, 0.17 mg/mL) were mixed. After 30 min, the emission intensity at 547 nm (an excitation wavelength of 410 nm) was measured. The H-SOM@SUM-T2 was retrieved by filtration using Omnipore™ Membrane Filters (0.2 μ m JG, Merck Milipore Ltd.). After being washed with water (200 mL), the H-SOM@SUM-T2 was dispersed in distilled water (1.5 mL). After TNP solution (1.5 mL, 1.0 mM) was added to the mixture, the emission spectrum (excitation wavelength: 410 nm) was obtained. These procedures were repeated.

Procedures of computational simulations

To simulate the frontier orbital energy levels of SUM-T, we carried out the density functional theory (DFT) calculations. First, we designed three model systems (SUM-T-1, SUM-T-5 and SUM-T- ∞) of SUM-T depending on the size of networks of SUM-T. (Fig. S5 in the ESI) The B3LYP/light-tier-1 level of theory was employed for the DFT calculations. The convergence criterion for structure optimizations was set as 0.01 eV/Å. For SUM-T- ∞ , PBE/light-tier-1 level of theory was used for full optimizations of atomic geometries as well as the unit cell parameters, because periodic boundary condition (PBC) calculation with hybrid functional requires huge computational cost. The unit cell parameters of SUM-T- ∞ are optimized as $a = 24.31$ Å, $b = 18.51$ Å and $c = 46.31$ Å within 0.02 eV/Å criteria. It is noted that we added the 40 Å of vacuum spacing along the c-axis to avoid the interaction between slabs in PBC condition. After unit cell optimization with PBE functional, single point calculation with B3LYP/light-tier-1 was performed to obtain the valence band and conduction band levels. The k-grid point grid was chosen as gamma point (1×1×1). All DFT calculations were carried out using FHI-aims codes.³ The molar volume calculations of TNP, DNP, 2NP and 4NP were conducted within B3LYP/6-31+G(d,p) level using Gaussian 09 program. (Fig. S8 in the ESI)

The fluorescence quenching process of nitrophenol sensing for SUM-T can be understood by the photo-induced electron transfer (PET) mechanism.⁴ Fig. S6 in the ESI shows the calculated HOMO and LUMO energy levels for three model systems of SUM-T and substrates. On the basis of SUM-T-1, SUM-T-5 and SUM-T- ∞ , we can estimate the frontier orbital energy levels of SUM-T including the deviations affected by organic polymer sizes. The LUMO energy levels for SUM-T were calculated to be around -1.87 ~ -2.32 eV. The calculated LUMO levels of nitrophenol moieties (TNP, DNP, 2NP and 4NP) are lower than those of SUM-T. For this reason, the photo-generated electrons of SUM-T can migrate to nitrophenols, resulting in fluorescence quenching. On the other hand, the fluorescence emission of SUM-T can be maintained for 4-chlorophenol, phenol and 4-methylphenol due to their higher LUMO energy levels compared with those of SUM-T.

References

1. Y. Xu, D. Chang, S. Feng, C. Zhang and J. -X. Jiang, *New J. Chem.* 2016, **40**, 9415-9423.
2. W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.* 1968, **26**, 62-69.
3. V. Blum, R. Gehrke, F. Hanke, P. Havu, V. Havu, X. Ren, K. Reuter and M. Scheffler, *Comput. Phys. Commun.* 2009, **180**, 2175–2196.
4. E. V. Anslyn and D. A. Dougherty, *Modern physical organic chemistry*, University Science Books, Sausalito, CA, 2006, 955-956.

Fig. S1 (a) SEM image and (b) PXRD pattern of KHSi_2O_5 formed by the reaction of silica templates and K_2CO_3 .

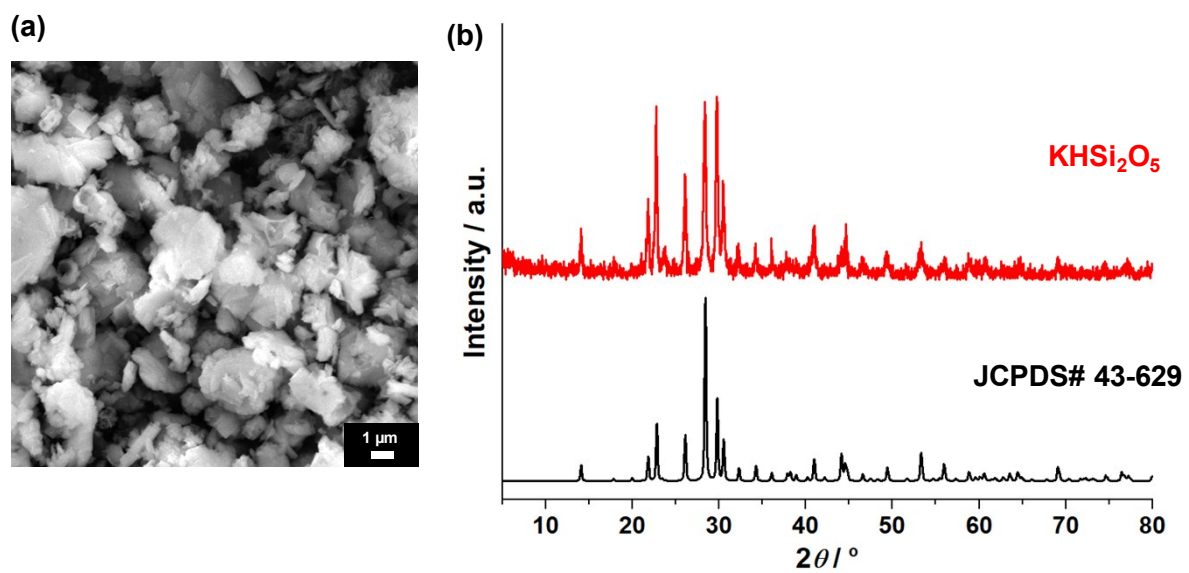


Fig. S2 SEM images of SUM-T.

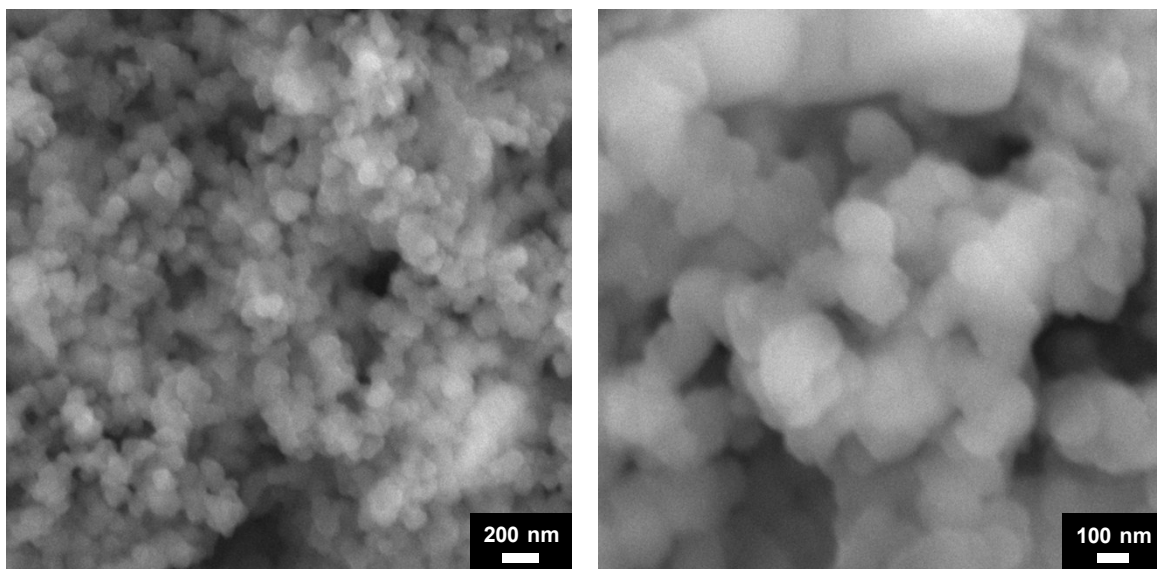


Fig. S3 PXRD patterns of H-SOM, H-SOM@SUM, and SUM-T.

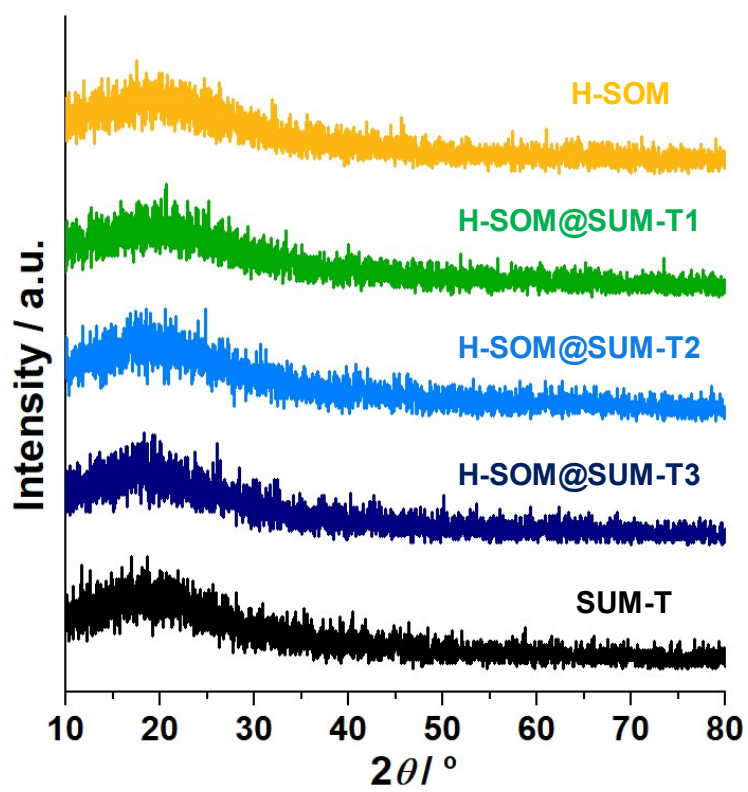


Fig. S4 Photographs of emission quenching of the H-SOM@SUM-T2 by TNP' (a) H-SOM@SUM-T2 dispersion in water and (b) the H-SOM@SUM-T2 powder on carbon tape.

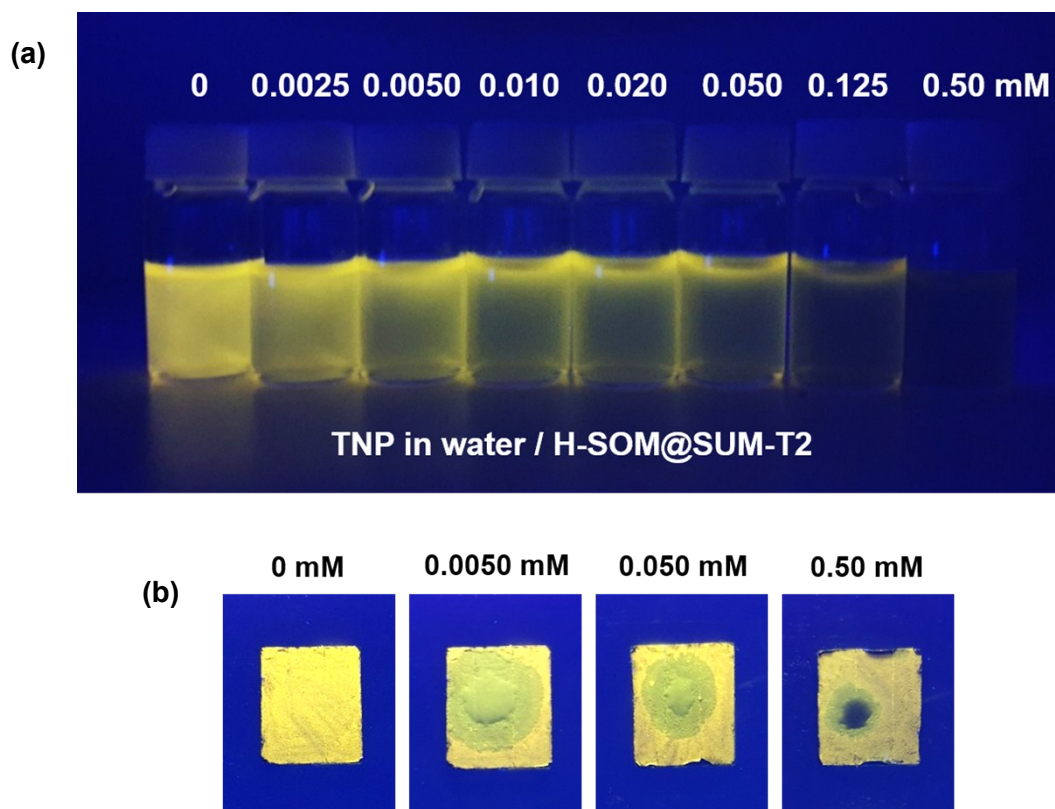
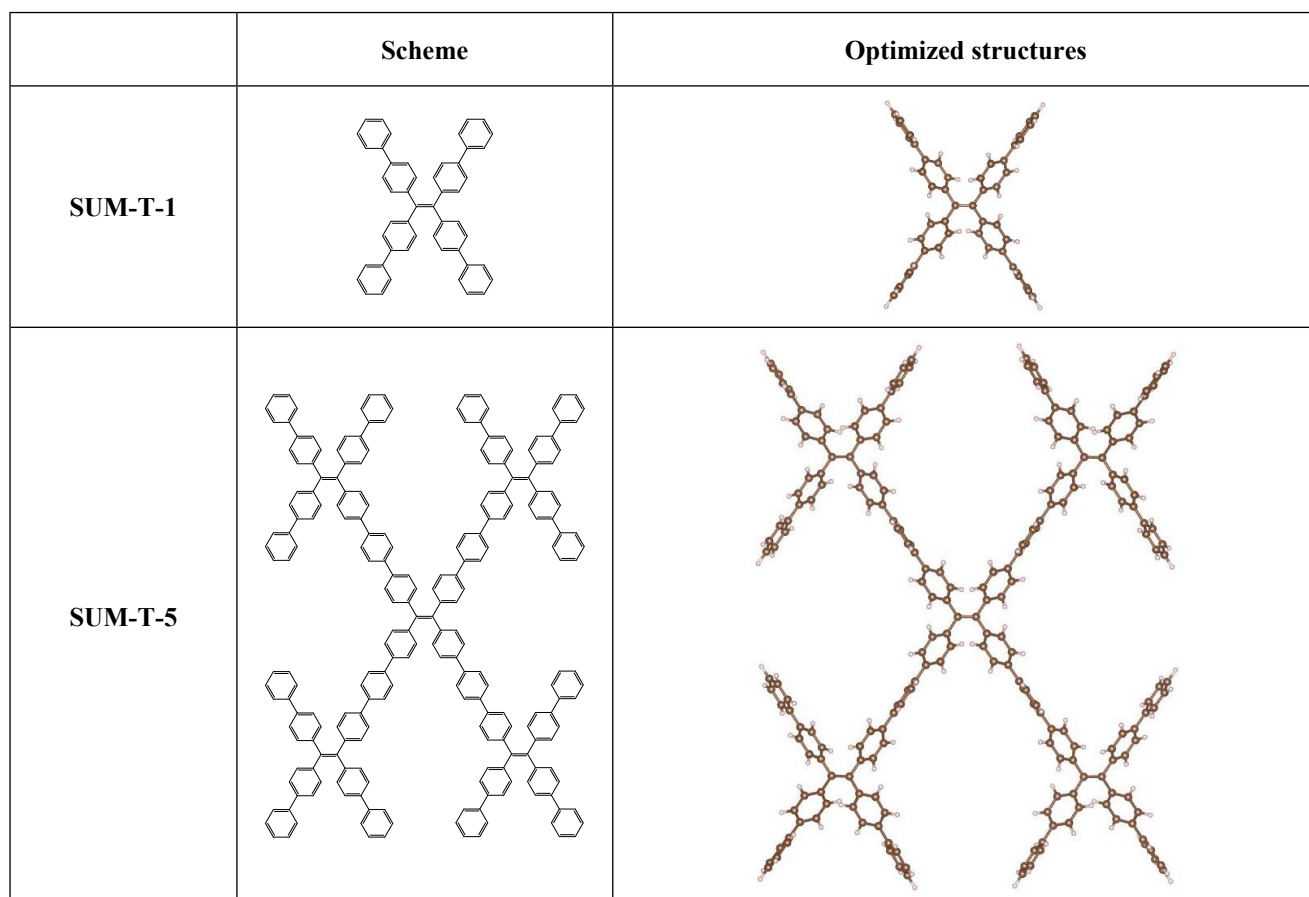


Fig. S5 The schematic figures for model systems (SUM-T-1, SUM-T-5, and SUM-T- ∞) which can represent the SUM-T with an increasing system size (left) and their optimized structures (right).



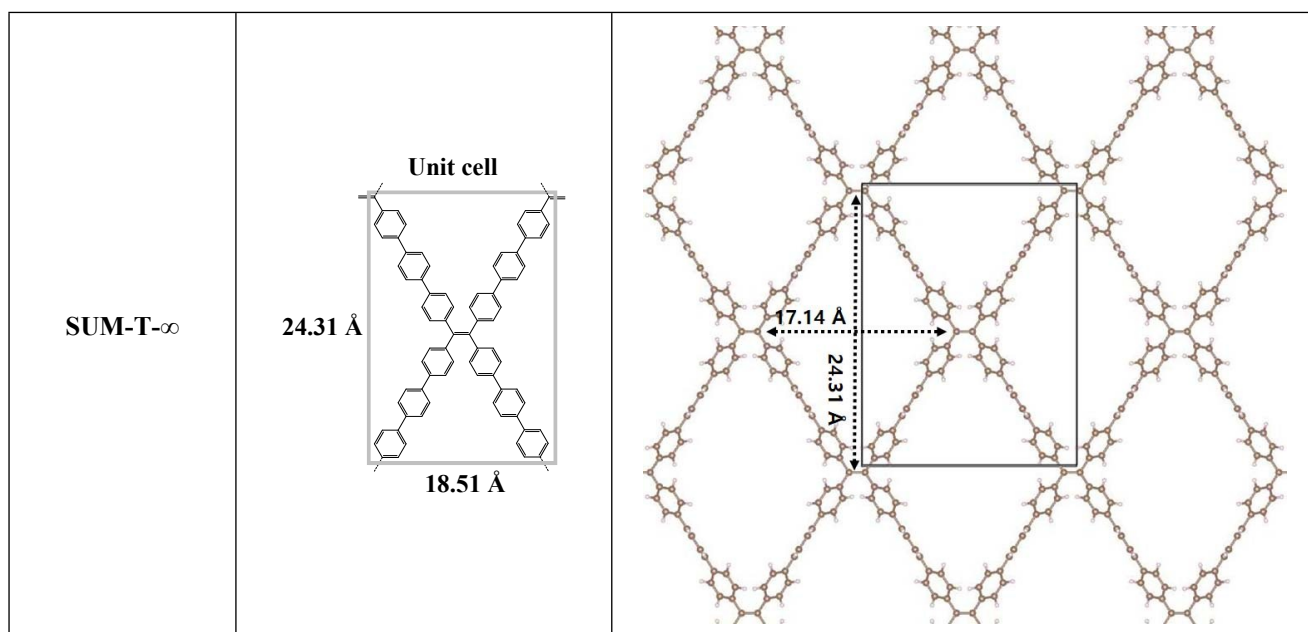
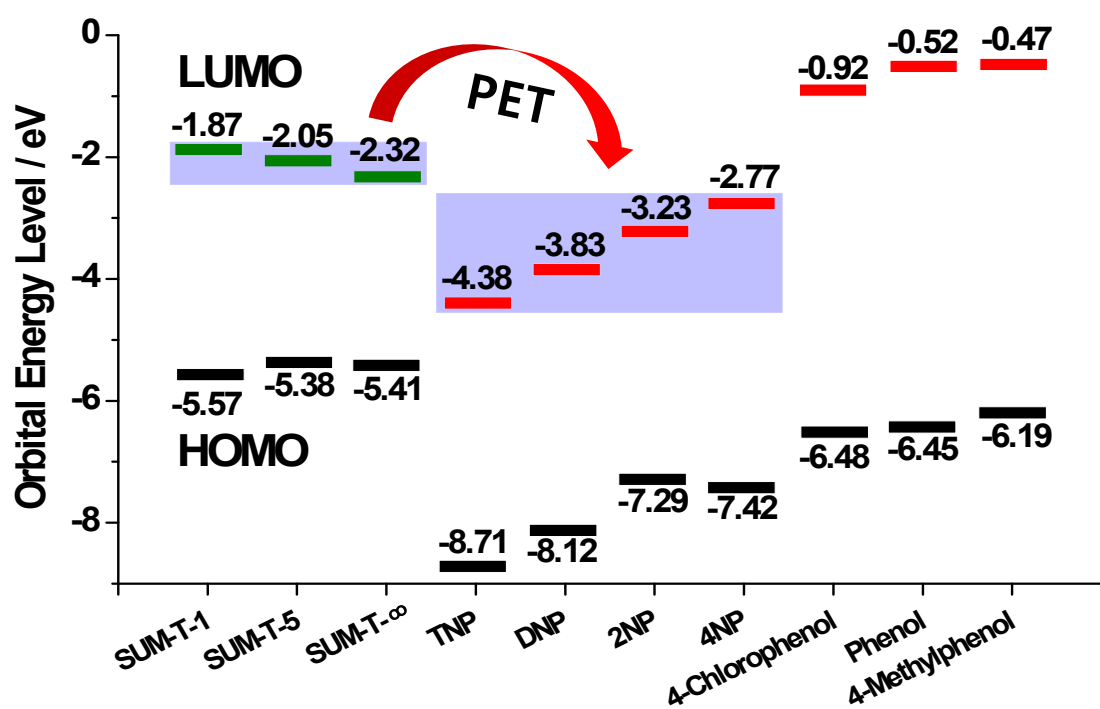


Fig. S6 The calculated HOMO and LUMO energy levels of model systems for SUM-T and substrates (TNP, DNP, 2NP, 4NP and 4-chlorophenol, phenol and 4-methylphenol).



C 15.312566	5.462167	2.609903	C 20.015467	14.146244	3.185323	H 16.873089	10.569595	1.531743
C 16.102067	6.752580	4.484860	C 21.267422	14.937013	3.201509	H 12.027385	11.597611	1.855754
C 16.320333	5.712789	3.500517	C 22.272568	14.674090	4.152468	H 10.608873	9.234666	5.167609
C 13.963878	10.280619	3.307613	C 21.494439	15.979391	2.282198	H 9.969746	12.954365	1.938591
C 14.176278	11.348402	4.201595	C 23.442856	15.426938	4.189706	H 8.557910	10.600124	5.265208
C 14.952072	10.035216	2.335573	C 22.656206	16.747693	2.333686	H 17.728539	4.792707	5.727829
C 15.347464	12.099769	4.161931	C 23.649713	16.498820	3.299337	H 17.731921	4.823059	1.416590
C 16.114672	10.802022	2.281913	C 0.596323	17.425480	3.457662	H 19.812445	3.477793	5.719478
C 16.347822	11.839527	3.205195	C 21.207260	1.519103	3.540598	H 19.787963	3.468792	1.408209
C 11.462345	10.291495	3.484803	C 21.426982	2.815883	2.584768	H 7.644465	4.850137	1.045240
C 11.258866	11.364820	2.595412	C 22.210655	0.737468	4.401107	H 7.645068	4.863648	5.356558
C 10.472890	10.051127	4.456823	C 22.579516	2.049540	2.541286	H 5.547022	3.556962	1.050322
C 10.094787	12.126949	2.639621	C 23.371933	0.974957	3.430319	H 7.667795	3.530703	5.361514
C 9.317612	10.828571	4.515113	C 23.570820	2.650152	3.226678	H 7.699036	12.771822	1.465864
C 9.093245	11.872226	3.596608	C 4.144062	2.650152	3.226678	H 7.699036	12.782226	5.777084
C 17.565590	4.911489	3.572520	C 3.144418	2.908847	4.184571	H 5.611793	14.126120	1.477042
C 18.183456	4.516926	4.774429	C 1.161688	1.611860	2.304076	H 5.615118	14.097062	5.788296
C 18.175755	4.518080	2.366123	C 1.974402	2.155752	4.225385	H 17.778140	12.715553	5.342183
C 19.352819	3.758202	4.769693	C 2.750207	0.843369	2.588831	H 17.755026	12.745296	1.031000
C 19.348727	3.768963	2.361400	C 1.762345	1.087870	3.331365	H 19.848117	14.048442	5.340769
C 19.964202	3.562838	3.562838	C 0.507183	0.288255	3.417214	H 19.852496	14.038499	1.029445
C 7.810412	4.958924	3.200851	C 4.206301	15.020831	3.622801	H 22.145280	13.847408	4.853962
C 7.187553	4.575327	1.997969	C 3.992573	16.061516	4.547223	H 20.732030	16.214093	1.336801
C 7.197286	4.567012	4.406237	C 3.196798	14.773778	2.672212	H 24.214114	15.187490	4.924456
C 6.010370	3.828790	2.000790	C 2.839762	16.843495	4.500814	H 22.794460	17.563136	1.622165
C 6.016656	3.830004	4.409087	C 2.035349	15.540411	2.639841	H 20.665736	1.293030	5.207886
C 5.959503	3.441017	3.206656	C 1.842256	16.610757	3.532444	H 22.089384	3.644186	1.884112
C 7.848064	12.673405	3.620241	H 12.012455	5.995213	4.934726	H 22.711941	-0.079698	5.111760
C 7.230113	13.072392	2.419649	H 10.592937	8.370269	1.631972	H 24.142148	2.280256	1.802748
C 7.237987	13.062428	4.827931	H 9.941581	4.657918	4.867027	H 3.275726	3.732416	4.888982
C 6.057159	13.821540	2.425983	H 8.528563	7.024186	1.549454	H 4.669737	1.380473	1.553219
C 6.068601	13.821089	4.834270	H 13.375008	5.995026	1.839903	H 1.207433	2.391934	4.965579
C 5.449429	14.216190	3.633210	H 14.815289	8.343906	5.152378	H 2.607808	0.031135	1.644463
C 17.600918	12.628420	3.187079	H 15.432948	4.637680	1.903719	H 4.758632	16.283971	5.292623
C 18.220667	13.015816	4.390543	H 16.866624	6.977753	5.230998	H 3.313497	13.948855	1.966810
C 18.217181	13.016487	1.982234	H 13.409110	11.585249	4.941368	H 2.711983	17.657263	5.216201
C 19.401344	13.752745	4.389682	H 14.809289	9.223092	1.621159	H 1.260412	15.313304	1.905134
C 19.394353	13.763062	1.981398	H 15.479410	12.923018	4.866588			

Fig. S8 The sizes and volumes of nitrophenols calculated by B3LYP/6-31+G(d,p) level of theory (Gaussian 09).

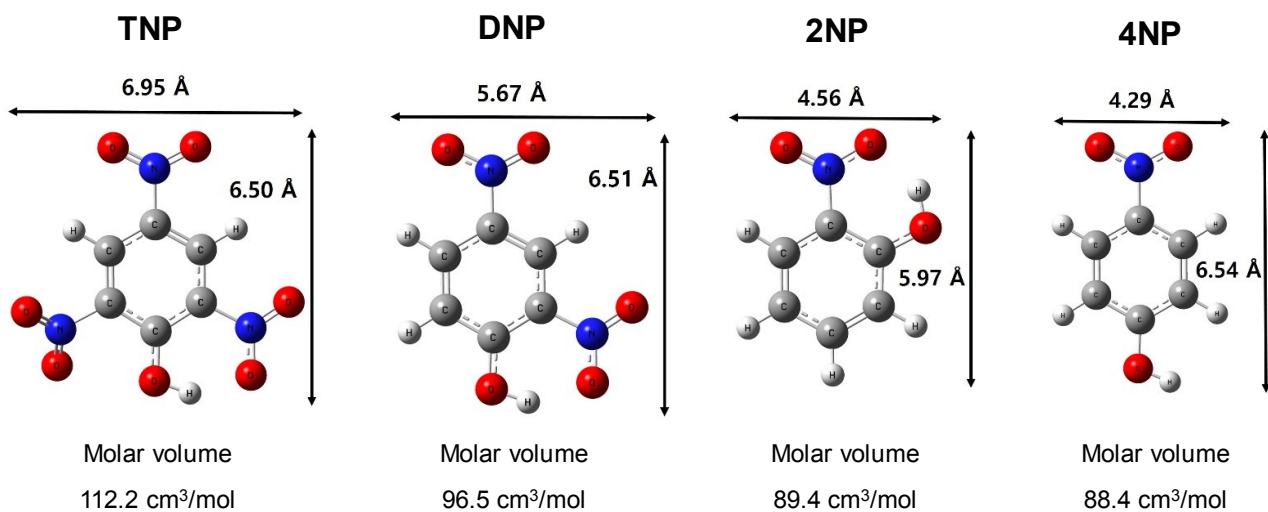


Fig. S9 TGA curve of H-SOM@SUM-T2.

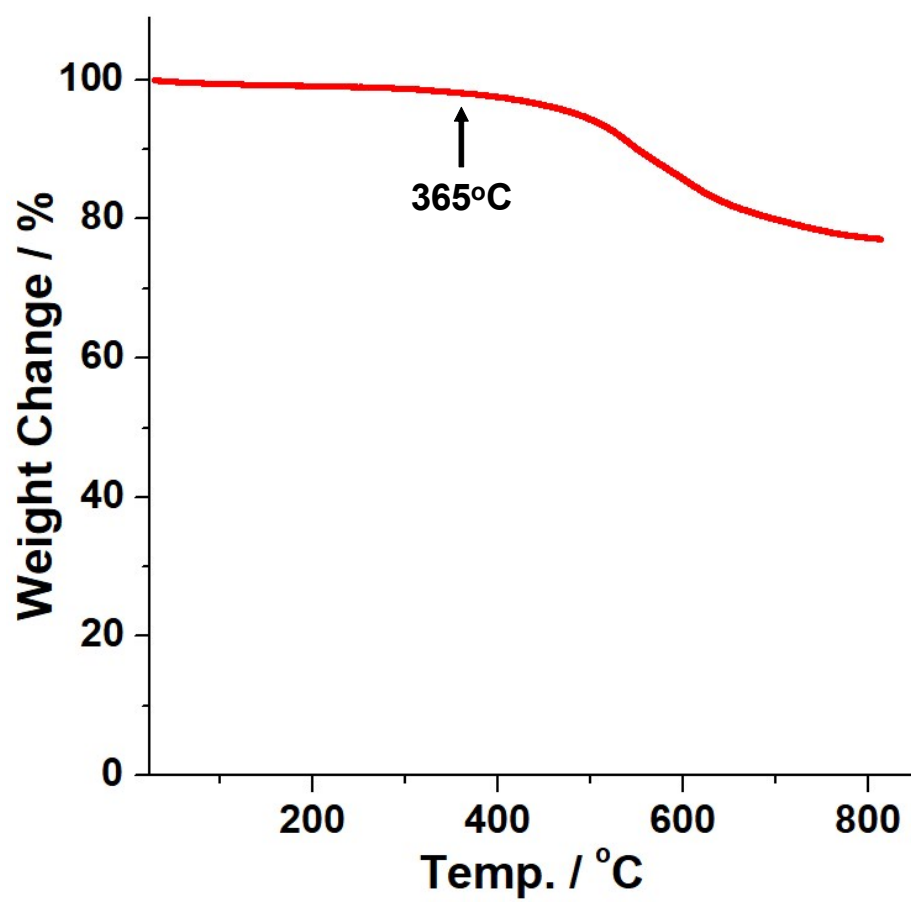


Fig. S10 (a) SEM images and (b) IR spectra of H-SOM@SUM-T2 before and after five successive sensing tests.

(a)

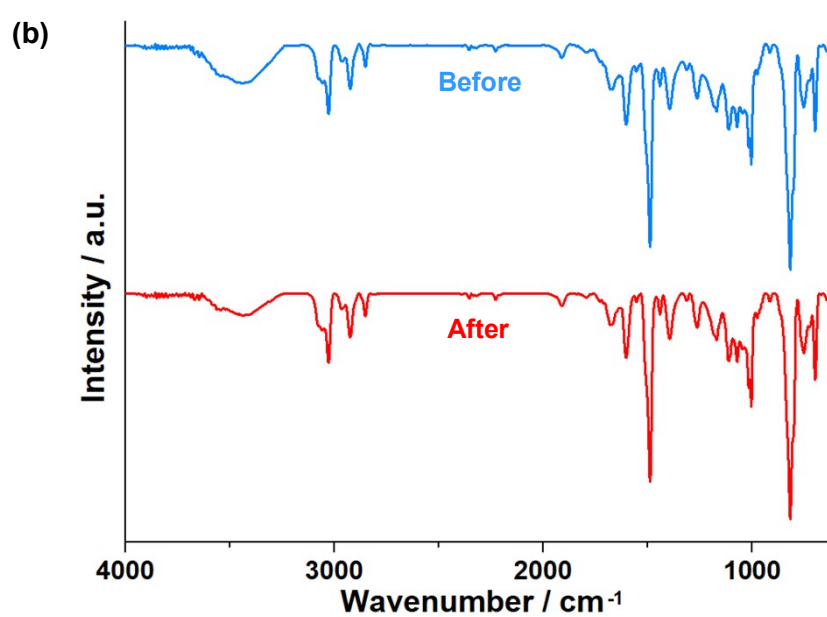
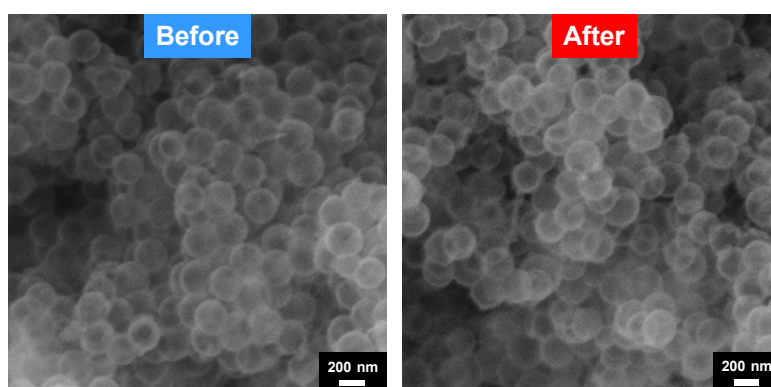


Table S1. Sensing performance of emissive MOP materials in the literature and H-SOM@SUM-T2 for the 2,4,6-trinitrophenols.

Materials	Solvent	Sensing Targets	K_{sv} (M^{-1})	Ref.
Core-shell porous aromatic framework	ethanol	TNP	5540	1d
Microporous polymer film with tetraphenylethylene	acetonitrile	TNP	64000	7b
Porous Troger's base polymer with tetraphenylethylene	ethanol	TNP	26000	7c
Microporous polymer nanoparticles with tetraphenylethylene	water	TNP	12600	8a
Sn-porphyrin network film	water	TNP	24000	8b
Luminescent microporous organic polymer with 1,3,5-tri(4-ethenylphenyl)benzene	THF/H ₂ O (9:1)	TNP	-	9a
Highly cross-linked fluorescent polymer microsphere	methanol	TNP	15200	9b
Hollow microporous organic network with isocoumarins	H ₂ O/THF (2:1)	TNP	15000	9c
CMP with fluorescein	THF	TNP	2080	9d
H-SOM@SUM-T2	water	TNP	73000	This work