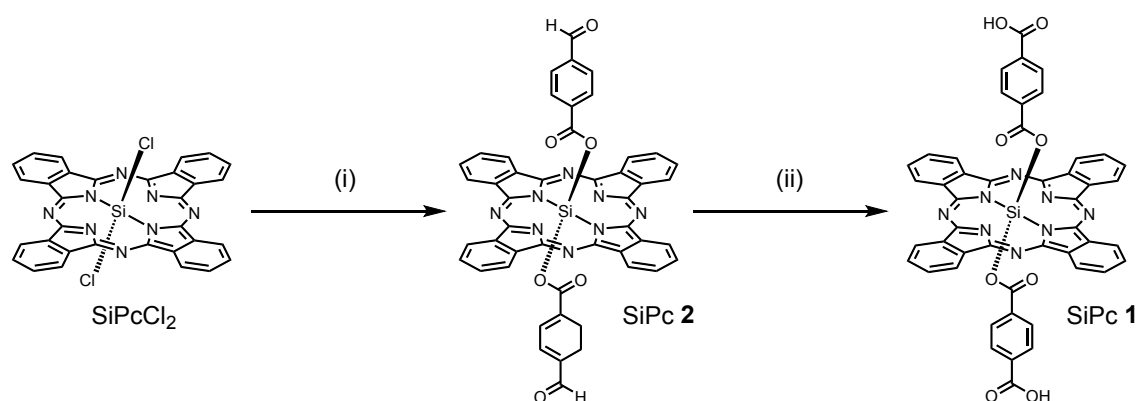


Supporting Information

Experimental methods

1. Synthesis of SiPc 1



(i) 4-formylbenzoic acid, Tol/diglyme/Pyr, 170 °C, 27%, (ii) amidosulfonic acid, sodium chlorite, THF/H₂O, RT, 85%

SiPc 1 has been synthesized following the depicted synthetic route, with slight variations of the already published method.¹ All chemicals and solvents were acquired from commercial sources and used as received, unless otherwise is stated.

NMR spectra were recorded with a Bruker AC 300 spectrometer, while mass and UV/vis spectra were acquired with a Bruker Microflex matrix-assisted laser desorption/ionization time of flight (MALDI-TOF) and a Helios Gamma spectrometer, respectively.

Synthesis of SiPc 2: A suspension of 50 mg silicon(IV) phthalocyanine dichloride (SiPcCl₂, 0.082 mmol), 37 mg 4-formylbenzoic acid (0.246mmol), 3 mL dry toluene, 2 mL diethylene glycol dimethylether (Diglyme) and 0.5 mL pyridine, is prepared in an 8 mL microwave tube. The mixture is then held at a constant temperature of 170°C for one hour, using a microwave reactor. After that, crude reaction is allowed to reach 60°C, diluted with ethylacetate and washed with 0.5

¹ L. Martín-Gomis, E. M. Barea, F. Fernández-Lázaro, J. Bisquert, Á. Sastre-Santos, *J. Porphyr. Phthalocyanines* **2011**, 15, 1004–1010.

M HCl, 0.5 M NaOH, H₂O and brine. The pure product was obtained as a blue-green solid (18.6 mg, 27%) after complete evaporation of the solvent under reduced pressure. ¹H NMR (300 MHz; 25°C; CDCl₃): δ=9.76–9.71 (8H, m, Pc- Ar-H), 9.40 (2H, s, CHO), 8.44–8.40 (8H, m, Pc-Ar-H), 6.76 (2H, d, *J*: 8.6 Hz, H-Ar) and 5.26 (2H, d, *J*: 8.6 Hz, H-Ar) ppm. HR MS (MALDI-TOF, dithranol): *m/z* [M⁺] calculated for C₄₈H₂₆N₈O₆Si 838.1739, found 838.1798. UV-Vis (CHCl₃) λ_{max}/nm (logε): 360 (4.87), 619 (4.57), 658 (4.51) and 688 (5.35)

Synthesis of SiPc **1**: SiPc **2** (150 mg, 0.179 mmol), amidosulfonic acid (HNH₂SO₃, 42 mg, 0.433 mmol) and sodium chlorite (30 mg, 0.332 mmol) in a 5:1 THF/H₂O mixture (36 mL) were stirred at room temperature for 12 h. The crude product was precipitated in water, filtered and redissolved in THF. The resulting organic solution was dried over anhydrous Na₂SO₄ and the pure product was obtained as a blue-green solid (140 mg, 90%) after the complete evaporation of solvent under reduced pressure. ¹H NMR (300 MHz; 25°C; CDCl₃): δ=9.75–9.71 (8H, m, Pc- Ar-H), 8.60–8.57 (8H, m, Pc-Ar-H), 6.84 (2H, d, *J*: 8.3 Hz, H-Ar) and 5.07 (2H, d, *J*: 8.3 Hz, H-Ar) ppm. HR MS (MALDI-TOF, dithranol): *m/z* [M⁺] calculated for C₄₈H₂₆N₈O₈Si 870.1643, found 870.1569. UV-Vis (CHCl₃) λ_{max}/nm (logε): 361 (4.79), 618 (4.50), 657 (4.44) and 686 (5.31).

2. Preparation of Substrate

For preparation of SURMOF in cavity, Ag-coated silicon wafer and glass substrates were used. The silicon wafers (with [100] orientation, from Silicon Sense (US)) were precleaned by ultrasonication in absolute EtOH absolute for 30 min and a silver (99.99%, Chempur) film of 30 nm thickness was thermally evaporated at 453 K under high-vacuum conditions (~10⁻⁷ mbar) with 2 nm-titanium as the adhesion layer. The thickness and deposition rate (10 Å s⁻¹) were monitored using a quartz crystal microbalance.

3. Preparation of SURMOF Thin Films

The Ag-coated substrate was cleaned by Ar-H₂ plasma treatment (Diener Plasma, airflow: 20 sccm, pure hydrogen) for 30 minutes and then immersed into a 1 mM ethanolic solution of 11-Mercapto-1-undecanol (MUD) solution for 24 h at room temperature. Subsequently, the substrate was rinsed with absolute ethanol and dried under a nitrogen stream. The Zn-Si-Pc SURMOF was fabricated in a layer-by-layer process using the spray coating method. Briefly, zinc acetate solution

(1 mM) and SiPc linker solution (20 μ M) were alternately sprayed on the pre-treated MUD-Ag - wafers 20 seconds and 30 seconds respectively by using the spray guns. After the metal or linker coating, the samples were rinsed with ethanol to remove unreacted metal/linker or by-products from the surface. By repeating this process, Zn-SiPc thin films with precise deposition thickness are prepared.

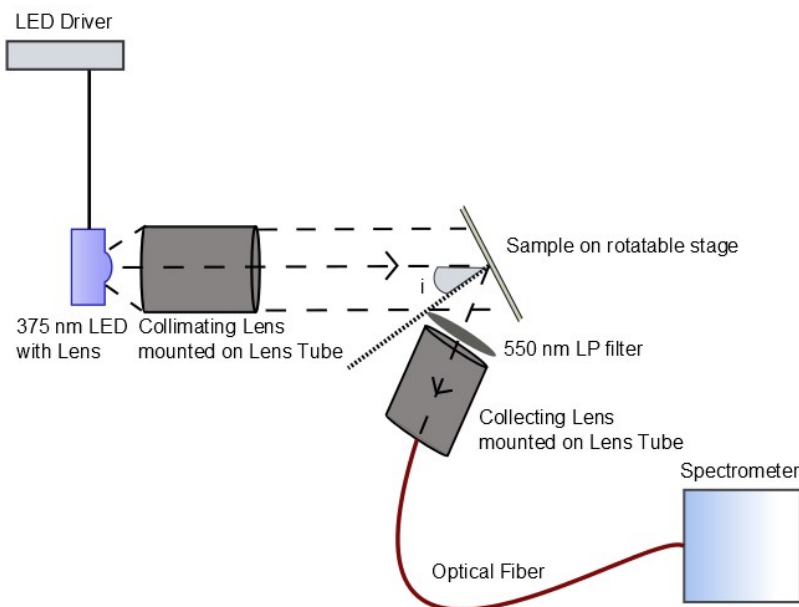
4. Cavity fabrication

Using layer-by-layer coating, an average Zn-SiPc film thickness of ~ 400 nm was realized, and a semitransparent 10 nm Ag mirror was evaporated on the top of the MOF films to form the cavity. Out-of-plane X-ray diffraction data, before and after top Ag-layer deposition confirmed the intact crystallinity of Zn-SiPc.

5. Characterization

UV-Vis spectroscopy: The UV-Vis spectra were measured in reflection mode with a Cary5000 UV-vis/NIR spectrometer with an UMA unit from Agilent. PerkinElmer Lambda 950 UV-vis/NIR spectrometer equipped with an integration sphere was used to determine the absorbance of the cavity formed using one semitransparent (10 nm Ag) and one non-transparent (30 nm Ag and glass) mirror.

Photoluminescence measurements: A 375 nm LED (Thorlabs, LED375L) is used as the light source, which is driven at constant current with the help of a driver (Thorlabs, ITC4001). It is collimated using a plano-convex lens (Thorlabs, LA1608) with 75 mm focal length mounted on a lens tube (Thorlabs, SM1L20). The collimated beam hits the sample at an angle of incidence 'i' and the emission from the sample is filtered using a long pass filter (Thorlabs, FEL0550) with 550 nm cut on wavelength and collected using a plano-convex lens (Thorlabs, LA1131) of 50 mm focal length mounted on another lens tube (Thorlabs, SM1L20), through an optical fiber (Thorlabs, FP1000URT) and detected using a CCD-cooled spectrometer (Avantes, AvaSpec-ULS2048 X 64TEC) which is calibrated for intensity using a calibration lamp (Ocean Optics, HL-3plus-INT-CAL-EXT) (See below appended schematic). The angle of incidence 'i' can be adjusted by rotating the sample.



Schematic of the incidence angle dependent fluorescence measurement set up.

Atomic force microscopy: AFM imaging was performed with the Bruker's Dimension® Icon™ SPM system. Then the process was performed in the Scanasyt in air mode (cantilever type: SCANASYST-AIR, BRUKER AFM probes) with the force of ~ 2 nN, scan rate of 0.5 Hz and the number of lines: 512.

6. Porosity measurement

For vapor uptake measurement using a quartz crystal microbalance (QCM, QSense), Zn-SiPc SURMOFs were grown on a 11-mercapto-1-undecanol (MUD) self-assembled monolayer (SAM) functionalized Au thin film deposited on a QCM sensor. Prior to the vapor uptake experiments, the SURMOF was activated by 8 h of Ar-flow at 50 °C.

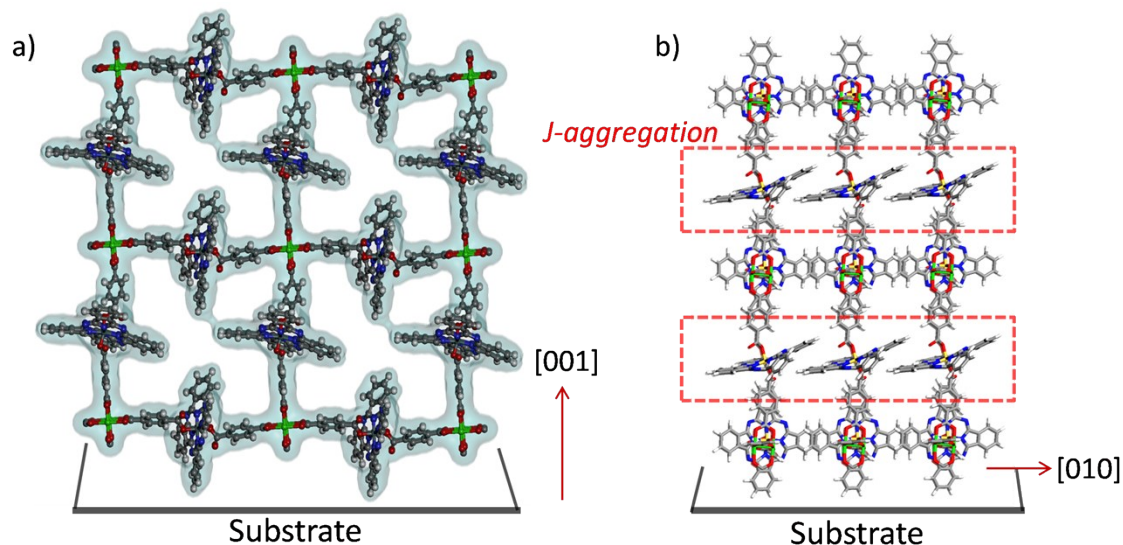


Fig. S1 a) van der Waals surface added view of the 1D pores in Zn-SiPc structure; b) View of close stacking along [010] axis leading to J-aggregation in Zn-SiPc SURMOF-2 structure.

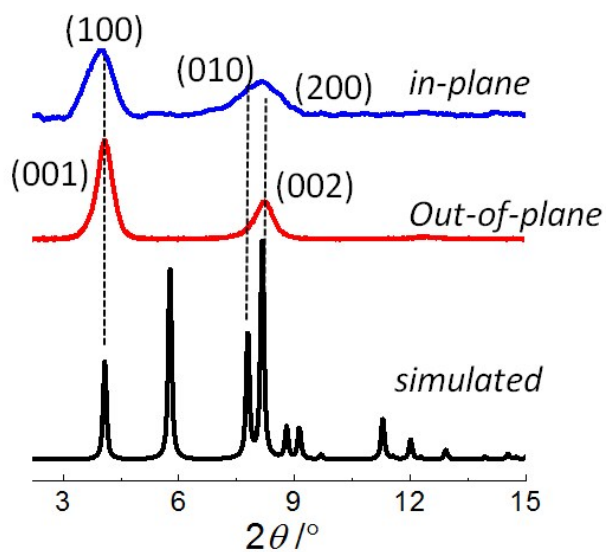


Fig. S2 Predicted, experimental out-of-plane and in-plane X-ray diffraction patterns of Zn-SiPc SURMOF-2 structure.

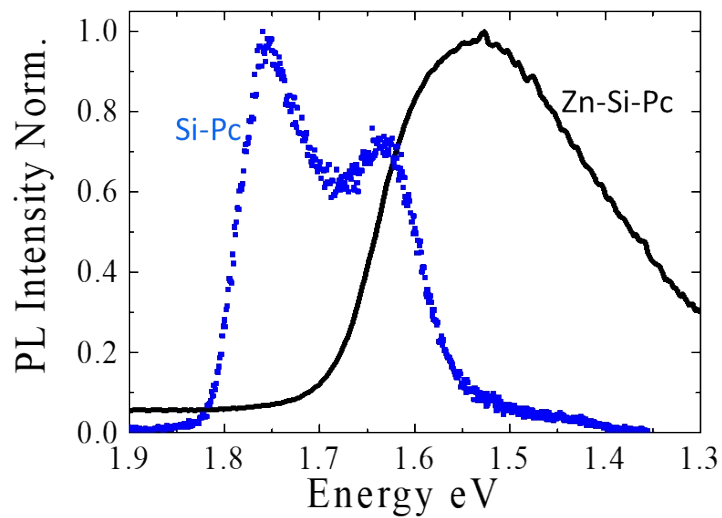


Fig. S3 Photoluminescence spectra of SiPc linker (solvated) and Zn-SiPc SURMOF ($E_x = 3.3$ eV).

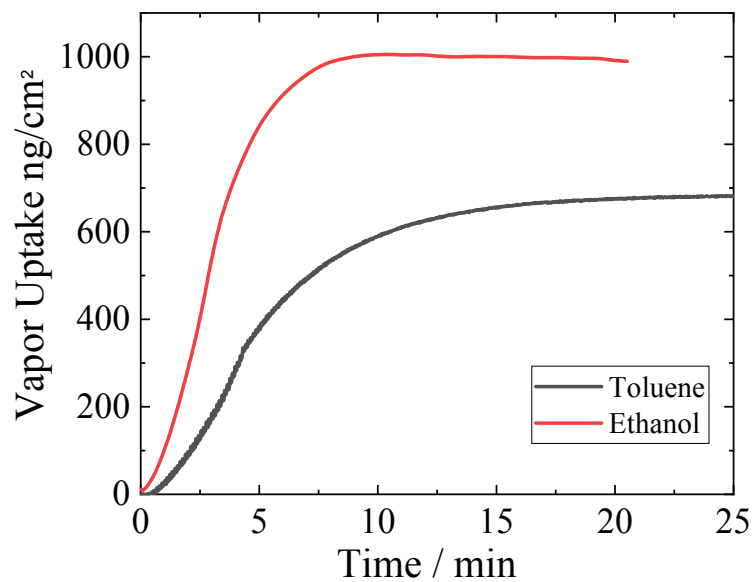


Fig. S4 Ethanol and toluene vapor uptake by Zn-SiPc, measured by a quartz crystal microbalance.

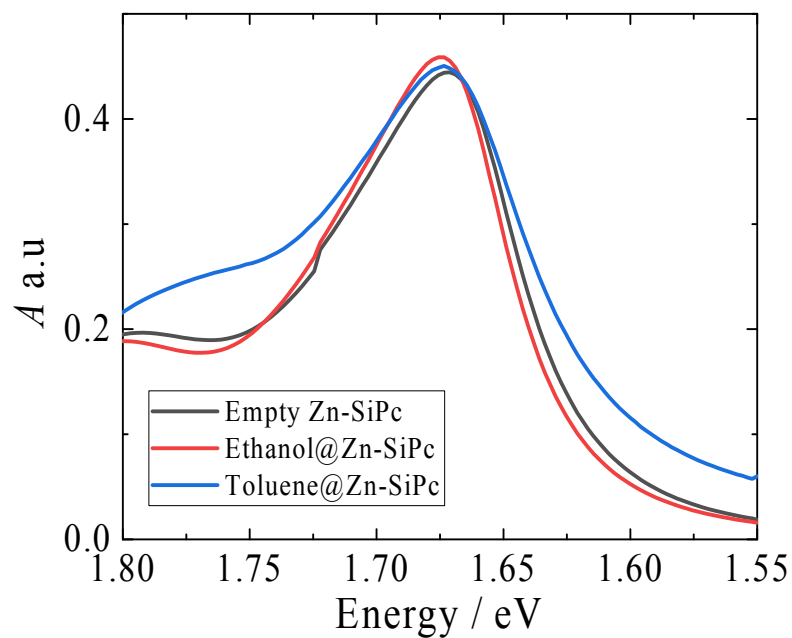


Fig. S5 UV-Vis spectra of the Zn-SiPc SURMOF in empty, ethanol and toluene adsorbed state.

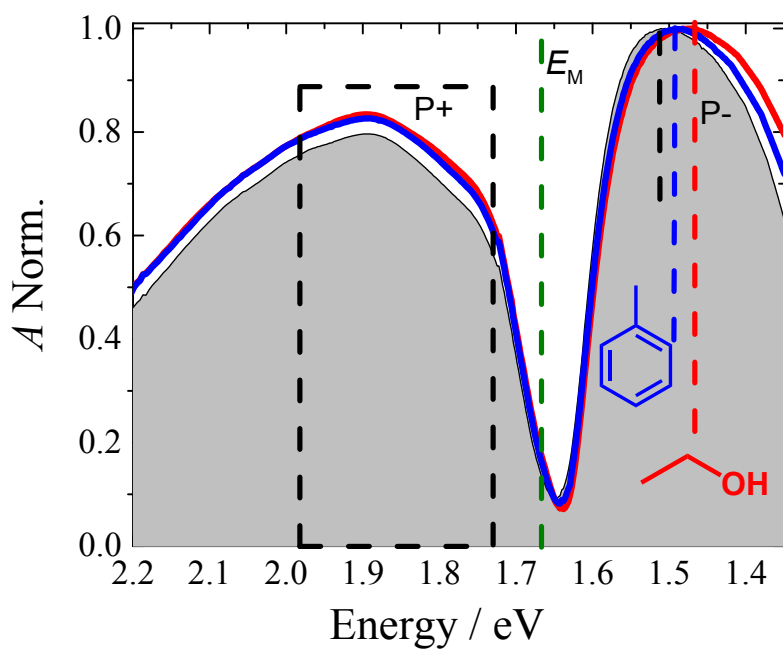


Fig. S6 Hybrid energy states in empty (black), ethanol (red) and toluene (blue) filled SURMOFs. The dotted lines show the respective energy states. The broad P+ state absorption is marked by a dotted box.

Table S1 Some of the different materials in optical cavity and corresponding Rabi splitting energies.

Material details	Rabi splitting
Liquid crystalline conjugated polymers (LCCPs)—poly(9,9-dioctylfluorene- <i>co</i> -benzothiadiazole) (F8BT), poly(9,9-dioctylfluorene) (PFO), and poly(9,9-dihexylfluorene- <i>co</i> -bithiophene) (F6T2) ¹	1.8 eV; 65% of the optical transition energy
tetra-(2,6- <i>t</i> -butyl)phenol-porphyrin zinc (4TBPPZn) ²	110 eV; 4% of the optical transition energy
photochromic spiropyran (SPI) molecules (10,30-dihydro-10,30,30-trimethyl-6-nitrospiro[2H-1-benzopyran-2,20-(2H)-indole]) in a PMMA (polymethyl methacrylate) matrix ³	700 meV; 32% of the optical transition energy
Colloidal CdSeTe/ZnS nanocrystals ⁴	110 meV; 7% of the optical transition energy
poly(vinyl alcohol) (PVA) film containing chlorosomes (4:1 weight ratio) ⁵	~103 meV; 6% of the optical transition energy
Anthracene ⁶	200 cm ⁻¹ ; 3% of the optical transition energy
For more examples, please see ⁷	

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