

Electronic Supporting Information

Influence of interpenetration on the flexibility of MUV-2

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1. General methods and materials

All reagents and solvents employed for the syntheses were of high purity grade and were purchased from Sigma-Aldrich Co., and TCI. ^1H NMR spectra were recorded using a Bruker DPX300 (300 MHz) spectrometer and Me_4Si as an internal standard. Powder X-ray diffraction spectra were recorded using 0.7 mm borosilicate capillaries that were aligned on an Empyrean PANalytical powder diffractometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056 \text{ \AA}$).

Synthesis of MUV-2-i: 20 mg of H_4TTFTB (0.03 mmol), 15 mg of $[\text{Fe}_3\text{O}(\text{CH}_3\text{COO})_6]\text{ClO}_4$ (0.02 mmol) and 1 mL of acetic acid were dissolved in 4 mL of DMF in a 10 mL Pyrex vial. The mixture was heated in an oven for 105°C for 48 h. After cooling down to room temperature, dark red crystals were collected by filtration. The crystals were washed with large amount of DMF in order to remove any unreacted starting material, immersed with EtOH at 65°C for 2h, filtered and dried at 150°C in the oven for 2h, yielding the dried material denoted **MUV-2-i(dry)**. These dark red crystals were soaked in pyridine resulting in **MUV-2-i(pyridine)**, which were used to determine the crystal structure by single-crystal X-ray diffraction.

2. Crystallographic data

Data Collection. X-ray data for compound **MUV-2-i** were collected at a temperature of 100 K using a synchrotron radiation at the single crystal X-ray diffraction beamline I19 in Diamond light Source,^{S1} equipped with an Pilatus 2M detector and an Oxford Cryosystems nitrogen flow gas system. Data were measured using GDA suite of programs.

Crystal structure determinations and refinements. X-ray data were processed and reduced using CrysAlisPro suite of programmes. Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. The crystal structure was solved and refined against all F^2 values using the SHELXL and Olex 2 suite of programmes.^{S2} All atoms were refined anisotropically. Hydrogen atoms were placed in the calculated positions. Phenyl and pyridine moieties were disordered and modelled over two positions. The C-O, C-C and C-S distances and O-C-C angles were restrained using SHELXs SADI commands. The atomic displacement parameters were also restrained using SHELXs SIMU and RIGU commands. The crystal was found to be a 50/50 inversion twin.

The formula unit has a fractional number of atoms due to the presence of 0.36 molecules of disordered pyridine in the asymmetric unit. Electron analysis from the crystal structure reveals that there are 793.8 electrons per void (i.e. 1587.6 electrons in the unit cell and 198.45 electrons per formula). This accounts for ca. 4.75 pyridines per unit cell.

CCDC-1897432 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge *via* www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

Table S1. Crystallographic information for **MUV-2-i**

Identification code	MUV-2-i
Empirical formula	$C_{72.79}H_{45.79}Fe_3N_{4.36}O_{13}S_6$
Formula weight	1549.35
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$C222_1$
$a / \text{\AA}$	34.2069(7)
$b / \text{\AA}$	57.0341(9)
$c / \text{\AA}$	12.1673(2)
$\alpha / ^\circ$	90
$\beta / ^\circ$	90
$\gamma / ^\circ$	90
Volume / \AA^3	23737.9(7)
Z	8
$\rho_{\text{calc}} / \text{g} \cdot \text{cm}^{-3}$	0.867
μ / mm^{-1}	0.461
F(000)	6328.0
Crystal size / mm^3	$0.04 \times 0.02 \times 0.02$
Radiation	($\lambda = 0.6889$)
2θ range for data collection / $^\circ$	3.512 to 49.038
Index ranges	$-41 \leq h \leq 41, -68 \leq k \leq 68, -14 \leq l \leq 14$
Reflections collected	141606
Independent reflections	21742 [$R_{\text{int}} = 0.1330, R_{\text{sigma}} = 0.0744$]
Data / restraints / parameters	21742 / 2130 / 1114
Goodness-of-fit on F^2	1.370
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.1143, wR_2 = 0.3166$
Final R indexes [all data]	$R_1 = 0.1221, wR_2 = 0.3262$
Largest diff. peak/hole / $e \text{\AA}^{-3}$	1.63/-1.18
Flack parameter	0.49(4)

3. ^1H -NMR of H_4TTFTB

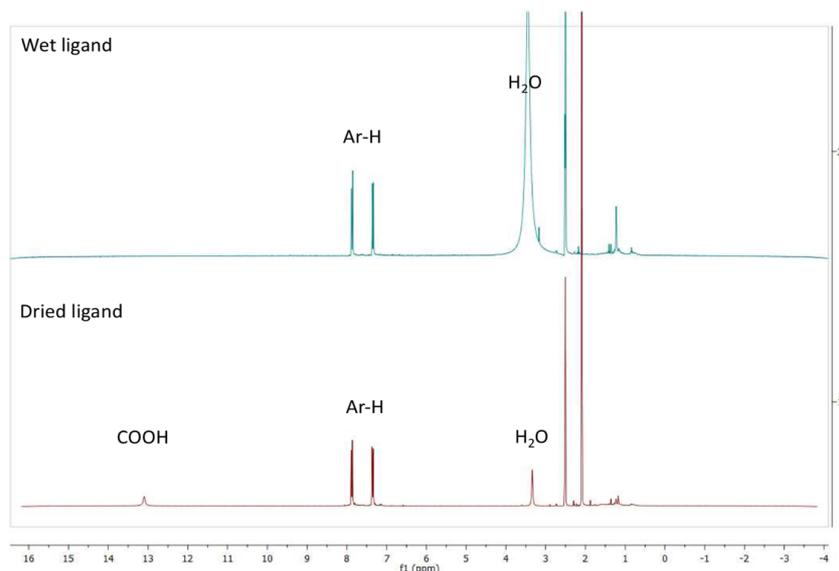


Figure S1. ^1H -NMR spectra of H_4TTFTB ligand in DMSO-d_6 before (used in the synthesis of interpenetrated **MUV-2-i**) and after drying under vacuum.

4. Powder X-ray diffraction

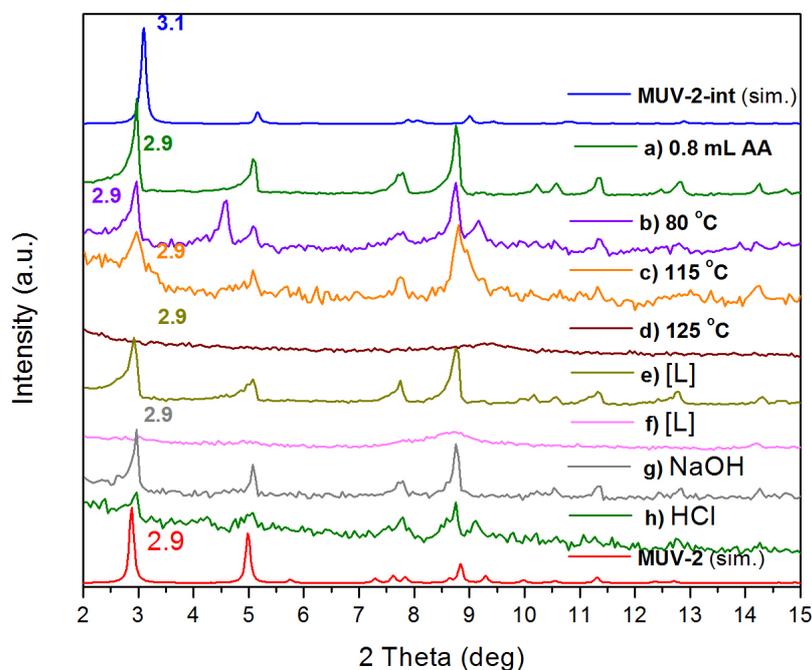


Figure S2. PXRD patterns for simulated **MUV-2** and **MUV-2-i** (soaked in pyridine) and for different products soaked with pyridine at room temperature obtained after modifying different synthetic parameters: a) adding 1.6 mL of acetic acid (1 eq.), b) reaction temperature = 85°C for 48 h, c) reaction temperature = 115°C for 48 h, d) reaction temperature = 125°C for 48 h,

e) 20 mg of L in 2 mL of DMF, f) 10 mg of L in 4 mL of DMF, g) adding 2 drops of NaOH, and h) adding 2 drops of HCl.

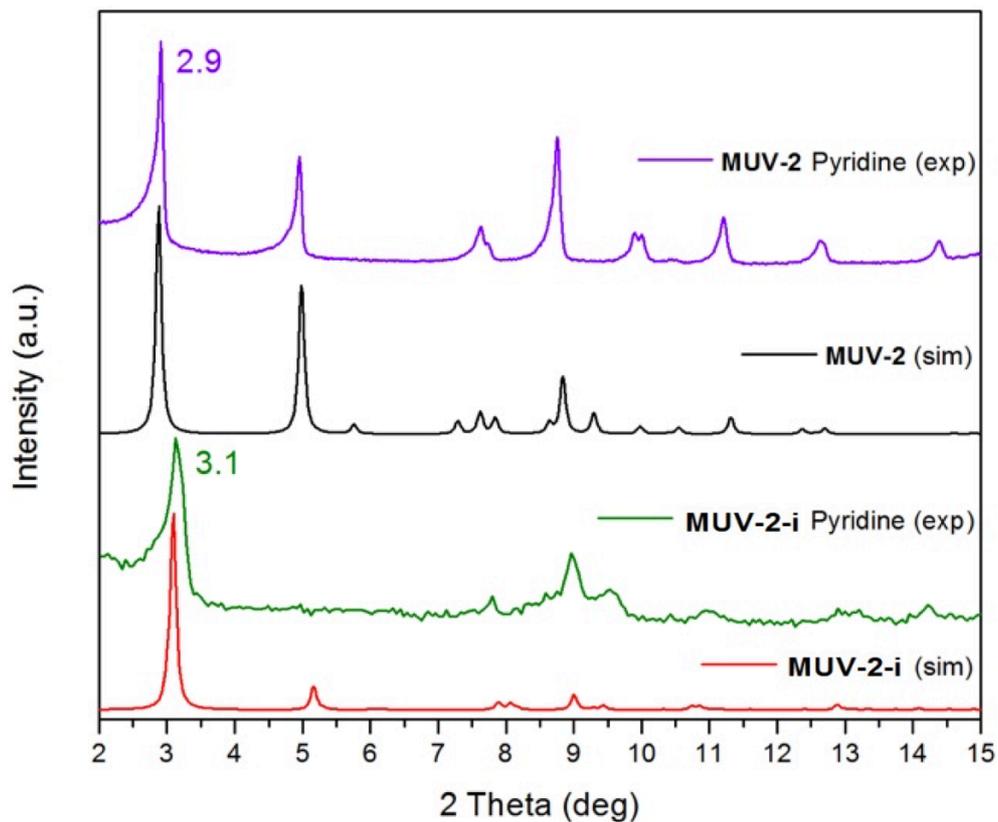


Figure S3. PXRD patterns for experimental and simulated MUV-2 and MUV-2-i after soaking with pyridine at room temperature.

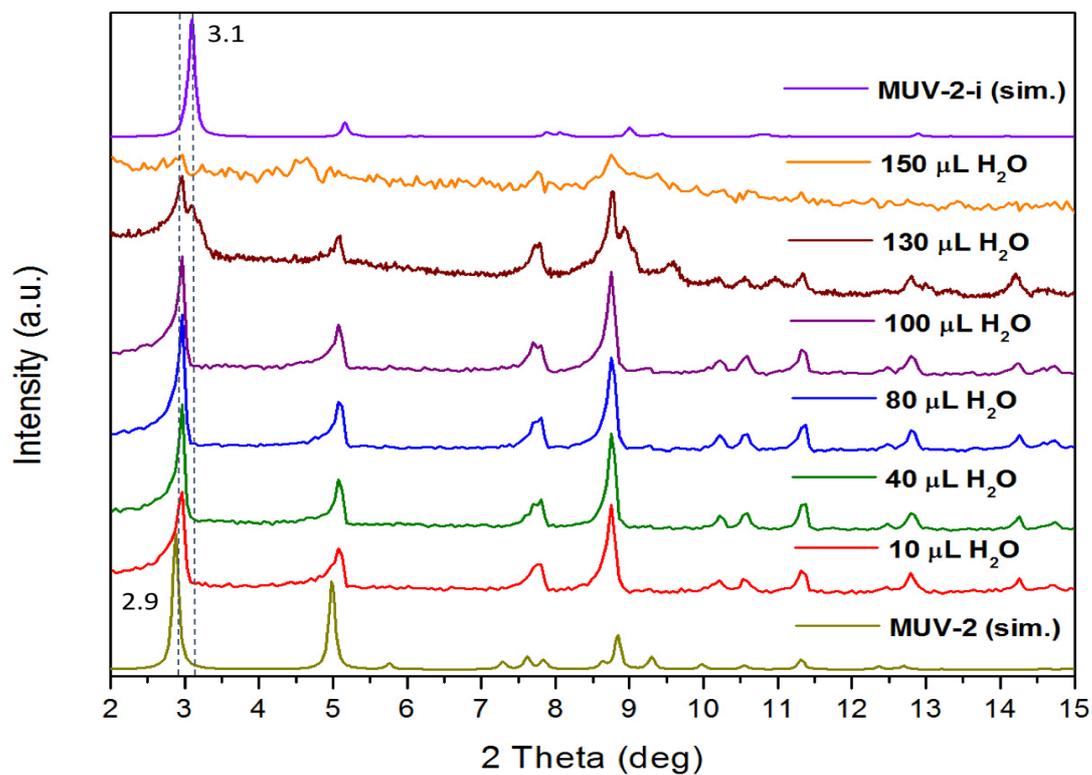


Figure S4. PXRD patterns for simulated **MUV-2(pyridine)** and **MUV-2-i(pyridine)** and for different products soaked with pyridine at room temperature obtained after adding different amount of water to the synthesis reaction.

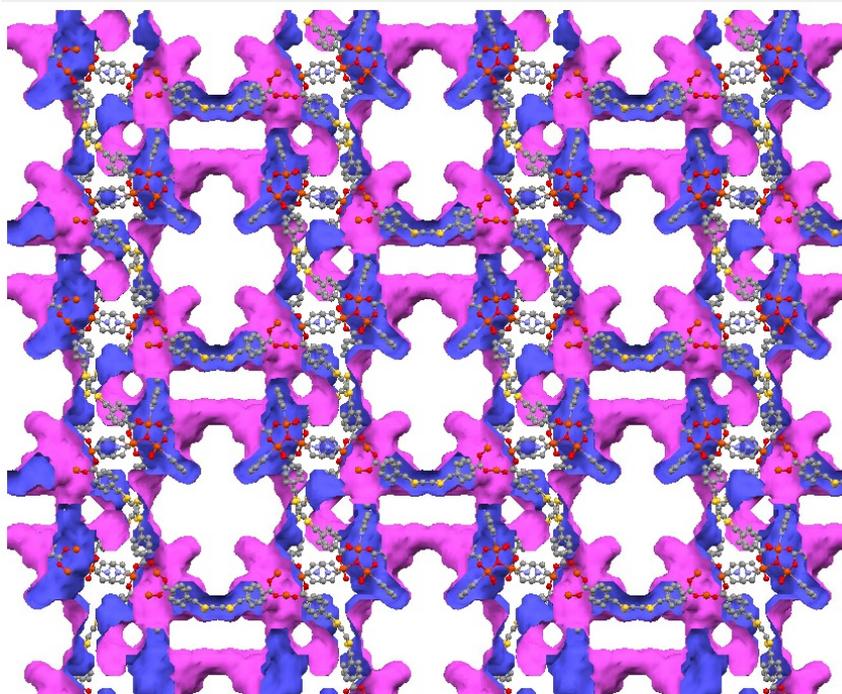


Figure S5. Representation of the crystal structure of **MUV-2-i** with the van der Waals surface shown in purple.

5. N₂ adsorption isotherms

Brunauer-Emmett-Teller (BET) surface area analysis were performed from nitrogen adsorption isotherms (77 K) recorded on a Micromeritics 3Flex apparatus. Samples were degassed at 150 °C and 10⁻⁶ Torr during 3 hours prior to analysis.

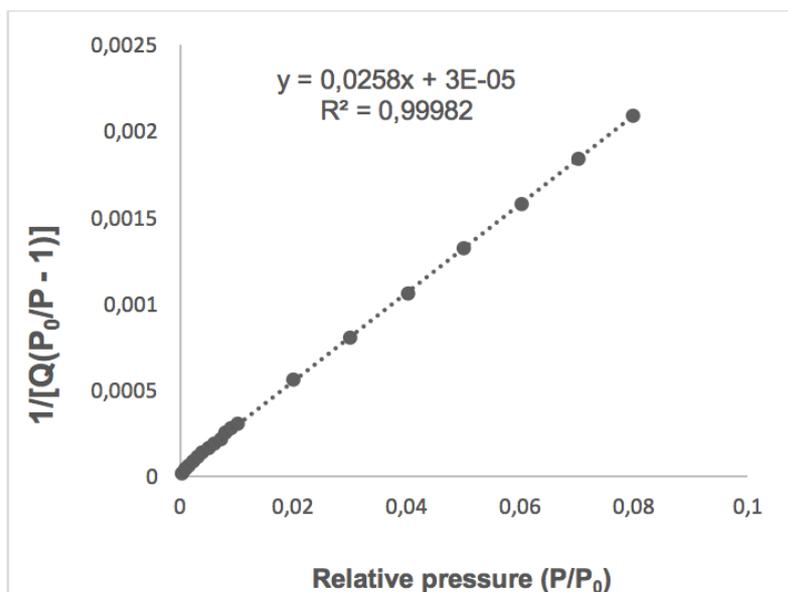


Figure S6. BET plot for the 0-0.09 relative pressure range for **MUV-2-i**.

6. References

- S1. Nowell H, Barnett SA, Christensen KE, Teat SJ, Allan DR. *J Synchrotron Radiat.*, **2012**, *19*, 435-441.
- S2. a) G. M. Sheldrick. *Acta Crystallogr.*, **2015**, *C71*, 3-8; b) O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.*, **2009**, *42*, 339–341