

Fast and reversible solvent-vapor-induced 1D to 2D transformation in emissive Ag(I)-organic networks

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§1. Reagents

AgOTf (98%, Alfa Aesar) CH₃CN (HPLC grade, Cryochrom) and CH₂Cl₂ (>99 %, Soyuzhimprom) were used as purchased. Diphenyl(2-pyrimidyl)phosphine (L) was synthesized according the known procedure.¹ Prior to syntheses, commercial AgOTf was additionally dried under vacuum.

§2. Methods and instrumentation

Powder X-ray diffraction analyses (PXRD) were made on a Shimadzu XRD-7000 diffractometer (Cu-K α radiation, Ni – filter, 3–35° 2 θ range, 0.03° 2 θ step, 5s per point). The baselines of the measured PXRD patterns were corrected using OriginPro suite.

Synchronic thermogravimetric analyses (TGA&DTG&c-DSC) were carried out in a closed Al₂O₃ pan under argon flow at 10 °C/min⁻¹ heating rate using a NETZSCH STA 449 F1 Jupiter STA instrument.

The CHN microanalyses were performed on a MICRO cube analyzer.

mid-IR spectra were recorded on a Bruker Vertex 80 FT-spectrometer in KBr pellets at ambient temperature.

Steady-state excitation and emission spectra were recorded on a Fluorolog 3 spectrometer (Horiba Jobin Yvon) equipped with a cooled PC177CE-010 photon detection module and an R2658 photomultiplier. The emission decays were recorded on the same instrument. The absolute PLQYs were determined at 298 K using a Fluorolog 3 Quanta-phi integrating sphere. Temperature-dependent excitation and emission spectra as well as emission decays were recorded using an Optistat DN optical cryostat (Oxford Instruments) integrated with above spectrometer.

§3. Synthetic procedures

[Ag₃L₂(CH₃CN)₂(OTf)₃] (1)

AgOTf (59 mg, 0.230 mmol) and diphenyl(2-pyrimidyl)phosphine (41 mg, 0.155 mmol) were dissolved in CH₃CN (3 mL) upon stirring for 3 min. The obtained solution was then evaporated. The colorless oil was then triturated with a diethyl ether-acetonitrile mixed solvent to give white crystalline product. Yield: 96 mg (91%). White powder. FT-IR (KBr, cm⁻¹): 432 (w), 492 (m), 505 (m), 517 (s), 575 (m), 635 (vs), 691 (m), 741 (m), 750 (m), 773 (w), 820 (w), 856 (w), 1024 (vs), 1094 (m), 1154 (s), 1231 (vs), 1273 (s), 1288 (s), 1395 (s), 1439 (m), 1481 (w), 1553 (m), 1570 (s), 2259 (w), 2278 (vw), 2307 (vw), 2934 (vw), 3080 (w). Anal. Calcd: C₃₉H₃₂Ag₃F₉N₆O₉P₂S₃ (1381.44); C, 33.9; H, 2.3; N, 6.1; S, 7.0 Found: C, 34.1; H, 2.1; N, 6.0; S, 7.2.

[Ag₃L₂(OTf)₃] (2)

AgOTf (35 mg, 0.136 mmol) and diphenyl(2-pyrimidyl)phosphine (24 mg, 0.09 mmol) were added to CH₂Cl₂ (5 mL) and stirred for 1 h. A precipitated white solid was washed with Et₂O, filtered and dried under vacuum. Yield: 48.7 mg (83%). White powder. FT-IR (KBr, cm⁻¹): 492 (s), 507 (s), 517 (s), 575 (m), 635 (vs), 691 (s), 743 (m), 824 (w), 997 (m), 1022 (vs), 1092 (m), 1155 (s), 1177 (s), 1231 (vs), 1261 (vs), 1271 (vs), 1287

(vs), 1396 (s), 1435 (m), 1481 (w), 1560 (m), 1572 (s), 3026 (w), 3051 (w), 3082 (m), 3138 (w), 3148 (w).
 Anal. Calcd: C₃₅H₂₆Ag₃F₉N₄O₉P₂S₃ (1299.33); C, 32.4; H, 2.0; N, 4.3; S, 7.4 Found: C, 32.5; H, 2.1; N, 4.2; S, 7.5.

§4. Single crystal X-ray crystallography

Single crystals of 1D MOF [Ag₃L₂(CH₃CN)₂(OTf)₃] (**1**) were grown by slow evaporation of a solution in a mixed CH₂Cl₂/CH₃CN solvent. The crystals of 2D MOF [Ag₃L₂(OTf)₃] (**2**) were obtained by a diffusion of Et₂O vapor into a solution in a mixed CH₂Cl₂/CH₃CN solvent. The data were collected on a Bruker Kappa Apex II CCD diffractometer using φ, ω -scans of narrow (0.5°) frames with Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$) and a graphite monochromator. The structures were solved by dual space algorithm (SHELXT)² and refined by the full-matrix least squares technique (SHELXL)³ in the anisotropic approximation (except hydrogen atoms). Positions of hydrogen atoms of organic ligands were calculated geometrically and refined in the riding model. The bridging triflate anion of **2** is disordered over the two positions.

Table S1. X-Ray crystallographic data for **1** and **2**.

Compound	[Ag ₃ L ₂ (CH ₃ CN) ₂ (OTf) ₃] (1)	[Ag ₃ L ₂ (OTf) ₃] (2)
CCDC number	2208216	2208215
Chemical formula	C ₃₉ H ₃₂ Ag ₃ F ₉ N ₆ O ₉ P ₂ S ₃	C ₃₅ H ₂₆ Ag ₃ F ₉ N ₄ O ₉ P ₂ S ₃
<i>M_r</i>	1381.44	1299.33
Crystal system, space group	Triclinic, <i>P</i> ⁻ 1	Monoclinic, <i>C2/c</i>
Temperature (K)	296	296
<i>a</i> , <i>b</i> , <i>c</i> (Å)	9.121(1), 14.6228(19), 19.074(3)	9.4645(4), 23.9337(11), 19.7003(9)
α , β , γ (°)	80.516(6), 78.591(6), 85.057(6)	96.227(2)
<i>V</i> (Å ³)	2455.8(5)	4436.2(3)
<i>Z</i>	2	4
μ (mm ⁻¹)	1.47	1.62
Crystal size (mm)	0.80 × 0.04 × 0.02	0.80 × 0.15 × 0.08
<i>T_{min}</i> , <i>T_{max}</i>	0.841, 0.928	0.714, 0.928
No. of measured, independent and observed [<i>I</i> > 2 σ (<i>I</i>)] reflections	43523, 9706, 5395	44751, 5124, 4433
<i>R_{int}</i>	0.102	0.040
(<i>sin</i> θ / λ) _{max} (Å ⁻¹)	0.620	0.651
<i>R</i> [<i>F</i> ² > 2 σ (<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.057, 0.113, 1.01	0.029, 0.077, 1.03
No. of reflections	9706	5124
No. of parameters	642	313
No. of restraints	12	18
$\Delta\rho_{\text{max}}$, $\Delta\rho_{\text{min}}$ (e Å ⁻³)	1.42, -0.70	1.08, -1.19

§5. Powder X-ray diffraction patterns

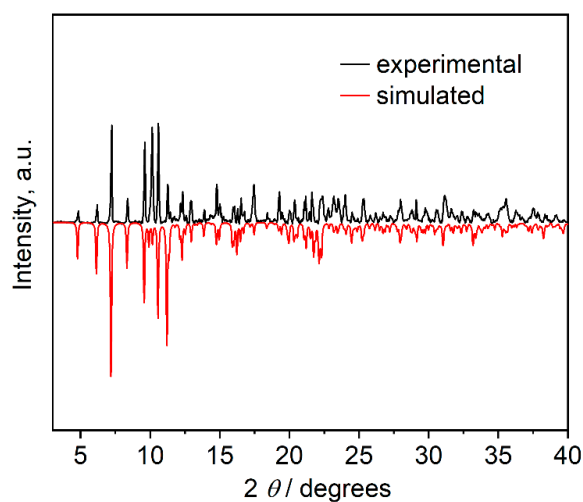


Figure S1. Experimental and simulated PXRD patterns of **1**.

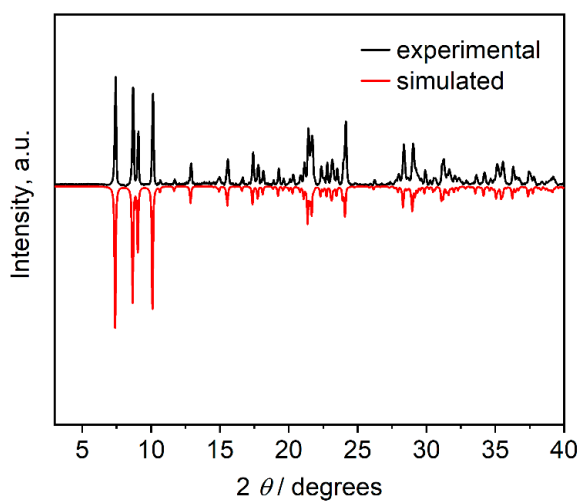


Figure S2. Experimental and simulated PXRD patterns of **2**.

§6. Thermal stability

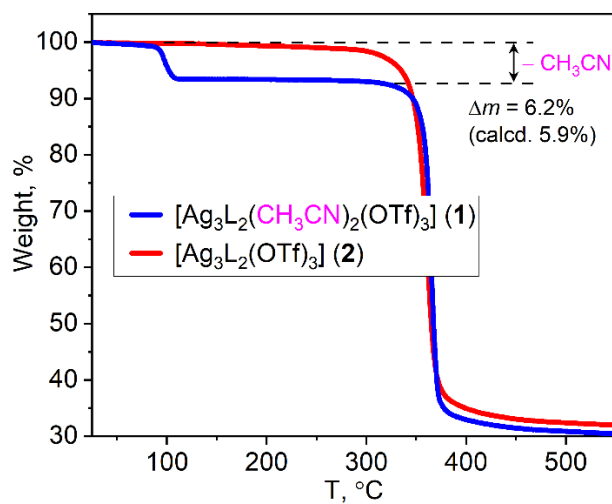


Figure S3. TGA traces for **1** and **2**.

§7. IR spectra

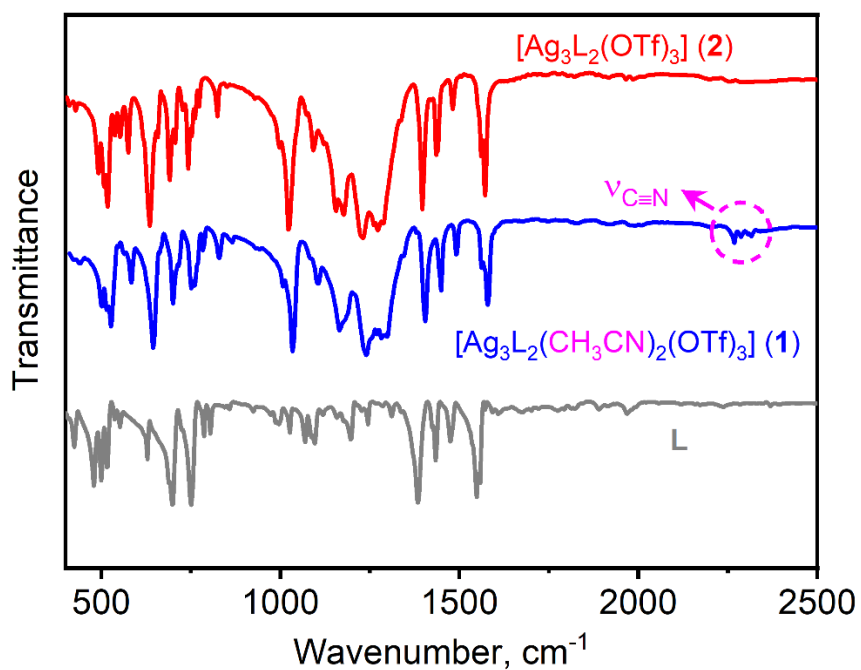


Figure S4. IR spectra of **1** and **2** compared with that of free diphenyl(2-pyrimidyl)phosphine ligand (**L**).

§8. Photophysical details

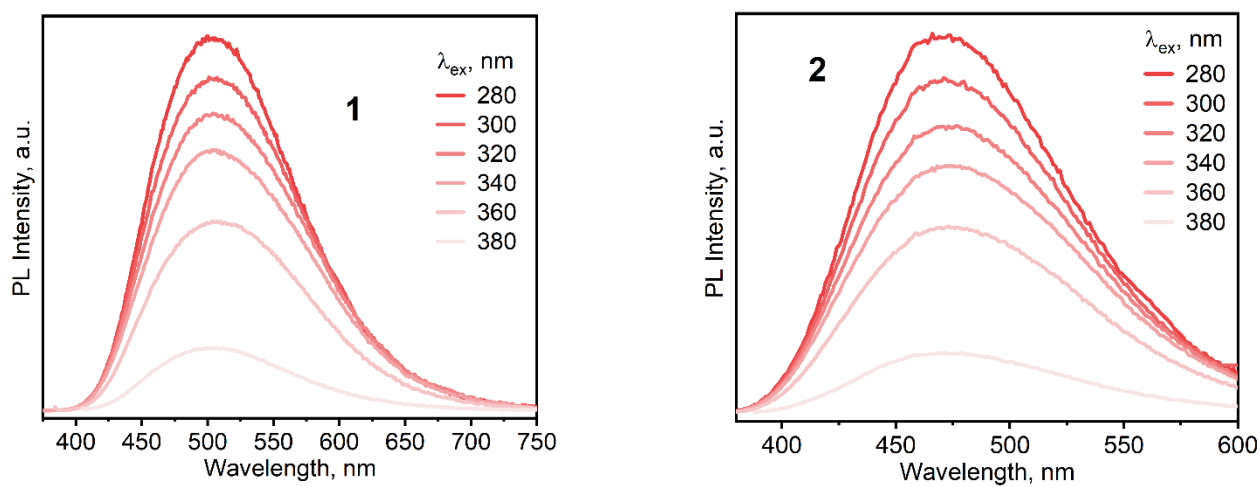


Figure S5. Excitation-dependent PL spectra of **1** and **2** at 298 K.

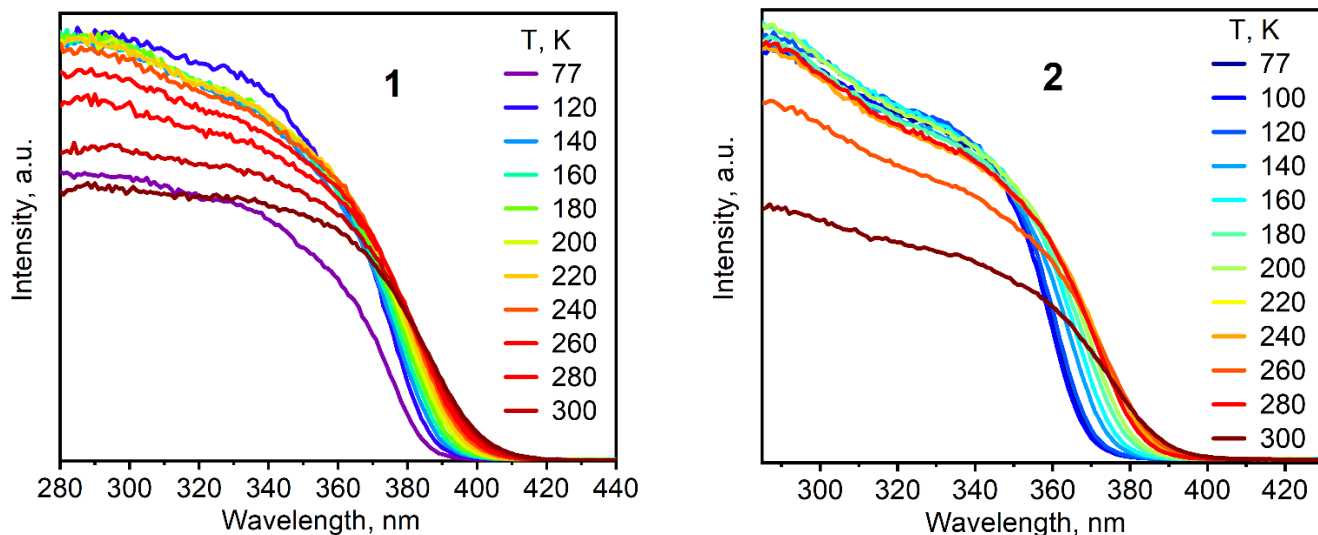


Figure S6. Temperature-dependent excitation spectra of **1** ($\lambda_{em} = 490$ nm) and **2** ($\lambda_{em} = 520$ nm).

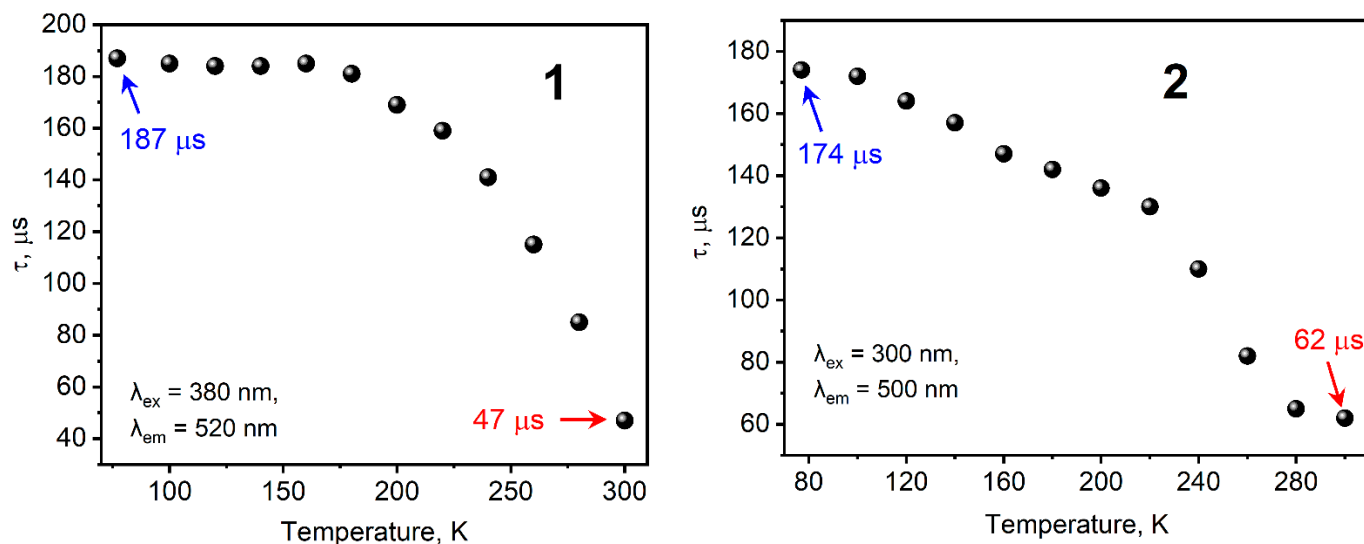


Figure S7. Emission lifetimes of MOFs **1** and **2** against temperature.

§9. Band structure calculations

The density of states of selected compounds was calculated using the Cambridge Serial Total Energy Package (CASTEP) in the Material's Studio 7.0 software⁴ using crystal structures obtained from single crystal x-ray diffraction (SCXRD). For the 1D-[Ag₃L₂(CH₃CN)₂(OTf)₃]_n structure, a k-point set of 7 x 4 x 3 was used. In the case of the 2D-[Ag₃L₂(OTf)₃]_n a k-point set of 8 x 3 x 4 was used. Generalized gradient approximations (GGA) with Perdew-Burke-Ernzerhof (PBE) exchange correlation functional (XC) were used for both calculations. The plane-wave kinetic energy cutoff was set as 10 eV, ultrasoft pseudopotentials were used for all chemical elements and the total energy tolerance was set to be 2×10^{-6} eV/atom.

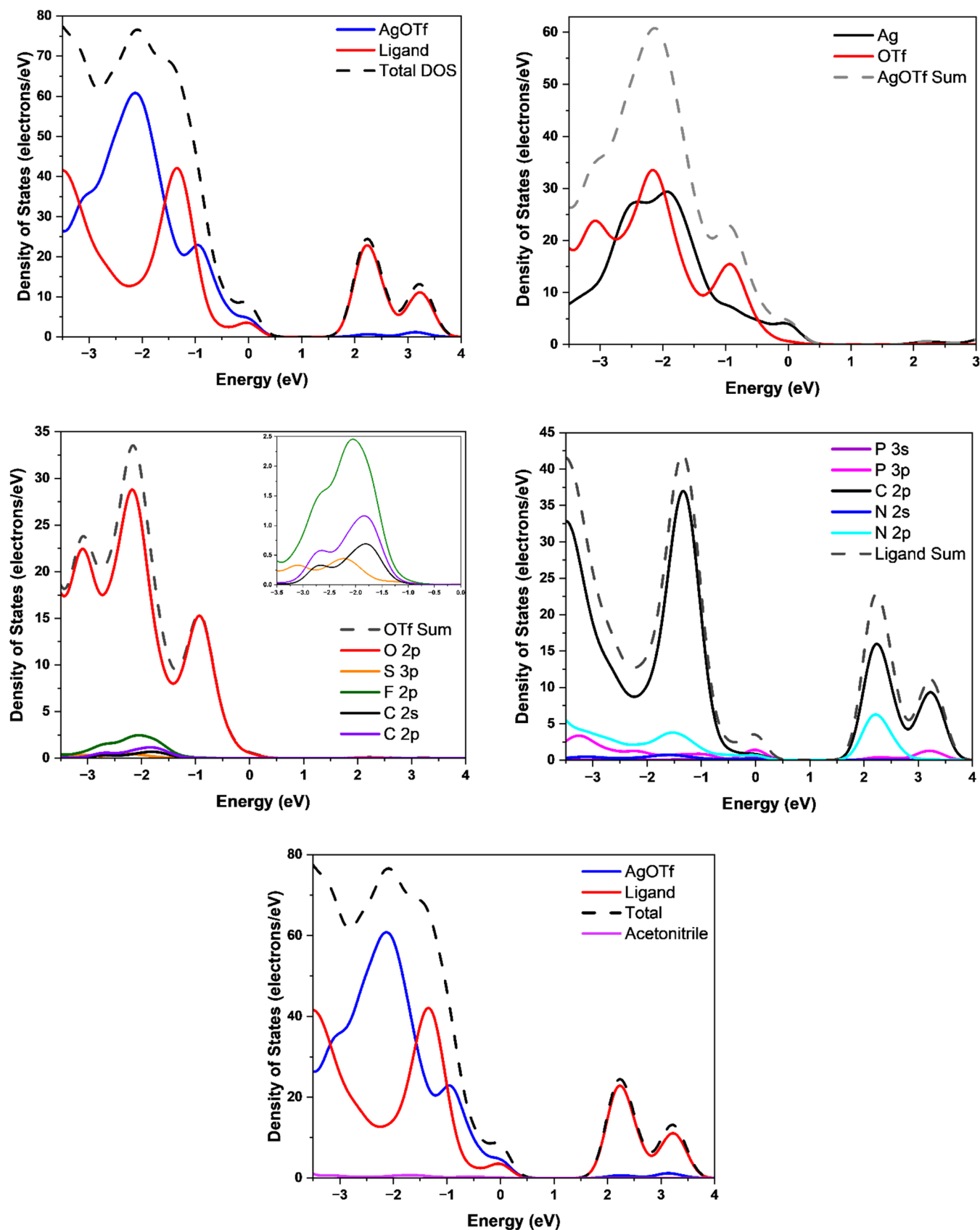


Figure S8. Projected density of states (PDOS) from selected components of 1.

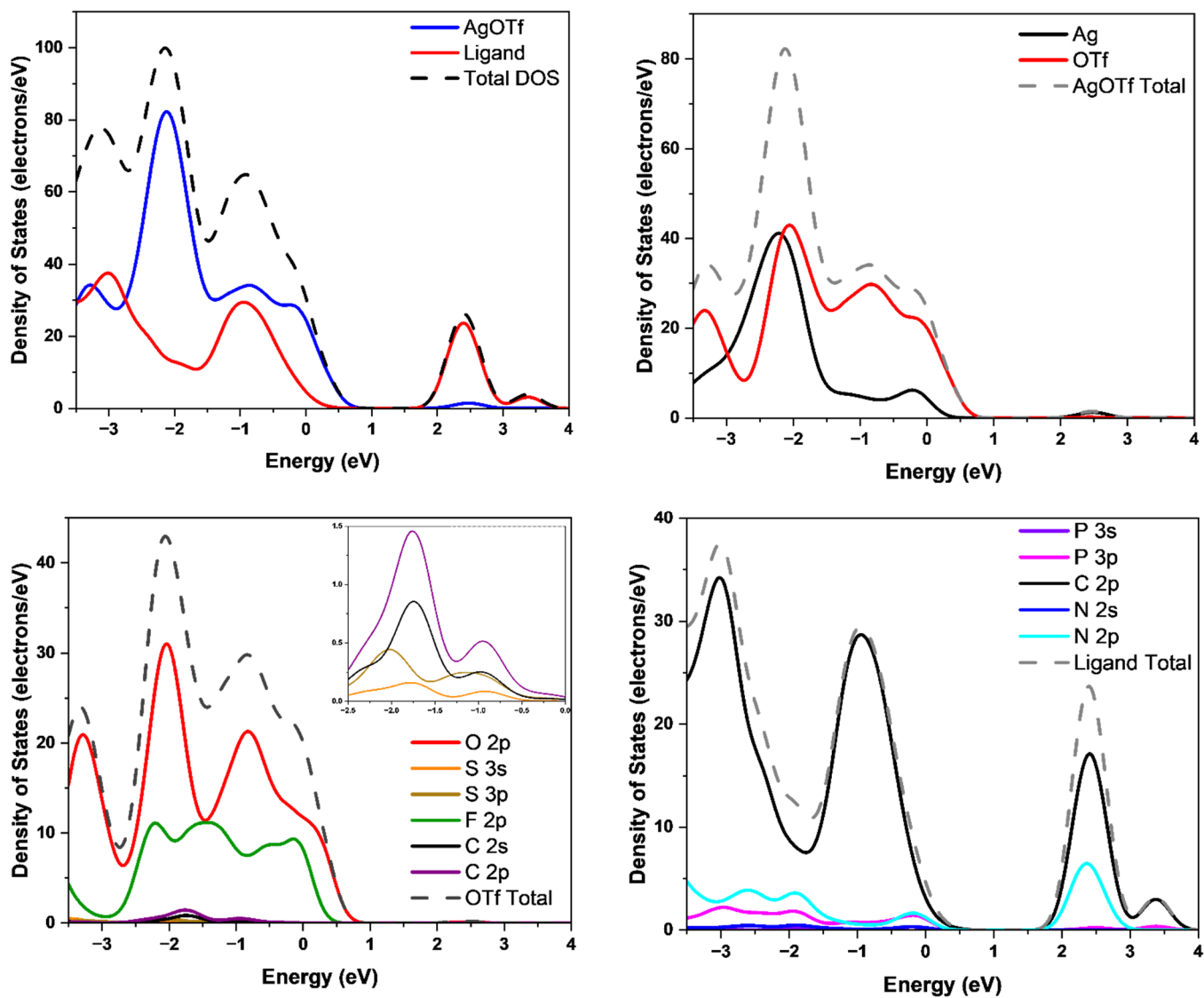


Figure S9. Projected density of states (PDOS) from selected components of **2**.

§10. Powder X-ray diffraction patterns of parent and recovered samples of **1** and **2**

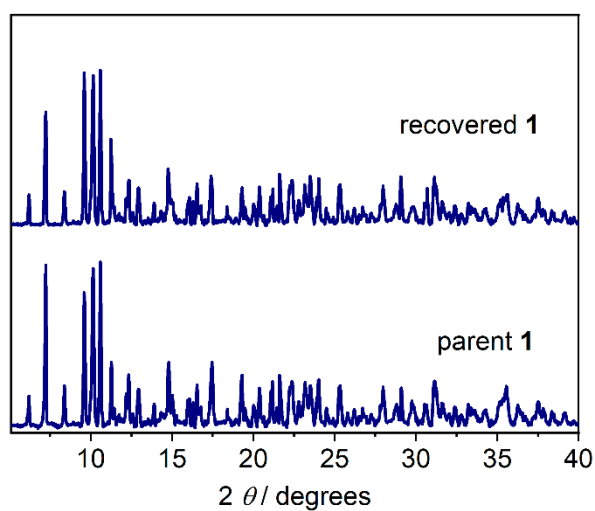


Figure S10. PXRD patterns of parent and recovered samples of **1**.

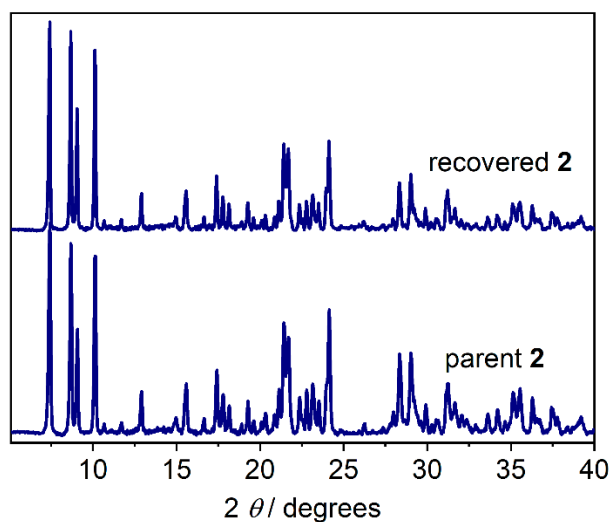


Figure S11. PXRD patterns of parent and recovered samples of **2**.

§11. Testing other solvents for vapor-induced **1** → **2** transformation

To reveal whether the **1** → **2** transformation can be induced by other solvent vapors, we have performed a series of experiments with CHCl_3 , CCl_4 , acetone, MeOH, and benzene. The experiments were carried out in a closed cuvette, on the bottom of which a solvent was poured (1–2 mL). After placing a microtube containing polymer **1** (about 10 mg) into the vial, the **1** → **2** transformation has been monitored visually using a UV lamp (365 nm). It was found that the emission color changes (from cyan to sky blue) more slowly than when using CH_2Cl_2 vapors. After 1 h exposing, the powder samples were examined by PXRD technique. As seen from **Figure S12**, CHCl_3 , CCl_4 and MeOH vapors induce a complete transformation of **1** into **2**. Whilst acetone and benzene vapors do not completely convert 1D polymer **1** to **2**: the resulting samples of **2** are contaminated by **1** (see additional peaks in red and dark-red PXRD curves in **Fig. S12**).

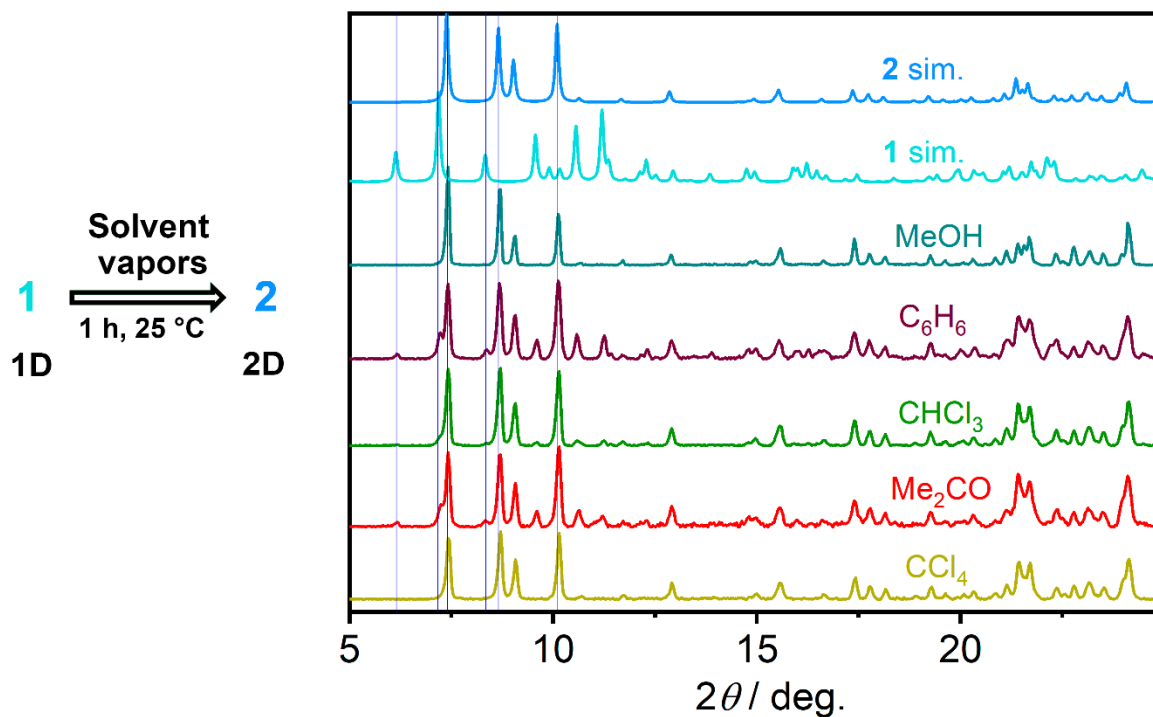


Figure S12. *Left:* transformation of **1** into **2** induced by different solvent vapors. *Right:* PXR D patterns of samples of **1** exposed under different solvent vapors (1 h at 25 °C) compared with the simulated PXR D patterns of **1** and **2**.

§12. References

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4. S. J. Clark, M. D. Segall, C. J. Pickard, P. J. Hasnip, M. I. J. Probert, K. Refson, M. C. Payne, *Z. für Krist. - Cryst. Mater.*, 2005, **220**, 567-570.