Electronic Supplementary Material (ESI) for Dalton Transactions.

Covalent Post-Synthetic Modification of Switchable Iron-based Coordination Polymers by Volatile Organic Compounds: A versatile strategy for environmental selective sensor development

Supporting Information

1) Experimental Section

Materials. Chemicals and reagents were purchased from commercial suppliers and used as received.

Physical measurements.

- Optical reflectivity measurements were performed using a MOTIC SMZ-171 optical stereoscope coupled with a MOTICAM 3. Images were collected in BMP format without any filter using the Motic Images Plus 3.0 software, with the mean value from each region of interest (ROI) analyzed under the ImageJ program. The temperature was controlled using a Linkam T95 system controller and a LNP 95 Liquid Nitrogen Cooling System.
- FT-IR spectra were recorded as neat samples in the range 400-4000 cm^{-1} on a Bruker Tensor 27 (ATR device) Spectrometer.
- Elemental analyses (C, H and N) were performed on a LECO CHNS-932 Analyzer at the "Servicio Interdepartamental de Investigación (SIdI)" at Autónoma University of Madrid.
- Magnetic susceptibility measurements were carried out in a Quantum Design MPMS-5S SQUID magnetometer under a 2000 Oe field. Each sample was secured inside a plastic capsule. Pascal constants were used to correct for the diamagnetic contribution.
- ^{1}H-NMR spectra were recorded on a Bruker Advance 300 (1H: 400 MHz) spectrometer at 298 K using partially deuterated solvents as internal standards. Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, t = triplet, m = multiplet.
- Powder X ray diffraction data was collected in a Rigaku Smartlab SE diffractometer with a Bragg-Brentano configuration, using Cu-Kα radiation (λ = 0.1541 nm). The sample was measured between 5 and 50° with a speed of 1.8° min^{-1} under an X ray fluorescence reduction mode, at room temperature.
- Ligand and complex images represented in Figure 1 and Figure 2 were simulated using the Avogadro Software.[1]

2) Synthesis of complexes 1-4

Compound **1** was synthetized in two steps at room temperature. First, 0.20 mmol of Fe(OTs)$_2$ (OTs = tosylate) were dissolved in 3 mL of distilled water. After that, the Fe(OTs)$_2$ aqueous solution was added on a drop by drop basis to a solution of 0.59 mmol of aminotriazole previously dissolved in 3 mL of ethanol. The Fe(OTs)$_2$ / aminotriazole H_2O:EtOH solution was stirred for 5 minutes, filtered and left in the freezer overnight. **1** was obtained as a pink powder in 87% yield.

Compounds **2-4** were synthetized by following the ensuing general procedure. A screw vial for chromatography (diameter 12 mm, height 32 mm) displaying 10 mg of **1** was placed in a clear glass vial (diameter 27 mm, height 55 mm) provided with 0.1 ml of the corresponding VOC (formaldehyde, benzaldehyde and acetone, **2-4**, respectively). The glass vial was sealed and kept at room temperature overnight to allow the gas-solid reaction between the corresponding volatile organic compound and **1**.Elemental analysis calculated (%) for **1·0.35H$_2$O**: C 36.93%, H 4.03%, N 25.84%; found C 36.34%, H 4.05%, N 25.79%. FTIR (cm^{-1}): 3441 (w), 3293 (m), 3210 (w), 3210 (m), 1631 (m), 1546 (w), 1496 (w), 1449 (w), 1396 (w), 1170 (s), 1122 (s), 1098 (m), 1033 (s), 1008 (s), 881 (w), 813 (m), 681 (s), 623 (s), 563 (s).

Elemental analysis calculated (%) for **2·0.1H$_2$O·1.95CH$_2$O**: C 40.12%, H 4.06%, N 22.5%; found C 40.4%, H 4.34%, N 22.33%. FTIR (cm^{-1}): 3264 (b), 3099 (m), 2954 (w), 1655 (m), 1600 (w), 1530 (m), 1497 (w), 1379 (m), 1166 (s), 1122 (s), 1066 (m), 1031 (s), 1007 (s), 919 (m), 680 (s), 632 (m), 563 (s).

Elemental analysis calculated (%) for **3·2H$_2$O**: C 51.79%, H 4.45% , N 17.68% ; found C 51.51%, H 4.13% and N 18.01%. FTIR (cm^{-1}): 3083 (m), 1696 (m), 1603 (m), 1575 (w), 1532 (m), 1494 (m), 1397 (m), 1335 (w), 1313 (w), 1295 (w), 1167 (s), 1120 (s), 1070 (m), 1032 (s), 1009 (s), 992 (m), 881 (w), 813 (m), 750 (m), 711 (w), 680 (s), 625 (s), 590 (m), 563 (s), 512 (w), 495 (w).

Elemental analysis calculated (%) for **4·0.55H$_2$O**: C 44.62%, H 5.05%, N 21.53%; found C 44.42%, H 5.07%, N 21.78%. FTIR (cm^{-1}): 3085 (m), 2922 (w), 1706 (w), 1633 (w), 1527 (m), 1496 (w), 1434 (m), 1373 (m), 3147 (w), 1218 (m), 1164 (s), 1119 (s), 1084 (w), 1063 (m), 1032 (s), 1008 (s), 923 (w), 900 (w), 872 (w), 814 (s), 765 (w), 710 (w), 678 (s), 628 (s), 563 (s), 519 (w), 492 (w).

3) Infrared spectra

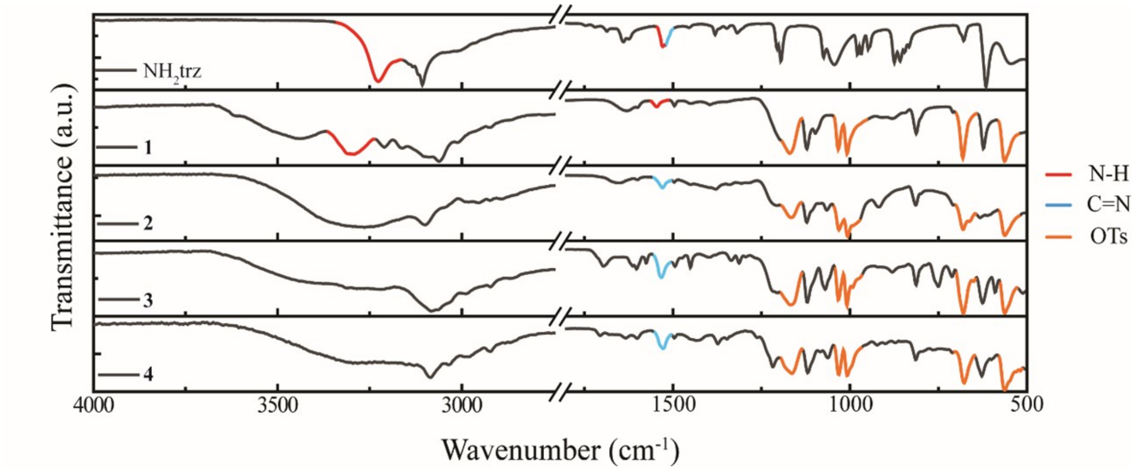

Figure S1. IR spectra of the pure organic ligand NH$_2$trz and coordination polymers **1**-**4**.

4) ^{1}H-NMR

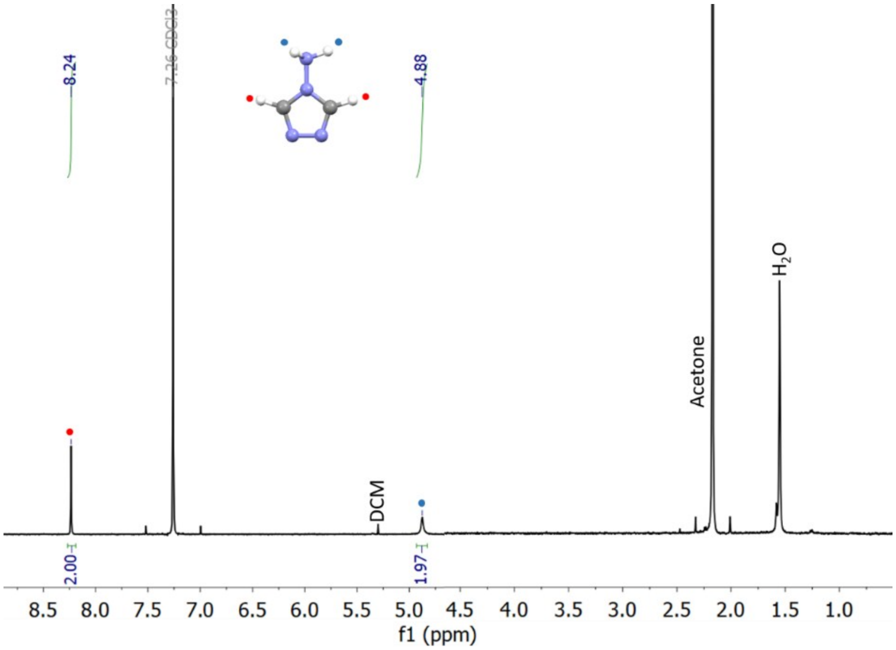

Figure S2. ^{1}H-NMR of **1** after digestion.

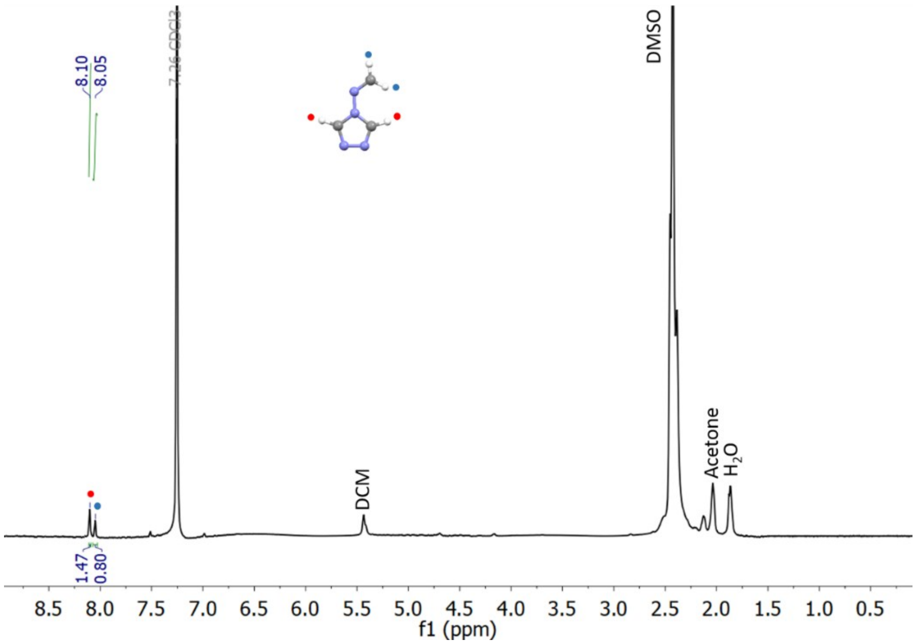

Figure S3. ^{1}H-NMR of **2** after digestion (CDCl$_3$+1 drop of DMSO-d$_6$).

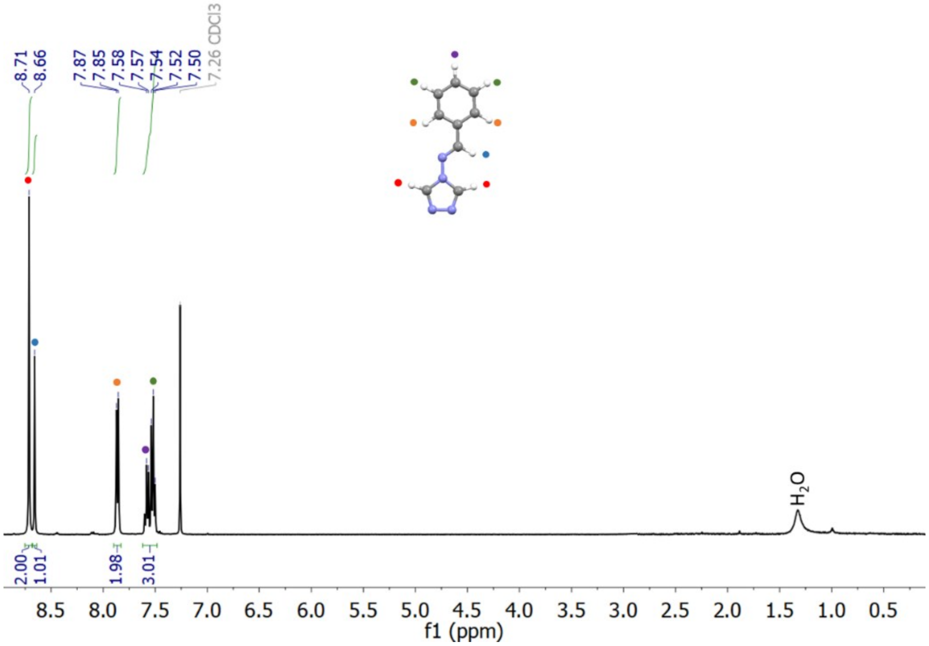

Figure S4. ^{1}H-NMR of **3** after digestion.

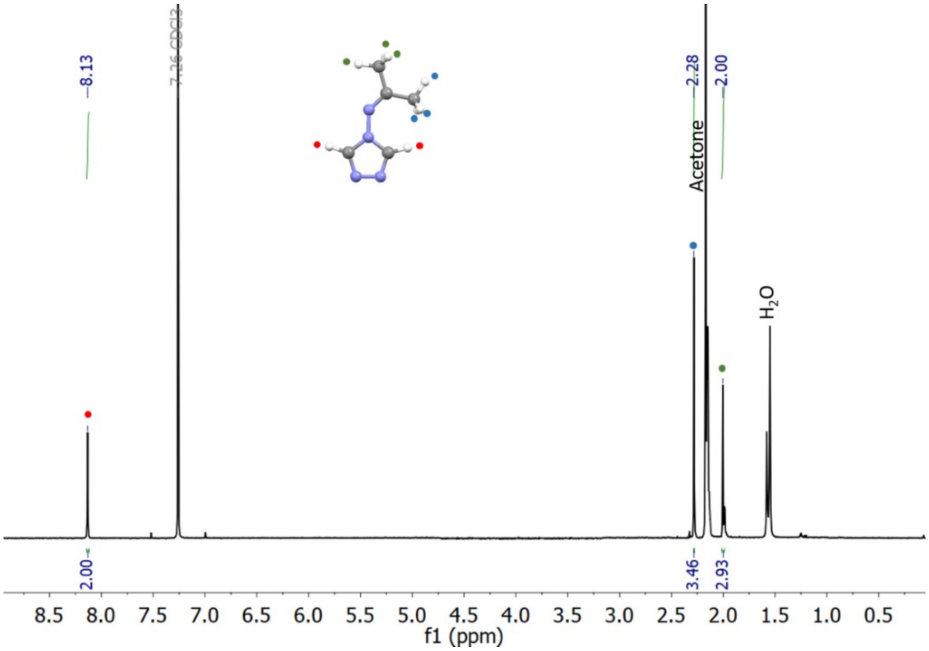

Figure S5. ^{1}H-NMR of **4** after digestion.

5) Powder X-ray diffraction

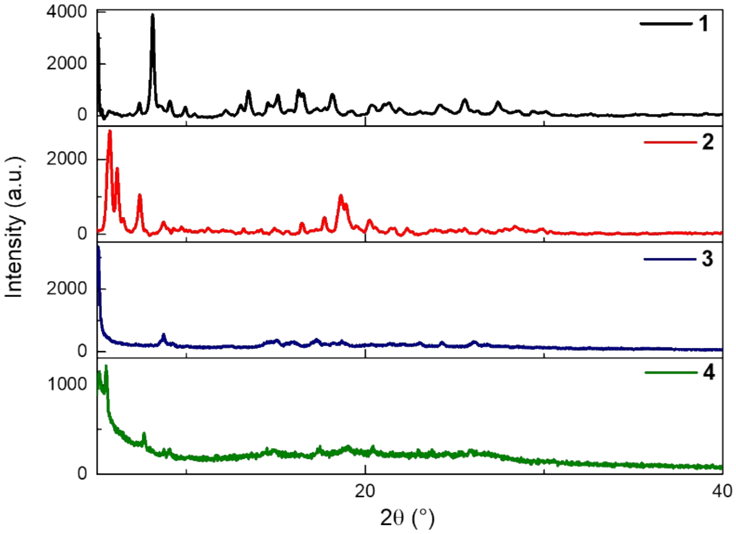

Figure S6. Powder X Ray diffractogram for compounds **1-4**.

6) Optical reflectivity measurements

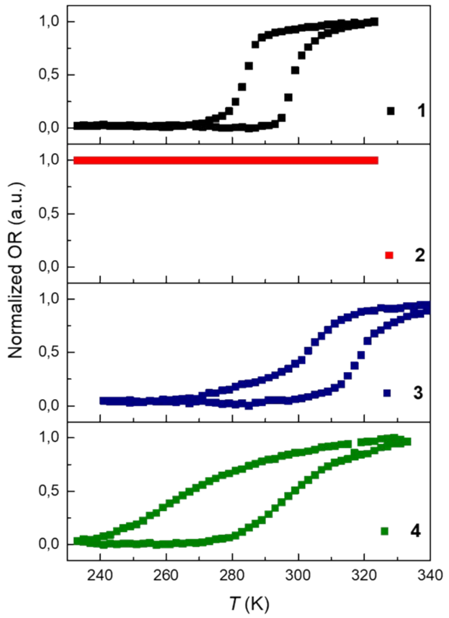

Figure S7. Normalized optical reflectivity (in respect to **1**) vs. *T* for **1-4**.

7) Complex 2 magnetic studies

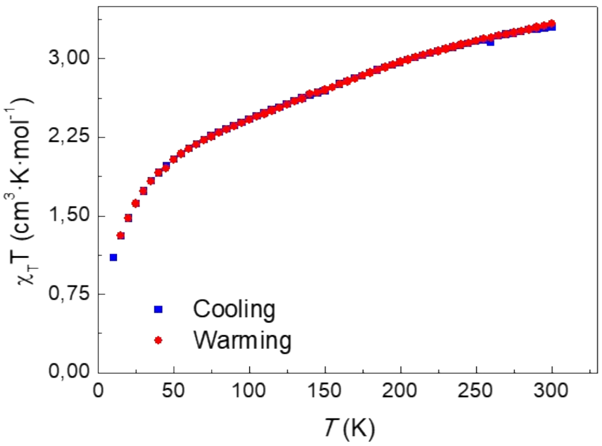

Figure S8. χ_MT vs. *T* for **2** between 2 K and 300 K.

1 M. D. Hanwell, D. E. Curtis, D. C. Lonie, T. Vandermeerschd, E. Zurek and G. R. Hutchison, *J. Cheminform.*, 2012, **4**, 1–17.