

Electronic Supplementary Information

Molecular tectonics: from a rigid achiral organic tecton to 3D chiral Co and Fe coordination networks

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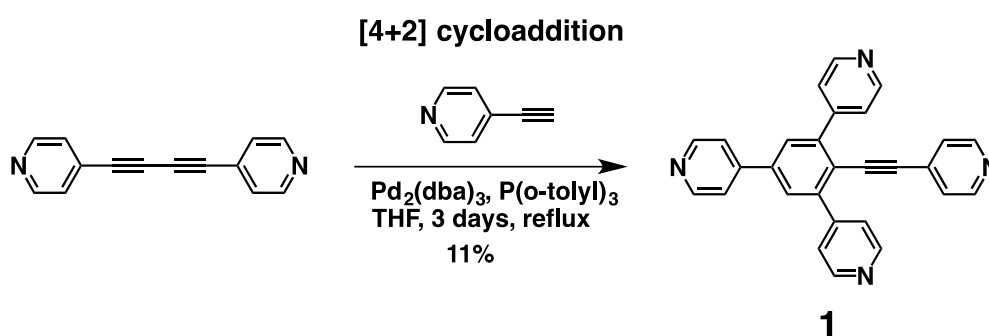
General

¹H- and ¹³C-NMR spectra were acquired at 25 °C on either Bruker AV 400 or Bruker AV 500 spectrometers in deuterated solvents and residual solvent peak was used as the internal reference. Elemental analyses were performed on a Thermo Scientific Flash 2000. For X-Ray diffraction on single crystals, data were collected at 173(2) K on a Bruker APEX8 CCD Diffractometer equipped with an Oxford Cryosystem liquid N₂ device, using graphite-monochromated Mo-Kα (λ = 0.71073 Å) radiation. For all structures, diffraction data were corrected for absorption. Structures were solved using SHELXS-97 and refined by full matrix least-squares on F² using SHELXL-97. The hydrogen atoms were introduced at calculated positions and not refined (riding model)¹.

All commercial reagents were used as received without further purifications. 4-ethynylpyridine and 1,4-Di(4-pyridyl)-1,3-diacetylene were prepared according to reported procedures.^{2,3}

Synthesis of organic compounds

Route A



Compound 1

Into a 25 mL 2-necked flask and under argon atmosphere was placed 1,4-Di(4-pyridyl)-1,3-diacetylene (25 mg, 0.12 mmol, 1eq) along with 4-ethynylpyridine (32 mg, 0.31 mmol, 2.5eq). Freshly distilled and degassed THF (10 mL) was then added to the flask via syringe. Finally, P(o-tolyl) (15 mg, 40% mol) and Pd₂(dba)₃ (6 mg, 5% mol) were added successively under an argon flow. The mixture was heated at 70°C for 3 days until no more evolution was observed on TLC. After cooling to RT, the mixture was evaporated to dryness. To the remaining solid was added CH₂Cl₂ (10 mL) and the mixture was filtered on paper. The filtrate was collected and evaporated to dryness. The solid beige residue was washed with Et₂O (10 mL) followed by CH₃CN (5 mL) to afford compound **1** as a beige

powder (5.5 mg, 11% yield). $^1\text{H-NMR}$ (400 MHz, CD_2Cl_2 , 25 $^\circ\text{C}$) δ (ppm): 8.78 (d, 4H, $^3J = 6.0$ Hz), 8.73 (d, 2H, $^3J = 6.1$ Hz), 8.48 (d, 2H, $^3J = 6.0$ Hz), 7.73 (s, 2H), 7.59 (d, 4H, $^3J = 6.0$ Hz), 7.57 (d, 2H, $^3J = 6.1$ Hz), 6.54 (d, 2H, $^3J = 6.0$ Hz).

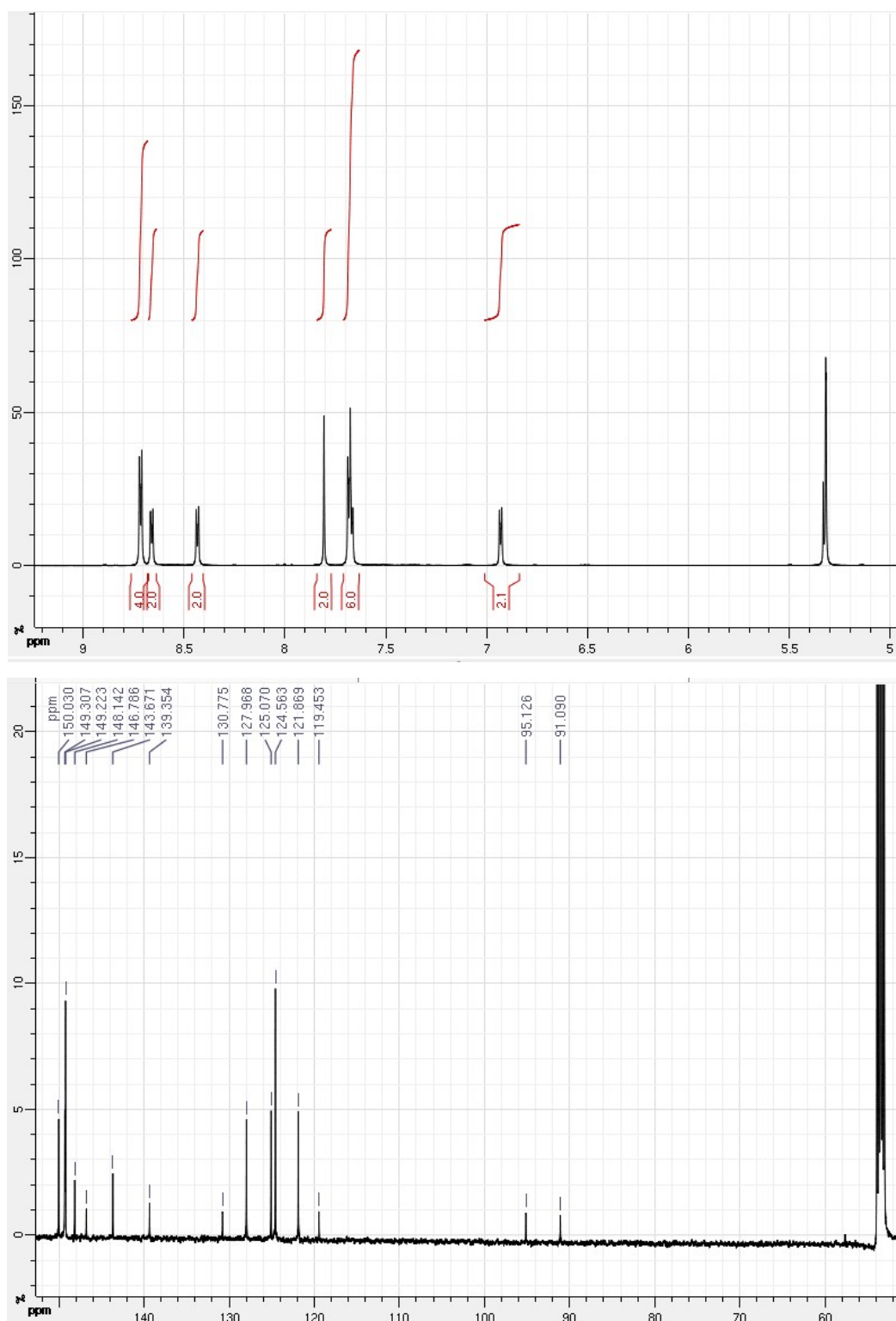
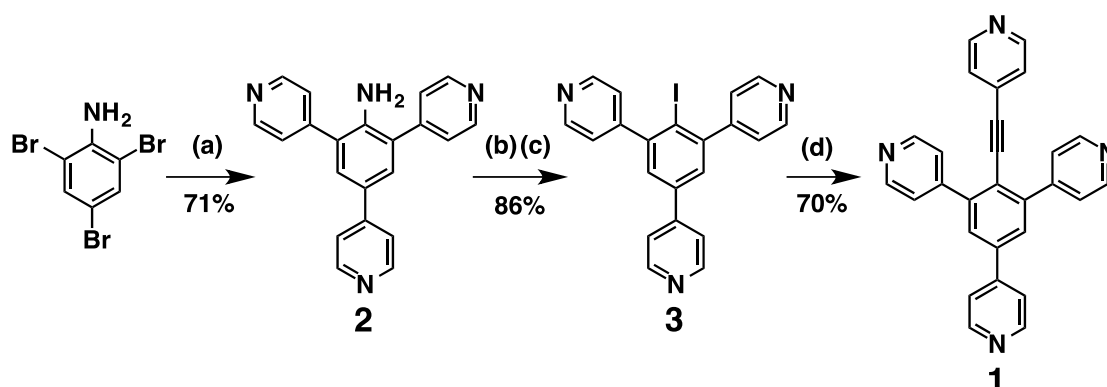


Figure S1. ^1H (400 MHz, top) and ^{13}C NMR (125 MHz, bottom) spectra of compound **1** (CD_2Cl_2 , 298K).

Route B



(a) 4-Pyridinylboronic acid, Pd(dppf)Cl₂, Na₂CO₃, H₂O/Dioxane, 100°C, 3 days (b) NaNO₂, HBF₄, H₂O, -5°C (c) KI, H₂O, 0°C (d) 4-ethynylpyridine, PdCl₂(PPh₃)₄, CuI, Et₃N, THF, 90°C, 48h

Compound 2

Into a 500 mL 2-necked round bottom flask was placed 1,4-dioxane (100 mL) and H₂O (100 mL). The mixture was degassed with argon for 20 min before 2,4,6-tribromoaniline (2.5 g, 7.58 mmol, 1eq), 4-pyridylboronic acid (4.6 g, 37.4 mmol, 5 eq) and Na₂CO₃ (20 g, 188 mmol, 24 eq) were added. The mixture was further degassed for 5 min before Pd(dppf)Cl₂ (1.5 g, 1.84 mmol, 24% mol) was added. The reaction media was heated at 100°C under argon for 3 days. After cooling to r.t. the mixture was filtered and the filtrate collected. It was then evaporated to dryness. The resulting residue was dissolved in CH₂Cl₂ (200 mL) and washed with water (3 x 200 mL). The organic phase was collected, dried over MgSO₄ and evaporated to dryness. The remaining solid was purified by column chromatography (SiO₂, eluent CH₂Cl₂/MeOH 3% then 5% then 10%) to yield a beige solid which, after precipitation from a CH₂Cl₂/Et₂O mixture afforded pure compound 2 as beige solid (1.75 g, 71% yield). ¹H-NMR (500 MHz, CDCl₃, 25 °C) δ (ppm): 8.73 (d, 4H, ³J = 5.8 Hz), 8.58 (d, 2H, ³J = 5.8 Hz), 7.47 (d, 6H, ³J = 5.8 Hz), 7.45 (s, 2H), 4.07 (s, 2H); ¹³C-NMR (125 MHz, CDCl₃, 25 °C) δ (ppm): 150.8, 150.1, 147.2, 146.7, 141.4, 128.9, 128.2, 125.9, 124.0, 120.7. Elemental analysis: calc. for C₂₁H₁₆N₄: C 77.76 %; H 4.97 %; N 17.27 % found C 77.95 %; H 4.85 %; N 17.25 %.

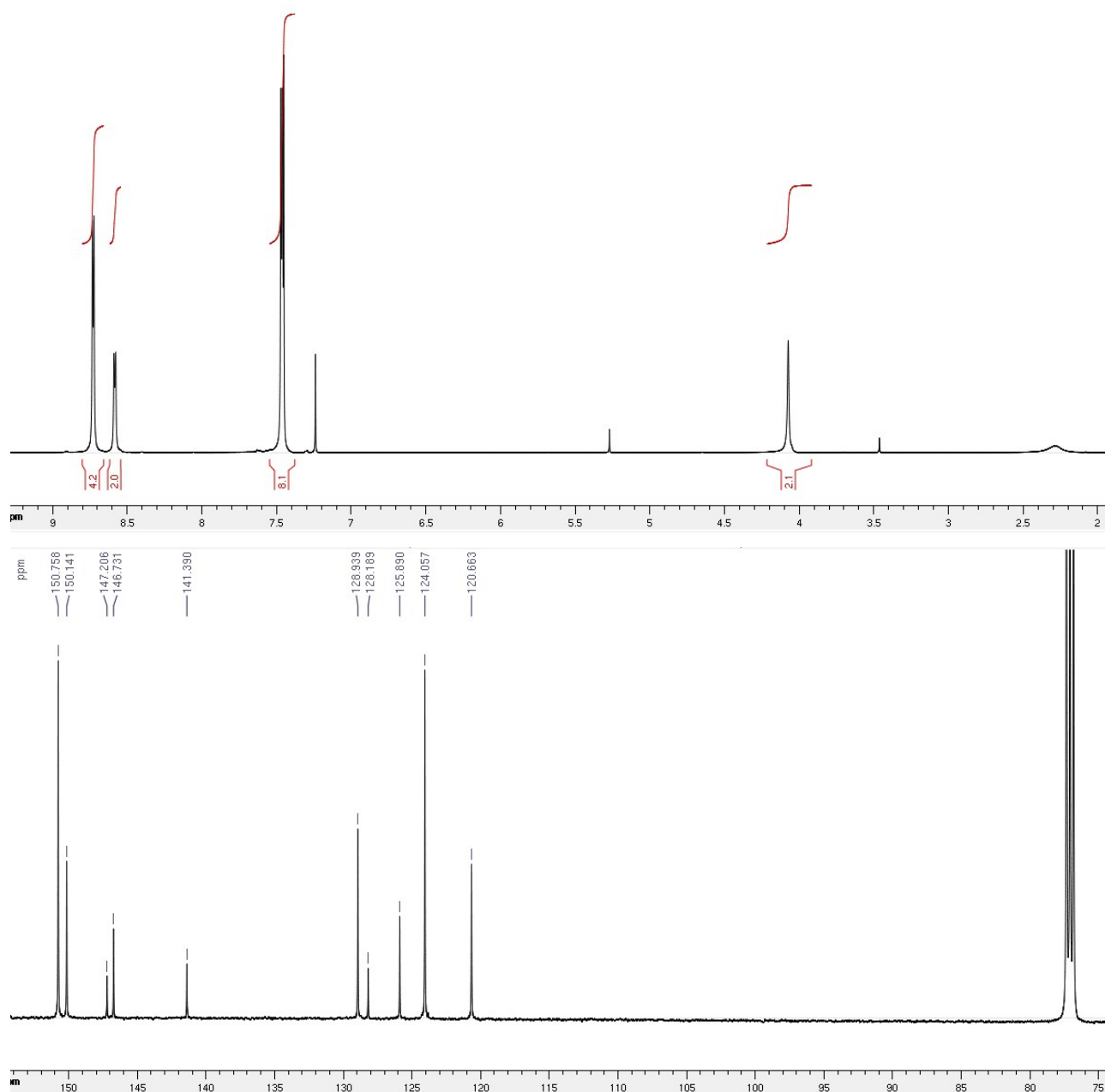


Figure S2. ^1H (500 MHz, top) and ^{13}C NMR (125 MHz, bottom) spectra of compound **2** (CDCl_3 , 298K).

Compound 3

Into a 50 mL 2-necked RBF was placed compound **1** (1.5 g, 4.62 mmol, 1eq) and HBF_4 (25 mL, 48% in H_2O) at -5°C . The mixture was stirred for 30 min before a solution of NaNO_2 (3.2 g, 46.3 mmol, 10 eq) in H_2O (15 mL) was added dropwise over a period of 1h while keeping the temperature at -5°C . The reaction media was further stirred for 30 min. This diazonium salt solution was then added via Pasteur pipette to a mixture of KI in $\text{H}_2\text{O}/\text{ice}$ (25 mL) contained in an ice bath. After stirring for 15 min, the resulting brown solution was decolorized by addition of Na_2SO_3 and basified to pH 8-9 by cautious addition of NaHCO_3 .

CH₂Cl₂ (300 mL) was added and stirring was continued for 30 min at RT. The mixture was transferred to a separating funnel and the organic phase was collected. It was then further washed with sat. aq. NaHCO₃ (3 x 300 mL), dried over MgSO₄ and evaporated to dryness. The resulting solid residue was purified by column chromatography (SiO₂, eluent CH₂Cl₂/MeOH 5% then 7% then 10%) to afford compound 3 as a beige solid (1.73 g, 86% yield). ¹H-NMR (400 MHz, CDCl₃, 25 °C) δ (ppm): 8.65 (d, 4H, ³J = 6.0 Hz), 8.59 (d, 2H, ³J = 6.1 Hz), 7.43 (d, 2H, ³J = 6.0 Hz), 7.42 (s, 2H), 7.25 (d, 4H, ³J = 6.0 Hz); ¹³C-NMR (100 MHz, CDCl₃, 25 °C) δ (ppm): 151.6, 150.3, 149.5, 146.5, 145.7, 138.2, 127.0, 123.7, 121.0, 100.8. Elemental analysis: calc. for C₂₁H₁₄IN₃: C 57.95 %; H 3.24 %; N 9.65 % found C 57.67 %; H 3.29 %; N 9.71 %.

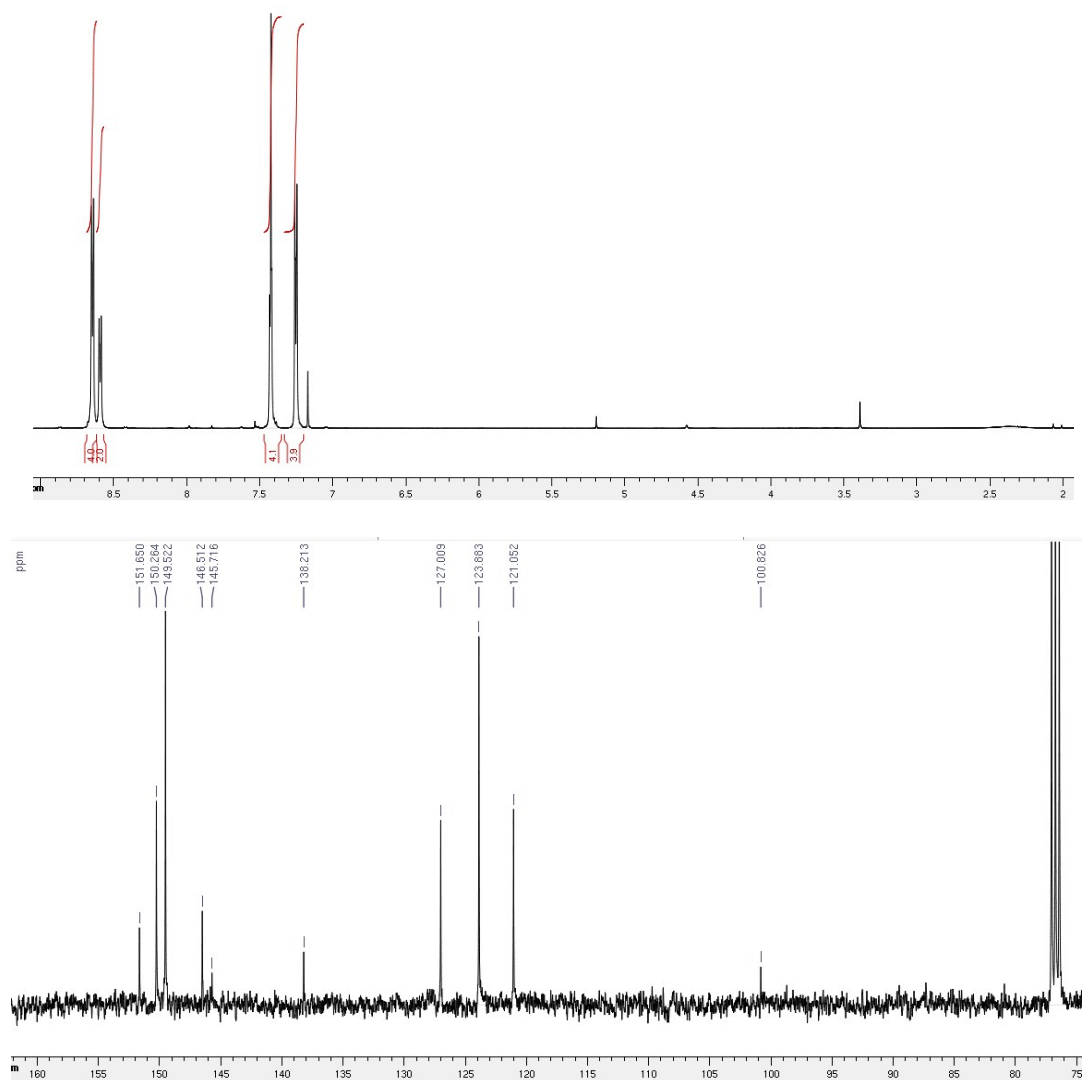


Figure S3. ¹H (400 MHz, top) and ¹³C NMR (125 MHz, bottom) spectra of compound 3 (CDCl₃, 298K).

Compound 1

A 100 mL 2-necked RBF was charged with compound 3 (300 mg, 0.69 mmol, 1 eq) and 4-ethynylpyridine (107 mg, 1.03 mmol, 1.5 eq) under an argon atmosphere. Distilled and degassed THF (20 mL) and Et₃N (20 mL) were added successively via syringe. The mixture was stirred under argon for 10 min before CuI (27 mg, 20% mol) and PdCl₂(PPh₃)₂ (48 mg, 10% mol) were added. The reaction media was then stirred at reflux temperature for 24h. After cooling to RT, the mixture was filtered and the filtrate collected. It was then evaporated to dryness. The resulting residue was purified by column chromatography (SiO₂, eluent CH₂Cl₂/MeOH 5% then 7%) to afford compound **1** as a beige solid (195 mg, 70% yield) which was stored under Argon at -25°C. ¹H-NMR (500 MHz, CD₂Cl₂, 25 °C) δ (ppm): 8.71 (d, 4H, ³J = 6.0 Hz), 8.66 (d, 2H, ³J = 6.3 Hz), 8.43 (d, 2H, ³J = 6.0 Hz), 7.81 (s, 2H), 7.68 (m, 6H), 6.93 (d, 2H, ³J = 6.0 Hz); ¹³C-NMR (125 MHz, CD₂Cl₂, 25 °C) δ (ppm): 150.0, 149.3, 149.2, 148.1, 146.7, 143.7, 139.3, 130.8, 127.9, 125.1, 124.6, 121.8, 119.4, 95.1, 91.0. Elemental analysis: calc. for C₂₈H₁₈N₄: C 81.93 %; H 4.42 %; N 13.65 % found C 81.87 %; H 4.59 %; N 13.39 %.

Crystallization procedure

Crystallisations were carried out by liquid-liquid diffusion techniques in glass crystallization tubes (height = 15 cm, diameter = 0.4 cm) at ca 25°C.

1·Co(SCN)₂ :

Through a buffered layer of a 1/1 CHCl₃/MeOH mixture (0.1 mL), diffusion of a MeOH solution (1 mL) of Co(SCN)₂ (1.3 mg, 7.4 μmol) into a CHCl₃ solution (1 mL) of tecton **1** (3.0 mg, 7.3 μmol) afforded pink needle single crystals after few days.

1·Fe(SCN)₂ :

Through a buffered layer of a 1/1 CHCl₃/MeOH mixture (0.1 mL), diffusion of a MeOH solution (1 mL) of Fe(SCN)₂(py)₄ (3.6 mg, 7.4 μmol) into a CHCl₃ solution (1 mL) of tecton **1** (3.0 mg, 7.3 μmol) afforded orange single crystals after few days.

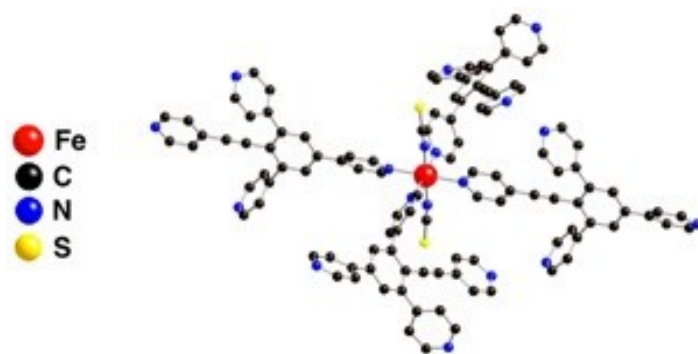


Fig S4: Portion of the X-ray structure of $1 \cdot \text{Fe}(\text{SCN})_2$ showing the Oh coordination geometry adopted by Fe(II) cation.

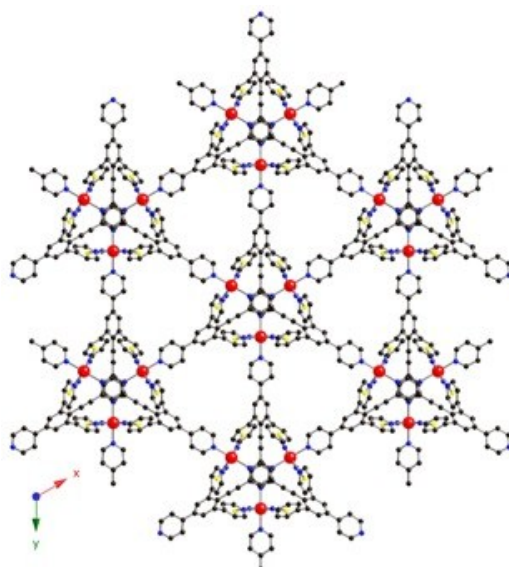


Fig S5: Portion of the X-ray structure along the z axis showing the porous 3D structure of $1 \cdot \text{Fe}(\text{SCN})_2$

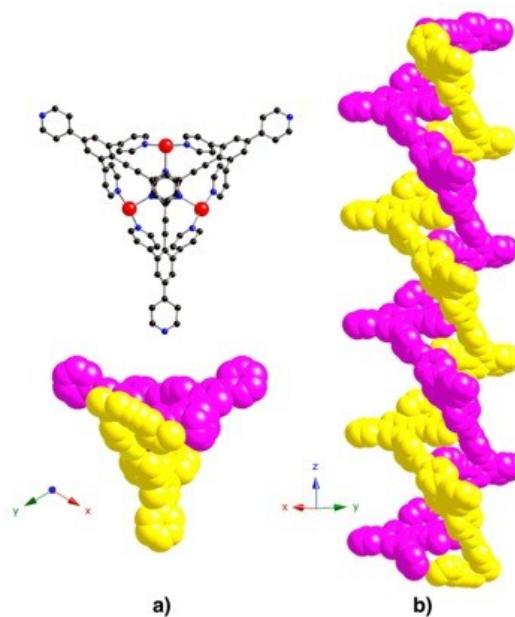


Fig S6: Portion of the X-ray structure of $1 \cdot \text{Fe}(\text{SCN})_2$ showing the double stranded helical repeating motifs.

Crystallographic data of 1·Co(SCN)₂ and 1·Fe(SCN)₂

	1·Co(SCN)₂	1·Fe(SCN)₂
Empirical formula	C ₃₀ H ₁₈ CoN ₆ S ₂	C ₃₀ H ₁₈ FeN ₆ S ₂
Molecular weight	588.55	582.47
Crystal system	Trigonal	Trigonal
Space group	<i>P3₁21</i>	<i>P3₁21</i>
a (Å)	18.3008(5)	18.3693(8)
b (Å)	18.3008(5)	18.3693(8)
c (Å)	15.2850(6)	15.2441(6)
α (°)	90	90
β (°)	90	90
γ (°)	120	120
V (Å ³)	4433.4(2)	4454.7(3)
Z	3	3
Colour	pink	orange
Crystal dim (mm ³)	0.05 x 0.04 x 0.04	0.05 x 0.04 x 0.04
D _{calc} (g.cm ⁻³)	0.658	0.651
F(000)	897	894
μ (mm ⁻¹)	0.375	0.339
Wavelength (Å)	0.71073	0.71073
Number of data meas.	8681	9015
Number of data with I>2σ(I)	8681	9015
R	0.0340	0.0484
R _w	0.0531	0.0897
GOF	1.066	1.046
Flack parameter	0.041(8)	0.022(15)

1. G. M. Sheldrick, *Acta Cryst.*, 2008, **A64**, 112.
2. J. G. Rodríguez, C. Díaz-Oliva, *Tetrahedron*, 2009, **65**, 2512.
3. L. Yu, J. S. Lindsey, *J. Org. Chem.*, 2001, **66**, 7402.