Supporting Information

Metallocenes@COF-102: Organometallic Host-Guest Chemistry of Porous Crystalline Organic Frameworks

Suresh Babu Kalidindi,[a] Kirill Yusenko, [a] and Roland A. Fischer*

[a] *Inorganic Chemistry II, Ruhr-University Bochum, Universitätsstrasse 150, 44801 Bochum, Germany; E-mail: roland.fischer@rub.de*

Materials, methods and experimental procedures

Starting Materials: All chemicals were purchased from Sigma-Aldrich and Alfa Aesar and used without further purification. Manipulations were carried out under Argon atmosphere using standard Schlenk-line and glovebox techniques. All the solvents were purified, dried using an automatic catalytic Solvent Purification System (MBraun, Garching). Ferrocene and cobaltocene were purchased from Alfa Aesar and further purified by sublimation. [Ru(cod)(cot)] was synthesized using literature procedure (K. Itoh, H. Nagashima, T. Ohshima, N. Oshima and H. Nishiyama, *J. Organomet. Chem.* **1984**, *272*, 179). Tetra(4-(dihydroxy)borylphenyl)methane was prepared from tertraphenylmethane using literature procedure(J- H. Fournier, T. Maris, J. D. Wuest, W. Guo and E. Galoppini, *J. Am. Chem. Soc.*, 2003, *125*, 1002)

Analytical Characterization:

Elemental analysis was performed by the Microanalytical Laboratory of the Department of Analytical Chemistry at the Ruhr-University Bochum, Germany. For Fe and Ru determination an AAS apparatus by Vario of type 6 (1998) was used, C, H, N analyses were carried out using a Vario CHNSO EL (1998) instrument. Infrared spectra were measured (inside a glovebox) on a bruker Alpha-P FT-IR instrument in the ATR geometry with a diamond ATR unit. Solid-state ^{1}H and^{13}C-CP MAS NMR spectra were measured with a Bruker DSX 400 MHz instrument in ZrO_2 rotors (diameter = 2.5 mm) with a rotational frequency of 20 kHz. All MAS NMR spectra were measured by using pulse programs written by H. -J. Hauswald at the Analytical Chemistry Departement at the Ruhr-University Bochum and based on standard parameters. For the ^{1}H and ^{13}C MAS(NMR) measurements ZG4PM and CP4C (cross-polarization) pulse programs were used, respectively. Thermo gravimetric analyses (TGA) studies were carried out using a Seiko TG/DTA 6300S11 instrument at a heating rate of 5°C/min in a temperature range from 30-600 °C at atmospheric pressure under N_2 flow (99.9999%; flow rate=300 mL min-1). The BET surface area measurements were carried out using N_2 gas, the samples were priorly degassed at 100 °C for 12 h. N_2 sorption measurements were performed on a Quantachrome Autosorp-1 MP instrument using optimized protocols.

Synthesis of COF-102

The reaction was carried out in a glass tube measuring o.d. × i.d. = 20 × 16 mm^2 and was charged with 100 mg (0.20 mmol) of *tetra*(4-(dihydroxy)borylphenyl)methane and 2.0 mL of a 1:1 v:v solution of mesitylene:dioxane under argon. The reaction tube was placed inside a liquid N_2 bath and evacuated. Later, the tube was flame sealed under vacuum and length of the tube was maintained around 18 cm. Self-condensation reaction was carried out by aging the reaction tube at 85 °C for 4 days. White color product was filtered from the reaction mixture using G2 crucible inside a glove box. The final product was washed with 40 mL of THF and stored overnight in fresh 20 mL of THF solvent. The solvent was removed under vacuum at room temperature to afford COF-102 as white powder. Yield: 50-60 mg (50-60 %)

IR: (cm^{-1}) 1593(s), 1397 (s), 1333 (vs), 1307 (s), 1188(w), 1080 (w), 1011 (s), 823 (w), 741 (s), 701(w), 601(w), 528(w), 500(w), 402(w)

NMR ^{13}C (MAS): δ (ppm) 151.6, 134.2, 128.4, 66.2

Elemental analysis: C, 67.6; H, 3.9.

Gas phase infiltration of COF-102 with organometallic precursors

In a typical experiment a sample of 30 mg(0.07 mmol) of dry and activated COF-102 and 100 mg of volatile organometallic precursors were placed in two separate glass boats in a Schlenk tube. The tube was then evacuated to 10^{-3} mbar for 5 min and sealed. The reaction tube was kept at 100 °C for 12 h, 25 °C for 24 h, and 50 °C for 7 days in case of ferrocene, cobaltocene, and [Ru(cod)(cot)], respectively. The obtained inclusion compounds (ML_n@COF-102) were isolated and were stored inside glove box later.

$FeCp_2$@COF-102: Yield: ~90 mg

Elemental analysis: Fe, 17.8; C, 66.4; H, 4.5

IR: 3066(w), 2996(vw), 1590(s), 1397(s), 1327(vs), 1305(s), 1186(w), 1097(s), 1077(w), 1010(w), 994(s), 808(s), 735(s), 694(s), 597(w), 485(s), 471(s), 404(w).

NMR ^{13}C (MAS): δ (ppm) 151.3, 135.7, 128.5, 68.7, 66.6

$CoCp_2$@COF-102: Yield: ~85 mg

IR: (cm^{-1}) 3063(w), 3007(vw), 1590(s), 1394(s), 1327(s), 1304(s), 1185(w), 1102(w), 1077(w), 1012(s), 989(s), 823(w), 772(s), 731(s), 693(s), 597(w), 526(w), 499(w), 395(w).

NMR: The peaks are too broad due to paramagnetic nature of the sample.

[Ru(cod)(cot)]@COF-102: Yield: ~60 mg

Elemental analysis: Ru, 18.5

IR: (cm^{-1}) 2935(w), 2895(w), 2840(w), 2792(w), 1951(w), 1593(s), 1392(s), 1331(vs), 1310(s), 1185(w), 1078(w), 1010(s), 861(w), 821(w), 737(s), 694(s), 600(w), 527(w), 499(w), 485(w), 459(w), 396(w), 380(w).

NMR ^{13}C (MAS): δ (ppm) 151.6, 135.2, 129.0, 102.0, 99.7, 77.1, 70.8, 66.3, 34.2, 32.1

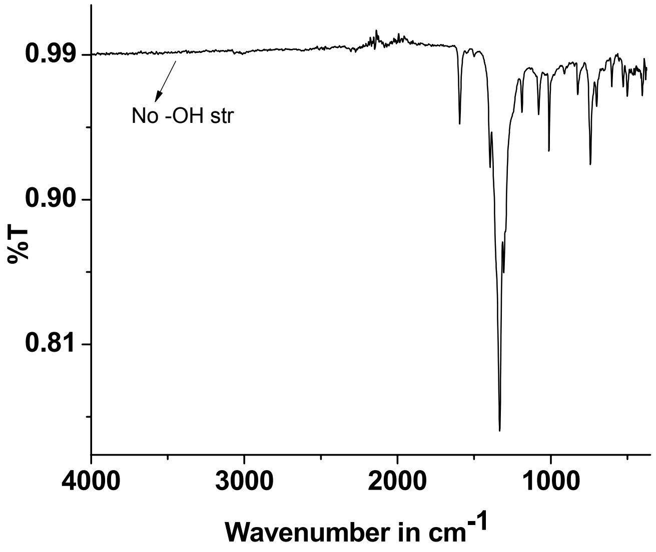

Fig. S1. IR spectrum of COF-102

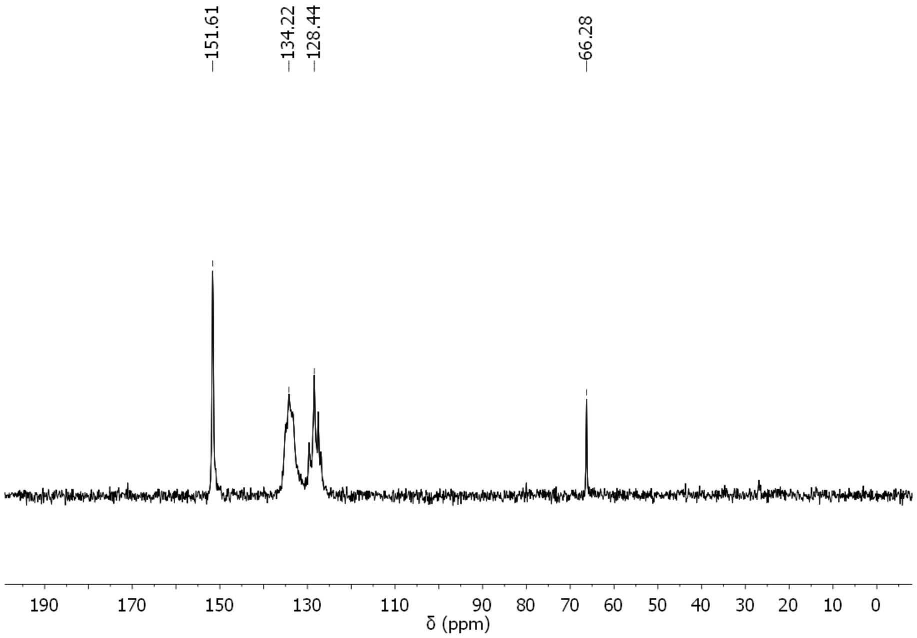

Fig. S2. ^{13}C NMR spectrum of COF-102

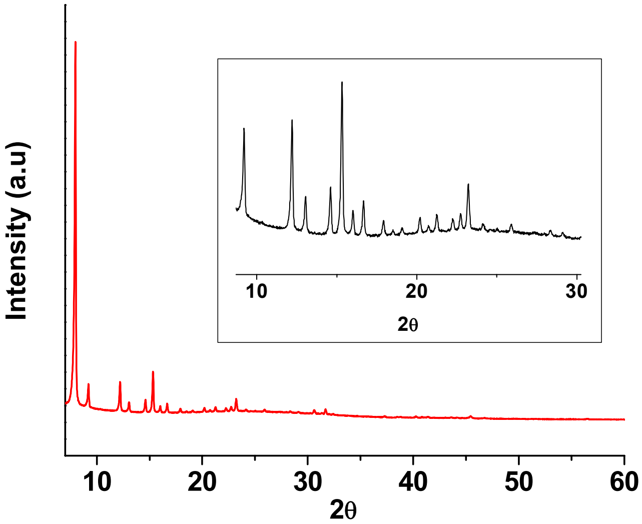

Fig. S3. Powder XRD pattern of COF-102, inset shows expanded view between 2θ = 8° to 30°

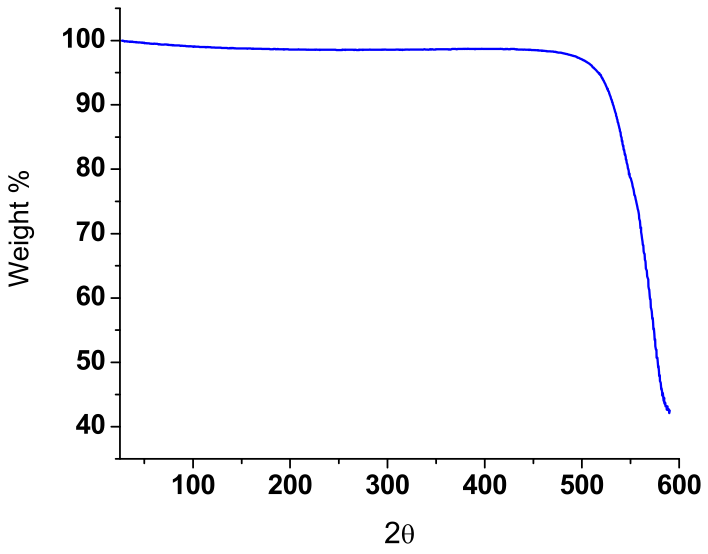

Fig. S4. TGA profile of COF-102, after activating overnight under vacuum at 100 °C

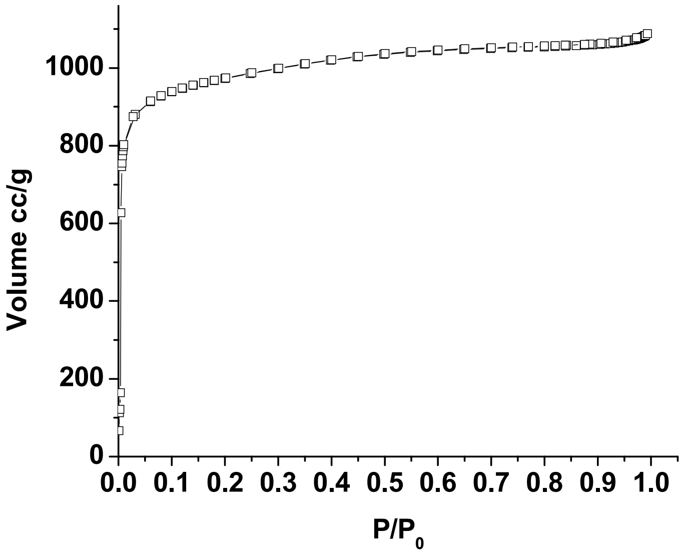

Fig. S5. N_2 adsorption/desorption isotherm of COF-102 sample; BET and Langmuir areas are found to be 3750 m^2/gm and 4378 m^2/gm, respectively.

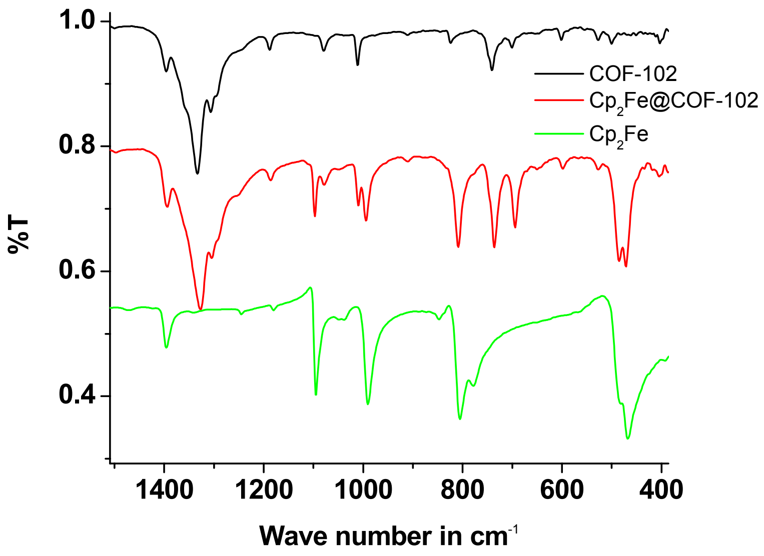

Fig. S6. Comparison of IR spectra of COF-102, Cp_2Fe@COF-102, and Cp_2Fe.

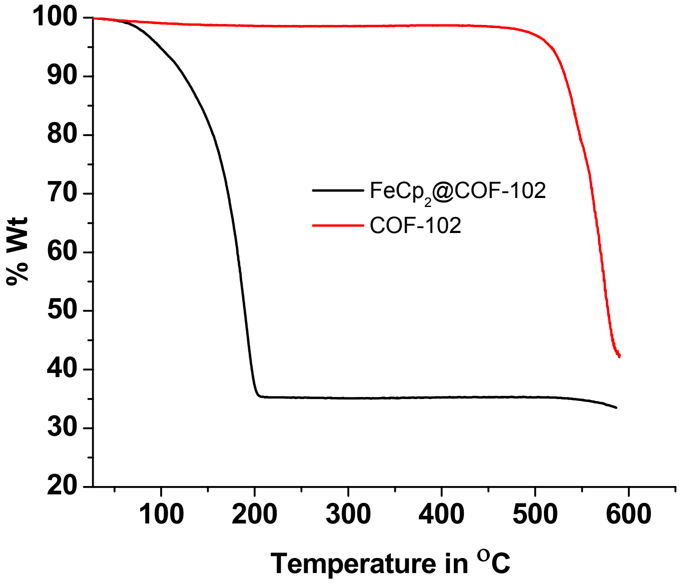

Fig. S7. Comparison of TGA profile of COF-102 and Cp_2Fe@COF-102

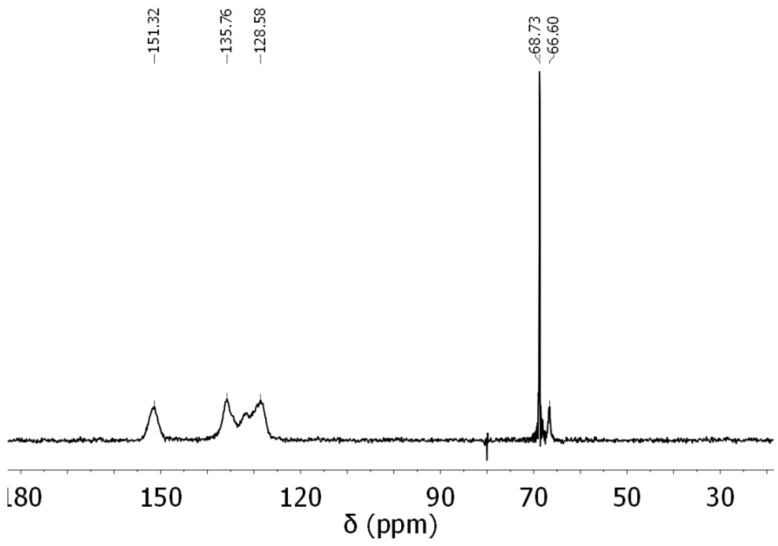

Fig. S8. ^{13}C NMR (MAS) spectrum of FeCp$_2$@COF-102 inclusion compound

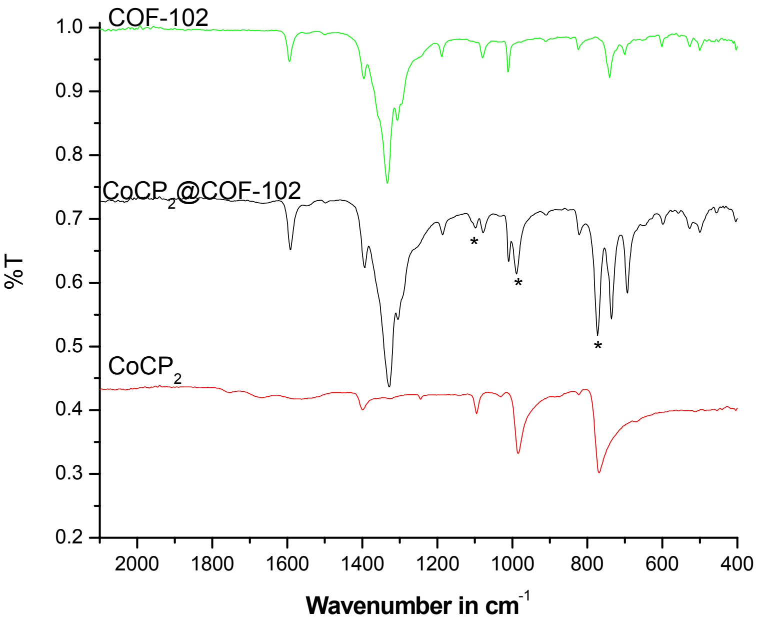

Fig. S9. Comparison of IR spectra of COF-102, CoCp2@COF-102 and CoCp$_2$

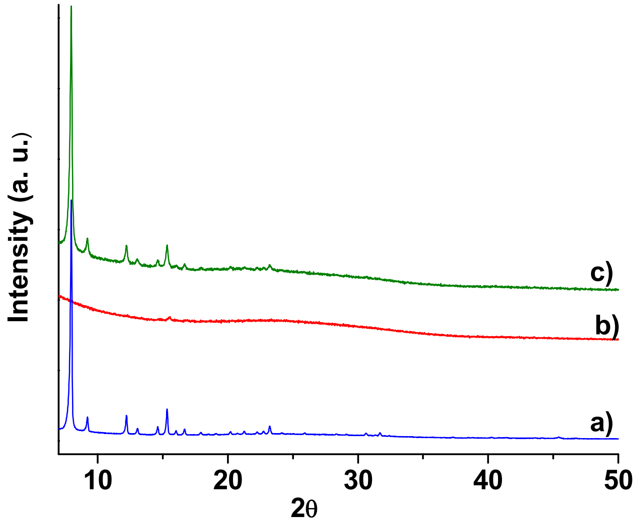

Fig. S10. Powder XRD pattern of a) COF-102; b) $CoCp_2$@COF-102; c) after heating $CoCp_2$@COF-102 compound at 100 °C for 3 h under vacuum.

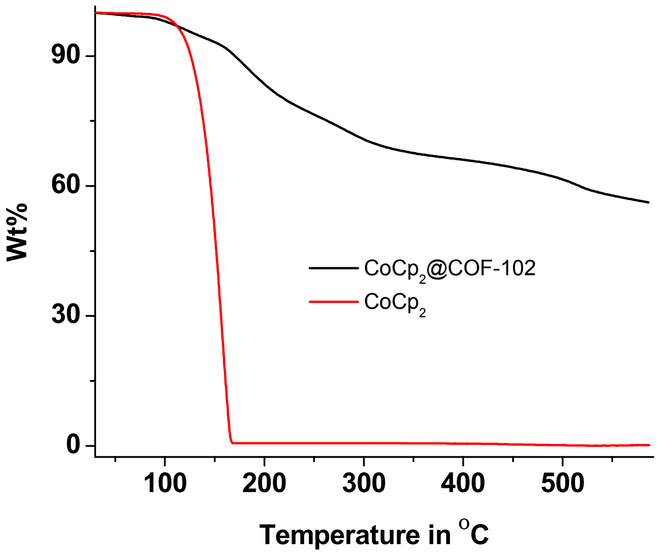

Fig. S11. Comparison TGa profiles of $CoCp_2$ and $CoCp_2$@COF-102

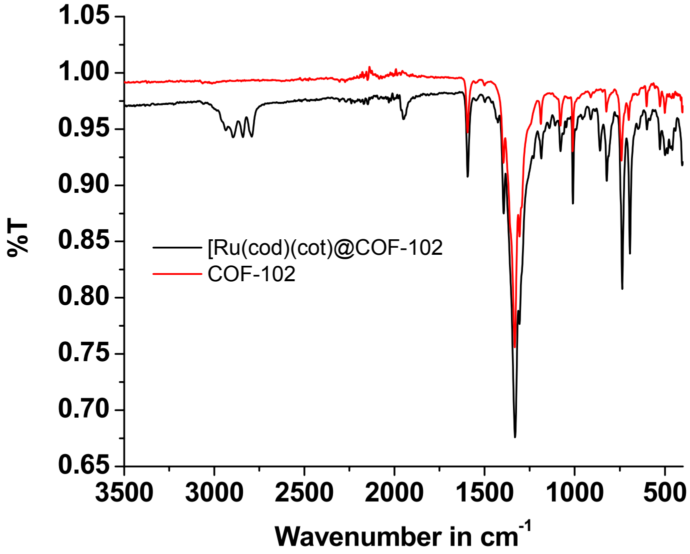

Fig. S12. Comparison of IR spectra between COF-102 and $[Ru(cod)(cot)]_2$@COF-102

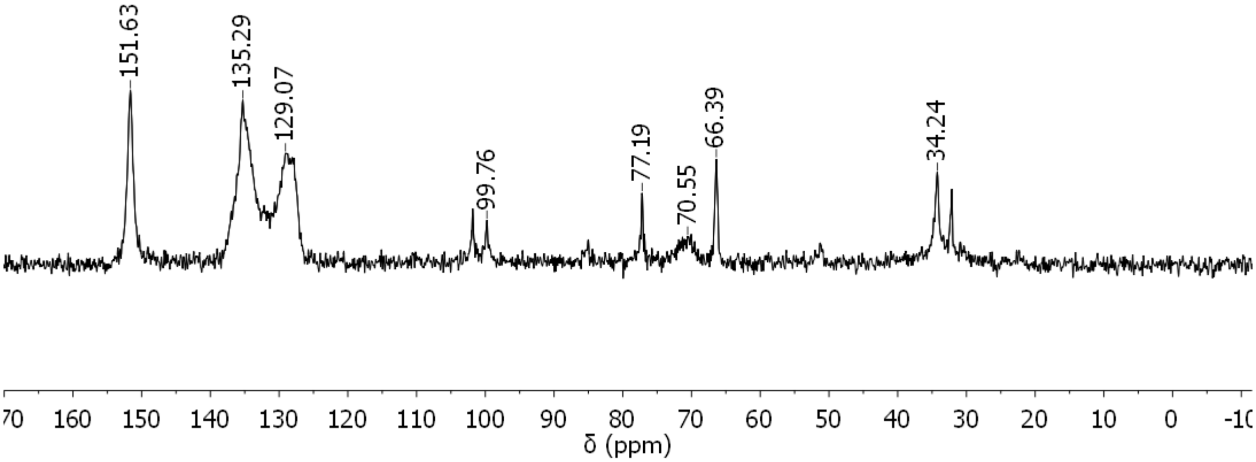

Fig. S13. ^{13}C NMR(MAS) spectrum of $[Ru(cod)(cot)]_2$@COF-102

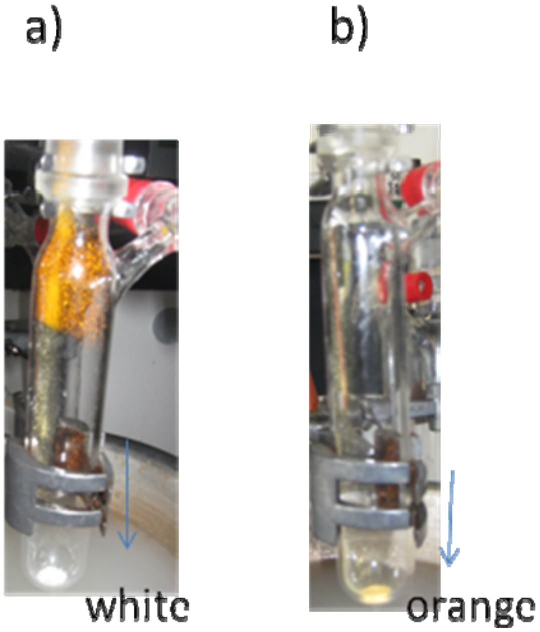

Fig. S14. The $FeCp_2$ uptake was found to be reversible; all the $FeCp_2$ molecules could be stripped off from compound **1** under vacuum at 100 °C in less than an hour. a) after heating $FeCp_2$@COF-102 for 1 h under static vacuum; b) after leaving the Schlenk tube at r. t. for 1 h.

Powder XRD data and structure solution:

X-ray powder diffractograms were recorded on a D8 Advance Bruker AXS diffractometer (Cu K_α -radiation, room temperature, Göbel mirror, step, data points) in θ–2θ geometry and with a position-sensitive detector. The data was collected in the 2θ range 5 – 90°. Measurements were carried out in capillary mode and by using 0.7 mm diameter capillaries. The glass capillaries were filled with the samples inside a glovebox, closed with grease and later flame sealed immediately outside the box.

The positions of the guest molecules were obtained by global optimization in the direct space using the parallel tempering algorithm of the FOX software starting from rigid "empty" COF-102 and ferrocene molecules as building blocks (V. Favre-Nicolin and R. Černý, *J. Appl. Crystallogr.*, 2002, **35**, 734–743: http://objcryst.sourceforge.net). The modeling of raw-data using FOX was based on the assumption that the interactions between the guest molecules and the host COF-102 framework are weak. Herewith, the geometries of the individual molecules and framework remain relatively unchanged during the formation of the inclusion complex. In this case, FOX is particularly robust because individual molecules can be added as mathematical objects in the form of a Fenske–Hall Z-matrix, thus retaining their geometry for the optimization algorithm. The Monte Carlo optimization, in which the parameters of the ferrocene Z-matrix were fixed (*i.e.*, the guest molecule was treated as a rigid body), was launched in FOX and the initial location of the crystallographically independent guest molecules were found after nearly $2*10^6$ movements (calculated R factors were between 0.15 and 0.20), whereas the atomic coordinates of COF-102 framework were fixed. Several independent runs starting from the different positions gave the identical minimum that shows correctness of the structure solution. Due to the less quality of the data final Rietveld refinement has not been performed for structure refinement. The same procedure have been performed for [Ru(cod)(cot)]@COF-102. The positions of the Ru atoms were obtained using pseudo-atom approach by other words cod and cot rings were replaced by two Rh atoms with Rh – Ru – Rh angle as 180°.

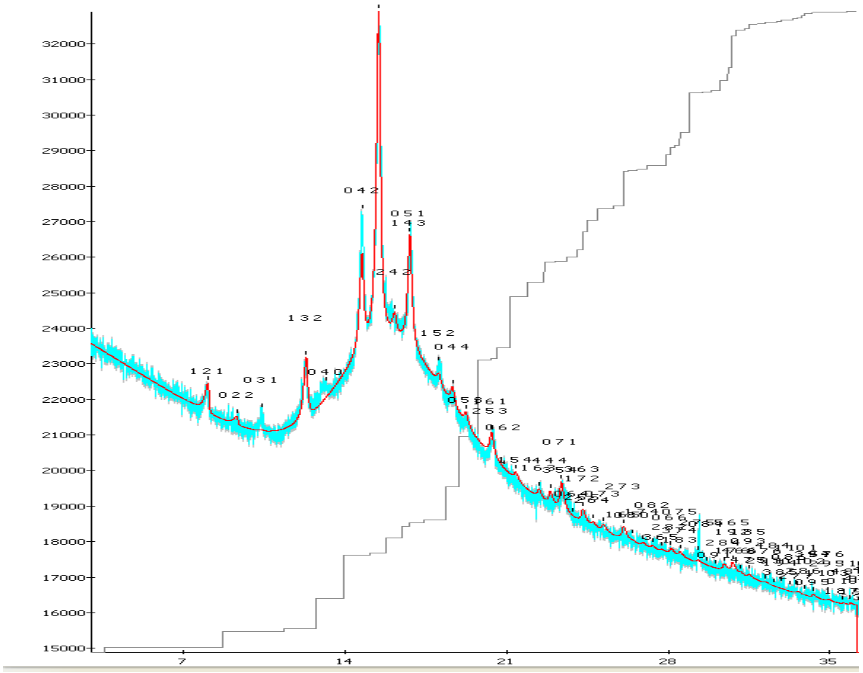

Fig. S15. Comparison of PXRD patterns of $FeCp_2$@COF-102 **-** experimental (red) and calculated (cyan) - obtained from crystal structure solution by direct space method with FOX software

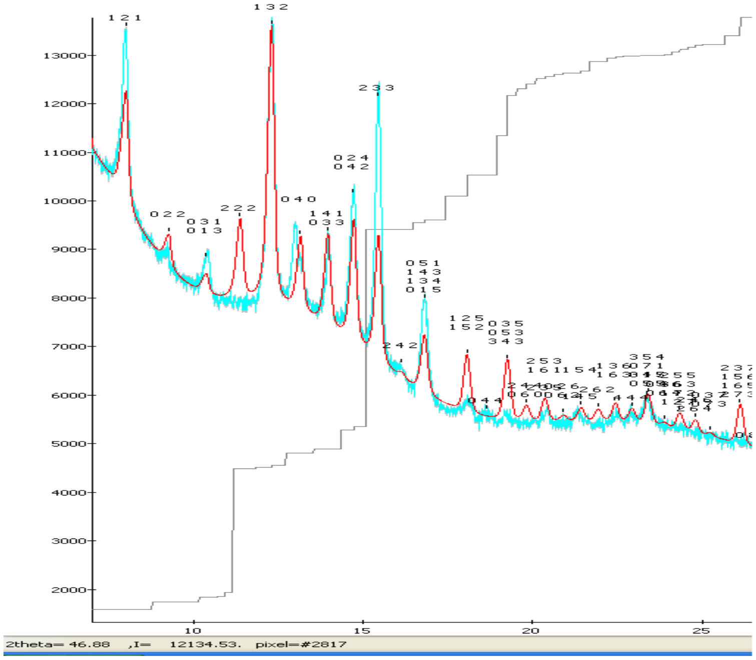

Fig. S16. Comparison of PXRD patterns of [Ru(cod)(cot)]$_2$@COF-102**-** experimental (red) and calculated (cyan) - obtained from crystal structure solution by direct space method with FOX software

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