

## SUPPORTING INFORMATION

### Prussian Blue Analogues for the Separation of Hydrocarbons in Humid Conditions

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## EXPERIMENTAL SECTION

**General Remarks:** all experiments were carried out under aerobic conditions using ultra pure water. The PBA were obtained following the general procedures. [1,2] The number of water molecules were obtained from TGA analysis. The ratio between the elements were obtained from EDS analysis.

### Syntheses

#### Synthesis of lacunary PBA $M[M(CN)_6]_{0.66}$ (1-3)

A solution of  $K_3[M(CN)_6]$  ( $M = Fe, Co$ ) (10 mmol) in 100 mL of ultrapure water added dropwise to a solution of  $M(NO_3)_2 \cdot 6H_2O$  ( $M = Co, Cu$ ) (18 mmol) in 100 mL of ultrapure water. A precipitate is formed immediately and is stirred overnight. The solid was then centrifuged, washed with ultrapure water and dried in the air.

Elemental analysis for  $Co[Co(CN)_6]_{0.66} \square_{0.33} \cdot 5.2H_2O$  (**1**) (calcd): % C 16.04 (16.06), % H 3.03 (3.51); % N 18.94 (18.91). IR (ATR,  $cm^{-1}$ ): 2171 (s)  $\nu(Co^{III}-CN-Co^{II})$ , 2138 (sh).

Elemental analysis for  $Cu[Co(CN)_6]_{0.66} \square_{0.33} \cdot 5.1H_2O$  (**2**) (calcd): % C 15.89 (16.13), % H 2.28 (3.43); % N 18.59 (18.81). IR (ATR,  $cm^{-1}$ ): 2185 (s)  $\nu(Co^{III}-CN-Cu^{II})$ , 2143 (sh).

Elemental analysis for  $Co[Fe(CN)_6]_{0.66} \square_{0.33} \cdot 4.6H_2O$  (**3**) (calcd): % C 16.24 (16.89), % H 2.88 (3.27); % N 19.50 (19.71). 2157 (s,  $\nu(Fe^{III}-CN-Co^{II})$ ), 2096 (sh,  $\nu(Fe^{II}-CN-Co^{II})$ ).

#### Synthesis of $Cs_{0.74}Co[Co(CN)_6]_{0.91} \square_{0.09} \cdot 3.6H_2O$ (**4**)

$MCl_2 \cdot 6H_2O$  (2.5 mmol) and CsCl (5 mmol) were dissolved in 50 mL of ultrapure water. This solution was added dropwise to a solution of  $K_3[Co(CN)_6]$  (2.5 mmol in 50 mL). The mixture was stirred for 3h. The solid was then centrifuged, washed with ultrapure water and dried in the air.

Elemental analysis for  $Cs_{0.74}Co[Co(CN)_6]_{0.91} \square_{0.09} \cdot 3.6H_2O$  (**4**) (calcd): % C 15.87 (15.68), % H 1.13 (1.72); % N 18.58 (18.29). IR (ATR,  $cm^{-1}$ ): 2171 (s)  $\nu(Co^{III}-CN-Co^{II})$ , 2140 (sh).

#### Synthesis of lacunary $M[M(CN)_6]_{0.50}$ (**5, 6**)

A solution of  $K_4[Fe(CN)_6]$  (3.1 mmol) in 50 mL of ultrapure water added dropwise to a solution of  $M(NO_3)_2 \cdot 6H_2O$  ( $M = Co, Cu$ ) (9.3 mmol) in 50 mL of ultrapure water. A precipitate is formed immediately and is stirred overnight. The solid was then centrifuged, washed with ultrapure water and dried in the air.

Elemental analysis for  $K_{0.96}Co[Fe(CN)_6]_{0.74} \square_{0.26} \cdot 3.0H_2O$  (**5**) (calcd): % C 17.21 (17.34), % H 1.61 (1.95); % N 20.31 (20.22). IR (ATR,  $cm^{-1}$ ): 2075 (s)  $\nu(Fe^{II}-CN-Co^{II})$ , 2116 (sh).

Elemental analysis for  $K_{0.17}Cu[Fe(CN)_6]_{0.54} \square_{0.46} \cdot 5.6H_2O$  (**6**) (calcd): % C 14.13 (13.57), % H 3.20 (3.95); % N 16.42 (15.82). IR (ATR,  $cm^{-1}$ ): 2097 (s)  $\nu(Fe^{II}-CN-Cu^{II})$ .

## **Experimental methods**

### **TGA analysis**

Thermogravimetric analyses were obtained with a thermal analyser STA 409 Luxx® (Netzsch) on the range 25 – 1000 °C at heating speed of 2 °C /min.

### **EDS analysis**

Scanning Electronic Microscopy (EDS) analyses were performed on a FEI Quanta FEG 200 instrument. The powders were deposited on an adhesive carbon film and analysed under vacuum. The quantification of the heavy elements was carried out with the INCA software, with a dwell time of 3  $\mu$ s.

### **PXRD**

X-ray powder diffraction patterns were recorded in the interval at room temperature with the XPERTPro analytical diffractometer mounted in a Debye–Scherrer configuration and equipped with a Cu radiation ( $\lambda = 1.5418 \text{ \AA}$ ).

### **Adsorption isotherms**

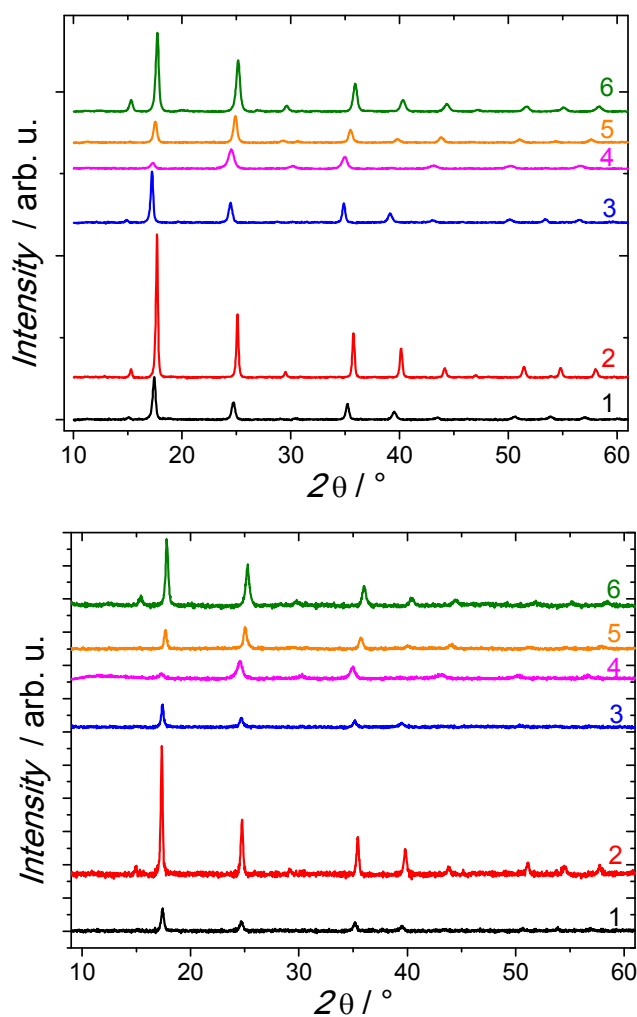
The vapor adsorption/desorption experiments have been performed with a home-made apparatus already described elsewhere.[3] This set-up is based on manometric measurements (with two capacitative pressure gauges (0-10 Torr and 0-1000 Torr). The sample cell can be disconnected from the system to undergo a thermal treatment up to 250°C (depending on the thermal stability of the sample) under a vacuum of  $10^{-3}$  Torr. The adsorption set-up presented above allows for the choice of the pressure of the adsorbate to be introduced (instead of the equilibrium pressure). The adsorbed amounts ( $Q_{ads}$ ) were determined as the difference between equilibrium pressure before adsorption and after adsorption for each adsorption step.

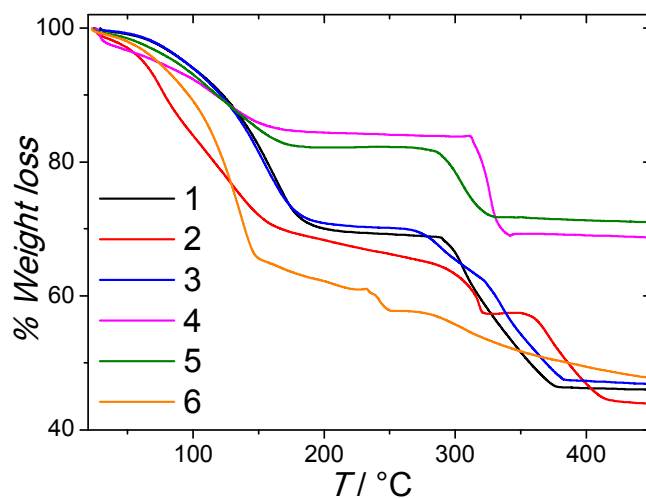
### **Chromatography**

The gas phase chromatographic separation set-up has been built in our laboratory. It is based on two mass flow controllers allowing the introduction of precise amounts of liquid (a few mg per hour) into a vaporization chamber. From this chamber, the vapor mixture was introduced into the separation column through an injection loop. This column of 30 cm long, 4 mm inner diameter was packed with PBA1 without pre-sieving and blocked by some glass wool. The column was activated at 250°C for 4 h under nitrogen flow before being put to the chromatographic test at 250°C. Distinct components were tested first for calibration and determination of elution times before the mixture was separated with or without water vapor.

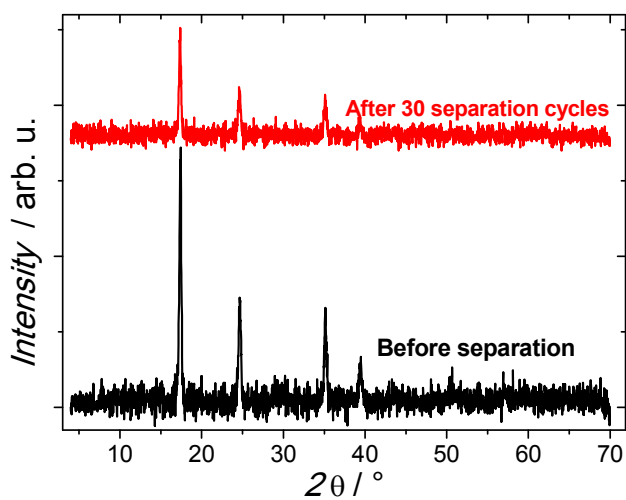
**Table S1:** Chemical composition and characterization of PBAs.

| Label | Formula                                                                                                           | $a / \text{\AA}$ | Particle size obtained from Scherrer's analysis (200) reflection / nm | $T_{\text{decomp.}} / ^\circ\text{K}$ |
|-------|-------------------------------------------------------------------------------------------------------------------|------------------|-----------------------------------------------------------------------|---------------------------------------|
| 1     | $\text{Co}[\text{Co}^{\text{III}}(\text{CN})_6]_{0.66}\square_{0.33} \cdot 5.2\text{H}_2\text{O}$                 | 10.16            | 45                                                                    | 563                                   |
| 2     | $\text{Cu}[\text{Co}^{\text{III}}(\text{CN})_6]_{0.66}\square_{0.33} \cdot 5.1\text{H}_2\text{O}$                 | 10.02            | 71                                                                    | 538                                   |
| 3     | $\text{Co}[\text{Fe}^{\text{III}}(\text{CN})_6]_{0.66}\square_{0.33} \cdot 4.65\text{H}_2\text{O}$                | 10.29            | 45                                                                    | 543                                   |
| 4     | $\text{Cs}_{0.74}\text{Co}[\text{Co}^{\text{III}}(\text{CN})_6]_{0.91}\square_{0.09} \cdot 3.6\text{H}_2\text{O}$ | 10.24            | 23                                                                    | 583                                   |
| 5     | $\text{K}_{0.96}\text{Co}[\text{Fe}^{\text{II}}(\text{CN})_6]_{0.74}\square_{0.26} \cdot 3.0\text{H}_2\text{O}$   | 10.09            | 29                                                                    | 553                                   |
| 6     | $\text{K}_{0.17}\text{Cu}[\text{Fe}^{\text{II}}(\text{CN})_6]_{0.54}\square_{0.46} \cdot 5.66\text{H}_2\text{O}$  | 10.00            | 33                                                                    | 503                                   |

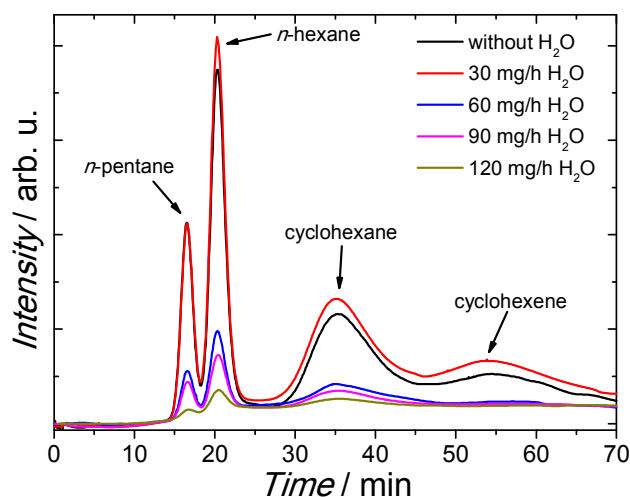
**Figure S1.** PXRD patterns of compounds **1 - 6** as synthesized (top) and after a dehydration (heating at 423 K) –rehydration cycle (bottom).



**Figure S2.** TGA analysis obtained with a 5°C/min heating rate for **1** – **6**.



**Figure S3.** PXRD patterns for **1** before and after hydrocarbons separation in humid conditions (50 RH, 200°C).



**Figure S4.** Chromatographic separation of humid hydrocarbons after 30 separation tests. The retention times are not modified after many chromatographic separations. The change in intensity is due to the dilution of the hydrocarbons mixture by water vapour (constant hydrocarbons flow = 30mg/h).

- [1] S.S. Kaye, J.R. Long, Hydrogen Storage in the Dehydrated Prussian Blue Analogues  $M_3[Co(CN)_6]_2$  ( $M = Mn, Fe, Co, Ni, Cu, Zn$ ), *J. Am. Chem. Soc.* 127 (2005) 6506–6507. doi:10.1021/ja051168t.
- [2] S.S. Kaye, J.R. Long, The role of vacancies in the hydrogen storage properties of Prussian blue analogues, *Catal. Today*. 120 (2007) 311–316. doi:10.1016/j.cattod.2006.09.018.
- [3] P. Trens, N. Tanchoux, A. Galarneau, D. Brunel, B. Fubini, E. Garrone, F. Fajula, F. Di Renzo, A macrothermodynamic approach to the limit of reversible capillary condensation., *Langmuir*. 21 (2005) 8560–4. doi:10.1021/la0507838.