

Electronic Supporting Information:

“Selective guest inclusion of linear C₆ hydrocarbons in a Zn(II) 1D coordination polymer”

Manfredi Caruso,^a Massimo Cametti,^a Kari Rissanen^b and Javier Martí-Rujas^{a,c}

a Department of Chemistry, Materials and Chemical Engineering “Giulio Natta”, Politecnico di Milano, Piazza L. da Vinci 32, 20133 Milan, Italy. E-mail: massimo.cametti@polimi.it, javier.marti@polimi.it.

b Department of Chemistry, University of Jyväskylä, Surfontie 9 B, FI-40014, Finland

c Center for Nano Science and Technology@Polimi, Istituto Italiano di Tecnologia, Via Pascoli 70/3, 20133 Milano, Italy

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Materials and Methods.

X-Ray Powder Diffraction Experiments

All the X-ray powder diffraction experiments were carried out using a Bruker D2-Phaser diffractometer equipped with Cu radiation ($\lambda = 1.54184 \text{ \AA}$) using Bragg-Brentano geometry. The experiments were performed at room temperature.

Single Crystal X-ray Diffraction

Single crystal data of **1·hexane** and **1·hexene** was recorded at the B13-XALOC beamline Macromolecular Crystallography beamline, Alba Synchrotron, Barcelona, Spain. The wavelength used was $\lambda = 0.82656 \text{ \AA}$ measured at 100 K. Data were indexed, integrated and scaled using the xia2 program with the DIALS pipeline for small molecule at the B13-XALOC Macromolecular Crystallography beamline. The structure was determined using direct methods (SHELXTL 97) and refined (based on F2 using all independent data) by full-matrix least-squares methods (SHELX 2014). All non-hydrogen atoms were located from different Fourier maps and refined with anisotropic displacement parameters. Hydrogen atoms were added in riding positions.

Single crystal X-ray data collection of **1·hexyne** was recorded with a Bruker X8 Prospector APEX-II/CCD diffractometer equipped with a microfocusing mirror (Cu-K α radiation, $\lambda = 1.54178 \text{ \AA}$) at low temperature (100 K).

Thermogravimetric Analysis (TG)

Thermogravimetric analysis was carried out using a Perkin Elmer Thermal Analysis instrument the Laboratorio Analisi Chimiche at the Dipartimento di Chimica, Materiali ed Ingegneria Chimica, Politecnico di Milano. Microcrystalline samples of **1·hexane**, **1·hexene** and **1·hexyne** obtained via solid/liquid reaction were heated within the 30 °C to 400 °C temperature range with a heating rate of 10 °C/min under N $_2$.

Synthesis of coordination polymer **1**

Microcrystalline CP **1** was synthesized according to a previously reported procedure.²

Briefly, 100 mg (0.22 mmol) of ligand **L** were suspended in 4 mL of CH $_3$ CN. To this suspension, a solution of ZnI $_2$ (71.8 mg, 1 Eq) in 1 mL of CH $_3$ OH was rapidly added and the mixture was vigorously stirred for 5 minutes. The resulting precipitate was collected by filtration and washed with CH $_3$ CN affording CP **1** as a white crystalline powder (174 mg, quantitative yield).

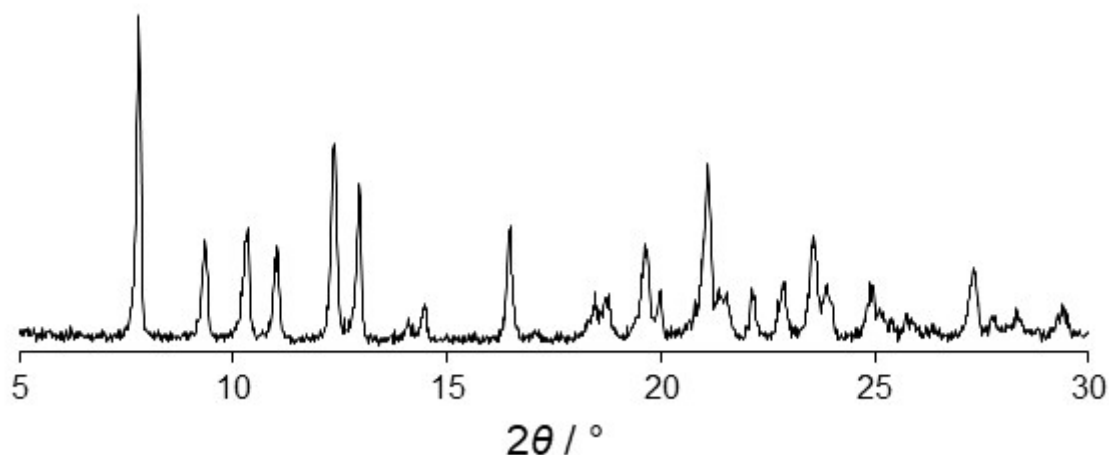


Figure S1. Powder XRD of the as synthesized CP **1**.

General procedure for gas/solid adsorption experiments using hexane, 1-hexene and 1-hexyne.

75 mg (0.1 mmol) of CP **1** were dried under dynamic vacuum for 6 h and then put onto a flat glass support and into a reaction chamber (of ca. 200 mL volume). Then, vials containing ca. 2 mL of each guest (hexane, 1-hexene or 1-hexyne) were added into the chamber which was then tightly sealed. After 24 h, the powder was removed from the chamber, left in open air under ambient conditions, and sampled at different times (4 h, 24 h, 168 h, 336 h).

For the competitive adsorption 100 mg of CP were exposed to *ca.* 1.5 mL of each guest (**1**·hexane, **1**·hexene and **1**·hexyne).

General procedure for gas/solid adsorption experiments using 1-hexyne, 2-hexyne and 3-hexyne.

75 mg (0.1 mmol) of CP **1** were dried under dynamic vacuum for 6 h and then put onto a flat glass support and into a reaction chamber (of ca. 200 mL volume). Then, vials containing ca. 1.5 mL of each guest were added into the chamber which was then tightly sealed. After 24 h, the powder was removed from the chamber, left in open air, and sampled at different times (4 h, 24 h, 168 h, 336 h).

General procedure for solid/liquid (dipping) adsorption experiments using hexane, 1-hexene and 1-hexyne.

75 mg (0.1 mmol) of CP **1** were dried under dynamic vacuum for 6 h and then put in glass chamber (of ca. 200 mL volume). CP **1** (25 mg) were immersed in 3 vials containing each vial ca. 2 mL of hexane, 1·hexene and 1·hexyne was added and the vials were tightly capped. After 24 h, the powders of each vial were filtered and used for TG analysis.

NMR sample preparation procedure

10 mg of the powder sample were introduced in an NMR tube and 500 mL of DMSO-d₆ were added. To the suspension 10 mL of a 4.5 mM solution of CH₃NO₂ in DMSO-d₆ were added.

From a previous study we found that the thermal disruption of CP is not needed for the complete released of the guest in DMSO-d₆.

NMR spectra were recorded at 305 K in a Bruker Advanced 400 (400 MHz, SW= 14 ppm, NS= 16).

The R factor, defined as the molar ratio between the solvent guest molecules and L·ZnI₂ units, was calculated according to the following equation:

$$R_{\text{Solvent Guest}} = \frac{\text{moles of solvent guest}}{\text{moles of L} \cdot \text{ZnI}_2 \text{ units}} = \frac{\text{Volume} \cdot [\text{solvent guest}]_{\text{NMR}}}{(mg_{\text{tot}} - MW_{\text{solvent guest}} \cdot \text{Volume} \cdot [\text{solvent guest}]_{\text{NMR}})}$$

Where:

- Volume= volume of the DMSO-d₆ used (500 mL + 10 mL of internal standard)
- [solvent guest]_{NMR}= concentration of the guest solvent as measured by ¹H-NMR by comparison of the integral value of an internal standard (Nitromethane)
- mg_{tot}= total amount of the material weighted (10 mg)
- MW_{solvent guest}= molecular weight of the solvent guest
- MF_{L·ZnI₂ units}= formula weight of the L·ZnI₂ unit

Single crystal X-ray data of 1·hexane.

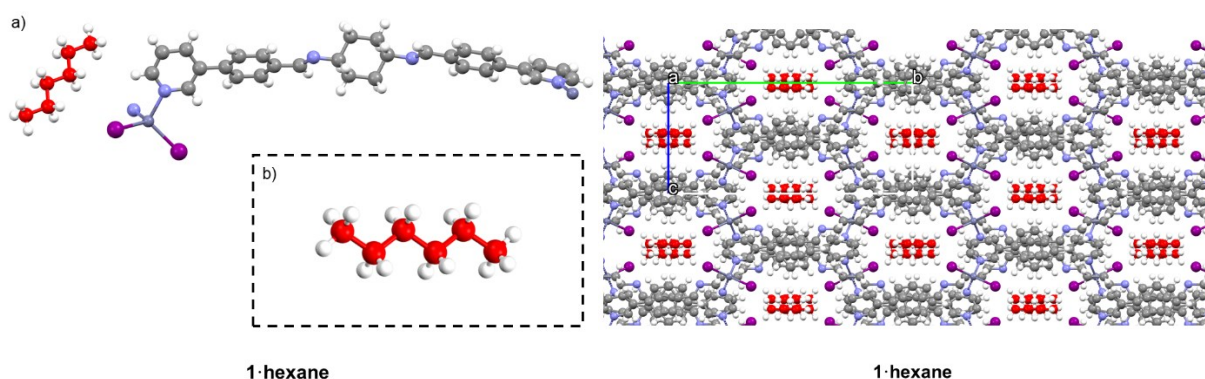


Figure S2. Structure solution for guest hexane in 1·hexane.

Single crystal X-ray data of 1·hexene.

The indexing procedure gave a new unit cell with the following parameters: $a = 14.63140(10) \text{ \AA}$, $b = 22.4021(2) \text{ \AA}$, $c = 10.88550(10) \text{ \AA}$; $V = 3567.98 (\times) \text{ \AA}^3$ for the hexene sample therefore the changes occur in the b -axis which increases ($\Delta 0.254 \text{ \AA}$) following an expansion, whereas the c -axis is the one that suffers a compression ($\Delta -0.204 \text{ \AA}$) as in the 1·TCM to 1·hexene SCSC transformation.

SQUEEZE calculation for:

1·hexene:

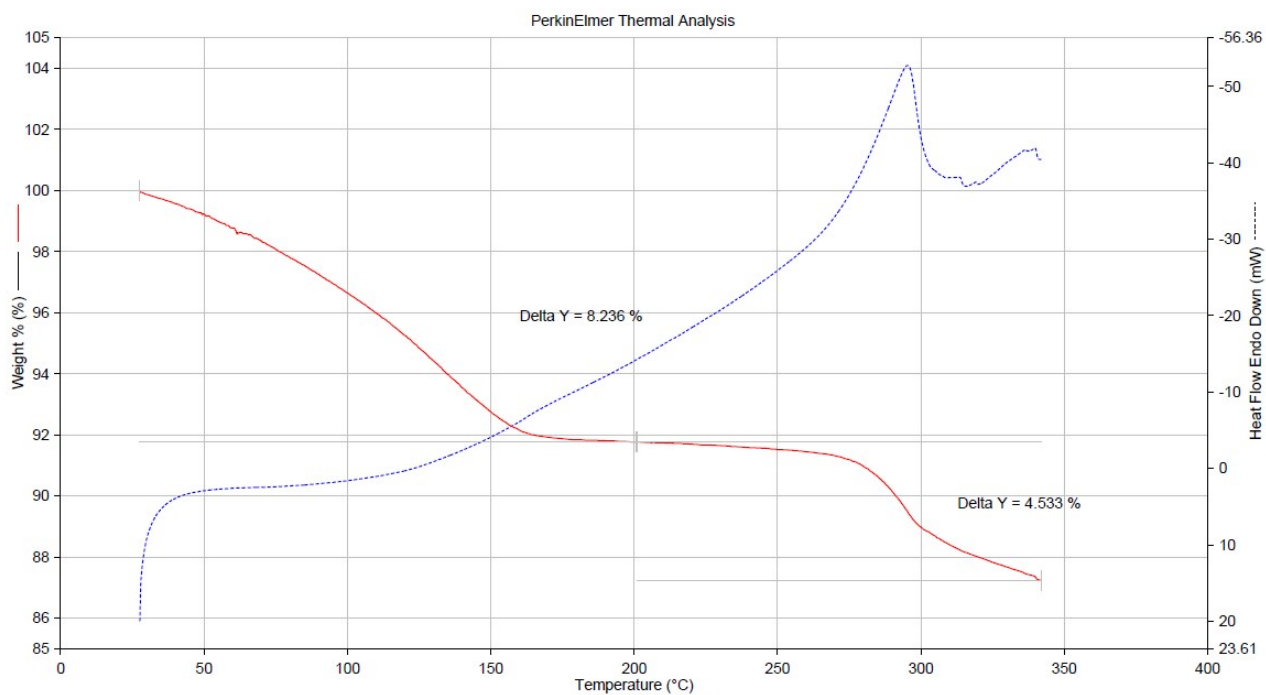
The obtained electron count (320 e, hexene has 48 electrons) in the whole unit cell corresponds to $320/48 = 6.67$ molecules of hexene in the unit cell. The cavity volume vs. molecular volume calculation, as following the Rebek's 55% rule, gives that one hexene molecule will take $121 \text{ \AA}^3/0.55 = 220 \text{ \AA}^3$. (CHCl_3 takes 136). The volume of the void space in the unit cell is 980 \AA^3 , thus $980 \text{ \AA}^3/220 \text{ \AA}^3 = 4.45 = 4.5$ hexene molecules in the unit cell. This value should be compared to the 6.67 molecules obtained by the electron count. As the electron count is too high, there has to be CHCl_3 too. A rough best fit calculation gives a minimum of 2.5 CHCl_3 and a maximum of 3 hexenes in a unit cell, giving an e count of 294 and a needed volume of 1000 \AA^3 .

1·hexyne:

The obtained electron count (276 e, hexyne has 46 electrons) in the whole unit cell corresponds to $276/46 = 6$ molecules of hexyne in the unit cell. The cavity volume vs. molecular volume calculation, as following the Rebek's 55% rule one, gives that 1-hexyne molecule will take $118 \text{ \AA}^3/0.55 = 215 \text{ \AA}^3$. (CHCl_3 takes 136 \AA^3). The volume of the void space in the unit cell is 896 \AA^3 , thus $896 \text{ \AA}^3/215 \text{ \AA}^3 = 4.2 = 4$ hexyne molecules in the unit cell. This value should be compared to the 6 molecules obtained by the electron count. As the electron count is too high, there has to be CHCl_3 too. A rough best fit calculation gives a minimum of two CHCl_3 and a maximum three 1-hexynes in the unit cell, giving an e count of 288 and volume of 917 \AA^3 .

In summary, in both SC structures, there is too much electron density in the cavities to be consistent with hexene or hexyne, only, to be included. A partial exchange must have been occurred.

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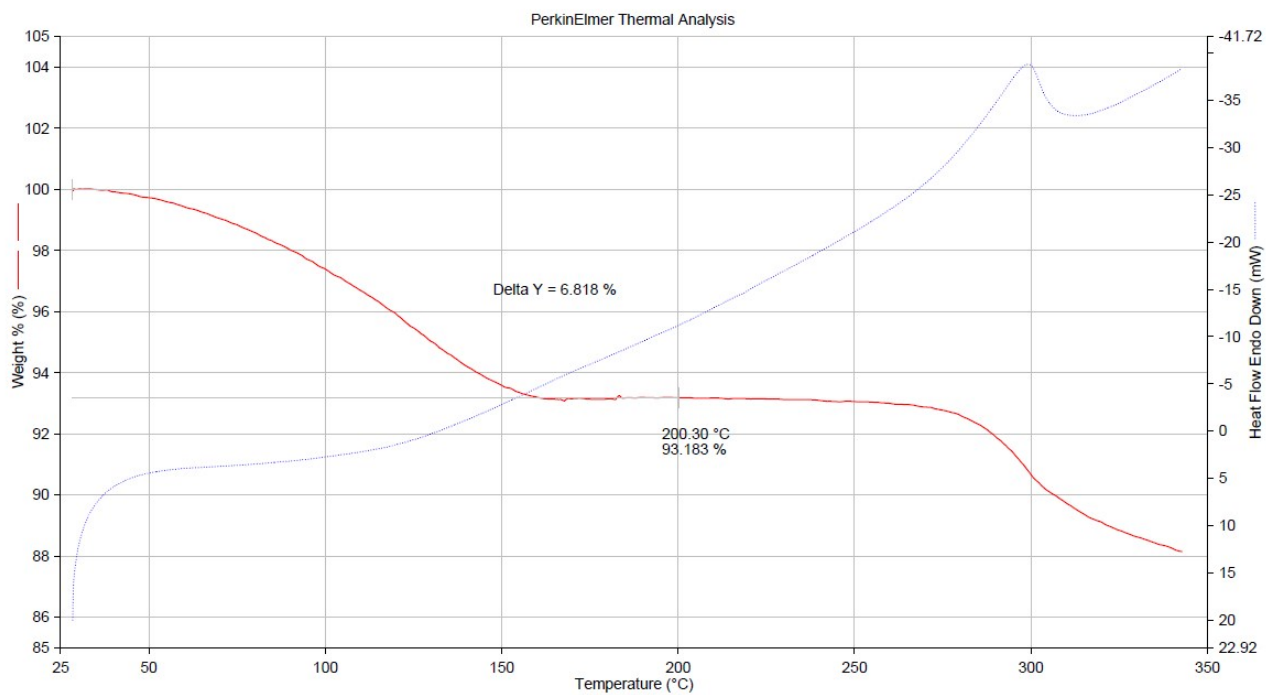


1) Heat from 30.00°C to 350.00°C at 10.00°C/min

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Figure S3. TG of microcrystalline **1**·hexane.

Filename: Y:\...LAC 13505 - CH494 Hexene Dipping.stad
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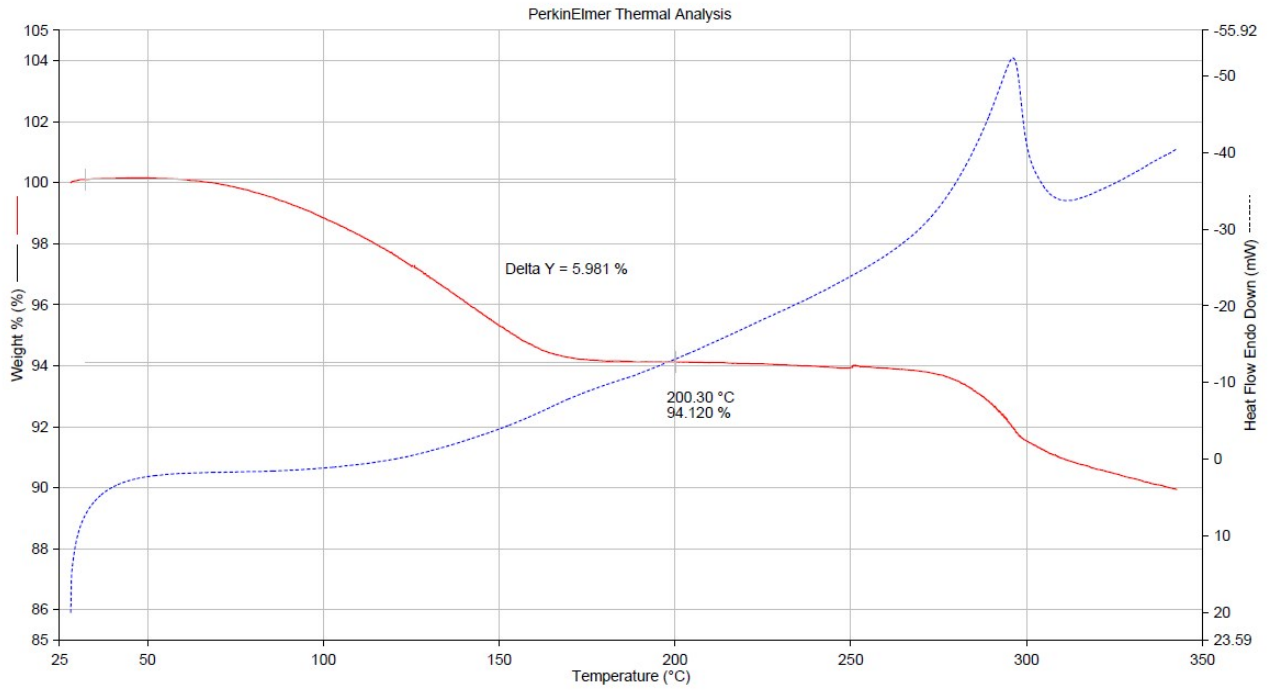


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1) Heat from 30.00°C to 350.00°C at 10.00°C/min

Figure S4. TG of microcrystalline **1**·hexene.

Filename: Y:\DATI PK...LAC 13506 - CH494 Hexine.stad
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1) Heat from 30.00°C to 350.00°C at 10.00°C/min

Figure S5. TG of microcrystalline **1**·hexyne.

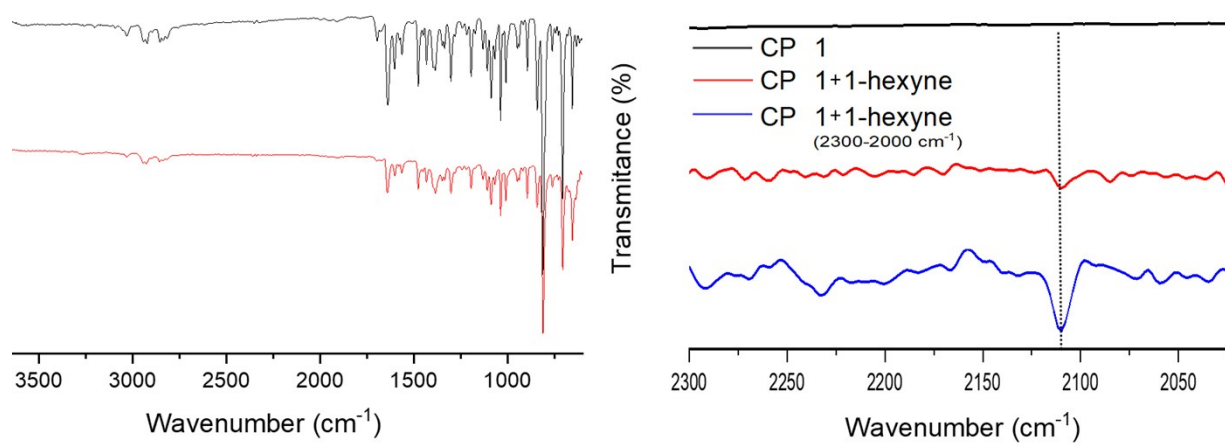


Figure S6. ATR-FTIR of CP **1** (black), **1**·**hexyne** (400-3600 cm⁻¹ spectral window acquisition) (red), and **1**·**hexyne** (2000-2300 cm⁻¹ spectral window acquisition) (blue).

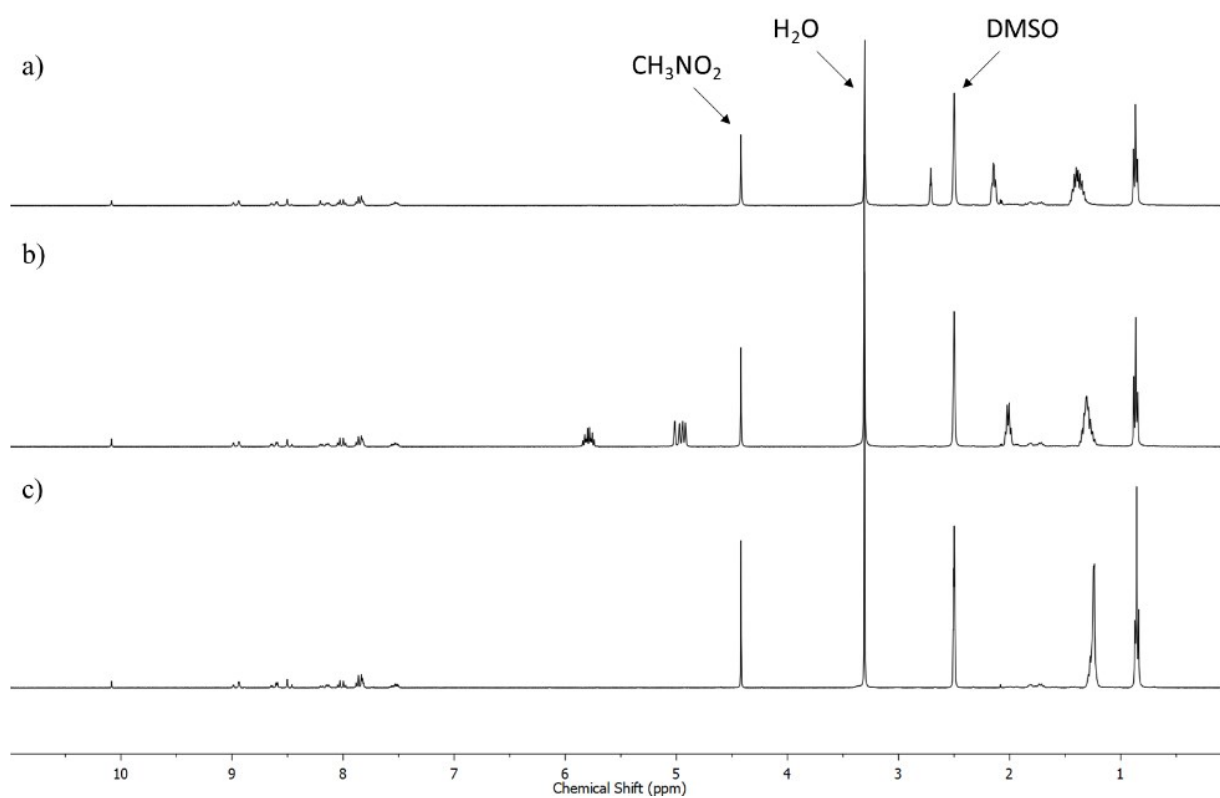


Figure S7. $^1\text{H-NMR}$ characterization in DMSO-d_6 of CP 1 containing a) hexane, b) 1-hexene, and c) 1-hexyne guests after exposure to open air for 4 h.

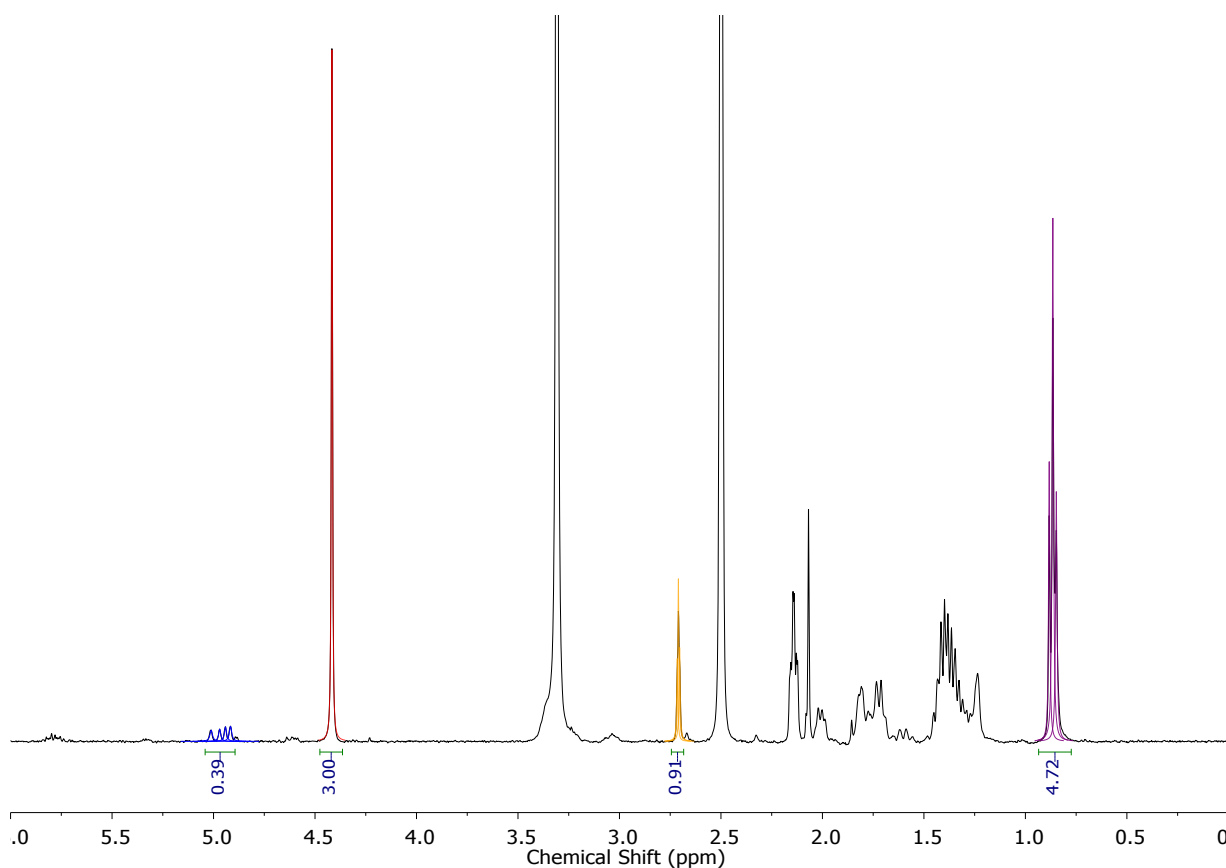


Figure S8. ¹H-NMR characterization in DMSO-d₆ of the CP containing hexane, 1-hexene, and 1-hexyne after competitive exposure for 24 h and being left in open air for 4 h. Characteristic peaks, considered for the calculation of the *R* factors, were colored as followed: nitromethane red, 1-hexene blue, 1-hexyne orange, 1-hexane purple (the area corresponding to hexane peak was calculated by difference with those of 1-hexene and 1-hexyne).

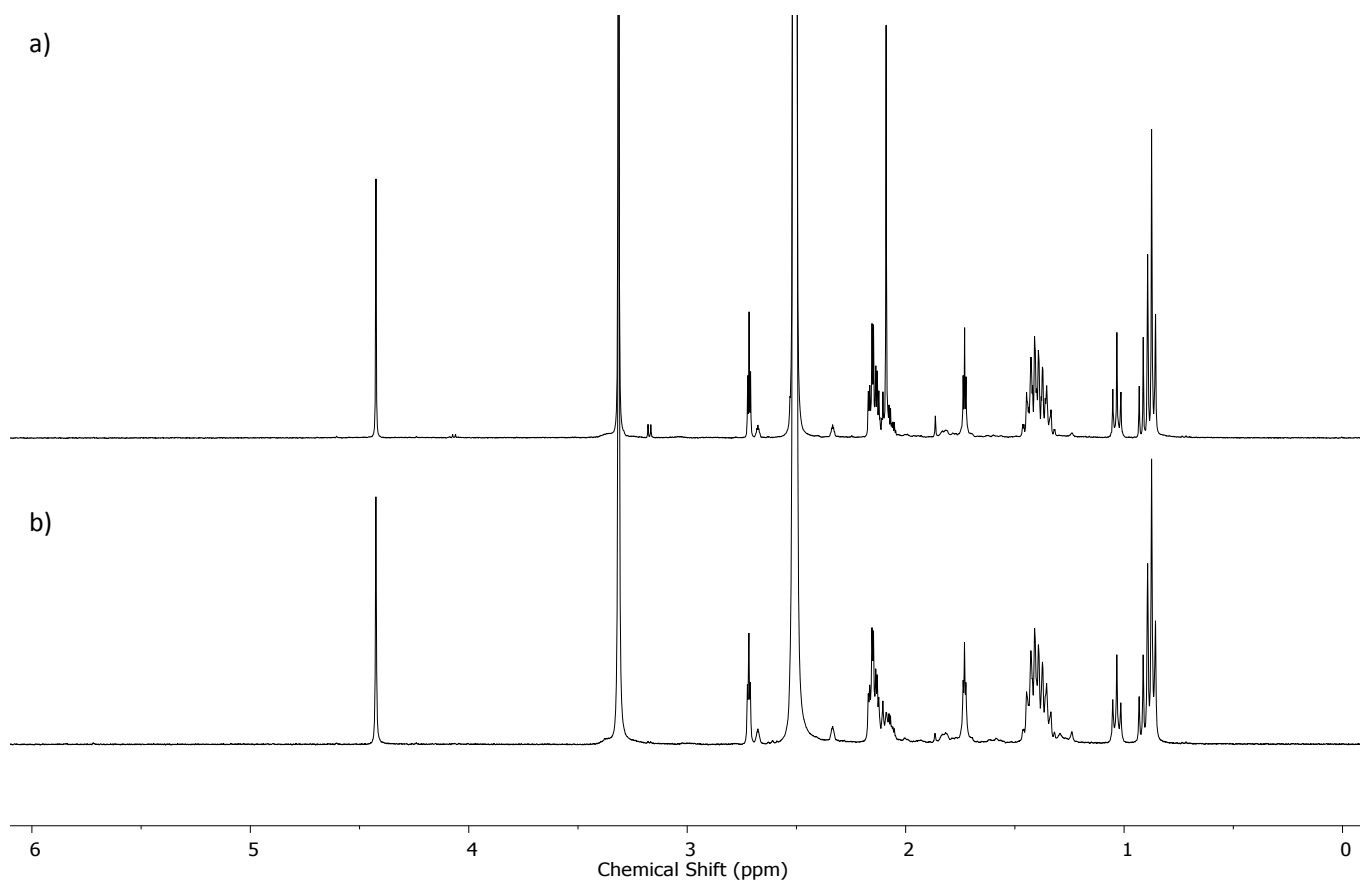


Figure S9. $^1\text{H-NMR}$ characterization in DMSO-d_6 of CP **1** containing 1-hexyne, 2-hexyne, and 3-hexyne after exposure to open air for a) 4 h, b) 48 h.