

Direct visualization of pyrrole reactivity by confined oxidation in a Cyclodextrin Metal-Organic Framework

Alejandro Nuñez-Lopez, Marta Galbiati, Natalia M. Padial, Carolina R. Ganivet, Sergio Tatay, Emilio Pardo, Donatella Armentano, Carlos Martí-Gastaldo*

Metal-Organic Frameworks can be used as porous templates to exert control over polymerization reactions. Here we show the possibilities offered by these crystalline, porous nanoreactors to capture highly-reactive intermediates for a better understanding of the mechanism of polymerization reactions. By using a cyclodextrin framework we are capable of restricting the polymerization of pyrrole to a low-degree, capturing the formation of terpyrrole cationic intermediates. Single-crystal X-Ray diffraction is used to provide definite information on the supramolecular interactions that induce the formation and stabilization of a conductive array of cationic complexes.

Metal-Organic Frameworks (MOFs) are crystalline, porous materials built from the interconnection of metal ions or clusters and organic linkers to produce porous architectures. MOFs found rapid application in gas storage and separation thanks to their unlimited chemical/structural versatility combined with a fine control over their porosity metrics.^[1] Compared to other porous materials like layered clays, zeolites, sol-gel matrices or polymers, these metal-organic scaffolds also offer important advantages when used as functional hosts to encapsulate molecules.^[2] For instance, as beautifully illustrated by the pioneering work of Kitagawa, Uemura and co-workers,^[3,4] the micro/nanoporous channels in these materials can be tailored to template the docking of monomers and confine polymerization reactions. In this way, the size, shape and morphology of the empty channels, together with their dimensionality and surface chemistry, can be effectively used to gain control over the molecular weight, stereoregularity, composition or sequence of the resulting polymers.^[5]

These works confirm the direct influence of MOFs over polymerization reactions when used as templates, either from restricting the packing of monomer guests to a confined nanospace or by chemical interaction with the groups decorating the surface of the pores. However, these experiments are generally limited to microcrystalline powders and do not enable direct visualization of monomer reactivity inside the channels of

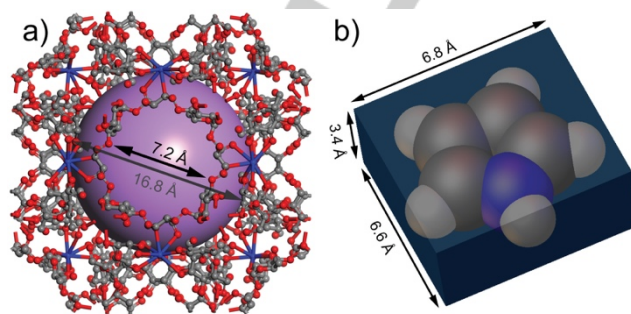


Figure 1. a) Structure of CD-MOF-2 featuring mesoporous cavities of 16.8 Å (purple sphere) interconnected in the solid by pore windows of 7.2 Å b) Dimensions of pyrrole. See S3 for details.

the MOF. As result, the structural information on the chemical and geometrical principles that dictate the assembly of the polymer for specific packing modes, local environments or conformations is often missing. This is in turn, inferred indirectly from the properties of the resulting polymers. We argued that translating this same concept to single crystal studies would be ideal for evaluating unambiguously the effect of the supramolecular interactions or geometrical restrictions (pore size and shape) imposed by the framework over the chemical reactivity of loaded monomers. Our work goes one step further in this regard and demonstrates the possibilities of MOF crystalline nanoreactors to capture highly-reactive intermediates for a better understanding of the mechanism of polymerization reactions. We make use of cyclodextrin (CD) metal-organic framework Rb-CD-MOF (or CD-MOF-2) to control the reactivity of redox-active pyrrole (Py) monomers by confining its chemical polymerization to 3D nanochannels. Compared to uncontrolled polymerization in solution, the use of a framework as host-guest template restricts the mobility and reactivity of pyrrole by supramolecular pinning of the confined monomers to enable the formation and stabilization of terpyrrole (Tpy) cations.

Rb-CD-MOF can be prepared as millimetre-size, colourless crystals by direct reaction of RbOH and CD.^[6] Rb-CD-MOF crystals have already proven to be robust enough to retain their original crystallinity upon impregnation of molecular guests or formation of metal nanoclusters inside their channels.^[7-9] This robustness was expected to simplify the crystallographic study and physical characterization. Previous works also confirm the ability of CDs to stabilize Py molecules by forming supramolecular inclusion complexes that can be then used as precursors for chemical polymerization.^[10] As shown in **Figure 1**, the structure of Rb-CD-MOF is based on the interconnection of (γ -CD)₆ units that adopt a body-centered cubic packing. This results in the intersection of 1D channels in the three crystallographic directions with internal cavities and pore windows of 16.8 and 7.2 Å, respectively, big enough to accommodate Py molecules (6.8 Å x 6.6 Å x 3.4 Å).^[6] We expected this 3D porous architecture to avoid the diffusion impediments intrinsic to 1D and 2D dimensionalities.

[*] A. Nuñez-Lopez, Dr. M. Galbiati, Dr. N. M. Padial, Dr. Carolina R. Ganivet, Dr. S. Tatay, Dr. E. Pardo, Dr. C. Martí-Gastaldo Instituto de Ciencia Molecular (ICMol), Universitat de València Paterna 46980, València (Spain)
E-mail: carlos.marti@uv.es

Dr. N. M. Padial (current address)
Department of Chemistry
The Scripps Research Institute
10550 North Torrey Pines Road
La Jolla, California, 92037 (United States)

Dr. D. Armentano
Dipartimento de Chimica e Tecnologie Chimiche
Università della Calabria
87030, Cosenza (Italy)

Supporting information for this article is given via a link at the end of the document.

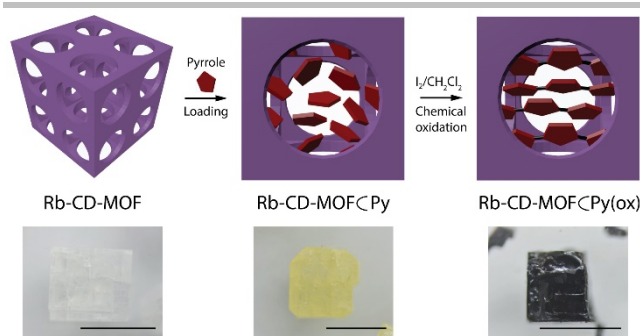


Figure 2. Schematic representation of the loading and chemical oxidation of pyrrole monomers within Rb-CD-MOF mesopores. The bottom panel shows the colour changes in the crystals of the MOF for the different stages of the process. Scale bars correspond to 250 μm .

Rb-CD-MOF crystals were synthesized by vapor diffusion of MeOH in an aqueous solution of RbOH and γ -CD, with slight modifications to the reported procedure.^[6] As-made crystals were thoroughly washed with MeOH and exchanged with CH_2Cl_2 . We used anhydrous solvents to avoid damage to the crystals, which were then stored in a glove box prior to be used. **Figure 2** summarizes the steps followed to study the reactivity of Py after MOF loading. Commercial grade pyrrole was distilled in vacuum (**Figure S1**), protected from light and stored under inert atmosphere. Solvent exchanged Rb-CD-MOF crystals were immersed at room temperature under static conditions in a pyrrole/ CH_2Cl_2 solution (30 % v/v) for 72 hours. The loading was carried out in the glove box by using freshly distilled Py and anhydrous solvents to prevent partial oxidation. The excess of Py was removed by thorough washing in CH_2Cl_2 . Loading of the monomer was preliminary identified by the change in colour of the crystals, from colourless to yellow, consistent with the presence of a few of the representative bands of Py in the FT-IR spectrum (**Figure S2**). Rb-CD-MOF@Py was fully dissolved in DMSO- d_6 . ^1H NMR spectra confirms the presence of CD@Py inclusion complexes in solution with an upfield shift of 0.038 ppm in H_b and H_e protons and 0.066 ppm in H_c and H_d protons of Py, compared to the free monomer, as result of the chemical interaction with CD (**Figure S3**).^[10] We estimated a total content of close to 12 Py molecules per unit formula of Rb-CD-MOF with NMR (**Figure S4**). This value is quite close to the theoretical uptake capacity calculated by Monte Carlo in Materials Studio R2.

Previous works report that polypyrrole (PPy) can be synthesized *in-situ* by oxidative polymerization reaction of Py monomers loaded into Cu(II) and Fe(III) redox-active

frameworks^[11,12] In our case, soaking of Rb-CD-MOF@Py in organic solutions of these metals at variable concentration always led to uncontrolled oxidation and irreversible damage to the crystals for a complete loss of crystallinity. We discarded this route and chose to use a mild oxidant such iodine as auxiliary oxidizing agent. This two-step strategy has proven to be more respectful with the crystallinity of inclusion compounds upon chemical oxidation.^[13,14] Accordingly, freshly prepared Rb-CD-MOF@Py crystals were soaked in a solution of iodine in dichloromethane (0.05 M) at 4 $^\circ\text{C}$ for 72 hours. Whereas reaction at 4 $^\circ\text{C}$ proceeded with no changes to the size or shape of the crystals (**Figure 2**), when the same experiment was conducted at room temperature we identified significant morphological damage likely due to more favourable conditions for the polymerization reaction. After 24 hours, chemical oxidation in the inclusion compound was evidenced by the black colour of Rb-CD-MOF@Py(ox) crystals. The reaction was maintained for 72 hours and the excess of iodine in Rb-CD-MOF@Py(ox) was washed off several times with aliquots of fresh solvent.

For a first analysis of the product of the reaction, we attempted to dissolve the crystals in DMSO- d_6 . They formed a black solid upon dissolution that was isolated by filtration. ^1H NMR spectra of the solution only displays signals from γ -CD, confirming the absence of unreacted pyrrole molecules (**Figure S5**). The solid-state ^{13}C magic angle spinning (MAS) NMR of the solid confirms the presence of a broad α carbon signal at 128.5 ppm indicative of the formation of cationic polypyrrole (**Figure S6**).^[13] The ^{13}C CP-MAS spectrum of Rb-CD-MOF@Py(ox) crystals is dominated by γ -CD with a very feeble signal associated to the product of the oxidation, preventing more detailed analysis of host-guest interactions (**Figure S7**).^[14] The thermogravimetric analysis (TGA) of Rb-CD-MOF before and after the pyrrole loading displays a weight loss (6%) at 180 $^\circ\text{C}$, below that corresponding to the decomposition of the framework, indicative of the filling of the pores with organic molecules. Rb-CD-MOF@Py(ox) presents a higher mass loss at low temperatures due to sublimation of iodide and also shows a significant mass loss at higher temperatures that can be linked to the presence of occluded iodide in the crystals that form RbI, which sublimates close to 650 $^\circ\text{C}$ (**Figure 3b**). N_2 adsorption isotherms were used to confirm the effect of Py loading and oxidation over the porosity of the material (**Figure 3c**). Rb-CD-MOF displays a BET surface area of 882 m^2/g , consistent with the reported value,^[6] that is reduced to 286 m^2/g after Py impregnation in Rb-CD-MOF@Py. In turn, chemical oxidation leads to complete loss of porosity probably due to the polymerization of Py in the pores combined

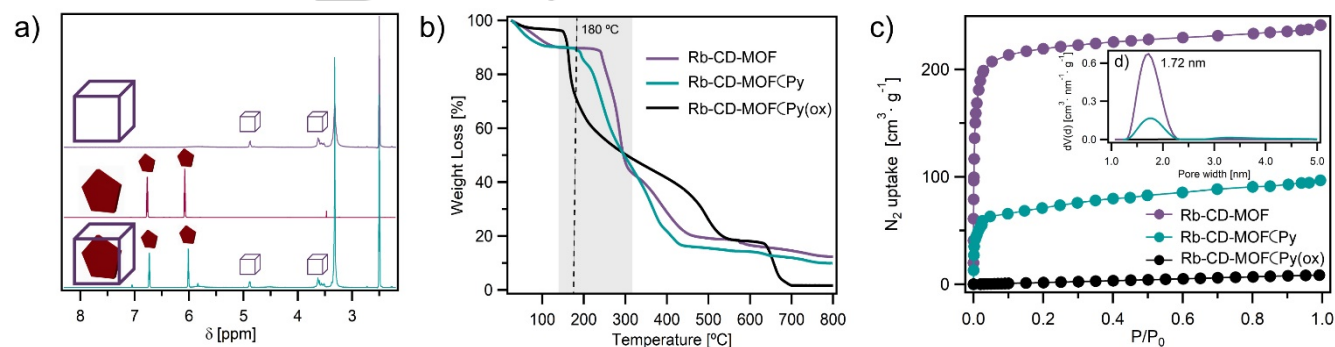


Figure 3. a) ^1H NMR of Rb-CD-MOF (purple), distilled pyrrole (maroon) and Rb-CD-MOF@Py (green). b) TGA profiles and c) N_2 adsorption isotherms of Rb-CD-MOF, Rb-CD-MOF@Py and Rb-CD-MOF@Py(ox) (black). d) Pore size distribution using density functional theory of c).

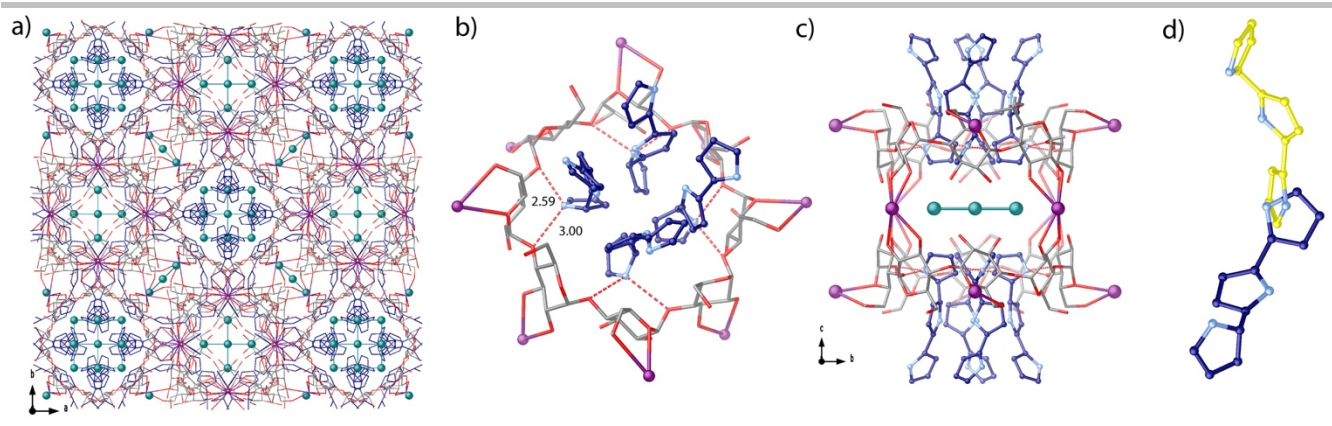


Figure 4. Views of different sections of the structure of **Rb-CD-MOFcTpy** determined by single-crystal X-Ray diffraction. a) View along the crystallographic *c* axis of a portion of the 3D **Rb-CD-MOFcTpy** crystal structure. b) Perspective views along the crystallographic *c* axis of the approximately spherical pores, located at the center of each $(\gamma\text{-CD})_6$ cube, filled by $[\text{TPy}]^+$ cations with details of host-guest interactions. c) Perspective view along the crystallographic *a* axis of the $[\text{TPy}]^+$ moieties; d) Perspective view of the observed crystallographic disorder for $[\text{TPy}]^+$ cations. Rubidium, nitrogen and iodine atoms are represented by purple, sky blue and green spheres respectively. Carbon atoms of the $[\text{TPy}]^+$ guests are depicted as blue spheres, whereas oxygen and carbon atoms from γ -cyclodextrin ligands are simplified as red and grey sticks. Free water solvent molecules are omitted for clarity. The yellow carbon atoms in figure d) highlight the two possible orientations of the guests.

with the inclusion of iodide anions formed during the oxidation. The analysis of the pore size distribution (PSD) by using density functional theory (DFT) shows that the cumulative pore volume corresponding to the mesoporous cages in the MOF centered at 1.72 nm, drop from 0.342 to 0.137 $\text{cm}^3\cdot\text{g}^{-1}$ after Py loading and down to 0.006 $\text{cm}^3\cdot\text{g}^{-1}$ after exposure to I_2 . PSD changes confirm that the fraction of empty space available for the diffusion of the oxidant in Rb-CD-MOFcPy is lost after the reaction (**Figure 3d**).

For a better understanding of the mechanism controlling the oxidative polymerization of confined Py we next studied crystals of Rb-CD-MOFcPy(α) by using single crystal X-Ray diffraction (SC-XRD). As shown in **Figure 4**, the structure of Rb-CD-MOF is robust enough to resist the oxidation of pyrrole with I_2 and undergoes a single-crystal to single-crystal (SCSC) transformation. In good agreement with our analysis of the bulk, density maps and structural analyses confirm the oxidation of the included Py to generate Rb-CD-MOFcTpy, that combines cationic terpyrrole (TPy) units and I_3^- anions in the pores of the solid (**Figures 4a** and **S10**). In accordance with BET and PSD analysis, the channels are almost entirely filled by these ionic molecular guests that account for close to 92% (13464.3 \AA^3) of the empty volume available. Similar to previous crystallographic studies analyzing confined chemical transformations in MOFs,^[15,16] the guests molecules suffer from a certain structural disorder that was restrained in the refinement (see Supporting Information for details).

Rb-CD-MOFcTpy retains the chiral *I*432 space group intrinsic to Rb-CD-MOF, that is built from the interconnection of $(\gamma\text{-CD})_6$ units and Rb(II) centers to conform a 3D solid with a body-centered cubic packing (**Figure 4a**). Crystals of Rb-CD-MOFcTpy are isomorphous to the parent material confirming the preservation of the network after loading and chemical oxidation. Unlike other indirect techniques, SC-XRD enables direct visualization of the formation of $[\text{TPy}]^+$ cations formed by the oxidative coupling of 3 Py units through 2,5-positions in the heterocycle. This intermediate is consistent with the mechanism generally accepted for the formation of polypyrrole by electropolymerization.^[17] However, the formation of such trimers during chemical oxidative polymerization reactions was unclear until now. $[\text{TPy}]^+$ cations and counterbalancing I_3^-

anions occupy the large spherical pores at the center of each $(\gamma\text{-CD})_6$ cube, and are stabilized by either ionic or supramolecular interactions (**Figure 4b,c**). The quality of the diffraction data evidence that, even though the crystallinity is maintained upon oxidative SCSC, $[\text{TPy}]^+$ molecules inherit a statistical disorder between two positions symmetrically related (**Figure 4d**). It is worth noting that the uncertainty of the X-Ray analysis makes difficult to exclude the formation of pentapyrrole $[\text{Py}_5]^+$ oligomers (with positional disorder on the central ring) even though $[\text{TPy}]^+$ units are by far the most probable resolution due to several reasons (see Crystallographic section in Supporting Information). This ambiguity was ruled out with MALDI-TOF after digestion of the crystals, by confirming the presence a strong peak at at m/z 199.11 in excellent agreement with the formation of cationic terpyrrole (**Figure S8**). The high reactivity of this cation in solution prevented its quantification by NMR (**Figure S9**). The two possible orientations of $[\text{TPy}]^+$ are grasped to the framework by the formation of bifurcated H-bonds between -NH groups of the terminal Py unit and the acetal oxygen bridges from the primary face of $\gamma\text{-CD}$ with $\text{N}\cdots\text{O}$ distances of 2.59(2) and 3.00(2) \AA (**Figure 4b-c** and **S10b**). Compared to this same interaction in the inclusion compound $\alpha\text{-CD/Py}$, 3.16(4) \AA ,^[10] the shorter distances in Rb-CD-MOFcTpy suggest more polar interactions for a stronger stabilization of the guest. This network of host-guest H-bond interactions, together with the limited number of confined Py molecules, is possibly the main responsible of restricting the polymerization of Py. The formation 4 $[\text{TPy}]^+$ cations per unit cell in Rb-CD-MOFcTpy agrees well with the 12 Py units estimated by NMR for Rb-CD-MOFcPy, confirming that the final product is formed exclusively by reorganization of the monomers loaded. A control experiment was used to discard the ability of free $\gamma\text{-CD}$ to produce similar results (**S6**). This is a striking difference with other porous hosts like mesoporous zeolites^[18] or microporous MOFs based on aromatic linkers,^[11,12,19,20] for which oxidation always proceeds completely until the formation of polypyrrole with changes to its dimensionality and polydispersity modulated by the template. In this case, the incorporation of CD rings to the surface of the channels provides a periodic distribution of conical cavities with a hydrophobic interior rich in -OH H-bond acceptor groups. These recognition sites are very effective in restraining the

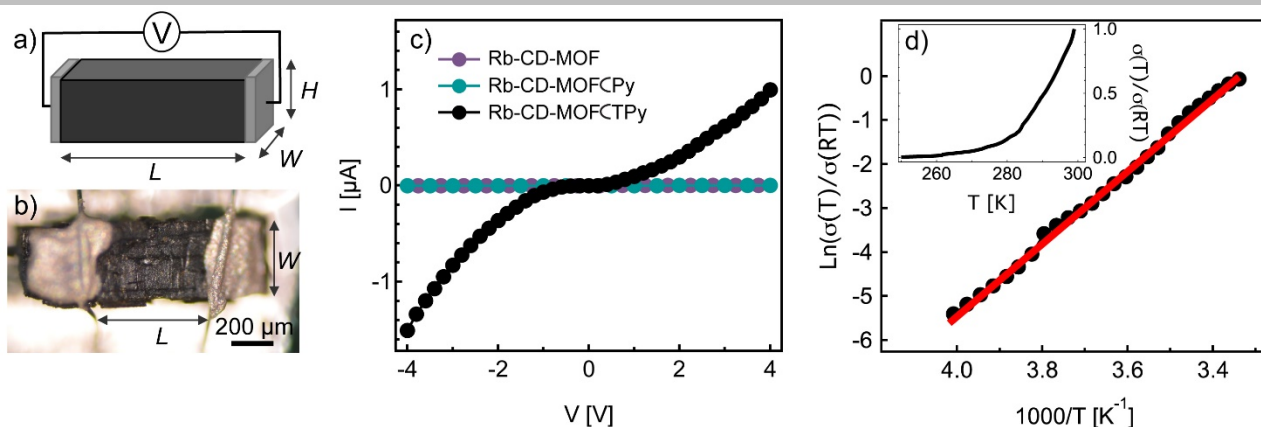


Figure 5. a) Scheme of electrical measurement in a two-probe configuration. b) Optical microscope image of a single crystal of Rb-CD-MOF_cTPy contacted with silver paint. c) I-V curves of Rb-CD-MOF (purple), Rb-CD-MOF_cPy (green) and Rb-CD-MOF_cTPy (black) at room temperature. d) $\text{Ln}(\sigma(T)/\sigma(RT))$ of Rb-CD-MOF_cTPy plotted as a function of the inverse of the temperature at a bias voltage of 1 V. Conductivity was calculated by estimating dimensional parameters from optical microscope images and approximating the crystal as rectangular structures. The activation energy (E_a) was calculated from the slope of the linear fit at room temperature. Inset shows the $\sigma(T)/\sigma(RT)$ as a function of temperature.

mobility and reactivity of the encapsulated Py monomers, that can only polymerize at a limited degree for the formation of the reactive intermediate $[\text{TPy}]^+$ that is also stabilized in the channels by supramolecular interactions. I_3^- molecular anions also display statistical disorder with some iodine atoms (I_2 and I_4) modelled on two sites with a half each other occupancy factors (**Figures S10-S12** in Supporting Information for further details). The average bond length within each crystallographically distinct I_3^- anion, 2.85 Å, agrees well with the value reported.^[21]

The impregnation and oxidative polymerization of pyrrole or thiophen is an effective strategy to endow insulating MOFs with extrinsic electrical conductivity, simply by backfilling the pores with the conducting polymers generated in-situ.^[11,12,19,20,22] Oxidation generally leads to morphological damage, that results in polycrystalline samples often amorphous. As a result, previous works on extrinsically conductive MOFs make use of pressed pellets to collect electrical measurements. However, Rb-CD-MOF crystals are hundreds of μm wide and robust enough to withstand SCSC transformation and can be directly contacted to minimize the influence of grain boundaries in the conductivity measurements. To investigate the effect of short-range polymerization over the conductivity of the inclusion compound, we measured the electrical conductivity of Rb-CD-MOF, _cPy and _cTPy single crystals by using a two-probe contacts method (**Figure 5a**).

Single crystals of the three materials were contacted by hand with conductive silver paint and measured at a base pressure of 7 torr in a Physical Properties Measurements System (PPMS) (**Figure 5b**). The first set of data collected proved the importance of using a controlled water-free atmosphere to collect reproducible measurements. **Figure 5c** shows a comparison of the I-V curves collected for all the crystals up to 4 V. As expected, Rb-CD-MOF and Rb-CD-MOF_cPy behave as insulators with conductivities in the range of $10^{-12} - 10^{-11} \text{ S cm}^{-1}$. In turn, Rb-CD-MOF_cTPy displays a million-fold enhancement of the electrical conductivity up to $5 \cdot 10^{-6} \text{ S cm}^{-1}$. Previous works on the oxidative synthesis of polymers by using MOFs as templates report a broad dispersion of conductivity values between 10^{-6} and $10^{-1} \text{ S cm}^{-1}$, depending on the dimensionality of the polymer and the characteristics of the MOF.^[10,18,19] The conductivity of Rb-CD-MOF_cTPy lies close to that reported for 2D PPy arrays growth in a redox-active layered coordination polymer.¹⁰ **Figure 5d** shows the thermal dependence of the conductivity with

temperature measured at a bias voltage of 1 V. The exponential decrease of conductivity with temperature suggests that Rb-CD-MOF_cTPy displays a semiconductive behavior. According to the Arrhenius law, the linear fit of $\text{Ln}(\sigma(T)/\sigma(RT))$ to the reciprocal of the temperature in the high-temperature range yields a E_a value of 709 meV. This value is considerably higher than the 0.2 eV reported for highly-oriented 1D PPy, for which unusually high conductivity was ascribed to percolating conducting paths with the templating framework,¹⁹ but comparable to that observed for electron tunneling between metal nanoclusters spatially separated in CD-MOF.⁷ This charge transport mechanism is possibly the origin for the electrical conductivity of the segregated iodine terpyrrole complexes formed in Rb-CD-MOF_cTPy.

In summary, we have used a cyclodextrin framework to control the chemical oxidation of pyrrole by confined reactivity. Compared to other MOFs based on π -rich aromatic linkers that lead to the formation of polypyrrole, interaction of the guest with the CD rings in the framework restrict the polymerization of pyrrole to a low degree for the formation and stabilization of a conductive array of cationic terpyrrole complexes. Our work offers unprecedented structural snapshots for definite information on the host-guest interactions that control this process by using SC-XRD. We are confident these findings will contribute to gain control over the transcription of MOF surface chemistry into controlled reactivity of confined redox-active molecules for targeted polymeric assemblies with controllable physical properties or even advanced functions.

Acknowledgements

This work was supported by the EU (ERC Stg Chem-fs-MOF 714122) and Spanish MINECO (CTQ2017-83486-P, RYC-2012-10894 and MDM-2015-0538). A.N.-L. thanks the Spanish MECD for FPU predoctoral grant (FPU10/02220). N.M.P. thanks the Marie Skłodowska-Curie Global Fellowships (749359-EnanSET). We thank XALOC beamline staff at ALBA Synchrotron for their help with preliminary experiments. Thanks are also extended to the Italian MIUR for the "Fondo per il finanziamento delle attività base di ricerca" (D.A.). Ismael Mullor-Ruiz, Gemma Peñalver, Neyvis Almora-Barrios and Isabel Solana are also acknowledged.

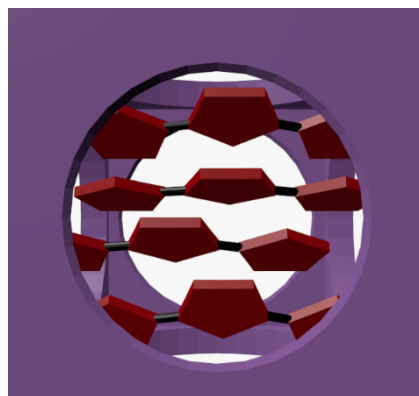
Keywords: metal-organic frameworks • confined reactivity • single-crystal to single-crystal transformation • terpyrrole • electrical conductivity

- [1] H. Furukawa, K. Cordova, M. O'Keeffe, O. M. Yaghi, *Science* **2013**, *341*, 1230444.
- [2] J. Juan-Alcañiz, J. Gascon, F. Kapteijn, *Journal of Materials Chemistry* **2012**, *22*, 10102-10118.
- [3] T. Uemura, N. Yanai, S. Kitagawa, *Chem. Soc. Rev.* **2009**, *38*, 1228-1236.
- [4] T. Uemura, S. Horike, S. Kitagawa, *Chem. Asian J.* **2006**, *1*, 36-44.
- [5] T. Uemura, S. Mochizuki, T. Kitao, *Chem. Commun.* **2018**, *54*, 11843-11856.
- [6] R. Smaldone, R. Forgan, H. Furukawa, J. Gassensmith, A. Slawin, O. Yaghi, J. Stoddart, *Angew. Chem. Int. Ed.* **2010**, *49*, 8630-8634.
- [7] S. Han, S. C. Warren, S. Yoon, C. D. Malliakas, X. Hou, Y. Wei, M. G. Kanatzidis, B. A. Grzybowski, *J. Am. Chem. Soc.* **2015**, *137*, 8169-8175.
- [8] S. Han, Y. Wei, B. A. Grzybowski, *Chem. Eur. J.* **2013**, *19*, 11194-11198.
- [9] R. S. Forgan, R. A. Smaldone, J. J. Gassensmith, H. Furukawa, D. B. Cordes, Q. Li, C. E. Wilmer, Y. Y. Botros, R. Q. Snurr, A. M. Slawin, et al., *J. Am. Chem. Soc.* **2012**, *134*, 406-417.
- [10] J. Storsberg, H. Ritter, H. Pielartzik, L. Groenendaal, *Adv. Mater.* **2000**, *12*, 567-569.
- [11] N. Yanai, T. Uemura, M. Ohba, Y. Kadowaki, M. Maesato, M. Takenaka, S. Nishitsuji, H. Hasegawa, S. Kitagawa, *Angew. Chem. Int. Ed.* **2008**, *47*, 9883-9886.
- [12] T. Uemura, Y. Kadowaki, N. Yanai, S. Kitagawa, *Chem. Mater.* **2009**, *21*, 4096-4098.
- [13] G. Street, T. Clarke, M. Krounbi, K. Kanazawa, V. Lee, P. Pfluger, J. Scott, G. Weiser, *Mol. Cryst. Liq. Cryst.* **1982**, *83*, 253-264.
- [14] A. Comotti, S. Bracco, M. Mauri, S. Mottadelli, T. Ben, S. Qiu, P. Sozzani, *Angew. Chem. Int. Ed.* **2012**, *124*, 10283-10287.
- [15] F. R. Fortea-Pérez, M. Mon, J. Ferrando-Soria, M. Boronat, A. Leyva-Pérez, A. Corma, J. Herrera, D. Osadchii, J. Gascón, D. Armentano, E. Pardo, *Nature Mater.* **2017**, *16*, 760-766.
- [16] M. Mon, F. Lloret, J. Ferrando-Soria, C. Martí-Gastaldo, D. Armentano, E. Pardo, *Angew. Chem. Int. Ed.* **2016**, *128*, 11333-11338.
- [17] J.-C. Lacroix, F. Maurel, P.-C. Lacaze, *J. Am. Chem. Soc.* **2001**, *123*, 1989-1996.
- [18] T. Bein, P. Enzel, *Angew. Chem. Int. Ed.* **1989**, *28*, 1692-1694.
- [19] Q. Wang, C. Zhang, *Macromol. Rapid Commun.* **2011**, *32*, 1610-1614.
- [20] B. Dhara, S. S. Nagarkar, J. Kumar, V. Kumar, P. Jha, S. K. Ghosh, S. Nair, N. Ballav, *J. Phys. Chem. Lett.* **2016**, *7*, 2945-2950.
- [21] H. Wang, J. Ge, C. Hua, C. Jiao, Y. Wu, C. F. Leong, D. M. D'Alessandro, T. Liu, J. Zuo, *Angew. Chem. Int. Ed.* **2017**, *129*, 5557-5562.
- [22] T. Uemura, R. Nakanishi, S. Mochizuki, S. Kitagawa, M. Mizuno, *Angew. Chem. Int. Ed.* **2016**, *55*, 6443-6447.

Entry for the Table of Contents

COMMUNICATION

Visualizing confined reactivity in MOFs: Compared to its uncontrolled polymerization in solution, we show that chemical oxidation of pyrrole can be regulated when confined to the channels of a cyclodextrin (CD) framework. Supramolecular interactions with the CD rings restrict the mobility and reactivity of pyrrole to enable the stabilization of terpyrrole cationic intermediates.

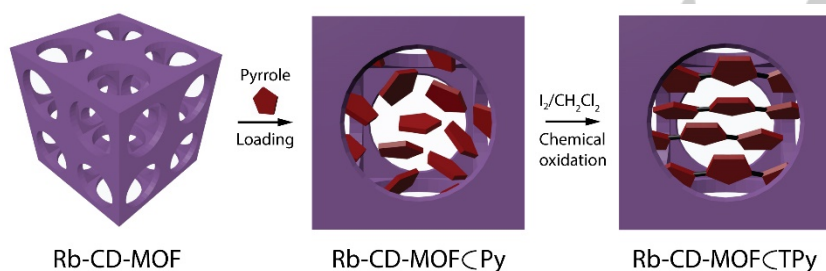


*Alejandro Nuñez-Lopez, Marta Galbiati, Natalia M. Padial, Carolina R. Ganivet, Sergio Tatay, Emilio Pardo, Donatella Armentano and Carlos Martí-Gastaldo**

Page No. – Page No.

Direct visualization of pyrrole reactivity by confined oxidation in a Cyclodextrin Metal-Organic Framework

COMMUNICATION



*Alejandro Nuñez-Lopez, Marta Galbiati, Natalia M. Padial, Carolina R. Ganivet, Sergio Tatay, Emilio Pardo, Donatella Armentano and Carlos Martí-Gastaldo**

Page No. – Page No.

Direct visualization of pyrrole reactivity by confined oxidation in a Cyclodextrin Metal-Organic Framework

Visualizing confined reactivity in MOFs: Compared to its uncontrolled polymerization in solution, we show that chemical oxidation of pyrrole can be regulated when confined to the channels of a cyclodextrin (CD) framework. Supramolecular interactions with the CD rings restrict the mobility and reactivity of pyrrole to enable the stabilization of terpyrrole cationic intermediates.