A Wavy Two-Dimensional Covalent Organic Framework from Core-Twisted Polycyclic Aromatic Hydrocarbons

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ABSTRACT: A high degree of crystallinity is an essential aspect in two-dimensional covalent organic frameworks, as many properties depend strongly on the structural arrangement of the different layers and their constituents. We introduce herein a new design strategy based on core-twisted polycyclic aromatic hydrocarbon as rigid nodes that give rise to a two-dimensional covalent organic framework with a wavy honeycomb (chair-like) lattice. The concave-convex self-complementarity of the wavy two-dimensional lattice guides the stacking of framework layers into a highly stable and ordered covalent organic framework that allows a full 3D analysis by transmission electron microscopy revealing its chair-like honeycomb facets and aligned mesoporous channels. Remarkably, the waviness of the framework does not disrupt the interlayer π-π stacking that shows charge transporting properties similar to those of planar covalent organic frameworks. The implementation of core-twisted aromatics as building blocks for covalent organic frameworks brings new possibilities in the design of highly ordered organic materials.

INTRODUCTION

Covalent organic frameworks (COFs) are long-range ordered porous organic structures held together by covalent bonds that have shown a lot of potential as materials for gas separation and storage, liquid filtration and purification, heterogenous catalysis, sensing, electronics and, energy conversion and storage applications.[1-10] Among these, two-dimensional COFs (2D COFs) are constituted by COF layers that upon packing give rise to organized porous channels and to piled-up organic components from which different adsorbing, catalytic and, electron and exciton transporting properties can emerge, among many others.[11-21]

A high degree of crystallinity is an essential aspect in 2D COFs, as many of the above-mentioned properties depend strongly on the structural arrangement of the different layers and their constituents. Furthermore, a high degree of crystallinity improves the ease of not only the screening and optimization of reaction conditions but also the ability to establish the structure of the resulting 2D COFs. Different approaches have been developed to increase the crystallinity of 2D COFs. These include reactivity- and condition-dependent approaches, such as those based on (i) the reversibility of the bond formation reactions[19] and on (ii) seeded growth,[22] in addition to structural-dependent approaches, such as the introduction of (iii) self-assembling motiffs[23-26] and of (iv) stackable precursors.[27-32]

In particular, the introduction of stackable precursors with distinct shapes, such as bowl-, propeller-, and armchair-shaped precursors,[27-32] rely on their structural self-complementarity that guides the stacking of COF layers during growth. However, current designs of stackable precursors[27-32] involve elements with a high degree of conformational freedom that allow several interconverting conformations that interfere with the stackability of the precursors and of the resulting layers, and therefore, conformational synchronization during COF formation is required.

We introduce herein a new design strategy that relies on the use of core-twisted polycyclic aromatic hydrocarbons as rigid non-planar nodes, namely 2,3,10,11,18,19-hexahydroxy-*cata*-hexabenzocoronene (HBC) nodes (Figure 1). HBC adopts a twisted and rigid structure that is conformationally-locked as the result of steric congestion between the hydrogens in the peripheral benzene rings (Figures 1 and 2a). The copolymerization of the twisted HBC with pyrene-2,7-diboronic acid (PDBA) produces a highly crystalline 2D COF with a wavy honeycomb (chair-like) lattice (Marta-COF-1, Figure 1).

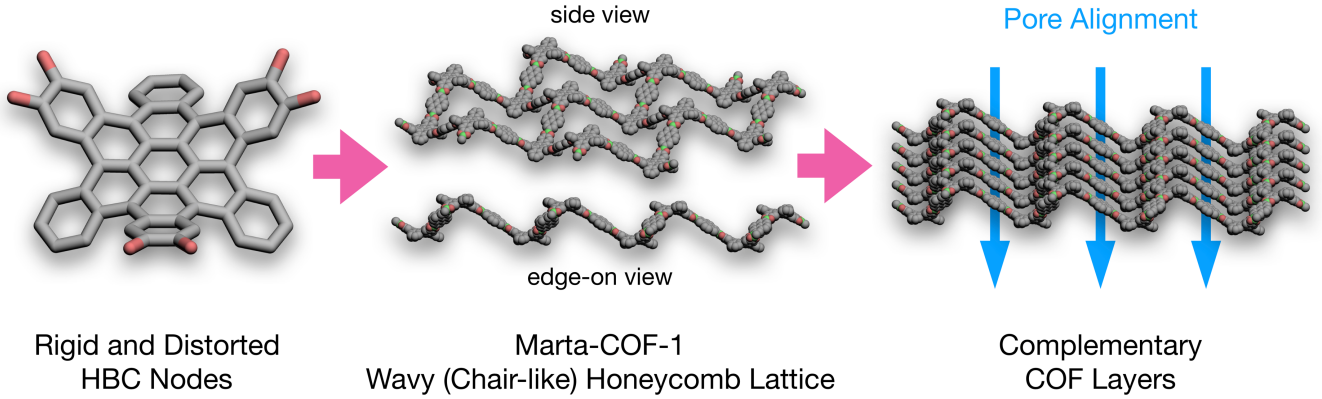


Figure 1. Schematic representation of the rigid and distorted HBC nodes and their incorporation in boronate ester COFs to obtain Marta-COF-1 with a wavy and highly complementary structure that guides the stacking of COF layers.

The concave-convex self-complementarity of the wavy lattice of Marta-COF-1, underpinned by the intrinsic rigidity and the tendency to self-assemble of the HBC nodes, line up the chair-like mesopores of the individual layers into open channels with a surface area close to the theoretical value. Remarkably, the high stability and crystallinity of Marta-COF-1 allows imaging its chair-like honeycomb facets and aligned mesoporous channels by high-resolution transmission electron microscopy (HR-TEM) and TEM tomography which provide unambiguous visual evidence of the wavy structural features of Marta-COF-1. Furthermore, the waviness of the framework does not disrupt the interlayer π-π stacking. In consequence, Marta-COF-1 shows charge transporting properties similar to those of the best performing planar 2D COFs.

RESULTS AND DISCUSSION

We selected *cata*-hexabenzocoronene derivatives as nodes because of their non-planar structure, their structural self-complementarity and their tendency to self-assemble.[33-37] We focused on the introduction of alternated catechol functionalities in the peripheral rings of *cata*-hexabenzocoronene core so these derivatives can be directly implemented as precursors of boronate ester COFs. HBC was synthesized by ether cleavage of 2,3,10,11,18,19-hexamethoxy-*cata*-hexabenzocoronene[38] in the presence of BBr_3 in a quantitative yield. Single crystal X-ray diffraction shows that HBC adopts a rigid contorted structure with a D_3 symmetry as the result of steric congestion between the hydrogens in the peripheral benzene rings that forces them below and above the plane (Figure 2a and Table S1). This alternated disposition of peripheral benzene rings generates a double-bowl structure that sets all the catechol groups above the coronene plane. The hexabenzocoronene core does not undergo any conformational change within the temperature range (–30-130 ºC) required for COF synthesis, as demonstrated by VT-NMR of 2,3,10,11,18,19-hexamethoxy-*cata*-hexabenzocoronene, in which the structure of the ^{1}H-NMR signals remain nearly invariable with the increase of temperature and only the typical chemical shifts associated to the temperature change are observed (Figure S1).

Marta-COF-1 was obtained as a yellow solid in a 95 % yield by solvothermal condensation of HBC and pyrene-2,7-diboronic acid (PDBA) in a mixture of 1,4-dioxane and mesitylene (2:1) at 120 °C for 72 hours in a sealed pre-scored ampoule (Figure 2b). The successful polymerization of the starting materials was ascertained by FT-IR that show the appearance of strong C-O stretching band distinctive for boronate ester five-membered rings at 1337 and 1347 cm^{-1} together with strongly attenuated signals of the hydroxyls of the boronic acid (Figure S2). The solid-state cross-polarization magic angle spinning (CP/MAS) ^{13}C NMR spectrum of Marta-COF-1 (Figure S3) shows the aromatic signals of the hexabenzocoronene and pyrene constituents, while the CP/MAS ^{11}B NMR spectrum (Figure S4) shows a single peak attributed to a single type of boronate ester linkage, both of which are consistent with the structure of Marta-COF-1. Marta-COF-1 shows the same solvent stability as other boronate ester COFs and hydrolizes in protic solvents such as MeOH and EtOH. The thermal stability was investigated by thermal gravimetric analysis under N_2 (Figure S5), revealing that Marta-COF-1 retained 95% of its mass up to 350 °C.

The PXRD diffractogram of Marta-COF-1 (Figure 3a) shows a large number of resolved reflections at 2.56°, 4.40°, 5.07°, 6.67°, 8.68°, 10.00° and 11.45°, which correspond to the (100), (2$\bar{1}$0), (020), (120), (2$\bar{4}$0), (400) and (4$\bar{5}$0) Bragg peaks. The presence of these sharp XRD peaks indicate that Marta-COF-1 exhibits a high degree of crystallinity with long-range periodic order. Pawley refinement using a unit cell of $a = b = 41.5$ Å and $c = 4.0$ Å confirmed the assignment (Figure S6).

The surface areas and pore size distribution of Marta-COF-1 were characterized by nitrogen adsorption measurements at 77 K (Figures 3b and 3c). Marta-COF-1 exhibits a reversible type IV isotherm with a microporous and mesoporous region. A Brunauer-Emmet-Teller (BET) surface area was calculated to be 1300 $m^2\ g^{-1}$ and a pore volume value of 0.677 $cm^3\ g^{-1}$. The estimated pore size from the Density Functional Theory (DFT) model is 3.5 nm.

The crystal structure of Marta-COF-1 was reconstructed with the expected slipped AA packing (Figures 3d, 3e and 3f) imposed by the complementary wavy lattice and by the HBC and pyrene constituents from a pre-optimized structure using semi-empirical Density Functional Theory Tight Binding (DFTB), followed by a final optimization using Density Functional Theory (DFT). The simulations of the slipped AA packing reproduce perfectly the PXRD pattern, meanwhile the AB packing models show a completely different PXRD pattern (Figure S7).[39] The reconstructed crystal structure reveals the chair-like honeycomb lattice (Figures 3e and 3f). Such chair-like lattice is the result of the alternated arrangement of HBC nodes with the cathecol groups above the coronene plane (all up) and HBC nodes with the cathecol groups below the coronene plane (all down) (Figure 3f).

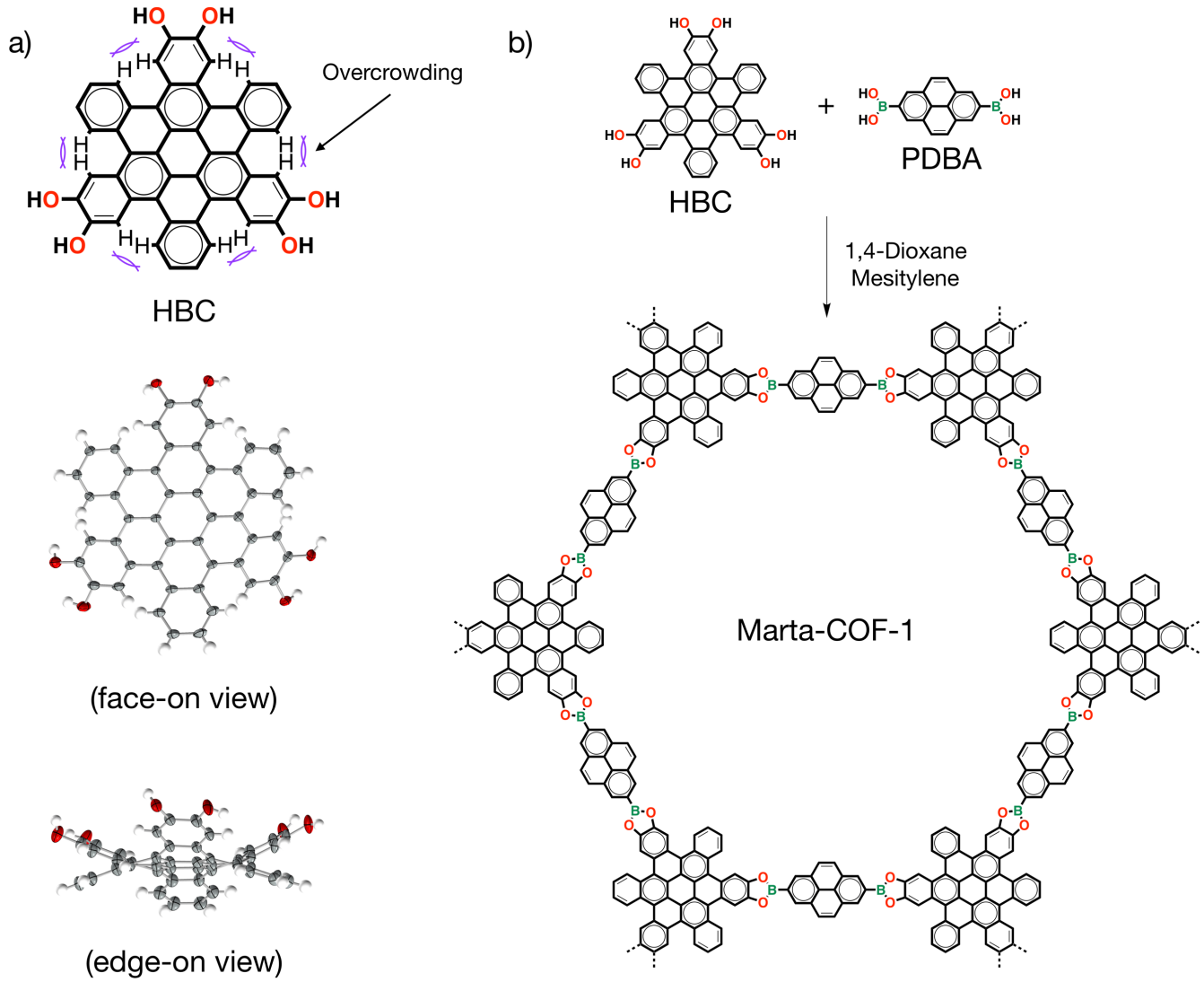


Figure 2. a) Chemical structure and face-on and edge-on views of the X-ray crystal structure of HBC. b) Synthesis of Marta-COF-1.

In addition, the reconstructed crystal structure exposes how the concave-convex complementarity between layers and the tight layer packing (centroid-to-centroid π-stacking distances are 3.4 Å at the pyrene segments and 3.7 Å at the HBC nodes) generates hexagonal mesoporous channels (Figures 3e and 3f). The calculated surface area and pore size obtained from the reconstructed crystal structure of Marta-COF-1 are 1570 m^2g^{-1} and 3.4 nm, respectively. The excellent agreement in the experimental and theoretical values surface area and pore size (Figures 3b and 3c) corroborates that Marta-COF-1 is a highly crystalline material.

Field-emission scanning electron microscopy (FE-SEM) and HR-TEM of Marta-COF-1 showed dahlia-like aggregates that extend beyond the μm in size (Figures S8 and S9, respectively). Upon closer inspection, the HR-TEM images reveal that Marta-COF-1 crystallizes with domains that extend from tens to hundreds of nm. Remarkably, the chair-like honeycomb facets of Marta-COF-1 can be easily observed, which provides direct evidence of the wavy structural features of Marta-COF-1 and also provides additional evidence of the high degree of crystallinity. In some areas, the crystallites are sitting face-on showing the lattice's highly ordered hexagonal mesopores (Figure 4a, red arrow and Figures S10) with a diameter 4.3-4.5 nm (pore size ca. 3.5 nm).[40] The mesoporous dimensions observed in HR TEM are also in agreement with the pore sizes estimated from the N_2 sorption measurements and the reconstructed crystal structure. In other areas, the crystallites are sitting edge-on revealing straight channels that extend across the crystalline domains consistent with the pore size (ca. 3.6 nm) and with the slipped AA packing (Figure 4b and S11). Other areas evidence chair-like features supportive of the chair-like structure of Marta-COF-1 (Figure 4a, green arrow and Figure 4c).

Individual layers of Marta-COF-1 can be distinguished at the edges (Figure 4a, circled area and Figure 4d), which allow investigating the structure of the unpacked honeycomb lattice lying in the vacuum. A closer inspection of such edges (inset of Figure 4a) reveals alternating bright (B) and dark (D) features in the nodes of each hexagon, which are consistent with the chair-like honeycomb lattice dimensions and with the estimated 6.6 Å height difference between the adjacent nodes estimated for an individual layer (Figure S12). Such alternating bright and dark features are ubiquitous to edges of COF particles when viewed face-on (Figures 4d-f).

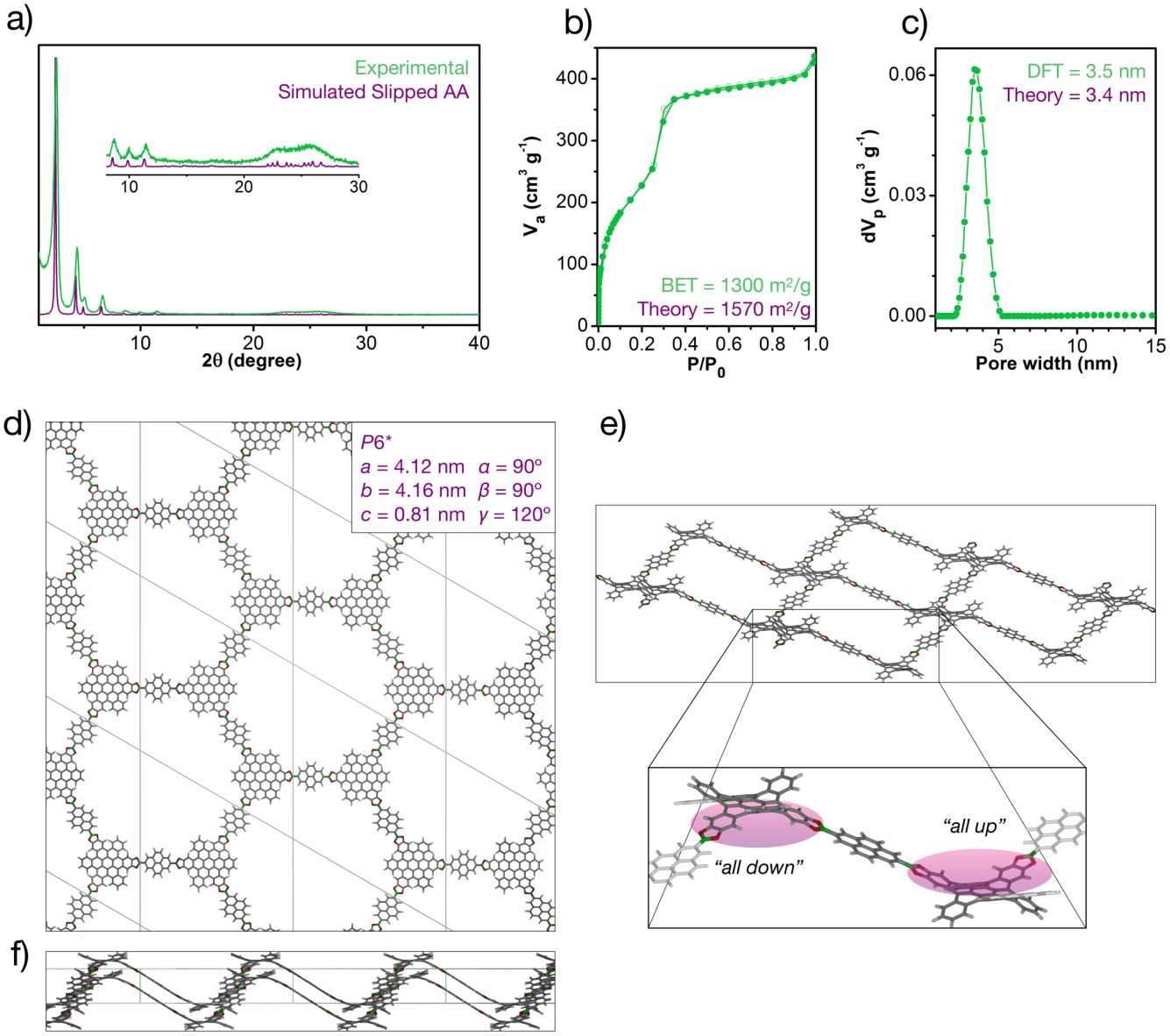


Figure 3. a) Experimental PXRD pattern (green line), simulated diffraction PXRD pattern for the simulated crystal structure. b) Nitrogen adsorption and desorption isotherms at 77 K. c) DFT pore size distribution. d) Face-on, e) lateral and f) edge-on views of the reconstructed crystal structure.

The high crystallinity also allows identifying both zigzag (Figure 4e) and armchair edges (Figure 4f). The hexagonal structures at the edges show a slightly larger hexagon diameter, ca. 4.7 nm (pore size ca. 3.7 nm), than those observed within the bulk of the structure, ca. 4.5 nm (pore size ca. 3.5 nm). This is confirmed by the line profiles from crystalline features in both the bulk structure and the edge that show smaller pore diameter in the bulk domains (Figure S13). These edge-bulk pore size differences can be rationalized in terms of the higher flexibility of the unpacked layers lying in the vacuum that gives rise to structures with a larger pore size in comparison to those packed in the bulk. This interpretation is also in agreement with the simulations on a free-standing Marta-COF-1 layer that shows larger diameters than those in a condensed phase (Figure S12).

TEM tomography, a process of sequential imaging and tilting of a particle has previously reported to be an excellent method to elucidate the internal structure of COFs and less crystalline conjugated microporous polymers,[41] however this technique is limited by the stability of the samples. Thanks to the high stability of Marta-COF-1, it was possible performing HR-TEM tilt experiments of individual crystallites over 70° (Figures 4g and S14). The images confirm that the observed hexagons, channel cross-sections and chair-like features are not only consistent with the dimensions and with the chair-like honeycomb structure of Marta-COF-1 but also interrelated to each other.[42] As a matter of fact, while the first frame of the tilt series shows hexagons corresponding to a view down the channels (Figure 4g, i), the tilting of the particle eventually shows wavy features and a side-view of the COF channel in a chair-like configuration (Figure 4g, ii). Additional tilting reveals how the hexagons transform into the previously observed channels (Figure 4g, iii). Such TEM image-structure correlations have been further confirmed by QSTEM[43] HR-TEM simulations of the geometry-optimized models of a bilayer of Marta-COF-1 in face-on (Figure 4h, i), chair-like

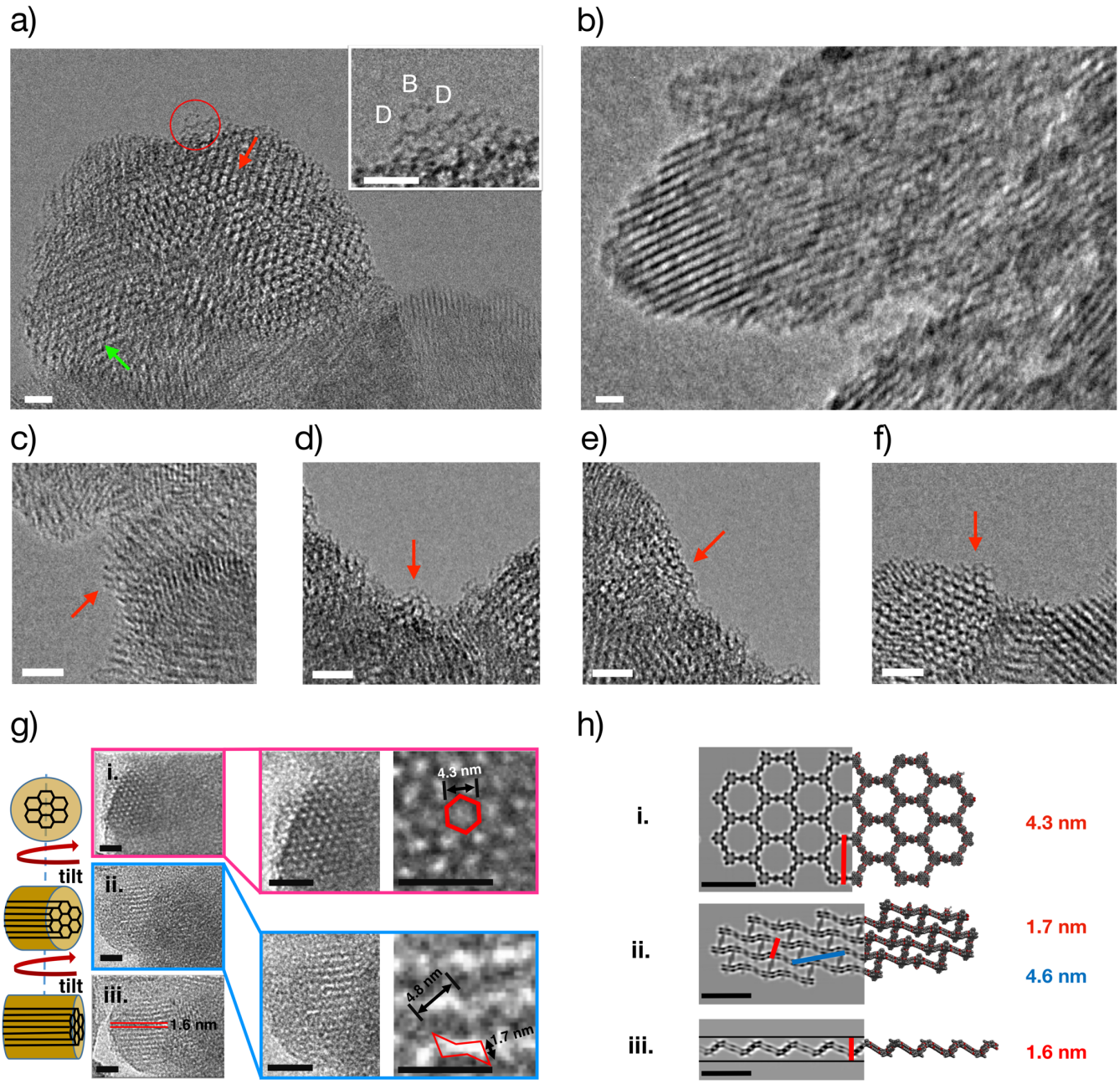


Figure 4. HR-TEM images of highly crystalline domains of Marta-COF-1 on a a) face-on, b) edge-on and c) chair-like configurations, of d) an individual hexagonal feature, and of e) zig-zag and f) armchair edges. The scale bars are 10 nm. g) HR-TEM images showing a Marta-COF-1 particle rotated and imaged over 70° tilt angle within the plane of the page (panels i-iii). The scale bars are 10 nm. Panels (i) and (ii) are magnified. h) Merged QSTEM HR-TEM simulations (left) with the corresponding geometry optimised models (right) showing the COF in (i) face-on (ii) chair-like and (iii) edge-on configurations. The scale bars are 5 nm.

(Figure 4h, ii), and edge-on (Figure 4h, iii) that reproduced the features, electron density profiles and distances observed experimentally (Figure 4g and Figure S14).

In planar 2D COFs, the π-stacking between layers can open up channels for charge transport across the columns obtained from the layers' π-stacked constituents. An open question is if the wavy structure of Marta-COF-1 could interfere with the charge transporting properties, since COFs with efficient charge transporting channels are obtained by the stacking of planar 2D COF. To assess the charge transporting properties of Marta-COF-1, we used the Flash-Photolysis Time-Resolved Microwave Conductivity (FP-TRMC) technique,[44] which has emerged as a standard to study the charge transporting properties of COFs. This is because interfacing COFs with electrodes is still a challenging task and FP-TRMC is an electrode-less technique that can be used to measure directly powders and films. FP-TRMC estimates the pseudo-photoconductivity ($\varphi\Sigma\mu$) that provides an estimation of the intrinsic mobility of the material. The $\varphi\Sigma\mu$ value is the product of the quantum yield (φ) and the sum of the charge carrier mobilities ($\Sigma\mu$). For comparison, samples of crystalline powders Marta-COF-1 and of thin films of crystalline powders of Marta-COF-1 dispersed in polytriarylamine were studied and compared. The samples of Marta-COF-1 dispersed in a polytriarylamine ($\varphi\Sigma\mu_{max}$ = 0.9

× 10^{-4} cm^2 V^{-1} s^{-1}) showed slightly higher $\varphi\Sigma\mu_{max}$ values (Figure 5), but in the same order of magnitude than the powders of Marta-COF-1 ($\varphi\Sigma\mu_{max}$ = 0.6 × 10^{-4} cm^2 V^{-1} s^{-1}). These nearly invariable $\varphi\Sigma\mu$ values for Marta-COF-1 are on the same order of magnitude than those observed in the best performing planar 2D COFs[45-53] (with $\varphi\Sigma\mu$ values between 10^{-5} and 10^{-4} cm^2 V^{-1} s^{-1}). This is consistent with the intimate π-stacking distances (3.4 Å at the pyrene segments and 3.7 Å at the HBC nodes) revealed by the reconstructed crystal structure that show how the framework's waviness does not interfere with charge transport across the layers.

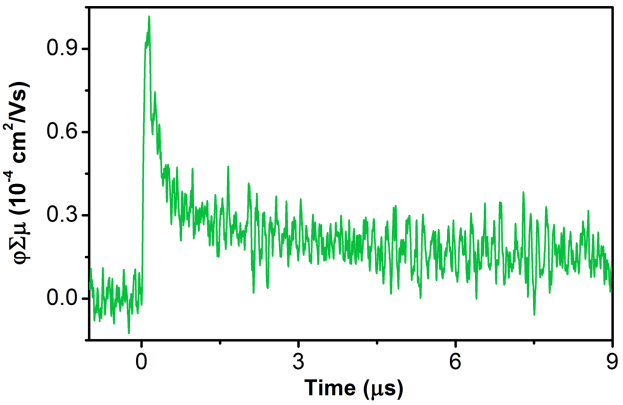


Figure 5. FP-TRMC of Marta-COF-1.

CONCLUSIONS

In summary, we have developed and implemented a design strategy for the synthesis of non-planar 2D COF based on the use of core-twisted polycyclic aromatic hydrocarbons as nodes. The rigid non-planar conformation of HBC expresses a 2D chair-like honeycomb lattice as the result of the alternated arrangement of HBC nodes with the cathecol groups facing above the coronene plane and HBC nodes with the cathecol groups below the coronene plane across the lattice. The structural self-complementarity of the twisted nodes and of the wavy lattice favours a slipped AA packing of the layers that line up the hexagonal chair-like mesopores of the individual layers into open channels with a surface areas (1300 m^2/g) and pore sizes (3.5 nm) close to the theoretically-predicted values (1587 m^2/g and 3.4 nm, respectively) that evidence that Marta-COF-1 is a highly crystalline material. The high stability and crystallinity of Marta-COF-1 have allowed an extraordinary level of characterization by HR-TEM. For instance, HR-TEM images show chair-like honeycomb facets and aligned mesoporous channels consistent with the experimental and predicted dimensions and packing, and also, it has been possible to identify both free-standing individual chair-like hexagons and, zig-zag and armchair edges. Furthermore, TEM tomography evidences how the observed hexagons, channel cross-sections and chair-like features of Marta-COF-1 are interrelated to each other. In addition, Marta-COF-1 exhibits similar $\varphi\Sigma\mu$ values as 2D COFs with high charge carrier mobilities since the wavy structure of the lattice does not interfere with the interlayer π-stacking. The implementation of core-twisted aromatics as COF precursors brings new possibilities in the design of highly crystalline 2D and 3D COFs with new architectures and properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.
Full synthesis and characterization of Marta-COF-1 (PDF)
X-ray structure of HBC (CIF)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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ABBREVIATIONS

COF, covalent organic framework; HBC, 2,3,10,11,18,19-hexahydroxy-*cata*-hexabenzocoronene; PXRD, powder X-ray diffraction; HR-TEM, high resolution transmission electron microscopy; FP-TRMC, flash-photolysis time-resolved microwave conductivity.

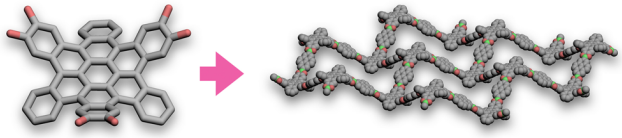
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We introduce herein a new design strategy based on core-twisted polycyclic aromatic hydrocarbon as rigid nodes that give rise to a two-dimensional covalent organic framework with a wavy honeycomb (chair-like) lattice.



From Twisted Aromatics to Wavy COFs