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Microtubular Self-Assembly of Covalent Organic Frameworks

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Dedicated to Sir Fraser Stoddart on the occasion of his 75th birthday

Abstract: Despite significant progress in the synthesis of covalent organic frameworks (COFs), reports on a precise construction of template-free nano- and microstructures for such materials have been rare. In search of dye-containing porous materials, a novel conjugated framework **DPP-TAPP-COF** with enhanced absorption capability up to 800 nm has been synthesized utilizing reversible imine condensations between 5,10,15,20-tetrakis(4-aminophenyl)-porphyrin (**TAPP**) and a diketopyrrolopyrrole (**DPP**) dialdehyde derivative. Surprisingly, the obtained COF exhibited spontaneous aggregation into hollow microtubular assemblies with outer and inner tube diameters of around 300 and 90 nm. A detailed mechanistic investigation revealed the time-dependent transformation of initial sheet-like agglomerates into the tubular microstructures.

The formation of well-defined nanoscale superstructures has been a major achievement for supramolecular chemistry in recent years.^[1] For a precise control over function and materials properties however, molecular organization often needs to be mastered on even larger spatial regimes, e.g. the μ m-scale.^[2] In natural systems, function often emerges from defined microarchitectures that are assembled via protein-templated biomineralization.^[3] While the defined bottom-up fabrication of artificial microstructures is still quite challenging, it would significantly improve the understanding of structure-property relationships for real applications.

Covalent organic frameworks (COFs), representing a class of crystalline porous polymers,^[4] have recently emerged as promising materials for potential applications in gas adsorption,^[5] energy storage,^[6] heterogeneous catalysis^[7] or sensing.^[8] In particular, two-dimensional (2D) COFs comprising extended π -systems or well-defined donor-acceptor heterojunctions in nm-sized regimes render such materials promising candidates for optoelectronic applications.^[9] In most cases, however, 2D COFs are prepared and isolated as microcrystalline powders. Thereby, the limited long-range crystal growth and morphological definition is presumably due to internal defects^[10] and kinetic trapping of smaller crystallites as a result of dispersive π -stacking of individual layers. Defined morphologies such as

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belts,^[11] fibers^[12] and spheres^[13] have been observed for some COFs, but detailed mechanistic investigations have so far only been conducted in two examples for COF-based hollow spheres.^[14] The template-assisted synthesis of COF nanotubes has also been reported.^[15] However, in this case additional effort was required to initially prepare and finally remove the templates without causing irreversible modifications of the COF properties.



Figure 1. a) Synthesis and b) proposed microtubular self-assembly of DPP-TAPP-COF.

Herein, we report on the synthesis of **DPP-TAPP-COF** containing diketopyrrolopyrrole (DPP) and tetraphenylporphyrin (TPP) moieties. This imine COF adopts a unique hollow microtubular morphology with uniform diameters, rendering it, to the best of our knowledge, the first example for bottom-up microtubular self-assembly based on COF materials.

During our quest for dye-containing COFs, we studied the reaction of 5,10,15,20-tetrakis(4-aminophenyl)-porphyrin (**TAPP**)^[16] and the organic semiconductor DPP^[17] dialdehyde derivative **DPP-1** bearing solubilizing ethylhexyl side chains. Microcrystalline precipitates were obtained after an AcOH-catalyzed solvothermal reaction in *n*-BuOH/mesitylene (3:1) at 120 °C for five days. Washing with anhydrous THF and acetone followed by drying under high vacuum yielded **DPP-TAPP-COF** (Figure 1a) as a dark purple material in 53% yield. Remarkably,

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even small deviations from these optimized conditions only resulted in amorphous products (see Table S1).

Figure 2. a), b) SEM and c) TEM micrographs of **DPP-TAPP-COF** nanotubes; d) high resolution TEM image of a microtube's outer wall indicating crystalline domains; e) STEM image of singular microtube indicating the hollow nature of the tube; f) statistical distribution of inner and outer tube diameters.

Strikingly, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) revealed that **DPP-TAPP-COF** predominantly assembles into well-defined

microtubular structures (Figure 2) that are extended up to 20 µm. The majority of the microtubes were aggregated into bundles, in some cases, however, individual tubes were observed, which were possibly separated mechanically by sonication and sample preparation. Energy-dispersive X-ray (EDX) spectroscopy on various spots of different tubes revealed a uniform atomic composition, thus indicating the homogeneous formation of a composite material (Figure S10). SEM and scanning transmission electron microscopy (STEM) images (Figures 2b,e) clearly demonstrated the hollow nature and remarkably smooth surface of the tubes. Statistical analysis yielded mean values for outer and inner diameters of 303 \pm 38 nm and 87 \pm 21 nm, respectively (Figure 2f), which corresponds to a mean wall thickness of 105 ± 9 nm (Figure S23). High-resolution TEM (Figure 2d) revealed a periodic rhomboidal framework with domain sizes in the range of several tens of nm.

Indeed, framework formation was proven by several analytical techniques. The FT-IR spectrum (Figure S5) shows almost complete disappearance of the aldehyde band at 1649 cm⁻¹ and the simultaneous rise of a new band at 1582 cm⁻¹ corresponding to the C=N stretching mode. In addition, the N-H stretching band for the amino groups of TAPP at 3316 cm⁻¹ is significantly weakened after polymerization. Similar spectral trends indicating identical functionalities and connectivity were observed for model compound M-1 as a representative "cutout" possessing two TPP units attached to one DPP-1. ¹³C Cross-polarization magic-angle spinning (CP-MAS) NMR spectra (Figure 3d-f) for both DPP-TAPP-COF and M-1 are in excellent agreement with ¹³C NMR solution data of **M-1** obtained in CDCl₃. The absence of any aldehyde signal, expected to appear beyond 180 ppm, indicates virtually quantitative consumption of the DPP precursor. Elemental analysis of DPP-TAPP-COF revealed the efficient formation of a polymeric material composed of both monomers (see SI for details). Thermogravimetric analysis (TGA) revealed a thermal stability up to 350 °C followed by a weight loss of around 20%, which is tentatively attributed to the loss of the alkyl side chains,^[18] and ultimate decomposition at 450 °C (Figure S6). Powder X-ray diffraction (PXRD) revealed Bragg reflections centered at low 20 angles of 2.68°, 3.51°, 4.26°, 5.49° and 7.17° corresponding to 110, 020, 120, 220 and 040 planes, respectively (Figure 3a), thus implying the formation of small



Figure 3. a) PXRD patterns of DPP-TAPP-COF: experimental (red), Pawley refinement (black), simulated pattern (green), and difference plot (blue). b) Simulated unit cell for a monoclinic crystal system of space group C2/m. c) Model compound M-1. d) ¹³C-CP-MAS-NMR spectra of DPP-TAPP-COF and e) of solid M-1. f) ¹³C-NMR spectrum (CDCl₃, 400 MHz, rt) of M-1.

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COF domains. A simulated diffraction pattern in the monoclinic *C2/m* space group (see SI for details) with an eclipsed but slightly offset (~ 1 Å) AA stacking provides a good description of **DPP-TAPP-COF** (Figure 3b). The final unit cell parameters were obtained by performing Pawley refinement and correspond to *a* = 45.3 Å, *b* = 48.1 Å, *c* = 3.9 Å; $\alpha = \gamma = 90^{\circ}$, $\beta = 74.3^{\circ}$ ($R_{wp} = 3.82\%$ and $R_p = 2.86\%$).



Figure 4. a) UV/Vis absorption spectra (CHCl₃, rt) of **M-1**, **NH**₂-**TPP** and **DPP-1**. Insets show enlarged region from 500 to 700 nm and the visual colors of the compounds in CHCl₃. b) Kubelka-Munk function for diffuse reflectance spectra of **DPP-TAPP-COF**, **M-1** and molecular precursors **TAPP** and **DPP-1**. Spectra are normalized to global absorption maximum.

Nitrogen sorption analysis was performed after activation at

elevated temperatures under high vacuum for 12 hours. The obtained sorption isotherm (Figure S9) and calculated BET surface area of 139 m² g⁻¹ indicate a fairly low N₂ uptake, which we attributed to the offset stacking and primarily to the sterically demanding side chains protruding into the pores.

The absorption spectrum of **M-1** nearly matches an overlay of **NH₂-TPP** and **DPP-1**, except for slightly increased *Q*-bands at 590 and 650 nm (Figure 4a). Steric interactions of the phenyl rings with the porphyrin possibly induce a significant twist, thus resulting in limited π -conjugation. Diffuse reflectance spectra for **DPP-TAPP-COF** showed a significant shift of the maximum absorption to 670 nm (Figure 4b), which can be rationalized by a planarization of the π -system and pronounced aggregation of the individual layers within the COF.^[16b] In addition, the relative intensity ratio for the *Q*- versus the Soret-bands increased from 0.4 and 0.41 for **TAPP** and **M-1**, respectively, to 1.47 for the COF. Due to this enhanced absorption, **DPP-TAPP-COF** more efficiently harvests photons in the visible and near IR region.

For time-dependent morphological studies, COF reactions were distributed to several pyrex tubes and guenched at different time intervals. SEM Images after one day indicated the formation of plate-like applomerates of small individual crystallites (Figure 5a). After four days, significantly smoother plate surfaces were observed alongside initial signs for a scrolling of some of the thin sheets (Figures 5b,c). After five days, hollow microtubes were isolated as the major product (Figure 5d) in addition to some remaining plate-like aggregates. Further increase of the reaction time up to 15 days resulted in roughening and fracturing of the tube walls as evidenced by SEM (Figures S17e,f) and PXRD (Figure S16). However, the isolated COF microtubes are stable for several months and PXRD measurements showed no signs for structural collapse. Based on these data, there is no evidence for tube growth via Ostwald ripening, as it was recently invoked for the formation of spherical COF particles.^[14a] Instead, we propose the following mechanism for microtube formation (Figure 5). Initially, small crystallites of imine-condensation products are formed that agglomerate into sheet-like aggregates, which is presumably induced by van der Waals interactions between the branched alkyl chains. Over time, initial crystallites grow further by condensation of unreacted precursors or grain boundary consumption via reactive aldehydes and amines at the interfaces (Figures S19 and S20). This transformation is



Figure 5. Proposed mechanism for microtube formation: a) agglomeration of small DPP-TAPP-COF crystallites into sheet-like aggregates, b) smoothing and densification of sheets by reversible imine condensations, c) rolling of the sheets due to solvent removal and d) tube formation and recombination by reversible imine condensations.

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supported by a change in thickness for the initial and uniform sheets from around 500 to 100 nm, respectively. Hence, we propose that the spontaneous scrolling into tubular arrangements (red arrows in Figure 5c) minimizes destabilizing interactions with solvent molecules, as it was previously shown for supramolecular nanotubes^[19] and microporous polymers.^[20] This assumption is also supported by similar wall thicknessess for the microtubes and the uniform sheets. Subsequently, well-defined uniform nanotubes are generated via dynamic imine formation of unreacted aldehyde and amino groups present at the edges.

In conclusion, we have demonstrated the successful implementation of DPP and TPP chromophores into one single conjugated COF via reversible imine condensations. UV/Vis studies revealed a significant redshift after framework formation that was attributed to enhanced conjugation and delocalization along and across the COF sheets. Remarkably, **DPP-TAPP-COF** crystallites self-assemble into microtubular aggregates with narrow size distribution as evidenced by SEM and STEM microscopy. Time-dependent studies support the hypothesis that the microtubes originate from rolled-up crystallite sheets. These findings pave the way for fascinating future experiments on single microtubes, as well as the inclusion of suitable guest molecules or even larger nanostructures thus allowing for an additional fine-tuning of materials properties.

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Rolling up the COFs: Tetraphenylporphyrins and Diketopyrrolopyrroles have been incorporated as functional dye components in covalent organic frameworks via reversible imine condensations. Upon formation, these crystalline polymers spontaneously self-assemble into hollow microtubes.

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