Lewis base mediated efficient synthesis and solvation-like host–guest chemistry of covalent organic framework-1†

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N-Lewis base mediated room temperature synthesis of covalent organic frameworks (COFs) starting from a solution of building blocks instead of partially soluble building blocks was developed. This protocol shifts COF synthetic chemistry from sealed tubes to open beakers. Non-conventional inclusion compounds of COF-1 were obtained by vapor phase infiltration of ferrocene and azobenzene, and solvation like effects were established.

Porous organic frameworks (POFs) are a vital class of organic polymers with technological importance.1 Until recently, organic frameworks have been mostly considered as amorphous or semi-crystalline materials. However, long range ordering and packing of molecules are very important in many technological applications. In a breakthrough work, Yaghi and co-workers reported synthesis of crystalline organic frameworks (COFs) by reversible self-condensation of aromatic diboronic acids or similar condensation between aromatic alcohols and aromatic diboronic acids.2 COFs exhibit permanent porosity and large specific surface areas on a par with metal organic frameworks (MOFs). COFs are attractive for gas storage applications because of their exceptionally low densities and higher gravimetric amounts of small gas molecules (CO₂, H₂, CH₄ and NH₃) can be stored.3 Recently developed COFs comprising photoactive building units such as pyrene and phthalocyanine were found to exhibit interesting optoelectronic properties.4

Despite their great potential, the synthetic protocols reported in the literature are very limited. The most common method is a one step solvothermal condensation approach which involves reversible formation of covalent bonds.5 Striking a balance between the thermodynamic and kinetic factors is essential to obtain crystalline COFs. This could be achieved by using sparingly soluble building blocks and by maintaining closed reaction conditions. The former controls the diffusion process and facilitates the nucleation of a crystalline material, and the latter helps in maintaining reversible conditions due to the availability of in situ generated H₂O. However, this approach is time consuming (at least 3–5 days) and difficult to scale up. New strategies that facilitate the synthesis of these materials on a large scale, in less reaction time and under milder conditions are sought after. In this regard, synthesis of COFs from their building solutions is one of the attractive ways. However, such attempts yielded only amorphous materials, so far.6

Herein, we present a novel approach for the efficient synthesis of the boroxine moiety based COF-1 framework from soluble building blocks. Condensation of 1,4-benzenediboronic acid (BDBA) in 1,4-dioxane in presence of N-Lewis base under reversible reaction conditions resulted in the formation of COF-1-L adduct (L = NH₃) material at room temperature. Activation of this intermediate compound at higher temperatures resulted in the formation of guest free COF-1. The high density of Lewis acidic sites and small

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pore dimensions make COF-1 an interesting host matrix. We investigated non-conventional host-guest chemistry of COF-1 using ferrocene [FeCp2] and trans-azobenzene (trans-AB). The choice of guests was motivated by anticipated stabilization of adsorbates within the framework via weak π-π interactions.

Unlike direct condensation of aromatic boronic acids, the formation of triorganoboroxine–amine complexes is highly favoured in the forward direction (Scheme 1), therefore, tuning the condensation equilibrium conducive to a crystalline framework is a challenging task.7 In our pursuit to synthesize COF-1 by this approach, we tested several alkyl amines as nitrogen containing bases. As expected, direct mixing of BDBA with alkyl amines resulted in the formation of only amorphous materials.

In order to tune the chemical equilibrium of the condensation reaction, we introduced additional water into the system to favor the reverse reaction and NH3 was introduced slowly by the vapor infiltration method to control the reaction kinetics. Slow infiltration of NH3–H2O vapor (from 33 wt% aqueous NH3 solution, BDBA : NH3 = 2 : 3) into a beaker containing BDBA dioxane solution resulted in the formation of a white precipitate at the bottom of the beaker. Here, an excess amount of NH3 was used to shift the equilibrium towards the condensation direction. The IR spectrum of this compound showed a Type I isotherm with hysteresis at high pressure, indicative of inclusion compounds by employing the solvent-free vapor infiltration method. The IR,13C and [11B NMR (MAS) and TGA analysis (Fig. S4, ESI†) of COF-1 shows two major weight losses one around 150 °C and another around 600 °C. The initial weight loss is assigned to the loss of solvent and ammonia from the framework and latter one to the decomposition of COF-1.

Activation of this material above 150 °C under vacuum gave guest free COF-1. This is confirmed by IR, XRD (Fig. 1a, ii), BET, SEM and elemental analysis data (Fig. S5–S10, ESI†). Using this method COF-1 was synthesized on a gram scale with a high yield (1.3 g, 83%). However, the peaks of the powder XRD pattern are broad, suggesting formation of smaller crystallites. The SEM and TEM data revealed the presence of COF-1 plates agglomerated as micron sized spheres. The thickness of the plates is in the range of 10 to 50 nm and their length is up to ~500 nm. The observed dimensions are smaller than those reported by Yaghi and co-workers (up to 100 μm). The N2 adsorption–desorption isotherm of this material showed a Type I isotherm with hysteresis at P/P0 = 0.42 (Type H4 loop).8 This indicates that the material is majorly microporous. We attribute the hysteresis at high pressure to slit-like mesoporous interparticulate voids.9 The BJH mesopore size distribution is centered at 3.7 nm (Fig. S8, ESI†). The calculated N2 BET surface area is 695 m2 g−1 and total pore volume is 0.4 cm3 g−1 vs. reported 711 m2 g−1 and total pore volume is 0.4 cm3 g−1 vs. reported 0.32 cm3 g−1.10 The agglomeration of COF-1, obtained by our optimized synthesis protocol, was further studied using transmission electron microscopy. The TEM bright field image (Fig. 1b) and the high angle annular dark field scanning TEM (HAADF-STEM) image (Fig. S10, ESI†) show a typical sample. To understand the 3D arrangement of the COF-1 plates electron tomography was performed. A slice through the reconstructed volume reveals the hollow structure of the spheres (Fig. 1c). The darker contrast in Fig. 1b results therefore from plates oriented parallel to the electron beam.

An ideally eclipsed COF-1 structure has boron nitride like layered structure with an interlayer spacing of 3.32 Å and hexagonally aligned 1D pores (~1 nm). The host–guest chemistry of COF-1 is so far limited to small molecules.3 However, the small pore dimensions, BN like layered structure and high density of Lewis acidic sites make COF-1 a quite interesting host matrix. In order to extend the host–guest chemistry to larger and more functional molecules, we have synthesized FeCp2@COF-1 and AB@COF-1 as representative inclusion compounds by employing the solvent-free vapor phase infiltration method. The IR,13C and [11B NMR (MAS) and TGA data confirm the intact nature of both guest and host in the inclusion compounds. The details of the characterization are given in the ESI† (Fig. S11 and S12). The powder XRD patterns of the two inclusion compounds are shown in Fig. 2. For the two inclusion compounds, substantial changes in the relative intensities of the framework diffraction peaks were observed due to the electron density changes resulting from incorporated guest molecules.
From AAS and TGA data the composition of inclusion compounds is established as [FeCp₂]_{0.20}@COF-1 and [AB]_{12.25}@COF-1 ([ML]_{a2}@COF, “a” refers to the number of guest molecules per COF formula unit). Moreover, additional peaks corresponding to bulk guest molecules are not observed. This indicates that the guest molecules are indeed present inside COF-1 pores and do not agglomerate on the surface of crystals. No significant change in the position of the (002) peak was observed for [FeCp₂]_{0.20}@COF-1 as inclusion of FeCp₂ between COF-1 layers is highly unlikely due to the steric hindrance. Therefore, FeCp₂ molecules predominately occupy 1D channels of the host. On the other hand, a certain amount of inclusion of trans-AB molecules in between the framework’s layers is possible in the case of [AB]_{12.25}@COF-1. This is evident from the 0.1 Å increase in the interlayer distance as deduced from the shift of (002) reflection.

The adsorption of FeCp₂ and trans-AB was completely reversible; all the guest molecules could be stripped off from inclusion compounds by heating to 100 °C at 0.1 Pa for 18 h. The powder XRD pattern of parent COF-1 was retrieved after removal of FeCp₂ or AB from the respective inclusion compounds. This suggests that both FeCp₂ and trans-AB are stabilized inside COF-1 by only weak interactions. The most likely ones are donor-acceptor (π-π) interactions between π-electron rich guest molecules and electron deficient boryl-substituted phenyl rings.¹⁰

The apparent changes in the physical properties of the probe molecules upon inclusion are evident from the DSC curves (Fig. 3a and b). The absence of a melting step or a boiling step in the case of AB inclusion compounds indicates solvation like effects experienced by probe molecules due to interaction with the host matrix. A consequence of such effects on electronic properties of AB inside COF-1 is shown in Fig. 3c. The electronic spectrum of neat trans-AB consists of a strong band at 315 nm (π → π*) and a very weak band at 440 nm (n → π*). As seen in Fig. 3c, the band corresponding to n → π* gained intensity after inclusion of AB inside COF-1. This suggests isomerization of a significant amount of trans-AB to thermodynamically unstable cis-AB upon inclusion into COF-1. Such a conversion is unprecedented in the absence of UV-light or strong acidic conditions.¹¹

Notes and references

12 Reversible condensation of building blocks was observed for the ligand tetra(4-dihydroxoboryl)pheny1methylene and 1,2-bis(4-dihydroxoborylphenyl)-1,2-diphenylethene in the presence of NH₄OH vapors. Further tuning of the reaction conditions is under progress.

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