Organic Framework Crystals with Carbon Nanotubes


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Abstract: The presence of tetrazine units in the organic nodes of UiO-68-TZCD controls the formation of ultrathin coatings of single wall nanotubes that decorate the surface of the crystal. These crystal hybrids can be prepared straightforwardly in one step and are extraordinarily respectful with the properties of the framework for combination of mesoporosity and surface areas near 4.000 m²·g⁻¹, with excellent stability in water, and conductivities at room temperature of 4·10⁻² S·cm⁻¹ even at very low carbon weight contents (2.3 wt%).

Metal-Organic Frameworks (MOFs) have gained increasing attention in fields like chemistry, biology, and materials science due to their unparalleled adaptability to different goals thanks to their modular nature. These hybrid reticular solids, built from the interlinking of inorganic and organic nodes, offer periodic structures for tailorable porosity, pore chemistry and structural diversity. However, MOFs can also suffer from weak chemical (hydrolytic), thermal and mechanical stabilities, and poor electrical conductivity, which limit their potential in fields as energy storage and conversion. In this regard, the preparation of composites by integration with other functional materials as polymers, metal nanoparticles and oxides, biomolecules, graphene, or carbon nanotubes (CNTs) is a powerful route to overcome some of these limitations. The combination, or even synergistic interaction of these components with the intrinsic properties of the MOF, can enable advanced performance of the resulting composites in proton transport, H₂ photogeneration or catalysis.

The intrinsic hydrophobicity and extraordinary mechanical and electrical properties of CNTs makes them particularly appealing in this context. CNT@MOF composites are often prepared by the addition of pre-formed MOF particles to bundles of nanotubes (ex-situ) or directly synthesized in their presence (in-situ). This results in the formation of necklace-like hybrids for an irregular distribution of MOF particles that are deposited/growth on top of the carbon matrix (Figure 1a). Oxidized CNTs incorporating superficial -OH and -CO₂H groups that act as nucleation sites are used to favor the growth of MOF nuclei. However, this often leads to unsought changes in the intrinsic properties of pristine nanotubes and is not sufficient to prevent the aggregation of MOF particles, control their distribution, or enable effective pathways for electronic hybridization. As beautifully illustrated for the case of MOF-polymer hybrids, a better integration mediated by strong covalent linkages that was respectful with the intrinsic proper-ties of both components would be arguably ideal to gain control over interfacial compatibility.

Figure 1. a) Hierarchical organization of CNT (grey) and MOF crystals (pink octahedra) in the composites obtained by conventional methodologies and b) MOF crystal hybrid prepared by conjugation of nanotubes to the crystal surface to form a permeable coating.

UiO-68-TZDC is built from the assembly of 4,4′-(1,2,4,5-tetrzine-3,6-diyldibenzoic acid (HTZDC)) linkers and 12-connected Zr₆ metal-oxo clusters (Figure 2a). This open framework combines intrinsic mesoporosity with the availability of reactive tetrzine tags, ideal for bulk post-synthetic modification by reaction with dienophiles. Also, the surface reactivity of these crystals will dominated by the (111) facets of their truncated octahedral morphologies (Figure 2b). According to the cleavage of the crystal structure along this direction, this would correspond to tetrazine terminations ideally suited to surface functionalization (Figure 2c). These features make UiO-68-TZDC an ideal candidate to approach the grafting of CNTs. Compared to our previous work with small molecule dienophiles, the low solubility and dispersibility in common organic solvents of the single-wall carbon nanotubes (SWCNTs) used in this case imposed specific changes to the experimental procedure. As general procedure, a dispersion of SWCNTs in organic solvent was treated with ultrasounds followed by addition of freshly made crystals of UiO-68-TZDC prepared according to our reported method. The mixture was then incubated in an orbital shaker. The resulting slurry was separated from the organic solvent and redispersed in a 1:1 mixture of DMF:hexane with ultrasounds. This facilitated isolating CNT@MOF crystals from the unreacted bundle of
nanotubes. Experimental conditions were optimized by systematic screening of different solvents, CNT concentration, incubation temperature and time, and different reaction vessels (Supporting Section S2.1-S.2.2). The impact of the conditions on the morphology of the crystal and the ease of purification due to variable dispersibility of the nanotubes in the solvents tested were considered as determining factors. Compared to toluene, \(N,N\)-dimethylformamide (DMF) or acetone, dioxane was the best choice for reaching a good compromise between CNT conjugation, minimum damage to the crystal and facile purification. \(\text{TZDC-CNT-1}\) was prepared by dispersing 80 mg of \(\text{UiO-68-TZDC}\) crystals in a suspension of 0.021 mg/mL of SWCNT in dioxane followed by incubation in a Schott glass bottle at 65 °C for 48 hours (Supporting Section S2.3). Higher nanotube concentrations (0.062 mg/mL) led to visible aggregates on the surface of the crystals which dificulted separation and purification. In turn, the reaction time and temperature had a negligible effect over the final product. CNT conjugation was first analyzed by optical microscopy. Figure 2d shows how the pink octahedra characteristic of \(\text{UiO-68-TZDC}\) do not change significantly in color after the reaction, suggesting the formation of a very thin coating not visible at a single crystal level. Scanning Electron Microscopy (SEM) analysis of the surface of the crystals reveals clear differences. Compared to the pristine material that shows a bare surface, \(\text{TZDC-CNT-1}\) confirms the formation of a clean coating layer with an internal structure reminiscent of a chainmail fabric (Figure 2e). The topography of the crystal surface was also analyzed with Atomic Force Microscopy (AFM). Single crystal images were captured in PeakForce Tapping Mode, placing the probe on top of the crystals and applying low force to ensure minimum effect over their surface (Figure 2f). Compared to the bare crystals, that present a rough surface with no observable terrace features indicative of a high supersaturation level during crystal growth, \(\text{TZDC-CNT-1}\) displays a dense array of intertwined nanotubes all over the surface which agrees well with the formation of a dense shell covering the crystal surface.

We argue CNT conjugation in our case is facilitated by an inverse demand [4+2] DA reaction between the nanotube sidewall and the tetrazine dienophiles covering the crystal surface. Similar sidewall functionalization of SWCNTs have been reported in solution, and compatibility with mild conditions is enabled by the low thermodynamic stability of the resulting adducts facilitates spontaneous rearomatization. The role of tetrazine units in controlling nanotube conjugation was confirmed by testing the same reaction with \(\text{UiO-68}\) crystals built from \([1,1′:4′,1′′-\text{terphenyl}]−4,4′-\text{dicarboxylic acid linkers}\). As expected, the absence of the dienophile resulted in a completely different behavior for unsuccessful grafting (Supporting Section S2.3). Surface functionalization was next confirmed by Raman spectroscopy (Figure 3a). Compared to \(\text{UiO-68-TZDC}\), only the spectrum of \(\text{TZDC-CNT-1}\) displays vibrations at 234, 270 and
corresponding PSD plots analyzed with NLDFT kernel. The differences between the CHN and thermogravimetric analysis (TGA), with negligible residue and equivalent thermal stability, for a 0.6 wt% content in nanotubes that agree well with the formation of a very thin coating. The structural integrity of the framework after reaction was confirmed with X-ray powder diffraction (PXRD, Figure 3c), for negligible changes to the unit cell parameters calculated by Le Bail refinement (Supporting Section S3.1). Concerning the nanotubes, the absence of the characteristic broad diffraction at 2θ is likely associated to the formation of a thin shell rather than aggregated bundles. Both materials were solvent-exchanged in hexane and evacuated at 10⁻⁶ torr overnight. They display almost identical non-hysteretic N₂ isotherms for BET surface area (SA) near 4150 m²·g⁻¹, and experimental pore size distributions (PSD) characteristic of UiO-68 type frameworks (Figure 3d).

Our results confirm the formation of a thin and permeable CNT coating layer, that is exquisitely respectful with the intrinsic properties of the framework in terms of the structure, thermal stability, and accessible surface area of the resulting crystal composite. To demonstrate the benefits associated to this superficial coating we next tested its ability to control wettability and electrical conductivity. We prepared TZDC-CNT-2, by following the protocol described above and keeping the same concentrations of nanotubes (0.019 mg/mL) but using Wheaton culture tubes as reactor. As summarized in Supporting Section S4, the same techniques used above suggest the formation of a thicker coating (2.3 wt%), probably due to the smaller surface area of the reactor for less effective CNT dispersion. This high loading was denoted by the darker color of the crystals (Figure 4a), that also has a negligible impact on the porosity of the framework. Contact angle measurements were used to test the hydrophobicity of the CNT@MOF hybrids (Figure 4b). Compared to the hydrophilic of UiO-68-TZDC, TZDC-CNT-1 and 2 show exterior surface hydrophobicity for similar contact angles of 120 and 125 °. This surface wettability is comparable to that attained by using fluorinated linkers or post-synthetic coating with hydrophobic organic polymers, and we argued it might be equally effective in protecting the crystals from chemical degradation and structural collapse in water for a particularly delicate MOF. After incubation for 24 hours, the PXRD of the crystals show a clear influence on the concentration of CNTs over the structural stability of the framework when immersed in liquid water as result of the formation of a denser shell (Figure 4d). Only TZDC-CNT-2 maintains its structural integrity compared to the collapse suffered by TZDC-CNT-1 and the pristine material This enhanced hydrolytical stability is also translated to the porosity of the crystals after the test (Figure 4e). Compared to CTN-2 that displays a SA of 4000 m²·g⁻¹, TZDC-CNT-1 and UiO-68-TZDC suffer from a reduction of near 50 and near to 100% of the original value. To investigate the electrical conductivity of the composites, we contacted single crystals to a chip by using Pt wires and silver painting with futile results due to their small size (Supplementary Section S5.3.). Instead, two-contact probe measurements of polycrystalline pellets revealed a bulk conductivity value of 4·10⁻² S·cm⁻¹ for TZDC-CNT-2, compared to the insulating character of both CNT-1and the pristine MOF (Figure 4f). The poor homogeneity and conductivity displayed by a pellet prepared from a physical mixture of both components (2.3 wt%) suggests the crucial role of covalent conjugation for their effective hybridization into a single crystal. Also, the steady state emission spectrum of TZDC-CNT-2 after UV excitation (λ=312 nm) shows a better defined, more intense emission at 375 and 405 nm (Figure S28), that suggest the creation of an interfacial Schottky barrier and
result in higher quantum yields from decreasing recombination rates of photogenerated electron-hole pairs.\(^\text{18}\)

Compared to other MOF/CNT composites,\(^\text{10}\) TZDC-CNT-2 displays an optimal compromise between porosity, conductivity, and stability at very low carbon weight contents, thus offering an alternative for the design of MOF hybrid composites not reliant on their growth but adapted to controlled modification of the surface of preformed crystals. We are confident this might open unprecedented opportunities for the exploitation of the potential of reticular chemistry in a variety of applications as photovoltaics, sensing, electrocatalysis, thermoelectrics or energy storage.

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Keywords: Metal-Organic Framework • Carbon Nanotubes • Crystal Hybrid • Click Chemistry • Tetrazine tags
and Hydrogen Storage Capacity of CNT@MOF-5 Hybrid Composite.


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We use tetrazine linkers to wrap up the surface of MOF crystals with ultrathin coatings of nanotubes. Nanotube linkage proceeds straightforwardly and is respectful with the properties of both components for water stable, mesoporous and electrically conductive CNT@MOF crystal hybrids. Compared to other composites, our route is adapted to controlled modification of the surface of preformed crystals to prevent aggregation and maximize the hybridization between components.

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