A porous, electrically conductive hexa-zirconium(IV) metal–organic framework†

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Engendering electrical conductivity in high-porosity metal–organic frameworks (MOFs) promises to unlock the full potential of MOFs for electrical energy storage, electrocatalysis, or integration of MOFs with conventional electronic materials. Here we report that a porous zirconium-node-containing MOF, NU-901, can be rendered electronically conductive by physically encapsulating C60, an excellent electron acceptor, within a fraction (ca. 60%) of the diamond-shaped cavities of the MOF. The cavities are defined by node-connected tetra-phenyl-carboxylated pyrene linkers, i.e. species that are excellent electron donors. The bulk electrical conductivity of the MOF is shown to increase from immeasurably low to 10−3 S cm−1, following fullerene incorporation. The observed conductivity originates from electron donor–acceptor interactions, i.e. charge-transfer interactions – a conclusion that is supported by density functional theory calculations and by the observation of a charge-transfer-derived band in the electronic absorption spectrum of the hybrid material. Notably, the conductive version of the MOF retains substantial nanoscale porosity and continues to display a sizable internal surface area, suggesting potential future applications that capitalize on the ability of the material to sorb molecular species.

Introduction

Metal–organic frameworks (MOFs) are a large and growing class of porous, or potentially porous, materials. They are characterized by well-ordered (i.e., crystalline) combinations of multi-topic organic ligands connected by coordination bonds to one or more metal ions, or metal-ion-containing clusters.1–4 The enormous potential and experimentally realized compositional variety of MOFs,5–8 together with their typically large surface areas and their molecular-scale voids, has inspired exploration of myriad candidate applications including, but not limited to, gas storage and release,9,10 chemical separations,11,12 chemical sensing,13 catalysis,14–17 energy transfer,18–20 drug delivery,21 and solar fuel production.22–24 Electrically conductive MOFs, while few in absolute number, constitute an intriguing and increasingly important sub-class of materials, especially in view of the insulating character (conductivity <10−10 S cm−1) of most MOFs. The insulating versions typically make use of redox-resistant d(0) or d(10) metal ions that are energetically poorly matched or otherwise ineffective at interacting with linker-based π–π* systems. Thus, nodes may behave as local insulators between otherwise potentially conductive arrays of linkers (and/or vice versa).

Nevertheless, the demonstrated feasibility of deploying electrically conductive MOFs in field-effect transistors (FETs),25 chemiresistive sensors,26 electrochromic devices,27,28 supercapacitors29,30 and batteries,31 has motivated the search for suitably conductive MOFs. The common design rule is to provide a low energy pathway for charge transport, and reported strategies include: (a) π stacking of conjugated organic ligands,32 (b) formulation of MOFs as laterally conjugated 2D coordination compounds,33 (c) templating the growth of conductive polymers within suitably large MOF channels,34,35 (d) intentionally matching energies of frontier orbitals of metal-ion nodes and organic linkers,36 (e) post-synthetic modification or augmentation of MOF nodes, either with metals featuring partially filled d-shells37 or with redox couples such as ferrocenium/ferroocene,37 to yield redox-hopping-type conductivity, and (f) electrochemically oxidizing or reducing the linkers of solution-immersed MOFs, again to enable redox-hopping-type conduction.38,39

The availability of free space within MOFs suggests another route to eliciting electrical conductivity, namely, the incorporation...
of guest molecules (electron acceptors or donors) that are complementary, in a charge-transfer sense, to MOF nodes or linkers. The approach has clear parallels, for example, to the formation of conductive, organic charge-transfer salts by combining (co-crystallizing) a strong electron donor (D), such as tetraethylvalene (TTF), with a strong electron acceptor (A) such as tetracyanoquinodimethane (TCNQ). Generally, in order to effectively transport charges, long-range ordering of donor and acceptor components is necessary. MOFs, with their inherent crystallinity and their ability to encapsulate guest molecules, offer platforms for achieving the desired long-range ordering of electronically complementary species. In a groundbreaking study, Talin et al. demonstrated that infiltration of the microporous MOF Cu4(btc)2 (also known as HKUST-1; btc = 1,3,5-benzenetricarboxylate) with TCNQ boosts the MOF’s electrical conductivity decreases from 1844 to 0.07 S cm⁻¹.

Aqueous stability may be paramount. Phase electrocatalysis processes such as water splitting, oxidative heterogeneous catalysis of gas phase reactions, etc. may be improved by installing redox-active guests to MOFs. One example of this is the incorporation of buckminsterfullerene (C60) as the complementary component by TCNQ in an otherwise insulating zirconium based MOF. NU-901 was synthesized by a slightly modified literature procedure. Infiltration with C60 was performed by soaking a microcrystalline powder sample of activated (i.e., solvent-evacuated and fully porous) NU-901 in a saturated o-dichlorobenzene solution of C60 for four days at 60 °C. The powder X-ray diffraction (PXRD) pattern of NU-901-C60 matches well with the experimentally obtained and computationally simulated patterns for pure NU-901, implying that guest uptake does not alter the material’s crystallinity (Fig. 2a). Preservation of microcrystal morphology was confirmed by comparing scanning electron microscopy images of NU-901 and NU-901-C60 (Fig. S1†). The presence of fullerene in NU-901-C60 was probed by Raman spectroscopy, based on 785 nm excitation (Fig. 2d). The scattering spectrum of NU-901-C60 displays peaks attributable to both the MOF and the fullerene, including the Aν(1) vibration of C60 at 492 cm⁻¹. Consistent with interactions with the fullerene, the vibrational peaks for NU-901 are slightly shifted in NU-901-C60.

The porosity of both NU-901 and NU-901-C60 was confirmed by nitrogen adsorption–desorption measurements (Fig. 2b). Both display approximately type I isotherms, albeit with slight hysteresis presumably arising from inter-crystallite macroporosity. Brunauer–Emmett–Teller (BET) analyses of the isotherms return gravimetric surface areas of 2120 m² g⁻¹ for guest-free NU-901 and 1550 m² g⁻¹ for NU-901-C60. DFT pore-size distribution analyses of the isotherms reveal a large peak centered at 12 Å, together with a small peak at 27 Å. The former is consistent with the crystallographically observed diamond-shaped pores of NU-901. The latter we speculate are a result of local defects.

After installation of C60, the incremental pore volume corresponding to the diamond shaped channels decreased from 0.54 cm³ g⁻¹ to 0.38 cm³ g⁻¹, whereas the pore volume remains unchanged for pores generated by defect sites, suggesting fullerenes primarily reside within the diamond channels of the MOF (Fig. 2c). From the decrease in gravimetric pore volume, we estimate that the fullerene incorporation to be ~0.6 per node (~0.6 per linker-defined diamond void). Notably, DFT calculations (geometry optimized) show sitting in diamond pores is overwhelmingly energetically favored (by ~0.8 eV) compared to sitting in the smaller pores defined by pairs of nodes along the c axis (Fig. S8b†). The representations in the bottom of Fig. 1 are derived from the DFT geometry.
C$_60$ encapsulation by NU-901 is accompanied by a change in color of the MOF from bright yellow to light brown. The visible color change is observable in corresponding diffuse reflectance UV-visible absorption spectra (Fig. S2a†). Guest-free NU-901 shows a broad absorption band beginning at 490 nm (2.53 eV) and maximizing in the UV, with no absorption beyond 490 nm. The spectrum of NU-901-C$_60$ likewise displays the UV-blue band, but also presents a broad band extending from 500 nm to 700 nm ($\lambda$/C$_24$1.77 eV). We attribute the new band to a donor/acceptor (pyrene linker/C$_60$) charge-transfer transition.\(^{55}\) Consistent with the introduction of a strong electron acceptor,\(^{56,57}\) the encapsulated fullerene quenches the steady-state luminescence of the tetra-phenyl-pyrene linker by ca. 90%; see Fig. S2b.†

Qualitative assessments of electrical conductivity were made by first dropcasting MOF suspensions on interdigitated array electrodes (IDEs; 5 μm gap) and then recording the current (I) transmitted between the electrodes, via electrode-gap-spanning MOF crystallites, in response to applied biases (V; two-point measurements). NU-901-C$_60$ samples yielded measurable currents whereas guest-free crystallites of NU-901 did not; see Fig. S7.† Unfortunately, we were unable with this approach to quantify the conductivity, \(\sigma\), of NU-901-C$_60$. We therefore turned to macroscopic, two-point, \(I-V\) measurements using pressed pellets. The stability of the MOF pellets before and after C$_60$ encapsulation was verified by PXRD and nitrogen adsorption isotherms (Fig. S3 and S4†). Consistent with IDE measurements, NU-901 alone displayed no measurable conductivity (where the lower limit of detection is estimated, from the magnitude of electrode noise, to be about 10$^{-14}$ S cm$^{-1}$). In contrast (Fig. 3), NU-901-C$_60$ shows remarkable electrical conductivity of \(\sigma \sim 10^{-3}$ S cm$^{-1}$,\(^{58}\) i.e. eleven orders of magnitude (or more) greater than NU-901 alone, and similar to that of organic semiconductors (\(\sigma > 10^{-6}$ S cm$^{-1}\)).\(^{59}\) Unlike conventional organic semiconductors, however, the MOF/fullerene material is characterized by substantial internal surface area and considerable molecular-scale porosity.

We reasoned that if TBAPy$^{4+}$/C$_60$ donor/acceptor interactions are responsible for the observed electrical conductivity, increasing the strength of the MOF linker as an electron donor would increase the conductivity. We therefore replaced TBAPy$^{4+}$ with a tetra-amino (phenyl-substituted) analogue.\(^{60}\) PXRD (Fig. S6†) and SEM (Fig. S1†) assessments of NU-901-amino-C$_60$ indicated formation of a material that is structurally similar (Fig. S5†) to NU-901-C$_60$ (see [Fig. S5†]). N$_2$ adsorption and desorption measurements established the permanent porosity of the material, and yielded BET surface area of 980 m$^2$ g$^{-1}$ for

\[\text{Fig. 1} \quad \text{Immobilization of C}_60\text{ within diamond shaped channels of NU-901. The chemical structures of the individual components of NU-901 are shown. The diameter of C}_60\text{ (~7 Å) is well suited for encapsulation in NU-901 with pore aperture of 12 Å. The top view and side view of the composite NU-901-C}_60\text{ are shown. The top and side views are DFT-optimized structures in the limit of full occupancy of the diamond pores by the fullerene guest, i.e. 1 : 1 occupancy.}\]

\[\text{Fig. 2} \quad \text{(a) PXRD pattern of simulated NU-901, experimental NU-901, and experimental NU-901-C}_60\text{. (b) N}_2\text{ adsorption–desorption isotherms (77 K) (NU-901 and NU-901-C}_60\text{). (c) density functional theory (DFT) pore size distribution (NU-901-C}_60\text{ and NU-901) and, (d) Raman spectra (NU-901, NU-901-C}_60\text{ and C}_60\text{).}\]

\[\text{Fig. 3} \quad \text{Current (I) vs. voltage (V) plot for pressed pellets of NU-901 and NU-901-C}_60\text{. The scan was performed from –2 V to 2 V and the scan rate was 50 mV s}^{-1}.\]
NU-901-amino and 370 m² g⁻¹ for NU-901-amino-C₆₀ (Fig. S6†). IDE based measurements show that C₆₀ incorporation imparts electrical conductivity to NU-901-amino, with the observed currents being larger for NU-901-amino-C₆₀ than for NU-901-C₆₀, see Fig. S7.†

Next we turn our attention to density functional theory (the details of the methods used are in the ESIF) to gain further insight into the nature of the observed electron-donor/electron-acceptor interactions and their manifestation as electrical conductivity in the MOF/fullerene assemblies. The results of electronic density of states (DOS) calculations for NU-901, NU-901-amino, NU-901-C₆₀ and NU-901-amino-C₆₀ are summarized in Fig. S9.† Briefly, for the guest-free MOFs, both the valence band maximum (VBM) and conduction band minimum (CBM) are dominated by contributions from linker p orbitals (i.e., those that contribute to the linkers' aromatic systems). For the C₆₀-containing materials, the VBM remains predominantly linker defined, but the CBM consists of fullerene p orbitals, consistent with donor/acceptor complex formation. The calculated CBM - VBM difference, i.e. the nominal bandgap, decreases by 1.2 eV with incorporation of C₆₀, a result that is qualitatively replicated in the visible-region reflectance spectra for fullerene-containing versus fullerene-free versions of the MOF (note that DFT methods often underestimate absolute magnitudes of bandgaps, particularly when local functionals like PBE are used).62,63

Given the spatial and energetic proximity of the putative donors and acceptors and their associated bands, we also calculated charge-transfer integrals for relevant clusters cut from the NU-901-C₆₀ and NU-901-amino-C₆₀ periodic structures (Table S1†). Both the electron-transfer and hole-transfer integrals are larger (by 2- and 4-fold, respectively) for NU-901-amino-C₆₀ compared to NU-901-C₆₀, consistent with larger IDE currents for the amino version.20

Conclusions

In summary, we find that the zirconium-based MOF, NU-901, can be rendered electrically conductive by installing isolated C₆₀ molecules in roughly half the linker-defined, diamond shaped pores presented by the MOF. Indeed, the experimentally evaluated conductivity increases from immeasurably small (<10⁻¹⁴ S cm⁻¹) to ~10⁻⁸ S cm⁻¹. The basis for the conductivity is in electron-donor (pyrene)/electron-acceptor (fullerene) interactions, as evidenced, in part, by the appearance of a visible-region charge-transfer band and by the results of DFT band structure calculations. Notably, the MOF internal surface area (gravimetric surface area) decreases by only about 27% with fullerene incorporation while the N₂-accessible void volume (as expressed gravimetrically) decreases by only about a third. DFT computes that appending NH₂ substituents (strongly electron-donating groups) to the linker phenyl groups of NU-901 increases hole- and electron-transfer integrals, which is consistent with the increased conductivity measured experimentally. These findings point to the potential for systematic chemical tunability of the observed conductivity.

Finally, while electrocatalysis applications are beyond the scope of this initial report, it is worth considering how much conductivity is needed for a MOF to function effectively in that context. A common motif for electrochemical applications of MOFs is a thin film (a fraction of a micron to several microns thick) sited on a conventionally conductive platform – for example, a planar glassy carbon or platinum electrode. A benchmark catalytic current density for solar-driven electrochemical processes is 10 mA cm⁻². For a hypothetical 10 micron thick MOF film having the modest conductivity observed here, i.e., ~10⁻⁵ S cm⁻¹, and operating at 10 mA cm⁻², the energetic penalty (i × R drop) due to film resistivity would be just 10 mV – a value barely within the reproducibility of kinetic over-potentials for many electrocatalytic systems. We suggest that for these types of applications, conductivities in the range of 10⁻³ S cm⁻¹, despite falling in the semiconducting regime (phenomenologically),24 will typically be sufficient.

Author contributions

J. T. H., O. K. F. and S. G. conceived the project, design the experiments and wrote the manuscript. S. G. performed the synthesis and experiments. D. R. and C. J. C. contributed to the theoretical studies. K. O. and C. W. C. assist in performing Raman spectroscopy and IDE measurements respectively. S. J. G., T. L. and A. A. contributed in amino linker synthesis. Y. C. assist in performing diffuse reflectance UV measurements.

Conflicts of interest

The authors declare no competing financial interests.

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Notes and references


54 The DFT calculations also indicate a slight change pore geometry in response to complete fullerene incorporation (1 : 1 incorporation). Based on PXRD measurements, the anticipated changes are absent suggesting minor differences in framework coordinates for $C_{60}$ incorporation at 0.6 : 1 versus 1 : 1. As yet, we have been unable to boost the loading beyond 0.6 : 1. Nevertheless, it will be interesting to see (eventually) if higher loading translates not only into detectable MOF structural changes, but also significant further changes in electronic conductivity (see subsequent results and discussion).

55 Based on the (+/0) redox potential of TBAPy linkers in NU-901 (1.4 V vs. Ag/AgCl) and (−/0) redox potential of $C_{60}$ (−0.33 V vs. Ag/AgCl), the charge transfer (CT) band should appear near 1.8 eV (690 nm). The experimental band maximum is at near 550 nm and the onset is near 700 nm (1.77 eV).


58 We recognize that two-point measurements with pelletized samples do exclude effects due to electrode/sample contact resistance and do not distinguish between inter-crystallite and intra-crystallite con-tributions to sample resistivity. Thus, the $\sigma$ value of $\sim 10^{-3}$ S cm$^{-1}$ should be regarded as a lower-limit estimate for electrical conductivity within a single crystallite. Also obscured by pellet-based measurements is any conductivity anisotropy – specifically, differences in conductivity in the MOF ab plane versus in the c direction (the direction aligned with the diamond-shaped channels).


61 Given uncertainties in MOF loading on the IDE platforms, we are unable to say with certainty that the conductivity of NU-901-amino-$C_{60}$ exceeds that of NU-901-$C_{60}$. Unfortunately, we lack sufficient NU-901-amino-$C_{60}$ to extend the study pelletized samples, i.e. samples that could yield quantitative conductivity data.


64 Definitive demonstration (or not) of the putative semiconducting behavior will require variable temperature conductivity measurements. We anticipate reporting on these in due course.