Through-space hopping transport in an iodine-doped perylene-based metal–organic framework

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Electrically conductive metal–organic frameworks (MOFs) have emerged in the past few years as promising materials towards applications in (opto)electronics, electrocatalysis and energy storage, among others. One of the most common strategies for the design of conductive MOFs is based on the use of electroactive organic ligands and their partial oxidation/reduction to increase the number of charge carriers. Although perylene salts were reported as the first molecular conductors, they have been scarcely explored as building blocks for the construction of conductive MOFs. Herein we report the electrical conductivity enhancement of a microporous perylene-based MOF upon partial ligand oxidation by using two-probe single-crystal devices. The origin of the conductivity enhancement is rationalised by means of spectroscopic studies and quantum-chemical calculations, supporting a through-space hopping transport along the herringbone perylene packing. This study opens the way for the design of conductive MOFs based on perylene building blocks.

Introduction

Metal–organic frameworks (MOFs) are crystalline porous materials constructed from multitiopic organic ligands and metallic nodes, which have received considerable attention towards a wide range of potential applications due to their considerable chemical and structural versatility.1,2 Besides their use in conventional applications, such as gas storage/separation and catalysis, electrically conductive MOFs have gained a great deal of interest especially in the fields of (opto)electronics, electrocatalysis and energy storage.3-5 In this direction, achieving efficient charge transport in MOFs is required towards their implementation in advanced multifunction electronic devices. Although most reported MOFs are insulators, certain synthetic strategies have been devised to increase their electrical conductivity.5 One such strategy, known as “through-space approach”, is based on noncovalent interactions between the organic moieties to promote efficient charge-transport pathways.5,6 In particular, different conjugated electroactive building blocks have been incorporated in MOFs giving rise to semiconducting properties ($\sigma = 10^{-7} - 10^{-9}$ S cm$^{-1}$) thanks to the short intermolecular interactions between the linkers.5,7,8 For example, conductive MOFs based on through-space conduction pathways are built from organic building blocks,
such as tetrathiafulvalenes,\textsuperscript{9–11} anthracenes,\textsuperscript{12} pyrenes,\textsuperscript{13} naphthalenes,\textsuperscript{14} naphthalene diimides,\textsuperscript{15,16} diazaphenalene radicals\textsuperscript{17} and pentacenes.\textsuperscript{18} Otherwise, encapsulation of doping molecules, such as iodine,\textsuperscript{19–22} within the pores is another efficient strategy to enhance the conductivity of MOFs by several orders of magnitude due to the spontaneous formation of free charge carriers.

The discovery of relatively high electrical conductivity in a perylene–bromine complex\textsuperscript{23} (considered the first organic conductor) in the 1950s initiated the vast field of molecular conductors.\textsuperscript{24,25} Since then, many perylene derivatives were extensively employed in the synthesis of molecular conductors, in combination with various inorganic anions (Br\textsuperscript{−}, I\textsuperscript{−} …) and organic acceptors, such as TCNQ.\textsuperscript{26,27} The conductivity of perylene salts originates from the \( \pi–\pi \) intermolecular interactions between these planar molecules, which should be optimally stacked in a close and parallel manner. The structural arrangement allied to the partial oxidation of perylenes may result in incompletely filled bands and metallic conductivities.\textsuperscript{26}

Despite their promising electrical properties, perylenes have been scarcely explored as building blocks for the construction of electrically conductive MOFs.\textsuperscript{3} Most perylene-based MOFs have been studied towards gas sorption and sensing applications due to the remarkable luminescence properties of perylene.\textsuperscript{28–35} On the other hand, the study of the electrical conductivity of alkali metal-based MOFs is limited to a very recently reported family of tetrathiafulvalene–tetracarboxylate MOFs.\textsuperscript{36} In this direction, the perylene-3,4,9,10-tetracarboxylate (PTC) ligand has been combined with potassium ions leading to two-\textsuperscript{37} and three-dimensional coordination polymers exhibiting permanent microporosity, humidity-dependent impedance and proton conductivity.\textsuperscript{31,32} However, the structure-dependent electrical conductivity and charge-transport mechanism of doped perylene-based MOFs have not been investigated in detail.

Inspired by the design of perylene-based molecular conductors, herein we report the electrical conductivity enhancement up to three orders of magnitude of a perylene-based MOF (\textit{Per-MOF})\textsuperscript{12} upon partial ligand oxidation by iodine doping using two-probe single-crystal devices. Solid-state cyclic voltammetry confirmed the possibility of oxidation of the electroactive ligands, whereas spectroscopic studies demonstrated the presence of perylene radical cation and polyiiodine anion species. Quantum-chemical calculations were performed to further understand the origin of the conductivity enhancement, which is explained in terms of a through-space hopping charge-transport mechanism. This study highlights the great potential of doped perylenes as building blocks for the construction of electrically conductive MOFs.

\section*{Results and discussion}

\subsection*{Synthesis and crystal structure}

\textit{Per-MOF} single-crystals were obtained by optimizing a previously reported method,\textsuperscript{32} consisting in mixing the ligand 3,4,9,10-perylenetetracarboxylic acid (H\textsubscript{4}PTCA) and KOH in water and heating the reaction mixture with infrared light for 24 h (see ESI\textsuperscript{†}). Crystals were exhaustively washed with DMF and EtOH to remove any unreacted ligand, as confirmed by IR spectroscopy (Fig. S1\textsuperscript{†}). Finally, the material was filtered off and dried at 100 °C.

\textit{Per-MOF} crystallises in the trigonal \( P\overline{3} \) space group. The 6- or 8-coordinated \( K^+ \) ions are connected through bridging carboxylate groups from the tetratopic perylene ligands (Fig. 1).\textsuperscript{32} The crystal structure reveals 1D hexagonal microporous channels of ca. 8.6 Å along the \( c \)-axis (Fig. 1a), resulting in a calculated solvent-accessible volume of ca. 20%...
of the total (see Table S1, ESI†). The perylene moieties stack to form one-dimensional chains along the \( a \)-axis (Fig. 1b and S2†). Perylene moieties are arranged in a herringbone stacking showing the shortest \( \cdots \) intermolecular distances of 3.6 Å between adjacent ligands (Fig. 1c). Note that such herringbone arrangement is a common molecular packing of many organic semiconductors.38,39

Thermogravimetric analysis and gas sorption properties

Thermogravimetric analysis (TGA) of Per-MOF (Fig. S3, ESI†) shows a mass loss (\( \sim \)5%) between 25 and 100 °C attributed to the removal of EtOH solvent molecules, followed by a wide plateau until the decomposition of the material at 450 °C, demonstrating its high thermal stability. Gas sorption (CO\(_2\), N\(_2\)) measurements were performed on activated Per-MOF (120 °C for 12 h under vacuum), to evaluate its porosity (Fig. S4, ESI†). The CO\(_2\) adsorption isotherm (273 K) reveals an uptake of 20 cm\(^3\) g\(^{-1}\) at 1 bar, indicating the presence of intrinsic micropores in the MOF. The pore size distribution was calculated by Grand Canonical Monte Carlo (GCMC) approach using a carbon slit-shaped pore model (Fig. S4b†) revealing a pore size range between 4 and 8 Å. The 77 K N\(_2\) adsorption isotherm shows a minimum uptake of N\(_2\), in line with other similar MOFs reported.31,36 This type of selective CO\(_2\) adsorption has been attributed to the high quadrupole moment of the CO\(_2\) molecules that strongly interact with the large \( \pi \)-electron cloud of the aromatic rings of \( \pi \)-conjugated ligands,10,31,40 in this case perylene.

Electrochemical properties

The electrochemical properties of Per-MOF and its organic building block were investigated by cyclic voltammetry (CV). The CV of the \( \text{H}_2\text{PTCA} \) ligand in DMF (Fig. S5, ESI†) shows a quasi-reversible redox process at \( -0.85 \) V (vs. Ag/AgCl) assigned to the reduction of the acid groups,41 and a more irreversible redox process at \( +1.10 \) V attributed to the oxidation of the perylene, in agreement with previous studies.42 The solid-state CV of Per-MOF in CH\(_3\)CN shows the oxidation process occurring at similar potentials, \(+1.17\) V (Fig. 2 and S6, ESI†), as expected for perylene derivatives,26,34 confirming the possibility of oxidation of the electroactive ligands. A quasi-reversible reduction process is observed at \( -0.76 \) V. The relatively large peak-to-peak separation can be explained by the partial dissolution of the ligand after several cycles (note that at negative potentials the reduction of the carboxylate groups takes place) or by the poor diffusion of the electrolyte through the micropores of the MOF. As expected, the perylene-based MOF oxidation process (\( \sim 1.2 \) V) occurs at lower potentials than for pyrene-based MOFs (\( \sim 1.4 \) V).33 The ionization potential (IP) was estimated from the oxidation potential to be 5.6 eV, in full agreement with theoretical calculations (see section 6 in the ESI† and Table S2).

Iodine doping

In view of the promising electrochemical properties and potential partial oxidation of the perylene moieties, chemical doping by iodine encapsulation was performed to obtain I\(_2@\)Per-MOF using a diffusion technique and adapting a reported procedure.19–22 The activated crystals (heated at 200 °C for 2 h) of Per-MOF were immersed in a saturated solution of iodine in cyclohexane (0.1 M) at room temperature for 24 h (Fig. S7, ESI†). Then, the crystals were washed with cyclohexane to remove the physisorbed iodine. The crystallinity and morphology of Per-MOF crystals after doping were preserved, as confirmed by powder X-ray diffraction (PXRD) (Fig. S8, ESI†) and scanning electron microscopy (SEM) (Fig. S9, ESI†), respectively. The pure crystalline phase of Per-MOF was confirmed by PXRD with some differences in relative intensity between simulated and experimental patterns that might be due to the preferred crystalline orientation. The PXRD reflections of I\(_2@\)Per-MOF did not change their positions relatively to Per-MOF, and only slight changes were observed in the relative intensities, as previously reported for other iodine-doped MOFs (Fig. S8†).19 Moreover, energy-dispersive X-ray spectroscopy (EDS) confirmed the homogeneous distribution of iodine through the I\(_2@\)Per-MOF crystals (Fig. S10 and S11, ESI†). IR (Fig. S12, ESI†) and Raman (Fig. S13a, ESI†) spectra of Per-MOF and I\(_2@\)Per-MOF did not show any significant differences in the 400–2000 cm\(^{-1}\) region. The most important changes are observed in the low-frequency spectral region (100–200 cm\(^{-1}\)) of the Raman spectrum of I\(_2@\)Per-MOF, in which four new bands at 178, 171, 153 and 139 cm\(^{-1}\) are observed (Fig. S13b, ESI†). Bands close to 180 cm\(^{-1}\) are attributed to symmetric stretching vibrations of I\(_2\) whereas bands at 130–142 and 150 cm\(^{-1}\) are related to I\(_3^–\) stretching vibrations.44–46 Thus, these results indicate that both molecular iodine (I\(_2\)) and polyiodine anions such as I\(_3^–\) are present within the framework. Importantly, the electron paramagnetic resonance (EPR) spectrum of I\(_2@\)Per-MOF crystals at room temperature showed an intense signal at \( g = 2.003 \) ascribed to perylene radical cation species (Fig. S14,
The photophysical properties of Per-MOF and I₂@Per-MOF were characterized in the solid state (Fig. 3). For comparison, the absorption, emission (λ_em = 366 nm) and excitation (λ_exc = 571 nm) spectra of the H₄PTCA ligand were also measured in solution (Fig. S16, ESI†). Upon the addition of an increasing amount of I₂ equivalents to the ligand, the UV-vis spectrum of H₄PTCA displays a growing intense absorption band at 360 nm (Fig. S17, ESI†) assigned to I₃⁻ species, suggesting the reduction of iodine upon oxidation of the perylene ligands. The emission spectra of the ligand H₄PTCA in solution upon addition of increasing amounts of I₂ were also measured as reference (Fig. S18, ESI†). The intensity of the band at 540 nm increases, which could also be related to the formation of I₃⁻ species (emission at 532 nm, Fig. S18, ESI†).

The solid-state emission spectra of Per-MOF and I₂@Per-MOF (λ_exc = 368 nm) display three main bands at 528, 559 and 605 nm (Fig. 3 and S19†), in agreement with other similar systems. The relative intensity of the 528 nm band increases in the case of I₂@Per-MOF (Fig. 3), a signature that could be related to the presence of chemisorbed I₃⁻ in the pore channels. Absolute quantum yields of Per-MOF and I₂@Per-MOF were determined using integrating sphere method obtaining values of 0.5% and 0.3%, respectively. To determine the Per-MOF and I₂@Per-MOF optical bandgaps (E_g), Tauc plots were obtained from diffuse reflectance UV-vis spectroscopy (Fig. S20, ESI†). Linear absorption onsets in Tauc plots of Kubelka-Munk-transformed data afforded E₉ of 2.37 and 2.34 eV for Per-MOF and I₂@Per-MOF, respectively. The slightly reduced bandgap for the doped I₂@Per-MOF is in agreement with first-principles calculations (see below).

![Figure 3](image-url) Solid-state emission spectra of Per-MOF and I₂@Per-MOF under 368 nm excitation.

Quantum-chemical calculations

Theoretical calculations were performed to shed light on the structural, electronic and conducting properties of Per-MOF before and after iodine doping (see section 6 in the ESI† for full computational details). The minimum-energy crystal structure of Per-MOF was obtained upon full ionic and lattice relaxation at the PBEsol level of theory without symmetry constraints. Lattice parameters for the optimized crystal structure are in good accord with the experimental X-ray data (Table S3, ESI†).

Band structure calculations were performed on the first Brillouin zone of the reciprocal space corresponding to the P3 space group. The electronic band structure of the evacuated Per-MOF framework displays flat bands along the full k-path (Fig. 4a), suggesting a hopping mechanism in case of efficient charge transport. The highest-occupied (HOCO) and lowest-unoccupied (LUCO) crystal orbitals are localized over the PTC moieties (Fig. 4b and S21†), and their shape resembles the typical frontier molecular orbitals of the perylene molecule.

Iodine doping was modelled by placing one iodine molecule per unit cell in the framework pore, according to the stoichiometry derived experimentally (1 I₂ molecule per 3 perylene units). The minimum-energy crystal structure indicates...
that iodine favourably interacts with the framework (Fig. S22, ESI†), displaying $I\cdots\text{perylene}$ intermolecular contacts in the range of 3.3–4.0 Å, and a short $I\cdots\text{O(COO)}^-$ interaction (2.43 Å). Upon iodine doping, electronic structure calculations predict a flat-band profile with a small reduction of the bandgap from 2.11 to 2.08 eV (Fig. 4a and S23a†), in good accord with the experimental evidence (see above). Atom-projected density of states (PDOS) calculations indicate that the frontier molecular orbitals of $I_2$ are close in energy to the HOCO and LUCO of Per-MOF, slightly shifted away from the bandgap (Fig. 5a; HOCO–3 and LUCO+3 in Fig. S24, ESI†). However, close inspection of the crystal orbital topology evidences an appreciable contribution of $I_3$ to HOCO (Fig. 4b). Relative PDOS confirms the active role of iodine in the frontier crystal orbitals of $[\text{Per-MOF} + I_2]$ (Fig. 5b).

According to the experimental evidence, iodine doping promotes the formation of the perylene radical cation due to oxidation by $I_2$ and formation of $I_3^-$ species. Theoretical calculations indicate that in the presence of $I_3^-$, the spontaneous oxidation of perylene moiety and formation of anion $I_3^-$ occurs. $I_3^-$ favourably interacts with the framework, with short $I\cdots\text{K}$ (3.5–3.9 Å) and $I\cdots\text{H}$ (3.2–3.6 Å) contacts (Fig. S25, ESI†). The spin density calculated for $[\text{Per-MOF} + I_3^-$ predicts the localization of an unpaired electron on one perylene moiety of the unit cell (Fig. 4b), whose accumulated charge ($\Delta q$) increases +0.90e with respect to Per-MOF, whereas the $I_3^-$ net charge is $-0.70e$. These results therefore confirm the formation of both a perylene radical cation and $I_3^-$. As a result, a half-empty valence band results (spin-$\beta$ bandgap of 0.09 eV; Fig. 5a), with a significant contribution of the $I_3^-$ species to HOCO-β (see Fig. S26, ESI†).

To get insight into the conducting properties of Per-MOF upon iodine doping (perylene cation formation), the electronic coupling ($J$) for hole carriers between perylene pairs was evaluated from molecular calculations. Recall that Per-MOF displays a band structure with flat states (Fig. 4a and S23†), which points towards a hopping regime as the dominant charge-transport mechanism. Moreover, the inefficient herringbone stacking pattern of PTC moieties in Per-MOF is typical of organic semiconductors reported to show a hopping charge transport. The size of the charge-carrier polaron species was estimated from the spin density contours calculated for perylene oligomers extracted from the crystal structure of Per-MOF and incorporating an oxidized perylene unit. The polaron is shown to be localized over few (1 or 2) perylene units (Fig. S27, ESI†), thus supporting a hopping mechanism. The $J$ values for the three perylene interacting pairs in the Per-MOF unit cell were calculated with very similar values, as expected from the experimental $P3$ symmetry (Fig. 6), with a mean $J$ value of 12 meV (a relatively small coupling as anticipated by the inefficient herringbone arrangement). Moving to the perylene pairs of $[\text{Per-MOF} + I_2]$ and $[\text{Per-MOF} + I_3]$ (see section 6 in the ESI† for details), the electronic couplings are comparable to Per-MOF (mean $J$ values of 11 and 9 meV, respectively; Table S4†), therefore suggesting a negligible structural effect of the iodine inclusion on the electronic communication between perylenes. On the other hand, the electronic effect of the iodine doping was assessed by calculating the lowest-lying

![Fig. 5](image-url)  
**Fig. 5** a) Atom-projected density of states (PDOS) and bandgap values calculated for Per-MOF, $[\text{Per-MOF} + I_2]$ and $[\text{Per-MOF} + I_3]$ at the HSE06 level. Spin-α and spin-β channels (with their corresponding bandgaps) are indicated in $[\text{Per-MOF} + I_2]$. The Fermi level was set to the valence band maximum. b) Relative PDOS of $[\text{Per-MOF} + I_3]$ calculated as the PDOS divided by the number of atoms of each type in the unit cell.

![Fig. 6](image-url)  
**Fig. 6** Electronic couplings for holes calculated at the PBE level for the three PTC interacting pairs in Per-MOF. Hydrogen and potassium atoms are omitted for clarity. The centroid-centroid intermolecular PTC distances are calculated to be 5.78, 5.81 and 5.89 Å and the closest C–H⋯C intermolecular distances are found at 2.67, 2.66 and 2.65 Å for interacting pairs 1, 2 and 3, respectively.

$J_1 = 12.16 \text{ meV}$  
$J_2 = 11.37 \text{ meV}$  
$J_3 = 11.82 \text{ meV}$
excited states of perylene-guest dimers under the time-dependent density functional theory, and considering the different charged species available (see the ESI†).

Interestingly, several charge-transfer (CT) states are predicted in the low-energy range, from very low to moderate probability (oscillator strength, f), and described by a net one-electron transfer from one moiety to the other (see Fig. S28†). For example, a charge-transfer state from perylene to I\(^+\) is predicted at 0.71 eV with a f = 0.029, whereas a CT from I\(^+-\) to [perylenyl] is calculated at 0.72 eV with a f = 0.001. As the conductivity depends on the charge mobility and carrier concentration, promoting hole carriers through perylene radical cations upon iodine doping, with the additional benefit of boosting perylene–perylene communication through guest-promoted charge transfer excitations, is expected to enhance significantly the electrical charge transport of Per-MOF.

The evolution of the Per-MOF experimental optical properties upon iodine doping was rationalized through theoretical modelling. Molecular calculations were performed on the lowest-lying singlet excited states of H\(_4\)PTCA, radical H\(_4\)PTCA cation, I\(_2\) and I\(_3\) at the PBE0 level. Simulated absorption and emission spectra including vibrational resolution of H\(_4\)PTCA are predicted with a mirror symmetry and a Stokes shift of 0.05 eV (Fig. S29a, ESI†). The most intense 0–0 PTC emission peak is predicted at 523 nm, in good accord with the experimental data recorded for Per-MOF (528 nm). Note that the excitonic coupling between MOF intense 000 PTC emission peak is predicted at 523 nm, in good accord with the experimental data recorded for Per-MOF (528 nm). Note that the excitonic coupling between MOF intense 000 PTC emission peak is predicted at 523 nm, in good accord with the experimental data recorded for Per-MOF (528 nm). Note that the excitonic coupling between MOF intense 000 PTC emission peak is predicted at 523 nm, in good accord with the experimental data recorded for Per-MOF (528 nm). Note that the excitonic coupling between MOF intense 000 PTC emission peak is predicted at 523 nm, in good accord with the experimental data recorded for Per-MOF (528 nm). Note that the excitonic coupling between MOF intense 000 PTC emission peak is predicted at 523 nm, in good accord with the experimental data recorded for Per-MOF (528 nm). Note that the excitonic coupling between MOF intense 000 PTC emission peak is predicted at 523 nm, in good accord with the experimental data recorded for Per-MOF (528 nm). Note that the excitonic coupling between MOF intense 000
Conclusions

In summary, we have reported the first evidence of increased conductivity in a perylene-based MOF upon iodine doping. This conductivity is ascribed to the partial oxidation of the perylene ligands, as witnessed by EPR and emission spectroscopy, and supported by theoretical calculations. The charge transport is described by means of a through-space hopping mechanism along the herringbone perylene packing, with highest conductivities of the order of \(10^{-5} \text{ S cm}^{-1}\) measured in two-contact single-crystal devices. Current research is focused on the design of extended perylene-based ligands to increase the MOFs porosity, allowing the encapsulation of larger electron-acceptor (doping) molecules. We highlight the potential of perylene building blocks for the design of electrically conductive and photoresponsive MOFs. In this direction, one of the main challenges is the construction of doped perylene-based MOFs in which electroactive ligands are arranged showing different stacking modes (e.g., face-to-face \(\pi\)-stacking) in order to modulate their electrical properties.

Author contributions

G. V. synthesised and characterised the doped material. A. P. and H. A. carried out and analysed the electrical measurements. A. R. D. and D. C. L. carried out and analysed the optical measurements. M. E.-R., E. O. and J. C. performed the Raman measurements. M. E.-R., E. O. and J. C. performed the Raman measurements. A. R. D. and D. C. L. analysed the crystal and H. A. carried out and analysed the electrical measurements. M. E.-R., E. O. and J. C. performed the Raman measurements. M. E.-R., E. O. and J. C. performed the Raman measurements. A. R. D. and D. C. L. analysed the crystal

Conflicts of interest

There are no conflicts to declare.

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