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Direct observation of the reduction of a molecule on nitrogen pairs in doped graphene

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Abstract

Incorporating functional atomic sites in graphene is essential for realizing advanced two-dimensional materials. Doping graphene with nitrogen offers the opportunity to tune its chemical activity, with significant charge redistribution occurring between molecules and substrate. The necessary atomic scale understanding of how this depends on the spatial distribution of dopants, as well as their positions relative to the molecule, can be provided by scanning tunneling microscopy. Here we show that a non-covalently bonded molecule such as CoPc undergoes a variable charge transfer when placed on N-doped graphene: on a nitrogen pair, it undergoes a redox reaction, with an integral charge transfer, whereas a lower fractional charge transfer occurs over a single nitrogen. Thus the charge state of molecules can be tuned by suitably tailoring the conformation of dopant atoms.

Keywords

Scanning tunneling microscopy, Doped graphene, Molecule, Charge transfer

Introduction

Integrating active atomic sites in graphene is a prerequisite for the realization of second generation two-dimensional materials. Particular attention has been focused on the doping of graphene by heteroatoms, due to the emergence of new physical and chemical properties at well defined point defects.¹⁻⁶ In nitrogen-doped graphene, the doping sites have different electronic properties depending on their atomic structure⁷ and the interaction of molecules with nitrogen sites induces a shift or renormalization of their electronic spectrum.^{8,9} However, redox reactions between doped graphene and molecules have not yet been directly visualized at the molecular scale, and therefore the site dependence of such reactions remains unknown. There is special interest in testing whether one can change the degree of

oxidation of adsorbed molecules containing a cobalt center binding to four nitrogens (Co-N₄), such as cobalt porphyrin (CoP), cobalt phthalocyanine (CoPc) and their derivatives. These molecules have been identified as efficient catalysts for the CO₂ reduction reaction.¹⁰⁻¹² Controlling the charge of these molecules is crucial, since an increase of electron density at the cobalt center amplifies the nucleophilicity, and hence improves its catalytic performance. This effect has been seen on functionalized carbon electrodes where the molecules bind to nitrogenated groups such as pyridine.^{10,13-15} Therefore, the control of the degree of oxidation of the Co-N₄ moiety on doped graphene is promising, but remains a challenging task. An atomic scale understanding and control of the charge transfer is still missing, and is highly desirable.

Here we directly observe redox reactions and various degrees of charge transfer between CoPc molecules and nitrogen-doped graphene, and we unveil the role of the adsorption site on the charge transfer. We show that the charge transfer varies from a fractional to an integer electron charge when a molecule is adsorbed on a single nitrogen atom or a nitrogen pair. Although previous studies have focused on single nitrogen or nitrogen-vacancy combinations, we show that nitrogen pairs can also play a vital role, and that they constitute a reduction center in doped graphene. An intermediate case is also observed, for a molecule centered on a single nitrogen dopant or moved around with respect to the position of a nitrogen pair on the graphene substrate, where the the Lowest Unoccupied Molecular Orbital (LUMO) splits into a singly occupied molecular orbital (SOMO) and a singly unoccupied molecular orbital (SUMO).

Results and discussion

The system that we study is represented in Fig. 1a. It consists of CoPc molecules on nitrogen-doped graphene, where the molecules can sit on a pristine graphene location, single nitrogen site or nitrogen pairs – the latter two are the main nitrogen configurations in our samples.

The nitrogen pairs consist of two nitrogen atoms separated by a few carbon atoms,⁷ with a N-N distance ranging from 2.5 to 10 Å. During the deposition process, the diffusion at room temperature leads to the formation of molecular clusters (Fig. 1b) that always include at least one molecule binding to two nitrogen atoms, suggesting that nitrogen pairs act as trapping sites. To locate the underlying nitrogen atoms, the molecules were removed with the STM tip in order to visualize the nitrogen atoms below. The topographs in Fig. 1c,d, taken at 1 V and -1.5 V respectively, show an inversion of the contrast between a CoPc adsorbed on a single nitrogen atom and a CoPc adsorbed on a nitrogen pair (the same area after spectroscopy measurements and removing the molecules reveals the position of the nitrogen atoms, as seen in Fig. 1e). Note that at higher positive bias (2 V), this contrast disappears, as is shown in Fig. 1b. The nitrogen pair corresponds to a 1-5 pair, with nitrogen atoms separated by two carbon atoms, according to our previous work.⁷ At -1.5 V, the CoPc adsorbed on single nitrogen appears with a lobe at the center of the molecule and four double lobes located at the end of the four arms of the molecule (only three are seen due to an overlap of the image of the neighboring molecule). For the molecule on a nitrogen pair, only a single broad lobe is observed on each arm. These contrasts at negative bias are typical of neutral CoPc⁰ and charged CoPc⁻ molecules.^{16,17} (The molecule is considered to be in a ‘neutral’ state when only a minute charge transfer occurs, while it is considered to be ‘charged’ when the charge transfer is close to one electron.) The spectrum of CoPc⁰ shows resonant states corresponding to a LUMO localized on the Co center, and Highest Occupied Molecular Orbital (HOMO) and LUMO+1 localized on the arms, as evidenced by the dI/dV spectra measured at the center and at the arms of the molecule (Fig. 1f). A close look at the spectra shows extra peaks close to the HOMO and LUMO (a shoulder on the right side of the LUMO peak at about 0.43 V and a small peak below the HOMO state around -1.65 V) that have also been observed in previous studies.^{16,17} The interaction between the CoPc and single nitrogen atom induces a downshift of the molecular spectrum due to a fractional charge transfer, which is similar to previous observations with other molecules^{8,18,19} (see

supplementary information Fig. S1). When the molecule is bound to two nitrogen atoms, the spectrum, which is shown in Fig. 1g, exhibits a series of peaks at negative bias, typical of a CoPc^- molecule,¹⁷ that are absent on CoPc^0 . This spectroscopy in the occupied states region can be analyzed as a series of pairs of peaks with the same localization corresponding to different states with vibrational replica. Four states at negative bias emerge: namely, S0 at -0.20 V, S1 at -0.29 V, S2 at -0.76 V, S3 at -1.0 V and S4 at -1.49 V. The dI/dV maps taken at the energies of the peaks of neutral and charged molecules are shown in Fig. 1h. On CoPc^- , the first state below the Fermi level, S0, is localised on the cobalt atom, like the LUMO of a neutral molecule, which confirms that the molecule is charged by an electron. The states S1 and S2 are localised on the four arms of the molecule, with one lobe on each arm for S1, and a double lobe on each arm for S2. Each of these states is accompanied by a replica at an energy separation between 0.1 V and 0.2 V, as seen in Fig. 1g,h, attributed to vibronic transitions (marked by the index v). At -0.39 V and -1.0 V, a mixing of a state and a vibrational replica appear, due to energy proximity of these features. This distribution of occupied states with vibronic replicas, and the localisation of the states, correspond to the spectrum and conductance maps of CoPc^- previously reported on another substrate,¹⁷ which confirms the assignment of the spectroscopic features that we measure on CoPc^- . In the unoccupied region, the conductance map of CoPc^- shows a broad feature, related to the broad peak around 1.2 V (less intense than the LUMO+1 of the neutral molecule) localized on the four arms of the molecule.

The observation of neutral and charged molecules raises the question of the strength of the molecule-surface binding when a molecule is charged or neutral. In order to gain some insight into this problem, we have investigated the possibility of observing a double tunnel barrier effect that is indicative of a weak interaction.^{19,20} In Fig. 2a, we show a cluster containing a CoPc^0 on a single nitrogen, and a CoPc^- on a nitrogen pair. The position of the nitrogen atoms is revealed in Fig. 2b after removing the molecules. The differential conductance curves of CoPc^0 (Fig. 2c) and CoPc^- (Fig. 2d) exhibit two new peaks at

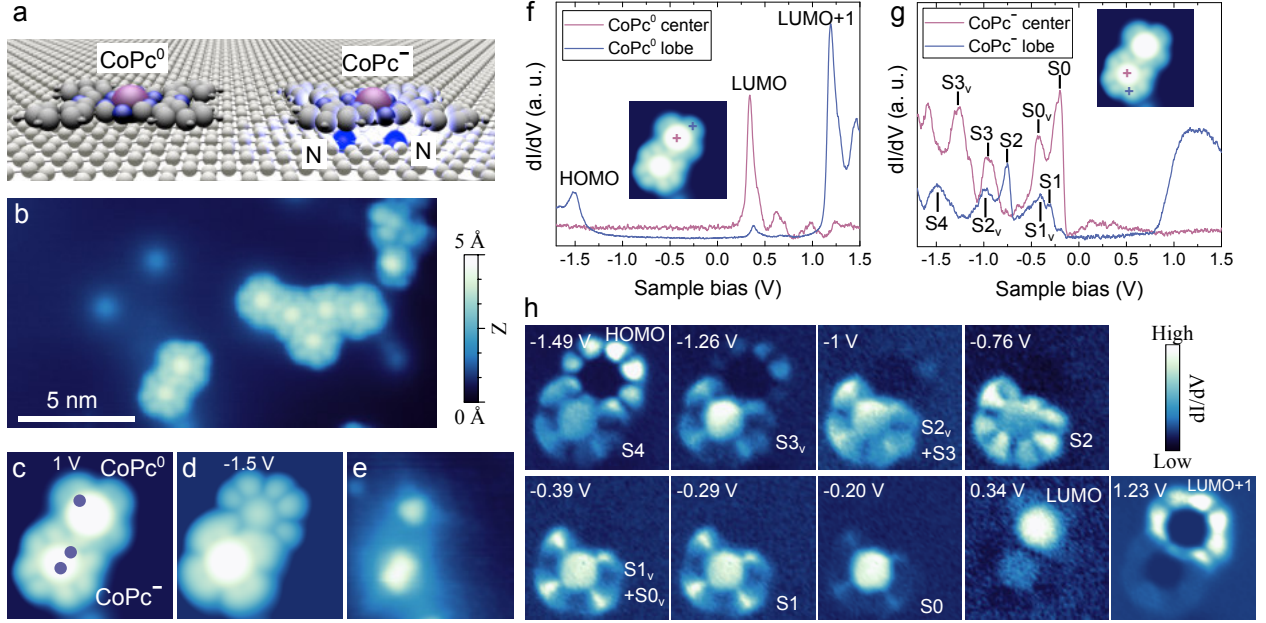


Figure 1: (a) Schematic view of a nitrogen-doped graphene sample with CoPc adsorbed in the neutral state on a pristine site, and negatively charged on a nitrogen pair site. (b) STM image (2 V, 10 pA) of CoPc molecules adsorbed on nitrogen-doped graphene. (c,d) Zoomed-in view of two molecules from image (b) measured at 1 V (c) and -1.5 V (d) (tunneling current 50 pA). The dark blue dots in (c) indicate the location of nitrogen atoms below the molecules. Image sizes $4 \text{ nm} \times 4 \text{ nm}$. (e) Image of the same area after removing the molecules, revealing the nitrogen atoms below the molecules (0.5 V, 100 pA). The dI/dV spectra of the two molecules of (c,d) are shown in (f,g). The insets in (f,g) indicate the locations where the spectra were measured. (h) Conductance maps of the same area as (c,d) at sample bias voltages corresponding to the peaks observed in (f,g).

negative (around -1.9 V) and positive (around 0.3 V) bias respectively, that have a different physical origin as compared to the resonant states. These peaks shift significantly upon changing the tip height, which is typical of a charging peak.¹⁹ For a weakly bound molecule, the potential drop of the tunneling junction is distributed between the tip-molecule barrier and the molecule-substrate area, behaving as a second tunneling barrier. Therefore, upon the application of a bias voltage, the molecular levels are shifted, and when a molecular state crosses the Fermi level of the sample, it gains or loses one electron, leading to a new charge state of the molecule. Such a charging effect has been seen on various systems where the molecule-surface interaction is weak or when a molecule is adsorbed on a metal covered by an insulating film.^{19,21-26} In Fig. 2, these peaks appear when the LUMO of a neutral molecule (Fig. 2c) or LUMO⁻ of a charged molecule (Fig. 2d) is shifted towards the Fermi level, leading to a temporary charging of the molecule. The charging peaks are not observed in the cases presented in Fig. 1, because they are outside the voltage range used in the spectroscopic measurements. For the neutral molecule in Fig. 1, the LUMO is at a higher energy (0.34 V) than in Fig.2, therefore its charging peak is expected to occur at a larger negative bias (below -1.9 V). The situation is similar for the charged molecule in Fig. 1 with a LUMO⁻ at a more negative bias (-0.2 V) than in Fig.2 (-0.08 V), therefore its charging peak is expected at a large bias voltage.

It has to be noted that the peaks corresponding to the resonant states are also slightly shifted when the tip height changes, though to a much lesser extent. To unambiguously identify the origin of the different peaks, we use a double tunneling barrier junction model in order to estimate the effect of the electric field.²⁷ In a double barrier, the condition for a resonant tunneling with a molecular level aligned with the Fermi level of the tip is obtained when $eV_b = E_0(1 + d/\epsilon z)$, where V_b is the sample bias voltage, E_0 is the energy of the states, z the distance between tip and sample, d the distance between the molecule and the surface and ϵ is the dielectric constant of the area between the molecule and the surface. For the charging peak, the condition to align the molecular level with the Fermi level of the sample is

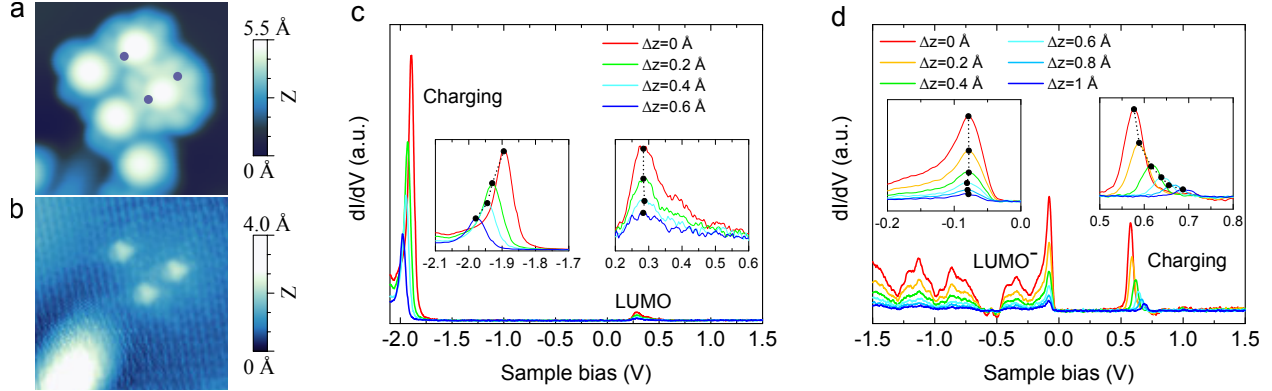


Figure 2: (a) STM image (1V, 50 pA) of a CoPc cluster including a molecule adsorbed on a nitrogen pair and a molecule on a single nitrogen site. The dark blue dots indicate the position of the nitrogen atoms below the molecules. Image size 5 nm \times 5 nm. (b) STM image (0.2 V, 300 pA) of the same area as in (a), after removing the molecules, revealing the location of nitrogen atoms. (c,d) dI/dV spectra measured at the center (above the Co atom) of the molecule shown in panel (a) that is (c) adsorbed on a single nitrogen and (d) on the nitrogen pair, for different tip heights. The tip-sample separation was increased by the amount Δz from the setpoint 1 V, 50 pA. The insets are zoomed-in views of the LUMO and charging peaks.

$eV_b = -E_0(1 + \epsilon z/d)$. It is important to note that these relations allow for an unambiguous determination of the origin of a peak, from its variation with the tip height. When the tip-sample distance increases, the energy of the peak is shifted away from the Fermi level for a charging peak, whereas it moves towards the Fermi level for a resonant molecular state. Moreover, for a given change in the tip-sample separation, the shift of a resonant peak is much smaller than the shift of a charging peak. From this model, the variation of the charging peaks of CoPc^0 and CoPc^- can be reproduced, together with a nearly absent shift for the resonant states (see supplementary information Fig. S2). As a result, the peak at positive bias measured at the center of the charged molecule can unambiguously be identified as a charging peak and not a LUMO state. The double barrier behaviour observed on the charged molecule shows that the molecule-graphene interface can be modeled as a tunneling barrier, indicative of a weak coupling between the molecule and the substrate. Note that in the case of CoPc on hexagonal boron nitride (h-BN) on Ir(111) the charging peaks were not observed.¹⁷ Another difference is that on h-BN the charging of CoPc involves the supporting

substrate, while here the reduction of CoPc is induced by the material itself and its dopants.

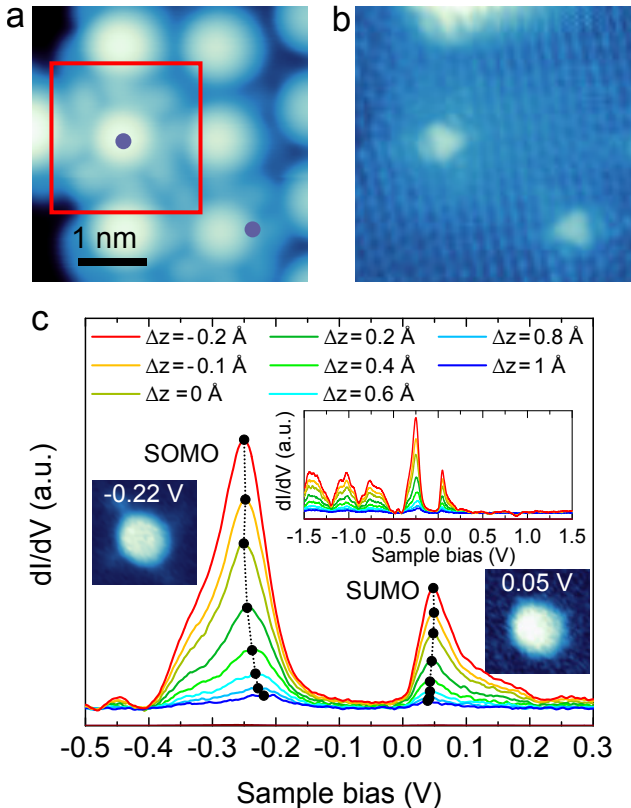


Figure 3: (a) STM image (1V, 50 pA) of CoPc molecules including a molecule (marked by a red square) adsorbed above a nitrogen atom located directly below the Co atom. The dark blue dots indicate the position of the nitrogen atoms below the molecules. (b) STM image (0.2 V, 300 pA) of the same area as in (a), after removing the molecules, revealing the location of nitrogen atoms. (c) dI/dV spectra measured at the center of the molecule marked by a square in (a). The tip-sample separation was changed by the amount Δz from the setpoint position at 1 V, 50 pA. Negative values of Δz correspond to a decrease of the tip-sample separation. The marks, linked by dotted lines, indicate the peak position of the SOMO and SUMO states. The inset curves show the spectra for a larger voltage range. The images in the two square insets correspond to the dI/dV maps in the area marked by a square in (a) at -0.22 and 0.05 V.

We have seen that nitrogen pairs lead to a stronger charge transfer than single nitrogen atoms. An intermediate case between the neutral and charged molecules described above is obtained when a molecule is adsorbed above a single nitrogen atom located at the center of the molecule. In that case, the dI/dV spectrum shows a series of peaks at negative bias, typical of a charged molecule, and also exhibits two peaks at positive and negative bias close to the Fermi level (Fig. 3), corresponding to a split LUMO state, as we will discuss below.

In contrast to the case shown in Fig. 2d, these two peaks shift towards the Fermi level when the tip is retracted, showing that no charging peak is present. This feature is typical of a half-filled molecular state that splits into two levels separated by a Coulomb repulsion energy, leading to the formation of a singly occupied molecular orbital (SOMO) and a singly unoccupied molecular orbital (SUMO). The dI/dV maps measured on the molecule at the energies of the SOMO and SUMO states reveal that these states are localised on the center of the molecule (inset in Fig. 3c). This shape is characteristic of the LUMO of a neutral molecule, which confirms that the two peaks around the Fermi level correspond to SOMO and SUMO states. The surrounding molecules do not show this feature, but instead exhibit the expected spectrum of a neutral molecule, more or less shifted depending on the amount of charge transfer (see supplementary information Fig. S3). The existence of SOMO and SUMO states could also be observed for a molecule adsorbed on a nitrogen pair that could be switched between neutral and charged states by lateral manipulation with the STM tip. In its charged state, the molecule showed a SOMO and SUMO state feature (see supplementary information Fig. S4-S5).

Our experimental data show that nitrogen atoms allow for charge transfer to non-covalently bonded molecules on graphene, and more particularly they show that nitrogen pairs induce an integer electron charge transfer. This is further supported by our Density Functional Theory (DFT) calculations. We present in Fig. 4a,b the spin-polarized Projected Density of States (PDOS) of the CoPc molecules on graphene and on a 1-5 nitrogen pair in N-doped graphene corresponding to the case of Fig. 1 (see also supplementary information Fig. S6). Since DFT is a ground state theory, it is well-known that HOMO-LUMO gaps are computed incorrectly, and one cannot therefore expect to obtain exact agreement between the PDOS computed theoretically, and the dI/dV spectrum obtained experimentally. For example, a standard feature of DFT computations of metal-phthalocyanines on substrates

is that the LUMO peak appears at the Fermi level, in disagreement with experimental observations. Similarly, absolute values for charges on atoms, as computed from DFT, can be unreliable, due to ambiguities in charge-partitioning schemes. However, DFT results for lowest-energy geometries and trends in charge transfer are accurate enough to provide considerable physical insight. In particular, DFT can reliably state when the charge transfer is larger or smaller, which is of interest to us here. When comparing the two PDOS computed on pristine and N-doped graphene, we can clearly observe a shift of the LUMO level below the Fermi level in the latter case, in good agreement with the experimental observations. This shift corresponds to a charging of the molecule from the nitrogen atoms doped in graphene. Indeed, the corresponding charge transfers computed from DFT are 0.20 e from graphene to CoPc on pristine graphene, and 0.61 e on N-doped graphene. Our calculations also reveal an inverse relationship between the Co-substrate distance and the charge transfer (see supplementary information Fig. S7). The addition of the electron charge also reduces the magnetic moment from $0.76 \mu_B$ on pristine graphene to $0.54 \mu_B$ on N-doped graphene. The charge transfer and the shift of the PDOS is found to be smaller on single nitrogen than on a nitrogen pair (see supplementary information Fig. S8-S9). Due to the DFT limitations discussed before, the calculated charge transfer does not correspond exactly to that deduced from the experiments, but, importantly, follows the same trend, and reproduces well the shift of the LUMO level below the Fermi level. Finally, when considering the isosurfaces of the charge density redistribution, shown in Fig. 4c,d, we find that the charge transfer is enhanced when a pair of nitrogen atoms is present in the graphene below the CoPc molecule. This is obviously due to the specific location of the molecule above these atoms, as represented in Fig. 4e.

In conclusion, we have shown that nitrogen pairs in doped graphene allow one to reduce cobalt phthalocyanine molecules. An integral charge transfer toward the molecules is evidenced by the shift of the LUMO state below the Fermi level. In some particular cases, when the molecule is sitting on a single nitrogen atom or a nitrogen pair, the downshifted peak

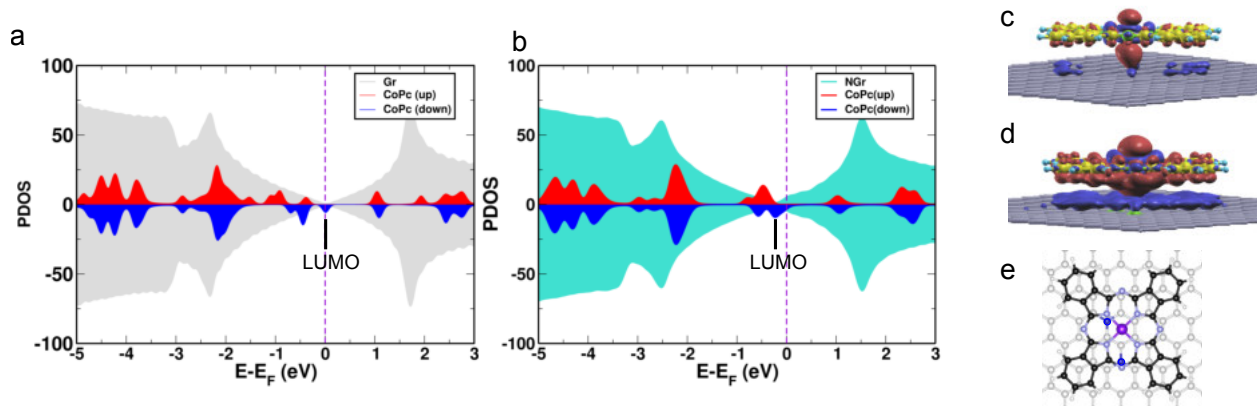


Figure 4: (a) PDOS computed from DFT, of graphene (gray) and CoPc (spin-up in red, spin-down in blue), for CoPc adsorbed on pristine graphene. (b) PDOS of graphene (light blue) and CoPc (spin-up in red, spin-down in blue), for CoPc adsorbed on doped graphene with two nitrogen atoms below the molecule. (c-d) Isosurfaces ($0.0005 e/\text{bohr}^3$) of the charge density redistribution for (c) CoPc on pristine graphene and (d) CoPc on a nitrogen pair in doped graphene. Red/blue lobes correspond to electron accumulation/depletion, respectively. (e) Top view of the structure used for the calculations of CoPc on a nitrogen pair in doped graphene. Color code: black for carbon in CoPc, gray for carbon in graphene, light blue for nitrogen in CoPc, dark blue for nitrogen in graphene, white for hydrogen, purple for Co.

gets split into a SUMO and SOMO. This effect on the molecules could have potential applications in improving the catalytic activity of CoPc, for reactions such as the reduction of CO_2 for energy conversion. More generally, nitrogen-doped graphene can be used to control the charge state of molecules on graphene.

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Supporting Information Available

Computational details, STM measurements, Shift of molecular spectrum on nitrogen atoms,

Double tunnel barrier model for charging peaks and resonant states, Spectroscopy of molecules around nitrogen atoms in a cluster, Manipulation of molecules on nitrogen pairs, Geometries used for DFT calculations, Comparison of DFT results for charge transfer, DFT Results for PDOS for CoPc over single N dopant in graphene.

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Graphical TOC Entry

