Mimicking Enzymatic Active Sites on Surfaces for Energy Conversion Chemistry

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ABSTRACT: Metal−organic supramolecular chemistry on surfaces has matured to a point where its underlying growth mechanisms are well understood and structures of defined coordination environments of metal atoms can be synthesized in a controlled and reproducible procedure. With surface-confined molecular self-assembly, scientists have a tool box at hand which can be used to prepare structures with desired properties, as for example a defined oxidation number and spin state of the transition metal atoms within the organic matrix. From a structural point of view, these coordination sites in the supramolecular structure resemble the catalytically active sites of metallo-enzymes, both characterized by metal centers coordinated to organic ligands. Several chemical reactions take place at these embedded metal ions in enzymes and the question arises whether these reactions also take place using metal−organic networks as catalysts.

Mimicking the active site of metal atoms and organic ligands of enzymes in artificial systems is the key to understanding the selectivity and efficiency of enzymatic reactions. Their catalytic activity depends on various parameters including the charge and spin configuration in the metal ion, but also on the organic environment, which can stabilize intermediate reaction products, inhibits catalytic deactivation, and serves mostly as a transport channel for the reactants and products and therefore ensures the selectivity of the enzyme. Charge and spin on the transition metal in enzymes depend on the one hand on the specific metal element, and on the other hand on its organic coordination environment. These two parameters can carefully be adjusted in surface confined metal−organic networks, which can be synthesized by virtue of combinatorial mixing of building synthons. Different organic ligands with varying functional groups can be combined with several transition metals and spontaneously assemble into ordered networks. The catalytically active metal centers are adequately separated by the linking molecules and constitute promising candiates for heterogeneous catalysts.

Recent advances in synthesis, characterization, and catalytic performance of metal−organic networks are highlighted in this Account. Experimental results like structure determination of the networks, charge and spin distribution in the metal centers, and catalytic mechanisms for electrochemical reactions are presented. In particular, we describe the activity of two networks for the oxygen reduction reaction in a combined scanning tunneling microscopy and electrochemical study. The similarities and differences of the networks compared to metallo-enzymes will be discussed, such as the metal surface that operates as a geometric template and concomitantly functions as an electron reservoir, and how this leads to a new class of bioinspired catalysts. The possibility to create functional two-dimensional coordination complexes at surfaces taking inspiration from nature opens up a new route for the design of potent nanocatalyst materials for energy conversion.
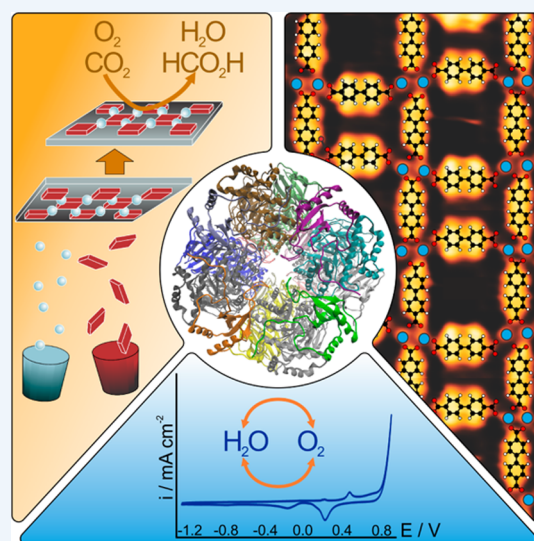
S upramolecular chemistry is a powerful design principle for the synthesis of functional molecular architectures.[1,2] Coordination chemistry at surfaces offers the salient possibility to create modular metal−organic networks (MONs) that are
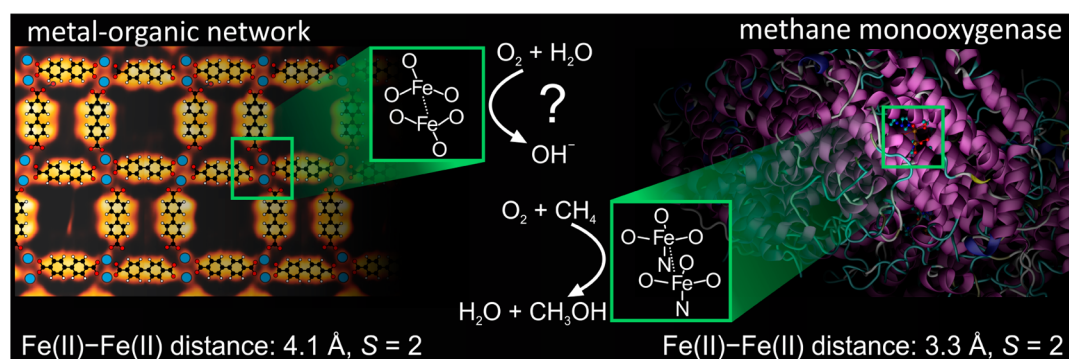
Figure 1. Analogous coordination environment as catalytically active sites in metal–organic network (left) and metallo-enzyme[15] (right). This example highlights the similarities between MONs and metallo-enzymes, like electronic and spin configuration, but also point out the differences, for example the 2D vs 3D structure, and the presence of a surface vs the amino acid side chains.
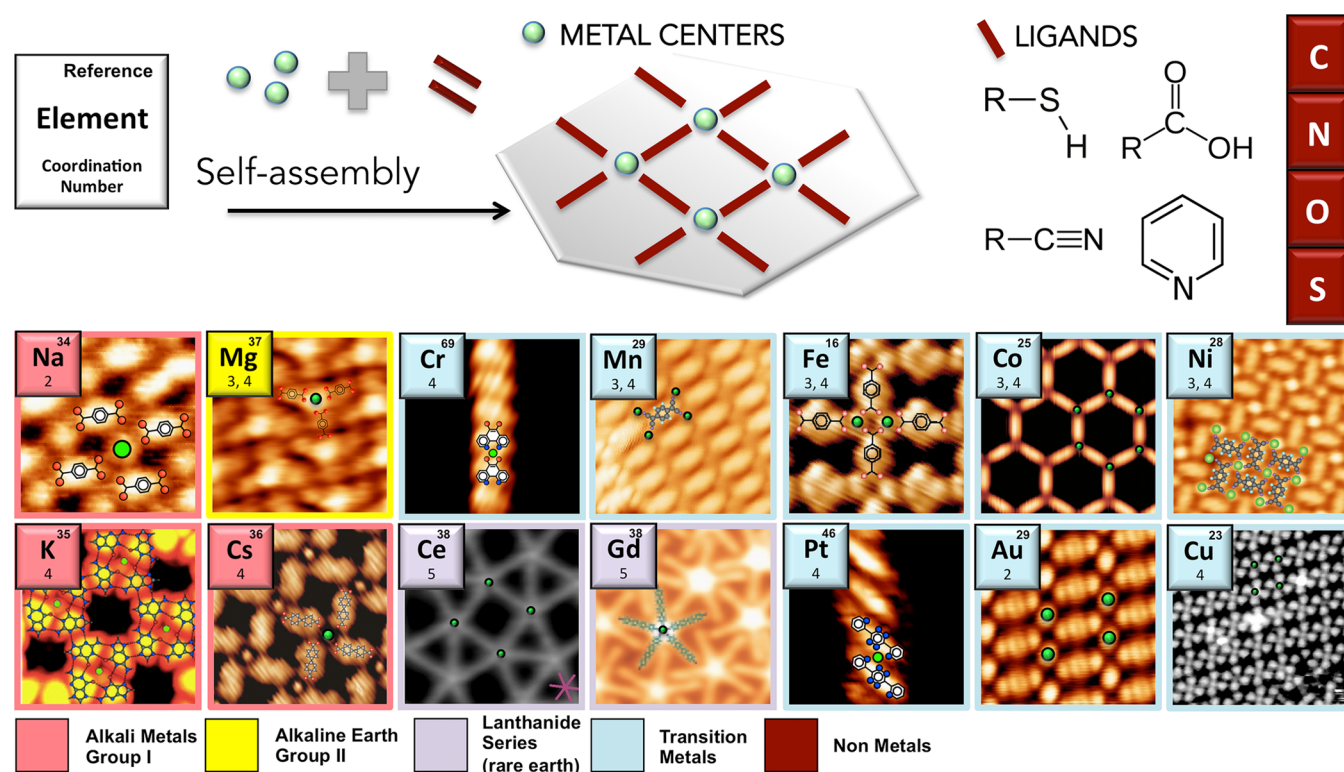
Figure 2. Table showing STM images of metal–organic networks incorporating different metal centers. Typical functional groups of the most common ligands are listed at the bottom. Adapted with permission from refs 16, 23, 25, 28, 29, 34–38, 45, and 69. Copyright American Chemical Society, American Institute of Physics, John Wiley & Sons, American Physical Society, and Royal Society of Chemistry.

self-assembled from relatively simple organic ligands and codeposited metal atoms on well-defined facets of metal substrates. This method has been employed to create a wide range of two-dimensional (2D) coordination motifs, with different metal centers coordinated within various organic environments.[3] The electronic structure and consequently the chemical properties of the incorporated metal ions is to a great extent defined by the elementary type of the metal, the number and geometry of the coordinating molecular functional groups, the electron affinity of the organic molecules, and the supporting metal surface.

Remarkable similarities exist between 2D coordination networks and the catalytically active site of metallo-enzymes (Figure 1).[4] Transition metal ions can be encountered embedded in the organic matrix of enzymes, which catalyze important biological processes like water oxidation, oxygen reduction, photosynthesis, and respiration.[5] During the enzymatic reaction, the substrate binds coordinatively to the metal within the three-dimensional organic pocket of the enzyme, ensuring substrate selectivity, reaction selectivity, and stereoselectivity.[6] The redox active sites of natural enzymes can comprise mono- or dinuclear metal ions of the same or different type of element, coordinated by specific groups of the amino acid side chain arranged in the polypeptide structure of the bulk protein. Few amino acid side chains including mostly carboxyl, hydroxyl, amine, thiol, and imidazole groups are involved in the metal coordination.[7–10] Inspired by these functional core units of metallo-enzymes, similar binding motifs can be synthesized on surfaces using coordination chemistry. By reducing the enzyme to its catalytically active metal center with its proximate organic environment, excluding the extended amino acid side chains but introducing the surface as a new

parameter, we envision surface-stabilized MONs as novel catalytic materials. The possibility to tune the atomic positioning of surface-confined under-coordinated metal atoms and their chemical properties make MONs excellent candidates for heterogeneous catalysts[11−13] due to their redox properties.[14]

The present Account delineates the approach toward the synthesis of surface-supported metal−organic networks as bioinspired artificial catalysts, highlighting the multifunctional properties of these networks for small-molecule adsorption and their chemical conversion. Starting from the discussion of the physical and chemical properties for a model class of structures, that is, iron-carboxylate networks, we will describe the key features of these novel architectures: a tunable design with exquisite positioning of unsaturated metal centers,[16−18] and unique magnetic[19] and catalytic properties[14,20] which depend critically on the coordination geometry. The interaction of these networks with molecular oxygen as a model system is elucidated on an atomic level as well as in the electrochemical reduction of O_2, exemplifying the suitability of MONs for energy conversion chemistry.

The scanning tunneling microscope (STM) has evolved as the instrument of choice for topographical characterization, as it allows imaging the networks with molecular resolution and the identification of the exact placement of the building blocks.[21] The use of space-averaging spectroscopic techniques is becoming more frequent, in particular for the investigation of electronic and magnetic properties.[22] In 2002, Lin et al. reported the first STM observation of a metal−organic coordination network by depositing benzene-1,3,5-tricarboxylic acid (TMA) molecules on Cu(100). STM images revealed the self-assembly of Cu(TMA) complexes by the spontaneous capture of Cu adatoms from the supporting surface.[23] This result inspired the on-surface synthesis of iron-carboxylate networks, where the Fe atoms were codeposited in ultrahigh vacuum (UHV) together with the aromatic linkers. A tunable set of 2D polymorphs has been fabricated, demonstrating that the coordination geometry on surfaces can be controlled by the metal/molecule ratio and the size of the organic ligands.[16,18,24] The flexible choice of the network's components has led to a rapid evolution of structural motifs with unusual coordination configurations (Figure 2). Metal-steered molecular self-assembly has thus become an intriguing research field on its own. The most prominent feature of the 2D MONs is the presence of low coordination numbers and open coordination sites mostly in the top position, which makes the networks highly reactive toward binding of ligands or reactants at these positions.

Chemical functionalization of the organic linker affords facile control over the pore size and the physical/chemical properties, while the metal center can be chosen to target specific reactions. The chemical structure of the ligand and its functional groups determines the interplay of molecule−surface and molecule-metal center interactions that finally favor one or more 2D polymorphs expressed on the surface. In this respect, carboxylate groups which are ubiquitous in protein active centers are also the most studied ligands for MONs.[16,23,24] Nitrile coordination, mostly driven by the intriguing electronic properties of TCNQ derivatives, was studied in detail for Co,[25] Mn,[26] Cs,[27] Ni,[28] Au,[29] and Na.[30] Other examples include pyridine,[31] hydroxyl,[32] and thiolate based structures.[33] The metal atom favors different coordination environments depending on its electronic configuration at a given ligand/metal ratio.

Recently, the approach has been extended from transition metals to group I (Na,[34] K,[35] Cs[27,36]) and group II (Mg[37]) elements. Ionic bonds are less directional than coordination bonds and therefore the networks based on alkalis often present a larger number of polymorphs under similar conditions. Interestingly, block *f* rare earths (Ce and Ga[38]) allow higher (5-fold) coordination motifs. The surface tends to act as a template favoring particular adsorption sites for both molecules and metal atoms. In general, the symmetry of the surface has a pronounced effect on the molecular arrangement that can be decisive for the coordination geometries, but sufficiently strong and flexible coordination bonds can override the constraints imposed by the substrate's surface potential landscape permitting the growth of nearly identical geometries on different surfaces.[31,39] The modular approach allows to combine multiple metals and ligands[40] enriching the chemistry of the system and making them the ideal platform to model bimetallic enzymes.

The structural similarities between MONs and the coordination environment of the active sites in enzymes naturally leads to questions about the electronic configuration of their metal centers, which is of critical importance for their functionality as catalysts. The enzyme's catalytic activity is encoded in the orbital structure of the metal centers and the redox-properties of the entire complex. The atomic character of the embedded metal ions in MONs was probed by X-ray absorption spectroscopy (XAS). Figure 3 shows well-defined
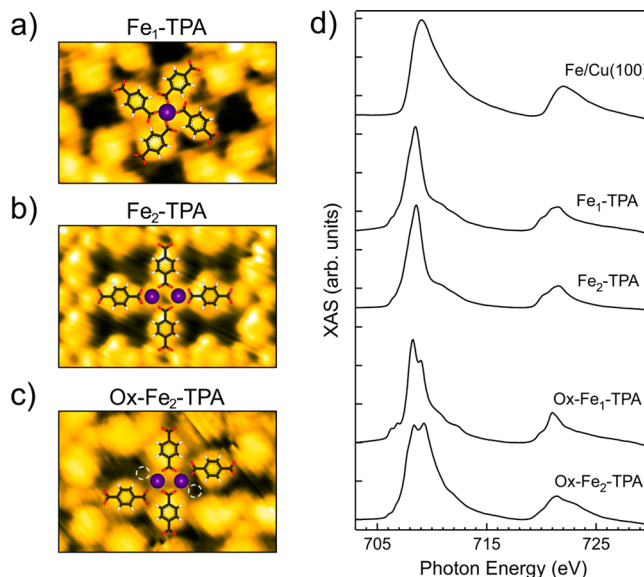
Figure 3. (a−c) Fe(TPA)$_4$ array; purple dots indicate the position of Fe atoms. Each Fe center is coordinated to four deprotonated oxygen ligands of the surrounding molecules. (d) X-ray absorption *L*-edge spectra of Fe/Cu(100), Fe$_1$-TPA, Fe$_2$-TPA, O$_2$-Fe$_1$-TPA, and O$_2$-Fe$_2$-TPA. Spectra were recorded in the electron-yield mode at *T* = 8 K at normal incidence.

absorption intensities with characteristic line shapes signifying localized Fe *d*-orbital states in carboxylate environments, which is in contrast to the metallic character of uncoordinated metal adatoms on surfaces.[19,28] Similar results were obtained for Mn and Ni centers embedded in other highly symmetric coordination sites.[19,28,41−43] Further, X-ray photoelectron spectroscopy investigations of Fe and Pt coordination centers indicate an oxidation state of mainly +2,[44,45] similar to the

ferrous active sites in enzymes encountered in dioxygenases.[46,47] Mixed-valence networks with Cu(II) and Cu(0) can also be realized.[48] Fe^{2+} is also the chemically active ion in the reduction of oxygen.[49] The XAS results demonstrate well-defined coordination bonds between metal centers and molecules with an effectively reduced hybridization between the ions and the metallic surface. Density functional theory (DFT) calculations corroborate this finding showing that the metal ions are lifted above from their adatom equilibrium position by about 0.6 Å.[19] The metal–organic adlayer is not perfectly planar and the organic ligands adopt a bent conformation accounting for the various attractive and repulsive forces occurring in the 2D complex.[17,19,26,27,29] Theoretical investigations find various degrees of charge transfer between metal centers, organic ligands and metal surface.[17,19,26,27,29,41] In the iron-carboxylate networks, the calculated total number of valence electrons is about 6.7, with a d-orbital occupation of approximately 5.6, in good agreement with the XAS measurements that find a d^6-configuration.[17,19] The projected density of states obtained from the DFT calculations demonstrates that the in-plane orbital character of the metal ions is mainly determined by the lateral bonding to the ligands and shows atomic-like localized spectral densities. The out-of-plane orbitals of the metal centers naturally interact more strongly with the metal surface states and exhibit a much broader spectral density in the PDOS resembling the character of free adatoms.[17,26,27,29,41] Thus, the metal centers possess a well-defined but hybrid electronic structure with properties being close to that of free metal–organic complexes but also show features of more strongly hybridized surface metal adatoms. In the systems studied so far, metal ions possess high-spin electronic configurations with evidence for weak magnetic coupling between adjacent centers.[19,26,28,29,41–43] Catalytically active metal centers in metallo-enzymes can likewise show high-spin configurations,[46,47] adding to the list of similarities between MONs and metallo-enzymes.

Knowing the structure and electronic configuration is a prerequisite to study the chemical response of MONs to gas adsorption and to correlate the reactivity with its physical properties. It is instructive to look into the interaction of small molecules with metallo-porphyrins and phthalocyanines bound to surfaces, which have been studied both in vacuum[50,51] and at the liquid/solid interface[52–54] as analogues of heme enzymes like cytochromes. In vacuum, monolayers of metallo-porphyrins were exposed to O_2, NO, and CO, and the adsorption geometry was investigated. On Fe- and Co-tetraphenylporphyrin, for example, two CO adducts bind to one metal atom on the same side of the macrocycle, reducing the metal to its 0 oxidation state.[55] Oxygen adsorption on Fe- and Co-phthalocyanines, however, leads to a discriminative response in the oxidation state. Co remains in its +2 state, while Fe^{2+} is oxidized to Fe^{3+}.[56] Manganese porphyrins homolytically cleave O_2 in vacuum, where the two O adducts bind to the metal centers of the molecules and increase their oxidation state from +2 to +3.[57] Exposing a monolayer of Fe phthalocyanine on Ag(110) to O_2 results in the reductive dissociation of oxygen between molecule and supporting surface.[58] The adsorption of O_2 on Mn- and Co-porphyrins is also studied at the liquid/solid interface.[52–54] Oxygen does not bind to these porphyrins when the molecules are dissolved in organic solvents; at the surface, however, O_2 adsorption on top of the metal centers is observed. All three studies attribute this to the surface *trans* effect,[59] a charge donating interaction from the surface to the metal,

which can stabilize the oxygen adducts. The surface can thus function as a cofactor to deliver electrons to chemical reactions, and also to adopt the role of organic ligands that stabilize redox active metal centers in enzymes, which due to rigid constraints are absent at the surface-confined networks.

The reactivity of the iron-carboxylate networks on Cu(100) toward molecular oxygen was studied to reveal the response of MONs to gas adsorption.[19,20,60] The networks consist of mono- or dinuclear Fe centers embedded in nearly square-planar coordination environments provided by the carboxylate ligands, that is, terephthalic acid (TPA) and biphenyl-dicarboxylic acid (BDA). STM imaging reveals that O_2 molecules adsorb on both the Cu(100) surface and the Fe centers. A remarkable difference was observed between the mononuclear and dinuclear Fe-TPA networks, which can be regarded as structural mimics of mono- and dinuclear metallo-enzymes such as lipoxygenases and dioxygenases in the former case and hemerythrin, ribonucleotide reductase, methane monooxygenase, and Δ^9 desaturase in the latter. For the monoiron phases of TPA, the structural motif remained stable at room temperature even in the saturation limit of oxygen adsorption, while the dinuclear Fe-TPA binding motif collapsed at relatively small oxygen doses.[19,20,60] DFT calculations find that O_2 adsorbs in a side-on binding mode on top of the monoiron centers.[19] Interestingly, the oxidation state of Fe remains nearly unchanged in the superoxo-adduct. The XAS spectra show a noticeable sharpening of the spectral features that is associated with the localization of the Fe d-states and a reduced hybridization with the Cu substrate (Figure 3) which is expressed in an increased Fe-surface distance. Despite the increased decoupling from the substrate, the electron donation to the O_2^- species stems mainly from the Cu substrate.

In contrast, O_2 reacts readily with the dinuclear Fe unit (Figure 4a,b). Individual reaction steps could not be followed via the STM at room temperature. XAS analysis showed a pronounced shift of L-edge intensity that can in part be attributed to a change in oxidation state of the Fe centers from +2 to +3. Similarly to the monoiron phase O_2 adsorbs molecularly on each Fe of the dinuclear unit. The dissociation of the first oxygen molecule has a finite but accessible barrier at room temperature, while the dissociation of the second oxygen molecule follows a correlated movement of the oxygen atoms on both Fe ions resulting in a much lowered barrier for the second dissociation step. As a consequence a new O_2 molecule with oxygen atoms from both Fe ions forms, which bridges the Fe dinuclear unit (Figure 4c).[20] The thermal activated release of this oxygen molecule leads to single oxygen atoms on each Fe atom. Finally, further relaxation of this structure leads to the collapse of the network, which is disadvantageous for continuous catalytic actions. However, an analogous diiron-carboxylate network formed by BDA molecules yields a stable structure after oxygen dosing. The main difference between Fe-TPA and Fe-BDA networks is the reduced Fe–Fe distance from ca. 4.7 to 4.1 Å, which emphasizes that the precise engineering of coordination structure on surfaces can be used to tune their chemical properties. For comparison, the di-iron site in Δ^9 desaturase shows an internal separation of 4.1 Å, yet most di-iron centers in other enzymes are separated by significantly less than 4 Å.[7]

The behavior of CO_2 adsorption on a metal–organic network was studied in ref 61. Metal–organic chains consisting of isocyanide bridged Au atoms were obtained on a Au(111) substrate. Upon CO_2 dosing the previously separated chains
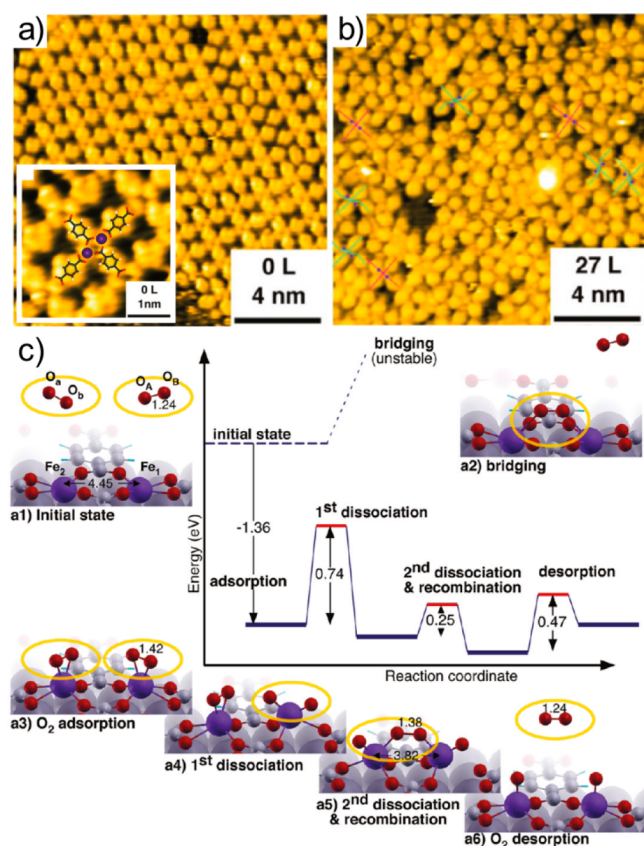
Figure 4. TPA/di-iron complex self-assembled on Cu(100). (a) Before oxygen exposure (see inset for a molecular model; purple circles represent Fe centers), and (b) after oxygen exposure. (c) Reaction mechanism for O_2 dissociation predicted by DFT. Reprinted with permission from ref 20. Copyright 2011 American Chemical Society.

show attractive interaction and form close-packed bundles with CO_2 binding in between. The CO_2 could be released by thermal annealing, showing that inert molecules can be reversibly bound to a coordination network. In Nature, CO_2 activation is catalyzed by the enzyme Ribulose-1,5-bisphosphate carboxylase oxygenase (RuBisCO). One of our current efforts aims toward the design of a 2D analogue of the RuBisCO active center (Figure 5a), which incorporates a Mg^{2+} ion. The modular assembly of Mg and TPA on Cu(100) constitutes the first MONs incorporating Mg centers (Figure 5c). STM and

XPS experiments on these bioinspired networks show initial evidence of CO_2 activation at room temperature.[37]

The exploitation of the resemblance of structural and electronic key features with natural enzymes for the use of MONs as catalytic materials is still in its infancy. There are only a handful of experiments reporting on the response to molecules from the gas phase, and little is known about the chemical properties of MONs at the liquid/solid interface. Insight into electrochemical processes can be gained by looking into studies on surfaces decorated with phthalocyanines or porphyrins. The activity toward the oxygen reduction reaction (ORR) of Fe and Cu phthalocyanines anchored to Au(111) can be enhanced by linking the molecules via aromatic thiol groups more strongly to the crystal surface.[63] Itaya and co-workers[64,65] and Tao[66] studied the ORR on metal-porphine derivate monolayers on Au(111) in a combined STM and electrochemical experiment, in which the Co-tetraphenyl-porphyrine-modified electrode showed an enhanced cathodic current for the ORR to H_2O_2. Further, monolayers of cobalt(II) porphine CoP and [2,3,7,8,-12,13,17,18-octaethyl-21H,23H-porphine]cobalt(II) CoOEP assembled on Au(111) showed that the ORR for CoP/Au proceeded mainly via a two-electron reduction of O_2 to H_2O_2 with a partial participation of the 4-electron reduction to H_2O. On the other hand, the two-electron reaction was the only reaction path for CoOEP/Au.[64] The first measurement of the electrochemical activity of a self-assembled metal−organic network was studied for a system comprising 4′,4′′′′-(1,4-phenylene)bis(2,2′:6′,2″-terpyridine) (PTPy) and metal ions (M^{2+}). Self-assembled structures of PTPy and PTPy-M^{2+} were characterized via cyclic voltammetry and electrochemical STM.[67] Disordered layers formed when iron ions were added, whereas well-ordered PTPy-Au adlayers were observed under controlled electrode potentials. The ORR activity depending on the metal ion was investigated for the PTPy-M layers.

Besides the catalytic action of metal coordination centers, the electrocatalytic activity can also be controlled by purely organic molecules. This is exemplified by a layer of calix[4]arene molecules self-assembled on a Pt electrode.[68] The organic molecules selectively block the ORR, whereas the hydrogen evolution proceeds with Pt-like activity. At optimal conditions, the Pt surface exhibits O_2-tolerant Pt sites that are highly active for the adsorption and dissociation of H_2.

Our current efforts focus on the electrochemical characterization of vacuum-fabricated MONs. To this end a special experimental setup was designed that consists of a flexible
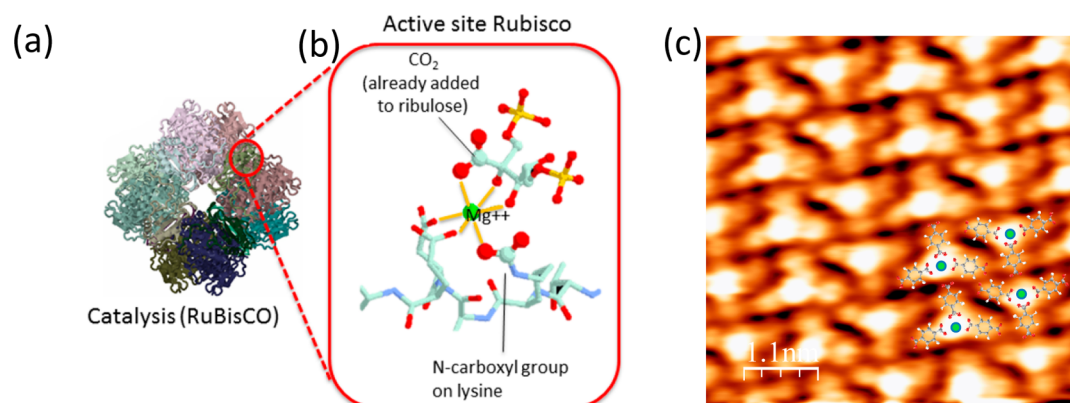
Figure 5. (a) Model of the enzyme RuBisCO and (b) its active center.[62] (c) STM image of a Mg-TPA MON.[37]

transfer system between UHV and electrochemical environment, thus facilitating sample transfer in a controlled and inert environment.[14] MONs of Fe with both TMA and 5,5′-bis(4-pyridyl)(2,2′-bipyrimidine) (PBP) were created and characterized first by STM in UHV, and then by cyclic voltammetry in a three-electrode conventional electrochemical cell. The TMA ligand provides a carboxylate coordination environment for Fe, whereas the metal is coordinated by pyridine and pyrimidine groups in the Fe-PBP network (Figure 6a,b). The activity
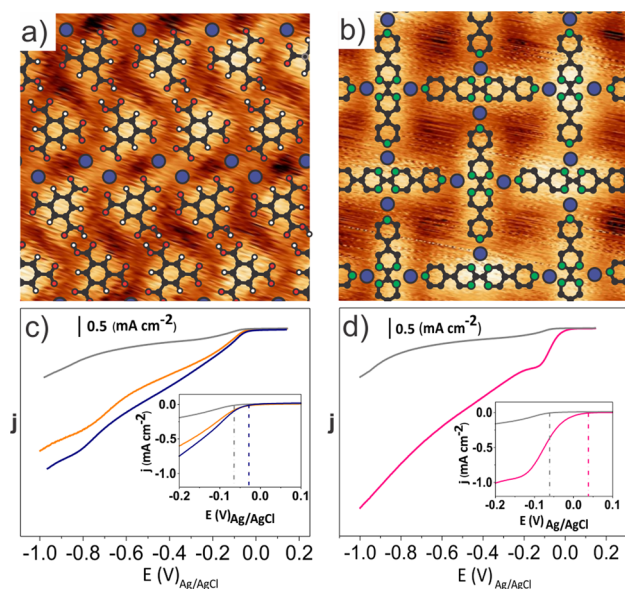
Figure 6. STM image of (a) TMA-Fe and (b) PBP-Fe network on Au(111). Color legend of model: N (green), C (black), O (red), and H (white). H is omitted in the PBP scheme. Polarization curves in O_2 saturated 0.1 M NaOH solution at 0.05 V/s for (a) bare Au(111) (gray line), TMA-Fe (orange line) and PBP-Fe (blue line) and (b) bare Au(111) (gray line) and TMA-Mn (pink line). The insets in the graphs show the different onset potential for the shoulder at −0.2 V. Reprinted with permission from ref 14. Copyright Macmillan Publishers Limited.

toward ORR of both networks was tested in prototypical experiments on the use of MONs for energy conversion. Figure 6c shows the polarization curves in O_2 saturated alkaline solutions for both Fe networks (TMA-Fe orange, PBP-Fe blue line). Compared to the bare gold electrode (gray line), the electrocatalytic activity of both networks is larger for the reduction of O_2. This effect is even clearer in the onset potential, which is shifted by 50 mV with respect to bare Au (inset Figure 6c). Around −0.3 V, O_2 is reduced to H_2O_2 in a two-electron pathway. More interesting is the presence of a second peak at larger cathodic potentials related to a second transfer of two electrons in which H_2O_2 is finally reduced to H_2O, and which was confirmed in additional experiments by the addition of H_2O_2 to the electrolyte. In comparison, the structural equivalent TMA-Mn network exhibits a dramatically different behavior (Figure 6d). Here, the reduction of O_2 to H_2O proceeds directly via a single path involving four electrons at low cathotic potentials. These results report the first controlled electrochemical characterization of vacuum-deposited and self-assembled metal−organic networks. The full potential of this approach is yet to be explored, but given the chemical richness of the MON synthesis, it represents a promising approach to novel functional catalytic materials.

The synthesis of surface-confined metal−organic networks has come a long way since its first demonstration to the recent characterization of their electrocatalytic activity. Creating redox active networks as heterogeneous catalysts is one of the many paths along which MONs can find novel applications. The focus so far rested mostly on the reduction of oxygen, but the wealth of reactions catalyzed by metallo-enzymes offers an enormous parameter space which remains to be explored. The resemblance between the catalytic active centers of MONs and enzymes thus nurtures the design of novel networks, but although being bioinspired materials, it is also clear that differences, for example, the presence of a surface functioning as electron reservoir, can be used as additional knobs for the adjustment of their catalytic properties. The here presented idealized system is of course currently not a match for any real catalyst. However, it offers the advantage of designing atomically well-defined new materials in a model environment and to study their behavior in detail. To bring MONs closer to practical applications, one possible path is using them in the functionalization of the surface of nanoparticles.

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Notes

The authors declare no competing financial interest.

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Rico Gutzler received his Ph.D. from the Ludwig Maximilians University in Munich in 2010 and is currently working as a research associate at the Max Planck Institute for Solid State Research. His research is focused on surface-confined molecular self-assembly and polymerization reactions.

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