Manipulating 2D metal–organic networks *via* ligand control

Nian Lin,*[a] Sebastian Stepanow,[a] Franck Vidal,[a] Johannes V. Barth[bc] and Klaus Kern[ac]

Received (in Cambridge, UK) 3rd December 2004, Accepted 19th January 2005
First published as an Advance Article on the web 2nd February 2005
DOI: 10.1039/b418174c

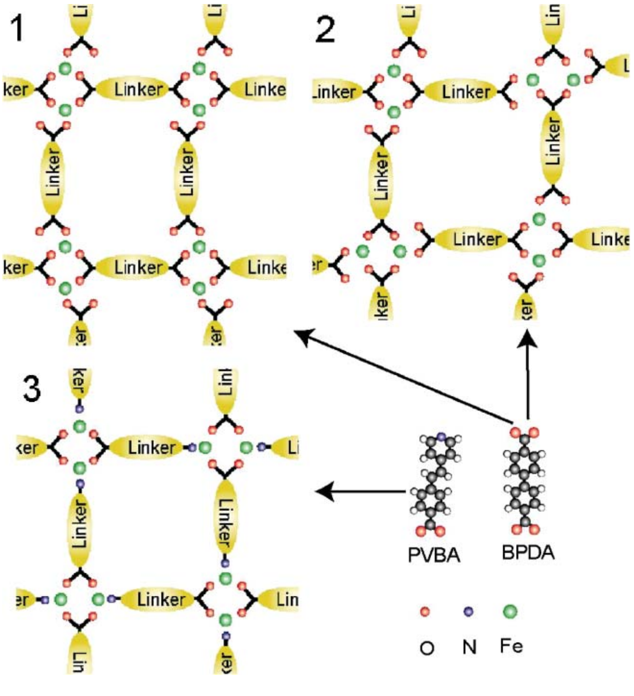
High-resolution scanning tunneling microscopy has revealed how ligand control can be successfully employed to eliminate isomeric phases and defects in 2D coordination networks that are self-assembled at a surface support by replacing symmetric dicarboxylato linker ligands to dissymmetric carboxylpyridyl linker ligands.

The metal-directed assembly of organic linker molecules at well-defined substrates is currently emerging as a promising approach toward the design of novel low-dimensional coordination architectures. Our previous studies revealed notably the suitability of polytopic carboxylate linkers in this respect, which were successfully used in conjunction with iron atoms for the engineering of a variety of two-dimensional networks.[1–4] These systems represent unique metal–organic supramolecular materials comprising distinctly arranged transition metal units, and significantly extend the spectrum of the impressive variety of 3D coordination systems.[5–7] A drawback in both 2D and 3D arrangements is the frequently encountered stereoisomerism, preventing from the realization of structurally homogenous phases.[1,3,8] However, a strategy to act on the assembly of supramolecular arrays – notably elaborated for the organization of open 3D dimetal-based systems using polycarboxylate and polypyridyl species – consists in the careful choice of bridging ligands.[9] Inspired by this concept we undertook a comparative study to explore homogenous coordination network formation and regular positioning of diiron centers at surfaces.

The key ideas are demonstrated in Scheme 1, where the effect of linker functionality and reduced symmetry on the 2D organisation of iron pairs mediated by exemplaric linear linkers is illustrated. (Note such configuration is stabilized by the surface. In 3D diiron carboxylate presents as paddle wheel units that are linked by the respective link.[10]) A ditopic carboxylato species may act as either equatorial or axial linker (following the definition in ref. 9), *i.e.*, both network isomers **1** and **2** may evolve.[1] In phase **1** each dicarboxylato species is employed strictly as an equatorial or as axial linker. Hence all diiron units are lying parallel. By contrast in phase **2** the dicarboxylate acts as equatorial linker at one side and as axial linker at the other side. As a result adjacent diiron units are rotated by 90°. Now, when we use a dissymmetric linker molecule with a carboxylato group at one end and a pyridyl group at the other end the isomerism vanishes. Rather, a unique favorable solution for network formation exists, since the pyridyl moiety couples preferentially in an axial fashion to the diiron units. As a consequence the iron pairs' orientations in phase **3** must alternate.

The scenario illustrated in Scheme 1 has been realized in a comparative investigation using appropriate molecules. Experimentally, the linkers and iron centers are sequentially evaporated onto an atomically clean Cu(100) surface in ultra-high vacuum. With appropriate surface concentrations and metal-molecule ratios 2D reticulated regular network structures comprising diiron units evolve after 450 K annealing for 5 min. The sample was characterized *in situ* by STM revealing exquisite structural details. Specifically, the two linkers used in this study are: 1,4′-biphenyldicarboxylic acid (BPDA) and 4-[*trans*-2-(pyrid-4-ylvinyl)]benzoic acid (PVBA). As illustrated in Scheme 1, both rodlike molecules are comparable in length, comprise two aromatic rings as backbones and two functional endgroups. Whereas BPDA is centrosymmetric with two terminal carboxyl moieties, the non-centrosymmetric species PVBA comprises a carboxyl and a pyridyl group at its extrema.[11] Under the employed preparation condition the molecules' carboxyl groups are deprotonated, providing reactive carboxylato ligands for metal coordination.[1,3] The aromatic backbones are crucial for the engineering of nanoporous metal–organic networks because they promote the flat adsorption and orientational ordering of the linkers at the surface.[1,3,12]

High-resolution STM topographs allow for the identification of the diiron units, thus permitting the unambiguous distinction of different phases. Representative STM data of the metallosupramolecular networks is shown in Fig. 1(a)–(c), where the iron atom pairs, *i.e.*, two iron atoms spaced by 3.6 Å, are clearly resolved.



Scheme 1 Concept of ligand control at 2D.

---

*n.lin@fkf.mpg.de

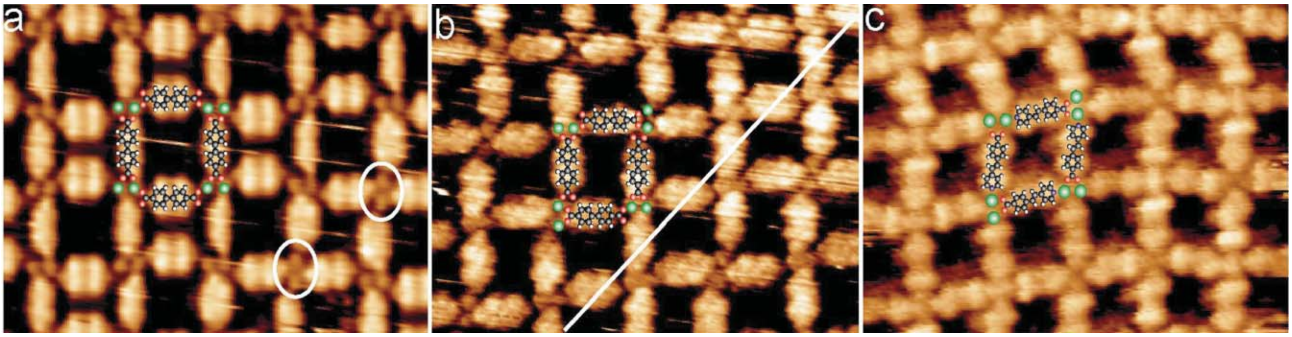


Fig. 1 High-resolution STM topographs of Fe–BPDA (a), (b) and Fe–PVBA (c) networks formed on the Cu(100) substrate. (image size: 8 × 6 nm). The diiron units, highlighted by green spheres, appear as spherical protrusions. Also the double-aromatic backbone structural feature of the linker molecules is clearly discernable. Tentative models are superimposed over the data (color code as in Scheme 1) indicating bidentate and monodentate coupling schemes. The circles in (a) indicate the structural defects of the diiron units and the line in (b) separates two anti-phase domains. The data were taken in the constant current mode with tunneling currents in the 0.5–1.0 nA range and a bias voltage of 0.5 V, applied to the sample.

Two phases, notably differing in the arrangement of the diiron units, are encountered in the Fe–BPDA system. As anticipated in Scheme 1, both parallel and alternating orientation of adjacent pairs exist, which is demonstrated in Fig. 1(a) and (b), respectively. It is obvious that in the former case (*cf.* Fig. 1(a)) the equatorial BPDA linkers (the vertical-aligned molecules) couple symmetrically to the diiron units, while the axial linkers (the horizontal-aligned molecules) are shifted upwards (downwards) relative to the diiron units, indicating an asymmetric bonding configuration. A tentative model is superimposed on the STM topology, where each diiron unit is coordinated by two equatorial bidentate carboxylato and two axial monodentate carboxylato linkages, respectively, reflecting phase **1** in Scheme 1. The equatorial linkers appear systematically narrower than the axial ones in the data, which is presumably related to differences in substrate coupling or other geometric effects. With the second Fe–BPDA network depicted in Fig. 1(b), the diiron units' coordination corresponds to that of phase **2** in Scheme 1. In this case each linker molecule acts as equatorial ligand at one end (bidentate coupling) and as axial ligand at the other end (monodentate coupling). As a result a given diiron unit is oriented by 90° with respect to adjacent units (*cf.* the model in Fig. 1(b)). Both phases **1** and **2** coexist in the form of $\approx$10 nm size single-phase domains, *i.e.*, they represent energetically equivalent products resulting from the same sample preparation. Thus large size single-domain networks comprising regular diiron unit arrays were not obtained. Rather, both Fe–BPDA networks typically comprise structural defects, as the irregularities in Fig. 1(a) where diiron units in **1** networks align in wrong orientations (marked by circles). Moreover, phase **2** networks are frequently divided in anti-phase domains, as shown by the highlighted boundary in Fig. 1(b). These imperfections are attributed to the small energy difference of the two coordination configurations. (The monodentate axial coupling in the present system contrasts the chelating bidentate motif encountered in related systems, where shorter dicarboxlyato linkers where employed.[1,3] This is ascribed to the BPDA–substrate interaction.)

In marked contrast, a pure phase with regularly arranged diiron units could be reproducibly obtained in the case of Fe–PVBA networks. The STM data reveal that the orientation of adjacent diiron pairs strictly alternates. In Fig. 1(c) a high-resolution image is reproduced, which corresponds to the realization of the network **3** established on the conceptual grounds presented in Scheme 1. As illustrated by the superimposed tentative model, for each PVBA molecule the carboxylato group forms a bidentate coordination bond with a diiron unit as an equatorial ligand, whereas the pyridyl moiety at the other side is engaged as an axial ligand in the linkage to the adjacent diiron unit. This asymmetric bonding necessarily implies an alternating orientation of neighboring iron pairs. Since this is the only favorable coupling scheme, the defect concentration is minute and the PVBA molecules serve for the construction of extended metallosupramolecular networks domains, where the oblique shape of the framework voids reflects the crooked shape of the linker backbone. The results furthermore nicely reveal that nitrogen containing units can be readily employed in metal-directed assembly of organic species at surfaces, which represents a field of its own that needs to be fully explored.

In conclusion, we achieved improved control of nanoporous systems and transition metal atom pairs at metal substrates by choosing dissymmetric linker molecules. Pyridyl ligands represent suitable axial linkers promoting homogenous coordination network formation and regular positioning of diiron centers. These findings exemplify the rational design principle in nanostructure synthesis at surfaces.

Nian Lin,*[a] Sebastian Stepanow,[a] Franck Vidal,[a] Johannes V. Barth[bc] and Klaus Kern[ac]
[a]Max-Planck-Institut für Festkörpeforschung, Heisenbergstrasse 1, Stuttgart, D-70569, Germany. E-mail: n.lin@fkf.mpg.de; Fax: 49 711 6891662; Tel: 49 711 6891617
[b]Institut de Physique des Nanostructures, Ecole Polytechnique Fédérale de Lausanne, Lausanne, CH-1015, Switzerland
[c]Advanced Materials and Process Engineering Laboratory, Departments of Chemistry and Physics & Astronomy, University of British Columbia, Vancouver, B.C., Canada V6T 1Z4

Notes and references

1 A. Dmitriev, H. Spillmann, N. Lin, J. V. Barth and K. Kern, *Angew. Chem., Int. Ed.*, 2003, **42**, 2670.
2 H. Spillmann, A. Dmitriev, N. Lin, P. Messina, J. V. Barth and K. Kern, *J. Am. Chem. Soc.*, 2003, **125**, 10725.
3 M. Lingenfelder, S. Stepanow, A. Dmitriev, H. Spillmann, N. Lin, J. V. Barth and K. Kern, *Chem. Eur. J.*, 2004, **10**, 1913.
4 S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, C. Cai, J. V. Barth and K. Kern, *Nat. Mater.*, 2004, **3**, 229.
5 O. M. Yaghi, M. O'Keeffe, N. W. Ockwing, H. K. Chae, M. Eddaoudi and J. Kim, *Nature*, 2003, **423**, 705.

6 S. Kitagawa, R. Kiraura and S. Noro, *Angew. Chem., Int. Ed.*, 2004, **43**, 2334.

7 C. N. Rao, S. Natarajan and R. Vaidhyanathan, *Angew. Chem., Int. Ed.*, 2004, **43**, 1466.

8 B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.

9 F. A. Cotton and R. A. Walton, *Multiple Bonds Between Metal Atoms*, Clarendon Press, Oxford, UK, 2nd edn., 1993; F. A. Cotton, C. Lin and C. A. Murillo, *Acc. Chem. Res.*, 2001, **34**, 759; F. A. Cotton, C. Lin and C. A. Murillo, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4810.

10 M. Eddaoudi, J. Kim, D. Vodak, A. Sudik, J. Wachter, M. O'Keeffe and O. M. Yaghi, *Proc. Natl. Acad. Sci. USA*, 2002, **99**, 4900.

11 C. Cai, B. Müller, J. Weckesser, J. V. Barth, Y. Tao, M. M. Bösch, A. Kündig, C. Bosshard, I. Biaggio and P. Günter, *Adv. Mater.*, 1999, **11**, 750.

12 J. V. Barth, J. Weckesser, G. Trimarchi, M. Vladimirova, A. D. Vita, C. Cai, H. Brune, P. Günter and K. Kern, *J. Am. Chem. Soc.*, 2002, **124**, 7991.