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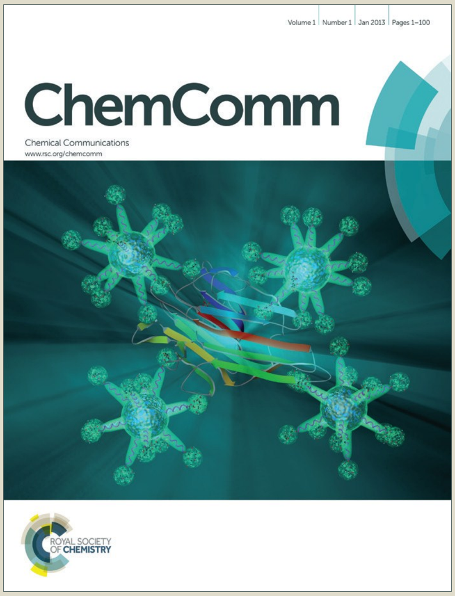

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Tunable lanthanide-directed metallosupramolecular networks by exploiting coordinative flexibility through ligand stoichiometry

Guoqing Lyu,[a] Qiushi Zhang,[a] José I. Urgel,[b] Guowen Kuang,[a] Willi Auwärter,[b] David Ecija,*[c] Johannes V. Barth*[b] and Nian Lin*[a]

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We report the self-assembly of multi-component lanthanide coordination metallosupramolecular structures on a Au(111) surface. Eu atoms coordinate with two heterotypic ligands of quarterphenyl-4,4”-dicarbonitrile and 4’,4””-(1,4-phenylene)bis(2,2’:6’,2”-terpyridine). For a concentration of carbonitrile ligands higher than 70% of the terpyridyl’s, Eu atoms are ligated in a four-fold coordination scheme. When carbonitrile ligand concentration is twice than terpyridyl´s, Eu atoms are ligated in a five-fold coordination sphere. Two types of coordination schemes result in structures exhibiting one-dimensional and two-dimensional morphologies, respectively. This study demonstrates that the flexible lanthanide coordination sphere facilitates rational design of metallosupramolecular architectures.

The assembly of supramolecular architectures with increasing complexity presents an auspicious strategy for the development of innovative materials.[1, 2] Hereof, self-assembly of metal-organic networks (MONs) directly on surfaces has been demonstrated as an efficient method to fabricate two-dimensional supramolecular architectures.[3-7] The morphology of these structures is dictated by the coordination sphere of the metal center. 2-, 3- and 4-fold coordination were frequently observed in surface-confined MONs using s-,[8-12] d-,[13-24] and p-block metals.[25] A major challenge is to find surface-confined coordination spheres with higher coordination numbers of five, six or even larger. As a matter of fact, rare-earth lanthanide metals are promising candidates because of their large ionic radii. However the lanthanide (Ln) chemistry is still far less explored in surface-confined supramolecular assembly, largely because of technical complexity of depositing Ln metals in vacuum. Only recently Ce or Gd coordination structures formed on surface were reported.[26, 27]

The coordination spheres of the Ln metals are determined by the nature of the Ln-ligand chemical bonds and by the geometrical arrangement of the ligands around the Ln atom.[28, 29] In Ln complexes, ligand-field effects are much weaker than the pertinent effects for d-transition metal complexes due to the shielding of the 4f orbitals by filled subshells of higher principal quantum number. As a result, Ln ions can easily adapt to many different coordination environments, making them the most versatile elements of coordination chemistry. This character on one hand very often leads to uncontrollable polymorphic structures, on the other hand, provides opportunities for construct coordination architectures that exhibit a designed morphology given a specific coordination sphere is expressed in high selectivity under certain conditions.[30, 31]

The design of surface-confined MONs via selective Ln-ligand interactions offers a novel and promising bottom-up approach to fabricate a broad range of 2D metal-organic architectures such as porous networks with desired morphologies and excellent structural stability. In this regard, 2D nanoporous MONs based on lanthanides metal ions, analogous to 3D lanthanide metal-organic frameworks (Ln-MOFs) can be attractive due to tunable pore geometry, potential application in optics, magnetism and heterogeneous catalysis.[32]

In this work, we demonstrate that Europium (Eu) atoms are able to coordinate with 2,2’:6’,2”-terpyridine (terpyridyl) and carbonitrile ligands on a Au(111) surface. Depending on ligand stoichiometry, they establish either a 4-fold coordination in which a Eu atom is linked to a terpyridyl and a carbonitrile ligand, or a 5-fold vertex in which a Eu atom is linked to a terpyridyl and two carbonitrile termini. Our results emphasize the adaptability of the Eu coordination sphere to adopt different coordination environments. These two types of coordination sphere can be expressed by tuning the stoichiometric ratio of the two ligands with a high degree of selectivity (up to 95%). Taking advantage of such a high selectivity, we have designed 1D and 2D Eu-directed nanoarchitectures, based on 4-fold and 5-fold nodes, respectively.

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[a] *Department of Physics, The Hong Kong University of Science and Technology, Clear Water Bay, Hong Kong, China*
[b] *Physik Department E20, Technische Universität München, James Franck Str. 1, D-85748 Garching, Germany.*
[c] *IMDEA Nanoscience, 28049 Madrid, Spain.*

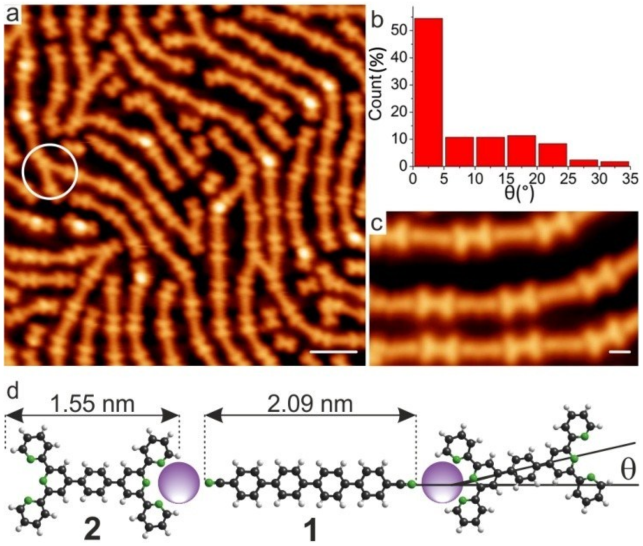

Fig. 1 One-dimensional multicomponent metal-organic structures formed at a stoichiometric ratio of [**1**]/[**2**]=0.7. (a) High resolution LT-STM image depicts 1D supramolecular chains comprising alternatively-linked molecules **1** and **2** (Scale bar: 5 nm). (b) Statistics of deviation angle distribution. (c) A magnified High resolution STM view of three 1D chains (Scale bar: 1 nm). (d) An atomistic model of the 1D chain structure illustrating the 4-fold coordination sphere of Eu. Color code: C, black; N, green; H, white; Eu, purple. The right side molecule **2** deviates from the collinear direction.

In the absence of Eu, molecules **1** and **2** behave as a 2D molecular gas on the Au(111) surface held at room temperature. Mixing **1** and Eu forms single-component two-dimensional networks. Mixing **2** and Eu forms single-component one-dimensional chains. When both **1** and **2**, and Eu atoms are co-deposited on the surface multi-component metallosupramolecular structures are expressed. For a molecular stoichiometric ratio of [**1**]/[**2**]=0.7, we observe the formation of 1D supramolecular chains, as represented in Fig. 1. These structures feature alternating molecules **2**, which are visualized as dog-bone shapes, and molecules **1**, which are visualized as linear rods. The chemistry of the two ligands, along with the control experiments, strongly indicates that **1** and **2** are linked *via* a Eu atom although the Eu atoms are not resolved in STM, which can be attributed to the weak density of states of the Eu as compared with those of the molecules.[22] The metallosupramolecular chains are based on 4-fold coordination nodes, whereby a Eu atom is coordinated by a terpyridyl and a carbonitrile moiety. The alternating arrangement of the two species in the chains corroborates heterotypic self-recognition coordination interactions of terpyridyl and carbonitrile ligands towards a Eu atom, highlighting the preference of the heterotopic coordination mode over homotopic coordination motifs. Hereby, the periodicity of the chain, defined as the center-to-center distance between two neighboring linker **2** molecules, is 4.26 ± 0.05 nm. An atomistic model based on the STM data is drawn in Fig. 1d, where the dimensions of the two molecular linkers are their intrinsic gas phase dimensions. The model features a Eu atom ligated by four nitrogen atoms, three from the chelate terpyridyl group and one from the carbonitrile group. In this configuration, the projected CN-Eu bond length is 2.5±0.2 Å, in good agreement with other on-surface assembled Ln-nitrile complexes.[26, 27] STM topographs show that molecular backbones of adjacent **2** and **1** molecules in a chain are frequently not collinear, indicating that the 4-fold coordination sphere has some degrees of flexibility in the bond direction, as illustrated by the right side molecule **2** in Fig. 1d. In this sense, we have conducted statistical analysis of the deviation angle and plot the results in a distribution histogram as Fig. 1b (0° defines the perfect collinear configuration). It shows that about 50% 4-fold coordination spheres are nearly collinear, i.e., deviate less than 5°, while the other 50% deviate relative greater angles, some as large as 35°.

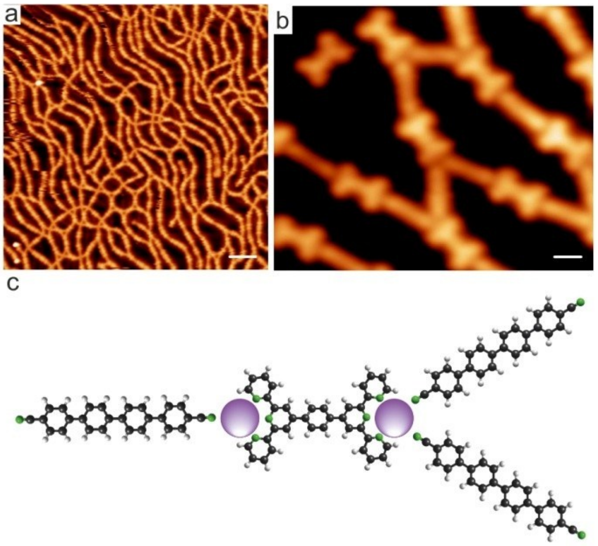

Fig. 2 Mixture of 1D supramolecular chains and three-way junctions inter-connected assemblies formed at a stoichiometric ratio of [**1**]/[**2**]=0.9. (a) A STM topograph showing mixed 1D supramolecular chains and inter-connected networks afforded by the three-way junctions (Scale bar: 10 nm). (b) A magnified STM view highlighting the two plausible Eu coordination schemes: 4-fold corresponding to 1D supramolecular chains and 5-fold assigned to the three-way junctions (Scale bar: 1 nm). (c) An atomistic model of the Eu coordination schemes of the 4-fold and 5-fold motifs. Color code: same as Fig. 1(d).

Additionally to 1D chains, three-way junctions, as marked with a circle in Fig. 1a, are observed. Such junction structures hint to a different coordination complex formed in the self-assembly. Remarkably, we have observed that when the amount of molecule **1** is increased, more junction structures emerged. Fig. 2a shows a STM image of a molecular ratio [1]/[2]=0.9, displaying a mixture of 1D chains and networks inter-connected by the three-way junctions. A closer inspection of Fig. 2b reveals that a junction comprises a terpyridyl attached to two carbonitrile groups. As detailed in the model shown in Fig. 2c, in a three-way junction a Eu atom is surrounded by five nitrogen atoms, three from the tridentate terpyridyl group and two from two carbonitrile groups, thus giving rise to a 5-fold coordination scheme. Assuming a symmetric configuration in the model, the two carbonitrile terminal nitrogen atoms and the central pyridyl nitrogen of the terpyridyl group are 2.6±0.2 Å to the Eu center, whilst the two side pyridyl nitrogens are 2.4±0.2 Å to the Eu center.

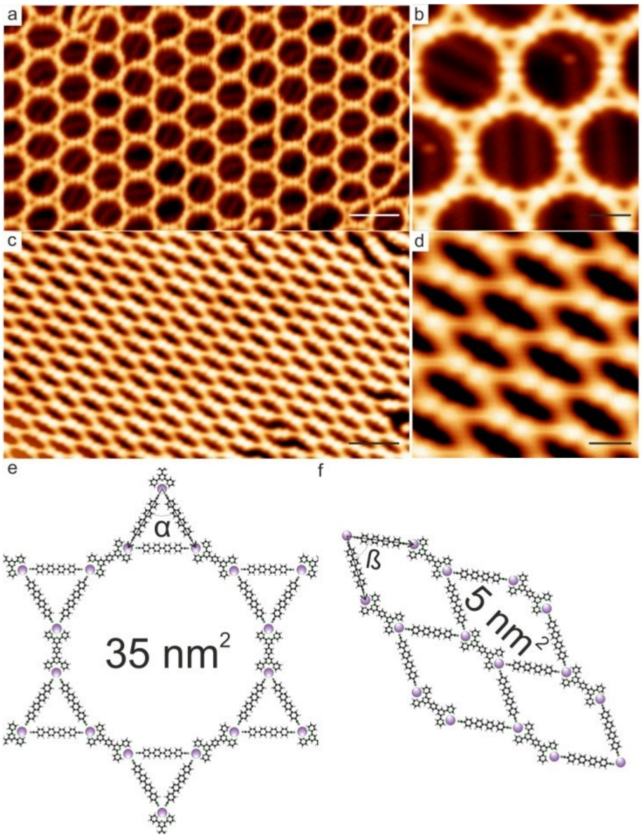

Fig. 3 Two-dimensional porous nanoarchitectures formed at a stoichiometric ratio of [**1**]/[**2**]=1.8. (a) A STM topograph showing well-ordered hexagonal porous 2D network structures (Scale bar: 10 nm). (b) High resolution STM image of (a) (Scale bar: 3 nm). (c) STM topograph displaying a fishing-net 2D metallosupramolecular network formed at the same molecular ratio as (a) (Scale bar: 10 nm). (d) High resolution STM image of (c) (Scale bar: 2 nm) (e, f) Atomistic models of the hexagonal and the fishing-net structures respectively.

For a molecular stoichiometric ratio of [**1**]/[**2**]=1.8, 5-fold coordination is predominant resulting in the formation of two segregation metallosupramolecular networks, which can be interpreted as a hexagonal and a fishing net assembly, respectively. Fig. 3a depicts the well-ordered 2D porous nanostructure exhibiting hexagonal geometry with a periodicity of 8.10 ± 0.05 nm. Fig. 3b shows a high-resolution STM topograph of the hexagonal phase. A detail inspection reveals pores of dodecagonal shape whereas each dodecagon has six molecular linkers **2** and six molecular linkers **1**, arranged alternatively, as its sides. Three Eu atoms are joined by an equilateral triangle comprising three molecular linkers **1**. An atomistic model is shown in Fig. 3e, featuring the dodecagonal pore and the triangles. The triangle corners are Eu atoms that ligated a terpyridyl and two carbonitrile termini in the 5-fold coordination sphere. The inner area of a dodecagonal nanopore is ~35 nm^2, which is, to the best of our knowledge the largest among 2D porous frameworks.[33, 34] The surface molecular density is 10 molecular linkers (**1**) and 5 molecular linkers (**2**) per 100 nm^2.

In addition to the hexagonal phase, Fig. 3c reveals a fishing-net 2D metallosupramolecular network self-assembly. A high-resolution STM topograph and an atomistic model of this phase are shown in Figs. 3d and 3f. Remarkably, this fishing-net structure contains elongated hexagonal pores, which are surrounded by two molecular linkers **2** and four molecular linkers **1**. The model in Fig. 3e illustrates two carbonitrile groups join a terpyridyl via a Eu atom in a 5-fold coordination sphere. The coordination sphere is similar to the one in the hexagonal phase. Nevertheless, the intersecting angle between the two carbonitrile groups is 67° in this structure, which is slightly larger than the 60° angle in the hexagonal phase. The inner area of nanopores in this structural mode is drastically reduced to ~5 nm^2 maintaining the stoichiometric ratio of the two ligands. However, the surface molecular density of this phase, 17.4 molecular linkers (**1**) and 8.7 molecular linkers (**2**) per 100 nm^2, is ~80% higher than those of the hexagonal phase giving rise to a dense 2D nanoarchitecture.

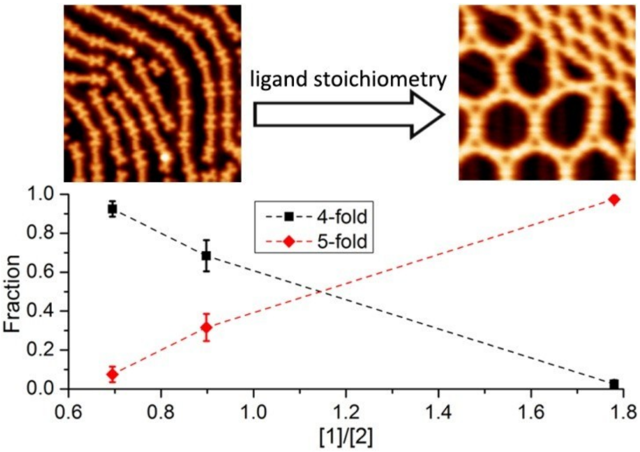

Fig. 4 The fraction of 4-fold and 5-fold Eu coordination schemes against the ligand stoichiometry and the distinct supramolecular phases formed at different ligand stoichiometry.

Co-existence of different coordination schemes for a particular combination of metal center and ligands is common in traditional coordination chemistry in three dimensions, but rarely reported in surface-confined coordination complexes presumably due to the reduced steric effects in the on-surface coordination systems, and the variation of the coordination number is unprecedented for binary metallosupramolecular networks.[35, 36] We attribute the 4-fold and 5-fold coordination schemes to the large ionic radii and unique coordinative characteristics of lanthanide elements, allowing many interactions and the remarkable adaptability of their coordination sphere to the variation of the coordination number. We have varied the stoichiometric ratio of the two molecular linkers and analyzed the population of two coordination spheres against stoichiometry. Fig. 4a reveals that the 4-fold coordination scheme is dominant (92%) at [**1**]/[**2**]=0.7. With increasing [**1**]/[**2**] ratio, the 4-fold coordination sphere decreases while the 5-fold coordination sphere increases. At [**1**]/[**2**]=1.8, the 4-fold coordination is almost completely converted to the 5-fold coordination with 95% selectivity. Hence, regulating the ligand stoichiometry allows us to choose a specific coordination sphere with very high selectivity.

In summary, we have demonstrated that Eu atoms can be ligated by terpyridyl and carbonitrile ligands in either a 4-fold or a 5-fold coordination scheme giving rise to 1D sinusoidal chains or 2D molecular porous networks, either in a hexagonal or a fish-net fashion. The two coordination schemes can be formed with over 95% selectivity at specific ligand stoichiometry. This high selectivity allows us to judiciously construct 1D linear and 2D porous structure using the same molecular building blocks. These findings reveal that surface-confined Ln-metal coordination may offer versatile and flexible coordination motifs for designing two-dimensional supramolecular structures.

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Notes and references

All the experiments were conducted in an ultrahigh-vacuum system (Omicron Nanotechnology), with a base pressure of 3×10^{-10} mbar. A single-crystalline Au(111) substrate was cleaned by repeated cycles of Ar^+ sputtering and annealing to about 620 °C afterwards. The linker molecules **1** and **2** were evaporated at 225 °C and 275 °C, respectively, and deposited onto the Au(111) surface held at room temperature. Subsequently, Eu atoms were sublimated by means of electron beam evaporation from an outgassed Eu rod (99.5%, Mateck GmbH, Germany). The samples were characterized by a scanning tunneling microscope at 5 K (Fig. 1) or 77 K (Fig. 2, 3 and 4) in a constant current mode.

1 J. L.,Atwood, J. E. D. Davies, D. D. MacNicol, F. Vogtle, J.-M. Lehn (ed), *Comprehensive SupramolecularChemistry*, New York: Pergamon, 1996.

2 J.-M. Lehn, *Supramolecular Chemistry, Concepts and Perspectives*, Weinheim: VCH, 1995.

3 A. Dmitriev, H. Spillmann, N. Lin, J.V. Barth and K. Kern, *Angew. Chem. Int. Ed*., 2003 **42**, 2670.

4 S. Stepanow, N. Lin, J. V. Barth, *J. Phys: Cond. Mat.* 2008, **20**, 184002.

5 N. Lin, S. Stepanow, M. Ruben, J. V. Barth, *Top. Curr. Chem.*, 2009, **287**, 1.

6 H. Liang, Y. He, Y. Ye; X. Xu, F. Cheng, W. Sun, X. Shao, Y. Wang, J. Li, K. Wu, *Coord. Chem. Rev.* 2009, **253**, 2959.

7 D. Bonifazi, S. Mohnani, A. Llanes-Pallas, *Chem. Eur. J.*, 2009, **15**, 7004.

8 S. Stepanow, R. Ohmann, F. Leroy, N. Lin, T. Strunskus, C. Woll, K. Kern, *ACS Nano*, 2010, **4**, 1813.

9 C. Wackerlin, C. Lacovita, D. Chylarecka, P. Fesser, T. A. Jung, N. Ballav, *Chem. Commun.*, 2011, **47**, 9146.

10 D. Skomski, S. Abb, S. L. Tait, *J. Am. Chem. Soc.*, 2012, **134**, 14165.

11 N. Abdurakhmanova, A. Floris, T. C. Tseng, A. Comisso, S. Stepanow, A. De Vita, K. Kern, *Nature Commun.*, 2012, **3**, 940

12 S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J.V. Barth, K. Kern, *Nature Mater.* 2004, **3**, 229.

13 W. Xu, J. Wang, M. Yu, E. Lægsgaard, I. Stensgaard, T. R. Linderoth, B. Hammer, C. Wang and F. Besenbacher, *J. Am. Chem. Soc.*, 2010, **132**, 15927.

14 L. Álvarez, S. Peláez, R. Caillard, P. Serena, J. A. Martín-Gago and J. Méndez, *Nanotechnology*, 2010, **21**, 305703.

15 M. Yu, W. Xu, N. Kalashnyk, Y. Benjalal, S. Nagarajan, F. Masini, E. Lægsgaard, M. Hliwa, X. Bouju, A. Gourdon, C. Joachim, F. Besenbacher, T. R. Linderoth, *Nano Res.*, 2012, **5**, 903.

16 M. Bieri, S. Blankenburg, M. Kivala, C. A. Pignedoli, P. Ruffieux, K. Müllen and R. Fasel, *Chem. Commun.*, 2011, **47**, 10239.

17 J. Björk, M. Matena, M. S. Dyer, M. Enache, J. Lobo-Checa, L. H. Gade, T. A. Jung, M. Stöhr and M. Persson, *Phys. Chem. Chem. Phys.*, 2010, **12**, 8815.

18 J. Zhang, A. Shchyrba, S. Nowakowska, E. Meyer, T. A. Jung and M. Muntwiler, *Chem. Commun.*, 2014, **50**, 12289.

19 M. Matena, J. Björk, M. Wahl, T.-L. Lee, J. Zegenhagen, L. H. Gade, T. A. Jung, M. Persson and M. Stöhr, *Phys. Rev. B*, 2014, **90**, 125408.

20 N. Henningsen, R. Rurali, C. Limbach, R. Drost, J. I. Pascual and K. J. Franke, *J. Phys. Chem. Lett.*, 2011, **2**, 55.

21 T. R. Umbach, M. Bernien, C. F. Hermanns, A. Krüger, V. Sessi, I. Fernández-Torrente, P. Stoll, J. I. Pascual, K. J. Franke and W. Kuch, *Phys. Rev. Lett.*, 2012, **109**, 267207.

22 T. Classen, G. Fratesi, G. Costantini, S. Fabris, F. L. Stadler, C. Kim, S. de Gironcoli, S. Baroni and K. Kern, *Angew. Chem. Int. Ed.*, 2005, **44**, 6142.

23 S. Barja, D. Stradi, B. Borca, M. Garnica, C. Díaz, J. M Rodriguez-García, M. Alcamí, A. L V. de Parga, F. Martín and R. Miranda, *J. Phys.: Cond. Matter*, 2013, **25**, 484007.

24 J. Cechal, C. S. Kley, T. Kumagai, F. Schramm, M. Ruben, S. Stepanow, K. Kern, *Chem. Commun.*, 2014, **50**, 9973.

25 G. Lyu, R. Zhang, X. Zhang, P. Liu, N. Lin, *J. Mater. Chem. C*, 2015, **3**, 322.

26 D. Ecija, D.; J. I. Urgel, A. C. Papageorgiou, S. Joshi, W. Auwarter, A. P. Seitsonen, S. Klyatskaya, M. Ruben, S. Fischer, S. Vijayaraghavan, J. Reichert, J. V. Barth, *Proc. Natl. Acad. Sci. U.S.A.*, 2013, **110**, 6678.

27 J. I. Urgel, D. Ecija, W. Auwarter, A. C. Papageorgiou, A. P. Seitsonen, S. Vijayaraghavan, S. Joshi, S. Fischer, J. Reichert, J. V. Barth, *J. Phys. Chem. C*, 2014, **118**, 12908.

28 N. Kaltsoyannis, P. Scott, *The f Elements*, Oxford Univesiity Press, Oxford, 1999.

29 J.-C.G. Bünzli, R. In: Saez-Puche, P. Caro, (Eds.), *Rare Earths*, Mardrid, 1998, 223.

30 L. C. Thompson, K. A. in Gschneider, L. Eyring, (Eds.), *Handbook on the Physics and Chemistry of Rare Earths*, North-Holland, Amsterdam, 1979, **3**, 209.

31 J.-C.G. Bünzli, N. Andre, M. Elhabiri, G. Muller, C. Piguet, *J. Alloy. Compd.*, 2000, **303**, 66.

32 Y. Chen, S. Ma, *Rev. Inorg. Chem.*, 2012, **32**, 81.

33 D. Kuhne, F. *Klappenberger,* R. Deck**er,** U. Schlickum, H. Brune, S. Klyatskaya, M. Ruben, J. V. Barth, *J. Am. Chem. Soc.*, 2009, **131**, 3881.

34 T. Lin, G. Kuang, X. Shang, P. Liu, N. Lin, *Chem. Commun.*, 2014, **50**, 15327.

35 A. Langner, S. L. Tait, N. Lin, C. Rajadurai, M. Ruben, K. Kern, *Proc. Natl. Acad. Sci. U.S.A.*, 2007, **104**, 17927.

36 Z. Shi, N. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 10756.