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Supramolecular squares of dirhodium(II) tetracarboxylate: combining carboxylate-exchange and metal–ligand coordination for self-assembly†

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Square self-assemblies are obtained from dirhodium(II) tetracarboxylate complexes using an isonicotinate-type ligand to act as an equatorial ligand to one dirhodium unit and an axial ligand to another. It is shown that the supramolecular squares are formed selectively out of a number of possible compounds in the dynamic carboxylate exchange library.

The use of multiple reversible orthogonal interactions is a fascinating synthetic route for the construction of complex multi-component assemblies.[1] Reversible interactions such as hydrogen bonds,[2] π–π stacking,[3,4] ion–dipole interactions,[5] and reversible covalent bond formation[6,7] have been employed concurrently with metal–ligand interactions to form a range of supramolecular structures. The combination of three independent interactions, aldehyde–amine condensations, metal–ligand interactions and formation of boronic esters has recently been demonstrated as a route to obtain a complex structure.[8]

Dimetal-tetracarboxylates, $M_2(O_2CR)_4$ are found for many transition metal elements in the +II oxidation state. The four carboxylates bridge the two metal ions and will be referred to as equatorial ligands, while two further ligands can bind along the metal–metal axis (the axial ligands). These two interactions are orthogonal: the carboxylate ion occupying the equatorial bridging site will not occupy the axial site, while a simple nitrogen donor will only bind to the axial site, and cannot bridge equatorially. Carboxylate ligand substitution and adduct formation with axial ligands are useful properties of dirhodium(II) tetracarboxylates $Rh_2(O_2CR)_4$ (R = organic substituents).[9] Partial or complete exchange of the carboxylate ligands of $Rh_2(O_2CR)_4$ with other carboxylic acids $R'CO_2H$ occurs in a stepwise fashion with replacement of O_2CR by O_2CR' to generate a library of six differently substituted products $[Rh_2(O_2CR)_{4-n}(O_2CR')_n]$, n = 0–4. Carboxylate ligand substitution has been employed as a scaffold for multichromophore assembly about the dirhodium(II) cores[10] and to control peptide structure.[11] Axial adduct formation by dirhodium(II) tetracarboxylate has been used to create liquid crystalline polymers,[12,13] in catalyst immobilisation,[14] molecular sensing,[15,16] and to assemble nanometric spheres from pentagonal units.[17]

The synthesis of square metallomacrocycles has been a subject of interest for more than twenty years.[18,19] Dirhodium units have previously been used to yield molecular squares only by employing "*cis*-protected" dirhodium precursors as corner components which allows di-substitutions to occur in a "*cis*"fashion at equatorial sites.[20–22] Herein we report a one-pot synthesis of two nano-sized supramolecular squares **2** and **3** based on dirhodium(II) tetracarboxylates using carboxylate exchange and metal–ligand coordination in the axial position. This work demonstrates the use of a new combination of two reversible orthogonal interactions for construction of self-sorting supramolecular assemblies.

A new dirhodium(II) tetra-3,5-di-*tert*-butylbenzoate precursor **1** which possesses high solubility in organic solvents was obtained in quantitative yield by reacting dirhodium(II) tetraacetate with 8-fold excess of 3,5-di-*tert*-butylbenzoic acid in refluxing toluene, with continuous removal of the liberated acetic acid from the reaction mixture (Scheme 1). The crystal structure of **1** is typical for dirhodium(II) tetracarboxylates (Fig. S1, ESI†).[23]

If compound **1** was reacted with one equivalent of isonicotinic acid, under reflux, a single product **2** was isolated in 83% yield. Compound **2** was confirmed as a tetramer from the crystal structure.‡ The carboxylate of the isonicotinate bridges one dirhodium unit while the pyridine binds to an axial site of an adjacent dirhodium (Fig. 1). The complex is distorted from planarity, with a S_4 axis passing through the centre of the pseudo-square, so that the asymmetric unit consists of one monomer. The centroids of the dirhodium units lie 1.02 Å from the mean plane, and the distance between neighbouring dirhodium centroids is 10.20 Å. The vacant axial coordination sites of the dirhodium units are occupied by methanol molecules which are linked by hydrogen bonding to neighbouring tetramers (Fig. S2, ESI†). The Rh–Rh and Rh–O-(acetate) distances are normal for dirhodium(II) tetracarboxylates.[9] The axial Rh–N(isonicotinate) distance is 2.151(13) Å.

The structure of **2** in solution is confirmed by the ^{1}H NMR spectrum showing (i) two signals for each aryl proton of the di-*tert*-butyl aromatic group in a 2 : 1 ratio (Fig. 2) and two signals for the *tert*-butyl protons as expected from the crystal structure

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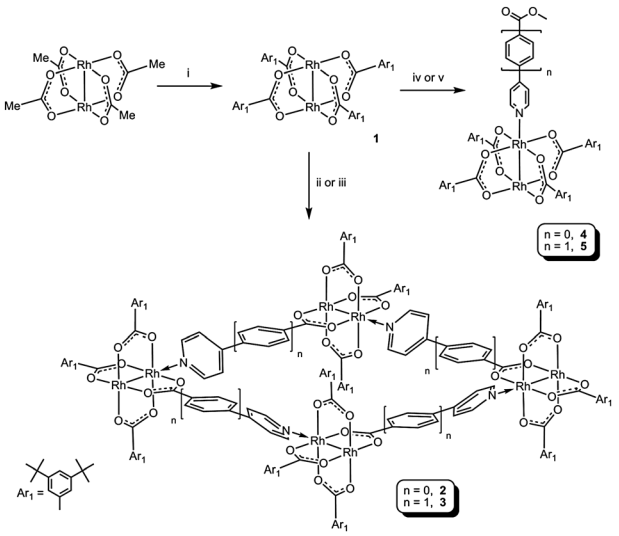

Scheme 1 Synthesis of the dirhodium tetracarboxylate species (**1–5**). Reagent and conditions: (i) 3,5-di-*tert*-butylbenzoic acid (8 eq.), toluene, overnight reflux; (ii) isonicotinic acid (1 eq.), toluene, overnight reflux; (iii) 4-(pyridin-4-yl)benzoic acid (1 eq.), benzene, overnight reflux; (iv) methyl isonicotinate (1 eq.), $CHCl_3$, r.t.; (v) methyl 4-(pyridin-4-yl)benzoate (1 eq.), $CHCl_3$, r.t.

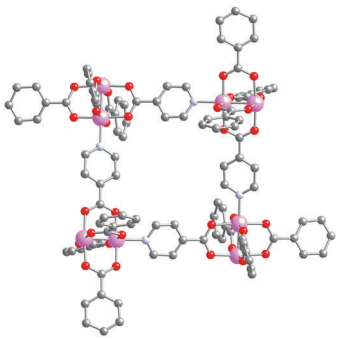

Fig. 1 X-ray crystal structure of **2**. The *tert*-butyl groups and hydrogen atoms are omitted for clarity (key: Rh pink, O red, N blue, C grey).

and (ii) a downfield shift of the pyridyl protons (Fig. S3, ESI†) showing the coordination of the pyridyl group to the dirhodium centre and comparable to shifts seen for the mono-adduct **4**. The electronic spectrum (Table S1, ESI†) also shows evidence for axial coordination since the absorption maximum for the dirhodium species attributable to the $\pi^*(Rh_2) \rightarrow \sigma^*(Rh_2)$ transition[9,24,25] shows a hypsochromic shift in comparison with precursor **1** (Fig. S4, ESI†). The UV absorption spectrum of **2** in $CHCl_3$ is concentration independent within the range 1.0×10^{-3} M to 4.9×10^{-7} M, suggesting that the dirhodium chromophores and the assemblies remain intact (Fig. S5, ESI†).

The MALDI-TOF mass spectrum of **2** shows the molecular ion (m/z = 4109.24, calculated 4109.20), along with peaks at m/z = 2054.88 and m/z = 1027.34 corresponding to the fragmented dimeric and monomeric units respectively (Fig. S6, ESI†). Finally the diffusion coefficient for the tetramers **2** determined by ^{1}H DOSY experiments at 25 °C in $CDCl_3$ is 430 $\mu m^2\ s^{-1}$, compared with that of the monomer **1** which is about 650 $\mu m^2\ s^{-1}$.

If the carboxylate function of isonicotic acid is blocked by esterification, its reaction with **1** under reflux in toluene gives

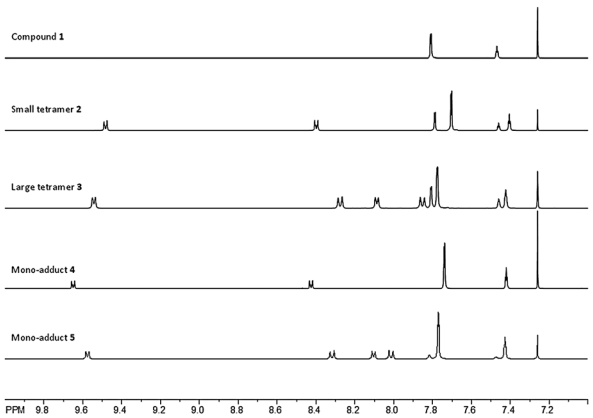

Fig. 2 The aromatic region of the ^{1}H NMR spectra in $CDCl_3$ of compounds **1** to **5**.

only a mono-adduct **4** whose ^{1}H NMR and electronic spectra show axial coordination, but no carboxylate exchange. On the other hand, if the pyridine is blocked by substitution by phenyl groups at the 2 and 6 positions no axial coordination is observed at room temperature. Refluxing overnight in toluene gave scrambling of carboxylates (Fig. S7, ESI†): mono-substituted $Rh_2[(O_2CR_1)_3(O_2CR_2)]$ (R_2 = 2,6-$(C_6H_5)_2C_5H_2N$) (25%), two inseparable di-substituted *cis*/*trans* isomers $Rh_2[(O_2CR_1)_2(O_2CR_2)_2]$ (combined yield of 20%), and tri-substituted $Rh_2[(O_2CR_1)(O_2CR_2)_3]$ (4%). Formation of the fully substituted product $Rh_2(O_2CR_2)_4$ was not observed.

From this we deduce that when the exchange of the carboxylate ligands occurs under reflux but the axial coordination of the pyridine is blocked, a library of substituted compounds is obtained. However, when the pyridine is available for axial Rh–N coordination, the dynamic combinatorial library[26] of six possible scrambled products in the carboxylate exchange is perturbed. Formation of the mono-substituted product is amplified from 25% to 83% because it can self-tetramerise to yield the discrete assembly **2**, and the four rhodium–nitrogen bonds formed in **2** shift the reversible carboxylate exchange towards mono-substitution. If the reaction between **1** and isonicotinic acid was carried out at room temperature only an orange brown insoluble material along with traces of the mono-adduct of **1**·L (L = 4-CO_2H–C_5H_4N) and isonicotinic acid were obtained. It is attributable to the formation of a mixture of polymers, the thermodynamically stable product being hindered by slow kinetics. An insoluble product was also obtained if two equivalents of isonicotinic acid were used in refluxing toluene, and this was attributed to multiple substitutions leading to polymer formation.

The strategy used for **2** was repeated using an elongated analogue of isonicotinic acid, 4-(pyridinyl)benzoic acid which gave with **1** in refluxing benzene the tetramer **3** in 49% yield. Despite the structural similarity with square **2**, compound **3** only shows moderate solubility in $CHCl_3$ and CH_2Cl_2. The ^{1}H NMR spectrum of **3** shows two sets of aryl protons in a 2 : 1 ratio in agreement with the mono-substituted nature of the dirhodium moiety (Fig. 2). The pyridyl protons in **3** appear in downfield region (9.55, 8.27 ppm), compared to methyl 4-(pyridine-4-yl)benzoate (8.68, 8.11 ppm) (Fig. S3, ESI†) showing coordination of the pyridyl group to dirhodium centre.

This is supported by the observation of similar ^{1}H NMR and electronic spectra for **3** and the model compound **5** (prepared by stoichiometric mixing of **1** with methyl 4-(pyridine-4-yl) benzoate). Despite numerous efforts, only an average mass for **3** was observed in the MALDI TOF spectrum, but exact masses were observed for monomeric, dimeric and trimeric fragments of **3**.

As expected for the greater size of the square the diffusion coefficient of **3** determined by ^{1}H DOSY experiments at 25 °C in $CDCl_3$ is 370 $\mu m^2\ s^{-1}$. Although the Stokes–Einstein equation is not suitable for determination of the hydrodynamic radius of these complexes due to their non-spherical shape, the order of the diffusion coefficients **1** > **2** > **3** is in good agreement with the expected size progression.

The monomer **1** has two vacant axial sites for binding ligands, and UV-visible titrations (Fig. S8–S10, ESI†) with a series of pyridine bases showed two-step binding with typical values of $\log_{10}K_1$ of 6 and $\log_{10}K_2$ of 3. The tetramers **2** and **3** have four binding sites and titrations confirmed four successive binding steps with slightly decreasing constants close to those observed for the second binding step of the monomer. The constants observed for the smaller tetramer **2** were slightly greater than those for **3**.

The cyclic voltammetry of complexes **1–5** was studied in CH_2Cl_2/NBu_4PF_6 (Table S1, ESI†). All measurements showed a single quasi-reversible system ($0.01 < v < 5$ V s^{-1}). In the case of monomeric complexes, we observed the one-electron oxidation of the dirhodium(II) species: $[Rh_2]^{4+} \rightarrow [Rh_2]^{5+} + e^-$ in the range observed for other tetracarboxylate dirhodium complexes.[27,28] The addition of an axial ligand to one of the two metal centres of compound **1** causes a negative shift of about −100 mV of the potential $E_{1/2}$ (Fig. S11, ESI†). This shift reflects stabilization of the oxidized state Rh(III)–Rh(II) due to increased electron density on the metal centres with the presence of an additional *N*-donor. For **2** and **3**, the cyclic voltammograms may be interpreted in terms of four independent one-electron oxidations showing negligible interaction. The peak observed for **2**, where the rhodium–rhodium distance is shorter, is slightly broader than that seen for **3** which may indicate slightly greater interaction (Fig. S12, ESI†). This affords a notable contrast with the systems where the dirhodium units are linked by equatorial–equatorial interactions (using terephthalate or oxalate[21,22]) where significant interaction was observed.

In conclusion, we have shown the facile one-step synthesis of nanometre-sized squares in high yields using a new combination of reversible orthogonal interactions. Two bonds have been used: dirhodium–carboxylate, and axial rhodium–nitrogen binding. Heating is required for carboxylate exchange, but when this occurs and axial coordination is possible, the mono-substituted product is selected out of the dynamic mixture as a result of the tetramerisation of the exchanged product. The resulting assemblies show Lewis acidity, binding up to four Lewis bases in the vacant axial positions, and are potentially available for the construction, *via* Lewis acid–Lewis base interactions, of more elaborate structures. They further show electrochemical behaviour compatible with four independent redox centres and could act as four electron reservoirs.

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Notes and references

‡ Crystal data for **2**: $C_{59}H_{78}NO_{9.5}Rh_2$ was collected on a IPDS II diffractometer at 180(2) K using MoKα radiation (λ = 0.71073 Å). Full-matrix, least-squares refinements on F^2 using all data. Total data 128 659, unique data 8666 (R_{int} = 0.2164), M_r = 1159.04, cubic, space group $Ia\bar{3}d$, $a = b = c$ = 59.616(3) Å, $\alpha = \beta = \gamma = 90°$, V = 211 879(17) Å^3, Z = 96, R_1 [$I > 2\sigma(I)$] = 0.1141, wR_2 = 0.2877.

1 M. Schmittel and K. Mahata, *Angew. Chem., Int. Ed.*, 2008, **47**, 5284.
2 I. Huc, M. J. Krische, D. P. Funeriu and J. M. Lehn, *Eur. J. Inorg. Chem.*, 1999, 1415.
3 M. Yoshizawa, J. Nakagawa, K. Kurnazawa, M. Nagao, M. Kawano, T. Ozeki and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 1810.
4 K. Ono, M. Yoshizawa, T. Kato, K. Watanabe and M. Fujita, *Angew. Chem., Int. Ed.*, 2007, **46**, 1803.
5 H. B. Yang, K. Ghosh, B. H. Northrop, Y. R. Zheng, M. M. Lyndon, D. C. Muddiman and P. J. Stang, *J. Am. Chem. Soc.*, 2007, **129**, 14187.
6 J. R. Nitschke and J. M. Lehn, *Proc. Nat. Acad Sci. U. S. A.* 2003, **100**, 11970.
7 K. S. Chichak, S. J. Cantrill, A. R. Pease, S. H. Chiu, G. W. V. Cave, J. L. Atwood and J. F. Stoddart, *Science*, 2004, **304**, 1308.
8 N. Christinat, R. Scopelliti and K. Severin, *Angew. Chem., Int. Ed.*, 2008, **47**, 1848.
9 F. A. Cotton, E. A. Hillard, C. Y. Liu, C. A. Murillo, W. N. Wang and X. P. Wang, *Inorg. Chim. Acta*, 2002, **337**, 233.
10 M. W. Cooke, G. S. Hanan, F. Loiseau, S. Campagna, M. Watanabe and Y. Tanaka, *J. Am. Chem. Soc.*, 2007, **129**, 10479.
11 A. N. Zaykov, B. V. Popp and Z. T. Ball, *Chem.–Eur. J.*, 2010, **16**, 6651.
12 M. Rusjan, B. Donnio, D. Guillon and F. D. Cukiernik, *Chem. Mater.*, 2002, **14**, 1564.
13 S. Takamizawa, E. Nakata, H. Yokoyama, K. Mochizuki and W. Mori, *Angew. Chem., Int. Ed.*, 2003, **42**, 4331.
14 H. M. L. Davies, A. M. Walji and T. Nagashima, *J. Am. Chem. Soc.*, 2004, **126**, 4271.
15 S. A. Hilderbrand, M. H. Lim and S. J. Lippard, *J. Am. Chem. Soc.*, 2004, **126**, 4972.
16 R. C. Smith, A. G. Tennyson and S. J. Lippard, *Inorg. Chem.*, 2006, **45**, 6222.
17 L. H. Tong, L. Guenee and A. F. Williams, *Inorg. Chem.*, 2011, **50**, 2450.
18 M. Fujita, J. Yazaki and J. Ogura, *J. Am. Chem. Soc.*, 1990, **112**, 5645.
19 M. Schmidtendorf, T. Pape and F. E. Hahn, *Angew. Chem., Int. Ed.*, 2012, **51**, 2195.
20 R. P. Bonar-Law, T. D. McGrath, N. Singh, J. F. Bickley and A. Steiner, *Chem. Commun.*, 1999, 2457.
21 S. Lo Schiavo, G. Pocsfalvi, S. Serroni, P. Cardiano and P. Piraino, *Eur. J. Inorg. Chem.*, 2000, 1371.
22 F. A. Cotton, L. M. Daniels, C. Lin and C. A. Murillo, *J. Am. Chem. Soc.*, 1999, **121**, 4538.
23 F. A. Cotton and R. A. Walton, *Multiple Bonds between Metal Atoms*, Oxford University Press, 1993.
24 L. Dubicki and R. L. Martin, *Inorg. Chem.*, 1970, **9**, 673.
25 J. W. Trexler, A. F. Schreiner and F. A. Cotton, *Inorg. Chem.*, 1988, **27**, 3265.
26 B. Brisig, J. K. M. Sanders and S. Otto, *Angew. Chem., Int. Ed.*, 2003, **42**, 1270.
27 J. G. Gaudiello, P. G. Bradley, K. A. Norton, W. H. Woodruff and A. J. Bard, *Inorg. Chem.*, 1984, **23**, 3.
28 R. S. Drago, R. Cosmano and J. Telser, *Inorg. Chem.*, 1984, **23**, 3120.