The dual role of Cu(I) as a protective group and a template in the synthesis of a tetra-rhodium(III)porphyrin [2]catenane

Maryline Beyler, Valérie Heitz* and Jean-Pierre Sauvage*

Received (in Montpellier, France) 1st June 2010, Accepted 11th June 2010
DOI: 10.1039/c0nj00414f

A new [2]catenane containing four Rh(III) porphyrins has been prepared following a three-step strategy: (i) Cu(I)-driven entwining of two free base porphyrin-bearing bidentate chelates, followed by (ii) insertion of rhodium in the porphyrin nuclei, and finally (iii) cyclisation *via* the formation of N–Rh coordination bonds. Direct metalation of porphyrinic compounds with $[Rh(CO)_2Cl]_2$ was not met with success when the bidentate chelate used as a connector was metal free, thus making the Cu(I) protecting approach very attractive.

The transition metal-induced formation of non-covalent assemblies has produced spectacular examples of large multifunctional architectures.[1] Most of the time, the assembly reaction is a dynamic process performed under thermodynamic control, ultimately leading to the most stable structure.[2] This is particularly true for first-row transition metals and Pd(II), whose coordination spheres are sufficiently labile to allow formation of the thermodynamic product. In contrast, second- and third-row transition metals can be very slow to exchange their ligands, and thus these metals may lead to non-equilibrium products rather than to thermodynamic ones. These differences are particularly well illustrated in the field of catenanes and rotaxanes. Use has been made of the Pd–N bond by Fujita and co-workers to prepare several types of catenanes,[3] including Cu(I)-complexed systems.[4] In all cases, the catenane formation reaction is performed under very mild conditions and it is quantitative. Porphyrin-incorporating interlocking systems are particularly promising in relation to electron and energy transfer processes, as well as molecular machines.[5] Several types of non-covalently-assembled porphyrinic catenanes or rotaxanes have been reported, either based on the formation of hydrogen bonds or coordination bonds.[6] In particular, advantage has been taken of the interaction between a pyridinic nitrogen atom or a related ligand and the central zinc atom of a porphyrin.

We would now like to report that Rh(III) porphyrins can also be used in the synthesis of catenanes assembled *via* the formation of coordination bonds, conferring to compounds obtained a relatively high stability compared to their zinc homologues. The principle is depicted in Scheme 1. Rhodium is an important metal in homogeneous catalysis. More specifically, rhodium-complexed porphyrins have been used as catalysts in various reactions such as cyclopropanations,[7] enolisations,[8] C–H bond activations,[9] the oxygenation of olefins,[10] and the reduction of ketones[11] or alkenes[12] in presence of a borohydride. It seemed to be promising to combine potential rhodium-based catalysts and photoactive copper complexes of the bis-dpp type (dpp: 2,9-diphenyl-1,10-phenanthroline).[13] The formation and the utilisation of the presently-described catenane appears to be an interesting approach in this respect.

The chemical structures of free-base bis-porphyrin **1**,[14] the non-metalated and metalated entwined species $\mathbf{2}^+$ and $\mathbf{3}^+$, respectively, 2,7-dipyridyl-naphthalene **4**,[14b] and final [2]catenane $\mathbf{5}^+$ are depicted in Scheme 2.

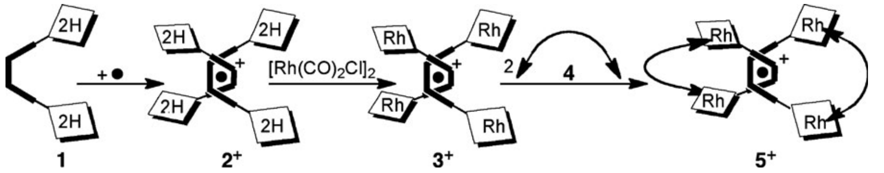
Porphyrin metalation with $[Rh(CO)_2Cl]_2$, followed by an oxidation step with I_2, according to the method described by Grigg *et al.*[15] and later by Sanders and co-workers,[16] was tried on free-base bis-porphyrin **1**. A complex mixture of products was obtained, including compounds originating from *ortho*-metalation of the dpp fragment component of **1**, *i.e.* the formation of complexes containing Rh–C and Rh–N bonds. Thus, the insertion of Rh(III) into a porphyrin in presence of a metal-free dpp unit seemed to be of no practical use. Therefore, the following strategy using Cu(I) as a protecting group for this dpp unit was chosen.

Complex $\mathbf{2}\cdot\mathbf{PF_6}$ was made quantitatively from **1** by adding 0.5 equivalents of $Cu(CH_3CN)_4\cdot PF_6$. In this entwined species, the 1,10-phenanthroline chelate is coordinated to Cu(I), implying that the dpp fragment is fully protected against *ortho*-metalation. Metalation of the four porphyrins with $[Rh(CO)_2Cl]_2$ was carried out on $\mathbf{2}^+$ according to the following procedure. To a solution of $\mathbf{2}\cdot\mathbf{PF_6}$ in CH_2Cl_2, were added 2.2 equivalents of $[Rh(CO)_2Cl]_2$ and exactly 2 equivalents of NaOAc per porphyrin. After stirring the mixture for 4 h at r.t., I_2 was added (8 equivalents) and the solution stirred for a further 16 h. The crude product was washed with a saturated solution of KI, followed by an exchange of counterion with a saturated solution of KPF_6. The resulting product was then purified by several precipitations in CH_2Cl_2–CH_3CN and CH_2Cl_2–CH_3OH. $\mathbf{3}\cdot\mathbf{PF_6}$ was obtained as a deep red solid in 62% yield. This complex was characterized by mass spectrometry ESI-MS, UV-vis spectroscopy and ^1H NMR, including COSY and ROESY. Since rhodium porphyrins are penta-coordinated and because the rotation of the phenyl groups in such metalloporphyrins is slow, the protons located above and below the plane (op protons) of the porphyrins are not equivalent.[17] Representative signals of complex $\mathbf{3}^+$ are shown in Fig. 1.

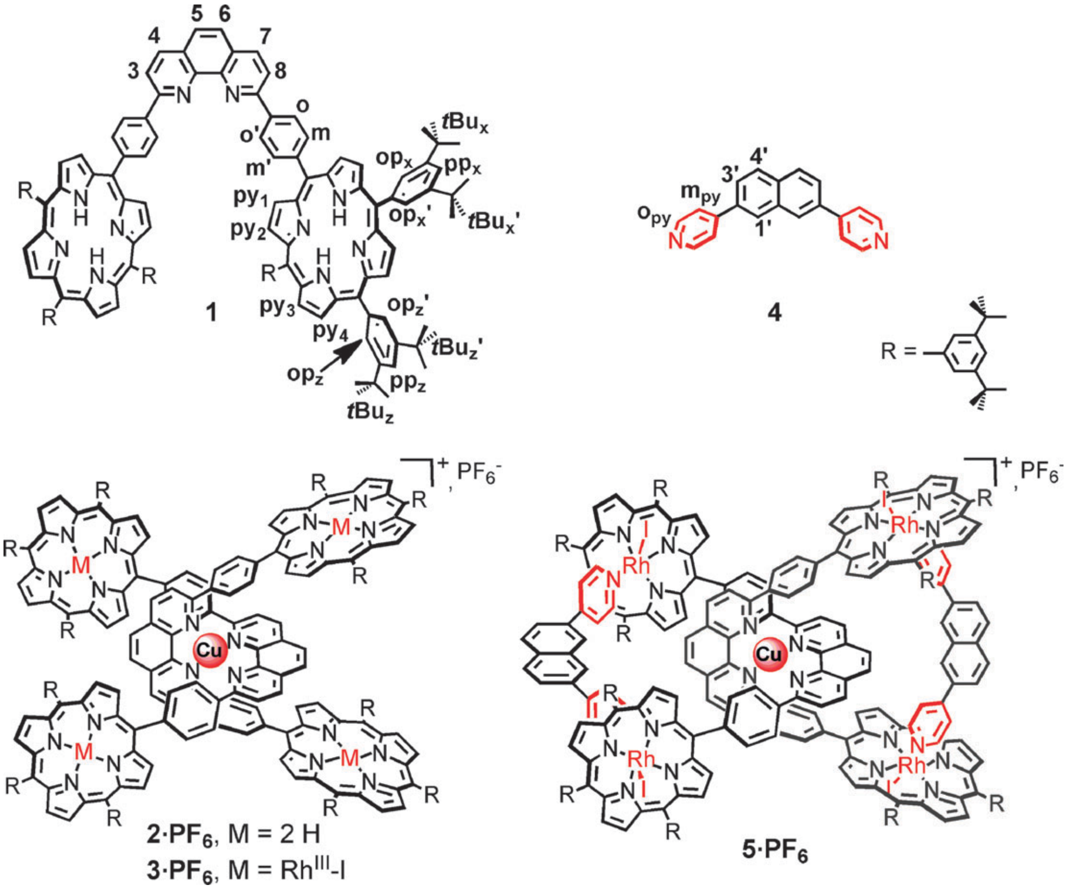
A recent report highlighted the importance of geometrical factors in terms of angles and distances in non-covalently-assembled edifices built using coordination chemistry.[14b] The

---

Laboratoire de Chimie Organo-Minérale, LC3 UMR 7177 du CNRS, Université de Strasbourg, Institut de Chimie, 4 rue Blaise Pascal, 67070 Strasbourg Cedex, France. E-mail: v.heitz@unistra.fr, sauvage@chimie.u-strasbg.fr; Fax: +33 3 6885 1368; Tel: +33 3 6885 1361



Scheme 1 The stepwise formation of a non-covalent [2]catenane. (i) Synthesis of the entwined precursor $\mathbf{2}^+$ due to a Cu(I) template effect followed by (ii) rhodium metalation to give $\mathbf{3}^+$ and finally (iii) a ring-closing reaction based on Rh(III)–pyridine interactions to afford $\mathbf{5}^+$. The diamonds stand for porphyrin units, the black dot is a Cu(I) atom and the U-shaped symbol designates a dpp connector. In **4**, the curved arc stands for a naphthalene unit. An arrow symbolises a 4-pyridyl nucleus and Rh indicates Rh(III)–I.



Scheme 2 Chemical structures of the free-base porphyrin **1**, the entwined Cu(I) complexes **2·PF$_6$** and **3·PF$_6$**, the dipyridyl naphthalene **4** and the tetra-rhodium(III)porphyrin-containing [2]catenane **5·PF$_6$**.

average angle between the two porphyrins linked on a dpp is 60°, and with pyridines coordinating zinc porphyrins approximately orthogonally, the two pyridyl group axes borne by the spacer must form an angle of 120° in order to obtain the best fit. This is the case if they are connected by positions 2 and 7 of the naphthalene unit, as in **4**. **4** (two equivalents) and **3·PF$_6$** are thus expected to lead to a very stable [2]catenane. Experimentally, **3·PF$_6$** and 2 equivalents of **4** were mixed in THF, allowed to react at r.t. for 2 h and the solvent pumped off. Contrary to a similar case[14b] in which a [2]catenane was formed with ligand **1** bearing Zn(II) in both porphyrins, **5·PF$_6$** was not formed quantitatively because the reaction is no longer performed under thermodynamic control but rather under kinetic control. Purification appeared to be delicate because of the high instability of the product on chromatography stationary phases, with no separation of the impurities on a size exclusion stationary phase (Sephadex LH-20, Biobeads). Nevertheless, after several cycles of flash chromatography on silica, the desired catenane, $\mathbf{5}^+$, could be isolated as a deep red solid, but with a low yield of 19% compared to the yield of the reaction, estimated to be 70%. The compound was characterized by mass spectrometry ESI-MS, UV-vis spectroscopy and ^{1}H NMR, including COSY and ROESY. Upon complexation, the pyridine protons of **4** undergo an expected strong upfield shift due to the porphyrin ring current (chemical shifts: 5.59 ppm for m_{py} and 1.15 ppm for o_{py} in $\mathbf{5}^+$ compared to 7.68 ppm for m_{py} and 8.74 for o_{py} in **4**), as already observed in similar systems (Fig. 1).[18] In addition, their signals are sharp, which means that, *a priori*, the N–Rh interaction is strong and there is no ligand exchange.

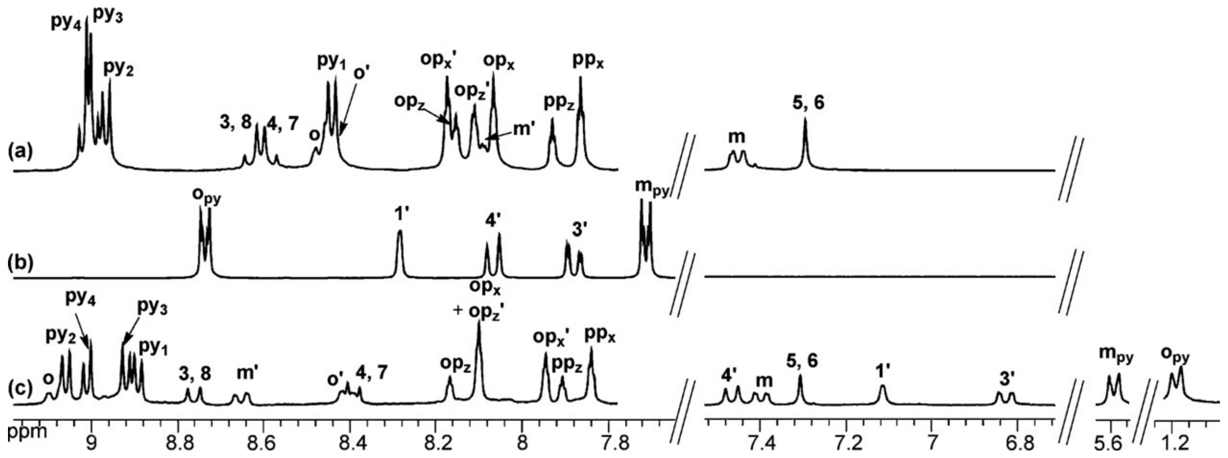


Fig. 1 Partial ^{1}H NMR (300 MHz, CD_2Cl_2, 25 °C) spectra of (a) $\mathbf{3}^+$, (b) **4** and (c) $\mathbf{5}^+$.

The present study illustrates the important role of Cu(I), which acts as a central template, but also as a dpp protective group for the rhodium metalation of the porphyrin units attached to the dpp fragment. A tetraporphyrinic[2]catenane was subsequently synthesised *via* the formation of four non-covalent but irreversible Rh(III)–pyridine interactions.

We thank the Ministry of Education for a Fellowship (to M. B.) and also COST D31 for financial support.

Experimental

Dry dichloromethane was distilled from calcium hydride. Thin layer chromatography was carried out using pre-coated polymeric sheets of silica gel (Macheray-Nagel, POLYGRAM, SIL G/UV$_{254}$). ^{1}H nuclear magnetic resonance (NMR) spectra were acquired on a Bruker AVANCE 300 spectrometer. The spectra were referenced to residual proton solvent reference (^{1}H: CD_2Cl_2 at 5.32 ppm). In the assignments, the chemical shift (in ppm) is given first, followed (in brackets) by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, m: multiplet or bs: broad singlet), the number of protons implied, the value of the coupling constants in Hz, if applicable, and finally the assignment. Mass spectra were obtained by using a Bruker MicroTOF spectrometer (ESI-MS). UV-visible spectra were recorded with a Kontron Instruments UVIKON 860 spectrometer at 25 °C with a 1 cm path cell.

All chemicals were of the best commercially available grade and were used without further purification (unless mentioned).

The syntheses of **1**[19] and **4**[14b] have already been reported.

Compound 2·PF$_6$

In a round-bottomed flask, was dissolved **1** (87 mg, 0.042 mmol) in 7 mL of freshly distilled CH_2Cl_2. The solution was de-gassed with three vacuum–argon cycles. In a Schlenk flask, was dissolved $Cu(CH_3CN)_4{\cdot}PF_6$ (8.2 mg, 0.022 mmol) in 3 mL of de-gassed CH_3CN. This solution was added *via* a cannula to the solution of **1** in CH_2Cl_2. The mixture was allowed to react for 3 h at room temperature under argon. The solvents were removed under a reduced pressure, and the purple solid was taken up in CH_2Cl_2 and washed with water (3 × 10 mL). The organic layers were dried under vacuum, and 94.1 mg of a purple solid, **2·PF$_6$**, were obtained (100%).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K). δ (ppm): 8.92 (d, 8 H, ^3J = 4.7 Hz, py$_2$), 8.91 (d, 8 H, ^3J = 4.8 Hz, py$_4$), 8.89 (d, 8 H, ^3J = 4.7 Hz, py$_3$), 8.61 (bs, 8 H, 3, 8 + 4, 7), 8.48 (d, 8 H, ^3J = 8.7 Hz, o), 8.38 (d, 8 H, ^3J = 4.8 Hz, py$_1$), 8.09 (d, 16 H, ^4J = 1.8 Hz, op$_x$), 8.08 (d, 8 H, ^4J = 2 Hz, op$_z$), 7.86 (t, 4 H, ^4J = 1.7 Hz, pp$_z$), 7.82 (t, 8 H, ^4J = 1.7 Hz, pp$_x$), 7.77 (d, 8 H, ^3J = 8.1 Hz, m), 7.37 (s, 4 H, 5, 6), 1.53 (s, 72 H, *t*Bu$_z$), 1.50 (s, 144 H, *t*Bu$_x$), −2.85 (s, 8 H, NH).

Compound 3·PF$_6$

A round-bottomed flask was charged with **2·PF$_6$** (94.1 mg, 0.022 mmol), NaOAc (14.3 mg, 0.172 mmol) and $[Rh(CO)_2Cl]_2$ (40.2 mg, 0.10 mmol). The mixture was de-gassed with three vacuum–argon cycles, dissolved in 10 mL of freshly distilled and de-gassed CH_2Cl_2, and stirred at room temperature under argon. After 4 h, I_2 (43.7 mg, 0.172 mmol) was added to the solution and the mixture allowed to react for a further 16 h. The crude product was washed with a saturated aqueous solution of KI (25 mL) and water (3 × 25 mL). The organic layers were taken up in a mixture of CH_2Cl_2–acetonitrile (5 : 1 v/v), and 1 mL of an aqueous saturated solution of KPF_6 added. The mixture was vigorously stirred under argon for 1 h. The organic solvents were removed under reduced pressure, and the red precipitate that formed was filtered and washed with water. The red powder was next dried under vacuum. The crude product was then purified by several precipitations from a mixture of CH_2Cl_2–MeOH and several precipitations from a mixture of CH_2Cl_2–acetonitrile. The impurities precipitated, allowing eventual isolation of **3·PF$_6$** from the filtrate as a deep red solid (72.5 mg, 62%).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K). δ (ppm): 9.02 (d, 8 H, ^3J = 5.1 Hz, py$_4$), 9.00 (d, 8 H, ^3J = 5.1 Hz, py$_3$), 8.97 (d, 8 H, ^3J = 5.1 Hz, py$_2$), 8.63 (d, 4 H, ^3J = 8.4 Hz, 3, 8), 8.58 (d, 4 H, ^3J = 8.2 Hz, 4, 7), 8.47 (dd, 4 H, ^3J = 8.4 Hz, ^4J = 1.7 Hz, o), 8.44 (d, 8 H, ^3J = 5.1 Hz, py$_1$), 8.44 (dd, 4 H, ^3J = 8.2 Hz, ^4J = 1.8 Hz, o′), 8.18 (t, 8 H, ^4J = 1.5 Hz, op$_x$′), 8.15 (t, 4 H, ^4J = 1.5 Hz, op$_z$), 8.11 (d, 4 H, ^4J = 1.6 Hz, op$_z$′), 8.10 (dd, 4 H, ^3J = 8.6 Hz, ^4J = 1.4 Hz, m′), 7.93 (t, 4 H, ^4J = 1.8 Hz, pp$_z$), 7.87 (t, 8 H, ^4J = 1.6 Hz, pp$_x$), 7.46 (d, 4 H, ^3J =

8.4 Hz, m), 7.30 (s, 4 H, 5, 6), 1.60 (s, 36 H, $t\mathrm{Bu}_z$), 1.60 (s, 36 H, $t\mathrm{Bu}_z'$), 1.56 (s, 72 H, $t\mathrm{Bu}_x$), 1.53 (s, 72 H, $t\mathrm{Bu}_x'$).

ESI/MS. *m*/*z* 5133.12 [**3**$^+$]; calc. 5132.65 for $C_{296}H_{312}N_{20}CuRh_4I_4$.

UV-vis (toluene). $\lambda_{\max}$ (log ε) = 436 (5.82), 543 (4.94), 580 (4.69) nm.

Compound 5·PF$_6$

A round-bottomed flask was charged with **3·PF$_6$** (46.3 mg, 0.009 mmol) and **4** (5 mg, 0.018 mmol), and de-gassed with three vacuum–argon cycles. The mixture was dissolved in 10 mL of freshly distilled and de-gassed THF. The mixture was then allowed to react for 2 h at room temperature under argon. The solvent was removed under a reduced pressure, the crude product absorbed onto neutral alumina and then purified by column chromatography on silica eluted with a gradient of CH_2Cl_2–MeOH (99.5/0.5 to 95/5) to yield a red solid (4 mg). Part of the product became stuck on the alumina and was desorbed by crushing it and adding CH_2Cl_2. The mixture was filtered and 6 mg of additional product isolated. Finally, **5·PF$_6$** was isolated as a red complex (19%).

^{1}H NMR (300 MHz, CD_2Cl_2, 298 K). δ (ppm): 9.08 (dd, 4 H, ^3J = 8.5 Hz, ^4J = 1.5 Hz, o), 9.06 (d, 8 H, ^4J = 5.1 Hz, py_2), 9.01 (d, 8 H, ^4J = 5.1 Hz, py_4), 8.92 (d, 8 H, ^4J = 4.9 Hz, py_3), 8.89 (d, 8 H, ^4J = 5.1 Hz, py_1), 8.76 (d, 4 H, ^3J = 8.6 Hz, 3, 8), 8.65 (dd, 4 H, ^3J = 8.1 Hz, ^4J = 1.3 Hz, m′), 8.41 (dd, 4 H, ^3J = 8.1 Hz, ^4J = 1.6 Hz, o′), 8.39 (d, 4 H, ^3J = 8.6 Hz, 4, 7), 8.17 (t, 4 H, ^4J = 1.8 Hz, op_z), 8.11 (m, 12 H, $\mathrm{op}_x + \mathrm{op}_z'$), 7.95 (t, 8 H, ^4J = 1.3 Hz, op_x'), 7.91 (t, 4 H, ^4J = 1.5 Hz, pp_z), 7.84 (t, 8 H, ^4J = 1.6 Hz, pp_x), 7.47 (d, 4 H, ^3J = 8.8 Hz, 4′), 7.40 (dd, 4 H, ^3J = 8.1 Hz, ^4J = 1.2 Hz, m), 7.31 (s, 4 H, 5, 6), 7.12 (bs, 4 H, 1′), 6.83 (dd, 4 H, ^3J = 8.6 Hz, ^4J = 1.3 Hz, 3′), 5.59 (d, 8 H, ^3J = 6.6 Hz, m_{py}), 1.60 (s, 72 H, $t\mathrm{Bu}_z$), 1.51 (s, 108 H, $t\mathrm{Bu}_x + t\mathrm{Bu}_z'$), 1.48 (s, 372 H, $t\mathrm{Bu}_x'$), 1.19 (d, 8 H, ^3J = 6.6 Hz, o_{py}).

ESI/MS. *m*/*z* 5697.4 [**5**$^+$]; calc. 5696.9 for $C_{336}H_{340}N_{24}CuRh_4I_4$.

UV-vis (toluene). $\lambda_{\max}$ (log ε) = 434 (5.77), 543 (4.85), 580 (4.57) nm.

Notes and references

1 (*a*) *Perspectives in Supramolecular Chemistry Vol. 5: Transition Metals in Supramolecular Chemistry*, ed. J.-P. Sauvage, John Wiley & Sons, New York, 1999; (*b*) M. Fujita, *Struct. Bonding*, 2000, **96**, 177–202; (*c*) S. Leininger, B. Olenyuk and P. J. Stang, *Chem. Rev.*, 2000, **100**, 853–908; (*d*) I. Bouamaied, T. Coskun and E. Stulz, *Struct. Bonding*, 2006, **121**, 1–47; (*e*) E. Zangrando, M. Casanova and E. Alessio, *Chem. Rev.*, 2008, **108**, 4979–5013.

2 (*a*) A. W. Maverick and F. E. Klavetter, *Inorg. Chem.*, 1984, **23**, 4129–4130; (*b*) A. W. Maverick, S. C. Buckingham, Q. Yao, J. R. Bradbury and G. G. Stanley, *J. Am. Chem. Soc.*, 1986, **108**, 7430–7431; (*c*) M. Fujita, S. Nagao, M. Iida, K. Ogata and K. Ogura, *J. Am. Chem. Soc.*, 1993, **115**, 1574–1576; (*d*) M. Fujita, D. Oguro, M. Miyazawa, H. Oka, K. Yamaguchi and K. Ogura, *Nature*, 1995, **378**, 469; (*e*) C. M. Hartshorn and P. J. Steel, *Inorg. Chem.*, 1996, **35**, 6902–6903; (*f*) A. Marquis-Rigault, A. Dupont-Gervais, P. N. W. Baxter, A. Van Dorsselaer and J.-M. Lehn, *Inorg. Chem.*, 1996, **35**, 2307–2310; (*g*) M. J. Hannon, C. L. Painting and W. Errington, *Chem. Commun.*, 1997, 307–308; (*h*) B. Olenyuk, A. Fechtenkötter and P. J. Stang, *J. Chem. Soc., Dalton Trans.*, 1998, 1707–1728; (*i*) D. M. Bassani, J.-M. Lehn, K. Fromm and D. Fenske, *Angew. Chem., Int. Ed.*, 1998, **37**, 2364–2367; (*j*) B. Olenyuk, J. A. Whiteford, A. Fechtenkötter and P. J. Stang, *Nature*, 1999, **398**, 796–799; (*k*) S. Leininger, J. Fan, M. Schmitz and P. J. Stang, *Proc. Natl. Acad. Sci. U. S. A.*, 2000, **97**, 1380–1384; (*l*) K. Umemoto, K. Yamaguchi and M. Fujita, *J. Am. Chem. Soc.*, 2000, **122**, 7150–7151; (*m*) M. Barboiu, G. Vaughan, R. Graff and J.-M. Lehn, *J. Am. Chem. Soc.*, 2003, **125**, 10257–10265; (*n*) M. Tominaga, K. Suzuki, M. Kawano, T. Kusukawa, T. Ozeki, S. Sakamoto, K. Yamaguchi and M. Fujita, *Angew. Chem., Int. Ed.*, 2004, **43**, 5621–5625; (*o*) B. H. Northrop, H.-B. Yang and P. J. Stang, *Chem. Commun.*, 2008, 5896–5908; (*p*) K. Suzuki, M. Tominaga, M. Kawano and M. Fujita, *Chem. Commun.*, 2009, 1638–1640.

3 (*a*) M. Fujita, F. Ibukuro, H. Hagihara and K. Ogura, *Nature*, 1994, **367**, 720–723; (*b*) A. Hori, K. Kumazawa, T. Kusukawa, D. K. Chand, M. Fujita, S. Sakamoto and K. Yamaguchi, *Chem.–Eur. J.*, 2001, **7**, 4142–4149; (*c*) A. Hori, H. Kataoka, T. Okano, S. Sakamoto, K. Yamaguchi and M. Fujita, *Chem. Commun.*, 2003, 182–183; (*d*) A. Hori, T. Sawada, K. Yamashita and M. Fujita, *Angew. Chem., Int. Ed.*, 2005, **44**, 4896–4899; (*e*) K. Yamashita, M. Kawano and M. Fujita, *J. Am. Chem. Soc.*, 2007, **129**, 1850–1851; (*f*) K. Yamashita, K. Sato, M. Kawano and M. Fujita, *New J. Chem.*, 2009, **33**, 264–270.

4 (*a*) F. Ibukuro, M. Fujita, K. Yamaguchi and J.-P. Sauvage, *J. Am. Chem. Soc.*, 1999, **121**, 11014–11015; (*b*) C. O. Dietrich-Buchecker, N. Geum, A. Hori, M. Fujita, S. Sakamoto, K. Yamaguchi and J.-P. Sauvage, *Chem. Commun.*, 2001, 1182–1183; (*c*) C. O. Dietrich-Buchecker, B. Colasson, M. Fujita, A. Hori, N. Geum, S. Sakamoto, K. Yamaguchi and J.-P. Sauvage, *J. Am. Chem. Soc.*, 2003, **125**, 5717–5725.

5 (*a*) L. Flamigni, V. Heitz and J.-P. Sauvage, *Struct. Bonding*, 2006, **121**, 217–261; (*b*) A. B. C. Deutman, C. Monnereau, J. A. A. W. Elemans, G. Ercolani, R. J. M. Nolte and A. E. Rowan, *Science*, 2008, **322**, 1668–1671; (*c*) J.-P. Sauvage, J.-P. Collin, J. A. Faiz, J. Frey, V. Heitz and C. Tock, *J. Porphyrins Phthalocyanines*, 2008, **12**, 881–905; (*d*) J. A. Faiz, V. Heitz and J.-P. Sauvage, *Chem. Soc. Rev.*, 2009, **38**, 422–442.

6 (*a*) K. Chichak, M. C. Walsh and N. R. Branda, *Chem. Commun.*, 2000, 847–848; (*b*) M. J. Gunter, N. Bampos, K. D. Johnstone and J. K. M. Sanders, *New J. Chem.*, 2001, **25**, 166–173; (*c*) C. A. Hunter, C. M. R. Low, M. J. Packer, S. E. Spey, J. G. Vinter, M. O. Vysotsky and C. Zonta, *Angew. Chem., Int. Ed.*, 2001, **40**, 2678–2682; (*d*) K. D. Johnstone, N. Bampos, J. K. M. Sanders and M. J. Gunter, *Chem. Commun.*, 2003, 1396–1397; (*e*) D. I. Schuster, K. Li, D. M. Guldi and J. Ramey, *Org. Lett.*, 2004, **6**, 1919–1922; (*f*) J. Wu, F. Fang, W.-Y. Lu, J.-L. Hou, C. Li, X.-K. Jiang, Z.-T. Li and Y.-H. Yu, *J. Org. Chem.*, 2007, **72**, 2897–2905; (*g*) M. J. Gunter and K. M. Mullen, *Inorg. Chem.*, 2007, **46**, 4876–4886; (*h*) K. M. Mullen and M. J. Gunter, *J. Org. Chem.*, 2008, **73**, 3336–3350.

7 (*a*) H. J. Callot, F. Metz and C. Piechoki, *Tetrahedron*, 1982, **38**, 2365–2369; (*b*) J. L. Maxwell, K. C. Brown, D. W. Bartley and T. Kodadek, *Science*, 1992, **256**, 1544–1547; (*c*) S. O'Malley and T. Kodadek, *Organometallics*, 1992, **11**, 2299–2302.

8 Y. Aoyama, Y. Tanaka, T. Yoshida, H. Toi and H. Ogoshi, *J. Organomet. Chem.*, 1987, **329**, 251–266.

9 (*a*) H. J. Callot and F. Metz, *Tetrahedron Lett.*, 1982, **23**, 4321–4324; (*b*) Y. Aoyama, T. Yoshida, K. Sakurai and H. Ogoshi, *J. Chem. Soc., Chem. Commun.*, 1983, 478–479; (*c*) H. J. Callot and F. Metz, *Nouv. J. Chim.*, 1985, **9**, 167–171.

10 Y. Aoyama, T. Watanabe, H. Onda and H. Ogoshi, *Tetrahedron Lett.*, 1983, **24**, 1183–1186.

11 Y. Aoyama, T. Fujisawa, T. Watanabe, H. Toi and H. Ogoshi, *J. Am. Chem. Soc.*, 1986, **108**, 943–947.

12 Y. Aoyama, Y. Tanaka, T. Fujisawa, T. Watanabe, H. Toi and H. Ogoshi, *J. Org. Chem.*, 1987, **52**, 2555–2559.

13 (*a*) C. O. Dietrich-Buchecker, P. A. Marnot, J.-P. Sauvage, J. R. Kirchhoff and D. R. McMillin, *J. Chem. Soc., Chem. Commun.*, 1983, 513–515; (*b*) C. O. Dietrich-Buchecker,

P. A. Marnot, J.-P. Sauvage, J.-P. Kintzinger and P. Maltesse, *Nouv. J. Chim.*, 1984, **8**, 573–582; (*c*) A. K. I. Gushurst, D. R. McMillin, C. O. Dietrich-Buchecker and J.-P. Sauvage, *Inorg. Chem.*, 1989, **28**, 4070–4072.

14 (*a*) M. Beyler, V. Heitz and J.-P. Sauvage, *Chem. Commun.*, 2008, 5396–5398; (*b*) M. Beyler, V. Heitz and J.-P. Sauvage, *J. Am. Chem. Soc.*, 2010, **132**, 4409–4417.

15 A. M. Abeysekera, R. Grigg, J. Trocha-Grimshaw and V. Viswanatha, *J. Chem. Soc., Perkin Trans. 1*, 1977, 1395–1403.

16 H.-J. Kim, J. E. Redman, M. Nakash, N. Feeder, S. J. Teat and J. K. M. Sanders, *Inorg. Chem.*, 1999, **38**, 5178–5183.

17 S. S. Eaton and G. R. Eaton, *J. Am. Chem. Soc.*, 1977, **99**, 6594–6599.

18 (*a*) N. C. Thomas, *Transition Met. Chem.*, 1986, **11**, 425; (*b*) Y. H. Liu, J. E. Anderson and K. M. Kadish, *Inorg. Chem.*, 1988, **27**, 2320–2325.

19 M. Beyler, C. Beemelmanns, V. Heitz and J.-P. Sauvage, *Eur. J. Org. Chem.*, 2009, 2801–2805.