

Self-assembly of a bis-porphyrinic supramolecular rectangle using two orthogonal binding strategies†

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A bis-porphyrinic rectangle is created *via* a double self-assembly algorithm using two orthogonal coordination themes, *i.e.* first a 90° building block composed of a dynamic heteroleptic Cu(I) or Ag(I) bisphenanthroline followed by a coordinative dimerization using the pyridine–zinc porphyrin motif; the spectroscopic and electrochemical properties as well as the dynamic nature of the supramolecule were tested.

Self-assembly, at its very best, involves the spontaneous and thermodynamically controlled formation of a single, well-defined, discrete supramolecular entity from a collection of components.^{1,2} Emplacement of double or multiple binding modes in dynamic self-assembly processes, although desirable, is not readily to hand.³ While the majority of known supramolecular structures to date are restricted to a single binding algorithm,² those that do utilise double or multiple binding interactions resort to multistep processes for introduction of diverse binding modes.⁴ Especially, in the case of metal based supramolecular grids, squares and rectangles, cases illustrating the use of two different dynamic metal coordination interactions are sparse. Even so, a one-pot approach seems to have little precedent other than the example of Lehn *et al.*⁵

A dynamic, hence thermodynamically controlled one-pot approach using a double binding algorithm is only feasible if the constituent binding interactions are pre-programmed to follow a non-interfering and self-contained pathway, thus ensuring the desired disposition of the metal ions in the final assembly. Consequently, compatibility and orthogonality of the metal-interactions are the most important factors to consider. We have, therefore, carried out several detailed metal and ligand exchange studies on dynamic heteroleptic bisphenanthroline assemblies.⁶

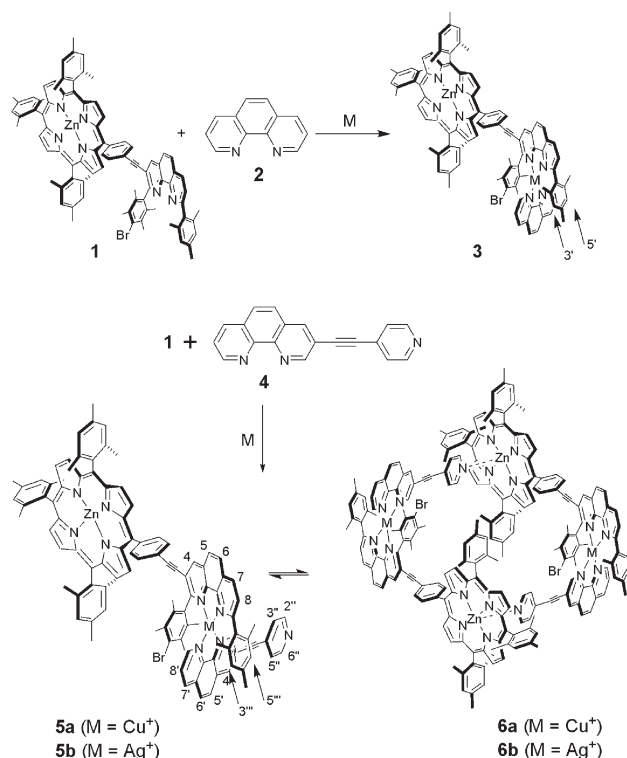
In the present communication we report on our success in generating dynamic heterometallic rectangles based on a dual binding algorithm allowing the use of a facile one-pot self-assembling process.

Our strategy towards a dynamic supramolecular heterometallic rectangle is based on two well-established binding motifs: (a) the Cu(I) or Ag(I) based heteroleptic complexation of modified 1,10-phenanthrolines as developed recently;⁷ and (b) the zinc(II) porphyrin–pyridine coordination. While other metal porphyrins, *e.g.* Ru(II)CO porphyrins, also strongly bind to nitrogen ligands,⁸ the Zn(II) counterparts are much more labile, thus enabling

formation of supramolecular structures under thermodynamic equilibration.⁹

The phenanthroline linked porphyrin **1** (Scheme 1) was synthesised by the Sonogashira method as based on an earlier report.^{6d} Ligand **4** was prepared readily in 48% yield using 3-ethynyl phenanthroline and 4-bromopyridine, again by a Sonogashira cross-coupling. Copper(I) mediated complexation of **1** with 1,10-phenanthroline afforded the heteroleptic complex **3** as an exclusive product in quantitative yield (detected by ESI-MS and ¹H NMR). A characteristic upfield shift to δ 6.06 ppm is noticed for the 3',5'-mesitylene protons (3',5'-MesH) of **1** due to the shielding from the second phenanthroline π system.

Ligand **4**, when combined with **1** and Cu(I) in dichloromethane, immediately furnished a deep red-coloured solution. In the ¹H NMR spectrum of **5a/6a** most peaks are shifted 0.1 ppm upfield compared to those of complex **3** (Fig. 1). Moreover, the ¹H NMR displayed a characteristic upfield shift of the signals corresponding to the 3''',5'''-mesitylene protons (3''',5'''-MesH). However, as against a single signal noticed for the enantiotopic 3',5'-MesH



Scheme 1 The bis-porphyrinic supramolecular assembly **6a,b** with the two orthogonal binding modes highlighted.

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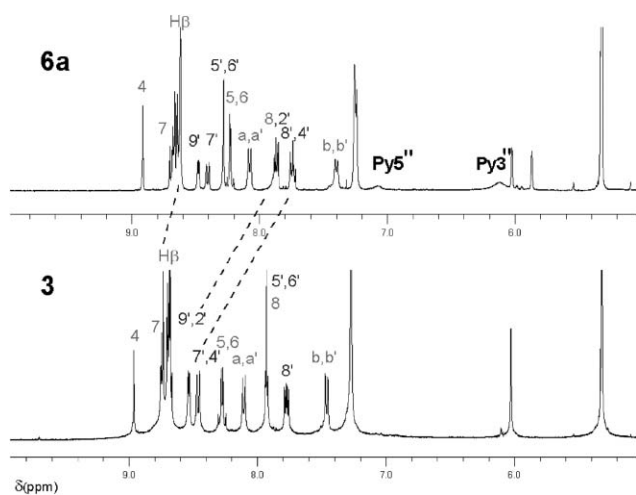


Fig. 1 Comparison of the aromatic region in the ^1H NMR of complexes **5a/6a** and **3** measured in CD_2Cl_2 .

protons of complex **3**, complex **5a/6a** exhibited two sets at δ 6.06 ppm and δ 5.89 ppm, due to the non-equivalence of the mesitylene protons. The two sharp doublets of the pyridyl protons Py5'' and Py3'' in **4** at δ 7.48 ppm and δ 8.64 ppm are drastically shifted upfield in **5a/6a** and appear as two broad singlets at δ 7.07 and 6.12. Such shifts are characteristic of pyridyl protons bound to zinc porphyrin.¹⁰ A H–H COSY revealed that the 2' and 4' protons of residue **4** in **5a/6a** also experience shielding from the π system of the porphyrin leading to their upfield shift from 8.44 and 8.52 ppm to 7.76 and 7.88 ppm, respectively. Hence, NMR evidence strongly supports the formation of **6a**. \ddagger

The ESI-MS of **5a/6a** showed a signal of 100% intensity at m/z 1681 corresponding to the molecular weight of **5a**. Also visible, however, is a signal at m/z 3397 (100%) corresponding to **6a** + Cl^- . The isotopic splitting of the signal at 1681 was dominated by the signals of a monocation, while the isotopic splitting for the dication could not be isolated due to the limits of the instrument.

To achieve further proof of the identity of the proposed rectangle **6a** formed through axial interaction of the pyridyl unit with the Zn(II) porphyrin in **5a**, NMR diffusion-ordered spectroscopy (DOSY) experiments were performed (Fig. 2).¹¹ This technique allows diffusion coefficients to be correlated with molecular composition by observing chemical shifts.

DOSY experiments were performed in CD_2Cl_2 for the complexes **3** and **5a/6a**. \S One single diffusion coefficient ($7.0 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) was found for **5a/6a**, indicative of a single species

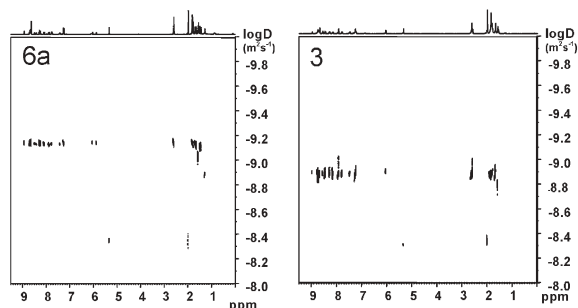


Fig. 2 DOSY plots of **6a** (left) and **3** (right) in CD_2Cl_2 at 298 K plotted for log D showing a marked difference in the diffusion coefficients.

present in solution. The finding that the diffusion coefficient measured for the complex **5a/6a** is much lower than that measured for **3** ($12.2 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$) suggests that **5a** exists in CD_2Cl_2 as the supramolecular dimer **6a**. In the case of negligible association, the diffusion coefficient of **6a** would have remained similar to that of **3**. As it is reasonable to assume similar viscosities in both solutions, one can additionally estimate the hydrodynamic radius r from the diffusion coefficients by the equation $D_x/D_y = r_y/r_x$. Accordingly, r_{6a} , the hydrodynamic radius of **6a** is $1.74 \times r_3$.¹² This value is within the range expected for **6a** vs. **3**.

Formation of an analogous complex was also observed with AgPF_6 in dichloromethane affording **6b**. The diffusion coefficient was measured to be $6.1 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ also confirming that **5b** exists as its dimer **6b**.

Metal exchange makes it possible to interrogate the dynamic nature of the supramolecular rectangles. When $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ was added to **6b**, the rectangle fully exchanged Ag^+ to Cu^+ affording **6a** within a few minutes of mixing as seen from the ESI-MS data. In contrast, when rectangles **6a** and **6b** were mixed together in a 1 : 1 ratio, no exchange of metal ions was noticed after 24 hours. Hence, although the rectangles exist in dynamic equilibrium, they do not show any ‘‘cross talk’’.

The thermodynamic driving force of the formation of rectangle **6a** was probed by UV–vis titrations in CH_2Cl_2 at 25 $^\circ\text{C}$. \P Titration of **4** against **1** provided an association constant of $4.4 \times 10^3 \text{ M}^{-1}$ ($\log K_{(1+4)} = 3.6 \pm 0.6$) in agreement with known binding constants of pyridine derivatives with zinc porphyrin.⁹ⁱ The association constant of complex **6a** was determined to be $2.3 \times 10^{21} \text{ M}^{-2}$ ($\log K_{6a} = 21.3 \pm 0.3$) (Table 1).

The global association constant for formation of **3** is thus $\log \beta_3 = \log K_{(1+\text{Cu})} + \log K_3 = 9.7$. The formation constant for **6a** would be $\log \beta_{6a} = 21.3 + (2 \times 3.6) = 28.5$. From the individual constants, $\log \beta_{6a}$ can be calculated as $2(\log \beta_3 + \log K_{(1+4)}) = 26.7$. Thus a small cooperative effect is noticed in the formation of **6a**. Using $\log \beta_{6a} = 28.5$ makes it possible to estimate $K_{(1+\text{Cu}^+)+4} = 19.1$ by a thermochemical cycle calculation (Fig. 3). This value may

Table 1 Binding constants for the various equilibrium processes involved in the dynamic rectangle

Reaction	$\log K (\text{M}^{-1})$
$1 + \text{Cu}^+ \rightleftharpoons (1 + \text{Cu}^+)$	4.7 ± 0.2
$(1 + \text{Cu}^+) + 2 \rightleftharpoons 3$	5.0 ± 0.3
$1 + 4 \rightleftharpoons (1 + 4)$	3.6 ± 0.6
$2(1+4) + 2\text{Cu}^+ \rightleftharpoons 6a$	21.3 ± 0.3

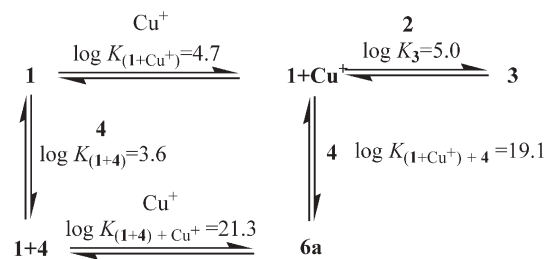


Fig. 3 Association constants of individual complexation steps leading to **3** and **6a**, as determined experimentally, except for $\log K_{(1+\text{Cu}^+)+4} = 19.1$ (obtained from a thermochemical cycle calculation).

Table 2 Redox potentials $E_{1/2}^a$ of **3** and **6a**

	$E_{1/2}/V^a$ (oxidation)		$E_{1/2}/V^a$ (reduction)
	Cu ⁺ /Cu ²⁺	Por/Por ²⁺	
3	0.70	1.14, $E_{pa} = 1.21$	-1.15
3 + py ^b	0.64		
6a	0.64	$E_{pa} = 1.47^c$	-1.11
6a + py ^d	0.63		

^a $E_{1/2}$ vs. SCE in CH₂Cl₂ with *n*-Bu₄NPF₆ (0.1 M); scan rate 100 mV.

^b Addition of 1 equiv. of pyridine. ^c Irreversible wave. ^d Addition of 2 equiv. of pyridine.

be compared to $2 \times (\log K_{(1+4)} + \log K_3) = 17.2$, again hinting at a small cooperative effect.

Electroanalytical studies of **6a** showed a marked difference in the redox potentials as against those of **3**. An anodic shift in the oxidation and reduction potentials of the porphyrin unit of **6a** was noticed which arises due to coordination of the pyridine to the zinc metal in the centre of the porphyrin (Table 2). In addition, a cathodic shift in the oxidation potential of the Cu(I) complex was noticed. Control experiments with **3** and **6a** in the presence of pyridine clearly indicated that the shift of the Cu(I)/Cu(II) wave in **6a** vs. **3** cannot be ascribed to a supramolecular effect, but that it is due to the electronic influence of the pyridine–Zn binding on the remote copper complex. Hence, the electroanalytical data confirm that **5a/6a** exists as a dimer with pentacoordinated Zn centres.

In conclusion, we have demonstrated that by appropriate choice of two non-interfering binding algorithms dynamic supramolecular heterometallic rectangles can be constructed. The dynamics of these assemblies was established by metal exchange experiments. The spectroscopically determined complexation constants suggest that the two binding modes in the rectangle exhibit a cooperative influence in the formation of the complex.

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Notes and references

‡ ¹H NMR experiments were carried out on 2 mM solutions of the samples. With the binding constants being in the order of 10²⁰ it is expected that the concentration range makes it possible to maintain a 99% yield of the supramolecular squares.^{9b}

§ Diffusion experiments were performed on the Bruker Avance 400 MHz NMR spectrometer, with a 5 mm BBI probe head, equipped with a pulsed field gradient unit capable of producing magnetic field gradients in the z-direction of about 5.35 G cm⁻¹. All experiments were carried out at 298 K in a 5 mm NMR tube at 2 mM concentration. The bipolar magnetic field pulse gradients (δ) were of 2.5–4.5 ms duration, and the diffusion time (Δ) was 50 ms. The pulse gradients were incremented from 0.10 to 5.08 G cm⁻¹ in 32 steps. Signals were averaged over 30–45 scans. In each experiment the peaks were analyzed using an inbuilt intensity fit function “simfit” which utilizes the formula

$$I = I_0 \exp[D(-\gamma^2 G^2 \delta^2)(\Delta - \delta/3)]$$

where γ is the gyromagnetic radius (rad s⁻¹ G⁻¹), δ = length of the diffusion gradients (G cm⁻¹) and Δ = time of separation between the gradients, G is the pulsed gradient strength and D = diffusion coefficient.

¶ UV–vis titrations were carried out by addition of a 1 mM solution of the titrant (either Cu(I) or **4**) at 298 K in CH₂Cl₂ to a 10 μ M solution of the other constituent(s) by a micro liter syringe. UV–vis titrations were analyzed by fitting the whole series of spectra at 0.5 nm intervals using the software SPECFIT.

- (a) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, VCH, Weinheim, 1995; (b) J. W. Steed and J. L. Atwood, *Supramolecular Chemistry*, Wiley, Chichester, 2000; (c) *Encyclopedia of Supramolecular Chemistry*, ed. J. L. Atwood and J. W. Steed, Marcel Dekker Ltd., New York, 2004.
- M. Schmittel and V. Kalsani, *Top. Curr. Chem.*, 2005, **245**, 1 and references therein.
- Attempts towards a bi-metallic grid led to two exclusive grids: M. Barboiu, E. Petit, A. van der Lee and G. Vaughan, *Inorg. Chem.*, 2006, **45**, 484.
- (a) D. M. Bassani, J.-M. Lehn, S. Serroni, F. Puntoriero and S. Campagna, *Chem.–Eur. J.*, 2003, **9**, 5936; (b) L. H. Uppadine and J.-M. Lehn, *Angew. Chem., Int. Ed.*, 2004, **43**, 240; (c) L. H. Uppadine, J.-P. Gisselbrecht, N. Kyritsakas, K. Näntinen, K. Rissanen and J.-M. Lehn, *Chem.–Eur. J.*, 2005, **11**, 2549.
- A. Petitjean, N. Kyritsakas and J.-M. Lehn, *Chem. Commun.*, 2004, **24**, 1168.
- (a) M. Schmittel, A. Ganz and D. Fenske, *Org. Lett.*, 2002, **4**, 2289; (b) M. Schmittel, H. Ammon, V. Kalsani, A. Wiegrefe and C. Michel, *Chem. Commun.*, 2002, **22**, 2566; (c) M. Schmittel, V. Kalsani and A. Wiegrefe, *Chem. Commun.*, 2004, **24**, 490; (d) M. Schmittel and R. S. K. Kishore, *Org. Lett.*, 2004, **6**, 1923; (e) V. Kalsani, H. Ammon, F. Jäckel, J. P. Rabe and M. Schmittel, *Chem.–Eur. J.*, 2004, **10**, 5481; (f) V. Kalsani, H. Bodenstedt, D. Fenske and M. Schmittel, *Eur. J. Inorg. Chem.*, 2005, 1841; (g) M. Schmittel, V. Kalsani and J. W. Bats, *Inorg. Chem.*, 2005, **44**, 4115; (h) M. Schmittel, V. Kalsani, R. S. K. Kishore, H. Cölfen and J. W. Bats, *J. Am. Chem. Soc.*, 2005, **127**, 11544.
- The concept of HETereoleptic PHENanthroline complexation (represented by an acronym HETPHEN): (a) M. Schmittel and A. Ganz, *Chem. Commun.*, 1997, 99; (b) M. Schmittel, U. Lüning, M. Meder, A. Ganz, C. Michel and M. Herderich, *Heterocycl. Commun.*, 1997, **3**, 493.
- (a) K. Funatsu, A. Kimura, T. Imamura, A. Ichimura and Y. Sasaki, *Inorg. Chem.*, 1997, **36**, 1625; (b) K. Funatsu, A. Kimura, T. Imamura, A. Ichimura and Y. Sasaki, *Inorg. Chem.*, 1998, **37**, 1798; (c) E. Alessio, S. Geremia, S. Mestroni, E. Iengo, I. Srnova and M. Slouf, *Inorg. Chem.*, 1999, **38**, 869; (d) E. Alessio, S. Geremia, S. Mestroni, I. Srnova, M. Slouf, T. Gianferrara and A. Prodi, *Inorg. Chem.*, 1999, **38**, 2527; (e) K. Campbell, R. McDonald, N. R. Branda and R. R. Tykwinski, *Org. Lett.*, 2001, **3**, 1045; (f) M. J. Gunter, N. Bampos, K. D. Johnstone and K. M. Sanders, *New J. Chem.*, 2001, **25**, 166; (g) E. Iengo, E. Zangrando, S. Mestroni, G. Fronzoni, M. Stener and E. Alessio, *J. Chem. Soc., Dalton Trans.*, 2001, 1338.
- (a) X. Chi, A. J. Guerin, R. A. Haycock, C. A. Hunter and L. D. Sarson, *J. Chem. Soc., Chem. Commun.*, 1995, 2567; (b) C. A. Hunter and R. K. Hyde, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1936; (c) F. Würthner, A. Sautter and C. Thalacker, *Angew. Chem., Int. Ed.*, 2000, **39**, 1243; (d) G. Ercolani, M. Ioele and D. Monti, *New J. Chem.*, 2001, **25**, 783; (e) T. S. Balaban, R. Goddard, M. Linke-Schaetzel and J.-M. Lehn, *J. Am. Chem. Soc.*, 2003, **125**, 4233; (f) C.-C. You and F. Würthner, *Org. Lett.*, 2004, **6**, 2401; (g) P. Ballester, A. Costa, P. M. Deya, A. Frontera, R. M. Gomila, A. I. Oliva, J. K. M. Sanders and C. A. Hunter, *J. Org. Chem.*, 2005, **70**, 6616; (h) A. Satake and Y. Kobuke, *Tetrahedron*, 2005, **61**, 13; (i) Y. Kobuke, *Eur. J. Inorg. Chem.*, 2006, **12**, 2333.
- (a) A. Tsuda, T. Nakamura, S. Sakamoto, K. Yamaguchi and A. Osuka, *Angew. Chem., Int. Ed.*, 2002, **41**, 2817; (b) E. Iengo, E. Zangrando, S. Geremia, R. Graff, B. Kieffer and E. Alessio, *Chem.–Eur. J.*, 2002, **8**, 4670.
- (a) W. S. Price, *Concepts Magn. Reson.*, 1997, **9**, 299; (b) W. S. Price, *Concepts Magn. Reson.*, 1998, **10**, 197; (c) For a recent review on the use of DOSY experiments in supramolecular chemistry, see: Y. Cohen, L. Avram and L. Frish, *Angew. Chem., Int. Ed.*, 2005, **44**, 520.
- M. S. Kaucher, Y.-F. Lam, S. Pieraccini, G. Gottarelli and J. T. Davis, *Chem.–Eur. J.*, 2005, **11**, 164.