In future studies we shall study other frondosins with a view to total synthesis, determination of absolute configuration, and biological evaluation.

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Self-Assembled Porphyrin Polymers**

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Supramolecular chemistry offers an attractive strategy for the construction of functional and responsive polymeric architectures.[1] Thermodynamically reversible noncovalent interactions such as hydrogen bonds and metal-ion coordination can be used to induce the self-assembly of suitably functionalized monomers into polymeric structures.[2, 3] However, the degree of polymerisation in such systems, N, depends critically on the stability constant of the monomer–monomer interaction, K:[3, 4]

$$N \approx (K\,[\text{monomer}])^{1/2} \qquad (1)$$

Most studies of supramolecular polymer systems have been limited to the solid or liquid-crystalline states, where the value of [monomer] is maximized and the requirement for a strong monomer–monomer interaction is relaxed.[2] However, if K is sufficiently large, it is possible to generate very high molecular weight polymers in solution.[3] These systems have all the physical properties of covalently bound polymers, but in addition are sensitive to both changes in environmental conditions and the presence of small molecules which alter the stability of the monomer–monomer interactions, and hence the degree of polymerisation may be changed in a reversible manner.[1]

We have previously used the coordination of zinc porphyrins by pyridine ligands to assemble small cyclic oligomers.[5] Thus, zinc porphyrins, covalently linked to an appropriate pyridine side arm, form macrocyclic dimers with stability constants in the range $K = 10^6 - 10^8\,\text{M}^{-1}$ in chloroform (Figure 1 a). These systems represent ideal building blocks for the formation of supramolecular polymers: Equation (1) predicts a degree of polymerisation of the order of $N = 10$ to 100 at millimolar monomer concentrations. Here, we show that this self-assembly strategy can indeed be used to generate soluble, high molecular weight porphyrin polymers. The rich photo- and electrochemical properties of the monomeric units make such polymers interesting from the point of view of charge storage and transport, solar energy conversion, and nonlinear optics.[6]

Figure 1 illustrates the approach. Changing the metal from zinc, which is five coordinate in a porphyrin, to cobalt, which is six coordinate, increases the number of vacant ligand binding sites from one to two,[7] and attachment of a second pyridine side arm yields a monomer with two identical

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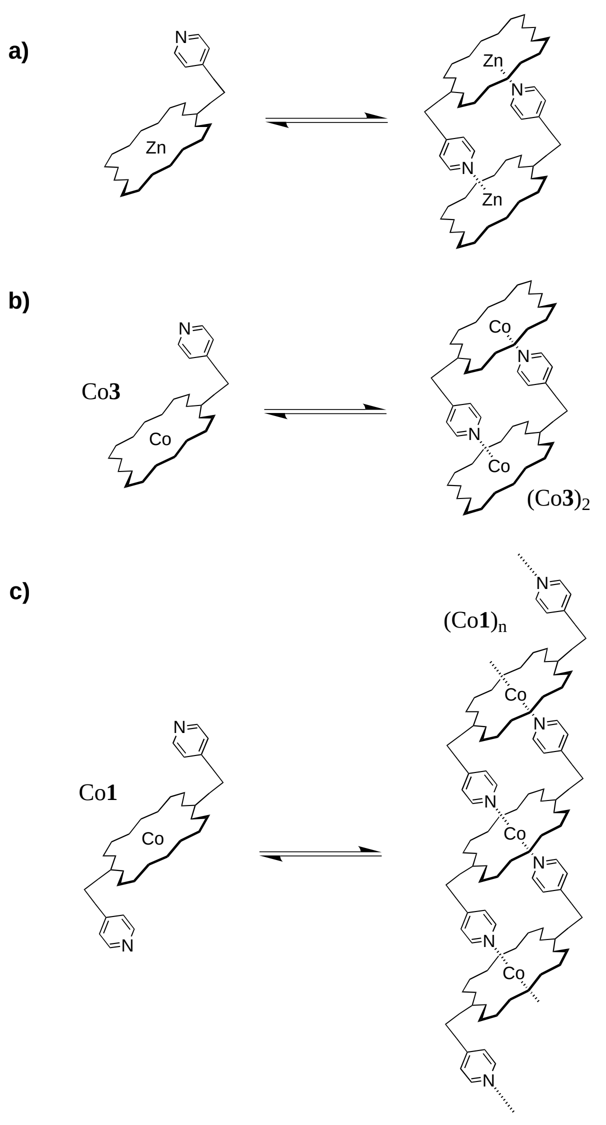
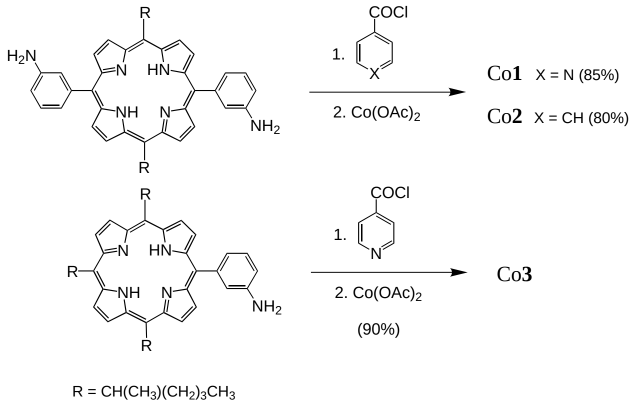


Figure 1. a) Self-assembly of a zinc porphyrin dimer via coordination of a covalently attached pyridine ligand. b) Self-assembly of a cobalt porphyrin dimer via coordination of a covalently attached pyridine ligand. This leaves a vacant ligand binding site on the six-coordinate cobalt center. c) Self-assembly of a cobalt porphyrin polymer via coordination of two covalently attached pyridine ligands, one on each face of the porphyrin.

dimerisation sites on the two faces of the porphyrin. This bifunctional analogue should polymerize through the same monomer–monomer interaction found in the zinc system (Figure 1c).

The synthesis of a suitable monomer for supramolecular polymerisation, Co**1**, is shown in Scheme 1.[8] In addition, we prepared two control compounds: Co**2** which is not capable of self-assembly, because both pyridine ligands have been replaced by noncoordinating phenyl groups, and Co**3** which can only assemble to give dimers, because it carries one pyridine ligand rather than two (Scheme 1). The incorporation of 2-ethylhexyl side chains was essential to ensure good solubility in organic solvents. Since cobalt(II) porphyrins are paramagnetic,[9] the products were characterized at the free base stage, H_2**1**, H_2**2**, and H_2**3**, and all gave satisfactory spectroscopic data. The metallation reaction of H_2**1** with cobalt acetate was sensitive to concentration: the solubility of Co**1** is much lower than that of the corresponding free base porphyrin H_2**1** and the control compounds Co**2** and Co**3**. At concentrations greater than 10 mM, Co**1** precipitated from the reaction mixture and could only be redissolved in coordinating solvents such as pyridine which is consistent with the polymerisation process illustrated in Figure 1c.



Scheme 1. The required aminoporphyrins were prepared from the corresponding nitroporphyrins using literature procedures.[8]

The UV/Vis absorption spectrum of the monomeric reference porphyrin Co**2** has a Soret band at 415 nm. Addition of pyridine at millimolar concentrations resulted in a red shift of the Soret absorption to 444 nm.[10] The Soret band of both Co**1** and Co**3** is at 440 nm at micromolar porphyrin concentrations.[9] This implies that cooperative self-assembly takes place in these systems giving rise to coordinated cobalt porphyrins at concentrations significantly lower than usually required for cobalt porphyrin–pyridine complexation.

Mass spectrometry, using soft ionization techniques, FAB, electrospray, and MALDI, provided no evidence for self-assembly: the only significant signals were due to the monomer units of Co**1**, Co**2**, and Co**3**. A weak signal corresponding to $(Co\mathbf{3})_2$ was detected, but it is clear that the coordination bonds are not stable under mass spectrometry conditions.[5]

The ^1H NMR spectra of the cobalt porphyrins were difficult to assign, because of the paramagnetic broadening associated with the cobalt(II) center and the complexity of the spectra. However, pulsed-gradient spin-echo (PGSE) NMR diffusion experiments did provide some insight into the relative sizes of the self-assembled complexes.[11] Figure 2 shows the change in

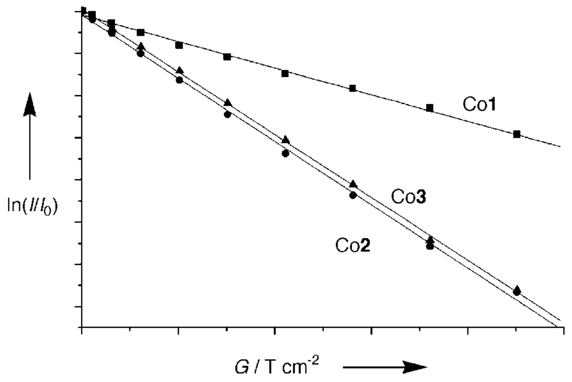


Figure 2. Variation in the intensity of the ^1H NMR signals of the aromatic protons of cobalt porphyrins ($\ln(I/I_0)$) in PGSE experiments, as a function of the field gradient (G). The measurements were carried out on a Bruker AMX-600 using 7 mM porphyrin solutions in chloroform/methanol (10/3).

intensity of the aromatic signals as a function of the field gradient. Clearly the diffusion coefficient of Co**1** is much smaller than that of Co**3** or Co**2**, which suggests that Co**1** forms a high molecular weight polymer (Figure 1 c). Porphyrin Co**3** appears to be marginally larger than the monomeric Co**2** as expected for simple dimerisation (Figure 1 b).

The best method for characterising these self-assembled complexes proved to be size-exclusion chromatography (SEC). The monomeric reference porphyrin Co**2** exhibits a retention time of 16.6 min, while the self-assembled dimer of Co**3** emerges after 15.7 min (Figure 3). For the self-assembled polymer of Co**1**, a single peak was observed, but the retention times ranged from 12 to 15 minutes depending on the concentration of the monomer (Table 1). No peak corresponding to the monomeric reference compound could be detected. This again indicates the formation of stable, high molecular weight polymers of Co**1**.

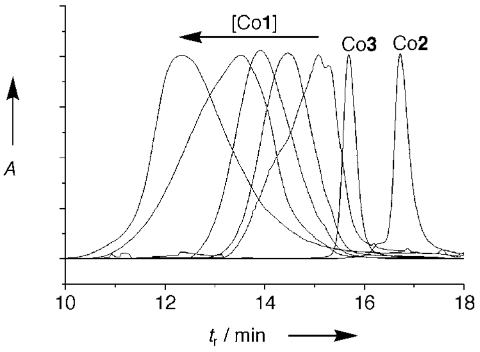


Figure 3. Normalized SEC trace (5 μm mixed-bed column) for Co**1** at various concentrations between 55 and 7000 μM, Co**2** and Co**3** (t_r: retention time; A: absorbance at 440 nm).

The SEC results were calibrated by titrating Co**3** into Co**1**. The monofunctional Co**3** has exactly the same binding site as Co**1** and so acts as a chain stopper, which can be used to control the mean molecular weight of the Co**1** polymer (Figure 4).[3] For the Co**1**/Co**3** mixtures, the length of the polymer decreases with increasing amounts of chain stopper Co**3**, and when the proportion of Co**3** is large, it is possible to assign clearly resolved SEC peaks to dimer, trimer, tetramer, and so forth (Figure 4). The molecular weights of these oligomers follow the expected logarithmic relationship with the retention time, and this calibration curve was used to determine the size of the pure Co**1** polymers (Table 1).

Table 1. Relationship between the concentration of the monomer and the mean molecular weight of the corresponding Co**1** polymers determined by SEC.

[M] [μM]	t_r [min]	M_w [g mol^{-1}]	N
7000	12.4	136000	95
2200	13.5	82500	58
550	13.9	26700	19
275	14.5	23100	16
55	15.1	17600	12

[M] is the monomer concentration, t_r is the SEC peak retention time, M_w is the mean molecular weight, and N is the corresponding degree of polymerisation (calibration based on the chain stopper experiment illustrated in Figure 4).

In pure samples of Co**1**, the degree of polymerization N clearly increases with the concentration of the monomer, as expected from Equation (1): the results in Table 1 give a monomer–monomer association constant of $K = 1.0 \pm 0.5 \times 10^6\,\text{M}^{-1}$. The polydispersity index of the polymers is between 1.5 and 2.5, as expected for an equilibrium polymerisation.[4] A solubility limit is reached at about 10 mM, at which point the longer polymers start to precipitate. Nevertheless, this self-assembly approach can be used to generate soluble porphyrin polymers of about 100 units long with an mean molecular weight of 136 kDa. This is significantly larger than the porphyrin systems obtained from covalent reactions which have only achieved modest degrees of polymerization (N = 10–15).[6c]

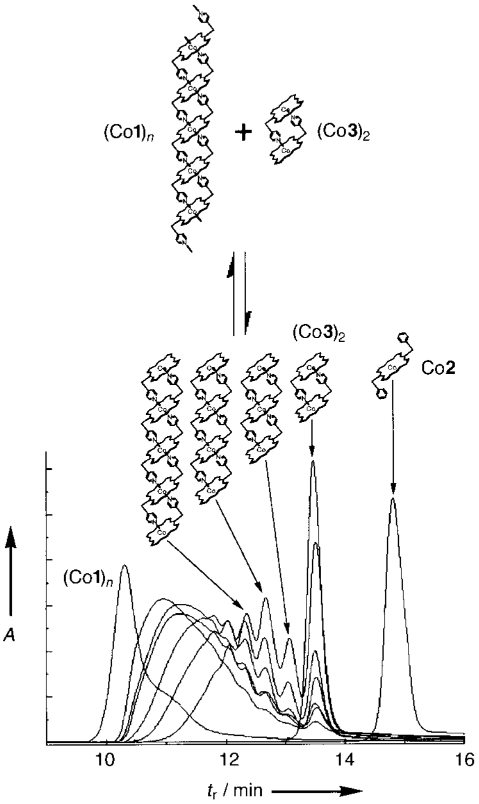


Figure 4. Co**3** acts as a chain stopper for the Co**1** polymers. The SEC traces (two 3 μm mixed-bed columns) for mixtures of Co**1** and Co**3** shift to shorter retention times as the proportion of Co**1** increases. The pure Co**1** polymer lies within the exclusion volume of the column, but this assembly is clearly larger than the mixtures. The trace for the monomeric reference compound Co**2** is included for comparison (t_r: retention time; A: absorbance at 440 nm).

This work demonstrates that it is possible to design large, self-assembling ordered arrays of rigid dye molecules using simple coordination chemistry. A variety of different polymer architectures can be obtained by varying the length and orientation of the pyridine ligand, and this could be used to control the communication between the porphyrin chromophores in the material. Investigations of the photophysical and electrochemical properties of these polymers are in progress.

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[9] Cobalt(II) porphyrins can undergo aerial oxidation to give cobalt(III) complexes, which have higher affinities for ligands and slower exchange kinetics. The NMR and EPR data suggest that cobalt(II) species dominate in this system, but it is not possible to rule out the presence of oxidation products, and the samples do show signs of ageing.

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Dinuclear π Complexes of Yttrium and Lutetium with Sandwiched Naphthalene and Anthracene Ligands: Evidence for Rapid Intramolecular Inter-Ring Rearrangements[**]

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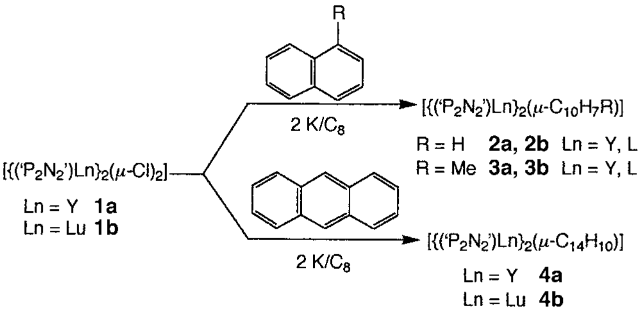
Steven J. Rettig

The coordination of aromatic hydrocarbons to transition metals is of considerable interest in organometallic chemistry not only from the point of view of bonding but also in organic synthesis.[1] In particular, benzene and substituted benzenes coordinated to Cr(CO)_3 have played a central role in this area. Less well developed, but potentially useful, are studies of the coordination of polycyclic arenes such as naphthalene and anthracene to metal atoms.[2–17] These aromatic systems can act as ligands for Group 3 and lanthanide elements, although the intrinsic electropositive nature of the metal ions means the bonding is best described as ionic, with the arene ligands formally carrying considerable negative charge.[4–6, 10, 11, 17, 18] Here we describe some dinuclear yttrium and lutetium complexes of naphthalene and anthracene, for which the solution and solid-state structures can only be correlated by invoking rapid intramolecular inter-ring migration of the metal-complex fragment.

A previous report described the synthesis of $[\{(\text{‘P}_2\text{N}_2\text{’})\text{Y}\}_2(\mu\text{-Cl})_2]$ (**1a**; $\text{‘P}_2\text{N}_2\text{’} = \text{PhP(CH}_2\text{SiMe}_2\text{NSiMe}_2\text{CH}_2)_2\text{PPh}$)[19] and its ability to couple aryl units to generate π-bound bis-arene moieties.[20] Given that yttrium could bind to an arene ligand, we examined the formation of yttrium and lutetium complexes with polycyclic aromatic compounds. The reaction of **1a** with potassium graphite (KC_8) in toluene/diethyl ether (75/25) in the presence of naphthalene generated the dark blue π-naphthalene complex $[\{(\text{‘P}_2\text{N}_2\text{’})\text{Y}\}_2(\mu\text{-C}_{10}\text{H}_8)]$ (**2a**) in moderate yield (Scheme 1). The ^{1}H NMR spectroscopic data show only two sets of coupled resonances for the C_{10}H_8 moiety, which demonstrates that the bridging naphthalene unit is symmetrically bound; in addition, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows equivalent phosphane donors on both yttrium(III) centers. A similar reaction with the lutetium complex **1b** (Scheme 1) produced the dark purple dinuclear naphthalene complex **2b**.



Scheme 1. Syntheses of polyarene complexes of yttrium and lutetium.

The crystal structure[21] of **2a** is shown in Figure 1. Each Y(‘P$_2$N$_2$’) unit binds in an η^4 fashion on the opposite sides of the different rings of the naphthalene unit. The naphthalene moiety is distorted slightly with elongated bond lengths, and the rings have a nonplanar step conformation.

A similar reaction with 1-methylnaphthalene ($\text{MeC}_{10}\text{H}_7$) gave $[\{(\text{‘P}_2\text{N}_2\text{’})\text{Ln}\}_2(\mu\text{-}\eta^4\text{:}\eta^4\text{-MeC}_{10}\text{H}_7)]$ (Ln = Y, **3a**; Ln = Lu, **3b**). The ^{1}H NMR spectrum of **3a** shows signals for the seven inequivalent protons on the naphthalene unit and a singlet for the 1-Me protons. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows equivalent phosphane donors (a doublet at $\delta = 21$, $^1J(\text{Y,P}) = 60$ Hz). The solid-state molecular structure[21] of **3a** is very similar to that of **2a**; the two yttrium ions are bound to opposite faces of the different rings. However, in this case the methyl group is disordered over all four equivalent positions (centrosymmetric). Nevertheless, since the behavior in solution of the

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