A supramolecular array assembled *via* the complementary binding properties of ruthenium(II) and tin(IV) porphyrins

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A new porphyrin trimer has been self-assembled by employing the mutually non-interfering coordination properties of the ruthenium(II) and tin(IV) centers to form a multi-metal array. The photo- and electro-chemical properties of this array are also reported.

Introduction

The recent resurgence in the coordination chemistry of metallo-porphyrins is largely due to the realization that metal–ligand interactions provide a convenient means of constructing functional supramolecular arrays.[1] The range of metals and ligands and also the multitude of interactions between them permit what is otherwise a synthetically cumbersome modulation of the photophysical and electrochemical properties of the resulting supramolecular species.[2] To this end, the well known binding of zinc(II) and ruthenium(II) to nitrogen and that of tin(IV) to oxygen has recently been employed to construct heterometallic porphyrin oligomers.[3] These oligomers were designed to exploit the complementary geometries and cooperative binding properties of the tailor-made metalloporphyrin building blocks. Building on these results we set out to determine if this theme can be 'amplified' to generate self-assembled, axially directed porphyrin arrays without relying on extended and inefficient syntheses of designed host and guest precursors. Our efforts in this direction resulted in the design of a prototype trimeric array **4**, the construction of which relies on the spontaneous self-assembly driven by the independent coordination properties of the ruthenium(II) and tin(IV) centers (Scheme 1). Unlike the case with the previously reported heterometallic porphyrins mentioned above which are characterized by the incorporation of the nitrogen and oxygen donor functionalities into their superstructures, the complementary binding achieved here is by an external, bifunctional ligand leading to the self-assembly of **4**. In addition to describing aspects related to the design, construction and spectral characterization of **4**, we also report the photophysical and electrochemical properties of this novel trimeric array.

Results and discussion

The monomeric precursors employed in this study; the five-coordinated (5,10,15,20-tetrakis(3,5-di-*tert*-butylphenyl) porphyrinato)ruthenium(II) carbonyl, **1** and the six-coordinated (5,10,15,20-tetrakis(4-methylphenyl)porphyrinato)-tin(IV) dihydroxide, **3** porphyrins, were prepared by modification of known procedures.[4] Trimer **4** was constructed by both step-wise and one-pot methods. In the former method, the pyridine-bound ruthenium(II) porphyrin **2** was assembled first with the 'pendant' carboxylic acid functionality being readily available for further coordination. The acid itself is not soluble in the organic solvents in which the porphyrin is soluble but the ruthenium porphyrin coordination to the pyridyl group solubilises the acid and allows us to obtain solutions of known concentration; the reaction reaches completion over a couple of hours. In the second preparation, two equivalents of **2** were reacted with the dihydroxy tin(IV) porphyrin **3** to obtain **4** in essentially quantitative yield. The array was also prepared in one pot by simply mixing **1**, **3** and pyridine-4-carboxylic acid in the appropriate stoichiometry.

Attempts were made to grow single crystals of **2** and **4**. As yet, crystals of **4** suitable for X-ray diffraction have not been isolated, but complex **2** crystallized out in the $P\bar{1}$ space group. The structure of **2** thus obtained clearly shows the H-bonded dimeric nature of the complex with an O–H···O distance of 1.843 Å (Fig. 1). Both the coordinated pyridyl ligand (Ru–N 2.201 Å) and CO [Ru–CO 1.839(4) Å] are near perpendicular to the porphyrin plane. Therefore, self-assembly of array **4** can be supposed to proceed with the breaking of these weak H-bonds prior to the competing Sn–O interaction.

The structure of **4** was probed in solution by ^{1}H NMR spectroscopy. The near perpendicular juxtaposition of the axial pyridine ligand with respect to the plane of the ruthenium porphyrin, as evident in the crystal structure of **2** (dihedral angle approx 90°), is expected to be retained in array **4**. As such, the α and β protons of the bound pyridine in **2** are shielded by the porphyrin ring-current[5] and resonate at 1.76 and 5.79 ppm, respectively (identified by COSY and NOESY experiments). The corresponding resonances in array **4** are seen to be further shifted upfield to 2.67 and 0.50 ppm respectively due to the additional shielding effect exerted by the tin(IV) porphyrin, as expected. Self-assembly of **4** is also accompanied by disappearance of the axial hydroxy proton resonances (−7.49 ppm) of **3**.

The UV/vis spectrum of the trimer is essentially a superposition of the spectra of its constituent components with the molar absorption coefficients at the peak maxima being close to the sum of those of **2** and **3**. This observation, coupled with the fact the λ_{max} values of **4** are also similar to those of **2** and **3**, clearly provides evidence for the absence of any electronic interaction between the porphyrin planes in this array. This is

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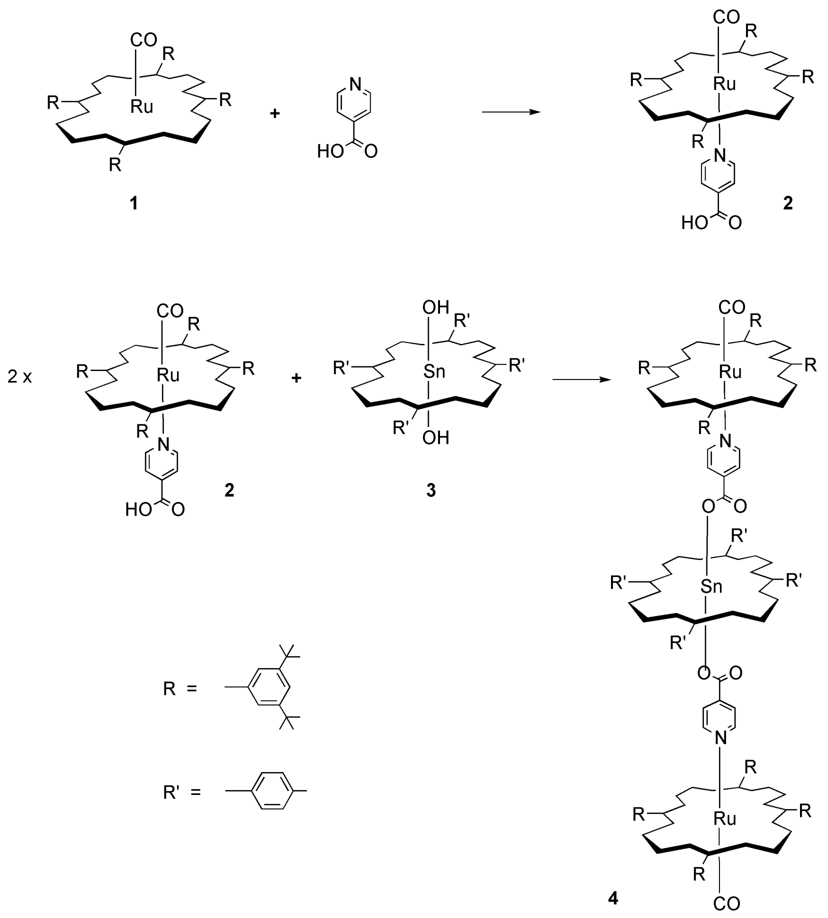

Scheme 1

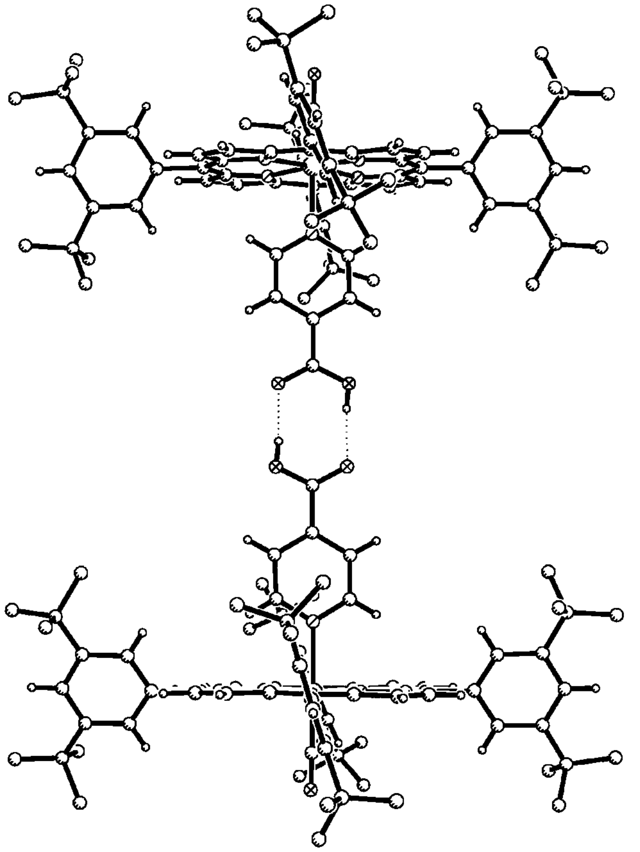

Fig. 1 X-Ray structure of **2** recorded at 180 K. The figure shows the dimer of molecules linked through the hydrogen bonded carboxylate groups. The *t*-butyl groups are disordered over two orientations, only one of which is shown for clarity. Hydrogen atoms have also been omitted from these groups.

not surprising if one considers that the array has ‘axial-bonding’ type architecture[6] and that the coordinated pyridine-acid spacer dictates that the separation distances between the porphyrin planes should be >4 Å (CPK molecular model). Further support for the presence of non-interacting porphyrin monomers in **4** comes from electrochemical experiments. Oxidation and reduction potentials of the trimer, as measured by differential pulse voltammetry (see Experimental), were found to be nearly identical to those of **2** and **3**. In contrast, the excited state properties of the tin(IV) porphyrin component of the array were found to be quite different from that of **3**, while the ruthenium(II) porphyrin component was found to be non-fluorescent, as is the case with the monomeric porphyrins **1** and **2**. The fluorescence quantum yield (ϕ_f) of the tin(IV) porphyrin part of the trimer is only 0.007 ($\lambda_{exc} = 600$ nm where the absorption is almost exclusively due to the tin(IV) porphyrin of the trimer) as against the corresponding reference compound **3** ($\phi_f = 0.024$). Analogously, the fluorescence life-time (τ) of the trimer was found to be 0.63 ± 0.05 ns while that of **3** is 1.48 ± 0.1 ns. This quenching of fluorescence observed for the trimer **4** can be interpreted in terms of a photo-induced electron transfer (PET) from the axial ruthenium(II) porphyrin to the excited state of the basal tin(IV) porphyrin.† Indeed, the free energy change ($\Delta G°$) for such a PET process is exoergic by 0.32 ± 0.04 eV, as estimated from the redox potential data of the trimer and the singlet state energy of the tin(IV) porphyrin (2.04 ± 0.03 eV).

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† Excitation energy transfer (between the two chromophores) and heavy atom effect (due to the ruthenium centre) are the other possible quenching mechanisms but, no direct/indirect evidence has been obtained to show that these processes are operative in this system. In addition, fluorescence of **3** was found to be unquenched in the presence of externally added **1** (2 or >2 mol equivalents).

Conclusion

In summary, a photochemically-functional, axial-bonding type hybrid porphyrin trimer has been assembled by an advantageous utilization of the well-known hard and soft acid–base (HSAB) principle and metal ion recognition by a ditopic ligand. Clearly, this new strategy provides scope for building more elaborate arrays having interesting photochemical functions. Such studies are currently in progress.

Experimental

^{1}H NMR (1D and 2D) spectra were recorded on Bruker DRX-400 or DRX-500 spectrometers respectively in CDCl$_3$. Resonances were referenced relative to residual solvent signals. UV/vis spectra were recorded with either a Uvikon model 810 or a Jasco Model 7800 UV-Visible spectrophotometer using 10 mm oven-dried cuvettes. Concentration of the samples used for these measurements ranged from about 2×10^{-6} M (Soret bands) to 5×10^{-5} M (Q bands). Steady-state fluorescence spectra were recorded using a Jasco Model FP-777 spectrofluorimeter. The emitted quanta were detected at right angles to the incident beam. The utilized concentrations of the fluorophores were such that the optical densities (O.D.) at the excitation wavelengths were always less than 0.2 in CH$_2$Cl$_2$. The fluorescence quantum yields (ϕ_f) were estimated by integrating the areas under the fluorescence curves and by using (5,10,15,20-(tetraphenyl)porphyrinato)zinc(II) ($\phi = 0.036$ in CH$_2$Cl$_2$) as the standard.[7] Fluorescence life times were measured by the time-correlated single photon counting method at the National Centre for Ultrafast Processes (Chennai, India) using their pico-second laser excitation and detection facility. The samples (solvent CH$_2$Cl$_2$) were excited at 440 nm and the emission was monitored at 610 ± 10 nm in each case. The count rates employed ranged typically from 10^3 to 10^4 s^{-1}. The dark count was <40 s^{-1}. Deconvolution of the data was carried out by the method of iterative reconvolution of the instrument response function and the assumed decay function, as described earlier.[8] Differential pulse voltammetric experiments (CH$_2$Cl$_2$ and 0.1 M tetrabutylammonium perchlorate, TBAP) were performed on a Princeton Applied Research (PAR) 174A polarographic analyzer coupled with a PAR 175 universal programmer and a PAR RE 0074 x–y recorder, as detailed in our previous studies.[6] Ferrocene was used to calibrate the potential axis.

Distilled solvents were used throughout and when used dry, were freshly obtained from solvent stills. CH$_2$Cl$_2$ was distilled from CaH$_2$ under argon.

Synthesis

Compound 2. 0.030 g (0.0126 mmol) of **1** was dissolved in 5 ml of CH$_2$Cl$_2$. To this solution, 0.0155 g (0.126 mmol) of pyridine-4-carboxylic acid was added and the resulting mixture was sonicated and then heated at 40 °C for a few minutes. The contents were passed through a pad of Celite and the filtrate was evaporated to give the desired product in quantitative yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 1.47 (s, 36H, *t*-butyl), 1.50 (s, 36H, *t*-butyl), 1.76 (d, 2H, $J = 6.8$ Hz, pyridyl-H$_\alpha$), 5.79 (d, 2H, pyridyl-H$_\beta$), 7.72 (br s, 4H, aryl-H), 7.87 (br s, 4H, aryl-H), 8.02 (br s, 4H, aryl-H), 8.65 (s, 8H, pyrrole-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 31.7 (*t* butyl *C*H$_3$), 34.9 and 35.0 [2 × *t*-butyl *C*(CH$_3$)$_3$], 120.5 (aromatic *C*H), 121.3 (pyridyl *C*$_\beta$), 122.7 (aromatic *C*), 128.8 (aromatic *C*H), 129.7 (aromatic *C*H), 131.9 (β-pyrrole *C*), 141.6 and 143.7 (porphyrin *C*), 145.3 (pyridyl *C*$_\alpha$), 148.2 and 148.5 (aromatic *C*); UV/vis $\lambda_{\max}$ (CH$_2$Cl$_2$)/nm (log[ε/M^{-1} cm^{-1}]) 415 (5.25), 532 (4.25), $E_{1/2}$ (V *vs.* SCE): +0.79, −1.76.

Trimer 4. 0.032 g (0.024 mmol) of complex **2** was dissolved in 5 ml of CH$_2$Cl$_2$. To this, 0.010 g (0.012 mmol) of **3** was added and the resulting solution was sonicated for a few minutes. Evaporation of the solvent first under a steady stream of N$_2$ and then under vacuum gave the desired product in quantitative yield. ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.50 (d, 4H, $J = 6.9$ Hz, pyridyl-H$_\alpha$), 2.67 (d, 4H, pyridyl-H$_\beta$), 1.39 (s, 72H, *t*-butyl), 1.43 (s, 72H, *t*-butyl), 2.62 (s, 12H, tolyl-CH$_3$), 7.32 (d, 8H, $J = 7.9$ Hz, Sn aryl-H), 7.45 (d, 8H, Sn aryl-H), 7.49 (br s, 8H, Ru aryl-H), 7.64 (br s, 8H, Ru aryl-H), 7.83 (br s, 8H, Ru aryl-H), 8.31 (s, 16H, Ru pyrrole-H), 8.64 (s, 18H, Sn pyrrole-H); ^{13}C NMR (100 MHz, CDCl$_3$): δ 21.5 (tolyl *C*H$_3$), 31.6 and 31.7 [2 × *t*-butyl *C*H$_3$], 34.8 and 34.9 [2 × *t*-butyl *C*(CH$_3$)$_3$], 118.6 (pyridyl *C*$_\beta$), 120.2 (Ru aromatic *C*H), 122.1 (Ru aromatic *C*), 127.5 (Sn aromatic *C*H), 127.8 (Sn aromatic *C*), 128.6 and 129.6 (2 × Ru aromatic *C*H), 131.1 (Sn β-pyrrole *C*), 132.9 (Ru β-pyrrole *C*), 134.0 (Sn aromatic *C*H), 137.6 (pyridyl *C*), 137.9 (Sn aromatic *C*), 142.7 (pyridyl *C*$_\beta$), 142.2 (Sn porphyrinic *C*), 146.4 (Ru porphyrinic *C*), 147.9 and 148.3 (Ru aromatic *C*), three unidentified resonances; UV/vis $\lambda_{\max}$ (CH$_2$Cl$_2$)/nm (log[ε/M^{-1} cm^{-1}]): 417 (5.38), 425 (5.37), 532 (4.26), 562 (4.10), 602 (3.92), $E_{1/2}$ (V *vs.* SCE): +0.79, +1.60, −0.93, −1.36, −1.76.

Crystallography

Crystals of **2** were grown by the layered addition of dry hexane onto a dry CDCl$_3$ solution of **2** and data collected on a Nonius Kappa CCD diffractometer: C$_{89}$H$_{111}$N$_5$O$_3$Ru, $0.20 \times 0.15 \times 0.10$ mm, $T = 180(2)$ K, $M = 1399.90$, triclinic, space group $P\bar{1}$, $a = 13.342(2)$, $b = 16.113(2)$, $c = 25.563(2)$ Å, $\alpha = 80.020(10)$, $\beta = 77.700(10)$, $\gamma = 69.650(10)°$, $U = 5004.6(10)$ Å^3, $Z = 2$, $D_c = 0.929$ Mg m^{-3}, $\lambda = 0.71069$ Å, $F(000) = 1496$, $\mu = 0.197$ mm^{-1}, $R_1 = 0.0779$ [15 643 reflections with $I > 2\sigma(I)$], $wR_2 = 0.2352$ for 22 773 independent reflections and 922 parameters.

CCDC reference number 152817. See http://www.rsc.org/suppdata/nj/b0/b010148f/ for crystallographic data in CIF or other electronic format.

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