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# Synthesis, spectral and electrochemical investigations of bichromophoric pentads possessing tetraazaporphyrin and $(bipy)_2Ru^{II}$/$(phen)_2Ru^{II}$ moieties†

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**Four $(bipy)_2Ru^{II}$ and $(phen)_2Ru^{II}$ moieties have been attached to the magnesium tepraazaporphyrin periphery by exploiting thioether coordination to obtain pentads 1 and 2 respectively. These molecules exhibit strong inter-chromophore electronic interaction as reflected by the changes in their spectral and oxidation potential shifts.**

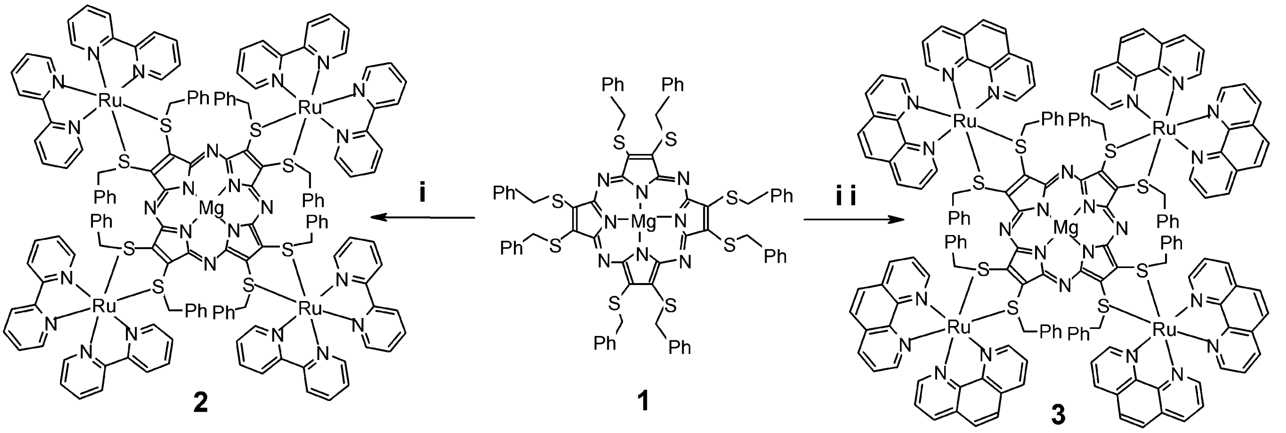
Porphyrinic[1] and porphyrin-metallo-polypyridyl[2,3] hybrid bichromophoric dyads, triads and higher-order arrays are the subject of great interest because of their potential use as novel functional materials for optical and electronic applications[4] and in catalysis.[5] These arrays commonly rely on linkers such as extended alkynes, phenylenes and other condensed ring hydrocarbons possessing terminal polypyridyl groups to place the two chromophores in optimal proximity. Owing to the fact that the electronic communication between components is critically affected by the distance between them, the dependence on linkages often results in a poor degree of electronic interaction between the chromophores. An alternative approach to build bichromophoric arrays exhibiting stronger electronic interactions, involves the attachment of the second chromophore directly onto the β-positions of the porphyrin macrocycle.[6] Because tetraazaporphyrins (TAPs) possess a diverse pool of β-substituents, they are an ideal choice to test the validity of this approach.

Recently we have reported the synthesis of molecular dyads that exploit the donor abilities of the β-thioether substituents on magnesium tetraazaporphyrin **1** to form co-ordination complexes with the $(PPh_3)CpRu^{II}$ and $(phen)_2Ru^{II}$ chromophores.[6] In an effort to build higher order arrays, we herein describe a convenient synthesis of two new pentad TAP assemblies, **2** and **3**, possessing four peripherally co-ordinated $(bpy)_2Ru^{II}$ and $(phen)_2Ru^{II}$ moieties respectively, their redox and electronic absorption and emission spectral characteristics.‡

[Mg(TAP)], **1** was synthesized as previously described.[6] The reaction of **1** with 4.4 molar equivalents of $Ru(bpy)_2Cl_2$ or $Ru(phen)_2Cl_2$ in methanol yielded the pentads **2** and **3** respectively, each in nearly 45% yield (Scheme 1). The compounds were purified by column chromatography using neutral alumina (eluent: 1:2 acetone/$CH_2Cl_2$). All these compounds are stable in air under ambient conditions but undergo slow decomposition upon exposure to intense light.

The $^1H$ NMR spectra of the pentads exhibit two groups of signals; a group of multiple multiplets between $\delta$ 6.0–11.0 ppm and three singlets below $\delta$ 5.5 ppm in $CH_2Cl_2$. Since the benzyl $CH_2$, and Ph groups could lie either off or within the TAP plane, they experience differing deshielding effects due to the TAP ring current. Thus, they are expected to give four groups of singlets, of which those corresponding to the in-plane deshielded Ph–H lie between $\delta$ 6.0–7.0 ppm while those corresponding to the off-plane shielded protons appear between $\delta$ 1.0–2.0 ppm. The bipyridyl/phenanthroline signals in **2** and **3** are complex multiplets due to the chair/boat orientations of the $(bpy)_2Ru^{II}$ moieties and the consequent differing deshielding influences of the TAP ring current *vis-a-vis* their mutual interactions. In the ESMS studies fragmentation leads to dissociation of the benzyl groups in these coordination compounds thereby giving the corresponding dithiolate cations. Thus, instead of $M^+$ peaks $(M - 8Bz)^{7+}$ peaks are observed in these complexes.

The lowest energy dπ(Ru) → π*(bpy/phen) MLCT band in the model alkenic-thioether complexes $[(bpy)_2Ru(mnt\text{-}Bn_2)]$, **4** and $[(phen)_2Ru(mnt\text{-}Bn_2)]$, **5**, (where, mnt-$Bn_2$ = *cis*-$(C_6H_5CH_2S)_2C_2(CN)_2$) are much less intense than the Soret and Q-bands of the TAP core in **1**. Linking the '$(bpy)_2Ru$' moieties to the TAP core through analogous thioether coordination in **2** further reduces the intensity of the MLCT band besides causing a moderate bathochromic shift to $\lambda_{max}$ 485 nm ($\Delta\lambda$ = 25 nm) in its position. This is suggestive of poor dπ(S) interaction with the '$(bpy)_2Ru$' in **2** than in **4**, probably because of their involvement with the TAP π-system. The Q-band undergoes a hypsochromic shift, which is more pronounced in compound **3**.



**Scheme 1** *Reagents and conditions*: i, $[(bpy)_2RuCl_2]$, MeOH, reflux 16 h; ii, $[(phen)_2RuCl_2]$, MeOH, reflux 16 h.

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A comparison of the fluorescence excitation spectra of **1** and **2** for the core [Mg(TAP)] $S_2$ emission at $\lambda_{em}$ 473 nm shows a major deviation in the excitatory component between 320–380 nm and around 460 nm in the latter compound (Fig. 1). These wavelengths correspond to the $\sigma(e_g) \rightarrow \sigma^*(e_g)$ LMCT and $d\pi(Ru) \rightarrow \pi^*(bpy)$ MLCT absorptions respectively in $(bpy)_2Ru^{II}$. Therefore, it could be discerned that significant channelization of the $(bpy)_2Ru^{II}$ absorption energy to the upper $S_2$ state of the [Mg(TAP)] core takes place in the pentad system. However, the $S_1$ emission as well as the excitation profile for $S_1$ emission from the [Mg(TAP)] core are not affected in **2** and **3**, probably due to existence of a large energy gap between $(bpy)_2Ru^{II}/(phen)_2Ru^{II}$ LMCT/MLCT absorptions and [Mg(TAP)] Q band.

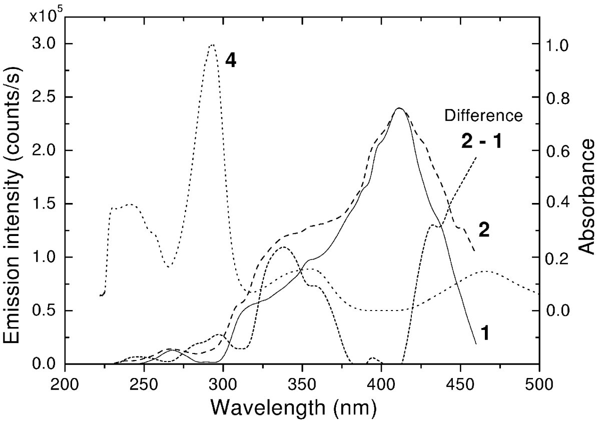

**Fig. 1** Fluorescence excitation spectra of **1** and **2** for emission at 473 nm and absorption spectra of **4** in $CH_2Cl_2$.

The binding of the $(bpy)_2Ru^{II}/(phen)_2Ru^{II}$ moieties to the [Mg(TAP)] core in **2** and **3** introduces a low lying reversible one electron oxidation wave with $E_{1/2}$ 0.45 V and 0.36 V *vs.* Ag/AgCl in acetonitrile, respectively (Fig. 2). Neither the [Mg(TAP)] **1** nor the ruthenium alkenic-thioether complexes **4** or **5** possess such low lying oxidation waves. Compounds **2** and **3** also exhibit a second reversible oxidation wave at $E_{1/2}$ 1.03 and 0.70 V respectively. It is likely that by moderating coupled chemical reaction, the coordination of $(bpy)_2Ru^{II}/(phen)_2Ru^{II}$ moiety has made the one electron oxidation wave of the [Mg(TAP)] core reversible. Thus, the two oxidation waves could tentatively be attributed to Ru(II)/Ru(III) and TAP/TAP$^+$ processes respectively. Comparing the corresponding Ru(II)/Ru(III) processes in compounds **4** and **5** this indicates weaker $d\pi(S)$–$d\pi(Ru)$ interactions in **2** and **3**. Consequently the ruthenium $d\pi$ orbitals are significantly destabilized resulting in the easy oxidation as well as the bathochromic shift of the MLCT transitions.

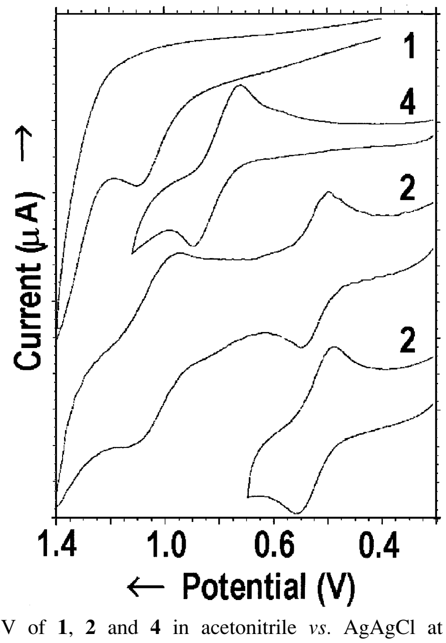

**Fig. 2** CV of **1**, **2** and **4** in acetonitrile *vs.* AgAgCl at Pt working electrode.

The absorption/emission spectral and redox data clearly show that binding of the polypyridyl moieties to the TAP periphery through β-substituent donors significantly alters the electronic state of the ruthenium–polypyridyl *vis-a-vis* TAP moieties.

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## Notes and references

‡ *Syntheses*. A suspension of **1** (210 mg, 0.16 mmol) and $[Ru(bpy)_2Cl_2]\cdot H_2O$ (370 mg, 0.71 mmol) in 40 mL methanol was heated at reflux for 16 h under $N_2$ atmosphere. The resulting solution was filtered and volume was reduced to *ca.* 1 mL at reduced pressure. To this was added a few drops of conc. methanolic $NH_4PF_6$ whereupon a greenish solid **2** separated out. It was collected, recrystallized from $CH_2Cl_2$/petroleum spirit and was purified by passing through a neutral alumina column (eluent, 1:2 acetone/$CH_2Cl_2$). Yield, 300 mg (45%).

Compound **3** was analogously prepared by heating at reflux **1** (210 mg, 0.16 mmol) and $[Ru(phen)_2Cl_2]\cdot H_2O$ (400 mg, 0.71 mmol) in 40 mL methanol for 16 h. Purification by column chromatography through a neutral alumina column yielded 290 mg (42%) of **3**.

**2** $^1$H NMR ($CD_2Cl_2$): $\delta$ = 1.5 (s, 15H, Ph–H), 2.1, 2.8 (s, 16H, $CH_2$), 5.6 (m, 16H, bpy–H), 6.0–11.0 (m, m, 89H, Ph/bpy–H): MALDI-TOF MS: *m/z*: 441 (calcd. for $[M + PF_6]^{7+}$ 441–448): ESMS: *m/z*: 336 (calcd. for $[M - 7Bn]^{7+}$ 330–337): UV/vis ($CH_2Cl_2$) $\lambda_{max}(\varepsilon)$ = 675 (56000), 485 (65000), 378 (111000), 297 nm (261000): CV ($CH_3CN$): $E_{1/2}$ = +0.45, +1.03 V Ag/AgCl.

**3** $^1$H NMR ($CD_2Cl_2$): $\delta$ = 0.8, 1.4 (s, 16H, $CH_2$), 1.9 (s, Ph–H), 6.4–10.6 (m, m, Ph/phen–H): MALDI-TOF MS ($BF_4$ salt): *m/z*: 497 (calcd. For $[M - 2Bn]^{6+}$ 492–499: ESMS: *m/z*: 345 (calcd. for $[M - 8Bn]^{7+}$ 344–351): UV/vis ($CH_2Cl_2$) $\lambda_{max}(\varepsilon)$ = 653 (30000), 367 (47000)), 267 nm (84000): CV ($CH_3CN$): $E_{1/2}$ = 0.36, +0.70 V Ag/AgCl.

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