

Highly coupled two-component Systems consisting of Porphyrins attached to a Rhodium(III) Bis-terpyridine Complex

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Abstract. A 2,2',6',2"-terpyridine (terpy) ligand bearing a porphyrin unit at its 4' position has been made as well as the corresponding rhodium(III) bis-terpy complex. The porphyrin site can be metallated by zinc(II).

Intramolecular photoinduced electron or energy transfer processes in multicomponent molecular systems are the object of intense research.¹ They are particularly promising for converting light signals to high energy charge separated states, in relation with molecular electronics or artificial photosynthesis. Numerous laboratories have developed elegant routes to make multi-functional porphyrin-based compounds.² Transition metal complexes have also been extensively utilized as building blocks for constructing di- or tripartite systems able to undergo intramolecular electron transfer under visible light irradiation.^{3,4}

Among the numerous multicomponent porphyrin containing systems described, only a few examples of transition metal complexes linked to a porphyrin have been reported in relation with photoinduced electron transfer.⁵⁻⁹

The use of terpy covalently attached to the porphyrin core is particularly promising for binding an electro-active function at the periphery of the ring.¹⁰ Furthermore, this approach may open the way to multiporphyrin arrays in which the individual components have been gathered via complexation of their peripheral chelates to transition metal.¹⁰ We now report the synthesis of a rhodium(III) bis-terpy complex bonded either to a free base porphyrin or to its zinc(II) complex.

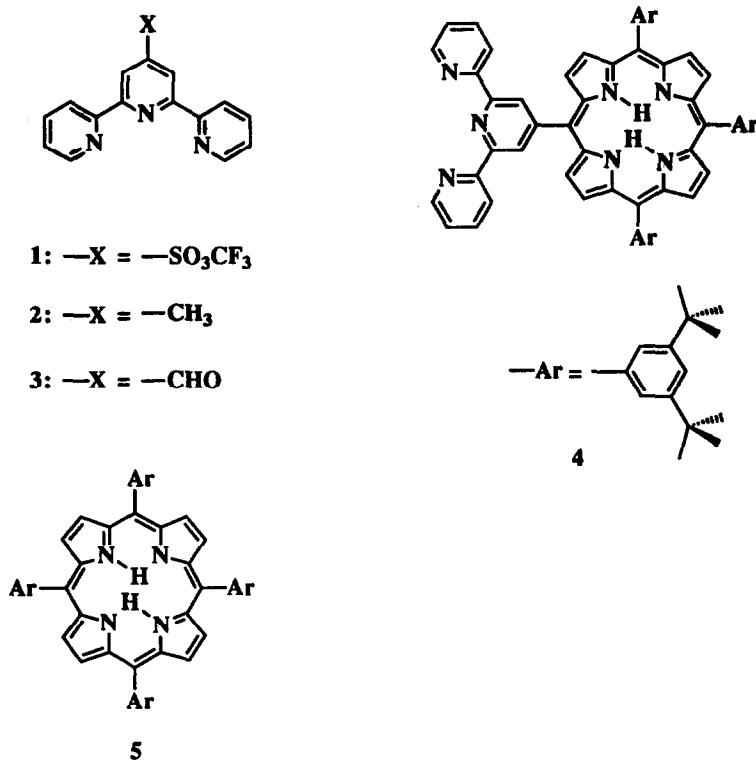


Figure 1

The precursor aromatic aldehyde **3** was prepared in two steps from the triflate terpy **1**.¹¹ **1** was reacted with $Sn(CH_3)_4$ in DMF at $130^\circ C$, in presence of $Pd(PPh_3)_2Cl_2$ (catalytic amounts) and LiCl. After work-up and chromatography on alumina (hexane/ethyl acetate, 9:1 v/v as eluent), an 88% yield of **2** was obtained. **2** had previously been prepared by a different routes.^{12,13} Oxidation of **2** to **3** using SeO_2 was reported a few years ago.¹³ However, we preferred to develop a new procedure based on a reaction recently published by Italian workers.¹⁴ A mixture of **2**, I_2 , CF_3COOH and *t*-BuI in DMSO was heated under argon at $110^\circ C$ for two hours. After work-up, the carboxaldehyde terpy **3** was isolated in 50% yield as a yellow white solid (mp : $170^\circ C$, IR (CHCl₃) ν_{CHO} 1715 cm^{-1} , litt¹³ IR (KBr) ν_{CHO} 1700 cm^{-1}).

The terpy porphyrin **4** was prepared following Adler's procedure.¹⁵ A mixture of **3** (0.7 mmol), 3,5-di-*t*-butyl-benzaldehyde (13.7 mmol) and pyrrole (14.4 mmol) dissolved in propionic acid (30 ml) was refluxed for two hours. After work-up and several chromatographies (alumina ; dichloromethane/methanol 97 : 3 v/v and silica ; hexane/ethyl acetate 99.5 : 0.5 v/v as eluents) **4** was obtained as a high melting point solid in 7% yield.¹⁶ As expected, substantial amounts (33%) of the symmetrical porphyrin **5** were also isolated.

The porphyrin-rhodium(III)-bis-terpy conjugates were prepared as indicated in Figure 2.

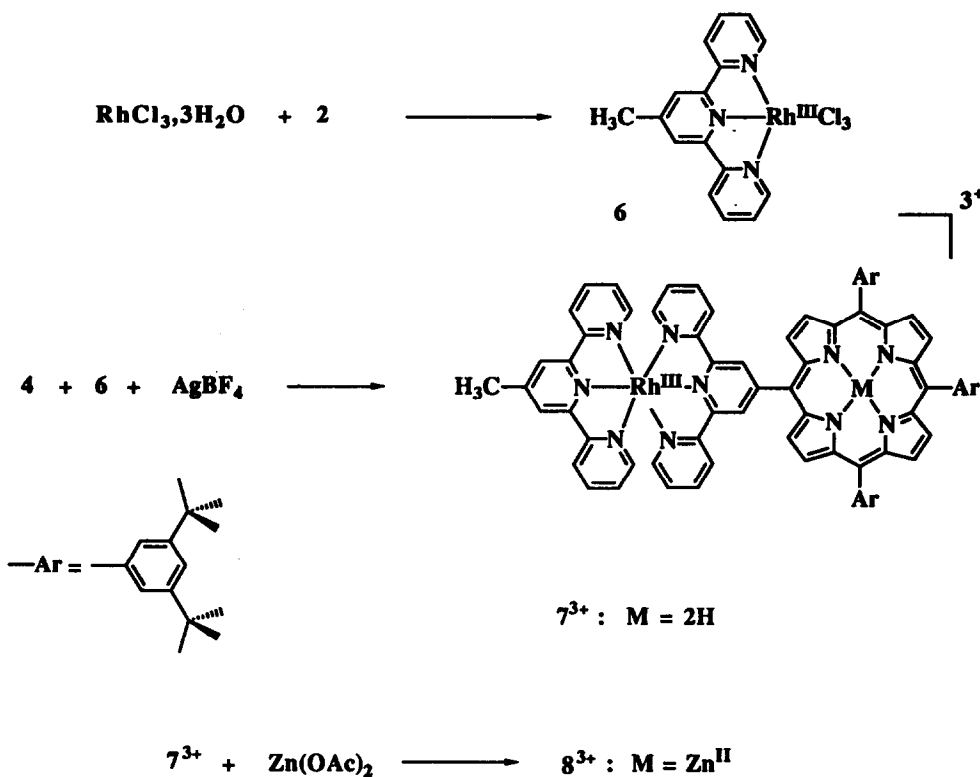


Figure 2

The neutral rhodium(III) precursor complex **6** was prepared from $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ and **2** (stoichiometric proportion) in refluxing ethanol. **6** was isolated as a fine yellow precipitate in 92% yield.¹⁶ It was suspended in acetone/ethanol (6:1 v/v) with four equivalents of AgBF_4 and the mixture was refluxed under argon for 3.5 hours. After removal of AgCl by filtration and partial solvent evaporation, the terpy porphyrin **4** was added (stoichiometric amount). The mixture was refluxed for 17 hrs. After work-up, the crude brown-green product was chromatographed (silica; $\text{CH}_3\text{CN-H}_2\text{O}$ -saturated aqueous KNO_3 89.5 : 10 : 0.5 v/v/v as eluent) to afford the free-base porphyrin rhodium bis-terpy conjugate $7^{3+} \cdot 3\text{PF}_6^-$ in 70% as a deep brown solid.¹⁶

Metallation of the porphyrin site was carried out using Zn(OAc)_2 in refluxing methanol-acetonitrile (5:2) under argon, leading to $8^{3+} \cdot 3\text{PF}_6^-$ after work-up, anion exchange (KPF_6) and column chromatography (silica; $\text{CH}_3\text{CN-H}_2\text{O}$ -saturated aqueous KNO_3 89.5 : 10 : 0.5 v/v/v as eluent). The metallated porphyrin $8^{3+} \cdot 3\text{PF}_6^-$ was obtained as a green black solid in 92%.¹⁶

Preliminary luminescence studies show that strong luminescence quenching takes place both in **7** and **8** as compared to **4**, due to the presence of the rhodium(III) complex. Presumably, very fast electron transfer occurs between the singlet excited state of the zinc(II) porphyrin component and the rhodium(III) bis-terpy subunit, acting as electron acceptor.

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- All the new compounds have been characterized by $^1\text{H-NMR}$, UV-vis spectroscopy and fast atom bombardment (FAB) or electro-spray (ES) mass spectroscopy (MS).
4 : FAB-MS $m/z = 1106.5$ ($4 + 2\text{H}$ requires 1106.7) ; vis. (CH_2Cl_2), λ_{max} nm (ϵ , $\text{mol}^{-1} \text{L.cm}^{-1}$): 422 (2.21×10^5), 518 (1.63×10^4), 553 (8.28×10^3), 592 (5.06×10^3), 648 (4.63×10^3). **6** : mp > 300°C ; FAB-MS : $m/z = 419.8$ ($6\text{-Cl}^- = \text{C}_{16}\text{H}_{13}\text{N}_3\text{RhCl}_2$ requires 419.9). $7^{3+} \cdot 3\text{PF}_6^-$: mp > 300°C ; ESMS : $m/z = 485.9$ ($\text{C}_{93}\text{H}_{95}\text{N}_{10}\text{Rh}^{3+}$ requires 485.2). vis (CH_3CN), λ_{max} nm (ϵ , $\text{mol}^{-1} \text{L.cm}^{-1}$) : 414 (1.87×10^5), 519 (1.48×10^4) ; 564 (9.10×10^3) ; 590 (8.51×10^3) ; 652 (5.56×10^3). $8^{3+} \cdot 3\text{PF}_6^-$; mp > 300° ; ESMS : $m/z = 506.7$ ($\text{C}_{93}\text{H}_{93}\text{N}_{10}\text{RhZn}^{3+}$ requires 506.4). vis (CH_3CN), λ_{max} nm (ϵ , $\text{mol}^{-1} \text{L.cm}^{-1}$) : 420 (2.06×10^5) ; 564 (1.20×10^4) ; 628 (8.50×10^3).

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