Photophysical properties of osmium(II) complexes with the novel 4′-*p*-phenylterpyridine-triarylpyridinium ligand

Philippe Lainé* and Edmond Amouyal

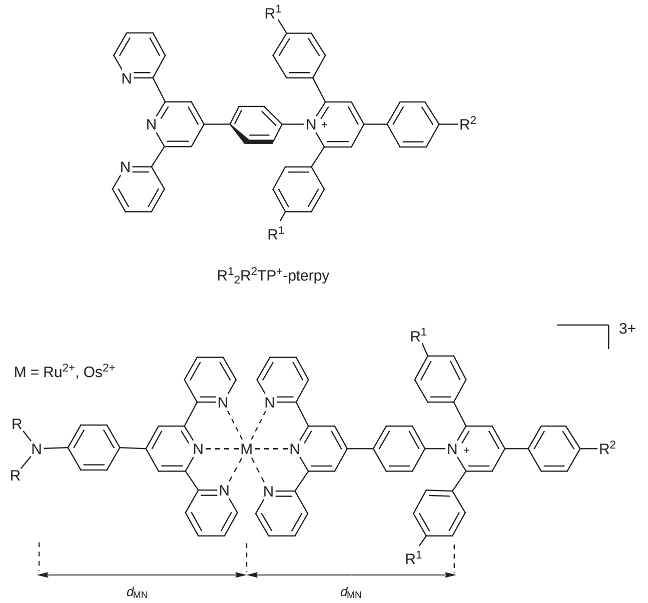
Molecular Photonics Group, Laboratoire de Physico-Chimie des Rayonnements, CNRS UMR 8610, Université Paris-Sud, Bâtiment 350, 91405 Orsay, France. E-mail: philippe.laine@lpcr.u-psud.fr

Received (in Basel, Switzerland) 14th February 1999, Accepted 11th April 1999

A new family of electron acceptor ligands complexed with osmium(II) and associated with appropriate electron donor subunits within heteroleptic compounds, results in multicomponent assemblies of potential interest for both synthetic chemistry and supramolecular photochemistry.

As part of our studies devoted to photochemical conversion of solar energy[1] we are interested in producing long-lived photoinduced charge separation (CS) states within inorganic supramolecular species. Determining criteria that govern intramolecular electron transfers (ET) in multicomponent systems (*i.e.* polyads) have already been addressed in previous work.[2,3] A representative composition for a polyad system devised for CS purposes consists of a linear disposition of peripheral electron donating (D) and withdrawing (A) groups borne by a central photosensitiser P in a *trans* configuration *e.g.* D–P–A (triad).[4] Spacers do play an important role in such constructions by providing the rigidity of the architecture and mediating the electronic coupling between the components. Regarding non-porphyrinic inorganic polyads, widespread strategy is to modulate the efficiency of A (and/or D) *vs.* intramolecular ET by varying the length and nature of saturated spacers; our approach hereby described is to preferably involve *intrinsically weak* electron acceptors *fairly strongly coupled* to P rather than the usual *good* acceptors *almost insulated* from P. The aim remains the same in both cases *i.e.* favour the formation of the CS state D^+–P–A^- by retarding the charge recombination (CR).

Based on hitherto established structural and energetic requirements, we have designed the new 4′-[4-*N*-(2,4,6-triarylpyridinio)phenyl]-2,2′:6′,2″-terpyridine ligand ($R^1{}_2R^2TP^+$-pterpy) depicted in Scheme 1. Related triphenylpyridinium derivatives are known to undergo charge transfer reactions when covalently linked to some donor groups as is the case for solvatochromic Reichardt's dyes like betaine 30,[5,6] the promoted electron being located on the pyridinium moiety. Our proposal is thus to replace the latter donor by a light-triggered electron donor, namely an inorganic chromophore (P) of the Ru/Os-bis(terpyridyl) type.



Scheme 1

It is noteworthy that $R^1{}_2R^2TP^+$-pterpy (A) specifically fits to polyad architectures where the electron-donating part (D) is built from 4′-(4-*N*,*N*-disubstituted-aminophenyl)terpy (R_2N-pterpy, R = alkyl, aryl). In such a structure, both pyridinio and amino nitrogen atoms are located at equal distance d_{MN} from the metal centre and connected to it with identical spacers (Scheme 1). From a topological viewpoint, the CS-state lifetime is expected to be increased in this particular arrangement that allows an optimal competition between the possible reductive quenching reactions of oxidised photosensitiser (D–P^+–$A^- \rightarrow D^+$–P–A^- *vs.* D–P^+–$A^- \rightarrow D$–P–A). Another advantage of $R^1{}_2R^2TP^+$-pterpy ligands comes from the tuneable redox properties of the pyridinium moiety[5,7] the potential of which can be varied systematically by altering substituents R^1 and R^2.

These acceptor-modified terpyridyl ligands (A) are readily synthesised following a general convergent approach[8] consisting in separately preparing the triarylpyrylium salt and the amino derivative of the chelating polyimine which are subsequently reacted together to afford the target molecule in reasonable yield (*ca.* 60% *vs.* amine). The chemical variability of $R^1{}_2R^2TP^+$-pterpy actually stems from pyrylium precursors, the chemistry of which is very rich and also well documented from the synthetic viewpoint.[9] In addition, this route to pyridinium derivatives can be successfully applied to other oligopyridine molecules.[10] Typically, the first element of the ligand family ($R^1 = R^2 = H$), H_3TP^+-pterpy, is obtained by the reaction of 4′-*p*-aminophenyl-terpy ($Na_2S_2O_4$-reduced 4′-*p*-nitrophenyl-terpy) with a triphenylpyrylium cation (HSO_4^- salt, 1 equiv.) in refluxing EtOH for 6 h in the presence of anhydrous NaOAc. Regarding the electron-donor component, the model ligand used is 4′-*p*-dimethylaminophenyl-terpy (Me_2N-pterpy) synthesised following the classical method for *para*-substituted phenyl terpy.[11] Up to 12 Ru^{II} and Os^{II} complexes were then synthesised corresponding to the different combinations between the following three ligands: H_3TP^+-pterpy, Me_2N-pterpy and 4′-*p*-tolyl-terpy (tterpy); after standard work-up purification these compounds prepared as PF_6^- salts afforded microcrystalline powders which were fully characterised;† experimental details will be given elsewhere.[10b] Owing to their better emission properties at room temperature than that of analogous Ru^{II} complexes, preliminary photophysical results are given for the Os^{II} complexes only *i.e.* $[Os(tterpy)_2]^{2+}$ **1**, $[Os(Me_2N\text{-pterpy})_2]^{2+}$ **2**, $[Os(\text{pterpy-}TPH_3{}^+)_2]^{4+}$ **3**, $[(Me_2N\text{-pterpy})Os(tterpy)]^{2+}$ **4**, $[(tterpy)Os(\text{pterpy-}TPH_3{}^+)]^{3+}$ **5** and $[(Me_2N\text{-pterpy})Os(\text{pterpy-}TPH_3{}^+)]^{3+}$ **6**. Properties of two H_3TP^+-pterpy complexes **5** and **6**, compared to that of **1** are more specifically discussed.

As illustrated in Fig. 1 for this series, the luminescence is shown to be gradually weakened when going from **1** to **6**. Compared to the reference chromophore **1** with an emission

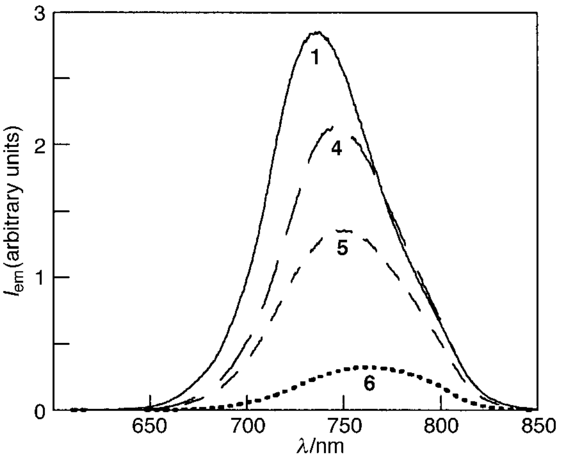


Fig. 1 Emission spectra of Os^{II} complexes in deaerated MeCN solutions at room temperature, measured in identical experimental conditions (in particular, same OD at $\lambda_{exc.}$ = 600 nm).

Table 1 Luminescence properties[a]

	$\lambda_{max}{}^{b}$/nm	$10^2\Phi^c$	$I_{rel}{}^{c,d}$(%)	τ^e/ns
1	734	2.00	100	247
4	747	1.48	74.3	206
5	750	1.02	50.9	168
6	764	0.24	12.1	57

[a] Room temperature measurements; deaerated MeCN solutions. [b] Emission maxima for uncorrected spectra. [c] Luminescence quantum yields were determined relative to $[Os(bpy)_3]^{2+}$ ($\Phi_{em} = 5 \times 10^{-3}$ in MeCN at 298 K).[12] [d] $I_{rel} = 100 \times [\Phi_{em}(\text{species})/\Phi_{em}(\mathbf{1})]$. [e] Determined by laser flash photolysis, λ_{exc} = 308 nm.[13]

quantum yield of 2.0×10^{-2}, ^{3}MLCT emission of the D–P–A triad **6** is *ca.* 90% quenched and lifetime shortened to 57 ns (Table 1).

Note that the contribution of the donor fragment to the quenching phenomenon should not be overestimated as revealed by I_{rel} values for **2** and **4**: 80.5 and 74.3%, respectively. A synergetic effect of electroactive subunits D and A upon emission is, however, clearly identified in the case of **6** when compared with luminescence properties of heteroleptic compounds **4** and **5**.

The rate constant k_Q for the bimolecular quenching reaction (1) of the excited state of the reference chromophore **1** (*P) by the model-acceptor species *N*-phenyl-2,4,6-triphenylpyridinium (p-TPH$_3^+$) was experimentally determined (Stern–Volmer plot). This k_Q value of *ca.* 6×10^7 dm^3 mol^{-1} s^{-1} (with τ_{em} of **1** = 247 ns) cannot account for the more efficient quenching process observed within the dyads and triad; therefore, the effective contribution of an *inter*-molecular ET to the quenching mechanism is negligible.

$$^*[Os(tterpy)_2]^{2+} + p\text{-}TPH_3^+ \longrightarrow [Os(tterpy)_2]^{3+} + p\text{-}TPH_3^{\bullet} \quad (1)$$

In addition, owing to photophysical properties of organic colourless D and A electroactive fragments (UV-absorbing) with respect to that of *P (NIR–VIS-emitting ^{3}MLCT state at *ca.* 740 nm), the above reported quenching effect cannot originate from energy transfer.

Further photophysical investigations at low temperature and picosecond time-scale are currently under way in order to elucidate whether the luminescence behaviour of this series results from effective *intra*-molecular ET or an alteration of the electronic properties of the complexes due to their intercomponent coupling.[14]

The chemical variability provided by R^1 and R^2 (Scheme 1) allows the modulation of the electron withdrawing ability of the acceptor as well as leading to the opportunity to expand the structure along the C_2-axis (*via* R^2) in polyads such as D–P–A$_1$–A$_2$ (redox cascade). Hence, $R^1_2R^2TP^+$-pterpy is a promising candidate to perform sequential and vectorial long-range ET over extended rod-like rigid systems engineered for CS.

Helpful discussions with Dr Valérie Marvaud were much appreciated by P. L.

Notes and references

† All new compounds exhibited satisfactory elemental, spectroscopic (^{1}H and ^{13}C NMR), spectral (UV–VIS–NIR) and mass (ES-MS for **2**–**6** and CI-MS for H$_3$TP$^+$-pterpy) data.

Selected spectroscopic data for H$_3$TP$^+$-pterpy. δ_H (Bruker AC300, 300 MHz, CDCl$_3$): 8.65 (d, *J* 4.8 Hz, 2 H), 8.57 (d, *J* 7.9 Hz, 2H), 8.46 (s, 2 H), 8.15 (s, 2 H), 7.94 (d, *J* 8.0 Hz, 2 H), 7.83 (dd, *J* 7.9, 7.6 Hz, 2 H), 7.75 (d, *J* 8.7 Hz, 2 H), 7.62 (m, 4 H), 7.59 (d, *J* 8.7 Hz, 2 H), 7.54 (m, 3 H), 7.33 (dd, *J* 4.8 Hz, 2 H), 7.29 (m, 6 H). For **6**: δ_H(300 MHz, CD$_3$CN): 8.98 (s, 2 H), 8.81 (s, 2 H), 8.60 (d, *J* 8.0 Hz, 2 H), 8.57 (d, *J* 8.3 Hz, 2 H), 8.50 (s, 2 H), 8.17 (dd, *J* 7.8, 1.4 Hz, 2 H), 8.08 (d, *J* 8.9 Hz, 2 H), 7.98 (d, *J* 8.6 Hz, 2 H), 7.80 (m, 4 H), 7.73 (m, 3 H), 7.62 (d, *J* 8.6 Hz, 2 H), 7.54 (m, 4 H), 7.47 (m, 6 H), 7.34 (d, *J* 5.4 Hz, 2 H), 7.18 (d, *J* 5.0 Hz, 2 H), 7.12 (dd, *J* 7.3, 5.7 Hz, 2 H), 7.04 (d, *J* 8.8 Hz, 2 H), 7.03 (dd, *J* 5.9 Hz, 2 H), 3.15 (s, 6 H). For **6** ES-MS (modified NERMAG R10-10 quadrupole mass spectrometer, solvent: MeCN): *m/z* 1448 (^{190}Os) and 1450 (^{192}Os), [M − PF$_6^-$]$^+$; 652 [M − 2PF$_6^-$]$^{2+}$; 386 [M − 3PF$_6^-$]$^{3+}$.

Selected electrochemical data [differential pulse voltammetry, $E_{1/2}$/V *vs.* SSCE in freshly distilled MeCN/0.1 M TBAPF$_6$ at 298 K]. For **6**: $E(Os^{III/II})$ = +1.03 (rev.), $E(dma^{+/0})$ = +0.77 (rev.), $E(TP^{+/0})$ = −0.93 (rev.), $E(TP^{0/-1})$ = −1.01 (rev.), $E(terpy^{0/-1})$ = −1.24 (rev.).

1 E. Amouyal, in *Homogeneous Photocatalysis*, ed. M. Chanon, John Wiley, Chichester, 1997, ch. 8, 263; E. Amouyal, *Sol. Energy Mater. Sol. Cells*, 1995, **38**, 249.
2 V. Balzani and F. Scandola, *Supramolecular Photochemistry*, Ellis Horwood, Chichester, 1991.
3 J.-P. Sauvage, J.-P. Collin, J.-C. Chambron, S. Guillerez, C. Coudret, V. Balzani, F. Barigelletti, L. De Cola and L. Flamigni, *Chem. Rev.*, 1994, **94**, 993; V. Balzani, A. Juris, M. Venturi, S. Campagna and S. Serroni, *Chem. Rev.*, 1996, **96**, 759.
4 E. C. Constable, *Adv. Inorg. Chem. Radiochem.*, 1986, **30**, 69; J.-P. Collin, S. Guillerez and J.-P. Sauvage, *J. Chem. Soc., Chem. Commun.*, 1989, 776; J.-P. Collin, S. Guillerez, J.-P. Sauvage, F. Barigelletti, L. de Cola, L. Flamigni and V. Balzani, *Inorg. Chem.*, 1992, **31**, 4112.
5 C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.
6 P. Chen and T. J. Meyer, *Chem. Rev.*, 1998, **98**, 1439.
7 M. Martiny, E. Steckhan and T. Esch, *Chem. Ber.*, 1993, **126**, 1671.
8 B. R. Osterby and R. D. McKelvey, *J. Chem. Educ.*, 1996, **73**, 260.
9 A. T. Balaban, A. Dinculescu, G. N. Dorofeyenko, G. W. Fischer, A. V. Koblik, V. V. Mezheritskii and W. Schroth, in *Pyrylium Salts: Synthesis, Reactions and Physical Properties. Advances in Heterocyclic Chemistry*, ed. A. R. Katritzky, Academic Press, New York, 1982, Supplement 2.
10 (*a*) Work in progress; (*b*) manuscript in preparation.
11 W. Spahni and G. Calzaferri, *Helv. Chim. Acta*, 1984, **67**, 450.
12 E. M. Kober, J. V. Caspar, R. S. Lumpkin and T. J. Meyer, *J. Phys. Chem.*, 1986, **90**, 3722.
13 E. Amouyal, M. Mouallem-Bahout and G. Calzaferri, *J. Phys. Chem.*, 1991, **95**, 7641.
14 M. Maestri, N. Armaroli, V. Balzani, E. C. Constable and A. M. W. Cargill Thompson, *Inorg. Chem.*, 1995, **34**, 2759.

Communication 9/01237K