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Terminal-to-Interior Energy Transfer in a “Linear” Oligomeric Diphosphine-Bridged Complex of Re(I)

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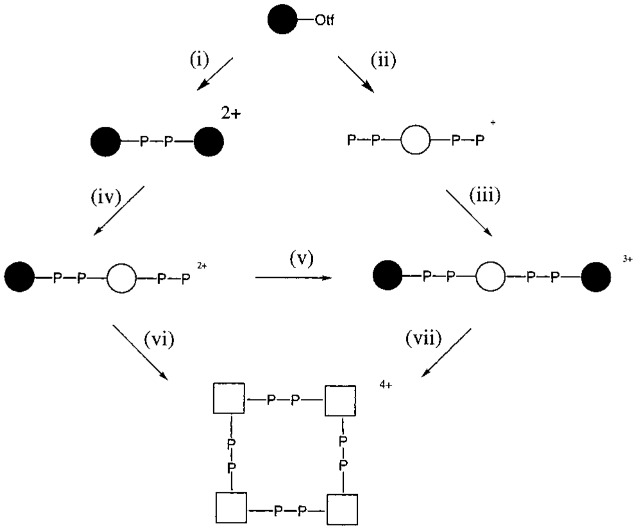
Oligomeric complexes containing metal-to-ligand charge transfer (MLCT) excited states are of interest in the study of the mechanisms of energy and electron transfer in extended molecular arrays, as well as in applications to molecular electronic circuits and solid−liquid junction solar cells.[1] A variety of approaches to the preparation of photoactive oligomers exist, but most are based on Ru(II)−chelate MLCT chromophores that emphasize linkages through the chelate (chelate is a polypyridine ligand such as 2,2-bipyridine, bpy, or 1,10-phenanthroline, phen).[2−5] Some notable exceptions include the *cis*-dicyano-bridged oligomers of Bignozzi et al.[6] and the Re(I) molecular squares bridged by 4,4′-bpy of Hupp et al.[7] Here we demonstrate new chemistry that allows the controlled preparation of “linear” oligomers by utilizing the trans-labilizing effect of diphosphine bridging ligands (from hereon denoted P-P). This overall strategy puts emphasis on the bridging diphosphine group for both control of linearity and electronic interactions between oligomer units while allowing electronic state energies to be controlled by the in-plane ligands. In addition to this new MLCT oligomer chemistry, we present the first example of a trimer containing solely Re(I)−chelate excited states, and of “parallel” energy transfer between the chromophores within the oligomer units.

Scheme 1. Preparative Routes to Oligomeric MLCT Excited States Based on Re(I)−Polypyridine Complexes[a]



[a] The dark circles represent *fac*-Re(chelate)$(CO)_3$ units; the light circles represent *cis*-Re(chelate)$(CO)_2$ units, and the squares represent *trans*-Re(chelate)$(CO)_2$ units. The bridging diphosphine (see text) is signified by P-P. Conditions for preparation of the complexes are as follows: (i) 0.5 equiv of P-P in EtOH at reflux for 48 h; (ii) excess P-P in *o*-DCB at reflux for 24 h; (iii) 1.0 equiv of *fac*-Re(chelate)$(CO)_3$OTf in acetone at reflux for 5 h; (iv) excess P-P in chlorobenzene at reflux for 24 h in an NMR tube; (v) excess *fac*-Re(chelate)$(CO)_3$OTf in acetone at reflux for 24 h; (vi) *o*-DCB at heated reflux for 5 h; (vii) 1.0 equiv of *cis-trans*-Re(chelate)$(CO)_2(P\text{-}P)^{2+}$ in *o*-DCB for 5 h.

The preparation of the Re(I) oligomers is based on the use of the precursor triflato (OTf) complex *fac*-Re(chelate)$(CO)_3$OTf, which substitutes under mild conditions to give *fac*-Re(chelate)-$(CO)_3(P\text{-}P)^+$, but under more forcing conditions with excess P-P to give *cis-trans*-Re(chelate)$(CO)_2(P\text{-}P)_2^+$ complexes.[8] Scheme 1 shows that by judicious choice of conditions and stoichiometry, a variety of complexes can be obtained with Re^I(chelate)$(CO)_2^+$ interior units and *fac*-Re^I(chelate)$(CO)_3^+$ terminal units.[9,10] The diphosphines used in our studies include *trans*-1,2-bis-diphenylphosphinoethylene (t-dppene), 1,2-bis-diphenylphosphinoacetylene, and 1,2-bis-diphenylphosphinobenzene. The chelates were either phen or bpy. The example of note for this work is the trimer $(CO)_3$(bpy)Re(μ^2-t-dppene)Re(bpy)$(CO)_2$(μ^2-t-dppene)Re(bpy)$(CO)_3[OTf]_3$ (**I**). Table 1 displays spectroscopic data on selected complexes including two dimers and two trimers based on the t-dppene bridge. Both ^{31}P NMR and IR spectroscopies are of particular help in characterizing the complexes, since the former gives the number of coordinated versus uncoordinated phosphorus nuclei and the latter enables the determination of the number of interior versus terminal units. As seen in Table 1 for several complexes, resonances occur in the region of −6 to −5 ppm (versus 85% H_3PO_4) that correspond to uncoordinated phosphorus (−7.6 ppm for free t-dppene). In contrast, Re(I)-coordinated phosphorus occurs in the region +13 to +18 ppm. In addition to satisfactory elemental analysis data, **I** yielded a large “parent” ion by FAB mass spectrometry corresponding to the loss of one OTf counterion ($m/e = 2333.4$).

A quite startling discovery was made during our initial attempts to refine the preparations, i.e., under the appropriate stoichiometric conditions new complexes that are *cyclic ligand bridged oligomers* are formed, e.g., $[Re(bpy)(t\text{-}dppene)(CO)_2]_4(OTf)_4$. These unusual materials contain trans carbonyl and cis phosphine ligands, and

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(1) See, for example: Meyer, G. J., Ed. Molecular Level Artificial Photosynthetic Materials. *Progress in Inorganic Chemistry*; Karlin, K. D., Ed.; 1996; Vol. 44.

(2) Although numerous examples of luminescent oligomeric complexes exist, only a few selected cases appear in refs 3−5, although see: Balzani, V.; Juris, A.; Venturi, M.; Campagna, S.; Seroni, S. *Chem. Rev.* **1996**, *96*, 759.

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(10) Preparation of **I**: *fac*-Re(bpy)$(CO)_3$OTf (135 mg, 0.235 mmol) and [*cis-trans*-Re$(CO)_2$(t-dppene)$_2$(bpy)](OTf) (159 mg, 0.119 mmol) were placed in a 50 mL round-bottom flask containing approximately 30 mL of dry acetone. The reaction mixture was purged with nitrogen for 20 min and refluxed with magnetic stirring for 48 h, after which time the acetone was removed by rotary evaporation, leaving a light yellow residue. The residue was dissolved in dichloromethane and reprecipitated by dropping into a stirring mixture of 2:1 diethyl ether:hexanes. The resulting light yellow solid was then purified by column chromatography on acidic alumina eluting with acetonitrile followed by methanol (266 mg, 91% yield). Anal. Calcd (found): C, 43.61 (43.69); H, 2.76 (2.76); N, 3.39 (3.31).

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Table 1. Key Spectroscopic Data for the Complexes[a]

complex[b−d]	^{31}P NMR shifts[e]	IR frequencies (cm^{-1})[c]	λ_{em}[c,f]
cis-trans-Re(bpy)(CO)$_2$(dppene)$_2$$^+$ (**III**)	+16.6, −5.7	1942, 1873	637
(CO)$_3$(bpy)Re(μ^2-dppene)Re(bpy)(CO)$_3$$^{2+}$ (**II**)	+14.9	2043, 1960, 1928	524
(CO)$_3$(bpy)Re(μ^2-dppene)Re(bpy)(CO)$_2$(dppene)$^{2+}$	+20.6, +19.6, +15.2, −3.5	2042, 1957, 1942, 1926, 1870	623
(CO)$_3$(bpy)Re(μ^2-dppene)Re(bpy)(CO)$_2$(μ^2-dppene)Re(bpy)(CO)$_3$$^{3+}$ (**I**)	+18.8, +14.4	2041, 1959, 1942, 1926, 1875	615
(CO)$_3$(bpy)Re(μ^2-dppene)Re(phen)(CO)$_2$(μ^2-dppene)Re(bpy)(CO)$_3$$^{3+}$	+18.9, +14.5	2042, 1958, 1945, 1926,1876	602

[a] All oligomers have *fac*-tricarbonyl capping groups and *cis*-dicarbonyl interior groups. [b] All complexes are OTf salts. [c] Data recorded in CH$_2$Cl$_2$ solution. [d] UV−visible absorption data have been omitted because the oligomers have no well-defined maxima. [e] Reported versus an 85% H$_3$PO$_4$ external standard; recorded in CH$_3$CN solution. [f] Corrected spectra recorded on an SLM model 8000C spectrofluorimeter.

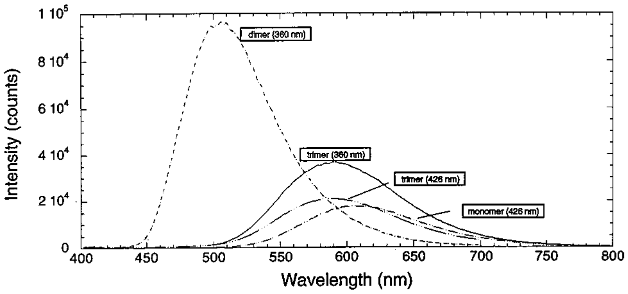

Figure 1. Uncorrected emission spectra for complexes/**I** (trimer), **II** (dimer), and **III** monomer in CH$_2$Cl$_2$ at 20 °C. Excitation wavelengths are either 360 or 426 nm (see text for discussion).

their properties are the subject of the following Communication in this issue.[11]

Of prime interest are the photochemical and photophysical properties of the linear oligomers. As demonstrated in Figure 1, results of steady state emission spectroscopy demonstrate that excitation energy can be transferred within complex **I** from a terminal unit to the interior unit. This is illustrated by the different behavior for the 360 nm excitation of the dimer (CO)$_3$(bpy)Re(μ^2-t-dppene)Re(bpy)(CO)$_3$(OTf)$_2$ (**II**), which serves as a photophysical model for the terminal units in **I**. For **II**, an extremely strong emission feature (ϕ_{360} = 0.35, CH$_2$Cl$_2$) is found in the 500 nm region, while for **I**, only a 600 nm emission is observed (ϕ_{360} = 0.036). That this lower energy emission is associated with the interior unit is supported by comparison with the monomer model, *cis-trans*-Re(bpy)(CO)$_2$(t-dppene)$_2$$^+$ (**III**). Both emissions occur at ca. 600 nm, although that of **I** is somewhat lower in energy. Since the absorption spectra of the MLCT region (ca. 340−600 nm) of **I** and that produced by the summation of **II** and **III** are superimposable, this blue shift is attributed to an excited state effect which could be electrostatically induced, as is found for Os(phen)$_3$$^{2+}$ ion pairs.[12,13] In addition to the blue-shifted emission, the lifetime of **I** has increased relative to **III** (0.40 versus 0.20 μs in CH$_2$Cl$_2$ at 20 °C at an excitation wavelength of either 360 or 440 nm).

The preparative techniques presented here offer the possibility to vary the electronic properties of the individual units as well as overall chain length in a straightforward fashion. The facile energy transfer at room temperature in **I** should be capable of being probed in a direct fashion by transient infrared spectral techniques[14] due to the presence of dicarbonyl versus tricarbonyl units.

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