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Synthesis of a linear-shaped tetramer and trimers of rhenium(I) diimine complexes†

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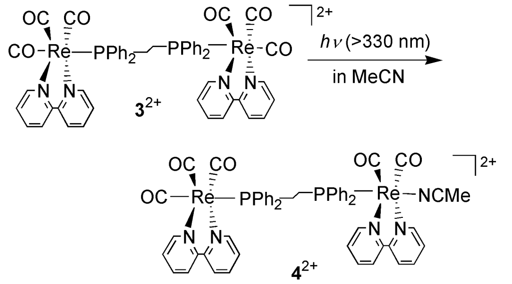
First examples of a linear-shaped tetramer and non-symmetrical trimers of rhenium(I) diimine complexes have been synthesized in good yields, and their UV–vis absorption and emission spectra are reported.

Linear-shaped multinuclear complexes have excited much interest as electron or photon relays.[1,2] However, only certain kinds of metal complexes, for example, ruthenium(II) bis-terpyridine derivatives[3] and *meso*-linked metalloporphyrins,[4,5] can be used as building blocks.[6] Also, rhenium(I) diimine complexes *fac*-$[Re(LL)(CO)_3X]^{n+}$ (LL = diimine ligand, X = monodentate ligand), for which the photophysics and photochemistry have been intensively studied,[7,8] have been used only as 'L-shaped' bent building blocks for supramolecules, such as molecular squares,[9–11] since only the ligands LL and X in positions *cis* to one another are easily modified.[12] In fact, only two 'linear-shaped' rhenium(I) diimine trimers, both having a symmetrical structure $[\{[Re(bpy)(CO)_3](dppene)\}_2Re(LL)(CO)_2]^{3+}$, have been reported so far because of the lack of general synthetic methods.[13]

We report here new synthetic routes for 'linear-shaped' but non-symmetrical trimers of rhenium(I) diimine complexes. This new synthesis strategy is also successfully applied to obtain for the first time a 'linear-shaped' rhenium(I) tetrameter $[\{Re(bpy)(CO)_3(dppe)Re(bpy)(CO)_2\}_2(py–py)]^{4+}$ $\mathbf{1}^{4+}$ (Scheme 1).

As a typical example, the synthetic procedure for $[Re(bpy)(CO)_3(dppe)Re(bpy)(CO)_2(py–py)Re\{(CF_3)_2bpy\}(CO)_3]^{3+}$ $\mathbf{2a}^{3+}$, where bpy = 2,2′-bipyridine, dppe = 1,2-bis(diphenylphosphino)ethane, py–py = 4,4′-bipyridine, and X_2bpy = 4,4′-X_2-2,2′-bipyridine, is now reported. An acetonitrile (MeCN) solution (50 dm^3) of the PF_6^- salts of $[\{Re(bpy)(CO)_3\}_2(dppe)]^{2+}$ $\mathbf{3}^{2+}$ (0.04 mmol) was irradiated under an argon atmosphere using a high-pressure mercury lamp with a glass filter (>330 nm) for 40 min, giving $[Re(bpy)(CO)_3(dppe)Re(bpy)(CO)_2(MeCN)]^{2+}$ $\mathbf{4}^{2+}$ [eqn. (1)].



(1)

After evaporation of the MeCN solvent, $[Re\{(CF_3)_2bpy\}(CO)_3(py–py)]^+(PF_6^-)$ and tetrahydrofuran (5 dm^3) were added and the solution was refluxed under an argon atmosphere for 3 h. A red–orange solid consisting of $(\mathbf{2a}^{3+})(PF_6^-)_3$ was precipitated in 72% yield [eqn. (2)]

$$4^{2+} + [Re(X_2bpy)(CO)_3(\eta^1\text{-py-py})]^+ \xrightarrow[\text{under Ar in THF}]{\text{reflux 3 h}} \begin{matrix} 2a^{3+}\ (X = CF_3) \\ 2b^{3+}\ (X = H) \end{matrix} \qquad (2)$$

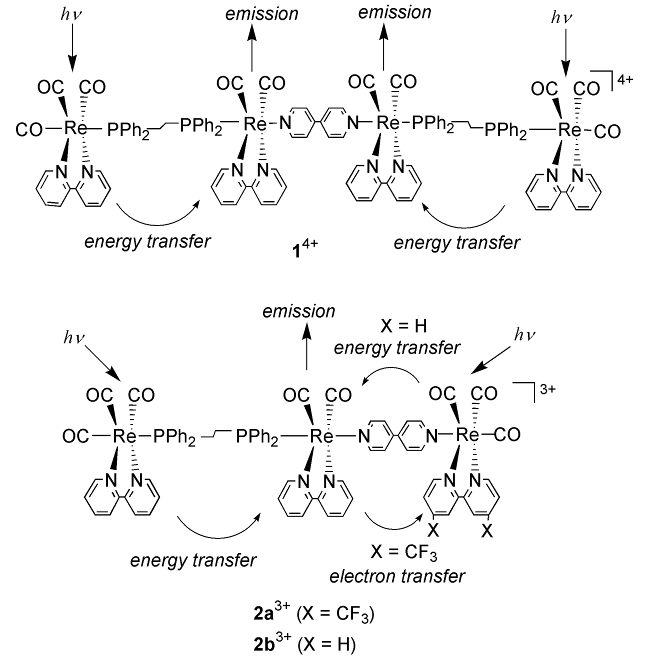
The further trimer $[Re(bpy)(CO)_3(dppe)Re(bpy)(CO)_2(py–py)Re(bpy)(CO)_3]^{3+}$ $\mathbf{2b}^{3+}$ was also synthesized by a similar procedure in 78% yield. This photochemical method should be applicable for the synthesis of various rhenium(I) trimers $[Re(X_2bpy)(CO)_3(PP)Re(X_2bpy)(CO)_2(BL)Re(LL)(CO)_3]^{3+}$ (PP = diphosphorus ligand; BL = bridge ligand), because photoexcitation of rhenium(I) diimine complexes with a phosphorus ligand generally gives a good yield of the *cis,trans*-$[Re^I(LL)(CO)_2(PR_3)(L')]^{n+}$ type complexes.[14]

The tetranuclear complex $\mathbf{1}^{4+}$ was also synthesized using the same photochemical product $\mathbf{4}^{2+}$. This product was dissolved in THF containing half molar concentration of py–py. The solution was refluxed for 3 h to give $(\mathbf{1}^{4+})(PF_6^-)_4$ at 60% yield, based on $\mathbf{3}^{2+}$ used [eqn. (3)]

$$2\ 4^{2+} + \text{py-py} \xrightarrow[\text{under Ar in THF}]{\text{reflux 3 h}} 1^{4+} \qquad (3)$$

The symmetrical dimers $[\{Re(LL)(CO)_2(MeCN)\}_2(dppe)]^{2+}$ are good candidates for synthetic building blocks for longer rhenium diimine oligomers because they have thermally-active acetonitrile ligands at both ends. Photochemical ligand substitution of $\mathbf{4}^{2+}$ was much slower than for $\mathbf{3}^{2+}$ because of the efficient energy transfer reaction from the excited state of the $[Re(bpy)(CO)_3(dppe)–]$ group to the other group (specified below), but then proceeded to give $[\{Re(bpy)(CO)_2(MeCN)\}_2(dppe)]^{2+}$. Attempts to synthesize longer rhenium diimine oligomers are in progress.

The electrospray ionization mass spectra of the complexes essentially show just a parent peak, and the elemental analysis



Scheme 1 Linear-shaped Re(I) oligomers.

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† Electronic supplementary information (ESI) available: IR and ^1H NMR data. See http://www.rsc.org/suppdata/cc/b1/b104220n/

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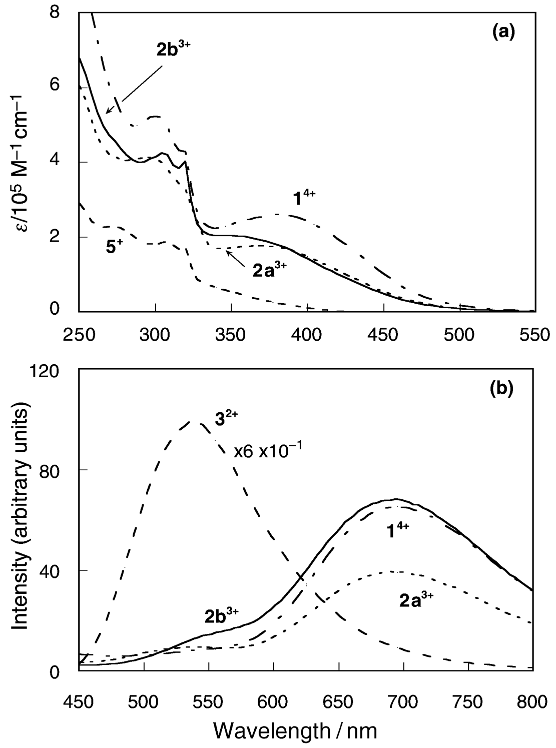

Fig. 1 (a) UV–vis absorption and (b) emission spectra (350 nm excitation) of **1**$^{4+}$, **2b**$^{3+}$, **3**$^{2+}$ and **5**$^{+}$ in acetonitrile.

data were in good agreement with the calculated values. The ^{1}H NMR spectra clearly indicate that the two pyridine rings of all the bpy and $(CF_3)_2$bpy ligands are magnetically equivalent and that the bridged ligands are in positions *trans* to one another, so that all the synthesized trimers and the tetrameter are linear-shaped.

We report preliminary spectroscopic data for the complexes synthesized. The UV–vis absorption spectra are shown in Fig. 1(a). The difference in the absorption maxima at 360–390 nm, due to metal-to-ligand charge transfer (MLCT), arises mainly from the differences in the constituent groups and their number. We chose two excitation wavelengths for emission measurements, at 350 and 440 nm: the higher energy photons can excite all the rhenium–complex groups in the oligomers while the other light is absorbed mainly by the central biscarbonyl group(s) $[-\{(dppe)Re^I(bpy)(CO)_2\}_2(py–py)–]$ and one of the terminal tricarbonyl groups $[Re^I\{(CF_3)_2bpy\}(CO)_3(py–py)–]$.

Fig. 1(b) illustrates the emission spectra of both the tetramer **1**$^{4+}$ and the corresponding dimer **3**$^{2+}$ under 350 nm excitation; these differ greatly even though both complexes have the same emissive group, $[Re^I(bpy)(CO)_3(dppe)–]$. The strong emission of **3**$^{2+}$, which arises from the triplet MLCT excited state (^{3}MLCT) of the $[Re^I(bpy)(CO)_3(dppe)–]$ groups, was observed at 540 nm. The emission of **1**$^{4+}$ at the same wavelength was much weaker, whereas another emission was observed at 695 nm, arising from ^{3}MLCT on the central groups $[–(dppe)Re^I(bpy)(CO)_2]_2(py–py)–]$. This assignment is supported by the following experimental results: excitation of **1**$^{4+}$ using 440 nm light absorbed mostly by the central groups gave emission only at 695 nm, and a model complex of the central groups $[Re^I(bpy)(CO)_2(PPh_2Pr)(\eta^1\text{-py–py})]^+$ emits at 710 nm. The strength of the 695 nm emission stimulated by the 440 nm excitation, normalized using the absorbance, was only 1.3 times greater than that stimulated by the 350 nm excitation. These results clearly show that efficient energy transfer occurs from the excited state of the terminal $[Re^I(bpy)(CO)_3(dppe)–]$ groups to the central $[-\{(dppe)Re^I(bpy)(CO)_2\}_2(py–py)–]$ groups in **1**$^{4+}$ as shown in Scheme 1.

The trimer **2b**$^{3+}$ has a different emission property: excitation using 350 nm light causes dual emission, at 540 and 670 nm [Fig. 1(b)], whereas 690 nm emission alone was observed with 440 nm excitation. The emission at 540 nm arises from ^{3}MLCT of the $[Re^I(bpy)(CO)_3(py–py)–]$ group, because the corresponding mononuclear complex $[Re^I(bpy)(CO)_3(\eta^1\text{-py–py})]^+$ **5**$^{+}$ emits at 570 nm and the excitation of another terminal $[Re^I(bpy)(CO)_3(dppe)–]$ group should cause efficient energy transfer to the central group, as described above. Energy transfer from the excited $[Re^I(bpy)(CO)_3(py–py)–]$ group to the central group is expected to occur (Scheme 1) because the emission strength from the $[Re^I(bpy)(CO)_3(py–py)–]$ group was much less than that of the model complex.

Emission from **2a**$^{3+}$ using either 350 or 440 nm light was weaker than that from **2b**$^{3+}$. It follows that the ^{3}MLCT state of the central $[-\{(dppe)Re^I(bpy)(CO)_2\}_2(py–py)–]$ group should be quenched by the terminal $[Re^I\{(CF_3)_2bpy\}(CO)_3(py–py)–]$ group. There are two possible quenching mechanisms: energy transfer and electron transfer. Energy transfer might not occur because the ^{3}MLCT energy of the central group is lower than that of the $[Re^I\{(CF_3)_2bpy\}(CO)_3(py–py)–]$ group, of which the model complex $[Re^I\{(CF_3)_2bpy\}(CO)_3(\eta^1\text{-py–py})]^+$ emits at 660 nm.

Further study of the intramolecular electron- and/or energy-transfer processes of rhenium(I) oligomers is in progress using laser flash photolysis.

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