CHAPTERWISE SUMMARY
Chapter 1

The luminescence properties, the electrochemical behaviour and the absorption spectra of six dinuclear heterometallic compounds have been investigated. The absorption spectra of the two components are slightly perturbed in the dinuclear compounds. The luminescence of Ru based unit is quenched by the connected Os based unit with practically unitary efficiency, regardless of the number of interposed phenylene spacers. Quenching is accompanied by quantitative sensitization of the Os-based luminescence. The rate of energy transfer at 293K is larger than $10^{10}$ s$^{-1}$ in all cases.
Chapter 2

A series of bimetallic complex of general formula \([(\text{phen})\text{Re(CO)}_3\text{LOs(trpy)}(\text{bpy})]^+\) (bpy = 2, 2' - bipyridine, phen = 1, 10, - phenanthroline, trpy = 2,2'; 6',2''-terpyridine and \(L = 4, 4'\) - bipyridine (4,4'-bpy), trans - 1,2-bis (4-pyridyl ethylene (t-bpe), or 1,2 - bis (4- pyridyl) ethane have been synthesised and their photophysical and photochemical properties studied. In the binuclear \([(\text{phen})\text{Re(CO)}_3\text{(t-bpe)Os(trpy)(bpy)}]^+\) complex, the trans to Os isomerization of the coordinated t-bpe ligand, characteristic of the \([(\text{phen})\text{Re(CO)}_3\text{(t-bpe)}]^+\) submit is inhibited by competitive intramolecular energy transfer.
Chapter 3

The binuclear complex \( \{\text{Os(bipy)}_2 \} (\mu - L^1) \{\text{Re (CO)}_3 (\text{H}_2\text{O})\} \) \([\text{PF}_6]_3\) (Os-crw-Re), and its monomeric counterpart \([\text{Os (bipy)}_2 (L^1)]^3 [\text{PF}_6]_2\), were synthesised. The bridging ligand \(L^1\) contains two bipyridyl binding sites which are attached via methylene spacers to each of the \(N\) atoms of a deaza-18-crown-6 macrocycle spacer (crw). The absorption spectra luminescence spectra and excited-state lifetimes, and electrochemical properties of acetonitrile solutions of these complexes were investigated. In fluid solutions at room temperature, there is no photoinduced \(\text{Re} \rightarrow \text{Os}\) energy transfer, instead photoinduced electron transfer occurs in the absence of \(\text{Ba}^{2+}\) \((K_{el} = 1.3 \times 10^{40}\ \text{Sec}^{-1})\), which is inhibited by the presence of \(\text{Ba}^{2+}\) and \(K_{en}^{\text{Ba}} = 6.9 \times 10^6\ \text{Sec}^{-1}\) in the presence of \(\text{Ba}^{2+}\) indicating that \(\text{Re} \rightarrow \text{Os}\) energy transfer is strongly affected by \(\text{Ba}^{2+}\) being hosted within the aza crown cavity, i.e. a switching effect.
Chapter 4

Synthesis of dinuclear bridged complex of osmium (II) [(Phen)$_2$Os(tatpp)Os(Phen)$_2$][PF$_6$]$_4$(E) (where phen is 1,10-phenanthroline and tatpp is 9,11,20,22-tetraazatetrapyrido[3,2-a:2'3'-c:3'',2''-l:2''',3'''']pentacene is found to accept up to four electrons and two protons on the central tatpp bridging ligand. The absorption spectra of seven distinct species related by reduction/protonation of the centre tatpp ligand were obtained and the two sequential photoproducts obtained from visible irradiation of E in acetonitrile as E$^{-}$ and HE$^{-}$ respectively. Absorption spectra were virtually obtained to those photochemically and the doubly reduced photoproducts were identified as E$^{2-}$, HE$^{-}$ and H$_2$E. A qualitative MO diagramme presents optical transition as a function of oxidation and protonation state.
Chapter 5

We have investigated the photochemistry of 
\([\text{(CO)}_4 \text{Re} (\mu-\eta^3: \eta^6-\text{C}_3\text{H}_4\text{C}_6\text{H}_5) \text{Cr} (\text{CO})_3] \) in low temperature matrices. In an argon 
matrix we see CO loss from only the Re end of the molecule and 
\([\text{(CO)}_3 \text{Re} (\mu-\eta^3: \eta^6-\text{C}_3\text{H}_4\text{C}_6\text{H}_5) \text{Cr} (\text{CO})_3] \) is the only observed photoprodut. How-
ever, in a \(\text{N}_2\) matrix photosubstitution is observed at both metal centres and we were 
able to identify \([\text{(CO)}_4 \text{Re} (\mu-\eta^3: \eta^6-\text{C}_3\text{H}_4\text{C}_6\text{H}_5) \text{Cr} (\text{CO})_2 (\text{N}_2)] \)
\([\text{(CO)}_3 \text{Re} (\mu-\eta^3: \eta^6-\text{C}_3\text{H}_4\text{C}_6\text{H}_5) \text{Cr} (\text{CO})_3] \) and \([\text{(CO)}_2 (\text{N}_2)_2 \text{ReC}_3\text{H}_4\text{C}_6\text{H}_5) \text{Cr} (\text{CO})_3] \) 
In all these experiments, characterisation of photoproduts was aided by 
comparison with experiments using the mononuclear fragments 
\((\eta^6-\text{C}_6\text{H}_5\text{C}_2\text{H}_3) \text{Cr} (\text{CO})_3] \) and \((\eta^3-\text{C}_3\text{H}_4\text{C}_6\text{H}_5) \text{Re} (\text{CO})_4] \) where we were able to 
characterise \([\text{(CO)}_3 (\text{N}_2)] \) and \([\text{(CO)}_2 (\text{N}_2)_2] \) and \([\text{(CO)}_3 (\text{N}_2)] \) and \([\text{(CO)}_2 (\text{N}_2)_2] \).