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Photoinduced energy and electron transfer processes in rigidly bridged dinuclear Ru/Os complexes

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Abstract

In an attempt to elucidate the role played by the various factors—distance, geometry, electronic nature of the bridging ligand—which control the occurrence of intercomponent electronic energy and electron transfer in dinuclear systems, several photophysical studies have been reported. In this contribution we discuss the photoinduced energy and electron transfer processes occurring in rigid systems containing ruthenium and/or osmium metal units prepared in our laboratories, and compare them with the results obtained with compounds described by other authors. The choice of spacers, connections, chelating sites, and metal units used to construct photoactive systems is described.

Keywords: Energy transfer; Electron transfer; Bridging ligands; Dinuclear metal complexes; Charge separation; Molecular wires; Polypyridine complexes; Excited-states; Emission lifetime; Ruthenium complexes; Osmium complexes

1. Introduction

The assembly of metal centers covalently linked in supramolecular structures has been object of several investigations in the past few years [1–4]. Such development is based on the new synthetic methodologies for preparing large polynuclear complexes [5–7], and is motivated by the interesting functions that a structurally organized system can perform elaborating the energy and information input of photons [8–12].

The use of transition metal complexes as building blocks is very appealing for several reasons. In particular these systems seem very flexible in terms of tailoring the energetics (excited-state energies, ground- and excited state redox potentials) by appropriate choice of metals and ligands. Furthermore they posses defined geometries and a possibility to tune the strength of the ligand coordination from very strong to very labile.

The photochemical and photophysical behavior on going from mononuclear to dinuclear or polynuclear systems is expected and found to be more complex and interesting for two principal reasons: (i) the properties of each metal-containing subunit may undergo perturbations upon incorporation into the multicomponent system, and (ii) a number of new processes involving different metal-containing units (intercomponent processes) may take place in the polynuclear complex. Important photoinduced inter-component processes are electron and energy transfer. A suitable choice of components (metal ions, peripheral ligands, and modular bridging ligands) leads to the possibility of controlling the overall structure (geometry, electronic interaction and distance between the chromophores) and allows the occurence of interesting and useful photoinduced processes such as vectorial transport of energy or electronic charge, charge separation, multiredox processes, etc.

Covalently linked two-component systems, dyads, are the simplest class of supramolecular architecture for the study of photoinduced energy and electron

transfer processes [13]. We have limited our discussion on dinuclear metal complexes and among them to those containing ruthenium and/or osmium units in which the connection between the metal centers is provided by a quite rigid bridging ligand. We will exclude bridges like CN^-, Cl^-, porphyrin system, and organometallic compounds and such contribution will cover only the past few years since a very complete review on polynuclear luminescent compounds has recently been published by Balzani et al. [5].

2. Dinuclear compounds for photoinduced processes

To build up dinuclear systems it is necessary to have a series of components each one having appropriate structural and electronic properties (Fig. 1). In order to produce defined architectures in a controlled fashion from multiple subunits, special care must be devoted to the choice of metals, ligands and connections [14–16]. Furthermore to perform light induced functions within the supramolecular structure, organization in space, energy, and time of the components is required. Prefabricated molecular components containing a metal ion coordinated to suitable ligands can be used as active units in order to obtain the desired electrochemical and photochemical properties. The connection between the two chromophoric units can be achieved by covalent bonding either directly between the two units or by another component. Such structural component, the bridging ligand (BL) should

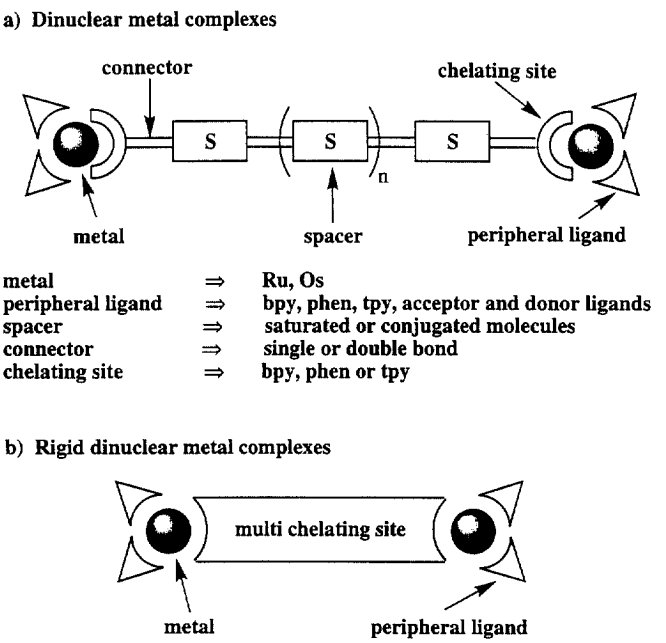


Fig. 1. Schematic representation for dinuclear metal complexes.

contain sites to coordinate the metal center, and suitable spacers in order to control distance and orientation of the chromophores.

The number of known dinuclear compounds is very large, however it is drastically smaller if one considers only the species containing luminescent metal units and in which the chromophores are linked by a rigid bridging ligand. Introducing rigidity as a structural requirement will allow the control of the overall geometry, to maintain fixed the distance between the metal units and provide a mean to draw pertinent conclusions about the processes of interest.

Most of the systems studied are molecules in which the two remote chromophore sites are linked by extended bridging spacers such alkanes, alkynes, saturated molecules (adamantane, *bicyclo*[2.2.2]octane, cyclobutane), polyphenyls. However the main drawback of such bridging ligands is the possible rotation around the σ-bonds (see Section 2.2) which can cause in some cases a change in the distance between the two metal units, or for conjugated bridges, a decrease in the long-distance electronic coupling because a loss of coplanarity of the π electrons or aromatic parts. Real rigid systems are therefore only those like 2,3-dpp [17], 2,5-dpp [18], a-bpt-b$^-$ [19–23], ppz [24,25], HAT [26], tpphz [27], tpp [28], FAF [29,78], PAP [30,78] (see Table 1 for ligand formulas—for details see Refs. [17–27,30,32–35,39,40,52,62,78,81,129–143]).

The number of real rigid dinuclear compounds is too limited, and therefore we will also consider some dinuclear compounds in which we have some flexibility that will not introduce a large structural change upon modification of the conformation.

2.1. Bridging ligands

In dinuclear compounds, a key component for assembling metal units in a desired spatial organization is the bridging ligand, BL.

For covalently linked systems the electronic coupling between the donor and the acceptor chromophoric units arises from their mutual interaction through the orbitals of the intervening medium, the bridging ligand. Therefore the electronic nature of the bridging ligand, its length, and configuration, provide not only the spatial organization of the active components but are responsible for the electronic interaction between them. The bridging ligand can be constituted by spacers, saturated [29,31–35] or conjugated molecules [35–40] connected to the chelating sites, or be a multichelating organic ligand connecting two metal ions through their π-systems (fragments as pyridine, pyrazine or pyrimidine) [24,28,41–56]. The bridging ligand can be a good electron acceptor possessing low-lying π^* orbitals, or act as a good π donor and poor π^* acceptor species like imidazole type ligands [57–60]. Structural formulas and abbreviations of bridging ligands are listed in Table 1, while Table 2 lists compounds without defined energy or electron transfer processes.

Table 1
Structural formulas and abbreviations of bridging ligands

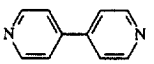
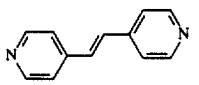
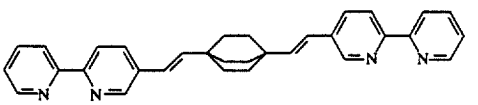
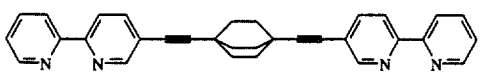
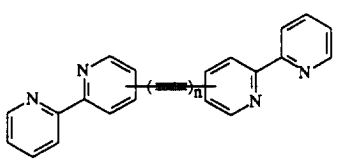
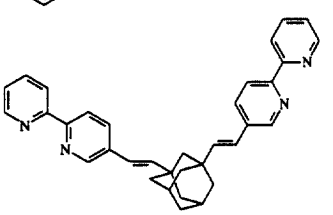
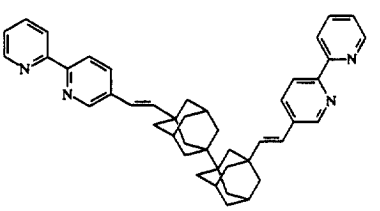
The bridging ligands	abbreviation of the compound (literature of the preparation)
	**[1] 4,4'-bpy** (commercially available)
	**[2] py-E4$_A$-py** (commercially available)
	**[3] bpy-E5$_A$-bpy** (32)
	**[4] bpy-E5$_B$-bpy** (32)
	**[5a1 + 5a2] ortho = ob-E$_n$-ob** (129) **[5b1 + 5b2] meta = mb-E$_n$-mb** (129) **[5c1 + 5c2] para = pb-E$_n$-pb** (129) **n = 1,2**
	**[6] bpy-a-bpy** (33)
	**[7] bpy-aa-bpy** (33)

Table 1 (Continued)

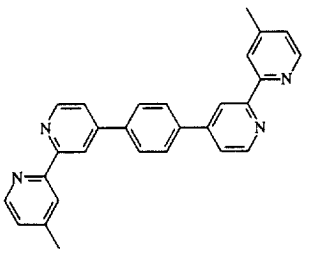
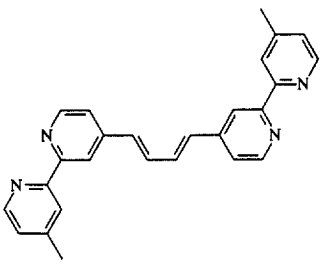
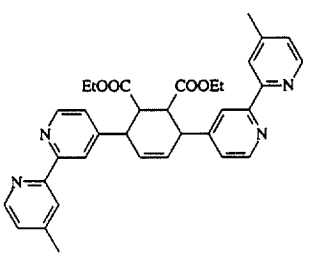
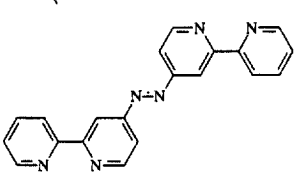
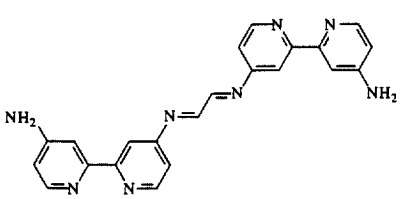
	abbreviation of the compound (literature of the preparation)
	**[8] bphb** (39)
	**[9] bbdb** (39)
	**[10] bchb** (39)
	**[11] b-azo-b** (130,143)
	**[12] DAB** (131)

Table 1 (Continued)

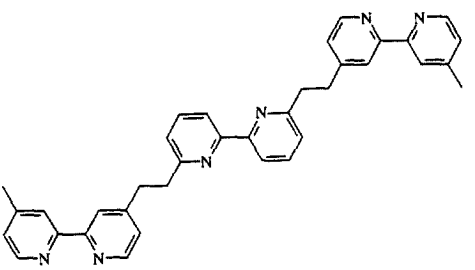
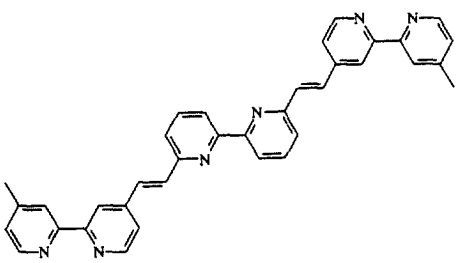
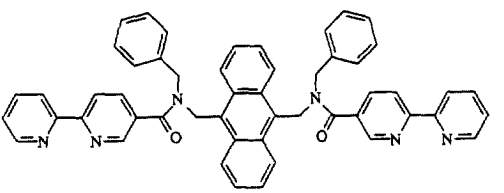
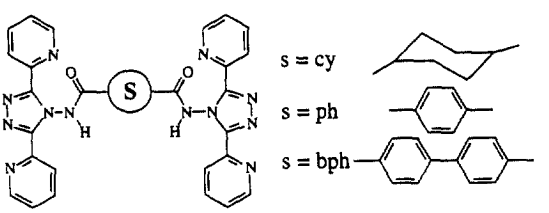
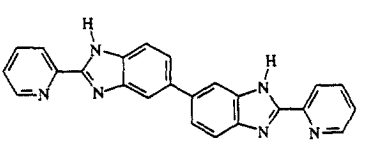
	abbreviation of the compound (literature of the preparation)
	**[13] bsbsb** (40)
	**[14] bdbdb** (40)
	**[15] bpy-A5$_A$-bpy** (81)
	**[16a] dpt-cy-dpt** (35,62) **[16b] dpt-ph-dpt** (35,62) **[16c] dpt-bdp-dpt** (35,62)
	**[17] bpbimH$_2$** (132)

Table 1 (Continued)

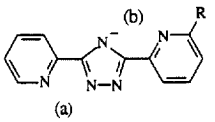
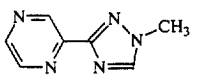
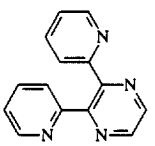
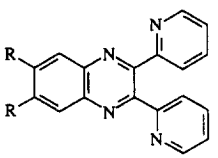
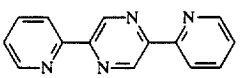
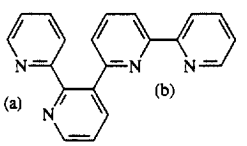
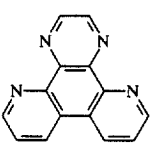
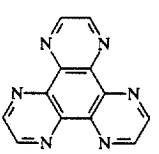
	abbreviation of the compound (literature of the preparation)
	**[18a]** **a-bpt-b⁻**, **R = H** (19,20) **[18b]** **a-mbpt-b⁻**, **R = CH_3** (21,22, 23,133)
	**[19]** **mpzt** (134)
	**[20]** **2,3-dpp** (17)
	**[21a]** **dpq** R = H **[21b]** **Me_2dpq** R = CH_3 **[21c]** **Cl_2dpq** R = Cl (according to 17)
	**[22]** **2,5-dpp** (18)
	**[23]** **bpy_a-bpy_b** (52,135)
	**[24]** **ppz** (24, 25)
	**[25]** **HAT** (26)

Table 1 (Continued)

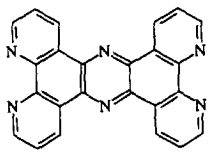
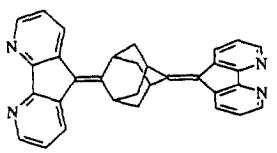
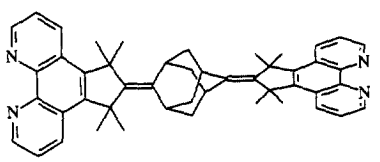
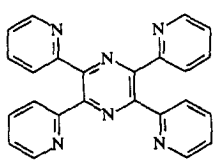
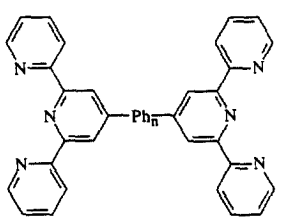
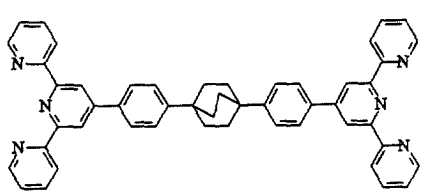
	abbreviation of the compound (literature of the preparation)
	**[26] tpphz** (27)
	**[27] FAF** (30,78)
	**[28] PAP** (30,78)
	**[29] tpp** (17) (commercially available)
	**[30a] tpy-tpy, n = 0** (136) **[30b] tpy-Ph-tpy, n = 1** (137) **[30c] tpy-Ph$_2$-tpy, n = 2** (138)
	**[31] tpy-Ph-bco-Ph-tpy** (34)

Table 1 (Continued)

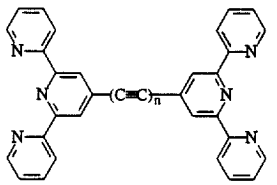
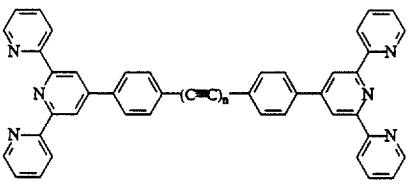
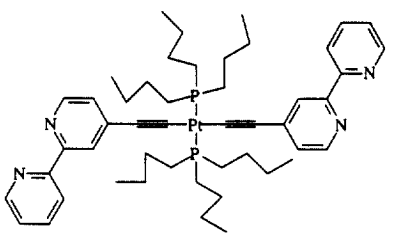
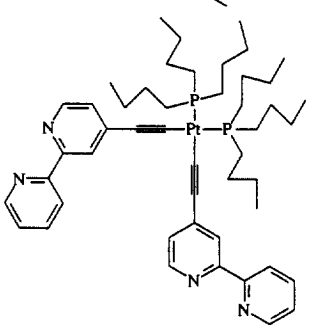
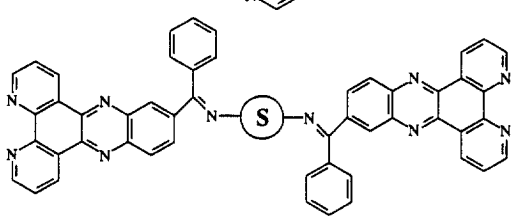
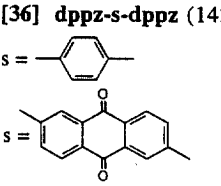
	abbreviation of the compound (literature of the preparation)
	**[32a, 32b] tpy-E$_n$-tpy** (139,140) **n = 1,2**
	**[33a, 33b] tpy-Ph-E$_n$-Ph-tpy** **n = 1,2** (139,140)
	**[34] bpy-*t*Pt-bpy** (141)
	**[35] bpy-*c*Pt-bpy** (141)
	**[36] dppz-s-dppz** (142) 

Table 2
Compounds without defined energy or electron transfer processes

Bridging ligand no.	Compound (solvent)	298 K						77 K				d_{MM} (nm)	Ref.(s)
		M_1			M_2			M_1		M_2			
		Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (μs)	Emission (nm)	τ (μs)		
1	$[Cl(dpte)_2Ru(4,4'\text{-bpy})Ru(bpy)_2Cl]^{2+}$ (AN/CH_2Cl_2)	706	51	<0.0002								1.13	[41]
1	$[(HO)(bpy)_2Ru(4,4'\text{-bpy})Os(tpy)(bpy)]^{3+}$ (H_2O; pH 11.9)				798	30	0.0011					1.13	[42]
1	$[(H_2O)(bpy)_2Ru(4,4'\text{-bpy})Os^{III}(tpy)(bpy)]^{5+}$ (H_2O; pH 1)				795	34	0.0022					1.13	[42]
1	$[(HO)(bpy)_2Ru^{III}(4,4'\text{-bpy})Os(tpy)(bpy)]^{4+}$ (H_2O; pH 10.9)				795	24	0.0025					1.13	[42]
2	$[Cl)(dpte)_2Ru(py\text{-}E4_A\text{-}py)Ru(bpy)_2Cl]^{2+}$ (AN/CH_2Cl_2)	700	60	<0.0004								1.35	[41]
3	$[(bpy)_2Ru(bpy\text{-}E5_A\text{-}bpy)Ru(bpy)_2]^{4+}$ (AN)	628	209	0.014				604	4.46			*Trans* = 1.84, *cis* = 1.65	[31,63,64]
3	$[(bpy)_2Os(bpy\text{-}E5_A\text{-}bpy)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	740	40	0.0023				727	0.89			*Trans* = 1.84, *cis* = 1.65	[31,63,64]
4	$[(bpy)_2Ru(bpy\text{-}E5_B\text{-}bpy)Ru(bpy)_2]^{4+}$ (AN)	635	231	0.015								*Trans* = 1.82, *cis* = 1.75	[32,64]
4	$[(bpy)_2Os(bpy\text{-}E5_B\text{-}bpy)Os(bpy)_2]^{4+}$ (AN)	787	29	0.0018								*Trans* = 1.82, *cis* = 1.75	[32,64]
5a1	$[(bpy)_2Ru(ob\text{-}E_1\text{-}ob)Ru\ (bpy)_2]^{4+}$ (AN)	615	4.1									0.71	[38]
5a2	$[(bpy)_2Ru(ob\text{-}E_2\text{-}ob)Ru\ (bpy)_2]^{4+}$ (AN)	625	8.6									0.87	[38]
5b1	$[(bpy)_2Ru(mb\text{-}E_1\text{-}mb)\ Ru(bpy)_2]^{4+}$ (AN)	680	1270									1.20	[38]
5b2	$[(bpy)_2Ru(mb\text{-}E_2\text{-}mb)\ Ru(bpy)_2]^{4+}$ (AN)	695	2200									1.43	[38]
5c1	$[(bpy)_2Ru(pb\text{-}E_1\text{-}pb)\ Ru(bpy)_2]^{4+}$ (AN)	690	1850									1.37	[38]
5c2	$[(bpy)_2Ru(pb\text{-}E_2\text{-}pb)\ Ru\ (bpy)_2]^{4+}$ (AN)	705	2400									1.65	[38]
6	$[(bpy)_2Ru(bpy\text{-}a\text{-}bpy)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	625	210	0.016				598	4.8			1.81 (max)	[33]
6	$[(bpy)_2Os(bpy\text{-}a\text{-}bpy)Os(bpy)]^{4+}$ (AN)	738	39	2.4×10^{-3}				725	1.0			1.81 (max)	[33]
7	$[(bpy)_2Ru(bpy\text{-}aa\text{-}bpy)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	621	217	0.014				600	4.6			1.81 (max)	[33]
7	$[(bpy)_2Os(bpy\text{-}aa\text{-}bpy)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	732	44	0.0024				723	1.1			2.23 (max)	[33]
8	$[(dmbpy)_2Ru(bphb)Ru\ (dmbpy)_2]^{4+}$ (AN)	641	1570	0.125				613, 664	5.09			1.55	[39]
9	$[(dmbpy)_2Ru(bbdb)Ru\ (dmbpy)_2]^{4+}$ (AN)	780		<0.001								1.57 (max), 1.55 (min)	[39]
10	$[(dmbpy)_2Ru(bchb)Ru\ (dmbpy)_2]^{4+}$ (AN)	628	1060	0.092				593, 645	4.61			1.27	[39]
11	$[(bpy)_2Ru(b\text{-}azo\text{-}b)Ru\ (bpy)_2]^{3+}$ (AN)	~645										1.30 (max)	[143]
11	$[(bpy)_2Os(b\text{-}azo\text{-}b)Os\ (bpy)_2]^{3+}$ (AN)	~750										1.30 (max)	[143]
12	$[(bpy)_2Ru(DAB)Ru\ (bpy)_2]^{4+}$ (DMF; 295 K)	666	130	0.0055								1.55 (max), 1.53 (min)	[131]
13	$[(bpy)_2Ru(bsbsb)Ru\ (bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	618	157	0.015				589	5500			2.25	[40]

Table 2 (Continued)

Bridging ligand no.	Compound (solvent)	298 K						77 K				d_{MM} (nm)	Ref.(s)
		M_1			M_2			M_1		M_2			
		Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (μs)	Emission (nm)	τ (μs)		
14	$[(bpy)_2Ru(bdbdb)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	661	190	0.0016				647	15600			2.23	[40]
15	$[(bpy)_2Os(bpy\text{-}A5_A\text{-}bpy)Os(bpy)_2]^{4+}$ (AN)	770	18									*Trans* = 2.07, *cis* = 1.80	[81]
16a	$[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = Et/Met)	638	110					585	4.37			1.65 (max)	[62]
16a	$[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = Et/Met 1:4)	638	100					578	4.38			1.65 (max)	[35]
16a	$[(bpy)_2Os(dpt\text{-}cy\text{-}dpt)Os(bpy)_2]^{4+}$	725	42					716	0.95			1.65 (max)	[35]
16a	$[(biq)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(biq)_2]^{4+}$ (RT = AN; 77 K = Et/Met 1:4)	740	235					735	2.40			1.65 (max)	[35]
16b	$[(bpy)_2Ru(dpt\text{-}ph\text{-}dpt)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = Et/Met 1:4)	635	115					585	4.70			1.64 (max)	[35]
16b	$[(biq)_2Ru(dpt\text{-}ph\text{-}dpt)Ru(biq)_2]^{4+}$ (RT = AN; 77 K = Et/Met 1:4)	740	240					735	2.40			1.64 (max)	[35]
16c	$[(bpy)_2Ru(dpt\text{-}bph\text{-}dpt)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = Et/Met 1:4)	630	105					580	4.80			2.06 (max)	[35]
16c	$[(biq)_2Ru(dpt\text{-}bph\text{-}dpt)Ru(biq)_2]^{4+}$ (RT = AN; 77 K = Et/Met 1:4)	745	240					735	2.35			2.06 (max)	[35]
17	$[(bpy)_2Ru(bpbimH_2)Ru(bpy)_2]^{4+}$ (AN)		560									1.11 (max), 0.72 (min)	[58,59]
	(BuCN)	629						611					[58,60]
	(Et/Met)							611	2.77				[58]
17	$[(bpy)_2Ru(bpbimH_2)Ru(4DCE\text{-}bpy)_2]^{4+}$ (BuCN)				678					649		1.11 (max), 0.72 (min)	[60]
17	$[(dmbpy)_2Ru(bpbimH_2)Ru(dmbpy)_2]^{4+}$ (RT = AN; 77 K = Et/Met)		480					611	2.22			1.11 (max), 0.72 (min)	[58]
17	$[(dmbpy)_2Ru(bpbimH_2)Ru(phen)_2]^{4+}$ (RT = AN; 77 K = Et/Met)		480					627				1.11 (max), 0.72 (min)	[58,59]
18a	$[(bpy)_2Ru(a\text{-}bpt\text{-}b)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = Et/Met)	648	100	0.002				608	3.6			0.60	[74,144]
	(Nitrile)							608	3.6				[74]
	(Nitrile)	648	100	0.0021				608	3.6				[75]
18a	$[(bpy)_2Ru(a\text{-}bpt\text{-}b)Ru(phen)_2]^{3+}$ (RT = AN; 77 K = EtOH)	640	66					606				0.60	[145]
18a	$[(phen)_2Ru(a\text{-}bpt\text{-}b)Ru(bpy)_2]^{3+}$ (RT = AN; 77 K = EtOH)				636	51		606		603		0.60	[145]
18a	$[(phen)_2Ru(a\text{-}bpt\text{-}b)Ru(phen)_2]^{3+}$ (RT = AN; 77 K = EtOH)	627	33					597				0.60	[145]

Table 2 (Continued)

Bridging ligand no.	Compound (solvent)	298 K						77 K				d_{MM} (nm)	Ref.(s)
		M_1			M_2			M_1		M_2			
		Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (μs)	Emission (nm)	τ (μs)		
18a	$[(bpy)_2Os(a\text{-}bpt\text{-}b)Os(bpy)_2]^{3+}$ (AN)	754	33									0.60	[74]
	(AN)	762	33										[146]
	(Nitrile)							742	0.34				[74]
	(Nitrile)							765	0.34				[146]
18b	$[(bpy)_2Ru(a\text{-}mbpt\text{-}b)Ru(bpy)_2]^{3+}$ (RT = AN; 77 K = nitrile)	655	65					610	3.8			0.60	[147]
19	$[(bpy)_2Ru(mpzt)Ru(bpy)_2Cl]^{3+}$ (RT = AN; 77 K = MeOH)	730						705				0.70	[148]
19	$[(bpy)_2Os(mpzt)Os(bpy)_2Cl]^{3+}$ (RT = AN; 77 K = MeOH)	n.o.						n.o.				0.70	[148]
20	$[(bpy)_2Ru(2,3\text{-}dpp)Ru(bpy)_2]^{4+}$											0.69	
	(AN)	756	134										[48]
		802	102	0.003									[49]
			125										
		802	125										[149]
		790	140	0.025				7.02	2.38				[45]
	(CH_2Cl_2)	770	154	0.065									[45]
	(EtOH)	753	84										[45]
				0.0030									[150]
		800	80	0.0012									[151]
	(Et/Met)							709	2.00				[49]
	(H_2O)	755	54										[150]
		755	53	0.0070									[24]
		800	55	0.012									[45]
	(MeOH)	797	100										[45]
20	$[(bpy)_2Ru(2,3\text{-}dpp)Ru(phen)_2]^{4+}$ (AN)	752	113									0.69	[48]
20	$[(bpy)_2Ru(2,3\text{-}dpp)Ru(biq)_2]^{4+}$											0.69	
	(AN)[a]	799	75										[49]
	(DMF)[a]	760	175										[152]
	(Et/Met)									710	3.17		[152]
										723	1.55		[49]
20	$[(dcbpyH_2)_2Ru(2,3\text{-}dpp)Ru(dcbpyH_2)_2]^{4+}$ (MeOH)	763	123					699	2.32			0.69	[45]

Table 2 (Continued)

Bridging ligand no.	Compound (solvent)	298 K						77 K				d_{MM} (nm)	Ref.(s)
		M_1			M_2			M_1		M_2			
		Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (μs)	Emission (nm)	τ (μs)		
20	$[(dcbpy)_2Ru(2,3\text{-}dpp)Ru(dcbpy)_2]^4$ (H_2O; pH 7)	778	87									0.69	[45]
20	$[(biq)_2Ru(2,3\text{-}dpp)Ru(biq)_2]^{4+}$											0.69	
	(AN)	789	65										[49]
	(DMF)	746	232										[152]
	(Et/Met)							714	2.24				[152]
								720	1.73				[49]
20	$[(biq)_2Ru(2,3\text{-}dpp)Ru(biq)_2]^{4+}$ (AN)[a]	746	153									0.69	[48]
		746	153										[45]
20	$[(bpy)_2Os(2,3\text{-}dpp)Os(bpy)_2]^{4+}$ (Et/Met)							928				0.69	[153]
21a	$[(bpy)_2Ru(dpq)Ru(bpy)_2]^{4+}$ (AN)	822	< 20									0.70	[48]
21a	$[(bpy)_2Ru(dpq)Ru(phen)_2]^{4+}$ (AN)	820	< 20									0.70	[48]
21a	$[(phen)_2Ru(dpq)Ru(phen)_2]^{4+}$ (AN)	810	20									0.70	[48]
21b	$[(bpy)_2Ru(Me_2dpq)Ru(bpy)_2]^{4+}$ (AN)	808										0.70	[50]
21c	$[(bpy)_2Ru(Cl_2dpq)Ru(bpy)_2]^{4+}$ (AN)	860										0.70	[50]
22	$[(bpy)_2Ru(2,5\text{-}dpp)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = Et/Met)[a]	824	155					771	0.94			0.70	[49]
22	$[(bpy)_2Ru(2,5\text{-}dpp)Ru(biq)_2]^{4+}$ (RT = AN; 77 K = Et/Met)[a]	830	190					792	1.00			0.70	[49]
22	$[(biq)_2Ru(2,5\text{-}dpp)Ru(biq)_2]^{4+}$ (RT = AN; 77 K = Et/Met)[a]	820	170					722	1.82			0.70	[49]
22	$[(bpy)_2Os(2,5\text{-}dpp)Os(bpy)_2]^{4+}$ (Et/Met)							984				0.70	[153]
23	$[(bpy)_2Ru(bpy_a\text{-}bpy_b)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	674	232	0.019				612	5.7			Planar = 0.73, ⊥ = 0.59	[51]
23	$[(bpy)_2Ru(bpy_a\text{-}bpy_b)Ru(bpy)_2]^{4+}$ (DMF/CH_2Cl_2)	656	340	0.022				615	5.3			Planar = 0.73, ⊥ = 0.59	[52]
23	$[(bpy)_2Os(bpy_a\text{-}bpy_b)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	814	21	0.00088				756	1.2			Planar = 0.73, ⊥ = 0.59	[51]
24	$[(bpy)_2Ru(ppz)Ru(bpy)_2]^{4+}$ (H_2O)	820	≤ 50	0.0157								0.69	[24]
25	$[(bpy)_2Ru(HAT)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = Et/Met)	> 800	550					727	2.7			0.69	[53]
	(H_2O)	825	148										[26]
	(H_2O)	> 800	160										[53]
25	$[(bpy)_2Ru(HAT)Ru(tap)_2]^{4+}$ (RT = AN; 77 K = Et/Met)				> 800	182			3.5			0.69	[53]
	(H_2O)				> 800	57							[53]

Table 2 (Continued)

Bridging ligand no.	Compound (solvent)	298 K						77 K				d_{MM} (nm)	Ref.(s)
		M_1			M_2			M_1		M_2			
		Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (μs)	Emission (nm)	τ (μs)		
25	$[(bpy)_2Ru(HAT)Ru(HAT)_2]^{4+}$ (RT = AN; 77 K = EtOH/MeOH)				>800	232		725	2.8			0.69	[53]
	(H_2O)				>800	54							[53]
25	$[(phen)_2Ru(HAT)Ru(phen)_2]^{4+}$ (RT = AN; 77 K = EtOH/MeOH)	>800	830					738	4.2			0.69	[53]
25	$[(phen)_2Ru(HAT)Ru(phen)_2]^{4+}$ (H_2O)	>800	260										[53]
26	$[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ (AN)	671										1.29	[54–56]
27	$[(bpy)_2Ru(FAF)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	605	0.3					577	5.5			1.60	[29]
27	$[(bpy)_2Os(FAF)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	720	41					577	5.5			1.60	[29]
28	$[(bpy)_2Ru(PAP)Ru(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	610	145					583	5.5			2.10	[30,78]
28	$[(bpy)_2Os(PAP)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	717	41					709	1.0			2.10	[30,78]
29	$[(tpy)Ru(tpp)Ru(tpp)]^{4+}$ (AN)	833	100									0.67	[28]
29	$[(tpy)Os(tpp)Ru(tpp)]^{4+}$ (AN)	820	120									0.67	[28]
30a	$[(ttpy)Ru(tpy\text{-}tpy)Ru(ttpy)]^{4+}$ (EtOH/MeOH)							674	12.9			1.10	[36]
30b	$[(tpy)Ru(tpy\text{-}E_1\text{-}tpy)Ru(tpy)]^{4+}$ (AN)	722	565	0.0014								1.37	[37,38]
30c	$[(tpy)Ru(tpy\text{-}E_2\text{-}tpy)Ru(tpy)]^{4+}$ (AN)	735	720	0.0021								1.63	[37,38]
33a	$[(tpy)Ru(tpy\text{-}Ph\text{-}E_1\text{-}Ph\text{-}tpy)Ru(tpy)]^{4+}$ (AN)	670	3.2									2.36	[37,38]
33b	$[(tpy)Ru(tpy\text{-}Ph\text{-}E_2\text{-}Ph\text{-}tpy)Ru(tpy)]^{4+}$ (AN)	665	5.5									2.62	[37,38]
34	$[(bpy)_2Ru(bpy\text{-}i\text{Pt}\text{-}bpy)Ru(bpy)_2]^{4+}$ (AN)	625	1300	0.084								1.93	[116]
34	$[(bpy)_2Os(bpy\text{-}i\text{Pt}\text{-}bpy)Os(bpy)_2]^{4+}$ (AN)	750	68	0.0048								1.93	[116]

[a] Lowest excited state is Ru → BL.

2.2. Spacers and connectors

In many dinuclear complexes the bridging ligand contains a spacer, a conjugated or saturated molecule that can be a modular unit providing a way to tune the distance, and the electronic interaction between the two chromophores. The spacer plays a very important role since it is one of the components responsible for the electronic coupling between the metal units. The use of phenyl or diphenyl derivatives as spacers has been described by several authors [36–39,61], and extremely rapid and efficient photoinduced processes have been reported. However when a saturated spacer, like *bicyclo*[2.2.2]octane, has been introduced as a component of the bridging ligand, even in the presence of phenyl spacer the electronic coupling between the chromophores drastically decreases and the photoinduced processes become much slower (see Section 4.1) [34,61]. Only recently the synthesis of derivatives of fully saturated spacers as cyclohexyl, adamantane, *bicyclo*[2.2.2]octane, cyclobutane [29–35,61–65], has allowed the construction of rigid dinuclear systems, and the investigations on these compounds have shown that all the photoinduced processes are quite slow and the bridging ligand acts as a poor contacting unit. It is clear therefore that one can modulate the rates of the energy and electron transfer processes with an appropriate choice of the spacer.

It is important to notice however that the use of rigid spacers as polyphenylenes or saturated molecules will provide in some cases a fixed metal–metal distance, but does not prevent conformational effects. In fact rotation around formally single bonds will confer some conformational freedom, and if the intercomponent interaction proceeds via the π system of the bridge, the tilt angle between the spacers can have relevant consequences [66] on metal–metal interactions and on electron transfer rates (Fig. 2a). Therefore the connections between the spacers and/or the chelating sites is another factor that should not be neglected. Many authors have reported the use of double [29–34,61,63,64] or triple bonds [32,37,38,64,67] as connecting units. The double bonds however can cause the existence of different conformers in solution and as a consequence a change in the distance between the two chromophoric units (Fig. 2b). Only when the double bond is the only connection between the spacer and the chelating sites we could talk of rigid system [29,30], otherwise the use of triple bond is more appealing [32,37,38,64,67].

2.3. Chelating sites and metal complexes

The transition metal complexes used as building blocks for the dinuclear systems described in this review are ruthenium and osmium containing mainly bidentate (N–N) or tridentate (N–N–N) polypyridine type ligands [68–71]. In Ru(II) and Os(II) complexes, the lowest excited state is a metal-to-ligand-charge-transfer (MLCT) state of formal triplet multiplicity (Os has a high degree of spin–orbit coupling). The energy of these states depends on the redox properties of the metal and of the ligands, which can be easily determined by electrochemical measurements. For the same metal the oxidation potential, that is metal centered, depends strongly on electron donating and/or electron withdrawing power of the coordi-

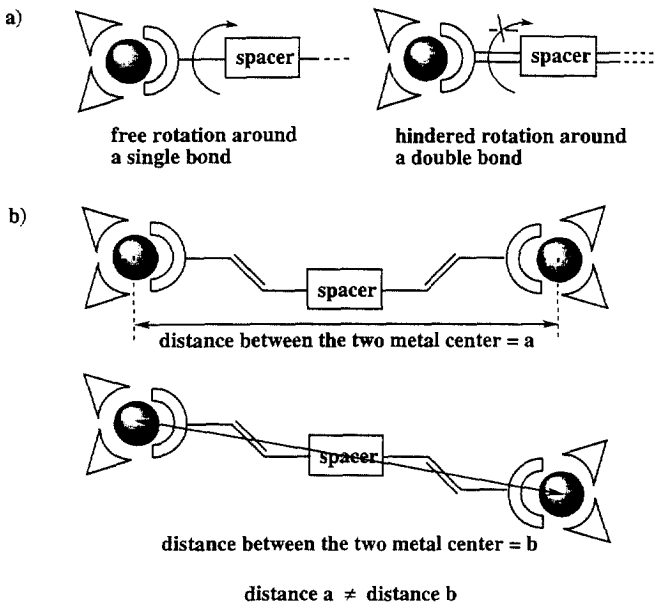


Fig. 2. (a) Free rotation around a single bond is the cause of the existence of different conformers. (b) Conformers have different distances between the two metal centers.

nated ligands, which can be tuned by changing the substituents on the ligands. In polypyridine complexes, Os(II) is easier to oxidize than Ru(II), and therefore for compounds of the same ligands the MLCT levels lie at higher energy in the Ru(II) than in the Os(II) complexes. The lifetime of the luminescent ^{3}MLCT states depends in a complex way on their energy: the absolute energy is relevant (because of the energy gap law for radiationless deactivation), but the energy gap to reach the ligand field or metal centered, MC states of the metal is also important. Indeed the possibility to populate such states by thermal activation is one of the main radiationless deactivation paths of the luminescent excited state. Bidentate N–N ligands like bpy and phen (bpy, 2,2′-bipyridine; phen, 1,10-phenanthroline) are much better chelating units than tridentate species like tpy (tpy, 2,2′:6′,2″-terpyridine) for Ru(II) because of the bite of the chelating sites. As a consequence at room temperature in fluid solution $[Ru(bpy)_3]^{2+}$ and $[Ru(phen)_3]^{2+}$ exhibit a strong and long-lived luminescence (τ of the order of 10^2–10^3 ns) ([8]a), whereas $[Ru(tpy)_2]^{2+}$ is very weakly luminescent (τ ca. 0.25 ns) ([6]a) because of the low energy of the MC states, that can be thermally populated from the luminescent ^{3}MLCT state (Fig. 3). Recently however the spectroscopic properties of Ru–tpy type complexes have been improved by appending suitable groups at the 4′ position of the tpy ligand. The use of electron withdrawing substituents [72] or groups that effect electronic delocalization [37] over the tpy fragment has made possible to obtain long-lived excited Ru–tpy type units. From a structural viewpoint, the dinuclear compounds containing a bridging ligand based on tpy derivatives posses a high degree of

geometrical control and the metal centers are kept at fixed distances and are linearly aligned with BL [73].

Very recently we have reported a new approach to combine the electronic properties of the tris bpy arrangement and the structural properties of a perfectly linear, rigid, aligned bridge [29,30]. The control of the energetic and geometric factors allows the mechanistic study of photoinduced processes, the manipulation of their rates, and finally to control the factors to build up photochemical molecular devices.

Another important consideration is concerned with the peripheral ligands. In many dinuclear compounds the lowest excited state involve the bridging ligand, since very often the lowest LUMO is localized on the more delocalized π system of the bridge. Therefore in such cases the peripheral ligands play only a minor role in the excited state properties of the complexes. On the other hand when the peripheral ligands have excited states lower in energy than the bridging ligand, upon light excitation the lowest MLCT will involve the ancillary ligands and the distance between the two examples chromophoric groups will be larger (Fig. 4). This consideration will in principle allow the construction of dinuclear compounds in which the lowest excited state can involve either the bridging ligand or the peripheral ligand depending on the substituents (electron donor or acceptor groups) on the ancillary ligands (Fig. 4).

A similar situation has been observed in the case of electron rich bridging ligands like for instance the a-bpt-b$^-$, in which the lowest excited state is localized on the peripheral ligands [74,75].

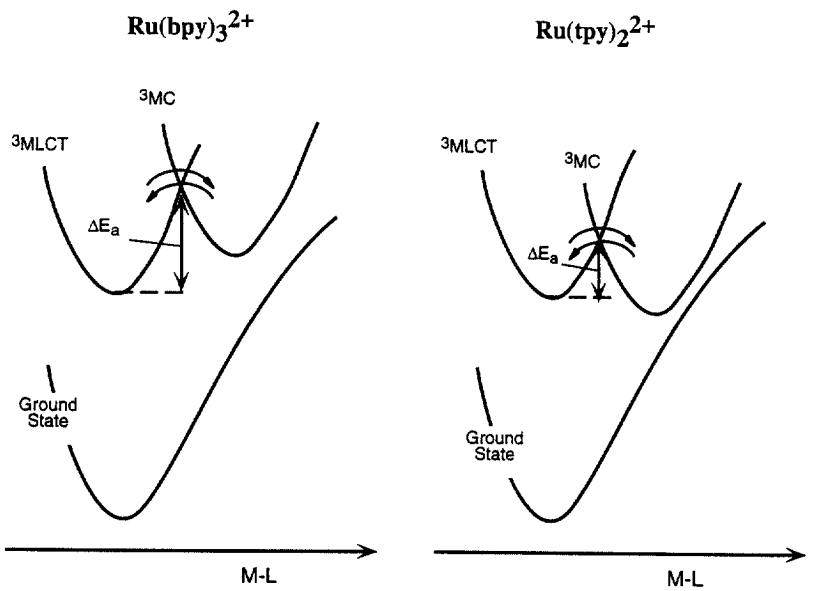


Fig. 3. ^{3}MC and ^{3}MLCT excited states in the two metal complexes $Ru(bpy)_3^{2+}$ and $Ru(tpy)_2^{2+}$. The smaller ΔE_a value for $Ru(tpy)_2^{2+}$ leads to very efficient deactivation of the luminescent excited state.

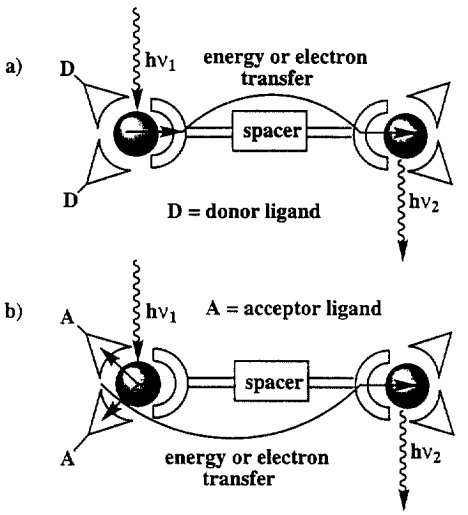


Fig. 4. The donor or acceptor ability of the ancillary ligands influences the energy or electron transfer process. The situation with (a) donor and (b) acceptor ligands.

3. Synthetic strategies

The general route for the synthesis of dinuclear compounds is given by the separate preparation of a bridging ligand, and of the mononuclear metal complex precursors. Difficulties during the preparation can be due either to the insolubility of the bridging ligand in common solvents or during the formation of the bridged heteronuclear metal complexes. The preparation of the bridging ligands is generally an organic synthesis that often requires a building block strategy. Few simple molecular fragments give after a coupling reaction a variety of new bridging ligands. An interesting example is given by the family of the ligands FAF and PAP in which the fragments are connected by the Barton reaction (double extrusion reaction) [29,30,76–78]. Other organic reactions which are often used as coupling reactions are the Wittig reaction [32], reductive homo-coupling reaction [16], cross-coupling reaction following the methodology developed by Suzuki et al. [79,80], the amide [81] or ester formation [82]. Other coupling reactions are described in Refs. [83–86]. Of course the choice of the spacers, the connections, the chelating sites is rather critical as discussed in Section 2. The introduction of a double bond as connector was an ideal choice in the case of the PAP and FAF bridging ligands in which a linear arrangement of the two metal centers and the connecting bridging ligand together with the desired photophysical properties of the donor and acceptor unit ($[M(bpy)_3]^{2+}$ or $[M(phen)_3]^{2+}$) was achieved [29,30,78].

One of the drawbacks of the synthesis of rigid, rod-like bridging ligands is their insolubility in common organic solvents that gives difficulties in the purification steps. Attaching long aliphatic or polyether chains either at the spacer unit or on the ligand part (py, bpy, phen, tpy) leads to a drastically change of the solubility of the whole system [87].

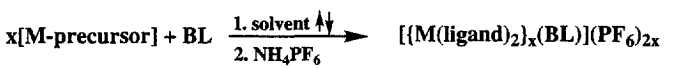
3.1. Metal complex formation

The synthesis of homo-, dinuclear metal complexes with bpy or phen as chelating sites of the bridging ligands, for example Ru-bridge-Ru and Os-bridge-Os, needs no special effort for their preparation. Heating of an appropriate metal precursor (e.g. $Ru(bpy)_2Cl_2$) and the corresponding bridging ligand in a polar solvent (ethylene glycol, methoxyethanol, butanol) gives in good yield the desired compound (see Scheme 1a) [88]. A very fast method for thermally inert ligand systems is the use of a microwave oven for the synthesis [89,90]. The heating time can then be shortened to some minutes.

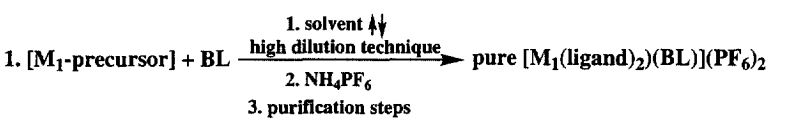
The situation for the preparation of heteronuclear, rigid, bridged metal complexes containing, bpy- or phen-type ancillary ligands is different (see Scheme 1b). Due to the often observed small solubility of the bridging ligands (organic material) in polar solvent only homo-, dinuclear compounds can be isolated and not the planned mononuclear metal complexes. A possible explanation for this behavior lies in the excellent solubility of the charged mononuclear complex (a very soluble organic salt) and therefore the enhanced reaction rate for the second metal center. To overcome such a problem, several methods were developed. High dilution technique combined with a slow addition of the reactants (by a syringe-pump) can help to improve the yield of the mononuclear metal complex [91]. A change of the

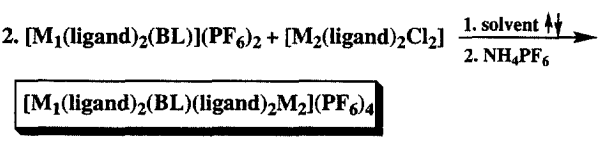
Complexes with bpy or phen as peripheral ligands

a) synthesis of homonuclear complexes (one step reaction)



b) synthesis of heteronuclear complexes (two step reaction)



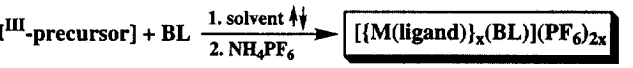


x = 1, 2
M, M_1, M_2 = Ru, Os
ligand = bpy, phen
BL = bridging ligand
[M-precursor] = $[M(ligand)_2Cl_2]$, $[M(ligand)_2DME](triflate)_2$
solvent = ethane-1,2-diol, 2-methoxy-ethanol, DME, $CHCl_3$

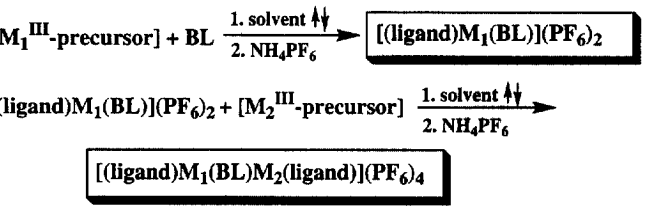
Scheme 1.

Complexes with tpy or ttpy as peripheral ligands

a) synthesis of homo mono- and dinuclear complexes



b) synthesis of heteronuclear complexes (two step reaction)



x = 1, 2
M, M_1, M_2 = Ru, Os
ligand = tpy, ttpy
BL = bridging ligand
[M-precursor] = [M(ligand)Cl_3],
[M(ligand)(acetone)$_3$]$^{3+}$,
[M(ligand)((CH)$_3$)$_2$$CO_3$)]$^{3+}$, [$Os^{IV}$(ligand)$(O)_2$(OH)]$^+$
solvent = ethane-1,2-diol, ethanol, ethanol/H_2O/NEt_3,
MeOH or THF/H_2O with H_2/platinum or H_2N-NH_2

Scheme 2.

metal precursor gives often better results. The preparation of the compound $[(bpy)_2Ru(PAP)Os(bpy)_2](PF_6)_4$ is only possible with the precursor $[(bpy)_2Ru(DME)](triflate)_2$ (Scheme 1) [92]. Both, the metal precursor and the bridging ligand are soluble in a mixture of DME (dimethoxyethane)/$CHCl_3$ and the charged mononuclear metal complex precipitate immediately after his formation. Another way to get a better yield of the mononuclear precursor is the modification of the bridging ligand. Adding long aliphatic- or poly-ether chains changes the solubility of the bridging ligands either towards non polar solvents or to more polar solvents [87].

The preparation of homo- and heteronuclear metal complexes with terpyridine as peripheral ligands follows in the most cases a two-step reaction [16] (see Scheme 2). In the first step the mononuclear species has been isolated, purified and then in a second step the dinuclear compound will be completed by addition of a second metal unit.

The oxidation state of the metal center of the precursor complexes in Scheme 2 is 3+. During the reaction process, the metal center is reduced to the oxidation state 2+ by a partial oxidation of the used polar solvent (e.g. ethane-1,2-diol).

3.2. New methodologies

New strategies for the preparation of bridged metal complexes were developed during the last few years. A first breakthrough was observed by the group of Balzani/Denti [93]. They developed the so called principle of complexes as metal and complexes as ligands [94]. The strategy works very well with the bridging ligand 2,3-dpp. Through a protection process (methylation on the pyridine-N), the 2,3-dpp can be transformed into a ligand system that contains only one binding site to metal center [95]. After complexation of the free site the protection can be removed. The now free ligand site is available for coordination to another metal center. A different approach was described by the group of Tor et al. [96]. They constructed the bridging ligand by a Pd-mediated coupling process with modified ruthenium complexes (positive charged) as reactants. The coupling process needs polar solvents (DMF) in which the metal precursors are highly soluble. A further system was described by McDonnell and co-workers [55,56]. The synthesis of the tpphz bridging ligand was performed by a coupling reaction between two different metal complexes. One complex contains the ligand 1,10-phenanthroline-5,6-dione and the other the ligand 1,10-phenanthroline-5,6-diamine. The condensation occurs by refluxing in a 1:1 $MeCN/H_2O$ mixture in nearly quantitative yield.

3.3. Purification and characterization

Several purification methods for the isolation of pure dinuclear metal complexes can be used. The usual purification can contain the following steps:

1. If the compounds are water-soluble (Cl^- as counter ion) an extraction of an aqueous solution with dichloromethane separates the remaining organic material.
2. Precipitation and isolation of the metal complex as PF_6^--salt.
3. A preliminary column chromatography on alox (with acetone/1–2% water as eluent) gives a raw product.
4. Preparative plate chromatography (silica gel; different polar eluents [29,97]) leads to a nearly pure sample. The technique of elution of the metal complexes from the silica gel is described in literature [29,97].
5. A further purification step is recrystallisation by the vapor-phase technique [29,97].

The characterization of the metal complexes includes the well-known analysis methods: ^1H- and ^{13}C-NMR, MS-technique with different ionization sources, elemental analysis, IR-, UV–vis- and fluorescence-spectroscopy, electrochemical analysis and crystal structure determinations.

4. Energy transfer

For complexes of the same ligands the MLCT levels lie at higher energy in the Ru(II) than in the Os(II) complexes [5,69–71,101], and therefore in $Ru^{II}BLOs^{II}$

complex an intercomponent energy transfer process from the Ru-based to the Os-based component can take place (Fig. 5). The free energy change ($\Delta G°$) for the energy transfer reaction can be expressed by the difference between the zero–zero spectroscopic energies of the donor and the acceptor excited state [98–102], that can be estimated from the luminescence band maxima of Ru and Os reference complexes taken at 77 K.

An evaluation of the rate constant of the energy transfer process can be obtained from Eqs. (1a) and (1b):

$$k_{en} = 1/\tau°(I°/I - 1) \tag{1a}$$

$$k_{en} = 1/\tau - 1/\tau° \tag{1b}$$

where $I°$ and $\tau°$ are the luminescence intensity and lifetime, respectively, of the species that can be quenched, the Ru(II)-based component, and I and τ the residual luminescence intensity and lifetime after quenching.

Evidence for energy transfer as the sole quenching mechanism can be obtained by sensitization experiments or by risetime measurements [31].

The measurements however can be somewhat complicated by the lack of selective excitation of the Ru-based chromophoric unit because of the similar absorption properties of the Os-unit, and therefore a substantial fraction of Os-based excited states are already present when the Os-based excited states originate from the energy transfer process. Furthermore, it is interesting to note that intramolecular energy transfer processes are almost temperature independent [36,67,102–104] because of the small reorganizational energy involved in such reactions.

The energy transfer processes can occur by two mechanisms: the Förster type mechanism (through space) [105] based on coulombic interactions, and the Dexter-type mechanism (through bond) [106], based on exchange interactions. The energy

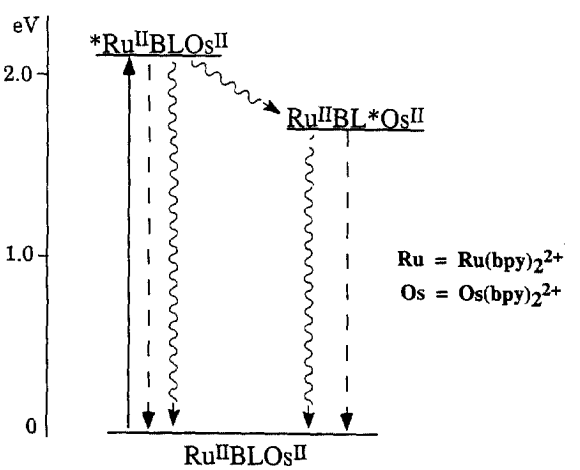


Fig. 5. Energy level diagram showing the photoinduced energy transfer deactivation process in Ru^{II}–BL–Os^{II}. Key: full line, excitation; dotted line, luminescence; wavy line, radiationless decay.

transfer rate constants according to Förster and Dexter treatments can be evaluated using Eq. (2) [103] and Eq. (3) [107], respectively:

$$k_F = \frac{8.8 \times 10^{-25} K^2 \Phi}{n^4 \tau r^6} J_F \quad (2)$$

$$k_D = \frac{4\pi^2 H^2}{h} J_D \quad (3)$$

where K is an orientation factor which accounts for the directional nature of the dipole–dipole interaction; Φ and τ are the emission quantum yield and mean lifetime of the donor, respectively; r the distance in nm between the donor and acceptor unit; n is the solvent refractive index; H is the intercomponent electronic interaction energy [98,108]; h is Planck's constant. J_F and J_D, are the overlap integrals, according to the two different theories, between the luminescence spectrum of the donor, and the absorption spectrum of the acceptor [103].

Both through bond and through space transfer mechanisms can operate in donor–acceptor systems. Very often these mechanisms occur competitively and in some cases they can practically add to each other and their relative contribution is difficult to evaluate. The coulombic mechanism ([8]b, [168–170]) is a long-range mechanism that does not require physical contact between donor and acceptor. The most important term for this mechanism is the dipole–dipole term, that obeys the same selection rules as the corresponding electric dipole transitions of the two partners. Therefore the typical example of an efficient coulombic mechanism is that of singlet–singlet energy transfer. In metal complexes the only excited state of appreciable lifetime is generally the lowest [170], spin forbidden excited state, so that coulombic energy transfer is not expected to be frequent in these systems. For metal units which weakly interact through bonds, for instance in the case of dinuclear compounds containing bridging ligands having saturated spacers, the Förster-type mechanism should be more efficient also in view of the partial singlet character of the ^{3}MLCT level of the Ru and Os–diimine complexes. A large electronic coupling between the energy donor and the energy acceptor units favors the Dexter mechanism and the experimental values for the rate of the energy transfer process become quite large, greater than the estimated value calculated using the Förster equation.

4.1. Selected examples

Table 3 collects the data for several dinuclear $Ru^{II}BLOs^{II}$ complexes. We have calculated the distances between the two metal units just considering a center-to-center average distance (see also [109]).

Even though is quite difficult to compare the systems reported, it is interesting to notice that there is a quite good correlation between the nature of the bridging ligand and the rate of the energy transfer processes if the distance is more or less constant. Bridges constituted by polyphenylenes, polyynes, or polyenes promote very fast through bond energy transfer, whereas introduction of a saturated spacer

Table 3
Energy transfer

Bridging ligand no.	Compound (solvent)	298 K						77 K				k (s^{-1})	ΔG (eV)	d_{MM} (nm)	Ref.(s)
		M_1			M_2			M_1		M_2					
		Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (μs)	Emission (nm	τ (μs)				
1	$[(H_2O)(bpy)_2Ru(4,4'\text{-bpy})Os(tpy)(bpy)]^{4+}$ (H_2O; pH 5)				798	31	0.0085							1.13	[42]
3	$[(bpy)_2Ru(bpy\text{-}E5_A\text{-}bpy)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	625	18	0.0014	740	39	0.0023	601	0.031	723	1.0	5×10^7	−0.35	*Trans* = 1.84, *cis* = 1.65	[31,63,64, 154]
4	$[(bpy)_2Ru(bpy\text{-}E5_B\text{-}bpy)Os(bpy)_2]^{4+}$ (AN)	638	22	0.0013	787	29	0.0018							*Trans* = 1.82, *cis* = 1.75	[32,64]
5a	$[(bpy)_2Ru(ob\text{-}E_1\text{-}ob)Os(bpy)_2]^{4+}$ (AN)				755	58						1.78×10^{10}	−0.45	0.71	[38]
5b	$[(bpy)_2Ru(mb\text{-}E_1\text{-}mb)Os(bpy)_2]^{4+}$ (AN)				835	52						2.7×10^{10}	−0.37	1.20	[38]
5c	$[(bpy)_2Ru(pb\text{-}E_1\text{-}pb)Os(bpy)_2]^{4+}$ (AN)				805	65						2.5×10^{10}	−0.34	1.37	[38]
6	$[(bpy)_2Ru(bpy\text{-}a\text{-}bpy)Os(bpy)_2]^{4+}$ (AN)	626	1.7	0.00013	736	38	0.0024	595	0.05	720	1.1	5.8×10^8	0.36	1.81 (max)	[33,154]
												1.4×10^8 and 2.0×10^7 (77 K)	0.36		[33]
11	$[(bpy)_2Ru(b\text{-}azo\text{-}b)Os(bpy)_2]^{3+}$ (AN)	~645	1.6		~750							6.8×10^8		1.30 (max)	[143]
15	$[(bpy)_2Ru(bpy\text{-}A5_A\text{-}bpy)Os(bpy)_2]^{4+}$ (AN)	640	2.1		770	16								*Trans* = 2.07, *cis* = 1.80	[81,127]
16a	$[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Os(bpy)_2]^{2+}$ (RT = AN; 77 K Et/Met)	620	56		724	34		580	4.85	715	0.90			1.65 (max)	[155]
16a	$[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(biq)_2]^{4+}$ (RT = AN; 77 K = Et/Met 1:4)	640	32		750	280		590	1.70	730	2.38	2.2×10^7 (298 K), 3.6×10^5 (77 K)	−0.20	1.65 (max)	[35]
16b	$[(bpy)_2Ru(dpt\text{-}ph\text{-}dpt)Ru(biq)_2]^{4+}$ (RT – AN; 77 K = Et/Met 1:4)	630	39		760	290		590	1.50	730	2.50	1.7×10^7, 4.4×10^5 (77 K)	−0.20	1.64 (max)	[35]
16c	$[(bpy)_2Ru(dpt\text{-}bph\text{-}dpt)Ru(biq)_2]^{4+}$ (RT = AN; 77 K = Et/Met 1:4)	630	92		750	280		580	3.06	730	2.56	2.0×10^6, 1.2×10^5 (77 K)	−0.20	2.06 (max)	[35]
18a	$[(bpy)_2Ru(a\text{-}bpt\text{-}b)Os(bpy)_2]^{3+}$ (RT = AN; 77 K = nitrile)				751	30				726	0.67			0.60	[74]
18a	$[(bpy)_2Ru(b\text{-}bpt\text{-}a)Os(bpy)_2]^{3+}$ (RT = AN; 77 K = nitrile)				758	28				730	0.59			0.60	[74]
19	$[(bpy)_2Ru(mpzt)Os(bpy)_2Cl]^{3+}$ (MeOH)									786				0.70	[148]

Table 3 (Continued)

Bridging ligand no.	Compound (solvent)	298 K						77 K				k (s^{-1})	ΔG (eV)	d_{MM} (nm)	Ref.(s)
		M_1			M_2			M_1		M_2					
		Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (μs)	Emission (nm	τ (μs)				
22	$[(bpy)_2Ru(2,5\text{-}dpp)Os(bpy)_2]^{4+}$ (Et/Met)									968				0.70	[153]
22	$[(bpy)_2Ru(2,5\text{-}dpp)Os(biq)_2]^{4+}$ (Et/Met)									900				0.70	[153]
23	$[(bpy)_2Ru(bpy_a\text{-}bpy_b)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)				756	41	0.0032			716	1.5			Planar = 0.73, ⊥ = 0.59	[51]
23	$[(bpy)_2Ru(bpy_b\text{-}bpy_a)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)				808	26	0.0013			756	1.0			Planar = 0.73, ⊥ = 0.59	[51]
27	$[(bpy)_2Ru(FAP)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	605	0.29		720	40		577	0.0039	703	1.1	2.6×10^8	−0.40	1.6	[29,154]
28	$[(bpy)_2Ru(PAP)Os(bpy)_2]^{4+}$ (RT = AN; 77 K = BuCN)	609	21		712	41		581	0.041	705	1.2	4.0×10^7	−0.38	2.1	[30,78,154]
30a	$[(ttpy)Ru(tpy\text{-}tpy)Os(ttpy)]^{4+}$ (BuCN)				800	110	0.0013					$\geq10^{10}$		1.10	[117–119]
30b	$[(ttpy)Ru(tpy\text{-}Ph\text{-}tpy)Os(ttpy)]^{4+}$ (BuCN)				746	190	0.015					$\geq10^{10}$		1.53	[117–119]
30c	$[(ttpy)Ru(tpy\text{-}Ph_2\text{-}tpy)Os(ttpy)]^{4+}$ (BuCN)				738	200	0.013					$\geq10^{10}$		1.96	[117–119]
31	$[(ttpy)Ru(tpy\text{-}Ph\text{-}bco\text{-}Ph\text{-}tpy)Os(ttpy)]^{4+}$ (DMF/CH_2Cl_2)	640	1.1		634	125		634	0.22	727	2.8	4.4×10^6 (77 K)		2.35	[34,61]
32a	$[(tpy)Ru(tpy\text{-}E_1\text{-}tpy)Os(tpy)]^{4+}$ (RT = AN; 77 K = EtOH)		0.014	<0.0001	746	225	0.016	640	$7.2\,10^{-4}$	730	2.4	7.1×10^{10}	−0.13	1.37	[38,156]
32b	$[(tpy)Ru(tpy-E_2-tpy)Os(tpy)]^{4+}$ (RT = AN; 77 K = EtOH)	700	0.027	<0.0001	760	200	0.010					5.0×10^{10}	−0.11	1.63	[38,156]
34	$[(bpy)_2Ru(bpy\text{-}t\text{Pt}\text{-}bpy)Os(bpy)_2]^{4+}$ (AN)	625	80	0.007	745	65	0.0050					1.3×10^7	0.35	1.93	[38,116]
35	$[(bpy)_2Ru(bpy\text{-}c\text{Pt}\text{-}bpy)Os(bpy)_2]^{4+}$ (AN)											1.0×10^7	0.35	1.37	[38]

reduce the rates and facilitate a mixed type mechanism where the through space (Förster-type) energy transfer has a strong influence. Dinuclear compounds containing alkyne spacers have been investigated by Harriman, Ziessel and coworkers [37,38,67,110], and can be considered molecular wires for their extremely efficient electronic transmission. In the systems $[(tpy)Ru(tpy\text{-}E_n\text{-}tpy)Os(tpy)]^{4+}$ [38,67], and $[(bpy)_2Ru(pb\text{-}E_n\text{-}pb)Os(bpy)_2]^{4+}$, $[(bpy)_2Ru(mb\text{-}E_n\text{-}mb)Os(bpy)_2]^{4+}$, $[(bpy)_2Ru(ob\text{-}E_n\text{-}ob)Os(bpy)_2]^{4+}$ [38] triplet energy transfer from the ruthenium(II) unit to the osmium(II) complex was quantitative and occured on a picosecond time scale ($k_{en} \sim 10^{10}$ s^{-1}; see Table 3). Such results indicate the remarkable superexchange properties of the bridge assuming an electron exchange mechanism for the observed energy transfer processes. The attenuation factor β estimated for energy transfer through alkyne bridges is of the order of 0.17 $Å^{-1}$ [38]. This is a rather small value, being smaller only for polyalkenes ($\beta = 0.06$ $Å^{-1}$) [105,106,111–113] for which, however, it should be noted that their use as bridging ligand can be prevented by their very low excited state, that can act as a very efficient triplet state quencher [114,115]. Very recently Ziessel et al. have also reported the $[(bpy)_2Ru(bpy\text{-}Pt\text{-}bpy)Os(bpy)_2]^{4+}$ complex (*cis* and *trans* form) in which coordination of a Pt unit into the bridge cause a switch in the mechanism of the energy transfer process [38,116].

In the field of molecular wires, even though the electronic conduction is not as efficient as for the polyalkynes, polyphenyls play an important role. Barigelletti, Sauvage, Scandola, Constable, Schmehl [39,117–120] have studied dinuclear compounds in which the bridging ligand is constituted by one or two phenyl units. The results obtained show that a very efficient and very fast ($k_{en} > 10^{10}$ s^{-1}) energy transfer occurs with a Dexter mechanism [117–119]. Temperature dependence studies on the energy transfer rate constants have also been performed [104].

For the phenyl spacer the attenuation factor is of the order of $\beta = 0.4$ $Å^{-1}$. The value was obtained for an electron transfer process [121,122], but recently the value of 0.33 $Å^{-1}$ [36,103] for an energy transfer process was obtained. Interposition of a saturated group like *bicyclo*[2.2.2]octane between two phenyl units causes a remarkable slowdown of the Ru→Os energy transfer rate ($k_{en} = 4.4 \times 10^6$ s^{-1}) [34,117–119]. This is not a surprising result since the *bicyclo*[2.2.2]octane unit is a well known poor contacting group because it breaks the π–π^* frame of molecular orbitals centred on the phenylene units and provide a σ–σ^* orbital mechanism which is less efficient for the transmission of the intermetal interaction.

We have prepared and investigated several systems containing saturated molecules, $[(bpy)_2Ru(FAF)Os(bpy)_2]^{4+}$, $[(bpy)_2Ru(PAP)Os(bpy)_2]^{4+}$, $[(bpy)_2Ru(bpy\text{-}E5\text{-}bpy)Os\ (bpy)_2]^{4+}$ [29–33,63,64]. In our investigations the distance between the metal centers ranges from 1.6 to 2.1 nm. It is interesting to notice that in the two dinuclear compounds where the two metal units are perpendicular to each other $[(bpy)_2Ru(FAF)Os(bpy)_2]^{4+}$, and $[(bpy)_2Ru(PAP)Os(bpy)_2]^{4+}$, the electronic coupling is extremely small (few wavenumber), but the energy transfer process is quite efficient ($k_{en} = 4.0 \times 10^7$ s^{-1} for the PAP system; see Table 3). Förster calculation have shown that the estimated value for the energy transfer rate constant is not too different from the experimental one, suggesting that for these type of complexes the Dexter contribution is minor.

5. Electron transfer

The theory of electron transfer has been described and reviewed by several authors [10,125,154,172] and only few basic concepts will be treated in this contribution.

In order to observe a photoinduced electron transfer the process must be thermodynamically allowed. If one considers a dinuclear system in which a metal unit can act as an electron donor D, and the other as an electron acceptor, A, it is possible using the ground-state redox potentials (reported in Table 5) to calculate the excited state redox potentials:

$$E°(D^+/D^*) = E°(D^+/D) - E_{00} \quad (4)$$

$$E°(A^*/A^-) = E°(A/A^-) + E_{00} \quad (5)$$

Thus for the photoinduced electron transfer reaction:

$$^*D\text{–}BL\text{–}A \rightarrow D^+\text{–}BL\text{–}A^-$$

the free energy change $\Delta G°$ can be estimated, neglecting the Coulombic stabilization energy of the products, as follows:

$$\Delta G° = E°(D^+/D) - E°(A/A^-) - E_{00} \quad (6)$$

In the nonadiabatic limit, if the electronic interaction is very small [123–125], the rate constant of an electron transfer process can be expressed by:

$$k_{el} = \nu_{el} \exp(-\Delta G^{\neq}_{el}/RT) \quad (7)$$

where ν_{el} is an effective frequency for nuclear motion, and $\Delta G^{\neq}_{el}$ is the free activation energy. $\Delta G^{\neq}_{el}$ depends on the driving force of the reaction and on the reorganizational energy λ, as expressed by the Marcus equation ([154]d):

$$\Delta G^{\neq}_{el} = (\lambda/4)(1 + \Delta G°/\lambda)^2 \quad (8)$$

Dealing with dinuclear metal complexes the electronic interaction is strongly dependent on the length, electronic nature and geometry of the bridging ligand.

The role of the bridging ligand in enhancing the electronic coupling between the two chromophoric groups in a supramolecular species has been described in terms of superexchange theory [173].

In homo-, dinuclear Ru or Os compounds the photoinduced electron transfer can be observed only if one metal unit is chemically or electrochemically oxidized. The oxidation of the ruthenium moiety is however rather difficult to achieve for several compounds since the oxidation potential of the Ru unit is rather high (Table 5) and the Ru(III) species is not stable in common organic solvents. In the case of the osmium complexes oxidation is easier and the Os(III) unit can be stabilized by the use of protic solvents. For weaker interacting metal units, where the two species are oxidized at the same potential, addition of the oxidant leads to a statistical distribution of the M^{II}–BL–M^{II}, M^{III}–BL–M^{II}, and M^{III}–BL–M^{III} species. The molar fractions of the three species are given by $(1-x)^2$, $2(1-x)x$, and x^2, where

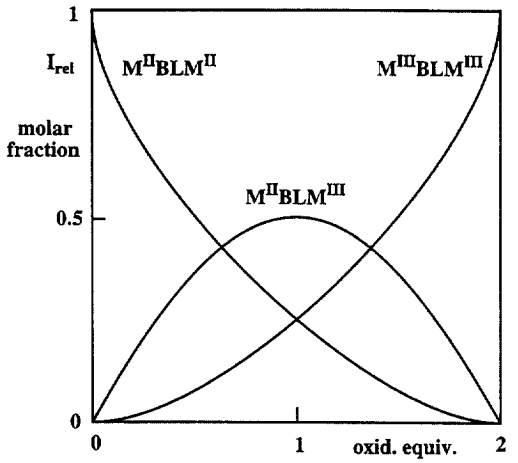


Fig. 6. Changes in the relative luminescence intensities of $M^{II}-BL-M^{II}$. The curves represent the molar fractions of the $M^{II}-BL-M^{II}$, $M^{II}-BL-M^{III}$ and $M^{III}-BL-M^{III}$ species, as a function of added oxidation equivalents.

x is the fraction of added oxidation equivalents (Fig. 6) [31]. Therefore in the presence of an efficient luminescence quenching due to an electron transfer process only the $M^{II}-BL-M^{II}$ species is responsible for the observed luminescence. Excited state lifetime measurements should also show a more complicated behavior since a double exponential decay, (the quenched and unquenched excited states lifetimes) must be observed. The rate constants for the electron transfer processes can be estimated from the quenched and unquenched lifetimes [30,32,33,78].

In the case of heterometallic Ru–BL–Os complexes the two metal ions generally have different oxidation potentials, and if the interaction between the metals is weak, Os-based oxidation can be selectively achieved. In the mixed metal compound $*Ru^{II}-BL-Os^{III}$ the Ru-based luminescence is quenched by an electron transfer process (see Fig. 7), leading to the $Ru^{III}-BL-Os^{II}$ according to the reaction:

$$*Ru^{II}-BL-Os^{III} \xrightarrow{el}{}^{tr} Ru^{III}-BL-Os^{II}$$

The transient $Ru^{III}-BL-Os^{II}$ species then decays to its intervalence ground state isomer $Ru^{II}-BL-Os^{III}$ (back electron transfer process) (see Fig. 7).

Electron transfer reactions can be directly observed by laser flash photolysis experiments since the reduced or oxidized species often have a characteristic absorption spectrum. In the absence of significant experimental data concerning intermediate species, electron transfer processes can be distinguished by energy transfer quenching mechanism because of the lack of the osmium sensitized luminescence upon excitation of the ruthenium moiety, and in some cases by the different temperature dependence behavior. It was mentioned (Section 4) that for an energy transfer process the change in temperature cause almost no change in the rate of the process. On the other hand an electron transfer reaction can be blocked

by freezing the solvent if the process is not exothermic enough [171]. This can be explained by the fact that solvent reorganization cannot take place in rigid matrices, and the products are therefore energetically destabilized in comparison with the fluid case.

The values of the experimental rate constants, free energy changes and distance between the metal units are reported in Table 4, while the electrochemical data for various compounds are listed in Table 5.

5.1. Selected examples

Table 4 collects all the electron transfer data available for rigid Ru and/or Os dinuclear compounds. Few data are available for highly conjugated bridging ligands [34]. Most of the systems reported contain saturated bridging ligands [174] where electron transfer reactions are rather slow. It is well known that saturated molecules behave as poor contacting units and large attenuation factors have been reported for such groups ($\beta = 0.85$–0.95 Å^{-1}).

An interesting case is represented by the dinuclear complexes involving the PAP bridging ligand (see Fig. 8). These systems are really rigid rod-like molecules in which the two metal centers are in a fixed geometric arrangement, perpendicular each other. For the homonuclear $Os^{II}PAPOs^{II}$ compound partial oxidation leads to the $Os^{II}PAPOs^{III}$ mixed valence species. In this case the luminescence lifetime of the $Os^{II}PAPOs^{III}$ unit at room temperature was 23 ns compared with 41 ns for the unoxidized $Os^{II}PAPOs^{II}$ species which leads to an electron transfer rate constant of 1.9×10^7 s^{-1} [126]. As we have mentioned above, in the case of the mixed metals compound $Ru^{II}PAPOs^{II}$ selective oxidation of the Os-based unit can be achieved. The luminescence from this unit decreases linearly upon addition of the oxidant and as expected, once the Os^{II} species is completely oxidized, the luminescence is

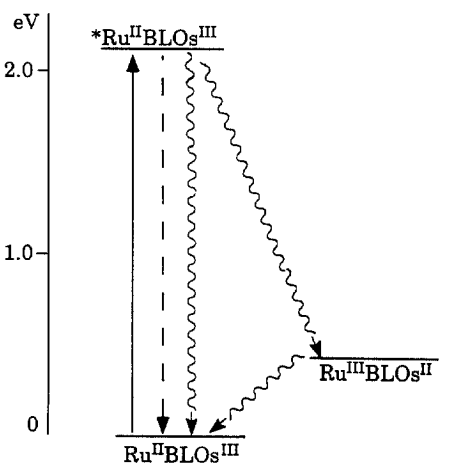


Fig. 7. Energy level diagram showing the photoinduced electron transfer deactivation process in Ru^{II}–BL–Os^{III}. Key: full line, excitation; dotted line, luminescence; wavy line, radiationless decay.

Table 4
Electron transfer

Bridging ligand no.	Compound (solvent)	M_1					k (s^{-1})	ΔG (eV)	d_{MM} (nm)	Ref.(s)
		298 K			77 K					
		Emission (nm)	τ (ns)	Φ	Emission (nm)	τ (ns)				
1	$[Cl(dpte)_2Ru(4,4'\text{-bpy})Ru^{III}(bpy)_2Cl]^{2+}$ (AN/CH_2Cl_2)	708	54	0.0002			$>10^7$ (220 K)		1.13	[41]
2	$[Cl)(dpte)_2Ru(py\text{-}E4_A\text{-}py)Ru^{III}\text{-}(bpy)_2Cl]^{3+}$ (AN/CH_2Cl_2)	704	50	<0.0004			$>10^7$ (220 K)		1.35	[41]
3	$[(bpy)_2Ru(bpy\text{-}E5_A\text{-}bpy)Ru^{III}(bpy)_2]^{5+}$ (AN)	628	0.94						*Trans* = 1.84, *cis* = 1.65	[31,154]
3	$[(bpy)_2Ru(bpy\text{-}E5_A\text{-}bpy)Os^{III}(bpy)_2]^{5+}$ (AN)	625	0.115				8.7×10^9	1.62	*Trans* = 1.84, *cis* = 1.65	[31,154]
3	$[(bpy)_2Ru^{III}(bpy\text{-}E5_A\text{-}bpy)Os(bpy)_2]^{5+}$ (AN)						1.0×10^6	−0.44	*Trans* = 1.84, *cis* = 1.65	[154]
3	$[(bpy)_2Os(bpy\text{-}E5_A\text{-}bpy)Os^{III}(bpy)_2]^{5+}$ (AN)	740	0.2				5.0×10^9	−1.71	*Trans* = 1.84, *cis* = 1.65	[31,154]
6	$[(bpy)_2Ru(bpy\text{-}a\text{-}bpy)Os^{III}(bpy)_2]^{5+}$ (AN)	620	0.35				2.8×10^9	−1.61	1.81 (max)	[33,154]
6	$[(bpy)_2Ru^{III}(bpy\text{-}a\text{-}bpy)Os(bpy)_2]^{5+}$ (AN)						4.0×10^7	−0.46	1.81 (max)	[154]
6	$[(bpy)_2Os(bpy\text{-}a\text{-}bpy)Os^{III}(bpy)_2]^{5+}$ (AN)	735	0.25				3.5×10^9	−1.71	1.81 (max)	[33,154]
7	$[(bpy)_2Os(bpy\text{-}aa\text{-}bpy)Os^{III}(bpy)_2]^{5+}$ (AN)	735	1.1				8.8×10^8	−1.71	2.23 (max)	[33,154]
26	$[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$ (AN)	618							1.29	[54–56]
27	$[(bpy)_2Ru(FAF)Os^{III}(bpy)_2]^{5+}$ (AN)		0.240				8.3×10^8	−1.69	1.60	[29,154]
27	$[(bpy)_2Ru^{III}(FAF)Os(bpy)_2]^{5+}$ (AN)						2.9×10^7	−0.46	1.6	[154]
27	$[(bpy)_2Os(FAF)Os^{III}(bpy)_2]^{5+}$ (AN)		2.4				3.9×10^8	−1.75	1.60	[29,154]
28	$[(bpy)_2Ru(PAP)Os^{III}(bpy)_2]^{5+}$ (AN)						7.5×10^6	−1.68	2.1	[154]
28	$[(bpy)_2Ru^{III}(PAP)Os(bpy)_2]^{5+}$ (AN)						8.3×10^3	0.44	2.1	[154]
28	$[(bpy)_2Os(PAP)Os^{III}(bpy)_2]^{5+}$ (AN)						2.7×10^7	−1.74	2.10	[30,78,154]
31	$[(ttpy)Ru(tpy\text{-}Ph\text{-}bco\text{-}Ph\text{-}tpy)Os^{III}(ttpy)]^{5+}$ (DMF/CH_2Cl_2)	640	1.1		632	10.5	$<10^8$	−1.65	2.35	[34]

Table 5
Electrochemical data

Bridging ligand no.	Compound	Solvent	Reference electrode	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	Ref.(s)
1	$[Cl(dpte)_2Ru(4,4'\text{-bpy})Ru(bpy)_2Cl]^{2+}$	AN	SCE	+1.20, +0.81		[41]
1	$[Cl(dpte)_2Ru(4,4'\text{-bpy})Ru^{III}(bpy)_2Cl]^{3+}$	AN	SCE	+1.20	+0.82	[41]
2	$[Cl(dpte)_2Ru(py\text{-}E4_A\text{-}py)Ru(bpy)_2Cl]^{2+}$	AN	SCE	+1.21, +0.79		[41]
2	$[Cl(dpte)_2Ru(py\text{-}E4_A\text{-}py)Ru^{III}(bpy)_2Cl]^{3+}$	AN	SCE	+1.21	+0.79	[41]
3	$[(bpy)_2Ru(bpy\text{-}E5_A\text{-}bpy)Ru(bpy)_2]^{4+}$	AN	SCE	+1.25 [2] (Ru)	−1.31 [2] (bpy)	[31,63,64]
3	$[(bpy)_2Ru(bpy\text{-}E5_A\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+1.25 [1] (Ru), +0.81 [1] (Os)	1.30 [2] (bpy)	[31,63,64]
3	$[(bpy)_2Os(bpy\text{-}E5_A\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+0.81 [2] (Os)	−1.25 [2] (bpy)	[31,63,64]
4	$[(bpy)_2Ru(bpy\text{-}E5_B\text{-}bpy)Ru(bpy)_2]^{4+}$	AN	SCE	+1.28 [2] (Ru)		[32,64]
4	$[(bpy)_2Ru(bpy\text{-}E5_B\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+1.27 [1] (Ru), +0.84 [1] (Os)		[32,64]
4	$[(bpy)_2Os(bpy\text{-}E5_B\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+0.84 [2] (Os)		[32,64]
5a1	$[(bpy)_2Ru(ob\text{-}E_1\text{-}ob)Ru(bpy)_2]^{4+}$	AN	SCE	+1.35 [2] (Ru)	−1.02, −1.26	[38]
5a1	$[(bpy)_2Ru(ob\text{-}E_1\text{-}ob)Os(bpy)_2]^{4+}$	AN	SCE	+0.85 [1] (Os)	−1.11, −1.21	[38]
5a2	$[(bpy)_2Ru(ob\text{-}E_2\text{-}ob)Ru(bpy)_2]^{4+}$	AN	SCE	+1.31 [2] (Ru)	−1.00, −1.18	[38]
5b1	$[(bpy)_2Ru(mb\text{-}E_1\text{-}mb)Ru(bpy)_2]^{4+}$	AN	SCE	+1.38 [2] (Ru)	−0.92, −1.16	[38]
5b1	$[(bpy)_2Ru(mb\text{-}E_1\text{-}mb)Os(bpy)_2]^{4+}$	AN	SCE	+0.81 [1] (Os)	−0.97, −1.11	[38]
5b2	$[(bpy)_2Ru(mb\text{-}E_2\text{-}mb)Ru(bpy)_2]^{4+}$	AN	SCE	+1.35 [2] (Ru)	−0.90, −1.12	[38]
5c1	$[(bpy)_2Ru(pb\text{-}E_1\text{-}pb)Ru(bpy)_2]^{4+}$	AN	SCE	+1.31 [2] (Ru)	−0.94, −1.19	[38]
5c1	$[(bpy)_2Ru(pb\text{-}E_1\text{-}pb)Os(bpy)_2]^{4+}$	AN	SCE	+0.82 [1] (Os)	−1.04, −1.14	[38]
5c2	$[(bpy)_2Ru(pb\text{-}E_2\text{-}pb)Ru(bpy)_2]^{4+}$	AN	SCE	+1.29 [2] (Ru)	−0.86, −1.04	[38]
6	$[(bpy)_2Ru(bpy\text{-}a\text{-}bpy)Ru(bpy)_2]^{4+}$	AN	SCE	+1.27 [2] (Ru)	−1.29 [2]	[33]
6	$[(bpy)_2Ru(bpy\text{-}a\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+1.26 [1] (Ru), +0.80 [1] (Os)	−1.27 [2]	[33]
6	$[(bpy)_2Os(bpy\text{-}a\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+0.80 [2] (Os)	−1.25 [2]	[33]
7	$[(bpy)_2Ru(bpy\text{-}aa\text{-}bpy)Ru(bpy)_2]^{4+}$	AN	SCE	+1.25 [2] (Ru)	−1.29 [2]	[33]
7	$[(bpy)_2Os(bpy\text{-}aa\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+0.81 [2] (Os)	−1.21 [2]	[33]
8	$[(dmbpy)_2Ru(bphb)Ru(dmbpy)_2]^{4+}$	AN	SSCE	+1.13 [2] (Ru)	−1.28, −1.40, −1.58	[39]
9	$[(dmbpy)_2Ru(bbdb)Ru(dmbpy)_2]^{4+}$	AN	SSCE	+1.14 [2] (Ru)	−1.05, −1.16, −1.57	[39]
10	$[(dmbpy)_2Ru(bchb)Ru(dmbpy)_2]^{4+}$	AN	SSCE	+1.13 [2] (Ru)	−1.37, −1.59, −1.82	[39]
11	$[(bpy)_2Ru(b\text{-}azo\text{-}b)Ru(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.79 [2] (Ru)	−0.69 [1] (BL), −1.12 [1] (BL), −1.84 [1] (bpy)	[143]
11	$[(bpy)_2Ru(b\text{-}azo\text{-}b)Os(bpy)_2]^{4+}$	AN	Fc/Fc^+	+1.11 [1] (Ru), +0.68 [1] (Os)	−0.57 [1] (BL), −0.97 [1] (BL), −1.65 [1] (bpy)	[143]

Table 5 (Continued)

Bridging ligand no.	Compound	Solvent	Reference electrode	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	Ref.(s)
11	$[(bpy)_2Os(b\text{-}azo\text{-}b)Os(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.52 [2] (Os)	−0.72 [1] (BL), −1.11 [1] (BL), −1.79 [1] (bpy)	[143]
12	$[(bpy)_2Ru(DAB)Ru(bpy)_2]^{4+}$	DMF	SCE	+1.01 [2] (Ru)	-0.83, −1.35, −1.59	[131]
13	$[(bpy)_2Ru(bsbsb)Ru(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.84		[40]
14	$[(bpy)_2Ru(bdbdb)Ru(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.85		[40]
16a	$[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(bpy)_2]^{4+}$	AN	SCE	+1.33 [2] (Ru)	−1.30 [2] (bpy), −1.54 [2] (bpy)	[62]
16a	$[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(bpy)_2]^{4+}$	AN	SCE	+1.33 [2]	−1.28 [2], −1.52 [2]	[35]
16a	$[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(biq)_2]^{4+}$	AN	SCE	+1.54 [1], +1.32 [1]	-0.58 [1], −0.88 [1]	[35]
16a	$[(biq)_2Ru(dpt\text{-}cy\text{-}dpt)Ru(biq)_2]^{4+}$	AN	SCE	+1.50 [2]	−0.60 [2], −0.90 [2]	[35]
16a	$[(bpy)_2Ru(dpt\text{-}cy\text{-}dpt)Os(bpy)_2]^{4+}$	AN	SCE	+1.30 [1] (Ru), +0.79 [1] (Os)	−1.33 [2] (bpy), −1.51 [2] (bpy)	[155]
16a	$[(bpy)_2Os(dpt\text{-}cy\text{-}dpt)Os(bpy)_2]^{4+}$	AN	SCE	+0.84 [2] (Os)	−1.27 [2] (bpy), −1.58 [2] (bpy)	[62]
16b	$[(bpy)_2Ru(dpt\text{-}ph\text{-}dpt)Ru(bpy)_2]^{4+}$	AN	SCE	+1.32 [2]	−1.30 [2], −1.55 [2]	[35]
16b	$[(bpy)_2Ru(dpt\text{-}ph\text{-}dpt)Ru(biq)_2]^{4+}$	AN	SCE	+1.54 [1], +1.30 [1]	0.62 [1], −0.80 [1]	[35]
16b	$[(biq)_2Ru(dpt\text{-}ph\text{-}dpt)Ru(biq)_2]^{4+}$	AN	SCE	+1.52 [1]	−0.60 [2], −0.86 [2]	[35]
16c	$[(bpy)_2Ru(dpt\text{-}bph\text{-}dpt)Ru(bpy)_2]^{4+}$	AN	SCE	+1.30 [1]	−1.26 [2], −1.50 [2]	[35]
16c	$[(bpy)_2Ru(dpt\text{-}bph\text{-}dpt)Ru(biq)_2]^{4+}$	AN	SCE	+1.50 [1], +1.30 [1]	−0.64 [1], −0.90 [1]	[35]
16c	$[(biq)_2Ru(dpt\text{-}bph\text{-}dpt)Ru(biq)_2]^{4+}$	AN	SCE	+1.50 [1]	−0.62 [2], −0.88 [2]	[35]
17	$[(bpy)_2Ru(bpbimH_2)Ru(bpy)_2]^{4+}$	AN	Fc/Fc+	+0.777 [1] (Ru)	-1.780 I [1] (BL), −1.875 [1] (bpy), −2.145 [1] (bpy)	[58]
		AN	Ag/AgCl	+0.94 [2] (Ru)		[132]
		AN/H_2O	Ag/AgCl	+0.98 [1] (Ru), +0.94 [1] (Ru)		[157]
17	$[(dmbpy)_2Ru(bpbimH_2)Ru(dmbpy)_2]^{4+}$	AN	Fc/Fc^+	+0.680 (Ru)		[58]
17	$[(dmbpy)_2Ru(bpbimH_2)Ru(phen)_2]^{4+}$	AN/H_2O	Ag/AgCl	+0.86 [1] (Ru-dmbpy), +0.97 [1] (Ru-phen)		[157]
18a	$[(bpy)_2Ru(a\text{-}bpt\text{-}b)Ru(bpy)_2]^{3+}$	AN	SCE	+1.34 [1] (Ru), +1.04 [1] (Ru)	−1.40 [2] (bpy), −1.62 [1] (bpy), −1.67 [1], −2.22 [1], −2.33 I [1]	[158]
18a	$[(bpy)_2Ru(a\text{-}bpt\text{-}b)Ru(phen_2]^{3+}$	AN	SCE	+1.07 [1], +1.38 [1]	−1.35 [1], -1.71 [1]	[145]
18a	$[(phen_2Ru(a\text{-}bpt\text{-}b)Ru(bpy)_2]^{3+}$	AN	SCE	+1.06 [1], +1.37 [1]	−1.33, −1.71	[145]
18a	$[(phen)_2Ru(a\text{-}bpt\text{-}b)Ru(phen)_2]^{3+}$	AN	SCE	+1.04 [1], +1.34 [1]	−1.48, −1.71	[145]
18a	$[(bpy)_2Ru(a\text{-}bpt\text{-}b)Os(bpy)_2]^{3+}$	AN	SCE	+1.20 [1] (Ru), +0.73 [1] (Os)	−1.33 [1] (bpy), −1.41 [1] (bpy)	[159]
18a	$[(bpy)_2Ru(b\text{-}bpt\text{-}a)Os(bpy)_2]^{3+}$	AN	SCE	+1.30 [1] (Ru), +0.65 [1] (Os)	−1.36 [2] (bpy)	[159]
18a	$[(bpy)_2Os(a\text{-}bpt\text{-}b)Os(bpy)_2]^{3+}$	AN	SCE	+0.64 [1], +0.85 [1]	-1.34 [2] (bpy), −1.58 [1] (bpy), −1.68 [1]	[146]
18b	$[(bpy)_2Ru(a\text{-}mbpt\text{-}b)Ru(bpy)_2]^{3+}$	AN	SCE	+1.34 [1], +1.04 [1]	−1.37 [1] (bpy), −1.42 [1] (bpy), −1.62 [1] (bpy)	[147]

Table 5 (Continued)

Bridging ligand no.	Compound	Solvent	Reference electrode	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	Ref.(s)
19	$[(bpy)_2Ru(mpzt)Ru(bpy)_2Cl]^{4+}$	AN	SCE	+1.41, +0.92	0.97, 1.51, 1.57, 1.76	[148]
19	$[(bpy)_2Ru(mpzt)Os(bpy)_2Cl]^{4+}$	AN	SCE	+1.41, +0.53	−0.95, −1.51, −1.75, −1.89	[148]
19	$[(bpy)_2Os(mpzt)Ru(bpy)_2Cl]^{4+}$	AN	SCE	+1.04, +0.86	−0.87, −1.49, −1.70, −1.87	[148]
19	$[(bpy)_2Os(mpzt)Os(bpy)_2Cl]^{4+}$	AN	SCE	+1.00, +0.50	−0.80, −1.53, −1.74, −1.89	[148]
20	$[(bpy)_2Ru(2,3\text{-}dpp)Ru(bpy)_2]^{4+}$	AN	SCE	+1.76 [1] (Ru), +1.57 [1] (Ru)		[150]
		AN	SCE	+1.52 [1] (Ru), +1.33 [1] (Ru)	−0.71, −1.18, −1.55	[24]
		AN	SCE	+1.65 [1] (Ru), +1.44 [1] (Ru)	−0.64, −1.13, −1.4	[48]
		AN	Ag/AgCl	+1.72 [1] (Ru), +1.50 [1] (Ru)		[151]
		AN	SCE	+1.55 [1] (Ru), +1.38 [1] (Ru)	−0.67 [1] (BL), −1.17 [1] (BL), −1.57 [2] (bpy), −1.89 [2] (bpy)	[49]
		AN	Ag/AgCl	+1.61 [1] (Ru), +1.43 [1] (Ru)	−0.61 [1] (BL), −1.09 [1] (BL)	[50]
		AN	Fc/Fc^+	+1.16 [1] (Ru), +0.99 [1] (Ru)	−1.05 (BL), −1.55 (BL), −1.95 (bpy)	[149]
		AN	SCE	+1.61 [1] (Ru), +1.41 [1] (Ru)	−0.69 [1] (BL)	[160]
		DMF	SCE		1.19 [1] (BL), ca. −1.4 (bpy), ca. −1.5 (bpy), −1.73 (bpy), −1.86 (bpy)	[160]
		DMF	Ag/AgCl		−0.60 [1] (BL), −1.04 [1] (BL), −1.37 [1] (bpy), −1.47 [1] (bpy), −1.64, −1.77	[151]
20	$[(bpy)_2Ru(2,3\text{-}dpp)Ru(phen)_2]^{4+}$	AN	SCE	+1.61 [1] (Ru), +1.41 [1] (Ru)	−0.6 i, −1.15 i, −1.4 i	[48]
20	$[(bpy)_2Ru(2,3\text{-}dpp)Ru(biq)_2]^{4+}$	AN	SCE	+1.48 [1] (Ru), +1.36 [1] (Ru)	−0.68 [1] (BL), −1.18 [1], −1.57 [2], −1.81 [2]	[49]
		DMF	SCE		−0.75 (biq), −0.93 (biq), −1.10 (BL)	[152]
20	$[(phen)_2Ru(2,3\text{-}dpp)Ru(phen)_2]^{4+}$	AN	SCE	+1.65 [1] (Ru), +1.44 [1] (Ru)	−0.64 [1] (BL), −1.13 (BL), −1.38	[161]
		DMF	Ag/AgCl		−0.62 [1] (BL), −1.03 [1] (BL), −1.34 [1] (bpy), −1.41 [1] (bpy), 1.61 [1] (bpy), −1.74 [1] (bpy)	
20	$[(biq)_2Ru(2,3\text{-}dpp)Ru(biq)_2]^{4+}$	AN	SCE	+1.57 [2] (Ru)	−0.45 [1] (BL), −0.81 [2] (biq), −0.95 [1] (BL), −1.19 [2] (biq)	[49]
		DMF	SCE		−0.71 (biq), −0.87 (biq), −1.07 (BL)	[152]
20	$[(bpy)_2Ru(2,3\text{-}dpp)Os(bpy)_2]^{4+}$	AN	Ag/AgCl	+1.56 [1] (Ru), +1.01 [1] (Os)		[162]
		DMF	SCE	> +1.60 (Ru), +0.90 (Os)	−0.73 (BL), −1.13 (BL), −1.45 (bpy), −1.55 (bpy), −1.73 (bpy), −1.89 (bpy)	[163]

Table 5 (Continued)

Bridging ligand no.	Compound	Solvent	Reference electrode	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	Ref.(s)
20	$[(bpy)_2Ru(2,3\text{-}dpp)Os(bpy)_2]^{4+}$	DMF	Ag/AgCl		−0.62 [1] (BL), −1.03 [1] (BL), −1.34 [1] (bpy), −1.41 [1] bpy), −1.61 [1] (bpy), −1.74 [1] (bpy)	[162]
20	$[(bpy)_2Os(2,3\text{-}dpp)Os(bpy)_2]^{4+}$	AN	SCE	+1.20 [1] (Os), +0.90 [1] (Os)	−0.68 [1] (BL), −1.10 [1] (BL), −1.38 [2] bpy), −1.62 [2] (bpy)	[164]
		AN	Ag/AgCl	+1.22 [1] (Os), +0.91 [1] (Os)	−0.68 [1] (BL), −1.06 [1] (BL)	[165]
		DMF	Ag/AgCl		−0.61 [1] (BL), −1.00 [1] (BL), −1.28 [1] (bpy), −1.38 [1] (bpy), −1.58 [1] (bpy), −1.76 [1] (bpy)	[165]
		DMF	SCE	+1.12 [1] (Os), +0.83 [1] (Os)	−0.72 (BL), −1.10 (BL), −1.39 (bpy), −1.50 (bpy), −1.69 (bpy), −1.89 (bpy)	[163]
21a	$[(bpy)_2Ru(dpq)Ru(bpy)_2]^{4+}$	AN	SCE	+1.62 [1] (Ru), +1.47 [1] (Ru)	−0.37 [0.96] (BL), −1.10 [1] (BL)	[166]
				+1.64 [1] (Ru), +1.48 [1] (Ru)	−0.40, −1.09, −1.4	[48]
				+1.68 [1] (Ru), +1.50 [1] (Ru)	−0.37 [1] (BL), −1.15 [1] (BL), ca. −1.4 [1] (bpy), ca. −1.5 [1] (bpy), −1.70 [1] (bpy), −1.82 [1] (bpy)	[160]
		AN	Ag/AgCl	+1.67 [1] (Ru), +1.52 [1] (Ru)	−0.32 [1] (BL), −1.10 [1] (BL)	[50]
21a	$[(bpy)_2Ru(dpq)Ru(phen)_2]^{4+}$	AN	SCE	+1.69 [1] (Ru), +1.51 [1] (Ru)	−0.36, −1.08, −1.41	[48]
21b	$[(bpy)_2Ru(Me_2dpq)Ru(bpy)_2]^{4+}$	AN	Ag/AgCl	+1.65 [1] (Ru), +1.48 [1] (Ru)	−0.41 [1] (BL), −1.15 [1] (BL)	[50]
21c	$[(bpy)_2Ru(Cl_2dpq)Ru(bpy)_2]^{4+}$	AN	Ag/AgCl	+1.72 [1] (Ru), +1.53 [1] (Ru)	−0.20 [1] (BL), −0.89 [1] (BL)	[50]
22	$[(bpy)_2Ru(2,5\text{-}dpp)Ru(bpy)_2]^{4+}$	AN	SCE	+1.58 [1] (Ru), +1.39 [1] (Ru)	−0.55 [1] (BL), −1.09 [1] (BL), −1.30 [>1] (bpy)	[46]
		AN	SCE	+1.54 [1] (Ru), +1.37 [1] (Ru)	−0.53 [1] (BL), −1.08 [1] (BL), −1.50 [2] (bpy), −1.81 [2] (bpy)	[49]
22	$[(bpy)_2Ru(2,5\text{-}dpp)Ru(biq)_2]^{4+}$	AN	SCE	+1.43 [2] (Ru)	−0.47 [1] (BL)	[49]
22	$[(biq)_2Ru(2,5\text{-}dpp)Ru(biq)_2]^{4+}$	AN	SCE	+1.48 [2] (Ru)	−0.45 [1] (BL), −0.82 [2] (biq), −0.99 [1] (BL), −1.26 [2] (biq)	[49]
22	$[(bpy)_2Os(2,5\text{-}dpp)Os(bpy)_2]^{4+}$	AN	SCE	+1.22 [1] (Os), +0.92 [1] (Os)	−0.56 [1] (BL), −1.00 [1] (BL), −1.46 [2] (bpy), −1.71 [2] (bpy)	[164]
23	$[(bpy)_2Ru(bpy_a\text{-}bpy_b)Ru(bpy)_2]^{4+}$	AN	Fc/Fc^+	+1.06 [1] (Ru), +0.99 [1] (Ru)	−1.46 (BL), −1.73 (bpy), −1.86 (bpy)	[51]
23	$[(bpy)_2Ru(bpy_a\text{-}bpy_b)Os(bpy)_2]^{4+}$	AN	Fc/Fc^+	+1.05 [1] (Ru), +0.60 [1] (Os)	−1.43 (BL), −1.66 (bpy), −1.85 (bpy)	[51]
23	$[(bpy)_2Ru(bpy_b\text{-}bpy_a)Os(bpy)_2]^{4+}$	AN	Fc/Fc^+	+1.09 [1] (Ru), +0.57 [1] (Os)	−1.42 (BL), −1.71 (bpy), −1.83 (bpy)	[51]

Table 5 (Continued)

Bridging ligand no.	Compound	Solvent	Reference electrode	E_{ox}, V [n] (site)	E_{red}, V [n] (site)	Ref.(s)
23	$[(bpy)_2Os(bpy_a\text{-}bpy_b)Os(bpy)_2]^{4+}$	AN	Fc/Fc^+	+0.65 [1] (Os), +0.56 [1] (Os)	−1.39 (BL), −1.63 (bpy), −1.81 (bpy)	[51]
24	$[(bpy)_2Ru(ppz)Ru(bpy)_2]^{4+}$	AN	SCE	+1.55 [1] (Ru), +1.35 [1] (Ru)	0.67 [1], −1.34 [1], −1.57 [1]	[24]
25	$[(bpy)_2Ru(HAT)Ru(bpy)_2]^{4+}$	AN	SCE	+1.78 [1] (Ru), +1.53 [1] (Ru)	−0.49 [1] (BL), −1.06 [1] (BL)	[26,53]
25	$[(bpy)_2Ru(HAT)Ru(HAT)_2]^{4+}$	AN	SCE	+1.68 [1] (Ru-bpy)	−0.37 [1] (BL), −0.77 [1] (BL), −0.95 [1]	[53]
25	$[(bpy)_2Ru(HAT)Ru(tap)_2]^{4+}$	AN	SCE	+2.18 [1] (Ru-tap), +1.57 [1] (Ru-bpy)	−0.38 [1] (BL), −0.85 [1] (BL), −1.03 [1]	[53]
25	$[(phen)_2Ru(HAT)Ru(phen)_2]^{4+}$	AN	SCE	+1.78 [1] (Ru), +1.52 [1] (Ru)	−0.49 [1] (BL), −1.07 [1] (BL)	[53]
		AN	SCE		−0.49 [1] (BL), −1.06 [1]	[167]
		H_2O(pH 5.9)	SCE		−0.64 [1] (BL)	[167]
26	$[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$	AN	SCE	+.34 [2] (Ru)	−0.71 [1], −1.31 [2], −1.51 [2], −1.72	[54]
26	$[(bpy)_2Ru(tpphz)Os(bpy)_2]^{4+}$	AN	SCE	+1.33 [1] (Ru), +0.89 [1] (Os)	−0.70 [1], −1.27 [2], −1.48 [2], −1.66, −2.06	[54]
26	$[(bpy)_2Os(tpphz)Os(bpy)_2]^{4+}$	AN	SCE	+0.89 [2] (Os)	−0.70 [1], −1.21 [2], −1.44 [2],	[54]
27	$[(bpy)_2Ru(FAF)Ru(bpy)_2]^{4+}$	AN	SCE	+1.265 [2] (Ru)	−1.285 [2]	[29]
27	$[(bpy)_2Ru(FAF)Os(bpy)_2]^{4+}$	AN	SCE	+1.260 [1] (Ru), +0.800 [1] (Os)	−1.275 [2]	[29]
27	$[(bpy)_2Os(FAF)Os(bpy)_2]^{4+}$	AN	SCE	+0.800 [2] (Os)	1.245 [2]	[29]
28	$[(bpy)_2Ru(PAP)Ru(bpy)_2]^{4+}$	AN	SCE	+1.235 [2] (Ru)	−1.380 [2] (bpy)	[29,30]
28	$[(bpy)_2Ru(PAP)Os(bpy)_2]^{4+}$	AN	SCE	+1.240 [1] (Ru), +0.795 [1] (Os)	−1.345 [2] (bpy)	[29,30]
28	$[(bpy)_2Os(PAP)Os(bpy)_2]^{4+}$	AN	SCE	+0.800 [2] (Os)	−1.305 [2] (bpy)	[29,30]
29	$[(tpy)Ru(tpp)Ru(tpp)]^{4+}$	AN	Ag/AgCl	+1.86 [1] (Ru), +1.51 [1] (Ru)	−0.30 [1] (BL), −0.82 [1] (BL)	[28]
29	$[(tpy)Os(tpp)Ru(tpp)]^{4+}$	AN	Ag/AgCl	+1.81 [1] (Ru), +1.17 [1] (Ru)	0.36 [1] (BL), −0.81 [1] (BL)	[28]
30a	$[(ttpy)Ru(tpy\text{-}tpy)Ru(ttpy)]^{4+}$	AN	SCE	+1.31 [2] (Ru)		[36]
30a	$[(ttpy)Ru(tpy\text{-}tpy)Os(ttpy)]^{4+}$	AN	SCE	+1.31 [1] (Ru), +0.94 [1] (Os)	−0.97 [1] (BL)	[119]
30b	$[(ttpy)Ru(tpy\text{-}Ph\text{-}tpy)Os(ttpy)]^{4+}$	AN	SCE	+1.29 [1] (Ru), +0.94 [1] (Os)	−1.16 [1] (BL)	[119]
30c	$[(ttpy)Ru(tpy\text{-}Ph_2\text{-}tpy)Os(ttpy)]^{4+}$	AN	SCE	+1.28 [1] (Ru), +0.94 [1] (Os)	−1.18 [1] (BL)	[119]
31	$[(ttpy)Ru(tpy\text{-}Ph\text{-}bco\text{-}Ph\text{-}tpy)Os(ttpy)]^{4+}$	AN	SCE	+1.24 [1] (Ru), +0.89 [1] (Os)		[34]
		DMF	SCE		−1.17 [2] (lig.), −1.45 [2] (lig.)	[34]
32a	$[(tpy)Ru(tpy\text{-}E_1\text{-}tpy)Ru(tpy)]^{4+}$	AN	SCE	+1.42 [2] (Ru)	−0.97, −1.19	[38]
32b	$[(tpy)Ru(tpy\text{-}E_2\text{-}tpy)Ru(tpy)]^{4+}$	AN	SCE	+1.41 [2] (Ru)	−0.92, −1.15	[38]
32b	$[(tpy)Ru(tpy\text{-}E_2\text{-}tpy)Os(tpy)]^{4+}$	AN	SCE	+1.39 [1] (Ru), +0.95 [1] (Os)	−1.04, −1.34	[116]
33a	$[(tpy)Ru(tpy\text{-}Ph\text{-}E_1\text{-}Ph\text{-}tpy)Ru(tpy)]^{4+}$	AN	SCE	+1.34 [2] (Ru)	−1.16, −1.40	[38]
33b	$[(tpy)Ru(tpy\text{-}Ph\text{-}E_2\text{-}Ph\text{-}tpy)Ru(tpy)]^{4+}$	AN	SCE	+1.39 [2] (Ru)	−1.08, −1.32	[38]
34	$[(bpy)_2Ru(bpy\text{-}t\text{Pt}\text{-}bpy)Ru(bpy)_2]^{4+}$	AN	SCE	+1.22 [2] (Ru)	−1.33, 1.52, −1.78	[116]
34	$[(bpy)_2Ru(bpy\text{-}t\text{Pt}\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+1.24 [1] (Ru), +0.80 [1] (Os)	−1.27, −1.36, −1.52, −1.78	[116]
34	$[(bpy)_2Os(bpy\text{-}t\text{Pt}\text{-}bpy)Os(bpy)_2]^{4+}$	AN	SCE	+0.79 [2] (Os)	−1.23, −1.53, −1.78	[116]

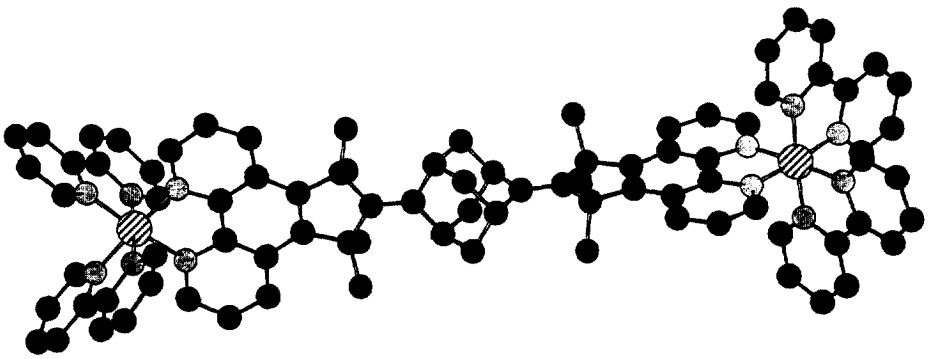


Fig. 8. Schematic representation of the dinuclear bridged metal complex $[(bpy)_2Ru(PAP)Ru(bpy)_2](PF_6)_4$ (CS Chem3D Pro calculation).

completely quenched. The luminescent Ru^{II}-based excited state is quenched by the Os^{III}-based component with rate constant $7.2 \times 10^6\ s^{-1}$ (see Table 4) [30,78]. Laser flash photolysis experiments showed the formation and the successive decay of the $Ru^{II}PAPOs^{III}$ intervalence species. It is interesting to note that the transient species decays to its ground-state isomer with a rate constant $8.3 \times 10^3\ s^{-1}$ [30,78]. The electronic coupling is very small and the direct electron transfer reactions involve the transfer of a π^* electron localized on one of the ligands of the M^{II}-based component to the t_{2g} orbital of the oxidized metal of the other unit. In the $Ru^{III}PAPOs^{II} \rightarrow Ru^{II}PAPOs^{III}$ back reaction the electron transfer takes place from a t_{2g} orbital of the Os^{II} to a t_{2g} orbital of Ru^{III}. Therefore the electronic factor should be different from that of the electron-transfer quenching reactions in the $*M^{II}PAPM^{III}$

6. Bridge as a switch

A special class of dinuclear compounds are those in which the bridging ligand can play the role of a molecular switch (see Fig. 9).

If the bridging ligand is directly responsible for the degree of electronic communication between the metal centres, energy and/or electron transfer processes can be switched on or off depending upon the state of the bridging ligand. In such

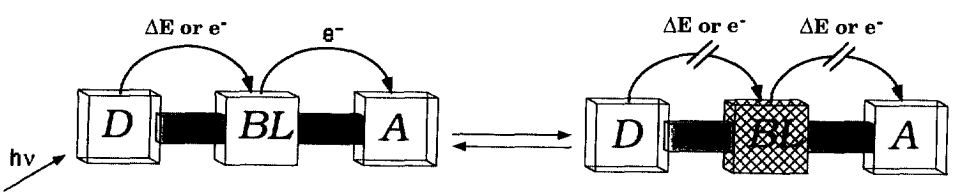


Fig. 9. Schematic representation of a molecular switch.

complexes the arrangement must be chosen so as to have a gradient for energy transfer or a driving force for electron transfer along the D–BL–A sequence (see Fig. 9). Furthermore in order to operate as a switch the bridging ligand must posseses special redox or chemical properties or be a photoactive unit. The different forms obtained upon reduction or oxidation, chemical changes (pH, coordination of an anion or cation), or light irradiation should be interconvertible, and in one of the two forms the bridging ligand must change its electronic properties enough to assure a different rate for energy or electron transfer processes.

The dinuclear complex $[(bpy)_2Ru(bpy\text{-}A5_A\text{-}bpy)Os(bpy)_2]^{4+}$ [81] is an interesting example of system where energy transfer can be switched. Excitation of the Ru-based component leads to an efficient energy transfer from the Ru-based excited state to the Os-based excited state through the triplet excited state of the anthracene bridge. Upon irradiation of an aereated solution of the dinuclear compound, the Os-based excited state is quenched by dioxygen with formation of singlet oxygen $^1O_2$ which is known to give $2+2$ cycloaddition reaction with aromatic molecules. Formation of the anthracene endoperoxide reduces the π delocalization on the anthracene bridge thereby moving the triplet excited state to much higher energy. The lack of a suitable energy level in the bridge precludes the occurence of energy transfer from the Ru-based to the Os-based component.

Dinuclear systems made of two chromophores and of a bridging ligand containing suitable receptors for cation or anion could act as a switch for photoinduced processes [128]. In such systems coordination of a chemical species could lead to strong perturbations and have profound effects on the photophysical behavior. Recently dinuclear compounds where the pH can control the photophysical properties of the system have been reported [157,175]. Several examples of supramolecular systems whose luminescent properties respond to the presence of metal ions have been reported, however examples of controlled photoinduced processes are very limited [12,81,82,143].

An example in which the bridging ligand is an electroactive unit has been very recently reported [143]. For the $[(bpy)_2Ru(b\text{-}azo\text{-}b)Os(bpy)_2]^{4+}$ complex [143], the energy transfer process depends on the oxidation state of the azo-derivative that acts as the bridging ligand. In the heterometallic Ru/Os complex weak emission is observed because of an almost complete quenching of both the Ru-based and Os-based emission, due to the lowest excited state localized on the bridging ligand. Upon electrochemical reduction of the azo-group energy transfer from the Ru-based component to the Os-unit is observed [143]. Homonuclear ruthenium compounds containing an electroactive bridging ligand have also been described recently [142].

7. Closing remarks

Rigid bridged dinuclear compounds have been discussed and photoinduced intercomponent energy and electron transfer have been compared in an attempt to elucidate which factors play a role in determining the rates of photoinduced

processes. Even though we have discussed only ruthenium and osmium complexes, the large choice of molecular components, and bridging ligands coupled to the use of rational synthetic strategies, can provide a remarkable variety of chemical architectures that could lead to the construction of useful photonic molecular devices.

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Appendix A. Abbreviations

$(a\text{-}bpt\text{-}b)^-$	deprotonated 3,5-bis(pyridin-2-yl)-1,2,4-triazole
$(a\text{-}mbpt\text{-}b)^-$	deprotonated 3-(6-methylpyridin-2-yl)-5-(pyridin-2-yl)-1,2,4-triazole
$(dcbpy)^{2-}$	deprotonated 4,4′-dicarboxy-2,2′-bipyridine
2,3-dpp	2,3-bis(2-pyridyl)pyrazine
2,5-dpp	2,5-bis(2-pyridyl)pyrazine
4,4′-bpy	4,4′-bipyridine
4DCE-bpy	4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine
A	acceptor
AN	acetonitrile
b-azo-b	4,4′-azo-bis(2,2′-bipyridine)
bbdb	1,4-bis(4-methyl-2,2′-bipyridin-4′-yl)buta-1,3-diene
bchb	1,4-bis(4-methyl-2,2′-bipyridin-4′-yl)-2-cyclo-hexene-5,6-dicarboxylic acid diethyl ester
bdbdb	see Table 1
biq	2,2′-biquinoline
BL	bridging ligand
$bpbimH_2$	2,2′-bis(2-pyridyl)bibenzimidazole
bphb	1,4-bis(4-methyl-2,2′-bipyridin-4′-yl)benzene
bpy	2,2′-bipyridine
bpy-a-bpy	1,3-bis[2-(2,2′-bipyridin-5-yl)ethenyl]-adamantane
bpy-$A5_A$-bpy	1,10-bis[[[(2,2′-bipyridinyl-5-yl)carbonyl]-benzyl-amino]methyl] anthracene
bpy-aa-bpy	1,1′-bis[2-(2,2′-bipyridin-5-yl)ethenyl]-3,3′-biadamantane
bpy-*c*Pt-bpy	*cis*-bis(tri-*n*-butylphosphine)bis(2,2′-bipyridine-4-ethynyl)platinum(II)
bpy-$E5_A$-bpy	1,4-bis[2-(2,2′-bipyridin-5-yl)ethenyl]-*bicyclo*[2.2.2.]octane
bpy-$E5_B$-bpy	1,4-bis[2-(2,2′-bipyridin-5-yl)ethynyl]-*bicyclo*[2.2.2.]octane

bpy-*t*Pt-bpy	*trans*-bis(tri-*n*-butylphosphine)bis(2,2′-bipyridine-4-ethynyl)platinum(II)
bpy_a-bpy_b	2,2′:3′,2″:6″,2‴-quaterpyridine
bsbsb	see Table 1
BuCN	butyronitrile
Cl_2dpq	6,7-dichloro-2,3-bis(2-pyridyl)quinoxaline
D	donor
DAB	see Table 1
$dcbpyH_2$	4,4′-dicarboxy-2,2′-bipyridine
dmbpy	4,4′-dimethyl-2,2′-bipyridine
DME	1,2-dimethoxyethane
DMF	dimethylformamide
dppe	1,2-bis(diphenylphosphino)benzene
dppz-s-dppz	see Table 1
dpq	2,3-bis(2′-pyridyl)quinoxaline
dpt-bph-dpt	see Table 1
dpt-cy-dpt	see Table 1
dpt-ph-dpt	see Table 1
dpte	1,2-bis(phenylthio)ethane
Et/Met	ethanol/methanol
EtOH	ethanol
FAF	adamantane-2,6-bis(4,5-diazafluorenylidene)
Fc	ferrocene
HAT	1,4,5,8,9,12-hexaazatriphenylene
mb-E_n-mb	see Table 4.1
Me_2dpq	6,7-dimethyl-2,3-bis(2-pyridyl)quinoxaline
MeOH	methanol
mpzt	1-methyl-3-(pyrazin-2-yl)-1,2,4-triazole
nitrile	propionitrile/butyronitrile
ob-E_n-ob	see Table 1
PAP	2,6-adamantanebis(1,3-dihydro-1,1,3,3-tetramethyl-7,8-diazacyclopenta[1]phenanthren)-2-ylidene
pb-E_n-pb	see Table 1
phen	1,10-phenanthroline
ppz	4′,7′-phenanthrolino-5′,6′:5,6-pyrazine
py-$E4_A$-py	*trans*-1,2-bis(4-pyridyl)ethylene
SCE	saturated calomel electrode
SSCE	sodium saturated calomel electrode
tpp	2,3,5,6-tetrakis(2′-pyridyl)pyrazine
tpphz	tetrapyrido[3,2-a:2′,3′-c:3″,2″-h:2″,3″-j]phenazine
tpy	2,2′,2″-terpyridine
tpy-E_n-tpy	see Table 1
tpy-Ph-bco-Ph-tpy	see Table 1

tpy-ph-E_n-Ph-tpy	see Table 1
tpy-Ph_n-tpy	see Table 1
tpy-tpy	see Table 1
triflate	trifluoromethanesulfonate
ttpy	4′-(*p*-tolyl)-2,2′,6′,2″-terpyridine

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