Electronic Supplementary Material for PCCP

Supporting information

for

Effect of Secondary Ligands Size on Energy Transfer and Electroluminescent Efficiencies for a Series of Europium (III) Complexes, A Density Functional Theory Study

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Table S1 Geometrical parameters in T_1 state of the seven complexes

	Eu-Phen	**Eu-PyPhen**	**Eu-MPP**	**Eu-DPPz**	**Eu-MDPz**	**Eu-DDPz**	**Eu-BDPz**
Eu - O1	2.398	2.480	2.402	2.404	2.405	2.405	2.406
Eu - O2	2.425	2.358	2.418	2.425	2.424	2.425	2.425
Eu - O3	2.381	2.381	2.450	2.382	2.383	2.385	2.385
Eu - O4	2.395	2.390	2.324	2.398	2.398	2.398	2.399
Eu - O5	2.353	2.415	2.424	2.417	2.418	2.419	2.419
Eu - O6	2.487	2.402	2.399	2.410	2.410	2.409	2.410
Eu - N1	2.676	2.679	2.696	2.680	2.679	2.679	2.679
Eu - N2	2.687	2.689	2.704	2.680	2.679	2.677	2.676

Table S2 Frontier molecular orbital composition of the seven complexes

orbital	**Eu-Phen**	**Eu-PyPhen**	**Eu-MPP**	**Eu-DPPz**	**Eu-MDPz**	**Eu-DDPz**	**Eu-BDPz**
L+5	π*(Phen)	π*(TTA)	π*(TTA)	π*(TTA)	π*(TTA)	π*(DDPz)	π*(BDPz)
L+4	π*(TTA)	π*(TTA)	π*(TTA+MPP)	π*(DPPz)	π*(MDPz)	π*(DDPz+TTA)	π*(TTA)
L+3	π*(TTA+Phen)	π*(PyPhen+TTA)	π*(TTA+MPP)	π*(TTA)	π*(TTA)	π(TTA)	π*(TTA)
L+2	π*(Phen+TTA)	π*(PyPhen+TTA)	π*(TTA)	π*(TTA)	π*(TTA)	π*(TTA)	π*(TTA)
L+1	π*(TTA+Phen)	π*(PyPhen)	π*(MPP)	π*(DPPz)	π*(MDPz)	π*(DDPz)	π*(BDPz)
L	π*(Phen)	π*(PyPhen)	π*(MPP)	π*(DPPz)	π*(MDPz)	π*(DDPz)	π*(BDPz)
H	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)
H-1	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)
H-2	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)
H-3	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)
H-4	π(TTA+Phen)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)
H-5	π(TTA+Phen)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)
H-6	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA+MPDz)	π(TTA)	π(TTA)
H-7	π(TTA+Phen)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)
H-8	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)
H-9	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)	π(TTA)

Table S3 Calculated absorption of the investigated complexes in CH_2Cl_2 media at the TD-B3LYP level, together with experimental values

Complex	state	energy	f	character	exptl[24]
Eu-Phen	S_1	357/3.47	0.0078	H→L/π(TTA)→π*(Phen)LLCT	
				H-1→L/π(TTA)→π*(Phen)LLCT	
	S_{16}	320/3.87	0.7919	H-2→L/π(TTA)→π*(Phen)ILCT	
				H→L+3/π(TTA)→π*(Phen+TTA)LLCT/ILCT	
	S_{70}	253/4.90	0.4313	H-9→L+3/π(TTA)→π*(Phen+TTA)ILCT/ILCT	
Eu-PyPhen	S_1	358/3.47	0.0098	H→L/π(TTA)→π*(PyPhen)LLCT	340
	S_{20}	321/3.87	0.7164	H-2→L+1/π(TTA)→π*(PyPhen)LLCT	
				H-2→L+3/π(TTA)→π*(PyPhen+TTA)LLCT/ILCT	
	S_{21}	318/3.90	0.2302	H-2→L+4/π(TTA)→π*(TTA)ILCT	298
	S_{89}	254/4.88	0.3928	H-12→L+5/π(PyPhen)→π*(TTA) ILCT/LLCT	
Eu-MPP	S_1	357/3.48	0.0100	H→L+1/π(TTA)→π*(MPP)LLCT	
				H-1→L+1/π(TTA)→π*(MPP)LLCT	
	S_{20}	320/3.87	0.8397	H→L+4/π(TTA)→π*(MPP+TTA)LLCT/ILCT	340
				H-2→L+1/π(TTA)→π*(MPP)LLCT	
	S_{86}	257/4.82	0.3595	H-14→L+5/π(MPP)→π*(TTA) LLCT	260
	S_{88}	255/4.85	0.3543	H-9→L+5/π(TTA)→π*(TTA)ILCT	
Eu-DPPz	S_1	401/3.09	0.0060	H→L/π(TTA)→π*(DPPz)LLCT	
	S_{24}	320/3.87	0.6323	H-2→L+1/π(TTA)→π*(DPPz)LLCT	342
				H→L+4/π(TTA)→π*(DPPz)LLCT	
	S_{53}	278/4.46	0.2468	H-6→L+1/π(TTA)→π*(DPPz)LLCT	
				H→L+3/π(TTA)→π*(TTA)ILCT	
	S_{54}	278/4.46	0.4908	H-3→L+5/π(TTA)→π*(TTA)ILCT	274
Eu-MDPz	S_1	394/3.15	0.0074	H→L/π(TTA)→π*(MDPz)LLCT	

				H-4→L/π(TTA)→π*(MDPz)LLCT	
	S_{21}	321/3.87	0.4820	H-4→L/π(TTA)→π*(MDPz)LLCT	342
				H→L+5/π(TTA)→π*(TTA)ILCT	
	S_{50}	282/4.40	0.3378	H-6→L+3/π(TTA+MDPZ)→π*(TTA)LLCT/ILCT	278
	S_{51}	281/4.41	0.2796	H-6→L+2/π(TTA+MDPZ)→π*(TTA)LLCT/ILCT	
Eu-DDPz	S_1	389/3.19	0.0010	H→L/π(TTA)→π*(DDPz)LLCT	
	S_{20}	321/3.87	0.6008	H-2→L+4/π(TTA)→π*(TTA+DDPz)LLCT/ILCT	340
				H-2→L+1/π(TTA)→π*(DDPz)LLCT	
	S_{44}	286/4.34	0.4911	H-5→L+2/π(TTA+DDPz)→π*(TTA)LLCT/ILCT	280
				H-3→L+5/π(DDPz)→π*(DDPz)ILCT	
Eu-BDPz	S_1	492/2.52	0.0203	H→L/π(TTA)→π*(BDPz)LLCT	
	S_{25}	327/3.79	0.4427	H-7→L/π(TTA)→π*(BDPz)LLCT	338
	S_{32}	317/3.92	0.1675	H-1→L+5/π(BDPz)→π*(BDPz)ILCT	
				H-2→L+5/π(TTA)→π*(BDPz)LLCT	
	S_{33}	316/3.92	0.1220	H-1→L+5/π(BDPz)→π*(BDPz)ILCT	