Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Theoretical study on photophysical properties of three high water solubility polypyridyl complexes for two-photon photodynamic therapy

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Table S-1. The absorption spectra of Ru-bpy were calculated by using different functionals.

Functionals	*E* (eV)	Wavelength (nm)	*f*
M06-2X	2.41	514.9	0.0001
TPSSh	2.43	511.1	0.0068
B3LYP	2.72	455.4	0.0058
PBE	2.90	426.8	0.0057
ωB97-XD	2.96	418.8	0.0001
LC-ωPBE	2.98	415.6	0.0057
CAM-B3LYP	3.04	408.5	0.0001
Exp.[1]		464	

1. H. Huang, B. Yu, P. Zhang, J. Huang, Y. Chen, G. Gasser, L. Ji and H. Chao, *Angewandte Chemie*, 2015, 127, 14255-14258.

Table S-2. The absorption spectra of Ru-bpy were calculated in different solvents by using B3LYP functional.

Solvent	States	E (eV)	λ_{max} (nm)	f	Main configurations	Exp.[1] (nm)
H_2O	S_1	2.72	455.4	0.0058	HOMO→LUMO (99%)	464
Methanol	S_1	2.72	455.4	0.0057	HOMO→LUMO (99%)	463
CH_3CN	S_1	2.72	455.4	0.0057	HOMO→LUMO (99%)	

1. H. Huang, B. Yu, P. Zhang, J. Huang, Y. Chen, G. Gasser, L. Ji and H. Chao, *Angewandte Chemie*, 2015, 127, 14255-14258.

Table S-3. The lowest vertical singlet excitation energies (*E* in eV), maximum one-photon absorption wavelengths (λ_{OPA} in nm), maximum two-photon absorption wavelengths (λ_{TPA} in nm), TPA cross-sections (σ_{TPA} in GM) of Ru-bpy were calculated by using different functionals and basis sets.

	E (eV)	λ_{OPA} (nm)	λ_{TPA} (nm)	σ_{TPA} (GM)
CAM-B3LYP/6-31G*	3.06	405.2	810.4	2.29E-02
B3LYP/6-31G*	2.68	462.7	925.4	2.22E-04
B3LYP/6-31+G*	2.65	467.9	935.8	2.18E-04
B3LYP/6-311+G*	2.62	473.3	946.6	6.31E-04
Exp.[1]			ca.900	

1. H. Huang, B. Yu, P. Zhang, J. Huang, Y. Chen, G. Gasser, L. Ji and H. Chao, *Angewandte Chemie*, 2015, 127, 14255-14258.

Table S-4. Partial molecular orbital (MO) energies (*E* in eV) and compositions in S_0 state of Ru-bpy, Zn-bpy and Zn-tpy in water solution. For Ru-bpy and Zn-bpy, the L1, L2 and L3 represent bipyridyl ligand. For Zn-tpy, the L1 and L2 represent terpyridyl ligand. Moreover, the M in the table represents the metal core.

	MO	*E* (eV)	Main Contribution (%)				Assignment
			M	L1	L2	L3	
Ru-bpy	LUMO+1	-3.13	7	61	13	19	d(Ru)+π*(bpy)
	LUMO	-3.27		33	33	32	π*(bpy)
	HOMO	-6.81	86				π(Ru)
	HOMO-1	-6.91	80		8	7	π(Ru)+π(bpy)
Zn-bpy	LUMO+1	-3.12		42	55		π*(bpy)
	LUMO	-3.12		24	10	65	π*(bpy)
	HOMO	-7.71		33	63		π(bpy)
	HOMO-1	-7.72		34	7	59	π(bpy)
Zn-tpy	LUMO+1	-3.28		50	50		π*(tpy)
	LUMO	-3.31		50	49		π*(tpy)
	HOMO	-7.59		50	50		π(tpy)
	HOMO-1	-7.59		50	50		π(tpy)

Table S-5. The lowest triplet excited energies (*E* in eV) and main configurations for Ru-bpy, Zn-bpy and Zn-tpy, calculated by using Gaussian program.

Molecule	States	*E* (eV)	Main configurations	Assignment
Ru-bpy	T_1	2.50	HOMO→LUMO (88%)	^{3}MLCT/^{3}LLCT
Zn-bpy	T_1	2.95	HOMO→LUMO (40%)	^{3}LLCT
			HOMO-1→LUMO+1 (27%)	^{3}LLCT
			HOMO-2→LUMO+2 (20%)	^{3}LLCT
Zn-tpy	T_1	2.87	HOMO→LUMO (95%)	^{3}LLCT

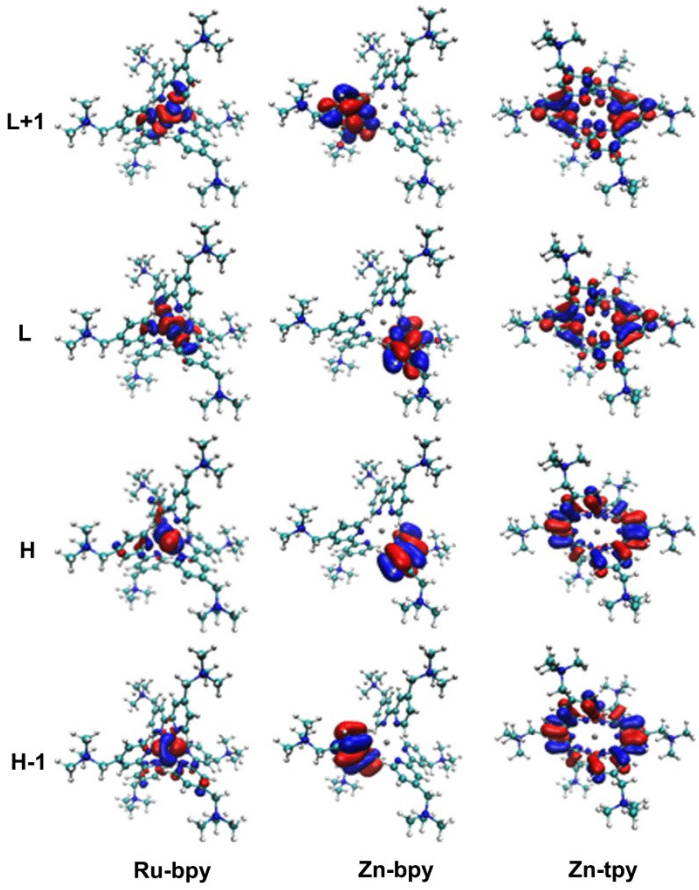

Fig. S-1 Partial frontier molecular orbitals map of the three compounds in ground state, calculated by using CAM-B3LYP functional.

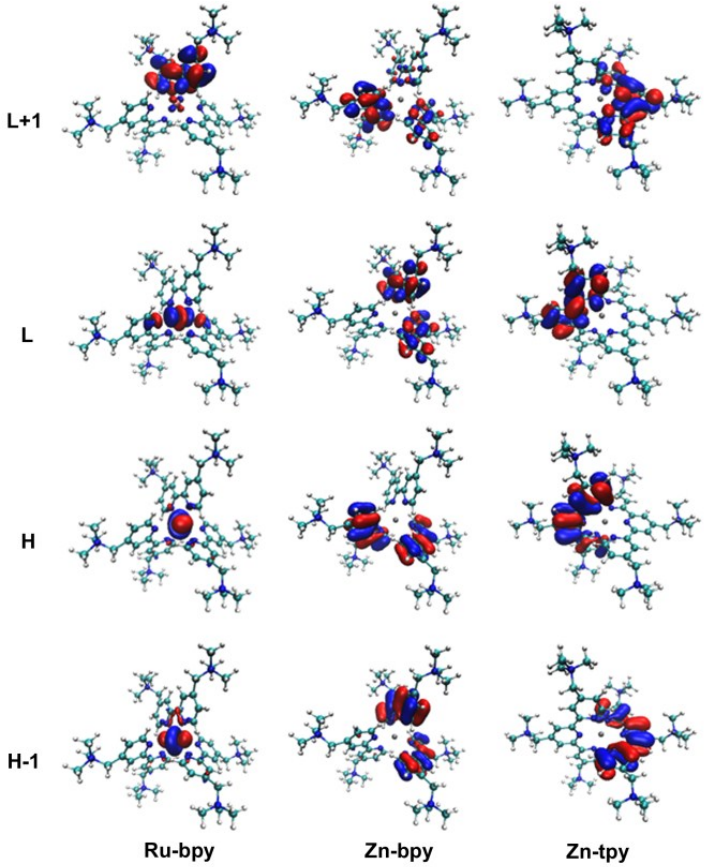

Fig. S-2 Partial frontier molecular orbitals map of the three compounds in triplet excited state, calculated by using B3LYP functional.