Near infrared-to-near ultraviolet triplet-triplet annihilation upconversion by strong spin-forbidden transition

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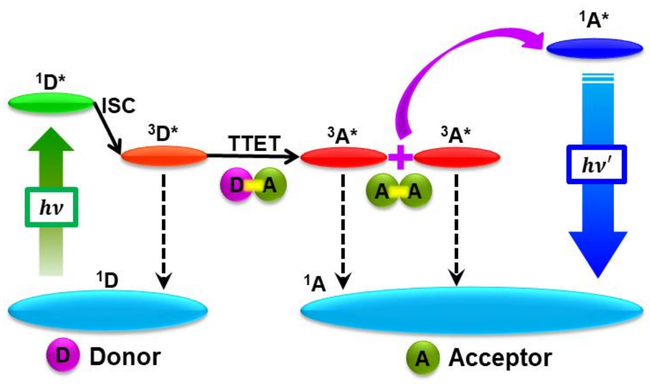
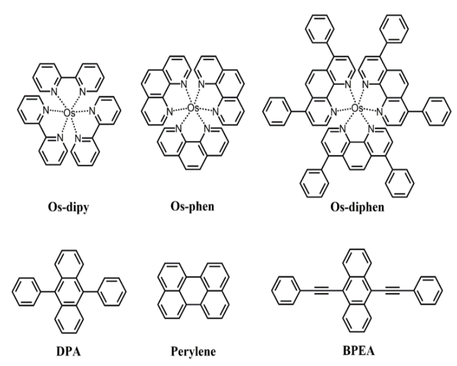
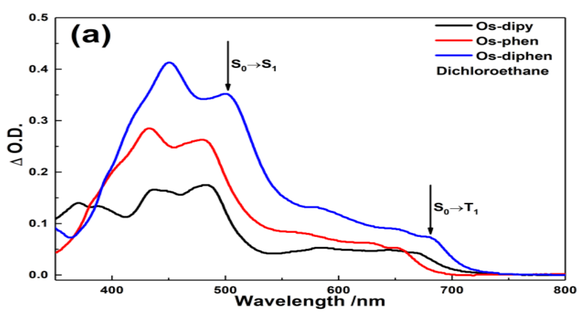
Introduction

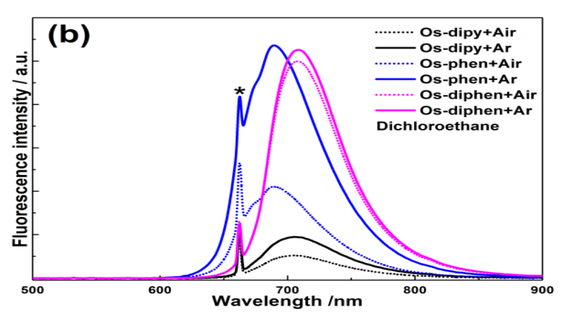
Due to the strong spin-orbit coupling, the osmium complex shows a considerable S_0-T_1 absorption, which can be utilized to overcome the energy loss of ISC. In this work, three new Os(II) complexes were designed and synthesized for triplet- triplet annihilation (TTA) upconversion with DPA, Perylene and BPEA as acceptor. These complex ligands were carefully selected in order to obtain much longer triplet lifetime and more accurately adjust the triplet energy levels of photosensitizers





UV-Vis absorption and phosphorescence spectra

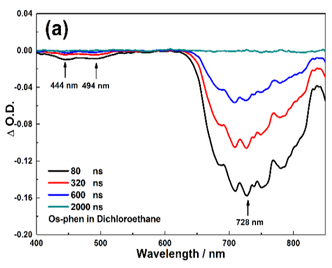


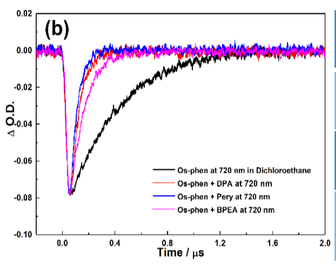


compound	λabs	ε(singlet)	λabs	ε(triplet)	λem	ΦP(Air)	ΦP(Ar)
Os-dipy	370/436/483	1.4/1.7/1.7	667	0.44	707	0.4	0.9
Os-phen	432/480	2.9/2.6	654	0.53	690	2.0	5.5
Os-diphen	450/501	4.1/3.5	682	0.73	711	2.2	4.4

✓The absorption transition of S_0-T_1 is clearly observed from the absorption spectrum and the energy level of the triplet changes with the structure of the ligand.

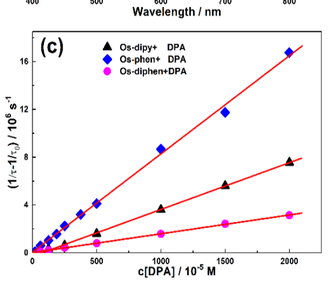
Transient absorption spectra and quench rate constant

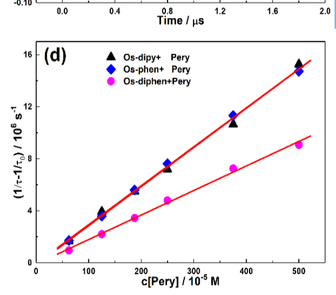


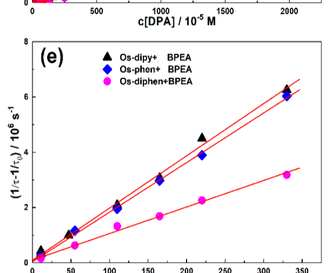


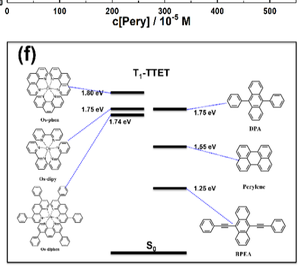
	τ_0 / ns	DPA[a]	Pery[a]	BPEA[a]
Os-dipy	107	0.39	3.01	1.89
Os-phen	373	0.82	2.99	1.79
Os-diphen	386	0.16	1.89	0.96

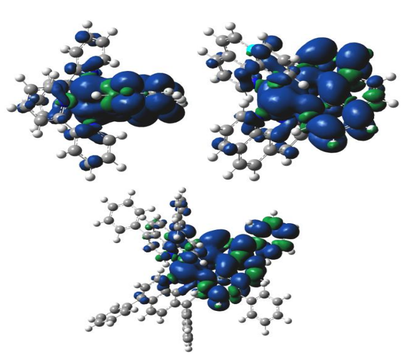
a.bimolecular quenching rate constant, $10^9\ M^{-1}s^{-1}$





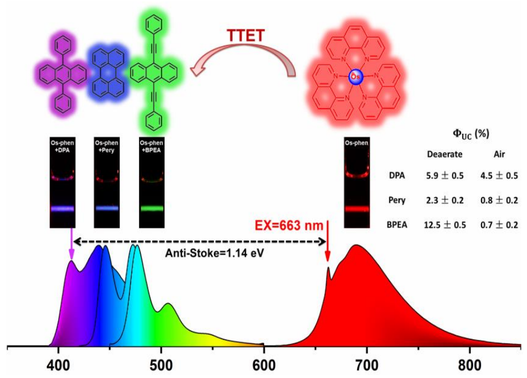




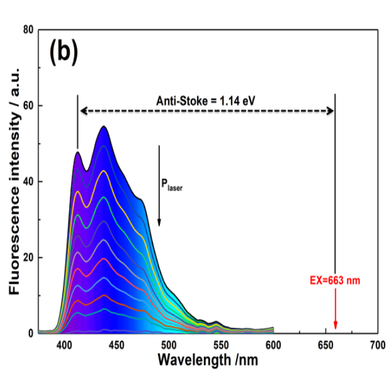


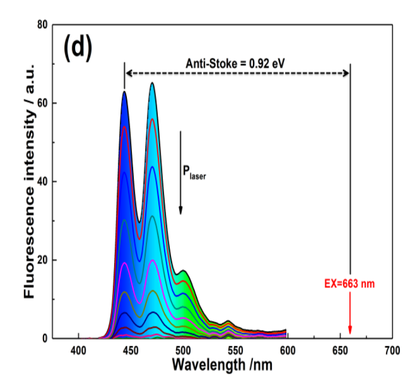
✓The rate of energy transfer between the photosensitizer and the acceptor molecule is mainly affected by the energy level, while steric hindrance is also a factor affecting the energy transfer.

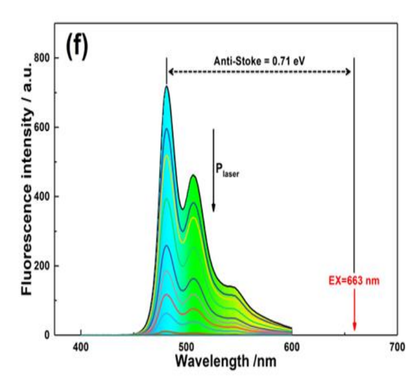
TTA upconversion fluorescence spectra



compound	ΦTTA (Dichloroethane, Ar, %)		
	DPA	Pery	BPEA
Os-dipy	0.40	1.1	3.0
Os-phen	5.9	2.3	12.5
Os-diphen	1.2	2.5	10.3







✓Using 532 nm laser as the excitation source, the up-conversion system consisting of photosensitizer and acceptor molecules BPEA, peryl and DPA can respectively emit green, blue and violet light, and the maximum anti-Stokes shift can reach 1.14 EV.

Conclusion

in this work, three Os(II) complexes photosensitizers of singlet-triplet excitation were designed and synthesized. To match the acceptor DPA ($T_1 = 1.75\ eV$) energy level, the triplet energy level was adjusted by precisely design photosensitizers and select ligand molecules and were determined as 1.80 eV for Os-phen, 1.75 eV for Os-dipy, and 1.74 eV for Os-diphen by the steady-state spectra. The TTA upconversion fluorescence emission of acceptor was clearly observed in the deaerated solution. For the TTA upconversion spectra, the upconversion quantum yield, Φ_{UC}, was determined to be 5.9 % for Os-phen/DPA, 2.3 % for Os-phen/Pery, and 12.5 % for Os-phen/BPEA in deaerated dichloroethane.

Reference AND Acknowledgement

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2. Zhou Q, Zhou M, Wei Y, et al. *Phys. Chem. Chem. Phys.* 2017, 19(2): 1516-1525.
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