Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information for

BODIPY-Modified Ru(II) arene Complex----a New Ligand Dissociation Mechanism and a Novel Strategy to Red Shift the Photoactivation Wavelength of Anticancer Metallodrugs

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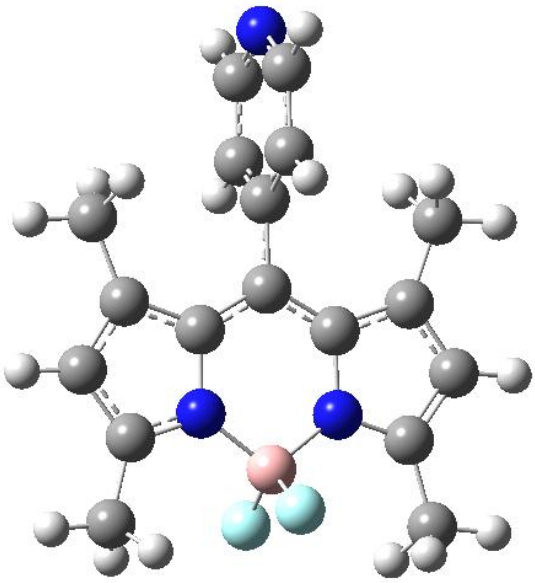


Fig. S1 The DFT calculated ground-state geometry of py-BODIPY in CH_3CN.

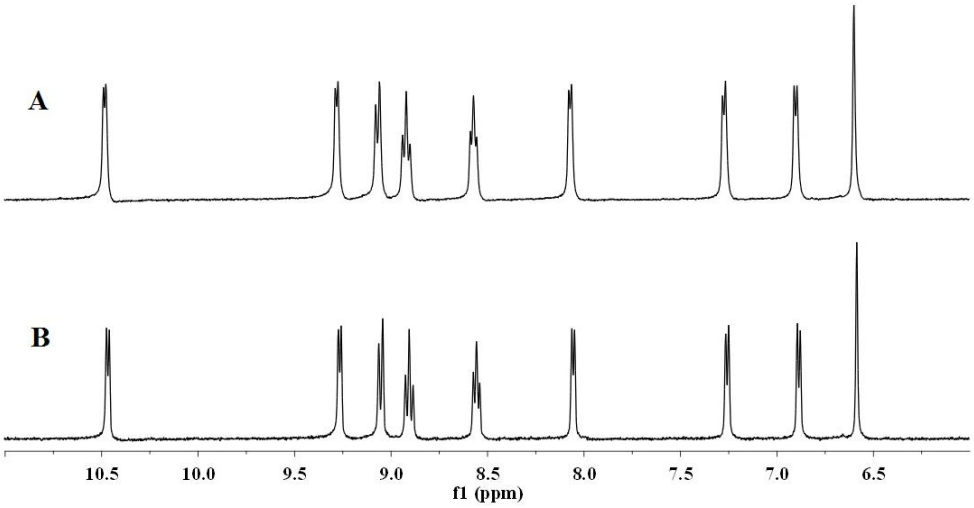


Fig. S2 The ^1H NMR spectra of complex **2** before (A) and after (B) storing for a month in the dark in CD_3COCD_3:D_2O (2:1).

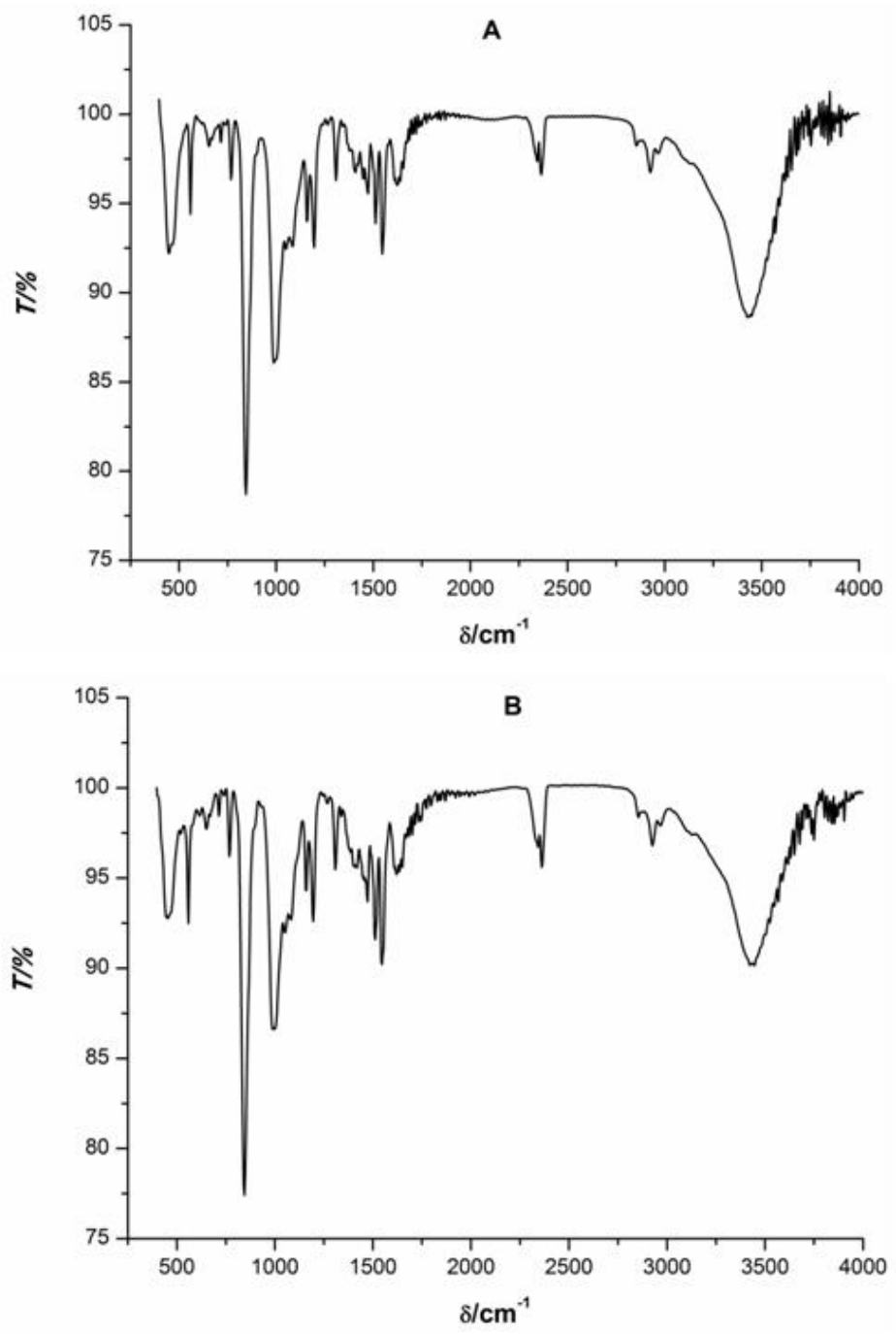


Fig. S3 The IR spectra of complex **2** before (A) and after (B) storing for a month in the dark in CD_3COCD_3:D_2O (2:1).

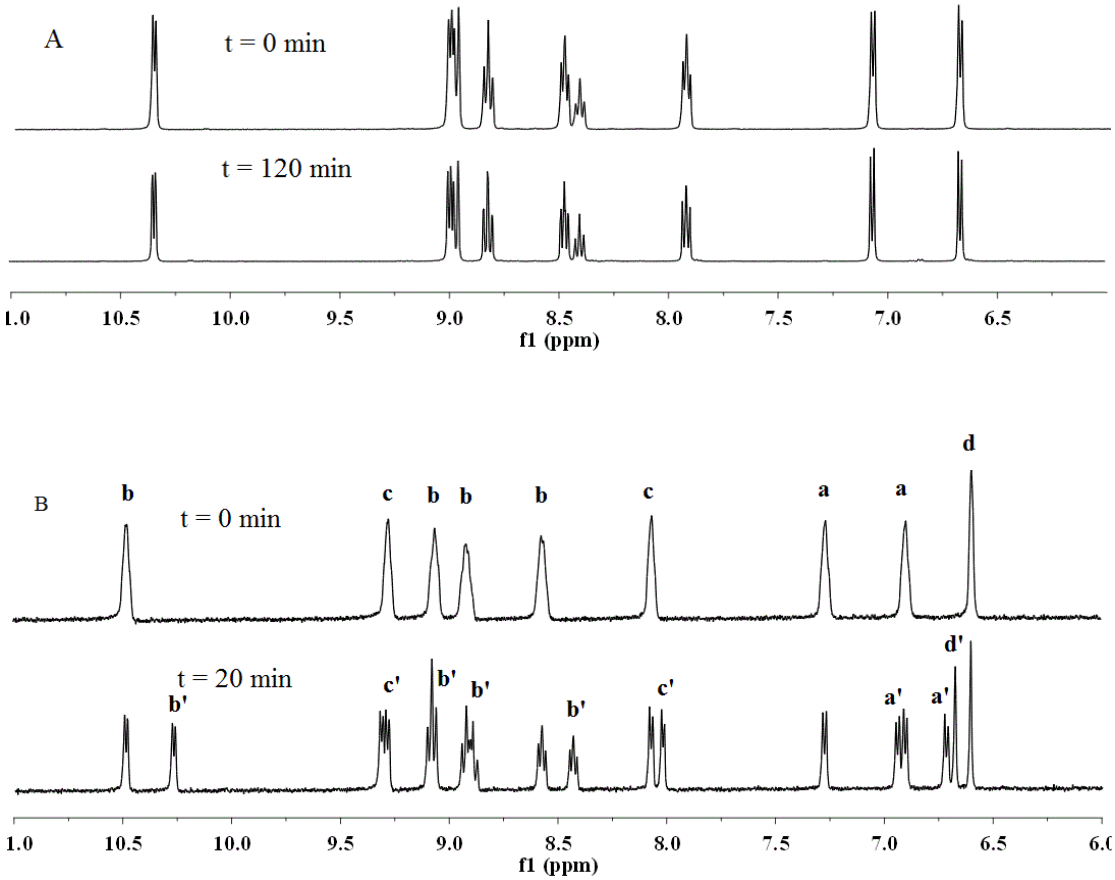
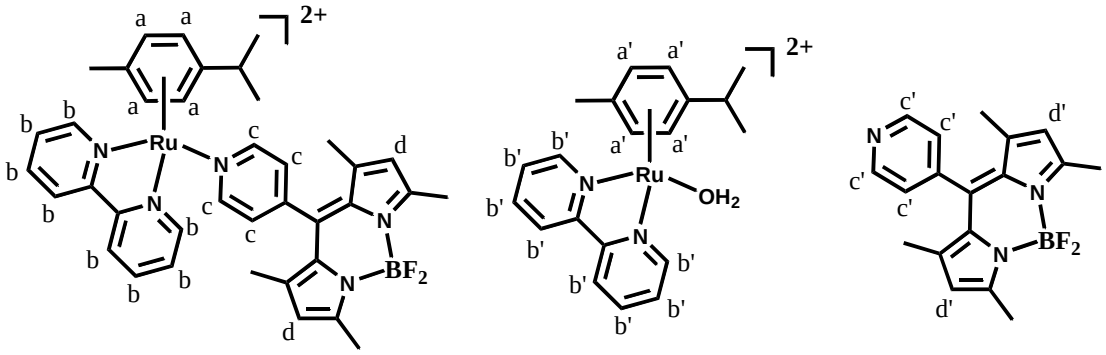


Fig. S4 The ^{1}H NMR spectra of **1** (A) and **2** (B) before and after irradiation (λ > 300 nm for **1** and λ > 500 nm for **2**) in CD_3COCD_3:D_2O (2:1).



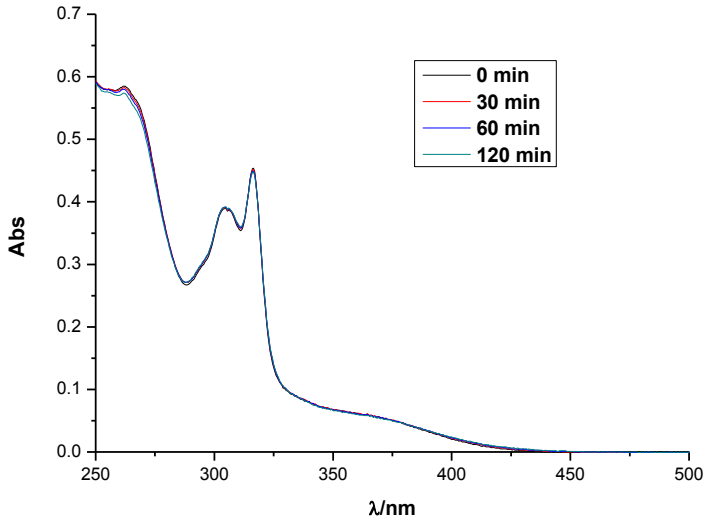


Fig. S5 The absorption spectral changes of **1** (25μM) with the irradiation (λ > 300 nm) time in aqueous solution.

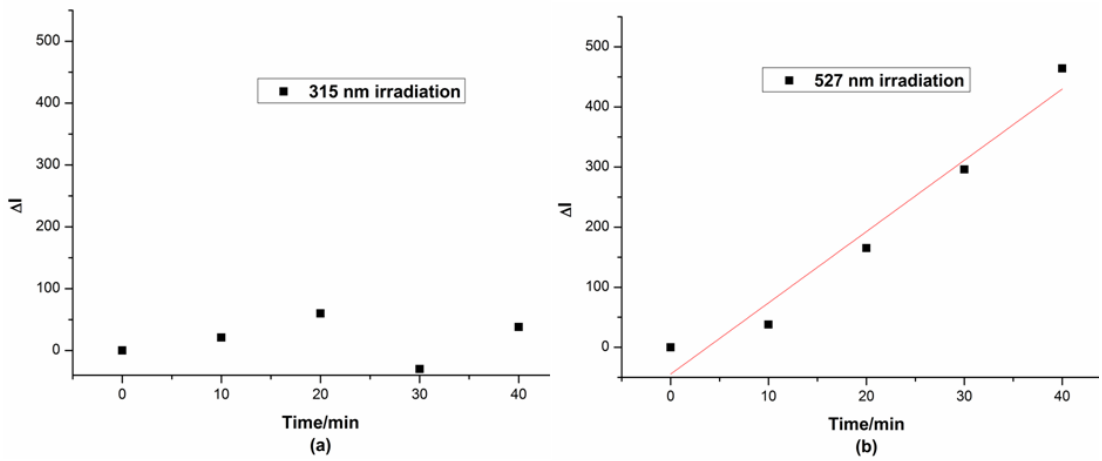


Fig. S6 The fluorescence intensity changes of complex **2** (5 μM) in aqueous solution upon irradiation at 315 nm (a) or 527 nm (b). Both the 315 nm light and the 527 nm light are from the Xe lamp of the Hitachi F-4500 fluorescence spectrophotometer with the excitation slit of 10 nm. The absorbance values of the sample at 315 nm and 527 nm are 0.090 and 0.025, respectively. The incident light intensity of the fluorescence spectrophotometer at 527 nm is about 3.3 times of that at 315 nm. Thus, the absorbed photons of the sample at 315 nm and 527 nm were estimated to be the same.

pK_a value of py-BODIPY ligand (acidic form)

The pK_a value of the acidic form of the py-BODIPY ligand was determined by monitoring the absorption changes as a function of the solution pH and fitting the data using the following equation :

$$A = \frac{A_{NH^+}}{1+10^{(pH - pKa)}} + \frac{A_N}{1+10^{(pKa - pH)}}$$

where A_{NH^+} and A_N are the absorbance of the solution when all the molecules are in the acidic form or basic form, respectively, and A is the absorbance of the solution at certain pH.

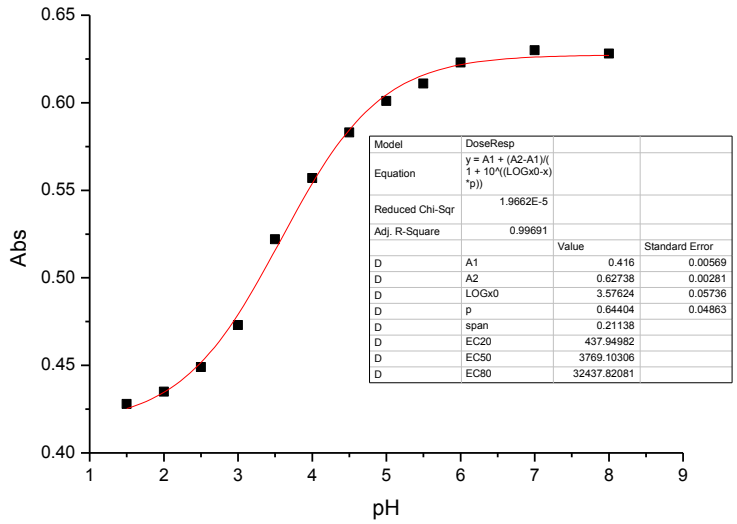
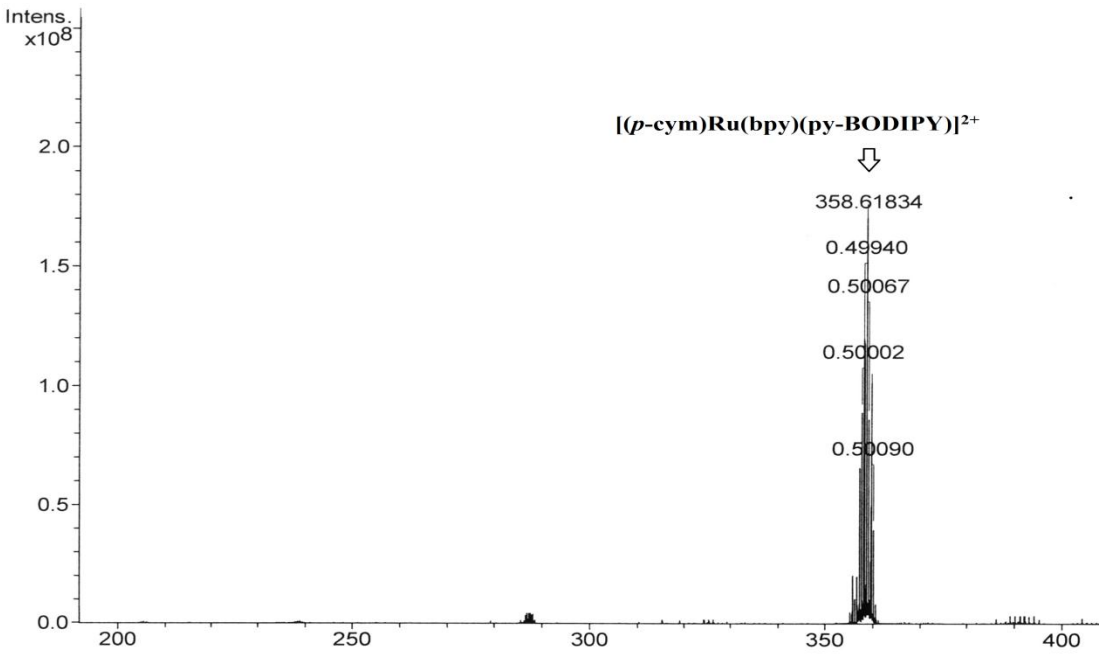


Fig. S7 The absorbance of py-BODIPY (10 μM) at 502 nm in aqueous solutions as a function of the solution pH.



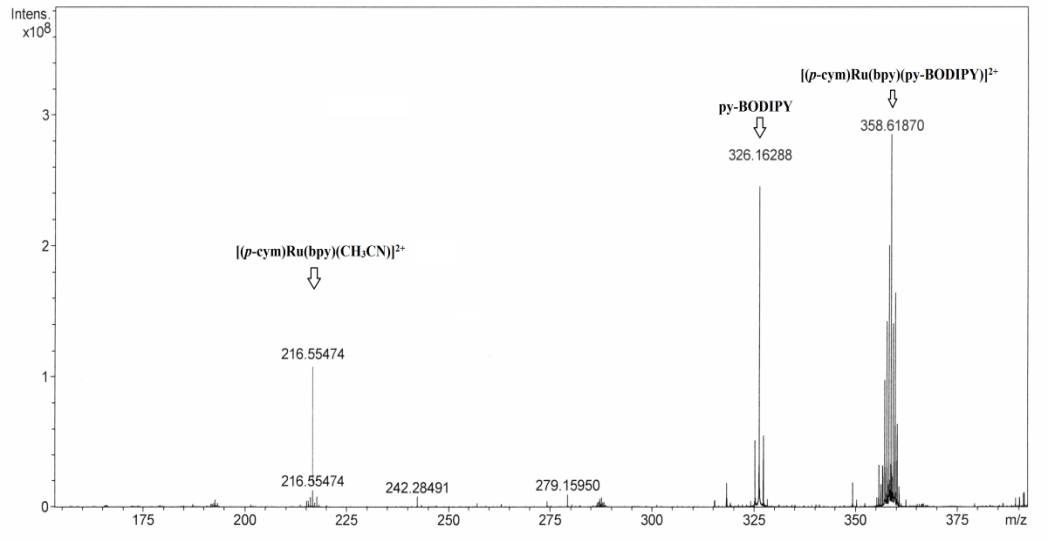


Fig. S8 The high-resolution ESI mass spectrum of complex **2** in CH_3COCH_3:H_2O (2:1) before (top) and after (bottom) irradiation (λ > 500 nm) for 20 min. The solvent for the ESI mass spectrum analysis is CH_3CN.

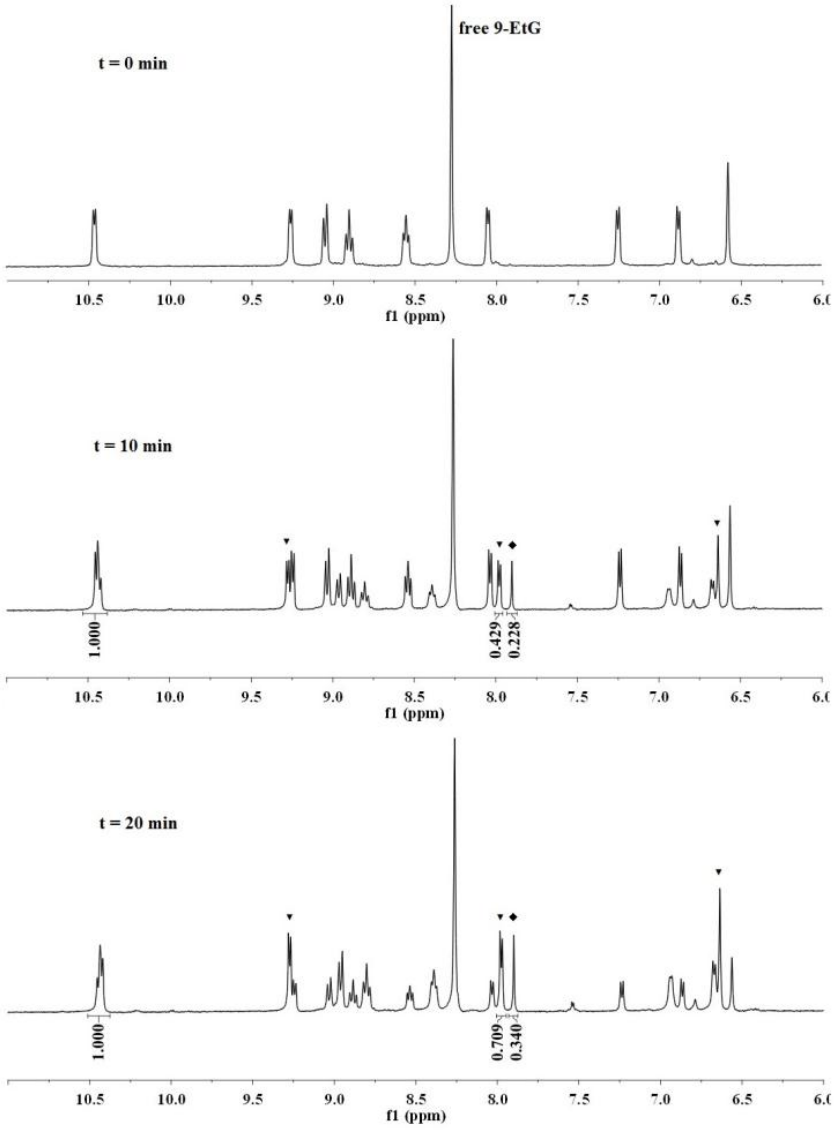


Fig. S9 ^{1}H NMR spectra of **2** in CD_3COCD_3/D_2O (2/1) before and after irradiation ($\lambda > 500$ nm) for 10 and 20 min in the presence of 9-EtG. The free py-BODIPY ligand based peaks are indicated with ▼, and the coordinated 9-EtG peak is indicated with ◆.

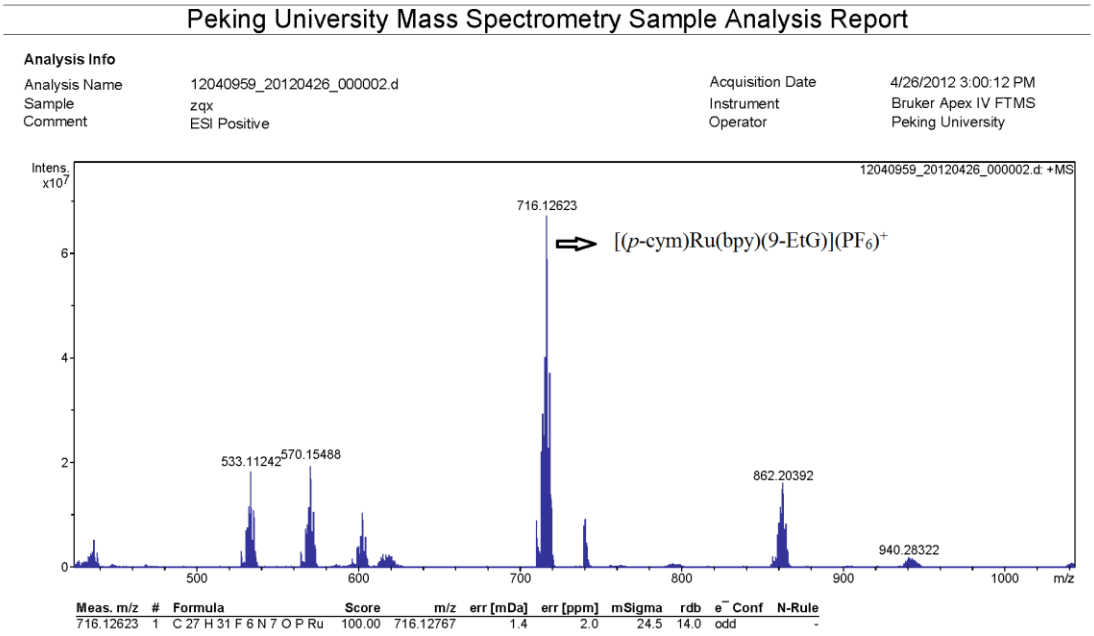


Fig. S10 The high-resolution ESI mass spectrum of complex **2** in CH_3COCH_3:H_2O (2:1) after irradiation ($\lambda > 500$ nm) for 20 min in the presence of 9-EtG.

Table S1. Selected TDDFT triplet transitions for complex **1** in the ground-state optimized geometry.

	Energy (eV)	**Wavelength (nm)**	**Oscillator Strength**	**Major Contributions**
1	2.32	535.29	0.0	HOMO → LUMO+1 (98%)
2	2.41	515.48	0.0	HOMO-1 → LUMO+1 (11%), HOMO → LUMO+2 (80%)
3	2.49	497.85	0.0	HOMO-1 → LUMO+1 (75%), HOMO-1 → LUMO+2 (15%)
4	2.63	471.09	0.0	HOMO-3 → LUMO+1 (25%), HOMO-1 → LUMO+2 (57%)
5	2.76	449.97	0.0	HOMO-3 → LUMO+1 (67%), HOMO-1 → LUMO+2 (-18%)

We met problems in the DFT calculation of complex **2**. The ground-state geometry optimization always fell into endless loop, possibly due to its large structure. In light of the fact that the absorption spectrum of **2** is nearly the superposition of **1** and py-BODIPY (Figure 2 shown in the main text), one may reasonable assume that the MLCT transition energy of **2** should be similar to

that of **1**. Thus, we use the calculated ^{3}MLCT energy of **1** (2.32 eV, 535.9 nm, Table S1) and the 0-0 transition energy of the coordinated py-BODIPY to estimate the driving force for the energy transfer from ^{1}py-BODIPY* to ^{3}MLCT in **2**, which is about -0.09 eV.