

# ADVANCED OPTICAL MATERIALS

## Supporting Information

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Photoresponsive Luminescence Switching of Metal-Free  
Organic Phosphors Doped Polymer Matrices

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and Jinsang Kim\**

## Supporting Information

### **Photoresponsive luminescence switching of metal-free organic phosphors-doped polymer matrices**

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Abstract: A new type of luminescence switching behavior based on phosphorescence enhancement from a series of metal-free organic phosphors doped polymers by UV-irradiation was investigated. This phenomenon is observed only from pairs of organic phosphors and polymer matrices having a combination of appropriate triplet exciton lifetime and oxygen permeability. Systematic investigation revealed that the luminescence switching behavior of organic phosphors embedded in a specific polymeric matrix stems from the conversion of triplet oxygens to singlet oxygens by UV-irradiation, leading to the unique phosphorescence enhancement of organic phosphors. Visualization of latent information by UV-irradiation was demonstrated toward novel secure information communication applications.

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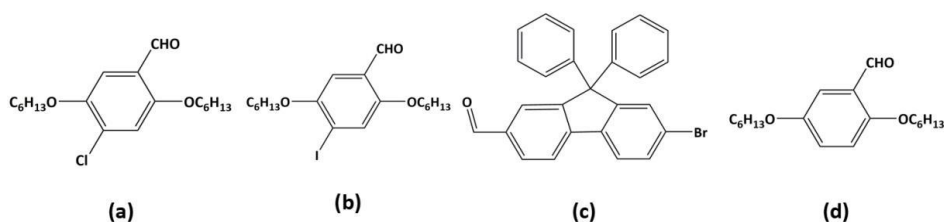
### 3 References

## 1 Experimental Procedures

### 1.1 Materials

All reagents were purchased from Sigma-Aldrich and used as purchased without additional purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories.

Br6A, 4-chloro-2,5-dihexyloxybenzaldehyde (Cl6A), and 2,5-dihexyloxy-4-iodobenzaldehyde (I6A) were synthesized following the method described in our previous work.<sup>[1]</sup> 7-Bromo-9,9-diphenyl-9H-fluorene-2-carbaldehyde (BrPhFlA) was synthesized according to a published method.<sup>[2]</sup> 2,5-Dihexyloxybenzaldehyde (6A) was synthesized as described previously.<sup>[3]</sup> Figure S1 shows the chemical structures of them. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) for 6A: δ 10.50 (1H), 7.30 (1H), 7.15 (1H), 6.85 (1H), 4.10 (2H), 3.90 (2H), 1.80 (4H), 1.43 (4H), 1.35 (8H), 0.88 (6H). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) for BrPhFlA: δ 10.00 (1H), 7.92 (3H), 7.73 (1H), 7.60 (2H), 7.30 (6H), 7.18 (4H). An optimum phosphor concentration of 1 wt% versus polymer mass<sup>17</sup> was used. A mixture of the phosphor and polymer was dissolved in chloroform at a concentration of 1 mg/mL for the phosphor (roughly, 1 mg Br6A and 100 mg a-PMMA in 1 mL chloroform). The solution was drop-cast on an unmodified glass substrate followed by annealing at 60 °C for 30 min in a glove box having the oxygen level of 1 ppm.



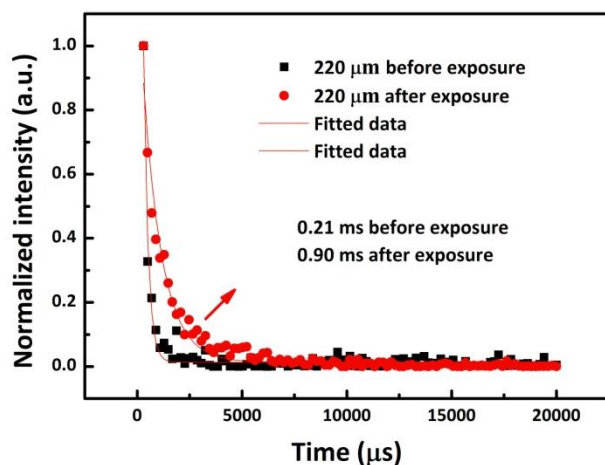
**Figure S1.** Chemical structures of Cl6A, I6A, BrPhFlA, and 6A.

## 1.2 Methods

Photoluminescence emission spectra, as well as quantum yields, were collected on a Photon Technologies International (PTI) QuantaMaster spectrofluorometer equipped with an integrating sphere. The gated emission and phosphorescence lifetime data were collected using a PTI LaserStrobe system equipped with a Xenon flash lamp. For these measurements, drop-cast samples were prepared. Singlet oxygen emission spectra were collected from an InGaAs NIR detector equipped on the PTI spectrofluorometer. For the video clips, the samples were excited by a 365 nm LED (Thorlab) at various power densities and responses were filmed with a digital camera (Nikon D7200).

## 2. Results and Discussion

### 2.1 Phosphorescence decay curves of Br6A/a-PMMA before and after the irradiation



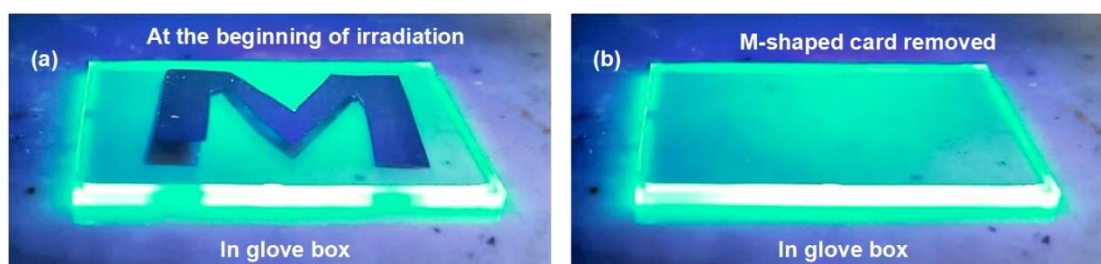
**Figure S2.** Phosphorescence decay curves of Br6A/aPMMA before and after the irradiation.

## 2.2 Phosphorescence quantum yield measurement data for Br6A in a-PMMA under sealed conditions

**Table S1.** Measurement data for the phosphorescence QY of Br6A on aPMMA under sealed condition

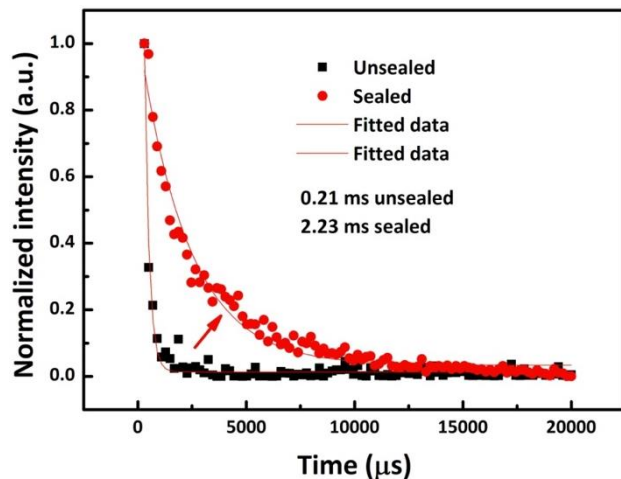
	Excitation (a.u.)	Emission (a.u)	QY
1	1970430	411603	20.9
2	2955200	556892	18.8
3	5396980	977145	18.1
4	2870400	524968	18.3
Average			19.0

## 2.3 Br6A/a-PMMA in a glove box before and after irradiation



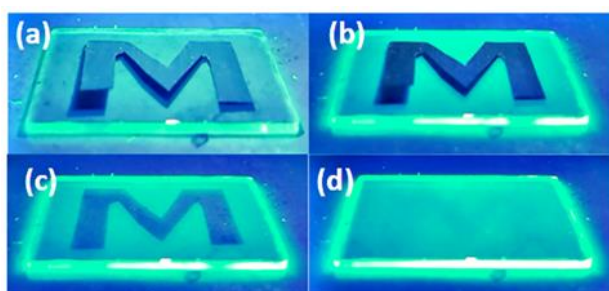
**Figure S3.1** wt% Br6A in aPMMA film excited by a 365 nm LED for 1 s and (b) after 30 s irradiation and followed by the removal of the M-shaped card in a glove box with the oxygen level below 1 ppm. No contrast is observed.

## 2.4 Phosphorescence decay curves of Br6A/a-PMMA film under sealed and unsealed conditions

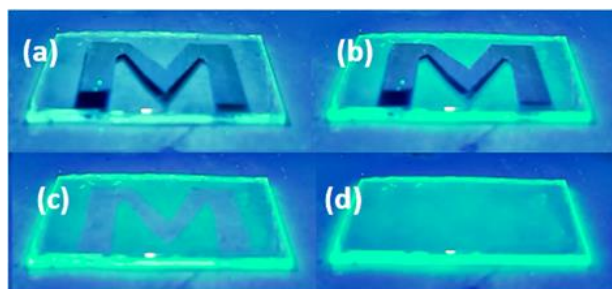


**Figure S4.** Phosphorescence decay curves of Br6A/ a-PMMA film under sealed and unsealed conditions.

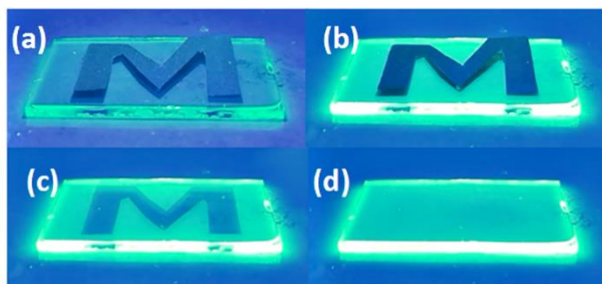
## 2.5 Emission enhancement of Cl6A, I6A and BrPhFIA in a-PMMA and no photochromism from R6G- and Ir(ppy)-doped a-PMMA as well as Br6A in i-PMMA



**Figure S5.** Emission enhancement of Cl6A in a-PMMA. (a) at the start of illumination, mask on; (b) after illumination for a while, mask on; (c) taking off the mask, photochromism behaviour was obvious; (d) kept illuminating for a while, phosphorescence from the masked area was recovered.

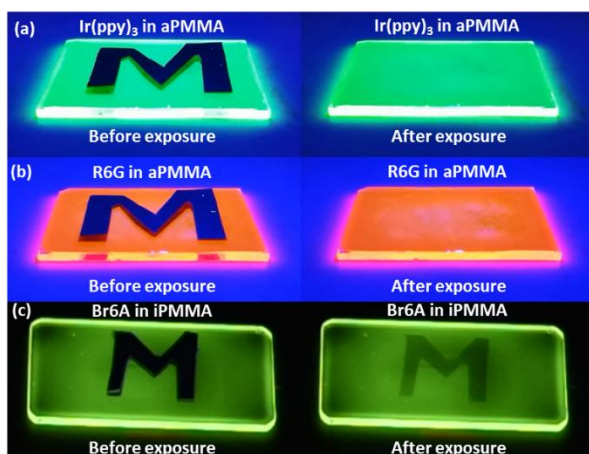


**Figure S6.** Emission enhancement of I6A in a-PMMA. (a) at the start of illumination, mask on; (b) after illumination for a while, mask on; (c) taking off the mask, photochromism behaviour was obvious; (d) kept illuminating for a while, phosphorescence from the masked area was recovered.



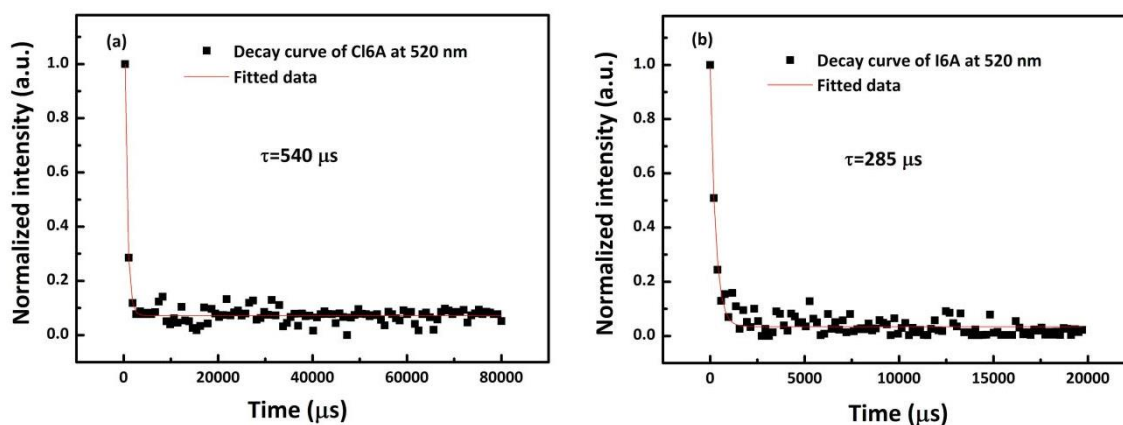
**Figure S7.** Emission enhancement of BrPhFlA in a-PMMA. (a) at the start of illumination, mask on; (b) after illumination for a while, mask on; (c) taking off the mask, photochromism behaviour was obvious; (d) kept illuminating for a while, phosphorescence from the masked area was recovered.





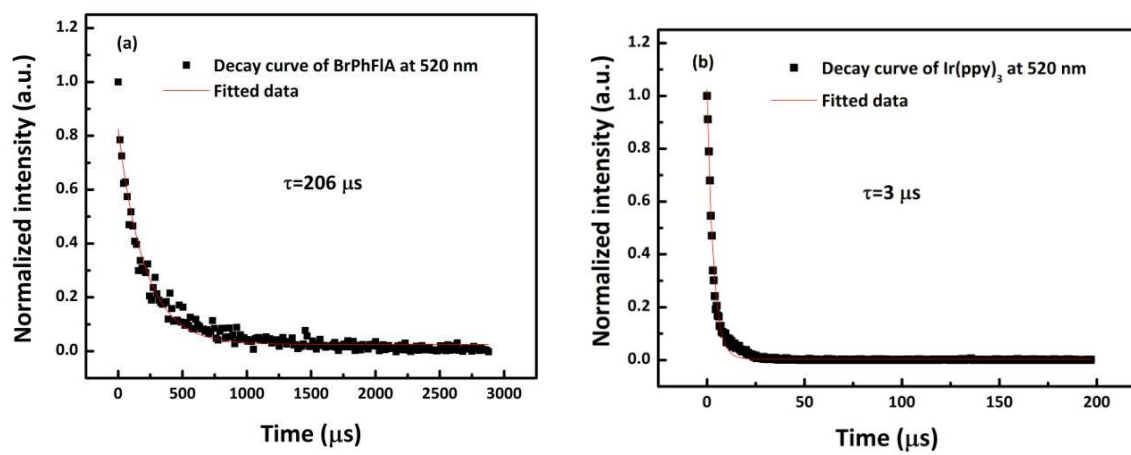
**Figure S8.** No emission enhancement of (a) Ir(ppy)<sub>3</sub> and (b) R6G in aPMMA, versus (c) obvious emission enhancement of Br6A in iPMMA before and after the irradiation.

## 2.6 Emission decay curves of Cl6A, I6A, BrPhFIA, and Ir(ppy)<sub>3</sub> as well as Br6A in

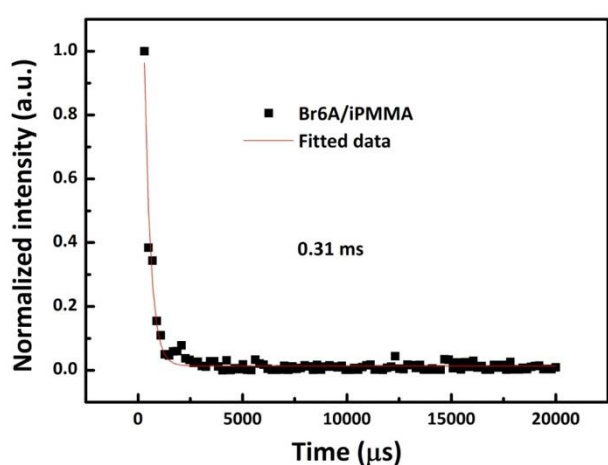


**i-PMMA**

**Figure S9.** Emission decay curves of (a) Cl6A and (b) I6A in a-PMMA.



**Figure S10.** Emission decay curves of (a) BrPhFlA and (b) Ir(ppy)<sub>3</sub> in aPMMA.



**Figure S11.** The phosphorescence decay curve of Br6A in iPMMMA.

## 2.7 The deduction of the relationship between the saturation time and the reciprocal of the power density

Considering the reaction kinetics between singlet oxygen and the substance in the polymer that can be oxidized by singlet oxygen, the concentration of the substance ( $[C]$ ) versus irradiation time ( $t$ ) should follow the first-order kinetic equation<sup>[4]</sup>,

$$[C] = [C]_0 \exp(-kPt) \quad (\text{S1})$$

where  $[C]_0$  is the initial concentration of the substance,  $P$  is the power density of the excitation source,  $k$  is the photodegradation rate constant of the substance. Thus, the reacted concentration of the substance can be expressed as,

$$[C]_{reacted} = [C]_0 - [C] = [C]_0[1 - \exp(-kPt)] \quad (S2)$$

We assume that the concentration of the reacted substance is the same

as the produced singlet oxygen concentration by UV irradiation. Then,

the concentration of the singlet oxygen produced by UV irradiation ( $[O_2^1]$ ) can be written as,

$$[O_2^1] = [C]_{reacted} = [C]_0[1 - \exp(-kPt)] \quad (S3)$$

Then, the concentration of the remaining triplet oxygen ( $[O_2^3]$ ) can be expressed as,

$$[O_2] = [O_2]_0 - [O_2^1] = [O_2]_0 - [C]_0[1 - \exp(-kPt)] \quad (S4)$$

With this expression for the oxygen concentration, we can write the Stern-Volmer equation

( $I_0/I_P = 1 + K_{SV}[O_2]$ , here,  $I_0$  is the emission intensity when oxygen cannot be consumed further.

We assume that this is the same emission intensity in the absence of oxygen.  $I_P$  is the intensity at a given oxygen concentration, and  $K_{SV}$  is the Stern-Volmer rate constant<sup>[5]</sup>)

for the irradiation process as,

$$I_0/I_P = 1 + K_{SV}\{[O_2]_0 - [C]_0[1 - \exp(-kPt)]\} = A_1 + A_2 \exp(-kPt) \quad (S5)$$

Here,  $A_1 = 1 + K_{SV}[O_2]_0 + K_{SV}[C]_0$  and  $A_2 = K_{SV}[C]_0$ , which are both constant. Based on

the result shown in Fig. 3, when the intensity reaches the saturation,  $I_0/I_P$  becomes the same for any

power density. Let's say that value of  $I_0/I_P = a$ , then,

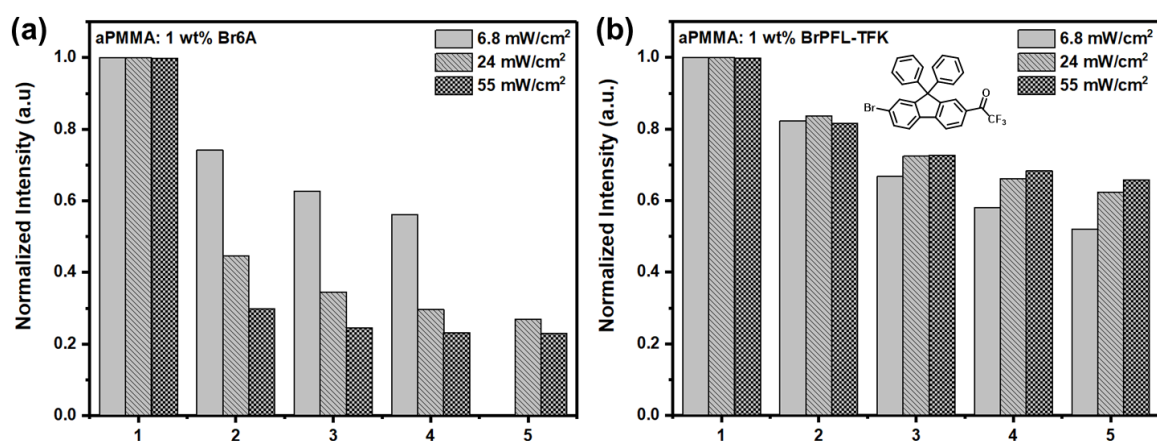
$$A_1 + A_2 \exp(-kPt) = a \quad (S6)$$

Then, we can get  $t = b/P$ . Here  $b = \ln[(A_1 - a)/A_2]/k$ . Therefore,

the relationship between the saturation time and  $1/P$  should be linear.

## 2.8 Reversibility study of the photoresponsive behavior

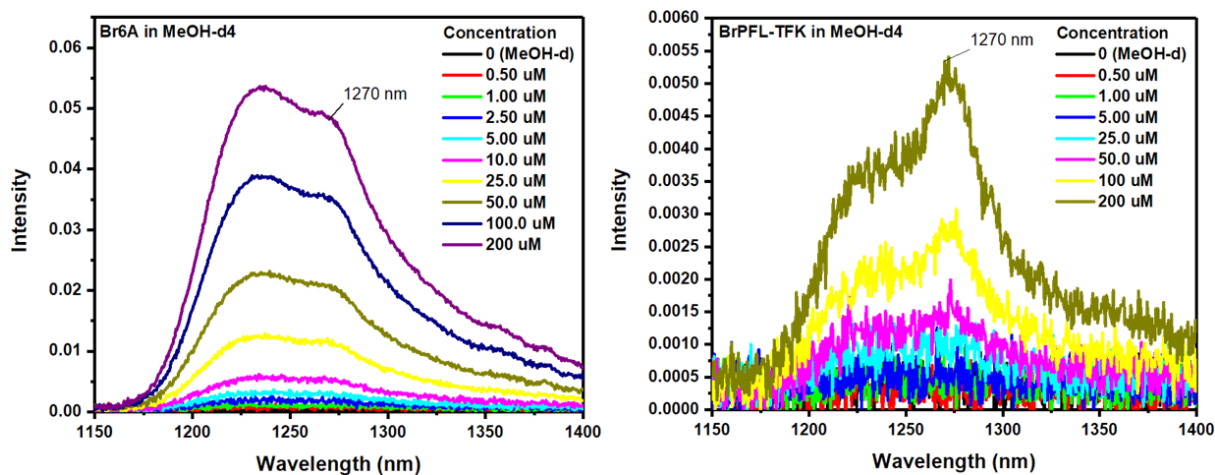
We studied the reversibility of the photoresponsive switching behavior of our system in order to discern whether the possible oxidation of matrix polymer by singlet oxygen could be the origin of the photoswitching. Directly after the films were fabricated, the achievable peak emission intensity of Br6A or BrPFL-TFK was tracked after one minute of 365 nm irradiation. After the emission intensity measurement, the film was left in ambient atmosphere for 3 minutes to ensure complete oxygen backfill before the subsequent cycle of measurement. Data were collected over 5 illumination cycles. Figure S12 shows the emission enhancement by UV irradiation is reversible even though the highest intensity reached in each cycle decreases over time due to photodegradation.



**Figure S12.** The highest achieved emission intensity in each illumination cycle at various excitation power densities of (a) aPMMA: 1 wt% Br6A drop-casted film and (b) aPMMA: 1 wt% BrPFL-TFK drop-casted film excited by 365 nm LED.

## 2.9 Singlet oxygen emission

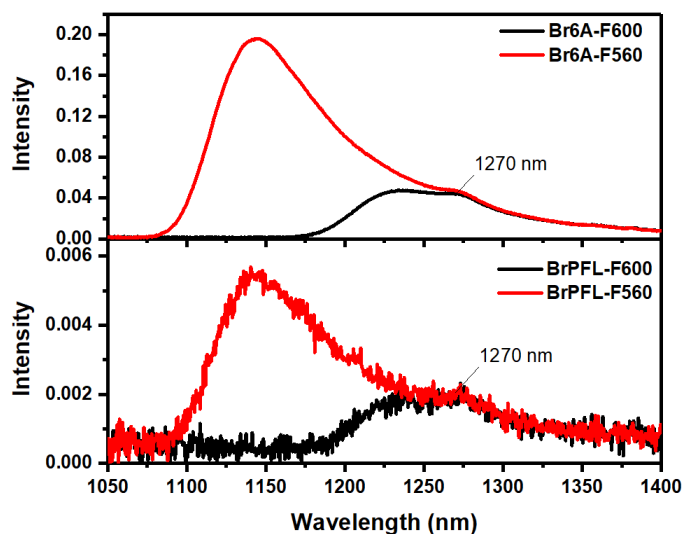
Methanol solutions of Br6A and BrPFL-TFK in various concentrations were prepared. Singlet oxygen emission was measured after 365 nm (for Br6A) or 345 nm (for BrPFL-TFK) UV irradiation.



**FigureS13.** NIR emissions spectra of Br6A and BrPFL-TFK in MeOH-d4

in various concentrations. The singlet oxygen emission is observed at 1270 nm.

The additional peak at around 1230 nm came from the second-order signal of the residual tail of the 600 nm long-pass filter could not remove. We confirmed this by using a 560 nm filter. When the 560 nm filter was used, the location of the artifact moved to ~ 1140 nm.



**FigureS14.** NIR emissionspectraof Br6A andBrPFL-TFK in MeOH-d4 withtwo differentlong-pass filters (F600: 600 nmfilter; F560: 560 nm Filter). The singleoxygenemissionpeak at 1270 nmismarked.

**References**

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