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## Visible light-absorbing rhenium(i) tricarbonyl complexes as triplet photosensitizers in photooxidation and triplet–triplet annihilation upconversion†

Xiuyu Yi, Jianzhang Zhao,\* Jifu Sun, Song Guo and Hongli Zhang

We prepared *N*^N Re(i) tricarbonyl chloride complexes (**Re-1** and **Re-2**) that give very strong absorption of visible light. To this end, it is for the first time that boron dipyrromethane (Bodipy) was used to prepare Re(i) tricarbonyl chloride complexes. The  $\pi$ -conjugation linker between the  $\pi$ -conjugation framework of the antenna Bodipy and the Re(i) coordination centre ensures efficient intersystem crossing (ISC). **Re-0** without visible light-harvesting ligand was prepared as a model complex in the photophysical studies. **Re-1** (with Bodipy) and **Re-2** (with carbazole-ethynyl Bodipy) show unprecedented strong absorption of visible light at 536 nm ( $\epsilon = 91\,700\text{ M}^{-1}\text{ cm}^{-1}$ ) and 574 nm ( $\epsilon = 64\,600\text{ M}^{-1}\text{ cm}^{-1}$ ), respectively. Interestingly, different from **Re-0**, **Re-1** and **Re-2** show fluorescence of the ligand, not the phosphorescence of the Re(i) coordination centre. However, long-lived triplet excited states were observed upon visible light excitation ( $\tau_T = 104.0\text{ }\mu\text{s}$  for **Re-1**;  $\tau_T = 127.2\text{ }\mu\text{s}$  for **Re-2**) vs. the short lifetime of **Re-0** ( $\tau_T = 26\text{ ns}$ ). With nanosecond time-resolved transient absorption spectroscopy and DFT calculations, we proved that the triplet excited states of **Re-1** and **Re-2** are localized on the Bodipy ligands. The complexes were used as triplet photosensitizers for two triplet–triplet-energy-transfer (TTET) processes, i.e.  $^1\text{O}_2$  mediated photooxidation and triplet–triplet annihilation (TTA) upconversion. With the strong visible light-harvesting ability, **Re-1** proved to be a better  $^1\text{O}_2$  photosensitizer than the conventional triplet photosensitizer tetraphenylporphyrin (TPP). Significant upconversion was observed with **Re-1** as the triplet photosensitizer. Our result is useful for preparation of Re(i) tricarbonyl chloride complexes that show strong absorption of visible light and long-lived triplet excited states and for the application of these complexes as triplet photosensitizers in photocatalysis, photodynamic therapy and TTA upconversion.

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## Introduction

Re(i) complexes have attracted much attention due to the application as luminescent bioprobes, photovoltaics and triplet photosensitizers for photocatalysis.<sup>1</sup> However, most of these complexes show weak absorption in the visible region, which is a clear disadvantage for the application of these complexes in the circumstances which require visible light excitation, such as photocatalysis.<sup>2</sup> Thus Re(i) complexes with strong absorption of visible light are highly desired, but similar to other conventional transition metal complexes, these complexes were rarely reported.<sup>3</sup> Previously we reported a Re(i) complex with coumarin-imidazole phenanthroline ligand that

shows strong visible-light absorption, but the absorption is still limited to the blue range (<500 nm).<sup>3b</sup>

The straightforward method to prepare transition metal complexes that show strong absorption of visible light is to attach a fluorophore to the coordination center.<sup>4</sup> The fluorophore should show strong absorption in the visible range, such as boron dipyrromethane (Bodipy).<sup>5</sup> However, the linker between the chromophore and the coordination centre is also crucial. In some cases the strong absorption of the complexes is *ineffective*, that is, the excitation energy harvested by the chromophore cannot be efficiently funnelled to the triplet state manifold of the complexes,<sup>6</sup> and the respective photophysics of the fluorophore ligand and the coordination centre collapse. For example, the emissive triplet excited state of the coordination center can be quenched.<sup>7</sup>

Basically there are two methods for attachment of a fluorophore to a coordination center. One is to *tether* the fluorophore to the coordination center, without  $\pi$ -conjugation linker between the two units.<sup>7,8</sup> In this case the respective energy

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†Electronic supplementary information (ESI) available: General experimental methods,  $^1\text{H}$  and  $^{13}\text{C}$  NMR data of the compounds, and the photophysical data of the Re(i) complexes. See DOI: 10.1039/c2dt32420b

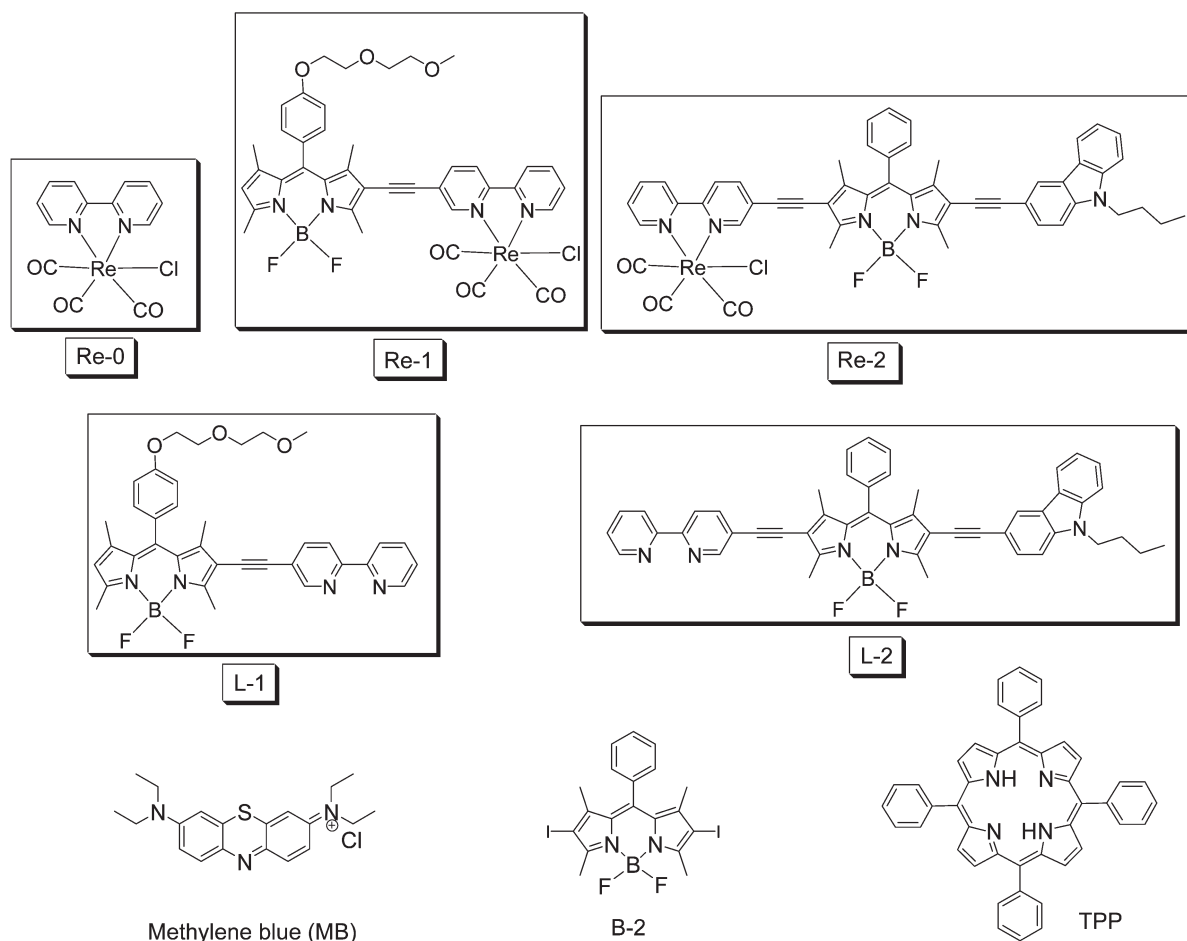
levels of the excited state of the ligands and the coordination centre have to be concerted in order to ensure an efficient energy transfer from the ligand to the coordination centre.<sup>6,9</sup> There will be a limitation on the maximal effective absorption wavelength for the ligand, that is, the excitation light with longer wavelength than this limit can be harvested by the ligand, but the energy will be trapped on the ligand and it cannot be transferred to the triplet excited state manifold of the complexes.<sup>6</sup>

Another method to enhance the absorption of transition metal complexes in the visible range is to connect a fluorophore to the coordination centre *via* a  $\pi$ -conjugation linker, such as a  $\text{C}\equiv\text{C}$  triple bond or the direct metalation method.<sup>3a,Ab,d,e,10</sup> In this case the effective absorption wavelength of the complex can be pushed further into the red end of the spectrum. One should be cautious because limitations also exist in this case, that is, the intersystem crossing (ISC) tends to be diminished with increasing the bulkiness of the ligand.<sup>10d,11,12</sup>

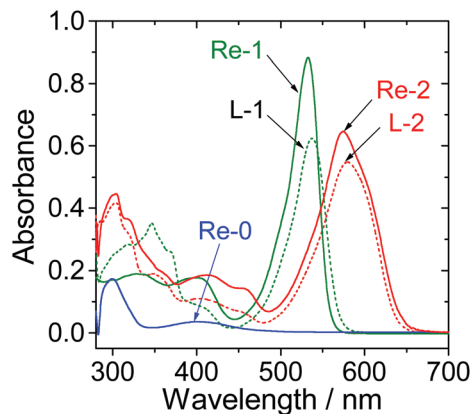
Only a few Re(i) complexes were reported to show strong visible light-absorption,<sup>1i,3a-c</sup> but the absorption wavelength is

not very long. To the best of our knowledge, no Bodipy fluorophore was used to prepare Re(i) complexes.<sup>1h,i</sup>

In order to address the above challenges, herein we designed two Re(i) complexes with Bodipy ligands (**Re-1**, **Re-2**, Scheme 1). The attachment of Bodipy to the coordination centre is based on the aforementioned  $\pi$ -conjugation method, which ensures *effective* absorption in the visible region. We used two Bodipy-conjugated  $N^N$  ligands, **L-1** shows absorption in 460 nm–560 nm and **L-2** shows absorption in 485 nm–650 nm range. We investigated the photophysical properties of the complexes with steady state and time-resolved spectroscopy, as well as DFT calculations. Both complexes show strong absorption of visible light, compared to the model complex **Re-0**, which is a typical Re(i) tricarbonyl chloride complex.<sup>1i</sup> Furthermore, the application of the complexes in *two* triplet-triplet-energy-transfer (TTET) processes was studied. We proved the triplet photosensitizing performance of the Re (i) complexes are better than the known triplet photosensitizer tetraphenylporphyrin (TPP) and Methylene Blue (MB, Scheme 1). Furthermore, the upconversion quantum yield of the Re(i) complexes are higher than a known bisiodo-



**Scheme 1** Molecular structures of the Re(i) complexes **Re-1** and **Re-2** and the ligands **L-1** and **L-2**. The known complex **Re-0** was used as a model complex in the study. Note the  $\pi$ -core of Bodipy is conjugated to the coordination centre in **Re-1** and **Re-2**. The model triplet photosensitizers tetraphenylporphyrin (TPP), MB and **B-2** are also shown (see ESI† for the synthetic details).



**Fig. 1** UV-Vis absorption of Re(i) complexes and the ligands.  $c = 1.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$  in toluene, 25 °C.

substituted Bodipy.<sup>13</sup> These results confirmed that the strong visible absorption of the Re(i) complexes is *effective*. Our results are useful for the design of transition metal complexes that show a strong absorption of visible light and long-lived triplet excited states, as well as the application of these complexes as triplet photosensitizers in photocatalysis, TTA upconversion, luminescent bio/molecular probing and photodynamic therapy, *etc.*

## Results and discussions

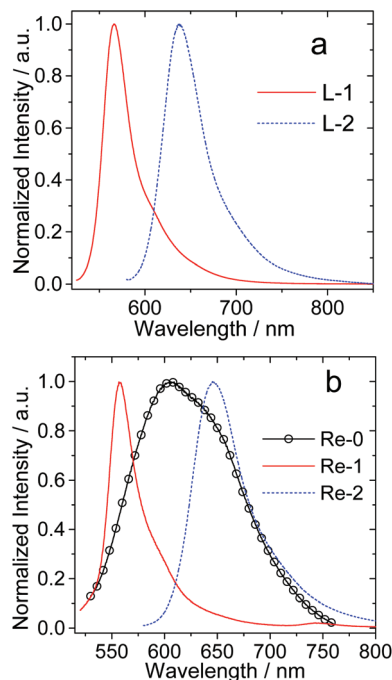
### Design and synthesis of the complexes

The Bodipy chromophore was connected to the coordination centre Re(i) *via* a  $\pi$ -conjugation linker in both complexes **Re-1** and **Re-2**.<sup>10a,c,d,14</sup> We envision that **Re-2** will show red-shifted absorption compared to **Re-1**, due to the larger  $\pi$ -conjugation framework of the ligand of **Re-2** (see ESI† for the synthetic details).

Ligands **L1** and **L2** were prepared by Stille and Sonogashira coupling reactions. The Pd(0) catalyzed Sonogashira coupling leads to ligand **L1**. In order to push the absorption wavelength to the red end of the spectra, the carbazole moiety was connected to the Bodipy core *via* a  $\text{C}\equiv\text{C}$  triplet bond linker.<sup>15</sup> Complex **Re-0** was used as a control compound in the photo-physical studies. All the compounds were obtained in moderate to good yields (see ESI† for the synthetic details).

### UV-vis absorption and emission spectra

The UV-vis absorption spectra of the ligands and the Re(i) complexes were compared (Fig. 1). The model complex **Re-0** shows very weak absorption in the visible range, which is typical for Re(i) tricarbonyl chloride complexes.<sup>18,16</sup> The Bodipy ligands **L1** and **L2** give absorption bands at 537 nm ( $\epsilon = 62\,400 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 579 nm ( $\epsilon = 54\,900 \text{ M}^{-1} \text{ cm}^{-1}$ ), respectively. Upon complexation with Re(i), slightly enhanced absorption was observed for both **Re-1** and **Re-2**, which show absorption at 536 nm ( $\epsilon = 91\,700 \text{ M}^{-1} \text{ cm}^{-1}$ ) and 574 nm ( $\epsilon = 64\,600 \text{ M}^{-1} \text{ cm}^{-1}$ ). We noted that the absorption band of **Re-2**



**Fig. 2** The normalized emission spectra of the Re(i) complexes and the ligands. (a) **L-1** ( $\lambda_{\text{ex}} = 525 \text{ nm}$ ), **L-2** ( $\lambda_{\text{ex}} = 578 \text{ nm}$ ), (b) **Re-0** ( $\lambda_{\text{ex}} = 400 \text{ nm}$ ), **Re-1** ( $\lambda_{\text{ex}} = 510 \text{ nm}$ ), **Re-2** ( $\lambda_{\text{ex}} = 570 \text{ nm}$ )  $c = 1.0 \times 10^{-5}$  mol  $\text{dm}^{-3}$  in deaerated toluene, 25 °C.

in the visible range is broader than in **Re-1**, the absorption profiles are similar to the respective ligands **L1** and **L2**. Attaching an electron-donating unit to the Bodipy moiety can broaden the absorption band.<sup>15</sup> Previously we prepared coumarin-containing Re(i) complex, which shows absorption maxima at 473 nm ( $\epsilon = 60\,800 \text{ M}^{-1} \text{ cm}^{-1}$ ).<sup>3b</sup> To the best of our knowledge, **Re-1** and **Re-2** are the Re(i) complexes that show to date the strongest absorption at the longest wavelength.<sup>11,3b</sup>

The emission of the ligands and the Re(i) complexes were studied (Fig. 2). Ligands **L1** and **L2** give intense emission at 566 nm ( $\Phi_{\text{F}} = 34.0\%$ ) and 637 nm ( $\Phi_{\text{F}} = 36.4\%$ ), respectively (Fig. 2a). Interestingly, similar emission profiles were observed for the Re(i) complexes **Re-1** and **Re-2**. However, the luminescence quantum yields of **Re-1** and **Re-2** decreased compared to that of free ligands (Table 1). Furthermore, the emission of **Re-1** and **Re-2** are not sensitive to  $\text{O}_2$ , which is different from the emission of **Re-0**, for which the emission intensity can be substantially decreased in the presence of  $\text{O}_2$  (see ESI† for detail). We also measured the luminescence lifetimes of the ligands as well as the Re(i) complexes (Table 1). Luminescence lifetimes in the range of ns were found for **Re-1** and **Re-2**. For **Re-0**, which is known to be phosphorescent, the luminescence lifetime is 23.6 ns. Based on these results, we concluded that the major luminescence bands of **Re-1** and **Re-2** are *fluorescence*, not *phosphorescence*. The characteristic phosphorescence of the Re(i) coordination centre, demonstrated by **Re-0**, was completely quenched in **Re-1** and **Re-2**. *Fluorescent* Re(i) tricarbonyl chloride complexes have been rarely reported.<sup>1p</sup>

**Table 1** Photophysical parameters of **Re-0**, **Re-1** and **Re-2**

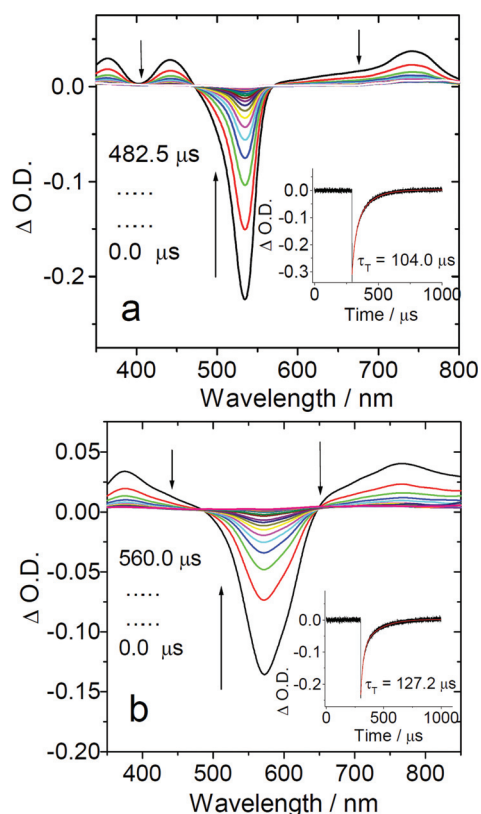
	$\lambda_{\text{abs}}^a$	$\epsilon^b$	$\lambda_{\text{em}}^c$	$\Phi_{\text{F}}^d$	$\tau_{\text{F}}^e$		$\tau_{\text{T}}^f$
					77 K	298 K	
<b>Re-0</b>	401	0.36	604	0.58%	4.1 $\mu\text{s}$	23.6 ns	26 ns <sup>g</sup>
<b>Re-1</b>	536	9.17	556, 742	0.13%	41.2, 114.8 $\mu\text{s}$	0.2 ns	104.0 $\mu\text{s}$
<b>Re-2</b>	574	6.46	647	17.1%	1.7, 282.0 $\mu\text{s}$	0.1 ns	127.2 $\mu\text{s}$
<b>L-1</b>	537	6.24	566	34.0%	—	4.34 ns	—
<b>L-2</b>	579	5.49	637	36.4%	—	1.56 ns	—

<sup>a</sup> In toluene ( $1.0 \times 10^{-5}$  mol dm<sup>-3</sup>). <sup>b</sup> Molar absorption coefficient at the absorption maxima.  $\epsilon$ :  $10^4/\text{cm}^{-1}$  mol<sup>-1</sup> dm<sup>3</sup>. <sup>c</sup> In toluene. <sup>d</sup> In toluene, with quinine sulfate ( $\Phi = 0.546$  in H<sub>2</sub>SO<sub>4</sub> (0.05 M)) for **Re-0**, bis-iodo-BODIPY ( $\Phi = 0.027$  in CH<sub>3</sub>CN) for **Re-1** and Rhodamine B ( $\Phi = 0.65$  in CH<sub>3</sub>OH) for **Re-2**, **L-1**, **L-2** as the standards. <sup>e</sup> Luminescence lifetime, at 298 K and 77 K (in C<sub>2</sub>H<sub>5</sub>OH–CH<sub>3</sub>OH = 4 : 1). <sup>f</sup> Triplet state lifetime, measured by time-resolved transient absorption.  $1.0 \times 10^{-5}$  mol dm<sup>-3</sup> in deaerated toluene. <sup>g</sup> Literature values.<sup>18</sup>

We noted the fluorescence quantum yield of **Re-2** is much higher than that of **Re-1**, indicating the ISC in **Re-2** is less efficient than **Re-1**. This result indicated that with the increase of the bulkiness of the ligand, the ISC becomes less efficient and the residual fluorescence of the ligand will be more significant.<sup>10d,11a–d</sup> However, since the fluorescence emission of the ligands was substantially reduced, the heavy atom effect of the Re(i) does exist, thus we postulate that the triplet excited state will be populated upon photoexcitation. The excitation spectra of the complexes are roughly superimposable to the UV-Vis absorption spectra (see ESI† for detail). Furthermore, it should be pointed out that the <sup>1</sup>MLCT → <sup>1</sup>Bodipy energy transfer cannot be excluded. The coumarin-Re(i) complex we prepared previously show only phosphorescence, no fluorescence was observed.<sup>3b</sup>

### Nanosecond time-resolved transient difference absorption spectra

In order to elucidate the triplet excited states of the Re(i) complexes, the time-resolved transient absorption of the complexes was studied (Fig. 3). Upon pulsed laser excitation at 532 nm, a significant bleaching band at 536 nm was observed for **Re-1**, which is due to the bleaching of the ground state of the Bodipy ligand in **Re-1**. TA bands in the range of 350 nm–450 nm and 600–800 nm were observed. The lifetime of the transient was determined as 104.0  $\mu\text{s}$  by following the decay trace at 530 nm. The transient can be substantially quenched in air saturated solution (lifetime of the transient was reduced to 0.42  $\mu\text{s}$ ). These results indicated that the transient observed is due to the triplet excited state. This conclusion was supported by the DFT calculated transient absorption of **Re-1**, which indicated absorption at 400 nm and 660 nm (see ESI† for detail), which is in agreement with the experimental observations. Similarly, a long-lived triplet excited state was also observed for **Re-2** upon pulsed photoexcitation at 532 nm ( $\tau_{\text{T}} = 127.2 \mu\text{s}$ ). The bleaching band at 570 nm is in agreement with the steady-state UV-vis absorption of the ligand **L2**. DFT calculations indicated broad transient absorption bands in the range of 350–500 nm and in the range of 650–850 nm (see ESI† for detail), which are in agreement with the experimental results.



**Fig. 3** Nanosecond time-resolved transient difference absorption spectra of (a) **Re-1**, inset is the decay trace at 530 nm, (b) **Re-2**, inset is the decay trace at 570 nm. In deaerated toluene at room temperature after pulsed excitation ( $\lambda_{\text{ex}} = 532$  nm).

These triplet excited state lifetimes are among the longest values for Re(i) complexes.<sup>1h,i</sup> Previously triplet excited state lifetimes up to 651  $\mu\text{s}$  were observed for a Re(i) complex with an excited state equilibrium.<sup>1k</sup> But the complex shows relatively weak absorption in the visible range ( $\lambda_{\text{abs}}^{\text{max}} = 408$  nm,  $\epsilon = 11\,980$  M<sup>-1</sup> cm<sup>-1</sup>).<sup>1k</sup> Re(i) complexes with dipyrinato ligand were reported,<sup>3a</sup> show strong absorption in the visible range ( $\lambda_{\text{ex}} = 490$  nm with  $\epsilon$  up to  $42\,100$  M<sup>-1</sup> cm<sup>-1</sup>), but the triplet excited states of the complexes were not studied. Recently we prepared Re(i) complexes with coumarin-phenanthroline ligands, the complexes show long-lived triplet excited



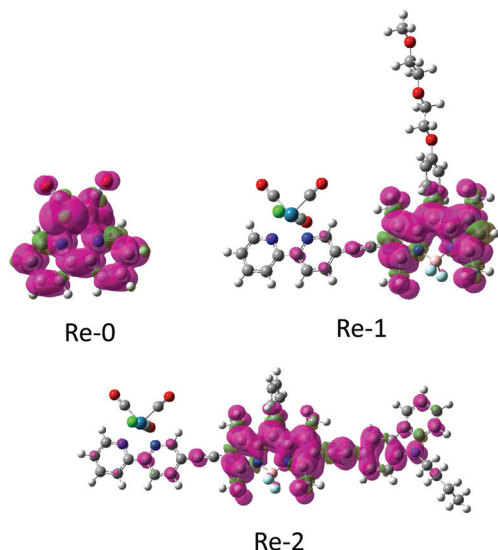


Fig. 4 Spin density of the complexes **Re-0**, **Re-1** and **Re-2**.

states ( $\tau = 86.0 \mu\text{s}$ ),<sup>3b</sup> but the complexes show blue-shifted absorption (in the range of 447–473 nm) compared to **Re-1** and **Re-2**. Re(i) complexes with strong absorption of visible light and long-lived triplet excited states will be beneficial for the application of these complexes in photocatalysis, photoluminescent biolabeling or probing and TTA upconversion. It should be noted that some of these applications do not need the complexes to be phosphorescent.<sup>17</sup>

#### DFT calculations on the photophysical properties of the Re(i) complexes

The triplet excited states of the Re(i) complexes were studied by DFT calculations on the spin density surfaces.<sup>4d,e,17a,19</sup> For **Re-0**, the spin density is localized on the Re(i) centre and the bpy ligand (Fig. 4). For **Re-1** and **Re-2**, however, the spin density surfaces are exclusively localized on the Bodipy ligands, the Re(i) centre and the bpy ligand do not contribute to the spin density surfaces. Therefore, the spin density analysis indicates that the triplet state is localized on the Bodipy ligands (intraligand state, <sup>3</sup>IL), which is in agreement with the transient absorption spectra (Fig. 3).

The geometry of the ground state of **Re-1** was optimized and the front molecular orbitals are presented (Fig. 5). The UV-vis absorption of the complexes were calculated with the TDDFT method based in the optimized  $S_0$  state geometry (Frank–Condon principle). The absorption maximum is located at 506 nm (Table 2), which is close to the experimental result at 536 nm (Fig. 1). The components of the  $S_0 \rightarrow S_1$  transition are mainly the HOMO and LUMO, both are localized on the Bodipy ligand. HOMO – 1 is also involved in the transition. The energy gap between the  $S_0$  state and the  $T_1$  state was also estimated with the DFT calculation (Table 2). The  $S_0 - T_1$  energy gap is estimated as 1.60 eV (776 nm), which is close to the phosphorescence band of **Re-1** at 742 nm (Fig. 2). Similar studies were carried out for **Re-2** (see ESI† for detail).

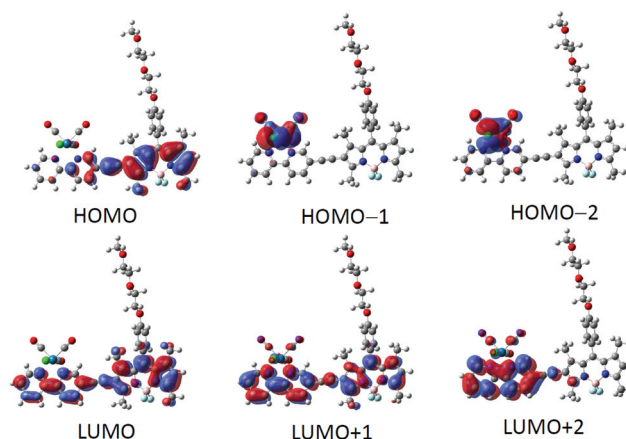


Fig. 5 Frontier molecular orbitals of **Re-1**. Calculated by DFT at the B3LYP/6-31G/LanL2DZ level using Gaussian 09W.

The photophysics of the Re(i) complexes can be summarized in Scheme 2. Note the energy level of the Bodipy ligand localized  $S_1$  state (<sup>1</sup>IL) is lower than the Re(i) coordination centre-localized state (MLCT state, based on the DFT calculations, Table 2). Therefore the energy transfer from the <sup>1</sup>Bodipy\* state to the <sup>1</sup>MLCT\* state is prohibited. The only available channel for the transformation from the <sup>1</sup>Bodipy\* state to the triplet state is ISC. In this case the heavy atom effect is crucial.

Non-efficient ISC will lead to the observation of more profound residual fluorescence of the Bodipy ligands (Fig. 2). Based on the quenching extent of the ligand fluorescence in **Re-1** and **Re-2**, we tentatively conclude that the ISC is more efficient for **Re-1** than that in **Re-2**. Also noticeable is the lower energy level of the <sup>3</sup>Bodipy\* state than the Re(i)-centred <sup>3</sup>MLCT\* state, which ensures an efficient energy transfer from <sup>3</sup>MLCT to the <sup>3</sup>Bodipy\* state, as a result the normal <sup>3</sup>MLCT emission in complexes **Re-1** and **Re-2** were completely quenched. This postulation is in full agreement with the experimental results (Fig. 2).

The Re(i) complexes **Re-1** and **Re-2** show strong absorption of visible light and long-lived triplet excited states, thus these complexes were used as triplet photosensitizers. Herein we studied two processes, the photooxidation *via* photosensitizing of the singlet oxygen (<sup>1</sup>O<sub>2</sub>) and the TTA upconversion. The application of the Re(i) complexes in these processes will reveal the ISC efficiencies in **Re-1** and **Re-2**. Furthermore, the performance of the Re(i) complexes will also be compared with some known efficient triplet photosensitizers, such as methylene blue (MB), tetraphenylporphyrin (TPP),<sup>20</sup> and **B-2**.<sup>13</sup>

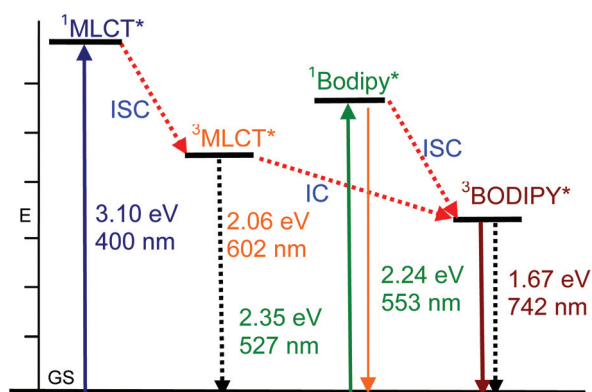
#### Photooxidation with the Re(i) complexes as the triplet photosensitizer

Firstly we studied the application of Re(i) complexes as triplet photosensitizers for <sup>1</sup>O<sub>2</sub> sensitizing. 1,5-Dihydronaphthalene (DHN) was used as the <sup>1</sup>O<sub>2</sub> scavenger (Scheme 3).<sup>2b,20</sup> DHN can be oxidized with <sup>1</sup>O<sub>2</sub> to produce Juglone, a synthetically important compound. The reaction kinetics can be easily followed

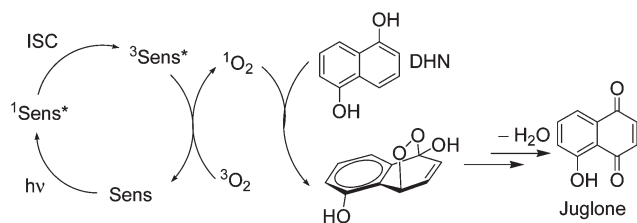
**Table 2** Electronic excitation energies (eV) and corresponding oscillator strengths ( $f$ ), main configurations and CI coefficients of the low-lying electronically excited states of complex **Re-1**, calculated by TDDFT//B3LYP/6-31G/LanL2DZ, based on the DFT//B3LYP/6-31G/LanL2DZ optimized ground state geometries

TDDFT//B3LYP/6-31G						
	Electronic transition	Energy (eV) <sup>a</sup>	$f^b$	Composition <sup>c</sup>	CI <sup>d</sup>	Character
Singlet	$S_0 \rightarrow S_1$	2.45 eV 506 nm	0.5885	H $\rightarrow$ L	0.5136	LLCT
	$S_0 \rightarrow S_2$	2.49 eV 498 nm	0.6173	H - 1 $\rightarrow$ L	0.3495	MLCT
	$S_0 \rightarrow S_3$	2.62 eV 473 nm	0.1505	H $\rightarrow$ L	0.4237	MLCT
Triplet	$T_1 \rightarrow S_0$	1.60 eV 776 nm	0.0000 <sup>e</sup>	H - 2 $\rightarrow$ L	0.5529	MLCT
	$T_1 \rightarrow S_0$			H $\rightarrow$ L	0.5726	LLCT
	$T_1 \rightarrow S_0$			H $\rightarrow$ L + 1	0.3226	LLCT
	$T_2 \rightarrow S_0$	2.15 eV 577 nm	0.0000	H $\rightarrow$ L + 1	0.3732	LLCT
	$T_2 \rightarrow S_0$			H $\rightarrow$ L	0.3408	LLCT
	$T_3 \rightarrow S_0$	2.43 eV 511 nm	0.0000	H - 1 $\rightarrow$ L	0.4506	MLCT
				H - 1 $\rightarrow$ L + 1	0.4170	MLCT

<sup>a</sup> Only the selected low-lying excited states are presented. <sup>b</sup> Oscillator strength. <sup>c</sup> H stands for HOMO and L stands for LUMO. Only the main configurations are presented. <sup>d</sup> The CI coefficients are in absolute values. <sup>e</sup> No spin-orbital coupling effect was considered, thus the  $f$  values are zero.

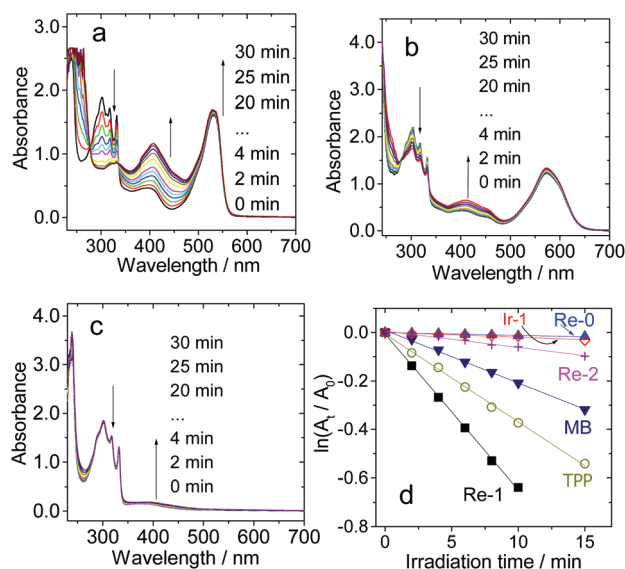


**Scheme 2** Qualitative Jablonski diagram for the photophysical process of the Re(I) complexes. Exemplified with **Re-1**. Solid lines represent excitation or radiative decay, dotted lines represent non-radiative processes. Note the  $^3\text{MLCT}$  phosphorescence is quenched by the low-lying  $^3\text{Bodipy}^*$  state. The energy levels are approximated by absorption or luminescence of the chromophores.



**Scheme 3** Mechanism for the photooxidation of DHN with a singlet oxygen ( $^1\text{O}_2$ ) photosensitizer.<sup>20a</sup>

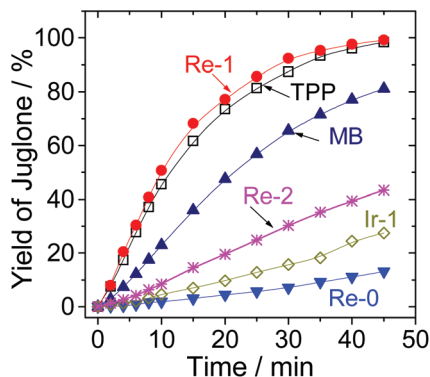
by monitoring the decay of the absorption of DHN at 301 nm, thus the  $^1\text{O}_2$  photosensitizing ability of the complexes can be compared.<sup>20</sup> Previously cyclometalated Ir(III) complexes were used for the photooxidation of DHN.<sup>20a</sup> But those conventional Ir(III) complexes show weak absorption in the visible range.<sup>20</sup> Organic triplet photosensitizers such as MB and TPP were also used for photooxidation and the performance of these visible



**Fig. 6** Photosensitizing of  $^1\text{O}_2$  with the complexes as photosensitizers. Irradiation time-dependent decrease of absorbance at 301 nm of DHN ( $2.0 \times 10^{-4}$  M) with different  $^1\text{O}_2$  sensitizers. (a) **Re-1**, (b) **Re-2**, (c) **Re-0**, (d) plots of  $\ln(A_t/A_0)$  vs. irradiation time. c [sensitizers] =  $2.0 \times 10^{-5}$  M. c [DHN] =  $2.0 \times 10^{-4}$  M. In  $\text{CH}_2\text{Cl}_2$ -MeOH (9 : 1, v/v). Broadband irradiation with 35 W xenon lamp ( $15 \text{ mW cm}^{-2}$ ) at  $25^\circ\text{C}$ .

light-absorbing chromophores is much better than the normal Ir(III) complex  $^1\text{O}_2$  photosensitizers.<sup>20a</sup> Recently we used cyclometalated Ir(III) complexes showing a strong absorption of visible light for the photooxidation of DHN, but the absorption wavelength is in the blue range.<sup>2b</sup> To the best of our knowledge, no visible light-absorbing Re(I) complexes have been used as triplet photosensitizers for photooxidation. Herein we will show that **Re-1** is more efficient than the well-known triplet photosensitizer TPP and RB (Scheme 1).

The three Re(I) complexes were used as  $^1\text{O}_2$  photosensitizers (Fig. 6). With **Re-1**, the change of UV-vis absorption is much more significant than that with **Re-0** as the photosensitizer



**Fig. 7** Plots of chemical yield as a function of irradiation time for the photooxidation of DHN using **Re-1**, **Re-0**, TPP, MB, [Ir(ppy)<sub>2</sub>(dpy)]<sup>+</sup> as triplet photosensitizers. *c* [sensitizers] =  $2.0 \times 10^{-5}$  M. Broadband irradiation with 35 W xenon lamp (light power  $15 \text{ mW cm}^{-2}$ ). In  $\text{CH}_2\text{Cl}_2$ –MeOH (9 : 1 v/v) at 25 °C.

**Table 3** Photophysical parameters of the Re(i) and the organic triplet photosensitizers<sup>a</sup>

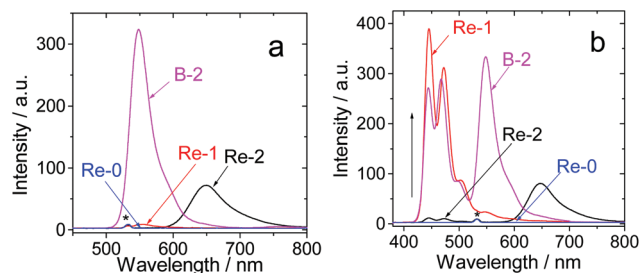
	$k_{\text{obs}}/\text{min}^{-1a}$	$\nu_i/\text{b}$	Yield <sup>c</sup> (%)	$\Phi_{\Delta}^d$
<b>Re-1</b>	65	6.5	99.3	0.88
<b>Re-2</b>	6	0.6	43.4	0.06
<b>TPP</b>	37	3.7	98.5	0.62 <sup>e</sup>
<b>MB</b>	21	2.1	81.1	0.57
<b>Ir(ppy)<sub>2</sub>bpy<sup>+</sup></b>	2	0.2	27.5	—

<sup>a</sup> Photoreaction rate constants:  $10^{-3} \text{ min}^{-1}$ . <sup>b</sup> Initial rate:  $10^{-5} \text{ M}$ . In  $\text{min}^{-1}$ . <sup>c</sup> Yield of Juglone after photoirradiation for 45 min. <sup>d</sup> Quantum yield of singlet oxygen ( $^1\text{O}_2$ ), with Rose Bengal as standard ( $\Phi_{\Delta} = 0.8$  in  $\text{CH}_3\text{OH}$ ). <sup>e</sup> Literature values.<sup>21</sup>

(Fig. 7c). For **Re-2**, however, the change of UV-vis absorption is not significant upon photoirradiation (Fig. 6b). Thus we propose that the  $^1\text{O}_2$  sensitizing ability of **Re-1** is more significant than **Re-0** and **Re-2**. The weak  $^1\text{O}_2$  sensitizing ability of **Re-0** can be attributed to its weak absorption of visible light. For **Re-2**, we propose the non-efficient ISC may be responsible for the weak  $^1\text{O}_2$  photosensitizing ability, which is supported by the strong fluorescence of **Re-2** rather than that of **Re-1**.

We also studied photooxidation with the known triplet photosensitizers TPP and MB (Fig. 6 and 7). The photooxidation rate with **Re-1** is more faster than that with TPP and MB as the triplet photosensitizers. It should be noted that TPP and MB proved to be much more efficient as  $^1\text{O}_2$  photosensitizers than the normal Ir(III) complex photosensitizers.<sup>20</sup> To the best of our knowledge, there is no transition metal complex reported to be more efficient than TPP and MB as  $^1\text{O}_2$  photosensitizers.<sup>20</sup>

The kinetic data of the photooxidation were compiled in Table 3.  $k_{\text{obs}}$  value of **Re-1** is 10-fold that of **Re-2**, and it is also at least 2-fold that of TPP. Furthermore, the  $^1\text{O}_2$  quantum yields ( $\Phi_{\Delta}$ ) of the Re(i) complexes were also determined. We found that **Re-1** gives the highest value ( $\Phi_{\Delta} = 0.88$ ). **Re-2** gives a  $\Phi_{\Delta}$  value of 0.06. The strong absorption of visible light and the high  $\Phi_{\Delta}$  value of **Re-1** may be responsible for the significant photooxidation capability of **Re-1**. The bis-iodo-BODIPY



**Fig. 8** Emission and upconversion of the complexes with perylene as the triplet acceptor with 532 nm (5 mW) laser excitation. (a) Emission of the complexes alone. (b) The upconverted perylene fluorescence and the residual luminescence of the photosensitizers **Re-1**, **Re-0** or **B-2**, respectively. *c* [perylene] =  $3.0 \times 10^{-5} \text{ M}$ ; *c* [photosensitizers] =  $1.0 \times 10^{-5} \text{ M}$  in deaerated toluene. The asterisks in (a) and (b) indicate the scattered 532 nm excitation laser at 25 °C.

**B-2** was used as a triplet photosensitizer as previously.<sup>13,22</sup>  $\Phi_{\Delta} = 0.79$  was determined for **B-2**. Based on these results, we concluded that the ISC is highly efficient in **Re-1**, at least 88%.

### Triplet-triplet annihilation upconversion

The Re(i) complexes were also used as triplet photosensitizers for TTA upconversion.<sup>23</sup> Compared to other upconversion methods, such as those with two-photon absorption dyes,<sup>24</sup> or with rare earth materials,<sup>25</sup> TTA upconversion shows the advantages of the requirement of low and non-coherent excitation light, strong absorption of the excitation light, high upconversion quantum yield and tunable excitation/emission wavelength.<sup>23g,i,j</sup>

One of the major areas of TTA upconversion research is to develop new triplet photosensitizers.<sup>23i</sup> Conventionally the triplet photosensitizers are limited to Pt(II)/Pd(II) porphyrin complexes.<sup>23a,f,26</sup> Recently we developed a series of Ru(II),<sup>6,17a</sup> Pt(II),<sup>10c,d,14b,27c,d</sup> Ir(III),<sup>27b</sup> and Re(i) complexes<sup>3b</sup> as triplet photosensitizers for TTA upconversion.<sup>23i,27</sup> These complexes share the common features of strong absorption of visible light and long-lived triplet excited states. The molecular diversity we developed for the triplet photosensitizers may offer an opportunity for further facile adaptation of the TTA upconversion for applications in other areas, such as photocatalysis,<sup>28</sup> photovoltaics,<sup>29</sup> luminescent bioimaging,<sup>23i,30</sup> and luminescent  $\text{O}_2$  sensing.<sup>31</sup>

Firstly the emission of the triplet photosensitizers alone upon 532 nm laser excitation were studied (Fig. 8a). **Re-2** gives intense emission, whereas **Re-0** and **Re-1** give very weak emission. The weak emission of **Re-0** and **Re-1** is due to the weak absorption of the complex at the excitation wavelength or the low fluorescence quantum yields. With addition of the triplet acceptor perylene, intense blue emission in the range of 430–550 nm was observed for **Re-1**. For **Re-2**, however, the emission band at the same position is much weaker. No upconverted emission was found with **Re-0** as the triplet photosensitizer. The new emission band is similar to the prompt fluorescence of perylene (see ESI†), therefore the new emission band was assigned as the TTA upconversion, *i.e.* the delayed fluorescence of perylene.

**Table 4** Photophysical parameters of **Re-0**, **Re-1** and **Re-2**

	$\epsilon^a$	$\tau_T/\mu\text{s}^b$	$\Phi_F^c$	$K_{SV}/\text{M}^{-1}$ ( $\times 10^5$ ) <sup>d</sup>	$k_q/\text{M}^{-1}\text{s}^{-1}$ ( $\times 10^9$ ) <sup>e</sup>	$\Phi_{UC}^f$	$\eta^g$
<b>Re-1</b>	8.83	104.0	0.13%	6.75	6.49	8.5%	7.5
<b>Re-2</b>	2.66	127.2	17.1%	6.42	5.05	2.0%	0.5
<b>B-2</b>	8.90	67.3	2.7%	3.28	4.87	5.3%	4.7

<sup>a</sup> Molar extinction coefficient at the excited wavelength (532 nm).  $\epsilon$ :  $10^4/\text{cm}^{-1}\text{mol}^{-1}\text{dm}^3$ . <sup>b</sup> Triplet state lifetimes. <sup>c</sup> Fluorescence quantum yield. <sup>d</sup> Quenching constant. <sup>e</sup> Bimolecular quenching constants. <sup>f</sup> Upconversion quantum yields, and with bis-iodo-BODIPY (**B-2**) as the standard ( $\Phi = 2.7\%$  in  $\text{CH}_3\text{CN}$ ). <sup>g</sup>  $\eta = \epsilon \times \Phi_{UC}$ . In  $10^3\text{M}^{-1}\text{cm}^{-1}$ .

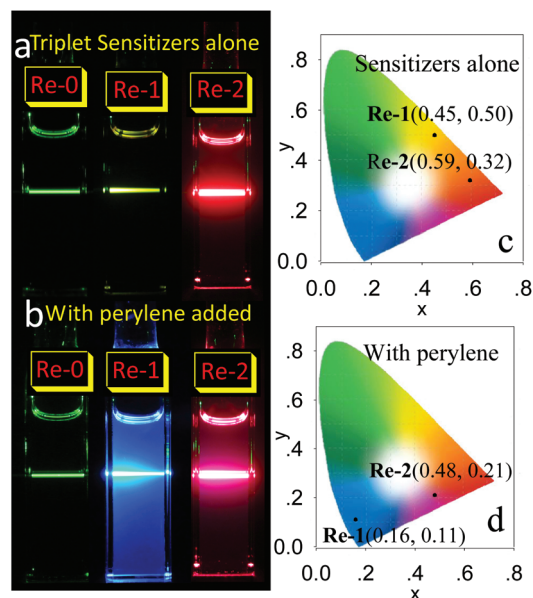
The upconversion quantum yields ( $\Phi_{UC}$ ) were determined (Table 4). **Re-1** shows an upconversion quantum yield ( $\Phi_{UC}$ ) of 8.5%, which is more than 4-fold that of **Re-2**. We proposed the overall upconversion capability of a triplet photosensitizer should be  $\eta = \epsilon \times \Phi_{UC}$  (where  $\epsilon$  is the molar extinction coefficient of the triplet photosensitizer at the excitation wavelength).<sup>23i</sup> The  $\eta$  value of **Re-1** is 15-fold that of **Re-2** with the 532 nm laser excitation.

The upconversions were compared with iodo-BODIPY (**B-2**, Scheme 1), which shows a similar molar extinction coefficient at 532 nm compared to **Re-1**. With bis-iodo substitution in **B-2**, the ISC of **B-2** is efficient ( $\Phi_{\Delta} = 79\%$ ).<sup>13,22</sup> **B-2** was used as a triplet photosensitizer.<sup>13</sup> A slightly smaller upconversion quantum yield of 5.3% was determined for **B-2**. This lower upconversion quantum yield can be attributed to its shorter triplet excited state lifetime ( $\tau_T = 57.1\text{ }\mu\text{s}$ ) compared with that of **Re-1** ( $\tau_T = 104.0\text{ }\mu\text{s}$ ).

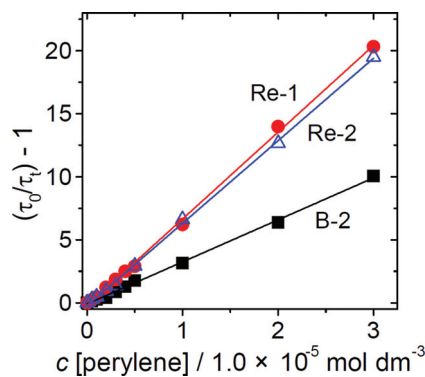
The TTA upconversion with the **Re(i)** complexes as the triplet photosensitizers are clearly visible by the naked eye (Fig. 9). For example, the emission color of **Re-1** or **Re-2** alone is green and cherry-red, which are due to the fluorescence emission of the complexes. In the presence of the triplet acceptor of perylene, the emission color of **Re-1** turns to bright-blue, which is due to the upconverted fluorescence of perylene. For **Re-2**, however, the emission color barely changed, which is in full agreement with the spectral observations (Fig. 9b). For **Re-0**, no upconversion was observed (the green color of **Re-0** or **Re-0**/perylene mixed solution is due to the scattered excitation laser). The changes of the emission color were quantified with the CIE coordinates (Fig. 9c and d).

In order to quantify the efficiency of the TTET process, the quenching of the triplet excited state lifetime of the triplet photosensitizers by the triple acceptor perylene was studied (Fig. 10). The quenching constants of **Re-1** ( $K_{SV} = 6.75 \times 10^5\text{ M}^{-1}$ ) and **Re-2** ( $K_{SV} = 6.42 \times 10^5\text{ M}^{-1}$ ) are close to each other (Table 4), which is due to the similar triplet excited state lifetime of the two complexes. The quenching constant of **B-2** is only half that of **Re-1** and **Re-2**, which is due to the shorter  $T_1$  state lifetime of **B-2**. Despite the similar quenching constants, **Re-2** shows much weaker TTA upconversion than **Re-1**, which can be assigned to the weak absorption of **Re-2** at the excitation wavelength and the less efficient ISC of **Re-2**.

In order to unambiguously confirm the TTA upconversion observed with **Re-1** as the triplet photosensitizer, the



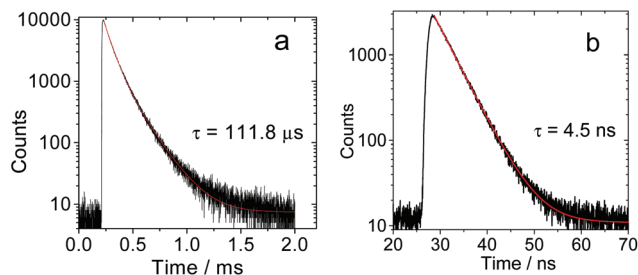
**Fig. 9** (a) Photographs of the emission of the photosensitizers alone and (b) the upconversion. (c) CIE diagram of the emission of sensitizers alone and (d) in the presence of perylene (upconversion).  $\lambda_{ex} = 532\text{ nm}$  (laser power: 5 mW). In deaerated toluene,  $c$  [sensitizer] =  $1.0 \times 10^{-5}\text{ M}$ ,  $c$  [perylene] =  $3.0 \times 10^{-5}\text{ M}$ , 25 °C.



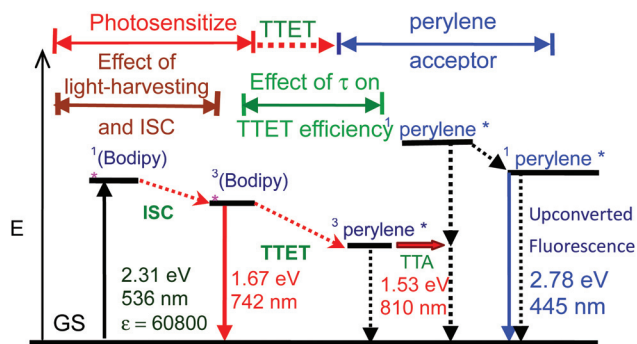
**Fig. 10** Quenching of the lifetime of the triplet photosensitizers with increasing concentration of perylene. Stern-Volmer plots for the lifetime quenching.  $c$  [photosensitizers] =  $1.0 \times 10^{-5}\text{ mol L}^{-1}$ , in deaerated toluene. The triplet excited state lifetimes were measured with a transient absorption spectrometer upon 355 nm nanosecond laser excitation, 25 °C.

luminescence lifetime of the upconversion observed in Fig. 8 were measured (Fig. 11). For **Re-1** as the triplet photosensitizer, the luminescence lifetime of the blue emission band observed in the presence of perylene was determined as 111.8  $\mu\text{s}$ . The prompt fluorescence lifetime of perylene determined in a different experiment was measured as 4.5 ns. Similar long-lived lifetimes were also observed with **Re-2** ( $\tau = 52.85\text{ }\mu\text{s}$ ) and **B-2** ( $\tau_T = 154.1\text{ }\mu\text{s}$ ) as the triplet photosensitizer in the TTA upconversion experiments (see ESI† for more details). The long-lived luminescence is the characteristic feature of the TTA upconversion.<sup>3b,14c,d,23d,27c,32</sup>





**Fig. 11** (a) Delayed fluorescence observed in the TTA upconversion with **Re-1** as triplet photosensitizer and perylene as the triplet acceptor. Excited at 532 nm (nanosecond pulsed OPO laser synchronized with spectrofluorometer) and monitored at 445 nm. Under these circumstances **Re-1** is selectively excited and the emission is due to the upconverted emission of perylene. (b) The prompt fluorescence decay of perylene determined in a different experiment (excited with EPL picosecond 405 nm laser, the decay of the emission was monitored at 445 nm). In deaerated toluene.  $c$  [sensitizers] =  $1.0 \times 10^{-5}$  M;  $c$  [perylene] =  $3.0 \times 10^{-5}$  M; 25 °C.



**Scheme 4** Jablonski diagram of TTA upconversion with **Re-1** as triplet photosensitizer.  $E$  is energy. GS is ground state ( $S_0$ ).  $^1\text{Bodipy}^*$  is intraligand singlet excited state localized on Bodipy ligand.  $^3\text{Bodipy}^*$  is intraligand triplet excited state localized on the Bodipy ligand. TTET is triplet–triplet energy transfer.  $^3\text{perylene}^*$  is the triplet excited state of perylene. TTA is triplet–triplet annihilation.  $^1\text{perylene}^*$  is the singlet excited state of perylene. The emission bands observed for the sensitizers along is the  $^1\text{IL}/^3\text{IL}$  emission. The emission bands observed in the TTA upconversion experiment is the delayed emission of perylene.

The photophysical processes involved in the photoexcitation and the TTA upconversion with **Re-1** can be summarized in Scheme 4. After photoexcitation of **Re-1**, the singlet excited state was obtained, which is localized by the Bodipy ligand ( $^1\text{Bodipy}^*$  state). Then through the process of intersystem crossing (ISC), the triplet excited state was produced ( $^3\text{Bodipy}^*$ ), facilitated by the heavy atom effect of Re(i). With the triplet–triplet energy transfer (TTET) from the triplet excited state of **Re-1** to perylene, the triplet excited state of perylene was populated. Note the energy level of the triplet acceptor must be lower than the energy level of the triplet photosensitizer. The biomolecular quenching constants are on the scale of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ , indicating diffusion-controlled quenching, *i.e.* the TTET is efficient. In turn the TTA process gives the singlet excited state of perylene. The delayed fluorescence was produced from the radiative decay of the  $S_1$  state of perylene, which was proved by the measurement of the

luminescence lifetime (for **Re-1**, the lifetime of the delayed fluorescence is 111.8  $\mu\text{s}$ , *vs.* the 4.5 ns for the prompt fluorescence of perylene).

## Conclusions

In conclusion,  $N^{\wedge}N$  Re(i) tricarbonyl chloride complexes with to date the strongest absorption in the visible range ( $\epsilon$  is up to  $91\,700 \text{ M}^{-1} \text{ cm}^{-1}$  at 536 nm) and long-lived triplet excited state (104  $\mu\text{s}$ ) were prepared. It is also for the first time that the well-known fluorophore of Bodipy was used to enhance the visible-light-absorption of the Re(i) tricarbonyl chloride Re(i) complexes. Different from the model complex (**Re-0**), in which no visible-light-harvesting chromophore is presented and showing phosphorescence, the new Re(i) complexes show the fluorescence of Bodipy ligands. Furthermore, Bodipy ligand-localized triplet excited states were identified with nanosecond time-resolved transient difference absorption spectroscopy and spin density analysis. The complexes were used as triplet photosensitizers in two different triplet–triplet-energy-transfer (TTET) processes, *i.e.* the singlet oxygen ( $^1\text{O}_2$ ) mediated photo-oxidation and the triplet–triplet annihilation (TTA) upconversion. We found that the  $^1\text{O}_2$  photosensitizing efficiency of the new Re(i) complexes are up to 3-fold that of the known efficient triplet photosensitizers such as tetraphenylporphyrin (TPP) and methylene blue (MB). The TTA upconversion quantum yields ( $\Phi_{\text{UC}}$ ) of the new Re(i) complexes are 1.6-fold that of the efficient bis-iodo-BODIPY triplet photosensitizer. Therefore we conclude that the strong visible-light absorption of the new Re(i) complex is *effective*, that is, the excitation energy harvested by the Bodipy ligand can be efficiently funnelled to the triplet excited states of the complexes. Our results are useful for preparation of Re(i) tricarbonyl complexes that show strong absorption of visible light and long-lived triplet excited states, as well as for the application of these complexes as triplet photosensitizers in photocatalysis, photodynamic therapy (PDT) and triplet–triplet annihilation upconversion.

## Experimental

### Analytical measurements

NMR spectra were recorded on a Bruker 400 MHz spectrometer ( $\text{CDCl}_3$  as solvent, TMS as standard, 0.00 ppm). High resolution mass spectra (HR MS) were determined on a LC/QTOF MS system (UK). Fluorescence spectra were measured on a RF-5301 PC fluorospectrometer (Shimadzu, Japan). Fluorescence lifetimes were measured with a OB920 lifetime spectrofluorometer (Edinburgh instruments, UK). Absorption spectra were recorded on a UV2550 UV/vis spectrophotometer (Shimadzu) and an Agilent 8453 UV/vis near-IR spectrophotometer. The nanosecond time-resolved transient absorption spectra were measured on a LP920 laser flash photolysis spectrometer (Edinburgh Instruments, UK) and recorded on a Tektronix TDS 3012B oscilloscope. The lifetime values (by

monitoring the decay trace of the transients) were obtained with LP900 software.

## Materials

All the chemicals were analytically pure and used as received. Solvents were dried and distilled for synthesis.  $\text{Re}(\text{CO})_5\text{Cl}$  was purchased from Sigma-Aldrich Corp. Compounds **1** to **6** were synthesized according to literature methods (see ESI† for detail). **7** to **10** were prepared by the reported method.<sup>34</sup>

**SYNTHESIS OF L1.** **4** (80 mg, 0.14 mmol) and 5-ethynyl-2,2'-bipyridine (**10**) (25 mg, 0.14 mmol) were added to deaerated triethylamine (15 mL). Then  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (5 mg, 5 mol%),  $\text{PPh}_3$  (4 mg, 10 mol%) and  $\text{CuI}$  (3 mg, 10 mol%) were added under an Ar atmosphere. The mixture was stirred and refluxed for 12 h under argon. After completion of the reaction, the mixture was cooled to RT and the light red precipitate was collected by filtration. The crude product was purified with column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ -ethyl acetate = 20 : 1, v/v) to give red solid, 59 mg (67.8%). M.p. > 250 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.78 (d, 2H,  $J$  = 13.7 Hz); 8.50–8.43 (m, 2H); 7.92–7.87 (m, 2H); 7.41–7.38 (m, 1H); 7.23 (d, 2H,  $J$  = 8.3 Hz); 7.12 (d, 2H,  $J$  = 8.1 Hz); 6.10 (s, 1H); 4.27 (t, 2H,  $J$  = 3.2 Hz); 3.98 (t, 2H,  $J$  = 3.2 Hz); 3.82 (t, 2H,  $J$  = 3.2 Hz); 3.67 (t, 2H,  $J$  = 4.0 Hz); 3.46 (s, 3H); 2.77 (s, 3H); 2.63 (s, 3H); 1.62 (s, 3H); 1.51 (s, 3H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 159.63, 158.23, 155.37, 154.11, 151.26, 149.11, 145.30, 142.42, 139.00, 137.31, 133.18, 130.60, 129.14, 126.76, 120.44, 115.40, 114.23, 92.75, 86.82, 71.99, 70.91, 69.79, 67.50, 59.21, 29.73, 14.78, 13.46 ppm. HRMS (MALDI): calcd  $[\text{C}_{36}\text{H}_{35}\text{BF}_2\text{N}_4\text{O}_3 + \text{H}]^+$ :  $m/z$  = 621.2849; found:  $m/z$  = 621.2795.

**SYNTHESIS OF L2.** The synthetic procedure was the same as that for **L1** except that compound **11** (97 mg, 0.14 mmol),<sup>13</sup> instead of **4**, was used. The crude product was purified by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{OH}$  = 100 : 1) to give a dark purple solid. Yield: 67 mg (63.8%). M.p. > 250 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.74 (s, 1H); 8.71 (d, 1H,  $J$  = 4.1 Hz); 8.46 (d, 2H,  $J$  = 8.4 Hz); 8.20 (s, 1H); 8.08 (d, 1H,  $J$  = 7.9 Hz); 7.88 (d, 2H,  $J$  = 8.5 Hz); 7.56–7.55 (m, 4H); 7.50 (t, 1H,  $J$  = 6.1 Hz); 7.41 (d, 1H,  $J$  = 7.9 Hz); 7.36–7.32 (m, 4H); 7.18–7.08 (m, 1H); 4.32 (t, 2H,  $J$  = 14.2 Hz); 2.79 (d, 6H,  $J$  = 16.5 Hz); 1.89–1.81 (m, 2H); 1.59 (d, 6H,  $J$  = 14.5 Hz); 1.44–1.34 (m, 2H); 0.96–0.92 (m, 3H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 157.57, 155.77, 154.04, 152.15, 148.51, 147.49, 145.87, 145.50, 144.54, 143.69, 142.64, 141.71, 141.00, 140.26, 139.19, 138.00, 134.57, 131.98, 129.23, 126.30, 123.08, 121.93, 119.52, 116.49, 113.35, 109.58, 109.14, 108.92, 93.14, 90.29, 87.05, 86.12, 61.91, 59.18, 43.17, 29.89, 20.71, 14.08, 13.79 ppm. HRMS (MALDI): calcd  $[\text{C}_{49}\text{H}_{40}\text{BF}_2\text{N}_5]^+$ :  $m/z$  = 747.3345; found:  $m/z$  = 747.3300.

**SYNTHESIS OF Re-0.**  $\text{Re}(\text{CO})_5\text{Cl}$  (30 mg, 0.08 mmol) and 2,2'-bipyridine (**L0**, 13 mg, 0.08 mmol) were dissolved in dry toluene and heated to 110 °C, the mixture was stirred under Ar for 1 h. The solvent was then removed under reduced pressure, and the product was obtained as a light yellow solid by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{OH}$  = 100 : 1). Yield: 34 mg (91.9%). M.p. > 250 °C.  $^1\text{H}$  NMR (400 MHz,

$\text{CDCl}_3$ ),  $\delta$  = 9.09 (d, 2H,  $J$  = 5.4 Hz); 8.22 (d, 2H,  $J$  = 8.1 Hz); 8.10 (t, 2H,  $J$  = 15.8 Hz); 7.58 (t, 2H,  $J$  = 12.9 Hz). HRMS (MALDI): calcd  $[\text{C}_{13}\text{H}_8\text{ClN}_2\text{O}_3\text{Re}-\text{Cl}]^+$ :  $m/z$  = 427.0093; found:  $m/z$  = 427.0082. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  = 2023 (s), 1890 (s), 1601 (m), 1471 (m), 1444 (m), 777 (m), 765 (m).

**SYNTHESIS OF Re-1.** The synthetic procedure was the same as that for **Re-0** except that **L1** (50 mg, 0.08 mmol) was used. The product was obtained as a red solid by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{OH}$  = 100 : 1). Yield: 56 mg (75.7%). M.p. > 250 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $\delta$  = 9.02–9.05 (m, 2H); 8.10–8.15 (m, 2H); 7.95–8.04 (m, 2H); 7.50 (t, 1H,  $J$  = 12.6 Hz); 7.17 (t, 2H,  $J$  = 13.2 Hz); 7.07 (d, 2H,  $J$  = 8.4 Hz); 6.09 (s, 1H); 4.22 (t, 2H,  $J$  = 7.9 Hz); 3.93 (t, 2H,  $J$  = 7.9 Hz); 3.76 (t, 2H,  $J$  = 8.4 Hz); 3.61 (t, 2H,  $J$  = 8.4 Hz); 3.42 (s, 3H); 2.71 (s, 3H); 2.60 (s, 3H); 1.58 (s, 3H); 1.48 (s, 3H) ppm.  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 196.74, 189.46, 159.83, 154.59, 153.33, 153.09, 146.37, 142.84, 140.05, 138.99, 133.82, 129.12, 127.00, 126.52, 125.21, 123.29, 122.69, 115.60, 112.65, 92.32, 90.36, 83.57, 72.08, 71.00, 69.87, 67.66, 59.23, 29.83, 15.08, 13.60 ppm. HRMS (MALDI): calcd  $[\text{C}_{39}\text{H}_{35}\text{N}_4\text{O}_6\text{ClBF}_2\text{Re}]^-$ :  $m/z$  = 926.1864, found:  $m/z$  = 926.1855. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  = 2924 (m), 2200 (m), 2022 (s), 1914 (s), 1887 (s), 1608 (m), 1540 (s), 1516 (s), 1478 (m), 1317 (m), 1277 (m), 1191 (s), 1108 (m), 1060 (m), 990 (m), 791 (m). Elemental analysis calcd (%) for  $[\text{C}_{39}\text{H}_{35}\text{N}_4\text{O}_6\text{ClBF}_2\text{Re} + 1.5 \text{H}_2\text{O}]$ : C 49.11, H 3.99, N 5.88; found: C 49.05, H 4.06, N 5.78.

**SYNTHESIS OF Re-2.** The synthetic procedure was the same as that for **Re-0** except that **L2** (60 mg, 0.08 mmol), which replaced **L0** was used. The product was obtained as a dark purple solid by column chromatography (silica gel,  $\text{CH}_2\text{Cl}_2$ - $\text{CH}_3\text{OH}$  = 100 : 1). Yield: 61 mg, (72.6%). M.p. > 250 °C. No  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectrum were not measured due to the poor solubility of the compound in common organic solvents. HRMS (MALDI): calcd  $[\text{C}_{52}\text{H}_{40}\text{N}_5\text{O}_3\text{ClBF}_2\text{Re}]^-$ :  $m/z$  = 1053.2438, found:  $m/z$  = 1053.2410. IR (KBr,  $\text{cm}^{-1}$ ):  $\nu$  = 3056 (w), 2924 (m), 2853 (m), 2197 (m), 2024 (s), 1899 (s), 1597 (w), 1530 (s), 1474 (m), 1322 (m), 1278 (m), 1185 (s), 1013 (m), 745 (w), 725 (m). Elemental analysis calcd (%) for  $[\text{C}_{52}\text{H}_{40}\text{N}_5\text{O}_3\text{ClBF}_2\text{Re} + 2.5 \text{H}_2\text{O}]$ : C 56.83, H 4.10, N 6.38; found: C 56.75, H 4.21, N 6.34.

## Triplet-triplet annihilation upconversions

Diode pumped solid state (DPSS) continuous laser (532 nm) was used as an excitation source for the upconversions. The power of the laser beam was measured with VLP-2000 pyroelectric laser power meter. For the upconversion experiments, the mixed solution of the compound (triplet photosensitizer) and perylene was degassed with  $\text{N}_2$  or Ar for at least 15 min (note the upconversion can be significantly quenched by  $\text{O}_2$ ). Then the solution was excited with laser. The upconverted fluorescence of perylene was observed with a spectrofluorometer. In order to repress the scattered laser, a black box was put behind the fluorescent cuvette to trap the laser beam.

The upconversion quantum yields ( $\Phi_{\text{UC}}$ ) were determined with the prompt fluorescence of bis-iodo-BODIPY (**B-2**,  $\Phi_{\text{F}}$  = 2.7% in  $\text{CH}_3\text{CN}$ ). The upconversion quantum yields were

calculated with the following equation, where  $\Phi_{\text{UC}}$ ,  $A_{\text{unk}}$ ,  $I_{\text{unk}}$  and  $\eta_{\text{unk}}$  represents the quantum yield, absorbance, integrated photoluminescence intensity and the refractive index of the solvents (eqn (1), where the subscript “std” is for the standard used in the measurement of the quantum yield and “sam” for the samples to be measured). Factor 2 is used in the equation in order to make the maximum quantum yield to be unity.<sup>23j</sup> Furthermore, the absorption correction factors  $1-10^{-A}$  are used in the equation, instead of the absorption ( $A$ ) in the previously reported equation,<sup>23g</sup> due to the strong absorbance of the samples compared to that of the dilute solutions, which are normally used for determination of the luminescence quantum yields.

$$\Phi_{\text{UC}} = 2\Phi_{\text{std}} \left( \frac{1 - 10^{-A_{\text{std}}}}{1 - 10^{-A_{\text{unk}}}} \right) \left( \frac{I_{\text{unk}}}{I_{\text{std}}} \right) \left( \frac{\eta_{\text{unk}}}{\eta_{\text{std}}} \right)^2 \quad (1)$$

The CIE coordinates ( $x$ ,  $y$ ) of the emission of the triplet photosensitizers alone and the emission of the TTA upconversion in the presence of a triplet acceptor were derived from the emission spectra with the software of CIE color Matching Linear Algebra.

### Delayed fluorescence

The delayed fluorescence of the TTA upconversion was measured with nanosecond pulsed laser (Opolette<sup>TM</sup> 355II+UV nanosecond pulsed laser, typical pulse length: 7 ns. Pulse repetition: 20 Hz. Peak OPO energy: 4 mJ. Wavelength is tunable in the range of 210–355 nm and 410–2200 nm. OPOTEK, USA), which is synchronized to FLS920 spectrofluorometer (Edinburgh, UK). The decay kinetics of the upconverted fluorescence (delayed fluorescence) was monitored with FLS920 spectrofluorometer (synchronized to the OPO nanosecond pulse laser). The prompt fluorescence lifetime of the triplet acceptor DPA was measured with EPL picosecond pulsed laser (405 nm) which is synchronized to the FLS 920 spectrofluorometer.

### DFT calculations

The density functional theory (DFT) calculations were used for optimization of both singlet and triplet states. The UV-vis absorption and the energy level of the  $T_1$  state (energy gap between  $S_0$  state and  $T_1$  state) were calculated with the time-dependent DFT (TDDFT), based on the optimized singlet ground state geometries ( $S_0$  state). The spin density surface of the complexes were calculated based on the optimized triplet state. All the calculations were performed with Gaussian 09W.<sup>35</sup>

### Photooxidation

A  $\text{CH}_2\text{Cl}_2$ -MeOH (9:1, v/v) mixed solvent containing DHN ( $2.0 \times 10^{-4}$  M) and triplet photosensitizer (10 mol% vs. DHN) was put into a two neck round bottom flask (25 mL). The solution was then irradiated using a 35 W xenon lamp through a cut off filter (0.72 M  $\text{NaNO}_2$  aqueous solution, which is transparent for light with wavelength  $>385$  nm). UV-vis absorption

spectra were recorded at intervals of 2–5 min. The consumption of DHN was monitored by the decrease of the UV absorption at 301 nm, and the concentration of DHN was calculated based on its molar extinction coefficient ( $\epsilon = 7664 \text{ M}^{-1} \text{ cm}^{-1}$ ). The Juglone production was determined by monitoring the increase of the absorption at 427 nm. The concentration of Juglone was calculated by using  $\epsilon = 3811 \text{ M}^{-1} \text{ cm}^{-1}$  at 427 nm, and the yield of Juglone was obtained by dividing the concentration of Juglone with the initial concentration of DHN.

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