Electronic Supporting Information

Iodo-BODIPY: a visible-light-driven, highly efficient and photostable metal-free organic photocatalyst

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I. Materials and methods

All reagents were purchased from commercial sources and used without further treatment, unless otherwise indicated. Solvents: Methanol was purified over magnesium and then distilled under vacuum. Dichloromethane (DCM) were predried over calcium hydride and then distilled under vacuum. UV-vis absorption spectra were recorded on a UV-2450 spectrometer and fluorescence emission spectra were recorded on a LS-55 fluorophotometer. Cyclic voltammetry (CV) measurements were performed on a CHI 660B electrochemical workstation.

II. Measurement of the optical properties of BODIPYs

A. Measurement of the extinction coefficients

Measurements for the extinction coefficients were performed according to the following protocol.

Around 1 mg of dye was weighed using a digital scale ($\Delta w = 0.01$ mg), and dissolved into 100 mL of methanol. A number of further diluted solutions with different dye concentrations (10^{-7} to 10^{-6} M) were prepared from this stock solution. The absorption spectra of these diluted solutions were measured, and the absorbance (A) and the concentration (C) were plotted on a graph of A versus C to determine the extinction coefficient (from the slope). This protocol was performed 2 times, and the average value of the extinction coefficient was calculated (Table 1 in main text).

B. Measurement of the fluorescence quantum yields

Measurements of fluorescence quantum yields were performed by following the method recommended by Horiba Jobin Yvon (see: <u>http://www.jp.jobinyvon.horiba.com/product_j/spex/</u> quantum_yields.pdf). A number of diluted solutions of different dye concentrations (A < 0.05, to prevent reabsorption) were prepared and the absorbance (A) and the integrated fluorescence intensity (F) at each concentration were recorded at 470 nm excitation wavelength. Quantum yield Φ was calculated using the following equation:

$$\Phi_{s} = \Phi_{R} \left(\frac{n_{s}}{n_{R}}\right)^{2} \left(\frac{F_{s}}{F_{R}}\right) \left(\frac{A_{R}}{A_{s}}\right)$$

The subscripts R and S denote the reference dye and the sample, respectively. n is the refractive index of the solvent. The PhBDP was used as reference dye ($\Phi = 0.65$ in metanol).¹ This protocol was performed 2 times, and the average value of the quantum yield was calculated.

C. Measurement of the singlet oxygen quantum yields

Singlet oxygen quantum yields were calculated according to the leterature.² Air satutared DCM was obtained by bubbling air for 15 minutes. The initial absorbance of DPBF was adjusted to about 1.0 in air satutared DCM. Then, the photosensitizer was added to the cuvette and photosensitizer's absorbance was adjusted to about 0.2–0.3 to minimize the possibility of singlet oxygen quenching by the dyes. The photooxidation of DPBF was monitored between 10 s to 2 min depending on the efficiency of the photosensitizer. The graphics recorded are shown in Figure S1 to S8. The quantum yields of singlet oxygen generation were calculated by a relative method comparing the quantum yield of photosensitzer to the methylene blue (MB) ($\Phi_{\Delta,MB} = 0.57$ in dichloromethane) as the reference. Φ_{Δ} were calculated according to the following equation:

$$\Phi^{BDP}_{\scriptscriptstyle \Delta} = \Phi^{MB}_{\scriptscriptstyle \Delta} \, \frac{m^{BDP} \; F^{MB}}{m^{MB} \; F^{BDP}} \label{eq:phi}$$

The superscript 'BDP' designates BODIPY derivatives, m is the slope of the plot ΔA of DPBF (at 414 nm) vs. irradiation time, and F is the absorption correction factor, which is given by F =

1-10^{-OD} (OD at the irradiation wavelength).



Figure S1. (A) Changes in the absorption spectrum of DPBF upon irradiation in the presence of HBDP. a) 0 s and h) 780 s (recorded at every 120 s interval). (B) Plot of ΔA of DPBF at 414 nm vs. irradiation time in the presence of HBDP against methylene blue as the standard.



Figure S2. (A) Changes in the absorption spectrum of DPBF upon irradiation in the presence of HBDP-2I. a) 0 s and f) 50 s (recorded at every 10 s interval). (B) Plot of ΔA of DPBF at 414 nm vs. irradiation time in the presence of HBDP-2I against methylene blue as the standard.



Figure S3. (A) Changes in the absorption spectrum of DPBF upon irradiation in the presence of MeBDP. a) 0 s and h) 840 s (recorded at every 120 s interval). (B) Plot of ΔA of DPBF at 414 nm vs. irradiation time in the presence of MeBDP against methylene blue as the standard.



Figure S4. (A) Changes in the absorption spectrum of DPBF upon irradiation in the presence of MeBDP-2I. a) 0 s and e) 80 s (recorded at every 20 s interval). (B) Plot of ΔA of DPBF at 414 nm vs. irradiation time in the presence of MeBDP-2I against methylene blue as the standard.



Figure S5. (A) Changes in the absorption spectrum of DPBF upon irradiation in the presence of PhBDP. a) 0 s and f) 600 s (recorded at every 120 s intervals). (B) Plot of ΔA of DPBF at 414 nm vs. irradiation time in the presence of PhBDP against methylene blue as the standard.



Figure S6. (A) Changes in the absorption spectrum of DPBF upon irradiation in the presence of 1I-PhBDP. a) 0 s and f) 600 s (recorded at every 120 s interval). (B) Plot of ΔA of DPBF at 414 nm vs. irradiation time in the presence of 1I-PhBDP against methylene blue as the standard.



Figure S7. (A) Changes in the absorption spectrum of DPBF upon irradiation in the presence of PhBDP-2I. a) 0 s and f) 50 s (recorded at every 10 s intervals). (B) Plot of ΔA of DPBF at 414 nm vs. irradiation time in the presence of PhBDP-2I against methylene blue as the standard.



Figure S8. Changes in the absorption spectrum of DPBF upon irradiation in the presence of methylene blue (MB). a) 0 s and g) 60 s (recorded at every 10 s interval).

III. Computational results

Samples	$-\epsilon_{HOMO}(eV)$	$-\epsilon_{LUMO}(eV)$	$\triangle E (eV)$
HBDP	5.38	2.42	2.97
HBDP-2I	5.73	2.82	2.91
MeBDP	5.38	2.31	3.07
MeBDP-2I	5.68	2.74	2.94
PhBDP	5.34	2.33	3.00
1I-PhBDP	5.46	2.47	2.99
PhBDP-2I	5.64	2.75	2.90

Table S1. The negative HOMO, LUMO energies and the H-L gaps obtained under DFT (PBE0) calculations

IV. Thioanisole oxidation catalyzed by BODIPYs

Taking PhBDP-2I as photocatalyst as an example: To a flame-dried 10 mL vial equipped with a magnetic stir bar were added PhBDP-2I (1.5 mg, 2.5 μ mol, 0.005 equiv) catalyst, thioanisole (62 μ L, 0.5 mmol, 1.0 equiv), and methanol (0.5 mL). A 24 W household fluorescent light bulb with a highpass filter ($\lambda = 395$ nm) was used as the visible light source.³ The reaction mixture was stirred at room temperature in air at a distance of *ca*. 5 cm from the lamp (the irradiance is about 17.5 W/m² for the distance). ¹H NMR was taken of the reaction mixture, and the integrated area ratio between the ¹H NMR peaks of the substrate and product was used to calculate the conversion yields.⁴

¹H NMR spectra



Figure S9. ¹H NMR spectra of the reaction mixture in $CDCl_3$ as a function of reaction time, with PhBDP-2I as the catalyst, the peak at 2.73 ppm of the product and the peak at 2.49 ppm of the substrate were used to calculate the conversion.

V. Reuse experiment

Table S2. Reuse of Iodo-BODIPYs

	SPhBDP-2I, 5 m methanol, in	air
	Time (h)	Conversion (%)
1 st use	3.5	99
2 nd use	3.5	99
3 rd use	3.5	99
4 th use	3.5	99
5 th use	3.5	98

VI. Measurement of oxidation potentials

Electrochemical experiments were performed using a conventional three-electrode system. A glassy carbon electrode served as a working electrode, a platinum plate as a counter electrode, and an Ag/AgCl electrode with saturated KCl solution as a reference electrode. Cyclic voltammetry (CV) measurements were performed on a CHI 660B electrochemical workstation (Shanghai Chenhua Apparatus, China), and carried out in saturated KCl solution at 25 °C, Magnetic stirring was used before the CV measurements to ensure the homogeneity of the electrolyte solution.

VII. References:

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