Supporting Information

Constructing a new platform for photo-peroxidase catalysis: ZIF-90 as a dual 'modulator' to overcome peroxide industrial application bottlenecks

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Experimental section

Preparation of Melem (MA)

The MA was calcined from melamine. Specifically, 5g of melamine was added to the alumina crucible and calcined in muffle furnace at 425℃ for 4h under air conditions (heating rate:7℃·min^{-1}), resulting in a beige MA powder[1].

Preparation of g-C_3N_4/PDI

After grinding 2.2g PMDA with 2.2g MA until well mixed, then the samples were calcined under air conditions by using muffle furnace for 4h (the temperature rises to 325℃ at a rate of 7℃·min^{-1}) to finally obtain a light yellow g-C_3N_4/PDI powder[2].

Fluorescently labelled HRP

Disperse 10mg HRP in 10ml PBS buffer (1X, pH=7.4), add 5mg EDC and 2.5mg NHS to the HRP-containing solution and stir for 2h, then add 100ug FITC to the HRP-containing solution and stir for 5h under dark conditions. Unreacted FITC, NHS and EDC were removed by dialysis (MWCO:12K-14K) for one day，then FITC-HRP was obtained.

Preparation of FITC-50%-CPZH

200mg g-C_3N_4/PDI with 187.6mg $Zn(NO_3)_2 \cdot 6H_2O$ in 1.5mL D.I. water and sonicate overnight to modify Zn^{2+} on g-C_3N_4/PDI as solution A. 240mg of ICA and 10mg of FITC-HRP were dissolved fully in 12.5mL D.I. water as solution B.

Then, slowly pour solution A into solution B and stir vigorously for 30 mins under dark condition, the FITC-50%-CPZH was obtained by centrifugation, washed three times with ethanol.

Determination of H_2O_2 by iodinometric method

1 mL of 0.1 mol L^{-1} potassium phthalate monobasic ($C_8H_5KO_4$) aqueous solution and 1 mL of 0.4 mol L^{-1} potassium iodide (KI) aqueous solution were added to the sample solution stand for 30 minutes.

Under acidic conditions, H_2O_2 molecules react with iodide anions (I^-) to form triiodide anions (I^{3-}) with strong absorption near 350nm as follows.

$H_2O_2 + 3I^- + 2H^+ \rightarrow I^{3-} + 2H_2O$

The amount of I^{3-} was determined by measuring the absorption intensity at 350 nm using UV–vis spectra.

Computational formula

Enzyme loading ability

Enzyme loading ability (%) were calculated by the HRP concentration before and after g-C3N4/PDI @ZIF-90 loading as follow:

$$\textit{Enzyme loading}\ (\%) = \frac{m_o - C_s \times V_s}{m_c} \times 100\% \qquad \text{(S1)}$$

In this formula, c_s is the concentration of HRP in the supernatant (quantified by Bradford method),$mg \cdot mL^{-1}$; V_s is the volume of the supernatant, *mL*; m_0 is the HRP amount of initial, *mg*; m_c is the amount of g-C_3N_4/PDI @ZIF-90, *mg*.

Relative activity (%)

Relative activity (%) were calculated from standard catalytic condition product concentrations and other catalytic condition product concentrations.

$$\textit{Relative activity (\%)} = \frac{C_o}{C_s} \times 100\% \tag{S2}$$

in which C_s means the product concentration of 50%-g-C_3N_4/PDI@HRP@ZIF-90 or HRP at pH=7 T=25°C (standard product concentration) and C_o means the product concentration under other catalytic conditions (other product concentration).

Dye degradation rate (%)

Dye degradation rate (%) were calculated by the dye maximum absorption wavelength before and after 50%-CPZH degradation.

$$\textit{Dye degradation rate (\%)} = \frac{A_0 - A_t}{A_0} \times 100\% \tag{S3}$$

Which, A_0 means the absorbance value before degradation, *nm*; A_t means the absorbance value after degradation, *nm*. Maximum absorption wavelength of CV, CR, RBBR, were in 594nm, 459nm and 595nm separately.

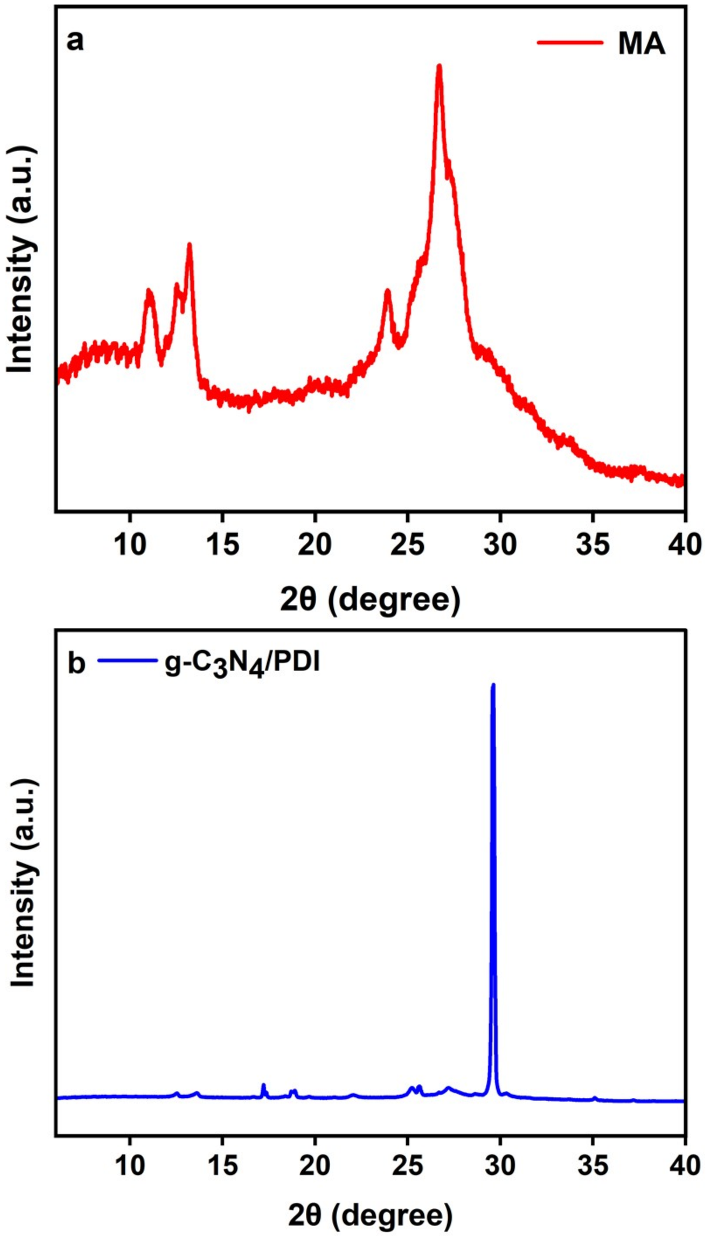


Figure S1. PXRD patterns of MA and g-C_3N_4/PDI.

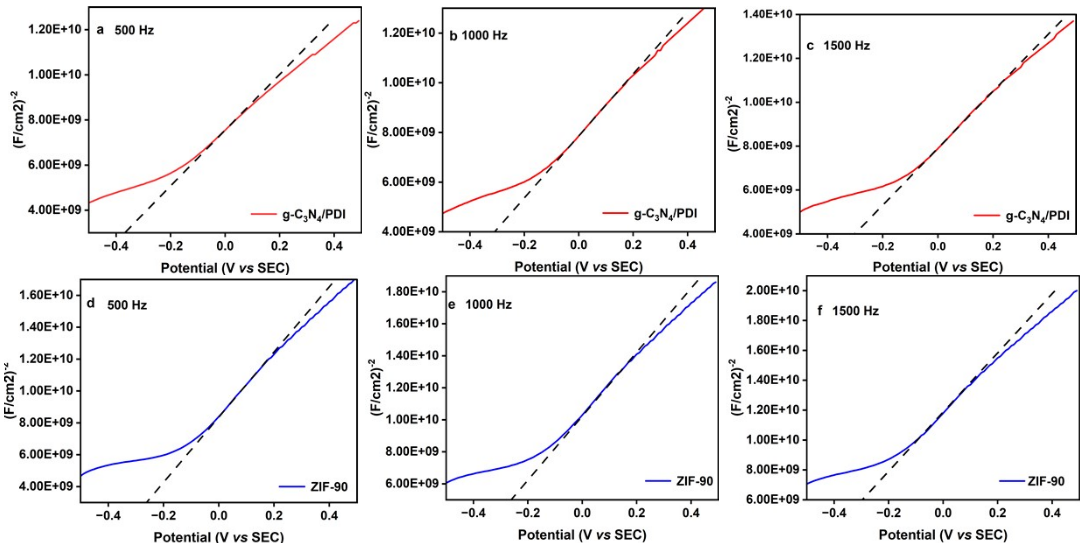


Figure S2. The Mott–Schottky (M-S) curves of ZIF-90 and g-C_3N_4/PDI.

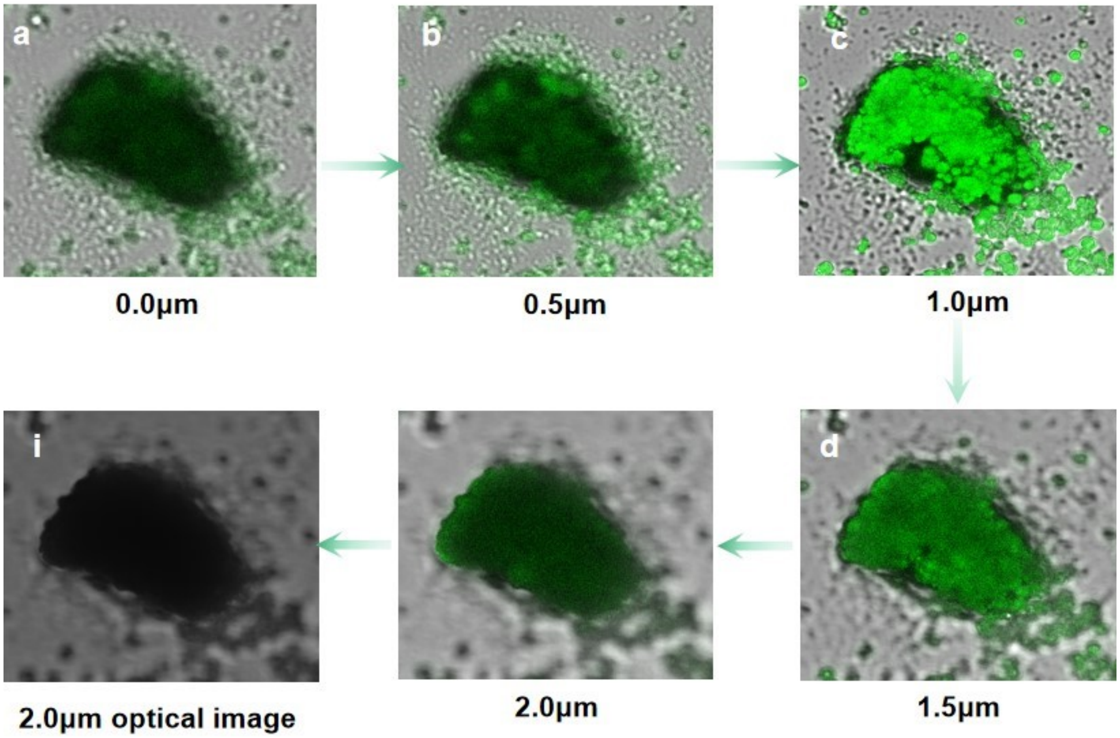


Figure S3. Super-resolution confocal microscopy Z-axis sectioning for 50%-CPZH (in overlap).

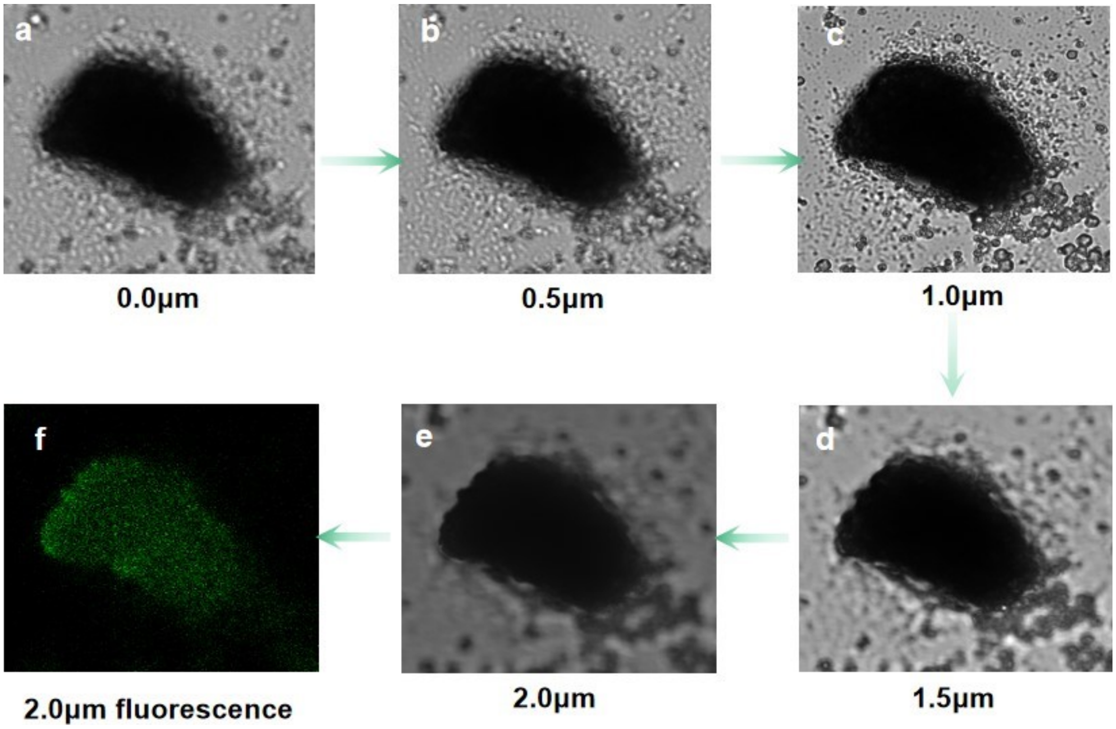


Figure S4. Super-resolution confocal microscopy Z-axis sectioning for 50%-CPZH (in optical image).

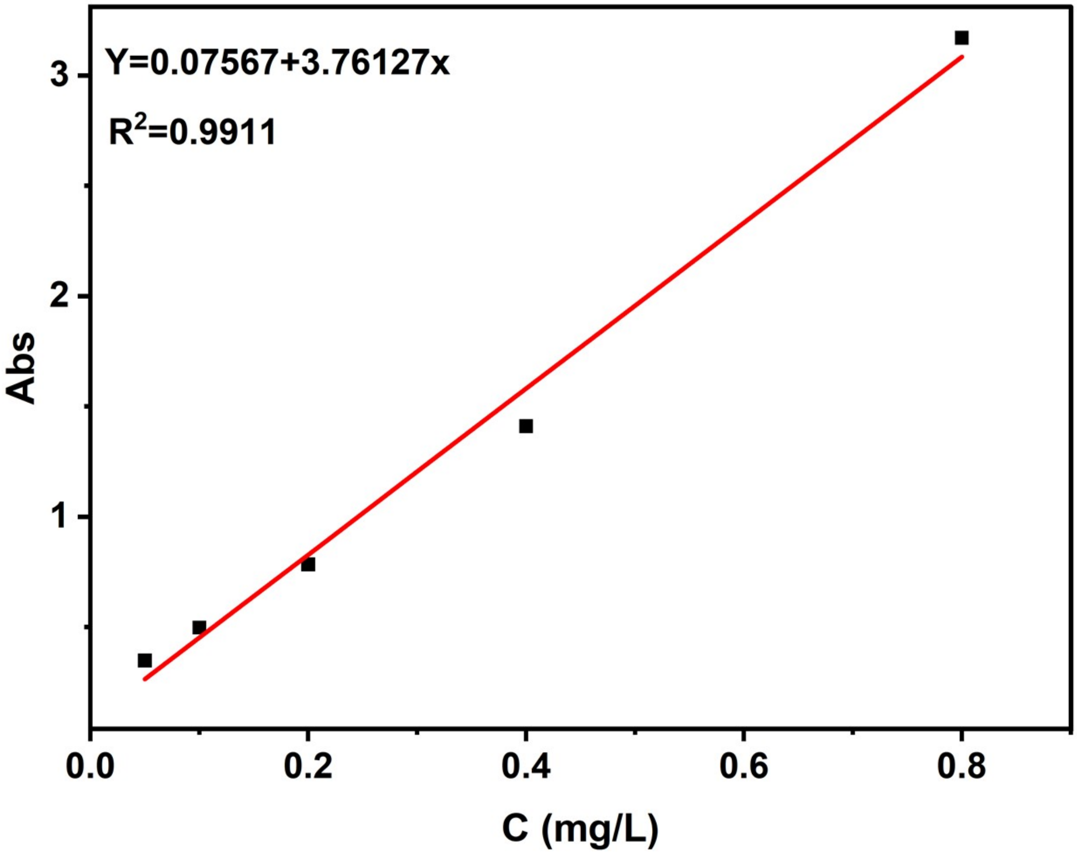


Figure S5. Standard curve for iodometric determination of H_2O_2.

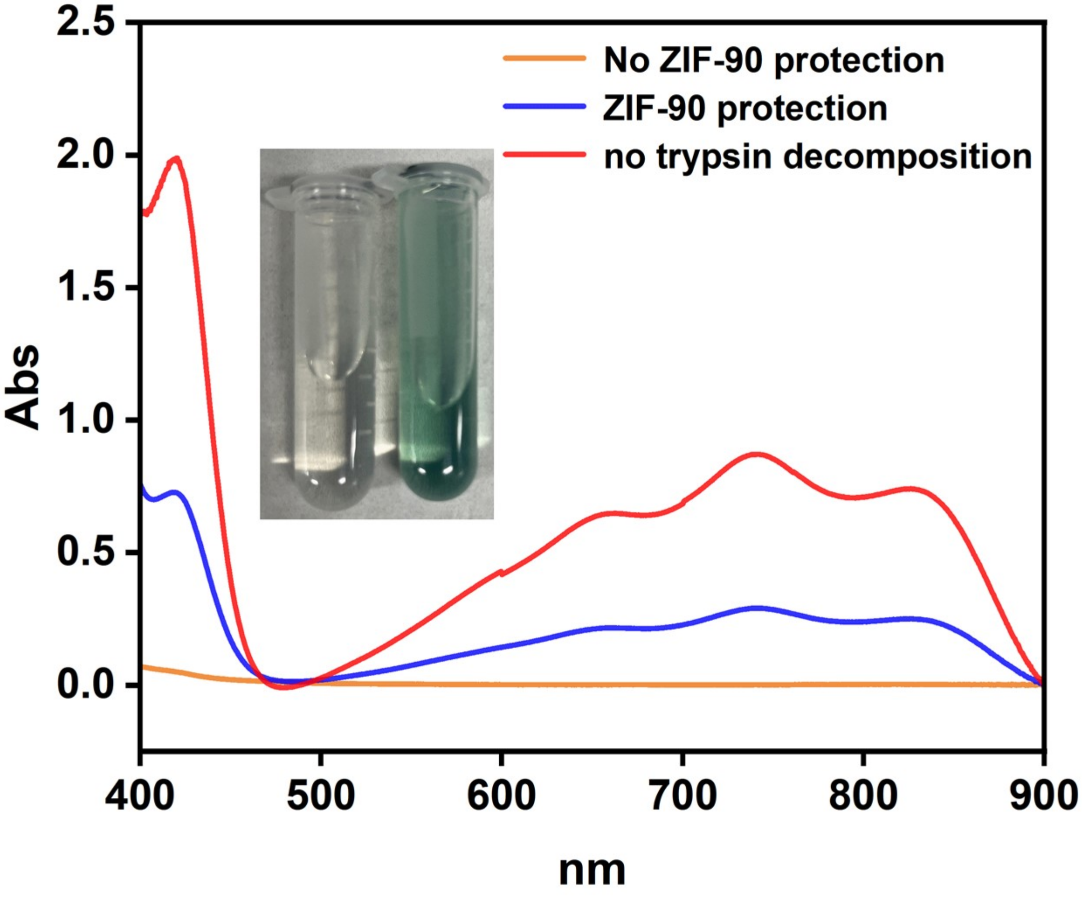


Figure S6: Framework protection of peroxidase by ZIF-90 as measured by trypsin catabolism.

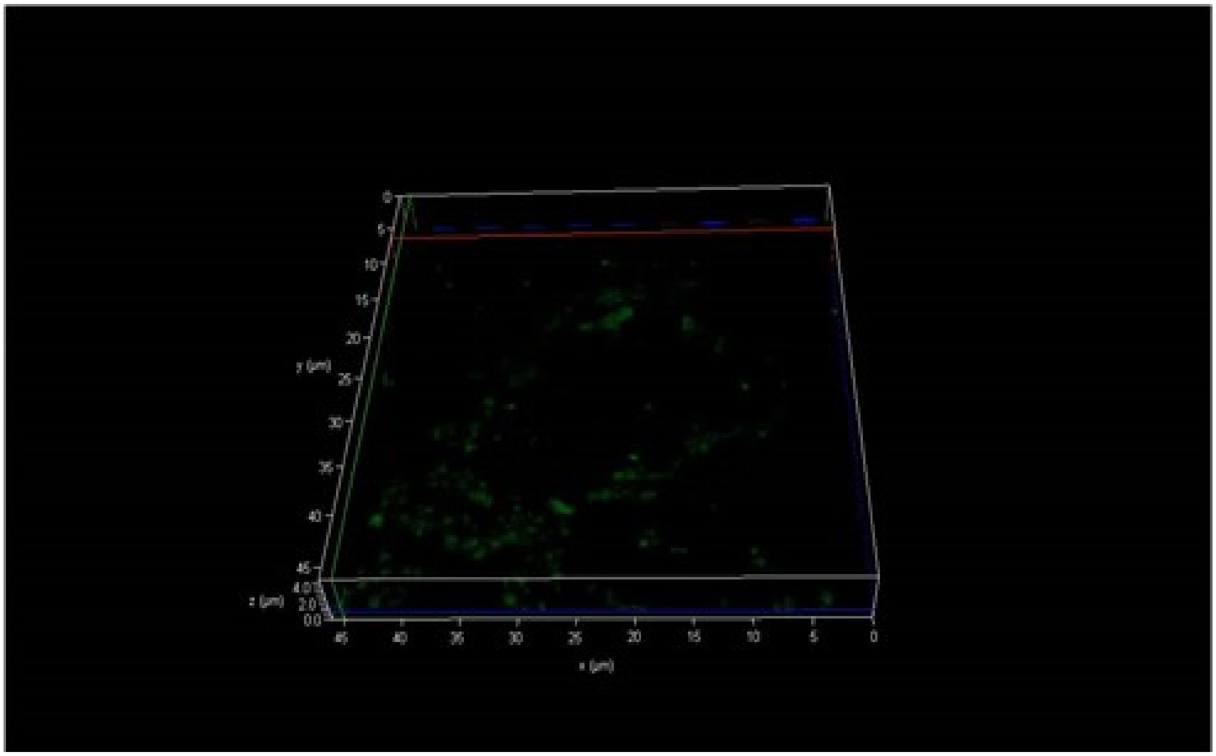
Table S1. The weight percentage of atoms in the 50%-CPZH measured by XPS.

Sample	N%	Zn%	C%	O%
g-C_3N_4/PDI	34.47	——	54.57	10.97
50%-CPZH	26.06	1.78	60.94	11.22
ZIF-90	18.83	3.75	65.21	12.21

Table S2. H_2O_2 production capacity of g-C_3N_4/PDI, physical mixing of g-C_3N_4/PDI with ZIF-90 and g-C_3N_4/PDI@ZIF-90.

Photocatalysts	$C_{(H2O2)}$ (λ>420nm, mM)
g-C_3N_4/PDI	0.34
physical mixing	4.2
g-C_3N_4/PDI@ZIF-90	11.3

Video S1. 50%-CPZH sunlight catalytic dye degradation



Video S2: CLSM Z-axis slices of 50%-CPZH.

References

(1) Chu, S.; Wang, C.; Feng, J.; Wang, Y.; Zou, Z. Melem: A metal-free unit for photocatalytic hydrogen evolution. *International Journal of Hydrogen Energy* **2014**, *39* (25), 13519-13526.

(2) Shiraishi, Y.; Kanazawa, S.; Kofuji, Y.; Sakamoto, H.; Ichikawa, S.; Tanaka, S.; Hirai, T. Sunlight-driven hydrogen peroxide production from water and molecular oxygen by metal-free photocatalysts. *Angew. Chem. Int. Ed.* **2014**, *53* (49), 13454-13459.