Supporting Information for

Ortho-Dihydroxyl-9,10-Anthraquinone Dyes as Visible-Light Sensitizers that Exhibit a High Turnover Number for Hydrogen Evolution

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a) Materials and Apparatus

All reagents were analytical grade and used without further purification. Degussa P25 TiO_2 powder was used as the source of TiO_2. Triethylolamine was supplied by Guangdong Guang hua Chemical Factory Co. Ltd. Alizarin Red was supplied by Kanto Chemical Co. Inc., and Alizarin was bought from Acros. Coumarin 343 was supplied by Sigma Aldrich, the 1-Hydroxyanthraquinone and 2-Hydroxyanthraquinone was supplied by TCI, the 1,8-Dihydroxyanthraquinone was supplied by Alfa Aesar, and the 2,6-Dihydroxyanthraquinone was supplied by Acros. The organic dye molecular structures are shown in Figure S9. For the UV-Vis diffuse reflectance spectra, a Hitachi U-3900 UV-Vis spectrophotometer was used. The reaction vessel and 300W Xe lamp used for the hydrogen evolution were supplied by China Education Aulight Co. Ltd. The photoelectrochemical behaviour of the photocatalysts was measured using a standard three-electrode cell at a computer-controlled Potentiostat/Galvanostat Model 283 (EG&G Co.) electrochemical workstation. The LC-ESI-MS analysis for product observation was carried on the Agilent 6310 Ion Trap LC/MS. The ESR experiments were conducted with a Bruker EPR ELEXSYS 500 spectrometer equipped with an in situ irradiation source (a Quanta-Ray Nd:YAG laser system with λ=532 nm).

b) Preparation of Dye-sensitized Pt/TiO$_2$ **for Hydrogen Evolution**

Pt was loaded on P25 by a typical photodeposition method.[1] In total, 1.5 g TiO_2, 2 ml isopropylalcohol, 3.19 ml of a 2.44×10^{-2}mol/L H_2PtCl_6 solution and 145 ml distilled water were added to a 200 ml Pyrex bottle, and then oxygen was removed from the bottle by Ar gas introduction. The mixture was irradiated by a 100W high pressure Hg lamp for 16 h. After filtration and washing with distilled water, the powders (denoted as Pt/TiO_2, Pt deposited amount: 0.8wt. %) were dried at 60°C in a vacuum drying chamber. Before photocatalytic hydrogen generation, 0.1 g Pt/TiO_2 was sensitized by the organic dyes in situ. Approximately 100mg of Pt/TiO_2 and a quantitative amount of dye (e.g. 0.25μmol) was added to 100ml of 0.6 M TEOA aqueous solution, and then the suspension was stirred in the dark for 2h before used for hydrogen evolution.

c) UV-vis diffuse reflectance spectra experiment

For the UV-vis diffuse reflectance experiment, the dyes were adsorbed onto Pt-TiO_2 by stirring the Pt-TiO_2 powder (100mg) in a mixture of anthraquinone dyes and TEOA-H_2O solution (1μmol of dye dissolved in 100ml of 8%（v/v)) at room temperature for 12h in the dark. The samples were filtered and washed with acetone and dried in vacuum desiccator. The reference for the diffuse reflection spectra is bare Pt/TiO_2 without any sensitization.

d) Photocatalytic Hydrogen Generation

Photocatalytic hydrogen generation was performed using a 350 ml quartz glass reactor connected to a closed gas-circulation system. The system was thoroughly evacuated by a vacuum pump before irradiation. The reaction suspension was prepared by the method in situ as mentioned above. The pH values of the suspension were adjusted by addition of perchloric acid. The suspension was irradiated from the top of the reactor by a 300W Xe lamp with a cut-off filter ($\lambda > 420$ nm). The evolution of hydrogen gas was analyzed by an on-line gas chromatograph (TCD, molecular sieve 5A).

e) Dye molecules detected by LC-MS

To detect the dye molecules more efficiently, the catalyst, Pt/TiO_2 (0.03g), was introduced to an aqueous solution (30ml) containing 1.5μmol of organic dye and 1.8mmolof TEOA as a sacrificial electron donor. These vessels were sealed and bubbled with Ar for 30 min. The suspensions were irradiated using a 300W Xe lamp with a cut-off filter ($\lambda > 420$ nm) for 18h. The adsorption is at equilibrium at 0h. The photocatalyst powder detected by the diffuse reflection spectra was separated from the suspension by centrifuge, washed with acetone, and then dried in a vacuum desiccator. The reference of the diffuse reflection spectra is bare Pt/TiO_2 without any sensitization.

The obtained solutions were filtered before detection. The HPLC analysis was proceeded with a Platisil ODS column (250mm× 4.6 mmi.d., dp=5μm) and mobile phases of 25% acetonitrile and 75% 0.01M ammonium acetate aqueous solution (Eosin-Y, measurement wavelength=254nm), 30% acetonitrile and 70% 0.01M ammonium acetate aqueous (Coumarin-343，measurement wavelength=254nm), 80% Methanol and 20% 0.01M ammonium acetate aqueous (2-hydroxyl anthraqinone, measurement wavelength=280nm), 70% Methanol and 30% 0.01M ammonium acetate aqueous (2.6-dihydroxyl anthraquinone, measurement wavelength=280nm), 80% Methanol and 20% 0.01M ammonium acetate aqueous (1-hydroxyl anthraquinone, measurement wavelength=280nm), 80% Methanol and 20% 0.01M ammonium acetate aqueous (1,8-dihydroxyl anthraquinone, measurement wavelength=254nm), 80% Methanol and 20% 0.01M ammonium acetate aqueous (1,2-dihydroxyl anthraquinone, measurement wavelength=254nm). The mobile phase of Alizarin Red consists of 0-15min of 100% 0.01M ammonium acetate aqueous solution and 18-30min of 30% acetonitrile and 70% 0.01M ammonium acetate aqueous solution at a flow rate of 0.2ml/min.

f) Measurement of produced H_2O_2

In order to detect the produced H_2O_2, the anthraquinone dye with obvious color change in hydrogen evolution (Fig. S4), such as 1-hydroxyl anthraqunine, had been used. The catalyst, Pt/TiO_2 (0.03g), was introduced to an aqueous solution (30ml) containing 3μmol of 1-hydroxyl anthraqunine and 1.8mmol of TEOA as a sacrificial electron donor. The vessel was sealed and bubbled with Ar for 30 min, and then were irradiated using a 300W Xe lamp with a cut-off filter (λ > 420 nm) for 18h. After that, the vessel was opened to air for 15min, and then the suspension was filtered to obtain the clear solution rapidly. The measurement of the produced H_2O_2 was carried out by the typical method. 1ml clear solution was mixed with 1ml buffer solution (pH=7) and then DPD (N,Ndimethyl-p-phenylenediamine) and POD (Horseradish peroxidase) were added into the mixed solution successively. At last, the solution was measured with UV-vis spectrum.[2]

g) Measurement of apparent quantum yield

The catalyst, Pt/TiO_2 (0.1g), was introduced to an aqueous solution (100ml) containing 1μmol AR and 60mmol TEOA as a sacrificial electron donor at a pH=9. After stirring in the dark for 2h, the suspension was introduced into a 350 ml quartz glass reactor connected to a closed gas-circulation system. The system was thoroughly evacuated by a vacuum pump before irradiation by a 300W Xe lamp with a bandpassfilter (λ = 520 nm). The photon flux of the incident light was determined using $KCr(NH_3)_2(NCS)_4$ as the detector.[3]

AQY% = number of reacted electrons/ number of incident photos×100%

=2×number of evolved H_2 molecules/ number of incident photos×100%

= 42.5 (μmol/h) ×2 / 7657.6(mmol/h) = 1.11%

h) Electrochemical Measurements

In total, 1g of P25 and 10μLof acetylacetone were added to 4 ml distilled water, stirred with a magnetic stir bar for 1 h, and then spun on the indium tin oxide (FTO) surface, which acted as the working electrode. The electrodes were calcined at 773 K for 3h in air. The working electrodes were sensitized by soaking in an organic dye solution (1×10^{-3} M) for 12 h. A Pt sheet and saturated calomel electrode (SCE) were used as the counter and reference electrodes, respectively. The supporting electrolyte was a 0.1M $NaClO_4$ aqueous solution. In the photocurrent experiments, the working electrodes were irradiated by a 300W Xe lamp with a cut-off filter ($\lambda > 420$ nm), and 0.6M TEOA were added as sacrificial agent. Before the experiments, Ar was bubbled through the reaction solution for 30min to completely remove oxygen.

i) ESR Experiment

The measured suspension contained 3g/L of Pt/TiO_2. The anthraquinone dyes were absorbed beforehand by adding Pt/TiO_2 into the dye solutions. The suspensions were stirred for 6 hours, filtered, washed and dried. The adsorption of organic dyes is listed in Table S3. Approximately 9mg of dye sensitized Pt/TiO_2 was added to a 3ml aqueous solution with or without TEOA, which was determined by the needed experiment. The prepared samples were then introduced into the NMR tubes quantifiably and pre-freezed in liquid nitrogen, and enough time was reserved to reach a temperature equilibrium before the ESR experiment. The experiment temperature was controlled by a liquid nitrogen vapour steam and a thermocouple temperature controller.

Figure S1. UV-Vis diffuse reflectance spectra of Pt/TiO_2 sensitized by anthraquinone dyes.

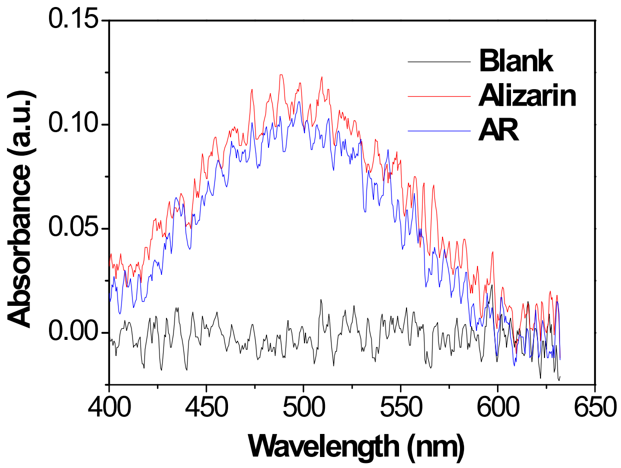


Figure S2. Transient photocurrent-time curves of Alizarin/TiO_2 (I), AR/TiO_2 (II), Eosin Y/TiO_2 (III, right Y axis) and Coumarin 343/TiO_2 (IV) working electrodes. The biasvoltageis 0.6V (vs. SCE). The supporting electrolyte is a 0.1M $NaClO_4$ aqueous solution.

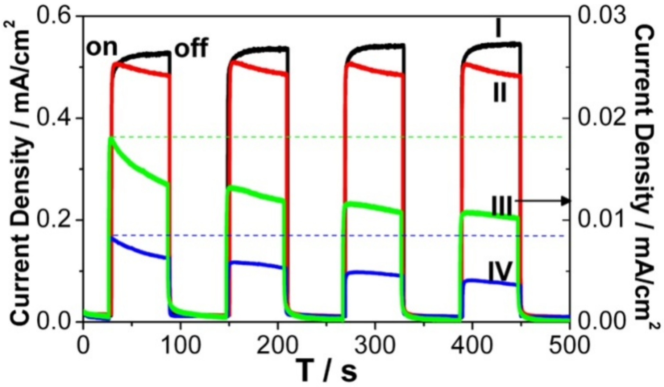


Figure S3. The diffuse reflection spectra of the (a) Pt/TiO_2 in Eosin Y sensitized system, (b) Pt/TiO_2 sensitized by 0.001 MEosin Y solution, (c) Pt/TiO_2 in C-343 sensitized system,and (d) Pt/TiO_2 sensitized by 0.001 MC-343 solution. The conditions of the former one were described in the LC-MS experimental section. For the latter, 60mg Pt/TiO_2 were added to 0.001M Eosin Y and C-343 solutions and stirred in the dark for 12h, then filtered and washed with distilled water, and then the powders were dried at 50°C in a vacuum drying chamber.

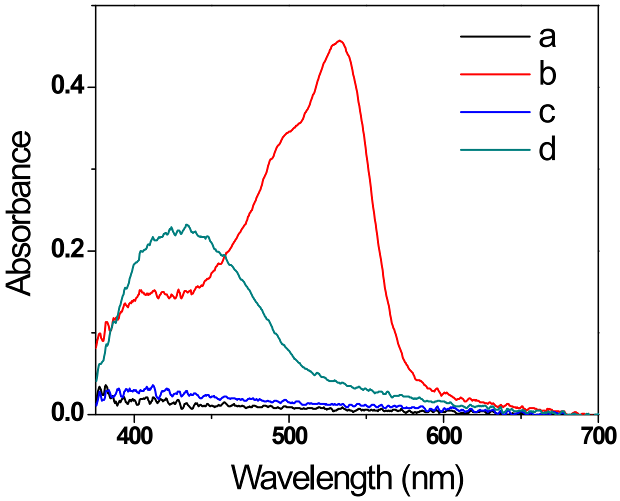


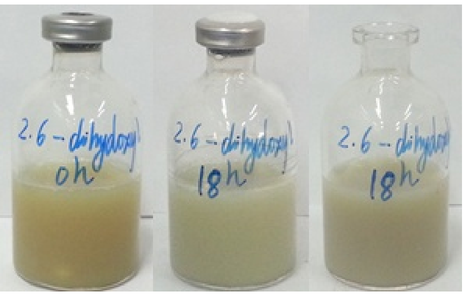
Figure S4. Photographs of suspension solutions for the systems: Alizarin red (a), Alizarin (b), 2-hydroxylanthraquinone (c), 2,6-dihydroxylanthraquinone (d), 1-hydroxylanthraquinone (e), 1,8-hydroxylanthraquinone (f), Eosin Y (g), and C-343 (h). The suspensions were exposed to air for 10min after 18h of irradiation. The conditions follow. The catalyst Pt/TiO_2 (0.03 g) was introduced to an aqueous solution (30ml) containing 1.5μmol organic dye and 1.8mmol TEOA as a sacrificial electron donor. These vessels were sealed and bubbled with Ar. The suspensions were then irradiated by a 300W Xe lamp with a cut-off filter (λ > 420 nm)

(a) 0 h 18 h in air

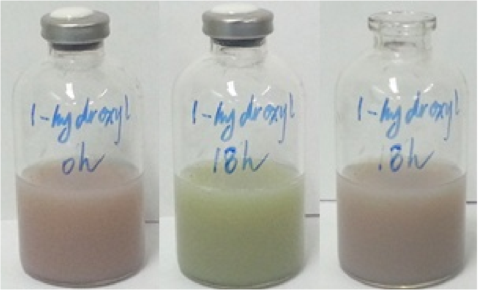
(b) 0 h 18 h in air

(c) 0 h 18 h in air

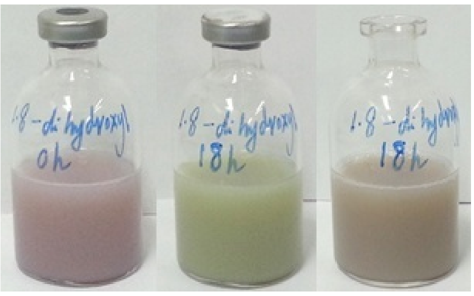
(d) 0 h 18 h in air



(e) 0 h 18 h in air



(f) 0 h 18 h in air



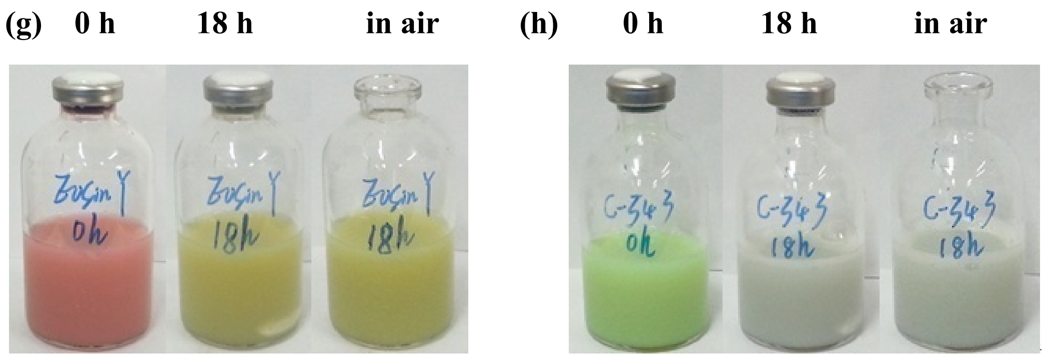


Figure S5. The UV-vis spectrum of the mixed clear solution in the experiment of H_2O_2 detection. A is the clear solution without DPD and POD and B is the clear solution mixed with DPD and POD. The characteristic absorption peak of H_2O_2 is around 500nm.

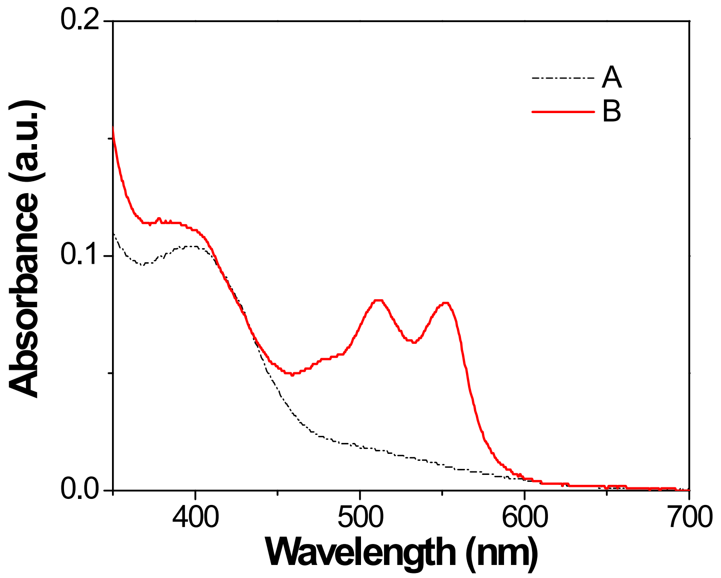


Figure S6. Effect of Pt loading content on the photocatalytic activity for hydrogen generation from the AR sensitized Pt/TiO_2 catalyst. The reaction conditions include: 100ml 0.6mol/L TEOA solution, pH 9.0, 100mg Pt/TiO_2, AR 1μmol, and irradiation time of 8h. Oxygen was removed before irradiation.

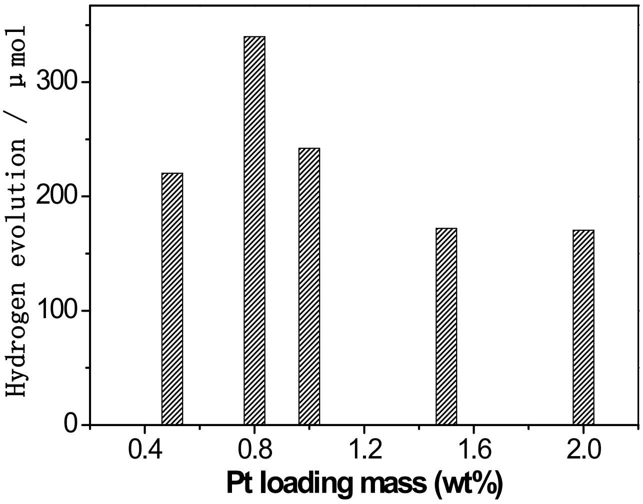


Figure S7. Effect of pH value on the photocatalytic activity for hydrogen generation from the AR sensitized Pt/TiO_2 catalyst. The reaction conditions include: 100ml 0.6mol/L TEOA solution, 100mg Pt/TiO_2 (0.8% w/w), AR: 1μmol, and irradiation time of 2h. Oxygen was removed before irradiation.

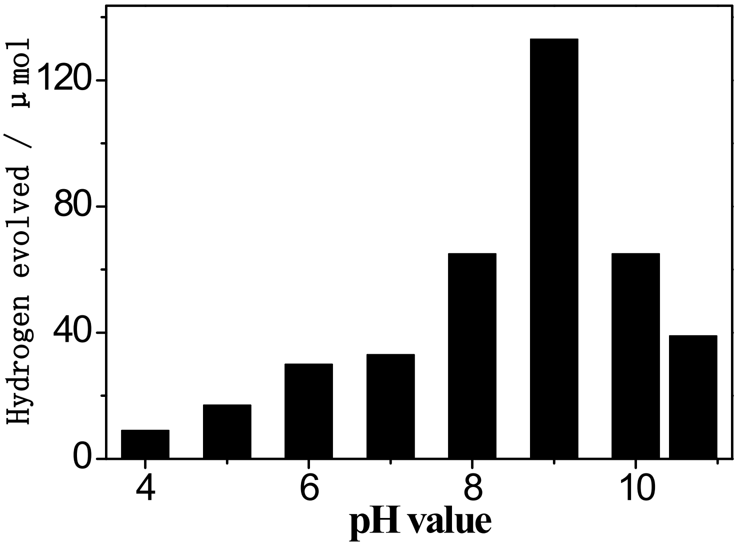


Figure S8. Effect of absorbance on the photocatalytic activity for hydrogen generation from the AR sensitized Pt/TiO_2 catalyst. The reaction conditions include: 100ml 0.6mol/L TEOA solution, pH 9.0, 100mg Pt/TiO_2 (0.8% w/w), and irradiation time of 6h. Oxygen was removed before irradiation.

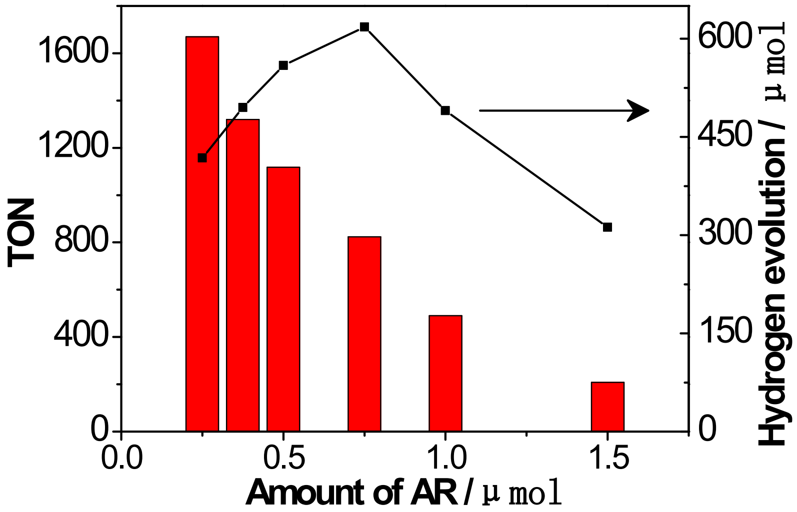


Figure S9. The ESR signals for the anthraquinone dyes. T=243.5K.

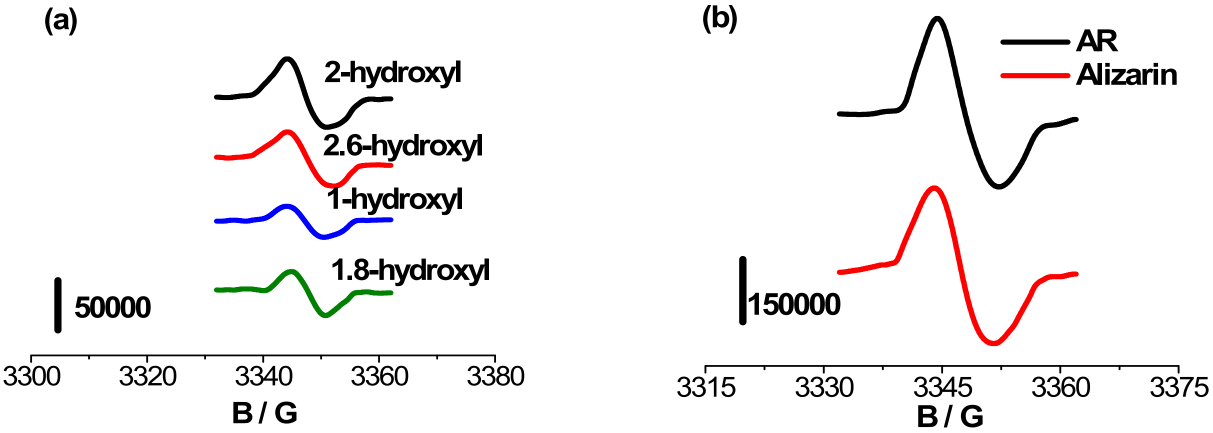


Figure S10. The time dependence of the ESR signals for the anthraquinone dye radicals. T=243.5K

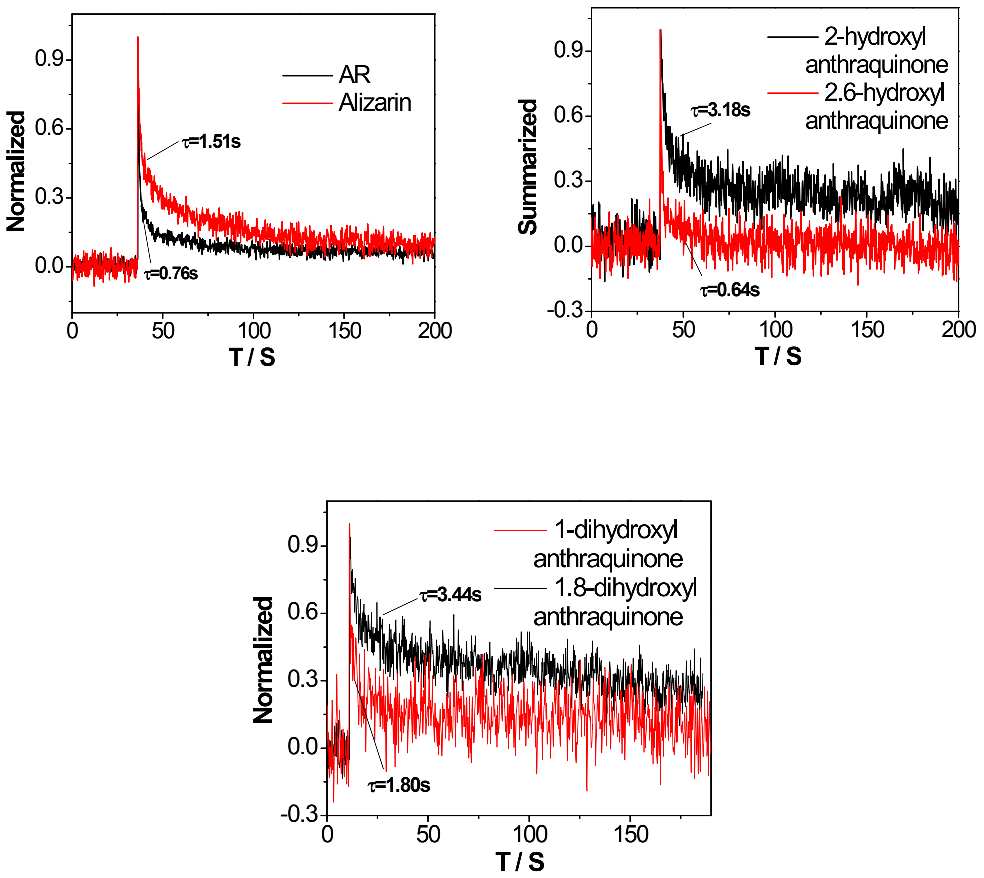
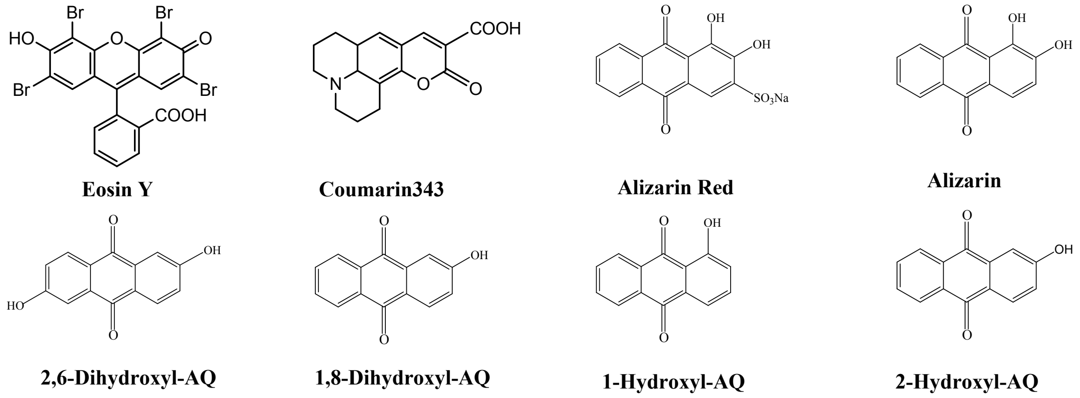


Figure S11. The molecular structures of Eosin Y, Coumarin 343, and anthraquinone dyes.



Eosin Y **Coumarin343** **Alizarin Red** **Alizarin**

2,6-Dihydroxyl-AQ **1,8-Dihydroxyl-AQ** **1-Hydroxyl-AQ** **2-Hydroxyl-AQ**

Table S1. The LC-MS adsorptions of different organic dyes for blank dye experiments. The catalyst, Pt/TiO$_2$ (1g/L), was introduced to an aqueous solution containing organic dye and 0.06mM TEOA. The suspensions were stirred in the dark for 2 hours.

Dye	Initial concentration	Adsorption / %
AR	2.5×10^{-6}M	>99%
Alizarin	2.5×10^{-6}M	>99%
Eosin Y	2.5×10^{-6}M	98.7%
C-343	2.5×10^{-6}M	97.9%
AR	5×10^{-5}M	15.2%
C-343	5×10^{-5}M	11.4%
Eosin Y	5×10^{-5}M	13.0%

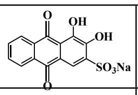
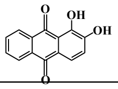
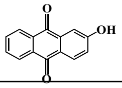
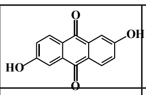
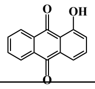
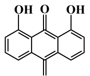
Table S2. AR sensitized Pt/TiO2 as a photocatalyst for hydrogen evolution. Hydrogen evolution was carried out for 6h in each run using a 300W Xe lamp with a 420nm cutoff filter. The reaction vessel was exposed to air and then evacuated every 6h. The turnover number of the dye is defined as n (1/2H2) / n(dye molecules). The reaction conditions include: 100ml 0.6mol/L TEOA solution, 100mg Pt/TiO2 (0.8% w/w), dyes: 0.25μmol, and a pH of 9.0. The reaction conditions include 100ml 0.6mol/L TEOA solution, 100mg Pt/TiO2 (0.8% w/w), AR: 0.25μmol, and a pH of 9.0.

Number	TON	Number	TON	Number	TON	Number	TON
1st run	1627	5	885	9	443	13	310
2	1225	6	731	10	392	14	287
3	1133	7	646	11	364		
4	1022	8	554	12	337		

Table S3. The adsorption amounts of the anthraquinone dyes sensitized Pt/TiO_2 used in ESR the experiments.

Dye	Solvent	Concentration (mol/L)	Adsorption (μmol/g catalyst)
AR	H_2O	5×10^{-5}	28.4
Alizarin	$CH_3CN:H_2O=1:1$(v:v)	2×10^{-5}	16.7
2-dihydroxyl	DMF	3.6×10^{-4}	12.6
2.6-dihydroxyl	DMF	3.6×10^{-4}	20.9
1-hydroxyl	DMF	3.6×10^{-4}	9.24
1.8-dihydroxyl	DMF	3.6×10^{-4}	20.2

Table S4. The light absorption of different hydroxyl-substituted 9,10-anthraquinone dyes. In the experiments, all anthraquinone dyes were dissolved in TEOA-H_2O solution (8% v/v) at a pH=9.

							
λ_{max}/ nm	520nm	520nm	470nm	420nm	420nm	440nm	500nm
ε_{max}/ $L\cdot mol^{-1}\cdot cm^{-1}$	5.50×10^3	6.66×10^3	3.70×10^3	10.4×10^3	1.52×10^3	2.08×10^3	1.98×10^3

References

(1) R. Abe, K. Sayama, H. Arakawa, Chem. Phys. Lett. 2003, 379, 230.

(2) H. Bader, V. Sturzenegger, J. Hoigne, Water Research 1988, 22, 1109.

(3) E. Wegner, A. Adamson, J. Am. Chem. Soc. 1966, 88, 394.