Supporting Information

Photocatalytic H$_2$ production in aqueous solution with host-guest inclusions formed by insertion of an FeFe-hydrogenase mimic and organic dye into cyclodextrins respectively

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Experimental Section

Chemicals. Eosin Y and Rose Bengal were purchased from Sigma-Aldrich and used as received. Diiron complex **1** was prepared according to the literature.[1] β-Cyclodextrin was purchased from Tianjin Chemical Factory, China and recrystallized twice before used. Triethylamine (TEA) was freshly distilled prior to use and stored under nitrogen atmosphere. The water used in this experiment was twice distilled deionized water.

UV-Vis, fluorescence, fluorescence lifetime and induced circular dichroism (ICD). UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. Photoluminescence spectra were recorded using a FluoroMax-4P fluorimeter (Horiba Jobin Yvon Inc.). Fluorescence lifetime was obtained with a Tempro−01 system time-correlated single-photon counting apparatus (Horiba Jobin Yvon Inc.) with a 450 nm LED excitation source. Induced circular dichroism spectra were measured by a Jasco J−810 dichrograph in a 1 cm optical path cuvette.

Electrochemistry. Electrochemical measurements were recorded in a three-electrode cell under

argon atmosphere using a BAS−100W electrochemical workstation. The working electrode was a glassy carbon disk (diameter, 3 mm) successively polished with 3 and 1 μm diamond pastes and sonicated in ion-free water for 10 min. The auxiliary electrode was a platinum wire and the reference electrode was a saturated KCl Ag/Ag$^+$ electrode. A solution of 1 M KCl in deionized water was used as electrolyte. All aqueous potentials are reported relative to the Ag/AgCl couple. Deionized water was used as solvent and the sample was bubbled with argon for 20 min before measurement.

MS and ^{1}H NMR spectroscopy. Electrospray ionization mass spectra were recorded on a Q−TOF Micromass spectrometer (Manchester, England). All ^{1}H NMR measurements were carried out in H_2O at 298 K with a Varian DLG−400 instrument. Chemical shifts were referenced to the internal water signal at 4.61 ppm.

Photodegradation of 1 monitored by IR spectroscopy. The IR spectra were recorded using an IFS 66v/S FTIR spectrometer (Bruker) equipped with a liquid nitrogen cooled MCT-A detector. The aqueous solution of **1** was freeze-pump-thaw deoxygenated three times and protected with argon before irradiated by Xe lamp (500 W) with a cutoff filter ($\lambda > 450$ nm). After the solution was irradiated for a certain period, the light was turned off and the probe was put into the solution under protection of argon before collection of an IR spectrum, because the AgBr-containing probe cannot be directly lighted. Upon completion of the IR measurement, the probe was removed from the Schlenk bottle and the solution was lighted again under argon.

Job's Plot method. Solutions for Job's plots were prepared by mixing appropriate quantities of **1** and β-CD in water to keep their sum concentration constant but make the molecular fraction of β-CD varied from 0 to 100%.

A general procedure for photocatalysis. The pH of the solution of TEA (10% v/v) in deionize

water was adjusted to the desired pH by addition of hydrochloric acid as required and measured with

a PHS-25 pH meter. In a typical experiment for photo-induced H_2 production, EY^{2-} (1.62 mg, 2.5

µmol), complex **1** (1.43 mg, 2.5 µmol), and β-cyclodextrin (28.4 mg, 25 µmol) were added to the 10

vol% TEA aqueous solution (5 mL) with magnetic stirring under nitrogen atmosphere. The solution

was then freeze-pump-thaw degassed three times and irradiated using a Xe lamp (500 W) with a

cutoff filter ($\lambda > 450$ nm).

The gas phase of the reaction system was analyzed by a GC 7890T instrument with a thermal

conductivity detector, a 5 Å molecular sieve column (2 mm × 2 m) with nitrogen as carrying gas. The

amount of hydrogen generated was determined by the external standard method and the hydrogen

dissolved in the solution was neglected.

Calculation method for TON. TON (turnover number) = molecules of H_2 per molecule of

catalyst, which was calculated by the following equations:

$$\text{TON}_{\text{cat.}} = \frac{n_{H_2}}{n_{\text{cat.}}} = \frac{V_{H_2}/V_{m,H_2,25\,°C}}{n_{\text{cat.}}}$$

The calculation of $V_{m,H2,25°C}$ was carried out using van der waals equitation as below:

$$V_{m,H_2,25\,°C} = \frac{RT}{p} + b - \frac{a}{RT} = 24.48 \text{ mL/mmol}$$

Where $R = 8.3145$ cm^3 Pa mol^{-1}K^{-1}; $T = 298.15$ K; $p = 101325$ Pa; $b = 26.6$ cm^3 mol^{-1}; $a = 24.7 \times$

10^9 cm^6 Pa mol^{-2}.

V_{H2} was determined by fitting the area of H_2 showed by GC to an external standard.

Quantum yield measurement. A sample containing **1** (5.0×10^{-4} M), TEA (10% v/v) in

deionized water was used as a blank. The solution containing EY (5.0×10^{-4} M), **1** (5.0×10^{-4} M),

and TEA (10% v/v) was used as a sample. The powers of the light passing through the blank and the

sample were measured with a L30 A−BB−13 thermal sensor and Nova II power meter using a 300 W

Xe lamp equipped with a 520 nm band pass filter. The difference between the power of light passing

through the blank and that through the sample was considered to be absorbed by the dye. Each value

of quantum yield was tested three times to reduce errors.

The photon flux was determined by equation (1):

$$F_{Photon} = 2 \frac{P\lambda}{S_{Beam}\, h\, c} \quad (1)$$

Where P (in W) is determined by the difference in the power of light passing through the blank and

the sample, respectively; λ is the irradiation wavelength number (520 nm); S_{Beam} is the beam area; h

is Plank's constant; and c is the speed of light.

The quantum yields (φ) were determined by equation (2):

$$\varphi\,(1/2H_2) = 2 \frac{n(H_2) \times N}{F_{Photon}\, S_{Beam}\, t} = 2 \frac{n(H_2) \times N\, h\, c}{P\lambda\, t} \quad (2)$$
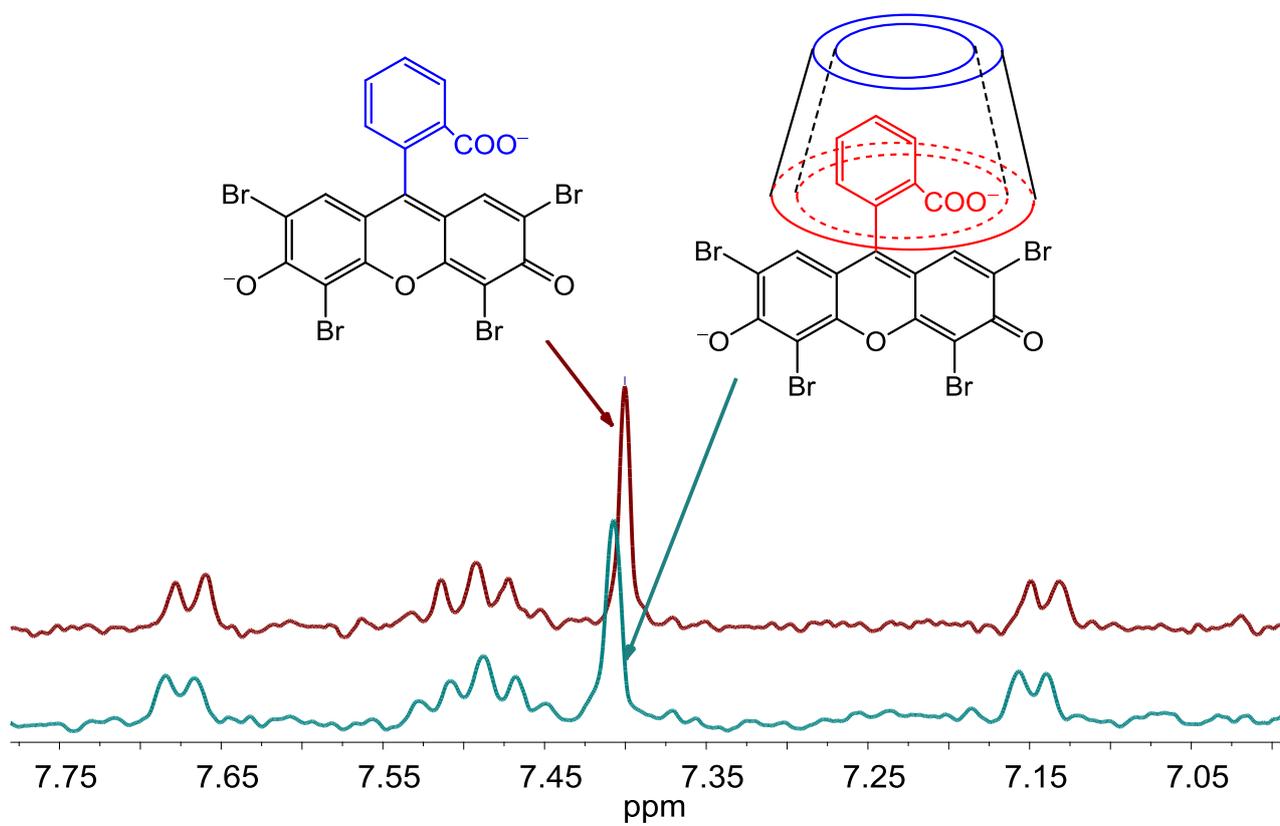
Where the amount of hydrogen produced ($n(H_2)$) was estimated form GC analysis; N is the Avogadro
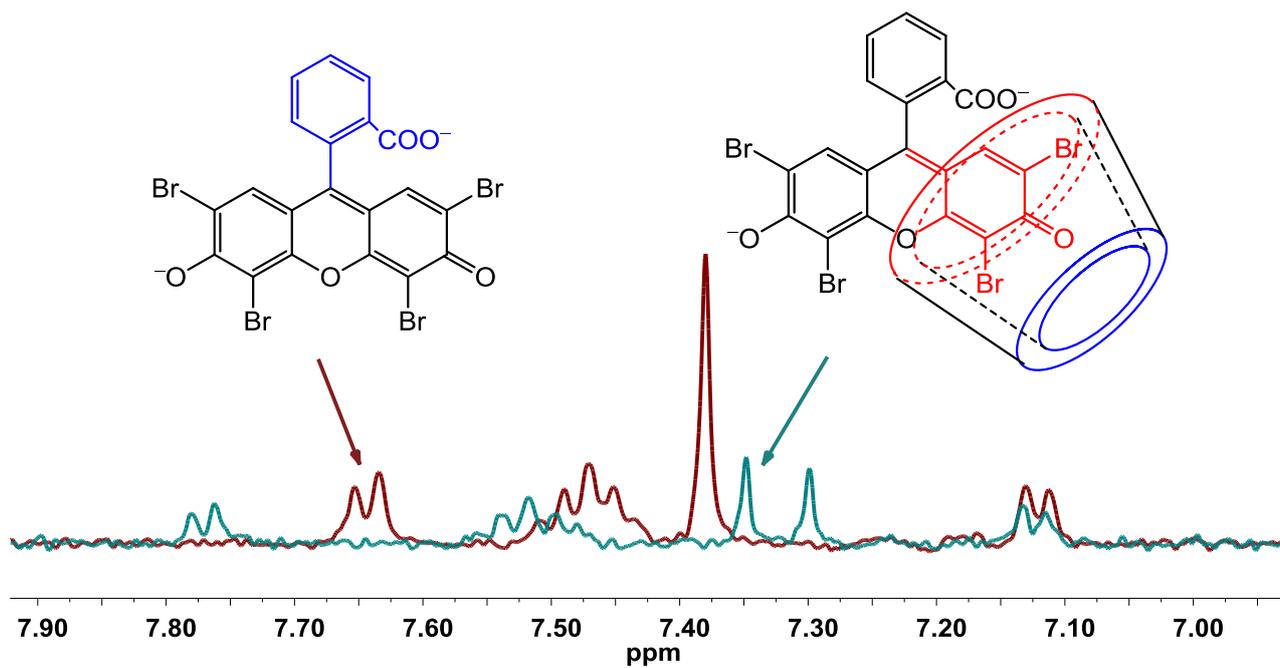
constant, and t is the irradiation period.
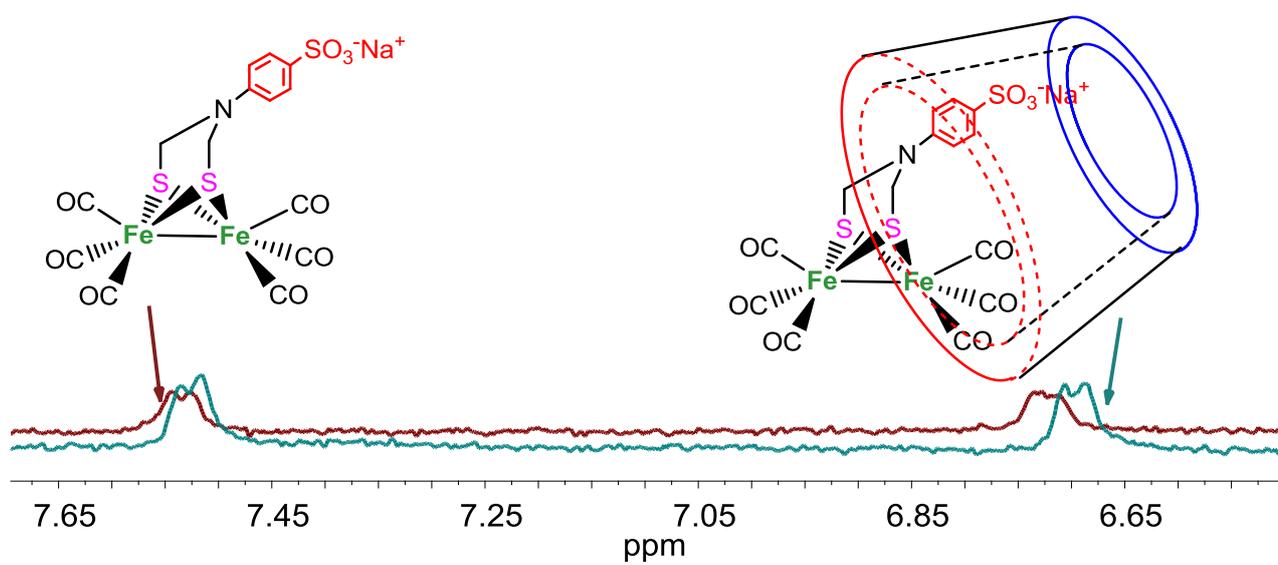
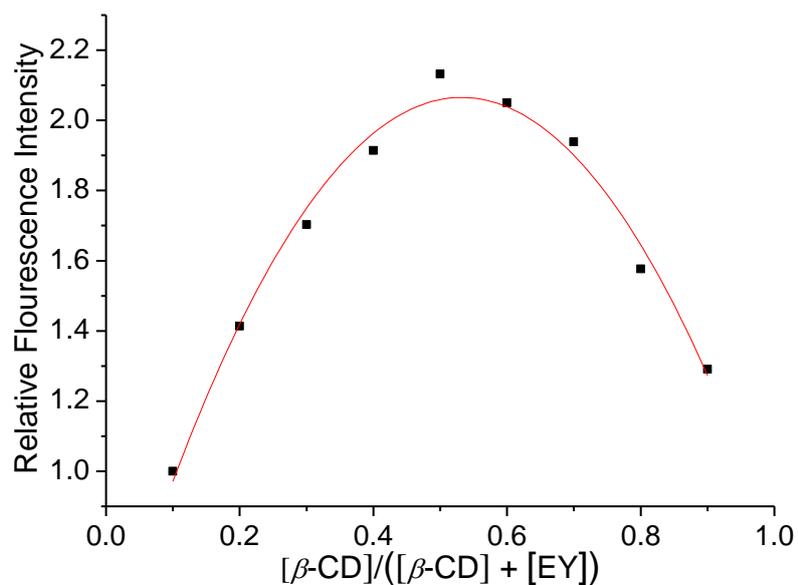**Fig. S1** ^{1}H NMR spectra of **1** (0.1 mM) and **1** with 5 equiv. γ–CD in D$_2$O at 298 K.
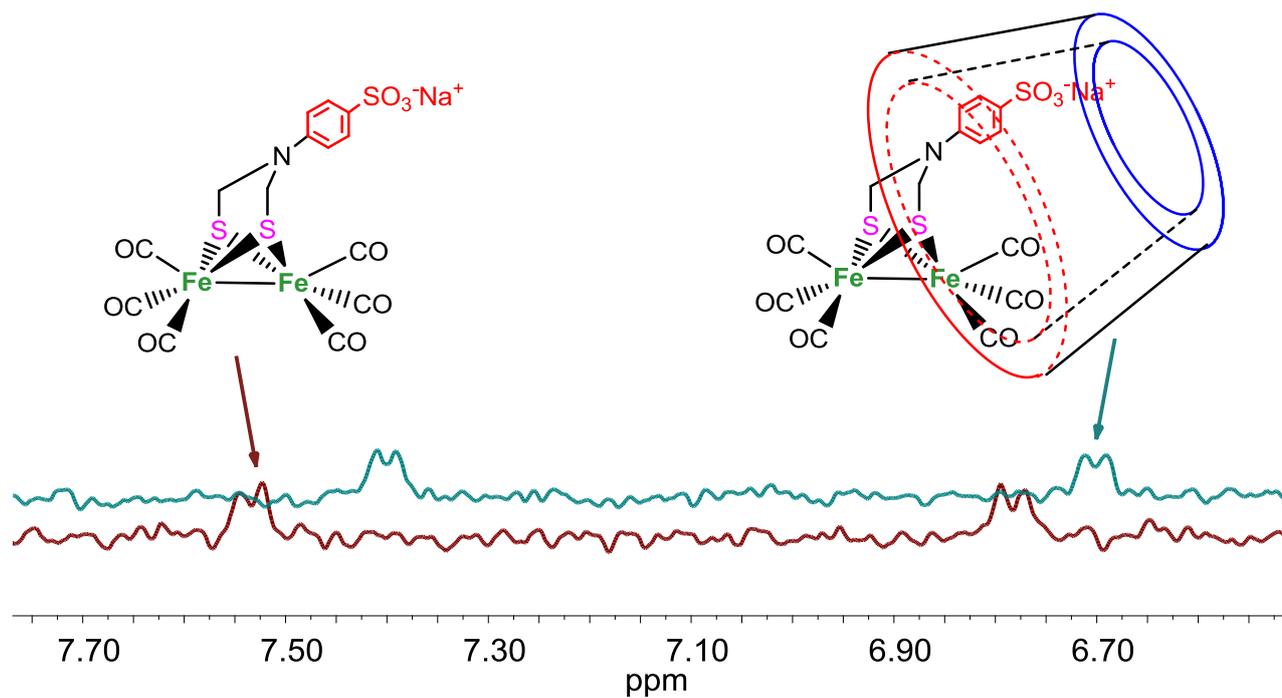
**Fig. S2** ^{1}H NMR spectra of **1** (0.1 mM) and **1** with 5 equiv. β–CD in D_2O at 298 K.

**Fig. S3** ^{1}H NMR of EY (0.1 mM) and EY with 5 equiv. β–CD in D$_2$O at 298 K.

**Fig. S4** ^{1}H NMR of EY (0.1 mM) and EY with 5 equiv. γ–CD in D_2O at 298 K.

Fig. S5 A Job plot based on the changes in fluorescence intensity with variation of the ratio of $[\beta–CD]/([\beta–CD]+[EY])$ in water ($[\beta–CD] + [EY] = 3 \times 10^{-5}$ M). Equation for the best fit line is: $y = 0.4069136 + 6.2326439x – 5.8558027x^2$ ($R^2 = 0.9800329$).
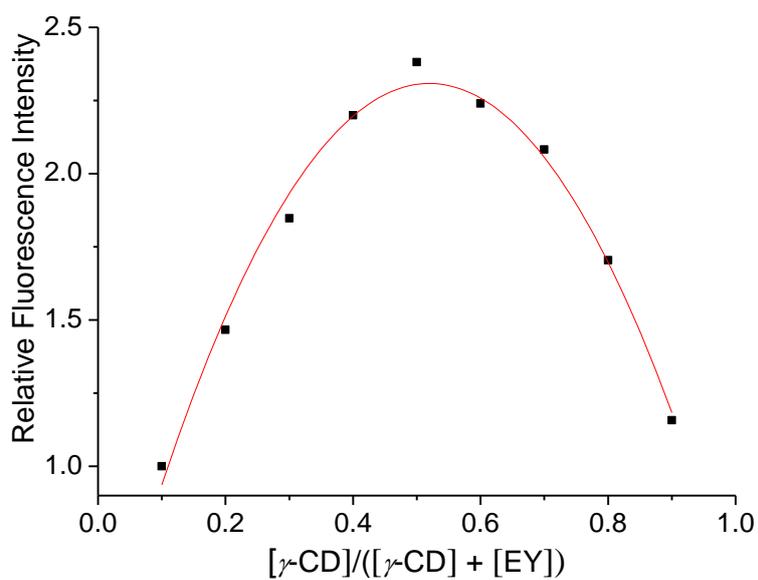
Fig. S6 A Job plot based on the changes in fluorescence intensity with variation of the ratio of

$[\gamma\text{–CD}]/([\gamma\text{–CD}]+[EY])$ in water ($[\gamma\text{–CD}] + [EY] = 3 \times 10^{-5}$ M). Equation for the best fit line is: $y = 0.2053163 + 8.0914859x - 7.7830231x^2$ ($R^2 = 0.9857499$).
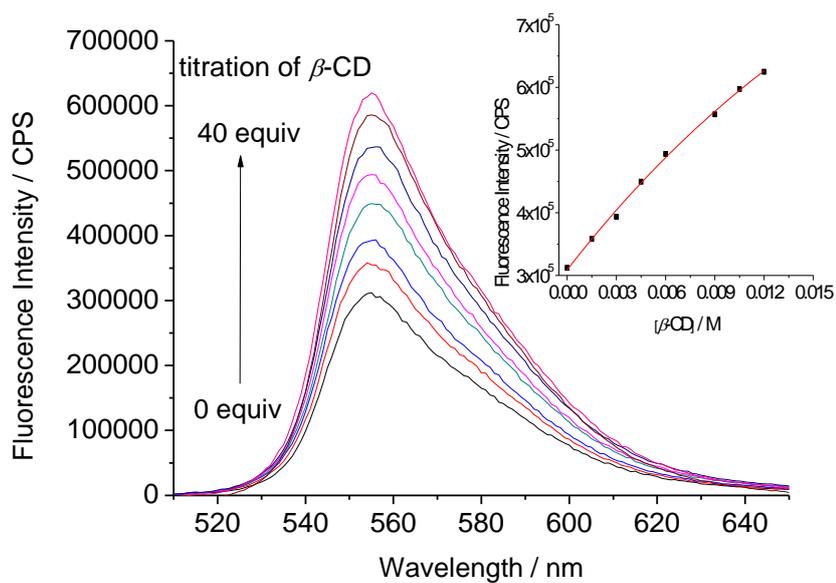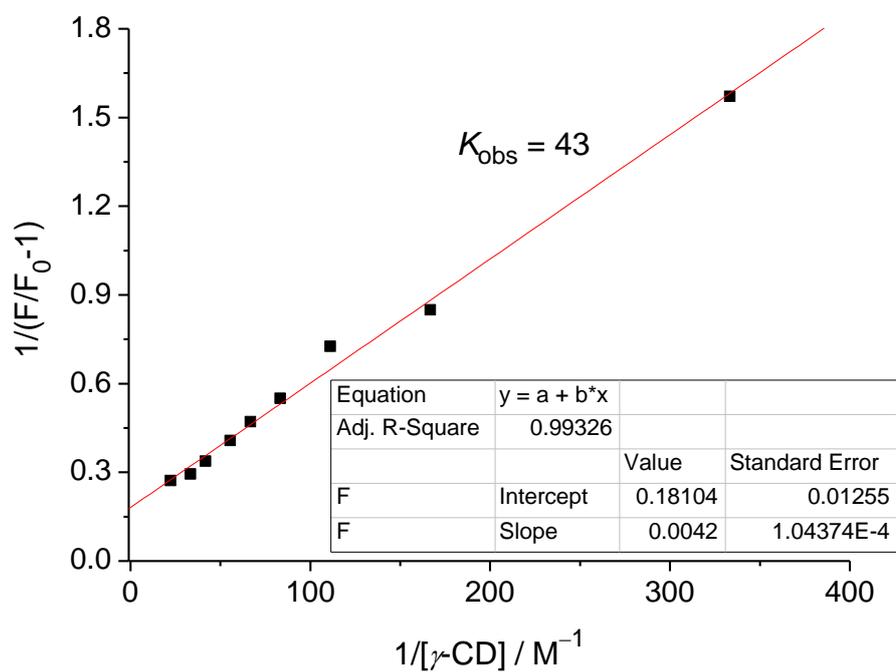
Fig. S7 Fluorescence spectra of EY in water with addition of β–CD ([EY] $= 3 \times 10^{-5}$ M); Inset:

Increase of the fluorescence intensity maximum of EY with addition of β–CD.
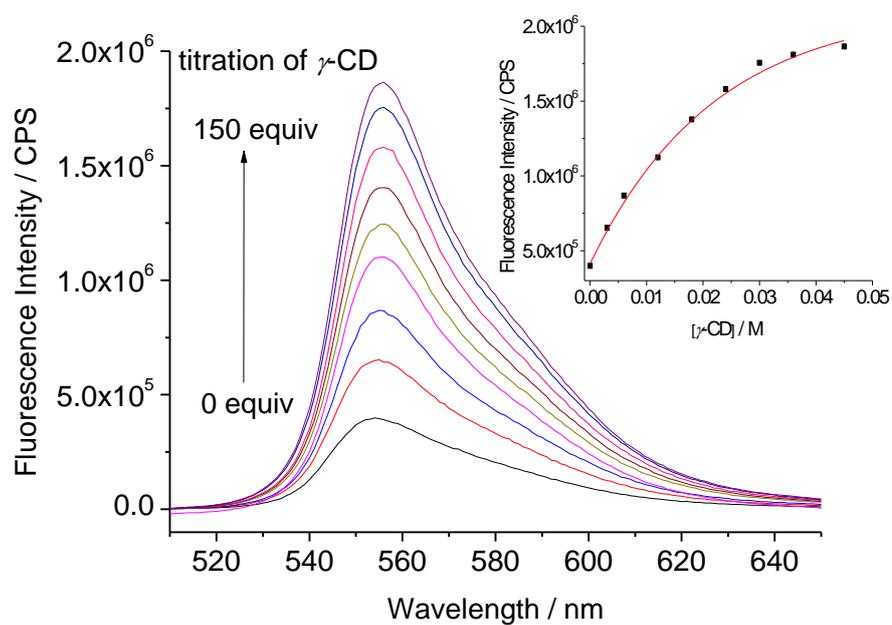
Fig. S8 Fluorescence spectra of EY in water with addition of γ–CD ([EY] = 3×10^{-5} M); Inset: Increase of the fluorescence intensity maximum of EY with addition of γ–CD.
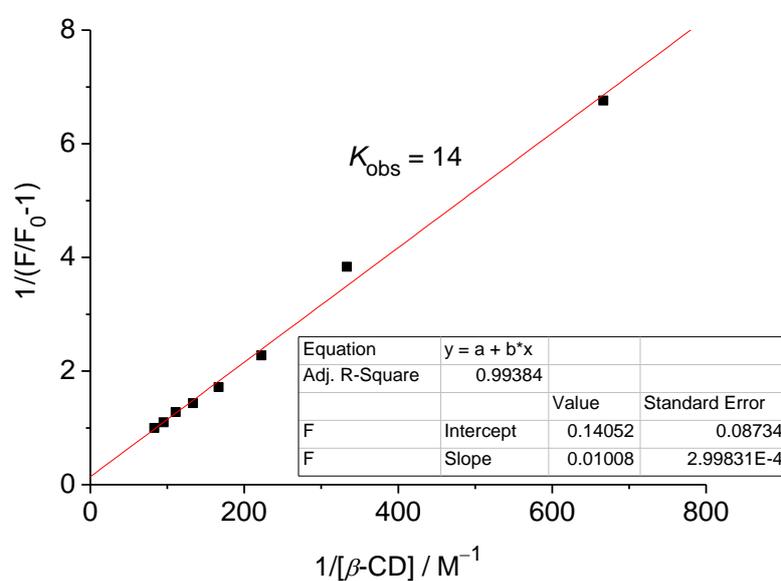
Fig. S9 The modified Stern−Volmer plot with $1/(F/F_0 − 1)$ against $1/[\beta\text{-CD}]$ for calculation of binding constant according to the data of Fig. S7.

| Equation	y = a + b*x	
Adj. R-Square	0.99326	
	Value	Standard Error
F	Intercept	0.18104	0.01255
F	Slope	0.0042	1.04374E-4

$K_{obs} = 43$

Fig. S10 The modified Stern−Volmer plot with $1/(F/F_0 − 1)$ against $1/[\gamma\text{-CD}]$ for calculation of binding constant according to the data of Fig. S8.
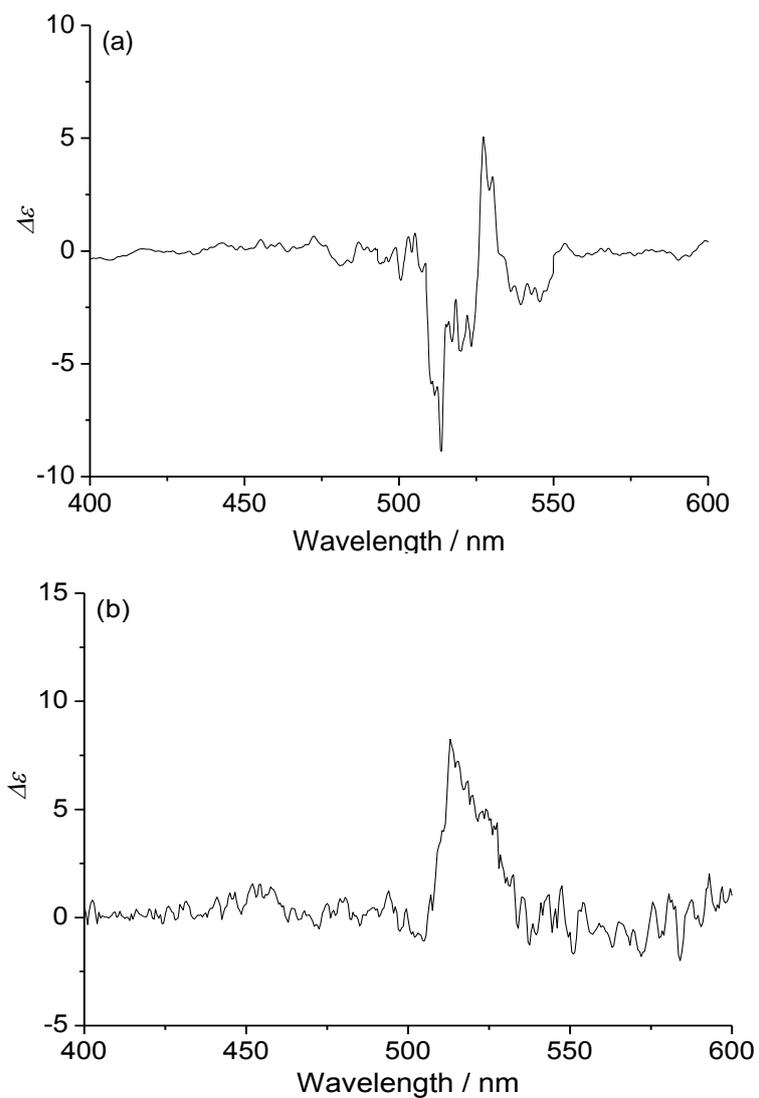
Fig. S11 Induced circular dichroism spectra of EY (1×10^{-5} M) in water with addition of (a) 10 equiv. β–CD and (b) 10 equiv. γ–CD.
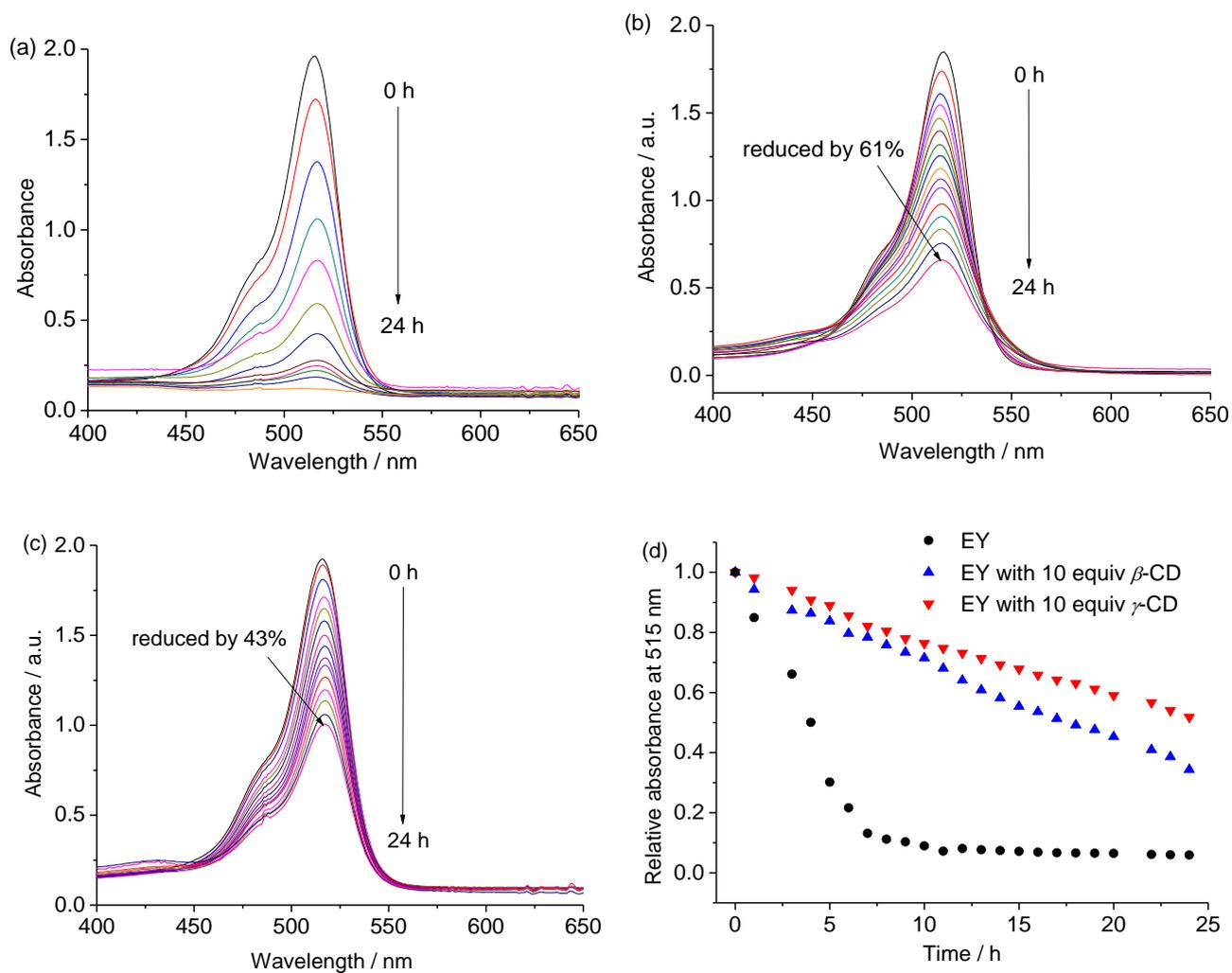
Fig. S12 Photodegradation of EY (30 μM) in water, (a) in the absence of CD; (b) [β-CD] = 300 μM;

(c) [γ-CD] = 300 μM; (d) plot of relative absorbance of EY at 515 nm versus irradiation time.
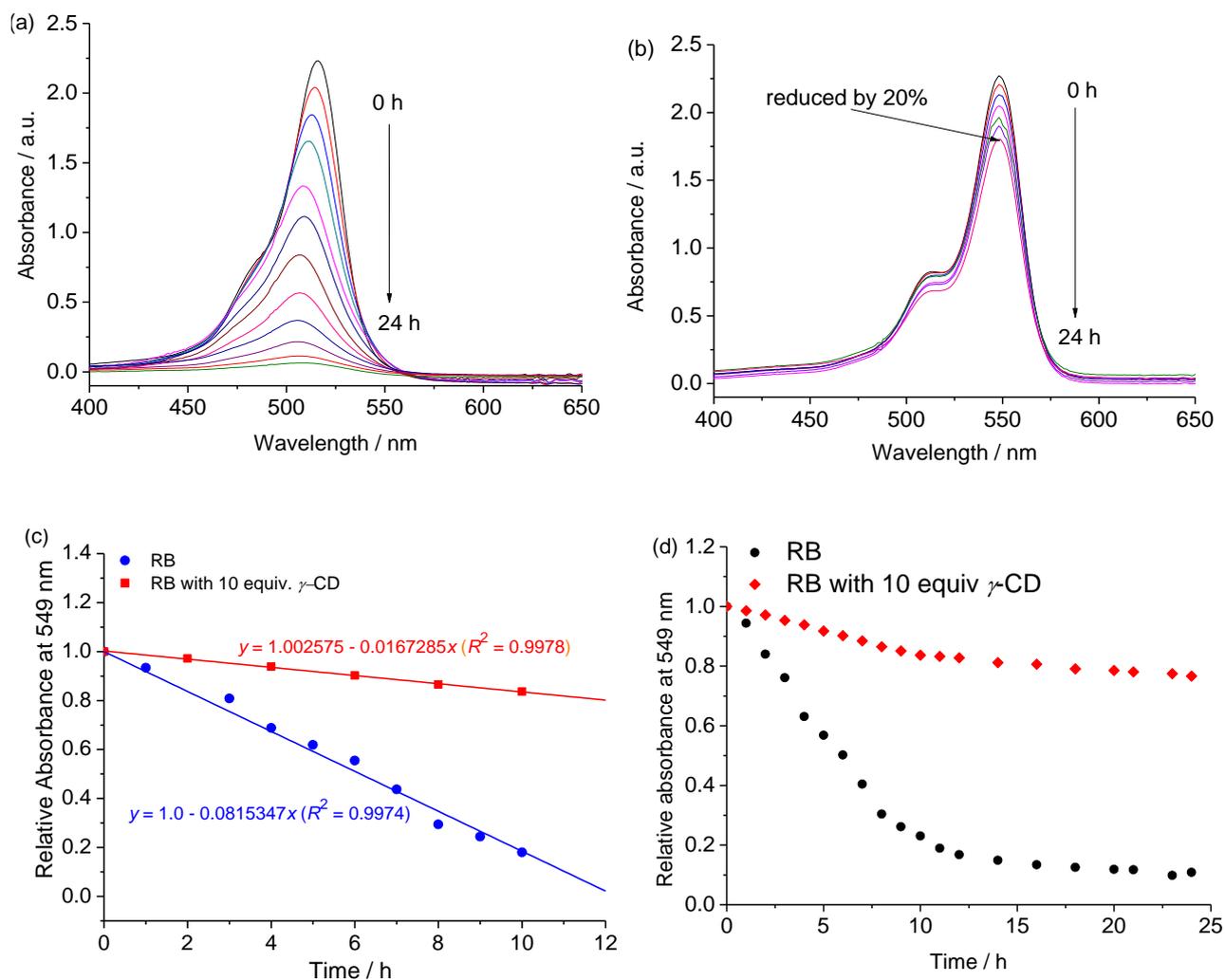
Fig. S13 Photodegradation of RB (30 μM) in water, (a) in the absence of CD; (b) [γ-CD] = 300 μM;

The UV-vis spectra for photodegradation of RB in the presence of 10 equiv. *β*-CD are essentially

identical with Fig. S13(a); (c) Photodegradation curves of RB (3.0×10^{-5} M) in the absence and

presence of *γ*-CD in water; (d) plot of relative absorbance of RB at 549 nm versus irradiation time.
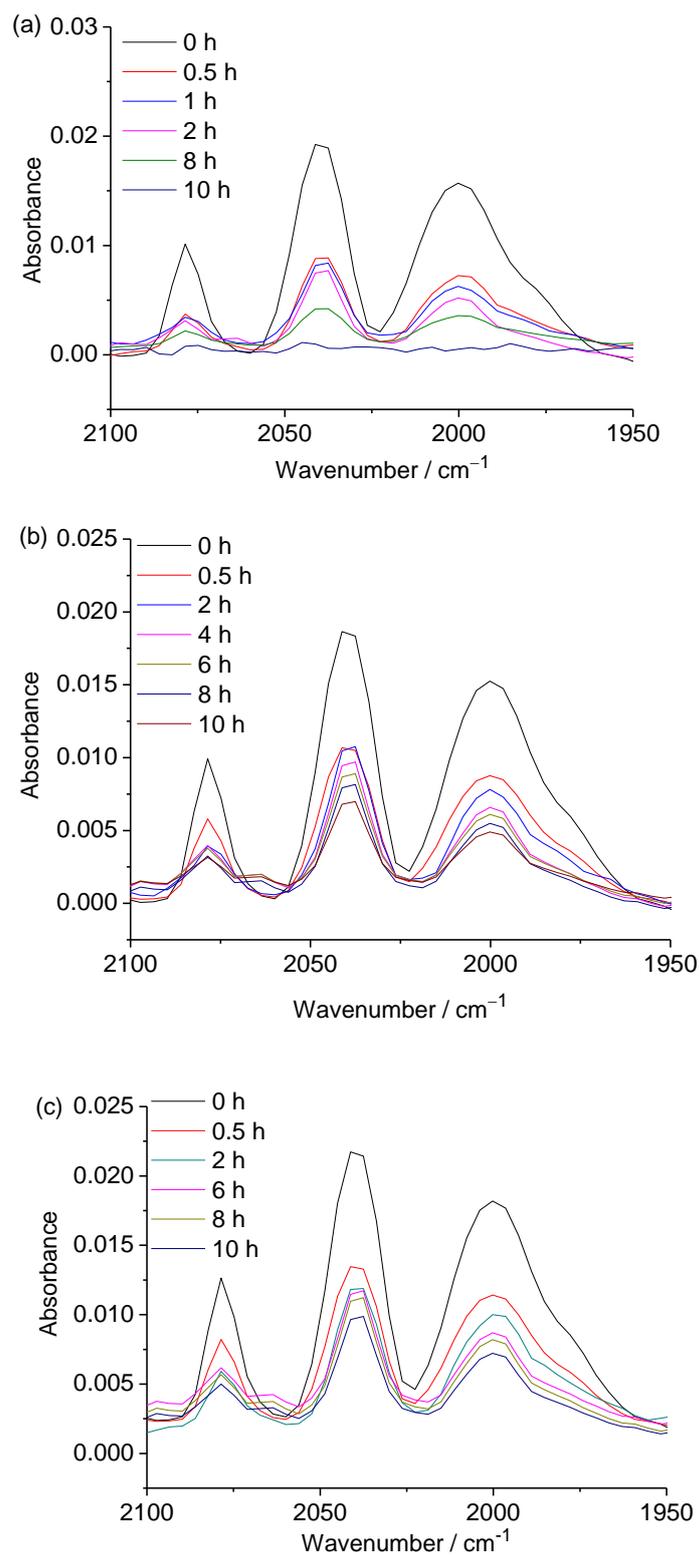
Fig. S14 Photodegradation of (a) **1** (60 µM), (b) **1** with 10 equiv. *β*-CD, and (c) **1** with 10 equiv. *γ*-CD

in water monitored by IR spectroscopy.

**Table S1** Photoinduced H_2 production of the EY/**1** system at different conditions[a]

Donor	pH	TON[b]
	pH = 8	0.1
	pH = 9	2.2
10 vol% TEA	pH = 10	8.0
	pH = 11	5.8
	pH = 12	1.1
5 vol% TEA	pH = 10	0.2
10 vol% TEA	pH = 10	8.0
15 vol% TEA	pH = 10	1.2
	pH = 6	0.5
	pH = 7	0.8
10 vol% TEOA	pH = 8	0.3
	pH = 9	0
	pH = 10	0

[a] Conditions: EY 5.0×10^{-4} M, **1** 5.0×10^{-4} M, in water at 25 °C.

[b] TONs were obtained over 10-h irradiation.
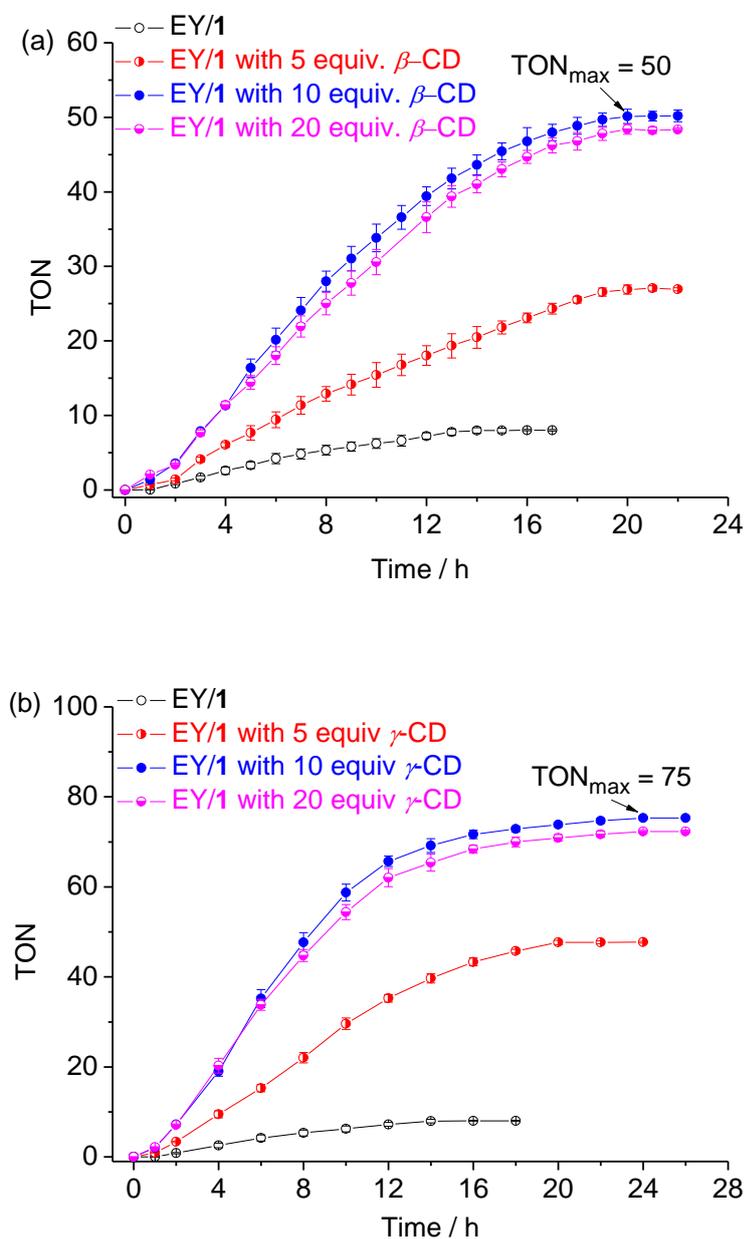
Fig. S15 Photocatalytic H_2 production by the EY/**1** system with different amounts of (a) β-CD and (b)

γ-CD in 10% TEA aqueous solution at pH 10 ([EY] = [**1**] = 5.0×10^{-4} M).
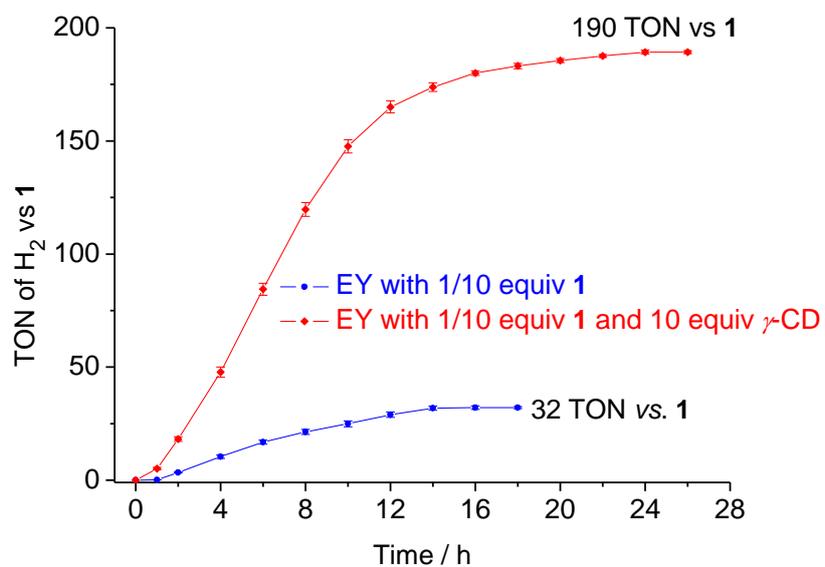
Fig. S16 Photocatalytic H_2 production with EY (5.0×10^{-4} M)/**1** (5.0×10^{-5} M) system in the absence

and presence of γ–CD in 10% TEA aqueous solution at pH 10.
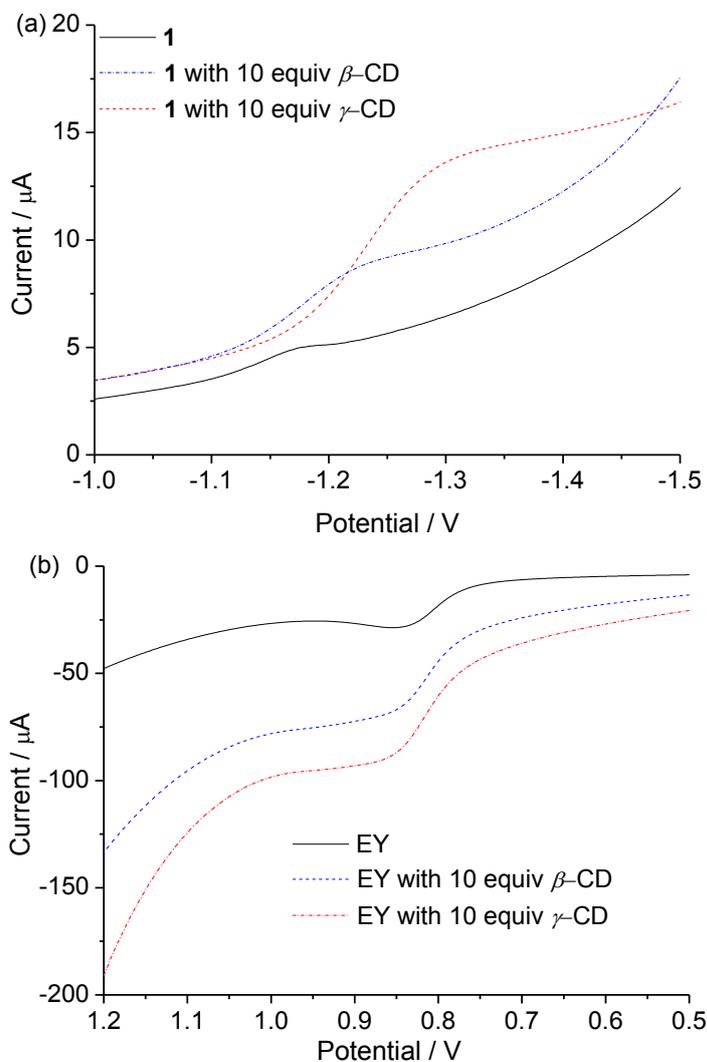
Fig. S17 Cyclic voltammograms of (a) **1** (1.0×10^{-5} M) and (b) EY (1.0×10^{-5} M) in water in the absence and presence of β-CD and γ-CD using a saturated KCl Ag/AgCl reference electrode.

Table S2 Redox potentials of **1**, EY, and RB as well as the calculated energies and redox potentials of the singlet and triplet excited states of EY and RB[a]

	E_{ox}/V	E_{red}/V	$^{1*}E_{00}/V$	$^{3*}E_{00}/V$	$^{1*}E_{ox}/V$	$^{1*}E_{red}/V$	$^{3*}E_{ox}/V$	$^{3*}E_{red}/V$
EY	0.841	−1.00	2.34	1.89	−1.499	1.34	−1.049	0.89
EY+β-CD	0.853	−0.97	2.34	1.89	−1.487	1.37	−1.037	0.92
EY+γ-CD	0.871	−0.95	2.34	1.89	−1.469	1.39	−1.019	0.94
RB	0.84	−1.00	2.21	1.83	−1.37	1.21	−0.99	0.83
RB+γ-CD	0.85	−0.99	2.21	1.83	−1.36	1.22	−0.98	0.84
1		−1.175						
1+β-CD		−1.222						
1+γ-CD		−1.294						

[a] All potentials are reported relative to Ag/AgCl in water using 1.0 M KCl as electrolyte.
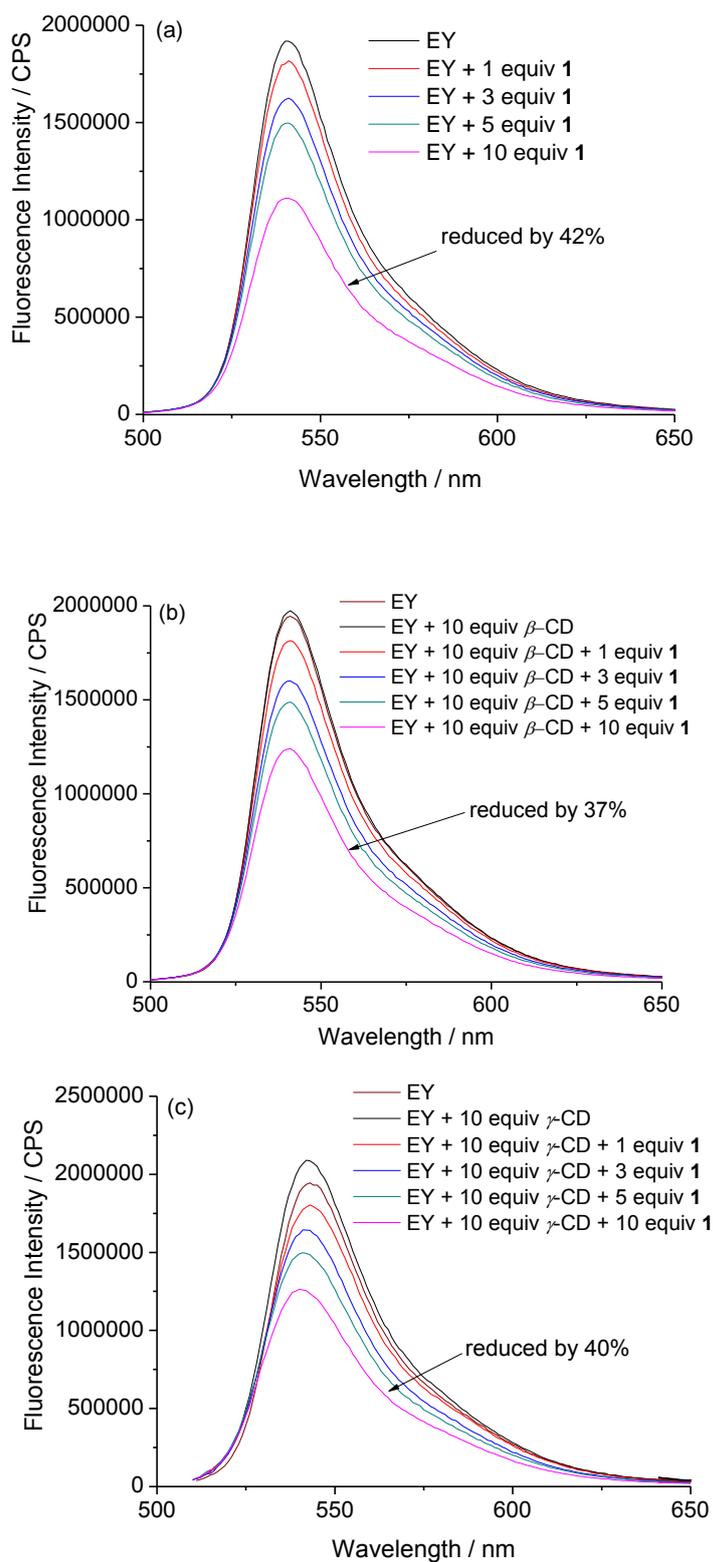
Fig. S18 The fluorescence spectra of EY (3×10^{-5} M) with addition of **1**: (a) in the absence of cyclodextrin; (b) in the presence of β-CD (3×10^{-4} M); (c) in the presence of γ-CD (3×10^{-4} M).
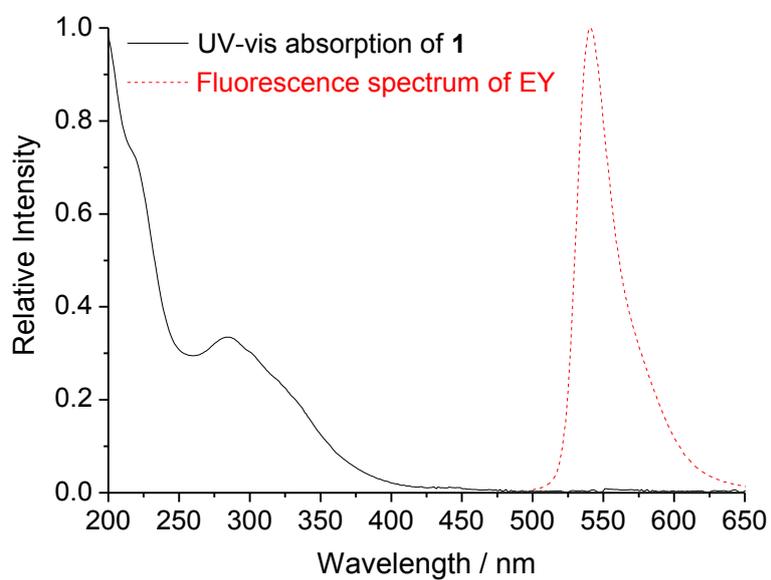
Fig. S19 The UV-vis absorption spectrum of **1** and fluorescence emission spectrum of EY (The intensity of each band is normalized by its initial intensity).

Table S3 Lifetime of EY and RB (3×10^{-5} M) with different concentration of β-CD and γ-CD in water

|	$\tau_f{}^a$/ ns	$\phi_f{}^b$
EY	1.2803	0.163
EY + 10 equiv. β-CD	1.2947	0.168
EY + 50 equiv. β-CD	1.3073	0.174
EY + 100 equiv. β-CD	1.3366	0.179
EY + 10 equiv. γ-CD	1.3187	0.176
EY + 50 equiv. γ-CD	1.4657	0.199
EY + 100 equiv. γ-CD	1.5365	0.219
RB	0.1059	0.018
RB + 10 equiv. β-CD	0.1066	0.020
RB + 10 equiv. γ-CD	0.1282	0.02439
RB + 50 equiv. γ-CD	0.1454	0.02443
RB + 100 equiv. γ-CD	0.1657	0.02539

[a] Fit by a single index model. [b] ϕ_f was calculated using following equation and taking the quantum yield of Rhodamine B in methanol as reference.[2]

$$Y_u = Y_s \times \left(\frac{F_u}{F_s}\right) \times \left(\frac{A_s}{A_u}\right) \times \left(\frac{n_u^2}{n_s^2}\right) \times \left(\frac{\lambda_{exs}}{\lambda_{exu}}\right)$$

Where Y_u is the fluorescence quantum yield of the sample solution to be measured and Y_s is the reference solution; F_u and F_s are the integral intensity; A_u and A_s stand for absorption values; n_u and n_s denote the refractive indexes of the solvents; and subscripts u and s refer respectively to the sample and standard substance. The fluorescence quantum yield of Rhodamine B in methanol is 0.69.[2]
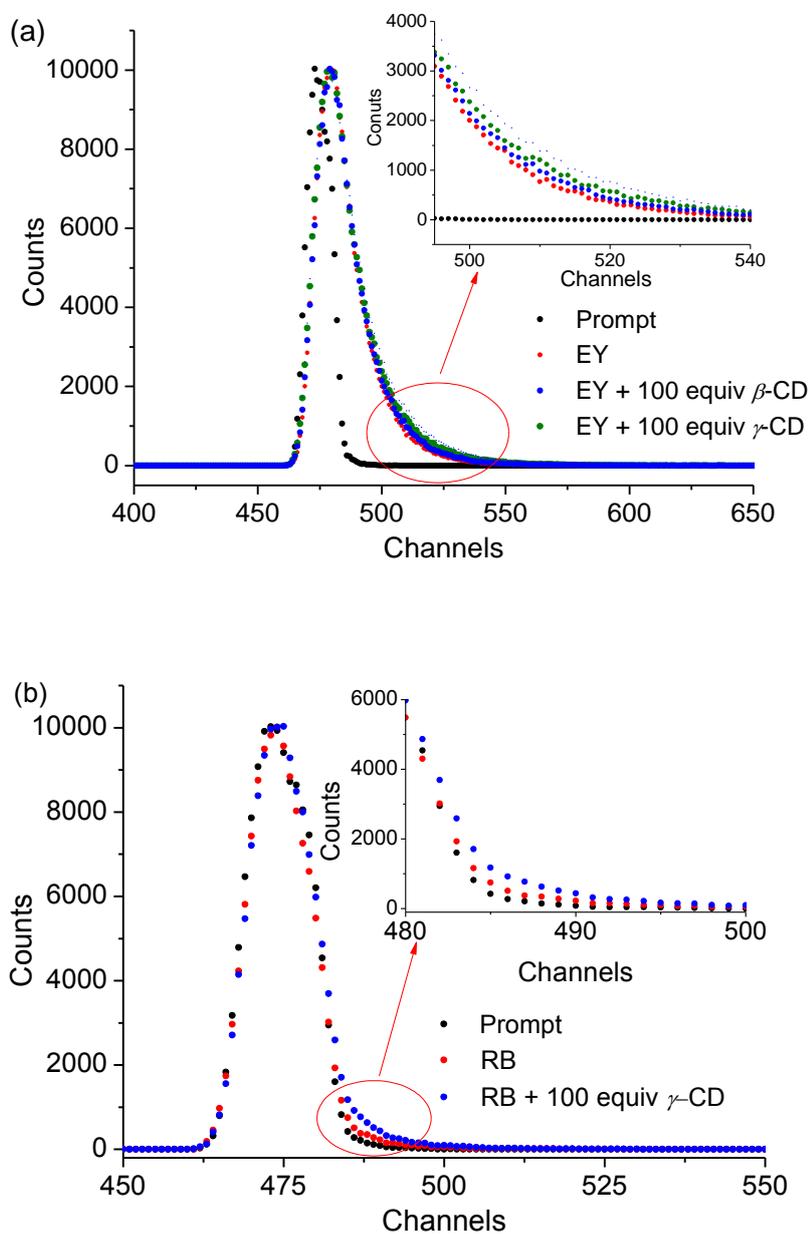
Fig. S20 The fluorescence lifetimes of (a) EY and (b) RB (3×10^{-5} M) in the absence and presence of cyclodextrin in water at 298 K. The samples were excited with a 450 nm LED and the signals were collected at 541 nm for EY and 573 for RB.
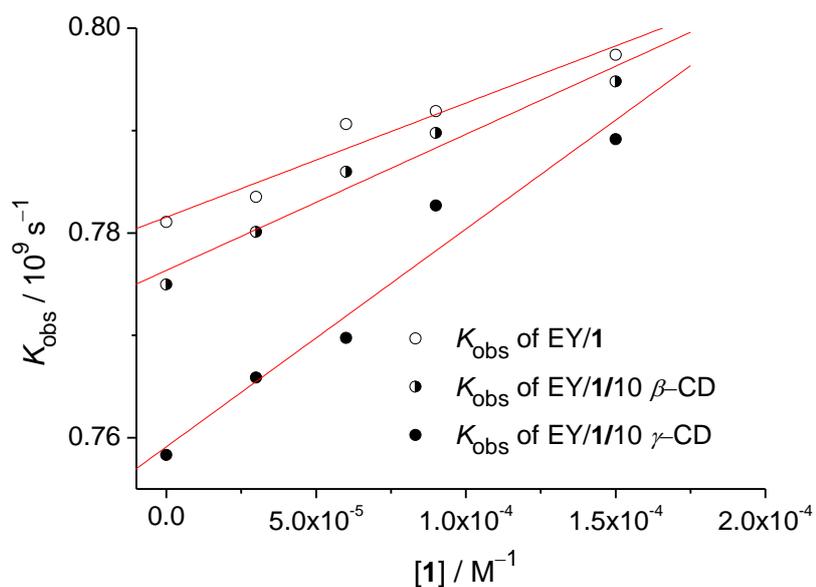
Fig. S21 The quenching constant plot of EY/**1** ([EY] = [**1**] = 3×10^{-5} M) system with addition of β-CD and γ-CD (3×10^{-4} M). Equations for the best fit line are: $y = 0.7815416 + 111.4792837x$ ($R^2 = 0.933$) for the EY/**1** system; $y = 0.7763433 + 132.9038063x$ ($R^2 = 0.950$) for the EY/**1**/β-CD system; $y = 0.7591164 + 212.6920464x$ ($R^2 = 0.940$) for the EY/**1**/γ-CD system.

References

1 M. L. Singleton, J. H. Reibenspies and M. Y. Darensbourg, *J. Am. Chem. Soc.*, 2010, **132**, 8870–8871.

2 R. A. Velapoldi and H. H. Tonnesen. *Journal of Fluorescence*, 2004, **14**, 465–472.