

## Supporting Information

### Photochemical hydrogen production from water catalyzed by CdTe quantum dots/molecular cobalt catalyst hybrid systems

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#### Materials and instruments

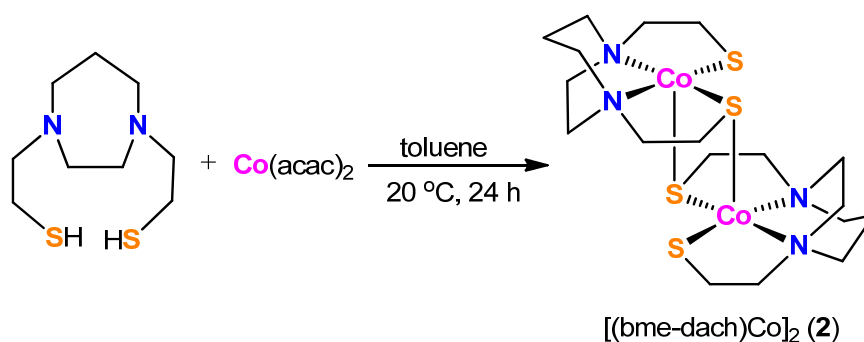
**Materials.** The reagents, 1,4-diazepane,  $K_2TeO_3$ , and  $Co(acac)_2$ , were purchased from Aladdin and thiirane was purchased from Sigma-Aldrich. 2-Thioglycolic acid,  $Cd(OAc)_2$ , NO gas, and other chemicals were purchased from local suppliers. All commercially available chemicals were used as received without further purification. Ligand  $H_2bme-dach$  (*N,N*-bis(2-mercaptoethyl)-1,4-diazacycloheptane), complexes  $[Co(bme-dach)]_2$  and  $[(bme-dach)Co(NO)]$  were prepared according to the literature protocols.<sup>S1-S4</sup>

**Instruments.** UV-Vis absorption measurements were carried out on an Agilent 8453 spectrophotometer. Infrared spectra were measured with a JASCO FT/IR 430 spectrophotometer. Mass spectra were recorded either on a TOF mass spectrometer (Micromass) or an Agilent 6224 Accurate-Mass TOF mass spectrometer. Elemental analyses were performed with a Thermoquest-Flash EA 1112 elemental analyzer. ICP-MS analysis was recorded on an Optima 2000 DV spectrometer (Perkin Elmer Inc.). Photoluminescence spectra were recorded using a FluoroMax-4P fluorimeter (Horiba Jobin Yvon Inc.).

## Characterization of cobalt complexes

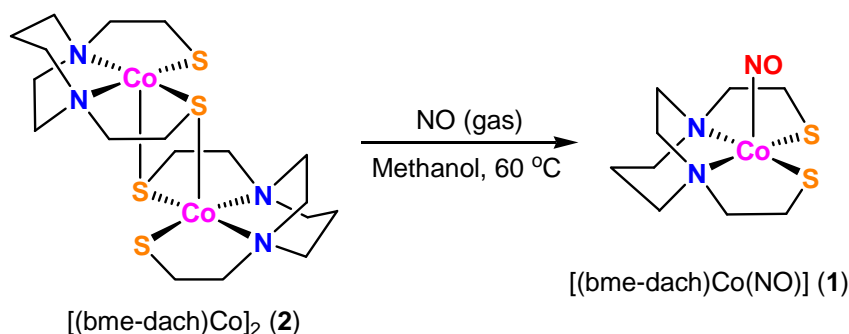
**[Co(bme-dach)]<sub>2</sub> (2, H<sub>2</sub>bme-dach = *N,N'*-bis(2-mercaptoethyl)-1,4-diazacycloheptane).**

Complex [Co(bme-dach)]<sub>2</sub> was obtained as green solid in 62% yield. HR-MS: Calcd for [M]<sup>+</sup>, *m/z* 554.0487; found, *m/z* 554.0442. IR (KBr, cm<sup>-1</sup>): 2915 (s), 2844 (s), 1459 (m), 1074 (s), 1039 (s), 737 (s) cm<sup>-1</sup>. Anal. calcd for C<sub>18</sub>H<sub>36</sub>Co<sub>2</sub>N<sub>4</sub>S<sub>4</sub>: C, 38.98; H, 6.54; N, 10.10%; found: C, 39.16; H, 6.67; N, 10.19%.



**[(bme-dach)Co(NO)] (1).** Complex 1 was obtained as dark-purple solid in 75% yield.

UV/vis spectrum in CH<sub>2</sub>Cl<sub>2</sub> [ $\lambda_{\max}$  ( $\epsilon$ , M<sup>-1</sup> cm<sup>-1</sup>): 268 (8460), 298 (5990), 364 (1740), 635 (341), 657 nm (250). IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu$ (NO) 1594 (m) cm<sup>-1</sup>. Anal. calcd for C<sub>9</sub>H<sub>18</sub>CoN<sub>3</sub>OS<sub>2</sub>: C, 35.17; H, 5.90; N, 13.67%; found: C, 35.04; H, 5.79; N, 13.51%.



## Preparation of CdTe QDs

The water-soluble 2-thioglycolic acid-stabilized CdTe (TGA-CdTe) quantum dots (QDs) were prepared according to a protocol in the literature.<sup>S5</sup> The TGA-CdTe QDs with desired photoluminescence spectra were obtained by controlling the reaction time (Fig. S1). The

diameter ( $D$ ) and extinction coefficient ( $\varepsilon$ ) of the TGA-CdTe QDs were calculated by the equations reported by Peng and coworkers:<sup>S6</sup>

$$D = (9.8127 \times 10^{-7})\lambda^3 - (1.7147 \times 10^{-3})\lambda^2 + 1.0064\lambda - 194.84$$

$$\varepsilon = 10043(D)^{2.12}$$

Wherein  $D$  (nm) is the diameter or size of a given nanocrystal sample,  $\lambda$  is the wavelength of the first absorption peak (from low energy) of the corresponding sample and  $\varepsilon$  is the extinction coefficient of the corresponding sample. The diameter ( $D$ ) and extinction coefficient ( $\varepsilon$ ) of the prepared TGA-CdTe QDs were calculated to be  $\sim 2.7$  nm and  $8.4 \times 10^5$  L mol<sup>-1</sup> cm<sup>-1</sup>.

### Preparation of CdTe QDs/1

The solution of cobalt catalyst **1** (15 mL,  $2.0 \times 10^{-4}$  M) was added to the solution of TGA-CdTe (15 mL,  $2.0 \times 10^{-4}$  M). After the mixture was vigorously stirred at room temperature for 5 h, isopropanol (30 mL) was added to the resulting solution. The precipitated fine solid was isolated by high speed centrifugation (15000 rpm). The solid was washed with diethyl ether and dried at 60 °C in vacuum for 8 h. The isolated solid, CdTe QDs/1, was characterized by UV-vis and IR spectroscopy. ICP analysis shows the loading amount of **1** on CdTe QDs is 0.45% (w/w), while the loading amount of **2** is negligible in the solid sample isolated from the same preparation procedure but using **2** as catalyst.

### Stern-Volmer equation

$$\frac{I_0}{I} = \frac{\tau}{\tau_0} = 1 + K_{SV}[Q] = 1 + k_q\tau_0[Q]$$

Where  $I_0$  and  $I$  are the luminescence intensity of the TGA-CdTe QDs in the absence and presence of catalyst in water;  $\tau_0$  and  $\tau$  are the luminescence lifetime of the TGA-CdTe QDs in

the absence and presence of catalyst, where  $\tau_0$  is the intrinsic excited state lifetime of QDs, which was determined to be 20.8 ns by time-correlated single photon counting (TCSPC) technique;  $k_q$  is the Stern-Volmer quenching constant and  $C$  is the concentration of catalyst.

### Langmuir adsorption isotherm

$$\frac{\Delta I}{I_0} = \frac{(\Delta I / I_0)_{\max} \cdot K_L \cdot [Q]}{1 + K_L \cdot [Q]}$$

$$\frac{I_0}{\Delta I} = \frac{1}{(\Delta I / I_0)_{\max}} \cdot \frac{1}{K_L [Q]} + \frac{1}{(\Delta I / I_0)_{\max}}$$

Where  $\Delta I$  ( $\Delta I = I_0 - I_Q$ ) is the amount of luminescence intensity quenched in the presence of quencher;  $I_0$  and  $I_Q$  are the luminescence intensities of TGA-CdTe QDs in the absence and presence of quencher;  $[Q]$  is the concentration of quencher,  $K_L$  is the association constant.<sup>S7,S8</sup>

### 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  $\mu\text{m}$  diamond pastes and sonicated in ion-free water for 10 min. Both auxiliary electrode and reference electrode were platinum wires. A solution of 0.1 M  $n\text{Bu}_4\text{NPF}_6$  in  $\text{CH}_3\text{CN}$  was used in the presence of an internal reference ( $E_{1/2}(\text{Fc}^{+/0}) = +0.63$  V vs. NHE).

### Photocatalysis

**A general procedure.** An aqueous colloidal TGA-CdTe solution ( $1.0 \times 10^{-4}$  M), ascorbic acid ( $\text{H}_2\text{A}$ , 0.28 M), and cobalt catalyst ( $1.0 \times 10^{-5}$  or  $1.0 \times 10^{-6}$  M) were added to a Schlenk bottle with magnetic stirring under  $\text{N}_2$  protection. The total volume of the aqueous solution was 10 mL. Prior to irradiation, the pH of the solution was adjusted by the 1.0 M NaOH or 1.0

M HCl solution and the pH value was determined by a PHS-25 pH meter. The solution was then freeze-pump-thaw degassed three times. The solution was vigorously stirred in the dark for 2 h before irradiated with a Xe lamp (300 W) fitted with a > 400 nm cutoff filter. 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 N<sub>2</sub> 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 of TON.** TON (turnover number) = molecules of H<sub>2</sub> per molecule of catalyst, which was calculated by the following equations:

$$\text{TON}_{\text{cat.}} = \frac{n_{\text{H}_2}}{n_{\text{cat.}}} = \frac{V_{\text{H}_2}/V_{\text{m,H}_2,25^\circ\text{C}}}{n_{\text{cat.}}}$$

The calculation of  $V_{\text{m,H}_2,25^\circ\text{C}}$  was carried out using van der waals equitation as below:

$$V_{\text{m,H}_2,25^\circ\text{C}} = \frac{RT}{p} + b - \frac{a}{RT} = 24.48 \text{ mL/mmol}$$

Where  $R = 8.3145 \text{ cm}^3 \text{ Pa mol}^{-1} \text{ K}^{-1}$ ;  $T = 298.15 \text{ K}$ ;  $p = 101325 \text{ Pa}$ ;  $b = 26.6 \text{ cm}^3 \text{ mol}^{-1}$ ;  $a = 24.7 \times 10^9 \text{ cm}^6 \text{ Pa mol}^{-2}$ .

The value of  $V_{\text{H}_2}$  was determined by fitting the area of H<sub>2</sub> showed by GC to an external standard.

**Quantum yield measurement.** A sample containing cobalt catalyst ( $1.0 \times 10^{-5} \text{ M}$ ), H<sub>2</sub>A (0.28 M) in deionized water (pH = 5.5) was used as a blank. The solution containing TGA-CdTe QDs ( $1.0 \times 10^{-4} \text{ M}$ ), cobalt catalyst ( $1.0 \times 10^{-5} \text{ M}$ ), and H<sub>2</sub>A (0.28 M) in water (pH = 5.5) was used as a sample. The powers (in Watts) 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 400 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 QDs. The average rate of hydrogen production “ $k$ ” (mol of

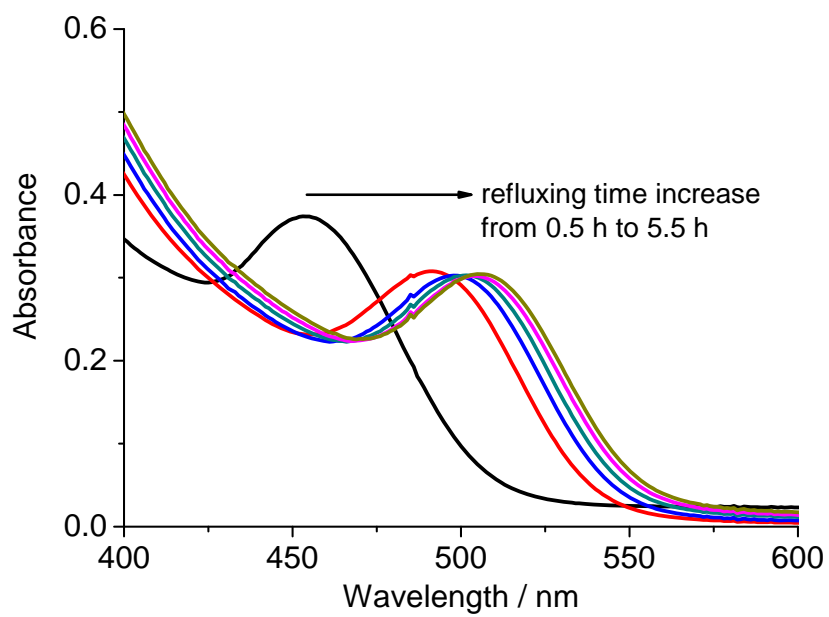
$\text{H}_2 \text{ s}^{-1}$ ) was derived from the amount of  $\text{H}_2$  generated from the first 5 hours of illumination. The quantum efficiency “ $\phi$ ” was calculated by determining the number of moles of hydrogen produced per second, and dividing it by the number of moles of photons absorbed by the system per second (two photons per  $\text{H}_2$ ). The average of the quantum yield for each sample was taken from multiple measurements.

$$P = \frac{c \times h \times n}{\lambda \times t}$$

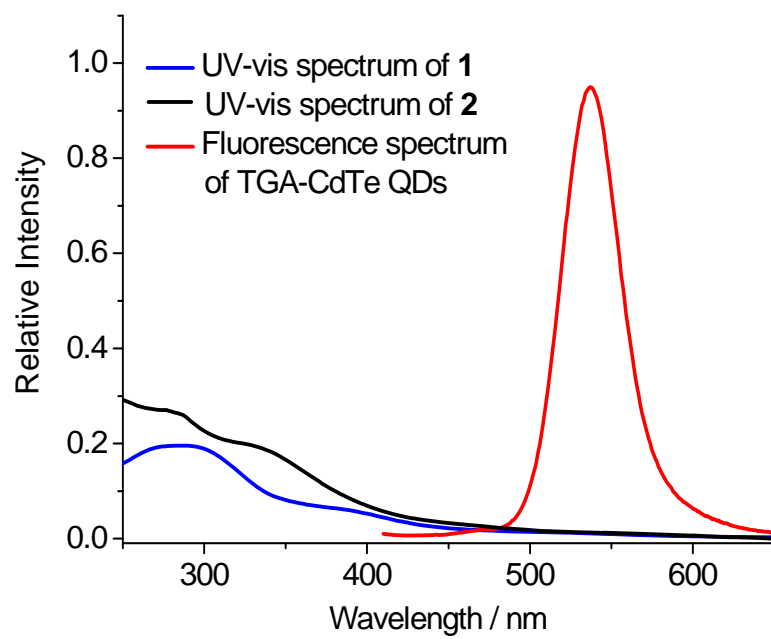
$$\phi = 2k/q_p$$

$$q_p = n/t_{(s)}$$

Where  $\lambda$  is taken to be 400 nm,  $h$  is Planck’s constant (in  $\text{J s}^{-1}$ ),  $c$  is the speed of light (in  $\text{m s}^{-1}$ ),  $n$  is the number of photons,  $t$  is the time (in second),  $q_p$  is the photon flux (number of photons per second).<sup>S9</sup>

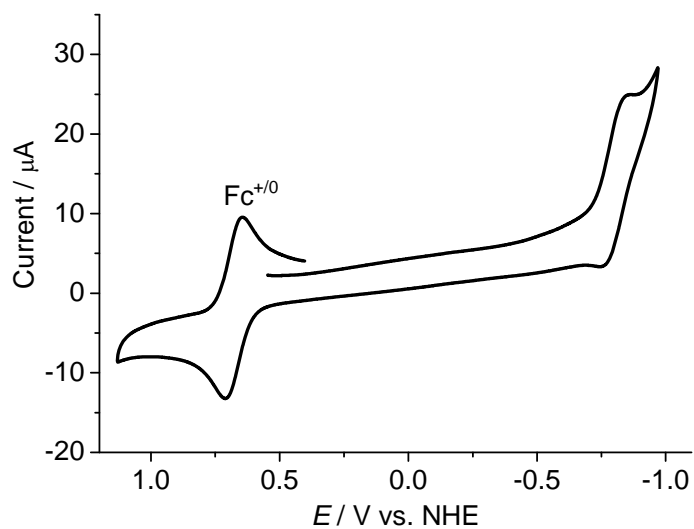


**Fig. S1** UV-vis spectra of TGA-CdTe QDs sampled at different refluxing intervals (0.5–5.5 h).

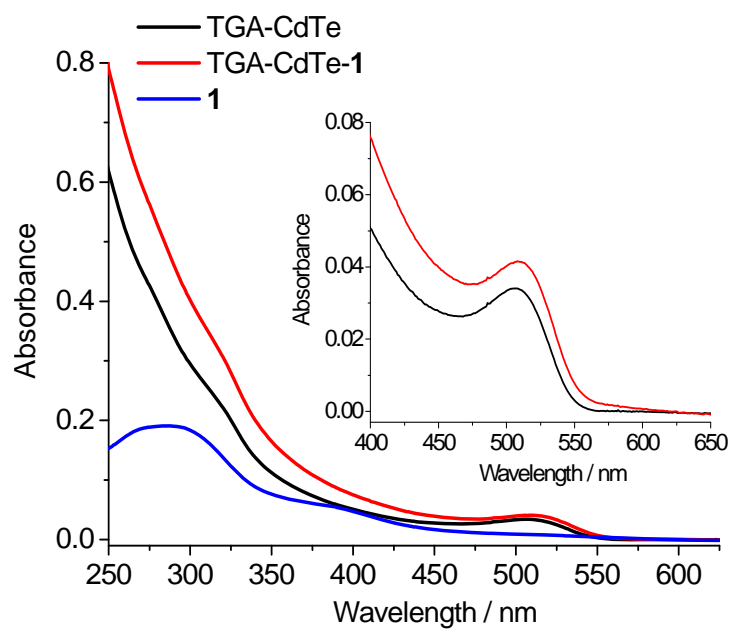


**Fig. S2** UV-vis spectra of [(bme-dach)Co(NO)] and [(bme-dach)Co]<sub>2</sub> in aqueous solutions at pH 5.5, together with the fluorescence spectrum of TGA-CdTe QDs in the absence of catalyst excited at 400 nm.

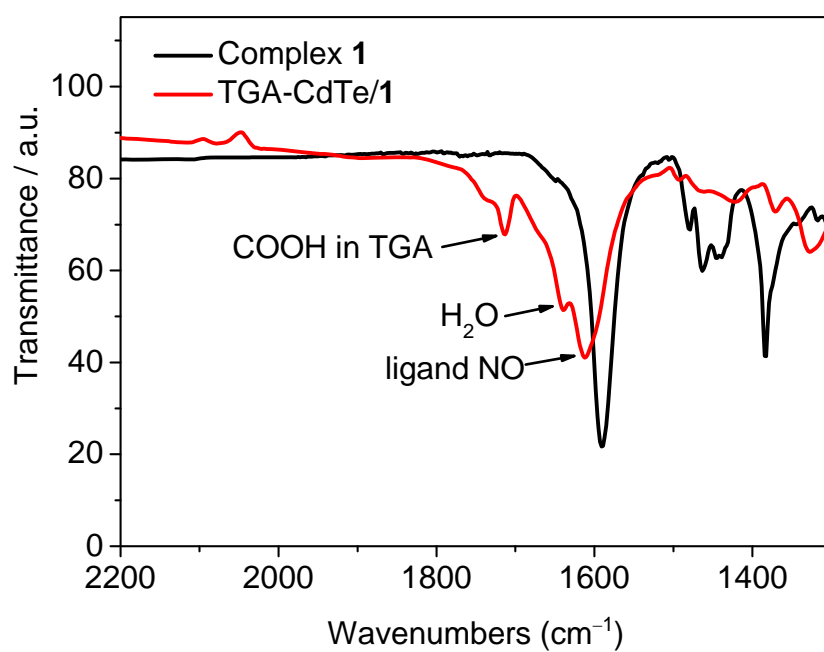




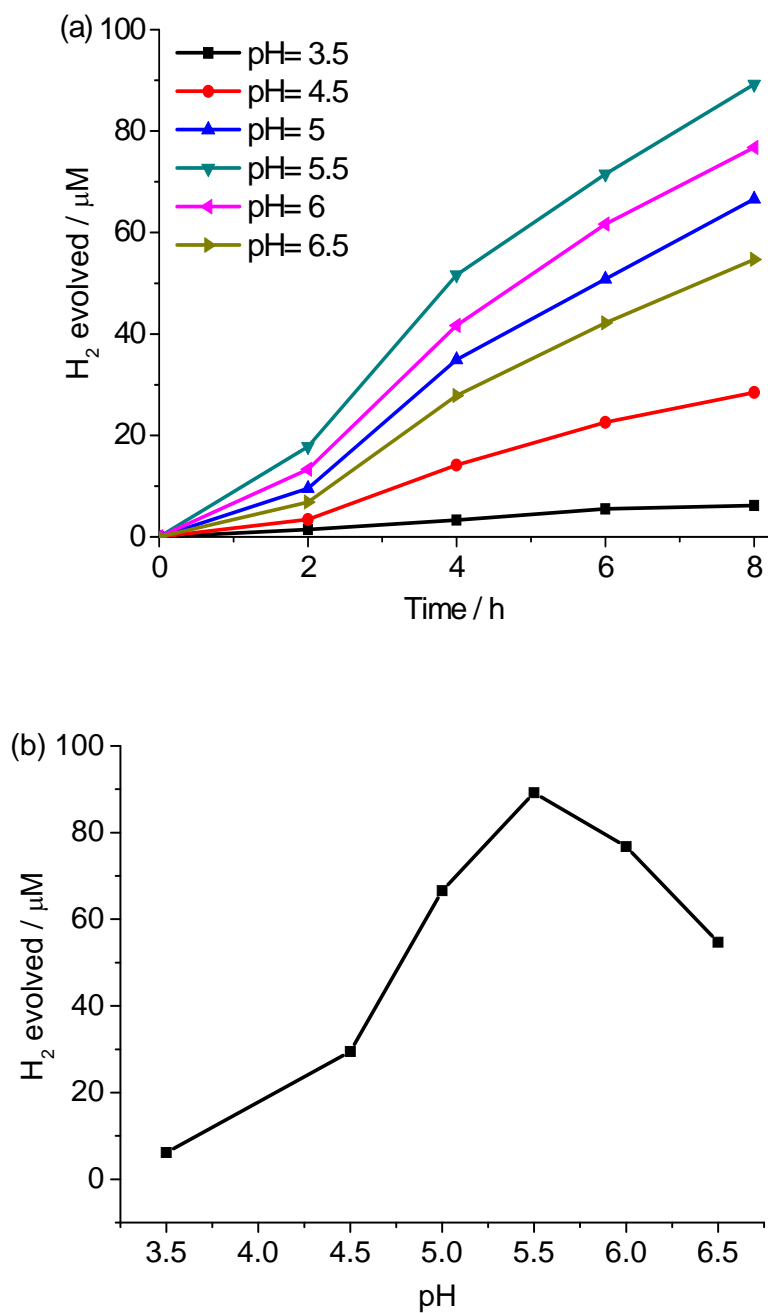
**Fig. S3** Cyclic voltammogram of  $[(\text{bme-dach})\text{Co}]_2$  (1.0 mmol) in 0.1 M  $n\text{Bu}_4\text{NPF}_6/\text{CH}_3\text{CN}$ , in a scan rate of  $100 \text{ mV s}^{-1}$  with glassy carbon as working electrode, Pt wires as both reference electrode and counter electrode, in the presence of an internal reference ( $E_{1/2}(\text{Fc}^{+/0}) = +0.63 \text{ V vs. NHE}$ ).



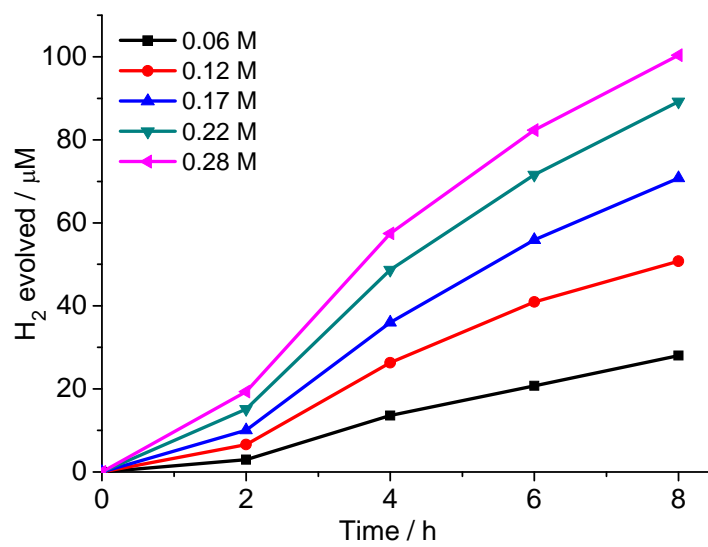
**Fig. S4** UV-vis spectra of the free complex **1**, TGA-CdTe, and TGA-CdTe-**1** hybrid assembly in aqueous solutions at pH 5.5 (inset: selected region of UV-vis spectra).



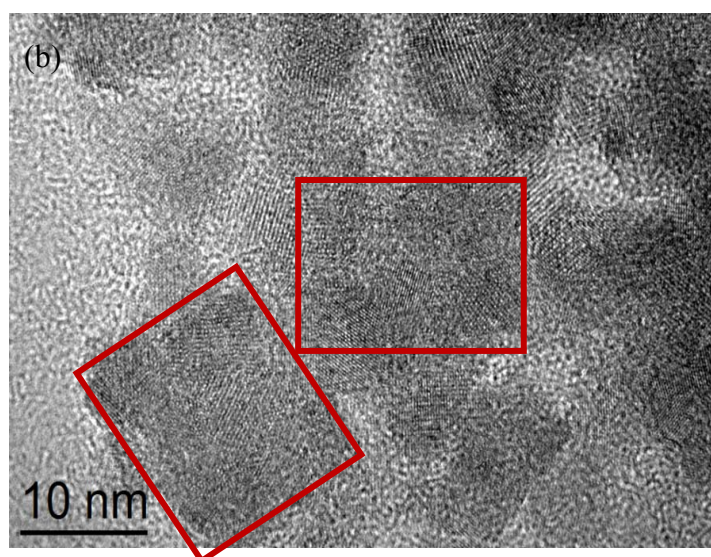
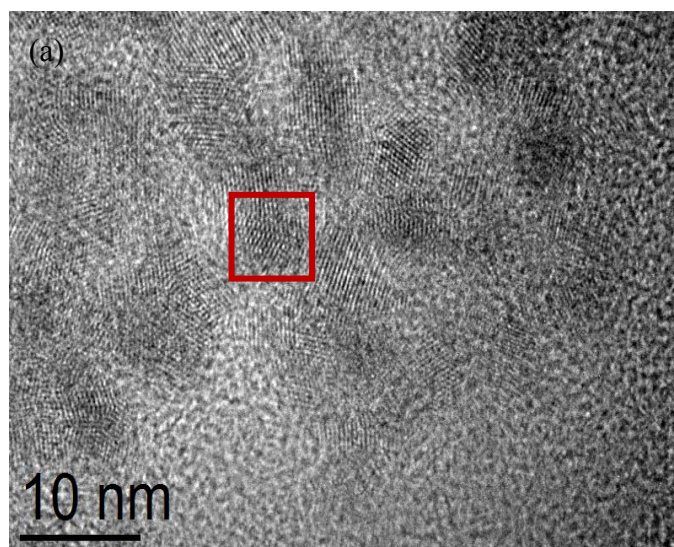
**Fig. S5** The NO stretching absorption region of IR spectra of **1** and TGA-CdTe-**1** hybrid assembly (KBr disc). The intensities of the  $\nu(\text{NO})$  bands for **1** and TGA-CdTe-**1** are normalized.



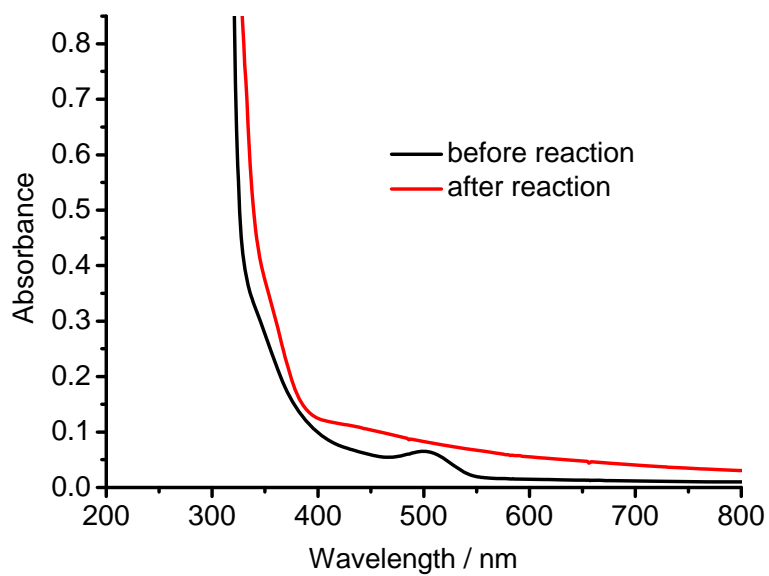
**Fig. S6** (a) Photocatalytic H<sub>2</sub> evolution from the systems comprising **1** ( $1.0 \times 10^{-5}$  M) and TGA-CdTe QDs ( $1.0 \times 10^{-4}$  M) in 0.17 M H<sub>2</sub>A aqueous solutions at pH values varied from 3.5 to 6.5 in irradiation using a Xe lamp (300 W) with a cutoff filter ( $\lambda > 400$  nm); (b) Plot of H<sub>2</sub> evolution as a function of pH values.



**Fig. S7** Influence of the concentration of H<sub>2</sub>A on the photocatalytic hydrogen production by self-assembly system of TGA-CdTe ( $1.0 \times 10^{-4}$  M) and **1** ( $1.0 \times 10^{-5}$  M) in aqueous solutions at pH 5.5.



**Fig. S8** TEM images of TGA-CdTe QDs before and after 70-h photocatalytic reaction, showing an apparent increase in the size of TGA-CdTe QDs after 30-h irradiation. Integration of QDs is one of the reasons for the decrease of H<sub>2</sub>-generation activity of the hybrid assembly.



**Fig. S9** UV-vis spectra of CdTe QDs before and after 70-h photocatalytic reaction.

**Table S1**

Photocatalytic production of H<sub>2</sub> using non-noble molecular catalyst/CdX (X = S, Se, Te) and /ZnS hybrid systems.

Catalyst <sup>a</sup> ([catalyst])	Semiconductor ( <i>d</i> <sub>av</sub> ) <sup>b</sup>	Donor	Solvent	Initial pH	Light $\lambda$ (irrad. time)	TON vs. catalyst	QE	Ref.
<b>1</b> ( $1.0 \times 10^{-6}$ M)	TGA-CdTe (2.7 nm)	HA <sup>-</sup>	H <sub>2</sub> O	5.5	> 400 nm (30 h)	14400	5.32% (400 nm)	Present work
<b>3</b> ( $1.6 \times 10^{-4}$ M)	MPA-CdTe <sup>c</sup> (3.4 nm)	HA <sup>-</sup>	H <sub>2</sub> O	4	> 400 nm (10 h)	505	–	[S10]
<b>4</b> + chitosan <sup>d</sup> ( $1.0 \times 10^{-6}$ M)	MPA-CdTe (2.8 nm)	HA <sup>-</sup>	MeOH/H <sub>2</sub> O (1:3)	4.5	410 nm LEDs (60 h)	52800	–	[S11]
<b>5</b> ( $2.3 \times 10^{-6}$ M)	MPA-CdSe (1.9 nm)	HA <sup>-</sup>	H <sub>2</sub> O	4	410 nm LEDs (82 h)	8781	–	[S12]
<b>5</b> ( $2.3 \times 10^{-6}$ M)	MPA-CdSe (1.9 nm)	HA <sup>-</sup>	H <sub>2</sub> O	4	> 400 nm (82 h)	6530	–	[S12]
<b>6</b> + PAA <sup>e</sup> ( $4.1 \times 10^{-6}$ M)	MPA-CdSe (1.8 nm)	HA <sup>-</sup>	H <sub>2</sub> O	4	450 nm LEDs (8 h)	27135	5.07% (450 nm)	[S13]
<b>7</b> ( $3.9 \times 10^{-6}$ M)	ZnS (50 nm)	HA <sup>-</sup>	DMF/H <sub>2</sub> O (9:1)	4.6	Xe lamp (38 h)	2607	2.5% (325 nm)	[S14]
<b>8</b> ( $4.0 \times 10^{-6}$ M)	ZnS (30 nm)	TEOA	DMF/H <sub>2</sub> O (~9:1)	11	Xe lamp (30 h)	4950	–	[S15]
<b>9</b> ( $4.0 \times 10^{-6}$ M)	ZnS (30 nm)	TEOA	DMF/H <sub>2</sub> O (~9:1)	11	Xe lamp (30 h)	3400	–	[S15]
<b>10</b> ( $2.5 \times 10^{-4}$ M)	CdS (50 nm)	TEOA	CH <sub>3</sub> CN/H <sub>2</sub> O (~9:1)	–	> 420 nm (15 h)	171	9.1% (420 nm)	[S16]
<b>10</b> ( $1.0 \times 10^{-3}$ M)	CdS (50 nm)	LA <sup>-</sup>	DMF/H <sub>2</sub> O (~9:1)	–	> 420 nm (3 h)	1.4	–	[S16]
<b>11</b> ( $1.0 \times 10^{-3}$ M)	CdS (50 nm)	LA <sup>-</sup>	DMF/H <sub>2</sub> O (~9:1)	–	> 420 nm (3 h)	2.3	–	[S16]
<b>12</b> ( $1.0 \times 10^{-3}$ M)	CdS (50 nm)	LA <sup>-</sup>	DMF/H <sub>2</sub> O (~9:1)	–	> 420 nm (3 h)	3.0	–	[S16]
<b>13</b> (NA)	CdSe/ZnS (NA)	TEOA	toluene	[Et <sub>3</sub> NH]Cl	> 400 nm (10 h)	151	–	[S17]
<b>14</b> ( $8.0 \times 10^{-7}$ M)	MBAA-CdSe <sup>f</sup> (NA)	HA <sup>-</sup>	H <sub>2</sub> O	4.5	520 nm LEDs (60 h)	$3 \times 10^5$	25% (520 nm)	[S18]
<b>14</b> ( $3.0 \times 10^{-6}$ M)	MBAA-CdSe (NA)	HA <sup>-</sup>	H <sub>2</sub> O	4.5	520 nm LEDs (46 h)	53303	–	[S18]
<b>15</b> ( $3.0 \times 10^{-6}$ M)	MBAA-CdSe (NA)	HA <sup>-</sup>	H <sub>2</sub> O	4.5	520 nm LEDs (46 h)	55238	–	[S18]
<b>16</b> ( $3.0 \times 10^{-6}$ M)	MBAA-CdSe (NA)	HA <sup>-</sup>	H <sub>2</sub> O	4.5	520 nm LEDs (46 h)	26815	–	[S18]
<b>17</b> ( $3.0 \times 10^{-6}$ M)	MBAA-CdSe (NA)	HA <sup>-</sup>	H <sub>2</sub> O	4.5	520 nm LEDs (46 h)	14375	–	[S18]
<b>18</b> ( $3.0 \times 10^{-6}$ M)	MPA-CdTe (NA)	HA <sup>-</sup>	H <sub>2</sub> O	4.1	> 400 nm (1.5 h)	650	10%	[S19]
<b>19</b> ( $1.0 \times 10^{-6}$ M)	DHLA-CdSe <sup>g</sup> (2.5-5.5 nm)	HA <sup>-</sup>	H <sub>2</sub> O	4.5	520 nm LED	$6.0 \times 10^5$	20-36%	[S20]



<sup>a</sup> For the structures of catalysts, see the figure below.

<sup>b</sup>  $d_{av}$  = average diameter of a quantum dot particle.

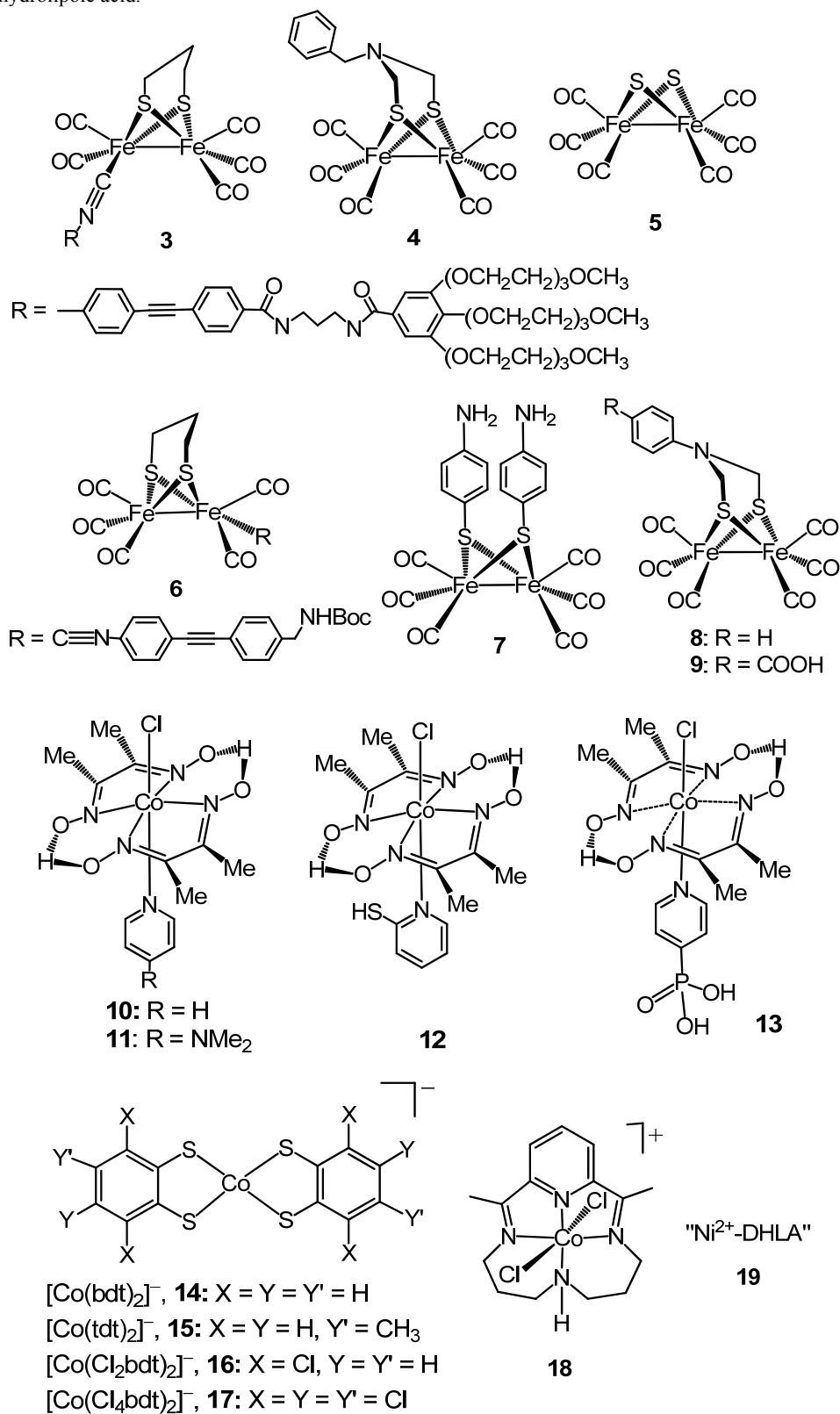
<sup>c</sup> MPA = 3-mercaptopropionic acid.

<sup>d</sup> chitosan  $1.0 \text{ mg mL}^{-1}$ .

<sup>e</sup> PAA = poly(acrylic acid),  $\sim 0.25 \text{ mg mL}^{-1}$ .

<sup>f</sup> MBPA = 3-mercapto-2,2-bis(mercaptomethyl)propanoic acid.

<sup>g</sup> DHLA = dihydrolipoic acid.



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