

Supporting Information

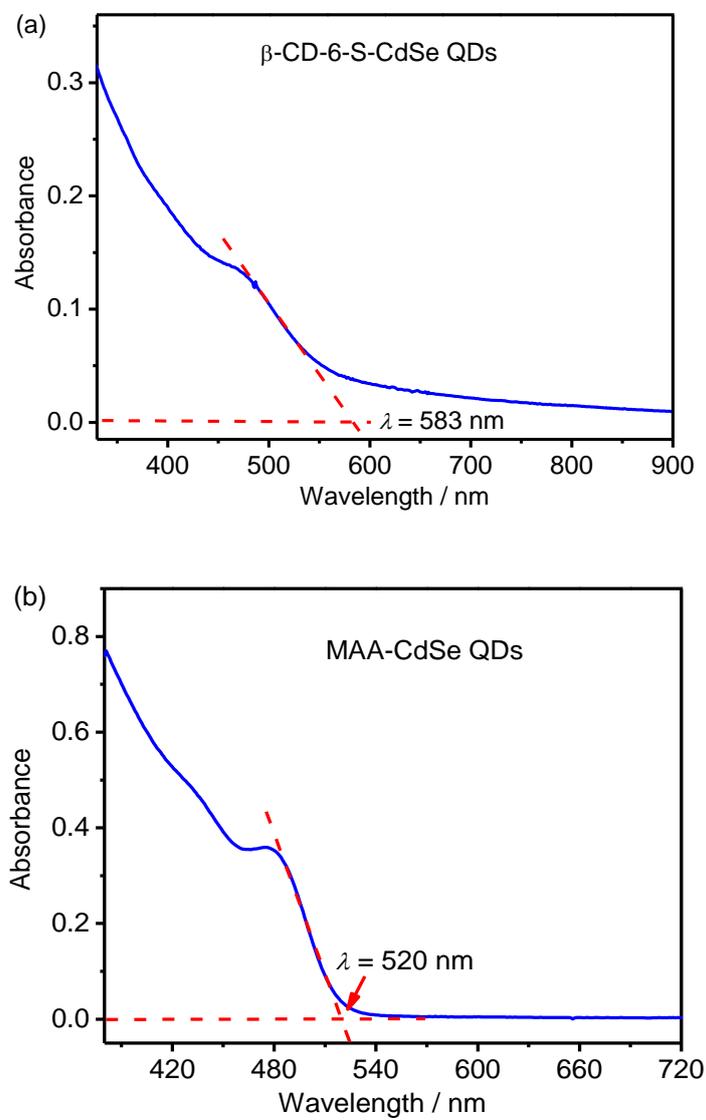
**Photocatalytic H<sub>2</sub> production by a hybrid assembly of [FeFe]-hydrogenase model and CdSe quantum dot linked through a thiolato-functionalized cyclodextrin†**

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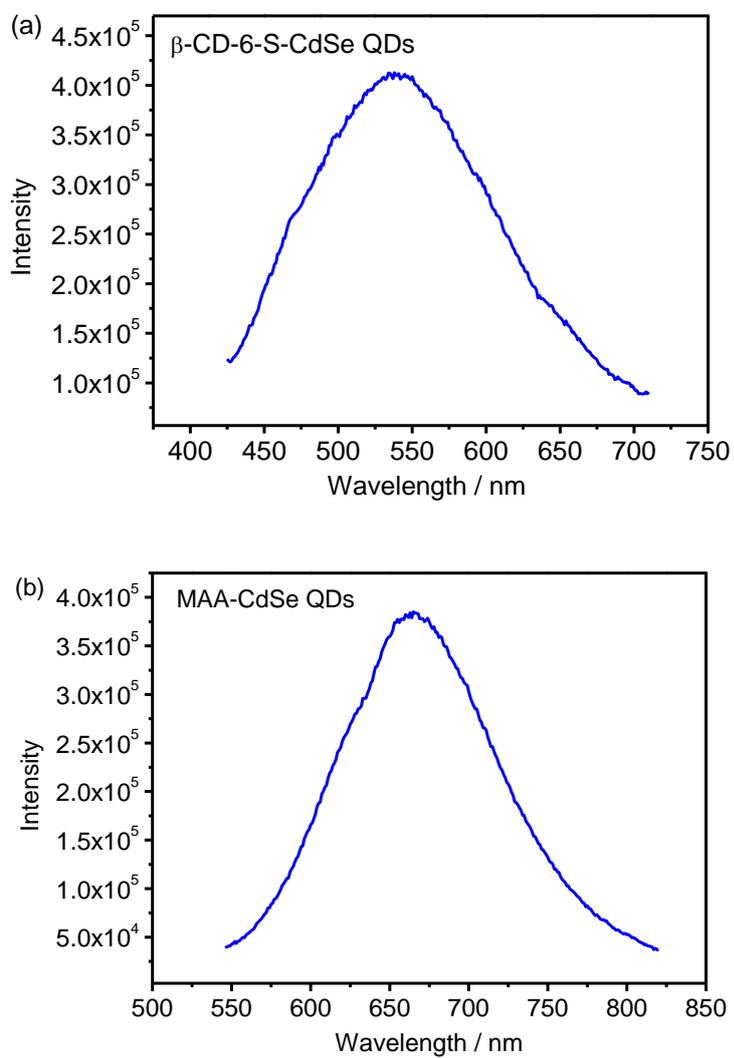
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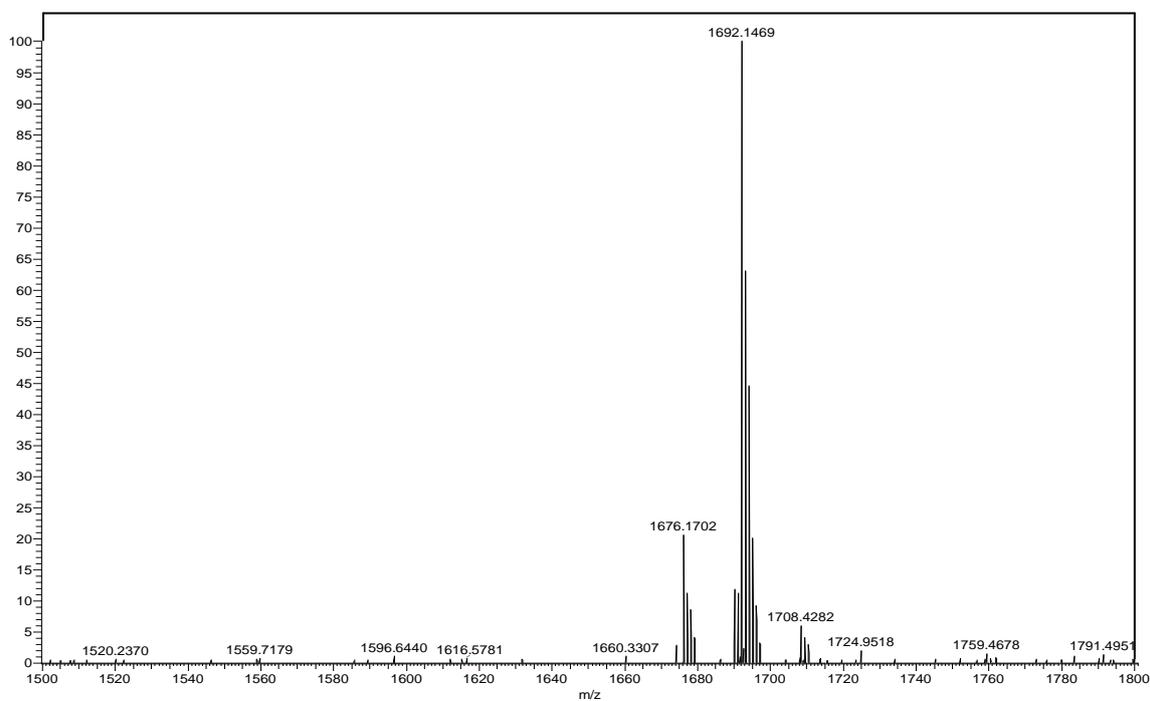
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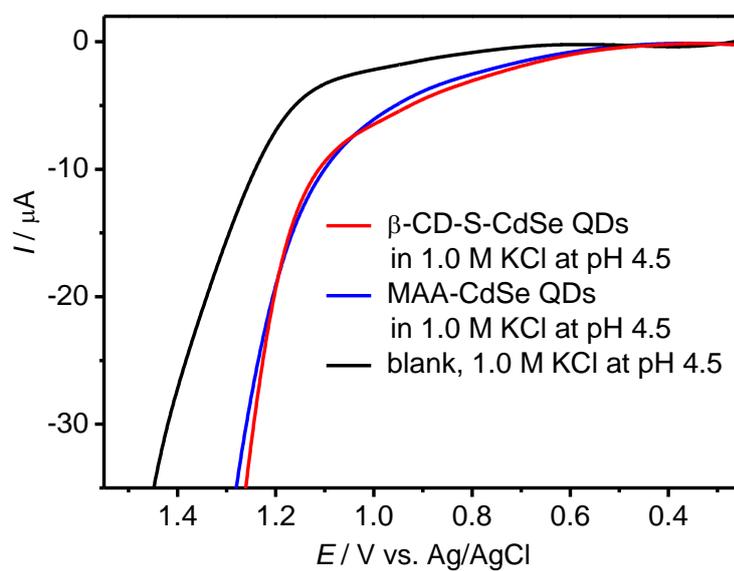
**Fig. S1** UV-vis spectra of (a)  $\beta$ -CD-6-S-CdSe QDs sampled at the refluxing interval of 30 min and (b) MAA-CdSe QDs sampled at the refluxing interval of 3 h.



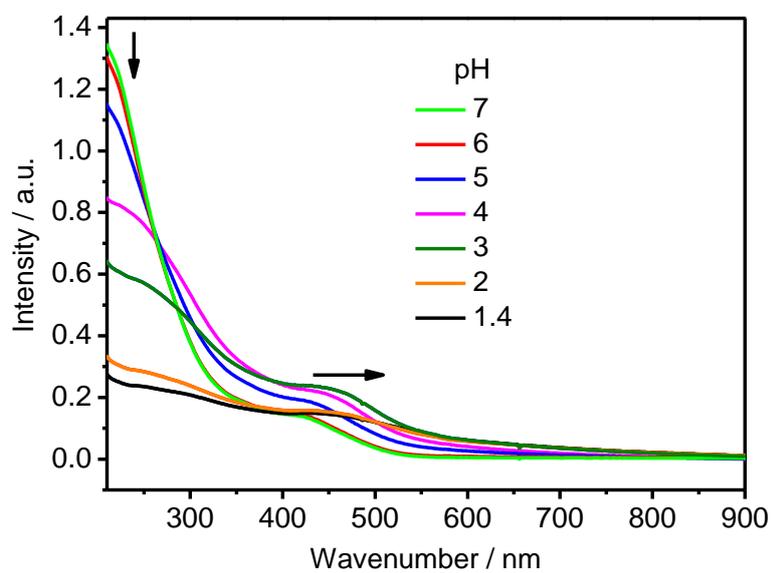
**Fig. S2** Fluorescence spectra of (a)  $\beta$ -CD-6-S-CdSe QDs sampled at the refluxing interval of 30 min and (b) MAA-CdSe QDs sampled at the refluxing interval of 3 h.



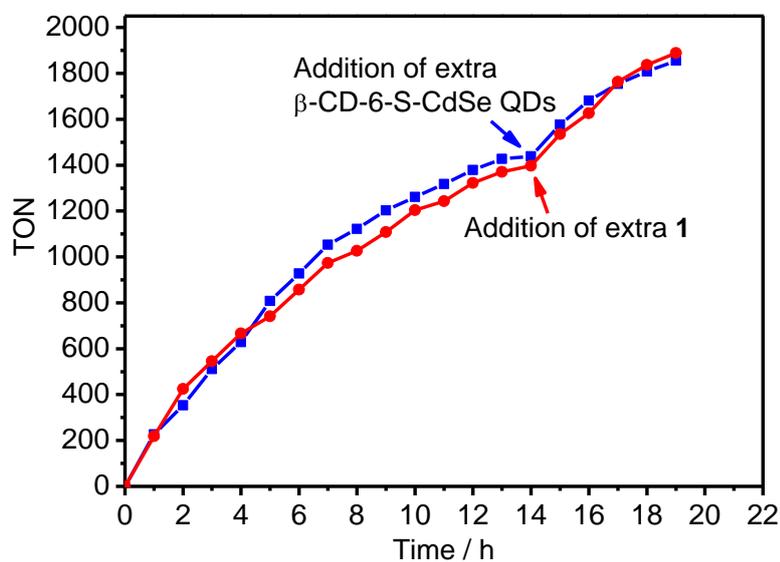
**Fig. S3** Mass spectrum of 1/β-CD-6-SH formed in situ in water.



**Fig. S4** Cyclic voltammograms of  $\beta$ -CD-6-S-CdSe and MAA-CdSe QDs in water using a saturated KCl Ag/AgCl reference electrode at pH 4.5.



**Fig. S5** Changes of UV-vis absorptions of  $\beta$ -CD-6-S-CdSe QDs in water at varying pH from 7 to 1.4.



**Fig. S6** Long-time photocatalytic H<sub>2</sub> evolution of the system of  $\beta$ -CD-6-S-CdSe QDs ( $1.0 \times 10^{-4}$  M), **1** ( $1.0 \times 10^{-5}$  M), and H<sub>2</sub>A (0.28 M) in water at pH 4.5 under illumination, with addition of extra **1** or  $\beta$ -CD-6-S-CdSe QDs after 14 h of illumination.