## Supporting Information

## Roles of Adsorption Sites in Electron Transfer from CdS Quantum Dots to Molecular Catalyst Cobaloxime Studied by Time-resolved Spectroscopy

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Fig. S1 <sup>1</sup>H-NMR of the prepared Co<sup>III</sup>(dmgH)<sub>2</sub>pyCl.

<sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ (ppm) = 8.27 (2H, Pyridine- $\alpha$ H), 7.68, 7.70, 7.72 (1H, Pyridine- $\gamma$ H), 7.23 (2H, Pyridine- $\beta$ H), 2.40 (12H, dimethylglyoxime).



**Fig. S2** The XPS survey spectra of the (1) CdS QDs, (2) QDs/Co-Py 50μM, (3) QDs/Co-Py 150μM, (4) QDs/Co-Py 200μM and (5) Co-Py.

In Fig. S2, the survey spectrum of CdS QDs shows the presence of Cd and S from CdS, also C and O from the QD surface and other polluted organics. Typical survey spectrum of Co-Py complex was also obtained, and it shows the presence of Co, Cl and N from Co-Py, C and O from Co-Py and other polluted organics. With the addition of Co-Py complex, the survey spectra of CdS QDs/Co-Py show both the

characteristic peaks of CdS QDs and Co-Py complex. For quantitative analysis of minor components and for other mathematical manipulations of the data, detail scans were obtained for precise peak location and for accurate registration of line shapes (Fig. S2, S3 and S4).



**Fig. S3** The XPS detailed spectra and their fittings for C 1s of (a) CdS QDs and (b) Co-Py complex respectively.

The C 1s spectra of CdS QDs in Fig. S3a show that there are three peaks centered at 284.26, 285.63 and 287.12 eV, which can be ascribed to  $-CH_2$ , C-SH and C=O (all from the 3-mercaptopropionic acid and other polluted organics) respectively. The position of C 1s line from hydrocarbon nearly always appears at 285.0 eV, so the shift from this value can be taken as a measure of the static charge. The same situation occurs in C 1s of Co-Py complex (Fig. S3b) except that the three fitting peaks at 284.33, 284.85 and 285.65 eV can be ascribed to C=C,  $-CH_2$  and C=N respectively. Therefore, all the peak positions related to CdS QDs and Co-Py complex were calibrated by the C 1s of  $-CH_2$  at 285.0 eV in this work.



**Fig. S4** The XPS detailed spectra of (a) Cd 3d and (b) S 2p for CdS QDs. The peak positions of Cd 3d and S 2p were both calibrated by the C 1s at 285.0 eV.

From XPS, a simplified expression to determine the atomic ratio of two elements is given in equation, <sup>1</sup>

$$\frac{n_i}{n_j} = \frac{I_i}{I_j} \times \frac{\sigma_j}{\sigma_i} \times \frac{Ek_j^{0.6}}{Ek_i^{0.6}}$$
(S1)

where *n* is the number of atoms of the element per cm<sup>3</sup> of sample, *I* is the peak area of photoelectrons from the element,  $\sigma$  is defined as the atomic sensitivity factor and the values for this factor have been experimentally determined and theoretically calculated for a variety of different types of XPS systems, <sup>2</sup> *Ek* is the kinetic energy of photoelectrons, and *Ek* = hv - BE (Al Ka, hv = 1486.6 eV), *i* and *j*, stand for the element studied. We use the fitting peaks of Cd 3d<sub>5/2</sub> and S 2p<sub>3/2</sub> to obtain the surface S/Cd ratio of CdS QDs. Fig.S3 shows the Cd 3d and S 2p peaks and their corresponding fittings. Peak locations and areas were determined by fitting each of the curves using a nonlinear Gaussian/Lorentz program. The Cd 3d spectrum has a doublet feature due to the spin orbit splitting resulting in 3d<sub>5/2</sub> and 3d<sub>3/2</sub> peaks with a spin orbit splitting of 6.72 eV. The signal at 404.76 and 411.50 eV can be attributed to Cd 3d<sub>5/2</sub> and Cd 3d<sub>3/2</sub> binding energy, respectively. On the other hand, the binding energy of S 2p<sub>3/2</sub> peak can be divided into two peaks centered at 161.22 eV and 162.49 eV, corresponding to sulfur in Cd-S and -HS respectively. The corresponding peak parameters of Cd 3d<sub>5/2</sub> and S 2p<sub>3/2</sub> are listed in Table S1.

According to the above semi-quantitative calculation formula, the surface S/Cd ratio for Cd-S was ca. 0.65, and -HS was ca. 0.24.

**Table S1** A summary of the peak parameters of Cd  $3d_{5/2}$  and S  $2p_{3/2}$  (for Cd—S and —HS species) according to the XPS detail scans and their corresponding fittings in Fig. S3

Element	Ι	σ	BE	Ek
Cd 3d <sub>5/2</sub>	90117.8	11.95	404.76	1081.84
Cd-S 2p <sub>3/2</sub>	6017.1	1.11	161.22	1325.38
—НS 2р <sub>3/2</sub>	2179.9	1.11	162.49	1324.11



**Fig. S5** The XPS detailed spectra of Co 3s. The peak positions were all calibrated by the C 1s at 285.0 eV. (2) QDs/Co-Py 50μM, (3) QDs/Co-Py 150μM, (4) QDs/Co-Py 200μM and (5) Co-Py.



**Fig. S6** UV-Vis absorption spectra of Co-Py complex, along with the steady state PL spectrum of CdS QDs. The PL excitation wavelength was 340 nm. [CdS QDs] =  $0.5 \mu$ M, [Co-Py] =100  $\mu$ M.

The decay curves for the band-edge and trap-related emissions of CdS QDs in the absence and presence of Co-Py complex can be fitted with the double and three exponentials respectively shown by equation

$$I(t) = \sum_{i=0}^{n} \alpha_{i} exp^{[i0]}(-t/\tau_{i})$$
(S2)

Then the average lifetime  $<\tau>$  is given by equation

$$<\tau>=\sum_{i=0}^{n}\beta_{i}\tau_{i}$$
  $(\sum_{i=0}^{n}\beta_{i}=1)$  (S3)

**Table S2** The band-edge emission ( $\lambda$  = 457 nm) decay parameters of CdS QDs with different concentrations of the added Co-Py

Conc. /µM	$\tau_1(\beta_1)/ns$	$\tau_2 \left(\beta_2\right)/ns$	<t>/ns</t>
0	4.53 (43.68%)	43.29 (56.32%)	26.36
25	4.13 (44.51%)	39.87 (55.49%)	23.96
50	4.19 (44.2%)	37.33 (55.8%)	22.68
75	4.10 (44.49%)	37.47 (55.51%)	22.62
100	4.18 (43.53%)	34.92 (56.47%)	21.54
125	4.19 (46.71%)	36.24 (53.29%)	21.27
150	3.75 (51.82%)	29.73 (48.18%)	16.27
175	2.62 (56.97%)	14.41 (43.03%)	7.69
200	2.49 (55.35%)	13.75 (44.65%)	7.52

Table S3 The trap-ralated emission ( $\lambda$  = 630 nm) decay parameters of CdS QDs with different

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	Conc. /µM	$\tau_1 \left( \beta_1 \right) /ns$	$\tau_2 \left(\beta_2\right)/ns$	$\tau_3$ ( $\beta_3$ ) /ns	< <b>t</b> >/ns
	0	11.06 (16.50%)	88.60 (52.24%)	402.49(31.26%)	173.93
	25	10.96 (16.96%)	84.39 (50.60%)	353.0 (32.44%)	159.07
	50	9.92 (14.75%)	77.52 (48.34%)	334.0 (36.90%)	162.18
	75	10.80 (15.06%)	77.88 (47.54%)	332.49(37.39%)	162.97
	100	10.60 (16.53%)	78.20 (49.68%)	331.06(33.79%)	152.47

concentrations of the added Co-Py

125	7.18 (18.29%)	66.34 (49.67%)	321.68(32.03%)	137.30
150	3.71 (28.40%)	35.22 (42.31%)	228.16(29.29%)	82.78
175	1.15 (36.13%)	8.18 (33.99%)	56.33 (29.89%)	20.03
200	0.82 (56.26%)	6.18 (25.03%)	41.96 (18.71%)	9.86

## References

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