Supporting Information
Observation of multiple, identical binding sites in the exchange of carboxylic acid ligands with CdS nanocrystals.

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Experimental section

Instrumentation. NMR (^{1}H, ^{13}C) spectra were recorded on a Varian Inova-400 MHz and Varian Inova-500 MHz spectrometer at room temperature. The ^{1}H and [13]C Chemical shifts (δ) are reported in parts per million and the residual solvent peak was used as an internal standard. UV-Vis was recorded with a Varian Cary 50 UV-vis spectrophotometer. Samples were prepared in ambient conditions with air-free cuvettes. Ensemble fluorescence data was taken with the Spex Fluorolog Tau-3 fluorescence spectrophotometer. Time-resolved photoluminescence experiment was done with Hamamatsu C4334 streakscope picosecond streak camera.

Synthesis. Chemical reagents were purchased from Aldrich Chemical Co, Strem, TCI America, or Alfa Aesar and were used as received. Cadmium oxide, octadecene and oleic acid were purchased from Alfa Aesar Aldrich Chemical and TCI America respectively. Dry and degassed acetone, toluene and dichloromethane were obtained from JC Meyer's solvent purification system.
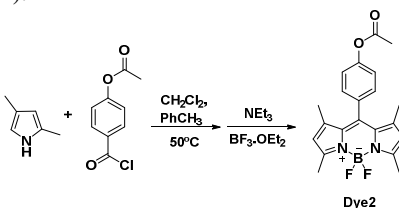
1) Dye Synthesis
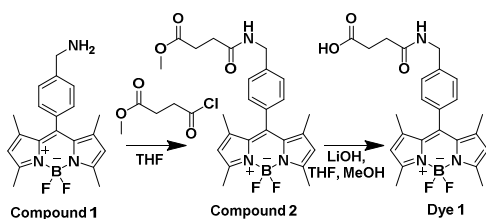
Scheme S1. Synthesis routine of Dye1

Compound 1 Compound 1[1] was synthesised and purified according to procedures published by Michel et. al.[3].

Compound 2 Compound 1(4.1 mg, 0.012mmol), methyl succinyl chloride (1.75mg,0.012mmol) and potassium carbonate (0.6 mg, 0.0042 mmol) in1.0 mL dry DMSO was bubbled under argon for 15 min. Then the reaction was heated to 90°C under protection of argon atomosphere and stirred overnight to yield a clear brown solution, which was then allowed to cool down to room temperature. After adding distilled water, a turbid orange-brown solution was obtained. This was extracted with dichloromethane to give a bright orange solution. ^{1}H NMR (CDCl$_3$, 400MHz): δ$_H$ 7.39(d, 2H, J=8Hz), 7.24(d, 2H, J=8Hz), 6.08(s, 1H), 5.97 (s, 2H), 4.55(d, 2H, J=6.0Hz), 3.70(s, 3H), 2.74(t, 2H, J=6.1Hz), 2.61(t, 2H), 2.52(s, 6H), 2.04(s, 3H), 1.36 (s, 6H). HRMS (+ESI/ APCI) *m/z*: 468.2270 (MH$^+$)

Dye 1 Dye 1 was obtained by deprotecting **compound 2** following a method published by Blum et. al[2]. Compound 2 (6.08mg, 0.013mmol) was dissolved in tetrahydrofuran (0.2 mL) and methanol (0.8 mL) were mixed and degassed under argon for 15 min. Then lithium hydroxide (1.64mg, 0.034mmol) in distilled water was added dropwise into the reaction flask. This reaction was stirred at room temperature and all solvent evaporated after 2h. The product was purified by column chromatography with dichloromethane. ^{1}H NMR (CDCl$_3$, 400MHz): δ$_H$ 7.37 (d, 2H, J=7.37Hz), 7.22(d, 2H, J=7.22Hz), 6.38(s, 1H), 5.96(s, 2H), 4.51(d, 2H, J=8Hz), 2.71(s, 2H), 2.53(s, 2H), 2.54(s, 6H), 1.35 (s,6H) ppm. ^{13}CNMR (600MHz, CDCl3) δ$_C$ 155.7, 143.2, 141.4, 139.2, 134.3, 131.5, 128.5, 128.3, 121.4, 43.4, 30.9, 29.8, 14.7, 14.2 ppm. HRMS (+ESI/ APCI) *m/z*: 453.2053 (MH$^+$).

Scheme S2. Synthesis routine of Dye 2

Dye 2 Dye 2 was synthesised by a method pubulished by Chang et. al.[3]. 2,4-Dimethylpyrrole (0.288mg, 3.03mmol) and 4-(acetoxy)benzoyl chloride (0.285mg, 1.436mmol) in 8.5 mL dichloromethane was refluxed at 50°C with an oil bath for 1h 30min to yield a light orange solution. Then dichloromethane was removed under vaccum until only 2~3 mL was left. 19.5mL toluene was added followed by triethylamine (0.667g, 6.58mmol) and boron trifluoride diethyl etherate (1.16g, 8.20mmol)to give a bright yellow suspension, which was heated at 50°C for another 1h. The reaction was cooled down to room temperature and put on vaccum for 20 min to remove all toluene. Product was extracted with dichloromethane, washed with water for 3 times and then dried with MgSO$_4$. Silica gel chromatography (dicholoromethane as eluent)

afforded a bright orange colored fraction that was collected (76.2 mg, 13.8%).^{1}H NMR (CDCl$_3$, 400MHz): δ_H 7.30-7.25(m, 2H), 7.23-7.19(m, 2H), 5.99(s, 2H), 2.55(s, 6H), 2.33(s, 3H), 1.42(s, 6H) ppm. ^{13}C NMR (600MHz, CDCl3): δ_C 169.0, 155.8, 143.2, 140.8, 132.5, 132.0, 131.6, 129.3, 122.6, 121.5, 21.3, 14.6, 14.9 ppm. HRMS (+ESI/ APCI) *m/z*: 382.1789 (MH[+])

2) CdS Nanocrystal

CdS nanocrystals were synthesized and purified by the procedure published by Peng et. al.[4].

0.128 g of cadmium oxide (1.00 mmol), 3.390 g of oleic acid (12.00 mmol), and 10 g of ODE (90%) were put under vacuum and heated to 100 ℃ for 1 hour. Then the mixture was heated to 300℃ under Ar until a clear solution was formed. It was then cooled to a 100 ℃ in an Ar atmosphere. 0.016 g (0.5 mmol) of S powder was added under Ar. The reaction was stirred for 30 min and cooled down to room temperature. As-prepared CdS nanocrystals were transferred to the glove box and cleaned with acetone and toluene at least three times. The final pellet was dissolved in toluene and stored inside glove box for future use. The concentration was determined by measuring the O.D. at first exciton peak and calculated according to Yu et. al[5]. In order to make sure the NC is fresh for the measurements, all the SSPL and TRPL experiments were performed within a month after the preparation of this NC. TEM of 5.0 ± 0.47.nm CdS is in Figure S1. The quantum yield of these particles is 0.19.
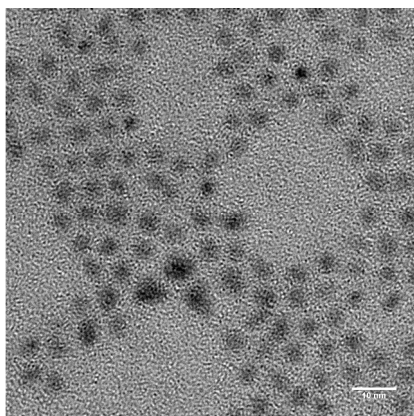

Figure S1. TEM of CdS nanocrystals with diameter of 5nm used in experiment. Scale bar is 10nm.

1) Steady State Photoluminescence
All sample preparation was performed in a nitrogen glovebox. NC-dye conjugate complexes were prepared by adding appropriate amounts of dye molecules dissolved in dichloromethane into pure toluene in a 1 cm path length fluorescence cuvette. Then 0.17 nmol of CdS NC were injected into cuvettes with different dye concentrations. Molar ratios of dye to QD were discretely varied among samples from 0-100. The final volume of each solution was fixed at 2.1 mL. The spectra of each sample were taken immediately after the mixing of CdS and Dye and then after reaching equilibrium (at least 5 hours) using the SPEX Fluorolog fluorimeter. All samples were excited at 405 nm, which is near the first exciton of CdS NC and also at the minimum of the dye absorption spectrum in order to reduce interference from direct excitation of the acceptor.

2) Time-resolved Photoluminescence
Fluorescence lifetime data were taken using front face detection with a Hamamatsu C4334 streakscope picosecond streak camera with a time resolution of 15 ps. The 400 nm excitation pulse was generated by frequency doubling the 800 nm pulse from a 1 kHz Coherent Libra regenerative amplifier. Scattered pump light was removed by placing a 400 nm long wave pass filter and 420 nm color filter on the input lens before the streak camera. The fluorescence was detected at 54.7° relative to the pump to eliminate rotational diffusion effects. Measurements of the fluorescence decay at different laser intensities yielded similar decays, indicating that exciton-exciton annihilation did not influence the results.

3) Multi-exponential decay model

CdS emission decay can be best fitted with 3 exponentials, which means there are 3 separate components. The photoluminescence for each component can be denoted as the below,

$$N_{D_1}(t) = N_{D_1}(0)e^{-k_1 t}, \ \ N_{D_2}(t) = N_{D_2}(0)e^{-k_2 t}, \ N_{D_3}(t) = N_{D_3}(0)e^{-k_3 t} \tag{S1}$$

where $N_{D_1}, N_{D_2}, N_{D_3}$ stands for the weights for each component respectively. In this case, the total photoluminescence can be represented as a sum of the intensity from each group,

$$I_{tot}(t) = N_{D_1}(0)e^{-k_1 t} + N_{D_2}(0)e^{-k_2 t} + N_{D_3}(0)e^{-k_3 t} \tag{S2}$$

We assume that each group of CdS can bind same average number, m, of acceptor ligands.

$$I_{tot}(t,m) = N_{D_1}(0)\exp[-k_1 t - m(1-e^{-k_q t})] + N_{D_2}(0)\exp[-k_2 t - m(1-e^{-k_q t})] + N_{D_3}(0)\exp[-k_3 t - m(1-e^{-k_q t})] \tag{S3}$$

The corresponding ensemble averaged decay curve can be expressed as,

$$I_{tot}(t,m) = \sum_{n=0}^{\infty} \frac{m^n e^{-m}}{n!}\left[N_{D_1}^0 \exp\left(-k_1 t - nk_q t\right) + N_{D_2}^0 \exp\left(-k_2 t - nk_q t\right) + N_{D_3}^0 \exp\left(-k_3 t - nk_q t\right)\right] \tag{S4}$$

To get the steady state expression, we can integrate the entire time range thus giving us the SSPL,

$$SSPL(m) = \int_0^{\infty} I_{tot}(t)dt = \sum_{n=0}^{\infty} \frac{m^n e^{-m}}{n!}\left[\frac{N_{D_1}^0}{k_1 + nk_q} + \frac{N_{D_2}^0}{k_2 + nk_q} + \frac{N_{D_3}^0}{k_3 + nk_q}\right]\left[\frac{k_1 k_2 k_3}{k_2 k_3 N_{D_1}^0 + k_1 k_3 N_{D_2}^0 + k_1 k_2 N_{D_3}^0}\right] \tag{S5}$$

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