

Supporting Information for:
Multivariable Response of Semiconductor Nanocrystal-Dye Sensors: the Case of pH
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Förster Energy Transfer Modeling: To model the integrated dye / NC emission data in Figs. 3B and S2B, we decomposed the absorption spectra of fluorescein dye into the pure acid and base forms in the same manner as the emission spectra as discussed in the main text. We next calculated the overlap integral of the two CdS/ZnS samples with the pure acid and base forms of fluorescein; with the quantum yields and coupled dye to NC ratios of the two samples (sample 1: QY 1.54%, dye/NC: 12.8; sample 2: QY 4.7%, dye/NC: 4.5) we calculated the distance (r) dependent efficiency of NC-to-dye FRET energy transfer $\varepsilon(r)_{acid}$ and $\varepsilon(r)_{base}$. The integrated emission of the dye / NC ratiometric response was then modeled as:

$$\text{Response}(r, \text{pH}) = \frac{\frac{[A(\text{pH})]}{[A(\text{pH})] + [B(\text{pH})]} \cdot \varepsilon(r)_{acid} \cdot QY_{acid} + \frac{[B(\text{pH})]}{[A(\text{pH})] + [B(\text{pH})]} \cdot \varepsilon(r)_{base} \cdot QY_{base}}{1 - \left[\frac{[A(\text{pH})]}{[A(\text{pH})] + [B(\text{pH})]} \cdot \varepsilon(r)_{acid} + \frac{[B(\text{pH})]}{[A(\text{pH})] + [B(\text{pH})]} \cdot \varepsilon(r)_{base} \right]}$$

where the pH dependent concentrations of the acid and base forms of fluorescein are taken from the polymer-bound dye data (see Fig. 1B of the text). The quantum yields $QY_{acid,base}$ (37% and 97% respectively)¹ are used to assure that the numerator accurately reflects the losses of energy transfer from the NC to either acid or base form of fluorescein. In other words, if energy transfer from the NC to the acid form of fluorescein is 100%, the total emission intensity drops by 37% as this is the quantum yield of the acid form of the dye (and similarly for the base). The denominator reflects the loss of NC emission through energy transfer to either form of the dye. We found that a constant value for the NC-dye distance cannot reproduce the trends in the data; we then used the NC-dye distance as a fitting parameter. Using Matlab, we calculated a smooth variation in r as a function of pH which matched the data as closely as possible as demonstrated in Figs. 3B and S4B.

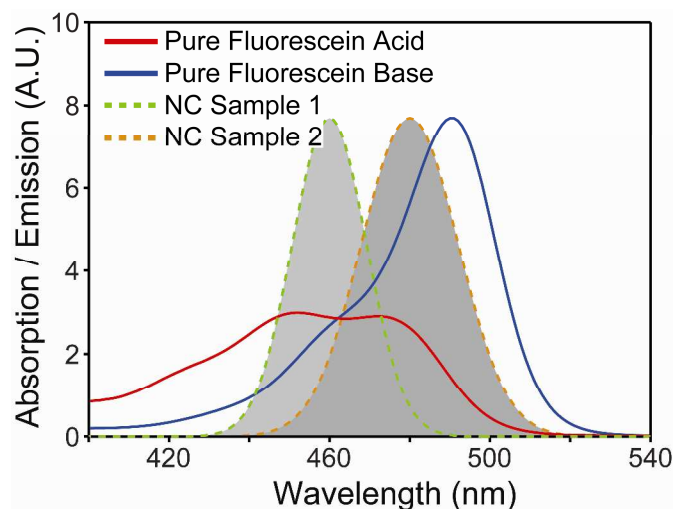


Figure S1. Emission of CdS/ZnS samples 1 & 2 overlap with the absorption spectra of the pure acid and base forms of fluorescein.

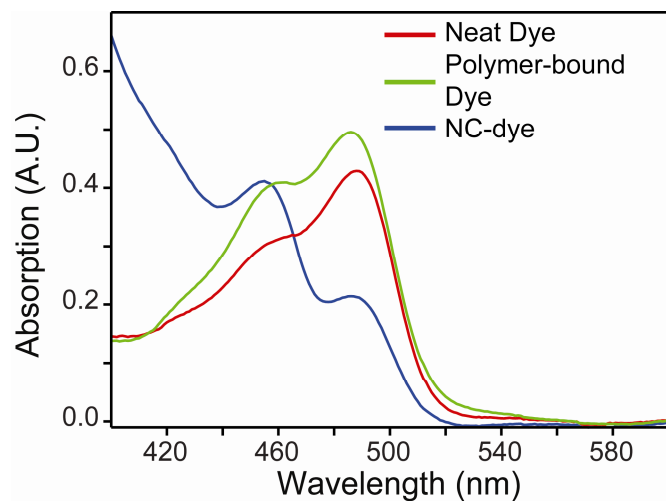


Figure S2. Absorption of the neat dye, polymer-bound dye, and the NC – dye conjugate (sample 1) at pH 6.4, the nominal pK_a of fluorescein dye. The emission of these species are presented in Fig. 4 of the main text.

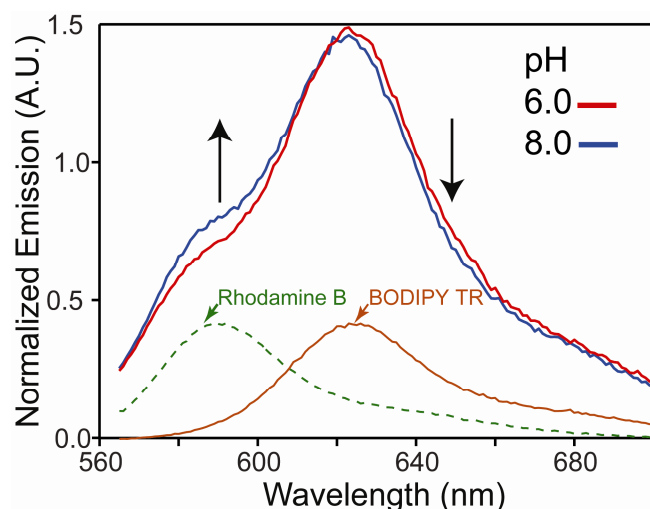


Figure S3. Emission of CdS/ZnS-rhodamine B-BODIPY TR coupled chromophores as a function of pH. The excitation wavelength was chosen to minimize excitation of the NC or FRET accepting BODIPY dye directly. The increase in rhodamine B donor with loss of BODIPY TR emission is consistent with an increase in the separation of the two dyes, most likely due to the swelling of the amphiphilic polymer that coats the CdS/ZnS NCs.

As shown in Fig. S3, the rhodamine donor emission slightly increases at the expense of the BODIPY TR acceptor from pH 6 to 8; this is indicative of a loss of FRET efficiency as the two dyes become more separated due to polymer swelling. Appropriate controls were also examined to assure the changes in the emission were not due solely to the photophysical properties of the polymer bound dyes alone.

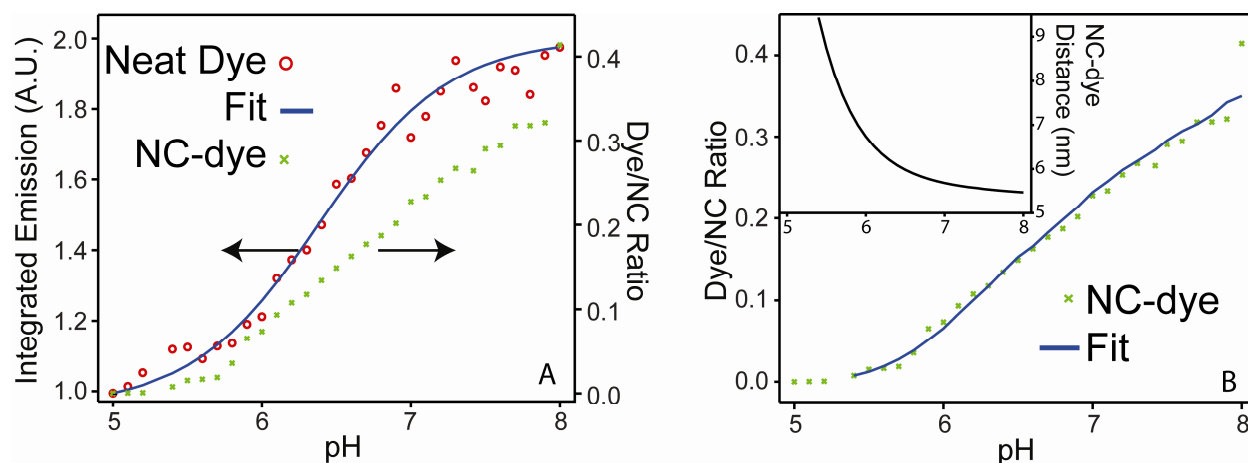


Figure S4. A. Integrated neat dye emission and dye/NC emission ratio (sample 2) versus pH. The fit to the neat dye data is derived from the Henderson-Hasselbalch equation. **B.** A fit to the NC/dye emission ratio through Förster theory where the NC-to-dye distance is a function of pH as shown in the inset. We were not able to fit the data < pH 5.5 due to the very low dye emission under these conditions.

Chemical Sources: All systems under study were synthesized according to the references provided in the main text. The following is a list of the chemicals used and their sources. All general use solvents were reagent grade from Fisher, except DMF (anhydrous, extra dry, Acros)

CdS/ZnS- cadmium oxide (Fluka), zinc oxide (Sigma-Aldrich), sulfur (Sigma-Aldrich), oleic acid (>99%, Sigma-Aldrich), octadecene (90%, Acros), dodecylamine (Sigma-Aldrich), tri-octylphosphine (97%, Strem), oleylamine (purified with vacuum distillation, Acros), diethyl zinc (Strem), bis-trimethylsilyl sulfide (Sigma-Aldrich)

RAFT 40% octylamine-modified poly(acrylic acid): carbon disulfide (Sigma-Aldrich), cesium carbonate (Acros), benzyl bromide (Sigma-Aldrich), anhydrous acrylic acid (Fluka), AIBN (Sigma-Aldrich), EDC (Advanced Chemtech), octylamine (TCI), sodium borohydride (98.5%, Sigma-Aldrich)

Fluorescein Iodoacetimide: resorcinol (Sigma-Aldrich), 4-nitrophthalic anhydride (Sigma-Aldrich), sodium hydrosulfide (Sigma-Aldrich), sodium sulfide nonahydrate (Sigma-Aldrich), chloroacetic anhydride (Sigma-Aldrich), sodium iodide (EM Science).

Reference:

(1) Sjoback, R.; Nygren, J.; Kubista, M. Absorption and Fluorescence Properties of Fluorescein. *Spectrochimica Acta Part a-Molecular and Biomolecular Spectroscopy* **1995**, 51, L7-L21.