

**Supplementary Information for:**

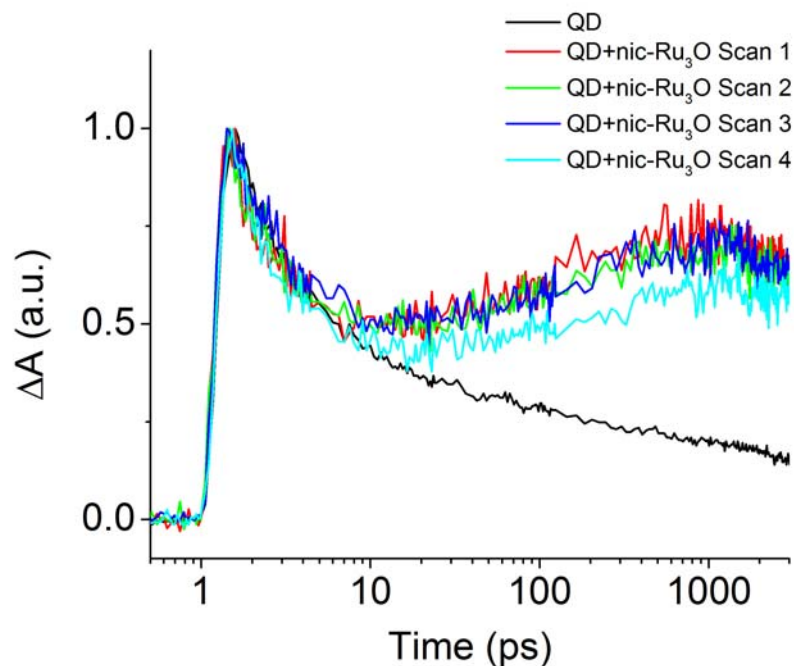
**Controlling the Rate of Electron Transfer between a Quantum Dot and a Tri-Ruthenium Molecular Cluster by Tuning the Chemistry of the Interface**

Adam J. Morris-Cohen<sup>a</sup>, Kenneth O. Aruda<sup>a</sup>, Andrew Rasmussen<sup>a</sup>, Gabriele Canzi<sup>b</sup>, Tamar Seideman<sup>a</sup>, Clifford P. Kubiak<sup>b</sup>, and Emily A. Weiss<sup>a,\*</sup>

<sup>a</sup>Department of Chemistry, Northwestern University, 2145 Sheridan Rd., Evanston, IL 60208-3113

<sup>b</sup>Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Dr., La Jolla, CA 92093-0358

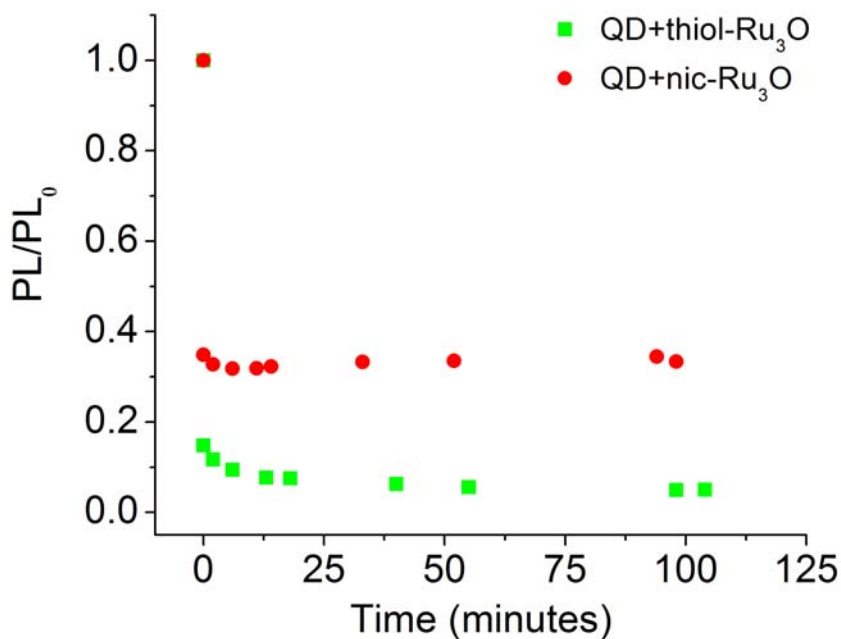
**Photochemical Stability of the QD-Ru<sub>3</sub>O Complexes.** To check the stability of the CdSe QD-Ru<sub>3</sub>O complexes during the TA measurements, we performed multiple consecutive scans on each sample. Each scan lasts approximately 35 minutes. Figure S1 shows four consecutive kinetic traces of the photo-induced absorption from the nic-Ru<sub>3</sub>O<sup>-</sup> transient and a QD-only trace at the same wavelength (for comparison). The first three scans produces traces that overlay each other, while the fourth trace shows a 20% decreases in amplitude. We attribute the loss in amplitude in the fourth kinetic trace to laser induced photo-degradation of the Ru<sub>3</sub>O clusters. Kinetic traces that exhibited significant loss of amplitude were not included in our kinetic analysis.



**Figure S1.** Transient absorption kinetic traces at a probe wavelength of 1200 nm of  $3.0 \times 10^{-5}$  M CdSe QDs ( $d = 2.4$  nm) in  $\text{CHCl}_3$  with no added  $\text{Ru}_3\text{O}$  (black), and of the same QDs with the nic- $\text{Ru}_3\text{O}$  added at a ratio of 20 clusters/QD. The first three kinetic scans retrace one another well while the fourth scan shows an approximately 20% decrease in amplitude of the signal from the  $\text{Ru}_3\text{O}^-$  anion due to photodegradation.

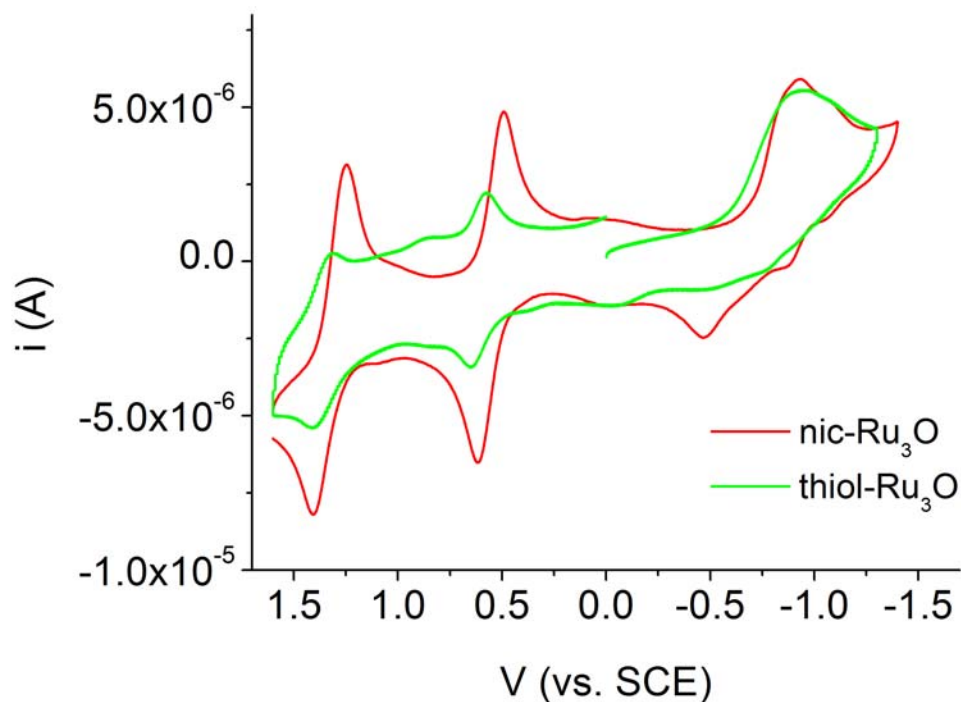
**Equilibration of QD- $\text{Ru}_3\text{O}$  Mixtures.** In addition to examining multiple TA kinetic traces, we also monitored the time dependence of the photoluminescence (PL) intensity of the QD- $\text{Ru}_3\text{O}$  complexes after preparing the samples, in order to ensure that the samples were equilibrated and stable during the TA measurement. Figure S2 shows the integrated PL intensity of the nic- $\text{Ru}_3\text{O}$ -QD (red) and thiol- $\text{Ru}_3\text{O}$  QD (green) complexes normalized to the PL intensity of the QD-only sample ( $\text{PL}/\text{PL}_0$ ) as a function of time after preparing the samples. Addition of the  $\text{Ru}_3\text{O}$  complexes to the solutions of QDs causes a rapid decrease in PL intensity in the first minute after mixing. At approximately 35 minutes after mixing, the PL intensity of both samples is stable and does not change. We attribute the initial quenching in the first minute after mixing to adsorption

of the  $\text{Ru}_3\text{O}$  complexes to the surface of the QDs. The stable PL intensity 35 minutes after mixing implies that the surface coverage of  $\text{Ru}_3\text{O}$  clusters on the QDs is constant and the samples are equilibrated. Samples prepared for TA measurement and used in the kinetic analysis in the main text stirred for at least 35 minutes prior to measurement.



**Figure S2.** Time dependence of the integrated photoluminescence intensity of  $3.0 \times 10^{-5}$  M CdSe QDs ( $d = 2.4$  nm) in  $\text{CHCl}_3$  with nic- $\text{Ru}_3\text{O}$  (red) or thiol- $\text{Ru}_3\text{O}$  added at a ratio of 20 clusters/QD. The PL is normalized to the integrated PL intensity of an identical sample with no added  $\text{Ru}_3\text{O}$  (black).

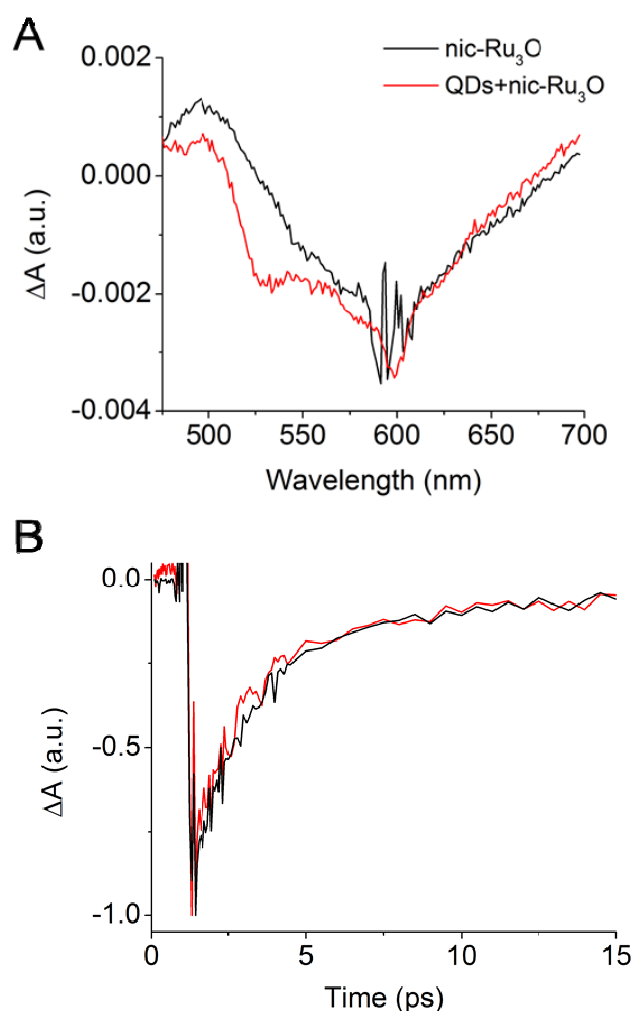
**Cyclic Voltammetry on the  $\text{Ru}_3\text{O}$  Clusters.** We performed the cyclic voltammetry with a Pt gauze working electrode, Pt counter electrode, and  $\text{Ag}/\text{Ag}^+$  reference, and a PINE bipotentiostat model AFCBP1. Figure S3 shows the cyclic voltammograms we used to calculate the redox potentials of the nic- $\text{Ru}_3\text{O}$  and thiol- $\text{Ru}_3\text{O}$  complexes. The first reduction peak is at  $\sim 930$  mV for both clusters.



**Figure S3.** Cyclic voltammograms used to calculate the HOMO and LUMO of the nic-Ru<sub>3</sub>O and thiol-Ru<sub>3</sub>O clusters. The first reduction peak is at ~930 mV for both clusters.

**Electron transfer does not occur upon selective excitation of the clusters.** To determine if incidental photoexcitation of the Ru<sub>3</sub>O clusters (as opposed to photoexcitation of the QDs) by the pump pulse resulted in any charge or energy transfer processes that would complicate our data analysis, we measured the TA spectra of Ru<sub>3</sub>O clusters photoexcited at a lower energy than the first excitonic peak of the QD (such that only the clusters, and not the QDs, are excited); these spectra show no signals indicative of electron transfer or other interactions between the excited Ru<sub>3</sub>O cluster and the QD. Figure S4 shows TA spectra 4.3 ps after photoexcitation (A) and kinetic traces at 585 nm for a sample of  $1.4 \times 10^{-4}$  M nic-Ru<sub>3</sub>O in CHCl<sub>3</sub> without and with CdSe QDs ( $d = 2.7$  nm,  $2.4 \times 10^{-5}$  M,  $E_g = 532$  nm) (B). The TA spectra show three main features: (i) a

broad negative peak centered a 600 nm which we assign as the ground state bleach of the Ru<sub>3</sub>O cluster; (ii) a positive feature centered at 500 nm which we assign to absorption from the excited state of Ru<sub>3</sub>O; and (iii) a negative feature centered at 530 nm which we assign to the ground state bleach of the QD. The first two features are present in both samples while third feature is only present in the sample with QDs. We also observe a bleach signal from a sample of QDs without any added Ru<sub>3</sub>O clusters excited at 600 nm ( $E_{\text{pump}} < E_{\text{g}}$ ) (spectra not shown). We therefore believe that the bleach from the QDs arises from a two-photon absorption and not from an energy or charge transfer process; it has previously been shown that CdSe QDs have a large two photon cross-section. The ground state bleach of the Ru<sub>3</sub>O clusters show a fast (< 10ps), multiexponential recovery after photoexcitation; this recovery is unaffected by the presence of CdSe QDs (S4B).

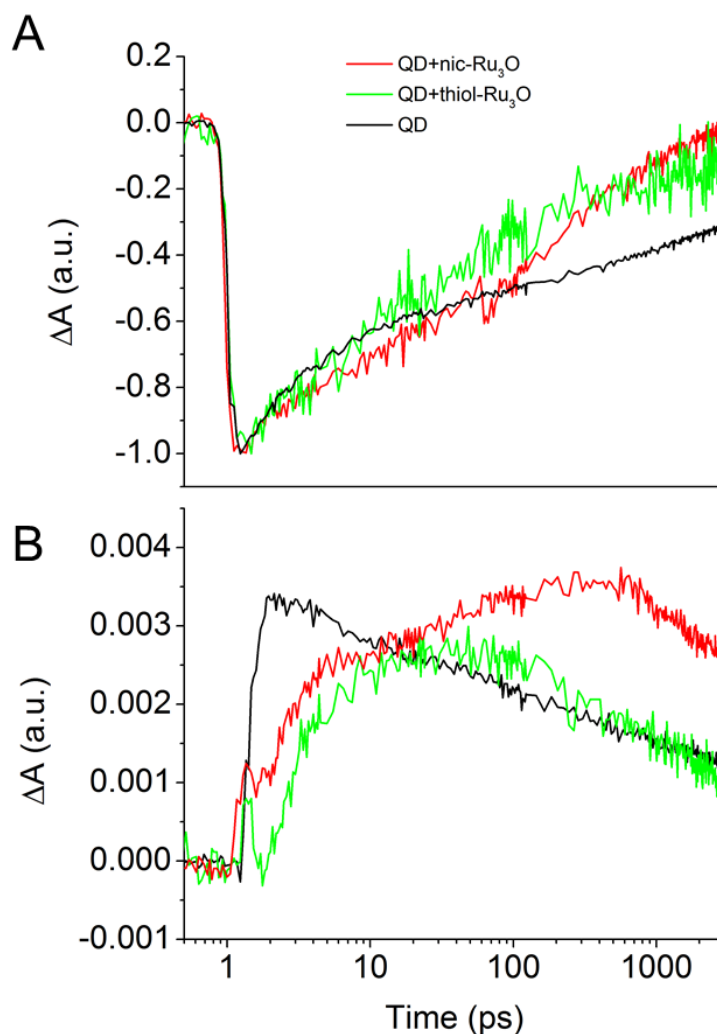


**Figure S4.** (A) Transient absorption spectra of  $1.4 \times 10^{-4}$  M nic-Ru<sub>3</sub>O in CHCl<sub>3</sub> (black) and of the same clusters with added M CdSe QDs ( $d = 2.7$  nm,  $2.4 \times 10^{-5}$ ; red) 4.3 ps after photoexcitation. The bleach centered at 600 nm corresponds to the ground state bleach of the Ru<sub>3</sub>O and the positive absorption at  $\sim 500$  nm corresponds to absorbance by nic-Ru<sub>3</sub>O\*. The increased noise at 600 nm results from scattered pump light and the additional peak in the QD + nic-Ru<sub>3</sub>O trace corresponds to bleaching of the QD via two photon absorption. (B) Kinetic traces of the same to samples from (A) taken at 585nm.

### Dynamics of the TA Features of the QD-Ru<sub>3</sub>O Complexes in the Visible Region.

Addition of Ru<sub>3</sub>O clusters to solutions of QDs induces a recovery of the ground state bleach of the QD and produces a new absorptive feature at lower energies than the QD. In principle, these

features also reflect the rate of the charge separation process, but it is much more difficult to isolate charge separation dynamics from competing processes in this region of the spectrum. The main text gives a detailed description of the competing processes in this region of the spectrum.



**Figure S5.** (A) Transient absorption kinetic traces, at a probe wavelength of 500 nm, of  $3.0 \times 10^{-5}$  M CdSe QDs ( $d = 2.4$  nm) in  $\text{CHCl}_3$  (with no added  $\text{Ru}_3\text{O}$ ) after photoexcitation (black), and traces for a sample of the same QDs with the nic- $\text{Ru}_3\text{O}$  (red) and thiol- $\text{Ru}_3\text{O}$  (green) clusters added at a ratio of 20 clusters/QD. The kinetic traces are normalized to their peak minimum at  $t_0$ . Electron transfer induces an additional, fast recovery of the ground state bleach. (B) Same as (A) but at 640 nm illustrating the dynamics of the new photoinduced absorption.

**Calculation of the Average Number of Clusters Adsorbed per QD.** To calculate the number of adsorbed Ru<sub>3</sub>O clusters, we must first estimate the number of surface sites. We estimated an upper bound for number of surface sites by calculating the number of the largest of ions in the QD (Se<sup>2-</sup>) that could be present at the surface of the QD. We calculate the number of surface atoms on a CdSe QD with eq S1, where  $r_{\text{QD}}$  is the radius of the QD and

$$n_{\text{sites}} = \frac{\pi}{4} \left( \frac{4\pi r_{\text{QD}}^2}{\pi r_{\text{Se}^{2-}}^2} \right) \quad (\text{S1})$$

$r_{\text{Se}^{2-}}$  is the radius of the selenide anion. Equation S1 yields approximate 110 surface sites per CdSe QD for the  $d=2.4$  nm QDs used in this study.

We have shown previously that the fraction of QD PL intensity remaining after addition of an efficient quenching ligand ( $\text{PL}/\text{PL}_0$ ) reveals the fraction of QDs with zero adsorbed ligands and the mean fractional surface coverage,  $\theta$ .<sup>1</sup> To find  $\theta$ , we first model the distribution of ligands bound to each QD using the binomial distribution, eq S2, where  $P(m|N, \theta)$  is the probability

$$P(m|N, \theta) = \binom{N}{m} (\theta)^m (1 - \theta)^{N-m} \quad (\text{S2})$$

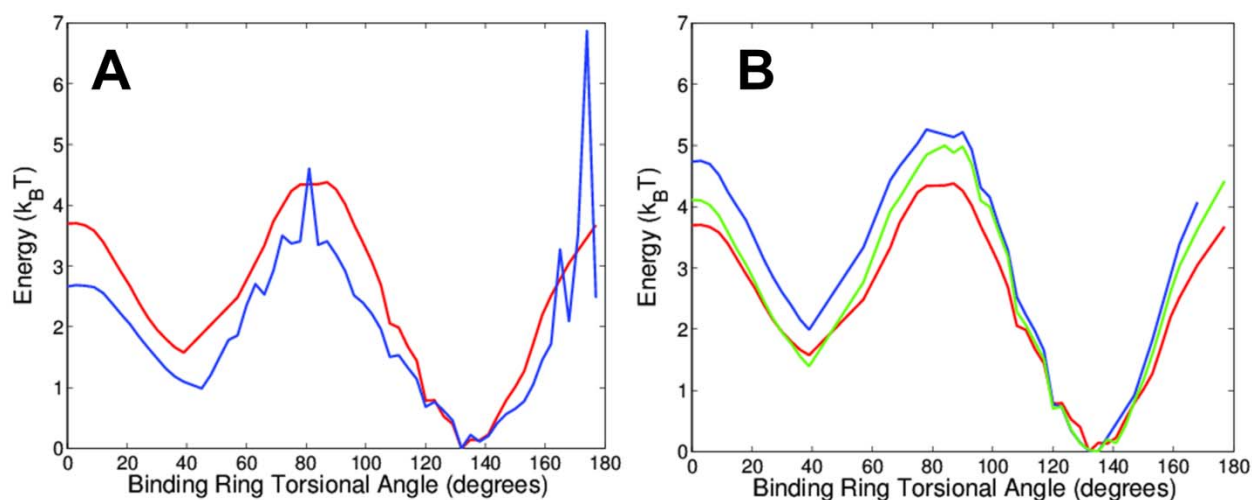
of finding a QD within the ensemble with  $m$  adsorbed ligands given that each QD has  $N$  surface sites and a mean fractional surface coverage of ligands is  $\theta$ . Since  $\text{PL}/\text{PL}_0$  equals  $P(0|N, \theta)$ , we substitute  $0$  in for  $m$  in eq S2 and solve for  $\theta$ , eq S3. Using eq S3 with  $N = 115$  and three separate

$$P(0|N, \theta) = \frac{\text{PL}}{\text{PL}_0} = (1 - \theta)^N \quad (\text{S3})$$

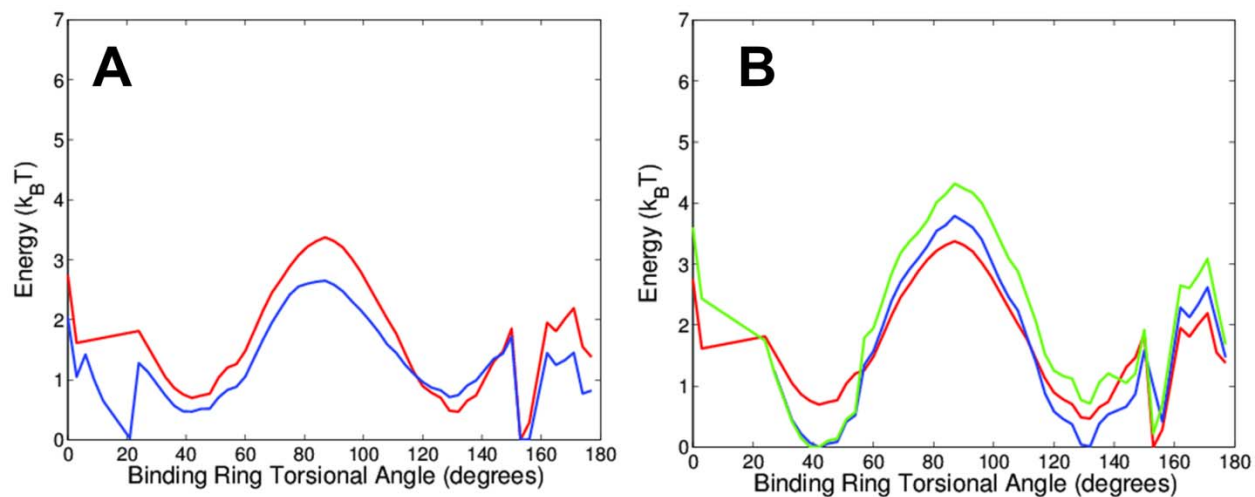
measurements of  $\text{PL}/\text{PL}_0$  on samples prepared identically to those we measured in the TA experiment, we find that there are an average of 2.9 thiol-Ru<sub>3</sub>O clusters adsorbed per QD and an average of 1.1 nic-Ru<sub>3</sub>O clusters adsorbed per QD at the concentrations of each component of the mixtures that we study with TA.



**Computational Methods and Details.** All computations were performed with the TURBOMOLE package at geometries optimized with the def2-SV(P) basis and B3LYP functional. We subsequently calculated torsional potential energy surfaces (TPES) using these geometries with a variety of density functionals and basis sets. Figures S6 and S7 demonstrate that the torsional potential energy surfaces (TPES) that we present in the main text (which are calculated with the PBE0 hybrid functional and the TZVPP basis set) are not qualitatively basis set- or functional-dependent. The energy units on the y-axis are  $k_B T$  at 300 K, and the y-axis is the same across all the subfigures.



**Figure S6:** A comparison of TPES for nic-Ru<sub>3</sub>O. In (A), the (red, blue) curve corresponds to the (def2-TZVPP, def2-SV(P)) basis set. In (B), the (red, green, blue) curve corresponds to the (B3LYP, PBE0, TPSSH) functional.



**Figure S7:** A comparison of TPES for thiol-Ru<sub>3</sub>O. In (A), the (red, blue) curve corresponds to the (def2-TZVPP, def2-SV(P)) basis set. In (B), the (red, green, blue) curve corresponds to the (B3LYP, PBE0, TPSSH) functional.

## References

- (1) Morris-Cohen, A. J.; Vasilenko, V.; Amin, V. A.; Reuter, M. G.; Weiss, E. A. Model for Adsorption of Ligands to Colloidal Quantum Dots with Concentration-Dependent Surface Structure. *ACS Nano* **2011**.