

Supporting Information

Electrogenerated Chemiluminescence of Solutions, Films and Nanoparticles of Dithienylbenzothiadiazole–Based Donor-Acceptor-Donor Red Fluorophore. Fluorescence Quenching Study of Organic Nanoparticles

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(1) *Digital simulations*

Digital simulations of the experimental CVs for the reduction and oxidation are shown in Figures S1 and S2, respectively. Experimental and simulated CVs for both reduction and oxidation performed at various scan rates from 0.02 V/s to 1.0 V/s fits very well. The double layer capacitance and the uncompensated resistance used in the simulation were measured from a potential step in the region where only double layer charging occurred, i.e. at 0 V vs SCE.

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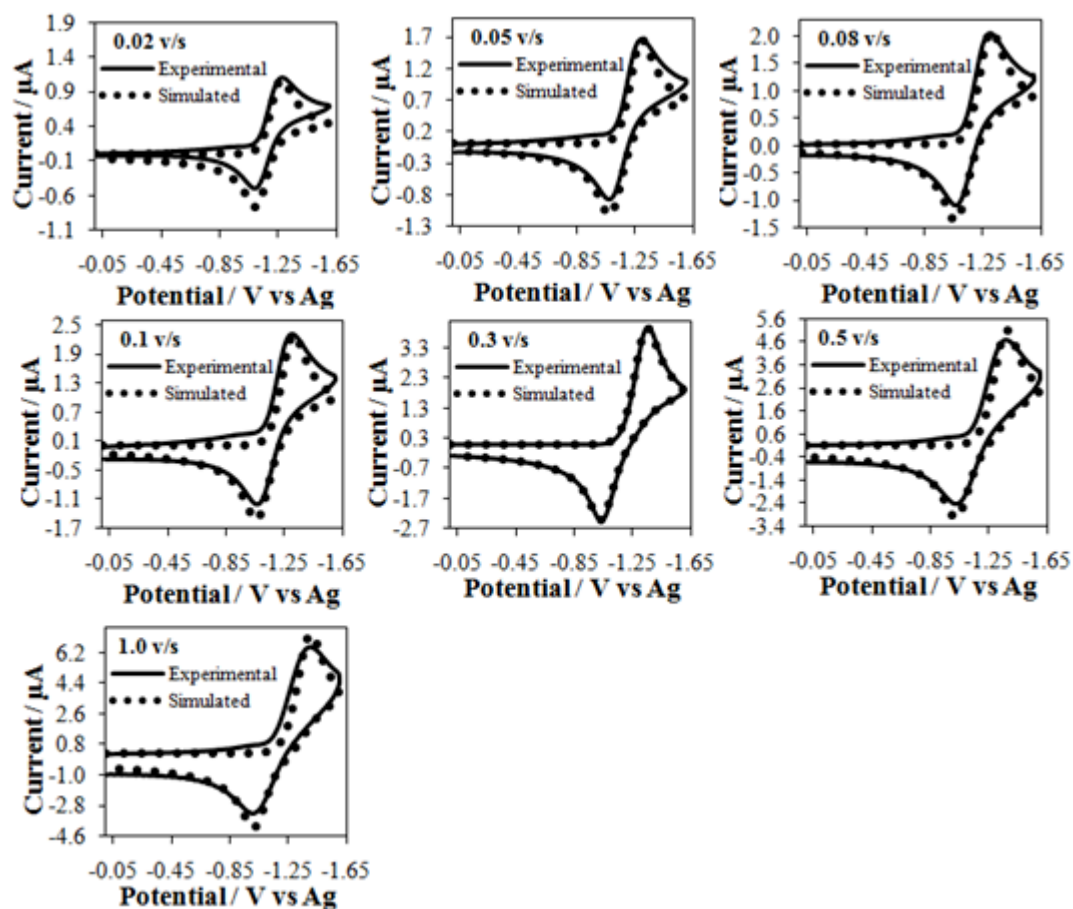


Figure S1. Simulation of 0.5 mM **1a** reduction in dichloromethane at (a) 0.02 V/s (b) 0.05 V/s (c) 0.08 V/s (d) 0.1 V/s (e) 0.3 V/s (f) 0.5 V/s (g) 0.75 V/s (h) 1 V/s. Simulation mechanism is one-electron reduction with $D = 6 \times 10^{-6} \text{ cm}^2/\text{s}$, $E_{\text{red}}^{\circ} = -1.18 \text{ V vs SCE}$, $k^{\circ} = 0.6 \times 10^{-3} \text{ cm/s}$, $\alpha = 0.5$, uncompensated solution resistance $R_u = 1972 \ \Omega$, and double layer capacitance $C_{\text{dl}} = 0.25 \ \mu\text{F}$.

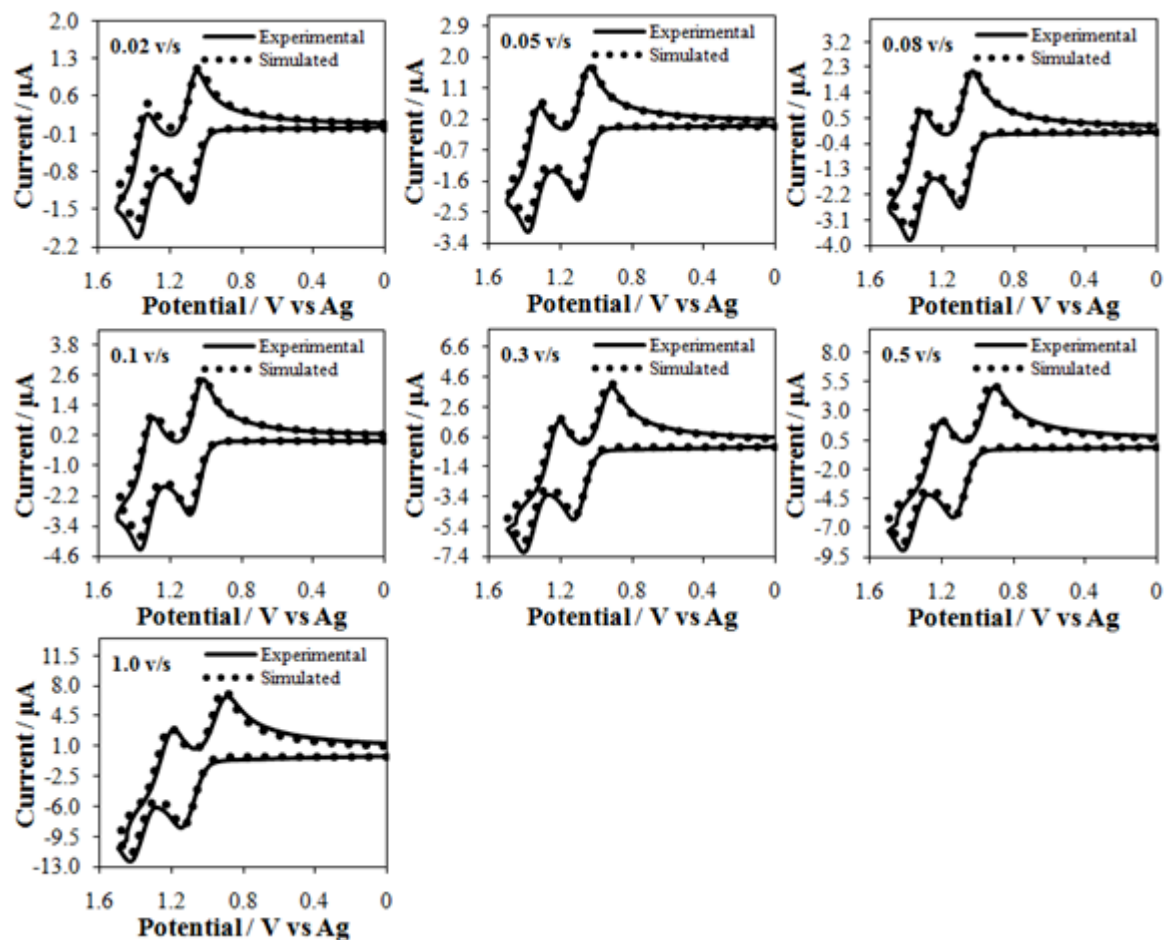


Figure S2. Simulation of 0.5 mM **1a** oxidation in dichloromethane at (a) 0.02 V/s (b) 0.05 V/s (c) 0.08 V/s (d) 0.1 V/s (e) 0.3 V/s (f) 0.5 V/s (g) 0.75 V/s (h) 1 V/s. Simulation mechanism is two stepwise 1e oxidations with $D = 6 \times 10^{-6} \text{ cm}^2/\text{s}$, $E_{1,\text{ox}}^0 = 1.01 \text{ V vs SCE}$, $E_{2,\text{ox}}^0 = 1.24 \text{ V vs SCE}$, $k^0 = 0.02 \text{ cm/s}$, $\alpha=0.5$, uncompensated solution resistance $R_u = 1972 \Omega$, and double layer capacitance $C_{\text{dl}} = 0.25 \mu\text{F}$.

(2) CV of film

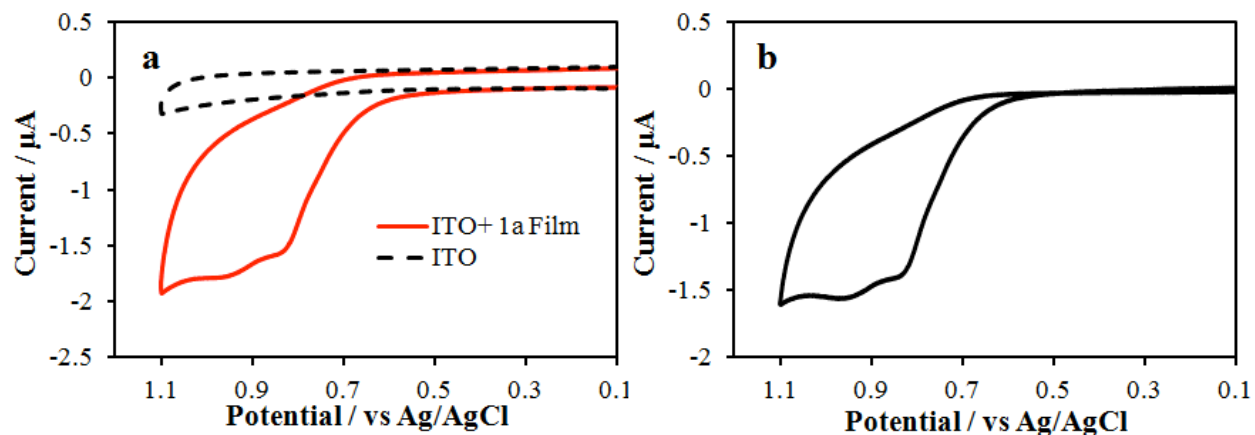


Figure S3. (a) Cyclic voltammetry of the film (b) background subtracted cyclic voltammetry.

The integrated charge in Figure b is 1.5×10^{-4} C, and 25 μL 0.5 mM **1a** is deposited, the calculated result is that 12% of the deposited material is electroactive.

(3) Excitation spectra and emission spectra

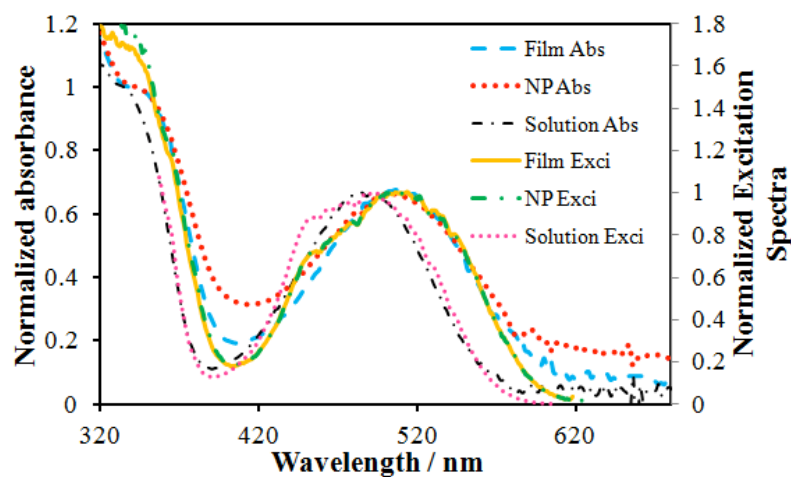


Figure S4. Normalized excitation spectra of **1a** nanoparticle (NP), solution and film and normalized absorbance spectra.

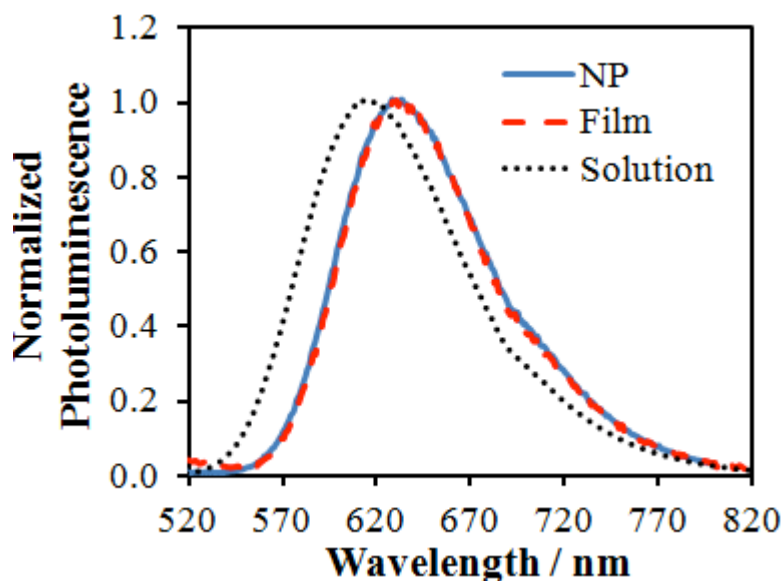


Figure S5. Normalized fluorescence emission spectra of NP, film and solution on Agilent Technologies Cary Eclipse Fluorescence spectrophotometer.

*(4) Supporting discussion and figures on fluorescence quenching of **1a** NPs.*

A static quenching mechanism is characterized by, $I_0/I = (1 + k_q\tau_0[Q]) \times e^{-V[Q]}$ (eqn S1) for the sphere of action static quenching model or $I_0/I = (1 + k_q\tau_0[Q]) (1 + Ka[Q])$ (eqn S2) for a ground-state complex static quenching model, where V is interaction sphere of volume and Ka is association constant between the fluorophore and quencher.¹

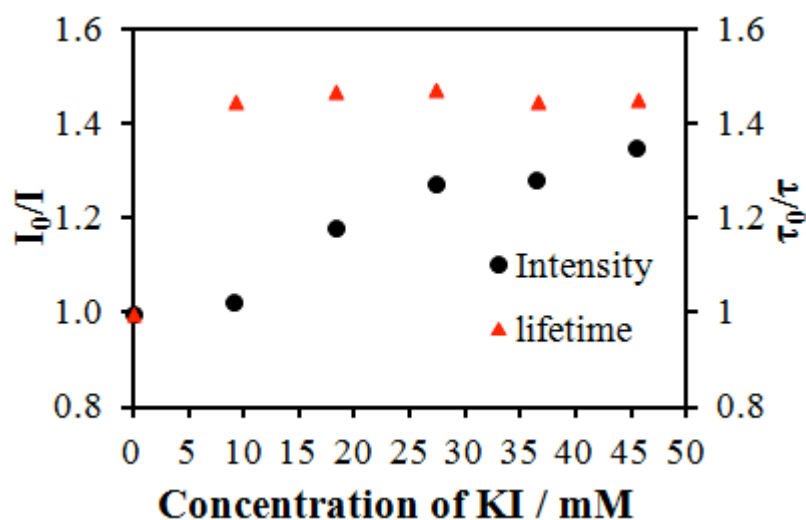


Figure S6. Plots of ratio of fluorescence intensity without and with quencher, (I_0/I), as well as ratio of fluorescence lifetime without and with quencher, τ_0/τ , versus concentration of KI.

Figure S7 shows the absorbance spectra of **1a** NPs in water upon adding I^- . As seen in Figure S7a, the absorbance of the **1a** NPs in water at 350 nm increases with increasing KI concentration; in contrast, no change was observed for the absorbance of **1a** NPs at 504 nm. In these studies, a very concentrated stock solution of KI (0.4 M) was used to minimize the volume change caused by dilution when adding KI. The absorbance at 350 nm upon adding KI could be related with interaction between **1a** NPs and KI. We also observed that the absorbance at 350 nm on adding certain concentration of KI is increasing with time and eventually reach a constant value.

Fluorescence excitation and emission of NPs on adding certain concentrations of KI shows no time dependency. The fluorescence emission of **1a** NPs in water upon adding KI were measured with excitation wavelength at 350 nm, and the result is shown in Figure S7b. In contrast to absorbance, a decrease in fluorescence emission intensity was observed on adding KI, indicating that the product of interaction between I^- and **1a** NPs are not fluorescent.

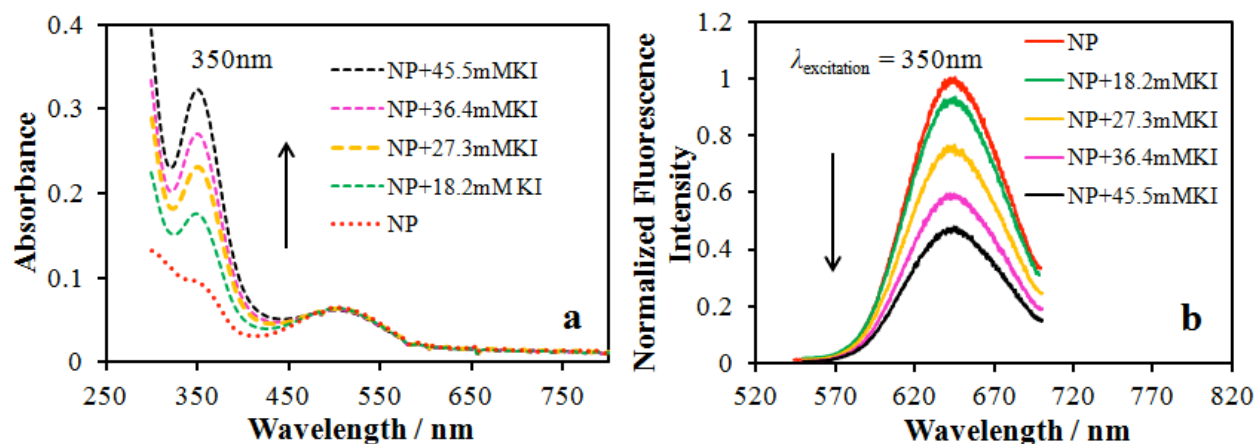


Figure S7. (a) Absorbance spectra and (b) fluorescence emission spectra of **1a** NPs in water in the presence of different concentrations of quencher (KI). For (b) the excitation wavelength was 350 nm. The absorbance at 350 nm change with time reaching a constant value plotted in (a) after about 5 min.

The absorbance as a function of concentration of **1a** in solution and of **1a** NPs follows linear relationships at 340 nm and 486 nm (solution) and 350 nm and 504 nm (**1a** NPs) (Figure S8).

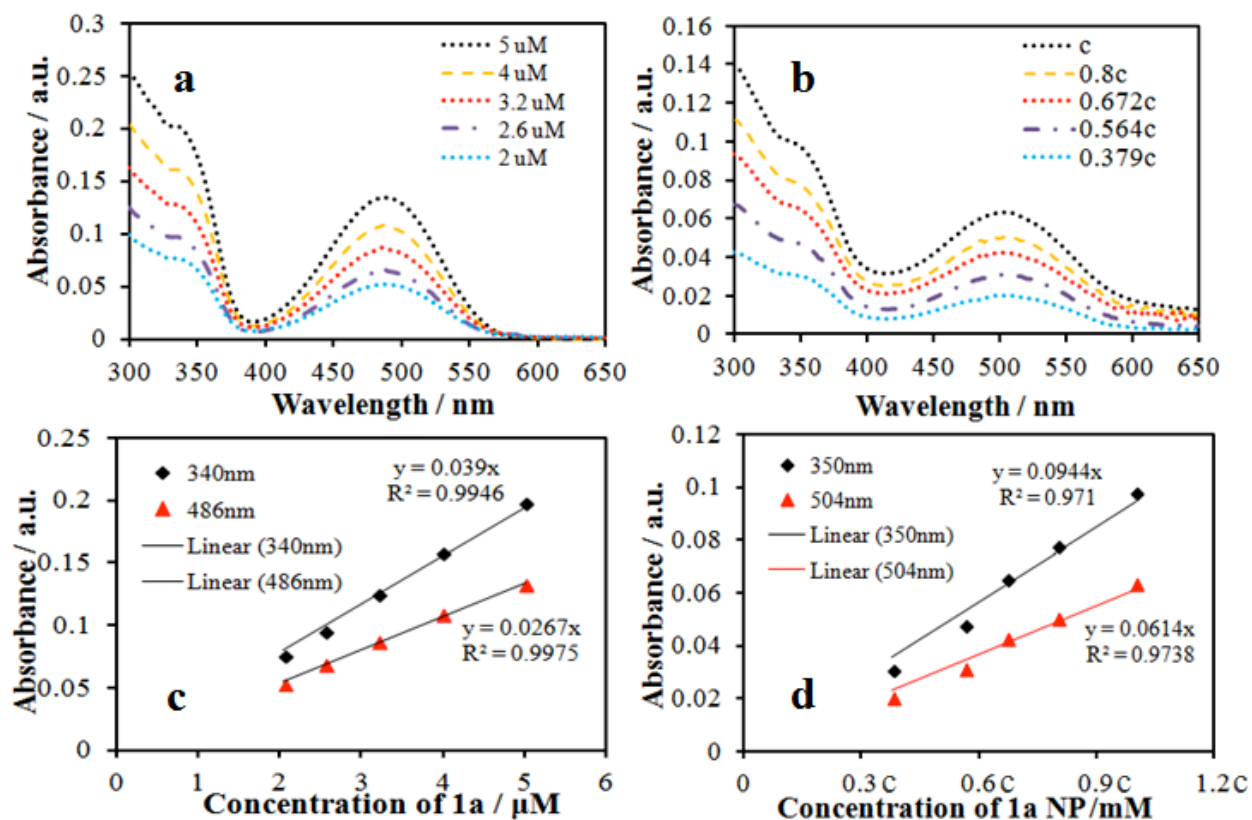


Figure S8. (a) Absorbance of different concentrations of **1a** solution with concentrations shown in the figure. (b) Absorbance of different concentrations of **1a** NPs in water. (c) Plots of two peak absorbance versus concentration of **1a** solution, where two peak absorbance occur at 340 nm and 486 nm. (d) Plots of two peak absorbance versus concentration of **1a** NPs in water, where two peak absorbance occurs at 350 nm and 504 nm. Molar absorptivity of $26700 \text{ M}^{-1}\text{cm}^{-1}$ at 486 nm and $38950 \text{ M}^{-1}\text{cm}^{-1}$ at 340 nm were calculated for **1a**.

Fluorescence emission spectra of **1a** NPs in water were measured at two different excitation wavelengths of 350 nm and 504 nm, the results are shown in Figure S9 where it can be seen that the normalized fluorescence emission spectra at 350 nm and 504 nm are overlapped very well, indicating that the same excited states are formed when excited at 350 nm and 504 nm.

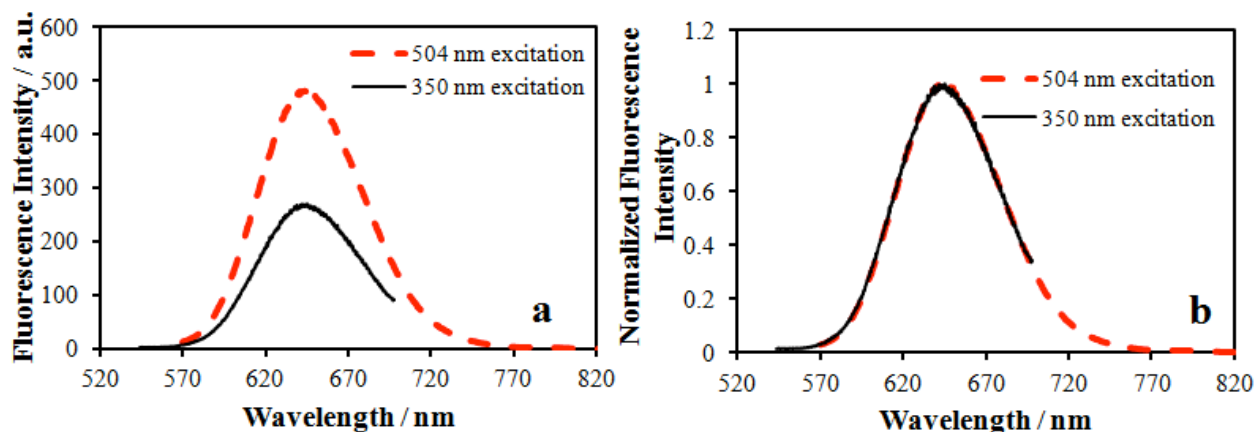


Figure S9. Fluorescence emission spectra (a) and normalized fluorescence emission spectra (b) at two different excitation wavelengths of 350 nm and 504 nm for **1a** NPs in water.

The complete expression for presence of dynamic and static quenching of a system with

heterogeneity is:

$$\frac{I_0}{I} = \left[\sum_{i=0}^n \frac{f(i)}{\{1+K_{sv}(i)[Q]\}\{1+K_a(i)[Q]\}} \right]^{-1} \quad (\text{Equation S3})$$

and

$$\frac{I_0}{I} = \left[\sum_{i=0}^n \frac{f(i)}{\{1+K_{sv}(i)[Q]\}e^{v(i)[Q]}} \right]^{-1} \quad (\text{Equation S4})$$

for the case of ground-state complex static quenching model and the sphere of action static quenching model respectively.¹

¹Laws, W. R.; Contino, P. B. *Method. Enzymol.* **1992**, *210*, 448-463.