Supporting Information

Hyper-Efficient Quenching of a Conjugated Polyelectrolyte by Dye-Doped Silica

Nanoparticles: Better Quenching in the Non-Aggregated State

Chunyan Tan,[a]   Yonghua Xie,[a,b] Xiaoxiao He,[c] Kemin Wang[c*] and Yuyang Jiang[a, d, *]

[a] Guangdong Province Key Laboratory of Chemical Biology, Graduate School at Shenzhen, Tsinghua University, Shenzhen 518055, P. R. China;
[b] Department of Chemistry, Tsinghua University, Beijing 100084, P. R. China
[c] State Key Laboratory of Chemo/Biosensing and Chemometrics, College of Chemistry and Chemical Engineering, Hunan University, Changsha 410082, P. R. China
[d] School of Medicine, Tsinghua University, Beijing 100084, P. R. China

jiangyy@sz.tsinghua.edu.cn

Experimental Section

Materials.   The synthesis and characterization of PPE-SO3 was previously described,[1, 2] and the sample was provided by Prof. Kirk S. Schanze in University of Florida.   Rubpy-doped SiNPs and non-dyed SiNPs were synthesized according to previously published procedures.[3] Triton X-100 and ruthenium trisbipyridinium chloride was purchased from Aldrich.   The water used in all experiments was prepared in a SG water purification system and displayed a resistivity of ≥ 18.2 MΩ-cm^{-1}.

Instrumentation.   Both steady state and time-resolved fluorescence spectra were recorded on a SPEX Flurolog 3-TCSPC instrument.   In steady-state measurements, 400 nm was used as the excitation wavelength, excitation and emission slits were set to be 2 nm, and the intergration time was 0.1 ms.   In time-resolved fluorescence spectra measurements, 370 nm NanoLed was used as the excitation light source, decays at 460 nm and 540 nm were recorded as needed.   Fluorescence decays were ananlyzed using Data Station developed by Horiba Jobin Yvon.   UV-visible absorption spectra were measured on a Beckmann DU800

spectrometer. Confocal fluorescence images were recorded on an Olymbus FluoView^{TM} FV1000 confocal microscope, combined with the IX81 inverted microscope.

Sample preparation. The polymer stock solution concentration was 1.8 mM (all concentrations are provided as polymer repeat unit concentration, [PRU]). The stock solution was diluted as needed to prepare solutions used for spectroscopic experiments. Final concentrations of the diluted PPE-SO3 solutions were determined based on the polymer's extinction coefficient $\varepsilon = 1.02 \times 10^5$ M^{-1}cm^{-1}. In order to calibrate the concentration of SiNPs, their absorption spectra were measured and their extinction coefficient at 455 nm on a per-mole-of-particles basis was determined as 1.7×10^8 M^{-1} cm^{-1}. The concentration of the stock solution of SiNPs was calibrated each time before the titration quenching experiment. For a typical quenching experiment, 2 mL of a PPESO3 solution was placed in a 1 cm quartz fluorescence cell. The UV-visible absorption and fluorescence spectra were recorded at room temperature. Then absorption and/or fluorescence spectra were repeatedly acquired after the addition of microliter aliquots of a concentrated quencher solutionDye (and polymer) solution by use of a calibrated Eppendorf microliter. For the confocal fluorescence image measurement, 5 µL of 50 µM PPE-SO3 in H$_2$O or the mixture of 50 µM PPE-SO3/1 nM Rubpy doped SiNPs were put on the glass slide and covered with a coverslip, and then placed under the confocal microscope.

Results
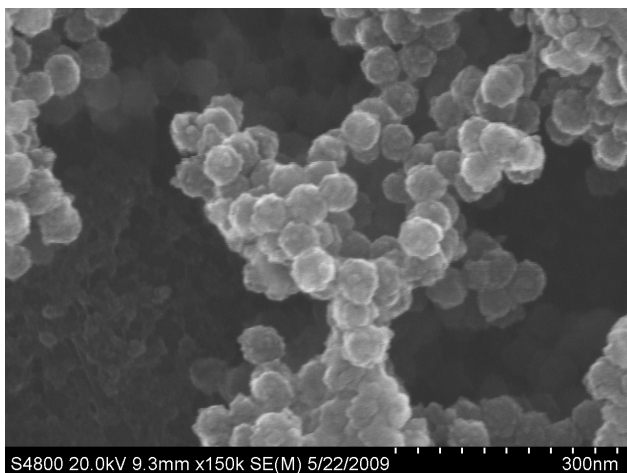
1. Characterization of the Rubpy doped SiNPs.

Figure S1.   SEM image of Rubpy doped SiNPs.

2. Steady-state fluorescence study.

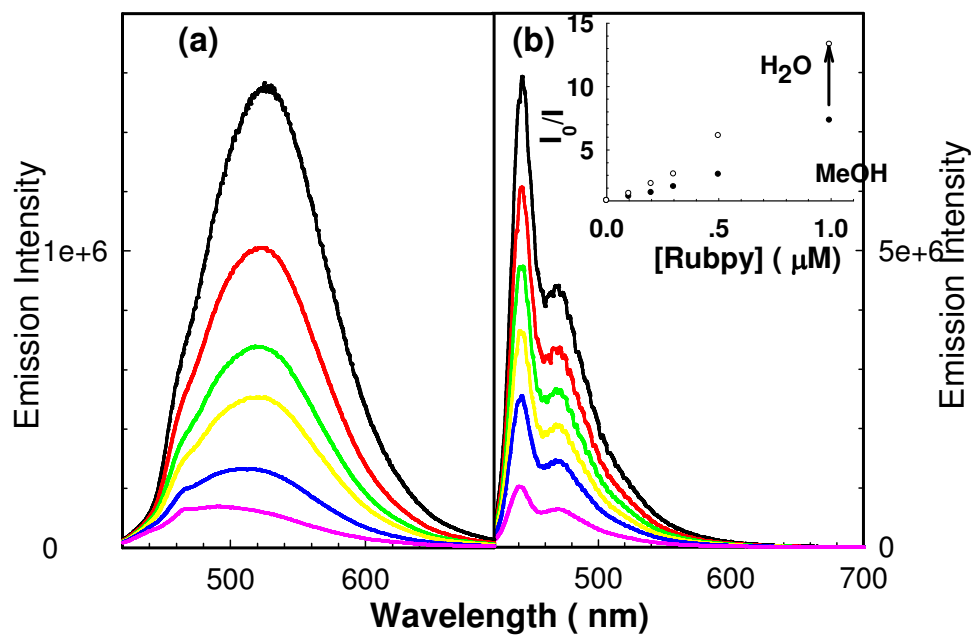### 1) Emission quenching of PPE-SO3 by Rubpy.

Figure S2.   Emission quenching spectra of PPE-SO3 by Rubpy in (a) water and (b) methanol solution, respectively. Inset: SV plots of PPE-SO3 quenching in water (○) and methanol (●), respectively.

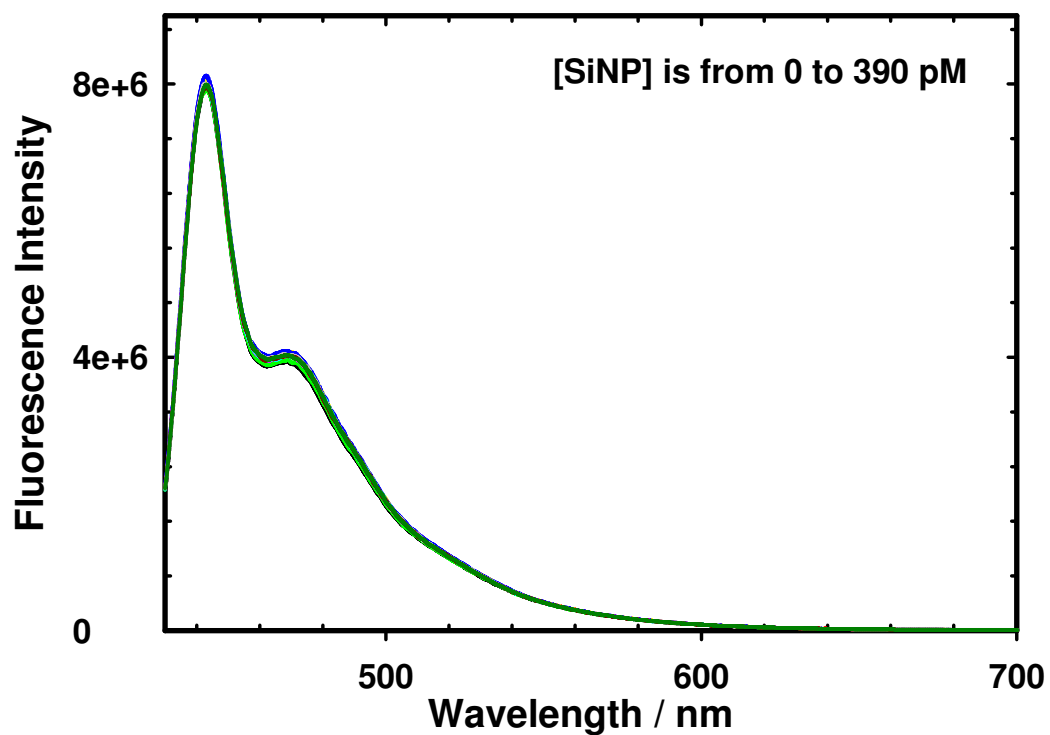**2) Emission quenching of PPE-SO3 by non-dyed SiNPs.**

Figure S3.   Fluorescence emission of 10 µM PPE-SO3 with different concentrations of non-dyed SiNPs in MeOH.

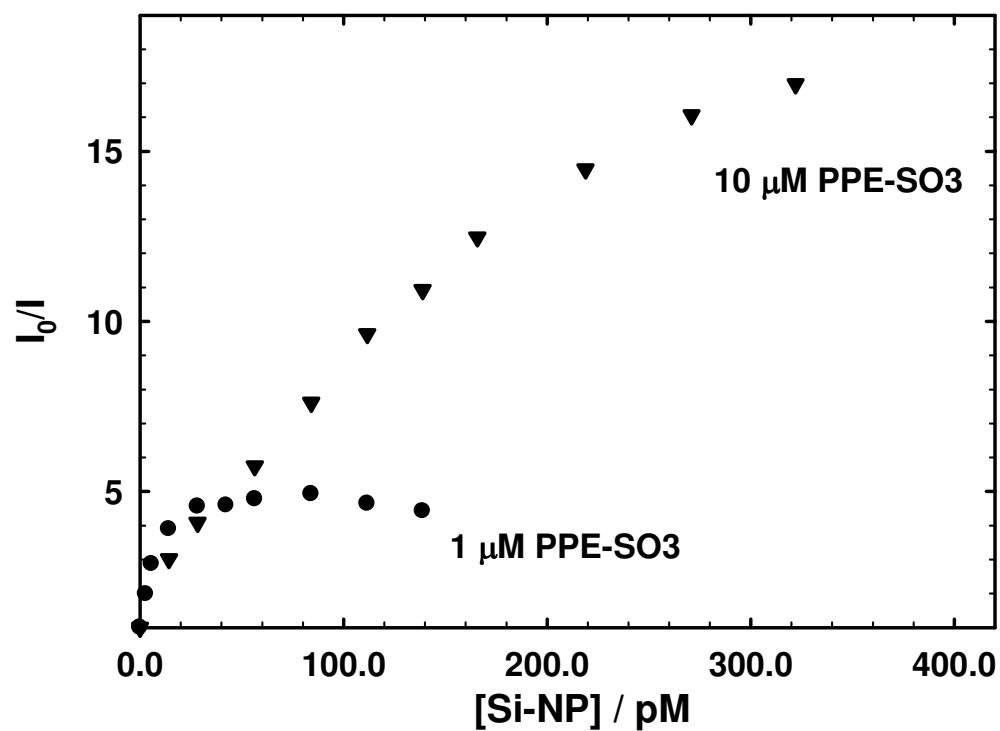**3) Emission quenching of different concentrations of PPE-SO3 by Rubpy doped SiNPs.**

Figure S4.   SV plots of 1 µM (●) and 10 µM PPE-SO3 (▼) by Rubpy doped SiNPs in methanol solutions.

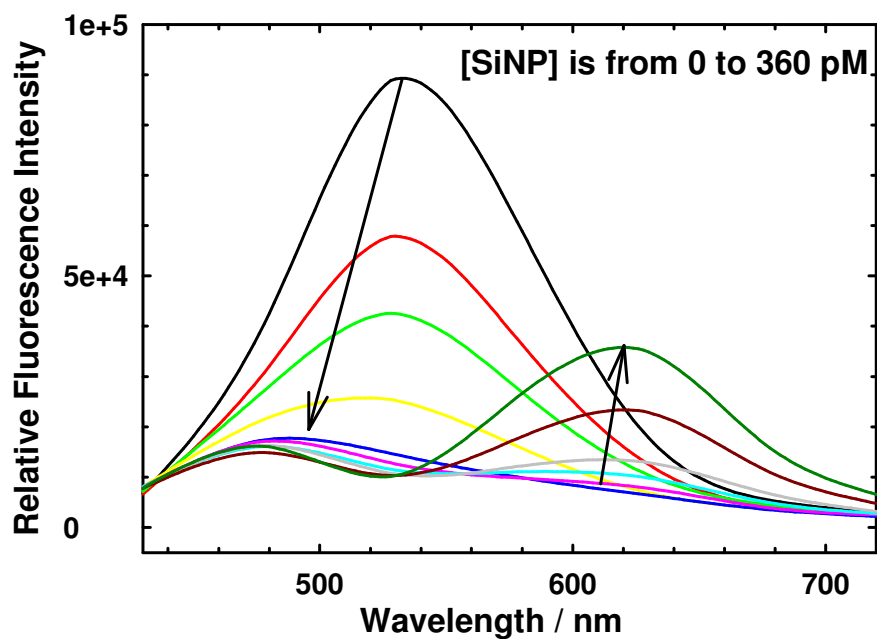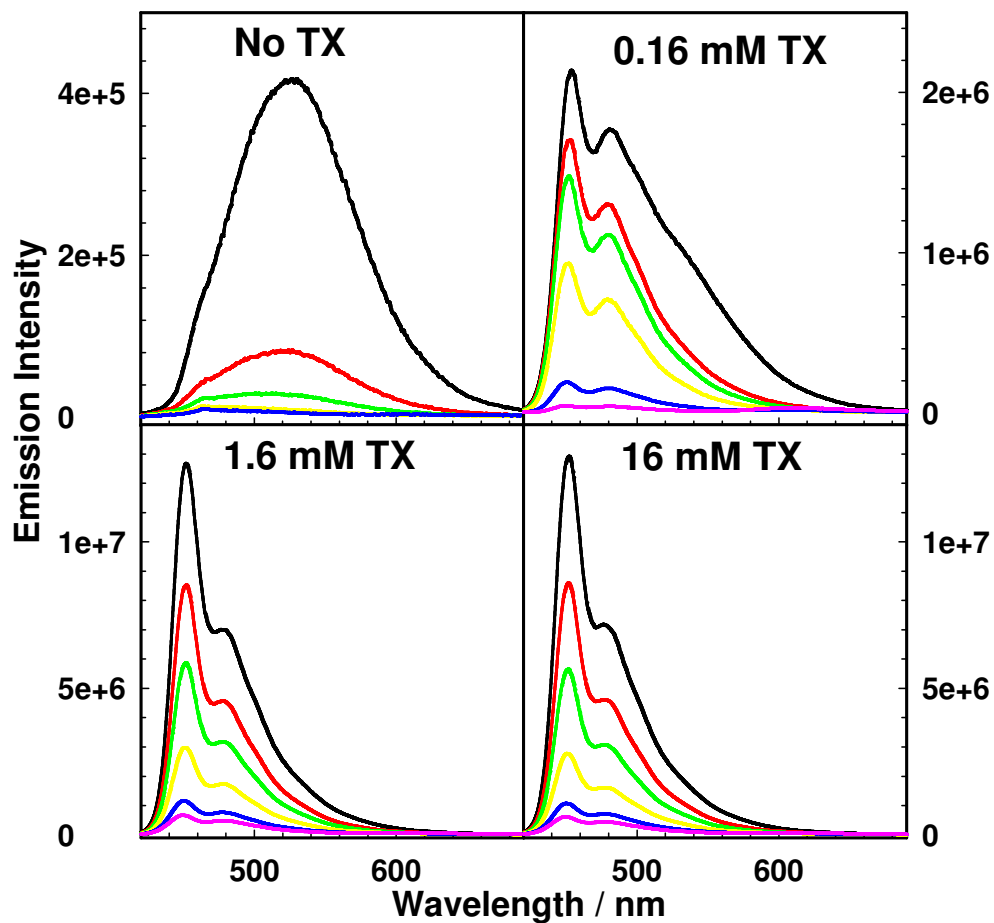**4) Emission quenching of PPE-SO3 by Rubpy doped SiNPs with N$_2$.**

Figure S5.   Emission quenching spectra of PPE-SO3 by Rubpy doped SiNPs in aqueous solution with the purge of N$_2$.

5) Emission quenching of PPE-SO3 by Rubpy in surfactant solutions.

$K_{SV} = 1.2 \times 10^7 \, M^{-1}$

$K_{SV} = 5.0 \times 10^6 \, M^{-1}$

$K_{SV} = 2.2 \times 10^6 \, M^{-1}$
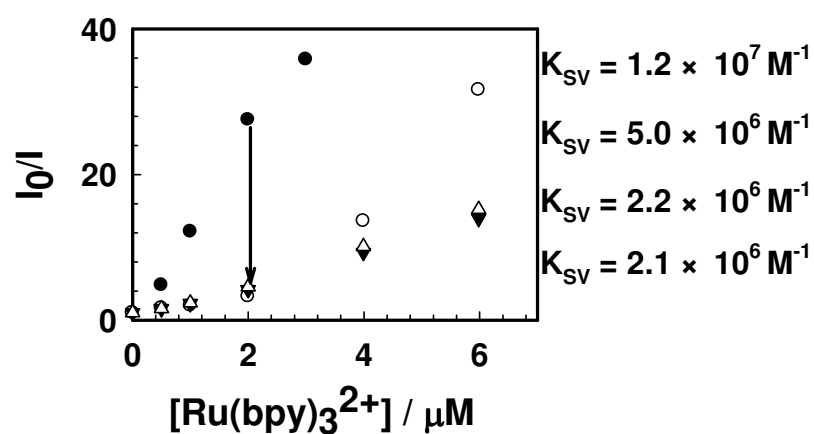
$K_{SV} = 2.1 \times 10^6 \, M^{-1}$

Figure S6. Emission quenching spectra of PPE-SO3 by Rubpy with the presence of 0, 0.16 mM, 1.6 mM and 16 mM Triton X-100 and corresponding SV plots of PPE-SO3 in aqueous solution with 0 (●), 0.16 mM (○), 1.6 mM (Δ) and 16 mM (▼)Triton X-100.

3. Time-resolved fluorescence study.

Table S1.   Lifetimes of PPE-SO3 with titrations of Rubpy doped SiNPs in methanol and aqueous solutions.[a]

Solvent	Wavelength / nm	[SiNP] / pM	Lifetime/ns		Amplitude/%	
			T1	T2	A1	A2
MeOH	460	0	0.44	1.40	93.6	6.4
		40	0.44	1.26	92.3	7.7
		100	0.44	1.10	88.7	11.3
		200	0.44	1.13	85.6	14.4
H_2O	540	0	0.59	2.79	64.3	35.7
		40	0.47	2.80	73.4	26.6
		100	0.37	2.81	78.3	21.7
		200	0.28	3.45	80.1	19.9

[a] T1/T2 and A1/A2 are lifetimes and relative amplitudes of each decay component.

References:
1.   Pinto, M. R.; Schanze, K. S., *Synthesis* **2002**, (9), 1293-1309.
2.   Tan, C. Y.; Pinto, M. R.; Schanze, K. S., *Chem Commun* **2002**, (5), 446-447.
3.   Santra, S. S.; Zhang, P.; Wang, K. M.; Tapec-Dytioco, R.; Tan, W. H., *Anal. Chem.* **2001,** 73, 4988-4993.