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Supporting Information

for

Efficient, Robust Surface Functionalization and Stabilization of Gold Nanorods with Quaternary Ammonium-Containing Ionomers as Multidentate Macromolecular Ligands

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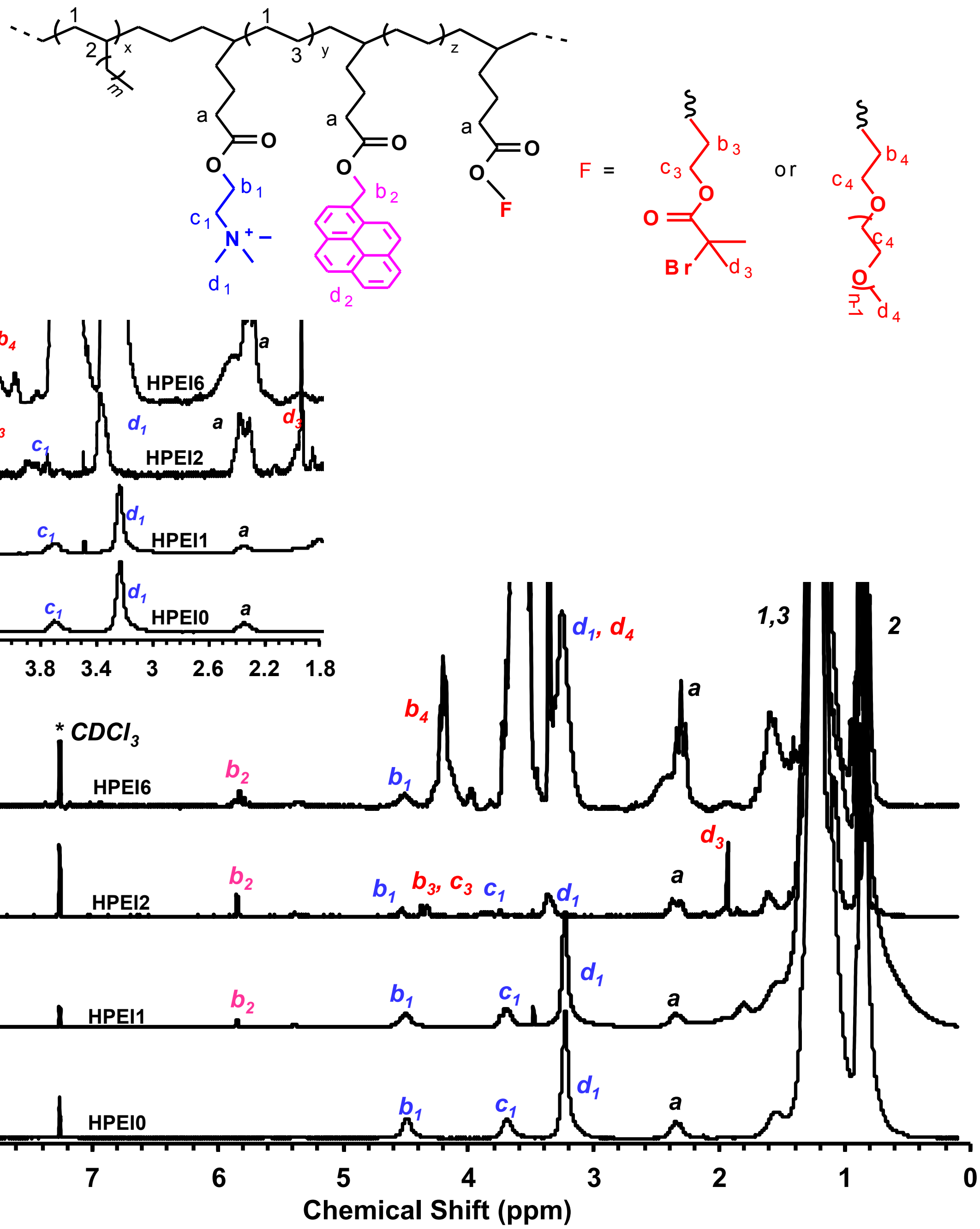

Figure S1. ^{1}H NMR spectra (in $CDCl_3$) of representative hyperbranched polyethylene ionomers (HPEI0–HPEI2 and HPEI6) containing different functionalities.

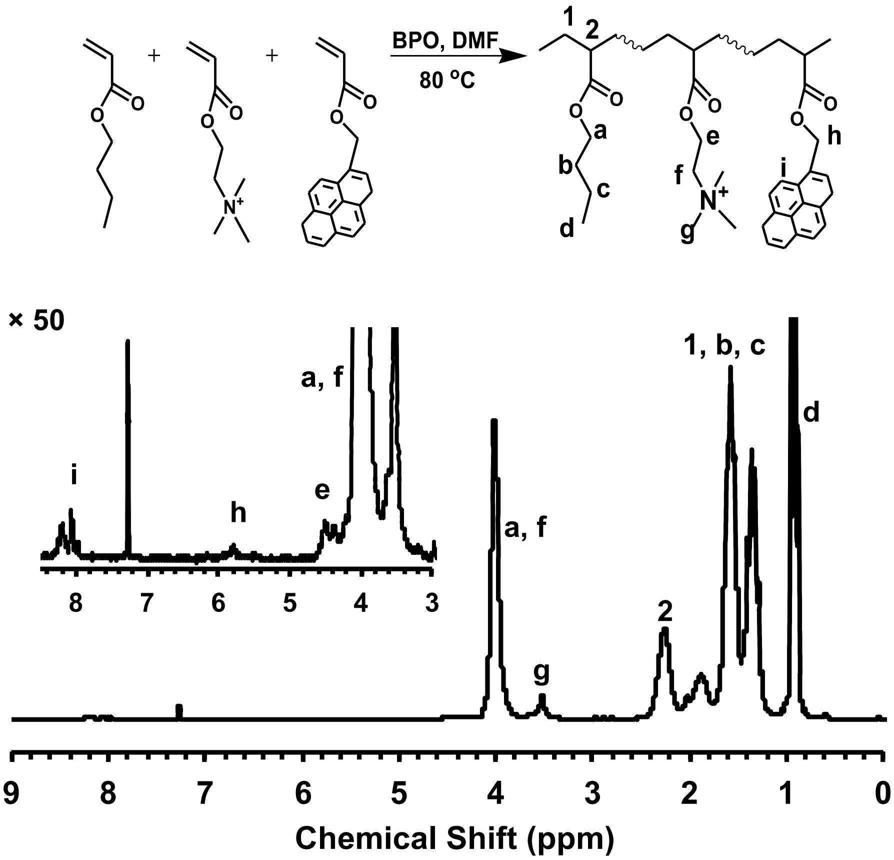

Figure S2. ^{1}H NMR spectrum of pyrene-labelled quaternary ammonium-containing poly(*n*-butyl acrylate) ionomers, PBAI.

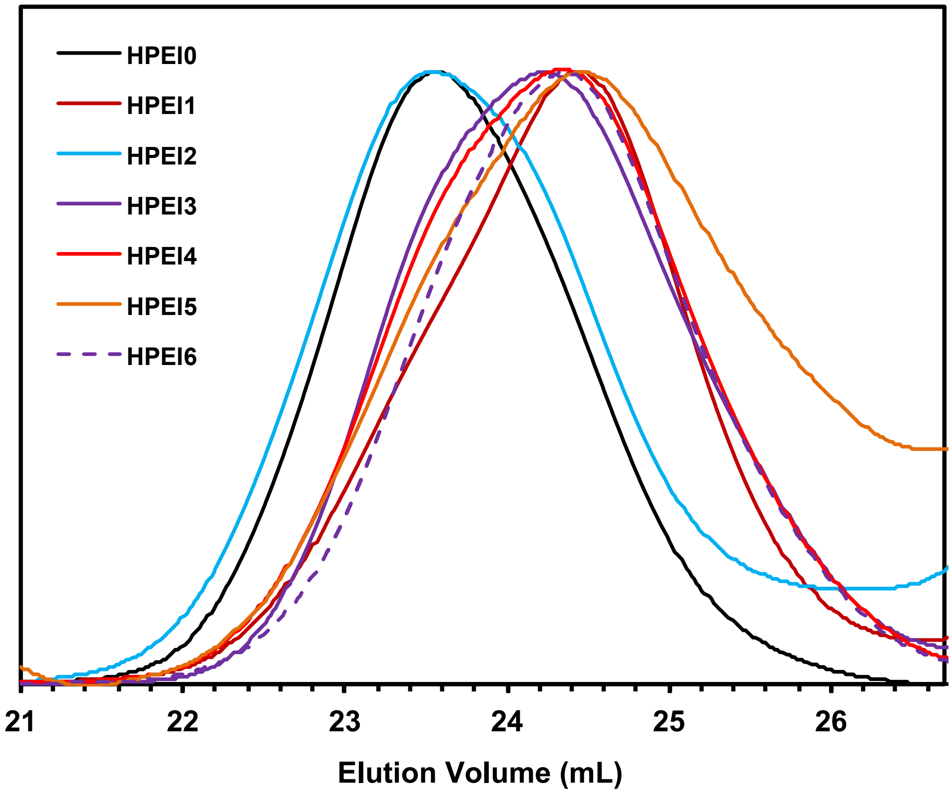

Figure S3. GPC elution curves (recorded with the DRI detector) of the hydrolyzed hyperbranched polyethylene ionomers. THF as the mobile phase at 1 mL/min and 33 ºC.

Table S1. Branching density, molecular weight data, and dilute solution properties of the hydrolyzed hyperbranched polyethylene ionomers. [a]

Ionomer	Branch density[b] (per 1000 C)	M_n[c] (kDa)	M_w[c] (kDa)	PDI[c]	M-H α[d]	η_n[e] (mL/g)
HPEI0[e]	83	13.3	18.8	1.42	0.35	12.1
HPEI1[f]	96	12.2	16.3	1.33	0.36	10.5
HPEI2	83	38.3	43.3	1.13	0.34	12.9
HPEI3	86	4.2	8.8	2.08	0.29	10.3
HPEI4	100	3.4	7.8	2.29	0.25	10.4
HPEI5	87	8.7	11.0	1.26	-0.05	9.1
HPEI6	96	3.1	8.3	2.69	0.13	12.3

[a] See Table 1 for details on the synthesis of the ionomers. [b] Branching density of ethylene sequences of the ionomers determined from their ^{1}H NMR spectra. [c] Number- and weight-average molecular weight, and polydispersity index of the hydrolyzed ionomers. [d] Mark-Houwink α constant of the hydrolyzed ionomers. [e] Number-average intrinsic viscosity of the hydrolyzed ionomers.

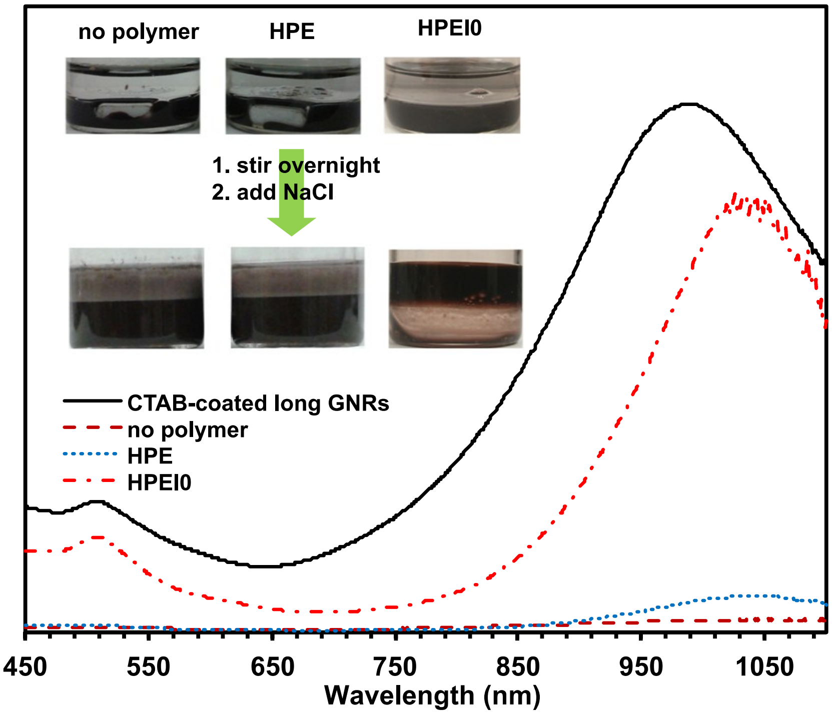

Figure S4. Control experiments showing the unsuccessful phase transfer of CTAB-coated long GNRs from aqueous phase to organic toluene phase in the case with no polymer or with nonionic hyperbranched polyethylene (HPE): UV-vis spectra of the resulting toluene phases (after the same dilution). The inset shows the photographs of the biphase mixtures before and after the process. The photographs and spectrum achieved with the use of HPEI0 are also included for comparison.

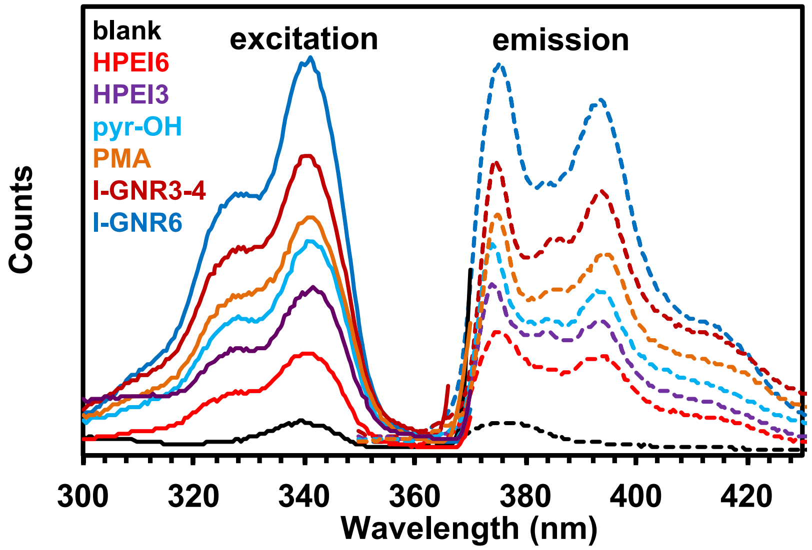

Figure S5. Fluorescent emission (em) and excitation (ex) spectra of pyrene-containing precursors, pyrene methanol (pyr-OH) and pyrenylmethyl acrylate (PMA), and representative pyrene-functionalized ionomers (HPEI3 and HPEI6) and corresponding ionomer-modified GNRs (I-GNR3-4 and I-GNR6). All the spectra were taken in THF as solvent. The emission spectra were collected at the excitation wavelength λ_{ex}=341.5 nm; the excitation spectra were collected at the emission wavelength λ_{em}=374.5 nm.

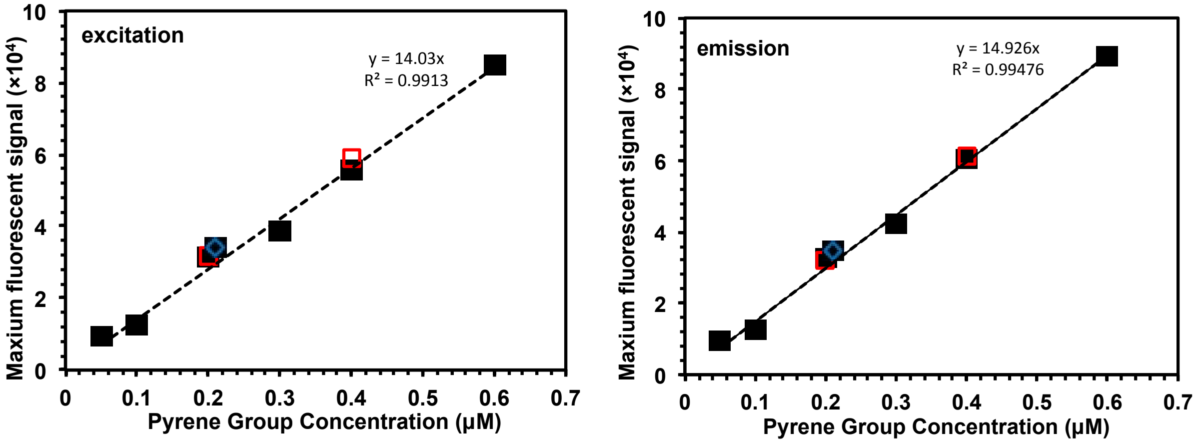

Figure S6. The fluorescence emission and excitation calibration curves (correlating the fluorescence intensity at 341.5 nm and 374.5 nm, respectively, vs. pyrene group concentration in THF) generated with pyrenylmethyl acrylate (PMA) as the concentration standard (○, concentration: 0.05, 0.1, 0.2, 0.3, 0.4, and 0.6 μmol/L). The fluorescence signals of with other pyrene-containing compounds/polyethylene ionomers with predetermined concentrations (□ for pyrene methanol with concentrations of 0.2 and 0.4 μmol/L; ◊ for HPEI2 with polymer concentration of 1 mg/L and pyrene group concentration of around 0.21 μmol/L) are also included, which fit the calibration curves well.

Table S2. Determination of ionomer content in representative ionomer-coated GNRs (I-GNR3-4 and I-GNR6) and the corresponding supernatant solutions by fluorescence quantification during the centrifugation purification procedure.

sample	ionomer feed mass[a] (mg)	Au mass, m_{Au} [b] (mg)	Solution volume [c] (mL)	Pyrene group conc.[d] (μM)	ionomer mass, m_{ionomer} [e] (mg)	$m_{\mathrm{ionomer}}/m_{\mathrm{Au}}$ [f] (mg/mg)
I-GNR3-4 [e]	**0.80**	0.46	40	0.14	0.08	0.17
Supernat. 1			200	0.24	0.66	
Supernat. 2			20	0.12	0.03	
Supernat. 3			20	0.05	0.01	
total					**0.78** [g]	
I-GNR6 [g]	**1.0**	0.1	8	0.08	0.014	0.14
Supernat. 1			200	0.16	0.72	
Supernat. 2			50	0.03	0.034	
Supernat. 3			5	0.10	0.011	
total					**0.78** [g]	

[a] The initial feed mass of ionomer to perform the ligand exchange with CTAB-coated GNRs. For other details, see Table 2 in the article on the preparation the two ionomer-coated GNRs [b] The mass of Au in the resulting ionomer-modified GNRs. [c] The volume of the resulting ionomer-modifiedd GNR dispersions or the supernatant solutions collected during the purification of ionomer-modified GNRs by centrifugation. [d] The pyrene concentration in the ionomer-modified GNR dispersions or the corresponding supernatant solutions quantified through fluorescence analysis. Negligible pyrene concentration was found in the supernatant solutions obtained after the first 3 centrifugations. [e] The ionomer mass in the dispersions of ionomer-modified GNRs or in the supernatant solutions. [f] The mass ratio of ionomer to Au in the ionomer-modified GNRs. [g] The total ionomer mass in the ionomer-modified GNRs and the supernatant solutions.

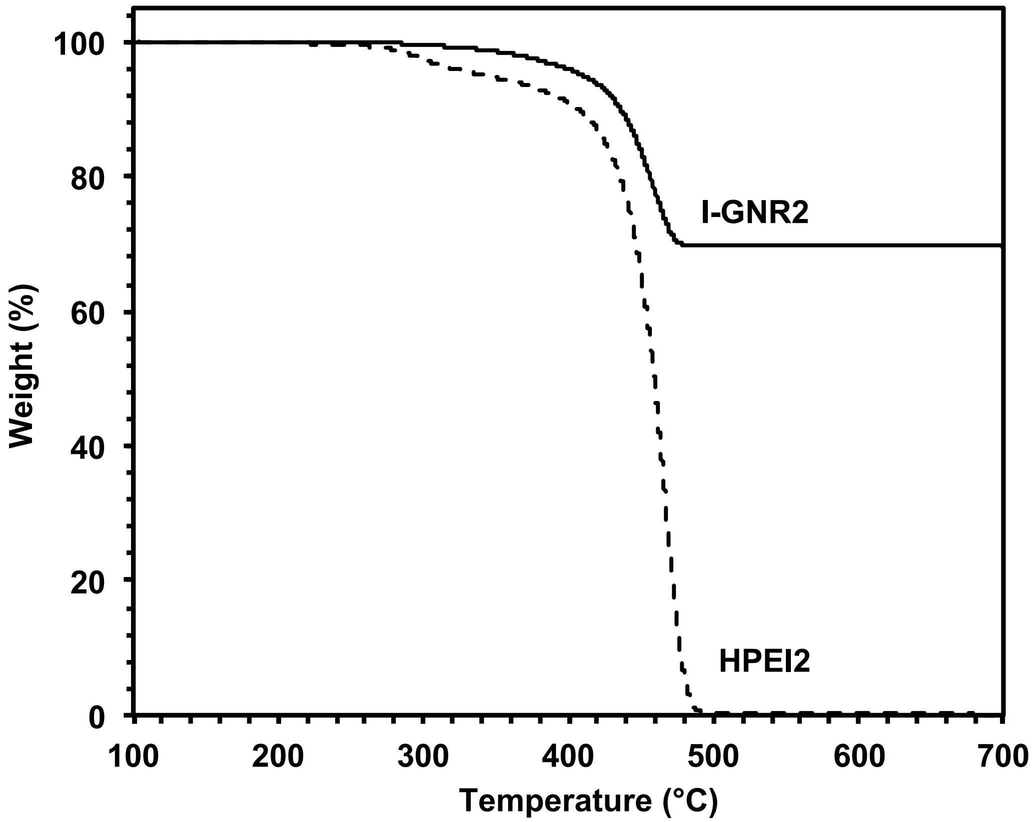

Figure S7. TGA curves of pure HPEI2 and the HPEI2-modified GNRs, I-GNR2. TGA was undertaken in a nitrogen atmosphere with a heating rate of 10 ºC/min. As per the TGA results, I-GNR2 has a HPEI2 content of 30.5 wt%, which agrees well with the value of 31.0 wt% determined by fluorescence measurement.

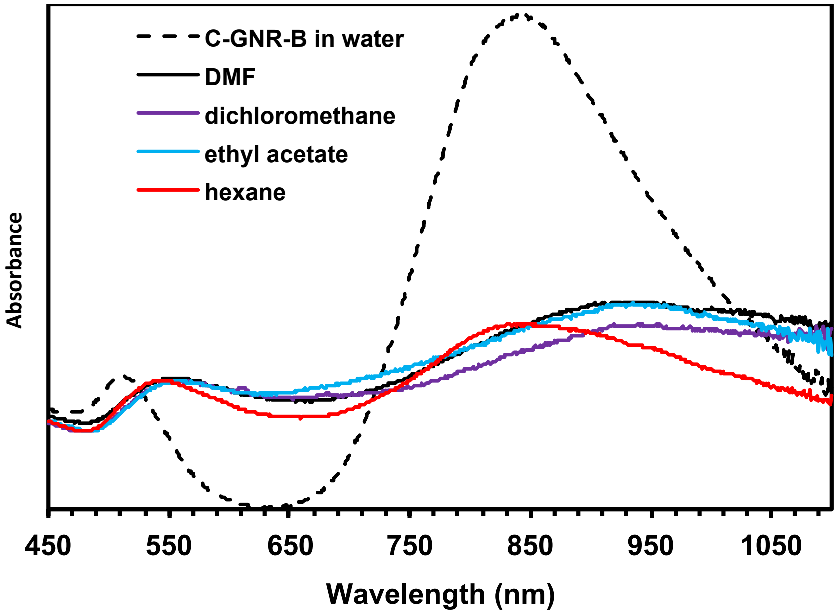

Figure S8. UV-vis spectra of I-GNR3-3 in DMF, dichloromethane, ethyl acetate, and hexane. The dispersions were prepared by adding a small volume of THF solution of I-GNR3-3 into the corresponding solvent (volume ratio = 1:9), followed with one round of centrifugation and the resuspension in the corresponding pure solvent.

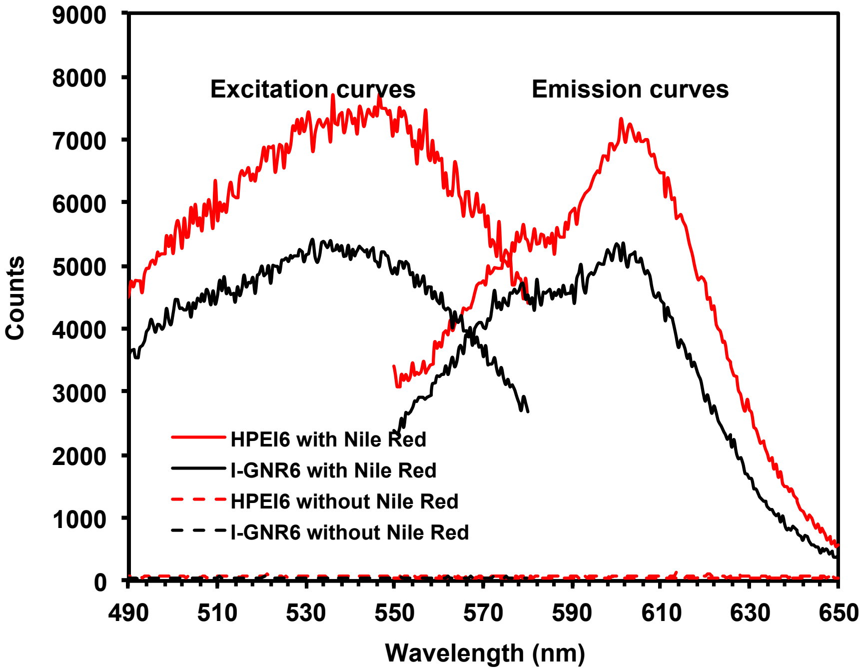

Figure S9. Fluorescence spectra of HPEI6 (concentration: 0.5 mg/mL) and I-GNR6 (concentration: 5.7 mg/mL) encapsulating Nile Red with the excitation spectra taken at emission wavelength λ_{em} = 601 nm and emission spectra taken with excitation wavelength λ_{em} = 535 nm. The spectra of HPEI6 and I-GNR6 without containing Nile Red are also included for comparison.

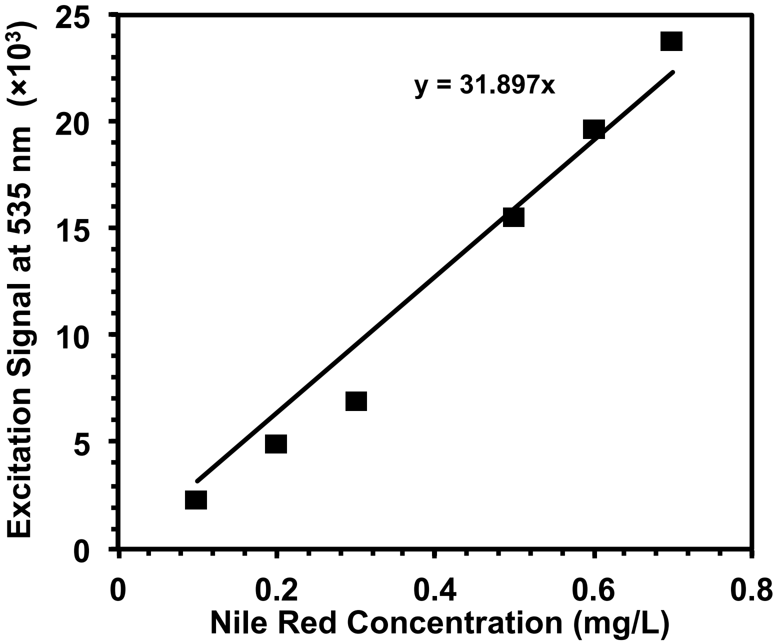

Figure S10. The calibration curve correlating the fluorescent excitation signal at 535 nm (λ_{em} = 601 nm) with the concentration of Nile Red encapsulated within sodium dodecyl sulfate (SDS) in aqueous dispersion. Standard dispersions containing different concentration (0.1, 0.2, 0.3, 0.5, 0.6, and 0.7 mg/L) of Nile Red encapsulated within SDS (a fixed concentration of 30 mg/mL in the dispersion) were prepared by referring to the work by Guan et al. (*J. Am. Chem. Soc.* **2004**, *126*, 2662–2663). Fluorescent excitation spectra of these dispersions were measured at λ_{em} = 601 nm, which show maximum intensity at 535 nm.