

Supporting Information

Graphene Oxide Enhanced Fluorescence of Conjugated Polyelectrolytes with Intramolecular Charge Transfer Characteristics

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Experimental Section

Materials. Poly[9,9-bis(6-*N,N,N*-trimethylammonium)ethoxy)ethoxy)ethyl)-fluorene-*alt*-4,7-(2,1,3-benzothiadiazole) dibromide] (PFBT), poly[9,9-bis(6'-*N,N,N*-dimethylamine)hexyl)-fluorenyldivinylene-*alt*-4,7-(2,1,3,-benzothiadiazole) dibromide] (PFVBT) and poly[9,9'-bis(6-*N,N,N*-trimethylammonium)-hexyl)-2,7-fluorenyldivinylene-*alt*-1,4-phenylene dibromide] (PFVP) were synthesized according to the previous reports.^[1, 2] GO was synthesized from graphite by a modified Hummers method.^[3] Toluene, *N,N*-dimethylformamide (DMF) and dichloromethane (DCM) were obtained from Merck (Germany). Milli-Q water was supplied by Milli-Q Plus System (Millipore Corporation, Bedford, USA).

Synthesis of GO. GO was synthesized from microwave-expanded graphite by a modified Hummers method.^[3] In brief, 0.3 g microwave-expanded graphite was added into a mixture of 2.4 mL 98% H₂SO₄, 0.5 g K₂S₂O₈, and 0.5 g P₂O₅. The solution was maintained at 80 °C for 4.5 h. The resulting pre-oxidized product was cleaned by water and dried in a vacuum oven. Then the pre-oxidized product was added into 12 mL of 98% H₂SO₄, followed by slow addition of 1.5 g KMnO₄ with the temperature maintained at below 20 °C in order to avoid overheating and explosion. The solution temperature was increased to 35 °C and maintained for 2 h. Then 25 mL of H₂O was added. After 2 h, additional 70 mL of H₂O was added to dilute the solution, and 2 mL of 30% H₂O₂ was injected into the solution to completely react with the excess KMnO₄. A bright yellow solution was obtained. The resulting mixture was washed with HCl and H₂O to yield the graphite oxide.

Characterization and Instrumentation. The UV-vis absorption spectra of CPEs were measured using a Shimadzu UV-1700 spectrophotometer. Their fluorescence measurements were carried out on a Perkin-Elmer LS-55 instrument equipped with a xenon lamp excitation source and a Hamamatsu (Japan) 928 photomultiplier tube (PMT), using 90° angle detection

for solution samples. The instrument was controlled by FL WinLab Software. The surface morphologies of CPEs/GO mixtures were studied by Atomic force microscopy (AFM) on a Digital Instrument Nanoscope III scanning probe microscope, operating at the tapping mode. Their morphologies were also studied by field emission transmission electron microscopy (FE-TEM) (JEM-2010F, JEOL, Japan).

Fluorescence Evolution Study. PFBT stock solution (6 μL , 0.5 mM) and Milli-Q water (1 mL) were transferred to a PMMA cuvette (1.5 mL) to yield a solution with [PFBT] = 3 μM (unit based). GO solution (0.2 $\text{mg}\cdot\text{mL}^{-1}$ or 2 $\text{mg}\cdot\text{mL}^{-1}$) was subsequently added dropwise with the desired amounts into the cuvette. Upon each addition, the mixture was gently mixed 5 times using pipette and then used for PL measurements directly. The fluorescence evolution of PFVBT and PFVP was also studied following the similar procedure.

Fluorescence Lifetime Study. Fluorescence lifetime measurements were performed on a FluoTime 200 TCSPC fluorescence platform from Picoquant GmbH (Berlin, Germany). A Titanium-sapphire 100 fs laser (Chameleon, Coherent) with second- and third-harmonic generation was used as the excitation source with excitation wavelength of 440 nm. In time correlated single photon counting (TCSPC) apparatus, the detector is a microchannel plate (MCP) PMT system HAM-R3809U-50 (Hamamatsu) and has a spectral sensitivity from 160 to 850 nm and instrument response function of 30 ps. Fluorescence lifetimes were extracted from the decay curves using commercially available fluorescence lifetime analysis software (FluoFit Pro. PicoQuant GmbH). Fluorescence decay curves were fitted using a two exponential mode.

Reference

1. K. Y. Pu, L. P. Cai, B. Liu, *Macromolecules* **2009**, *42*, 5933.
2. C. Wang, R. Y. Zhan, K. Y. Pu, B. Liu, *Adv. Func. Mater.* **2010**, *20*, 2597.

3. Y. Xu, H. Bai, G. Lu, C. Li, G. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 5856.

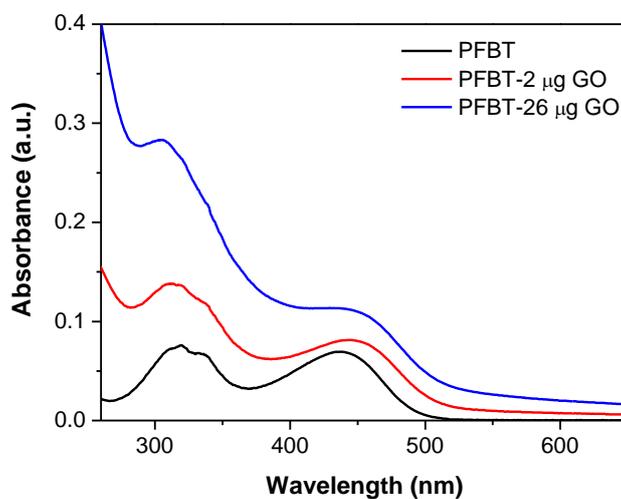


Figure S1. The absorption spectra of 3 μM PFBT in the absence (black) and presence of 2 μg GO (red) as well as 26 μg GO (blue).

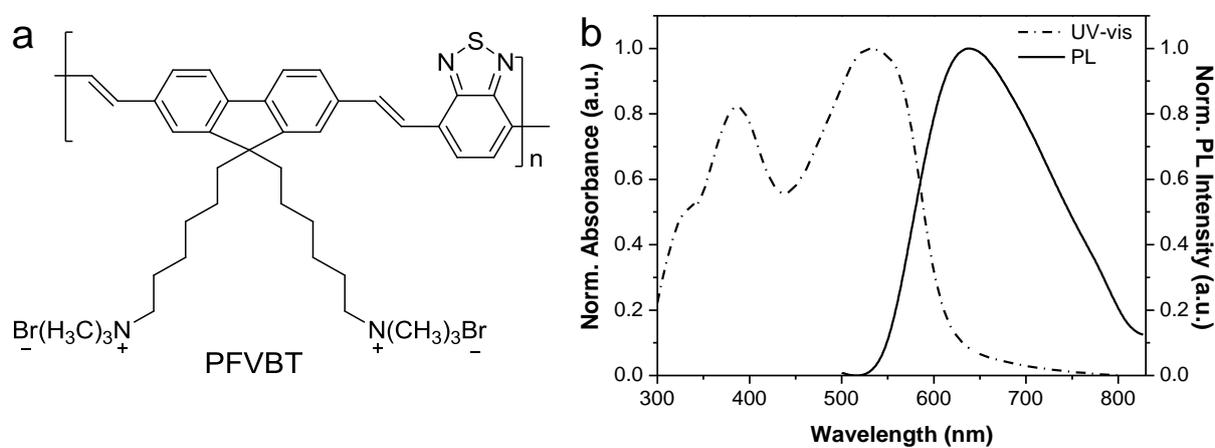


Figure S2. (a) Chemical structure of PFVBT. (b) Normalized UV-vis absorption and PL spectra of PFVBT in water.

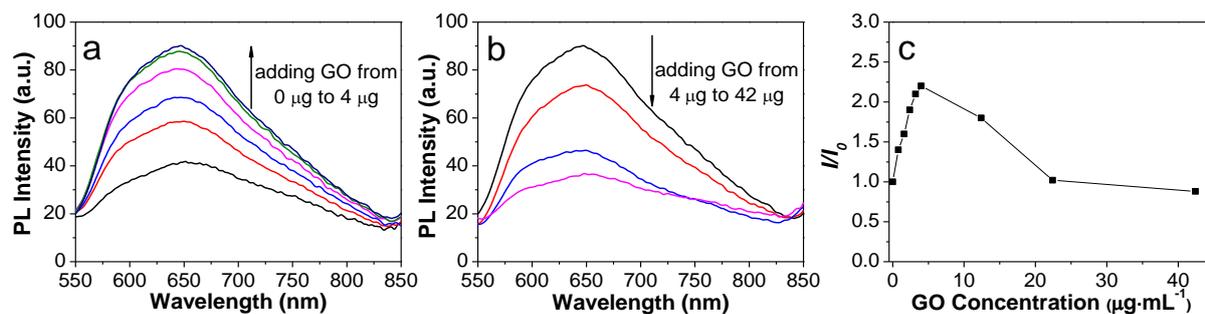


Figure S3. (a) PL spectra of 3 μM PFVBT in water with adding GO from 0 to 4 μg·mL⁻¹ at 0.8 μg interval. (b) PL spectra of 3 μM PFVBT in water in the presence of GO at concentrations of 4, 12, 22 and 32 μg·mL⁻¹. (c) I/I_0 as a function of [GO] in water, where I_0 is the fluorescence intensity of PFVBT in water and I is the fluorescence intensity of the same amount of PFVBT in the presence of GO. $\lambda_{\text{ex}} = 540$ nm.

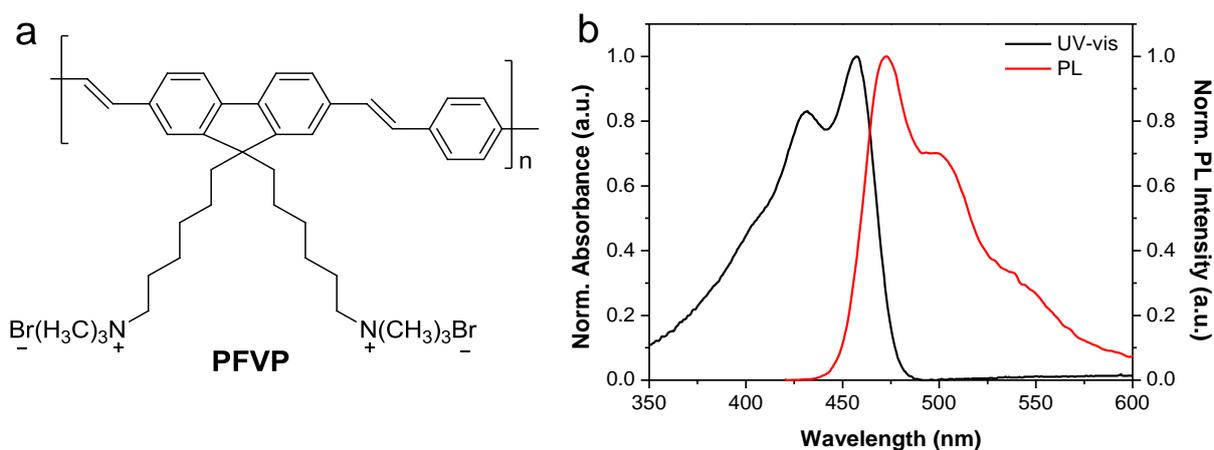


Figure S4. (a) Chemical structure of PFVP. (b) Normalized UV-vis absorption and PL spectra of PFVP in water.

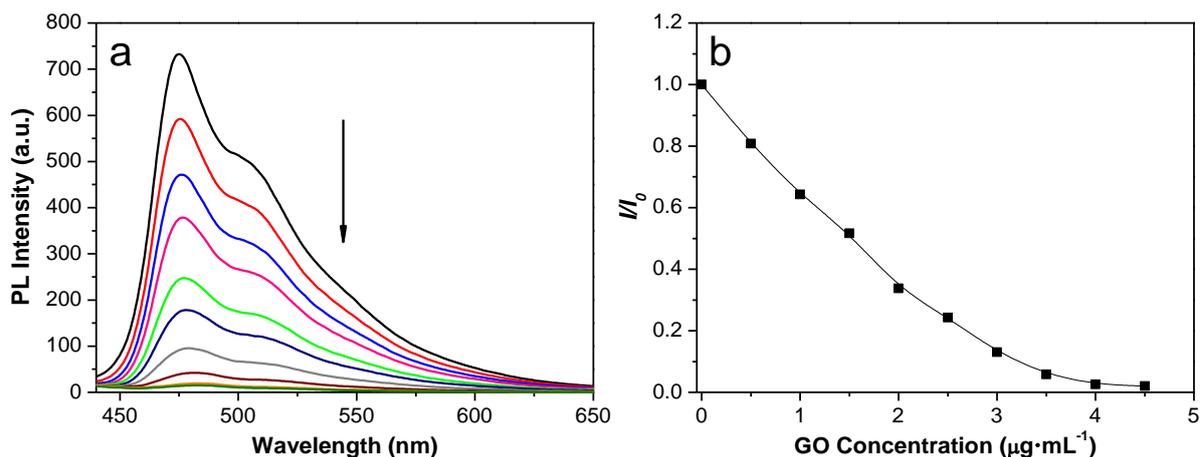


Figure S5. (a) PL spectra of 3 μM PFVP in water upon addition of GO from 0 to 4.5 μg at an interval of 0.5 μg upon excitation at 420 nm. (b) I/I_0 as a function of [GO] in water, where I_0 is the fluorescence intensity of PFVP in water and I is the fluorescence intensity of the same amount of PFVP in the presence of GO.

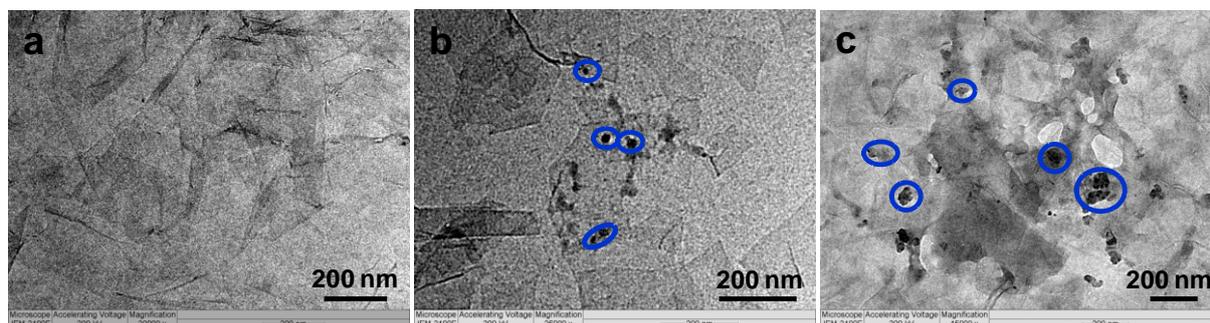


Figure S6. FE-TEM images of (a) GO, (b) GO/PFBT with enhanced PFBT fluorescence at $[\text{GO}] = 2 \mu\text{g}\cdot\text{mL}^{-1}$, $[\text{PFBT}] = 3 \mu\text{M}$ and (c) GO/PFBT with quenched PFBT fluorescence at $[\text{GO}] = 26 \mu\text{g}\cdot\text{mL}^{-1}$, $[\text{PFBT}] = 3 \mu\text{M}$. PFBT aggregates are marked by the blue circles.

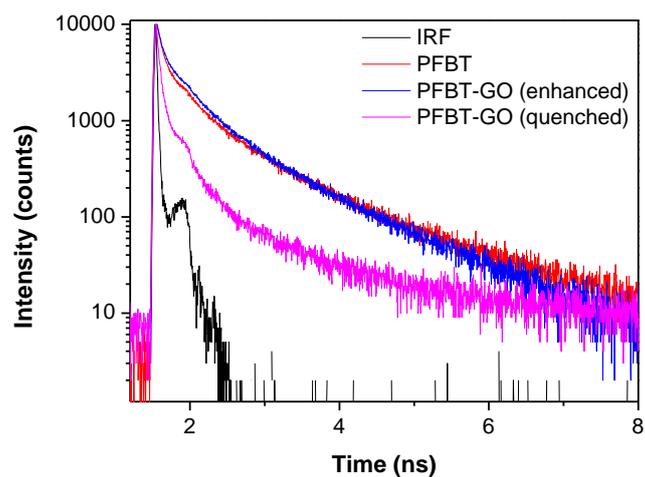


Figure S7. Fluorescence decay curves for of PFBT (red), GO/PFBT (blue) at $[GO] = 2 \mu\text{g}\cdot\text{mL}^{-1}$, GO/PFBT (pink) at $[GO] = 26 \mu\text{g}\cdot\text{mL}^{-1}$.