
Supporting Information for

Ultrafast Electron Injection at the Cationic Porphyrin- Graphene Interface Assisted by Molecular Flattening

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Table of Contents

Experimental Section.

Materials. 5,10,15,20-tetra(4-pyridyl)-porphyrin (TPyP), 5,10,15,20-tetra(1-methyl-4-pyridino)-porphyrin tetra(p-toluenesulfonate) (TMPyP) and 5,10,15,20-tetra(4-trimethyl-ammoniophenyl)-porphyrin tetra(p-toluene-sulfonate) (TMAP) were supplied by Frontier Scientific. Carboxyl Graphene (GC) purchased from ACS Materials.

Instsurmentation

Stationary Spectroscopy. Absorption spectra were measured on a Cary 5000 UV-VIS-NIR spectrophotometer (Varian Inc.), while the steady-state photoluminescence spectra were measured using a Jobin-Yvon-Horiba Fluoromax-4 spectrofluorometer.

Raman Spectroscopy. Raman spectra were measured on a LabRam Aramis Raman specrometer from Horiba Jobin Yvon, using a laser wavelength of 473 nm and an integration time of 60 seconds.

Time-resolved Spectroscopy. Time-resolved absorption decays were measured with a pump-probe setup in which a white light continuum probe pulse was generated in a 2 mm-thick sapphire plate contained in an Ultrafast System LLC spectrometer by pulse energy of a few µJ. The fundamental output came from a Ti:Sapphire femtosecond regenerative amplifier operating at 800 nm with 35 fs pulses and a repetition rate of 1 kHz. Spectrally tunable (240-2600 nm) femtosecond pulses generated by an Optical Parametric Amplifier (Light Conversion LTD) and a white light continuum were used, respectively, as the pump (excitation)- and probe beams in the pump-probe experimental setup (Helios). To detect the entire time resolved fluorescence spectrum simultaneously, we decided to use a Halcyone MC multichannel fluorescence upconversion spectrometer with 150 fs temporal resolution (Ultrafast Systems, USA). In these experiments a 2 mm thick cuvette containing a solution of DHAQ was excited with 0.5 mW of 440 nm light. The fundamental pulse was used as a gate pulse for the up-conversion process. Finally, the sample fluorescence was mixed with the gate pulses in a nonlinear crystal (BBO) and the sum-frequency signal was detected by a photon-counting method. *Finally,* Time-Correlated Single Photon Counting (TCSPC) was used for lifetime measurements. The excitation wavelength for both TCSPC and fluorescence upconversion was 440 nm.

Raman Data.

The interaction has been confirmed by Raman Spectroscopy,the spectra recorded for GC, free porphyrins and porphyrin-GC mixtures as given in Figure S4-S6. The Raman spectra of GC shows two peaks, the E_{2g} vibration mode of sp^2 bonds at 1595 cm^{-1} and breathing modes of six-atom rings at 1365 cm^{-1}.[1] These bands show a spectral shift in the presence of TMPyP, indicating less freedom upon binding. A similar behavior is observed upon interaction between electrondonor and electron-acceptor molecules.[2,3] Raman spectra of TMPyP upon GC addition show evidence of the interaction as well. The band appearing at 1299 cm^{-1} is assigned to pyridine bending and the A_{1g} symmetry almost disappears in the TMPyP-CG spectra that indicate the flipping or twisting of the pyridine ring when porphyrin is attached with GC surface. The band at 658 cm^{-1} assigned to the bending of the pyridine ring ($C-N^+-CH_3$) shifted to 673 cm^{-1}.[4, 5] The TMPyP band at 402 cm^{-1} assigned to in-plane bending of the porphyrin core and pyridine ring, is shifted to 380 cm^{-1} with a strong shoulder band at 407 cm^{-1} in the TMPyP-GC spectra, which confirms that the interaction takes place through the porphyrin cavity as well as with the pyridine ring.[4] A similar behavior has been observed for the TMAP (See Figure S5). On the other hand, no changes in the Raman spectra are observed for the neutral TPyP upon GC addition (see Figure S6)

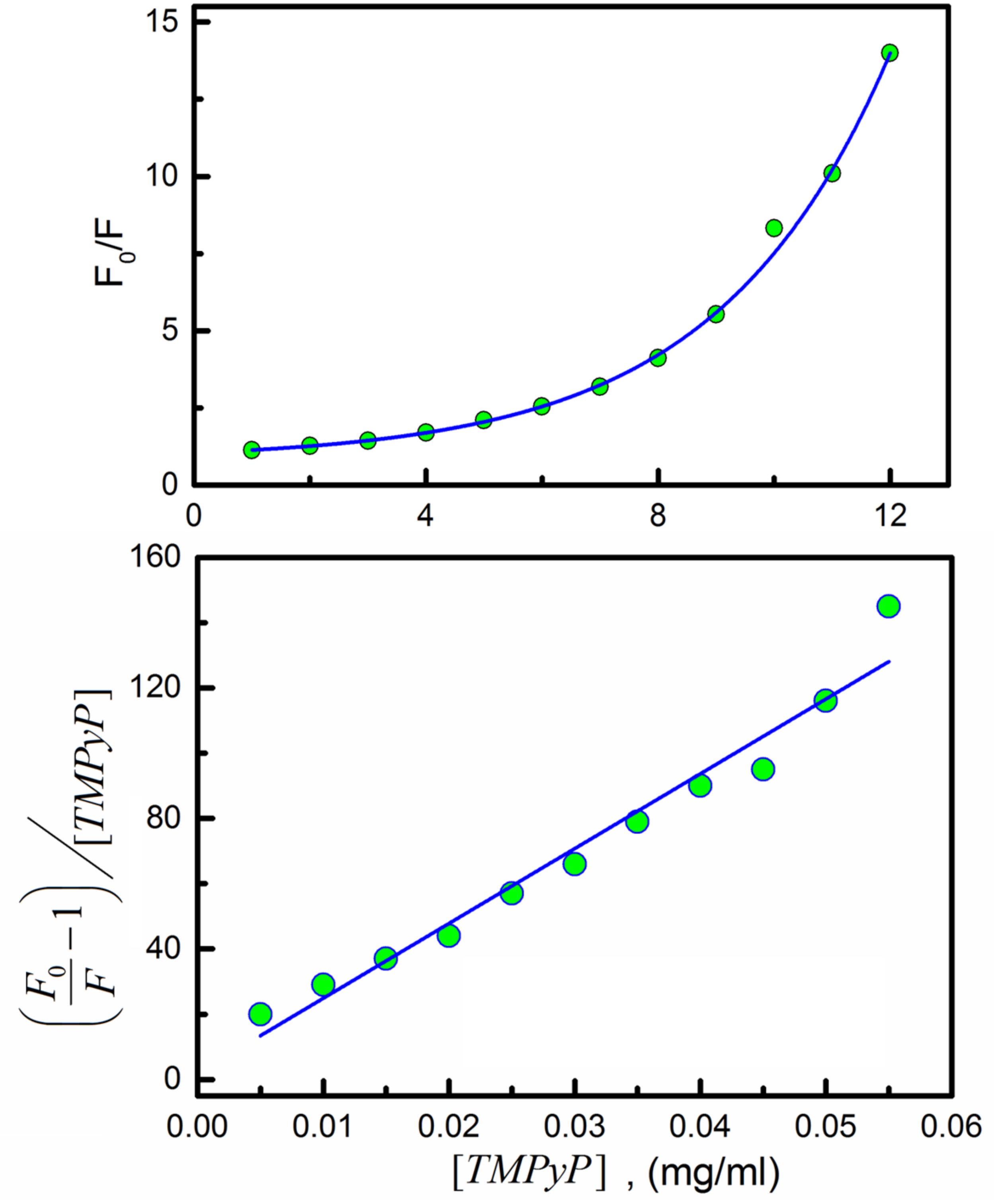

Figure S1. (A) Stern-Volmer and (B) Modified Stern-Volmer plots for the quenching of TMPyP by GC.

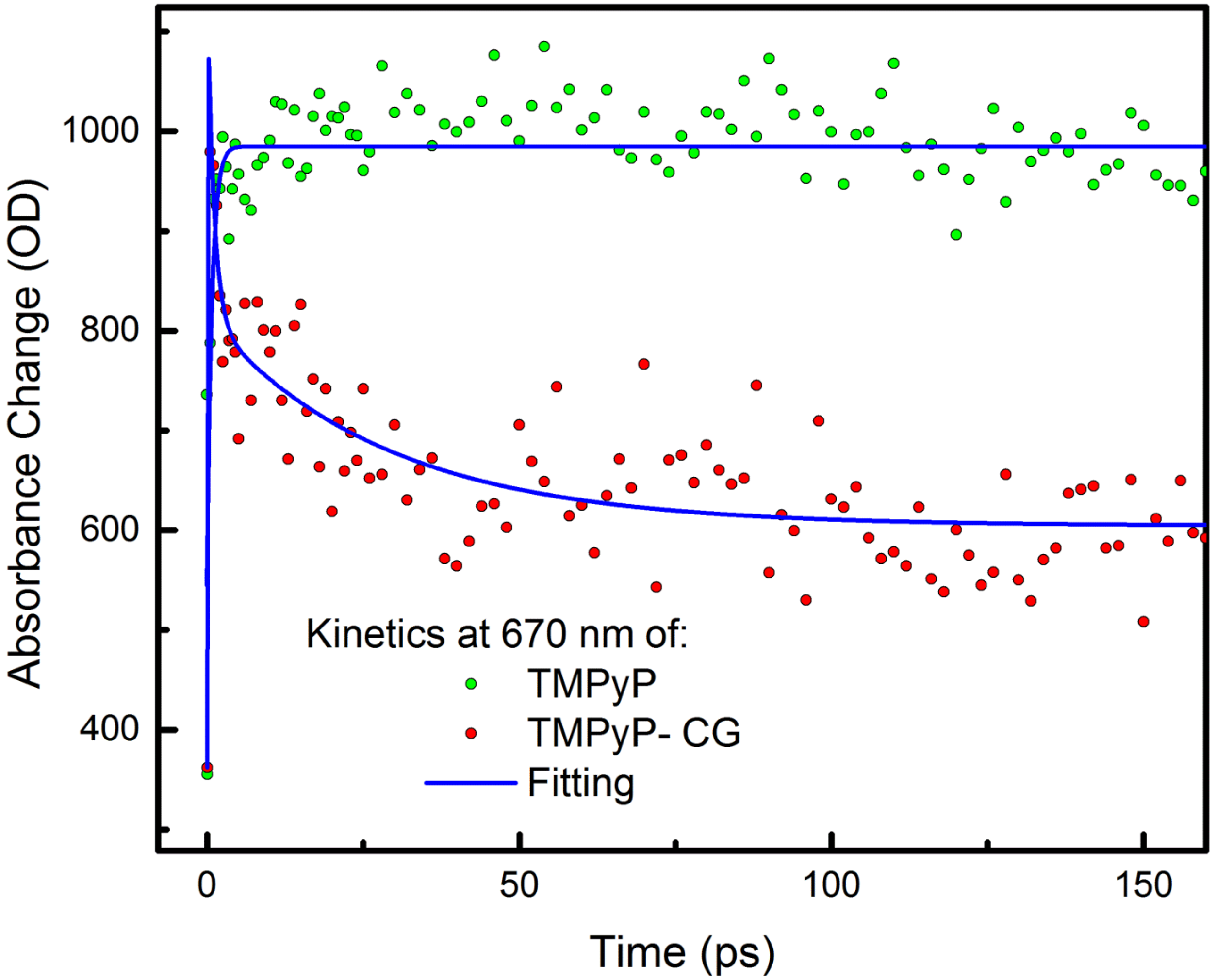

Figure S2. Fluorescence upconversion kinetic profile collected using excitation at 440 nm of TMPyP (green) and TMPyP- GC (red) monitored at 670 nm.

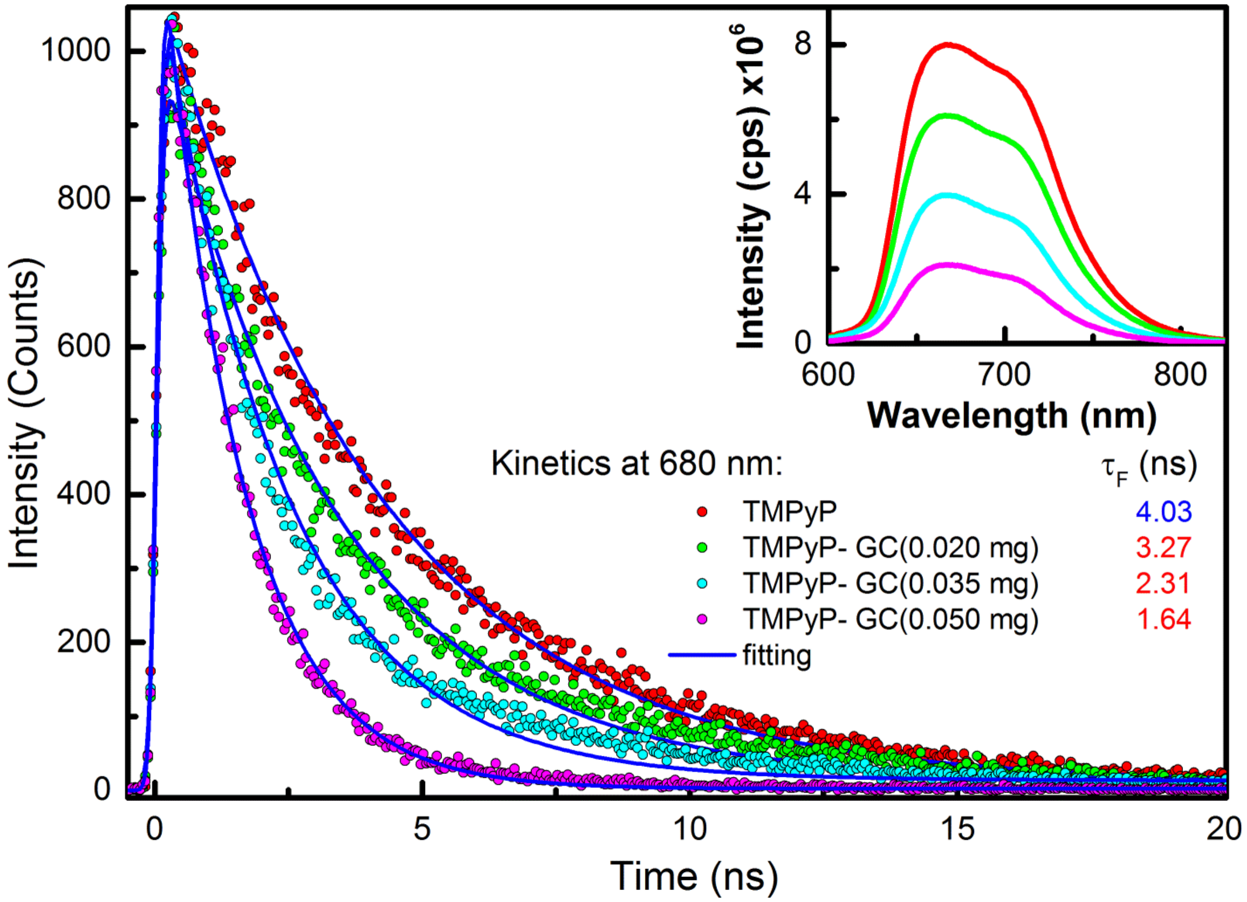

Figure S3. Time correlated single photon counting (TCSPC) kinetic profile collected using excitation at 440 nm of TMPyP and TMPyP- GC (concentrations indicated on graph) monitored at 680 nm. Inset showing the fluorescence of the solutions used for the TCSPC measurements. Fluorescence lifetimes are given on the graph.

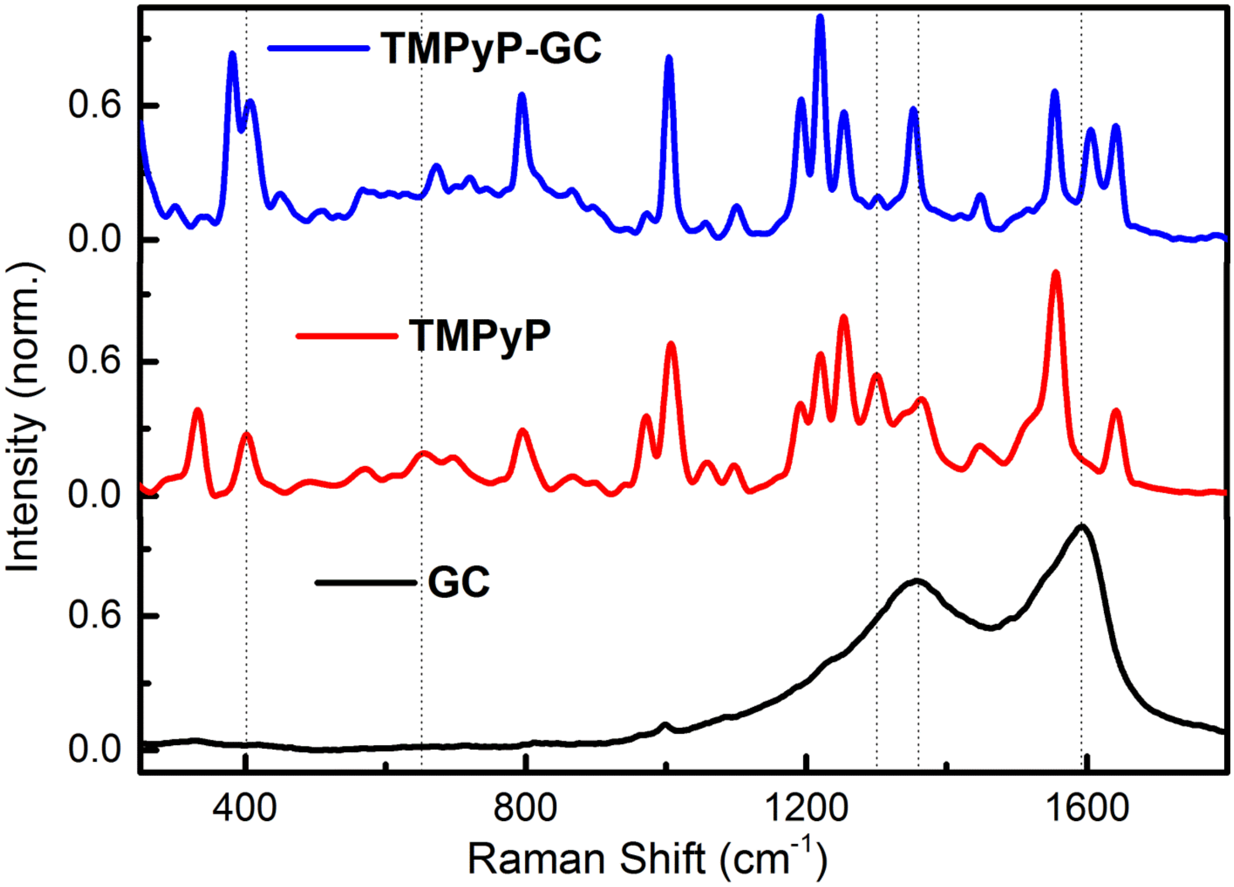

Figure S4. Raman Spectra of GC(black), TMPyP(red), and TMPyP-GC(blue) measured using 473 nm excitation.

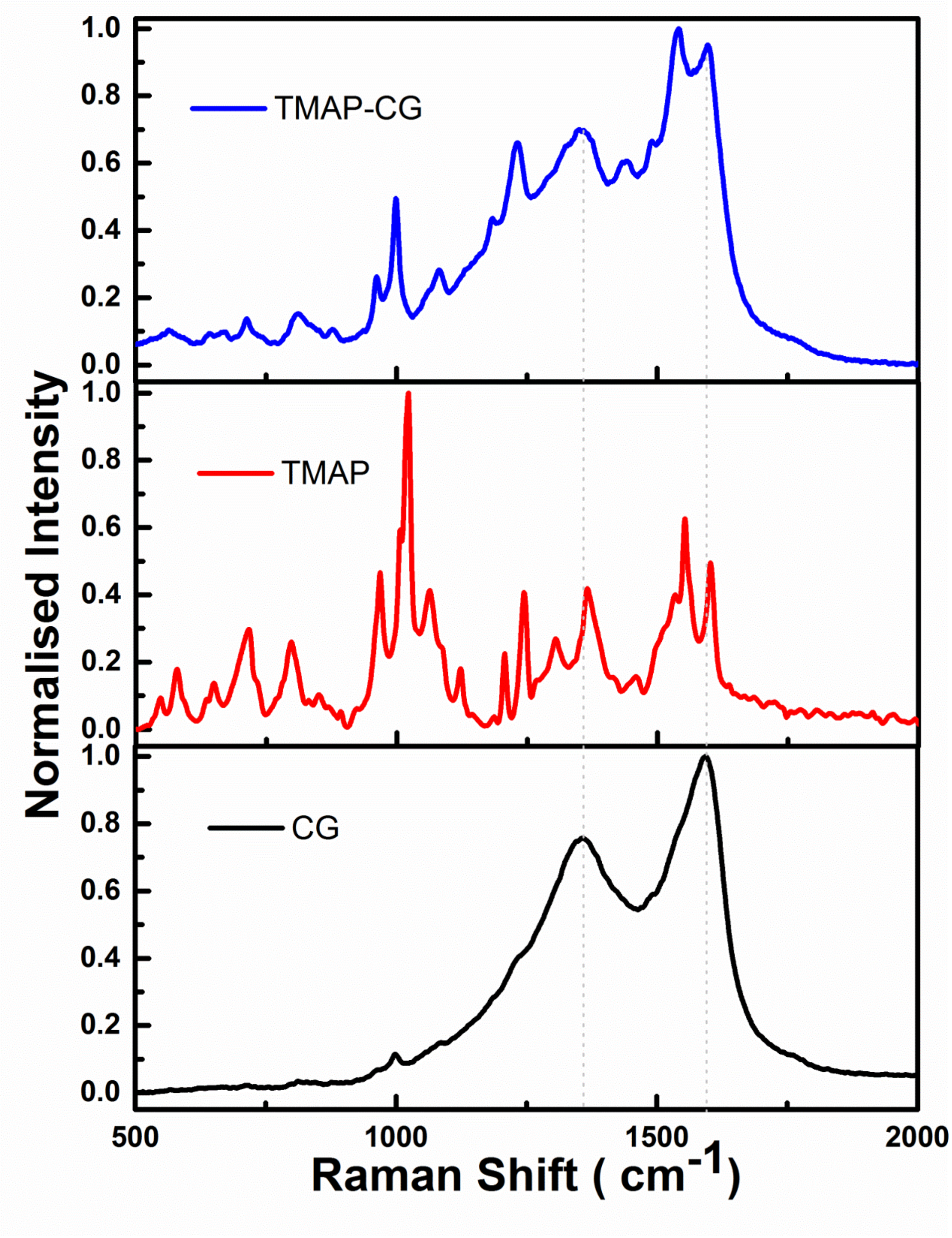

Figure S5. Raman Spectra of GC(black), TMAP(red), and TMAP-GC(blue) measured using 473 nm excitation.

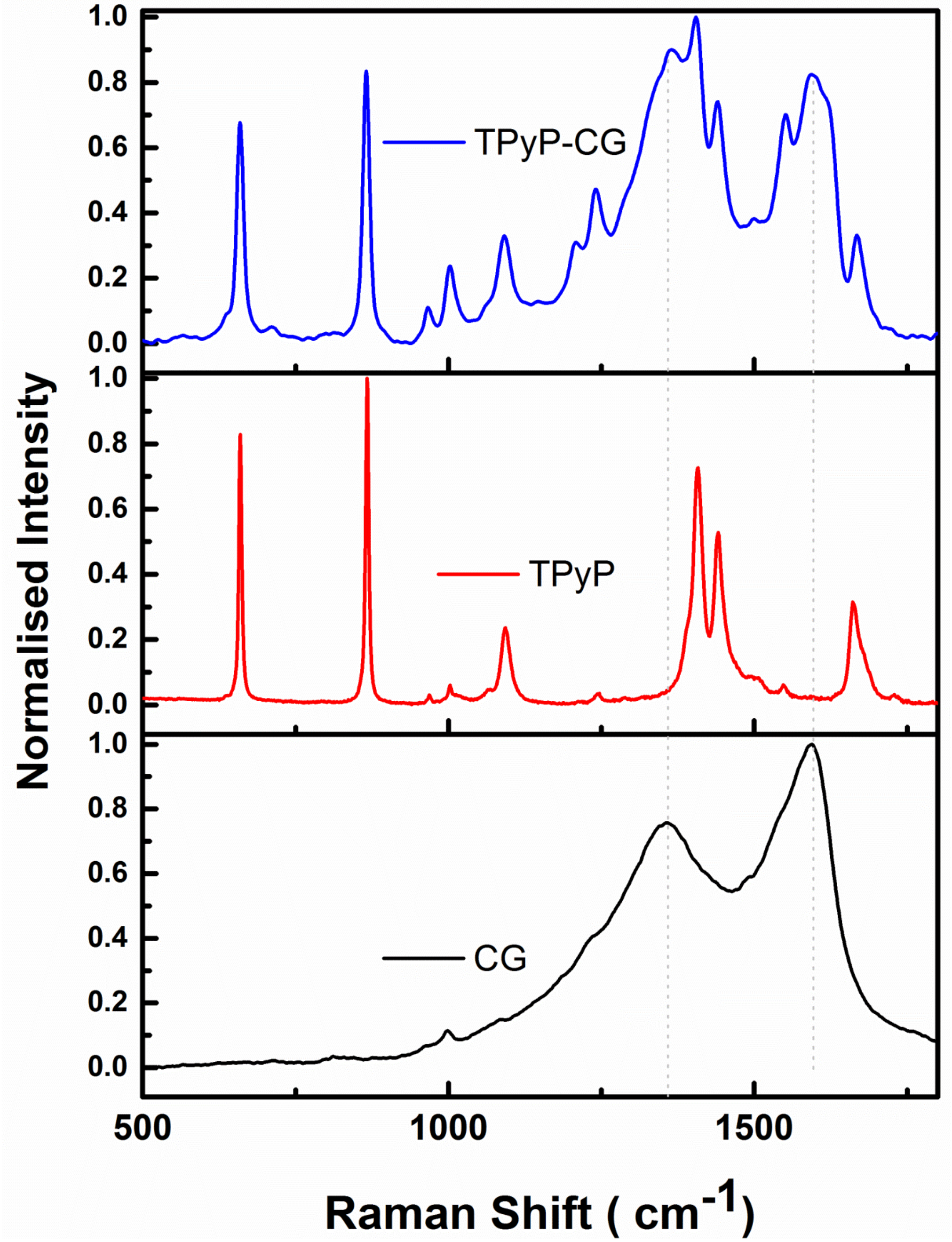

Figure S6. Raman Spectra of GC(black), TPyP(red), and TPyP-GC(blue) measured using 473 nm excitation.

References.

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