Supplementary Information

To what extent can charge localization influence electron injection efficiency at graphene-porphyrin interfaces?

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Experimental Section.

Materials. 5,10,15,20-tetra(1-methyl-4-pyridino)-porphyrin tetra(p-toluenesulfonate) (TMPyP) was supplied by Frontier Scientific. Graphene Carboxylate (GC) purchased from ACS Materials. β-Cyclodextrin (CD) purchased from sigma Aldrich.

Instrumentation

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).

Cyclic Voltammetry. Cyclic voltammetry (CV) was carried out using 10 mM $K_4[Fe(CN)_6]$ containing 0.1 M KCl as supporting electrolyte at a scan rate of 50 mV/s. The studies were carried out by VMP3 biologic instrument with a three electrode electrochemical cell comprising of glassy carbon electrode (3 mm dia.) as working electrode, Ag/AgCl (3 mM KCl solution) as reference electrode, and Pt wire as counter electrode.

Raman Spectra. The band at 1364 cm^{-1} assigned to the stretching of the (C_α-N) appears at shifted 1353 cm^{-1} indicating the less freedom occurred to this vibration upon binding. The band appearing at 1299 cm^{-1} is assigned to pyridine bending and the A_{1g} symmetry almost disappears in the TMPyP-CD-GC spectra that indicate the flipping or twisting of the pyridine ring when porphyrin is attached with GC surface.[1] The band at 970 assigned to the in-plane bending of the pyridyl ring also appear with decreased intensity in the TMPyP-CD-GC spectra indicating the permissible bending of the pyridine ring after binding onto GC surface which is considered as absent of metalation process.[1,2] 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. In the TMPyP spectra, the band appearing at 332 cm^{-1} assigned to in-plane bending of the porphyrin core, and the A_{1g} symmetry, also appears in the TMPyP-CD-GC spectra with decreased intensity as a signature of absent of metalation process.[2]

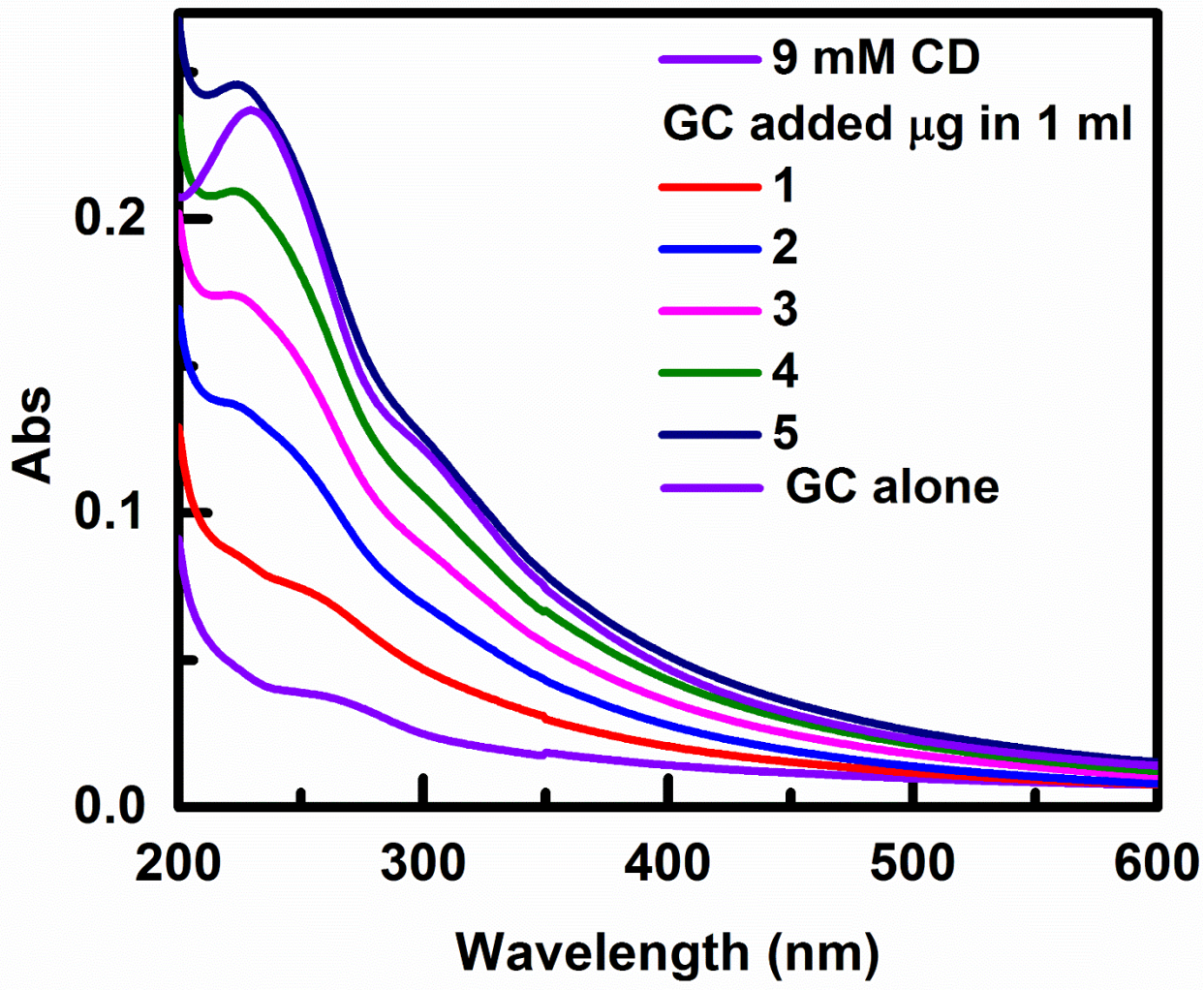

Fig S1. Effect of successive additions of GC (concentration on the graph) on ground-state absorption of CD.

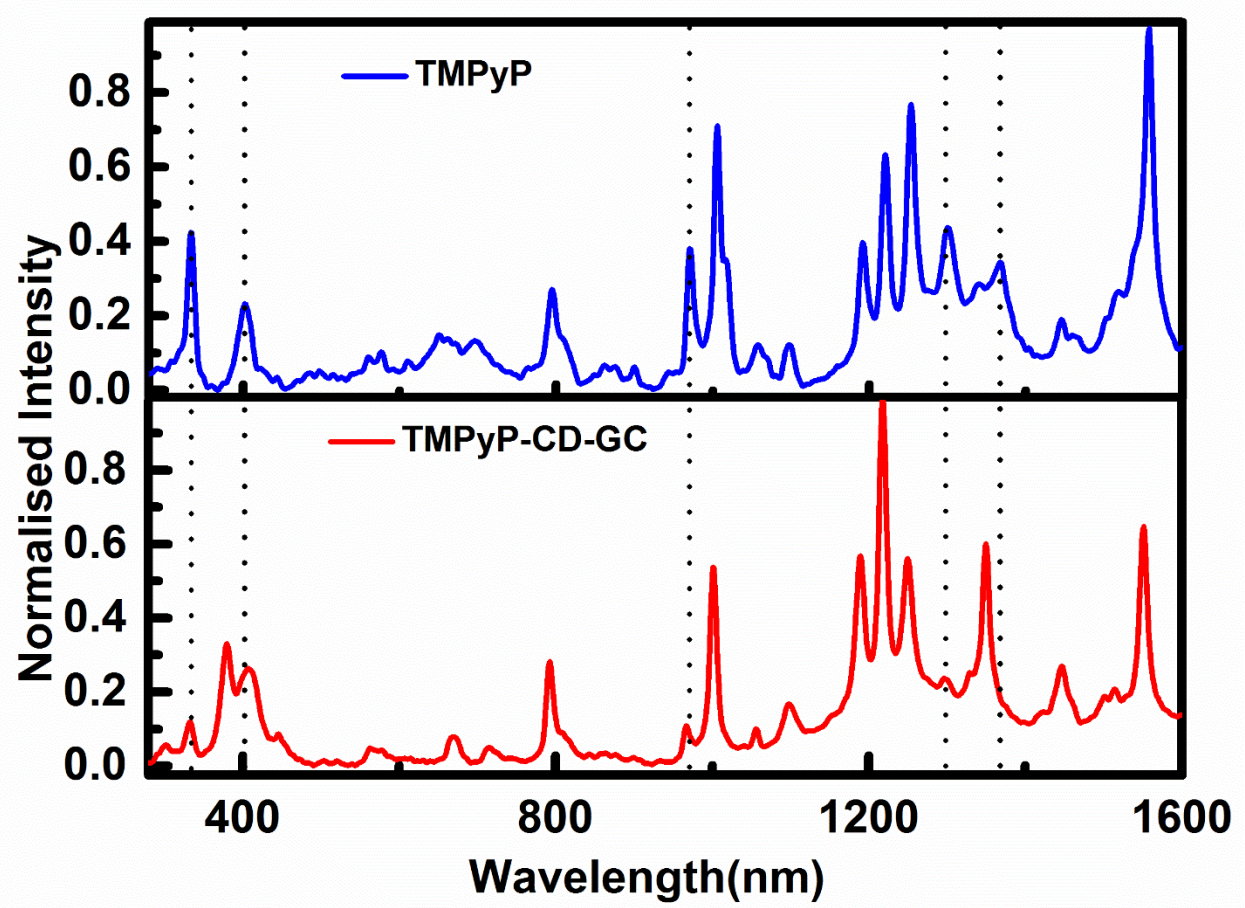

Fig S2. Raman spectra of TMPyP and TMPyP-CD-GC

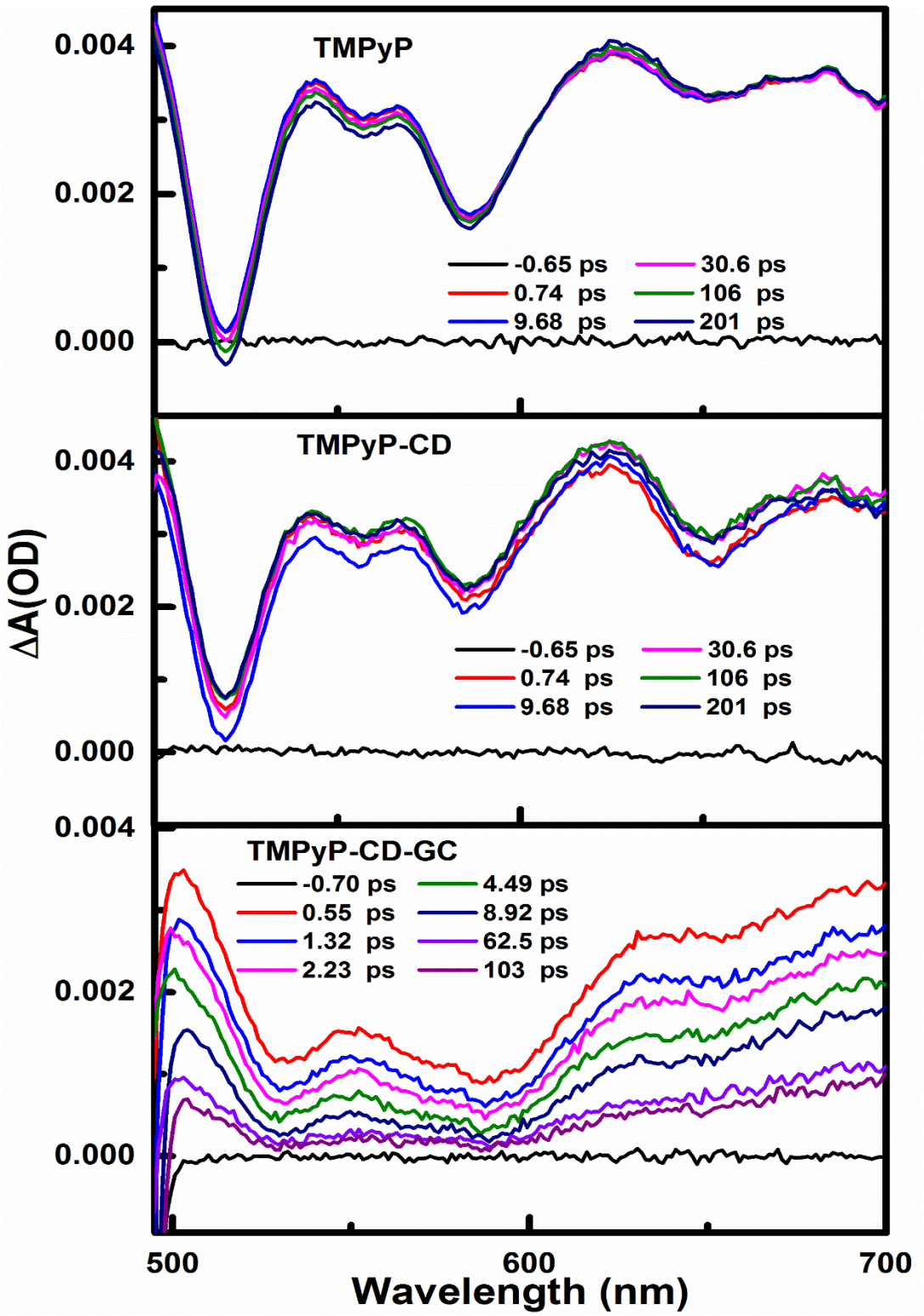

Fig S3. Femtosecond transient absorption spectra recorded after 475 nm pulsed laser 120 fs excitation for TMPyP, TMPyP-CD and TMPyP-CD-GC.

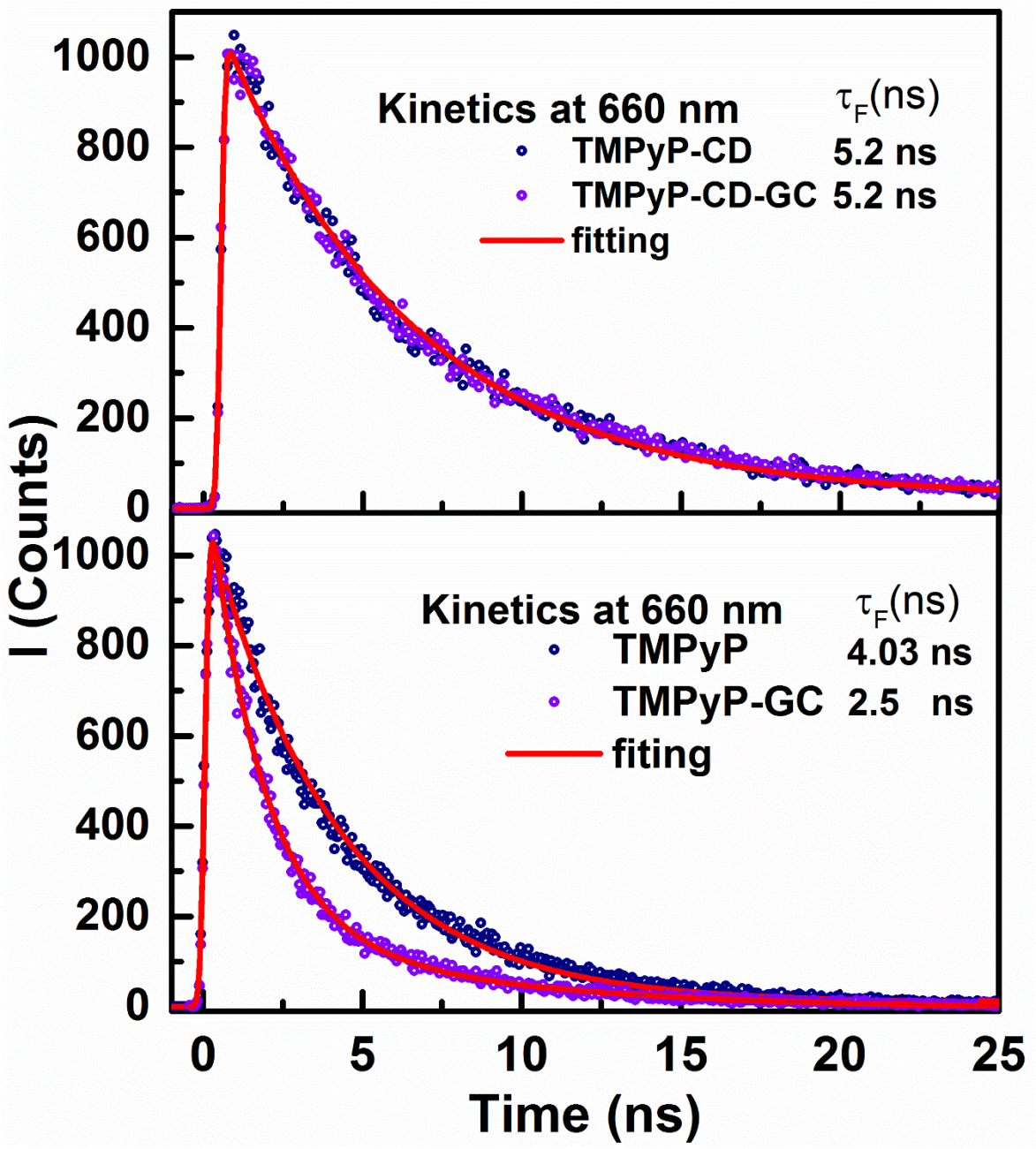

Fig S4. Time correlated single photon counting (TCSPC) kinetics excitation at 475 nm

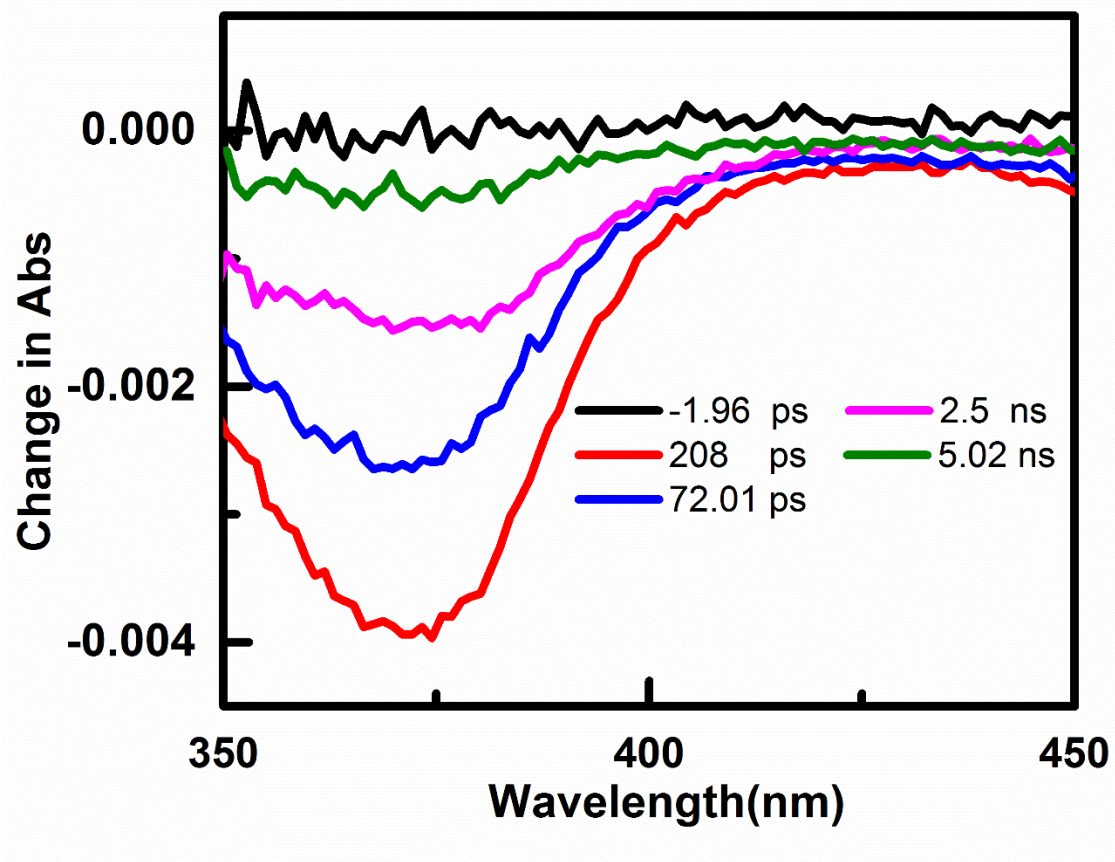

Fig S5. Femtosecond TA showing the ground state bleach of GC in TMPyP-CD-GC after excitation at 650 nm.

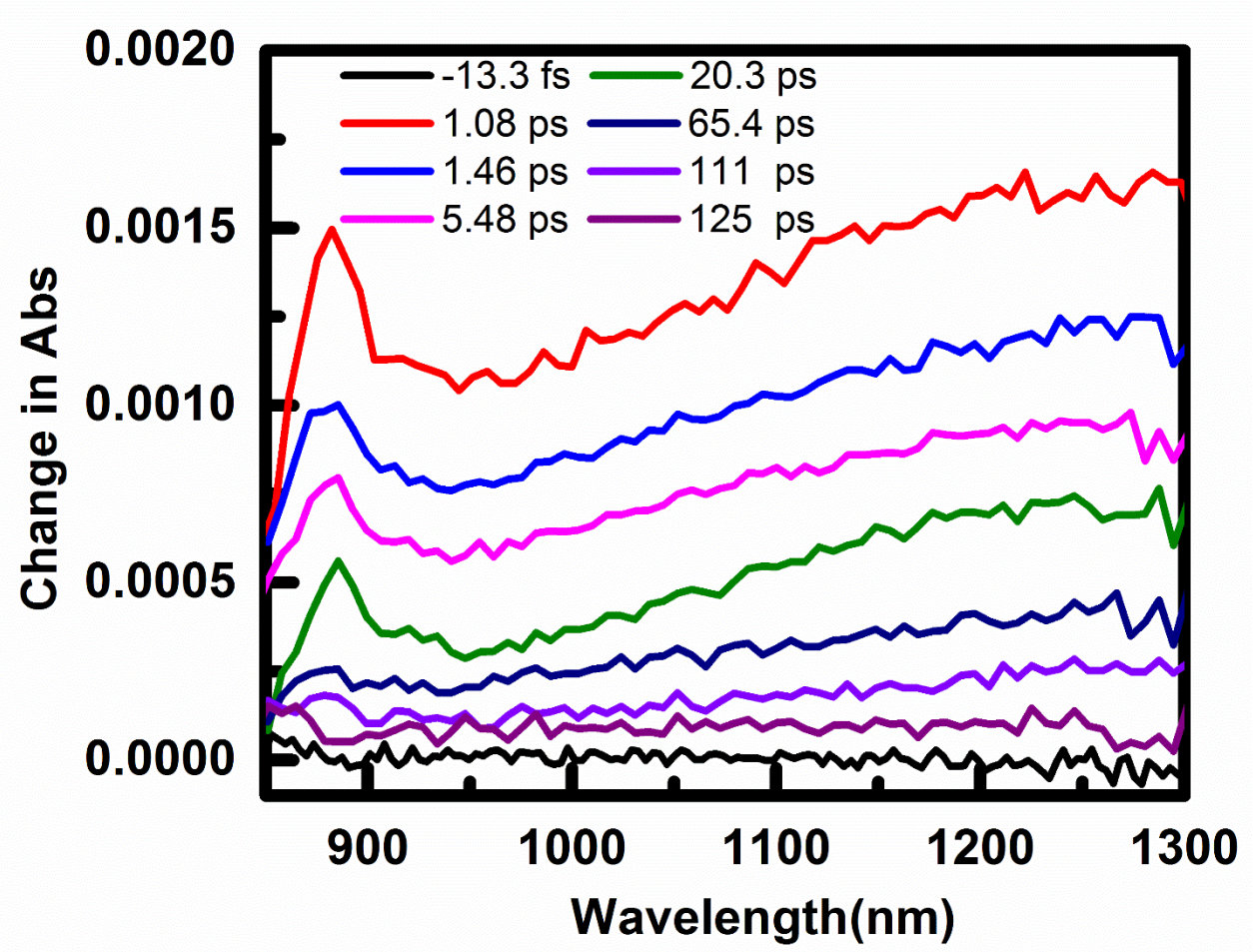

Fig S6. Femtosecond TA of TMPyP-CD-GC after excitation at 475 nm

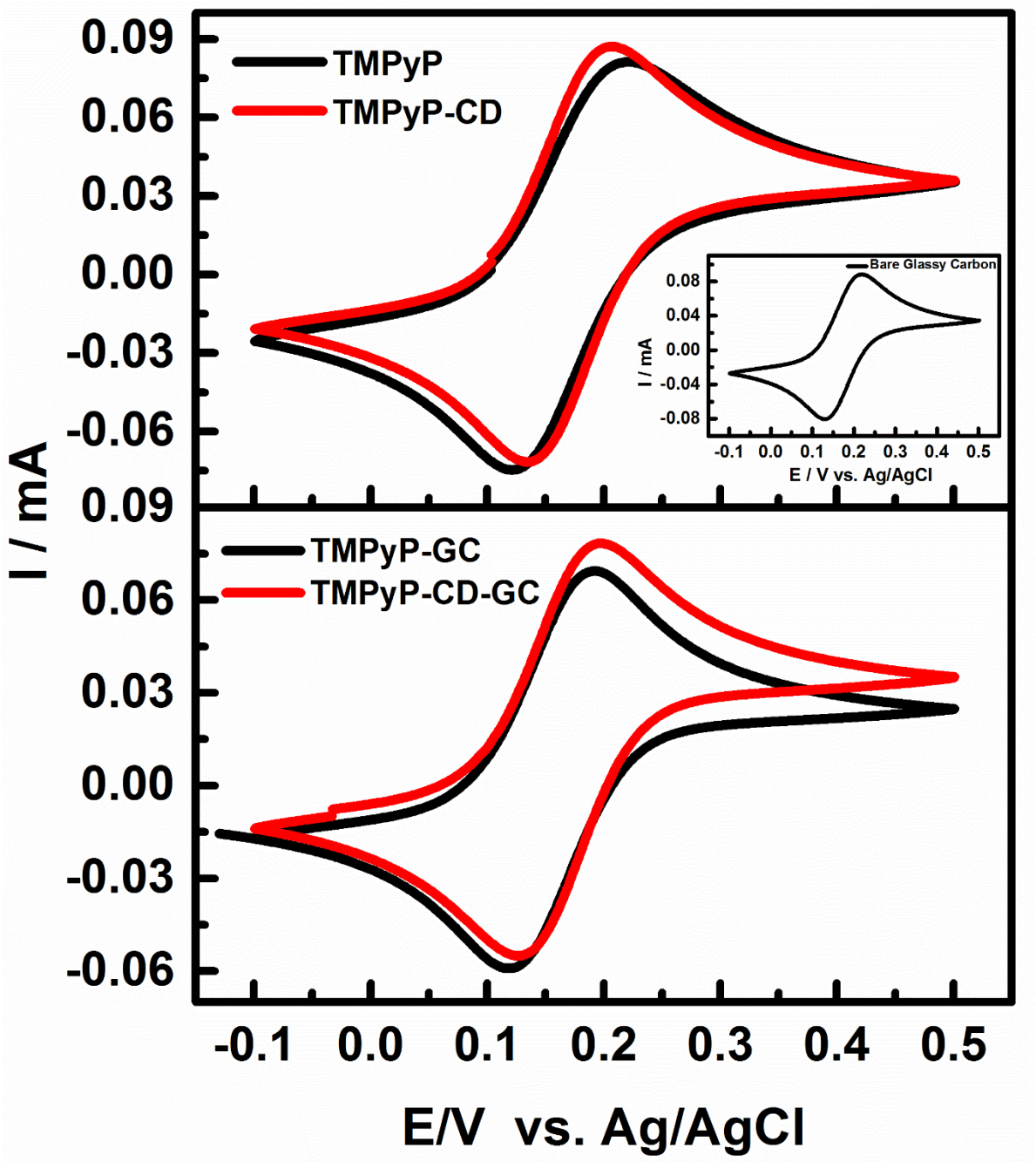

Fig S7. Cyclic Voltammetry results for: Upper panel) TMPyP (black) and TMPyP-CD (red); Lower panel) TMPyP-GC (black) and TMPyP-CD-GC (red)

References:

(1) N. Blom, J. Odo, K. Nakamoto, D. P. Strommen, *J. Phys. Chem.* 1986, ***90***, 2847-2852.
(2) J. Qu, D.P. Arnold and P.M. Fredericks, *J. Raman Spectrosc.* 2000, ***31***, 469-473