--Electronic Supplementary Information--

Photoinduced charge separation in ordered self-assemblies of perylenediimide–graphene oxide hybrid layers

Mustafa Supur, Kei Ohkubo, and Shunichi Fukuzumi*

Department of Material and Life Science, Graduate School of Engineering, Osaka University, ALCA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan

EXPERIMENTAL SECTION

Materials. *N*,*N'*-di(2-(trimethylammonium iodide)ethylene)perylenediimide (PDI) was synthesized in accordance with the reported procedures.[9] Graphene oxide (GO; as dispersion in water, 2.0 mg ml^{-1}, Sigma-Aldrich), polyethylene glycol (PEG 200; average M_w: 190-210, Nacalai Tesque) were used as received from commercial sources. Purification of water (18.2 MΩ cm) was performed with a Milli-Q system (Millipore, Direct-Q 3 UV). GO was sonicated at least 20 min. before use. Supramolecular gel of TAIPDI was obtained by adding 2.1 mg PDI to 2 ml of hot GO aqueous dispersion (2.0 mg ml^{-1}, ~70ºC). Then, the viscous mixture was sonicated at least 15 min. to form gelation. As a second method, 20 µl of 2.7 mg ml^{-1} PDI aqueous solution was mixed with 30 ul of GO aqueous dispersion (4.8 mg ml^{-1}). Then, mixture was sonicated at least 15 min. to obtain supramolecular gel. Extensive sonication-centrifugation-decantation (SCD) cycles were applied to the samples for further measurements to completely remove the weakly physisorbed and non-adsorbed TAIPDI moieties on GO surface. The samples were again sonicated for good dispersion in water.

Instruments. Steady-state absorption measurements were recorded on a Hewlett Packard 8453 diode array spectrophotometer. Fluorescence measurements were carried out on a Shimadzu spectrofluorophotometer (RF-5300PC).

Powder X-ray diffraction (PXRD) patterns were recorded by a Rigaku Ultima IV. Incident X-ray radiation was produced by Cu X-ray tube, operating at 40 kV and 40 mA with Cu K_α radiation of 1.54 Å. A scanning rate was 4°/min from 4 to 50° in 2θ. PXRD samples were prepared by drying the GO dispersion and TAIPDI–GO supramolecular gel for overnight.

Electrochemical measurements were performed on an ALS630B electrochemical analyzer in water containing 0.10 M Na_2SO_4 as supporting electrolyte. A conventional three-electrode cell was used with a glassy carbon working electrode and a platinum wire as the counter electrode. The measured potentials were recorded with respect to a saturated calomel electrode (SCE).

Femtosecond laser-induced transient absorption spectroscopy experiments were conducted using an ultrafast source: Integra-C (Quantronix Corp.), an optical parametric amplifier: TOPAS (Light Conversion Ltd.) and a commercially available optical detection system: Helios provided by Ultrafast Systems LLC. The source for the pump and probe pulses was derived from the fundamental output of Integra-C (780 nm, 2 mJ per pulse and fwhm =

130 fs) at a repetition rate of 1 kHz. 75% of the fundamental output of the laser was introduced into TOPAS, which has optical frequency mixers resulting in a tuneable range from 285 nm to 1660 nm, while the rest of the output was used for white light generation. Typically, 2500 excitation pulses were averaged for 5 seconds to obtain the transient spectrum at a set delay time. Kinetic traces at appropriate wavelengths were assembled from the time-resolved spectral data. Time profiles obtained from femtosecond transient absorption spectra were analyzed by using a computer program, Igor Pro version 6.2. The formation and decay curves were fitted to a mono and double exponential function of the form: $y = y_0 + A\exp(-\mathrm{invTau}x)$ and $y = y_0 + A_1\exp(-\mathrm{invTau}_1 x) + A_2\exp(-\mathrm{invTau}_2 x)$, respectively.

The EPR spectra were taken on a JEOL X-band spectrometer (JES-RE1XE) under photoirradiation with a high-pressure mercury lamp (USH-1005D) through a water filter focusing the sample cell in the EPR cavity at 4 K.

SUPPLEMENTARY FIGURES

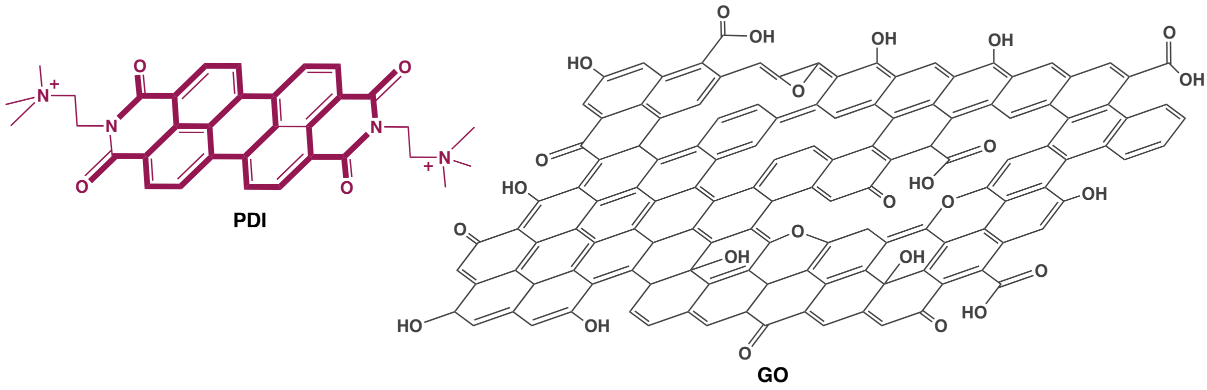

Fig. S1 Molecular structure PDI and proposed structural model of a single layer GO.

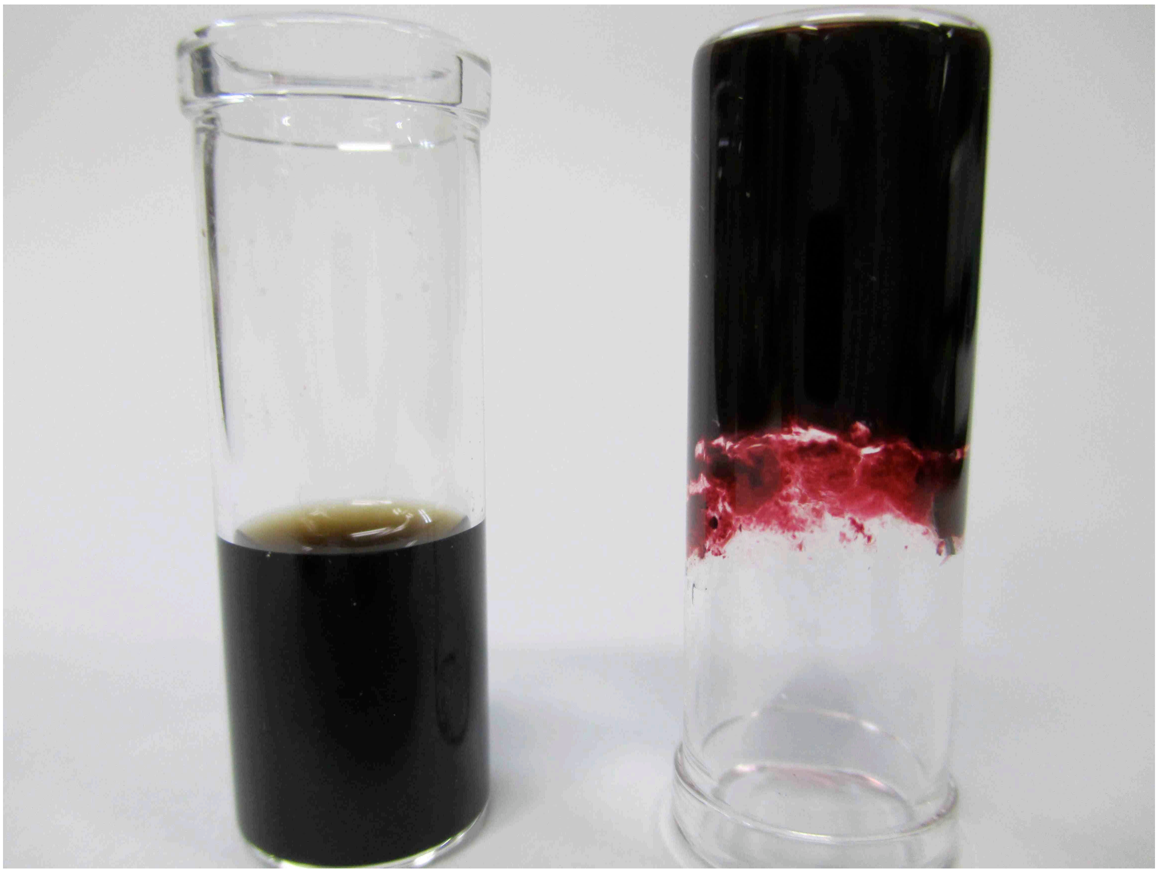

Fig. S2 Photographic image of GO dispersion (left vial) and TAI–GO gel (right vial) prepared by adding 2.1 mg PDI to 2 ml of hot GO aqueous dispersion (2.0 mg ml^{-1}, ~70ºC). ~15 min. of sonification resulted in gelation.

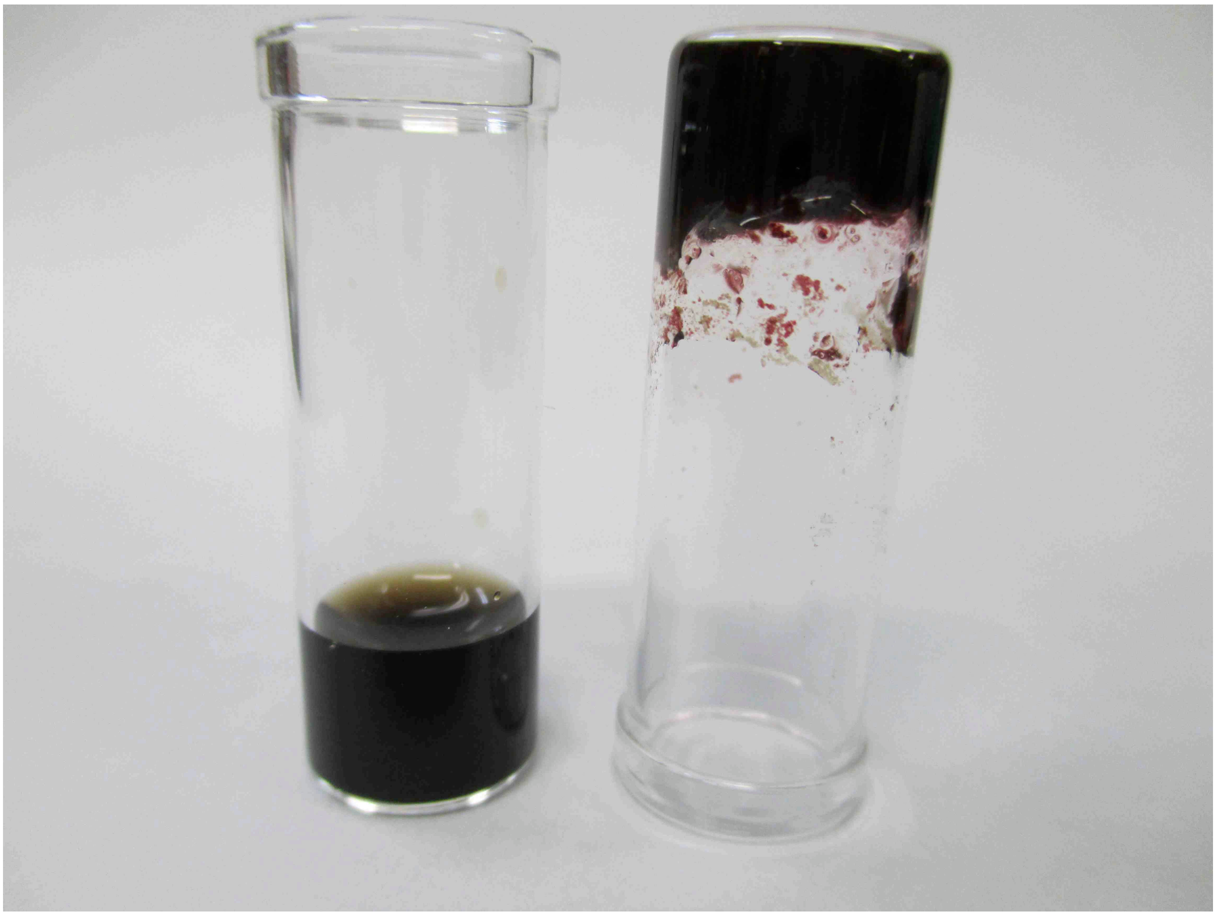

Fig. S3 Photographic image of GO dispersion (left vial) and TAI–GO gel (right vial) prepared by mixing 20 μl of 2.7 mg ml^{-1} PDI aqueous solution with 30 ul of GO aqueous dispersion. ~15 min. of sonification resulted in gelation.

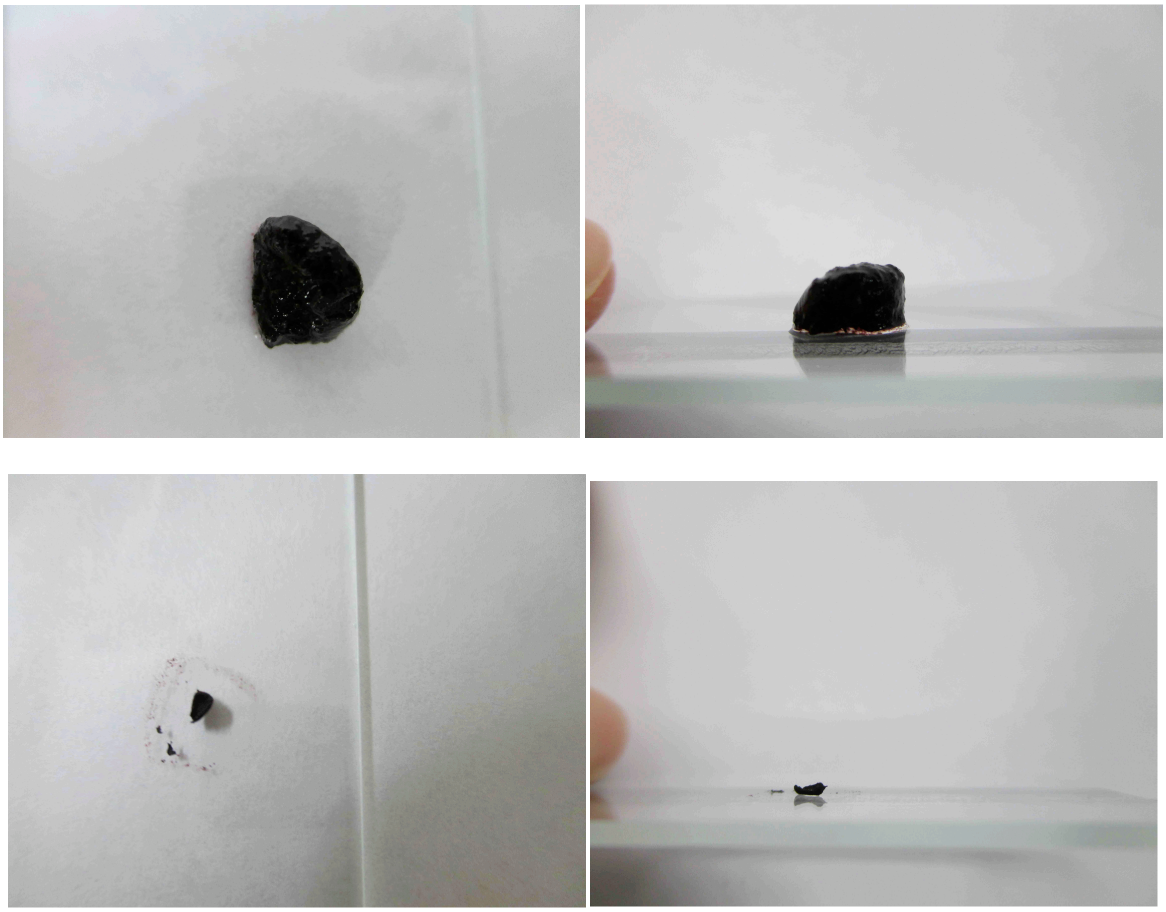

Fig. S4 Photographic image of TAIPDI–GO supramolecular gel before (upper panel) and after (lower panel) drying for overnight.

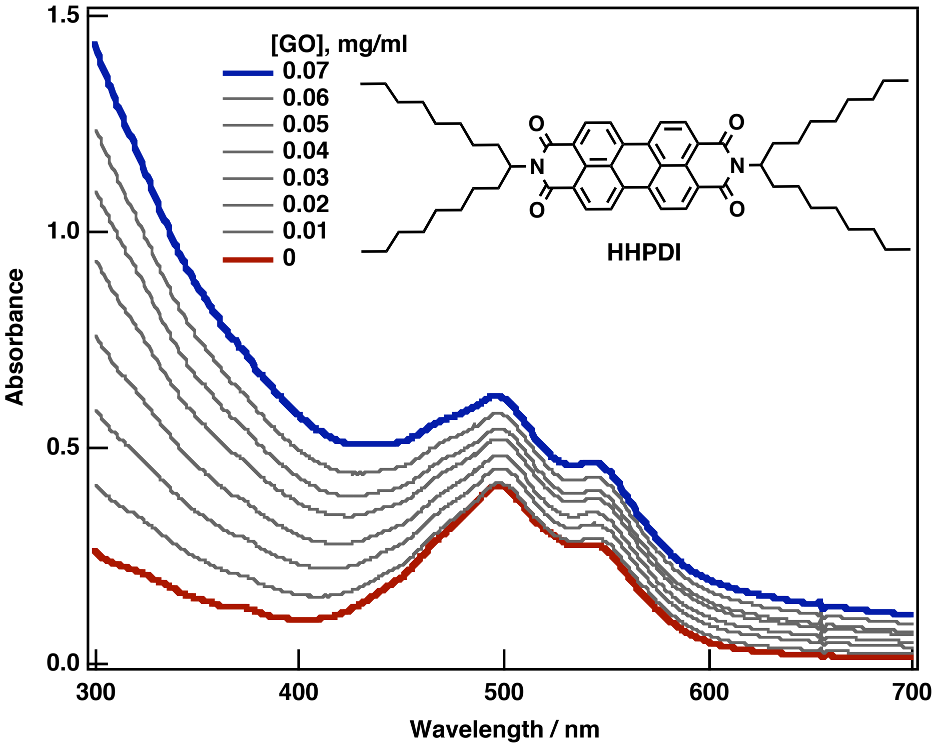

Fig. S5 Absorption spectral changes during the addition of GO to the aqueous solution of 0.022 mM HHPDI in water/ACN (1:1 v/v).

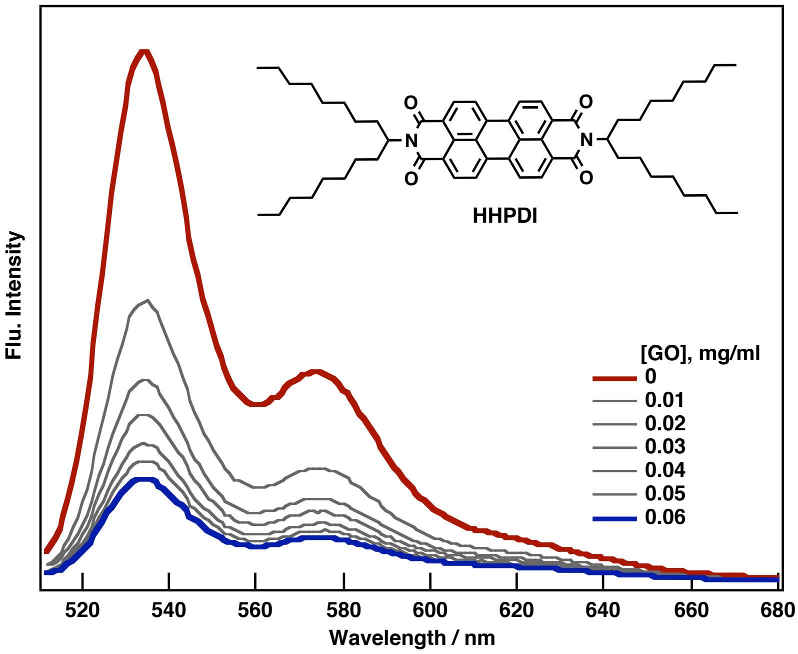

Fig. S6 Fluorescence emission spectral changes during the addition of GO to the solution of 0.022 mM HHPDI in water/ACN (1:1 v/v), λ_{exc}=510 nm.

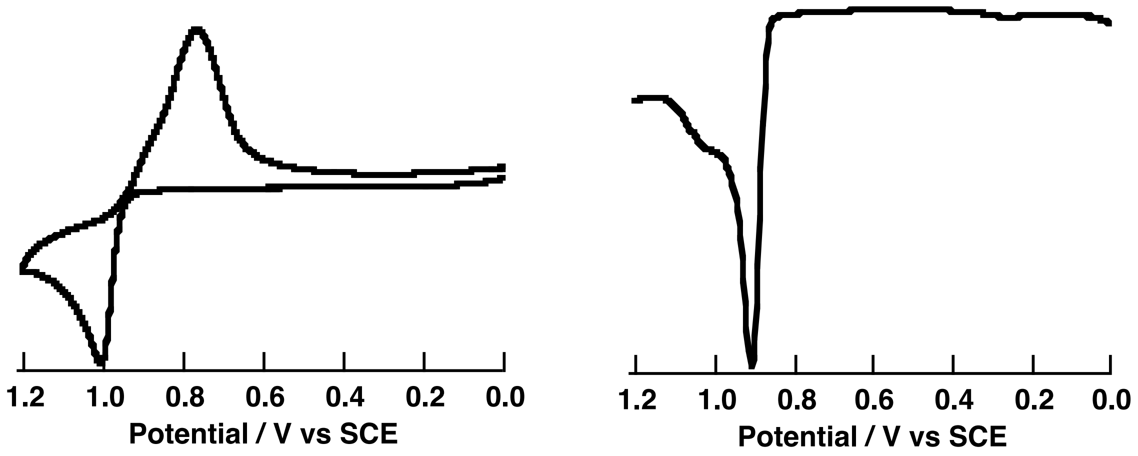

Fig. S7 Cyclic (left) differential pulse (right) voltammograms of GO in water containing 0.10 M Na_2SO_4 (sweep rate: 0.1 mV/s).

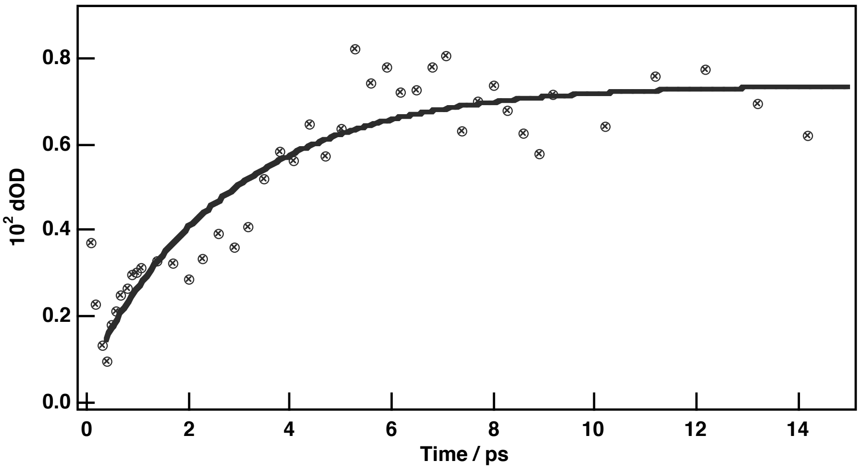

Fig. S8 Time profile of transient absorbance of 0.25 mM TAIPDI and 0.6 mg ml^{-1} GO in water at 720 nm, $\lambda_{exc} = 510$ nm.

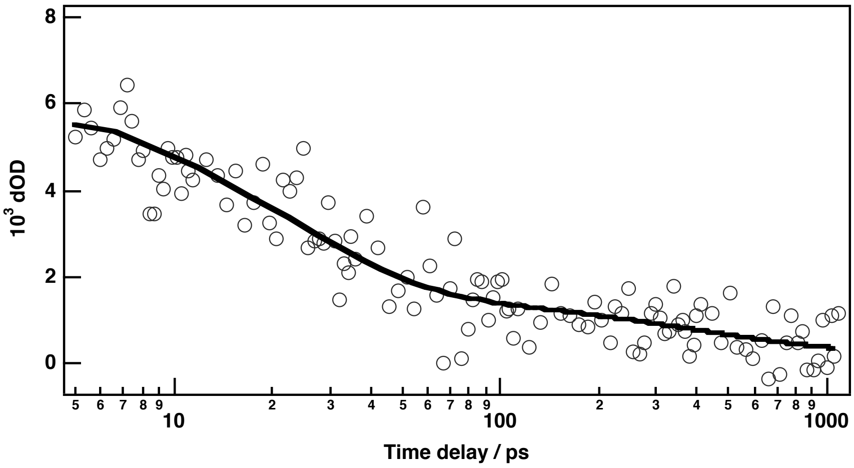

Fig. S9 Decay time profile of transient absorbance of 0.25 mM TAIPDI and 0.9 mg ml^{-1} GO in water at 720 nm, $\lambda_{exc} = 510$ nm.

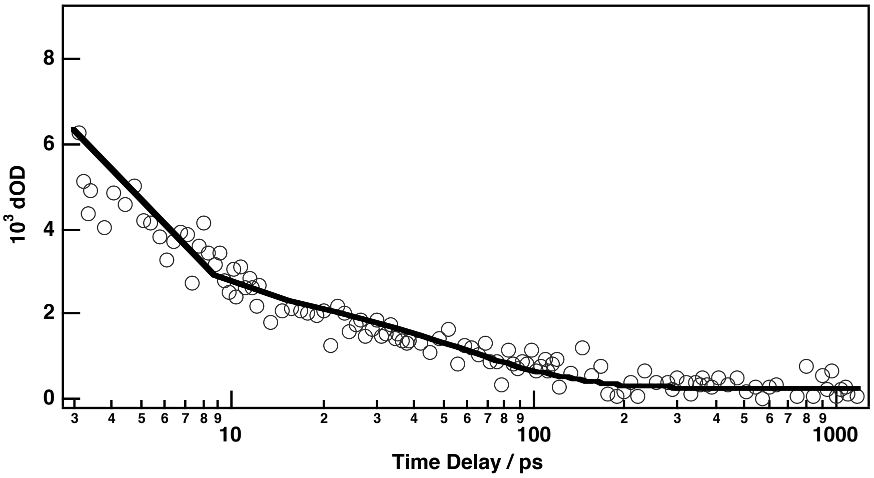

Fig. S10 Decay time profile of transient absorbance of 0.25 mM TAIPDI and 0.3 mg ml^{-1} GO in water at 720 nm, λ_{exc} = 510 nm.

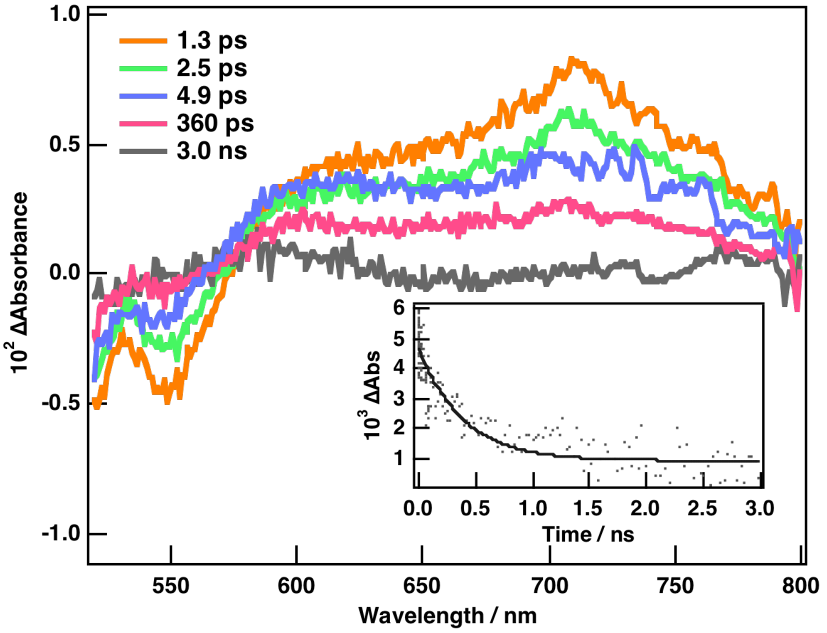

Fig. S11 Femtosecond laser-induced transient absorption spectra of GO–PDI in PEG 200 at indicated time delays, λ_{exc}=510 nm. Inset: Time profile at 710 nm.

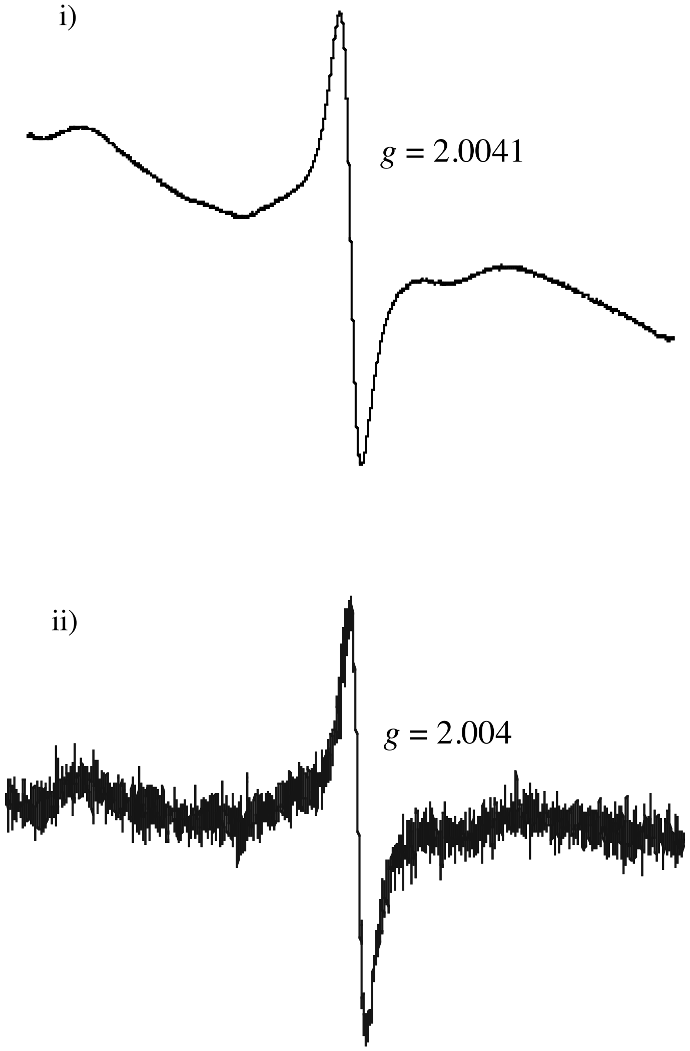

Fig. S12 EPR spectra of PDI–GO in water (i) and in aqueous PEG 20000 solution (ii) showing radical anion signal of PDI with corresponding *g* values measured at 4 K observed after photoirradiation.

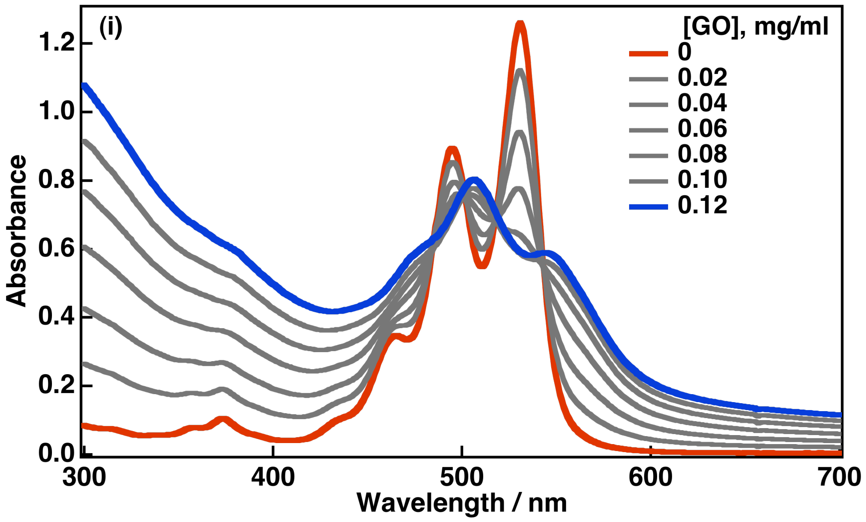

Fig. S13 Absorption spectral changes during the addition of GO to the aqueous solution of 0.021 mM PDI containing PEG 200 (v/v 1:1).

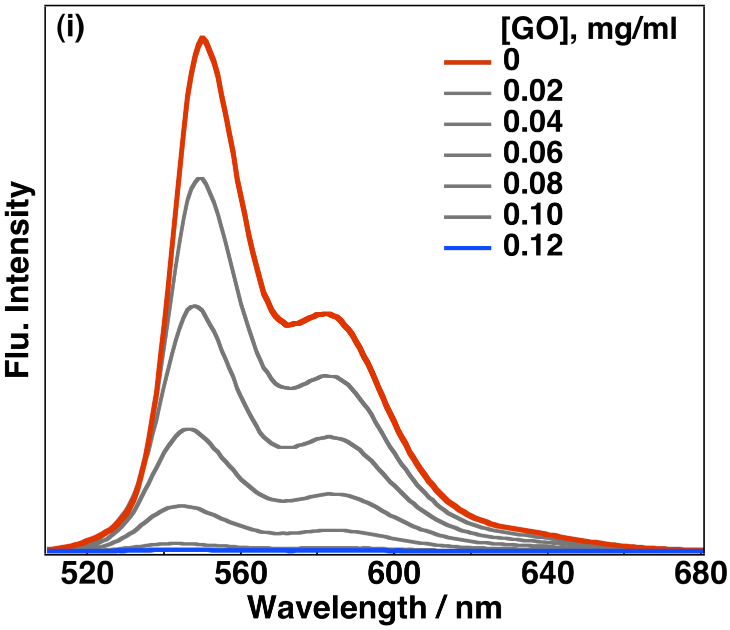

Fig. S14 Fluorescence emission spectral changes during the addition of GO to the aqueous solution of 0.021 mM PDI containing PEG 200 (v/v 1:1), λ_{exc}=510 nm.