Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Enhanced optical limiting and hydrogen evolution of graphene oxide nanohybrids covalently functionalized by covalent organic polymer based on porphyrin

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Experimental Section

Materials and reagents

All reactions and manipulations were carried out under nitrogen atmosphere with the use of standard Schlenk techniques. All materials and reagents are of chemical or analytical grade. Dimethyl formamide (DMF) was dried over CaH_2 and distilled before use. The other chemicals were directly used unless otherwise stated.

Instruments and measurements

The ultraviolet–visible (UV–Vis) absorption spectra were obtained with a JASCO V-570 spectrophotometer. For comparison, the concentration of all samples was adjusted to be about 0.05 mg/mL in DMSO. Steady-state fluorescence spectra were measured on a Fluoro-Max-P instrument. The sample for the fluorescence measurement was dissolved in dry DMSO, filtered, transferred to a long quartz cell, and then capped and bubbled with N_2 for at least 10 min before measurement. The spectra were recorded in DMSO with the absorbance matching 0.8 at an excitation wavelength of 435 nm. Column chromatography was performed with silica gel (100-200 mesh, Qingdao Haiyang Chemical Co., Ltd, China). Fourier transform infrared (FTIR) spectra were recorded on a MB154S-FTIR spectrometer (Canada). All infrared (IR) samples were prepared as thin films using spectroscopic grade KBr. The FTIR spectra were recorded by accumulating 32 scans at a spectral resolution of 4 cm^{-1} at room temperature. Raman spectra were performed on a Renishaw Invia Raman Microscope with Ar+ radiation (532 nm). The laser light was focused onto samples by using a microscope equipped with a×100 objective. X-ray photoelectron spectroscopy (XPS) measurements were recorded on a RBD upgraded PHI-5000C ESCA (Perkin-Elmer) with Mg Kα radiation (hν = 1253.6 eV). Scanning electron microscopy (SEM) images were acquired using a Hitachi S4800 instrument to investigate the morphology of the samples. The molecular weights and polydispersity indices of TPPCOP were obtained via gel permeation chromatography (GPC) by using a WAT044207 refractive index detector at 35 ^{o}C. UV-Vis diffuse reflection spectra (DRS) were recorded on a Varian Cary 500 spectrophotometer in the range 200-800 nm with $BaSO_4$ pellet as the reference. Thermogravimetric analysis (TGA) measurements were run on a Perkin-Elmer Pyris 1 system under N_2 purge with a heating rate of 10 ^{o}C/min.

The Z-scan method is a well-known technique used to investigate the NLO properties of materials involving nonlinear absorption and optical limiting. The NLO properties of the samples were measured by performing Z-scan measurements. DMSO solutions of the samples were placed in quartz cells of 2 mm thickness for the nonlinear optical measurements, which were carried out using a Nd:YAG 532 nm laser (Continuum, Surelite II) with a pulse width 4 ns (fwhm), repetition rate of 2 Hz. The quartz with the samples was placed at the focus of a lens with a focal length of 300 mm controlled by a computer and moved along the axis of the incident beam (*z*-direction). The incident and transmitted laser pulses were monitored by two energy detectors (Rjp-765 energy probe), which were linked to an energy meter (Rj-7620 ENERGY RATIOMETER, Laserprobe). A personal computer was used to collect and process data coming from energy meter through a GPIB interface. Investigation of the optical limiting responses of the samples was performed by the Z-scan technique with the laser system as in the NLO experiments. The samples were placed in quartz cells of 5 mm thickness and positioned at the focus, and cures of transmittance and energy *vs* incident energy were obtained.

All electrochemical experiments including photocurrent, electrochemical impedance spectroscopy (EIS) and HER activity were carried out on a CH Instrument (CHI 614 E electrochemical workstation) with a conventional three-electrode cell system at room temperature. For the HER measurements, a sample-covered glassy carbon electrode was used as the working electrode, with Pt gauze (0.5×0.5 cm^2) as the counter electrode and silver/silver chloride (Ag/AgCl) as the reference electrode. The measured potential in N_2-saturated 0.5 M H_2SO_4 was then calibrated with the reversible hydrogen electrode potential (RHE) using the following Nernst equation, $E_{RHE} = E_{Ag/AgCl} + 0.0592pH + 0.199$. EIS was performed at frequencies ranging from 10^{-2} to 10^5 Hz. For the photocurrent experiments, a sample-covered fluorine-doped indium tin oxide (ITO) substrate was employed as the working electrode. A 350W xenon arc lamp with an incident density of 100 mW/cm^2 was utilized as the light source.

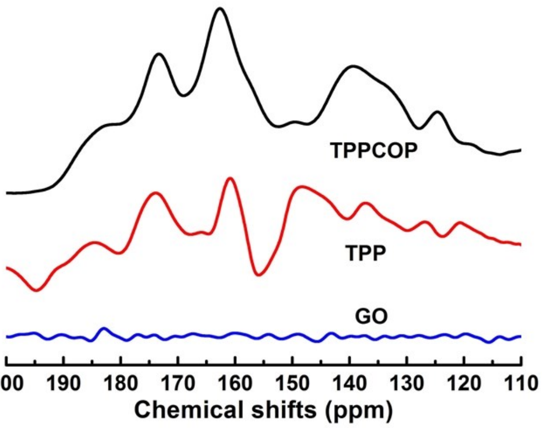

Figure S1. Solid-state ^{13}C NMR spectra of GO, TPP and TPPCOP.

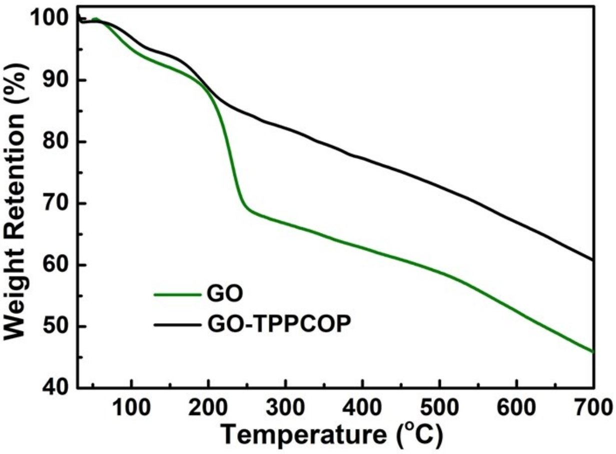

Figure S2. TGA curves of GO and GO-TPPCOP.

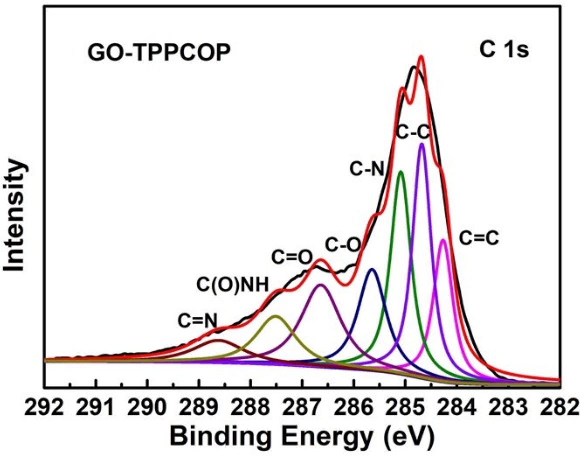

Figure S3. High-resolution C 1s XPS spectra of GO-TPPCOP.

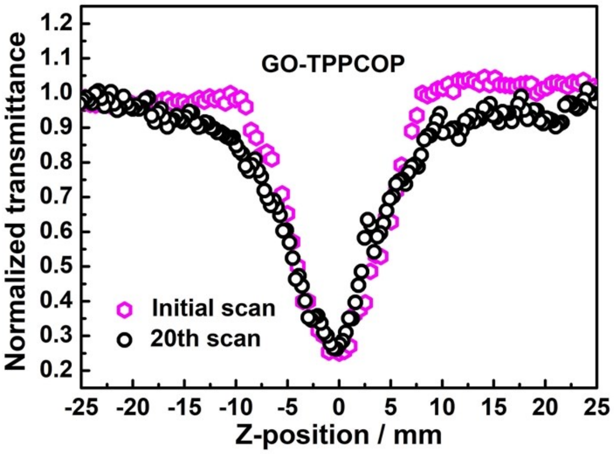

Figure S4. Cycle stability of GO-TPPCOP.

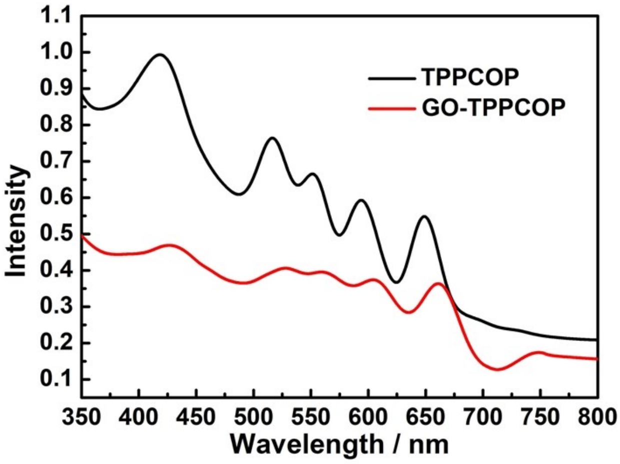

Figure S5. UV-Vis DRS spectra of TPPCOP and GO-TPPCOP.

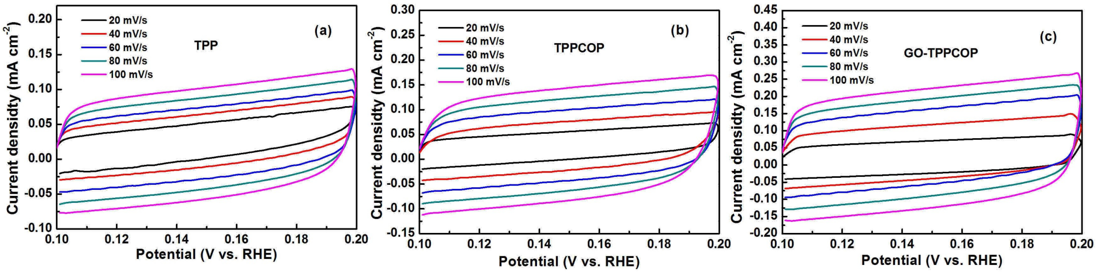

Figure S6. CV curves of (a) TPP, (b) TPPCOP, and (c) GO-TPPCOP measured from 20 to 100 mV/s.