

Supplementary Information

Stacked graphene platelet nanofibers dispersed in the liquid electrolyte for highly efficient cobalt-mediator-based dye-sensitized solar cells

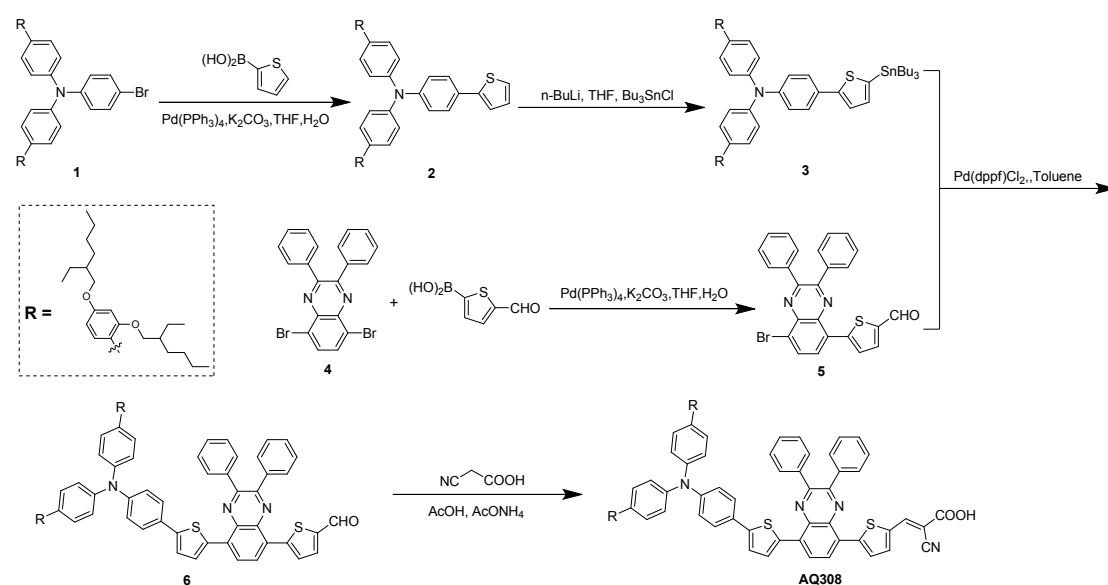
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Materials

[4-bis(2',4'-bis((2-ethylhexyl)oxy)biphenyl-4-yl)amino]phenylbromide (**1**)¹ and 5,8-dibromo-2,3-diphenylquinoxaline (**4**)² were synthesized according to published procedures.

All chemicals and solvents were purchased from commercial sources and were used without further purification. Stacked graphene platelet nanofibers (length 0.1-10 μm \times width 40-50 nm, SGNF) was purchased from ABCR, Germany.

Synthesis



Scheme S1. Synthetic Route of the AQ308 Dye

Synthesis of 2. Under an argon atmosphere, compound **1** (950 mg, 0.96 mmol), K_2CO_3 (5 mL, 2 M aqueous solution) and $\text{Pd}(\text{PPh}_3)_4$ (42 mg, 0.036 mmol) were dissolved in 20 mL of THF. After the mixture was stirred for half an hour and heated to 50 $^\circ\text{C}$, a solution of 2-thiopheneboronic acid (147 mg, 1.2 mmol) in THF (5 mL) was added slowly, and the mixture was refluxed for further 12 h. After cooling to room temperature, the mixture was extracted with CH_2Cl_2 . The combined organic layers were washed with brine water and dried with anhydrous Na_2SO_4 . After removing the solvent under

reduced pressure, the residue was purified by column chromatography on silica gel with PE/CH₂Cl₂ (10/1-5/1, v/v) as eluent to give compound **2** (790 mg, 82.9 % yield). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 7.52 (d, *J* = 8.6 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 4H), 7.30-7.25 (m, 4H), 7.19 (d, *J* = 8.8 Hz, 6H), 7.11-7.09 (m, 1H), 6.59-6.58 (m, 4H), 3.92-3.88 (m, 8H), 1.79-1.71 (m, 4H), 1.51-1.29 (m, 32H), 1.00-0.89 (m, 24H).

Synthesis of 3. Under an argon atmosphere, compound **2** (445 mg, 0.45 mmol) was dissolved in distilled THF (15 mL) then n-BuLi (0.32 mL, 0.58 mmol) was added at -78 °C. The solution was stirred for an hour at -50 °C before adding the solution of Bu₃SnCl (0.73 mL, 0.72mmol) at -78 °C. The solution was allowed to reach room temperature and stirred for 2 hours. The reaction was quenched with water and the organic phase was extracted with n-hexane, dried with Na₂SO₄, filtered and concentrated under reduced pressure. The resulting oil **3** was engaged without any further purification in a Stille coupling with **5**.

Synthesis of 5. Compound **5** was obtained by using a similar procedure to that of **2** (235 mg, 35 %). ¹H NMR(400 MHz, CDCl₃, ppm): δ = 9.98 (s, 1H), 8.09 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 8.8 Hz, 1H), 7.89 (d, *J* = 4.4 Hz, 1H),7.81 (d, *J* = 4.4 Hz, 1H), 7.70-7.68 (m, 4H), 7.42-7.36 (m, 6H).

Synthesis of 6. Under an argon atmosphere, compound **3** and compound **5** (190 mg, 0.43 mmol), Pd(dppf)Cl₂ (7.3 mg, 0.01 mmol) were dissolved in anhydrous toluene (20 mL) and refluxed for 12 h. The mixture was then poured into HCl (1 M). The organic phase was extracted with CH₂Cl₂, washed with HCl (1 M), dried over Na₂SO₄ and concentrated under reduced pressure. The crude solid was purified by chromatography on silica gel using PE/CH₂Cl₂ (3/1-1/1, v/v) as eluent to give red solid **6** (180 mg, 0.13 mmol, 30.5 %). ¹H NMR (400 MHz, CDCl₃, ppm): δ = 9.98 (s, 1H), 8.19 (d, *J* = 4.8 Hz, 2H), 7.93 (t, *J* = 4.8 Hz, 2H), 7.82 (d, *J* = 4.8 Hz, 1H), 7.79-7.73 (m, 4H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.46-7.39 (m, 10H), 7.34 (d, *J* = 4.8 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 2H), 7.21-7.17 (m, 6H), 6.56-6.55 (m, 4H), 3.89-3.86 (m, 8H), 1.76-1.72(m, 4H), 1.46-1.28 (m, 32H), 0.97-0.86 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, ppm): δ = 159.89, 157.21, 148.52, 148.39, 147.75, 145.51, 144.83, 138.40, 138.26, 137.54, 137.10, 136.43, 135.78, 133.46, 130.70, 130.56, 130.42, 128.46, 128.27, 126.39, 123.94, 123.29, 123.12, 117.03, 105.17, 100.29, 85.65, 70.54, 45.02, 39.48, 39.39, 30.64, 30.57, 29.14, 29.00, 24.06, 23.90, 23.09, 23.07, 14.13, 11.20, 11.17. HRMS (ESI-MS): *m/z* calcd for C₉₁H₁₀₄N₄O₅S₂: 1382.7417 [M+H⁺]; found: 1382.7445.

Synthesis of AQ308. Under an argon atmosphere, a mixture of **6** (145 mg, 0.11 mmol), cyanoacetic acid (85 mg, 1 mmol) and ammonium acetate (120 mg) in the mixed solvent of acetic acid (15 mL) and THF(5 mL) were refluxed for 12 h heat to 90 °C. After cooling down, the mixture was poured into water. The precipitate was collected by filtration and washed with water. The residue was purified by column chromatography on silica gel column with CH₂Cl₂/ethanol (10:1, v/v) to yield a purple solid (120 mg, 66.5 % yield). ¹H NMR (400 MHz, Acetone, ppm): δ = 8.47 (d, *J* = 8.4 Hz, 1H) , δ = 8.45 (s,

¹H), 8.37 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 4.8 Hz, 1H), 8.06 (d, *J* = 4.8 Hz, 1H), 8.00 (d, *J* = 4.6 Hz, 1H), 7.92-7.86 (m, 4H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.52-7.46 (m, 10H), 7.29-7.25 (m, 3H), 7.19-7.16 (m, 6H), 6.70-6.69 (m, 2H), 6.63-6.61 (m, 2H), 3.97-3.95 (m, 8H), 1.77-1.71 (m, 4H), 1.48-1.36 (m, 32H), 0.97-0.86 (m, 24H). ¹³C NMR (100 MHz, CDCl₃, ppm) δ = 160.28, 156.38, 149.46, 146.41, 143.98, 137.92, 130.91, 130.83, 129.79, 129.02, 128.81, 127.16, 124.51, 124.33, 123.37, 123.15, 105.75, 100.67, 88.52, 71.35, 70.51, 39.47, 39.35, 30.62, 30.56, 29.70, 29.33, 29.13, 28.99, 27.22, 24.05, 23.89, 23.09, 23.06, 22.70, 14.13, 11.16. HRMS (ESI-MS): *m/z* calcd for C₉₄H₁₀₅N₄O₆S₂: 1449.7475 [M+H⁺]; found: 1449.6638.

Solar cells assembly

A compact TiO₂ layer was firstly deposited on the FTO glass by immersing into 40 mM TiCl₄ aqueous solution at 70 °C for 30 min two times. Then one layer of Dyesol 90-T TiO₂ paste and a scattering layer (4+4 μm) were screen printed onto and sintered gradually up to 500 °C and kept at this temperature before cooling. The photoanodes were immersed into 40 mM TiCl₄ aqueous solution at 70 °C for 30 min and sintered at 450 °C for 30 min again. After cooling to room temperature, these films were dipped into a 3×10⁻⁴ M solution of dyes (**AQ308**) in dichloromethane for 3 h. After this, the electrodes were rinsed with CH₂Cl₂ and ethanol and then dried. The Pt-counter electrodes were prepared by spin coating of H₂PtCl₆ solution (20 mM in isopropanol) onto FTO glass at 400 °C for 15 min. For assembly of DSSCs as a sandwich type, the TiO₂ photoelectrodes and Pt-counter electrodes were sealed with a hot-melt gasket of 25 μm thickness. The cobalt electrolyte consists of 0.22 M [Co(II)(bpy)₃](TFSI)₂, 0.06 M [Co(III)(bpy)₃](TFSI)₃, 0.1 M LiClO₄, 0.5 M tert-butylpyridine and a certain amount of SGNF (0, 0.1 mg/mL, 0.2 mg/mL, and 0.4 mg/mL graphene nanoplatelets, respectively) in acetonitrile (bpy = 2,2'-bipyridine, TFSI = bis(trifluoromethane)sulfonamide), then the electrolyte was sonicated for 5 min to produce dispersion of SGNF in electrolyte. The active area of all DSSCs is 0.12 cm².

Instruments and Characterization

¹H NMR and ¹³C NMR spectra were measured at 400 and 100 MHz, respectively. Chemical shifts δ, were calibrated against TMS as an internal standard. HRMS measurements were performed by using a Waters LCT Premier XE spectrometer. The absorption spectra of the sensitizer dyes in solution and adsorbed on TiO₂ films were measured with a Varian Cary 500 spectrophotometer. Scanning electron microscopy (SEM) images were taken with a S4800 transmission electron microscope operated at 15.0 kV. Fourier transform infrared (FTIR) spectra was carried out using NICOLET 380 spectrometer in the frequency range of 4000-450 cm⁻¹. Powder X-ray diffraction (XRD) was performed on a Bruker D8-Advance X-ray diffractometer with monochromatized Cu Kα radiation (λ = 1.5418 Å). Electrical conductivity of SGNF dispersed in CH₃CN were measured at room temperature by DDS307 conductivity meter (LeiCi Co. Ltd, Shanghai, China).

The cyclic voltammograms were determined by using a CHI660C electrochemical workstation (Chenhua Co. Ltd, Shanghai, China) in a three-electrode cell. The working electrode was a glassy

carbon electrode, used in conjunction with a Pt auxiliary electrode and an Ag/AgCl wire reference electrode. The electrolyte consisted of 0.1 M TBAP solution in dichloromethane containing 10^{-3} M of the dye. The Fc/Fc⁺ redox couple was used as an external potential reference. The scan rate was 100 mV/s.

A Zahner IM6e Impedance Analyzer (ZAHNER-Elektrik GmbH & CoKG, Kronach, Germany) was employed to carry out the electrochemical impedance spectroscopy. The frequency range was 0.1 Hz-100 kHz and the applied bias was from -0.60 V to -0.85 V. The magnitude of the alternating signal was 5 mV.

Transient photocurrent measurements were performed under an AM 1.5 solar simulator equipped with a 300 W xenon lamp (Model No.91160, Oriel), and the data were collected by CHI660C electrochemical workstation (Chenhua Co. Ltd, Shanghai, China). The transient photocurrent was measured several times to obtain a stable current response by switching on/off illumination of simulator.

Photovoltaic measurements employed an AM 1.5 solar simulator equipped with a 300 W xenon lamp (Model No.91160, Oriel). The power of the simulated light was calibrated to 100 mW cm⁻² by using a Newport Oriel PV reference cell system (Model 91150 V). *J-V* curves were obtained by applying an external bias to the cell and measuring the generated photocurrent with a Keithley model 2400 digital source meter. The voltage step and delay time of the photocurrent were 10 mV and 40 ms, respectively. Action spectra of the incident monochromatic photon-to-electron conversion efficiency (IPCE) for the solar cells were obtained with a Newport-74125 system (Newport Instruments). The intensity of monochromatic light was measured with a Si detector (Newport-71640).

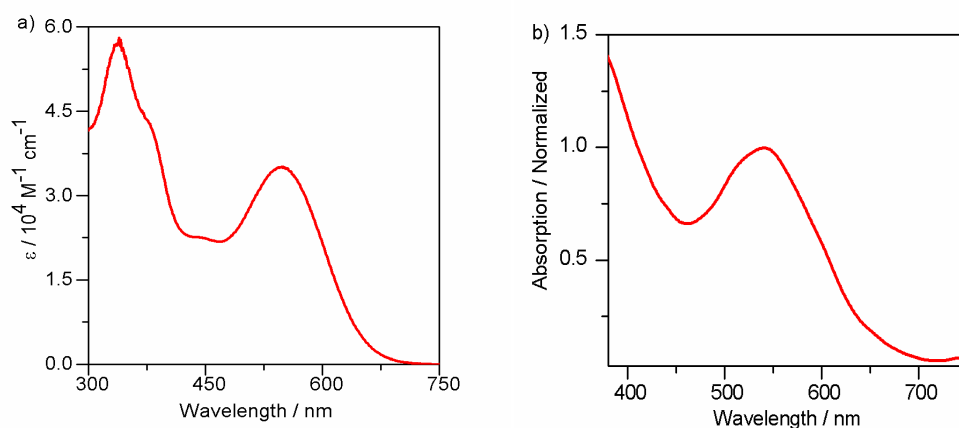


Fig. S1. (a) Absorption spectra of AQ308 in CH₂Cl₂. (b) Normalized absorption spectra of AQ308 on 4 μm TiO₂ film.

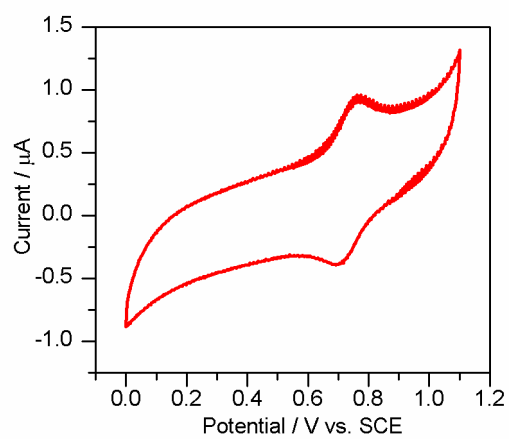


Fig. S2. CV profile of AQ308 in CH_2Cl_2 containing 0.1 M TBAP as a supporting electrolyte. The scan rate was 100 mV s^{-1} .

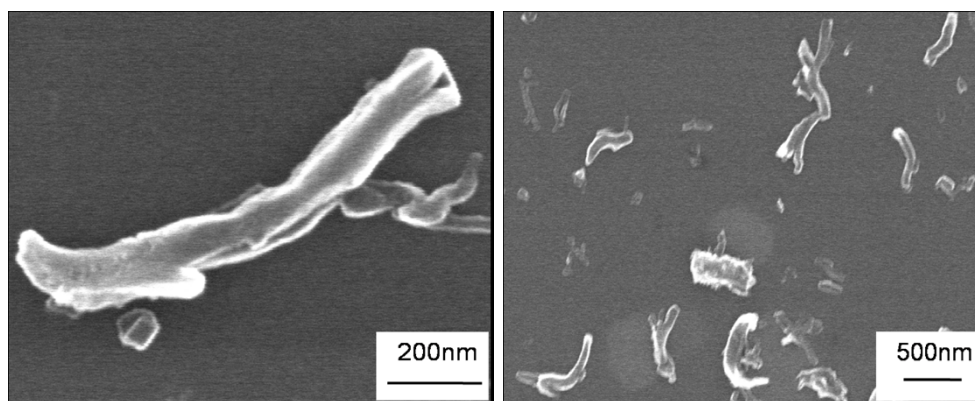


Fig. S3. SEM images of SGNF.

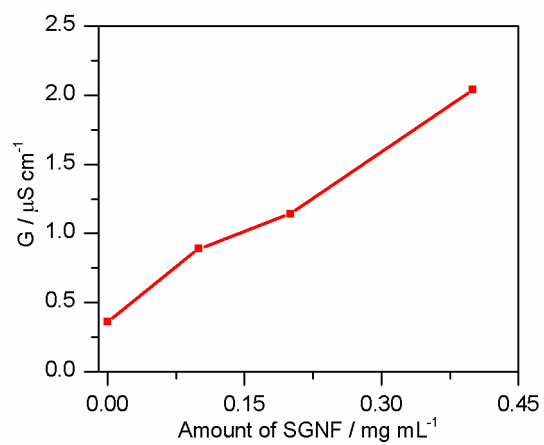


Fig. S4. Electrical conductivity profile of the dispersion of different amounts SGNF in CH_3CN .

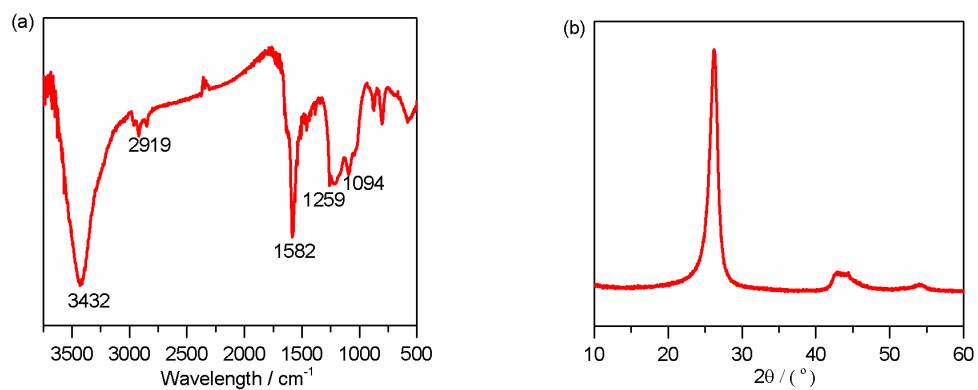


Fig. S5. (a) Fourier transform infrared (FTIR) spectrum and (b) XRD pattern of SGNF.

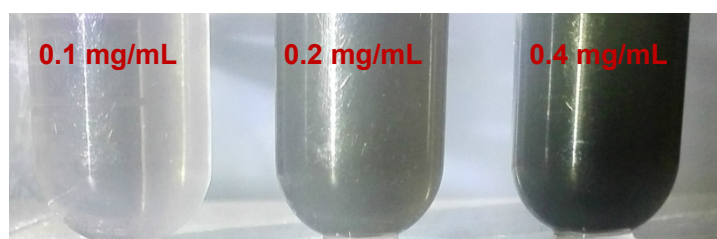


Fig. S6. Images with different amounts of SGNF dispersed in CH₃CN.

References:

1. D. W. Chang, H. J. Lee, J. H. Kim, S. Y. Park, S.-M. Park, L. M. Dai and J.-B. Baek, *Org. Lett.*, 2011, **13**, 3880.
2. H. N. Tsao, C. Yi, T. Moehl, J.-H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin and M. Grätzel, *ChemSusChem*, 2011, **4**, 591.