

Spectroscopic investigation of photoinduced processes in graphene-dye hybrid materials.

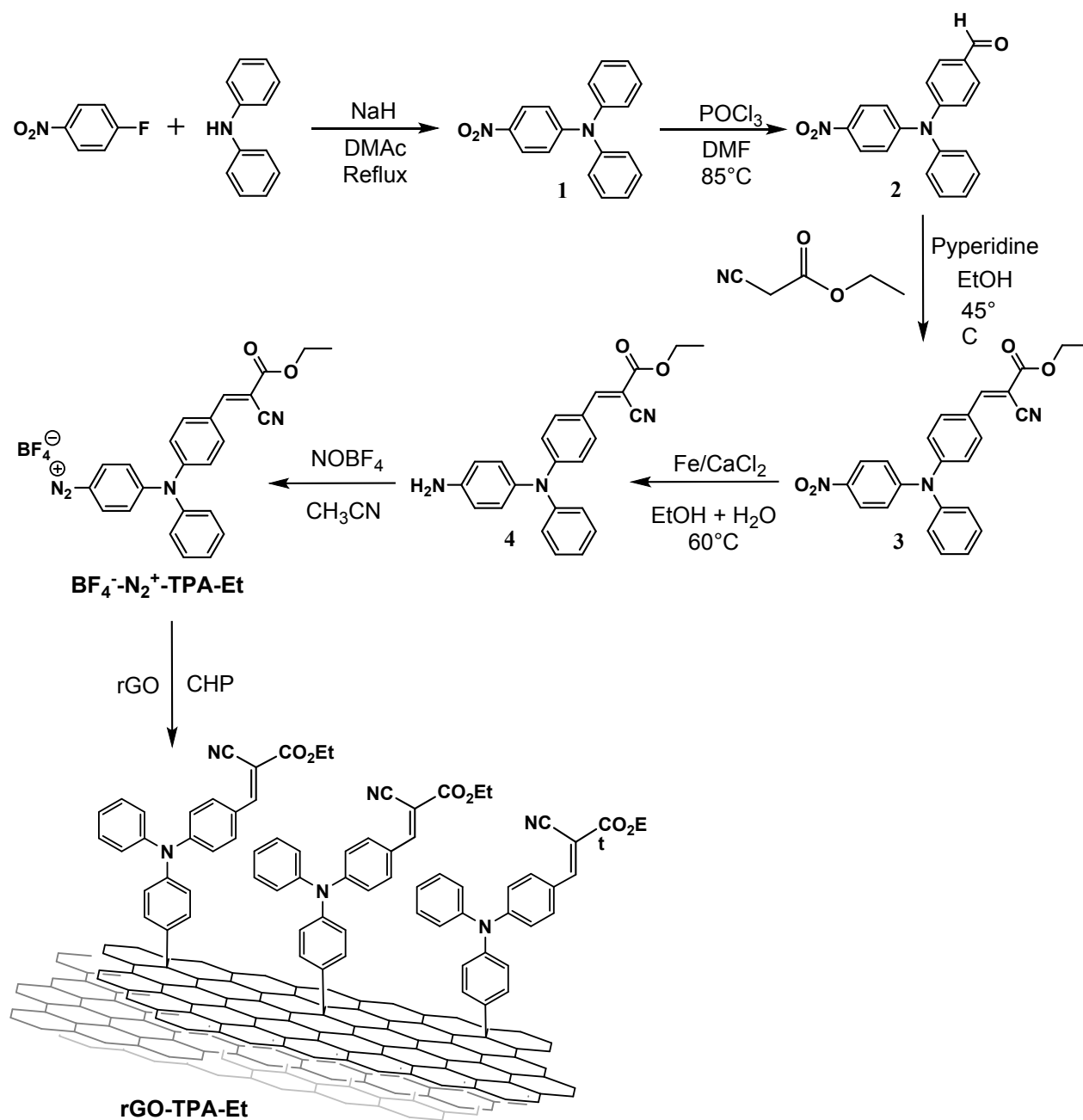
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SUPPLEMENTARY INFORMATION

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Scheme SI-1: Synthetic route towards rGO-TPA-Et

Synthetic procedures for compounds 1-4 and for BF₄⁻-N₂⁺-TPA-Et

4-nitro-N,N-diphenylamine (1). Diphenylamine (1.009 g, 5.96 mmol) was added to a solution of sodium hydride (0.267 g, 11.1 mmol) in anhydrous DMAc (20 mL) under nitrogen atmosphere. The solution was stirred at room temperature for 30 minutes and cooled to 0 °C. A solution of 1-Fluoro-4-nitrobenzene (1.26 g, 8.94 mmol) in dehydrated DMAc (20 mL) was added dropwise to this mixture. After the addition was complete, the mixture was stirred at 125 °C for 3 h. Then the mixture was cooled to room temperature and poured into a cold dilute hydrochloric acid solution. The precipitate was collected by filtration and dissolved in dichloromethane. The solution was then washed with a saturated sodium bicarbonate solution. The organic phase was dried with anhydrous sodium sulfate, and the crude product was obtained by rotary evaporation. Purification by flash chromatography in toluene was executed to give the final product as orange crystals (1.41 g) in 82% yield. ¹H NMR (500 MHz, CDCl₃, δ, ppm) 8.04 (d, *J* = 9.3 Hz ArH, 2H), 7.37 (m, ArH, 4H), 7.22-7.17 (m, ArH, 6H), 6.92 (d, *J* = 9.3 Hz, ArH, 2H).

4-((4-nitrophenyl)(phenyl)amino)benzaldehyde (2). DMF (6.9 g) was added dropwise with vigorous stirring to 8.25 ml (90 mmol) of POCl₃ in an ice bath for 0.5 h to form the Vilsmeier reagent. Then, 5 g (20 mmol) of 4-nitro-N,N-diphenylamine were added, followed by stirring at 85 °C under N₂ atmosphere for 21 h, cooled, and then poured slowly into ice water. The mixture was then neutralized with 10% NaOH solution, and then extracted with dichloromethane, filtered, washed with water, and dried. After evaporation of dichloromethane, the crude product, orange/brown oil, was purified by flash chromatography in gradient eluent polarity (from pure petroleum ether to 7:3 petr.eth/Ethyl acetate). After evaporation of the solvent the pure product was obtained as orange-yellow crystals with an 86% yield (946 mg). ¹H NMR (300 MHz, DMSO-d₆) δ 9.92 (s, 1H, CHO), 8.16 (d, *J* = 9.2 Hz, 2H, ArH), 7.89 (d, *J* = 8.6 Hz, 2H, ArH), 7.50 (t, *J* = 7.7 Hz, 2H, ArH), 7.35 (t, *J* = 7.4 Hz, 1H, ArH), 7.30 – 7.21 (m, 3H, ArH), 7.10 (d, *J* = 9.2 Hz, 2H, ArH). ¹³C NMR (300 MHz, DMSO-d₆, δ ppm): δ 191.48, 152.21, 150.90, 144.77, 141.23, 131.91, 131.42, 130.57, 127.33, 126.90, 125.63, 123.76, 121.03. APCI-MS (CH₃CN, positive mode): *m/z*: 319.1 ([M+H]⁺, calcd. 319.1) 341.4 ([M + Na]⁺, calcd. 341.09). Elemental analysis: calcd. %: C: 71.69, H: 4.43, N: 8.80; found %: C: 67.75, H: 4.20, N: 8.32.

(E)-ethyl-2-cyano-3-(4-((4-nitrophenyl)(phenyl)amino)phenyl)acrylate (3). 4-((4-nitrophenyl)(phenyl)amino)benzaldehyde (0.911 g) was added to a solution of ethyl cyanoacetate (1.5 mL) and piperidine (0.06 mL) in Ethanol (90 mL) under nitrogen atmosphere. The mixture was stirred at 45 °C under N₂ atmosphere for 5 h. After cooling the solution, Dichloromethane was added and the mixture was washed first with brine, then with water. The organic phase was dried with sodium sulfate and the solvent was removed by rotary evaporation. The crude product, orange oil, was purified by flash chromatography in gradient eluent polarity (from 9:1 to 8:2 petr.eth:ethyl acetate). After evaporation of the solvent, the pure product was obtained as orange oil with an 80% yield (938 mg). ¹H NMR (300 MHz, DMSO-d₆) δ 8.30 (s, *J* = 8.7 Hz, 1H, vinyl proton), 8.16 (d, *J* = 9.2 Hz, 2H, ArH), 8.05 (d, *J* = 8.8 Hz, 2H, ArH), 7.50 (t, *J* = 7.7 Hz, 2H, ArH), 7.35 (t, *J* = 7.4

Hz, 1H, ArH), 7.24 (t, $J = 8.5$ Hz, 4H, ArH), 7.13 (d, $J = 9.2$ Hz, 2H, ArH), 4.31 (q, $J = 7.1$ Hz, 2H, CH₂), 1.30 (t, $J = 7.1$ Hz, 3H, CH₃). ¹³C NMR (300 MHz, DMSO-d₆) δ 162.19, 153.66, 151.79, 149.94, 144.47, 141.45, 132.91, 130.50, 127.34, 126.95, 126.40, 125.54, 123.26, 121.45, 115.99, 99.83, 62.18, 13.99. APCI-MS (CH₃CN, positive mode): m/z : 414.1 ([M+H]⁺, calcd. 414.14), 342.2 ([M+H -NO₂ -CN]⁺, calcd. 342.15). Elemental analysis: calcd. %: C: 69.72, H: 4.63, N: 10.16; found %: C: 61.45, H: 5.04, N: 8.74.

(E)-ethyl-2-cyano-3-(4-((4-nitrophenyl)(phenyl)amino)phenyl)acrylate (4). To a solution of (E)-ethyl-2-cyano-3-(4-((4-nitrophenyl)(phenyl)amino)phenyl) acrylate (938 mg, 2.27 mmol) in a mixture of ethanol (5 mL) and water (0.5 mL), iron powder (746 mg, 13.36 mmol) and calcium chloride (480 mg, 4.33 mmol) were added. After stirring at 60 °C for 5 hours, the same amounts of iron and calcium chloride were added and the mixture was left stirring at 60 °C overnight. After completion, the reaction mixture was filtered on celite to remove the iron residues, which were washed with ethyl acetate (2 x 20 mL). The organic extracts were washed with water and brine, and dried over sodium sulfate. After evaporation of the solvent, the crude product was purified by flash chromatography (1:1 petroleum ether/ethyl acetate) to give red crystals in 75% yield (656 mg). ¹H NMR (300 MHz, DMSO-d₆) δ 8.10 (s, 1H, vinyl proton), 7.87 (d, $J = 9.1$ Hz, 2H, ArH), 7.43 – 7.36 (m, 2H, ArH), 7.24 – 7.17 (m, 3H, ArH), 6.93 (d, $J = 8.6$ Hz, 2H, ArH), 6.73 (d, $J = 9.0$ Hz, 2H, ArH), 6.63 (d, $J = 8.6$ Hz, 2H), 5.27 (s, 2H), 4.26 (q, $J = 7.1$ Hz, 2H), 1.27 (t, $J = 7.1$ Hz, 3H). ¹³C NMR (300 MHz, DMSO-d₆) δ 162.99, 153.75, 153.01, 147.68, 145.16, 133.27, 132.73, 129.79, 128.45, 125.97, 125.39, 121.17, 116.86, 116.05, 114.90, 94.80, 61.68, 14.05. APCI-MS (CH₃CN, positive mode): m/z : 384.1 ([M+H]⁺, calcd. 384.17). Elemental analysis: calcd. %: C: 75.18, H: 5.52, N: 10.96; found %: C: 73.93, H: 5.81, N: 10.37.

BF₄⁻-N₂⁺-TPA-Et. Nitrosyl tetrafluoroborate (117 mg, 1 mmol) was added to a solution of (E)-ethyl 3-(4-((4-aminophenyl)(phenyl)amino)phenyl)-2-cyanoacrylate (343 mg) in acetonitrile (10 mL), cooled in an ice bath. After removal of the ice bath, the solution was stirred at room temperature for 30 minutes. The reaction was then stopped by adding 50 mL of cold diethyl ether, and the solvent was removed by vacuum. The product, a dark red solid, was directly used for the subsequent functionalization reaction. ¹H NMR (200 MHz, DMSO-d₆) δ 8.13 (s, 1H), 7.90 (d, $J = 8.9$ Hz, 2H), 7.53 – 7.33 (m, 2H), 7.23 (d, $J = 7.0$ Hz, 3H), 6.98 (d, $J = 8.4$ Hz, 2H), 6.73 (t, $J = 9.0$ Hz, 4H), 4.27 (q, $J = 7.1$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H). FT-IR (KBr): $\tilde{\nu}_{\max}$ (cm⁻¹): 2214 (CN/N=N stretching), 1715 (CO stretching).

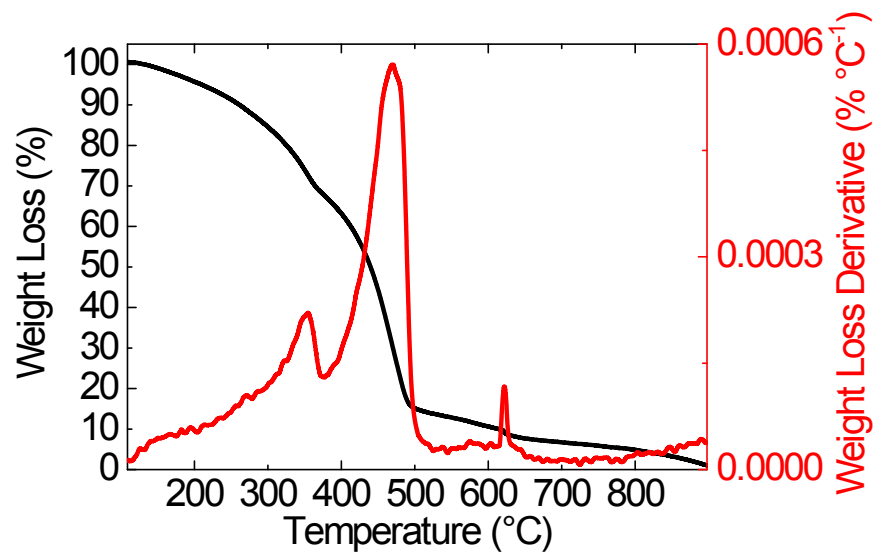


Figure SI-1. Thermogram of rGO-TPA-Et acquired under a nitrogen atmosphere. The black line represents the weight percentage loss, while the red line is the corresponding derivative curve.

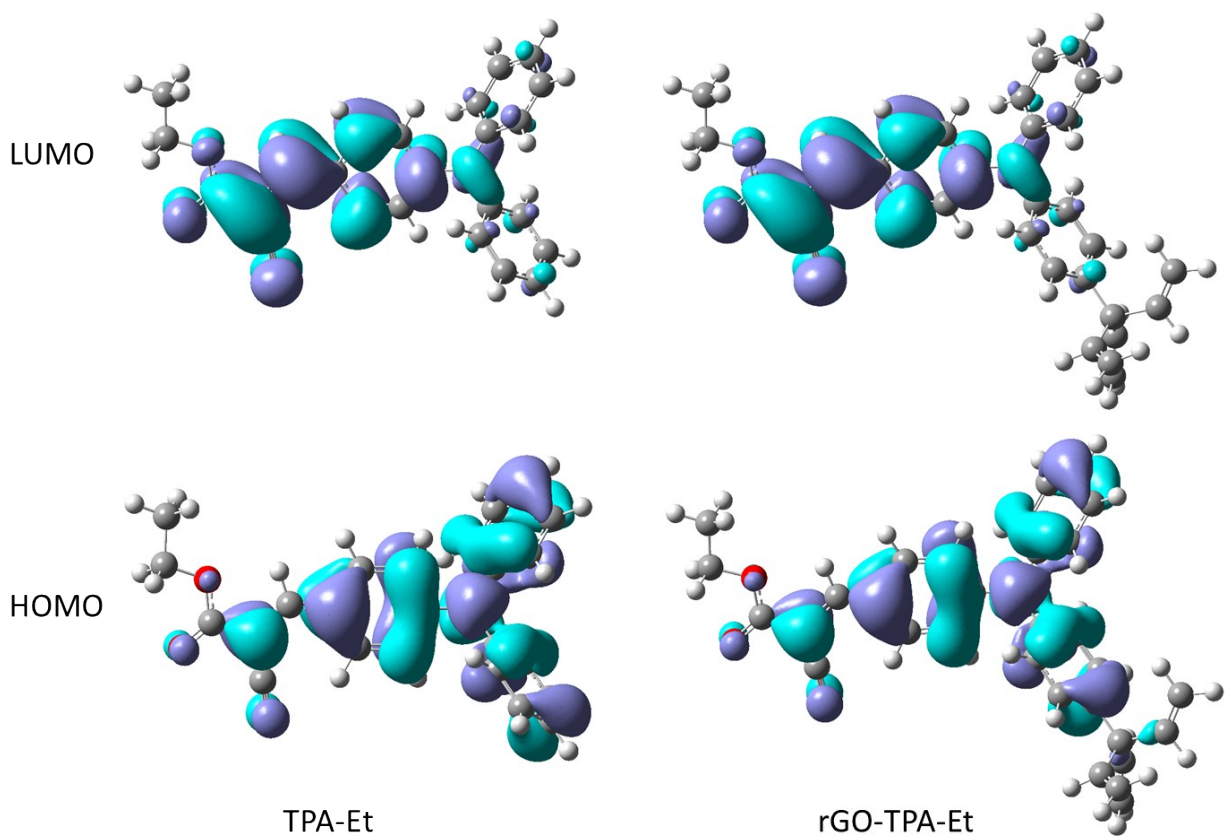
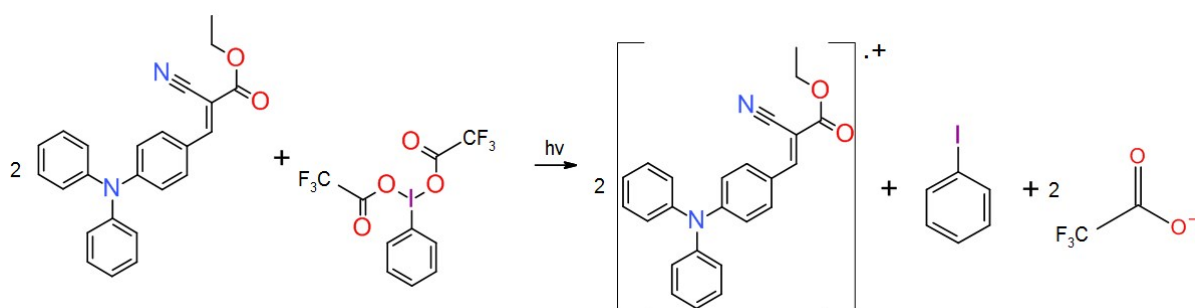


Figure SI-2. Isodensity surface plots of HOMO and LUMO orbitals for neutral TPA-Et (left) and for rGO-TPA-Et model system (right).



Scheme SI-2: Oxidation reaction of TPAEt by PIFA, under UV-VIS irradiation.

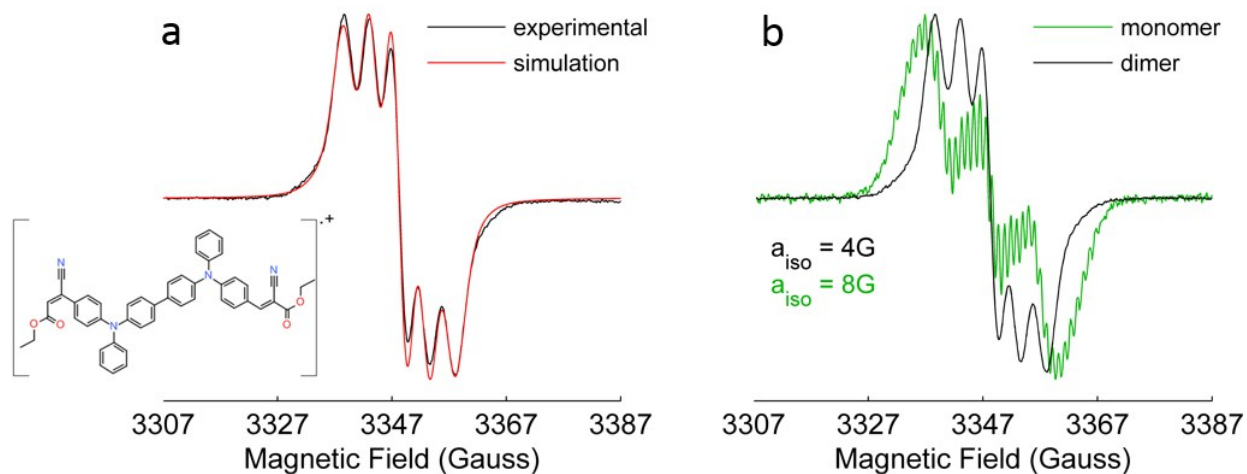


Figure SI-3: **a)** Black line: experimental EPR spectrum of the solution of concentrated TPAEt after oxidation with PIFA (T=290K). Red line: simulated spectrum. **b)** Comparison between the experimental EPR spectra (T=290K) of the monomeric and dimeric TPAEt radicals.

	g_{iso}	$a_{N,iso}$ (Gauss)
dimer	2.0027	4.1
monomer	2.0028	8.5

Table SI-1: Isotropic g-factor and ^{14}N Hyperfine coupling constant of TPA-Et monomer and dimer radical cations.

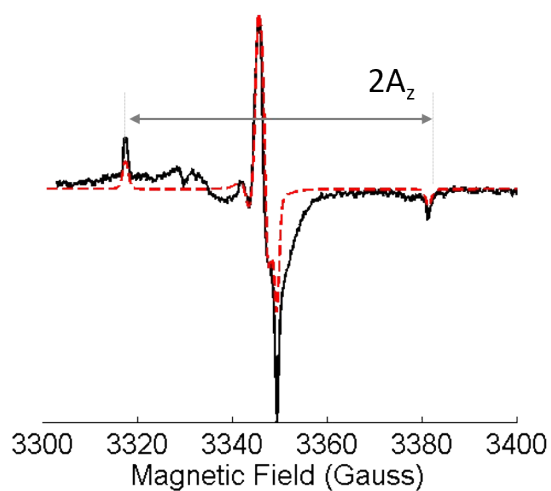
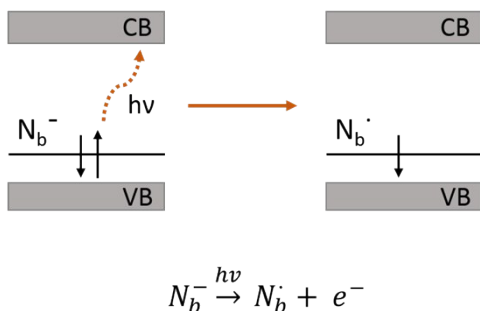


Figure SI-4. Light-induced EPR spectrum (light on – dark), of TiO₂ powder at T=130K (black). Simulation of the light-induced spectrum (red dashed line) obtained using the parameters listed in Table SI-2.



Scheme SI-3. Scheme showing the localized energy levels introduced by nitrogen defects in TiO₂ and the photogeneration of paramagnetic Nitrogen-related defects in TiO₂. Adapted from reference 50.

	g_{ii}	A_{ii} (Gauss)
x	2.0051	2
y	2.0042	3.6
z	2.0027	32

Table SI-2: Principal values of Zeeman (g) and hyperfine (A) tensors of ¹⁴N of the nitrogen defects in TiO₂, used for the simulation of the light-induced EPR spectrum in Figure SI-4.

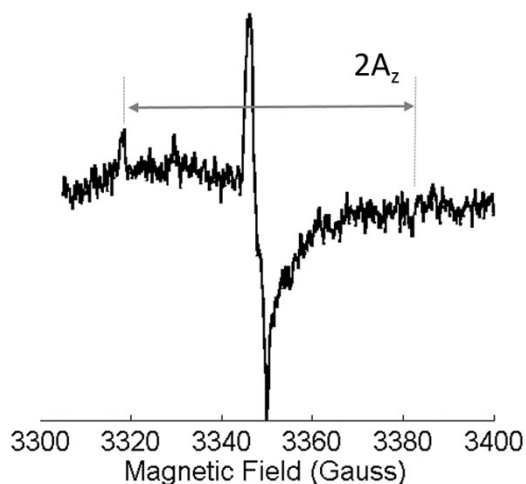


Figure SI-5: Light-induced EPR spectrum of the rGO/TiO₂ mixed material (T=130K). The spectrum is identical to the one obtained in pure TiO₂ powder (Figure SI-4).

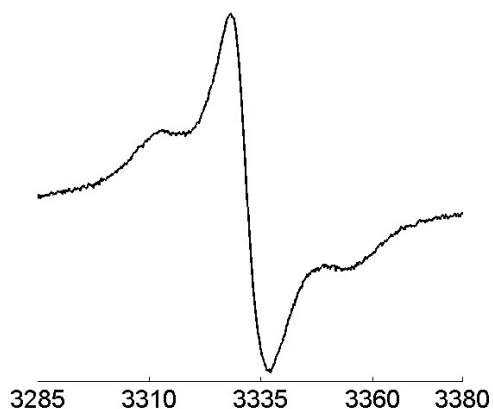


Figure SI-6: Light-induced EPR spectrum of the TPA-H/TiO₂ mixed material (T=130K). *TPA-H* is the carboxylic acid derivative of the TPA-Et molecule. The EPR spectrum belongs to the TPA-H radical cation, indicating the occurrence of a photoinduced electron transfer towards TiO₂. The same spectrum is obtained using TPA-Et (Figure 4 in the paper), proving that the ester dye molecule can interact with TiO₂ and produce electron photo-injection in the conduction band of the semiconductor.