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Electronic Supporting Information

Light assisted rechargeable battery: Proof of concept with Bodipy derivatives acting as combined photosensitizer and electrical storage unity

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A Synthesis

The starting organic materials were purchased from Acros Organics, Alfa Aesar and Sigma-Aldrich and were used without further purification. The purity of the synthesized compounds has been checked by ^{1}H NMR, ^{13}C NMR, IR and elemental analysis. NMR and IR spectra have been recorded using a Bruker 400 MHz and a Perkin Elmer apparatus respectively.

Elemental analyses were performed by the Département de Chimie Moléculaire (DCM) at Saint Martin d'Hères (France).

Thermal analyses were carried out using a Mettler Toledo DSCi star system under nitrogen flow at a heating rate of 20°C min^{-1}.

Fourier transform infrared (FT-IR) spectra were recorded on a Bruker Vertex 70v FT-IR spectrometer using KBr pellets.

Gel Permeation Chromatography (GPC) measurements were performed on a Waters apparatus equipped with a SOPARES RI2000 detector using THF as solvent at a rate of 1.0 mL.min^{-1}. 20 μL of 1.0% (w/v) sample solutions were injected for each analysis. Calibration was accomplished with ASTM D 5296 polystyrene standards.

2,8-Diethyl-5,5-difluoro-10-(3-hydroxypropyl)-1,3,7,9-tetramethyl-5*H*-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (1). 4-Bromobutyryl chloride (742 mg, 464 μL, 4.00 mmol) was added dropwise to a solution of 3-ethyl-2,4-dimethyl-1*H*-pyrrole (986 mg, 1.08 mL, 8.00 mmol) in anhydrous dichloromethane (45 mL). The mixture was heated at 50°C for 2.5 h. After cooling at room temperature, the crude mixture was concentrated *in vacuo* and used in next step without further purification. To a solution of the crude mixture in anhydrous toluene (95 mL) and anhydrous dichloromethane (5 mL), triethylamine (1.94 g, 2.67 mL, 19.2 mmol) was added over 30 min, followed by a slow addition of $BF_3 \cdot Et_2O$ (3.91 g, 3.40 mL, 27.5 mmol). The mixture was heated at 50°C for 1.5 h. After cooling at room temperature, dichloromethane was added and the reaction mixture was treated with water. The organic layer was washed with water followed by 2 M aqueous sodium hydroxide. Purification by flash chromatography on silica gel (eluent: pentane-EtOAc, 9:1 to 1:1) afforded **1** as a dark red-violet solid.

1 (336 mg, 0.93 mmol, 23%). mp 188-192°C; IR (thin film): ν_{max}/cm^{-1} 3565, 3400br, 2960, 2930, 2870, 1540, 1475, 1465, 1405, 1195, 1060, 975; δH (400 MHz, $CDCl_3$, 300 K) = 3.83 (2H, dd, ^1J(H,H) = 5.6 and 10.5 Hz, CH_2), 3.14 (2H, m, CH_2), 2.50 (6H, s, CH_3), 2.40 (q, 4H, ^1J(H,H) = 7.6 Hz, CH_2), 2.37 (6H, s, CH_3), 1.90 (2H, m, CH_2), 1.40 (1H, t, ^1J(H,H) = 4.8 Hz, OH), 1.05 (6H, t, ^1J(H,H) = 7.6 Hz, CH_3) ppm; δB (128 MHz, $CDCl_3$, 300 K) = 0.63 (1B, t, ^1J(B-F) = 34 Hz, B) ppm; δF (282 MHz, $CDCl_3$, 300 K) = −145.81 to −146.14 (2F, m, F) ppm; δC (128 MHz, $CDCl_3$, 300 K) = 152.3 (C_q), 144.3 (C_q), 135.7 (C_q), 132.7 (C_q), 131.0 (C_q), 62.6 (CH_2), 34.4 (CH_2), 25.0 (CH_2), 17.2 (CH_2), 14.8 (CH_3), 13.5 (CH_3), 12.4 (CH_3) ppm; MS (ESI$^+$): m/z (%): 385 (50) $[M+Na]^+$, 363 (100) $[M+H]^+$.

2,8-Diethyl-5,5-difluoro-10-(3-(methacryloyloxy)propyl)-1,3,7,9-tetramethyl-5*H*-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinin-4-ium-5-uide (2). To a solution of compound **1** (100 mg, 0.28 mmol) in anhydrous THF (400 μL), 4-dimethylaminopyridine (31 mg, 0.25 mmol) and methacrylic anhydride (50 μL, 0.34 mmol) were added sequentially. The reaction mixture was stirred at room temperature for 15 minutes and then quenched with MeOH (5.7 μL, 0.14 mmol). The mixture was stirred for additional 30 min and the solvent was evaporated *in vacuo*. The crude mixture was dissolved in dichloromethane, washed with 0.1 M aqueous solution of HCl then with water. The organic layer was dried over anhydrous $MgSO_4$, filtered and concentrated *in vacuo*. Purification by flash chromatography on silica gel (eluent: pentane-EtOAc, 95:5 to 90:10) afforded **2** as a dark red-violet solid.

2: (88 mg, 0.20 mmol, 71%). m.p. 131-133°C; IR (thin film): ν_{max}/cm^{-1} 2960, 2925, 1710, 1540, 1480, 1405, 1360, 1295, 1225, 1190, 1065, 1040, 980; δH (400 MHz, $CDCl_3$, 300 K) = 6.13 (1H, s, CH), 5.61 (1H, s, CH), 4.33 (2H, t, ^1J(H,H) = 6.2 Hz, CH_2), 3.11-3.16 (2H, m, CH_2), 2.50 (6H, s, CH_3), 2.40 (4H, q, ^1J(H,H) = 7.6 Hz, CH_2), 2.36 (6H, s, CH_3), 2.05-2.01 (2H, m, CH_2), 1.98 (3H, s, CH_3), 1.05 (6H, t, ^1J(H,H) = 7.6 Hz, CH_3) ppm; δB (128 MHz, $CDCl_3$, 300 K) = 0.61 (1B, t, ^1J(H,H) = 33 Hz, B) ppm; δF (282 MHz, $CDCl_3$, 300 K) = −145.83 to −146.14 (m, 2F, F) ppm; δC (128 MHz, $CDCl_3$, 300 K) = 167.4 (C=O), 152.6 (C_q), 143.2 (C_q), 136.2 (C_q), 135.5 (C_q), 132.8 (C_q), 130.9 (C_q), 125.7 (CH_2), 64.4 (CH_2), 30.7 (CH_2), 25.3 (CH_2), 18.4 (CH_3), 17.2 (CH_2), 14.8 (CH_3), 13.4 (CH_3), 12.4 (CH_3) ppm; MS (ESI$^+$): m/z (%): 453 (60) $[M+Na]^+$, 431 (100) $[M+H]^+$.

Poly(Bodipy-Butyl-Glycidyl)-methacrylate) (denoted Terpol). To a **2** (40.0 mg, 0.093 mmol), freshly distilled glycidyl-methacrylate (25.3 μL, 0.186 mmol) and freshly distilled butyl-methacrylate (103 μL, 0.650 mmol) in degazed toluene (0.7 mL) solution, 0.036 molar equiv of 2,2′-Azobis(2-methylpropionitrile) (AIBN) (4.64 mg, 3.32 10^{-5} mol) were added. After 48 h of stirring at 90°C, the solution was reduced under evaporation and then dichloromethane (5 mL) and pentane (50 mL) were poured into the solution and the polymeric material was filtered and thoroughly washed with pentane. The product was obtained as a brownish powder. The GPC with a polystyrene equivalent shown a M_n of 26900 g mol^{-1}, which corresponds to approximately 16 repetitions of patterns made of 1 Bdp, 3 Gly and 6 Bu with a polydispersity of 4.7.

Terpol (101 mg, 64%). T_g 74°C; Found: C, 64.32; H, 8.79; N, 2.14. Calc. (%) for Bdp/Gly/Bu = 0.08/0.33/0.58 : C, 65.36; H, 8.69; N, 2.02; ; IR (KBr): ν_{max}/cm^{-1} 1729 (C=O acrylate), 1548 (C=C Ar), 1477 (C-H alkyle), 1269 (C-O epoxy ring), 1198 (C-O acrylate), 1156 (C-O acrylate); δH (400 MHz, CD_3Cl_3, 300 K) = 0.67-1.19 (4H, m, CH_3); 1.19-1.51 (1.48H, m, CH_2 & CH_3); 1.51-1.72 (1.12H, m, CH_2); 1.72-2.24 (1.58H, m, CH_2 & CH_3); 2.24-2.59 (1.05H, m, CH_2 & CH_3); 2.62 (0.2H, s, CH); 2.83 (0.20H, s, CH); 3.10 (0.10H, s, CH_2); 3.20 (0.20H, s, CH); 3.81 (0.20H, s, CH); 3.94 (1.03H, s, CH_2); 4.08 (0.10H, s, CH_2); 4.27 (0.20H, s, CH) ppm; δF NMR (377 MHz, $CDCl_3$, 300 K) = -145.9 (2F, m, FB) ppm; δB NMR (128 MHz, $CDCl_3$, 300 K) = 0.60 (^{1}B, s, BF) ppm.

B Photophysical properties measured in solution

Electronic absorption spectra were recorded on a Shimadzu UV-2501 PC UV-Vis Spectrophotometer using dichloro-1,2-ethane as solvent.

Emission spectra were recorded in dichloro-1,2-ethane at room temperature on a Varian Cary.

Eclipse fluorescence spectrophotometer. Samples were placed in 1 cm path length quartz cuvettes.

Luminescence lifetime measurements in liquid solutions were performed after irradiation at λ = 400 nm obtained by the second harmonic of a titanium:sapphire laser (picosecond Tsunami laser spectra physics 3950-M1BB and 39868-03 pulse picker doubler) at a 800 kHz repetition rate. Fluotime 200 from AMS technologies was used for the decay acquisition. It consists of a GaAs microchannel plate photomultiplier tube (Hamamatsu model R3809U-50) followed by a time correlated single-photon counting system from Picoquant (PicoHarp300). The ultimate time resolution of the system is close to 30 ps. Luminescence decays were analyzed with Fluofit software available from Picoquant. Emission quantum yields ϕ were determined at room temperature in dichloro-1,2-ethane solutions (λ_{ex} = 470-480 nm) using the optically dilute method[37]. Fluoresceine in ethanol solution was used as quantum yield standard (ϕ = 0.79).

Experimental uncertainties are as follows: absorption maxima, 2 nm; molar absorption, 20%; emission maxima, 5 nm; emission lifetimes, 10%; emission quantum yields, 20%.

C Crosslinking

Terpol was drop coated (20 µL) onto an ITO electrode (surface area: 2 cm^2) from a solution of THF (1.0 mg in 1 mL). Once the film is formed by THF evaporation, the electrode is put into an argon atmosphere glove box. A solution of HBF_4 complexed with diethyl ether at a 0.73 M concentration is drop coated (10 µL) onto the **Terpol** film before heating the ITO electrode to 75°C for 5 minutes. A rest time of 5 minutes allows the electrode to reach R.T. and to finalize the crosslinking process. In the case of further electrochemical measurements, the ITO is immerged in ACN for one minute and then rinsed with ACN, this step is repeated 3 times.

For UV measurements, two ITOs were drop coated with Terpol solution. One of them was crosslinked following the previous procedure. Both ITOs were then each rinsed with 3 mL of DMF and a 1 cm UV cuvette was filled with this solution.

D Electrochemistry

All electrochemical measurements were performed in a dry-glove box under an argon atmosphere at room temperature. If I present terpol-2 results, the experimentation was not carried out in a glove-box. Add Dimethylformamide if I present results in DMF + LiTFSI 10^{-1} M. Acetonitrile (CH_3CN, Rathburn, HPLC grade), tetra-*n*-butyl-ammonium perchlorate (TBAP, Fluka), were dried under vacuum and stored under an argon atmosphere allowing to reach an amount of H_2O in electrolyte less than 10 ppm. Cyclic voltammetry experiments were performed using a Biologic SP-300 potentiostat/galvanostat equipped with a standard three electrodes electrochemical cell. Potentials were referred to an Ag|$AgNO_3$ 0.01 M reference electrode in CH_3CN + 0.1 mol.L^{-1} TBAP. Potentials can be converted to Li/Li$^+$ scale by adding 3.588 V or to SHE reference electrode by adding 548 mV[38]. The working electrode platinum disk (diam. 5 mm), was polished with 2 µm diamond paste (MecaprexPresi). For cyclic voltammetry. $E_{p,a}$ and $E_{p,c}$ correspond to the anodic peak and the cathodic peak potentials respectively :

$$E_{1/2} = \frac{E_{p,a} + E_{p,c}}{2} \text{ and } \Delta E_p = E_{p,a} - E_{p,c}$$

$E_{1/2,1}$ and $E_{1/2,2}$ relate to the cathodic and anodic redox processes, respectively.

Polymers were analyzed by drop coating (20 µL) onto ITO electrodes (surface area: 2 cm^2) from a solution of THF (1.0 mg in 1 mL).