



Synthesis, photophysical and electrochemical properties of perylene dyes



Érica Torres^{a, b}, Mário Nuno Berberan-Santos^b, Maria João Brites^{a, *}

^a LNEG, UES Unidade de Energia Solar, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal

^b CQFM-IST, CQFM – Centro de Química-Física Molecular and IN – Institute of Nanoscience and Nanotechnology, Instituto Superior Técnico, Universidade de Lisboa, 1049-001 Lisboa, Portugal

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ABSTRACT

Perylene dyes comprising: (i) 4-alkoxyphenylamino moiety in the 9-position as a strong donating group, (ii) cyanoacrylic acid as electron acceptor and anchoring group and (iii) a triple bond as short and rigid linker between perylene core and the acceptor group have been successfully synthesized. Their photophysical (i.e. absorption and emission spectra, molar extinction coefficients, fluorescence quantum yields and lifetime measurements) and electrochemical properties were investigated. The dyes display intense absorption in the visible exhibit high molar absorption coefficients making them good light harvesting materials for ss-DSCs.

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1. Introduction

Perylene derivatives have been widely applied in various optical devices due to their excellent photophysical properties (e.g. high absorption coefficient and high fluorescence quantum yield), charge transfer properties, as well as outstanding chemical, thermal and photochemical stability [1,2].

Perylene monoimides (PMI) or monoanhydrides (PMA) are being intensively investigated as sensitizers in dye-sensitized solar cells (DSCs) [3]. Keeping only one acceptor group, i.e. imide or anhydride, and introducing a donor group in the 9-position (such as diarylamine) proved to be important in order to obtain a favorable orbital partitioning strength and dipole moment of perylene compounds for DSCs. One way to control optical and electrochemical properties of perylene dyes is achieved by functionalizing *peri* and *bay* positions of perylene core with different substituents. In a simplified view, the *peri* groups coarsely tune the spectroscopic and electrochemical properties whereas the *bay* functional groups provide an additional fine tuning [4–7]. To date, the PMA derivative with a bis (4-(2,4,4-trimethylaminopentan-2-yl)phenylamino in 9-position and phenylthio groups in 1 and 6 positions of perylene core has shown to be the highest efficient perylene sensitizer in

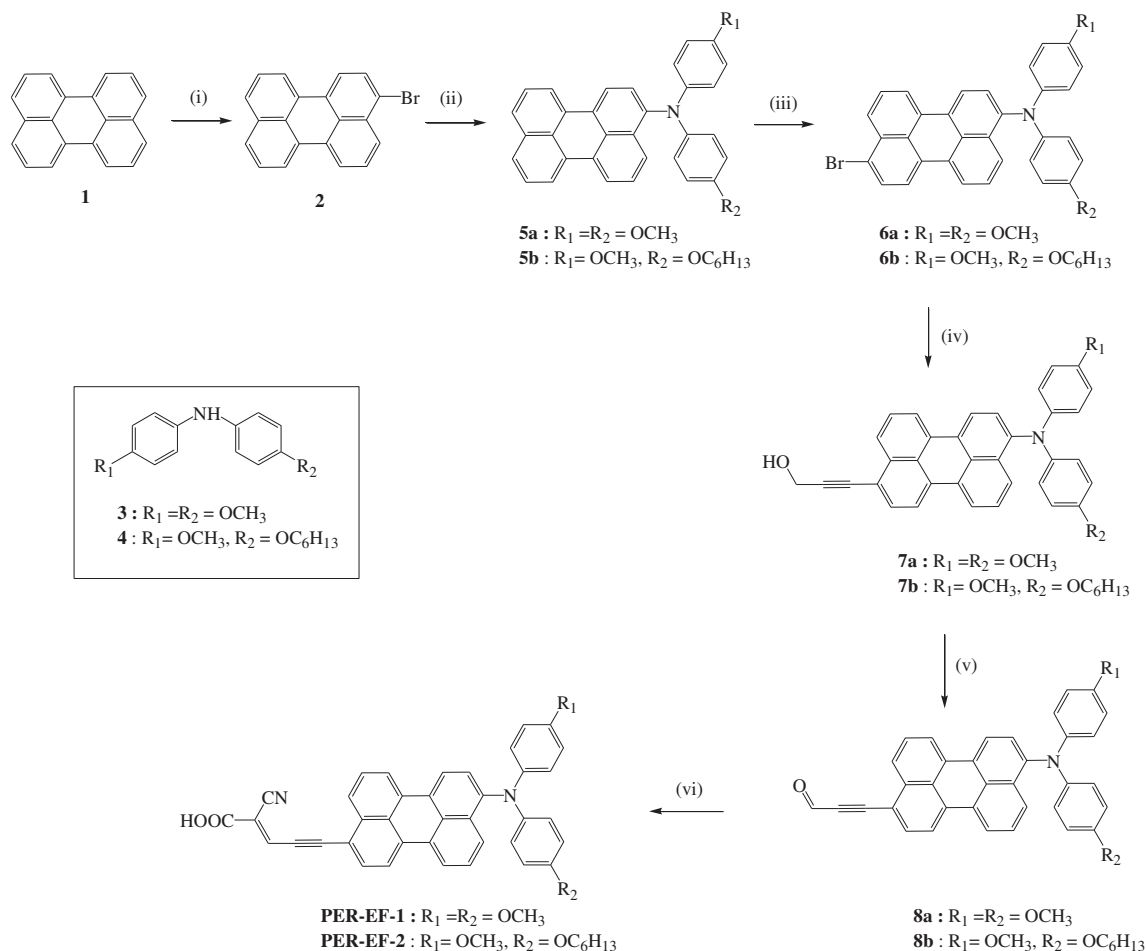
DSCs with liquid electrolyte (iodide/tri-iodide redox couple), delivering an incident monochromatic photo-to-current conversion efficiency of 87% and yielding a power conversion efficiency of 6.8% (6 μm thick mesoporous TiO₂ film) under standard AM 1.5 solar conditions [8]. In comparison, the same sensitizer tested in solid-state DSC (ss-DSC) yield a power conversion efficiency of only 1.8% (1.8 μm thick mesoporous TiO₂ film), showing that sensitizer design needs to be adapted according to the cell type.

Based on the aforementioned, the key challenge is to obtain efficiencies that are comparable to that for the optimized I⁻/I₃⁻/volatile solvent cell by using a Hole Transport Material (HTM), which may be a solid-state material. However, the poor filling of the mesoporous semiconductor and short diffusion length of charge carriers in HTM have limited the mesoscopic titania layer to a thickness of 2–3 μm. To increase the amount of light harvesting by ss-DSCs, organic dyes with high molar extinction coefficients, broad absorption in visible spectrum and with suitable geometry for control of molecular orientation and arrangement on the TiO₂ surface are needed [9,10].

Here we report the design, synthesis and characterization of new perylene dyes (Scheme 1) comprising: (1) a 4-alkoxyphenylamino moiety in the 9-position as a strong donating group, (2) a cyanoacrylic acid as electron acceptor and anchoring group and (3) a triple bond as short and rigid linker between perylene core and the acceptor group. The photophysical and electrochemical properties of these dyes were investigated, and the

* Corresponding author. Tel.: +351 210924600; fax: +351 217127195.

E-mail address: mjoao.brites@lneg.pt (M.J. Brites).



Scheme 1. (i) NBS (1.0 equiv), anhydrous THF, 24 h, r.t.; (ii) diarylamine (1.0 equiv), Pd(OAc)₂ (0.020 equiv), P(*t*-Bu)₃ (0.04 equiv), NaOt-Bu (1.5 equiv), anhydrous toluene, 120 °C; (iii), NBS (1.0 equiv), anhydrous THF, 24 h, r.t.; (iv) Pd(PPh₃)₄ (0.1 equiv), PPh₃ (0.1 equiv), CuI (0.1 equiv), 2-propyn-1-ol (2.0 equiv), anhydrous THF and diisopropylamine, 90 °C; (v) Dess-Martin, anhydrous CH₂Cl₂, 24 h; (vi) cyanoacetic acid (1.5 equiv), ammonium acetate (0.4 equiv), glacial acetic acid, 120 °C.

results obtained (high molar absorption coefficients and broad absorption in solar spectrum) make them promising sensitizers for solar cells applications.

2. Experimental section

2.1. Materials

Chemicals were purchased from commercial sources and used without further purification. Solvents were dried and distilled immediately prior to use by standard procedures [11]. Vacuum filtration purification was performed using silica gel (230–400 mesh) as the stationary phase in a filter funnel with porous plate. Tetrabutylammonium hexafluorophosphate (TBAPF₆-98%) used for cyclic voltammetry (CV) was purified by recrystallization from ethanol and dried under vacuum prior to use. The polymeric films were prepared from cyclic polyolefin Zeonex 480 R (average Mw ≈ 480,000, pellets) from Zeon Chemicals L.P.

2.2. Synthesis

The diarylamines bis(4-methoxyphenyl)amine **3** and 4-(hexyloxy)-*N*-(4-methoxyphenyl)aniline **4** were synthesized by following reported procedures [12].

2.2.1. 3-bromoperylene (**2**)

A solution of *N*-bromosuccinimide (NBS) (70.5 mg, 1.0 mmol) in dry THF (5 mL) was added to a solution of compound **1** (100 mg, 1.0 mmol) in dry THF (5 mL) and stirred at room temperature under nitrogen atmosphere for 24 h. The mixture was poured into water (30 mL) and extracted with dichloromethane (30 mL). The organic layer was dried over anhydrous MgSO₄. After filtration, the solvent was removed under reduced pressure to afford compound **2** as a yellow solid (128 mg, 98%). m.p.: 237–240 °C; IR ν_{max} (KBr): 2921 (C–H alkyl), 1504, 1493 (C=C aromatic ring), 814, 804 (C–H aromatic ring), 764 (C–Br); ¹H RMN δ (400 MHz; CDCl₃): 7.48 (2H, *t*, *J* = 8.0 Hz), 7.58 (1H, *t*, *J* = 8.0 Hz), 7.70 (2H, *d*, *J* = 8.0 Hz), 7.76 (1H, *d*, *J* = 8.4 Hz), 7.99 (1H, *d*, *J* = 8.4 Hz), 8.08 (1H, *d*, *J* = 8.4 Hz), 8.15 (1H, *d*, *J* = 7.6 Hz), 8.20 (1H, *d*, *J* = 7.6 Hz), 8.23 (1H, *d*, *J* = 7.2 Hz); HRMS (ESI): found [M+H]⁺ 330.0045; molecular formula C₂₀H₁₁Br requires [M+H]⁺ 330.0044.

2.2.2. General procedure for Buchwald–Hartwing cross-coupling (**5a–b**)

A mixture of 3-bromoperylene **2** (1.0 equiv), diarylamine (1.0 equiv), Pd(OAc)₂ (0.02 equiv), P(*t*-Bu)₃ (0.04 equiv), NaOt-Bu (1.5 equiv) and dry toluene were stirred at 120 °C in nitrogen atmosphere for 24 h. After cooling, water was added and the product was extracted with ethyl acetate (2 × 30 mL). The organic layer was washed with brine solution and dried over anhydrous MgSO₄. After

filtration, the solvent was removed under vacuum and the product was quickly purified by vacuum filtration over a short pad of silica using a mixture of petroleum ether/CH₂Cl₂ (9:1 to 8:2) as eluent.

2.2.2.1. Bis-(4-methoxy-phenyl)-perylene-3-yl-amine (5a). The general method was used with 3-bromoperylene **2** (100 mg, 0.303 mmol) and bis(4-methoxyphenyl)amine **3** (70 mg, 0.303 mmol) to afford **5a** (116.6 mg, 45%) as an orange solid. m.p.: 217–220 °C; IR ν_{\max} (KBr): 2924, 2831 (C–H alkyl), 1507, 1500 (C=C aromatic ring), 1242 (C–N), 829, 810 (C–H aromatic ring) cm⁻¹; ¹H RMN δ (400 MHz; CDCl₃): 3.77 (6H, s, OCH₃), 6.78 (4H, d, *J* = 8.0 Hz), 6.98 (4H, d, *J* = 8.0 Hz), 7.47 (1H, t, *J* = 8.0 Hz), 7.46 (1H, t, *J* = 8.0 Hz), 7.67 (2H, m), 7.83 (1H, d, *J* = 8.0 Hz), 7.34 (1H, t, *J* = 8.0 Hz), 7.20 (1H, brs), 7.83 (1H, d, *J* = 8.0 Hz), 8.13 (2H, d, *J* = 8.0 Hz), 8.15 (2H, d, *J* = 8.0 Hz); ¹³C NMR δ (400 MHz, CDCl₃): 154.7, 144.4, 142.6, 134.8, 131.7, 131.4, 131.2, 130.4, 128.4, 127.8, 127.3, 126.5, 126.4, 124.5, 123.6, 120.9, 120.5, 120.2, 119.8, 114.7, 55.8; HRMS (ESI): found [M+H]⁺ 479.1872; molecular formula C₃₄H₂₅NO₂ requires [M+H]⁺ 479.1879.

2.2.2.2. (4-hexyloxy-phenyl)-(4-methoxy-phenyl)-perylene-3-yl-amine (5b). The general method was used with 3-bromoperylene **2** (100 mg, 0.303 mmol) and 4-(hexyloxy)-N-(4-methoxyphenyl)aniline **4** (90.7 mg, 0.303 mmol) to afford **5b** (193.4 mg, 60%) as an orange solid. m.p.: 127–128 °C; IR ν_{\max} (KBr): 2956, 2852 (C–H alkyl), 1508 (C=C aromatic ring), 1239 (C–N), 811 (C–H aromatic ring) cm⁻¹; ¹H RMN δ (400 MHz; CDCl₃): 0.91 (3H, t, *J* = 8.0 Hz), 1.34 (4H, m); 1.44 (2H, m), 1.76 (2H, m), 3.78 (3H, s, OCH₃), 3.91 (2H, t, *J* = 8.0 Hz), 6.79 (4H, d, *J* = 8.0 Hz), 6.98 (4H, d, *J* = 8.0 Hz), 7.21 (1H, brs), 7.34 (1H, t, *J* = 8.0 Hz), 7.49 (2H, m), 7.67 (2H, m), 7.83 (1H, d, *J* = 8.0 Hz), 8.15 (4H, m); ¹³C NMR δ (500 MHz, CDCl₃): 154.8, 154.5, 131.6, 131.3, 131.2, 130.4, 128.5, 127.9, 127.5, 126.5, 126.2, 124.5, 123.7, 123.6, 121.7, 120.9, 120.5, 120.2, 119.8, 115.2, 114.5, 68.3, 55.5, 31.6, 29.4, 25.8, 22.6, 14.1; HRMS (ESI): found [M+H]⁺ 549.2656; molecular formula C₃₉H₃₅NO₂ requires [M+H]⁺ 549.2662.

2.2.3. General procedure for compounds 6a–b

The products **6a** and **6b** were synthesized according to the procedure described in the subchapter 2.2.1.

2.2.3.1. (9-bromo-perylene-3-yl)-bis-(4-methoxy-phenyl)-amine (6a). The general method was used with **5a** (60.3 mg, 0.126 mmol) and NBS (22.4 mg, 0.126 mmol) in dry THF (20 mL) to afford **6a** (131.4 mg, 94%) as a red solid. m.p.: 208–210 °C; IR ν_{\max} (KBr): 2925, 2832 (C–H alkyl), 1506, 1502 (C=C aromatic ring), 1240 (C–N), 828 (C–H aromatic ring), 611 (C–Br) cm⁻¹; ¹H RMN δ (400 MHz; DMSO): 3.71 (6H, s, OCH₃), 6.86 (4H, d, *J* = 8.0 Hz), 6.90 (4H, d, *J* = 8.0 Hz), 7.17 (1H, d, *J* = 8.0 Hz), 7.46 (1H, t, *J* = 8.0 Hz), 7.72 (1H, t, *J* = 8.0 Hz), 7.80 (1H, d, *J* = 8.0 Hz), 7.91 (1H, d, *J* = 8.0 Hz), 8.02 (1H, d, *J* = 8.0 Hz), 8.19 (1H, d, *J* = 8.0 Hz), 8.39 (1H, d, *J* = 8.0 Hz), 8.41 (1H, d, *J* = 8.0 Hz), 8.48 (1H, d, *J* = 8.0 Hz); ¹³C NMR δ (500 MHz, THF): 155.4, 145.4, 142.6, 133.0, 131.9, 131.4, 131.3, 131.1, 130.8, 129.9, 129.5, 127.8, 127.2, 126.4, 126.3, 125.9, 125.0, 123.8, 121.5, 121.2, 121.1, 120.0, 114.3, 54.6, 29.2; HRMS (ESI): found [M+H]⁺ 557.0974; molecular formula C₃₄H₂₄BrNO₂ requires [M+H]⁺ 557.0985.

2.2.3.2. (9-bromo-perylene-3-yl)-(4-hexyloxy-phenyl)-(4-methoxy-phenyl)-amine (6b). The general method was used with **5b** (105.4 mg, 0.197 mmol) and NBS (35.1 mg, 0.197 mmol) in dry THF (20 mL) to afford **6b** (115.1 mg, 93%) as a red solid. m.p.: 188–191 °C; IR ν_{\max} (KBr): 2925, 2853 (C–H alkyl), 1501 (C=C aromatic ring), 1239 (C–N), 825, 803 (C–H aromatic ring), 622, 611 (C–Br) cm⁻¹; ¹H RMN δ (400 MHz; CDCl₃): 0.90 (3H, t, *J* = 8.0 Hz), 1.34 (4H, m), 1.45 (3H, m), 1.75 (2H, m), 3.78 (3H, s, OCH₃), 3.92 (2H, t, *J* = 8.0 Hz), 6.76 (4H, d, *J* = 8.0 Hz), 6.78 (4H, d, *J* = 8.0 Hz), 7.18 (1H,

brs), 7.48 (1H, t, *J* = 8.0 Hz), 7.58 (1H, m), 7.68 (1H, d, *J* = 8.0 Hz), 7.86 (2H, m), 7.94 (1H, d, *J* = 8.0 Hz), 8.07 (1H, d, *J* = 8.0 Hz), 8.18 (2H, m); ¹³C NMR δ (500 MHz, CDCl₃): 132.5, 132.4, 131.6, 130.6, 130.1, 128.3, 127.7, 126.7, 126.2, 125.2, 125.0, 124.8, 121.3, 121.1, 121.0, 115.2, 114.8, 71.0, 68.3, 55.5, 31.6, 29.7, 29.4, 25.8, 22.6, 14.1; HRMS (ESI): found [M+H]⁺ 627.1761; molecular formula C₃₉H₃₄BrNO₂ requires [M+H]⁺ 627.1767.

2.2.4. General procedure for Sonogashira–Hagihara cross-coupling (7a–b)

To a solution of **6a/6b** (1.0 equiv) in anhydrous THF-diisopropylamine (10–10 mL) were added Pd(PPh₃)₄ (0.1 equiv), CuI (0.1 equiv) and PPh₃ (0.1 equiv) under nitrogen atmosphere, refluxed at 90 °C. 2-propyn-1-ol (2.0 equiv) was added after 2 h. The reaction mixture was stirred for 24 h. After cooling down to room temperature, the solvents were removed under vacuum to dryness. The powdery product obtained was purified by vacuum filtration over short pad of silica using a mixture of hexane/AcOEt (9:1 to 8:2) as eluent.

2.2.4.1. 3-[9-[bis-(4-methoxy-phenyl)-amino]-perylene-3-yl]-prop-2-yn-1-ol (7a). The general method was used with **6a** (131.0 mg, 0.235 mmol) and 2-propyn-1-ol (27.4 μ L, 0.470 mmol) to afford **7a** (108.9 mg, 87%) as a red solid. m.p.: 170–172 °C; IR ν_{\max} (KBr): 2928, 2833 (C–H alkyl), 2215 (C≡C), 1501 (C=C aromatic ring), 1239 (C–N), 1035 (C–O alcohol), 829, 810 (C–H aromatic ring) cm⁻¹; ¹H RMN δ (400 MHz; CDCl₃): 3.77 (6H, s, OCH₃), 4.67 (2H, s), 6.78 (4H, d, *J* = 8.0 Hz), 6.97 (4H, d, *J* = 8.0 Hz), 7.18 (1H, d, *J* = 8.0 Hz), 7.33 (1H, t, *J* = 8.0 Hz), 7.53 (1H, t, *J* = 8.0 Hz), 7.62 (1H, d, *J* = 8.0 Hz), 7.83 (1H, d, *J* = 8.0 Hz), 8.00 (1H, d, *J* = 8.0 Hz), 8.09 (1H, d, *J* = 8.0 Hz), 8.15 (1H, d, *J* = 8.0 Hz), 8.16 (1H, d, *J* = 8.0 Hz), 8.18 (1H, d, *J* = 8.0 Hz); ¹³C NMR δ (400 MHz, CDCl₃): 154.9, 145.2, 142.3, 134.7, 133.9, 132.6, 132.5, 132.1, 132.0, 131.6, 131.4, 131.3, 130.7, 130.1, 128.6, 128.5, 128.1, 127.9, 127.5, 127.3, 127.1, 126.2, 126.0, 125.1, 124.8, 123.9, 121.7, 120.9, 120.7, 119.1, 114.6, 93.1, 84.3, 69.7, 60.4, 55.5, 52; HRMS (ESI): found [M+H]⁺ 533.1973; molecular formula C₃₇H₂₇NO₃ requires [M+H]⁺ 533.1985.

2.2.4.2. 3-[9-[4-(4-hexyloxy-phenyl)-(4-methoxy-phenyl)-amino]-perylene-3-yl]-prop-2-yn-1-ol (7b). The general method was used with **6b** (87.6 mg, 0.140 mmol) and 2-propyn-1-ol (16.3 μ L, 0.279 mmol) to afford **7b** (67.7 mg, 80%) as a red solid. m.p.: 105–107 °C; IR ν_{\max} (KBr): 2924, 2853 (C–H alkyl), 2218 (C≡C), 1500 (C=C aromatic ring), 1238 (C–N), 1029 (C–O alcohol), 825, 808 (C–H aromatic ring) cm⁻¹; ¹H RMN δ (400 MHz; CDCl₃): 0.90 (3H, t, *J* = 8.0 Hz), 1.34 (4H, m); 1.44 (2H, m), 1.75 (4H, m), 3.77 (3H, s, OCH₃), 3.90 (2H, t, *J* = 8.0 Hz), 4.67 (2H, s), 6.77 (4H, d, *J* = 8.0 Hz), 6.96 (4H, d, *J* = 8.0 Hz), 7.19 (1H, d, *J* = 8.0 Hz), 7.34 (1H, t, *J* = 8.0 Hz), 7.56 (1H, t, *J* = 8.0 Hz), 7.64 (1H, d, *J* = 8.0 Hz), 7.84 (1H, d, *J* = 8.0 Hz), 8.03 (1H, d, *J* = 8.0 Hz), 8.11 (1H, d, *J* = 8.0 Hz), 8.16 (1H, d, *J* = 8.0 Hz), 8.18 (1H, d, *J* = 8.0 Hz), 8.21 (1H, d, *J* = 8.0 Hz); ¹³C NMR δ (400 MHz, CDCl₃): 154.9, 154.6, 152.3, 145.3, 142.7, 142.4, 132.1, 131.4, 130.6, 130.0, 128.2, 127.9, 127.5, 127.3, 127.1, 126.6, 126.1, 125.9, 125.1, 124.9, 123.8, 121.7, 121.5, 120.9, 120.7, 119.1, 118.9, 118.8, 115.2, 114.6, 92.9, 84.4, 68.4, 60.3, 55.5, 52.0, 31.6, 29.4, 25.8, 22.6, 14.0; HRMS (ESI): found [M+H]⁺ 603.2762; molecular formula C₄₂H₃₇NO₃ requires [M+H]⁺ 603.2768.

2.2.5. General procedure for the compounds (8a–b)

To a solution of 1,1,1-Tris(acetyloxy)-1,1-dihydro-1,2-benziodoxol-3-(1H)-one (Dess–Martin periodinane) (1.5 equiv) in anhydrous CH₂Cl₂ (10 mL) was added a solution of compounds **7a/7b** in anhydrous CH₂Cl₂ (10 mL). The mixture was stirred at room temperature for 24 h. After complete consumption of the starting material, a saturated NaHCO₃ solution containing 2.5 g of Na₂S₂O₃

(15 mL) and ethyl ether (15 mL) were added and the mixture was stirred for more 10 min. The product was extracted with ethyl ether (2 × 30 mL). The organic layer was dried over anhydrous MgSO₄ and the solvent was evaporated under vacuum.

2.2.5.1. {9-[bis-(4-methoxy-phenyl)-amino]-perylene-3-yl}-propynal (8a). The general method was used with **7a** (108 mg, 0.203 mmol) and Dess-Martin reagent (130 mg, 0.305 mmol) to afford **8a** (104 mg, 96%) as a dark red solid. m.p.: 162–163 °C; IR ν_{\max} (KBr): 2921, 2851 (C–H alkyl), 2170 (C≡C), 1640 (C=O aldehyde), 1507, 1499 (C=C aromatic ring), 1240 (C–N), 851, 807 (C–H aromatic ring) cm⁻¹; ¹H RMN δ (400 MHz; CDCl₃): 3.77 (6H, s, OCH₃), 6.79 (4H, d, *J* = 8.0 Hz), 6.97 (4H, d, *J* = 8.0 Hz), 7.19 (1H, d, *J* = 8.0 Hz), 7.35 (1H, t, *J* = 8.0 Hz), 7.62 (1H, t, *J* = 8.0 Hz), 7.82 (1H, d, *J* = 8.0 Hz), 7.87 (1H, d, *J* = 8.0 Hz), 8.05 (1H, d, *J* = 8.0 Hz), 8.16 (1H, d, *J* = 8.0 Hz), 8.18 (1H, d, *J* = 8.0 Hz), 8.19 (1H, d, *J* = 8.0 Hz), 8.23 (1H, d, *J* = 8.0 Hz), 9.56 (1H, s, -CHO); ¹³C NMR δ (400 MHz, CDCl₃): 176.5, 155.2, 154.4, 146.4, 142.5, 141.8, 135.4, 134.9, 134.3, 131.9, 131.8, 130.9, 130.5, 130.1, 129.4, 128.3, 128.2, 128.0, 126.7, 126.5, 125.8, 125.5, 125.4, 125.0, 124.2, 124.0, 123.0, 122.5, 121.2, 121.0, 120.1, 118.9, 118.1, 114.9, 114.6, 113.4, 94.8, 94.6, 65.8, 59.3, 55.5, 20.4, 15.4; HRMS (ESI): found [M+H]⁺ 531.1820; molecular formula C₃₇H₂₅NO₃ requires [M+H]⁺ 531.1829.

2.2.5.2. {9-[(4-hexyloxy-phenyl)-(4-methoxy-phenyl)-amino]-perylene-3-yl}-propynal (8b). The general method was used with **7b** (122.0 mg, 0.203 mmol) and Dess-Martin reagent (129.0 mg, 0.304 mmol) to afford **8b** (108 mg, 92%) as a dark red solid. m.p.: 117–120 °C; IR ν_{\max} (KBr): 2923 (C–H alkyl), 2170 (C≡C), 1647 (C=O aldehyde), 1499 (C=C aromatic ring), 1238 (C–N), 807 (C–H aromatic ring) cm⁻¹; ¹H RMN δ (400 MHz; CDCl₃): 0.90 (3H, t, *J* = 8.0 Hz), 1.34 (4H, m), 1.44 (2H, m), 1.76 (2H, m), 3.78 (3H, s, OCH₃), 3.91 (2H, t, *J* = 8.0 Hz), 6.78 (4H, d, *J* = 8.0 Hz), 6.96 (4H, d, *J* = 8.0 Hz), 7.20 (1H, d, *J* = 8.0 Hz), 7.36 (1H, t, *J* = 8.0 Hz), 7.65 (1H, t, *J* = 8.0 Hz), 7.84 (1H, d, *J* = 8.0 Hz), 7.90 (1H, d, *J* = 8.0 Hz), 8.01 (1H, d, *J* = 8.0 Hz), 8.17 (1H, d, *J* = 8.0 Hz), 8.18 (1H, d, *J* = 8.0 Hz), 8.19 (1H, d, *J* = 8.0 Hz), 8.20 (1H, d, *J* = 8.0 Hz), 9.56 (1H, s, -CHO); ¹³C NMR δ (500 MHz, CDCl₃): 175.6, 155.1, 154.8, 146.2, 142.6, 142.3, 140.8, 136.3, 135.2, 131.7, 131.5, 130.0, 129.7, 129.6, 129.0, 128.3, 128.0, 126.7, 125.9, 125.3, 124.1, 124.1, 122.6, 121.5, 121.3, 120.8, 117.1, 117.9, 115.2, 114.6, 112.9, 68.3, 55.5, 55.4, 31.6, 29.7, 29.4, 25.8, 22.6, 14.0; HRMS (ESI): found [M+H]⁺ 601.2604; molecular formula C₄₂H₃₅NO₃ requires [M+H]⁺ 601.2611.

2.2.6. General procedure for the compounds (PER-EF-1 and PER-EF-2)

A mixture of aldehyde **8a/8b** (1.0 equiv), 2-cyanoacetic acid (1.5 equiv), ammonium acetate (0.4 equiv) and glacial acetic acid were refluxed at 120 °C for 1 h under nitrogen atmosphere. The reaction mixture was then cooled to room temperature and taken up in sodium bicarbonate solution. The organic phase was separated, washed with water, dried over anhydrous MgSO₄, filtered and concentrated under reduced pressure. The residue obtained was purified by silica preparative chromatography using mixtures of AcOEt/MeOH (9:1) as eluent.

2.2.6.1. 5-{9-[bis-(4-methoxy-phenyl)-amino]-perylene-3-yl}-2-cyano-pent-2-en-4-ynoic acid (PER-EF-1). The general method was used with **8a** (43.7 mg, 0.082 mmol) and 2-cyanoacetic acid (10.5 mg, 0.123 mmol) to afford **PER-EF-1** (16.5 mg, 34%) as a purple solid. m.p.: 234–235 °C; IR ν_{\max} (KBr): 3447 (COOH), 2921, 2851 (C–H alkyl), 2345 (C≡N), 2172 (C≡C), 1507, 1499 (C=C aromatic ring), 1241 (C–N), 826, 808 (C–H aromatic ring) cm⁻¹; ¹H RMN δ (400 MHz; DMSO): 3.71 (6H, s, OCH₃), 6.74 (4H, d, *J* = 8.0 Hz), 6.90 (4H, d, *J* = 8.0 Hz), 7.17 (1H, d, *J* = 8.0 Hz), 7.34 (2H, m), 7.56 (1H, s),

7.62 (2H, m), 8.15 (1H, d, *J* = 8.0 Hz), 8.23 (2H, d, *J* = 8.0 Hz), 8.28 (2H, d, *J* = 8.0 Hz); ¹³C NMR δ (400 MHz, CDCl₃): 176.5, 155.2, 146.6, 142.5, 141.9, 135.4, 135.3, 134.6, 132.0, 131.8, 131.1, 131.0, 130.0, 128.3, 128.1, 128.0, 126.7, 126.5, 125.8, 125.5, 125.4, 124.5, 124.2, 124.1, 123.0, 121.6, 121.0, 119.0, 115.0, 114.7, 94.8, 94.5, 65.8, 55.5, 15.2; HRMS (ESI): found [M+H]⁺ 598.1876; molecular formula C₄₀H₂₆N₂O₄ requires [M+H]⁺ 598.1887.

2.2.6.2. 2-cyano-5-{9-[(4-hexyloxy-phenyl)-(4-methoxy-phenyl)-amino]-perylene-3-yl}-pent-2-en-4-ynoic acid (PER-EF-2). The general method was used with **8b** (40.0 mg, 0.067 mmol) and 2-cyanoacetic acid (8.5 mg, 0.001 mmol) to afford **PER-EF-2** (25.5 mg, 55%) as a purple solid. m.p.: 215–216 °C; IR ν_{\max} (KBr): 3448 (COOH), 2923, 2852 (C–H alkyl), 2345 (C≡N), 2171 (C≡C), 1507, 1499 (C=C aromatic ring), 1239 (C–N), 825, 807 (C–H aromatic ring) cm⁻¹; ¹H RMN δ (400 MHz; CDCl₃): 0.83 (3H, t, *J* = 8.0 Hz), 1.26 (4H, m), 1.36 (2H, m), 1.64 (2H, m), 3.67 (3H, s, OCH₃), 3.82 (2H, t, *J* = 8.0 Hz), 6.72 (4H, d, *J* = 8.0 Hz), 6.84 (4H, d, *J* = 8.0 Hz), 7.12 (1H, d, *J* = 8.0 Hz), 7.31 (1H, m), 7.59 (1H, t, *J* = 8.0 Hz), 7.71 (1H, d, *J* = 8.0 Hz), 7.75 (1H, d, *J* = 8.0 Hz), 8.16 (1H, brs), 8.24 (2H, brs), 8.28 (2H, d, *J* = 8.0 Hz); ¹³C NMR δ (500 MHz, CDCl₃): 154.5, 154.0, 145.3, 141.8, 141.6, 133.8, 132.3, 131.0, 130.4, 129.2, 128.5, 127.8, 127.3, 126.4, 125.6, 123.6, 122.5, 120.9, 114.9, 114.3, 91.9, 67.5, 55.0, 40.0, 39.8, 39.7, 39.5, 39.3, 39.2, 31.0, 25.0, 22.0, 14.0; HRMS (ESI): found [M+H]⁺ 668.2660; molecular formula C₄₅H₃₆N₂O₄ requires [M+H]⁺ 668.2669.

2.3. Film sensitization

The TiO₂ films (with average thickness of 1.5 μ m) were prepared according to previous reported method [13] onto alkali free (AF54) thin glass substrates (Präzisions & Optik GmbH). These were immersed into a 2.5 × 10⁻⁵ M solution of dye in dichloromethane and kept for 24 h at room temperature in the dark.

2.4. Instruments and measurements

¹H and ¹³C NMR spectra were recorded on a Bruker Avance III 400 or a Bruker AV 500b spectrometer, operating at 400 and 500 MHz, respectively. Chemical shifts are reported in ppm downfield from tetramethylsilane, and coupling constants (*J*) are reported in Hz. Melting points were measured on a Reichert Thermovar apparatus fitted with a microscope and are uncorrected. The absorption spectra were recorded at room temperature in quartz cuvettes using a Shimadzu UV-3101PC UV–Vis–NIR spectrophotometer and the fluorescence measurements were obtained using a Horiba Jobin Yvon Fluorolog 3 spectrometer. Fluorescence quantum yields of dyes **PER-EF-1** and **PER-EF-2** were determined by a comparative method at 298 K using rhodamine 101 in ethanol (ϕ = 0.96) as the fluorescence standard [14]. Fluorescence measurements in Zeonex films were obtained with a Fluorolog F112A fluorimeter (Spex, www.jobinyvon.com) in right-angle configuration. Emission spectra were corrected for the spectral response of the optics and photomultiplier. The films were mounted slightly away from a 45° angle geometry to minimize specular reflection of the excitation light. All fluorescence decays were measured by single-photon timing. The system is formed by a diode-pumped solid state mode-locked Nd:YVO₄ laser (Vanguard, Spectra Physics) delivering 2W of 532 nm light at repetition 76 MHz and pulse duration of ~ 12 ps that synchronously pumped a cavity-dumped dye laser (701-2, Coherent, delivering 5–6 ps pulses with 40 nJ pulse⁻¹ at 3.4 MHz) working with rhodamine 6G. Intensity decay measurements were made by alternating collection of impulse and decays with the emission polarizer set at the magic angle position. Impulses were recorded slightly away from the excitation

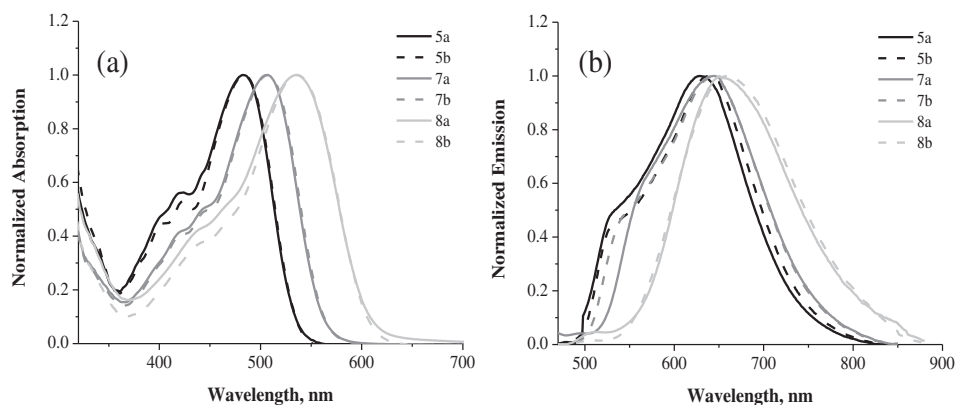


Fig. 1. (a) Normalized absorption spectra of intermediates **5a**, **5b**, **7a**, **7b**, **8a** and **8b** in toluene (2.5×10^{-5} M); (b) Normalized emission spectra of intermediates **5a**, **5b**, **7a**, **7b**, **8a** and **8b** in toluene (2.5×10^{-5} M, $\lambda_{exc} = 450$ nm).

wavelength at 562 nm with a scattering suspension, thus defining the instrument responds function (IRF). For the decays, a cut-off filter was used to effectively remove excitation light. Emission light was passed through a depolarizer before reaching the Jobin-Yvon HR320 monochromator with a grating of 100 lines/mm which select the fluorescence light from the samples with a bandwidth of 15–20 nm. The fluorescence was detected by a Hamamatsu 2809U-01 microchannel plate photomultiplier. No less than 20,000 counts were accumulated at the maximum channel. Solutions of the samples were contained in 1 cm path-length quartz cells at the optical density below 0.1 for fluorescence studies. Cyclic voltammetry (CV) was carried out at room temperature using a three electrode cell in potentiostat/galvanostat Gamry Instrument reference 600. The scan rate was 50 mV/s. A platinum disk, platinum wire and Ag/AgCl (3 M KCl solution) were used as working (WE), counter (CE) and reference electrodes, respectively. The supporting electrolyte was a solution of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in anhydrous *N,N*-dimethylformaldehyde, with concentration of dyes fixed at 1×10^{-3} M. The potential was calibrated against ferrocene/ferrocenium couple (Fc/Fc⁺). The HOMO energy level was calculated using the following equation: $E_{HOMO} = -(E_{ox}^{onset} + 4.75)$ eV, where E_{ox}^{onset} is the onset oxidation potential versus Ag/Ag⁺ [15].

3. Results and discussion

3.1. Synthesis and characterization

The synthetic route towards **PER-EF-1** and **PER-EF-2** is shown in Scheme 1. The diarylamines bis(4-methoxyphenyl)amine **3** and 4-(hexyloxy)-*N*-(4-methoxyphenyl)aniline **4** were synthesized according to earlier published procedures [12]. The synthesis commences with the monobromination of **1** with *N*-bromosuccinimide (NBS) in dry THF to afford 3-bromoperylene **2** in very high yield (98%) which was used in the next step without further purification. Introduction of donor group in perylene core was carried out by Buchwald-Hartwig coupling reaction of compound **2** with diarylamine **3** and **4** to afford **5a** and **5b** in moderated yields (45% and 60% respectively). Selective bromination of **5a** and **5b** with NBS in THF, followed by Sonogashira-Hagihara cross-coupling reaction of **6a** and **6b** with 2-propyl-1-ol afforded **7a** and **7b** in 87% and 80% yields respectively. Synthesis of **PER-EF-1** and **PER-EF-2** was fulfilled through selective oxidation of allylic alcohols **7a** and **7b** with Dess-Martin reagent followed by Knoevenagel reaction of aldehydes **8a** and **8b** with cyanoacetic acid. Compounds **2**, **6a**, **6b**, **8a** and **8b** were used in the next step without further purification and

compounds **5a**, **5b**, **7a** and **7b** were purified by rapid vacuum filtration through a pad of silica, in lieu of column chromatography, which is more amenable to scale-up. All the new compounds were characterized by IR, NMR, and high-resolution mass spectral analysis. The spectral data were consistent with the proposed structures. The dyes are reasonable soluble in dichloromethane, chloroform, tetrahydrofuran, dimethylformamide and toluene.

3.2. Spectroscopic characterization

Fig. 1 shows the absorption (Fig. 1a) and emission (Fig. 1b) spectra of intermediates **5a**, **5b**, **7a**, **7b**, **8a** and **8b** in toluene and the results are summarized in Table 1. It is noteworthy that the spectra of these compounds are almost identical. This implies that the substituents at the donor group have a small influence on the frontier orbitals of the perylene π -system. The peak position and the shape are similar for all pairs of intermediates showing that there is little difference in the electronic structure of the excited singlet state.

As expected, the introduction of the ethyne-bridge (**7a** and **7b**) followed by the aldehyde functional group (**8a** and **8b**) led to a red-shift of the absorption maximum of 21 and 30 nm respectively, observed for both alkyl substituents (methyl or hexyl).

The normalized emission spectra of all intermediates in toluene solution present an emission maximum between 630 nm and 655 nm, however in the case of **5a**, **5b**, **7a** and **7b**, a high energy shoulder is observed around 530 nm, which could be due to an excited-state rotamer with weak intramolecular charge-transfer (ICT). To clarify this situation, drop-cast films of each intermediate in zeonex were prepared and the emission spectra recorded. In

Table 1

Optical properties of intermediates **5a**, **5b**, **7a**, **7b**, **8a**, **8b**, perylene molecule and dyes **PER-EF-1** and **PER-EF-2** (2.5×10^{-5} M) in toluene at room temperature.

Compounds	λ_{max} (nm) ($\epsilon/M^{-1} cm^{-1}$) ^a	λ_{max} (nm) ^b	Stokes shift ($\Delta\lambda/nm$) ^c
Perylene	440 (34,000)	444	4
5a	485 (36,000)	630	145
5b	486 (36,400)	638	152
7a	506 (37,000)	644	138
7b	507 (37,000)	645	138
8a	535 (37,600)	651	116
8b	536 (39,800)	655	119
PER-EF-1	506 (41,000)	695	189
PER-EF-2	493 (40,000)	695	202

^a Maximum of absorption spectra and respective molar absorption coefficient.

^b Maximum of emission spectra.

^c Stokes shift.

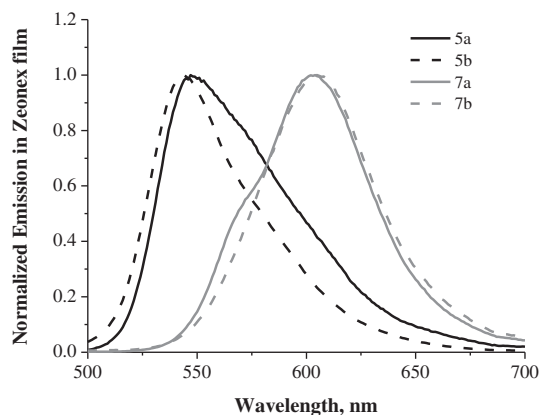


Fig. 2. Normalized emission spectra of intermediates **5a**, **5b**, **7a** and **7b** in Zeonex films. ($\lambda_{exc} = 450$ nm).

this rigid medium, excited-state intramolecular rotation of bulky groups is prevented. As shown in Fig. 2, the aforementioned shoulder around 530 nm almost disappears for **7a** and **7b**, but becomes dominant for **5a** and **5b**, thus reflecting a different angular distribution of conformers in the ground state. In the case of **5a** and **5b**, where ICT is weaker, the short wavelength emitting conformer dominates, whereas the opposite is observed for **7a** and **7b**, as expected.

The absorption spectra recorded for **PER-EF-1** and **PER-EF-2** in toluene, at different concentration, are displayed in Fig. 3. At low concentration (2.5×10^{-6} M) both dyes exhibit a unique and broad band, with a maximum at 506 and 493 nm respectively, which are assigned to ICT band as a result of charge transfer from the donor group (triphenylamine) to the acceptor group (cianoacetic acid) via the π -conjugated linker. However at higher concentrations (2.5×10^{-5} M) **PER-EF-1** shows a new broad band in the longer wavelength range (above 700 nm), which indicates the formation of dye aggregates. In the case of **PER-EF-2**, this is not observed since dye aggregation is suppressed by the presence of hexyl chain in the triarylamine donor group. The molar absorption coefficients of **PER-EF-1** and **PER-EF-2** are $41,000 \text{ M}^{-1} \text{ cm}^{-1}$ (506 nm) and $40,000 \text{ M}^{-1} \text{ cm}^{-1}$ (493 nm), respectively. Based on previous reported in literature [5–8] **PER-EF-1** and **PER-EF-2** present the highest molar absorption coefficients, indicating that these dyes have good light-harvesting ability. The six intermediates and two dyes have large Stokes shifts, which might be attributed to an

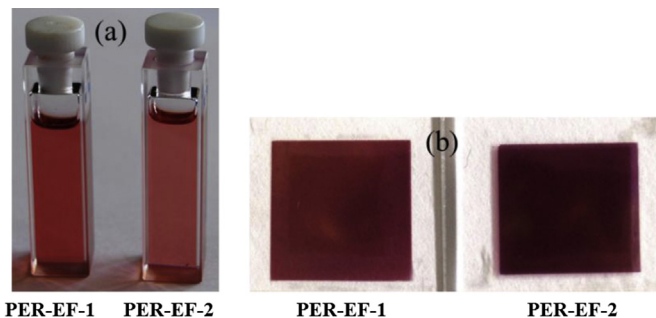


Fig. 4. (a) Dyes in toluene solution and (b) adsorbed on TiO_2 films.

Table 2

Fluorescence quantum yield (ϕ_F), radiative lifetime (τ /ns), radiative rate constants (k_R/s^{-1}) and non-radiative rate constants (k_{NR}/s^{-1}) of compounds in toluene.

Compounds	ϕ_F	τ (ns)	k_R (s^{-1})	k_{NR} (s^{-1})
Perylene	0.95	4.0	2.4×10^8	1.3×10^7
5a	0.63	7.2	8.8×10^7	5.1×10^7
5b	0.66	7.2	9.2×10^7	4.7×10^7
7a	0.97	6.5	1.5×10^8	4.6×10^6
7b	0.94	7.0	1.4×10^8	8.7×10^6
8a	0.66	4.4	1.5×10^8	7.7×10^7
8b	0.72	4.0	1.8×10^8	7.0×10^7
PER-EF-1	0.89	5.1	1.8×10^8	2.2×10^7
PER-EF-2	0.88	5.1	1.7×10^8	2.4×10^7

excited-state intramolecular charge transfer between the donor and acceptor in the dyes. Large Stokes shift could help to reduce self-quenching and measurement error by excitation light and scattered light [18].

The two dyes showed red-shifted absorption profile (Fig. 3a) when adsorbed on TiO_2 as compared to the corresponding spectra in solution, being this more pronounced in the case of **PER-EF-2** (38 nm). The observed bathochromic shift is attributed to the formation of *J*-aggregates of the dyes at the TiO_2 surface, which is opposite to the blue-shift observed for most organic dyes because of partial deprotonation of the carboxylic acid unit due to the dye- TiO_2 interaction [16,17]. The fluorescence spectra for dyes in toluene were obtained by excitation at 450 nm. Both dyes exhibit a broad structure less emission peaking at 695 nm which is compatible with the proposed assignment.

Fig. 4 shows a photograph of **PER-EF-1** and **PER-EF-2** in toluene solution (Fig. 4a) and adsorbed on TiO_2 film (Fig. 4b).

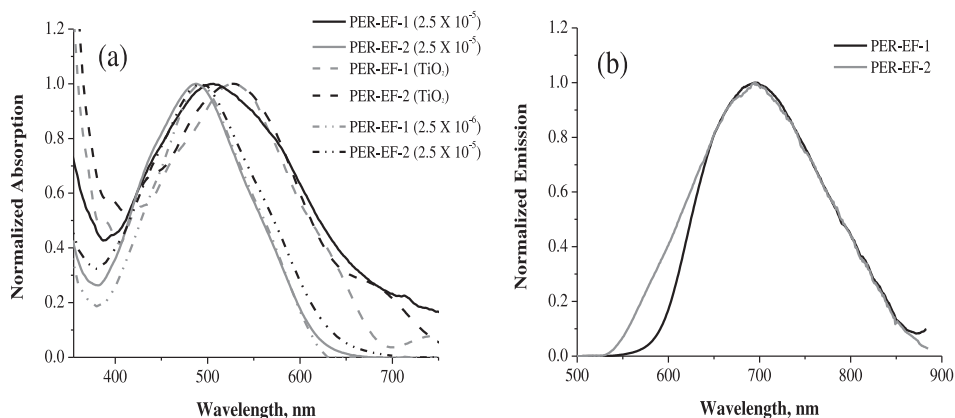


Fig. 3. (a) Normalized absorption spectra of **PER-EF-1** (black) and **PER-EF-2** (gray) at low and high concentration in toluene solution (2.5×10^{-6} M and 2.5×10^{-5} M) and adsorbed on TiO_2 films; (b) Normalized emission spectra of **PER-EF-1** (black line) and **PER-EF-2** (gray line) in toluene (2.5×10^{-5} M, $\lambda_{exc} = 450$ nm).

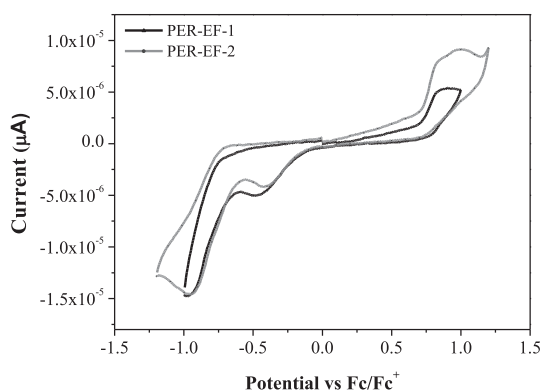


Fig. 5. Cyclic voltammograms recorded for the dyes **PER-EF-1** (black line) and **PER-EF-2** (gray line) in DMF solutions with TBAPF₆ (0.1 M) as the electrolyte; scan rate: 50 mV s⁻¹. All voltammograms were referenced to internal ferrocene (Fc/Fc⁺).

Table 3
Electrochemical properties of perylene dyes in DMF.

Dye	λ_{int} (nm) ^a	E_{0-0} (eV) ^b	E_{HOMO} (eV) ^c	E_{LUMO} (eV) ^d
PER-EF-1	600	2.07	-5.88	-3.81
PER-EF-2	557	2.22	-5.81	-3.59

^a The intersect of the normalized absorption and the emission spectra.

^b E_{0-0} values were estimated from the intercept of the normalized absorption and emission spectra.

^c Deduced from the equation $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.75)$.

^d Deduced from the equation $E_{\text{LUMO}} = E_{\text{HOMO}} - E_{0-0}$.

Photophysical parameters of the all intermediates and dyes were obtained and the results are shown in Table 2. All dyes have high fluorescence quantum yields. The average fluorescence lifetimes measured in toluene at room temperature of intermediates **5a**, **5b**, **7a**, **7b**, **8a** and **8b** result from fits with a sum of three exponentials while for dyes **PER-EF-1** and **PER-EF-2** the decays were single exponential. Fluorescence rate constants of all intermediates and dyes are close to those of the perylene molecule, whereas the absorption and emission spectra are significantly red-shifted.

3.3. Electrochemical properties

The electrochemical properties of **PER-EF-1** and **PER-EF-2** were investigated by cyclic voltammetry (CV) in deoxygenated DMF solution containing 0.1 M of TBAPF₆ as supporting electrolyte (Fig. 5). The potential was externally calibrated by ferrocene/ferrocenium couple (Fc/Fc⁺) and then was calculated versus NHE electrode. The HOMO energy level was calculated using the following equation: $E_{\text{HOMO}} = -(E_{\text{ox}}^{\text{onset}} + 4.75)$ eV, where $E_{\text{ox}}^{\text{onset}}$ is the onset oxidation potential versus Ag/Ag⁺ [15]. The dyes displayed irreversible waves and the HOMO and LUMO level (Table 3) were found to be -5.88 and -3.81 eV for **PER-EF-1** and -5.81 and -3.59 eV for **PER-EF-2**, respectively.

Both dyes exhibit LUMO levels more positive than the conduction band of TiO₂ (-4.26 eV) [9,19] and hence should in theory have enough driving force for effective injection, when used as sensitizers in DSCs.

4. Conclusion

In summary, we have successfully designed and synthesized new perylene dyes following a synthetic strategy and purification

procedures liable for scale-up. **PER-EF-1** and **PER-EF-2** display intense absorption in the visible range. In addition, these dyes exhibit high molar absorption coefficients which make them good light harvesting materials for ss-DSCs because of their ability to absorb light effectively in very thin films. The performance characterization of these dyes in DSCs is underway and will be reported in a future article.

Acknowledgements

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