Electronic Supplementary Material (ESI) for RSC Advances.

UV-vis and EPR spectroelectrochemical investigations of triaryl amine functionalized arylene bisimides

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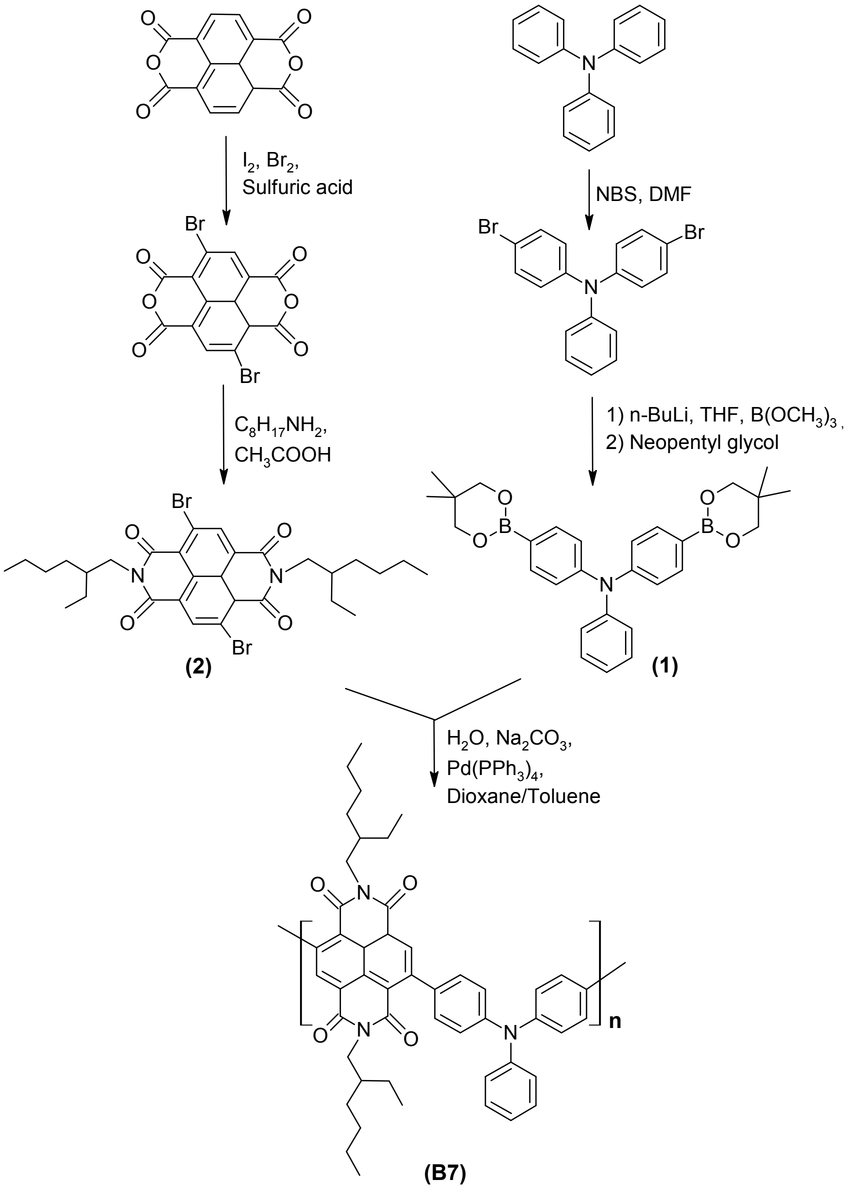
Synthetic procedures

1. Synthesis of alternating copolymer of 4,4'-bis(4-diphenylamino)phenyl and N,N'-bis(2-etylhexyl)naphtalene bisimide (B7).

Compound (**B7**) was prepared using the reaction sequence depicted in *Scheme 1.*



Scheme 1

1.1. 4,4'-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))triphenylamine **(1)** and 2,6-dibromo-N,N’-bis(2-etylhexyl)naphtalene bisimide **(2)** were prepared following the procedures described in detail in the literature.[1,2]

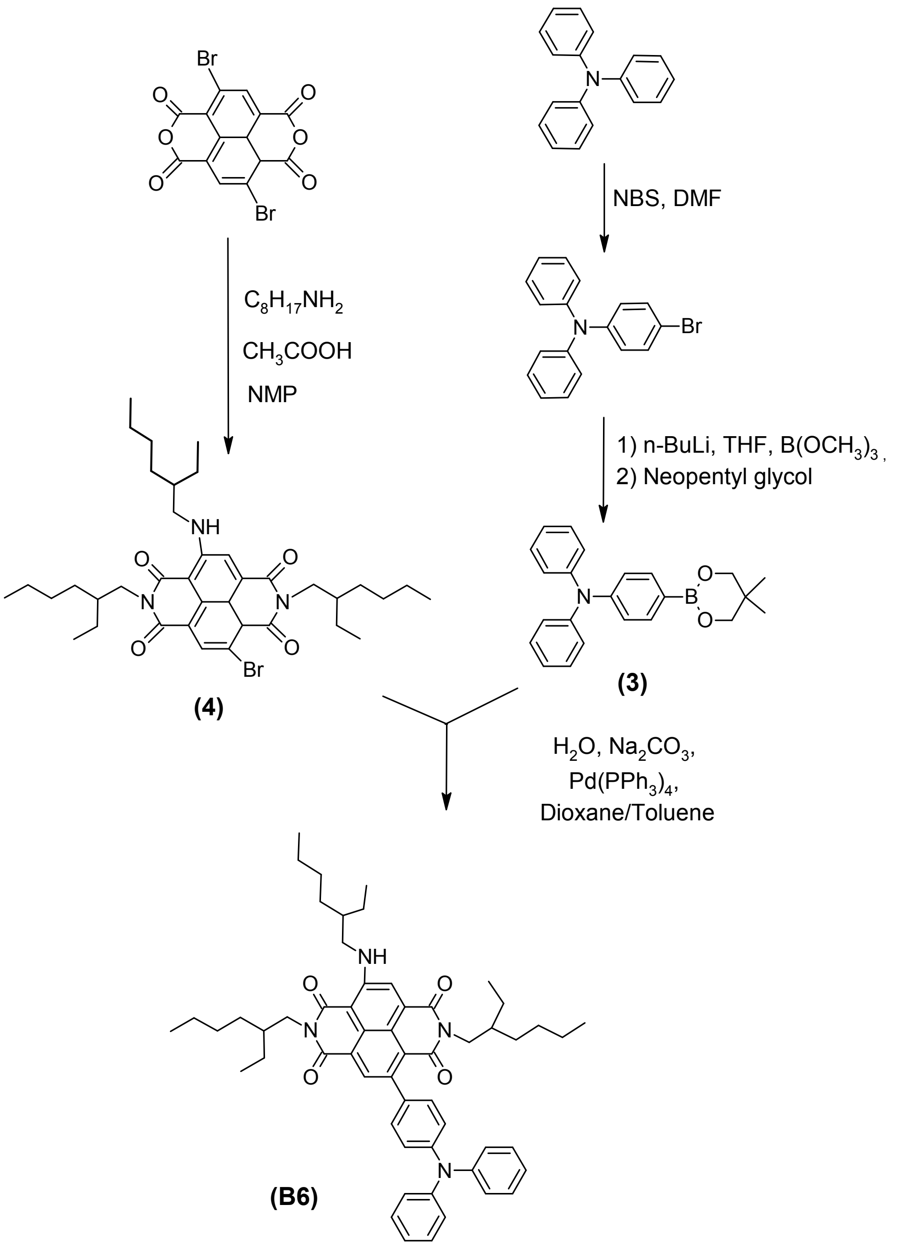
1.2. Polycondensation of 4,4'-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2yl))triphenylamine (1) and 2,6-dibromo-N,N’-bis(2-etylhexyl)naphtalene bisimide (2) to yield (B7).

2,6-dibromo-N,N’-bis(2-etylhexyl)naphtalene bisimide (2) (0.45 g, 0.58 mmol) and 4,4'-(Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl))triphenylamine (1) (0.33 g, 0.7 mmol) were dissolved in a mixed solvent consisting of 5 mL of dioxane and 10 mL of toluene. A solution of sodium carbonate (0.87 g, 4.08 mmol) in 2 ml of water was added to this mixture and the reaction vessel was then purged with argon. After 10 minutes tetrakis(triphenylphosphine)palladium(0) (20 mg, 0.13 mmol) and one drop of benzyltriethylammonium chloride were added to the reaction mixture. It was then stirred at 110°C for 14 hrs under argon atmosphere and subsequently poured into 100 ml of water. The obtained precipitate was filtered off, washed with water and dried in a desiccator. In the next step the crude product was vigorously stirred with 50 ml of methanol for 2 hours, then was purified using a Soxhlet extractor to obtain 0.4 g of dark purple solid (78% reaction yield).

^{1}H NMR ($CDCl_3$; 400 MHz; ppm) δ: 8.70 (s, 2H), 7.47 –7.27 (m, 8H), 7.24 – 7.04 (m, 5H), 4.19 – 3.97 (m, 4H), 1.98 -1.81 (m, 2H), 1.68 – 1.10 (m, 16H), 1.01 – 0.76 (m, 12H).

2. Synthesis of 2-(N-ethylhexyl)-6-(4-(diphenylamino)phenyl)-N,N'-bis(2-ethylhexyl)-naphtalenetetracarboxylic-1,4:5,8-bisimide (B6).

The applied synthetic pathways are depicted in **Scheme 2**.


NBS, DMF
C8H17NH2
CH3COOH
NMP
1) n-BuLi, THF, B(OCH3)3,
2) Neopentyl glycol
(4)
(3)
H2O, Na2CO3,
Pd(PPh3)4,
Dioxane/Toluene
(B6)

Scheme 2

2.1 Synthesis of 4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine (3).

(3) was prepared using the procedure described in detail in the literature.[3] The product was obtained as white powder (93 % reaction yield).

2.2. Synthesis of 2-monobromo-6-ethylhexyl-N,N'-2-bis(ethylhexyl)naphtalene-bisimide (4).

2,6-dibromo-naphtalene dianhydride (1.2 g, 2.81 mmol) suspended in 20 ml of N-methylpyrrolidone was mixed with 20 ml of glacial acetic acid. It was then heated at 60°C for 20 min and 2-ethylhexyl-amine (0.91 ml, 7.05 mmol) was consecutively added. The temperature was raised to 120°C and the reaction was carried out for additional 12 h with constant stirring and under argon atmosphere. The reaction mixture was then poured into 200 ml of water and the precipitated product was filtered. Next, it was washed with methanol and purified using a chromatographic column (silica gel, eluent: methylene chloride/hexane, 4/1) to give the desired product (42 % reaction yield).

^{1}H NMR ($CDCl_3$, 400 MHz, ppm) δ: 10.18 (t, J = 7.6Hz, 1H), 8.85 (s, 1H); 8.28 (s, 1H); 4.18 ÷ 4.06 (m, 4H); 3.49 (t, J = 5.8Hz, 2H); 1.99 ÷1.87 (m, 2H); 1.83-1.73 (m, 1 H), 1.51-1.43 (m, 2H), 1.42 ÷ 1.23 (m, 22H); 1.12 ÷ 0.85 (m, 18H).

2.3. Synthesis of 2-(N-ethylhexyl)-6-(4-(diphenylamino)phenyl)-N,N'-bis(2-ethylhexyl)-naphtalenetetracarboxylic-1,4:5,8-bisimide (B6).

2-monobromo-6-ethylhexyl-N,N'-2-bis(ethylhexyl)naphtalene-bisimide **(4)** (0.5 g, 0.62 mmol) and 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)triphenylamine **(3)** (0.33 g, 0.93 mmol) were dissolved in a mixed solvent consisting of 5 mL of dioxane and 10 mL of toluene. A solution of sodium carbonate in 2 ml of water was added and the reaction mixture was purged with argon for 10 minutes. Then, the catalyst, tetrakis(triphenylphosphine)palladium(0) (10 mg) was added. The mixture was stirred at 110°C for 14 hrs under argon atmosphere and then poured into 100 ml of water. The obtained precipitate was filtered off, washed with water and dried in a desiccator. In the next step the crude product was purified using a chromatographic column (silica gel, and the following eluent: methylene chloride/hexane 4/1 + 1 vol% triethylamine), yielding 60% of violet solid.

^{1}H NMR ($CDCl_3$; 400 MHz; ppm) δ: 10.15 (t, J = 7.6, 1H), 8.55 (s, 1H), 8.30 (s, 1H), 7.37 - 7.16 (m, 10H), 7.13 (d, J = 6.8, 2H), 7.06 (t, J = 7.4, 2H), 4.22 - 4.10 (m, 2H), 4.10 - 3.98 (m, 2H), 3.52 (t, J = 5.8 Hz, 2H); 1.98 ÷1.84 (m, 2H); 1.83-1.75 (m, 1 H), 1.52-1.44 (m, 2H), 1.42 ÷ 1.17 (m, 22H); 1.14 ÷ 0.76 (m, 18H). **^{13}C NMR** ($CDCl_3$; 400 MHz; ppm) δ: 166.60; 163.34;

163.30; 163.14; 152.07; 147.55; 147.21; 141.36; 135.87; 134.64; 129.55; 129.26; 128.81; 128.17; 124.80; 123.07; 122.74, 122.48; 122.42; 120.49, 120.05; 99.99; 46.40; 44.27; 43.89; 39.38; 37.80; 37.42; 31.42; 31.16; 30.70; 30.66; 29.71; 28.83; 28.61; 28.54; 24.53; 24.05; 23.98; 23.09; 22.99; 22.71; 14.11; 14.04; 10.98; 10.70; 10.64. **HRMS [ESI$^+$]:** Calcd. for $C_{56}H_{68}N_4O_4$; $[M+Na]^+$ 860.5241, found: 860.5225.

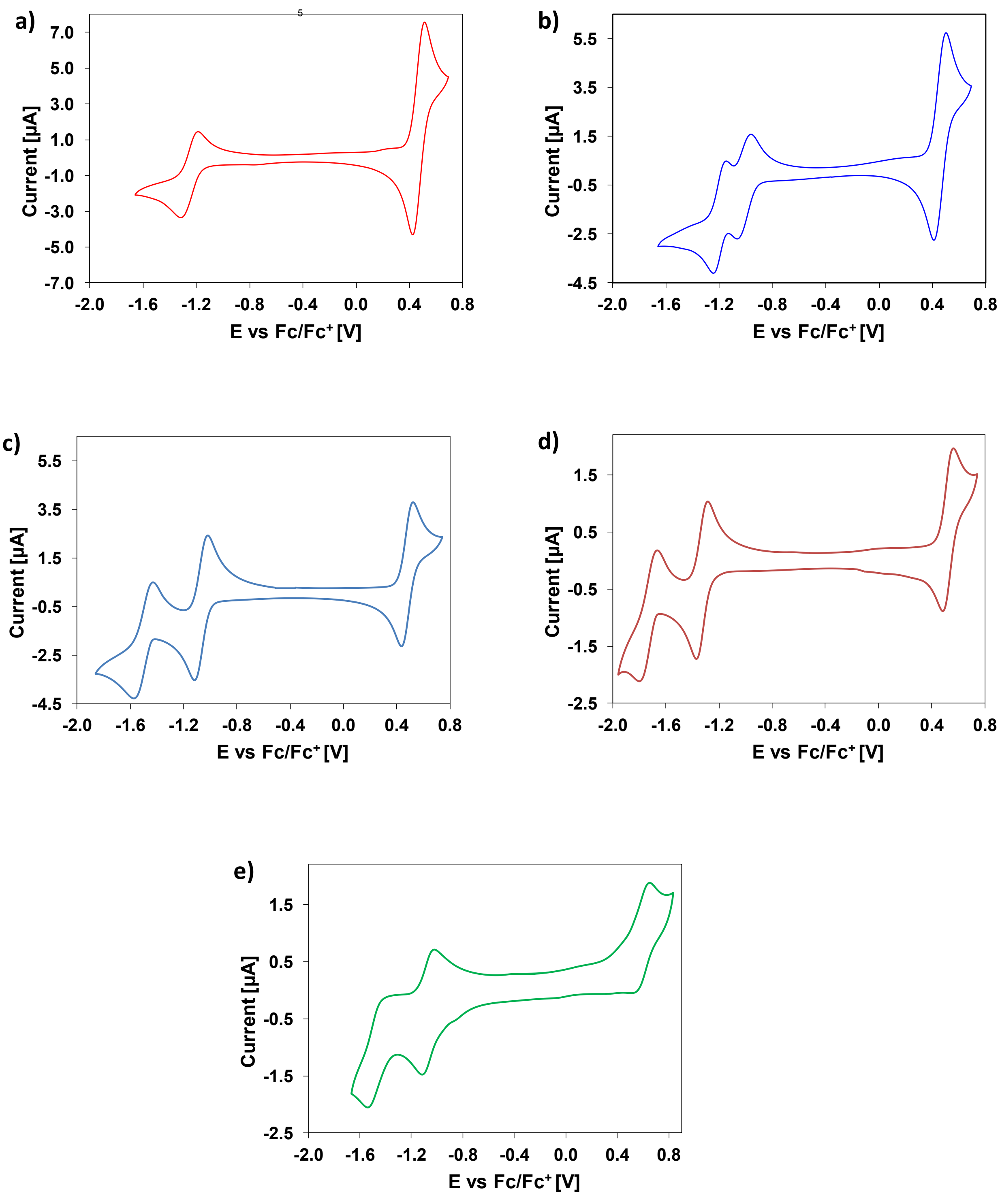


Fig. S1. Cyclic voltammograms of: (a) **B1** (1 × 10^{-3}M), **(b) B3** (1 × 10^{-3}M), **(c) B4** (1 × 10^{-3}M), **(d) B6** (5 × 10^{-4}M), **(e) B7** (1 × 10^{-4}M); electrolyte 0.1M Bu_4NBF_4 in CH_2Cl_2; scan rate 50 mV/s.

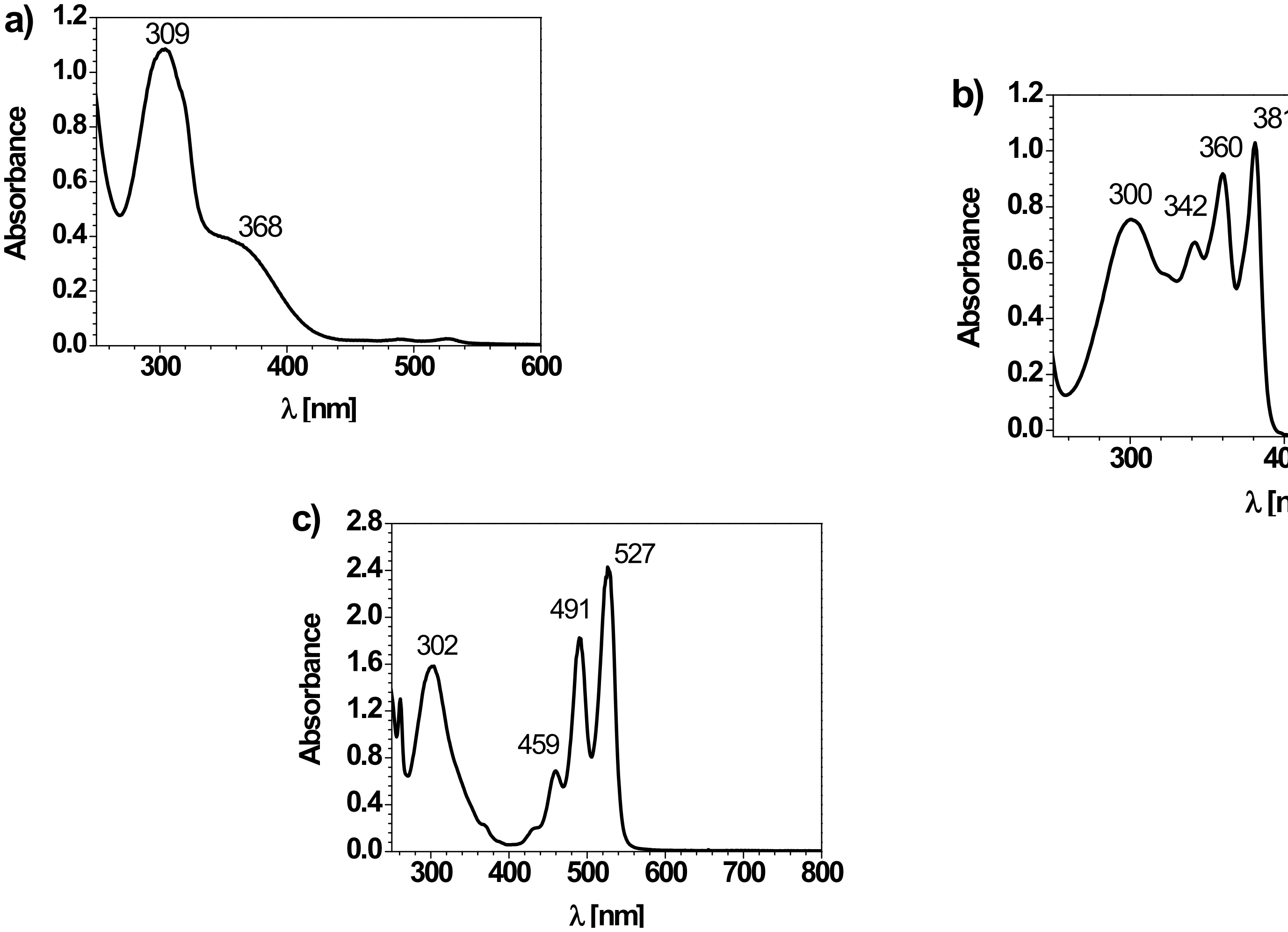


Fig. S2. Solution UV-vis spectra of neutral **B1 (a), B3 (b)** and **B4 (c)** (concentration: 1 × 10^{-4}M).

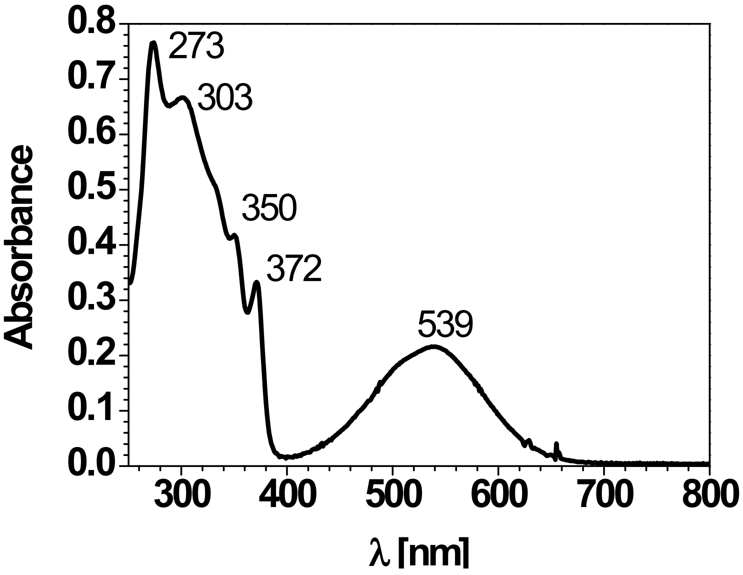
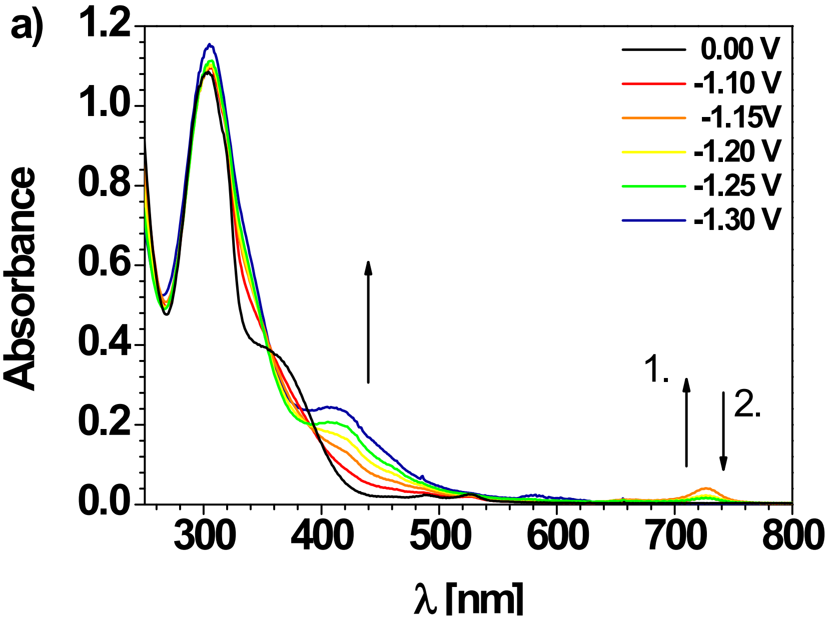


Fig. S3. Solution UV-vis spectrum of neutral **B6** (concentration: 1 × 10^{-4}M).



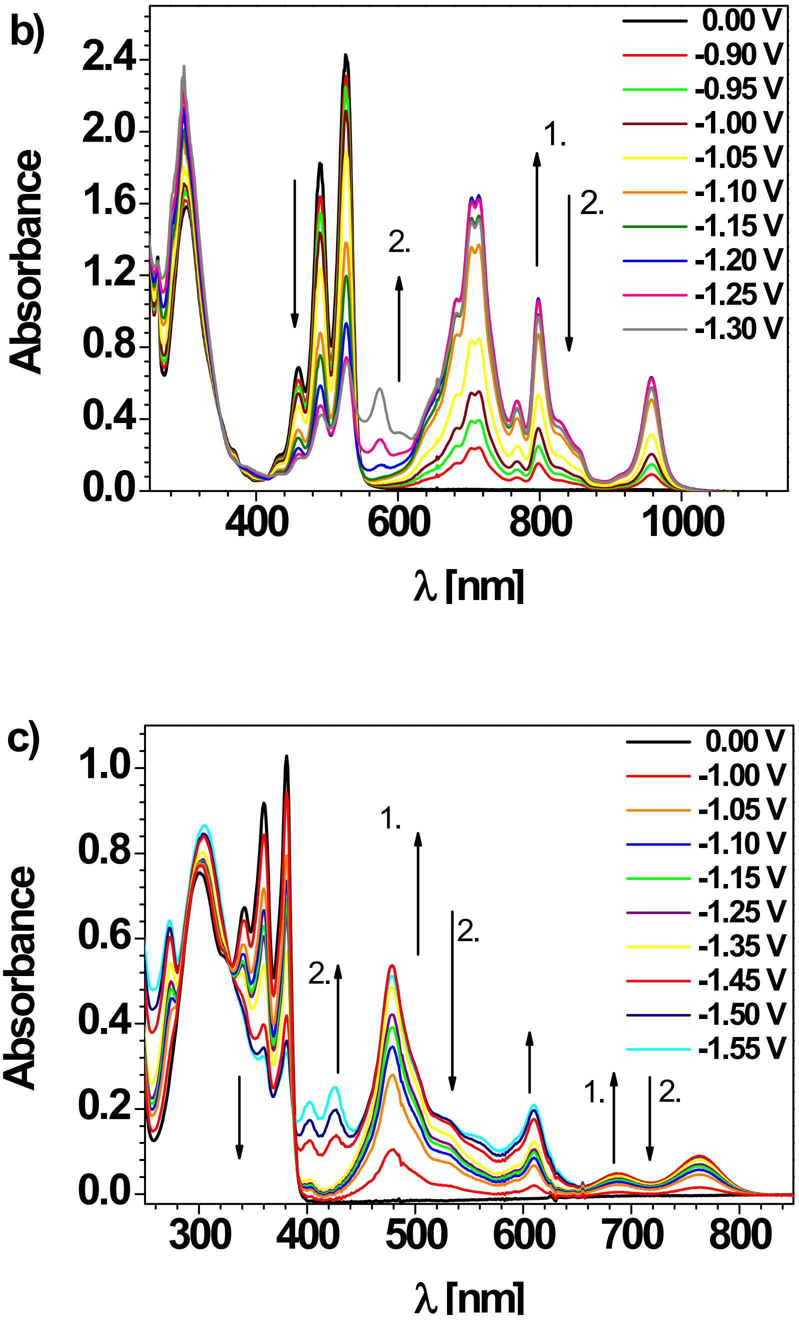


Fig. S4. UV-vis spectra of **B1 (a), B3 (b) and B4 (c)** registered for decreasing working electrode potential (concentration: 1 × 10^{-4}M**;** electrolyte 0.1M Bu_4NPF_6 in CH_2Cl_2).↑$^{1.}$ - absorption bands which grow during the first step of reduction; ↑$^{2.}$ - absorption bands which grow during the second step of reduction; ↓$^{2.}$ - absorption bands which decrease during the second step of reduction.

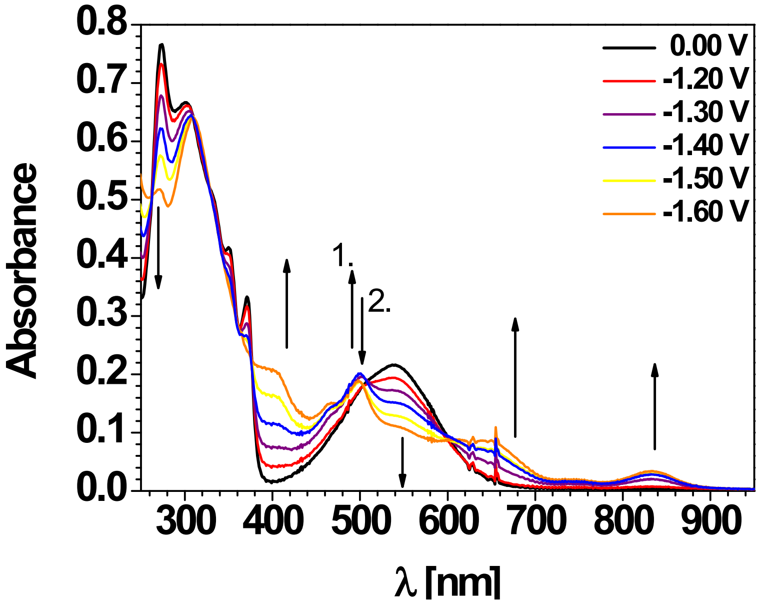
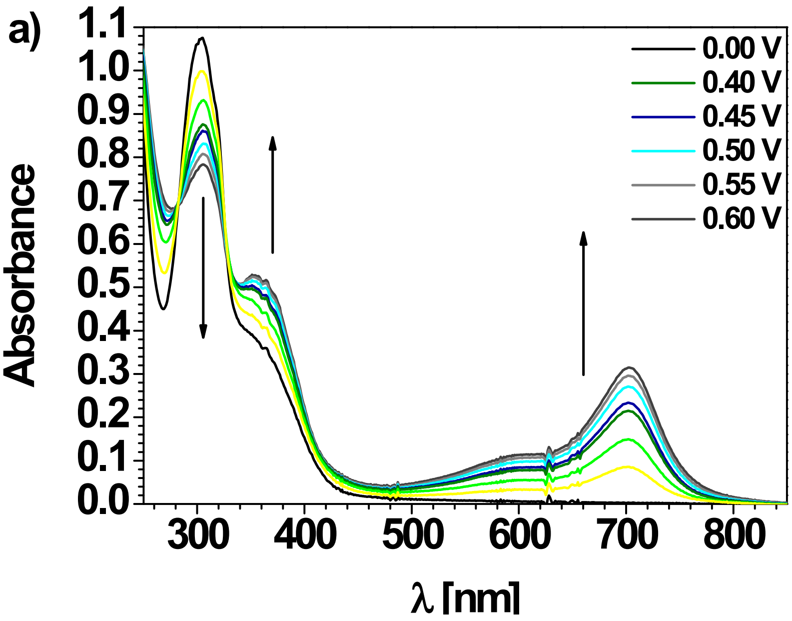


Fig. S5. UV-vis spectra of **B6** registered for decreasing working electrode potential (concentration: 1 × 10^{-4}M; electrolyte 0.1M Bu_4NPF_6 in CH_2Cl_2). ↑1. - absorption bands which grow during the first step of reduction; ↓2. - absorption bands which decrease during the second step of reduction.



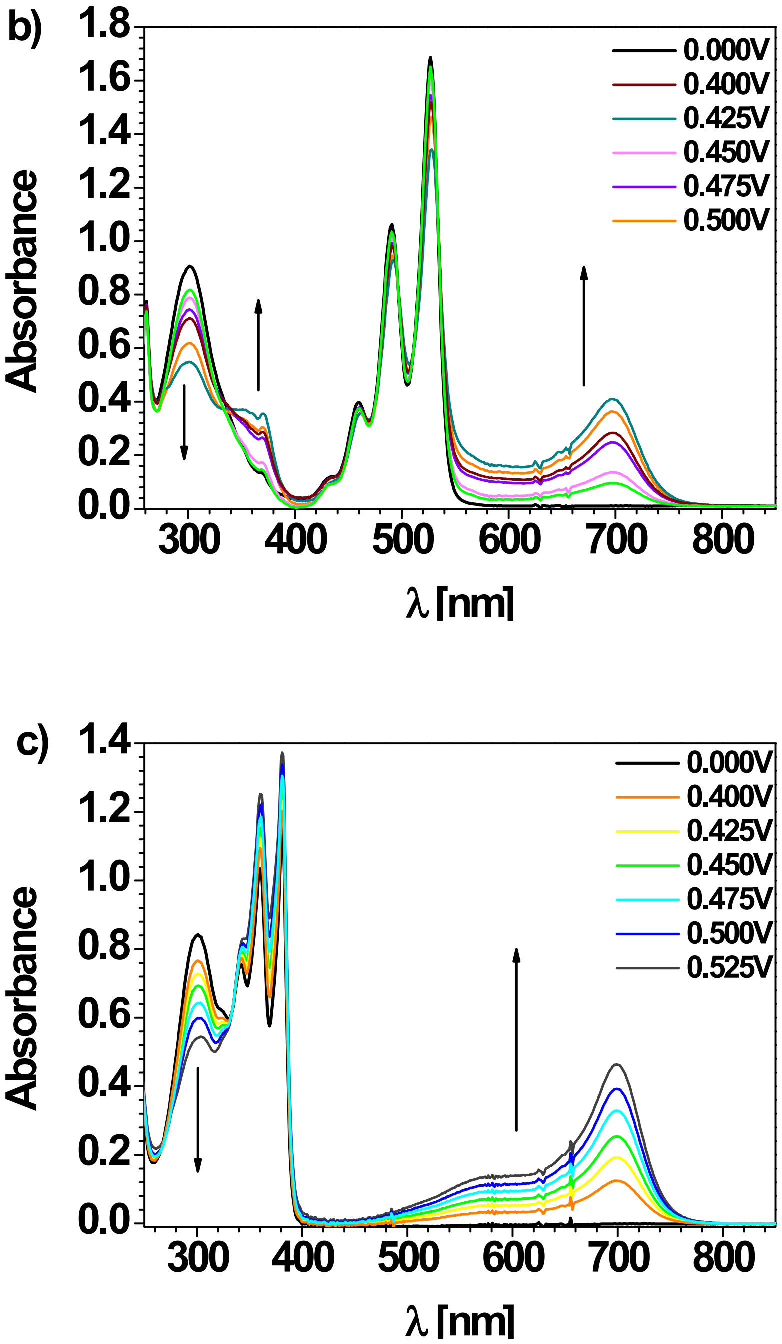


Fig. S6. UV-vis spectra of **B1 (a), B3 (b)** and **B4 (c)** registered for increasing working electrode potential (concentration: 1 × 10^{-4}M**;** electrolyte 0.1M Bu_4NPF_6 in CH_2Cl_2).

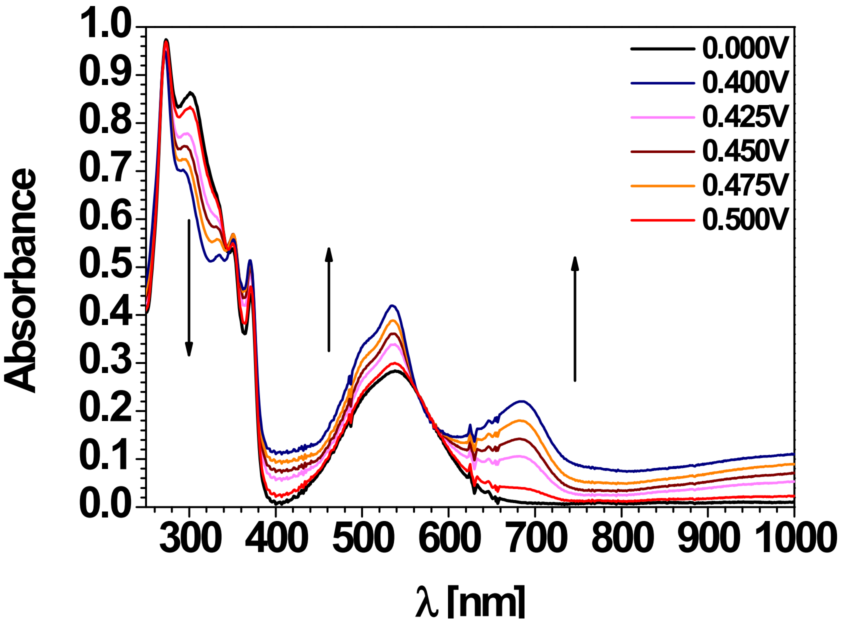


Fig. S7. UV-vis spectra of **B6** registered for increasing working electrode potential (concentration: 1 × 10^{-4}M**;** electrolyte 0.1M Bu_4NPF_6 in CH_2Cl_2).

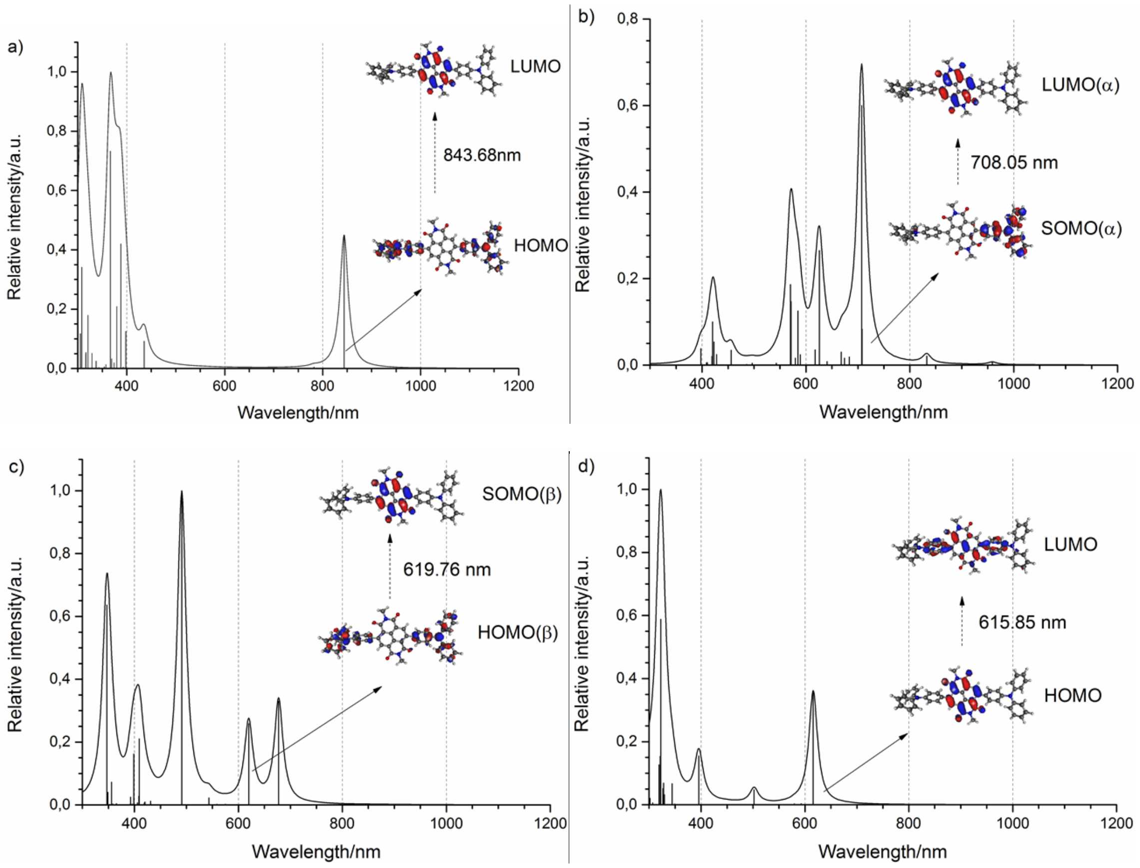
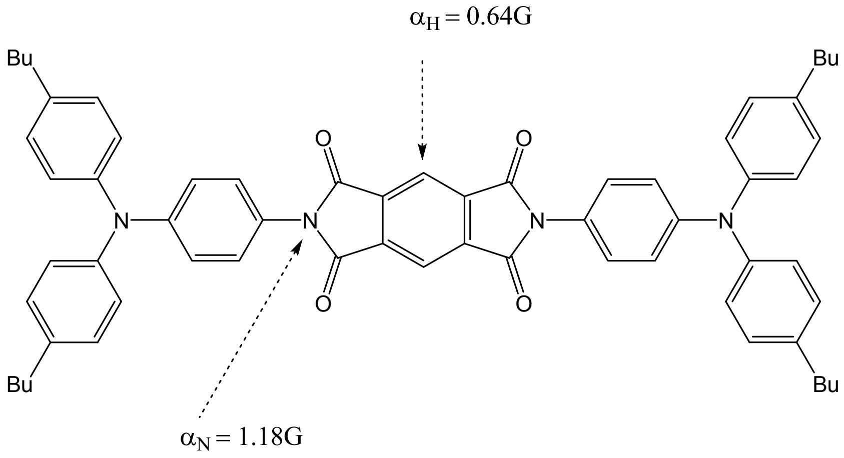


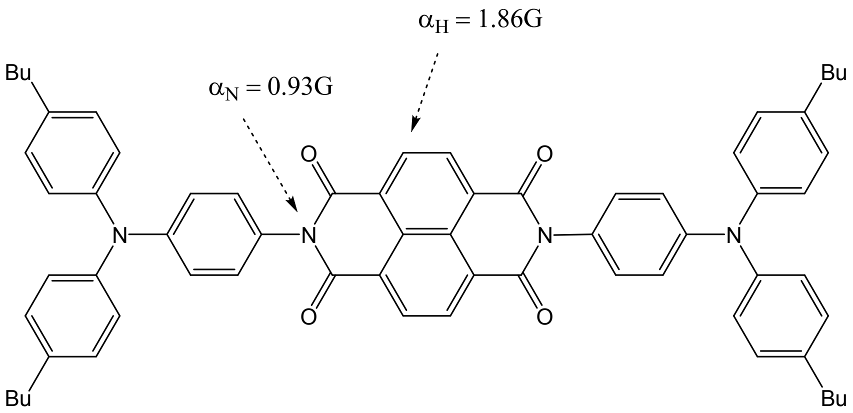
Fig. S8. Simulated UV-Vis spectra of four forms of **B5**: a) neutral form, b) radical cation, c) radical anion and d) dianion; calculated at TDDFT/B3LYP/6-31G(d). Inset shows the orbitals responsible for CT transition.

B1



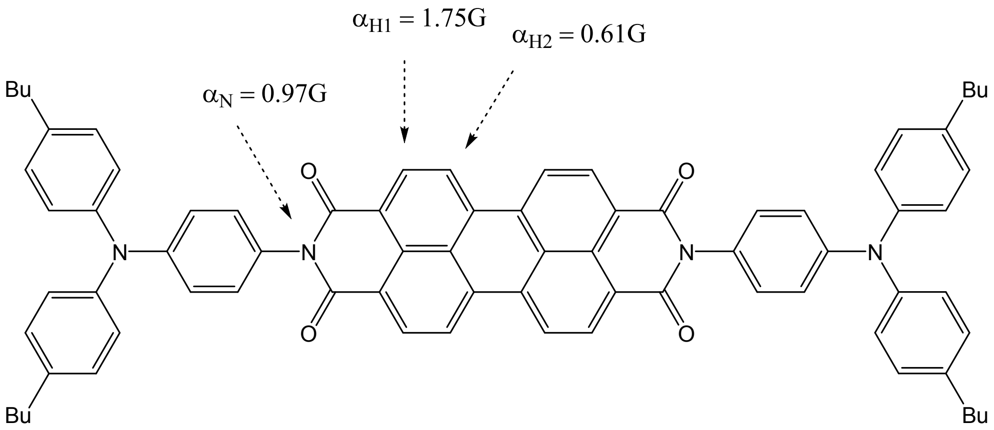
Linewidth: 0.09G
Line shape: 23% Lorentz, 77% Gaussian

B2



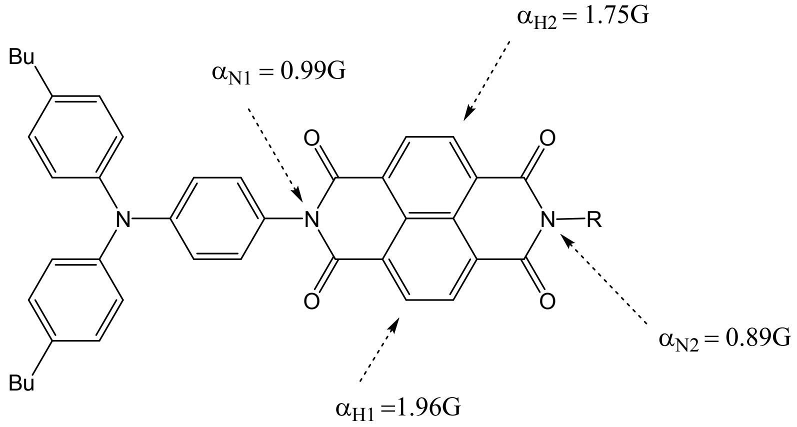
Linewidth: 0.42G
Line shape: 100% Lorentz

B3



Linewidth: 0.20G
Line shape: 92% Lorentz, 8% Gauss

B4



$\alpha_{H2} = 1.75G$

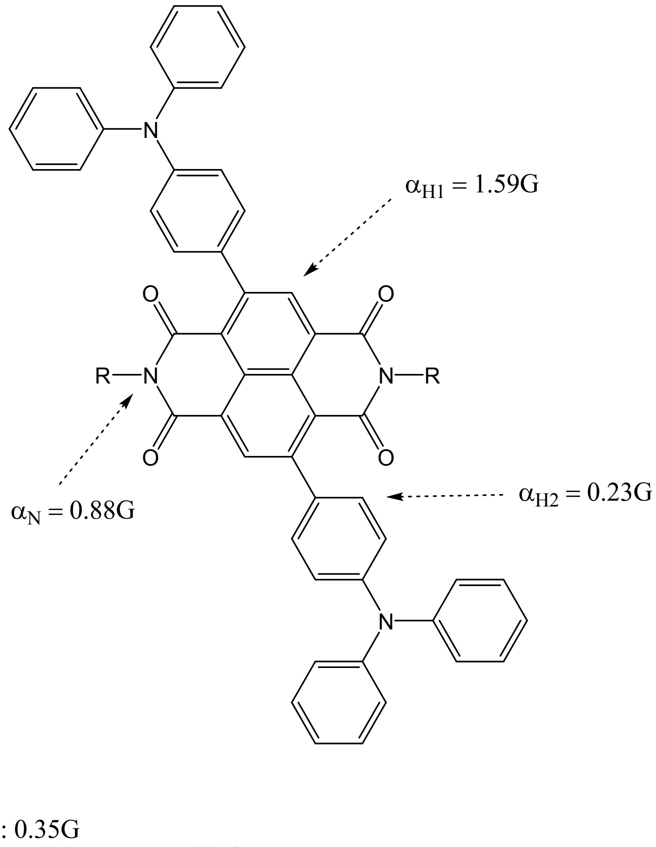
$\alpha_{N1} = 0.99G$

$\alpha_{N2} = 0.89G$

$\alpha_{H1} = 1.96G$

Linewidth: 0.20G
Line shape: 88% Lorentz, 12% Gauss

B5



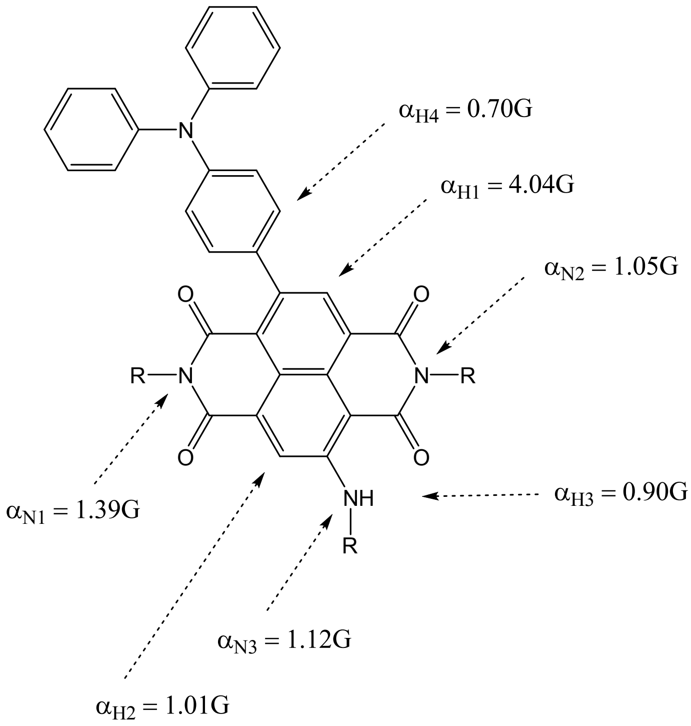
$\alpha_{H1} = 1.59G$

$\alpha_{N} = 0.88G$

$\alpha_{H2} = 0.23G$

Linewidth: 0.35G
Line shape: 56% Lorentz, 34% Gauss

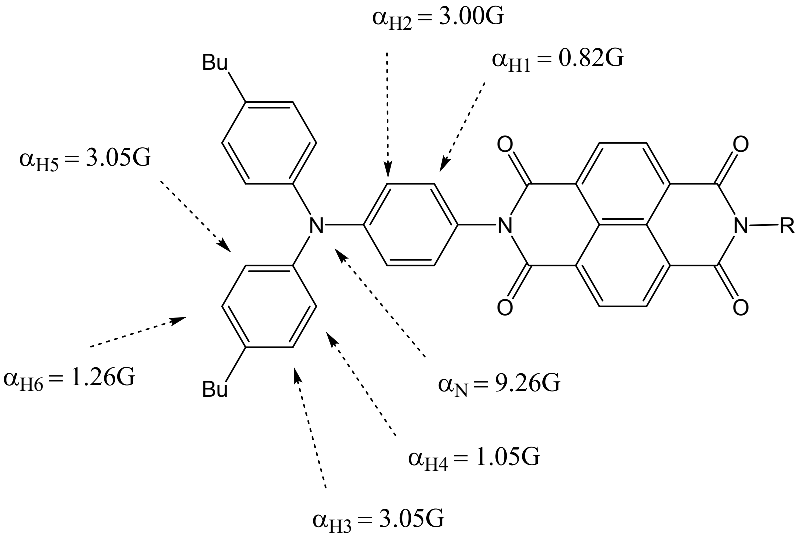
B6



Linewidth: 0.40G
Line shape: 82% Lorentz, 18% Gauss

Chart S1. Fitting parameters for EPR spectra of radical anions of low molecular weight substituted arylene bisimides.

B4



Linewidth: 1.30G
Line shape: 100% Lorentz

Chart S2. Fitting parameters for EPR spectra of radical cations of **B4**.

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3 L. Shi, C. He, D. Zhu, Q. He, Y. Li, Y. Chen, Y. Sun, Y. Fu, D. Wen, H. Cao, J. Cheng, *Journal of Material Chemistry*, 2012 ,**22**, 11629.

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