

Photoinduced Charge Separation in Two Bis(phenylethynyl)anthracene Based Triads : Inverted Region Effect vs Distance Effect on Back Electron Transfer

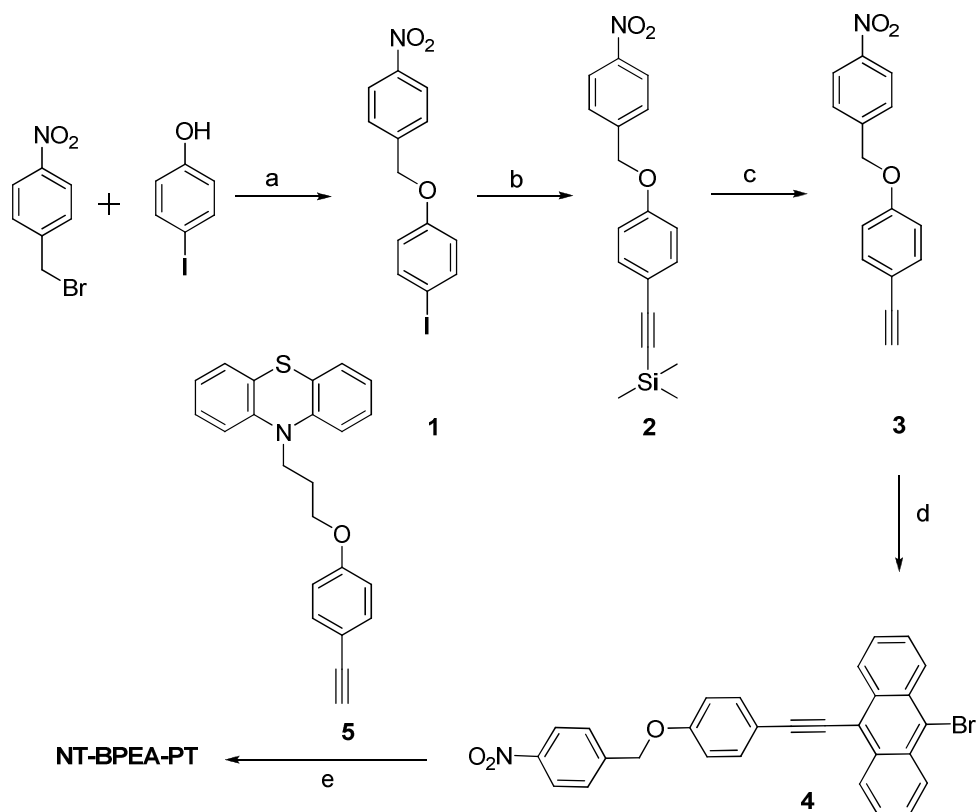
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Supporting information

Synthesis of NT-BPEA-PT.

NT-BPEA-PT were synthesized as shown in Scheme S1.



Conditions: (a) K_2CO_3 , Acetone, 8 h, reflux; (b) TMS acetylene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , NH^iPr_2 , THF, 24 h, RT; (c) TBAF, THF, 0 °C-RT; (d) 9,10-dibromoanthracene, $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , NH^iPr_2 , Toluene, 24 h, 70 °C; (e) $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$, CuI , NH^iPr_2 , Toluene, 24 h, 70 °C.

Scheme S1. Scheme for the synthesis of NT-BPEA-PT.

Synthesis of 1: 4-iodophenol (2.24 g, 10.18 mmol) was dissolved in dry acetone (20 mL). Potassium carbonate (2.42 g, 18.52 mmol) and 4-nitrobenzyl bromide (2 g, 9.26 mmol) in dry acetone (20 mL) were added and the mixture refluxed under argon for 24 h. It was poured into water and extracted with dichloromethane. The extract was washed with 20% sodium hydroxide solution and then with water. The organic layer was dried and evaporated at reduced pressure to get **1**, (3.16 g, 96%). mp 139-140 °C. Mass (GC-MS): calcd. for $\text{C}_{13}\text{H}_{10}\text{INO}_3$: 355; found: 355. ^1H NMR (CDCl_3 , 500 MHz) δ : 5.06 (s, 2H), 6.66 (d, 2H), 7.50 (m, 4H), 8.16 (d, 2H).

Synthesis of 2: **1** (1.55g, 4.36 mmol), dichlorobis(triphenylphosphine) palladium(II) (123 mg, 0.17 mmol) and copper(I) iodide (83 mg, 0.44 mmol) were dissolved in dry THF (50 mL). Dry diisopropylamine (10 mL) and trimethylsilylacetylene (555 mg, 5.66 mmol) were added under argon and the mixture stirred for 24 h. Solvent was removed and residue was purified by column chromatography on silica using chloroform/hexane (20:80) to get **2** (1.2 g, 85%). mp 95-96 °C. Mass (GC-MS): calcd. for C₁₈H₁₉NO₃Si: 325; found: 325. ¹H NMR (CDCl₃, 500 MHz) δ: 0.258 (s, 9H), 5.17 (s, 2H), 6.89 (d, 2H), 7.44 (d, 2H), 7.60 (d, 2H), 8.25 (d, 2H).

Synthesis of 3: **2** (1.36 g, 4.19 mmol) was dissolved in THF (20 mL). The solution was cooled to 0 °C and TBAF (1M in THF, 4.2 mL) added. The mixture was then stirred for 2 h at RT, poured into ice-cold water and extracted with dichloromethane. The solvent was removed and residue was purified over alumina column using chloroform/hexane (20:80) to obtain **3** (900 mg, 85%). mp 151-152 °C. Mass (GC-MS): calcd. for C₁₅H₁₁NO₃: 253; found: 253. ¹H NMR (CDCl₃, 500 MHz) δ: 3.01 (s, 1H), 5.17 (s, 2H), 6.91 (d, 2H), 7.44 (d, 2H), 7.60 (d, 2H), 8.24 (d, 2H).

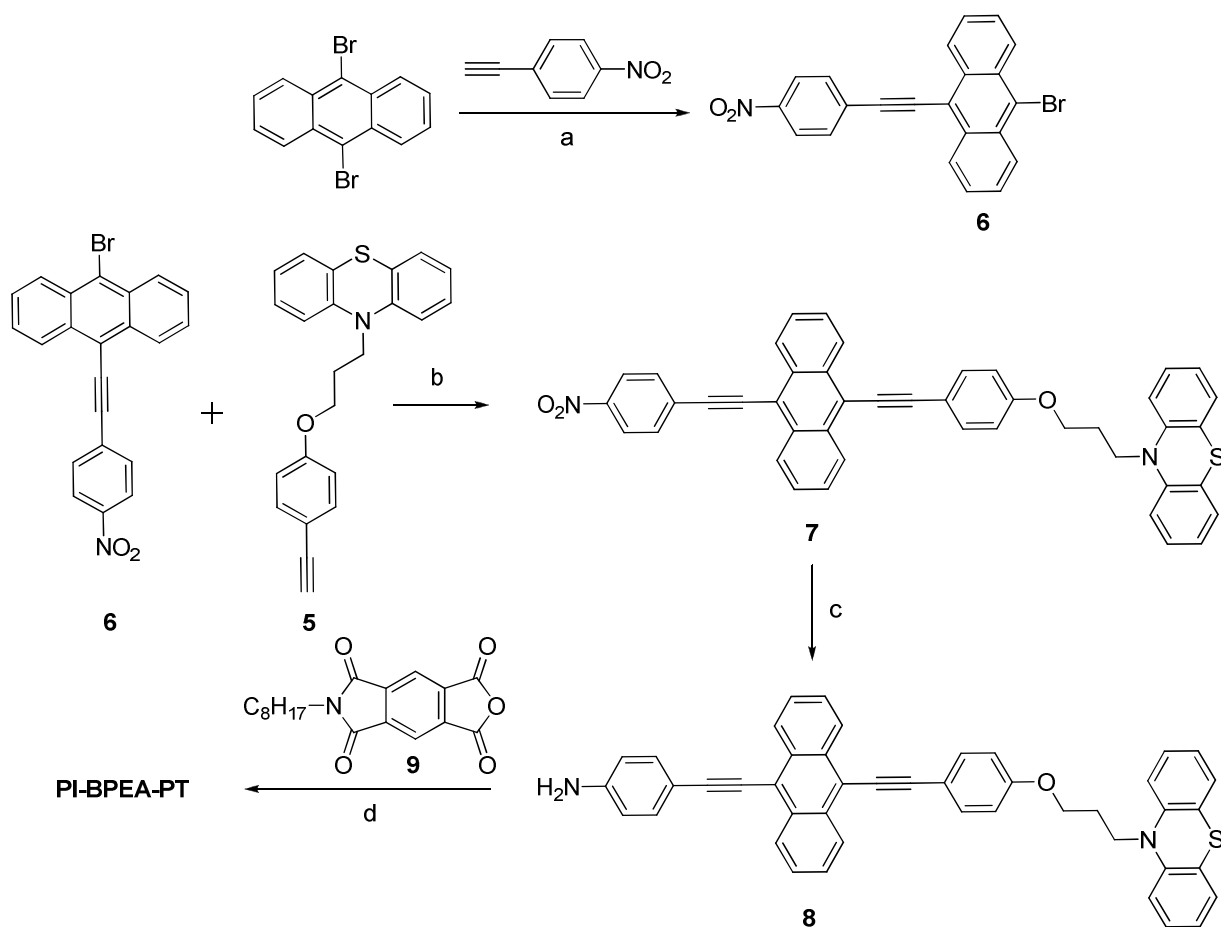
Synthesis of 4: To an argon degassed RB flask, 9, 10-dibromoanthracene¹ (300 mg, 0.89 mmol), dichlorobis(triphenylphosphine)palladium(II) (19 mg, 0.026 mmol), copper(I) iodide (5 mg, 0.026 mmol), dry toluene (60 mL) and dry diisopropylamine (15 mL) were added. **3** (270 mg, 1.07 mmol) in dry toluene (10 mL) was added drop wise to it and the reaction mixture was stirred for 24 h at 70 °C under argon. Solvent was removed and the residue obtained was purified by column chromatography over silica gel using chloroform/hexane (3:7) to obtain **4** (158 mg, 35%). mp 178-179 °C. FAB-MS (M⁺) calcd. for C₂₉H₁₈BrNO₃: 508.36; found: 508.79. ¹H NMR (CDCl₃, 300 MHz) δ: 5.17 (s, 2H), 6.92 (d, 2H), 7.44 (m, 6H), 7.60 (d, 2H), 8.24 (d, 2H), 8.55 (d, 2H), 8.68 (d, 2H).

Synthesis of NT-BPEA-PT: To an argon degassed RB flask, **4** (100 mg, 0.19 mmol), dichlorobis(triphenylphosphine)palladium(II) (5 mg, 0.006 mmol), copper(I) iodide (2 mg, 0.009 mmol), dry toluene (25 mL) and dry diisopropylamine (5 mL) were added. **5**² (85 mg, 0.23 mmol) in dry toluene

(10 mL) was added and the reaction mixture stirred for 24 h at 70 °C under argon. Solvent was removed and the residue obtained was purified by column chromatography over silica gel using chloroform/hexane (3:1) to obtain NT-BPEA-PT, (75 mg, 50%).

Synthesis of PI-BPEA-PT.

PI-BPEA-PT was synthesized as shown in Scheme S2.



Conditions: (a) Pd(PPh₃)₂Cl₂, CuI, NHⁱPr₂, Toluene, 24 h, 70 °C; (b) Pd(PPh₃)₂Cl₂, CuI, NHⁱPr₂, Toluene, 24 h, 70 °C; (c) SnCl₂, HCl, THF, reflux, 5 h; (d) DMF, 140 °C, 48 h.

Scheme S2. Scheme for the synthesis of **PI-BPEA-PT**.

Synthesis of 6: To an argon degassed RB flask, 9, 10-dibromoanthracene (300 mg, 0.89 mmol), dichlorobis(triphenylphosphine) palladium(II) (19 mg, 0.026 mmol), copper(I) iodide (5 mg, 0.026 mmol), dry toluene (60 mL) and dry diisopropylamine (15 mL) were added. 1-ethynyl-4-nitrobenzene³

(157 mg, 1.07 mmol) in dry toluene (10 mL) was added drop wise to it and the reaction mixture was stirred for 24 h at 70 °C under argon. Solvent was removed and the residue obtained was purified by column chromatography over silica gel using chloroform/hexane (1:1) to obtain **6**, (130 mg, 36%). mp 215-216 °C. FAB-MS (M^+) calcd. for $C_{22}H_{12}BrNO_2$: 402.24; found: 402.65. 1H NMR ($CDCl_3$, 300 MHz) δ : 7.68 (m, 4H), 7.90 (d, 2H), 8.32 (d, 2H), 8.62 (m, 4H).

Synthesis of 7: To an argon degassed RB flask, **6** (100 mg, 0.25 mmol), dichlorobis(triphenylphosphine)palladium(II) (7 mg, 0.01 mmol), copper(I) iodide (3 mg, 0.012 mmol), dry toluene (30 mL) and dry diisopropylamine (5 mL) were added. **5**¹ (105 mg, 0.3 mmol) in dry toluene (10 mL) was added and the reaction mixture stirred for 24 h at 70 °C under argon. Solvent was removed and the residue obtained was purified by column chromatography over silica gel using chloroform/hexane (3:1) to obtain **7**, (54 mg, 32%). mp 193-194 °C. FAB-MS (M^+) calcd. for $C_{45}H_{30}N_2O_3S$: 678.80; found: 678.26. 1H NMR ($CDCl_3$, 300 MHz) δ : 2.32 (t, 2H), 4.17 (m, 4H), 6.94 (m, 6H), 7.18 (m, 4H), 7.67 (m, 6H), 7.89 (d, 2H), 8.32 (d, 2H), 8.62 (d, 2H), 8.70 (d, 2H).

Synthesis of 8: **7** (30 mg, 0.044 mmol) and $SnCl_2 \cdot (H_2O)_2$ (180 mg, 0.79 mmol) were added to THF (15 mL) with 4 drops 37% HCl and stirred under reflux condition for 5 h. The reaction mixture was diluted with 50 mL of DCM and washed once with 0.1 M sodium bicarbonate and two times with water. The organic solvent was removed on a rotary evaporator and the crude product was purified by filtration through an alumina pad using DCM as the eluent to afford **8** (23 mg, 80%). mp 182-183 °C. FAB-MS (M^+) calcd. for $C_{45}H_{32}N_2OS$: 648.81; found: 648.42. 1H NMR ($CDCl_3$, 300 MHz) δ : 2.32(t, 2H), 3.92 (s, 2H), 4.15 (m, 4H), 6.73 (d, 2H), 6.94 (m, 6H), 7.18 (m, 4H), 7.61 (m, 8H), 8.68 (m, 4H).

Synthesis of PI-BPEA-PT: **8** (15 mg, 0.023 mmol) and **9**⁴ (12 mg, 0.035 mmol) were dissolved in dry DMF (10 mL) in a 25 mL RB flask. The reaction mixture was heated at 140 °C for 48 hours under argon atmosphere. The DMF was removed by evaporation under reduced pressure. The residue was

chromatographed on a silica gel column using chloroform as eluent to obtain **PI-BPEA-PT** (11 mg, 50%).

Electrochemical data

The redox potentials of the triads were determined using square wave votammetry. The square wave voltammogram is shown in Figure S1.

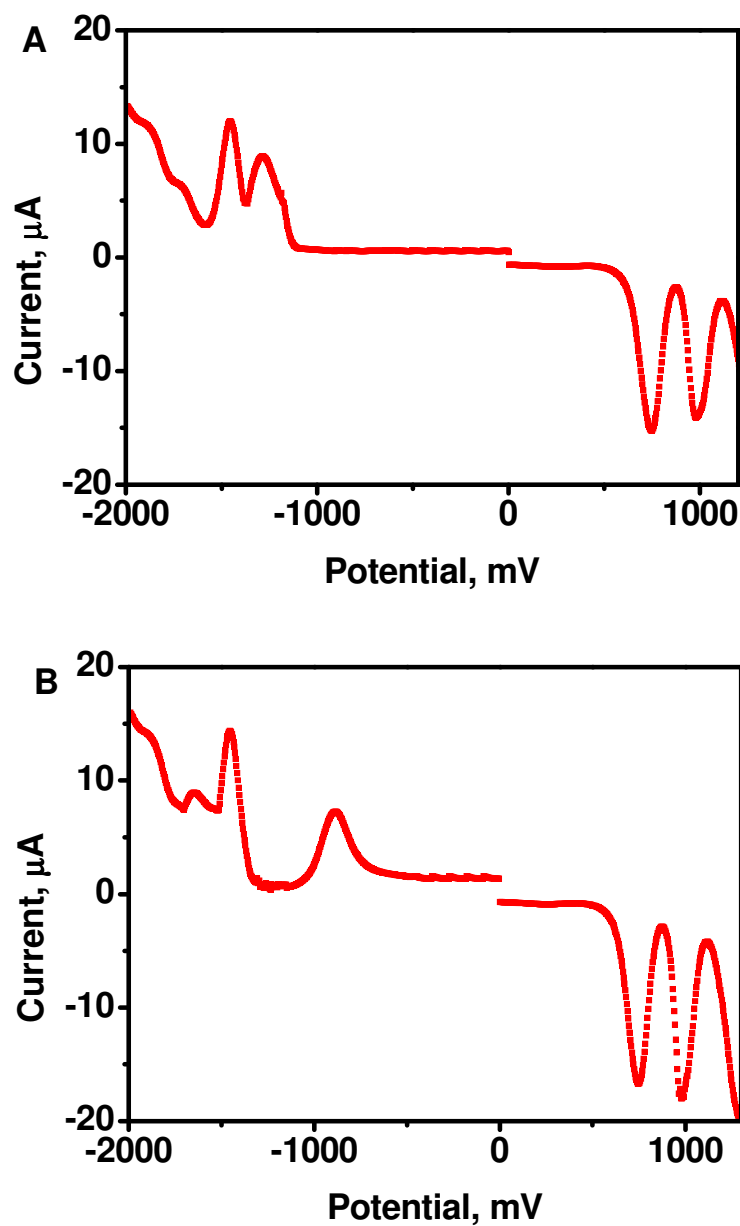


Figure S1. Square wave voltammogram of (A) NT-BPEA-PT (B) PI-BPEA-PT in DCM

Fluorescence decay profiles

Flourescece decay profiles of **BPEA** and **BPEA-PT** and **NT-BPEA-PT** are shown in Figure S2

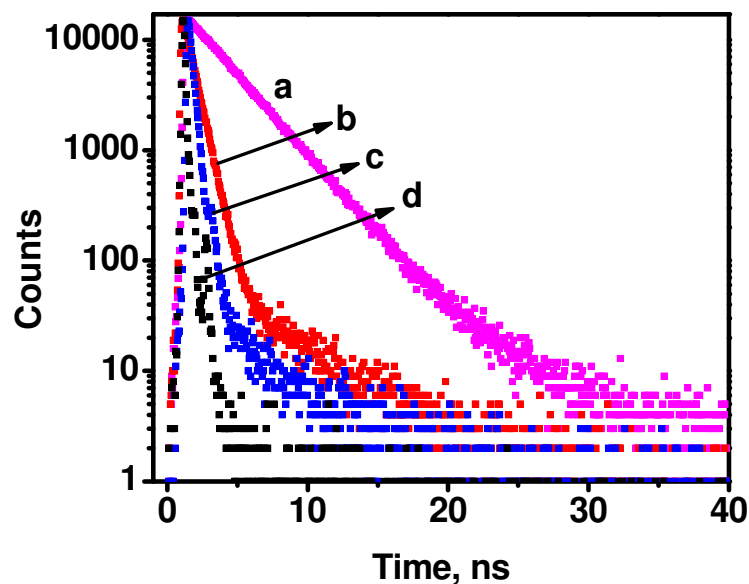


Figure S2. Fluorescence decay profiles of (a) **BPEA** (b) **BPEA-PT** and (c) **NT-BPEA-PT** in DCM. (d) Instrument profile. Excitation was at 440 nm

Minimum Energy Conformations

Minimum energy conformations of the triads were obtained by AM1 calculation using Gaussian 03 (Revision-D.01). It is shown in Figure S3.

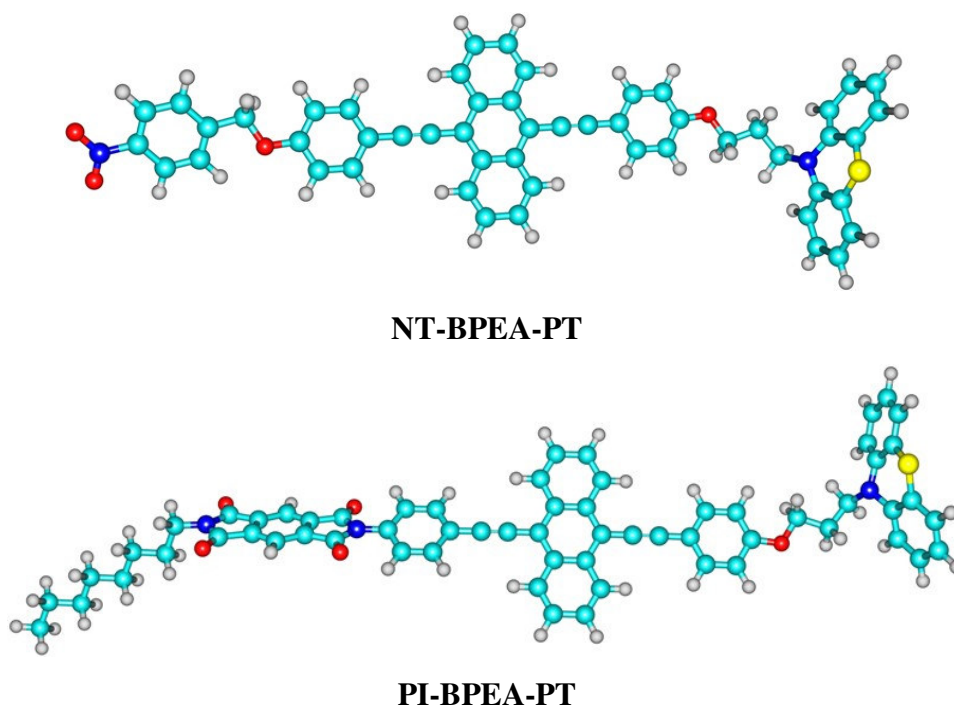


Figure S3. Minimum energy conformation of triads

References

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