

**Long-Lived Photoinduced Charge Separation in flexible 9,10-
Bis(phenylethynyl)anthracene – Phenothiazine Dyads**

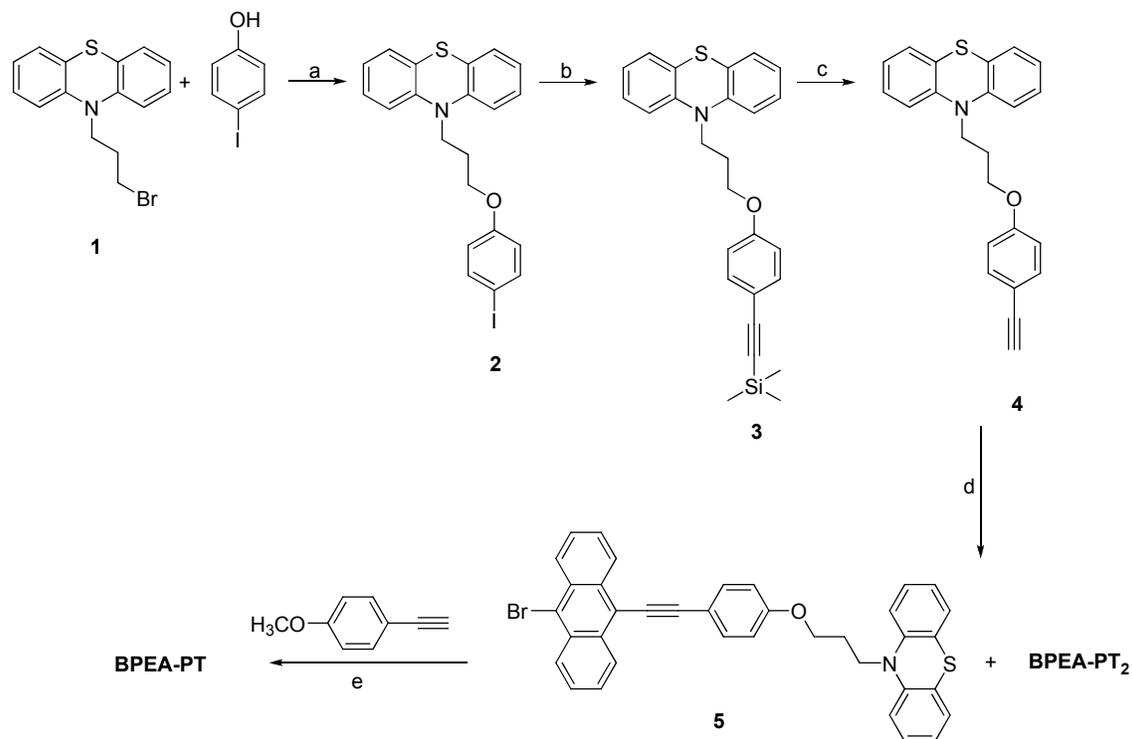
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Supporting information

Synthesis of dyads:

BPEA-PT and **BPEA-PT₂** were synthesized as shown in Scheme S1.



Conditions: (a) K₂CO₃, Acetone, 8 h, reflux; (b) TMS acetylene, Pd(PPh₃)₂Cl₂, CuI, NH^tPr₂, THF, 24 h, RT; (c) TBAF, THF, 0 °C-RT; (d) 9,10-dibromoanthracene, Pd(PPh₃)₂Cl₂, CuI, NH^tPr₂, Toluene, 24 h, 70 °C; (e) Pd(PPh₃)₂Cl₂, CuI, NH^tPr₂, Toluene, 24 h, 70 °C.

Scheme S1. Scheme for the synthesis of **BPEA-PT** and **BPEA-PT₂**.

Synthesis of 2: 4-iodophenol (1.65 g, 7.5 mmol) was dissolved in dry acetone (20 mL). Potassium carbonate (2.15 g, 15.6 mmol) and **1** (2 g, 6.25 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 **2**, (2.86 g, 97%). mp: 68-69 °C. Mass (GC-MS): calcd. for C₂₁H₁₈INOS: 459; found: 459. ¹H NMR (CDCl₃, 300 MHz) δ: 2.23 (m, 2H), 4.07 (m, 4H), 6.61 (d, 2H), 6.91 (t, 4H), 7.13 (m, 4H), 7.49 (d, 2H).

Synthesis of 3: **2** (2g, 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 alumina using ethyl acetate/hexane (5:95) to get **3**. (1.8 g, 95%). mp: 71-72 °C. Mass (GC-MS): calcd. for C₂₆H₂₇NOSSi: 429; found: 429. ¹H NMR (CDCl₃, 300 MHz) δ: 0.233 (s, 9H), 2.24 (m, 2H), 4.07 (m, 4H), 6.73 (d, 2H), 6.91 (t, 4 H), 7.15 (m, 4H), 7.33 (d, 2H).

Synthesis of 4: **3** (1.8 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 ethyl acetate: hexane (5:95) to obtain **4**. (1.2 g, 81%), mp: 100-101 °C. Mass (GC-MS): calcd. for C₂₃H₁₉NOS: 357; found: 357. ¹H NMR (CDCl₃, 300 MHz) δ: 2.23 (m, 2H), 2.94 (s, 1H), 4.05 (m, 4H), 6.73 (d, 2H), 6.89 (t, 4H), 7.12 (m, 4 H), 7.32 (d, 2H).

Synthesis of BPEA-PT₂ and 5: To an argon degassed RB flask, 9, 10-dibromoanthracene (493mg, 1.47 mmol), dichlorobis(triphenylphosphine)palladium(II) (52 mg, 0.073mmol), copper(I) iodide (28 mg, 0.028 mmol), dry toluene (40 mL) and dry diisopropylamine (20 mL) were added. A solution of Compound **4** (1.1 g, 3.1mmol) in dry toluene (15 mL) was added and the mixture was refluxed for 24 h at 70 °C under argon. The solvent was removed and residue was purified by column chromatography over silica using chloroform: hexane (1:1) to obtain **5** as yellow solid, (260 mg, 29 %). FAB-MS (M⁺) calcd. for C₃₇H₂₆BrNOS: 611.09; found: 611.82. ¹H NMR (CDCl₃, 300 MHz) δ: 2.23 (q, 2H), 4.07 (q, 4H), 6.85 (m, 6H), 7.10 (d, 4H), 7.54 (m, 6H), 8.47 (m, 2H), 8.60 (m, 2H).

Further elution with chloroform: hexane (1:1) gave **BPEA-PT₂**, (630 mg, 49%).

Synthesis of BPEA-PT: To an argon degassed RB flask, **5** (200 mg, 0.327 mmol), dichlorobis(triphenylphosphine)palladium(II) (20 mg, 0.013 mmol), copper(I) iodide (10 mg, 0.049 mmol), dry toluene (40 mL) and dry diisopropylamine (15 mL) were added. 4-methoxyphenylacetylene (40 mg, 0.39 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 (3:7) to obtain **BPEA-PT**, (120 mg, 59 %).

BPEA (R = OCH₃) is synthesized by a reported procedure.¹ Data for this compound is given below.

BPEA (R = OCH₃): Mp: 244-245 °C. ¹H NMR (CDCl₃, 300 MHz) δ: 3.89 (s, 6H), 6.99 (d, 4H), 7.63 (q, 4H), 7.73 (d, 4H), 8.69 (q, 4H). ¹³C NMR (CDCl₃, 125 MHz) δ : 55.40, 85.37, 102.42, 114.22, 115.61, 118.44, 126.61, 127.30, 131.97, 133.17, 159.97. FAB-MS (M⁺) calcd. for C₃₂H₂₂O₂: 438.52; found: 438.55. Anal. calcd. for C₃₂H₂₂O₂: C, 87.65; H, 5.06; found: C, 87.39; H, 4.93.

References

1. Gimenez, R.; Pinol, M.; Serrano, J. L. *Chem. Mater.* **2004**, *16*, 1377-1383.