Supporting Information

The mutual interplay of light harvesting and triplet sensitizing in a perylene bisimide-antenna fullerene dyad

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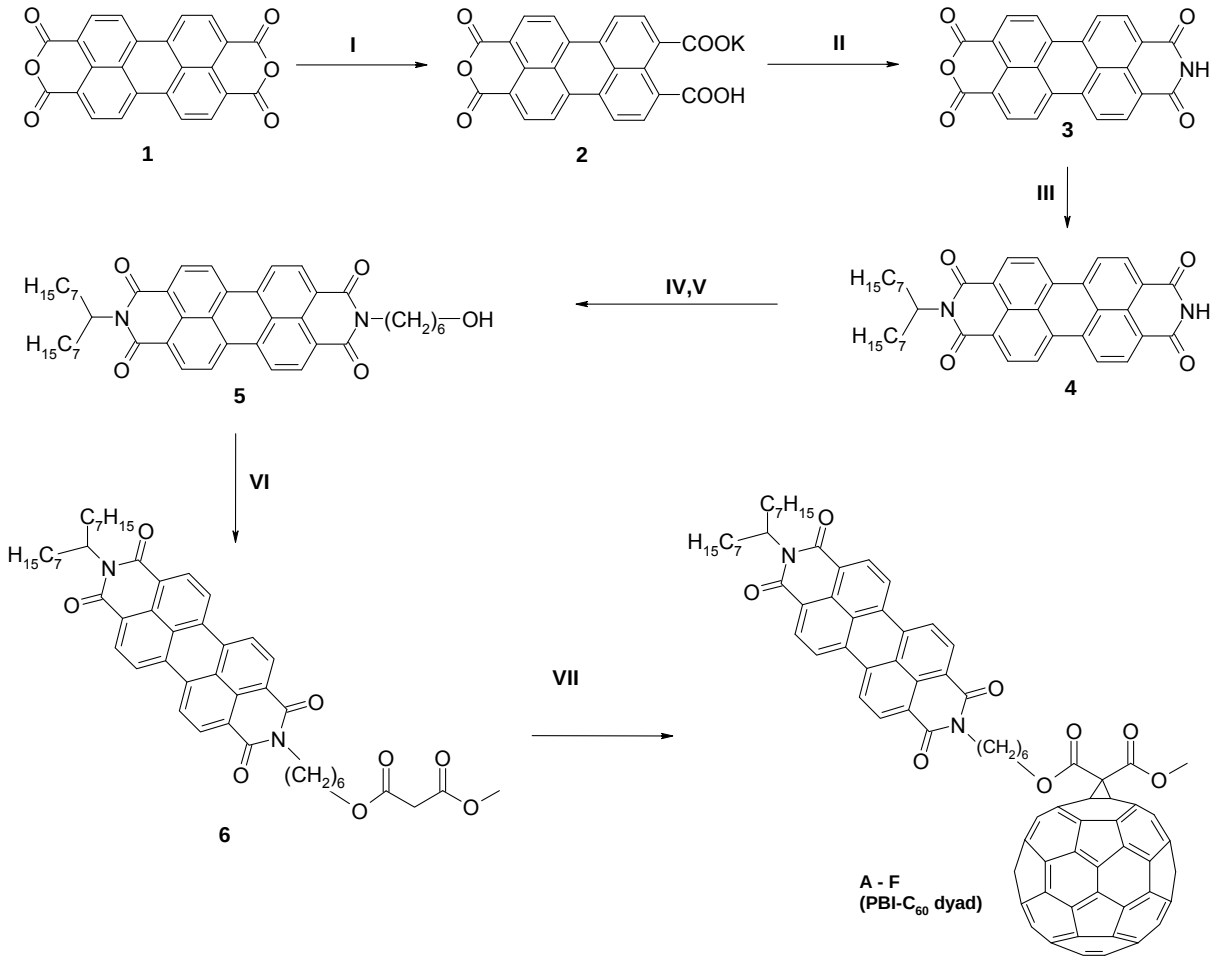
Synthesis

The synthetic route for the preparation of fullerene with covalently linked perylene bisimide is shown in scheme 1. The synthesis starts with the opening of one of the anhydride groups in the perylene-3,4:9,10-tetracarboxylic dianhydride **1** to form the mono potassium salt **2**. The ring is closed again to get the unsymmetrical monoanhydride monoimide **3** [1]. As the imide group is stable against basic and acidic reactions, only the anhydride group reacts with 8-aminopentadecane, forming a swallow-tail substituted product **4**. In contrast to most perylene bisimide derivatives these swallow-tail substituted perylene bisimides are highly soluble in organic solvents. The unsymmetrical perylene bisimide **4** was coupled with 1-bromo-6-tetrahydropyranyloxyhexane and afterwards the free hydroxyl group was obtained by removing the THP protecting group under acidic conditions. The hydroxyl functionalized perylene bisimide was then coupled with methyl malonyl chloride or malonyl dichloride to get the mono substituted malonate (6). The cyclopropanation of C_{60} was carried out by a modified Bingel reaction[2] of the malonate 6 with iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene[3]. This coupling reaction was performed with good yield of 57% to obtain PBI-fullerene dyad (**A-F**).



Scheme 1: Synthetic strategy of **A-F** (PBI-C60 dyad). *Reagents and conditions:* (I) KOH, H_20; AcOH; (II) NH_3, H_20; (III) 8-aminodecane, imidazole, quinoline, 160 °C; (IV) Br-$(CH_2)_6$-OTHP, K_2CO_3, DMF, THF, 60 °C; (V) PPTS, HCl, THF, ethanol, 55°C; (VI) methyl malonyl chloride, pyridine, CH_2Cl_2; (VII) C_{60}, I_2, DBU, toluene.

Experimental

Compounds **2**, **3** and **PBI** were prepared according to literature[1]. PCBM was purchased from ADS Inc. All reagents and solvents were of analytical grade or purified using standard methods.

Synthesis of (1-Heptyloctyl)-perylene-3,4:9,10-tetracarboxylic bisimide (4)

Perylene-3,4:9,10-tetracarboxylic monoanhydride monoimide (**3**) (3.13 g, 8 mmol) and 8-aminopentadecane (2.91 g, 12.8 mg) were stirred in imidazole (30 g) and quinoline (5 ml) under argon (160 °C, 2h). The mixture was dissolved in THF and precipitated in 400 ml of a mixture of ethanol and 2N HCl (1:1). The precipitate was collected by vacuum filtration, treated with boiling aqueous K_2CO_3 solution (100 ml, 10%), washed with distilled water and dried under vacuum. The compound was purified by extractive recrystallization[20] and traces of N,N'-di(1-heptyloctyl)-perylene-3,4:9,10-tetracarboxylic bisimide were removed by extraction with hexane to yield a red solid (3.64 g, 77%). ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 0.81 (t, ^3J = 6.95 Hz, 6H), 1.28 (m, 16H), 1.87 (m, 2H), 2.21 (m, 2H), 5.16 (m, 1H), 8.56 (m, 8H). MS (EI) m/z: 600 [M^+-1]. IR (Si) v: 3067, 2958, 2927, 2855, 1698, 1659, 1594, 1432, 1403, 1343, 1269, 1179, 810, 741, 655 cm^{-1}.

Synthesis of 5

1202 mg (2 mmol) **4**, 743 mg (2.8 mmol) 1-bromo-6-tetrahydropyranyloxyhexane and 498 mg (3.6 mmol) K_2CO_3 were stirred in a mixture of 30 ml DMF and 10 ml THF under argon at 60 °C for 24 h. The mixture was precipitated in 200 ml methanol, collected by vacuum filtration and dried in vacuum. The precipitate was dissolved in 20 ml THF and 50 mg (0.2 mmol) pyridinium para-toluenesulfonate (PPTS) and three drops of hydrochloric acid in 10 ml ethanol were added and stirred at 55 °C for 3 hours. The product was precipitated in 200 ml cold methanol, collected by vacuum filtration and dried in vacuum. It was purified by column chromatography (silica gel, hexanes/THF = 4/1) to yield 823 mg (1.17 mmol, 59%).

^{1}H-NMR ($CDCl_3$, 250 MHz) δ: 0.80 (t, ^{3}J = 6.56 Hz, 6H), 1.20 (m, 20H), 1.46 (m, 4H), 1.64 (m, 2H), 1.84 (m, 4H), 2.20 (m, 2H), 3.35 (s, 2H), 4.10 (m, 4H), 5.10 (m, 1H), 8.20 (m, 8H) ppm. MS (EI) m/z: 390, 701 [M^+]. IR (Si) v: 2954, 2925, 2856, 1698, 1648, 1596, 1578, 1405, 1346, 1255, 1179, 1082, 810, 746 cm^{-1}.

Synthesis of the unsymmetrical malonate 6

100 mg (0.14 mmol) **5** was dissolved in 50 ml CH_2Cl_2 and 14 µl (0.17 mmol) pyridine was added under protecting gas. The mixture was cooled on an ice bath and 18 µl (0.17 mmol) methyl malonyl chloride in 10 ml CH_2Cl_2 was added dropwise. The mixture was stirred for 12h at room temperature. Compound **6** was purified by column chromatography (silica gel, CH_2Cl_2/ethyl acetate = 80/20) to yield 110 mg (0.14 mmol, 98%).

^{1}H-NMR ($CDCl_3$, 300 MHz) δ: 0.83 (t, ^{3}J = 6.61 Hz, 6H), 1.20 (m, 20H), 1.45 (m, 4H), 1.65 (m, 4H), 1.85 (m, 2H), 2.20 (m, 2H), 3.35 (s, 2H), 3.57 (s, 3H), 4.10 (m, 4H), 5.10 (m, 1H), 8.20 (m, 8H) ppm. ^{13}C-NMR ($CDCl_3$, 75MHz) δ: 14.00, 22.60, 25.50, 26.60, 27.00, 27.95, 28.15, 29.40, 29.50, 31.80, 32.20, 40.20, 41.20, 52.50, 54.80, 65.45, 122.60, 122.70, 122.80, 125.60, 125.70, 129.00, 129.10, 130.80, 133.90, 134.10, 160.60, 166.50, 167.00 ppm. MS (FAB) m/z: 801 [M^+].

Synthesis of A –F (PBI-C_{60} dyad)

33 mg (0.13 mmol) iodine were added to a solution of 140 mg (0.20 mmol) C_{60} in 150 ml toluene. The malonate **6** which is dissolved in toluene was added and the mixture was degassed with argon for 30 minutes. 40 µl (0.26 mmol) 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in 30 ml toluene was added dropwise within one hour and the reaction was

stirred over night. The Per_1C_{60} (**7**) was purified with column chromatography (silica gel, toluene/ethyl acetate = 98/2) to yield 112 mg (0.08 mmol, 57%).

^{1}H-NMR ($CDCl_3$, 400 MHz) δ: 0.82 (t, ^{3}J = 6.78 Hz, 6H), 1.20 (m, 20H), 1.50 (m, 4H), 1.75 (m, 4H), 1.85 (m, 2H), 2.25 (m, 2H), 4.05 (s, 3H), 4.15 (t, ^{3}J = 7.32 Hz, 2H), 4.50 (t, ^{3}J = 6.32 Hz, 2H), 5.15 (m, 1H), 8.40 (m, 8 H) ppm. ^{13}C-NMR ($CDCl_3$, 100.5 MHz) δ: 14.00, 22.60, 25.50, 26.60, 27.00, 27.95, 28.15, 29.20, 29.50, 31.80, 32.20, 40.5, 52.50, 54.80, 55.00, 67.45, 71.40, 122.60, 122.70, 122.80, 125.60, 125.70, 129.00, 129.10, 130.80, 133.90, 134.10, 140.85, 141.80, 141.85, 142.50, 142.10, 142.82, 142.86, 142.90, 143.00, 143.70, 143.82, 144.48, 144.52, 144.54, 144.58, 144.6, 144.80, 145.04, 145.07, 145.10, 145.20, 145.30, 163.20, 163.60, 164.10 ppm. MS (FAB) m/z: 720 [C_{60}^+], 1519 [M^+]. IR (Si) v: 2954, 2927, 2855, 1746, 1697, 1658, 1594, 1578, 1435, 1405, 1341, 1254, 1242, 810, 745, 528 cm^{-1}.

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