

Supporting Information

The influence of π - π -stacking on the light-harvesting properties of perylene bisimide antennas that are covalently linked to a [60]fullerene

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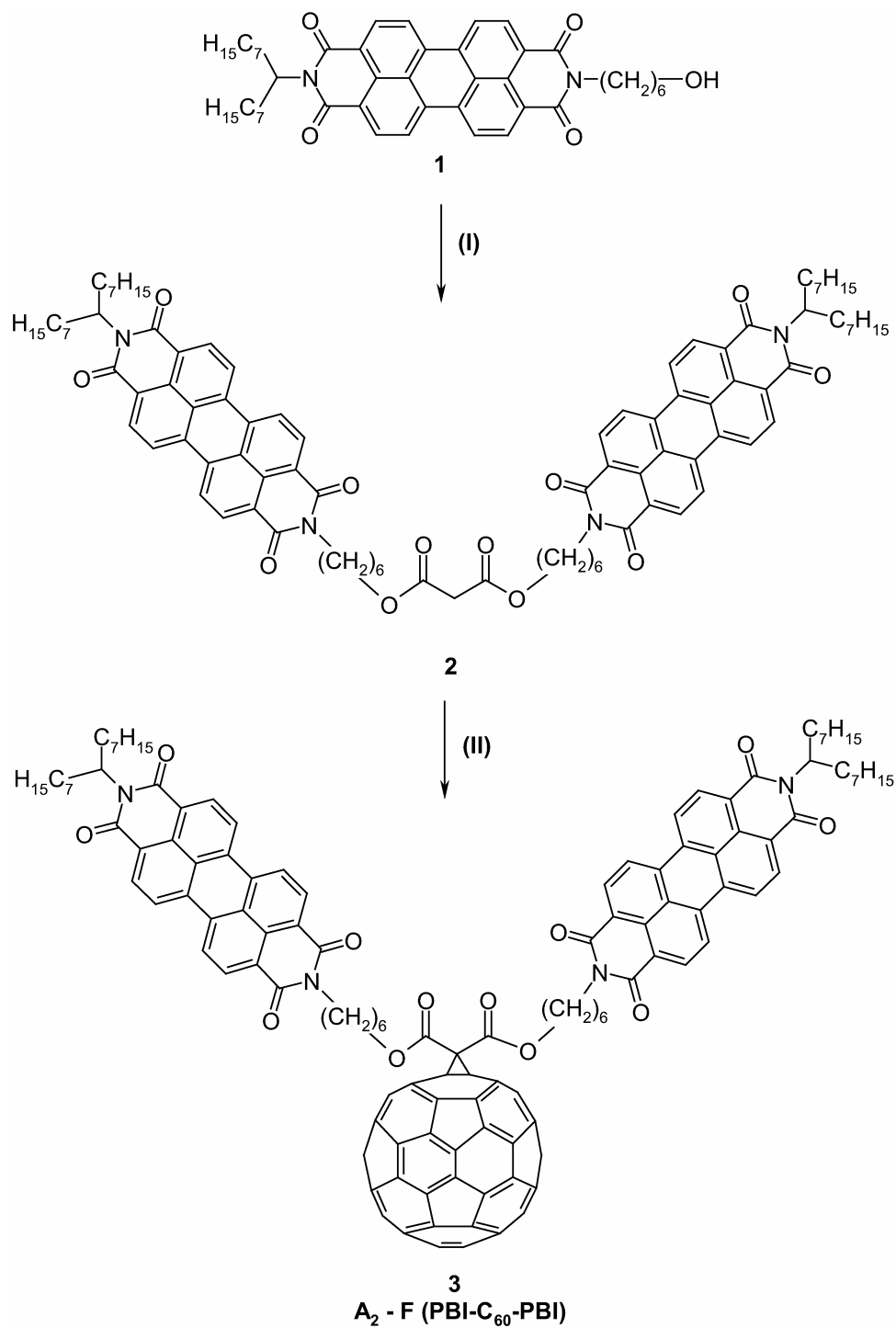
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Synthesis

The synthetic route for the preparation of fullerene with two covalently linked perylene bisimides, **A₂-F (3)** is shown in scheme 1. The hydroxyl functionalized perylene bisimide (**1**) reported elsewhere^{1,2} was coupled with malonyl dichloride to get the disubstituted malonate (**2**). The cyclopropanation of C₆₀ was carried out by a modified Bingel reaction³ of the malonate **2** with iodine and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) in toluene⁴. This coupling reaction was performed with good yield of 47% to obtain PBI-fullerene-PBI triad, **A₂-F (3)**.



Scheme 1: Synthetic strategy of A_2-F (PBI- C_{60} -PBI triad). *Reagents and conditions:*

(I) malonyl dichloride, pyridine, CH_2Cl_2 ; (II) C_{60} , I_2 , 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), toluene.

Experimental

The synthesis of compound **1** and **A-F** were reported earlier^{1,2}. All reagents and solvents were of analytical grade or purified using standard methods.

Synthesis of the symmetrical substituted malonate (**2**)

1 (100 mg, 0.14 mmol) was dissolved in CH₂Cl₂ (50 cm³) and pyridine (14 μl, 0.17 mmol) was added under protecting gas. The mixture was cooled in an ice bath and malonyl dichloride (10 μl, 0.11 mmol) in CH₂Cl₂ (10 cm³) was added dropwise. The mixture was stirred for 12h at room temperature. The product was purified by column chromatography (silica gel, CH₂Cl₂/ethyl acetate 80/20) to yield **2** (104 mg, 99%) as a red solid. λ_{\max} (CH₂Cl₂)/nm 462, 491 and 526 ($\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ 24 000, 51 000 and 56 000); ν_{\max} (film)/cm⁻¹ 3054, 2986, 2929, 2857, 1695, 1655, 1595, 1421, 1342, 1266, 1258 and 748; δ_{H} (300 MHz; CDCl₃) 0.83 (12H, t, *J* 6.57 Hz, CH₃), 1.30 (40H, m, CH₂), 1.50 (8H, m, CH₂), 1.75 (8H, m, CH₂), 1.90 (4H, m, CH₂), 2.20 (4H, m, CH₂), 3.40 (2H, s, OCCH₂CO), 4.15 (8H, m, NCH₂, CH₂O), 5.10 (2H, m, N-CH(CH₂)₂), 8.10 (4H, d, *J* 8.15 Hz, Ar-H), 8.20 (4H, d, *J* 8.15 Hz, Ar-H), 8.30 (4H, d, *J* 7.98 Hz, Ar-H) and 8.40 (4H, d, *J* 7.55 Hz, Ar-H); δ_{C} (75MHz; CDCl₃) 14.10, 22.60, 25.50, 26.70, 27.00, 27.80, 28.25, 29.20, 29.60, 31.80, 32.20, 42.00, 44.00, 55.00, 65.50, 122.60, 125.80, 129.00, 131.00, 134.10, 162.80 and 166.60; *m/z* (FAB) 1469 (M⁺).

Synthesis of A₂-F (PBI-C₆₀-PBI) (**3**)

To a solution of C₆₀ (74 mg, 0.10 mmol) in toluene (150 cm³), iodine (18 mg, 0.07 mmol) and **2** (100 mg, 0.07 mmol) were added and the mixture was degassed with argon for 30 minutes. 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) (20 μl, 0.14 mmol) in toluene (15 cm³) was added dropwise within one hour and the reaction was stirred over night. The product was purified with column chromatography (silica gel, toluene/ethyl acetate 90/10) to yield **3** (70 mg, 47 %) as a dark-red solid. λ_{\max} (CH₂Cl₂)/nm 260, 325, 461, 492 and 528; ν_{\max} (film)/cm⁻¹ 3054, 2928, 2304, 1695, 1655, 1595, 1421, 1342, 1257 and 757; δ_{H} (400 MHz; CDCl₃) 0.83 (12H, t, *J* 6.53 Hz, CH₃), 1.30 (40H, m, CH₂), 1.60 (8H, m, CH₂), 1.90 (8H, m, CH₂), 2.20 (4H, m, CH₂), 4.30 (4H, m, NCH₂), 4.53 (2H, t, *J* 6.22 Hz, CH₂O), 5.10 (2H, m, N-CH(CH₂)₂), 8.20 (8H, m, Ar-H), 8.40 (8H, m, Ar-H); δ_{C} (75MHz; CDCl₃) 14.10, 22.60, 25.50, 26.70, 27.00, 27.80, 28.25, 29.20, 29.60, 31.80, 32.20, 42.00, 52.00, 55.00, 65.50, 71.60,

122.60, 122.80, 123.00, 125.80, 129.30, 131.00, 134.10, 140.85, 141.90, 142.10, 142.90, 142.95, 143.00, 143.20, 143.80, 144.50, 144.60, 144.80, 145.10, 145.20, 145.40, 163.10, 163.90; m/z (FAB) 720 (C_{60}^+), 2188 (M^+).

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