Supporting Information

Synthesis of Rigid Cores Based on 1,1'-Biadamantane

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Experimental Section

3, 3', 5, 5', 7, 7'-Hexabromo-1, 1'-biadamantane (2c). 1,1'-Biadamantane (2.70g, 9.98mmol) was added portionwise over 30 min to a stirred mixture of Br₂ (50mL) and anhydrous AlCl₃ (2.66g, 19.96mmol) at 0°C, and then heated to 85°C over a period of 1h and kept at that temperature for 48h. Hydrogen bromide was evolved copiously during the addition and heating. The cooled mixture was treated subsequently with saturated aqueous NaHSO₃ solution and hydrochloric acid. The solids were removed by filtration, washed and air-dried. The crude product was extracted with CHCl₃ for 24h and then recrystallized from N-Methyl-2-pyrrolidinone (NMP), giving 5.20g (70%) of 2d as white solid. ¹H NMR (400 MHz, Pyridine-d₅) δ 2.83 (s, 12H), 2.26 (s, 12H); ¹³C NMR (101 MHz, Pyridine-d₅) δ 59.44, 55.63, 48.63, 43.49. Anal. Calcd for C₂₀H₂₄Br₆: C, 32.29; H, 3.25. Found: C, 32.32; H, 3.33.

General Procedure for the Synthesis of Poly(aryl)-1, 1'-biadamantane (4a-c). To a 100ml flask were successively added bromobenzene (50mL), anhydrous FeCl₃ (0.01mol) and 2a-2c (0.01mol). The mixture was magnetically stirred at room temperature for 30min and then heated to reflux until hydrogen bromide ceased to release. The reaction mixture was cooled to room temperature and then poured into a mixture of 50mL of 0.1M HCl aqueous solution and 100mL of CH₂Cl₂. The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3×50mL). The combined organic layers were washed successively with saturated NaHCO₃ solution, water and brine. The organic layer was transferred to a separatory chamber and added, as a slow stream, to 1L methanol to precipitate a solid during 1h. After the addition was complete, the methanol suspension was stirred vigorously for another 1h. The methanol suspension was filtered and dried in the vacuum-oven.

3, 3'-Bis(4-bromophenyl)-1,1'-biadamantane (4a). The crude product was purified by silica gel chromatography eluted with petroleum ether. The first fraction was concentrated and recrystallized from DMF to afford 4a as white crystals with the yield of 3.31 g (57%). ¹H NMR (400 MHz, CDCl₃) δ 7.48-7.36 (m, 4H), 7.28-7.17 (m, 4H), 2.23-2.12 (m, 4H), 1.87-1.51 (m, 24H); ¹³C NMR (101 MHz, CDCl₃) δ 150.34, 131.12, 126.86, 119.36, 42.46, 41.70, 37.66, 36.88, 36.39, 34.48, 29.33. Anal. Calcd for C₃₂H₃₆Br₂: C, 66.22; H, 6.25. Found: C, 66.13; H, 6.20.

3, 3', 5'-Tetrakis(4-bromophenyl)-1,1'-biadamantane (4b). The crude product was purified by silica gel chromatography eluted with CH₂Cl₂: hexane= 1:50. The fraction with an Rₜ value of 0.68 was concentrated and recrystallized from DMF to afford 4b as white crystals with the yield of 4.72 g (53%). ¹H NMR (400 MHz, CDCl₃) δ 7.50-7.13 (m, 16H), 2.27-1.70 (m, 24H); ¹³C NMR (101 MHz, CDCl₃) δ 150.34, 131.12, 126.87, 119.36, 42.46, 41.70, 37.66, 36.88, 36.39, 34.47, 29.32. Anal. Calcd for C₄₄H₄₂Br₄: C, 59.35; H, 4.75. Found: C, 59.24; H, 4.70.

3, 3', 5', 7'-Hexakis(4-bromophenyl)-1,1'-biadamantane (4c). The crude product was recrystallized from DMF to give 2.64g (44%) of 3d as a white solid. ¹H NMR (400 MHz, CDCl₃) δ 7.46 (dt, J=9.21, 2.03 Hz, 12H), 7.26 (dt, J=9.21, 2.03 Hz, 12H), 2.06 (d, J=11.97 Hz, 6H), 1.93 (d, J=11.97 Hz, 6H), 1.80(s, 12H); ¹³C NMR (101 MHz, CDCl₃) δ 148.16, 131.52, 126.84, 120.23, 46.65, 40.41, 38.92, 38.58. Anal. Calcd for C₅₆H₄₈Br₆: C, 56.03; H, 4.03. Found: C, 56.14; H, 4.12.