Supplementary Material (ESI) for Chemical Communications
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Supplementary Informations

Synthesis, and Two Photon Absorption properties of 7,7'-(iminundecahydro-*closo*-dodecaborate)-9,9'-(dihexyl)-2,2'-bifluorene.

Rémy Bernard*[a], Cyril Barsu[b], Patrice L. Baldeck[c], Chantal Andraud[b], David Cornu [a], Jean-Pierre Scharff[a] and Philippe Miele[a].

[a] *Laboratoire des Multimatériaux et Interfaces, Université Claude Bernard-Lyon I, CNRS (UMR 5615), 43 Bd du 11 Novembre 1918, F69622 Villeurbanne cedex, France*
[b]*Ecole Normale Supérieure de Lyon, Laboratoire de chimie CNRS (UMR 5182), 46 allée d'Italie 69364 Lyon Cedex 07, France*
[c] *Laboratoire de Spectrométrie Physique, Université Joseph Fourier, CNRS (UMR 5588) 140 Avenue de la Physique - BP 87,*

General Procedure

All reactions were carried out under atmosphere of pure argon using vacuum-line and Schlenk techniques with solvents purified by standard methods[1]. Zn dust was activated according to the literature.[2] $NiCl_2(PPh_3)_2$.[3] $(Et_3NH)_2[B_{12}H_{12}]$ and 2,7-dibromofluorene were purchased respectively from KATCHEM Ltd., Prague, and Aldrich and used without further purification. Chromatographic separations were carried out using Merck silica gel 60 (0.040-0.063 mm). ^{1}H-, ^{13}C- and ^{11}B-NMR spectra were recorded on a Brüker AM 300 spectrometer at 300MHz, 75MHz, and 96.29MHz with $Et_2O.BF_3$ as external reference (positive values downfield), respectively. High resolution Mass spectra of ionic species were measured on Esquire 3000 Ion Trap System, and alternatively on Brüker Esquire-LC Ion Trap Instrument using Electrospray Ionization. Negative ions were detected. Samples dissolved in acetonitrile (1 ng μL^{-1}) were introduced to ion source by infusion of 3 μL min^{-1}; drying temperature was 300°C, drying gas flow 5 L min^{-1}, nebulizing gas pressure 10 psi. UV-VIS linear absorption curves were recorded in acetonitrile solution (10 mm cell) on Varian CARY 1E spectrometer. Differential scanning calorimetry (DSC) analysis was performed on a TA8000 Mettler-Toledo apparatus.

Synthesis of compound 1

To a mixture of 2,7-dibromofluorene (10.0 g, 30.86 mmol) and triethylbenzylammonium chloride (387 mg, 1.70 mmol) in 45 mL DMSO and 11.5 mL of aqueous NaOH (50 % ww),

1-bromohexane (15.3 g, 13.06 mL) was added. The reaction mixture is stirred for 2 h, warmed at 60 °C and stirred for 2 h at this temperature. An excess of ethylacetate was added to the reaction mixture. NaOH precipitate formed was filtered off. The organic layer was washed with dilute HCl, H_2O and brine, and dried over $MgSO_4$. Purification by column chromatography on silica using pentane as eluent to give **1** (14.6g, 96%) as a white solid (Found: C, 60.90; H, 6.49. $C_{25}H_{32}Br_2$ requires: C, 60.99; H, 6.55%); mp 52 °C; δ_H(300 MHz; $CDCl_3$; Me_4Si) 7.42-7.51 (6H, m), 1.85-1.93 (4H, m), 1.04-1.15 (12H, m), 0.72-0.79 (6H, m), 0.57 (4H, m); δ_C (75 MHz; $CDCl_3$; Me_4Si) 152.08, 138.58, 129.66, 125.69, 120.97, 120.63, 55.20, 39.69, 30.95, 29.07, 23.15, 22.07, 13.48.

Synthesis of compound 2

To a solution of compound **1** (2.5 g, 5.08 mmol) in THF (23 mL) was added *n*-BuLi (2.5 M in hexane, 2.0 mL, 5.08 mmol) dropwise at –78 °C. After 1 h at -78 °C, DMF (0.51 mL, 6.60 mmol) was added dropwise via a syringe and the mixture was stirred for 2 h at –78 °C and then for 2 h at room temperature. The mixture was cooled at 0 °C and HCl (3M, 10 mL) was added. The organic layer was separated and then washed with water (4 times) and brine before dried over Na_2SO_4. Upon evaporating off the solvent, the residue was purified with column chromatography on silica using a mixture pentane/dichloromethane (2/1) to afford **2** (1.8g, 80%) as an yellow oil (Found: C, 70.74; H, 7.45; O, 3.75. $C_{26}H_{33}BrO$ requires C, 70.74; H, 7.53; O, 3.62); mp 43 °C; δ_H(300 MHz; $CDCl_3$) 10.05 (1 H, s), 7.85-7.75 (3 H, m), 7.60 (1 H, d, *J*8,0), 7.51-7.44 (2 H, m), 2.03-1.93 (4 H, m), 1.12-1.00 (12 H, m), 0.71 (6 H, t, *J*6.6,), 0.59-0.52 (4 H, m); δ_C (75 MHz; $CDCl_3$) 192.05; 154.30; 151.17; 146.32, 138.60, 135.71, 130.54, 130.48, 126.50, 123.15, 122.27, 120.12, 55.64, 40.13, 31.45, 29.56, 23.74, 22.55, 13.99.

Synthesis of compound 3

A mixture of $NiCl_2(PPh_3)_2$ (889 mg, 1.36 mmol), triphenylphosphine (2.85 g, 10.87 mmol), zinc powder (533 mg, 8.15 mmol), and dry DMF (10 mL) was stirred at room temperature for 0.5 h under argon atmosphere, resulting in the change of the color from green blue to reddish brown. A solution of **2** (1.2 g, 2.72 mmol) in dry DMF (6 mL) was added and the mixture heated at 50 °C for 70h. Water (10 mL) was then added to the mixture followed by filtration through Celite. The filtrate was diluted with chloroform and the layers were separated. The organic layer was washed with water (4 times) and brine before dried over Na_2SO_4. Upon

evaporating off the solvent, the residue was purified by column chromatography on silica using a mixture pentane/dichloromethane (1/1) as eluent to afford **3** (500mg, 51%) as a yellow solid which is recristallised in hexane (Found: C, 86.25; H, 9.38. $C_{52}H_{66}O_2$ requires: C, 86.38; H, 9.20%); mp 125 °C; δ_H (300 MHz; $CDCl_3$) 10.07 (2H, s), 7.90-7.84 (8H, m,), 7.70-7.64 (4 H, m), 2.12-2.04 (8H, m), 1.12-1.05 (24 H, m), 0.77-0.70 (20H, m), δ_C(75 MHz; $CDCl_3$) 192.31, 153.06, 151.82, 147.11, 141.86, 139.11, 135.39, 130.63, 126.64, 123.15, 121.69, 121.32, 120.12, 55.47, 40.19, 31.45, 29.57, 23.80, 22.52, 13.98.

Synthesis of compound 4. The synthesis of compound **4** was conducted using a method described by Hertler and Raash.[4]

Synthesis of compound 5. 0.057 g (0.0536 mmol) of compound 1 and 0.085 g (0.214 mmol) of compound 2 were dissolved in 30 mL of dimethylformamide. Few drops of an aqueous solution of sodium hydroxide (5 wt %) were then added to the mixture. The reaction mixture was stirred over night at room temperature. The solvent was removed under vacuum at 60°C. and further purification was performed by chromatography on silica using a miture acetonitrile/dichloromethane (4/1) as eluent to afford **5** (0.029mmol, 55%) as a yellow powder; δ_H(300MHz; $CDCl_3$; Me_4Si) 0.6(12H, u, CH_3), 0.7(8H, m, CH_2), 1.0(48H, m, CH_2 and CH_3), 1.4 (16H, m, CH_2), 1.6 (16H, m, CH_2), 2.1 (m, 8H, CH_2); 3.2 (16H, m, CH_2), 7.7 (8H, m, C_6H_3), 7.9 (4H, m, C_6H_3), 8.7 (2H, d, HC=NH), 9.5 (2H, d, HC=NH); $\delta_{B\{1H\}}$ (96,29MHz; CH_3CN): -3,8 (s, 2B); -15,3 (s, 22B); δ_B(96,29MHz; CH_3CN) -2,8 (s, 2B); -15,3 (d, 22B); δ_C(75MHz; CD_2Cl_2) 13.8, 14,1, 20.1, 23.0, 24.1, 24.3 , 29.8, 31.8, 40.6, 56.2, 59.4, 121.2, 122.1, 123.3, 127.2, 127.6, 131.3, 138.0, 142.4, 149.2, 153.0, 153.6, 165.7; m/z (EI) 500,5; DSC : strong exothermic effect starting at 230 °C.

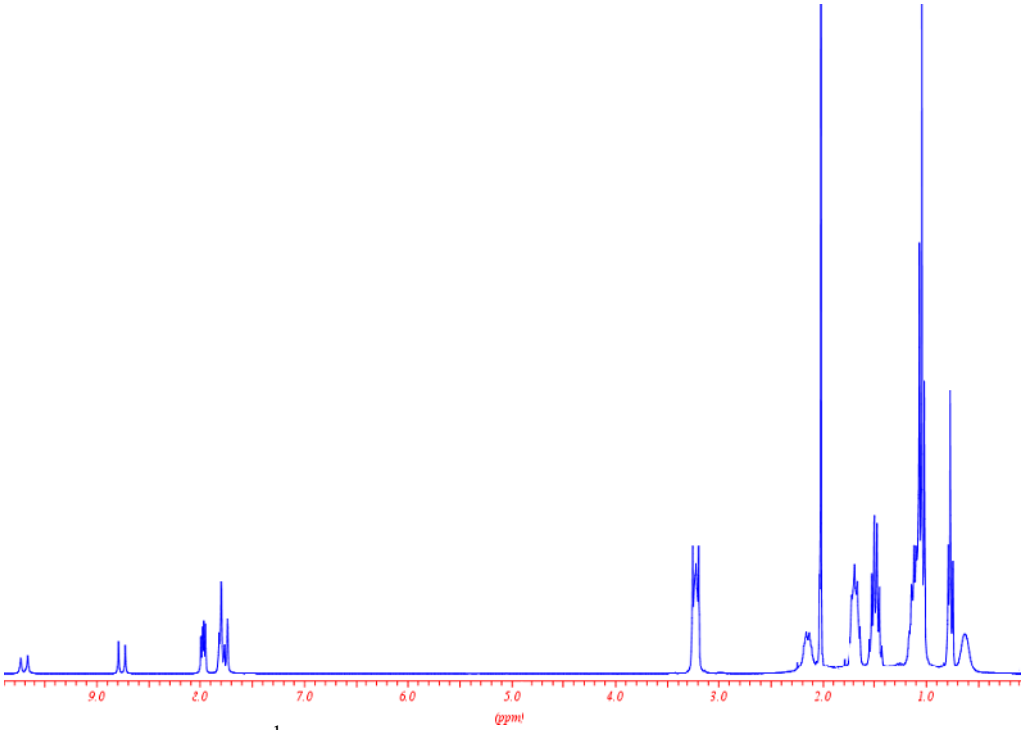

Fig 1 ^{1}H NMR ($CDCl_3$) spectrum of compound 5

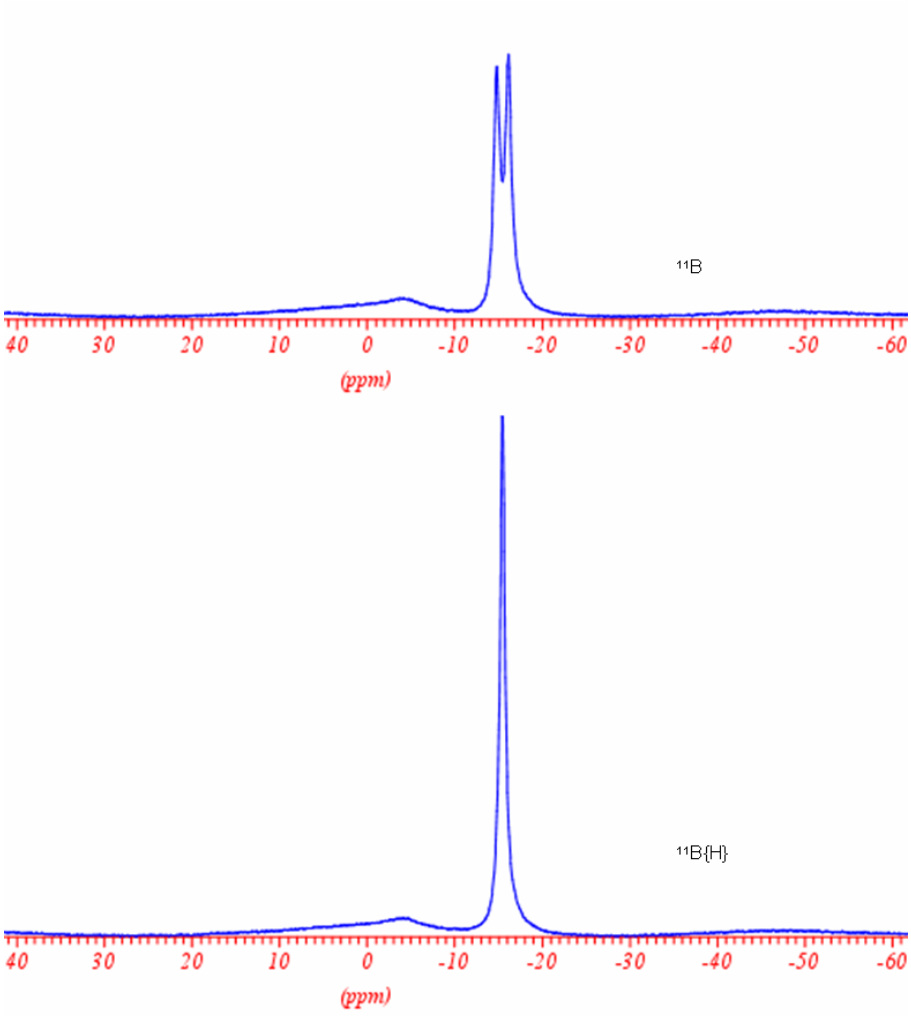

Fig 2 ^{11}B NMR ($CDCl_3$) spectrum of compound 5

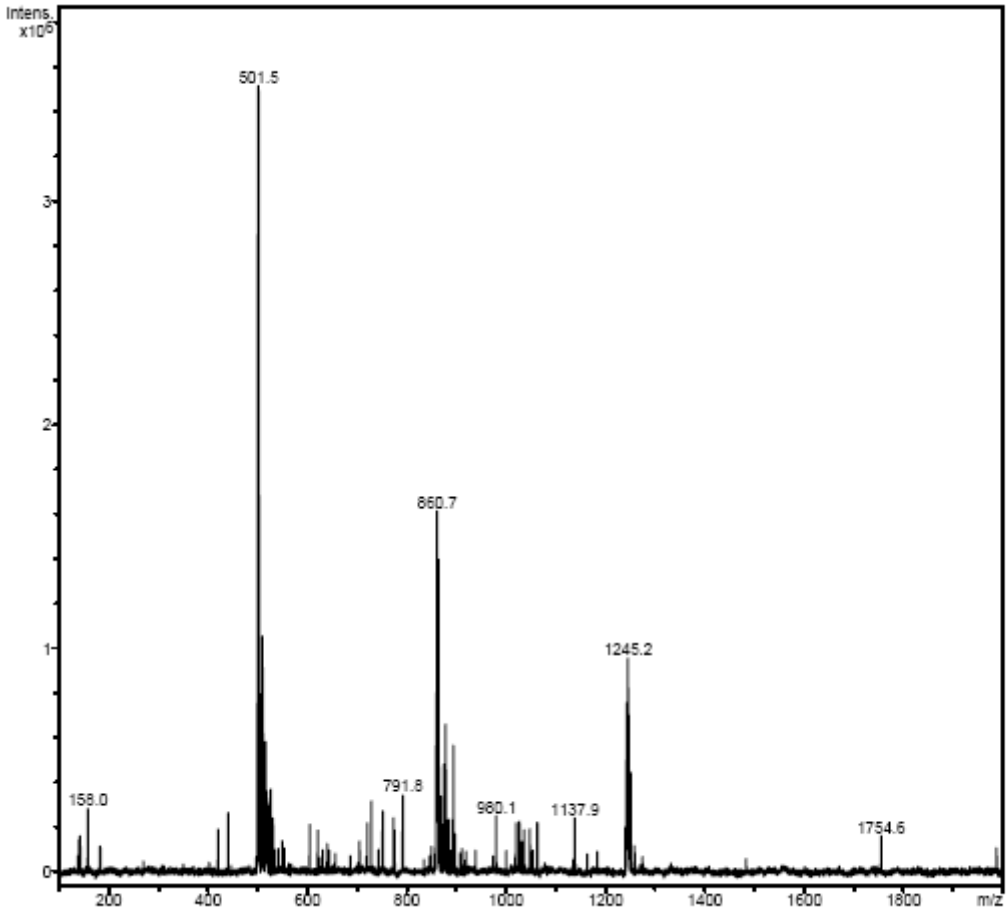

Fig 3 MS spectrometry spectrum of compound 5

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