Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting information

Synthesis and characterization of a ferrocene-linked bis-fullerene[60] dumbbell

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^{1}H NMR spectra and assignment of compounds

1,1′-N,N’-(2-(3,4-bis(octadecyloxy)benzene)-3,4-fulleropyrrolidinyl) ferrocenedicarboxamide (dumbbell **1**)

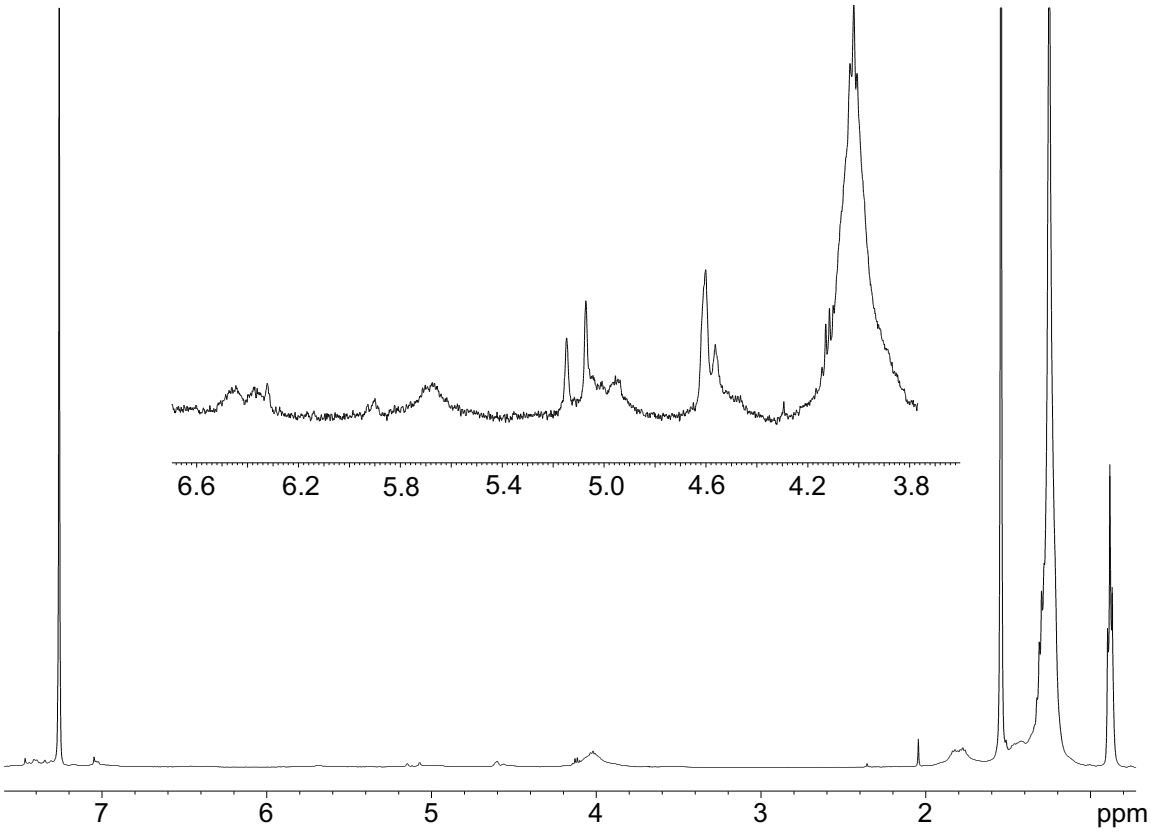

Figure 1. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) spectrum of compound **1**. Inset shows an expansion of the area between 6.6 – 3.8 ppm.

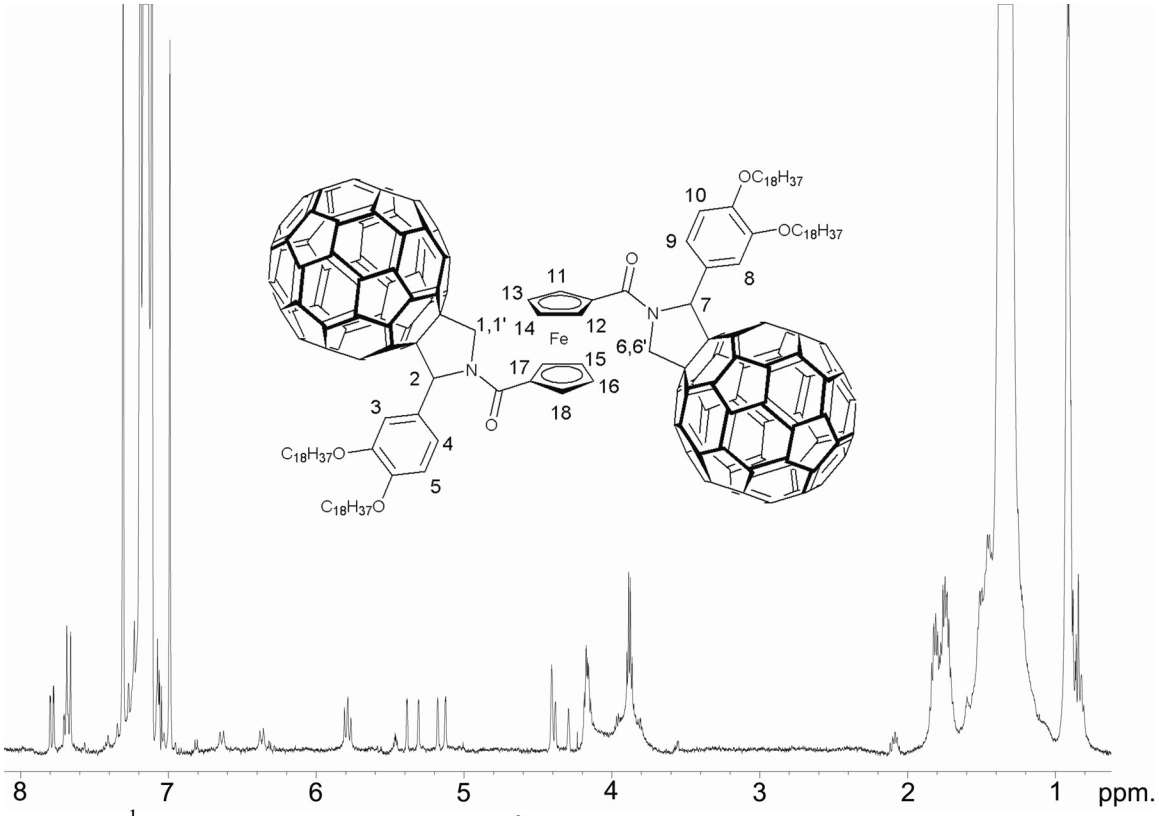

Figure 2. ^{1}H NMR (500 MHz, C_6D_6, 70°C) spectrum of compound **1**

Assignment:

δ_H (500 MHz, C_6D_6, 70°C): 7.80 (1H, d, J = 2.2 Hz, H^3), 7.78 (1H, d, J = 2.2 Hz, H^8), 7.68 (2H, m, H^4 and H^9), 7.07 (1H, d, J = 8.2 Hz, H^5), 7.05 (1H, d, J = 8.2 Hz, H^{10}), 6.64 (1H, d, J = 12 Hz, H^1), 6.37 (1H, d, J = 12 Hz, H^6), 5.80 (1H, d, J = 12 Hz, $H^{1'}$), 5.78 (1H, d, J = 12 Hz, $H^{6'}$), 5.47 (2H, m, H^2 and H^7), 5.39 (1H, m, H^{11}), 5.31 (1H, m, H^{17}), 5.18 (1H, m, H^{18}), 5.12 (1H, m, H^{12}), 4.41 (2H, m, H^{13} and H^{15}), 4.38 (1H, m, H^{16}), 4.29 (1H, m, H^{14}), 4.17 (4H, m, aliphatic, (-O-$\mathbf{CH_2}$-R)$_2$), 3.89 (2H, t, J = 6.5 Hz, aliphatic, (-O-$\mathbf{CH_2}$-R)), 3.87 (2H, t, J = 6.5 Hz, aliphatic, (-O-$\mathbf{CH_2}$-R)), 1.81 (4H, m, aliphatic, (-O-CH_2-$\mathbf{CH_2}$-R)$_2$), 1.75 (4H, m aliphatic, (-O-CH_2-$\mathbf{CH_2}$-R)$_2$), 1.34 (120H, m, aliphatic), 0.92 (12H, m, aliphatic, (-O-((CH_2)$_{17}$-$\mathbf{CH_3}$)$_4$) ppm.

2-(3,4-bis(octadecyloxy)benzene)-3,4-fulleropyrrolidine (**5**)

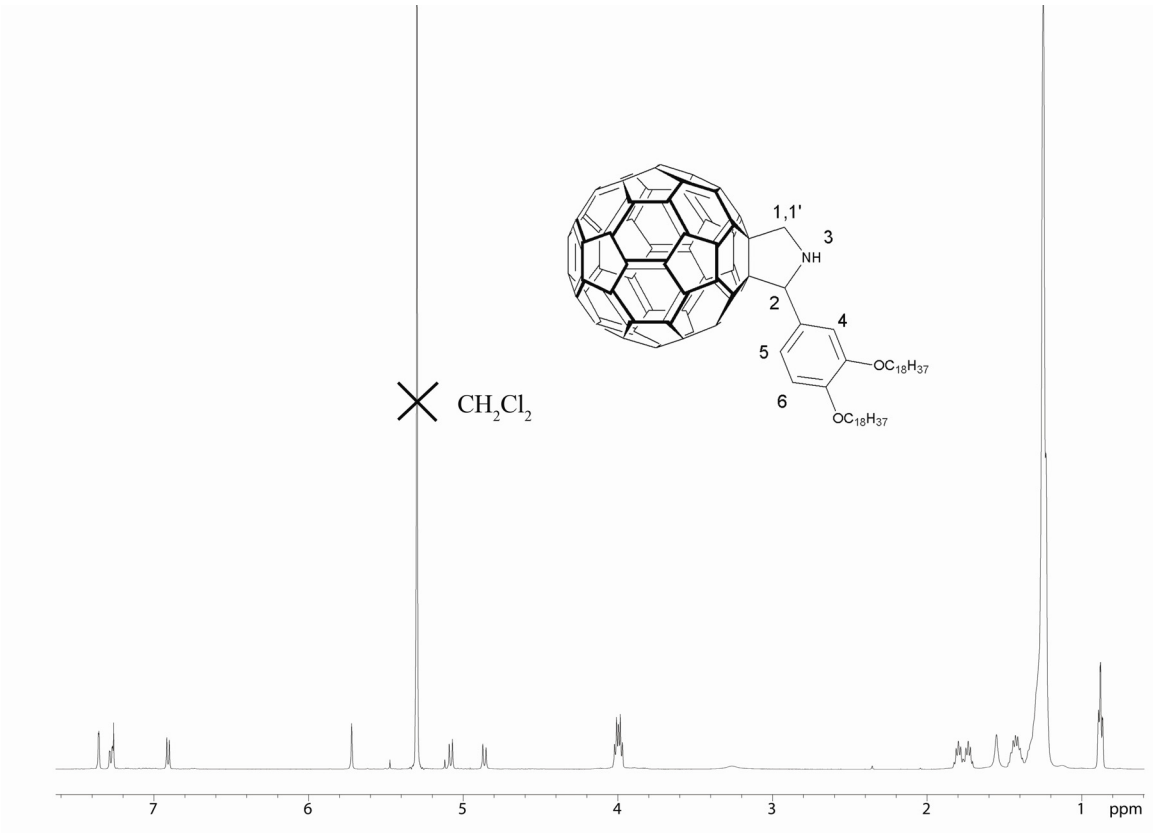

Figure 3. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) spectrum of compound **5**

Assignment:

δ_H(500 MHz, $CDCl_3$, 25 °C): 7.36 (1H, d, J = 2.1 Hz, H^4), 7.28 (1H, dd, J = 8.3, 2.1 Hz, H^5), 6.91 (1H, d, J = 8.3 Hz, H^6), 5.72 (1H, s, H^2), 5.08 (1H, d, J = 10.3 Hz, H^1), 4.86 (1H, d, J = 10.3 Hz, $H^{1'}$), 4.01 (2H, t, J = 6.8 Hz, aliphatic (-O-**CH_2**-R)), 3.98 (2H, t, J = 6.8 Hz, aliphatic (-O-**CH_2**-R)), 3.26 (1H, br s, H^3) 1.80 (2H, m, aliphatic (-O-CH_2-**CH_2**-R)), 1.74 (2H, m, aliphatic (-O-CH_2-**CH_2**-R)), 1.43 (4H, m, aliphatic (-O-CH_2-CH_2-**CH_2**-R)), 1.34-1.19 (56H, m, aliphatic), 0.88 (6H, m, aliphatic (–O-$(CH_2)_{17}$-**CH_3**)) ppm.

3,4-bis(octadecyloxy)benzaldehyde

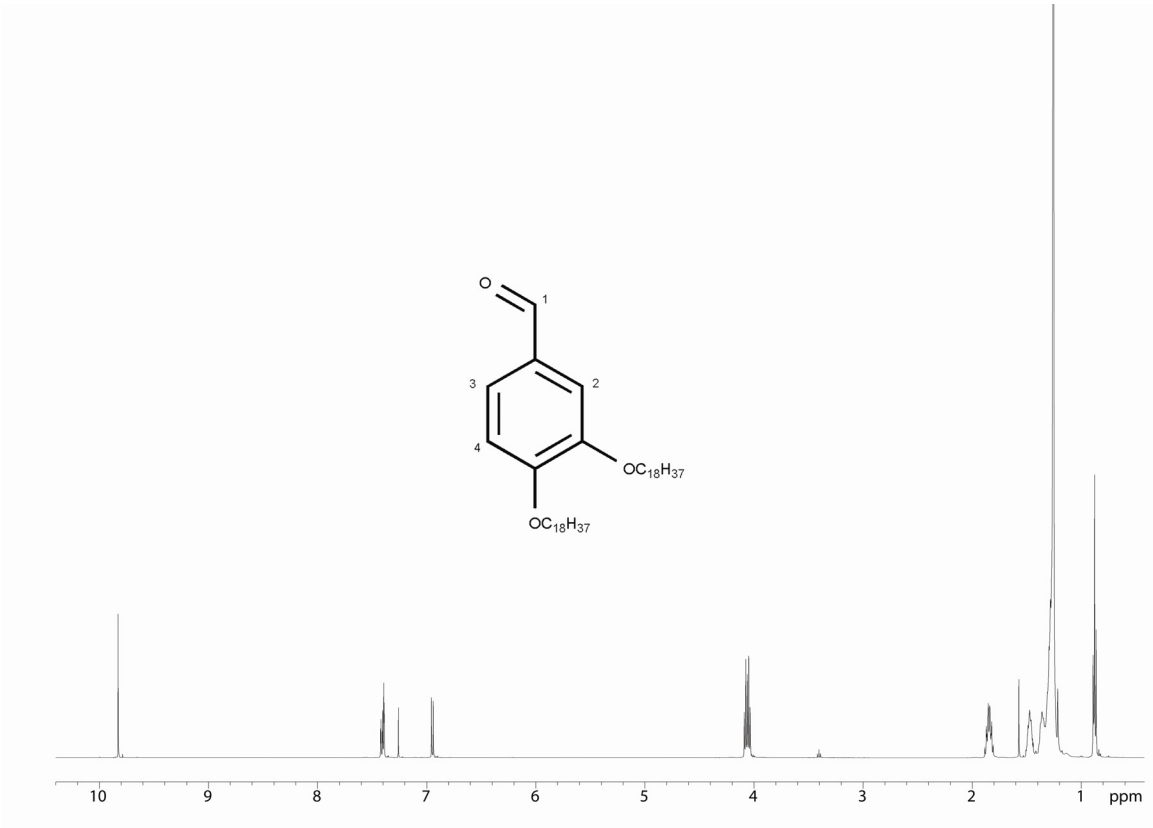

Figure 4. ^{1}H NMR (500 MHz, $CDCl_3$, 25°C) spectrum of 3,4-bis(octadecyloxy) benzaldehyde

Assignment:

δ_H (500 MHz, $CDCl_3$, 25 °C): 9.83 (1H, s, H^1), 7.41 (1H, dd, J = 8.1, 1.9 Hz, H^3), 7.39 (1H, d, J = 1.9 Hz, H^2), 6.95 (1H, d, J = 8.1 Hz, H^4), 4.08 (2H, t, J = 6.6 Hz, aliphatic (-O-**CH_2**-R)), 4.05 (2H, t, J = 6.6 Hz, aliphatic (-O-**CH_2**-R)), 1.85 (4H, m, aliphatic (-O-CH_2-**CH_2**-R)), 1.48 (4H, m, aliphatic (-O-CH_2-CH_2-**CH_2**-R)), 1.41-1.20 (56H, m, aliphatic), 0.88 (6H, m, aliphatic (–O-$(CH_2)_{17}$-**CH_3**)) ppm.

UV/Vis spectra of compounds **1**, **5**, **6**, **7**

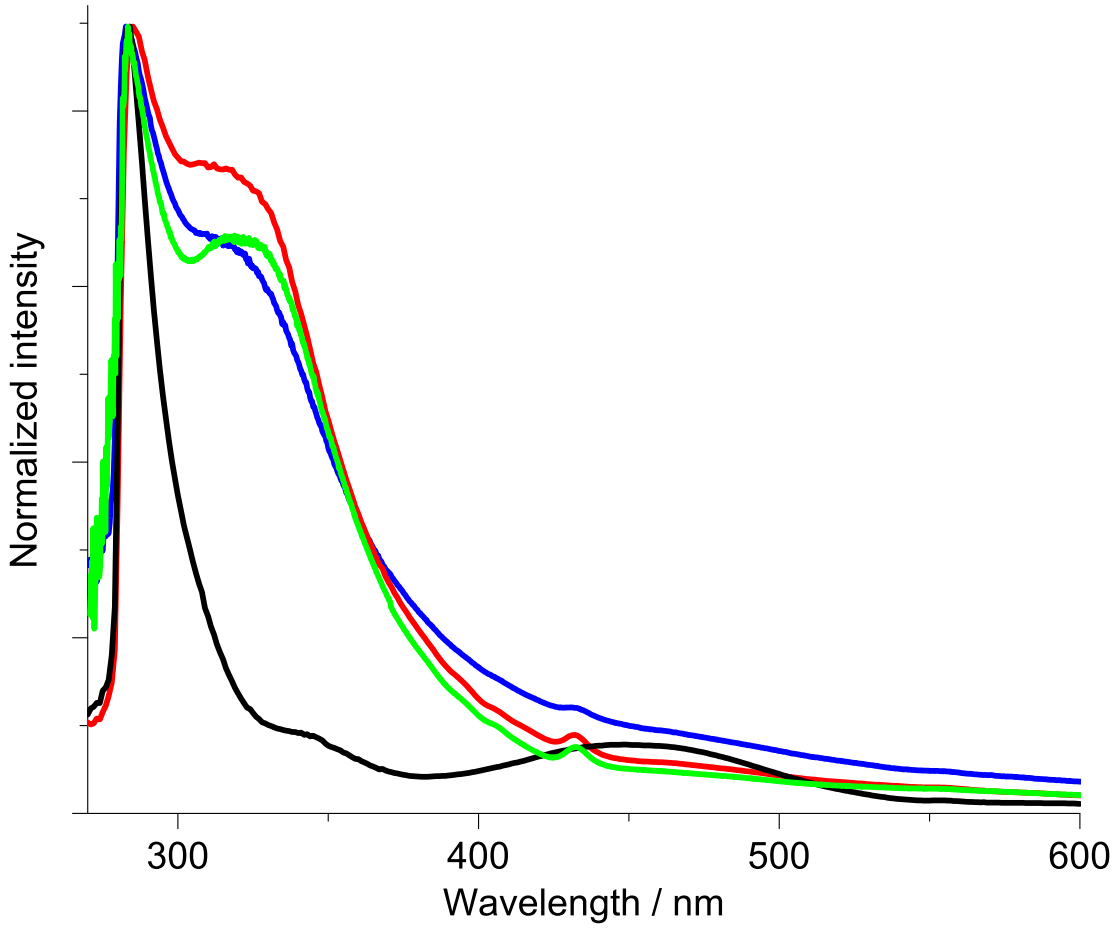

Figure 5. UV/Vis spectra of dumbbell **1** (blue), fulleropyrrolidine **5** (red), fulleropyrrolidine **6** (green), and ferrocene derivatives **7** (black). Spectra are recorded in toluene.

Experimental details for synthesis of compounds **8-13**

Synthesis of *N*-(4-iodophenyl)glycine ethyl ester **8**

4-iodoaniline (2.0g, 9.1 mmol), ethyl bromoacetate (1.54g, 9.28 mmol), anhydrous sodium acetate (0.75g, 9.14 mmol) and absolute ethanol (100 mL) was added to a round-bottomed flask and the mixture was refluxed over night under nitrogen atmosphere. The solvent was evaporated and dichloromethane (100 mL) was added. The organic phase was washed with water (2 x 100 mL) and evaporated. The residue was then dissolved in absolute ethanol, and water was added to precipitate the product that was filtered off. The solid product was washed with water and then dried in vacuo to yield N-4-iodophenylglycine ethyl ester as a white solid (yield: 1.35g, 48%). ^{1}H NMR (500 MHz,

$CDCl_3$, 25 °C): δ = 7.44 (AA´BB´, 2H), 6.39 (AA´BB´, 2H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.86 (s, 2H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm.

Synthesis of *N*-((4-trimethylsilylethynyl)phenyl)glycine ethyl ester **9**

N-(4-iodophenyl)glycine ethyl ester **8** (1,03 g, 3,38 mmol), Ethynyltrimethylsilane (0.55 mL, 3.89 mmol), $Pd(PPh_3)_2Cl_2$ (48 mg, 0.068 mmol), CuI (27 mg, 0.14 mmol), diethylamine (5.6 mL) and DMF (1.6 mL) was added to a microwave vial. The vial was sealed and flushed with nitrogen. The vial was heated under nitrogen atmosphere in a microwave at 120°C for 45 minutes. The content in the vial was poured into HCl (0.1 M, 40 mL). The suspension was extracted with diethyl ether (3 x 40 mL) and the organic phase was washed with aqueous $NaHCO_3$ (2 x 20 mL) and with water (40 mL). The organic phase was evaporated leaving a residue that was partly soluble in *n*-pentane. The pentane dispersion was filtrated through a pad of celite and the filtrate was evaporated giving compound 9 as a brown solid (yield: 637 mg, 69%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.31 (AA´BB´, 2H), 6.50 (AA´BB´, 2H), 4.45 (br t, *J* = 5.2 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.89 (d, *J* = 5.2 Hz, 2H), 1.30 (t, *J* = 7.1 Hz, 3H), 0.22 (s, 9H) ppm.

Synthesis of *N*-((4-ethynyl)phenyl)glycine ethyl ester **10**

9 (415 mg, 1.51 mmol), K_2CO_3 (522 mg, 3.78 mmol), CH_2Cl_2 (20 mL) and ethanol (50 mL) was added to a round-bottomed flask and the mixture was stirred under nitrogen atmosphere at RT over night. The solvent was evaporated and the residue was redissolved in CH_2Cl_2 and the solution was washed with water (2 x 20 mL). Yield: 74%. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.33 (AA´BB´, 2H), 6.52 (AA´BB´, 2H), 4.48 (br t, *J* = 5.4 Hz, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 3.89 (d, *J* = 5.4 Hz, 2H), 2.96 (s, 1H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm.

Synthesis of 1,1´-bis(tri-*n*-butylstannyl)ferrocene

Ferrocene (10.0g, 53.7 mmol) was added to a flame-dried 1000 mL flask equipped with a septum. The flask was evacuated for 2 hours and then kept under nitrogen atmosphere. Dry diethyl ether (90 mL) was added and the flask was cooled to 0°C. Butyl lithium (2.5 M in hexanes, 48 mL) and TMEDA (18 mL) was added in portions to the cooled solution via syringe. The solution was then allowed to stir over night under nitrogen atmosphere in room temperature. The resulting red suspension was cooled to 0°C and tributyltin chloride (37 g, 114 mmol) was added to the mixture in portions. The resulting dark solution was allowed to slowly reach room temperature over a 6 hour period and was then stirred over night. The solution was washed with water (3 x 50 mL) and brine and was then dried using K_2CO_3. The solvent was evaporated and a portion of the crude product was subjected to column chromatography on neutral Al_2O_3 using pentane as eluent. A broad orange band was collected and dried in vacuo to afford 1,1´-bis(tri-n-butylstannyl)ferrocene that was pure enough for the next step. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.26 (m, 4H), 3.99 (m, 4H), 1.59 (m, 12H), 1.38 (m, 12H), 1.04 (m, 12H), 0.94 (m, 18H) ppm.

Synthesis of 1,1´-diiodoferrocene **11**

1,1´-bis(tri-n-butylstannyl)ferrocene (2.0g, 2.6 mmol) was dissolved in dichloromethane (15 mL) in a round-bottomed flask. The flask was cooled to -79°C and I_2 (1.48g, 5.83 mmol) was added under nitrogen atmosphere. The solution was allowed to slowly reach room temperature under a period of several hours and was then stirred over night. The dark mixture was washed with $Na_2S_2O_3$ (1M, 20 mL) and the orange organic phase was collected and filtrated through a plug of neutral Al_2O_3. The plug was rinsed with dichloromethane to elute all of the orange product. The filtrate was evaporated and the resulting oil was dissolved in methanol (30 mL). KF (0.7g, 12 mmol) was added to the solution to precipitate stannyl by-products. The heterogeneous mixture was filtrated and the filtrate was evaporated. The residue was then treated with diethyl ether and the solution was filtrated through a plug of neutral Al_2O_3 two times to yield 1,1´-diiodoferrocene (0.8g, 70%) as a brown oil. ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 4.37 (t, *J* = 1.8 Hz, 4H), 4.18 (t, *J* = 1.8 Hz, 4H) ppm.

Synthesis of compound **12**

1,1´-diiodoferrocene (230 mg, 0.53 mmol), compound **10** (286 mg, 1.41 mmol), $Pd(Ph_3)_2Cl_2$ (50 mg, 0.071 mmol), CuI (15 mg, 0.079 mmol) and diisopropylamine (5 mL) was added to a 10 mL round-bottomed flask and the flask was flushed with nitrogen. The mixture was heated to 90°C under nitrogen atmosphere for 2 days. The solvent was evaporated leaving a brown solid. The material was subjected to column chromatography (silica, pentane/CH_2Cl_2 1:1) and the last band was collected (yield: 120 mg, 39%). ^{1}H NMR (500 MHz, $CDCl_3$, 25 °C): δ = 7.35 (AA´BB´, 2H), 7.27 (CC´DD´, 2H), 6.52 (AA´BB´, 2H), 6.49 (CC´DD´, 2H), 4.52 (br t, 1H), 4.49 (t, *J* = 1.8 Hz, 4H), 4.47 (br t, 1H), 4.27 (q, *J* = 7.1 Hz, 4H), 4.27 (t, *J* = 1.8 Hz, 4H), 3.91 (d, *J* = 5.3 Hz, 2H), 3.90 (d, *J* = 5.3 Hz, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 1.30 (t, *J* = 7.1 Hz, 3H) ppm. MS (Maldi-TOF, α-cyano-4-hydroxycinnamic acid, positive mode) m/z: 588 (M^+).

Synthesis of compound **13**

Compound **12** (58 mg, 0.098 mmol), NaOH (100 mg, 2.5 mmol) and ethanol (15 mL) was added to a round-bottomed flask. The mixture was refluxed for 5 hours under nitrogen atmosphere after which the solvent was evaporated. H2O (10 mL) was added followed by HCl (0.1 M) to precipitate the compound as a brown solid. The solid was collected by filtration and the product was then washed with water (yield: 28 mg, 55%). ^{1}H NMR (500 MHz, dmso-d_6, 25 °C): δ = 7.22 (m, 2H), 7.05 (m, 2H), 6.51 (m, 2H), 6.39 (m, 2H), 4.55 (m, 4H), 4.32 (m, 4H), 3.59 (m, 4H) ppm. MS (Maldi-TOF, α-cyano-4-hydroxycinnamic acid, positive mode) m/z: 532 (M^+).