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Electronic Supporting Information

for:

An unexpected stereoisomerism in enantiomerically pure trisadducts of C_{60} with the inherently chiral *trans*-3,*trans*-3,*trans*-3 addition pattern

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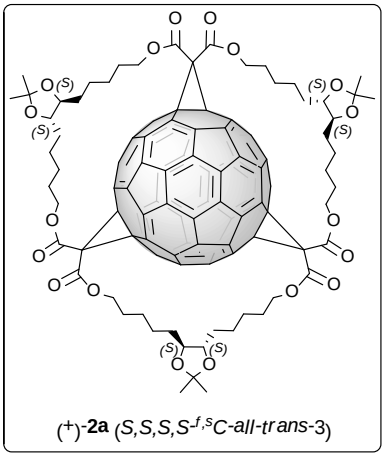
General Experimental

The solvents were dried using standard techniques. Reactions were monitored by thin layer chromatography on silica gel 60 F_{254} (Merck) aluminium plates. Products were isolated by column chromatography (silica gel 60, particle size 0.04-0.063 mm, Merck). HPLC measurements of the fullerene adducts were carried out on a Shimadzu Prominence system using a Nucleosil 100-5 analytical HPLC column at a flow rate of 1mL/min. The fullerene adducts were detected at 340 nm with an SPD-M20A Prominence Diode Array Detector. ^{1}H- and ^{13}C NMR spectra were recorded on a Bruker Avance III 500 Ultrashield Plus 500 MHz spectrometer. The chemical shifts are given in ppm relative to the appropriate solvent peak as standard reference. The resonance multiplicity is indicated as s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), or combinations of these. Broad resonances are designated with br. High resolution MALDI TOF mass spectra were recorded on a Bruker Autoflex III Smartbeam instrument using DCTB as a matrix. UV/Vis spectra were recorded on a Shimadzu UV-3600 spectrometer. Circular Dichroism (CD) spectra were recorded on a JASCO J-815 spectrometer.

Experimental procedure for the synthesis of the *trans*-3,*trans*-3,*trans*-3 trisadducts (+)-2a, (–)-2b

In a dry 250 mL three-necked round-bottomed flask equipped with gas inlet, dropping funnel and magnetic stirrer, C_{60} (48.6 mg, $6.74*10^{-5}$ mol) was dissolved in dry toluene (55 mL) under an argon atmosphere. Subsequently, macrocycle (–)-**1** (63.0 mg, $6.13*10^{-5}$ mol) and iodine (42.0 mg, $1.65*10^{-4}$ mol) were added followed by the dropwise addition of a solution of DBU (0.07 mL, $4.60*10^{-4}$ mol) in dry toluene (25 mL) over a period of 75 min. The solution was stirred at RT for one day and the crude reaction mixture was subjected to flash column chromatography on SiO_2. Unreacted C_{60} and other impurities were eluted with toluene and then the eluent was changed to toluene/EtOAc = 8:2. Diastereomers (+)-**2a**, (–)-**2b** were obtained as a mixture and were separated by column chromatography on SiO_2 using a mixture of cyclohexane/EtOAc = 9:3, as an eluent. Precipitation from DCM/hexane afforded (+)-**2a** and (–)-**2b** in pure form.

Trisadduct (*S,S,S,S-^{f,s}C-trans-3,trans-3,trans-3*) (+)-2a



Red solid (5.4 mg, 5.1%).

R_f = 0.57 (SiO_2, cyclohexane/EtOAc = 9:3).

HPLC, Retention time = 20.19 min (toluene/EtOAc = 95:5).

^{1}H NMR (500 MHz, $CDCl_3$): δ_H 4.82 (m, 2H, OC*H*$_2$CH$_2$), 4.71 (m, 2H, OC*H*$_2$CH$_2$), 4.60 (m, 2H, OC*H*$_2$CH$_2$), 4.36 (m, 2H, OC*H*$_2$CH$_2$), 4.20 (m, 4H, 2 x OC*H*$_2$CH$_2$), 3.46 (m, 4H, 4 x OC*H*CH$_2$), 3.31 (m, 2H, 2 x OC*H*CH$_2$), 1.79 (m, 14H, 7 x C*H*$_2$), 1.50-1.25 (m, 52H, 3 x (C*H*$_3$)$_2$C & 17 x C*H*$_2$).

^{13}C NMR (125 MHz, $CDCl_3$): δ_C 163.79 (*C*=O), 162.89 (*C*=O), 162.57 (*C*=O), *148.64, 148.38, 148.34, 147.80, 147.61, 147.42, 147.39, 147.26, 147.08, 147.00, 146.77, 146.42, 145.69, 145.67, 145.60, 145.27, 143.39, 143.34, 143.09, 142.65, 142.42, 142.37, 142.13, 142.02, 141.60, 141.56, 141.24,* 108.17 ((CH$_3$)$_2$*C*), 108.06 ((CH$_3$)$_2$*C*), 81.26 (O*C*HCH$_2$), 80.83 (O*C*HCH$_2$), 80.75 (O*C*HCH$_2$), 72.09 (sp^3 *C* of C$_{60}$), 72.03 (sp^3 *C* of C$_{60}$), 71.87 (sp^3 *C* of C$_{60}$), 67.28 (CH$_2$*C*H$_2$O), 67.10 (CH$_2$*C*H$_2$O), 66.85 (CH$_2$*C*H$_2$O), 52.53 (CO*C*CO), 32.97 (*C*H$_2$), 29.35 (*C*H$_2$), 28.71 (*C*H$_2$), 28.53 (*C*H$_2$), 28.34 (*C*H$_2$), 27.34 ((*C*H$_3$)$_2$C), 27.30 ((*C*H$_3$)$_2$C), 27.28 ((*C*H$_3$)$_2$C), 26.71 (*C*H$_2$), 26.59 (*C*H$_2$), 26.53 (*C*H$_2$), 26.43 (*C*H$_2$), 26.24 (*C*H$_2$), 25.78 (*C*H$_2$).

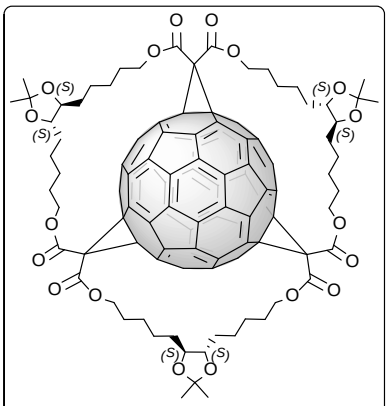
**27 signals for the sp^2 C of C$_{60}$.*

UV/Vis ($CHCl_3$) λ_{max}/nm (ε/dm^{3}mol^{-1}cm^{-1}): 297 (41437), 324 (24329), 372 (6858), 480.5 (3494), 568 (1695), 692 (111).

CD ($CHCl_3$): 273 nm ($\Delta\varepsilon$ = -23.7), 289.4 (-47.6), 315.8 (-19.9), 344.8 (-34.6), 380 (-0.63), 396.0 (10.3), 402.6 (-0.23), 411.0 (9.3), 470.0 (29.4), 530.0 (-11.6), 609.2 (-4.2).

HRMS (MALDI TOF, negative mode, DCTB matrix): calculated for $C_{114}H_{86}O_{18}$ $[M+2H]^-$ 1742.5809; found 1742.5730.

Trisadduct (*S,S,S,S-*^{f,s}*A-trans-3,trans-3,trans-3*) (–)-2b



(–)-**2b** (*S,S,S,S-*^{f,s}*A-all-trans-3*)

Red solid (10.9 mg, 10.2%).

R_f = 0.54 (SiO_2, cyclohexane/EtOAc = 9:3).

HPLC, Retention time = 22.23 min (toluene/EtOAc = 95:5).

^{1}**H NMR** (500 MHz, $CDCl_3$): δ_H 4.80 (m, 2H, OC*H*$_2$CH$_2$), 4.65 (m, 4H, 2 x OC*H*$_2$CH$_2$), 4.35 (m, 2H, OC*H*$_2$CH$_2$), 4.27 (m, 2H, OC*H*$_2$CH$_2$), 4.17 (m, 2H, OC*H*$_2$CH$_2$), 3.55 (m, 2H, 2 x OC*H*CH$_2$), 3.43 (m, 2H, 2 x OC*H*CH$_2$), 3.31 (m, 2H, 2 x OC*H*CH$_2$), 1.83-1.67 (m, 14H, 7 x C*H*$_2$), 1.37-1.25 (m, 52H, 3 x (C*H*$_3$)$_2$C & 17 x C*H*$_2$).

^{13}**C NMR** (125 MHz, $CDCl_3$): δ_C 163.80 (*C*=O), 162.96 (*C*=O), 162.42 (*C*=O), *148.64, 148.38, 148.33, 148.09, 147.73, 147.37, 147.34, 147.12, 146.92, 146.90, 146.82, 146.67, 145.76, 145.69, 145.30, 143.41, 143.31, 143.03, 142.68, 142.46, 142.40, 142.23, 142.21, 141.83, 141.73, 141.43, 140.98,* 108.24 ((CH$_3$)$_2$*C*), 108.06 ((CH$_3$)$_2$*C*), 80.89 (O*C*HCH$_2$), 80.86 (O*C*HCH$_2$), 80.77 (O*C*HCH$_2$), 72.14 (sp^3 *C* of C_{60}), 71.97 (sp^3 *C* of C_{60}), 71.90 (sp^3 *C* of C_{60}), 67.94 (CH$_2$*C*H$_2$O), 67.45 (CH$_2$*C*H$_2$O), 66.97 (CH$_2$*C*H$_2$O), 52.53 (CO*C*CO), 33.22 (*C*H$_2$), 32.52 (*C*H$_2$), 28.81 (*C*H$_2$),

28.73 (*C*H_2), 28.26 (*C*H_2), 27.38 ((*C*H_3)$_2$C), 27.25 ((*C*H_3)$_2$C), 27.24 ((*C*H_3)$_2$C), 26.99 (*C*H_2), 26.84 (*C*H_2), 26.59 (*C*H_2), 26.27 (*C*H_2), 26.15 (*C*H_2), 26.05 (*C*H_2).

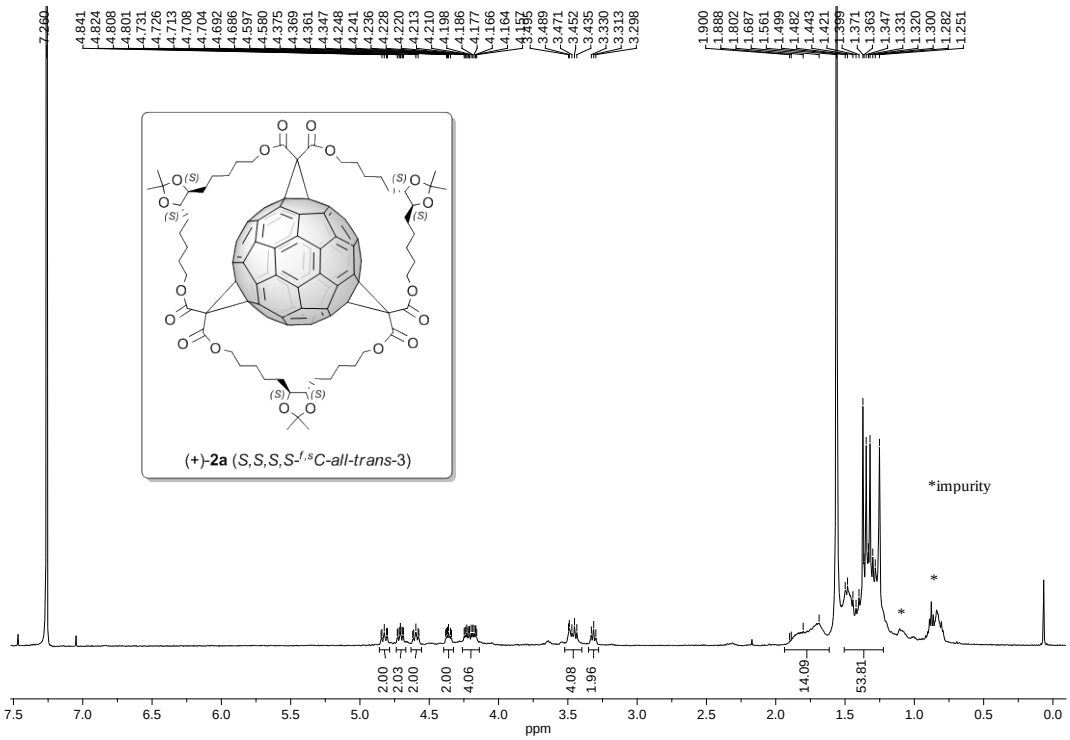
**27 signals for the sp^2 C of C_{60}.*

UV/Vis ($CHCl_3$) λ_{max}/nm (ε/$dm^3mol^{-1}cm^{-1}$): 296.5 (53041), 323 (25029), 372 (8681), 401.5 (4401), 479 (4449), 566 (2104), 691 (96).

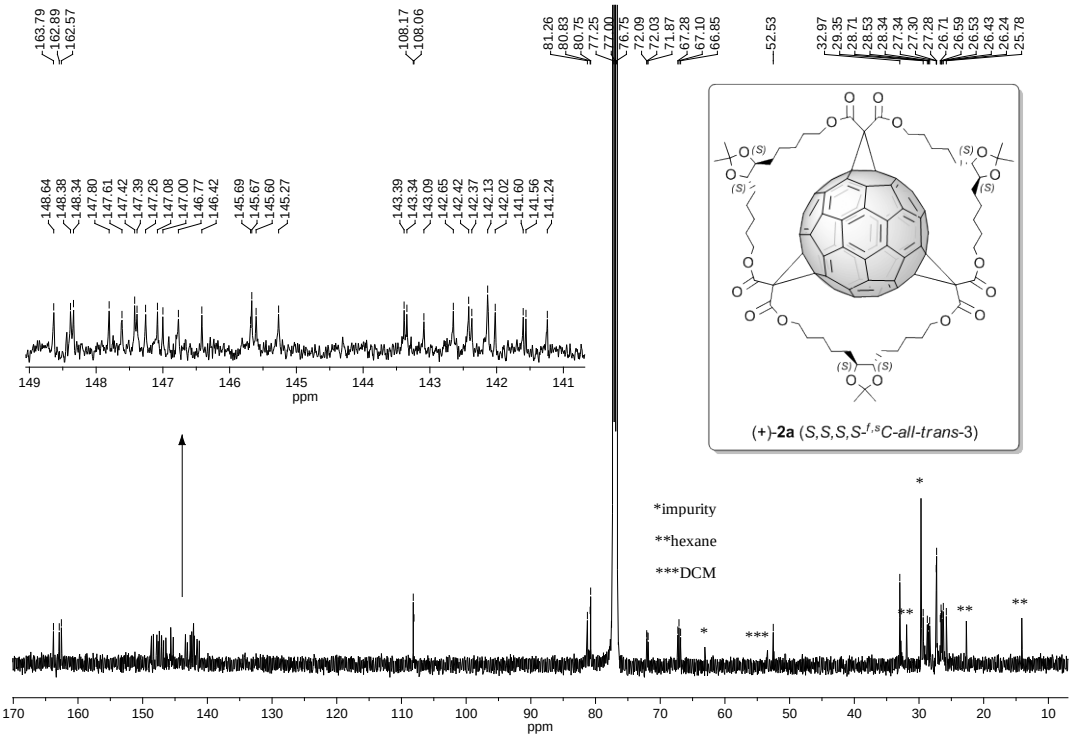
CD ($CHCl_3$): 273 nm (Δ*ε* = 23.0), 289.4 (46.3), 318 (20.6), 344.6 (35.4), 380.2 (0.8), 396 (-9.6), 402.8 (0.9), 468.2 (-29.0), 531 (11.8), 610 (6.3).

HRMS (MALDI TOF, negative mode, DCTB matrix): calculated for $C_{114}H_{85}O_{18}$ $[M+H]^-$ 1741.5686; found 1741.5674.

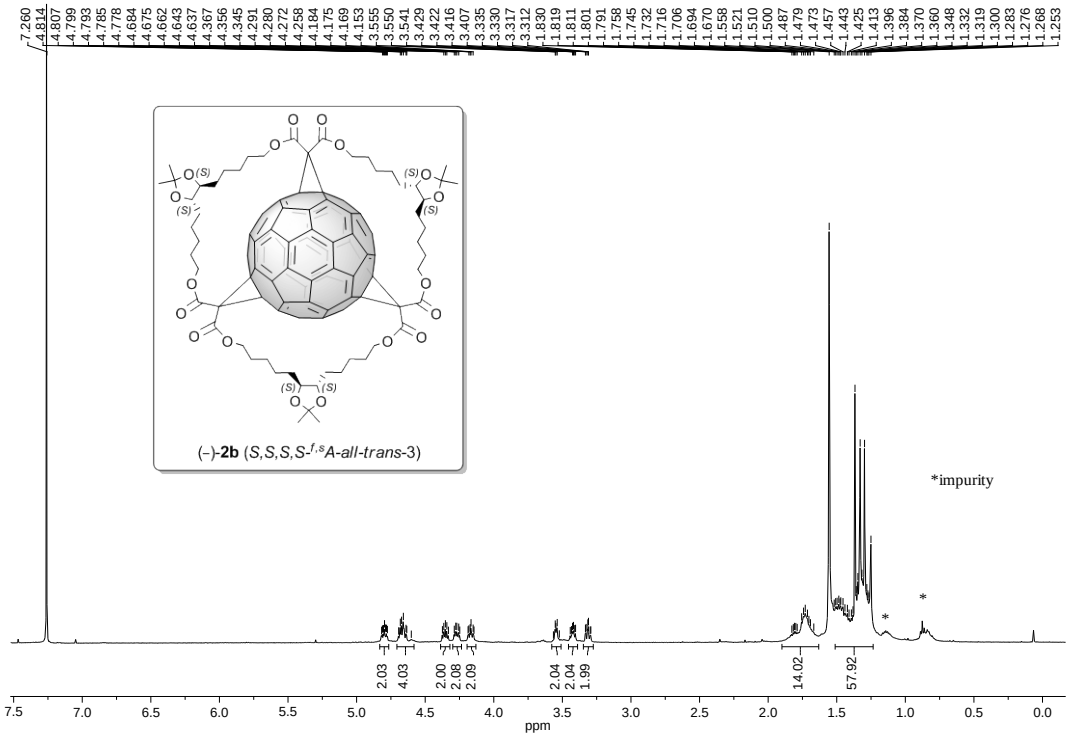
^{1}H NMR spectrum of (+)-**2a** (500 MHz, $CDCl_3$, 25 °C)



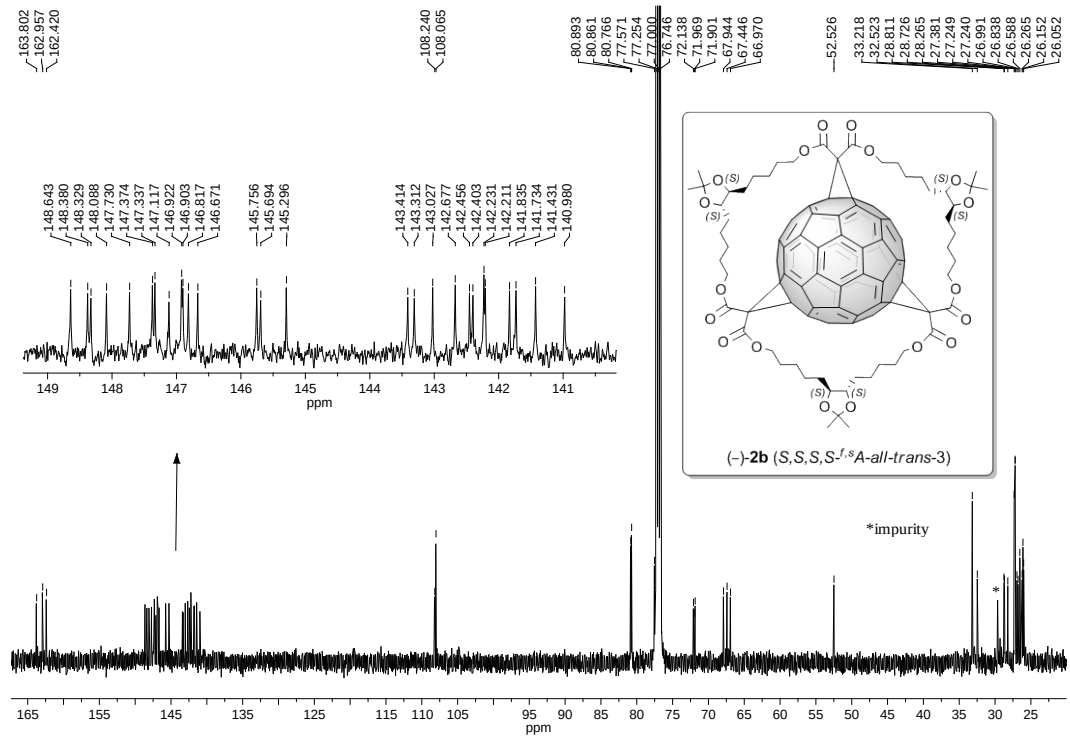
^{13}C NMR spectrum of (+)-**2a** (125 MHz, $CDCl_3$, 25 °C)



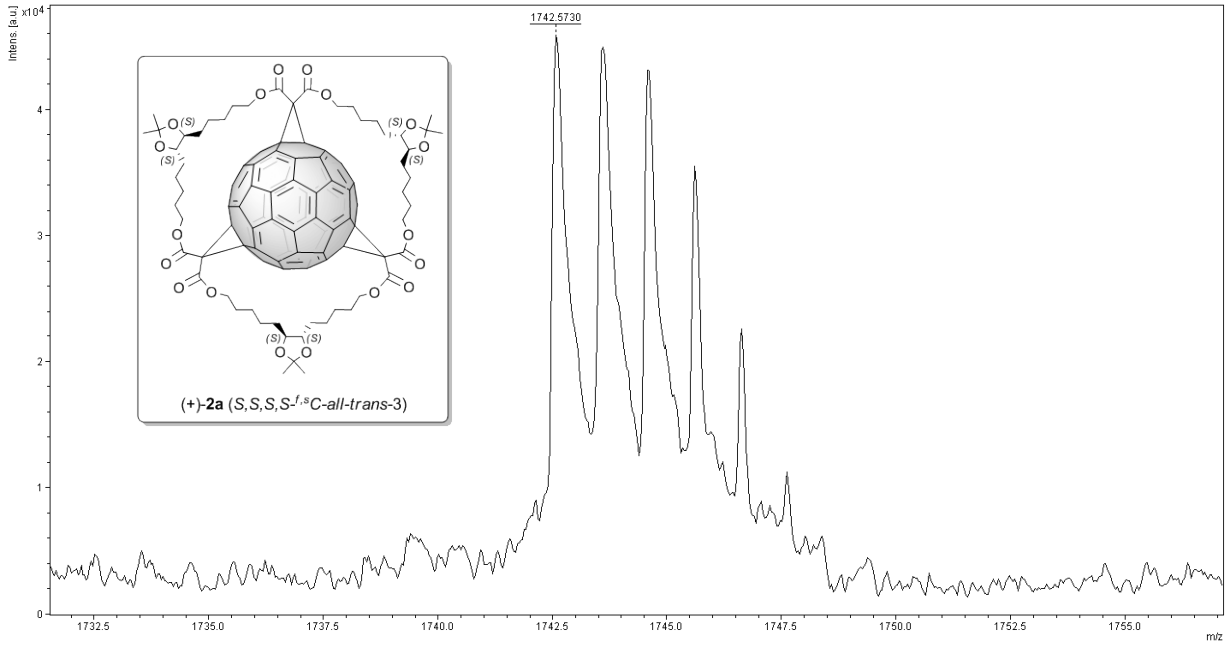
^{1}H NMR spectrum of (–)-**2b** (500 MHz, $CDCl_3$, 25 °C)



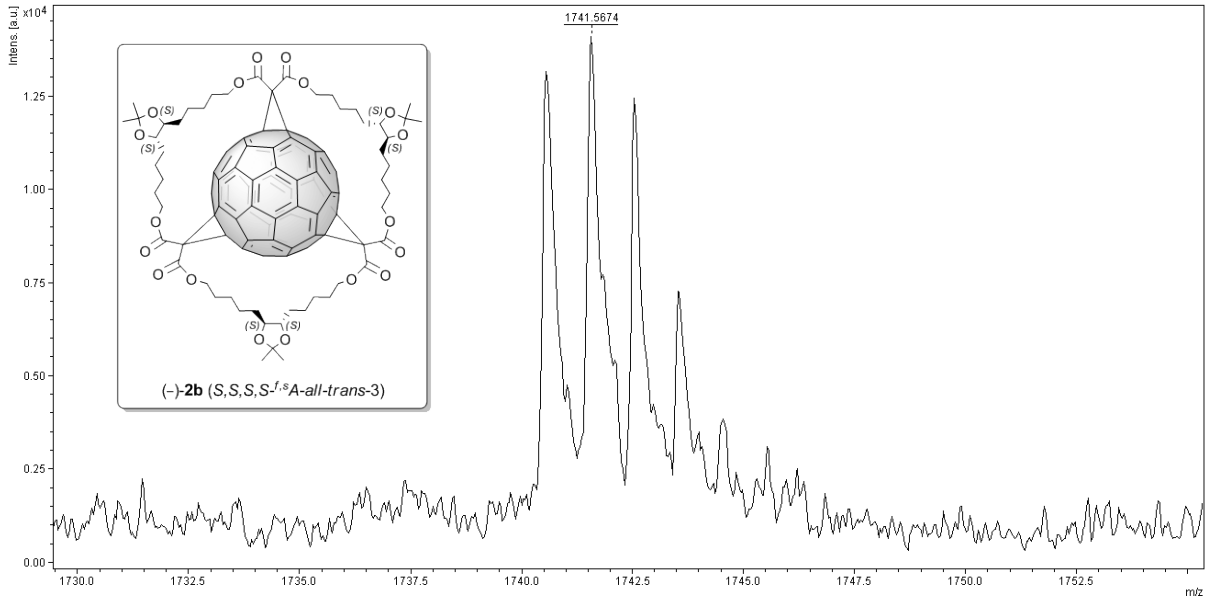
^{13}C NMR spectrum of (–)-**2b** (125 MHz, $CDCl_3$, 25 °C)



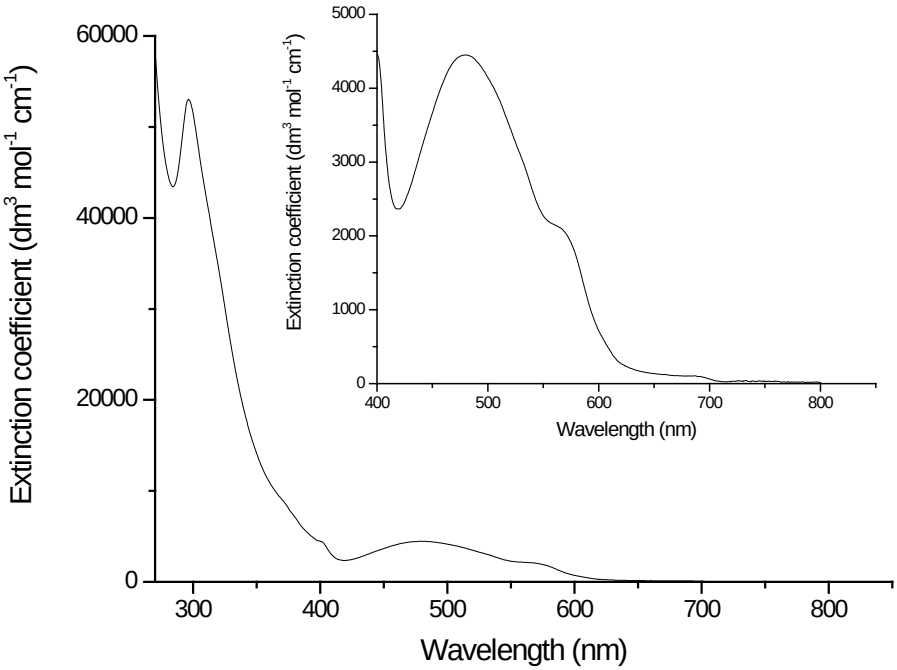
MALDI-TOF mass spectrum of (+)-**2a** (negative mode, DCTB matrix)



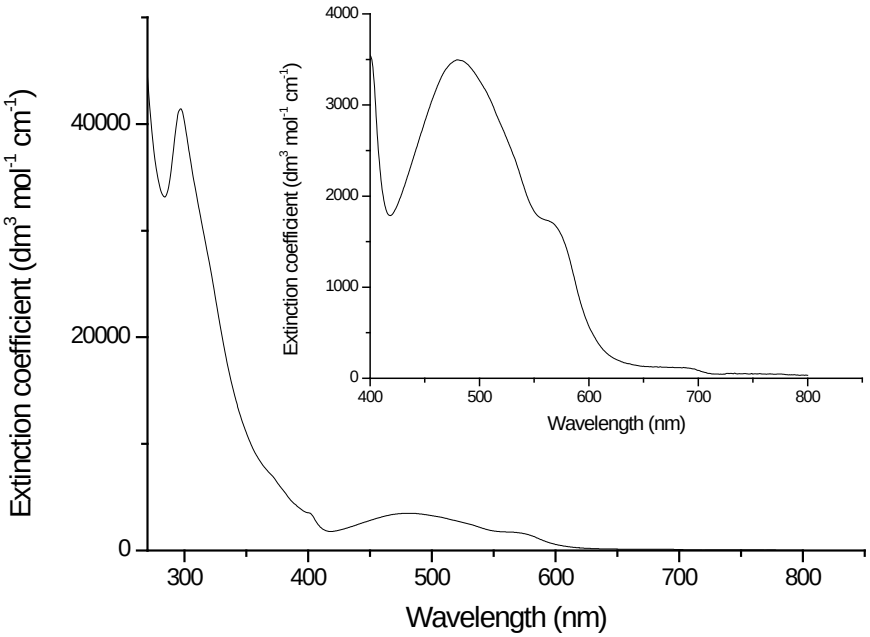
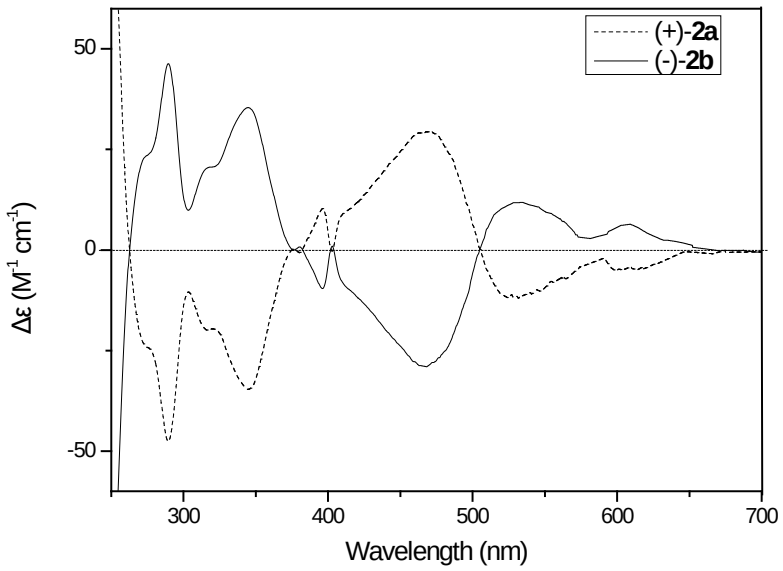
MALDI-TOF mass spectrum of (–)-**2b** (negative mode, DCTB matrix)



UV-Vis spectrum ($CHCl_3$) of **(+)-2a**



UV-Vis spectrum ($CHCl_3$) of (–)-**2b**



CD spectra ($CHCl_3$) of **(+)-2a/(–)-2b**