Supporting information

For

Time-resolved EPR investigation of [70]fulleropyrrolidine nitroxide isomers

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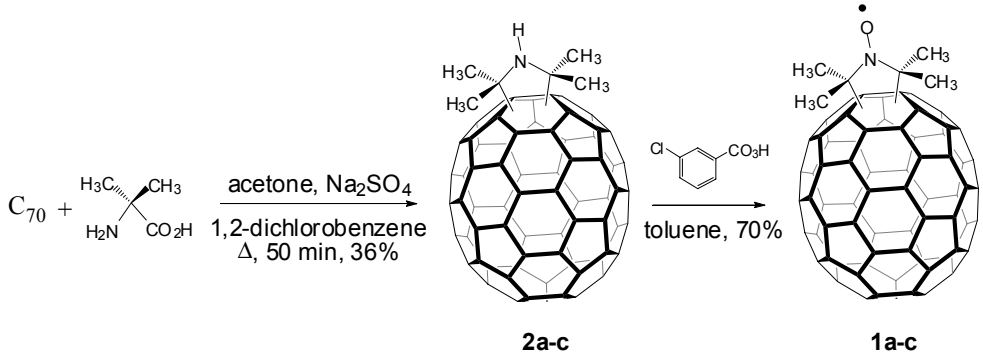
Contents



Instrumentation

HPLC station: Shimadzu LC 8A pump coupled to a controller SCL 8A; detector: TSP Spectrasystem UV6000LP diode array detector.
HPLC column: Phenomenex Luna 5 μm, 250 × 4.6 mm, SiO_2 colum.
NMR spectrometer: Bruker AC 250 operating at 250.1 MHz.
MALDI-MS: Bruker mass spectrometer: Reflex^{TM} time-of-flight, positive linear mode, 15 KV acceleration voltage. 2,5-dihydroxybenzoic acid as matrix.
ESI-MS: Thermo Finnigan AQA LC/MS: -4 kV spray voltage; -10 V capillary voltage; 180 °C capillary temperature; nitrogen as nebulizing gas. The samples were dissolved in tetrahydrofuran containing 1% trifluoroacetic acid.

Synthesis of 2,2,5,5-tetramethyl[70]fulleropyrrolidine 2a-c.[1]
In a 10 ml high-pressure glass vial, C_{70} (29.8 mg, 35 μmol) was dissolved in 1,2-dichlorobenzene (8 ml). Then acetone (0.5 ml), α-aminoisobutyric acid (11.8 mg, 114 μmol) and anhydrous Na_2SO_4 (200 mg) were added. The suspension was heated to 180 °C, kept at that temperature for 50 min. and then cooled to ambient temperature (TLC, SiO_2, eluent: toluene/ethyl acetate 9:1, R_f(**2a-c**) = 0.43). The reaction mixture was filtered through a cotton plug and loaded on top of a SiO_2 flash chromatography column (3 × 10 cm). The mixture of isomeric NH-[70]fulleropyrrolidines was purified from unreacted C_{70} (eluent: toluene, 11.1) and from traces of higher molecular weight adduct. 11.9 mg (36%) of **2a-c** were isolated as a brownish powder.

MALDI-MS. $C_{76}H_{13}N$: *m/z* 940 $[M+H]^+$
^1H NMR (250 MHz, CS_2/C_6D_6 5:1): δ 3.21 (s, 1H), 1.98 (s, 12H α), 1.66 (s, 12H β), 1.25 (s, 12H γ).
IR (KBr): 3417, 3303, 2963, 2921, 2849, 1454, 1443, 1428, 1415, 1379, 1368, 1160, 795, 735, 672, 535 cm^{-1}
UV-Vis (cyclohexane): λ_{max} 196, 209, 235, 396, 460 nm.

Oxidation of 2a-c with MCPBA. To a solution of NH-[70]fulleropyrrolidines **2a-c** (see above, 8 mg, 8.5 μmol) in toluene (18 ml), MCPBA (10.6 mg, 61 μmol) in toluene (2 ml) was added at room temperature. After stirring for 20 min. (TLC, SiO_2, eluent: toluene/ethyl acetate 9:1, R_f(**1a-c**) = 0.86) the solution was washed with 5% aqueous $NaHCO_3$ (3 × 15 ml). The organic phase, dried over Na_2SO_4, was concentrated at reduced pressure and purified by SiO_2 flash chromatography column (2 × 12 cm, eluent: toluene). 5.7 mg (70%) of **1a-c** were isolated as a brownish powder.

MALDI-MS. $C_{76}H_{12}NO$: *m/z* 954 $[M]^+$
IR (KBr): 3547, 3464, 3415, 3236, 2979, 2926, 2849, 1638, 1628, 1618, 1444, 1428, 1415, 1376, 1369, 1362, 1183, 796, 727, 589, 542, 535 cm^{-1}
UV-Vis (cyclohexane): λ_{max} 290, 237, 396, 459 nm.

1. (a) G. Schick, M. levitus, L. Kvetko, B. A. Johnson, I. Lamparth, R. Lunkwitz, N. Ma, S. I. Khan, M. A. Garcia-Garibay, Y. Rubin *J. Am. Chem. Soc.* **1999**, *121*, 3246. (b) M. Mazzoni, L. Franco, C. Corvaja, G. Zordan, E. Menna, M. Maggini *ChemPhysChem* **2002**, *3*, 527.

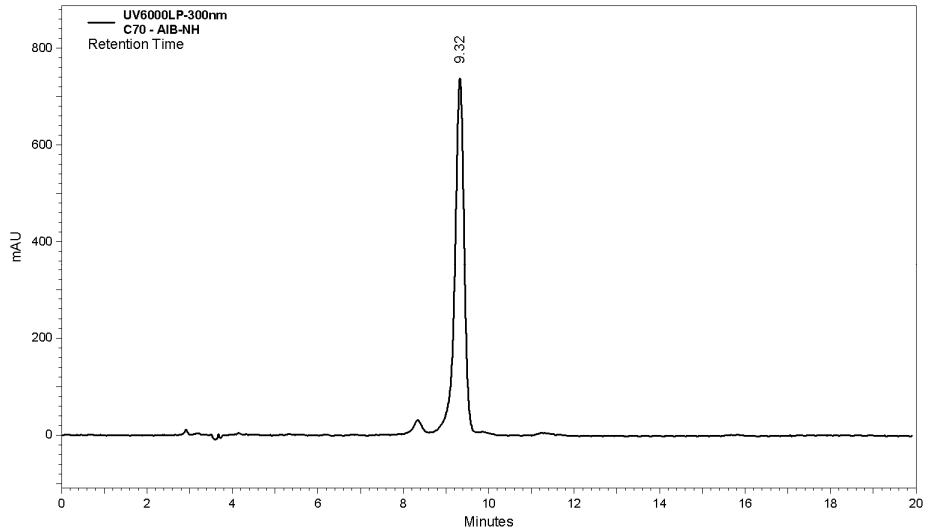


Figure S1. HPLC trace of **2a-c** (Phenomenex Luna SiO_2, 5µ, 250 × 4.6 mm; toluene/ethyl acetate 9:1, 1ml/min; λ = 300 nm).

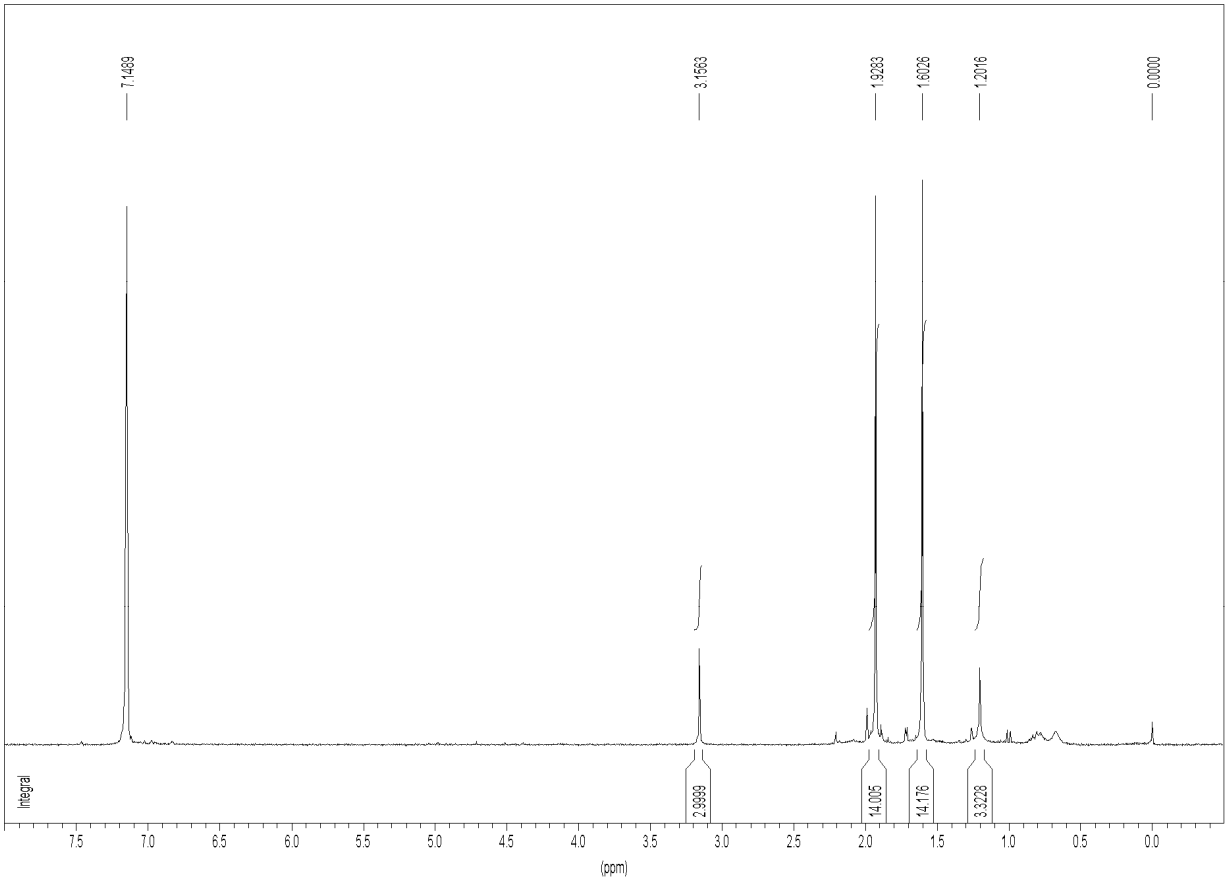


Figure S2. ^{1}H NMR spectrum of **2a-c** (250MHz, CS_2/benzene-C_6D_6 5:1)

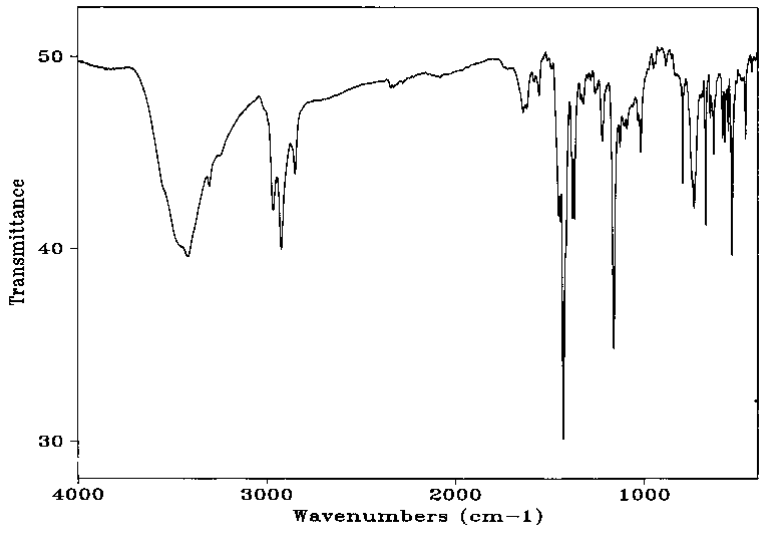


Figure S3. FT-IR spectrum (KBr) of **2a-c**

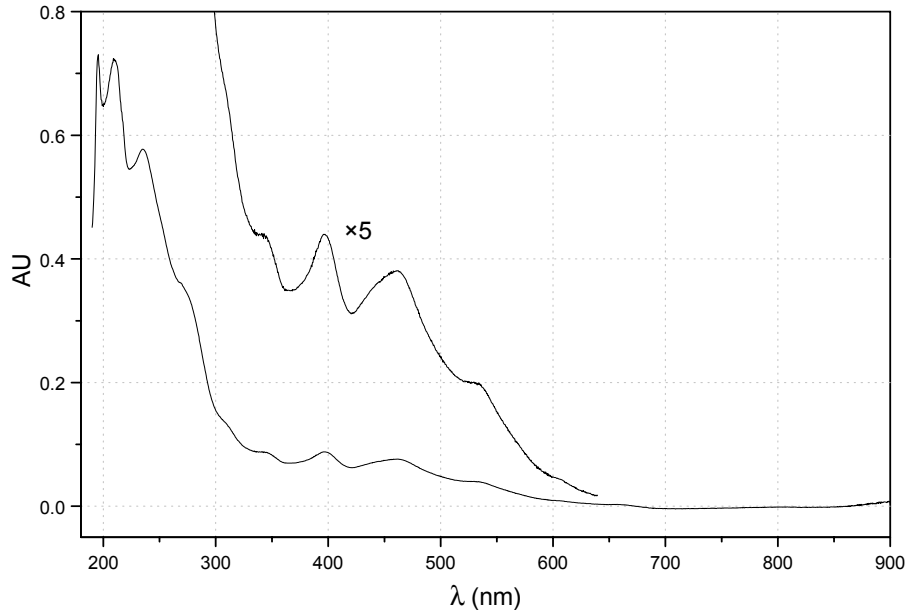


Figure S4. UV-Vis spectrum of **2a-c** in cyclohexane.

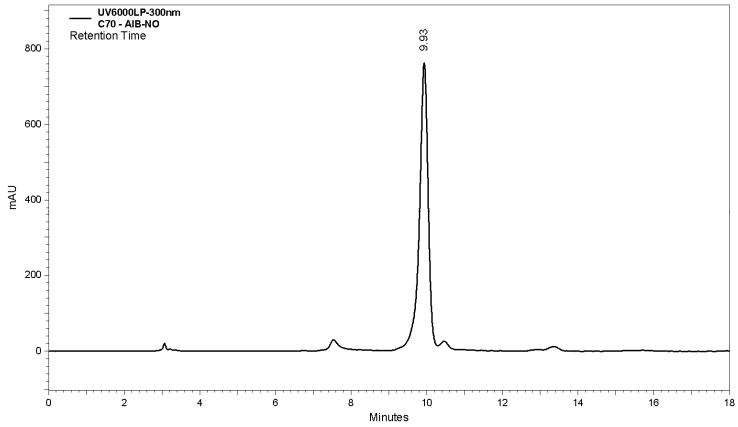


Figure S5. HPLC trace of **1a-c** (Phenomenex Luna SiO_2, 5µ, 250 × 4.6 mm; toluene/ethyl acetate 9:1, 1ml/min; λ = 300 nm).

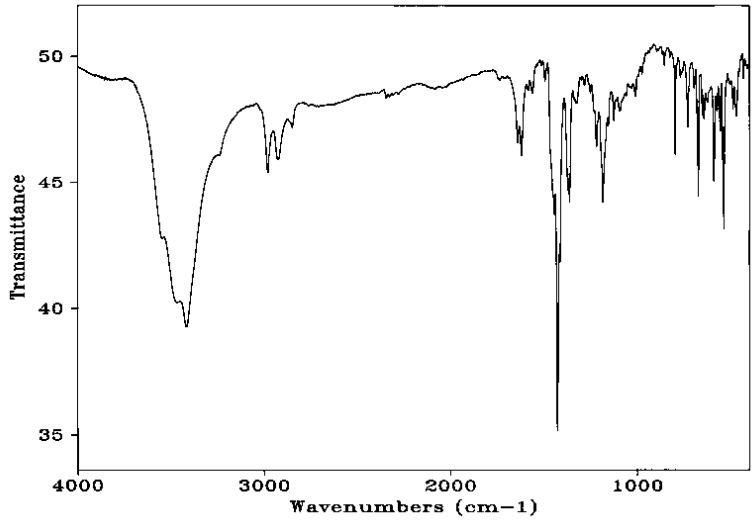


Figure S6. FT-IR spectrum (KBr) of **1a-c**

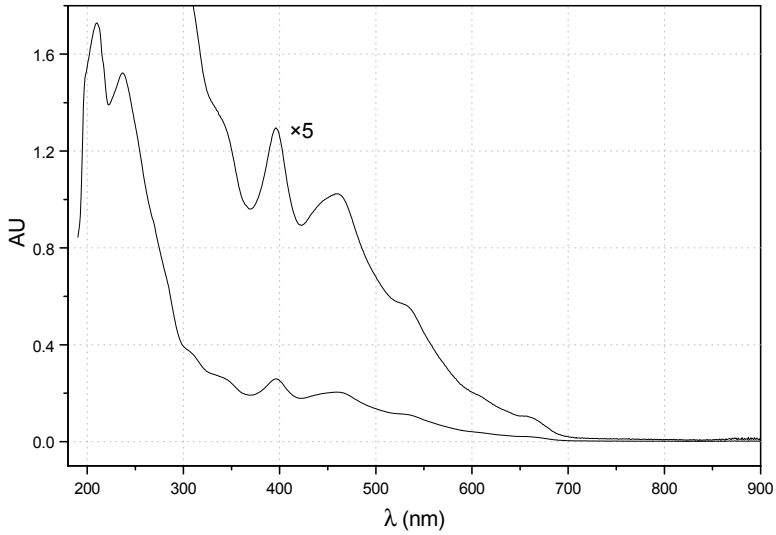


Figure S7. UV-Vis spectrum of **1a-c** in cyclohexane.