Endohedral Metallofullerenes in Self-Assembled Monolayers

Supporting Information

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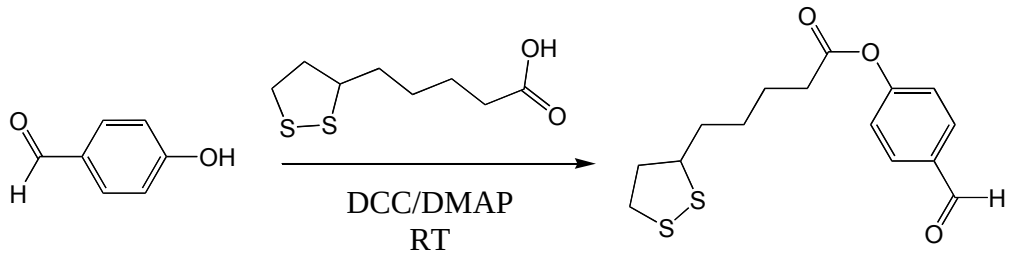
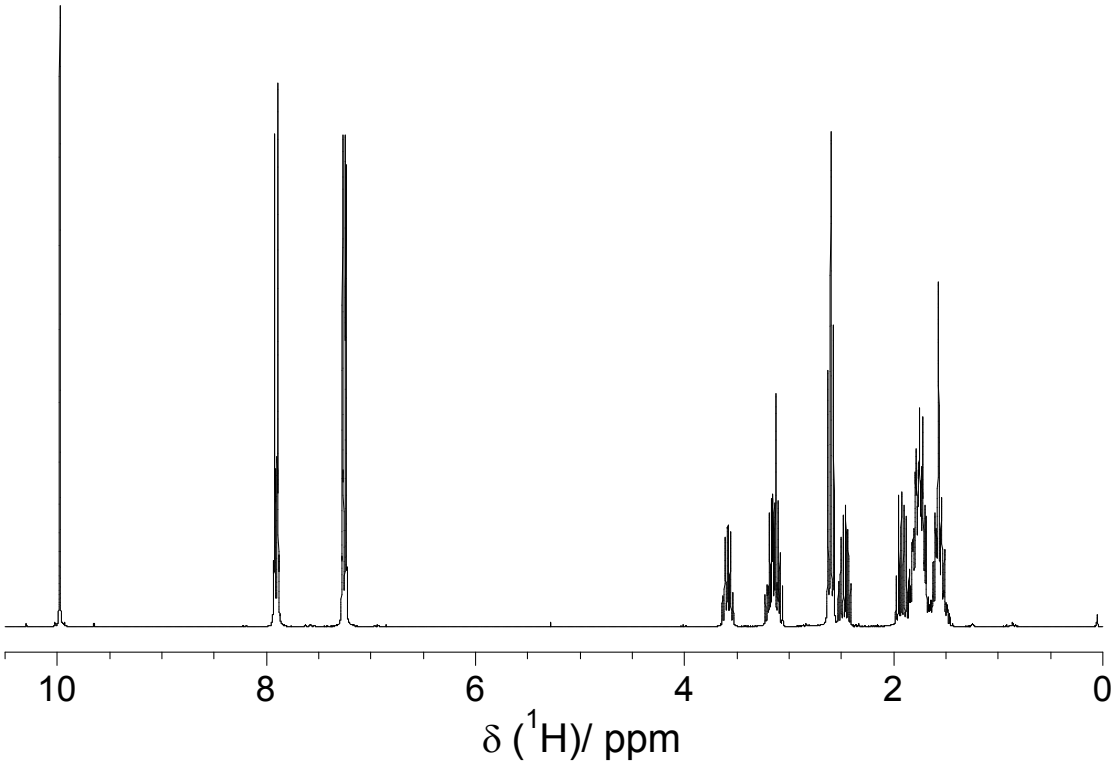
S1. Synthesis of **4-(liponyloxy)benzaldehyde (3)**

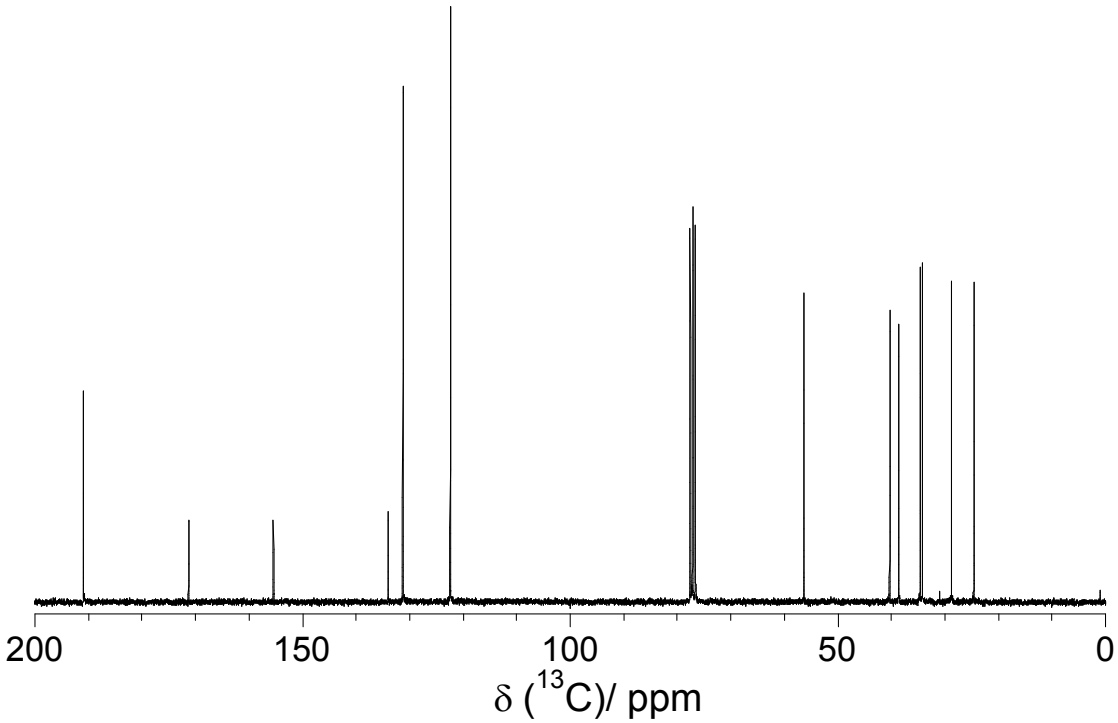
In a slenck flask, (±)-α-Lipoic acid (412.6 mg, 2 mol) and 4-hydroxybenzaldehyde (280.4 g, 2.25 mol) were dissolved in dry-THF (20 mL). The solution was stirred and cooled in an ice bath to 0°C while a clear solution of 4-dimethylaminopyridine (195.5 g, 1.6 mol) and dicyclohexylcarbodiimide (464.2 g, 2.25 mol) in minimum quantity of dry-THF was added drop wise. After a further 30 min at 0°C the ice bath is removed and the reaction mixture is stirred for 2 days at room temperature. At the end the dicyclohexylurea that precipitated was removed by filtration and the solvent was removed *in vacuo*. The residue was purified by column chromatography (SiO_2; dichloromethane) to afford yellow oil in a yield of 49 % (300 mg). ^{1}H-NMR {270 Mz, $CDCl_3$, 300 K} δ_H 9.98 (s, 1H, CHO), 7.90, 7.25 (d, *J*=4.2 Hz, 2H each, ArH), 3.64–3.54 (m, 1H, –CH), 3.21–3.06 (m, 2H, –CH_2), 2.60 (t, *J*=7.2 Hz, 2H, –CH_2– alkyl chain), 2.53–2.41 (m, 1H, –CH_2), 1.97–1.85 (m, 1H, –CH), 1.82–1.70 (m, 4H, –CH_2– alkyl chain), 1.62–1.51 (m, 2H, –CH_2– alkyl chain). ^{13}C-NMR {270 Mz, $CDCl_3$, 300 K} δ_C 191.00, 171.34, 155.46, 134.04, 131.30, 122.43, 56.35, 40.34, 38.61, 34.66, 34.22, 28.65, 24.59. IR(KBr) cm^{-1}: 3425, 3120, 1676, 1076. ESI-MS (m/z): 310.07 (M^+).



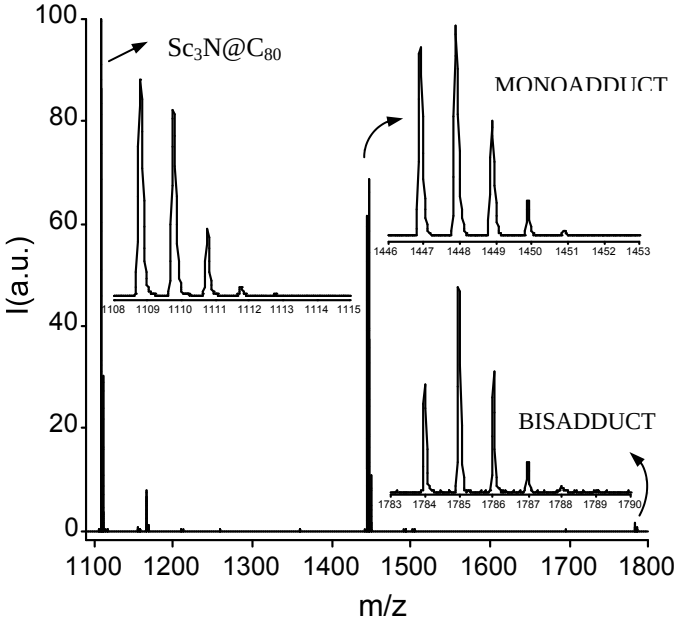
Esterification scheme of Lipoic acid with 4-Hydroxybenzaldehyde.

^{1}H NMR and ^{13}C NMR {270 Mz, $CDCl_3$, 300 K} spectra of **3.**

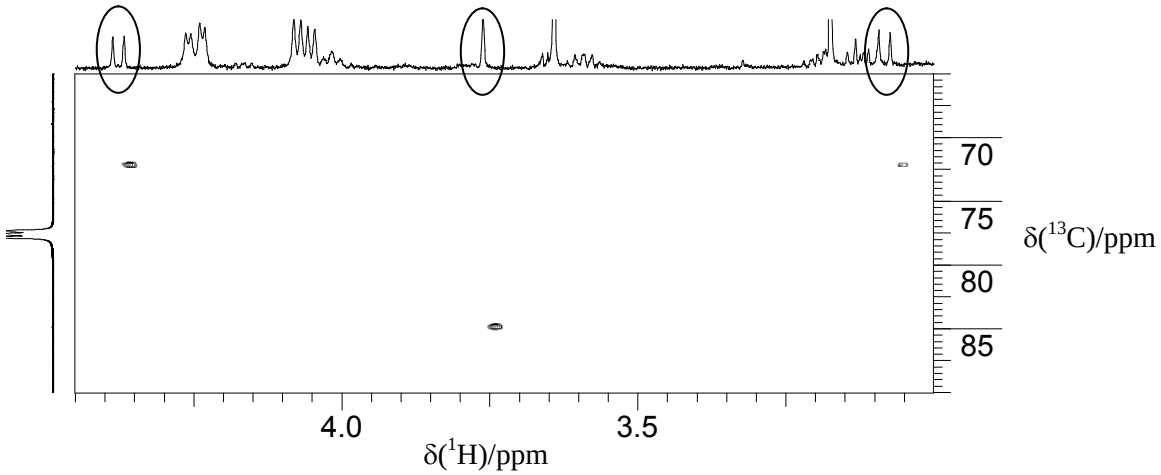




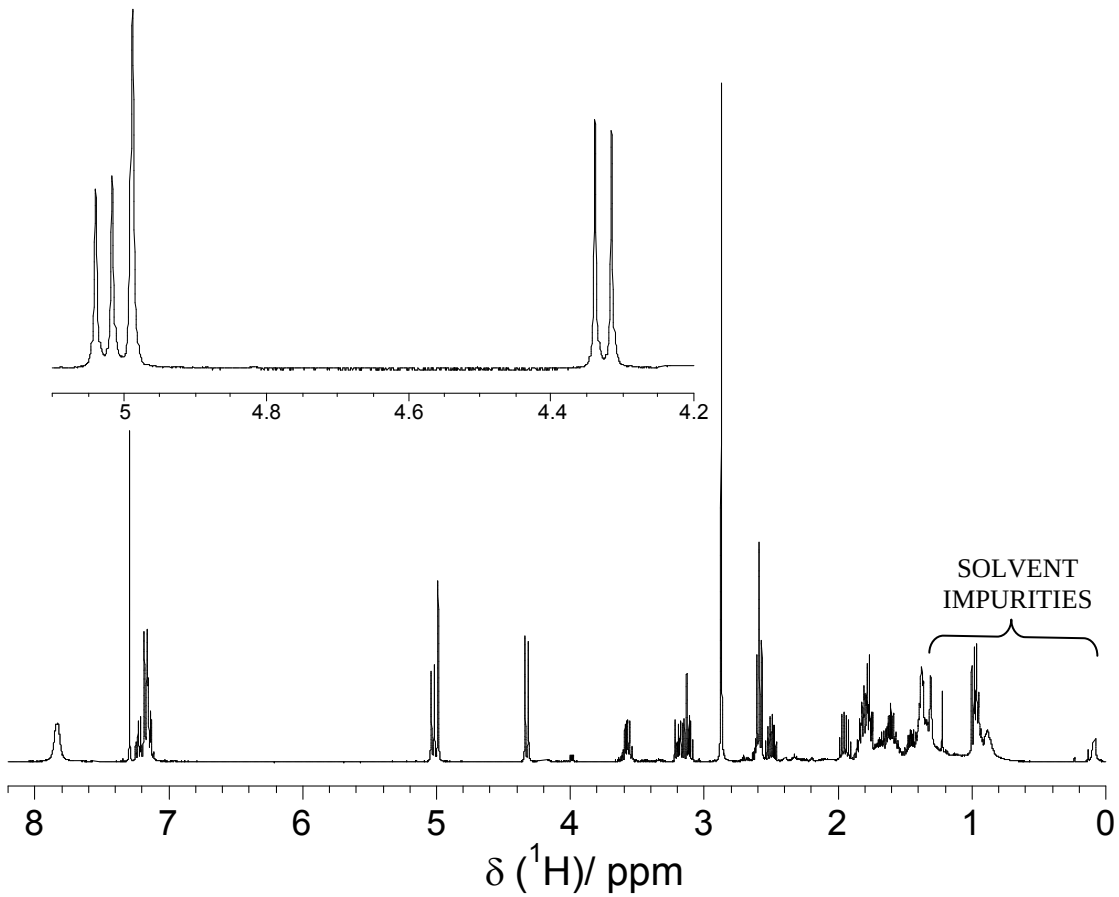
S2. MALDI-TOF mass spectrum of the crude mixture of the cycloaddition of azomethine ylides to $Sc_3N@C_{80}$ after 270 min using a DCTB matrix and negative ionization.

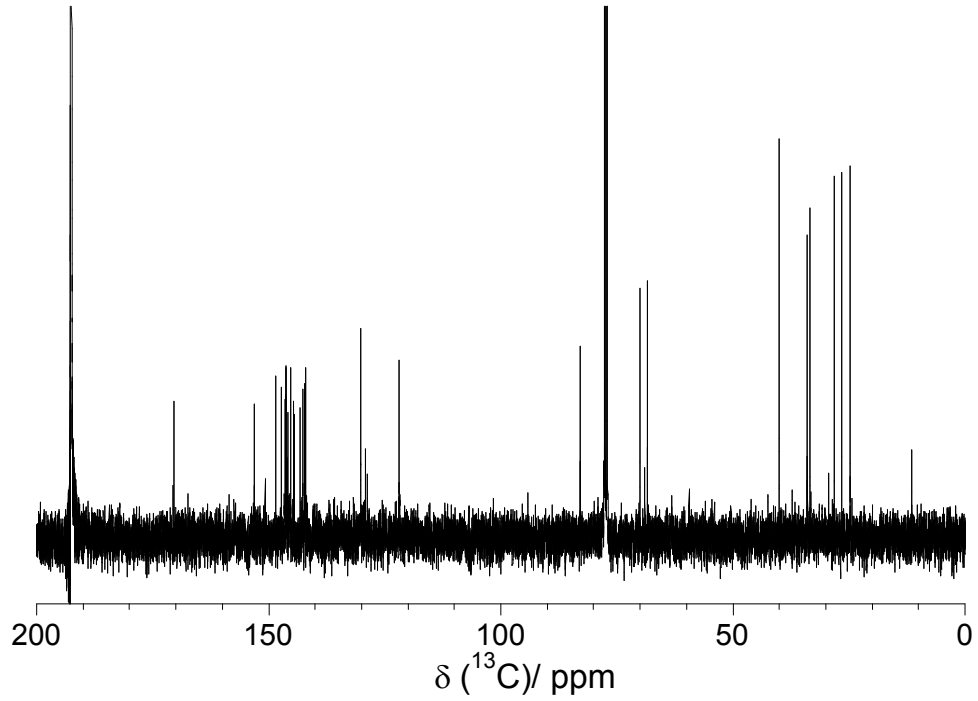


S3. HMQC spectrum {500 Mz, $CDCl_3$:CS_2 (1:6), 300 K} of ***N*-methyl-2-(4-(liponyloxy)benzyl)-$Sc_3N@C_{80}$ (1)**

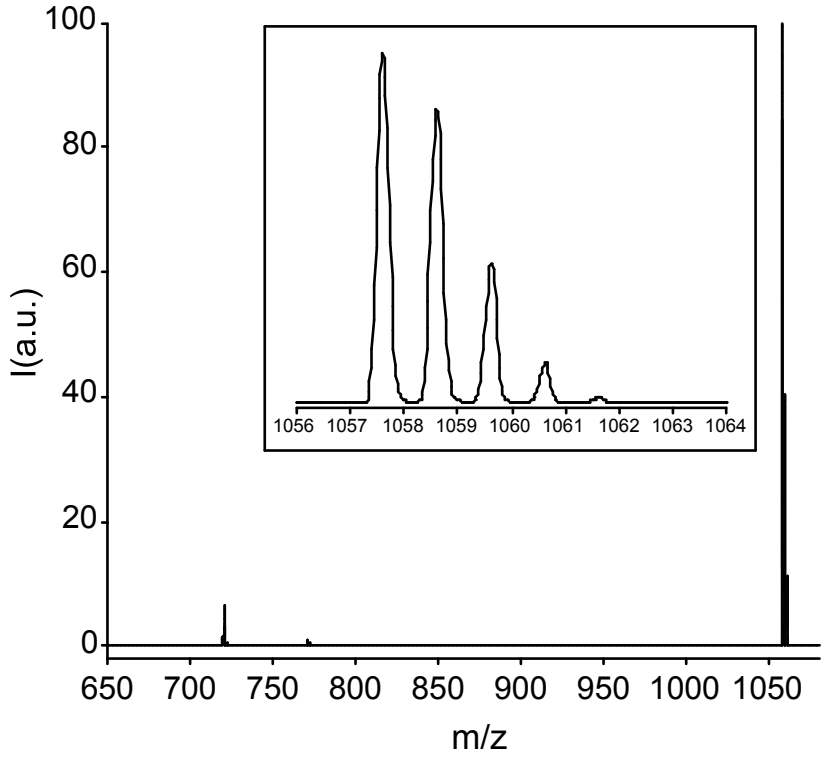


S4. ^{1}H and ^{13}C NMR {400 Mz, $CDCl_3$:CS_2 (1:6), 300 K} spectra of the *N*-methyl-2-(4-(liponyloxy)benzyl)-[6,6]-C_{60} **(4)**

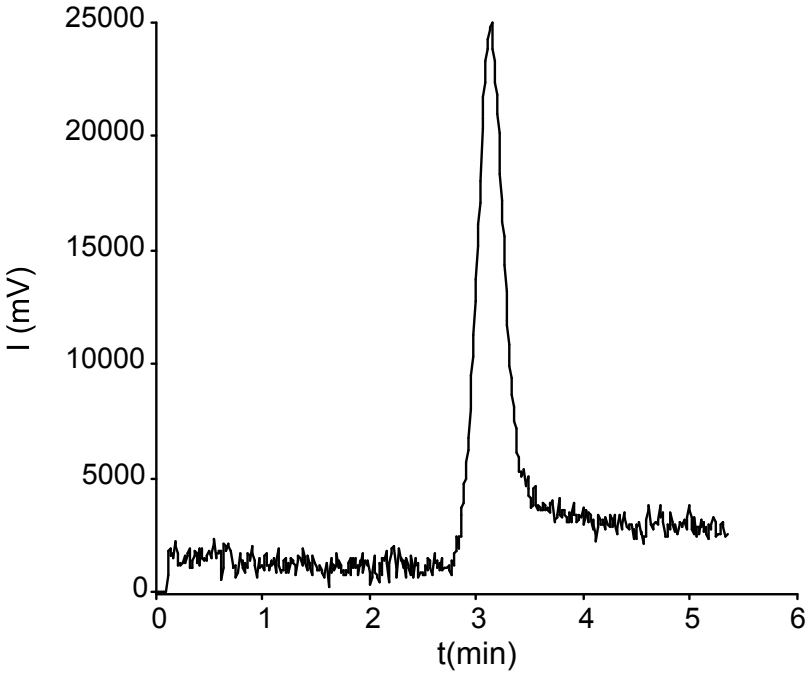




S5. MALDI-TOF mass spectrum of pure ***N*-methyl-2-(4-(liponyloxy)benzyl)-[6,6]-C_{60}** fulleropyrrolidine (**4)** using a DCTB matrix and negative ionization.



S6. HPLC chromatogram of ***N*-methyl-2-(4-(liponyloxy)benzyl)-[6,6]-C_{60}** (**4)** using using 3% ethylacetate in toluene as eluent and SiO_2 FORTIS HILIC (5μ) (250 mm x 21 mm) column.



S7. (a) Evolution of mono- (♦), bis- (■), tris- (●) and tetra-functionalised (▲) fullerenes in the reaction of 1,3-dipolar cycloaddition of dithiolane aldehyde **3** with (a) C_{70} and (b) C_{78} as a function of time. I_{rel} is a relative conversion rate calculated as $I_{rel}(\%) = [I_{adduct} / (\Sigma I_{adduct\,(i)} + I_{C60})] \cdot 100$ measured by MALDI-TOF mass spectrometry. The appearance of peak shoulders (b) may be related to the presence of minor isomers of C_{78}.