Supporting information: A two-step approach to the synthesis of N@C_{60} fullerene dimers for molecular qubits†

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1 Materials and characterization methods

Materials: C_{60} powder (99.5+%) was supplied by the MER corporation. The toluene was HPLC grade (99.8%) purchased from Fisher, and was distilled over Na before use in microscale reactions and reactions with N@C_{60}. *N*-(4-(hexyloxy)benzyl)glycine was synthesized as previously reported[1]. All other reagents and solvents were purchased from Sigma–Aldrich or Fisher and were used without further purification.

N@C_{60} was produced by the ion implantation method using a beam energy of 40 eV.[2] This method yields soot consisting of N@C_{60}:C_{60} in the ratio of typically 1:10^5. The soot was dissolved in toluene and filtered to remove particles greater than 0.2 μm. Batches of fullerene soot containing ^{15}N@C_{60} were produced using isotopically enriched nitrogen gas. Whenever necessary, solutions were purified (enriching N@C_{60} with respect to C_{60}) using a LC-250HS recycling preparative HPLC (high performance liquid chromatography) apparatus connected to a Nacalai Tesque 15PBB fractionating column, and then a LC-908W HPLC apparatus connected to a 5PBB column, when appropriate.

Characterization: Product characterization was undertaken using MALDI-TOF mass spectrometry (with negative ionization and a DCTB matrix) and optical absoprtion, ^{1}H NMR and ^{13}C NMR spectroscopies. For optical absorption spectroscopy, samples were collected in toluene directly following separation by HPLC. The solutions were then transferred to quartz cuvettes suitable for measurements in the UV-visible range. Optical absorption spectra were recorded using a JASCO V-570 spectrophotometer in ambient conditions. NMR spectroscopy was undertaken using a Bruker AV(III) 500 instrument fitted with a cryoprobe. Continuous-wave (CW) EPR measurements on samples in liquid solution were made using a benchtop Magnettech Miniscope MS200 spectrometer at X-band (∼9.5 GHz). CW EPR measurements were made on frozen solution samples using a Bruker EMX CW EPR spectrometer, operating at X-band in the range 9.2-9.9 GHz, and equipped with an ESR900 cryostat from Oxford Instruments. ^{15}N@C_{60}–C_{60} dimers were dissolved in toluene and flash frozen within a quartz EPR tube using liquid nitrogen, in order to form an amorphous solid.

2 Synthesis

All reactions were carried out under an argon atmosphere. For characterisation purposes, we performed the reaction initially to form dimer samples on a preparative scale. C_{60}:terephthaldehyde:*N*-(4-(hexyloxy)benzyl)glycine in the molar ratios of 2:1:10 were dissolved in toluene and refluxed for a period of ∼5 minutes, and the dimer fraction was separated out using column chromatography with silica gel as the stationary phase. These molar ratios favour formation of the dimer. Two diastereomers of the dimer, (I) and (II), were separated using recycling HPLC (column: Buckyprep-M; eluent: toluene; flow rate: 18 ml/min).

Scheme 1 applied to ^{14}N@C_{60}/C_{60} (Step 1) and ^{15}N@C_{60}/C_{60} (Step 2): In Step 1, 0.59 mg of material consisting of ^{14}N@C_{60}:C_{60} (in the ratio of 1:10^5) and 1.85 mg of *N*-(4-(hexyloxy)benzyl)glycine were added to an NMR tube, which was used as the reaction vessel. 0.466 ml of a terephthaldehyde stock solution (toluene) was then added (1 molar equivalent of terephthaldehyde). The reaction vessel was shielded to prevent exposure of N@C_{60} and its derivatives to light. The tube was heated to 110 °C for 2 minutes, and the reaction was quenched by placing the tube into cold water to quench the reaction. The

reaction products were filtered through a 0.22 μm membrane to remove insoluble particles and were then passed through a Buckyprep-M column (eluent: tolune, flow rate: 18 ml/min). The dimers (yield: 11 %), monoadduct (yield: 37 %) and unreacted $^{14}N@C_{60}/C_{60}$ were isolated in separate fractions using HPLC. In Step 2, an excess of $^{15}N@C_{60}$ (purity: 10^{-5}) and the $^{14}N@C_{60}/C_{60}$ monoadduct from Step 1 were mixed in 0.5 ml of toluene. The mixture was then transferred to an NMR tube and 1.32 mg of *N*-(4-(hexyloxy)benzyl)glycine was added. The reaction mixture was heated to 110 °C for 15 minutes under reflux conditions. (This was also protected from light). The reaction was quenched at the end of 15 minutes by placing the tube into cold water. Any remnant *N*-(4-(hexyloxy)benzyl)glycine was removed by passing the solution through a short plug of silica gel eluting with toluene. The solution was filtered using a 0.22 μm membrane and then passed through a Buckyprep-M column (eluent: tolune, flow rate: 18 ml/min) to isolate the dimer products (yield: 17 %).

Microscale N@C_{60}–C_{60} dimer synthesis: Stock solutions of terephthaldehyde (89.5 μmol/L) and $^{15}N@C_{60}$ of purity 10^{-5} (0.151 mmol/L) were prepared in separate volumetric flasks. 50 μL of each solution was added to an NMR tube – used as the reaction vessel – already containing 10 molar equivalents of *N*-(4-(hexyloxy)benzyl)glycine. A small stirrer bar was added to the tube to ensure agitatation of the reaction mixture. The reaction proceeded at 110 °C for 15 minutes, whilst shielding the vessel from ambient light. The reaction was quenched by immediately inserting the tube into a chilled water bath to cool the contents as rapidly as possible. The reaction mixture was further diluted in 1ml of toluene, filtered and then analyzed by HPLC.

3 Characterization data

C_{60} monoadduct: ^{13}C NMR (125.76 MHz, $CDCl_3$) δ (ppm) = 191.90, 158.82, 156.05, 153.86, 152.73, 152.54, 147.36, 147.33, 146.43, 146.32, 146.29, 146.23, 146.22, 146.17, 146.14, 145.98, 145.97, 145.69, 145.67, 145.61, 145.54, 145.50, 145.46, 145.37, 145.36, 145.33, 145.29, 145.24, 145.20, 144.74, 144.56, 144.44, 144.35, 144.30, 143.19, 143.10, 143.03, 142.73, 142.62, 142.61, 142.58, 142.31, 142.22, 142.16, 142.13, 142.09, 142.04, 142.00, 141.85, 141.83, 141.68, 141.58, 140.22, 140.19, 139.93, 139.48, 137.06, 136.51, 136.36, 136.10, 135.60, 130.17, 128.80, 114.69, 80.74, 76.36, 68.68, 68.13, 66.52, 56.19, 31.63, 29.33, 25.81, 22.64, 14.07. ^{1}H NMR (500 MHz, $CDCl_3$) δ (ppm) = 10.06 (s, 1H, **H-15**), 8.16 (s, 2H, **H-14**), 8.01 (d, *J* = 8.0 Hz, 2H, **H-13**), 7.55 (d, *J* = 8.6 Hz, 2H, **H-12**), 7.03 (d, *J* = 8.7 Hz, 2H, **H-11**), 5.27 (s, 1H, **H-10**), 4.88 (d, *J* = 9.6 Hz, 1H, **H-9**), 4.47 (d, *J* = 13.2 Hz, 1H, **H-8**), 4.21 (d, *J* = 9.6 Hz, 1H, **H-7**), 4.04 (t, *J* = 6.6 Hz, 2H, **H-6**), 3.69 (d, *J* = 13.2 Hz, 1H, **H-5**), 1.89–1.79 (m, 2H, **H-4**), 1.55–1.48 (m, 2H, **H-3**), 1.43–1.34 (m, 4H, **H-2**), 0.94 (t, *J* = 7.1 Hz, 3H, **H-1**).

C_{60}–C_{60} dimer: ^{13}C NMR (126 MHz, CS_2:C_6D_6 (1:1)) δ (ppm) = 158.83, 156.13, 153.86, 153.02, 147.20, 147.17, 146.49, 146.33, 146.30, 146.28, 146.17, 146.11, 146.10, 146.05, 145.92, 145.84, 145.69, 145.54, 145.51, 145.40, 145.38, 145.35, 145.27, 145.25, 145.17, 145.16, 145.07, 144.64, 144.52, 144.38, 144.26, 143.15, 142.96, 142.70, 142.59, 142.53, 142.30, 142.17, 142.12, 142.09, 142.06, 141.97, 141.89, 141.84, 141.65, 141.24, 140.21, 140.17, 139.79, 137.72, 136.84, 136.47, 135.95, 135.66, 129.95, 114.68, 81.08, 76.51, 68.47, 67.76, 66.55, 56.35, 31.97, 29.66, 26.18, 23.15, 14.40 (Diastereomer I). ^{1}H NMR (500 MHz, CS_2:C_6D_6 (1:1)) δ (ppm) = 8.27 (s, broad, 2H, **H-14**), 7.56 (d, broad, *J* = 8.3 Hz, 2H, **H-13**), 7.40 (s, broad, 4H, **H-12**), 6.84 (d, *J* = 6.9 Hz, 4H, **H-11**), 5.05 (s, 2H, **H-10**), 4.71 (d, *J* = 9.4 Hz, 2H, **H-9**), 4.42 (d, broad, 2H, **H-8**), 3.98 (d, *J* = 9.4 Hz, 2H, **H-7**), 3.80 (t, *J* = 6.4 Hz, 4H, **H-6**), 3.47 (d, *J* = 12.9 Hz, 2H, **H-5**), 1.76–1.56 (p, 4H, **H-4**), 1.38 (p, 4H, **H-3**), 1.32–1.10 (m, 8H, **H-2**), 0.86 (t, *J* = 6.8 Hz, 6H, **H-1**) (Diastereomer I). MS (MALDI-TOF, DCTB): m/z = 1981.9 $[M]^-$. UV-vis-NIR (toluene): λ_{max} = 433, 706 nm.

3.1 NMR spectra

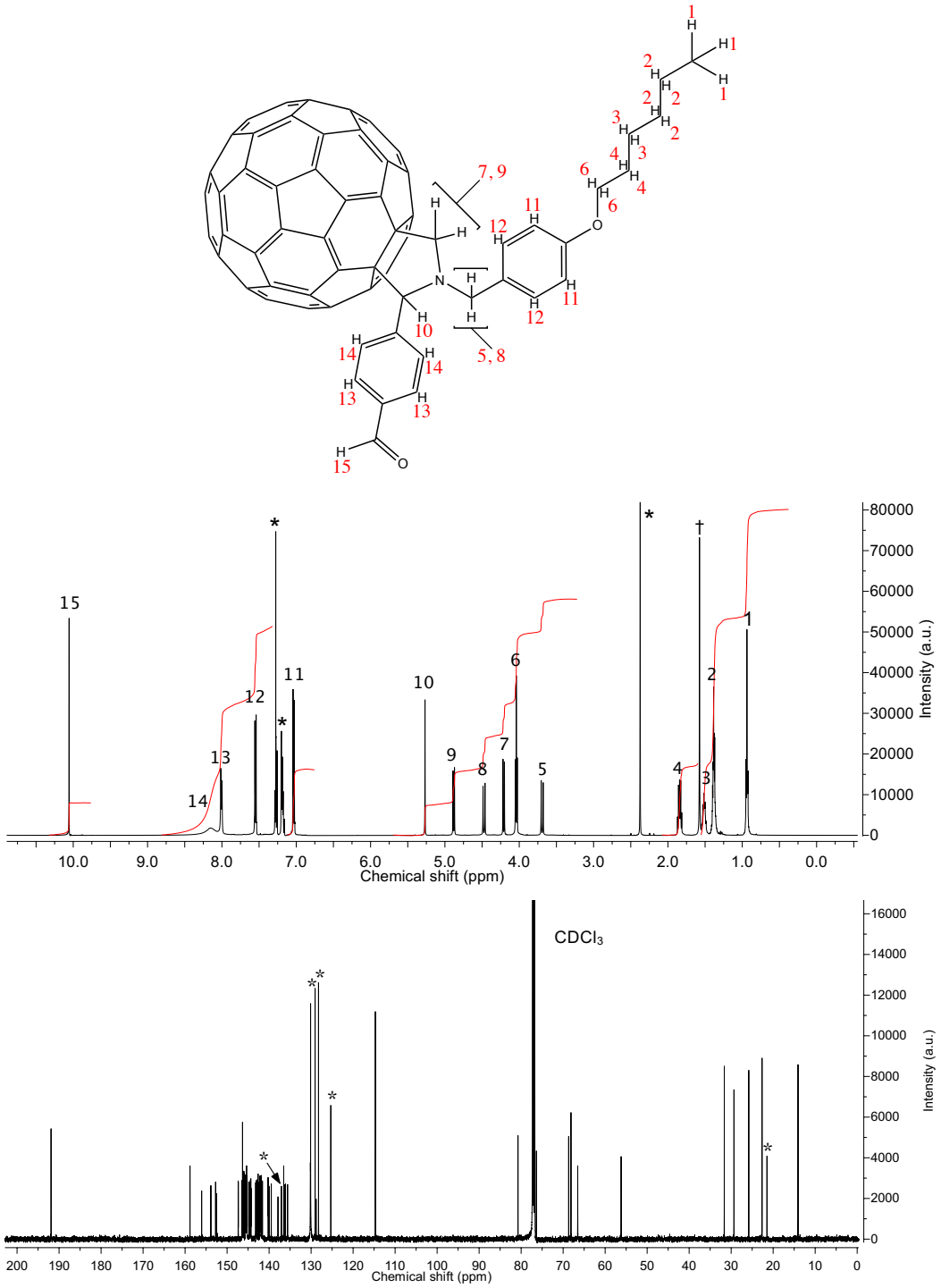

Fig. 1 Top: ^{1}H NMR spectrum (500 MHz, $CDCl_3$) for the C_{60} monoadduct. Protons are labelled on the diagram corresponding to the observed resonances. Peaks arising from remnant solvent (toluene) are marked (∗); water is also marked (†). Integrals of the peaks are shown in red. **Bottom**: ^{13}C NMR spectrum (126 MHz, $CDCl_3$) of the C_{60} monoadduct. Peaks arising from remnant solvent (toluene) are marked (∗).

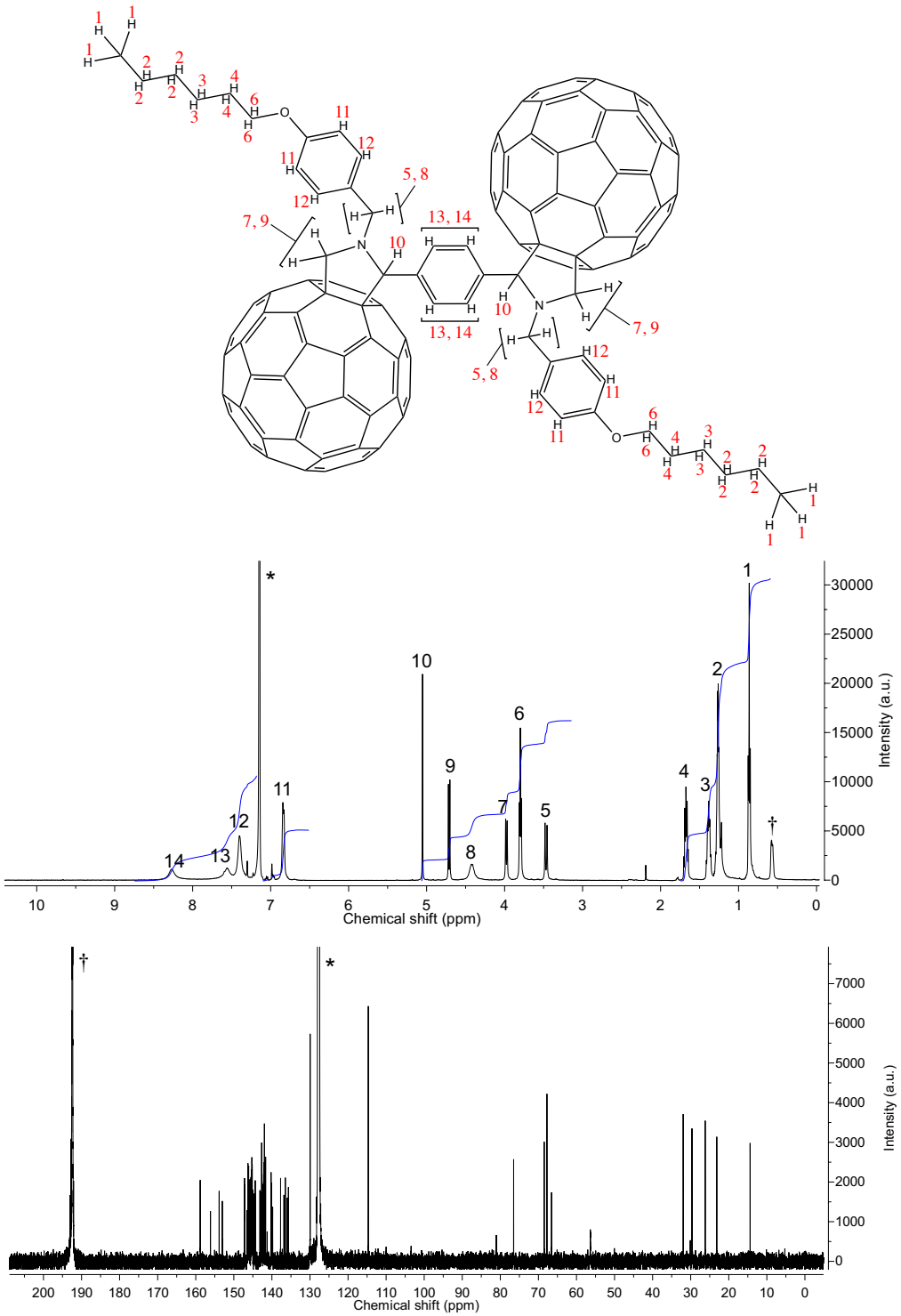

Fig. 2 .**Top**: ^{1}H NMR spectrum (500 MHz, CS_2:C_6D_6 (1:1)) for the C_{60}–C_{60} dimer (diastereomer I). Protons are labelled on the diagram corresponding to the observed resonances. The peak arising from the solvent (benzene) is marked with (∗); a minor impurity is marked with (†). Integrals of the peaks are shown in blue. **Bottom**: ^{13}C NMR spectrum (126 MHz, CS_2:C_6D_6 (1:1)) for the C_{60}–C_{60} dimer. Peaks arising from the solvent are marked with (∗) for C_6D_6 and with (†) for CS_2.

3.2 UV-vis-NIR spectra

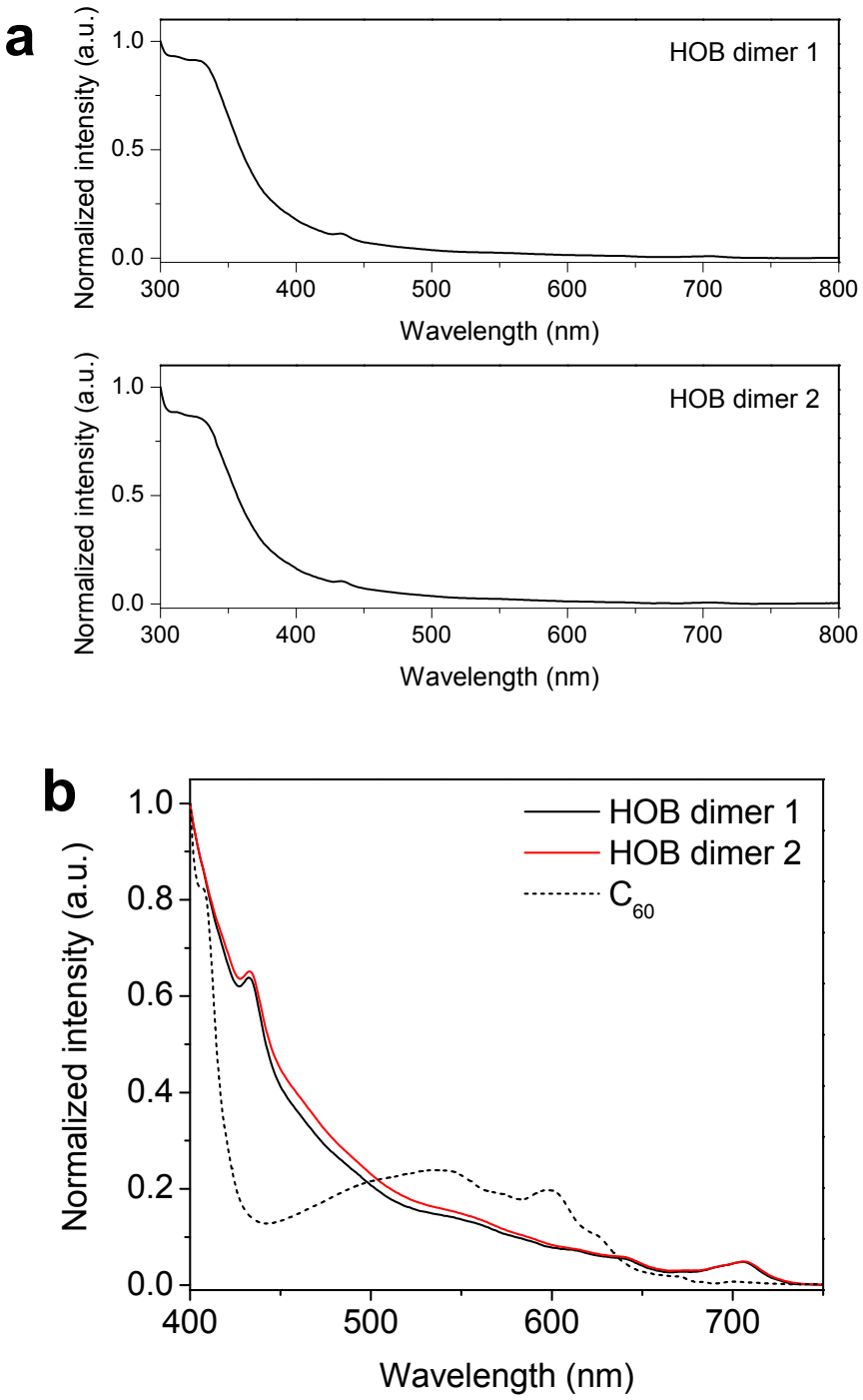

Fig. 3 **(a)** Optical absorption spectra for diastereomers I and II of the C_{60}–C_{60} dimer. **(b)** The spectra of the diastereomers overlaid and normalized at 400 nm, revealing peaks at 433 and 706 nm. The spectrum of C_{60} is also shown, again normalized at 400 nm, for comparison.

3.3 Mass spectra

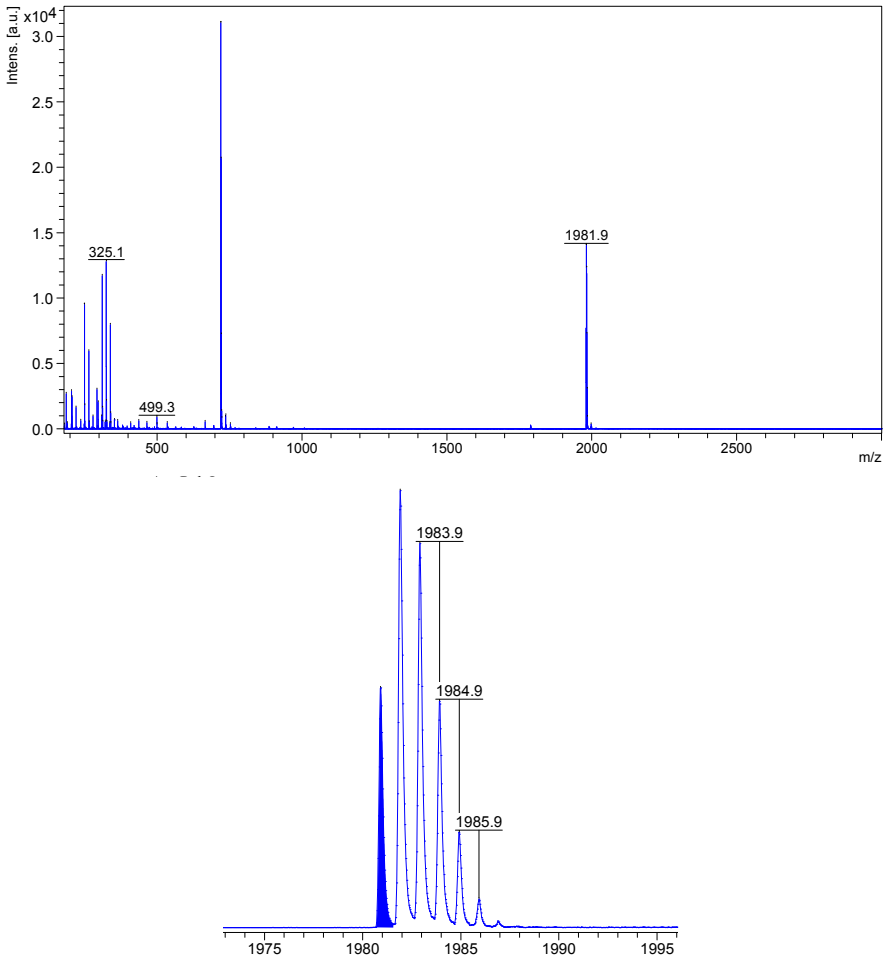

Fig. 4 **Top**: Mass spectrum of C_{60}–C_{60} dimer (diastereomer II), m/z = 1981.9. Peaks at lower m/z values arise due to fragmentation. **Bottom**: Isotopic distribution.

3.4 Stereoisomers of the C_{60}-C_{60} dimer

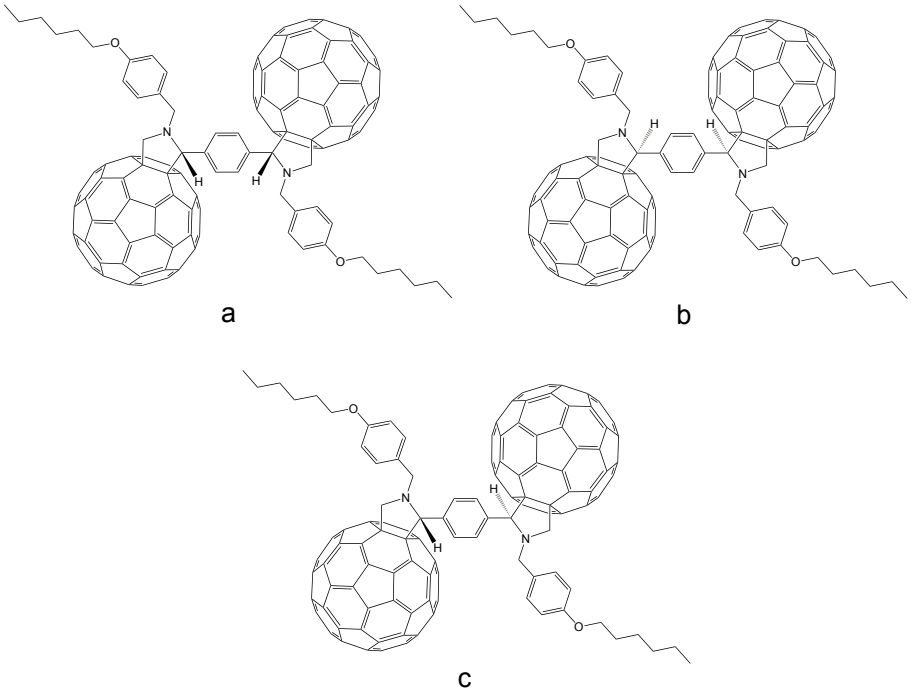

Fig. 5 The stereoisomers of the C_{60}-C_{60} dimer: (a) RR, (b) SS and (c) meso (RS = SR).

References

1 B. J. Farrington, M. Jevric, G. A. Rance, A. Ardavan, A. N. Khlobystov, G. A. D. Briggs and K. Porfyrakis, *Angew. Chem., Int. Ed.*, 2012, **51**, 3587–3590.
2 K. Lips, M. Waiblinger, B. Pietzak and A. Weidinger, *Phys. Status Solidi A*, 2000, **177**, 81–91.