

Synthesis of Ar@C₆₀ using molecular surgery.

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Note added after first publication: This Supplementary Information file replaces that originally published on 04 Aug 2020. The UV-Vis and IR data of Ar@C₆₀ and C₆₀ were missing from the original file. This has been added in section S2.4 and figure S2.2 in this updated version.

S1 General methods

Reactions were conducted under an argon atmosphere using standard Schlenk and syringe techniques with freshly distilled solvents. All apparatus was dried in a hot oven (>140 °C, 12 h) before being cooled in a sealed desiccator over silica gel or assembled while hot and cooled under vacuum (0.1 mm Hg).

Toluene was freshly distilled from sodium benzophenone ketal under argon. MeCN was freshly distilled from CaH₂ under argon. Technical grade 1-chloronaphthalene (≥85 %) was filtered through a short column of activated Al₂O₃ and distilled under argon at reduced pressure (117 °C, 13 mbar). Solutions in 1-chloronaphthalene were degassed under reduced pressure (<0.4 mm Hg) until evolution of gases had ceased. Triisopropyl phosphite was distilled over sodium at reduced pressure (67 °C, 14 mbar). Dimethyldioxirane¹ and di-(2-furyl)phenylphosphine² were prepared according to the published procedures. All other reagents, solvents or gases were used as received from commercial suppliers.

NMR spectra were recorded on a Bruker AVIIIHD400 or AVIIIHD500 FT-NMR spectrometer, or Bruker Ascend 700 NB magnet with Bruker AVANCE NEO console and Bruker TCI prodigy 5 mm liquids cryoprobe; in the indicated solvent at 298 K. ¹H chemical shifts are reported as values in ppm referenced to residual solvent. ¹H NMR spectra collected in 1,2-dichlorobenzene-*d*₄ are referenced to residual solvent at δ_H = 6.93 ppm; and this solvent chemical shift is referenced to TMS (δ_H = 0.00 ppm). The following abbreviations are used to assign multiplicity and may be compounded: s = singlet, d = doublet, t = triplet, q = quartet and m = multiplet. Coupling constants, *J*, are measured in Hertz (Hz). ¹³C NMR spectra were ¹H decoupled unless otherwise stated, and are referenced to solvent, including to 1,2-dichlorobenzene-*d*₄ at δ_C = 127.19 ppm (centre of the 1:1:1 triplet); the solvent chemical shift is referenced to TMS (δ_C = 0.00 ppm). The confidence limits of the absolute chemical shift are dominated by the chemical shift of reference solvents, reported to 2 d.p.

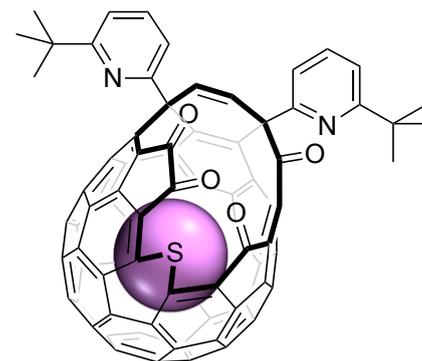
Positive ion atmospheric pressure photoionization (APPI) mass spectra were recorded using a solariX Fourier transform ion cyclotron resonance mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) equipped with a 4.7 T actively shielded superconducting magnet and an Infinity cylindrical analyser cell. The sample was diluted using toluene and directly infused into the APPI source using a Hamilton syringe driver at a flow rate of 2 μL/min. The capillary voltage was set at -2000 V, drying temperature of 180 °C, a drying gas flow rate of 4 μL/min and a nebuliser gas pressure of 2 bar. The source was equipped with a 10.6 eV krypton lamp and a vaporisation temperature of 320 °C was utilised. 16 scans were summed over the *m/z* range 150-1500 with a data set size of 1 M resulting in a resolving power of 120,000 at *m/z* 400. Data were acquired using Solarixcontrol v 1.5.0 and processed using BrukerDataAnalysis v 4.0. Positive ion electrospray mass spectra were recorded using a MaXis time of flight (TOF) mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany). IR spectra of Ar@C₆₀ and C₆₀ were obtained by deposition of the solid from CS₂ solution, using a Nicolet 380 FTIR instrument with Smart orbit ATR accessory. UV measurements were recorded on an Ocean Optics DH-2000-BAL spectrometer with a 1 cm path length cell.

Open-fullerene **2**^{3,4} and sulfide open-fullerene **3**^{5,6} were prepared according to the published methods.

S2 Synthesis and characterisation

S2.1 Ar@3

A glass reactor tube was charged with powdered open-fullerene **3** (302 mg, 0.266 mmol) and loosely plugged with glass wool. The tube was inserted into a purpose-built steel housing and then heated under a dynamic vacuum (0.4 mm Hg) at 140 °C for 2 h in order to remove endohedral water from the open-fullerene. After cooling to room temperature, the reactor was charged with argon to 1000 atm. using a Sitec 750.01 hand-operated pressure intensifying syringe (1000 bar working pressure, 30 mL capacity). The reactor was then heated to 180 °C and maintained at this temperature for 17.5 h, with a stable internal pressure of 1421 – 1427 atm during this time, before cooling to room temperature and slow release of the pressure. The title compound was obtained as a dark red/brown solid (311 mg, 100 %).



>99 % Argon filling was estimated from the ^1H NMR and ESI+ mass spectrum. Empty open-fullerene **3** is known to uptake water at room temperature⁷ and no resonance corresponding to endohedral water is seen in the ^1H NMR spectrum (expected at $\delta_{\text{H}} -11.50$ ppm⁵). No peaks corresponding to empty **3** were present in the high resolution ESI+ mass spectrum of Ar@**3** (expected at $m/z = 1135.1667$ [$^{12}\text{C}_{82}\text{H}_{27}\text{N}_2\text{O}_4\text{S}$]⁺ from ionisation of a sample of **3** under identical conditions).

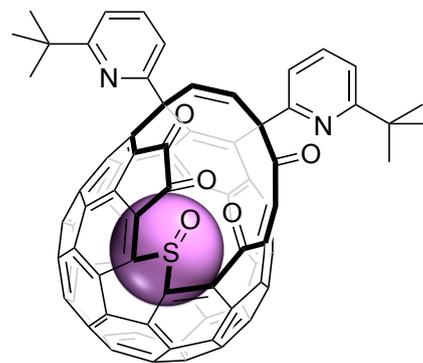
^1H NMR (500 MHz, CD_2Cl_2) δ_{H} 7.64 (1H, t, $J = 7.9$ Hz), 7.54 (1H, t, $J = 7.9$ Hz), 7.25 (2 \times 1H, dd, $J = 7.9, 0.8$ Hz), 7.13 (1H, dd, $J = 7.9, 0.8$ Hz), 7.11 (1H, dd, $J = 7.9, 0.8$ Hz), 7.01 (1H, d, $J = 10.3$ Hz), 6.42 (1H, d, $J = 10.3$ Hz), 1.22 (9H, s), 1.11 (9H, s) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CD_2Cl_2) δ_{C} 191.70, 185.96, 183.51, 181.43, 168.96, 168.85, 163.90, 162.60, 156.73, 152.88, 151.76, 151.15, 150.66, 150.48, 150.31, 150.20, 150.07, 149.81, 149.72, 149.52, 149.41, 149.40, 147.62, 147.03, 146.30, 145.70, 145.56, 145.40, 145.30, 145.14, 144.85, 144.62, 143.74, 143.69, 143.64, 143.58, 142.99, 142.56, 142.03, 141.58, 141.56, 140.93, 140.16, 139.57, 138.74, 138.24, 138.16, 138.15, 137.91, 137.81, 137.67, 137.62, 137.57, 137.15, 136.96, 136.45, 136.37, 136.15, 134.55, 133.22, 133.10, 131.81, 131.39, 131.13, 128.54, 126.56, 126.06, 120.44, 120.09, 117.86, 117.70, 60.06, 54.95, 37.97, 37.93, 30.05, 29.95 ppm. There is 1 overlapping ^{13}C resonance in the spectrum.

HRMS-ESI+ (m/z): Calcd. for [$^{12}\text{C}_{82}\text{H}_{26}\text{ArN}_2\text{NaO}_4\text{S}$]⁺, 1197.1140; found 1197.1165. Calcd. for [$^{12}\text{C}_{81}\text{C}^{13}\text{H}_{26}\text{ArN}_2\text{NaO}_4\text{S}$]⁺ isotope, 1198.1174; found 1198.1199. Calcd. for [$^{12}\text{C}_{80}\text{C}_2\text{H}_{26}\text{ArN}_2\text{NaO}_4\text{S}$]⁺ isotope, 1199.1205; found 1199.1266. Calcd. for [$^{12}\text{C}_{79}\text{C}_3\text{H}_{26}\text{ArN}_2\text{NaO}_4\text{S}$]⁺ isotope, 1200.1239; found 1200.1330. Calcd. for [$^{12}\text{C}_{78}\text{C}_4\text{H}_{26}\text{ArN}_2\text{NaO}_4\text{S}$]⁺ isotope, 1201.1274; found 1201.1381.

S2.2 Ar@4

To a stirred solution of Ar@3 (276 mg, 0.234 mmol) in toluene (23 mL) at 0 °C, was added dimethyldioxirane (3.85 mL of a 91.4 mM solution in acetone, 0.35 mmol) rapidly using an ice-chilled syringe. The resulting mixture was stirred at 0 °C for 5 min. before removal of the cooling bath and stirring for 50 min., during which time the mixture warmed to room temperature. Solvents were removed *in vacuo* to give the title compound as a crude brown powder (277 mg, 99 %) that was used directly in the next step without purification.



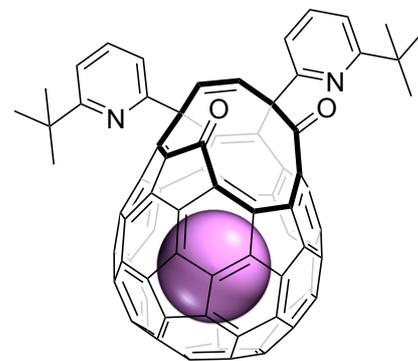
^1H NMR (400 MHz, CD_2Cl_2) δ_{H} 7.64 (1H, t, $J = 7.9$ Hz), 7.63 (1H, t, $J = 7.9$ Hz), 7.26 (1H, dd, $J = 7.9, 0.7$ Hz), 7.25 (2 \times 1H, d, $J = 7.8$ Hz), 7.21 (1H, dd, $J = 7.9, 0.7$ Hz), 7.17 (1H, d, $J = 10.3$ Hz), 6.68 (1H, d, $J = 10.3$ Hz), 1.19 (9H, s), 1.16 (9H, s) ppm.

$^{13}\text{C}\{^1\text{H}\}$ NMR (125.7 MHz, CD_2Cl_2) δ_{C} 191.80, 186.23, 184.28, 181.94, 169.21, 168.93, 163.68, 162.56, 156.89, 156.54, 151.55, 151.28, 151.00, 150.69, 150.62, 150.40, 150.20, 150.07, 149.97, 149.86, 149.67, 149.40, 149.02, 148.15, 147.85, 147.84, 147.48, 145.84, 145.72, 145.19, 144.55, 144.40, 144.38, 144.30, 143.84, 143.78, 143.63, 143.33, 142.33, 141.66, 141.12, 140.25, 139.78, 139.22, 138.99, 138.27, 138.16, 138.10, 137.88, 137.80, 137.69, 137.67, 137.54, 137.36, 137.10, 137.07, 135.13, 134.64, 133.65, 133.48, 132.94, 131.83, 131.48, 128.54, 127.40, 127.04, 126.30, 120.55, 120.12, 118.12, 117.85, 60.10, 55.23, 38.03, 37.97, 30.01 ppm. There is 1 overlapping ^{13}C resonance in the spectrum.

HRMS-ESI+ (m/z): Calcd. for $[\text{}^{12}\text{C}_{82}\text{H}_{27}\text{ArN}_2\text{O}_5\text{S}]^+$, 1191.1259; found 1191.1243. Calcd. for $[\text{}^{12}\text{C}_{81}\text{}^{13}\text{CH}_{27}\text{ArN}_2\text{O}_5\text{S}]^+$ isotope, 1192.1292; found 1192.1277. Calcd. for $[\text{}^{12}\text{C}_{80}\text{}^{13}\text{C}_2\text{H}_{27}\text{ArN}_2\text{O}_5\text{S}]^+$ isotope, 1193.1324; found 1193.1298. Calcd. for $[\text{}^{12}\text{C}_{79}\text{}^{13}\text{C}_3\text{H}_{27}\text{ArN}_2\text{O}_5\text{S}]^+$ isotope, 1194.1358; found 1194.1317. Calcd. for $[\text{}^{12}\text{C}_{78}\text{}^{13}\text{C}_4\text{H}_{27}\text{ArN}_2\text{O}_5\text{S}]^+$ isotope, 1195.1392; found 1195.1338.

S2.3 Ar@6

A dry Schlenk flask was charged with Ar@4 (115 mg, 0.096 mmol) and the apparatus placed under an atmosphere of argon. MeCN (80 mL), AcOH (16 mL of a degassed 10% v/v aqueous solution) and toluene (30 mL) were added and the resulting mixture was vigorously stirred under irradiation with a low-pressure sodium lamp (35 W) at 15 mm distance, for 35 h, without cooling. Temperature monitoring using a thermocouple in the reaction flask indicated a stable temperature of 50 °C during the irradiation. Solvents were removed *in vacuo* and purification by rapid, repeat column chromatography (SiO₂ eluted with a 90:8:2 mixture of toluene:EtOAc:AcOH; then SiO₂ eluted with a gradient of toluene → 5 % AcOH in toluene) gave Ar@5 as a black solid (29 mg, 26 %) which was used directly in the next step.



Ar@5 obtained above (20 mg, 0.0174 mmol) was heated at 140 °C under vacuum (0.4 mm Hg) for 36 h before cooling to room temperature under vacuum, and dissolution in toluene (5 mL). Di-(2-furyl)phenylphosphine (77 mg, 0.317 mmol) was added and the resulting mixture stirred at 50 °C for 119 h with exclusion of light. After cooling to room temperature, solvents were removed *in vacuo*. Purification by column chromatography (SiO₂ eluted with a gradient of 1:1 hexane:toluene → toluene) gave the title compound, Ar@6, as a shiny brown/black solid (16.8 mg, 87 % yield from Ar@5). >95 % Filling was estimated from the HRMS-ESI+ spectrum by comparison of the peak intensities for peaks $m/z = 1111.1691$, [¹²C₈₂H₂₇ArN₂O₂]⁺ and $m/z = 1071.2081$, [¹²C₈₂H₂₇N₂O₂]⁺.

¹H NMR (500 MHz, THF-*d*₈) δ_H 7.76 (1H, t, *J* = 7.8 Hz), 7.73 (1H, t, *J* = 7.8 Hz), 7.59 (1H, dd, *J* = 7.8, 0.8 Hz), 7.50 (1H, dd, *J* = 7.8, 0.8 Hz), 7.32 (1H, d, *J* = 7.9 Hz), 7.31 (1H, d, *J* = 7.9 Hz), 7.18 (1H, d, *J* = 10.0 Hz), 7.14 (1H, d, *J* = 10.0 Hz), 1.27 (9H, s), 1.18 (9H, s) ppm.

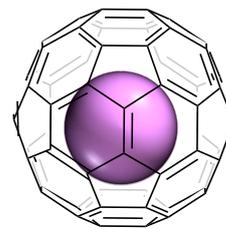
¹³C {¹H} NMR (125.7 MHz, THF-*d*₈) δ_C 198.91, 191.27, 169.57, 169.18, 166.12, 162.96, 155.99, 150.83, 149.62, 148.65, 148.56, 148.44, 148.17, 147.67, 147.60, 147.55, 147.53, 146.90, 146.84, 146.68, 146.57, 146.50, 146.49, 146.32, 146.23, 146.18, 145.87, 145.69, 145.36, 145.33, 145.03, 144.82, 144.79, 143.49, 143.41, 143.35, 143.15, 142.82, 142.71, 142.64, 141.72, 141.52, 141.45, 141.29, 141.16, 140.57, 140.27, 140.17, 140.04, 139.41, 139.32, 138.90, 138.28, 138.11, 138.02, 137.70, 137.53, 136.78, 135.85, 135.29, 134.23, 133.92, 133.59, 132.96, 132.40, 130.67, 121.08, 120.41, 118.30, 117.60, 61.72, 55.65, 38.29, 38.18, 30.11, 30.10 ppm.

HRMS-ESI+ (m/z): Calcd. for [¹²C₈₂H₂₇ArN₂O₂]⁺, 1111.1691; found 1111.1716. Calcd. for [¹²C₈₁¹³CH₂₇ArN₂O₂]⁺ isotope, 1112.1724; found 1112.1748. Calcd. for [¹²C₈₀¹³C₂H₂₇ArN₂O₂]⁺ isotope, 1113.1758; found 1113.1782. Calcd. for [¹²C₇₉¹³C₃H₂₇ArN₂O₂]⁺ isotope, 1114.1791; found 1114.1809. Calcd. for [¹²C₇₈¹³C₄H₂₇ArN₂O₂]⁺ isotope, 1115.1825; found 1115.1841.

HRMS-APPI (m/z): Calcd. for [¹²C₈₂H₂₆ArN₂O₂]⁺, 1110.1613; found 1110.1628. Calcd. for [¹²C₈₁¹³CH₂₆ArN₂O₂]⁺ isotope, 1111.1646; found 1111.1668. Calcd. for [¹²C₈₀¹³C₂H₂₆ArN₂O₂]⁺ isotope, 1112.1680; found 1112.1719. Calcd. for [¹²C₇₉¹³C₃H₂₆ArN₂O₂]⁺ isotope, 1113.1713; found 1113.1769. Calcd. for [¹²C₇₈¹³C₄H₂₆ArN₂O₂]⁺ isotope, 1114.1747; found 1114.1840.

S2.4 Ar@C₆₀

Triisopropyl phosphite (242 μ L, 0.979 mmol) was added to a solution of Ar@6 (68 mg, 0.0612 mmol) in toluene (14 mL) and the resulting mixture was stirred at reflux for 22 h. After cooling to room temperature, the mixture was concentrated *in vacuo* and purified by column chromatography (SiO₂ eluted with toluene) to afford a black solid (38 mg) which was taken into 1-chloronaphthalene (8 mL) and transferred to a Schlenk tube charged with N-phenyl maleimide (24 mg, 0.141 mmol). The mixed solution was degassed and placed under an atmosphere of argon before stirring at 245 °C for 42 h. After cooling to room temperature, the mixture was flushed through a SiO₂ column packed with toluene, collecting a purple band. Purification by recycling HPLC (figure S2.3) gave the title compound Ar@C₆₀ as a black solid (20 mg, 43 % yield from Ar@6).



¹³C NMR (176 MHz, 1,2-dichlorobenzene-*d*₄) δ = 142.98 ppm.

HRMS-APPI (*m/z*): Calcd. for [¹²C₆₀Ar]⁺, 759.9618; found 759.9620. Calcd. for [¹²C₅₉¹³CAr]⁺ isotope, 760.9652; found 760.9660. Calcd. for [¹²C₅₈¹³C₂Ar]⁺ isotope, 761.9685; found 761.9700.

IR: ν = 1429, 1182, 576 cm⁻¹; for comparison, C₆₀ ν = 1428, 1182, 576 cm⁻¹.

UV (toluene): λ_{max} 333.7 nm, ϵ 45000 M⁻¹cm⁻¹.

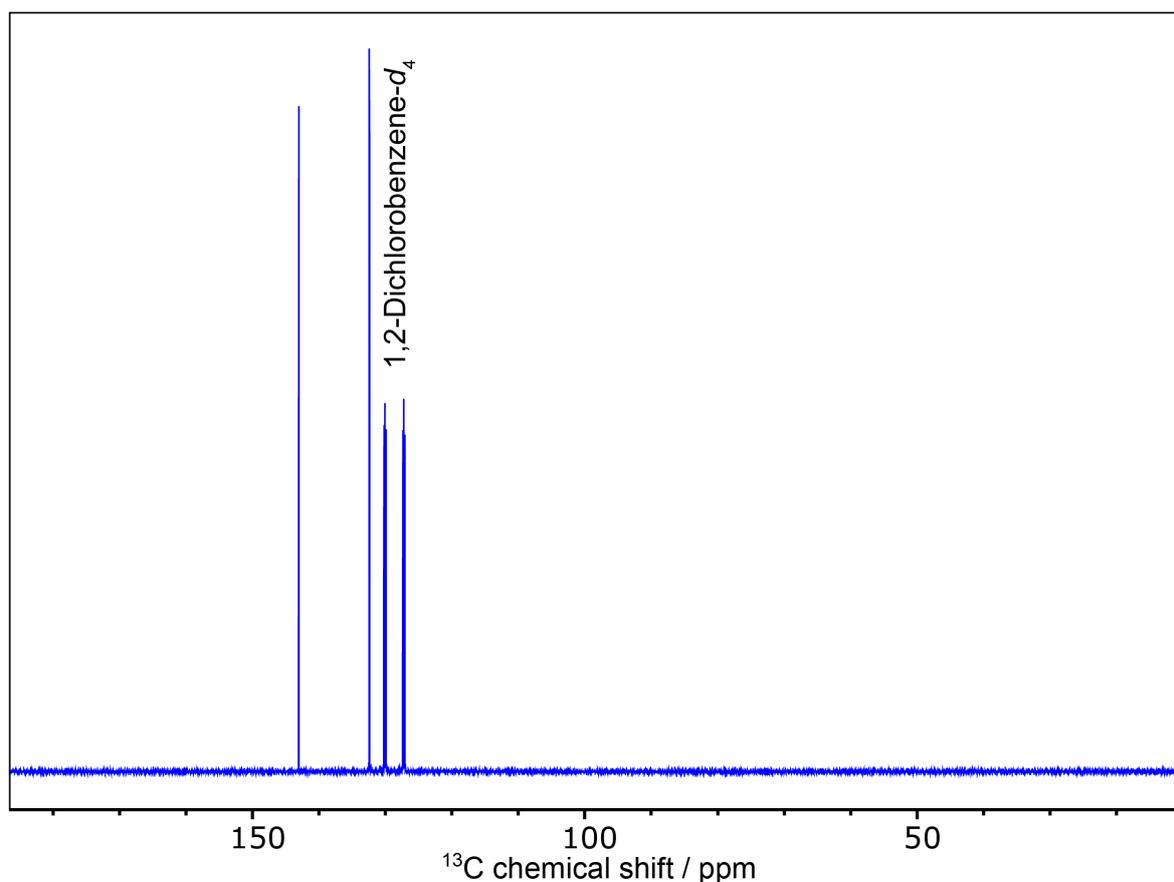


Figure S2.1 ¹³C NMR spectrum of Ar@C₆₀ (100% argon filling), 24 mM solution in degassed 1,2-dichlorobenzene-*d*₄ at 298 K, acquired with 32 transients. The spectrum was processed using Lorentzian line broadening, 0.2 Hz.

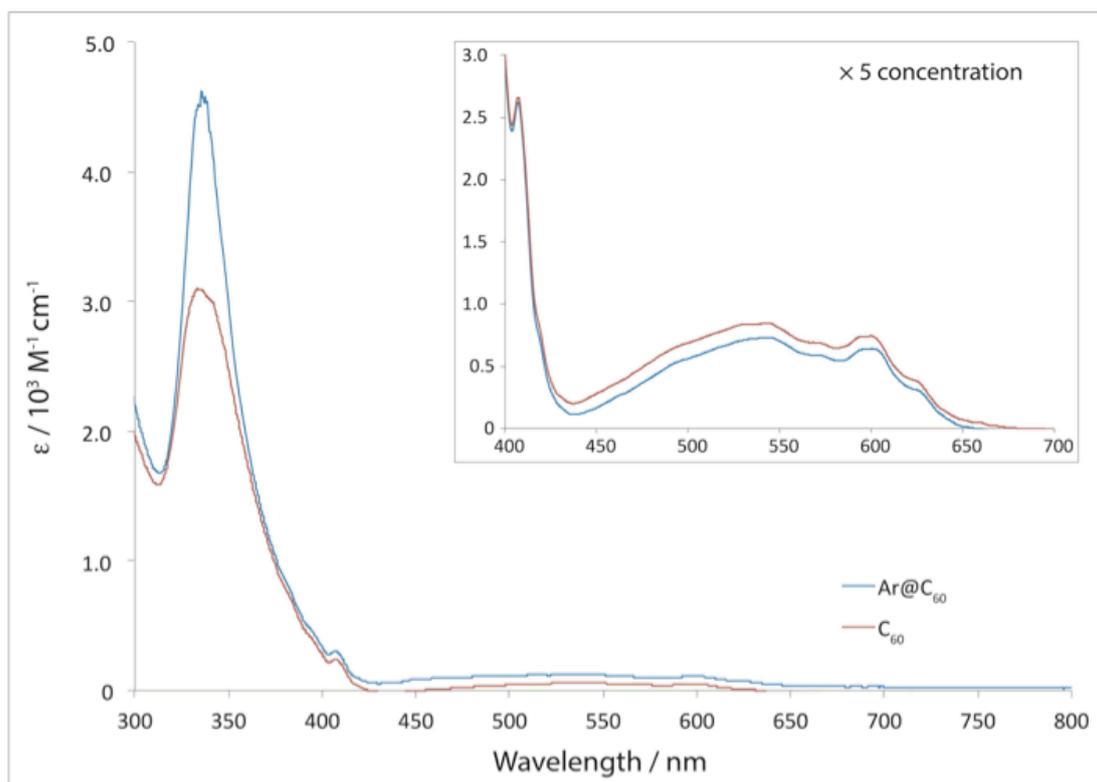


Figure S2.2 UV-vis spectra of Ar@C₆₀ and C₆₀. The spectra in the main figure were each obtained from a solution of the fullerene in toluene (Ar@C₆₀ approx. 5.26×10^{-5} M, C₆₀ approx. 5.55×10^{-5} M) following serial dilution of a 0.2 mg mL⁻¹ solution in toluene. Spectra in the insert were obtained from the undiluted solution.

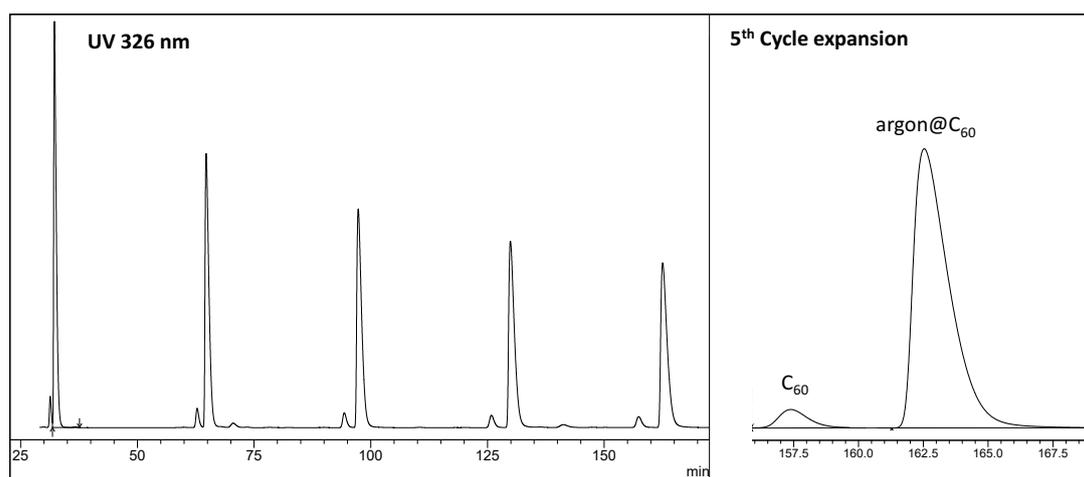


Figure S2.3 Recycling HPLC chromatogram for the isolation of Ar@C₆₀. Conditions: Cosmosil™ Buckyprep column eluted with toluene at a flow rate of 10.0 mL min⁻¹ at 30 °C.

S3 Summary of DFT calculations

Model structures **2b**, **3b** and **4b** were used to represent compounds **2**, **3** and **4**, in which the 5-tert-butylpyridyl groups were replaced by methyl groups. Calculations were carried out using Gaussian 09,⁸ using the M06-2X functional⁹ with cc-pVDZ¹⁰ basis set to locate minimum energy and transition state structures and to characterise them through frequency calculations. The cc-pVTZ¹⁰ basis set with an ultrafine integration grid was used to calculate electronic energies and to correct for Basis Set Superposition Error using the counterpoise method.¹¹ Thermal corrections to the electronic energy to give the enthalpy at 298 K and 1 atm were derived from frequency calculations at the M06-2X/cc-pVDZ level using the Gaussian freqchk utility. The frequencies were not scaled and low frequency modes were not removed.

	$\Delta H(\text{binding}) \text{ kJ mol}^{-1}$	$\Delta H^\ddagger (\text{entry}) \text{ kJ mol}^{-1}$	$\Delta H^\ddagger (\text{exit}) \text{ kJ mol}^{-1}$
$\text{Ar} + \mathbf{3b} \rightleftharpoons \text{Ar@}\mathbf{3b}$	-45.9	54.8	100.7
$\text{Ar} + \mathbf{4b} \rightleftharpoons \text{Ar@}\mathbf{4b}$	-46.8	63.2	110.0
$\text{CH}_4 + \mathbf{3b} \rightleftharpoons \text{CH}_4\text{@}\mathbf{3b}$	-50.1	86.3	136.4
$\text{CH}_4 + \mathbf{4b} \rightleftharpoons \text{CH}_4\text{@}\mathbf{4b}$	-52.0	98.1	150.2
$\text{Ar} + \mathbf{2b} \rightleftharpoons \text{Ar@}\mathbf{2b}$	-49.1	167.1	216.2
$\text{H}_2\text{O} + \mathbf{2b} \rightleftharpoons \text{H}_2\text{O@}\mathbf{2b}$	-53.6	46.6	100.2

Table S3.1 Summary of outcomes of DFT calculations.

S4 References

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