Supporting Information

Open-cage fullerene with a stopper acts as a molecular vial for a single water molecule

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Preparation of Compounds 2b and 3b.

Acetic acid (20 drops, 384 mg) and diaminobenzene (132 mg, 1.22 mmol) were added to a solution of 1b (128 mg, 0.121 mmol) in CH2Cl2 (60 mL) at room temperature. After 14 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate (20:1). The solution was concentrated, and chromatographed again on a silica gel column eluting with dichloromethane/ethyl acetate (100:1). The first band was collected and evaporated to give 2b (58 mg, 0.051 mmol, 43%). The second band was collected and evaporated to give 3b (51 mg, 0.045 mmol, 37%).

**Characterization Data for 2b.** 1H NMR (400 MHz, C6D4Cl2) δ: 8.34-8.32 (d, 1H, J = 8.0 Hz), 8.21-8.19 (d, 1H, J = 8.2 Hz), 7.89-7.84 (m, 4H), 7.74-7.70 (t, J = 7.5 Hz, 2H), 7.61 (s, 1H), 7.08 (s, 1H), 7.03-6.95 (m, 2H), 6.81-6.79 (m, 1H), 6.15-6.09 (m, 2H), 5.47-5.39 (m, 1H), 4.47-4.42 (m, 2H), 4.00 (s, 3H), -10.90 (s). 13C NMR spectrum could not be obtained due to low solubility. ESI-FT-ICR-HRMS: C79H22N5O6 (M + H+) calcd 1136.1565, found 1136.1563.

**Characterization Data for 3b.** 1H NMR (400 MHz, C6D4Cl2) δ: 8.39 (s, 1H), 8.01-7.99 (d, 1H, J = 8.0 Hz)), 7.90-7.88 (d, 2H, J = 8.0 Hz),
7.58-7.55 (t, $J = 7.1 \text{ Hz}$, 2H), 7.46-7.42 (t, $J = 7.3 \text{ Hz}$, 1H), 7.31 (s, 1H), 6.91-6.87 (m, 2H), 6.85-6.83 (m, 1H), 6.42-6.41 (m, 1H), 6.37-6.34 (m, 1H), 6.02-5.99 (t, $J = 7.2 \text{ Hz}$, 1H), 4.79-4.75 (m, 1H), 4.54-4.44 (m, 1H), 4.07-4.03 (m, 1H), 3.86 (s, 1H), 3.60 (s, 3H), -11.50 (s). $^1$H NMR (400 MHz, CDCl$_3$/CD$_3$OD) $\delta$: 8.49-8.47 (m, 1H), 8.31-8.29 (m, 1H), 8.04-8.03 (m, 1H), 8.03-8.02 (m, 1H), 7.99-7.92 (m, 2H), 7.88-7.85 (m, 1H), 7.55-7.47 (m, 1H), 7.18-7.15 (m, 2H), 6.78-6.77 (d, 1H, $J = 7.4 \text{ Hz}$), 6.67-6.63 (m, 1H), 6.26-6.21 (m, 1H), 5.15-5.09 (m, 1H), 5.05-5.01 (m, 1H), 4.79-4.68 (m, 1H), 4.16-4.15 (m, 1H), 4.00 (s, 3H), -11.14 (s). $^{13}$C NMR (125 MHz, C$_6$D$_4$Cl$_2$): all signals represent 1C except noted, $\delta$: 190.13, 159.48, 158.75, 154.10, 150.24, 150.09, 150.06, 149.39, 148.79, 148.71, 148.54, 148.38, 148.13, 147.98, 147.93, 147.90, 147.79, 147.77, 147.75, 147.59, 147.46, 147.17, 147.03, 146.80, 146.67, 146.48, 146.12, 146.00, 145.88, 145.33, 145.19, 144.42, 144.28, 144.08, 143.17, 142.68, 142.66, 142.64, 142.45, 142.24, 142.22, 141.71, 141.61, 141.59, 141.22, 140.62, 139.91, 138.83, 138.58, 138.39, 138.11, 138.06, 137.85, 136.82, 135.19, 133.93, 121.15, , 119.29, 116.40, 113.41, 113.11, 112.84, 106.51, 77.74, 76.95, 76.59, 75.99, 63.72, 54.34 (3C). ESI-FT-ICR-HRMS: C$_{79}$H$_{22}$N$_5$O$_6$ (M + H$^+$) calcd 1136.1565, found 1136.1556.
Acetic acid (1 ml) was added to a solution of 2b (17 mg, 0.015 mmol) in PhCl (10 mL) at 80°C. After 18 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate. The solution was concentrated, and chromatographed on a silica gel column eluting with dichloromethane. The first red band was collected and evaporated to give 4b (14 mg, 0.014 mmol, 91%).

Acetic acid (1 ml) was added to a solution of 3b (14 mg, 0.012 mmol) in PhCl (10 mL) at 80°C. After 18 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate. The solution was concentrated, and chromatographed on a silica gel column eluting with dichloromethane. The first red band was collected and evaporated to give 4b (10 mg, 0.010 mmol, 79%).
**Characterization Data for 4b.** $^1$H NMR (400 MHz, CDCl$_3$) $\delta$: 8.21-8.13 (m, 3H), 8.09-8.07 (m, 2H), 7.82-7.74 (m, 2H), 7.17-7.15 (d, $J$ = 8.6 Hz, 2H), 6.81-6.69 (d, $J$ = 7.4 Hz, 1H), 4.00 (s, 3H), -12.87 (s). $^{13}$C NMR (125 MHz, CDCl$_3$): all signals represent 1C except noted, $\delta$: 184.63, 184.49, 184.42, 184.37, 184.25, 184.20, 184.17, 183.97, 160.40, 160.37, 158.81, 158.77, 155.55, 155.50, 150.03, 149.76, 149.73, 149.68, 149.66, 149.62, 149.60, 149.59, 149.57, 149.55, 149.46, 149.43, 149.40, 149.36, 149.31, 149.27, 148.30, 148.29, 148.27, 148.23, 148.20, 148.18, 148.15, 147.91, 147.90, 147.39, 147.29, 147.27, 147.11, 147.01, 146.88, 146.69, 146.53, 146.35, 146.23, 146.21, 146.06, 146.01, 145.83, 145.76, 145.70, 145.63, 145.53, 145.45, 145.43, 145.34, 145.25, 145.20, 145.16, 144.89, 144.81, 144.71, 144.67, 144.64, 144.55, 144.49, 144.47, 144.42, 144.34, 144.30, 144.26, 143.72, 143.69, 143.65, 143.50, 143.43, 143.42, 143.39, 143.34, 143.31, 143.27, 142.85, 142.69, 142.60, 142.49, 142.47, 141.75, 141.73, 141.59, 141.55, 141.05, 140.90, 140.68, 140.66, 140.44, 139.78, 139.76, 136.82, 136.66, 136.57, 136.49, 136.47, 136.32, 135.96, 135.81, 131.82, 131.17, 129.60, 129.58, 129.24, 127.74, 127.70, 127.64, 127.33, 126.95, 126.66, 113.69, 78.31, 78.26, 77.60, 77.55, 55.69. ESI-FT-ICR-HRMS: C$_{73}$H$_{14}$N$_3$O$_6$ (M + H$^+$) calcd 1028.0877, found 1028.0867. C$_{146}$H$_{27}$N$_6$O$_{12}$ (2M + H$^+$) calcd 2055.1682, found 2055.1590.

Acetic acid (15 drops, 288mg) and diaminobenezene (58 mg, 0.52 mmol) were added to a solution of 4a (103 mg, 0.0978 mmol) in CH$_2$Cl$_2$.
(60 mL) at room temperature. After 14 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate (40:1). The solution was concentrated, and chromatographed again on a silica gel column eluting with dichloromethane. The first band was collected and evaporated to give 2a (27 mg, 0.023 mmol, 24%). The second band was eluted with dichloromethane/ethyl acetate (100:1) and evaporated to give 3a (68 mg, 0.059 mmol, 60%).

Acetic acid (6 drops, 115 mg) and diaminobenzene (17 mg, 0.16 mmol) were added to a solution of 4b (15 mg, 0.013 mmol) in CH₂Cl₂ (10 mL) at room temperature. After 14 h, the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate (20:1). The solution was concentrated, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate = 100:1. The first band was collected and evaporated to give 2b (4 mg, 0.004 mmol, 29%). The second band was collected and evaporated to give 3b (8 mg, 0.008 mmol, 59%).
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 15050385_20150517_000001.d
Sample: sJ-Ar
Comment: ESI Positive

Acquisition Date: 2015/05/11 10:44:01
Instrument: Bruker Apex IV FTMS
Operator: Peking University

Bruker Compass DataAnalysis 4.0
printed: 2015/05/11 18:12:28
Page 1 of 1
$\text{Ar} = 4^\prime\text{-Bu-C}_8\text{H}_4^-$

solvent: CDCl$_3$/CD$_2$OD
Peking University Mass Spectrometry Sample Analysis Report

Analysis Info
Analysis Name: 10031019_20150027_000003.d
Sample: 3
ESI Positive
Acquisition Date: 5/27/2015 3:11:54 PM
Instrument: Bruker Apex V FTMS
Operator: Peking University

Bruker Compex DataAnalysis 4.0
printed: 5/27/2015 3:02:57 PM
Page 1 of 1
Ar = 4'-BuC₆H₄⁺

solvent: CDCl₃

Ar = 4'-BuC₆H₄⁺

solvent: C₆D₆/C₆D₆/CD₂OD

water and grease
$^1$H NMR spectra for water encapsulation and release and D$_2$O exchange with 4a
(the experiments were carried out in CDCl$_3$ in a sealed flask)

$^1$H NMR spectra for addition of o-diaminobenzene to 4a and dehydration of
2a and 3a with Na$_2$SO$_4$ (the experiments were carried out in CDCl$_3$ in a sealed flask)
$^1$H NMR spectra for dehydration of 3a with Na$_2$SO$_4$

(the experiments were carried out in CDCl$_3$ in a sealed flask)