Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Highly selective encapsulation and purification of U-based C_{78}-EMFs within a supramolecular nanocapsule

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1. Material and instrumentation.

Reagents and solvents used were commercially available reagent quality unless indicated otherwise. Tetragonal prismatic nanocapsule **1·(BArF)$_8$** was synthesized according to published procedures.[1] All soot containing uranium EMFs were synthesized in an electrical arc discharge reactor using a Krätschmer–Huffman type apparatus. For soot containing Sc species of endohedrals, hollow graphite rods were packed with a 0.0103:0.0079:1 molar ratio of uranium oxide (U_3O_8) / scandium oxide (Sc_2O_3) and graphite powder mixture. Packed graphite rods were vaporized in an arc plasma under a partial He and H_2 atmosphere (200 torr and 20 torr respectively). Scandium free endohedral soot was produced using hollow graphite rods packed with a 0.0095:1 molar ratio of uranium oxide (U_3O_8) / graphite powder mixture vaporized in arc plasma under a partial He and NH_3 atmosphere (200 torr and 30 torr respectively). Endohedral species were extracted from the resulting carbon soot using CS_2 in a Soxhlet extractor under reflux for 4-6hrs. Laser desorption/ionization time-of-flight (LDI-TOF) mass spectrometry was conducted on a Bruker Microflex LRF mass spectrometer. ESI-MS experiments were collected and analyzed on a Bruker MicroTOF-Q-II, using acetonitrile as the mobile phase.

The liberation of entrapped fullerenes and endohedral metallofullerenes from **1·(BArF)$_8$** was achieved following a reported procedure,[1] consisting in charging the filled nanocapsule in a column and applying consecutive washings with 1,2-dichlorobenzene/CS_2 (1/1 v/v mixture).

2. Selective molecular recognition of U-based EMFs and Host-Guest adduct characterization:

The amount of a given EMF present in a soot sample cannot be precisely quantified, because they are produced as a mixture of compounds. In order to have an approximate idea of the amount of nanocapsule needed for the quantitative encapsulation of the desired EMF, we took an aliquot from the soot and we add 50 μL of a suspension of **1·(BArF)$_8$** (1 mg) in toluene (1 ml) (corresponding to 0.05 mg of **1·(BArF)$_8$**). Monitoring by MALDI the EMFs left in the supernatant of the sample, we can infer the amount of the target EMF encapsulated and thus the total amount of it present in the initial mixture. Then, these results are used as a guideline for the purification of the Soot sample, adding stoichiometric amounts of capsule with respect to the target EMF.

Selective encapsulation of $U_2@C_{78}$ and $U_2C@C_{78}$ from soot sample-1 using 1·(BArF)$_8$ in the solid phase: 0.40 mg of nanocapsule **1·(BArF)$_8$** (0.0336 μmols) in the solid phase are added to a toluene solution of sample-1. The suspension is stirred at room temperature for 3h. Aliquots of the supernatant are filtered, and analyzed by LDI-TOF every 60 minutes (Fig 2).

Selective encapsulation of $U_2@C_{78}$ from soot sample-2 using $\mathbf{1\cdot(BArF)_8}$ in the solid phase: 0.12 mg of nanocapsule $\mathbf{1\cdot(BArF)_8}$ (0.01 µmols) in the solid phase are added to a toluene solution of sample-2. The suspension is stirred at room temperature for 1h. Aliquots of the supernatant are filtered, and analyzed by LDI-TOF every 15 minutes (Fig 3).

Selective encapsulation of $U_2C@C_{78}$ from soot sample-3 using $\mathbf{1\cdot(BArF)_8}$ in the solid phase: 0.12 mg of nanocapsule $\mathbf{1\cdot(BArF)_8}$ (0.01 µmols) in the solid phase are added to a toluene solution of sample-3. The suspension is stirred at room temperature for 45 minuts. Aliquots of the supernatant are filtered, and analyzed by LDI-TOF every 15 minutes (Fig 4).

Selective encapsulation of $U_2@C_{78}$ from soot sample-4 using $\mathbf{1\cdot(BArF)_8}$ in the solid phase: 0.10 mg of nanocapsule $\mathbf{1\cdot(BArF)_8}$ (0.0083 µmols) in the solid phase are added to a toluene solution of sample-4. The suspension is stirred at room temperature for 20 minuts. Aliquot of the supernatant is filtered, and analyzed by LDI-TOF (Fig 5).

Sequential molecular recognition of $U_2@C_{78}$ and $U_2C@C_{78}$ from soot sample-5 using $\mathbf{1\cdot(BArF)_8}$ in the solid phase: For the purification of $U_2@C_{78}$, 0.25 mg of nanocapsule $\mathbf{1\cdot(BArF)_8}$ (0.017 µmols) in the solid phase are added to a toluene solution of the sample-5. The suspension is stirred at room temperature for 45 minutes. Aliquots of the supernatant are filtered, and analyzed by LDI-TOF at different times (Fig. 6). The Host-Guest adducts are isolated by filtration. Subsequently, for the purification of $U_2C@C_{78}$, 0.25 mg of nanocapsule $\mathbf{1\cdot(BArF)_8}$ (0.017 µmols) in the solid phase are added to a toluene solution of the remaining sample-5 (after complete removal of $U_2@C_{78}$). Then, the suspension is stirred at room temperature for 2h, analyzing aliquots of the supernatant by LDI-TOF every 30 minutes (Fig. 6).

Competition experiment between $U_2C@C_{78}$ and $Sc_3N@C_{78}$ using $\mathbf{1\cdot(BArF)_8}$ in the solid phase: 0.25 mg of nanocapsule $\mathbf{1\cdot(BArF)_8}$ (0.017 µmols) in the solid phase are added to a toluene solution of $U_2C@C_{78}$ and $Sc_3N@C_{78}$ equimolar mixture.[2] The suspension is stirred at room temperature for 3 h. The Host-Guest adducts are isolated by filtration and analyzed by HRMS.

Spectrometric characterization of $U_2C@C_{78}\subset\mathbf{1\cdot(BArF)_8}$ host-guest adducts formed during the purification of soot sample-5: The HRMS spectrum of the host-guest adducts formed show ions corresponding to the $\mathbf{U_2C@C_{78}\subset 1\cdot(BArF)_8}$ complex with consecutive loss of counteranions (Fig. S1).

HRMS m/z:
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_4\}^{+4}]$: calculated 2418.468 and found 2418.468
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_3\}^{+5}]$: calculated 1762.161 and found 1762.163
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_2\}^{+6}]$: calculated 1324.611 and found 1324.611
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_1\}^{+7}]$: calculated 1011.953 and found 1011.953
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_0\}^{+8}]$: calculated 777.575 and found 777.577

Spectrometric characterization of $Sc_3N@C_{78}\subset\mathbf{1\cdot(BArF)_8}$ host-guest adducts formed during the competition experiment between $U_2C@C_{78}$ and $Sc_3N@C_{78}$: The HRMS spectrum of the host-guest adducts formed show ions corresponding to the $\mathbf{Sc_3N@C_{78}\subset 1\cdot(BArF)_8}$ complex with consecutive loss of counteranions (Fig. S2).

HRMS m/z:
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_4\}^{+4}]$: calculated 2333.744 and found 2333.748
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_3\}^{+5}]$: calculated 1694.352 and found 1694.354
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_2\}^{+6}]$: calculated 1268.091 and found 1268.095
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_1\}^{+7}]$: calculated 963.619 and found 963.621
$[\{U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_0\}^{+8}]$: calculated 735.265 and found 735.266

Competition experiment, $Sc_3N@C_{80}\subset$1·(BArF)$_8$ exposed to $Sc_3N@C_{78}$. A encapsulated sample of $Sc_3N@C_{80}$ in **1**·(BArF)$_8$ was prepared following previously reported protocols (Chem. Eur. J. 2017, 23, 3553 – 3557),[3] and its full encapsulation checked by HRMS. The $Sc_3N@C_{80}\subset$**1**·(BArF)$_8$ adduct in the solid state (0.043 mmols) was exposed to a toluene solution of $Sc_3N@C_{78}$ (0.043 equiv, 5 mL) for 48 hours, followed by filtration and analysis by HRMS of the solid adduct (Figure S3).

Competition experiment, 1 equiv. of $Sc_3N@C_{80}$ and 1 equiv. of $Sc_3N@C_{78}$ with 2 equiv. of nanocapsule 1·(BArF)$_8$ monitored by HRMS at 2.5 hours. A toluene solution (7 mL) of 1 equiv. of $Sc_3N@C_{80}$ (0.043 mmol) and 1 equiv. of $Sc_3N@C_{78}$ (0.043 mmol) was stirred with 2 equivalent of **1**·(BArF)$_8$ (0.086 mmol) in the solid state for 2.5 hours. The suspension was then filtered and analysed by HRMS (in CH_3CN). The spectra showed the sole uptake of $Sc_3N@C_{78}$ despite empty nanocapsule was still remaining (only traces of $[Sc_3N@C_{80}\subset$**1**·(BArF)$_4]^{4+}$). The latter experiment and HRMS spectrum is depicted in Figure S4.

3. Computational details

All geometry optimizations and single point calculations were carried out with the ADF 2017 package[4] using BLYP exchange-correlation functional.[5, 6] To describe valence electron we employed Slater triple-zeta polarization (TZP) basis sets whereas frozen cores were described by means of single Slater functions, consisting of the 1s shell for C and N, the 1s to 2p shells for Zn and the 1s to 4f shells for U. Scalar relativistic corrections were included by means of the ZORA formalism. Dispersion corrections by Grimme were also included.[7]
A data set collection of computational results is available in the ioChem-BD repository[8] and can be accessed via https://doi.org/10.19061/iochem-bd-2-XX.

4. Supplementary figures

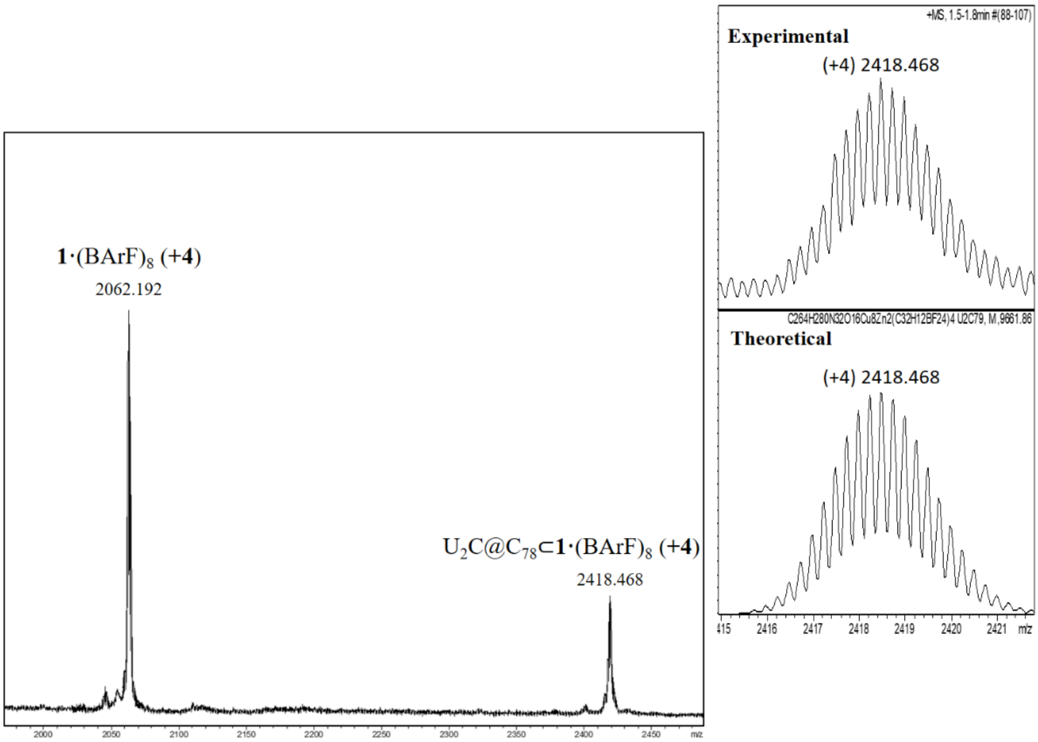


Figure S1. ESI-MS characterization of $U_2C@C_{78}\subset\mathbf{1}\cdot(BArF)_8$.

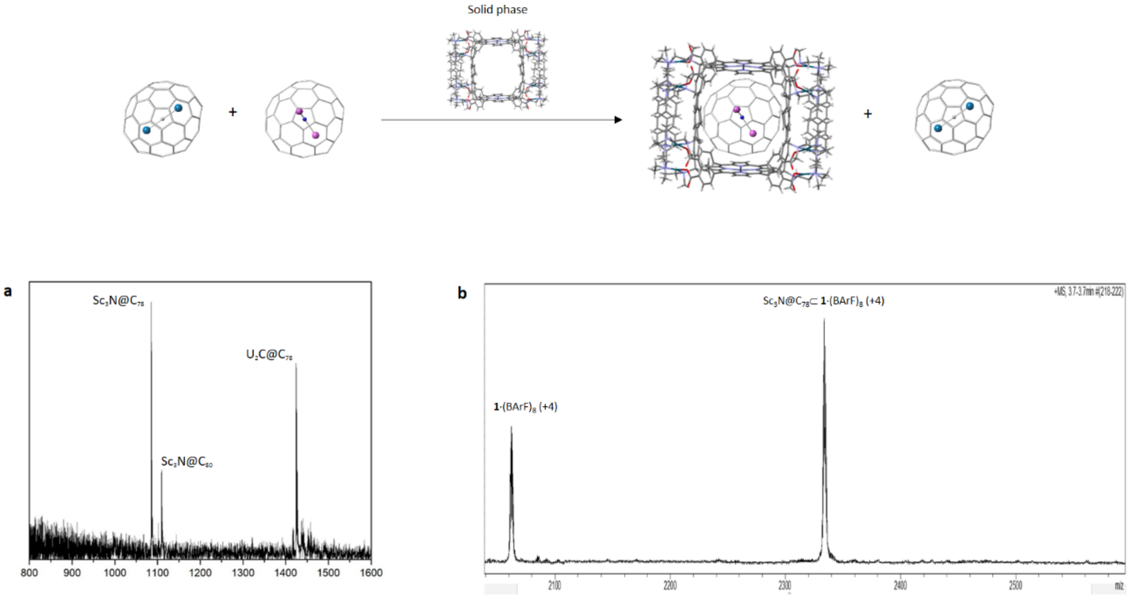


Figure S2.A) MALDI-MS showing the composition of the starting mixture of $U_2C@C_{78}$ and $Sc_3N@C_{78}$ (sample contains traces of $Sc_3N@C_{80}$ as an impurity). B) ESI-MS characterization of the host guest complex produced during the competition experiment between $U_2C@C_{78}$ and $Sc_3N@C_{78}$.

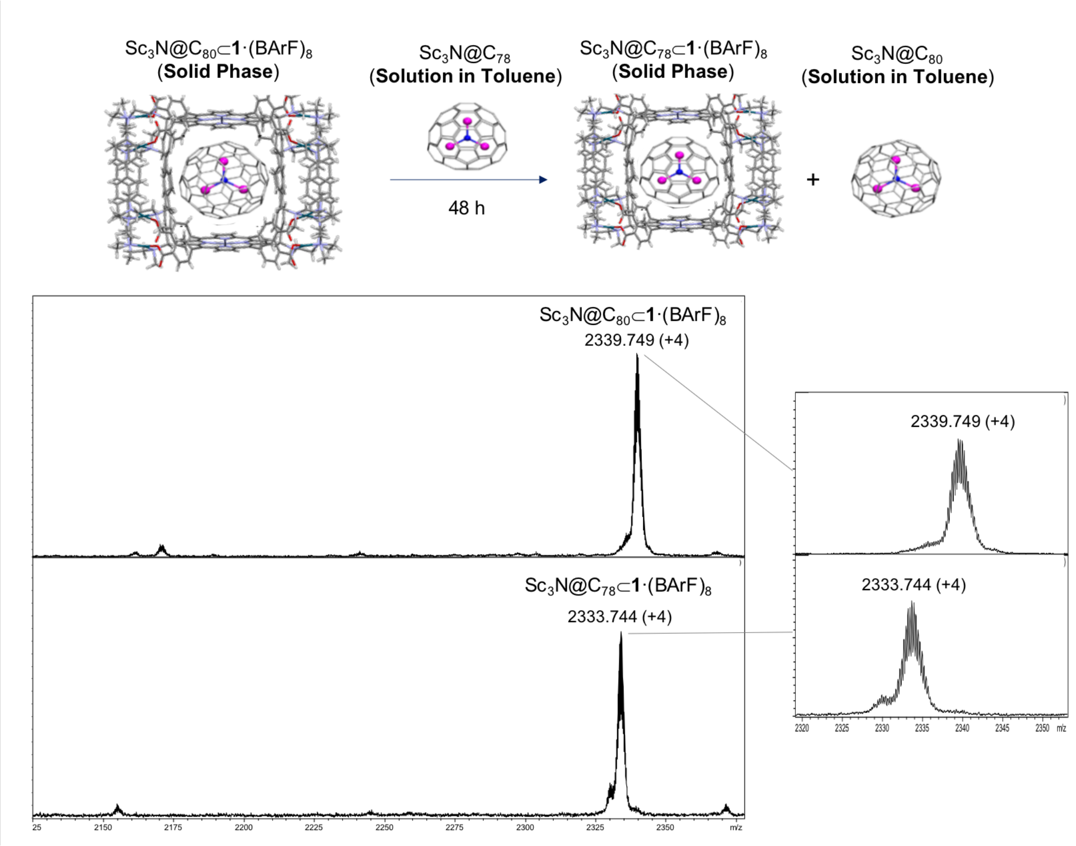


Figure S3. HRMS showing the starting encapsulated $Sc_3N@C_{80}\subset\mathbf{1}\cdot(BArF)_8$ and the complete exchange with $Sc_3N@C_{78}$ to form exclusively the corresponding adduct $Sc_3N@C_{78}\subset\mathbf{1}\cdot(BArF)_8$ (reaction time 48 h).

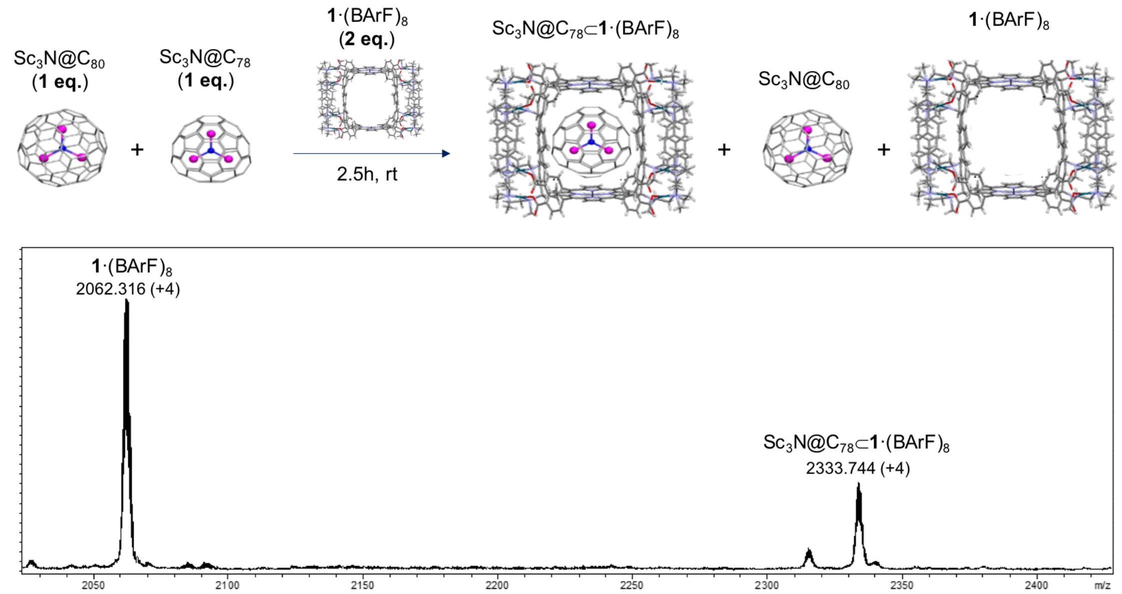


Figure S4. HRMS showing the sole encapsulation of $Sc_3N@C_{78}$ upon mixing (2.5 hours) 1 equiv. of $Sc_3N@C_{80}$ and 1 equiv. of $Sc_3N@C_{78}$ with 2 equiv. of nanocapsule $\mathbf{1}\cdot(BArF)_8$.

d(Zn···Zn)[b)]	$U_2@C_{78}$	$U_2C@C_{78}$
13.0	-41.1	-41.9
13.2	-50.6	-50.4
13.4	-56.0	-55.2
13.6	-58.2	-57.0
13.8	-58.1	-56.7
14.0	-56.6	-55.1

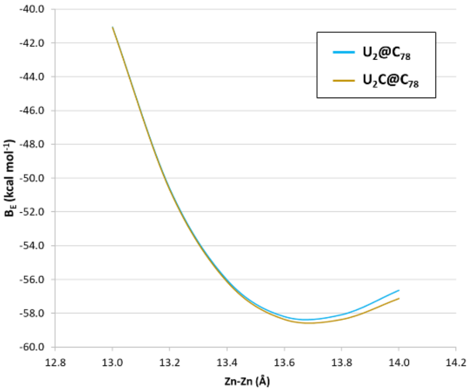
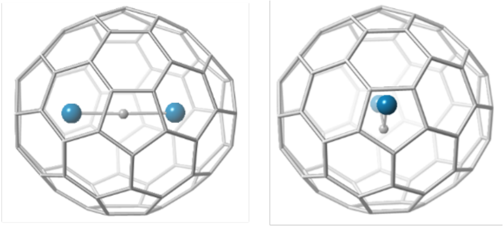


Figure S5. Energy scan and binding energies (kcal mol^{-1}) along the Zn···Zn separation maintaining porphyrins and fullerenes fixed for $U_2@D_{3h}$-C_{78} orientation **2** and $U_2C@D_{3h}$-C_{78} in the same orientation.



U-C-U angle (º)	178.4	128.8
U-C distance (Å)	2.028	2.025
ΔE (kcal mol^{-1})	0.00	49.84

Figure S6. U-C-U angle (º), U-C distance (Å) and relative energies (kcal mol^{-1}) for $U_2@D_{3h}$-C_{78} with the cluster in an almost linear form (this work) and in the geometry reported in ref [8].[9]

Supplementary References

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