

Supramolecular complexation of C₆₀ and C₇₀ by helical nanographene incorporating N-heterotriangulene and hexabenzocoronene subunits

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Contents

1. Reference MS ¹ Spectra	2
2. Breakdown graph of (HB-HBC) ₂ (C ₆₀) ⁺	3
3. MS ¹ Spectra of NTH and C ₇₀	4
4. Breakdown graphs of NTH(C ₇₀)	5
5. MS ² Spectra of NTH(C ₇₈) ²⁺	6
6. E ₅₀ values of the NTH complexes with C ₆₀ and C ₇₀	6
7. DFT calculations: complex structures	7
8. Calculated fragmentation and ionization energies	8
9. Energies and cartesian coordinates of the host-guest complexes	9
10. ¹ H-, ¹³ C-NMR spectra and crystal structure of NTH	9

1. Reference MS¹ Spectra

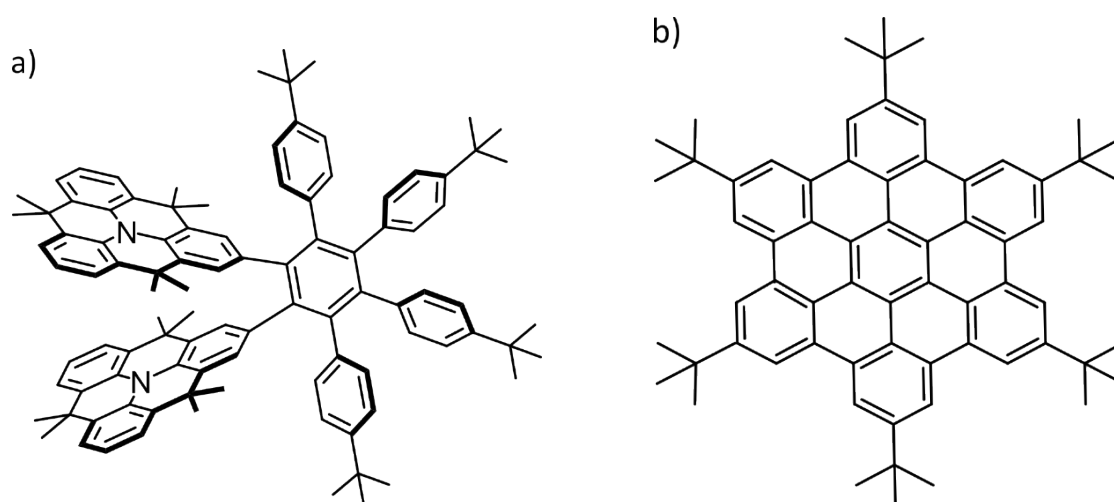


Figure S 1: Reference molecules for comparison with NTH. a) NTH precursor (M), b): hexa-tert-butyl-hexa-peri-hexabenzocoronene (HB-HBC)

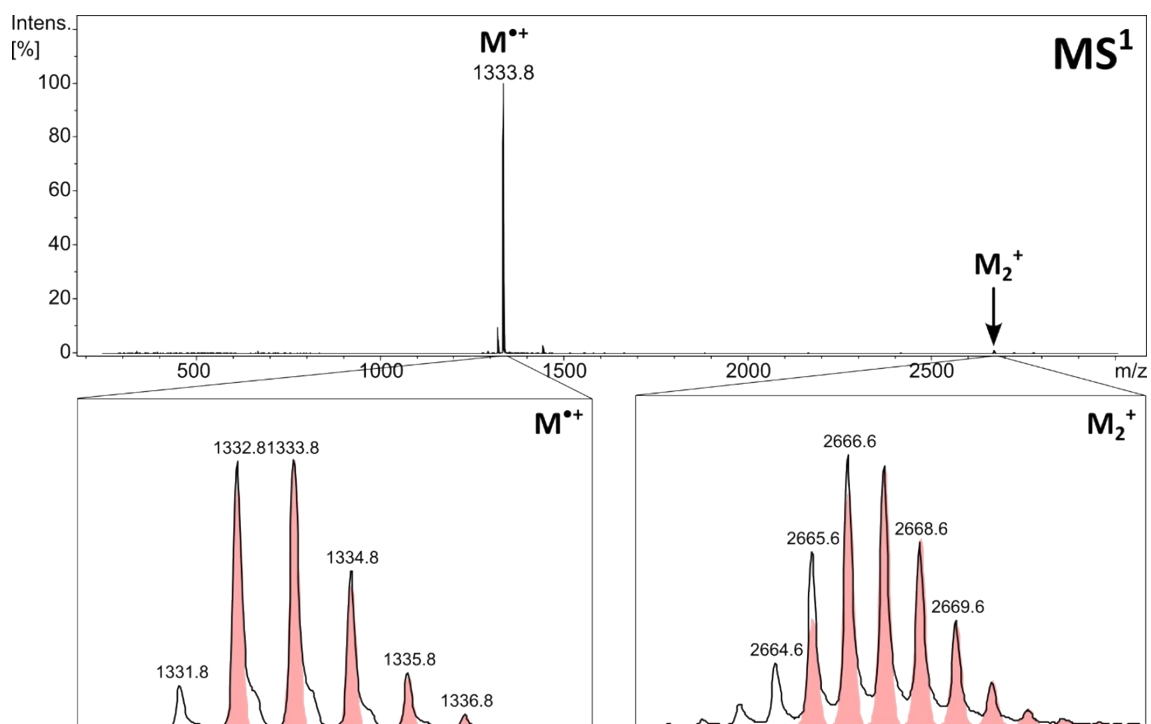


Figure S 2: MS¹ of the NTH precursor/C₆₀ analyte solution. No molecule-fullerene complexes could be observed.

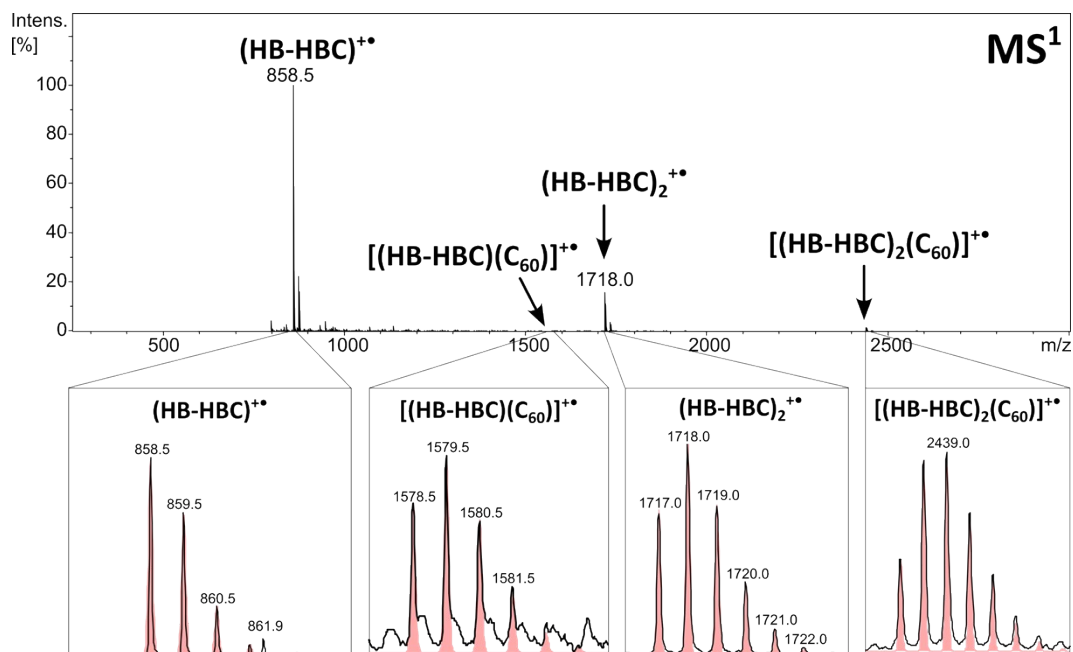


Figure S 3: MS¹ of the HB-HBC/C₆₀ analyte solution. Only minor amounts of [1:1] and [2:1] HB-HBC fullerene complex was observed in the experiment.

2. Breakdown graph of (HB-HBC)₂(C₆₀)⁺

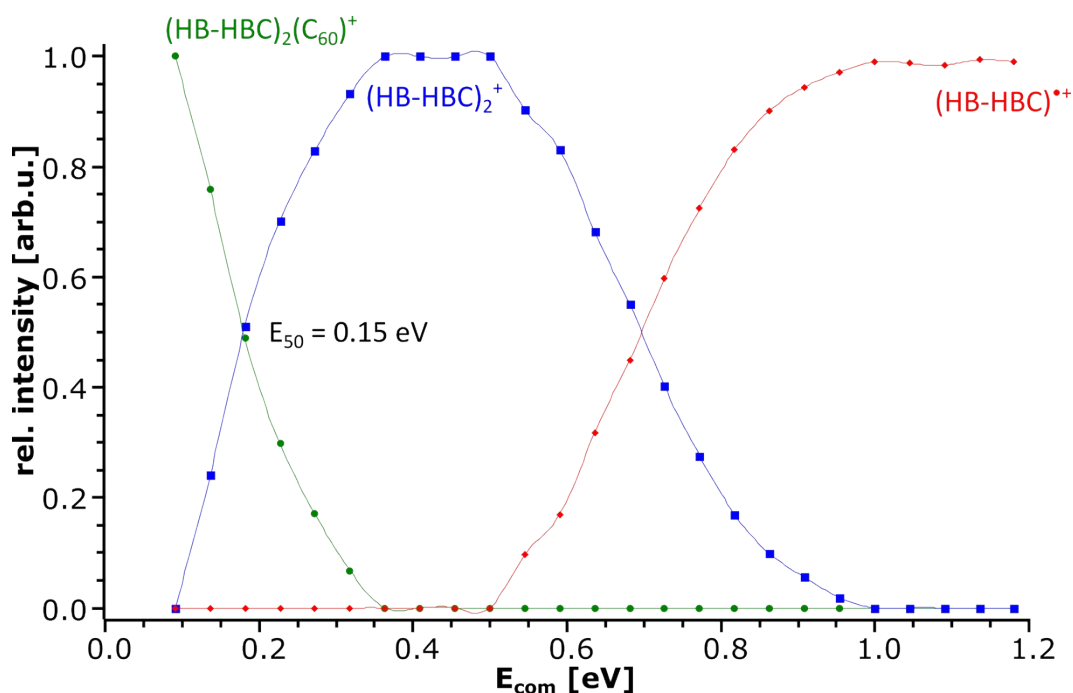


Figure S 4: Breakdown graph of the HB-HBC:C₆₀ [2:1] complex, showing the loss of neutral C₆₀ at low collision energy followed by the dissociation of the HB-HBC dimer at higher collision energy. This indicates that the C₆₀ is only loosely bound to an HB-HBC dimeric structure.

3. MS¹ Spectra of NTH and C₇₀

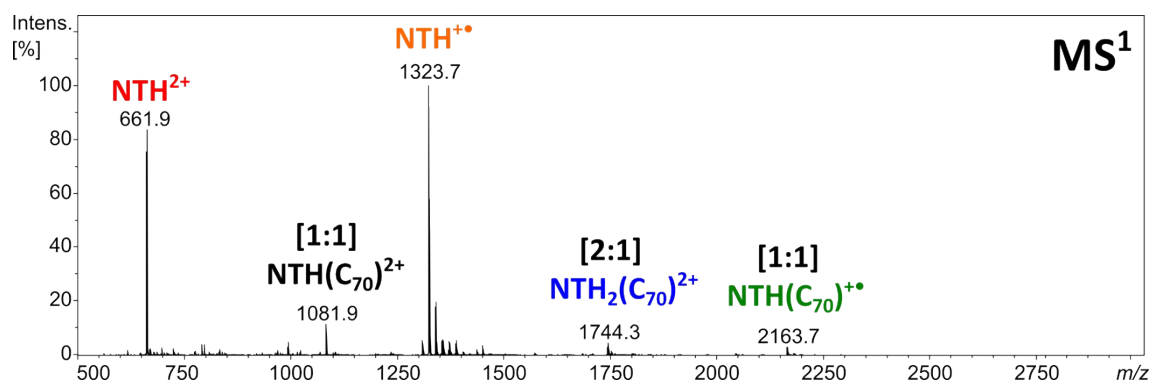


Figure S 5: MS¹ spectra of the NTH/C₇₀ analyte solution.

4. Breakdown graphs of NTH(C₇₀)

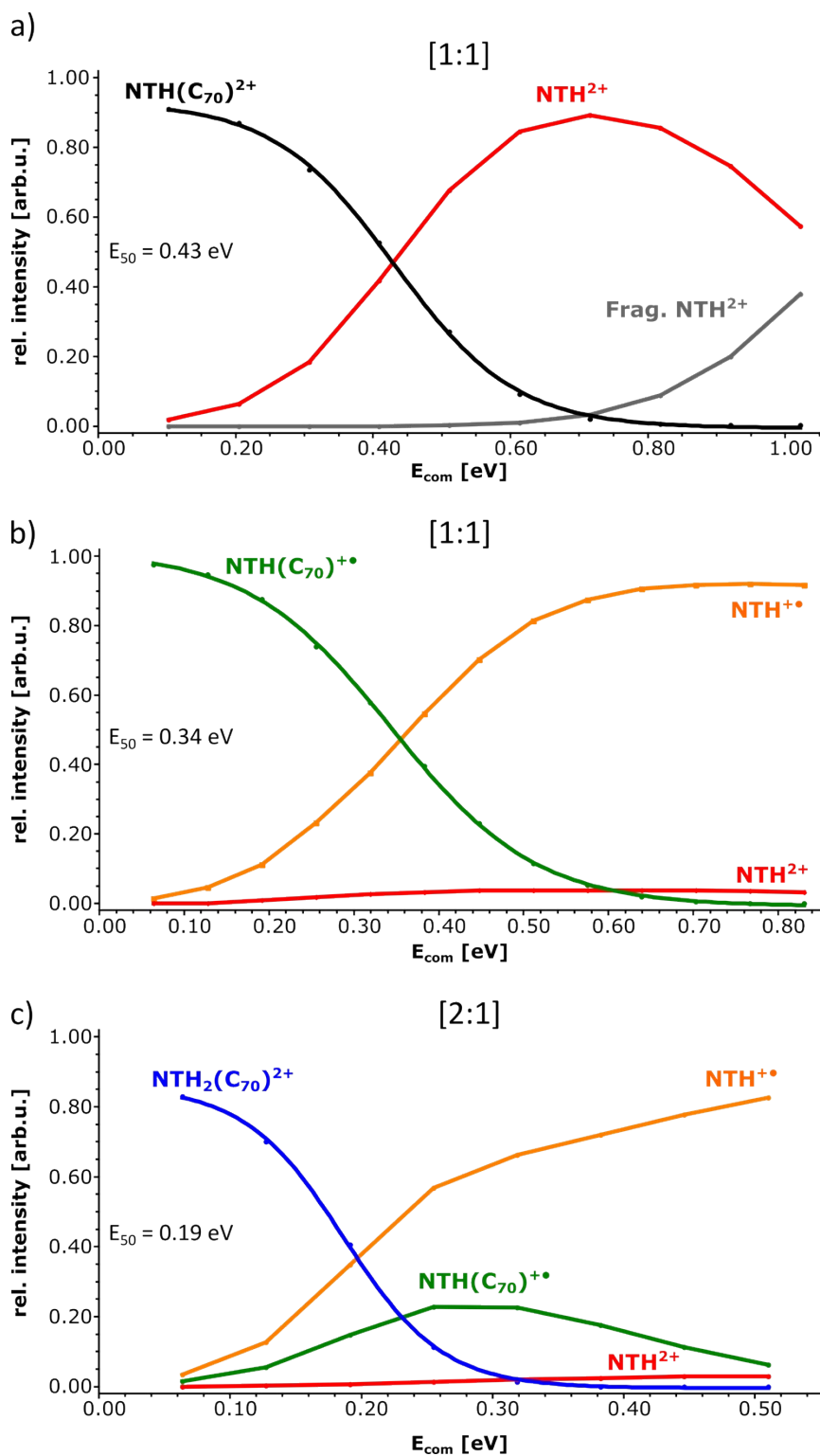


Figure S 6: Breakdown graphs of the selected NTH/C₇₀ complexes.

5. MS² Spectra of NTH(C₇₈)²⁺

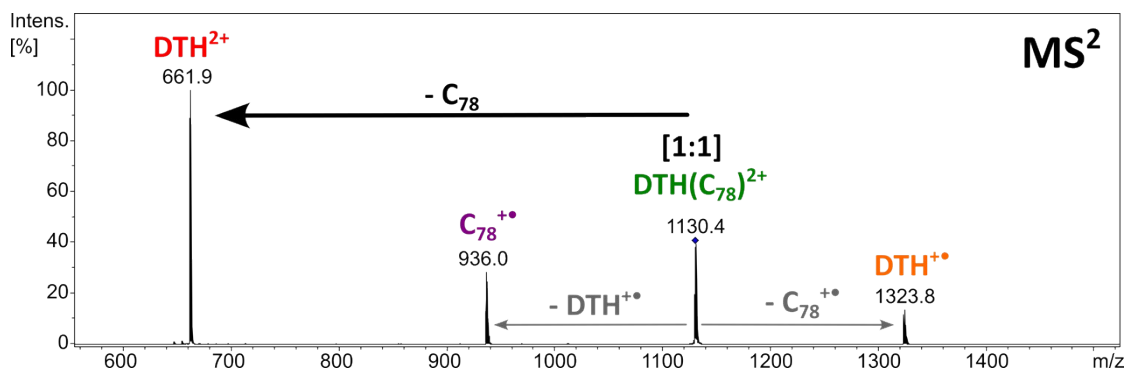


Figure S 7: MS² spectra of the doubly charged [1:1] complex of NTH and C₇₈ (m/z 1130.4). Two fragmentation processes can be observed. The loss of neutral C₇₈ (black) and the fragmentation into C₇₈^{+•} and NTH^{+•} (grey) indicate a charge transfer from the dicationic NTH to the fullerene.

6. E₅₀ values of the NTH complexes with C₆₀ and C₇₀

Table S 1: relative stability of the observed NTH/fullerene (C₆₀ and C₇₀) complexes in eV

E ₅₀ in [eV]	[1:1] NTH(C _{60/70}) ²⁺	[1:1] NTH(C _{60/70}) ⁺	[2:1] NTH ₂ (C _{60/70}) ²⁺	[1:2] NTH(C _{60/70}) ₂ ⁺	[2:3] NTH ₂ (C _{60/70}) ₃ ²⁺
C₆₀	0.31	0.28	0.15	0.18	0.18
C₇₀	0.43	0.34	0.19	---	---

7. DFT calculations: complex structures

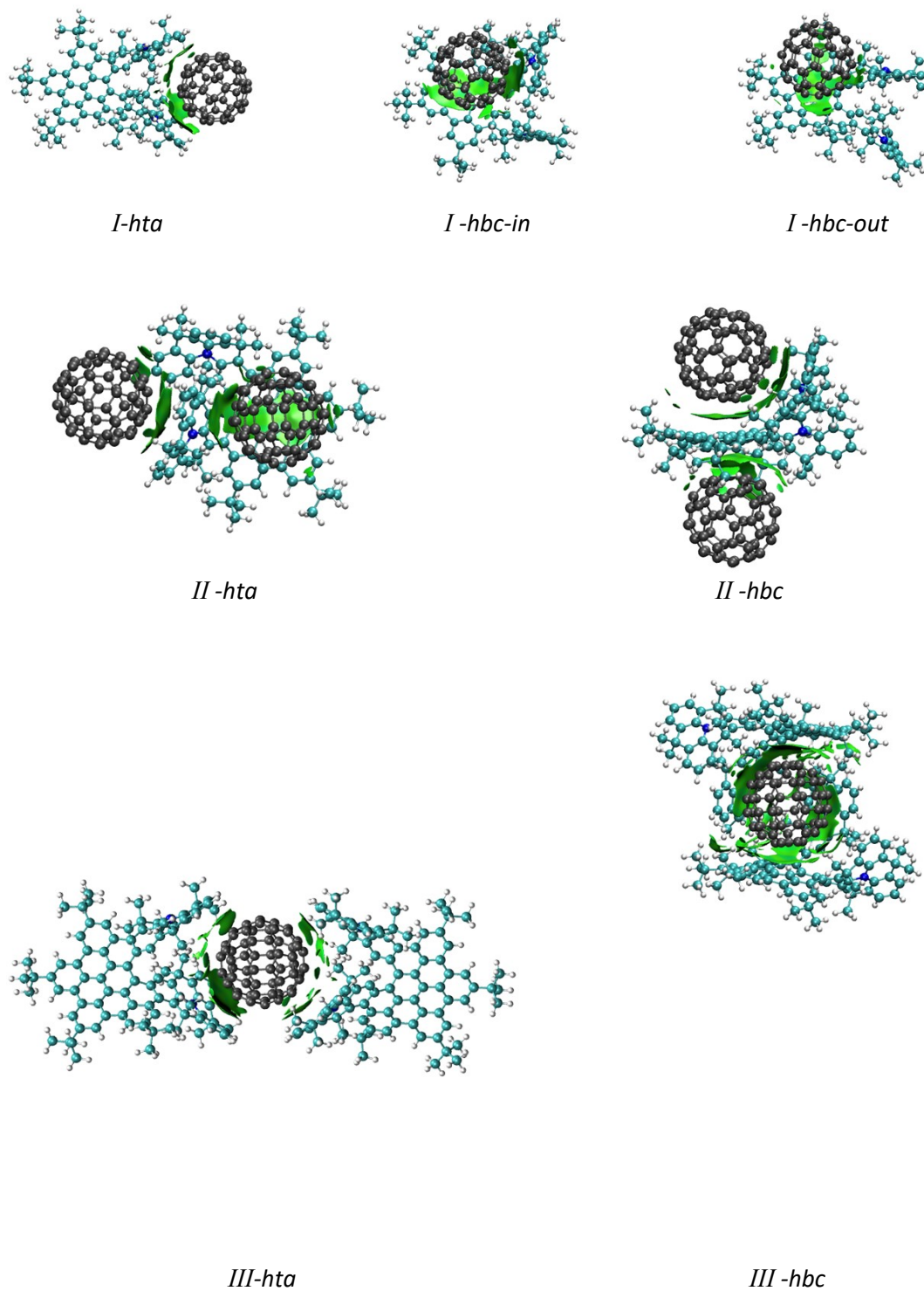


Figure S 8: structures for the [1:1] (top), [1:2] (middle) and [2:1] (bottom) NTH/C₆₀ complexes.

8. Calculated fragmentation and ionization energies

Table S 2: Fragmentation energies of NTH/C₆₀ [1:1] complexes in eV

[1:1] NTH / C ₆₀	Neutral	Monocation		Dication	
	NTH/C ₆₀	NTH ⁺ /C ₆₀	NTH/C ₆₀ ⁺	NTH ⁺ /C ₆₀ ⁺	NTH ²⁺ /C ₆₀
<i>I-hta</i>	0.90	0.88	2.95	0.79	0.96
<i>I-hbc-in</i>	1.16	1.14	3.20	1.05	1.22
<i>I-hbc-out</i>	1.08	1.07	3.13	0.45	0.63

Table S 3: Fragmentation energies of NTH/C₆₀ [2:1] complexes in eV

[2:1] NTH / C ₆₀	Neutral	Monocation			Dication	
	NTH / NTH / C ₆₀	NTH ⁺ / NTH / C ₆₀	NTH / NTH / C ₆₀ ⁺	NTH ⁺ / NTH / C ₆₀ ⁺	NTH ⁺ / NTH ⁺ / C ₆₀	NTH ²⁺ / NTH / C ₆₀
<i>II-hta</i>	1.72	2.15	4.22	2.33	0.26	2.50
<i>II-hbc</i>	3.24	3.52	5.18	3.50	1.44	3.67

Table S 4: Fragmentation energies of NTH/C₆₀ [1:2] complexes in eV

[1:2] NTH / C ₆₀	Neutral	Monocation		Dication		
	NTH / C ₆₀ / C ₆₀	NTH ⁺ / C ₆₀ / C ₆₀	NTH / C ₆₀ ⁺ / C ₆₀	NTH ⁺ / C ₆₀ ⁺ / C ₆₀	NTH ²⁺ / C ₆₀ / C ₆₀	NTH / C ₆₀ ⁺ / C ₆₀ ⁺
<i>III-hta</i>	1.97	1.91	3.97	1.30	1.47	3.36
<i>III-hbc</i>	2.20	2.18	4.24	1.67	1.84	3.73

We estimated the BSSE error for the fragmentation energies of the neutral DTH/C₆₀ complex (Table S2, first column) using the counterpoise (CP) correction method. We obtain:

I-hta: CP correction = -0.05 eV

I-hbc-in: CP correction = -0.06 eV

I-hbc-out: CP correction = -0.05 eV

Thus, the CP correction yields a nearly uniform shift of the fragmentation energies, and the relative stabilities of the complexes are unaffected.

Table S 5: Calculated vertical ionization energies (PBE/def2-TZVP)

	Ionisation energy
NTH	¹ IE = 5.33 eV
NTH	² IE = 7.49 eV
C ₆₀	¹ IE = 7.32 eV
C ₇₀	¹ IE = 7.24 eV
C ₇₈ (D3)	¹ IE = 6.63 eV
C ₇₈ (D3h)	¹ IE = 6.93 eV
C ₇₈ (D2v)	¹ IE = 6.88 eV

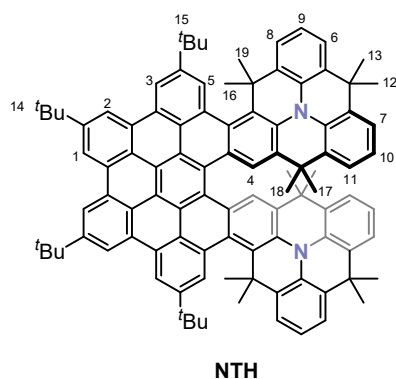
9. Energies and cartesian coordinates of the host-guest complexes

The calculated structures and energies (in Hartrees) can be found at:

<https://doi.org/10.5281/zenodo.14534357>

10. ^1H -, ^{13}C -NMR spectra and crystal structure of NTH

Nuclear Magnetic Resonance. ^1H - and ^{13}C -NMR spectra were recorded on a Bruker Avance 600 (Bruker, 601 MHz, for ^1H , 151 MHz for ^{13}C) spectrometer. Chemical shifts (δ) are reported in ppm and were referenced to the residual solvent signal as an internal reference ($(\text{CD}_3)_2\text{CO}$: 2.05 ppm for ^1H , 206.26 and 29.84 ppm for ^{13}C). Coupling constants (J) are given in Hz as observed and the apparent resonance multiplicity is reported as s (singlet), d (doublet), t (triplet), or m (multiplet). All signals of solvents and impurities are assigned according to literature.^[1] All spectra were recorded at ambient probe temperature if not otherwise stated.



N-Heterotriangulene [5]helicene (NTH).

^1H NMR (600 MHz, $(\text{CD}_3)_2\text{CO}$) δ 9.38 (s, 2H, H¹), 9.33 (s, 2H, H²), 9.24 (s, 2H, H³), 8.82 (s, 2H, H⁴), 8.30 (s, 2H, H⁵), 7.78 (dd, J = 7.6, 1.2 Hz, 2H, H⁶), 7.71 (td, J = 7.7, 1.3 Hz, 4H, H⁷, H⁸), 7.50 (t, J = 7.5 Hz, 2H, H⁹), 7.30 (t, J = 7.5 Hz, 2H, H¹⁰), 7.04 (dd, J = 7.5, 1.2 Hz, 2H, H¹¹), 1.91 (s, 6H, H¹²), 1.88 (s, 6H, H¹³), 1.82 (s, 18H, H¹⁴), 1.72 (s, 18H, H¹⁵), 1.66 (s, 6H, H¹⁶), 1.33 (s, 6H, H¹⁷), 1.03 (s, 6H, H¹⁸), 0.78 (s, 6H, H¹⁹) ppm.

^{13}C NMR (151 MHz, $(\text{CD}_3)_2\text{CO}$) δ 150.6, 146.5, 141.3, 134.1, 132.3, 131.94, 131.86, 131.85, 131.7, 131.4, 131.1, 130.7, 129.6, 128.7, 128.4, 127.4, 126.8, 126.3, 126.0, 125.1, 125.0, 124.7, 124.1, 123.9, 123.6, 123.5, 123.1, 121.44, 121.36, 120.1, 120.5, 119.9, 119.7, 41.0, 36.5, 36.2, 36.1, 35.90, 35.87, 35.8, 34.3, 34.2, 32.3, 32.1, 30.4, 24.4 ppm.

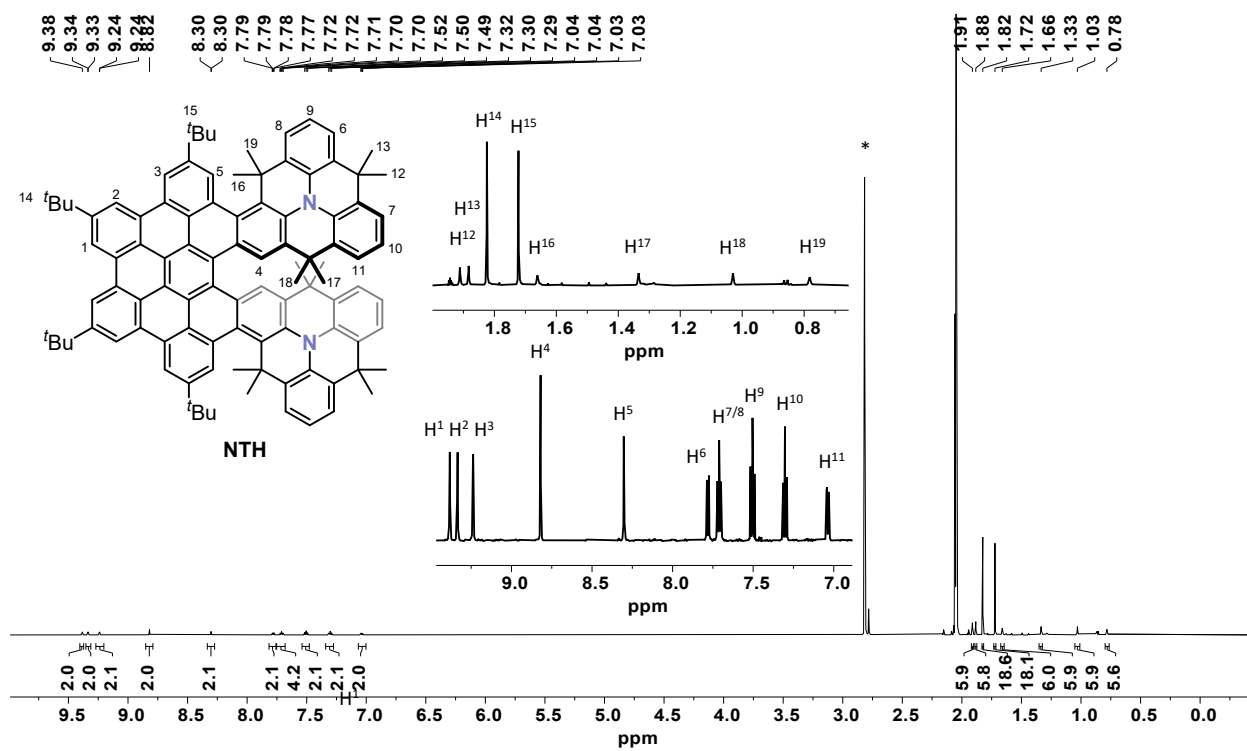


Figure S9:: ¹H NMR spectrum (601 MHz, (CD₃)₂CO) of NTH; * H₂O.

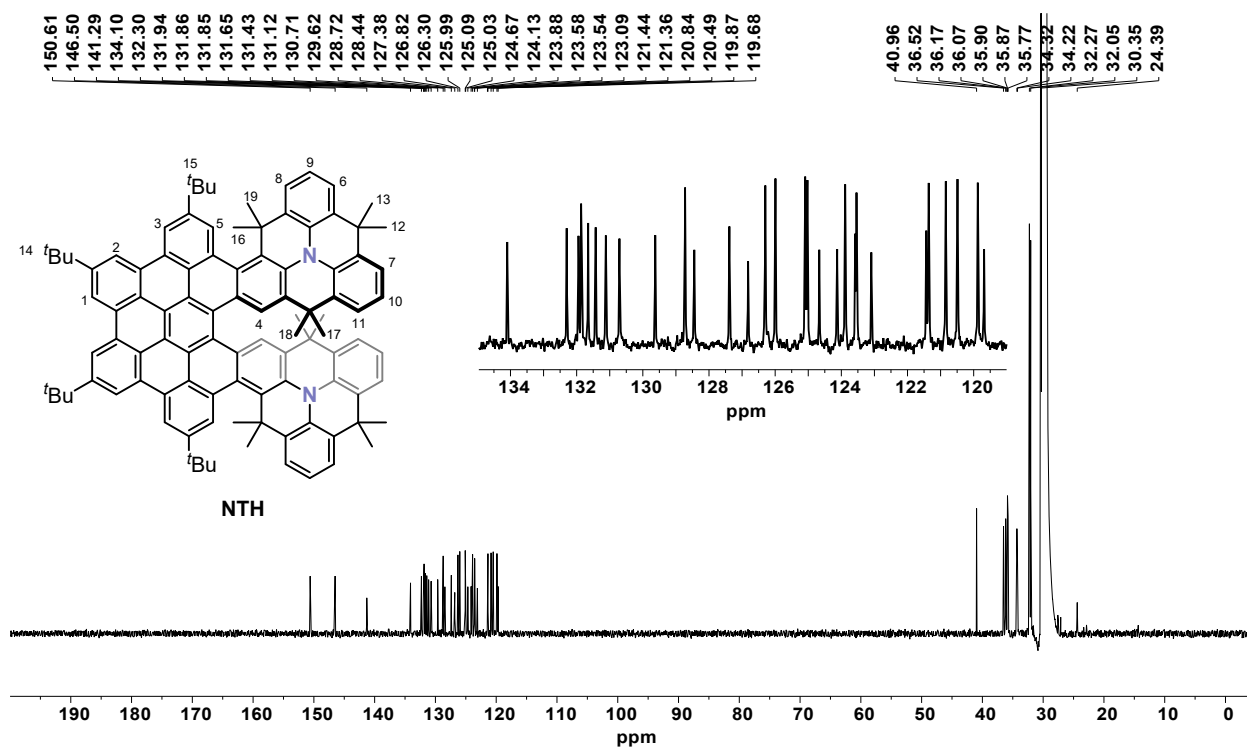


Figure S10: ¹³C NMR spectrum (151 MHz, (CD₃)₂CO) of **NTH**.

[1] H. E. Gottlieb, V. Kotlyar, A. Nudelman, *J. Org. Chem.* **1997**, *62*, 7512.

Deposition number CCDC 2406553 contains the supplementary crystallographic data for **NTH**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures.