

## Supporting Information

### A Persistent Concealed Non-Kekulé Nanographene: Synthesis and in-situ Characterization

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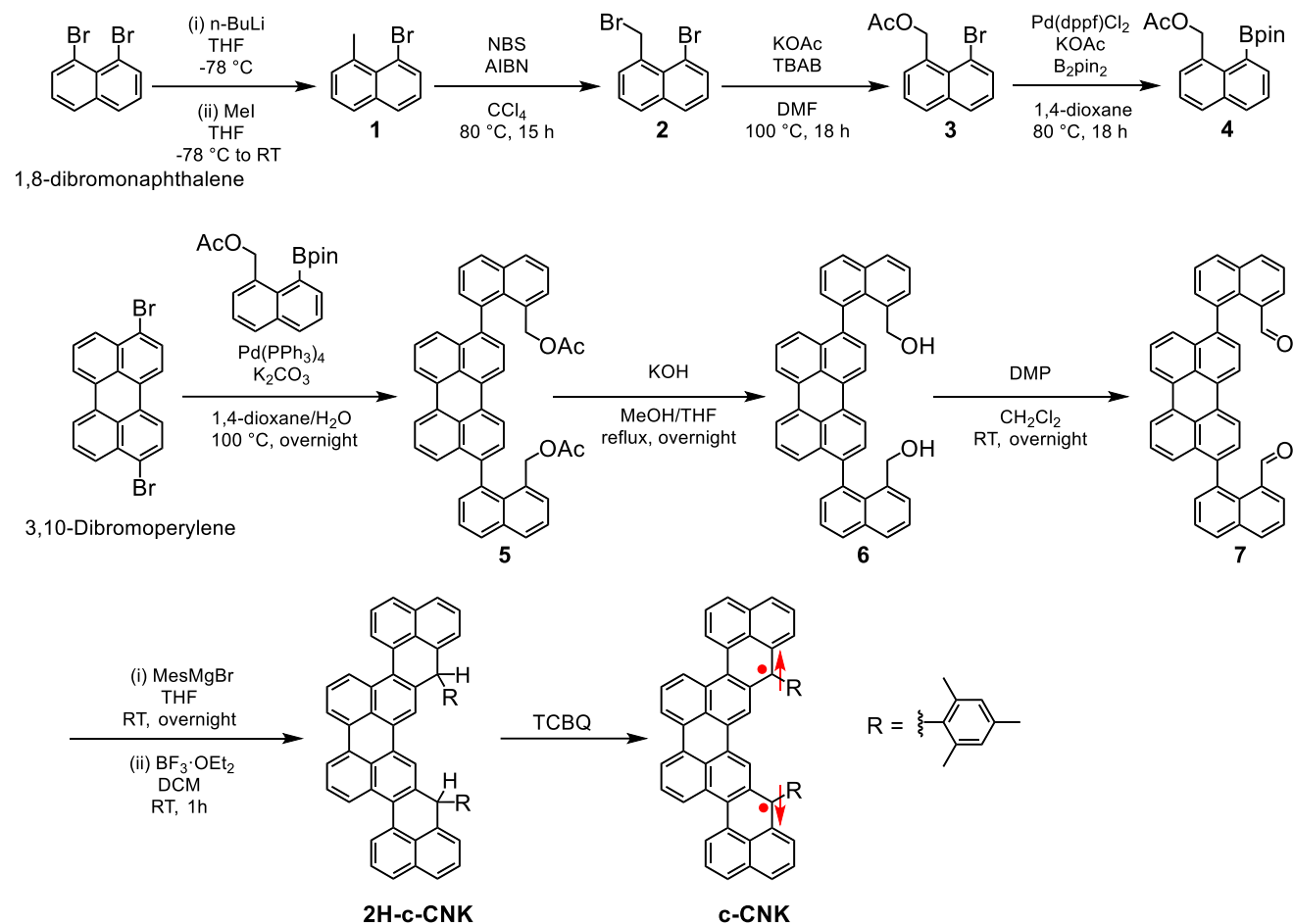
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## I. General Synthetic Methods

Unless otherwise noted, commercially available starting materials, reagents, catalysts, and dry solvents were used without further purification. Reactions were performed using standard vacuum-line and Schlenk techniques. All starting materials were obtained from TCI, Sigma Aldrich, BLD, Alfa Aesar, Acros Organics, or Fluorochem. Catalysts were purchased from Strem. All reactions dealing with air- or moisture-sensitive compounds were carried out in a dry reaction vessel under argon (Ar) atmosphere using standard vacuum-line and Schlenk techniques. Anhydrous dichloromethane was obtained from MBRAUN MB-SPS-5 solvent purification system. Column chromatography was performed on silica (SiO<sub>2</sub>, particle size 0.063-0.200 mm, purchased from VWR). Silica-coated aluminum sheets with a fluorescence indicator (TLC silica gel 60 F254, purchased from Merck KGaA) were used for thin-layer chromatography. Recycling gel permeation chromatography (rGPC) was carried out on a Japan Analytical Industry JAI-HPLC LC 9110 II Next equipped with a JAIGEL-2HH and a JAIGEL-1HH column. Chloroform was used as the eluent in a flow rate of 5 mL/min. NMR data were recorded both on a Bruker AV-II 300 spectrometer operating at 300 MHz for <sup>1</sup>H and 75 MHz for <sup>13</sup>C. The <sup>1</sup>H NMR titration experiment was performed in toluene-d<sub>8</sub> at 30 °C. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, t = triplet and m = multiplet. High-resolution matrix-assisted laser desorption/ionization time-of-flight mass spectra (HR-MALDI-TOF MS) were recorded on a Bruker Autoflex Speed MALDI-TOF MS (Bruker Daltonics, Bremen, Germany). All of the samples were prepared by mixing the analyte and the matrix trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile (DCTB, purchased from Sigma Aldrich, purity > 99%) in the solid state. UV-visible (UV-Vis) spectra were measured on an Agilent Cary 5000 UV-VIS-NIR spectrophotometer by using 10 mm optical-path quartz cell at room temperature. EPR measurements were performed using a CW X-band EMXplus spectrometer with a premiumX microwave bridge (Bruker, Germany) and a high-sensitivity resonator (ER 4119 HS, Bruker). The EPR spectra were registered at 100 kHz modulation and the microwave power of 2 mW. For the precise determination of g-values, an NMR teslameter (ER036TM, Bruker) was used. Variable-temperature EPR measurements were performed using an integrated variable temperature controller.

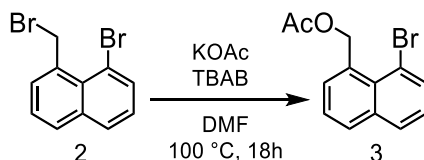
## II. Synthetic Procedures and Characterization

Compounds **1** and **2** were synthesized as reported in the literature report. [S1]



Scheme S1. Synthesis scheme for *c*-CNK and all the intermediate compounds.

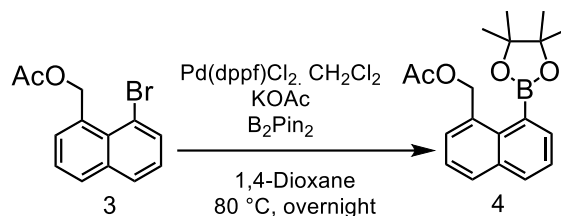
### (8-bromonaphthalen-1-yl)methyl acetate (**3**)



To a mixture of 1-bromo-8-(bromomethyl)naphthalene (**2**, 5 g, 16.7 mmol), KOAc (8.18g, 83.3 mmol) and tetra-*n*-butylammonium bromide (2.69 g, 8.33 mmol) were dissolved in 70 mL DMF under Argon atmosphere. The mixture was heated at  $100^\circ\text{C}$  for 18 h. After cooling to room

temperature, 30 mL of ammonium chloride solution was added to the reaction mixture. The mixture was extracted with DCM. The combined organic extracts were dried over MgSO<sub>4</sub>. The solvent was removed under vacuum and the residue was used directly for the next step.

**(8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-yl)methyl acetate (4)**



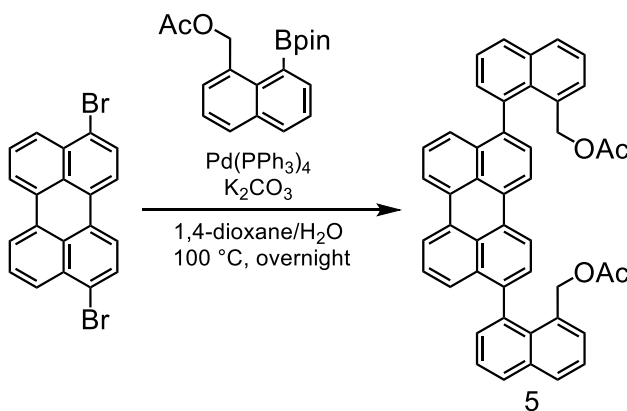
A mixture of compound (8-bromonaphthalen-1-yl)methyl acetate (**3**, 2 g, 7.17 mmol), B<sub>2</sub>pin<sub>2</sub> (2.73 g, 10.8 mmol), K<sub>2</sub>CO<sub>3</sub> (1.41 g, 14.3 mmol) and Pd(dppf)Cl<sub>2</sub>·CH<sub>2</sub>Cl<sub>2</sub> (585.1 mg, 0.72 mmol) was added to a 25 mL Schlenk flask, and degassed with Ar for 30 min. Then, degassed 1,4-dioxane (15 mL) was added via syringe. The reaction mixture was stirred at 80 °C overnight. After being cooled to room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography (silica gel, isohexane/EtOAc = 10/1 to 5/1) to afford the product (8-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)naphthalen-1-yl)methyl acetate (**4**, 72%, over two steps).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.92–7.89 (d, 1H), 7.83–7.80 (m, 2H), 7.62–7.58 (d, 1H), 7.49–7.42 (m, 2H) 2.08 (s, 3H), 1.45 (s, 12H).

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) 170.91, 134.28, 133.94, 133.21, 131.57, 129.98, 127.56, 125.19, 124.83, 84.53, 83.64, 77.58, 77.16, 76.74, 66.61, 25.17, 25.13, 21.29.

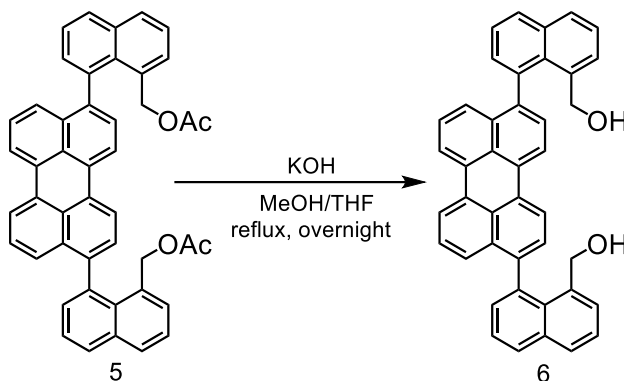
HR-ESI-MS (m/z): Calc. for [M+Na<sup>+</sup>]. 349.1587 found, 349.1583

**Synthesis of the intermediate compound 5**



3,10-dibromoperylene (500 mg, 1.22 mmol)  $K_2CO_3$  (1.68 g, 12.2 mmol) and  $Pd(PPh_3)_4$  (140.9 mg, 0.122 mmol) was added to a 100 mL Schlenk flask, and degassed with Ar for 30 min. Then, degassed 1,4-dioxane/ $H_2O$  (10/1, 66 mL) was added via syringe. The reaction mixture was stirred at 100 °C for 18 h. After being cooled to room temperature, the solvent was removed under reduced pressure, and the residue was subjected to column chromatography to afford the mixture of **5** (48%, yellow solid), which was used directly for next step.

### Synthesis of the intermediate compound **6**



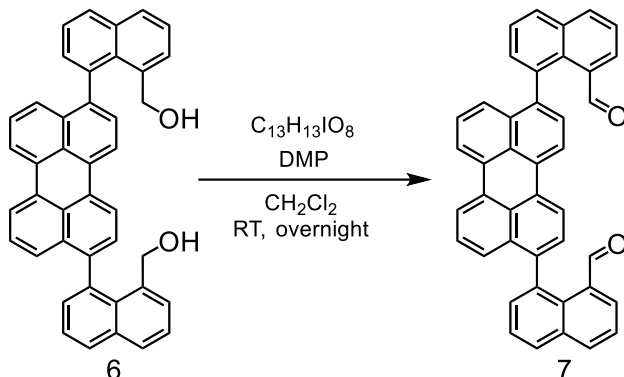
Compounds **5** (200 mg, 0.308 mmol), KOH (345.9 mg, 6.17 mmol) were dissolved in MeOH/THF (1/1, 10 mL) under argon atmosphere. The mixture was refluxed overnight. After cooling down to room temperature, the solvent was removed under vacuum to get crude product. The residue was subjected to column chromatography (silica gel, isohexane/DCM/EtOAc = 10/1/1 to 4/1/1) to afford the product (perylene-3,10-diylbis(naphthalene-8,1-diyl))dimethanol **6** (43%, yellow solid).

$^1H$  NMR (300 MHz,  $CDCl_3$ ) 8.36–8.22 (m, 4H), 8.03–8.00 (d, 2H), 7.97–7.94 (d, 2H), 7.69–7.66 (d, 2H), 7.62–7.52 (m, 6H), 7.46–7.43 (d, 2H), 7.43–7.31 (m, 2H), 7.23–7.20 (d, 2H), 4.43–4.38 (d, 2H), 4.18–4.13 (d, 2H).

$^{13}C$  NMR 75 MHz,  $CDCl_3$ ) 141.97, 141.93, 137.88, 136.95, 135.18, 134.46, 131.66, 131.52, 131.34, 131.19, 130.76, 130.52, 129.73, 129.37, 128.63, 127.95, 127.31, 126.97, 126.51, 125.88, 125.08, 120.94, 120.77, 120.06, 119.90, 77.58, 77.16, 76.74, 64.30.

HR-MS MALDI-TOF (m/z): calc. 564.2083 found, 564.2068

## Synthesis of the intermediate compound 7



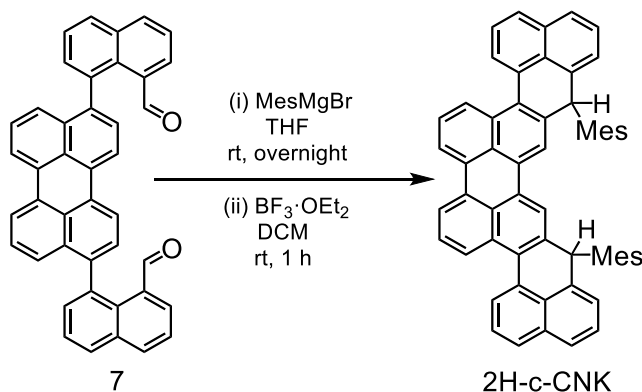
Compound **6** (10 mg, 17.7  $\mu$ mol), and Dess-Martin oxidant (18.1 mg, 42.5 mmol) were dissolved in DCM (2 mL) under air atmosphere. The mixture was stirred at room temperature overnight. Then,  $NaHCO_3$  was added to quench the reaction, the solvent was removed under vacuum to get a crude product. The residue was subjected to column chromatography (silica gel, isohexane/DCM = 1/1 to 2/3) to afford the product 8,8'-(perylene-3,10-diyl)bis(1-naphthaldehyde) **7**, (41%, yellow solid).

$^1H$  NMR (300 MHz,  $C_2D_2Cl_4$ ) 9.51–9.45 (d, 2H), 8.29–8.22 (m, 4H), 8.16–8.13 (d, 2H), 8.04–8.01 (m, 2H), 7.85–7.81 (m, 2H), 7.68–7.64 (m, 4H), 7.59–7.54 (m, 2H), 7.47–7.44 (m, 4H), 7.40–7.35 (m, 2H).

$^{13}C$  NMR (75 MHz,  $C_2D_2Cl_4$ ) 192.20, 192.02, 140.71, 136.35, 134.93, 134.64, 133.08, 131.47, 131.31, 131.24, 129.27, 129.14, 128.84, 127.62, 126.32, 126.22, 125.59, 121.43, 120.61, 120.34, 74.31, 74.20, 73.94, 73.58.

HR-MS MALDI-TOF (m/z): calc. 560.1781, found 560.1795

## Synthesis of the precursor compound 2H-c-CNK



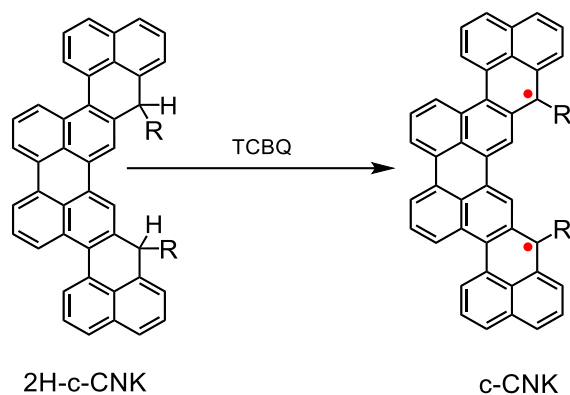
To a solution of compound **7** (10 mg, 17.8  $\mu\text{mol}$ ) in 7.5 mL of dry THF, mesityl magnesium bromide (0.178 mL, 1M in diethylether, 178  $\mu\text{mol}$ ) was added under an argon atmosphere and the reaction mixture was stirred at room temperature for overnight. Then the reaction mixture was poured into 50 mL water and extracted by DCM. The organic layer was dried over anhydrous  $\text{MgSO}_4$  and the solvent was removed under reduced pressure. The residue was redissolved in 15 mL of dry DCM under argon atmosphere and 0.5 mL of  $\text{BF}_3 \cdot \text{OEt}_2$  was added at 0  $^\circ\text{C}$  dropwise. The mixture was stirred for 1 h at room temperature and quenched with water at 0  $^\circ\text{C}$ . Then the reaction mixture was washed with  $\text{NaHCO}_3$  solution (3x20 mL) and brine and dried over anhydrous  $\text{MgSO}_4$ . The solvent was removed under reduced pressure. After a flash column, the residue was purified by preparative TLC (isohexane/DCM = 5/1) to get the target compound **2H-c-CNK** (9.2 mg, 68%).

$^1\text{H}$  NMR (300 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.64 (d, 8.6 Hz, 2H; 8), 8.26 (d, 7.5 Hz, 2H; 10), 8.26 (d, 7.4 Hz, 2H; 7), 7.81 (d, 8.1 Hz, 2H; 5), 7.71 (d, 8.2 Hz, 2H; 4), 7.58 (t, 8.2 Hz, 2H; 6), 7.55 (dd, 8.5 Hz, 2H; 9), 7.35 (t, 8.1 Hz, 2H; 3), 7.23 (s, 2H; 11), 7.21 (m, 2H), 6.90 (m, 2H; 2), 6.79 (m, 2H), 6.06 (m, 2H; 1), 2.45 (s, 6H), 2.37 (s, 6H), 1.49 (s, 6H).

$^{13}\text{C}$  NMR (75 MHz,  $\text{CD}_2\text{Cl}_2$ ) 138.95, 137.80, 136.51, 136.40, 133.94, 131.42, 130.34, 128.66, 127.36, 126.56, 126.28, 126.13, 125.52, 125.25, 125.14, 123.03, 120.49, 120.33, 54.15, 53.79, 53.43, 53.07, 52.71, 44.30, 29.68, 20.83, 20.76.

HR-MS MALDI-TOF (m/z): calculated for  $\text{C}_{64}\text{H}_{44} [\text{M}]^+$ , 764.3443; found, 764.3451.

### In-situ synthesis of c-CNK



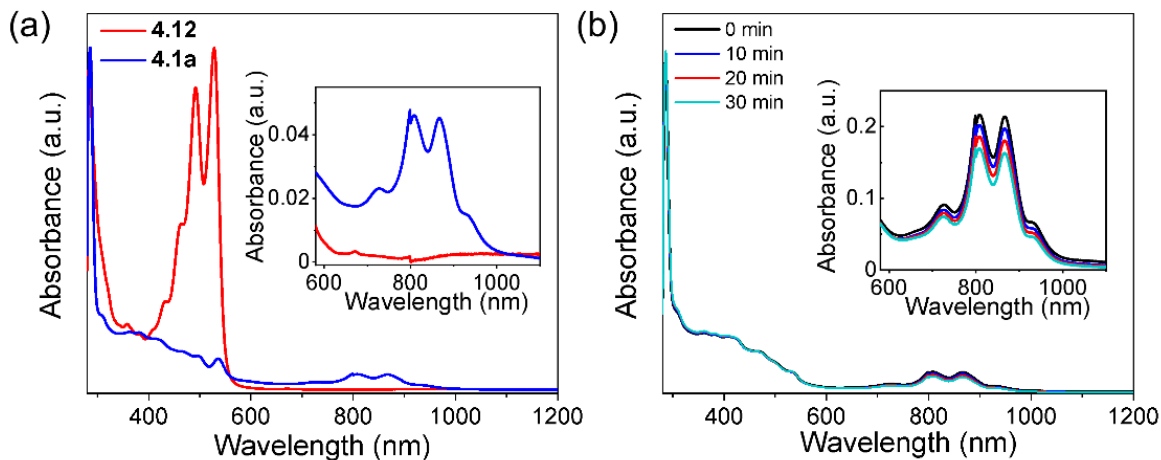
To a degassed solution of **2H-c-CNK** (10mg) in toluene (3mL) at 100  $^\circ\text{C}$  was added TCBQ (1eq, 3.21mg). The reaction mixture was stirred for 6 hours. The reaction was monitored by UV-Vis-NIR spectroscopy and MALDI-TOF mass analysis.

HR-MS MALDI-TOF (m/z): calculated for  $\text{C}_{64}\text{H}_{44} [\text{M}]^+$ , 762.3272; found, 762.3281.



### III. UV-Vis-NIR Absorption spectroscopy

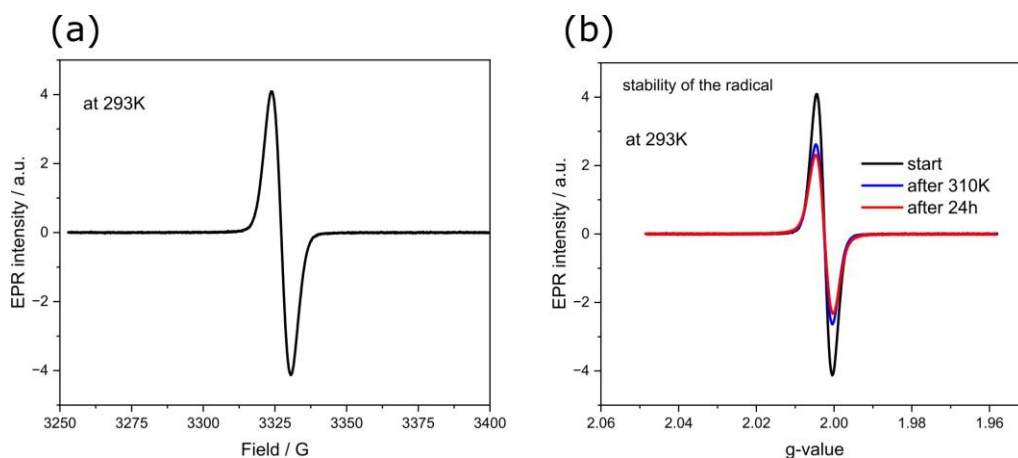
UV-Vis-NIR spectral data were measured at room temperature (298 K) with a Varian Cary 5000 spectrophotometer. All solvents used for solution samples were dried and degassed before use. Wavelengths are shown in nanometers (nm), and absorption is reported in arbitrary units (normalized).



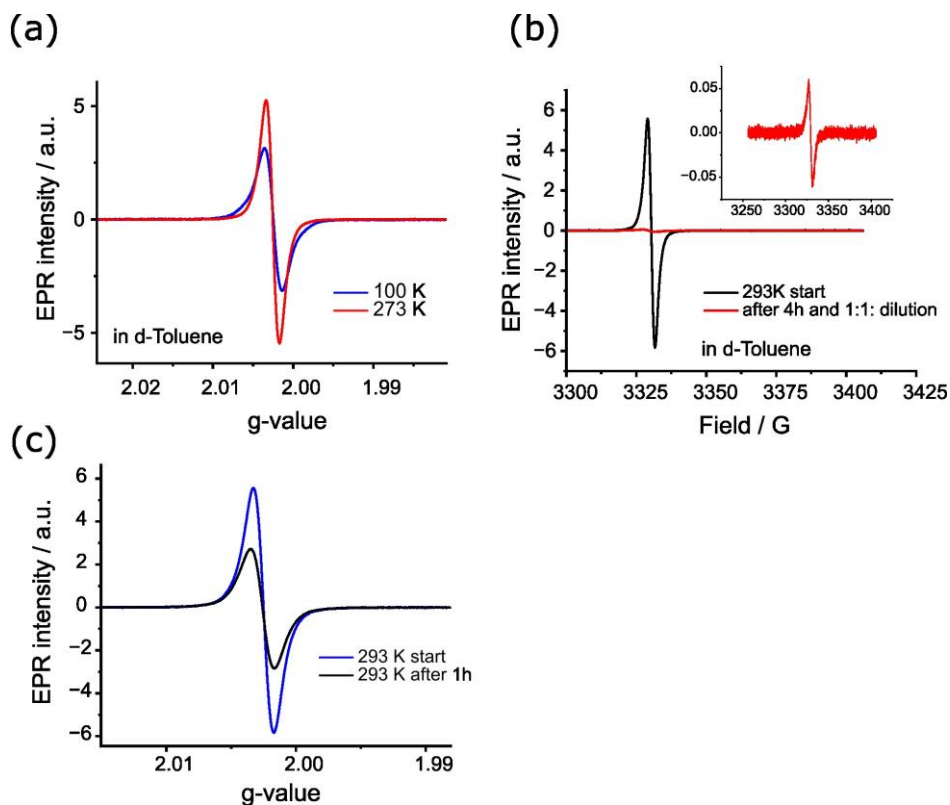
**Figure S1.** (a) UV-Vis-NIR absorption spectra of compounds **c-CNK** and the precursor **2H-c-CNK**. (b) Time-dependent UV-Vis-NIR absorption spectra of compound **c-CNK**. The spectra were recorded in dry and degassed DCM under ambient air and light irradiation.

## IV. EPR spectroscopy

The compound **c-CNK** exhibits a strong EPR signal with a  $g$  value of 2.0026 at 293K.



**Figure S2.** (a) EPR spectrum of in-situ generated **c-CNK** at 293 K. (b) EPR spectrum of in-situ generated **c-CNK** at the beginning of experiment at 293 K, after 24 h at 293K and at slightly higher temperature 310K. The EPR signal intensity is lower both at 310K and after 24h due to possible degradation of the **c-CNK** due to its high reactivity.

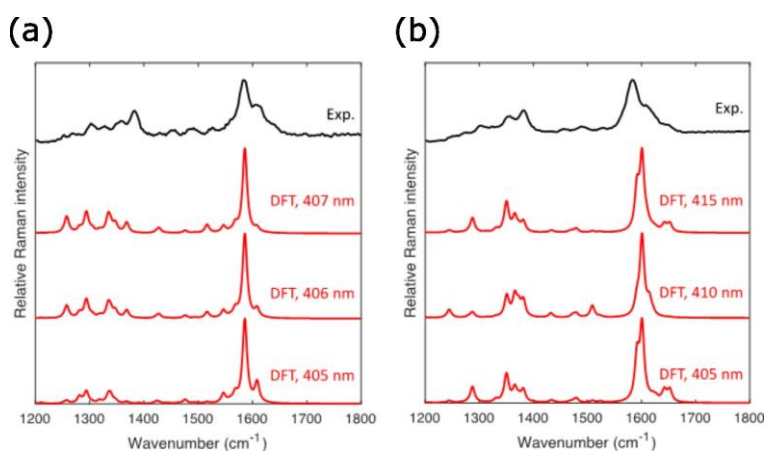


**Figure S3.** (a) EPR spectrum of **c-CNK** (2mM) in *d*-toluene formed at 100K and 273K (b) EPR spectrum of **c-CNK** (2mM) at the start of experiment and after four hours (c) EPR spectrum of **c-CNK** (2mM) at 293K at the start and after one hour in *d*-toluene.

## V. Raman spectroscopy

The reported spectra were recorded using an HR800 UV dispersive Raman HORIBA Jobin-Yvon instrument coupled to an Olympus BX41 optical microscope and a Peltier-cooled CCD. The excitation line was 405 nm. A film of the samples was deposited on brass from a dichloromethane solution. The measurements were carried out in micro-Raman mode with a spot size of about 1 micron, focusing the laser on the sample using a 50x objective with a numerical aperture of 0.75. The laser power on the sample varied from 0.01 mW to 0.1 mW. The single accumulation time was 20 seconds, and each Raman spectrum was the result of the average of two accumulations. To minimize unwanted photodegradation effects, during the measurements, the sample was translated with the micro stage of the instrument at a constant focusing distance.

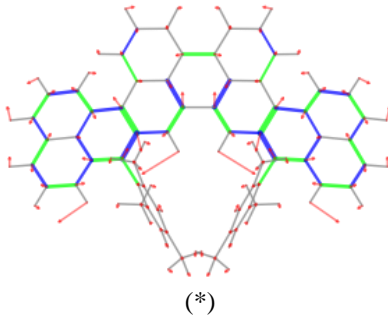
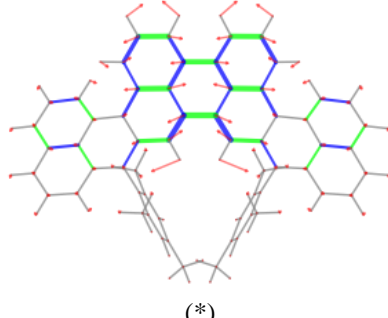
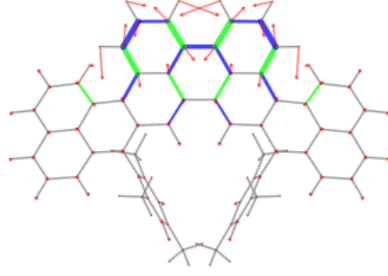
Density-functional theory (DFT) calculations were performed at the CAM-B3LYP/6-311G(d,p) level on gas-phase molecular models of **2H-c-CNK** and **c-CNK**. We used the Gaussian code [S2]. After verifying that **c-CNK** decreases its energy by more than 35 kcal/mol when optimized with broken symmetry unrestricted calculations as opposed to closed-shell calculations, we continued the investigation of the Raman spectra by considering unrestricted calculations. In these conditions, the triplet state of **c-CNK** is higher in energy than the singlet state by about 0.9 kcal/mol. Therefore, we limited ourselves to analyzing the simulated Raman spectra for the unrestricted broken symmetry singlet states. The Raman intensities were computed for finite excitation wavelengths in the range 405 – 415 nm. Resonance Raman spectra were simulated from the intensities computed by DFT after complete geometry optimization. We applied a scaling factor of 0.97 to the wavenumbers of the computed vibrational normal modes to account for the known systematic overestimation of wavenumbers produced by DFT. The value of the scaling factor was determined through a least-square regression performed on selected pairs of experimental and computed peaks of **2H-c-CNK**.



**Figure S4.** (a) Resonance Raman spectra of **c-CNK**; (b) Resonance Raman spectra of **2H-c-CNK**. Each spectrum has been normalized to unity. Experimental (black lines) and computed (red lines). Computed spectra are labeled with the excitation wavelength considered in the calculation.

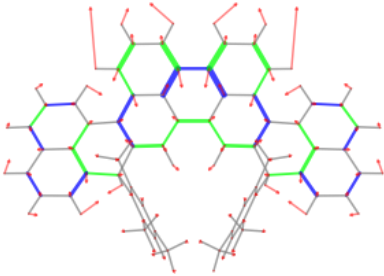
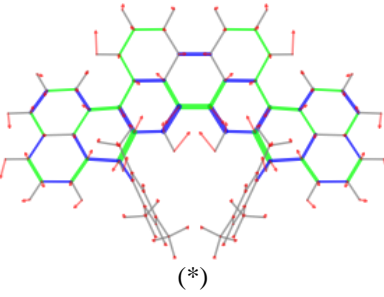
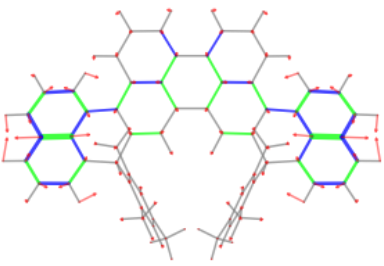
**Table S1**

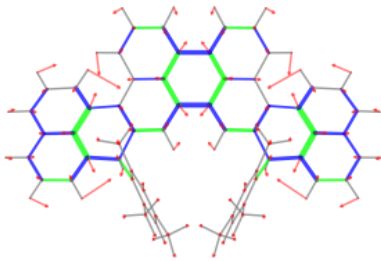
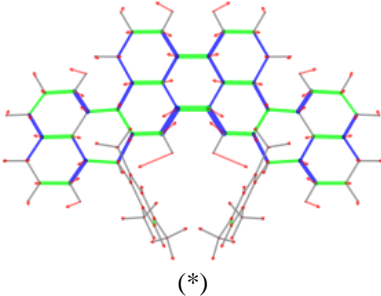
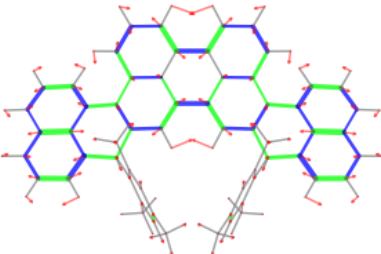
Representation of the vibrational modes of **c-CNK** associated to the Raman peaks mentioned in the main text. In the first column, the wavenumber computed by DFT; in the second column, the DFT wavenumber multiplied by the shift factor; in the third column, the correspondent experimental peak position; in the fourth column, the computed Raman activity; in the fifth column, a cartoon representing the computed vibrational normal mode, where the green and blue segments. Cartoons indicated with (\*) are referred to in the main text.

DFT wavenumber (cm <sup>-1</sup> )	Scaled DFT wavenumber (cm <sup>-1</sup> )	Experimental peak position (cm <sup>-1</sup> )	Computed Raman activity (Å <sup>4</sup> /amu; $\lambda_{exc} = 406 \text{ nm}$ )	Computed vibrational mode
1410	1368	1383	$2.0 \cdot 10^6$	 (*)
1635	1586	1582	$2.1 \cdot 10^7$	 (*)
1658	1608	1607	$2.2 \cdot 10^6$	

**Table S2**

Representation of the vibrational modes of **2H-c-CNK** associated to the Raman peaks mentioned in the main text. In the first column, the wavenumber computed by DFT; in the second column, the DFT wavenumber multiplied by the shift factor; in the third column, the correspondent experimental peak position; in the fourth column, the computed Raman activity; in the fifth column, a cartoon representing the computed vibrational normal mode, where the green and blue segments represent stretching and contracting bonds, respectively, and the red arrows represent nuclear displacements. Cartoons indicated with (\*) are referred to in the main text.

DFT wavenumber (cm <sup>-1</sup> )	Scaled DFT wavenumber (cm <sup>-1</sup> )	Experimental peak position (cm <sup>-1</sup> )	Computed Raman activity (Å <sup>4</sup> /amu; λ <sub>exc</sub> = 410 nm)	Computed vibrational mode
1391	1349	1357	6.4 · 10 <sup>7</sup>	
1408	1366	1383	1.5 · 10 <sup>9</sup>	
1415	1373	1383	8.2 · 10 <sup>8</sup>	

1424	1381	1383	$1.2 \cdot 10^9$	
1650	1601	1582	$5.8 \cdot 10^9$	
1664	1614	1607	$1.1 \cdot 10^9$	

## VI. Single Crystal XRD

Crystal data and structure refinement for **2H-c-CNK**.

Bond precision: C-C = 0.0030 Å

Wavelength = 1.54184

Cell: a = 9.2019(2) b = 13.3162(2) c = 20.6547(4)

Alpha = 90 beta = 94.599(2) gamma = 90

Temperature: 100 K

	<b>Calculated</b>	<b>Reported</b>
Volume	2522.76(8)	2522.76(8)
Space group	P 2/n	P 1 2/n 1
Hall group	-P 2yac	-P 2yac
Moiety formula	C <sub>60</sub> H <sub>44</sub> , 2(C <sub>6</sub> H <sub>5</sub> Cl)	C <sub>6</sub> H <sub>5</sub> Cl, C <sub>30</sub> H <sub>22</sub>
Sum formula	C <sub>72</sub> H <sub>54</sub> Cl <sub>2</sub>	C <sub>36</sub> H <sub>27</sub> Cl
Mr	990.05	495.02
Dx, g cm <sup>-3</sup>	1.303	1.303
Z	2	4
Mu (mm <sup>-1</sup> )	1.505	1.505
F000	1040.0	1040.0
F000'	1043.95	
h,k,l max	11,16,26	11,16,26
Nref	5349	5045
Tmin,Tmax	0.860,0.860	0.785,1.000
Tmin'	0.860	

Correction method = # Reported T Limits: Tmin = 0.785 Tmax = 1.000

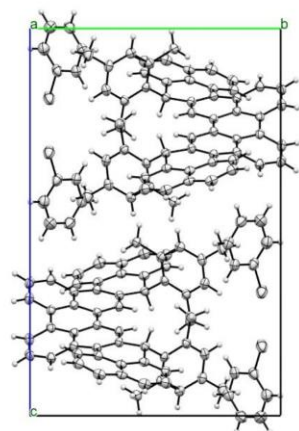
AbsCorr. = MULTI-SCAN

Data completeness = 0.943 Theta (max) = 76.984

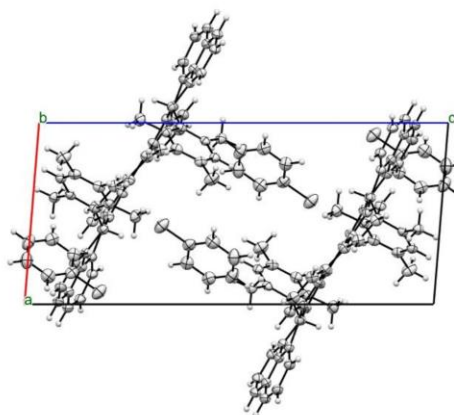
R(reflections) = 0.0486(3899)

wR<sup>2</sup>(reflections) = 0.1437(5045)

S = 1.047 Npar= 337



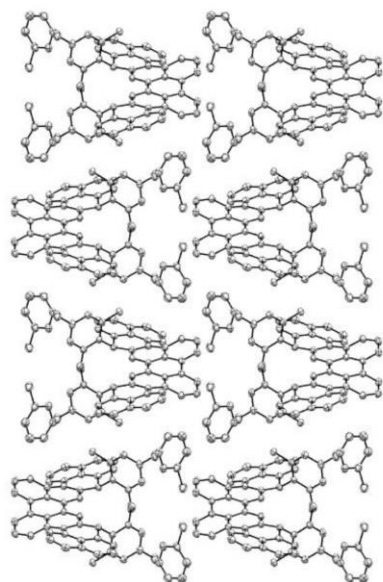
Unit cell along a-axis



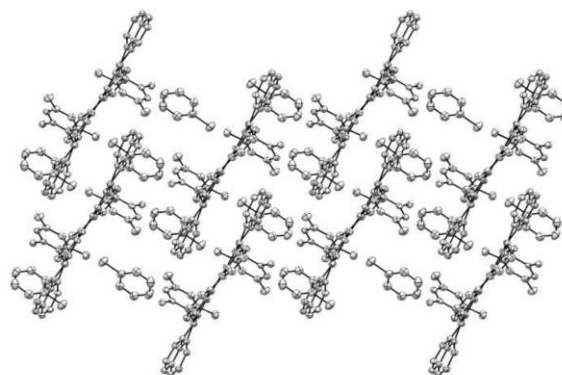
Unit cell along b-axis

**Figure S5.** Unit cell of single crystal structure of 2H-c-CNK.

(a)



(b)



**Figure S6.** Unit cell packing of single crystal structure of 2H-c-CNK. Hydrogen atoms omitted for clarity. (a) along a-axis (b) along b-axis.



## VII. Mass spectrometry

Organische Chemie

HRMS Report

XEVO-G2XS-QTOF

A: H<sub>2</sub>O (0.5 mM NH<sub>4</sub>OAc); B: MeCN; C: MeOH

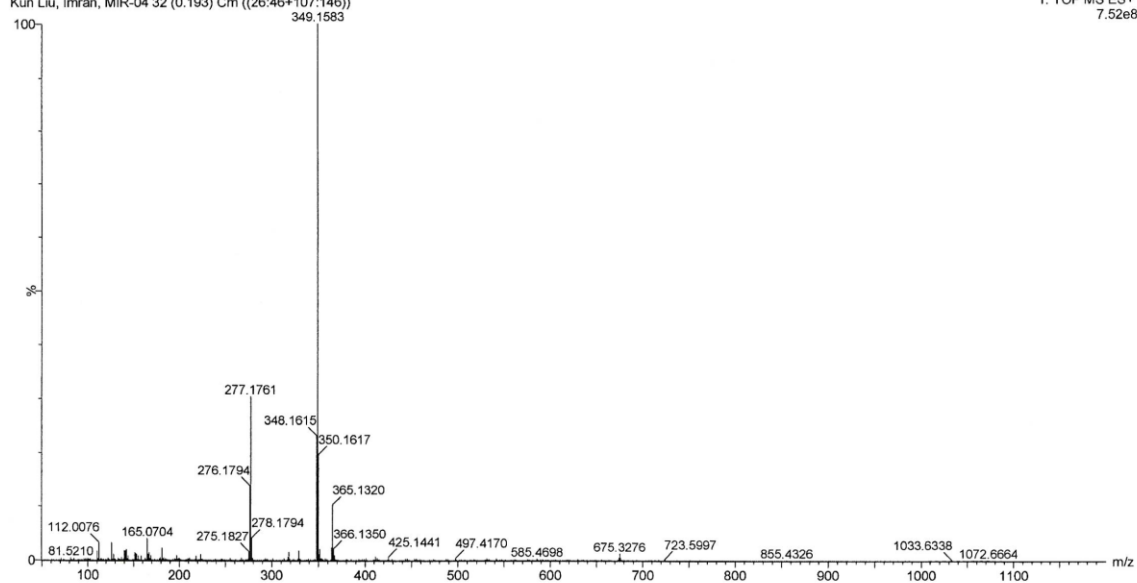
Kun Liu/Imran, MIR-04, m 326.1687, ESI\_MS\_PosSens\_50\_1200\_t1, C\_Isocratic\_02ml\_t1\_col2

25-Nov-2024

Kun Liu, Imran, MIR-04 32 (0.193) Cm ((26:46+107:146))

1: TOF MS ES+

7.52e8



Kun Liu/Imran, MIR-04, m 326.1687, ESI\_MS\_PosSens\_50\_1200\_t1, C\_Isocratic\_02ml\_t1\_col2

25-Nov-2024

Kun Liu, Imran, MIR-04 32 (0.193) Cm ((26:46+107:146))

1: TOF MS ES+

7.52e8

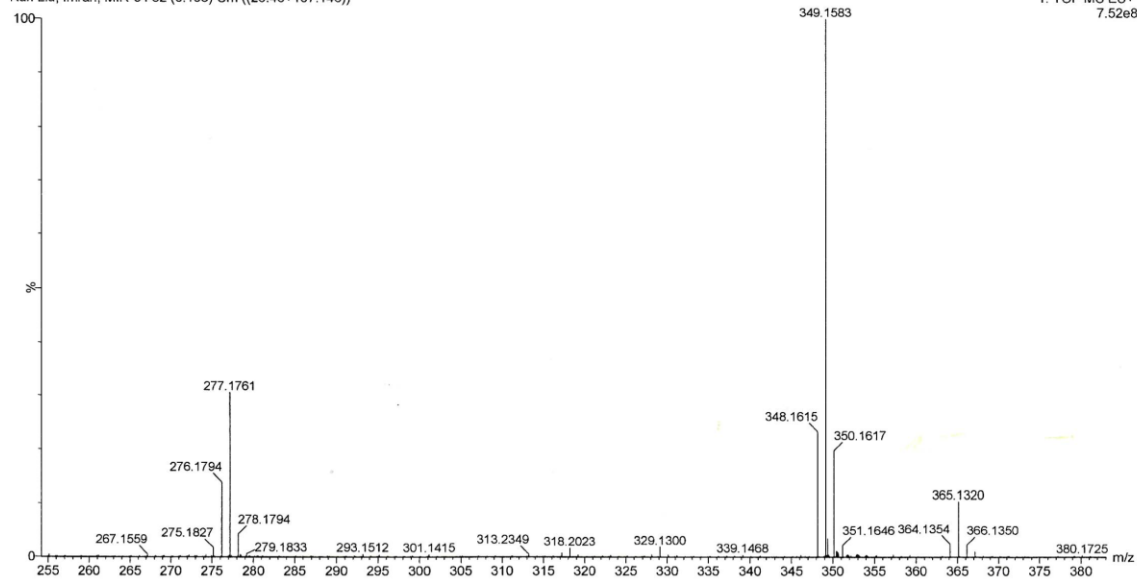


Figure S7. HR-ESI-MS mass spectrum of compound 4 [M+Na<sup>+</sup>].

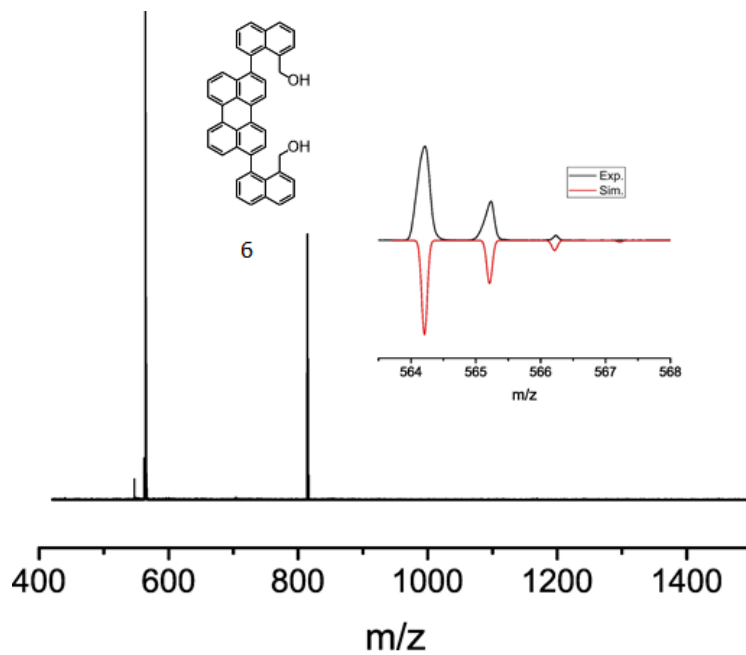


Figure S8. HR-MALDI-TOF mass spectrum of compound 6.

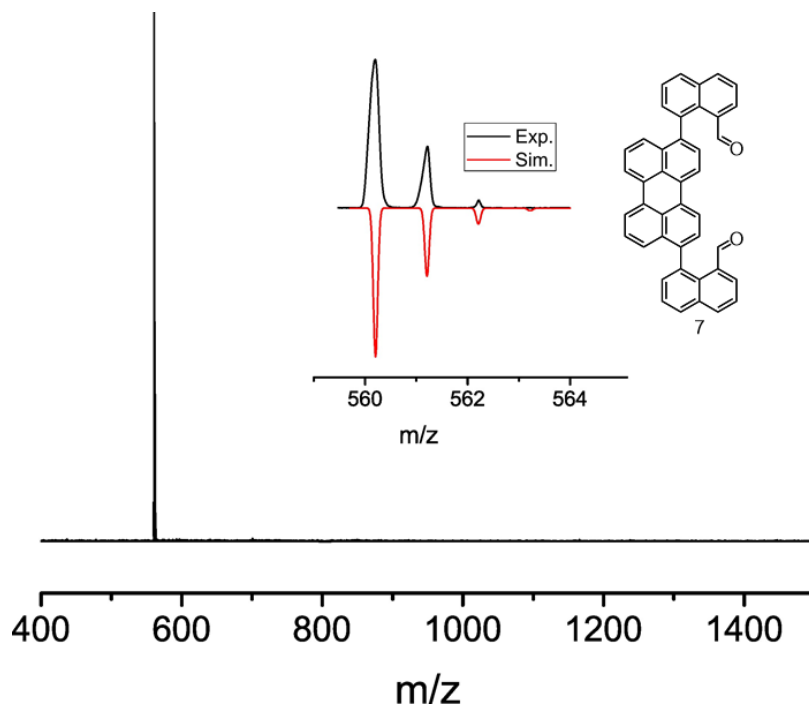


Figure S9. HR-MALDI-TOF mass spectrum of compound 7.

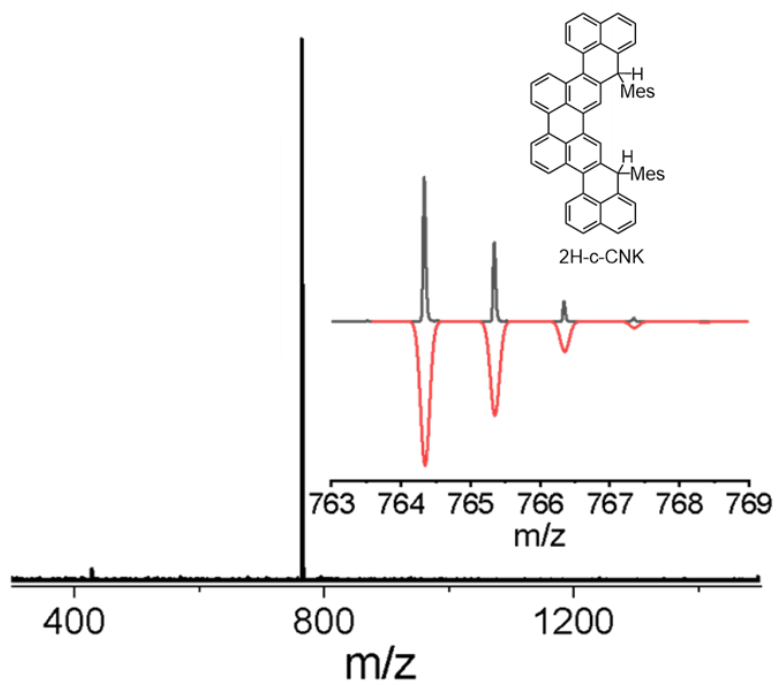


Figure S10. HR-MALDI-TOF mass spectrum of compound 2H-c-CNK.

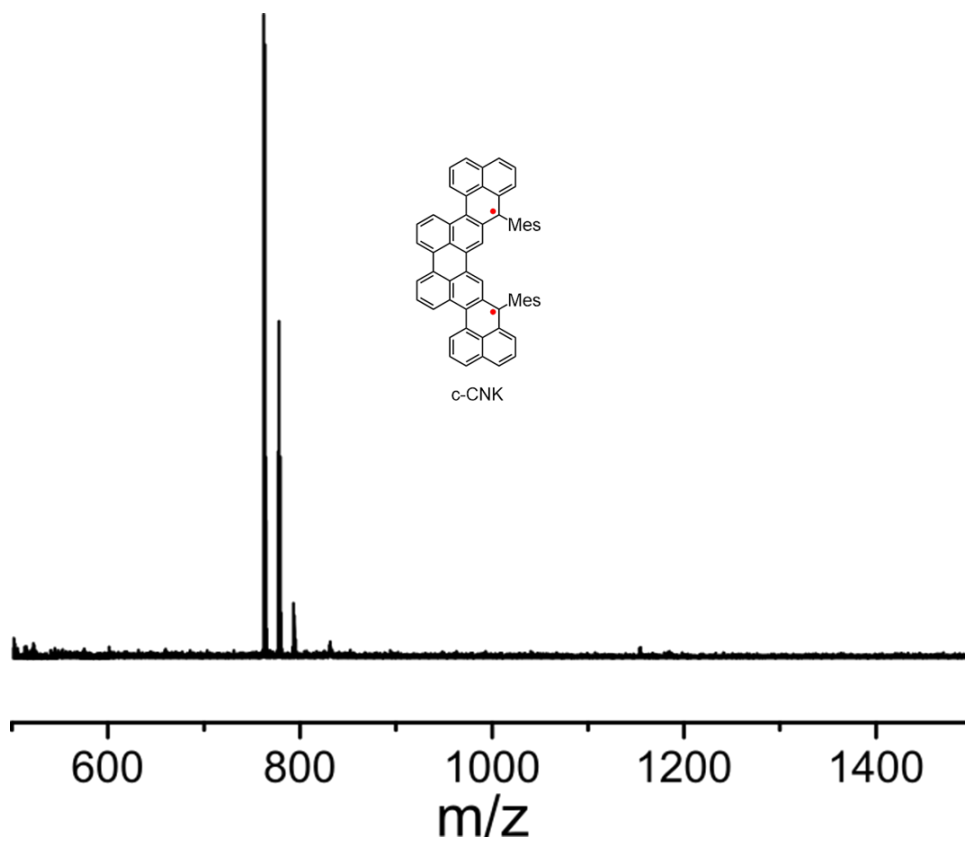
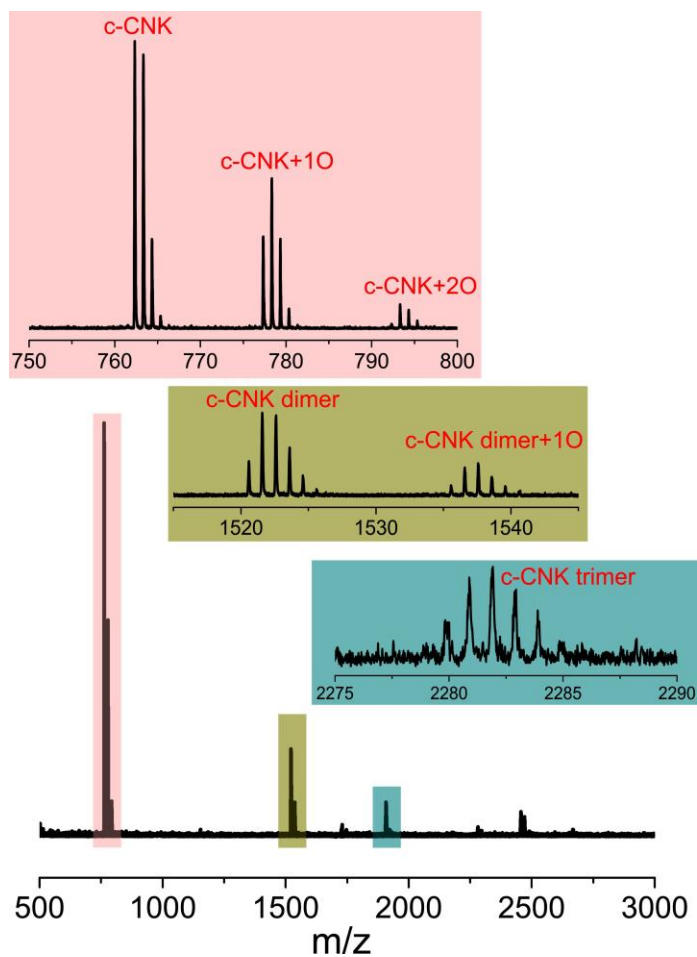
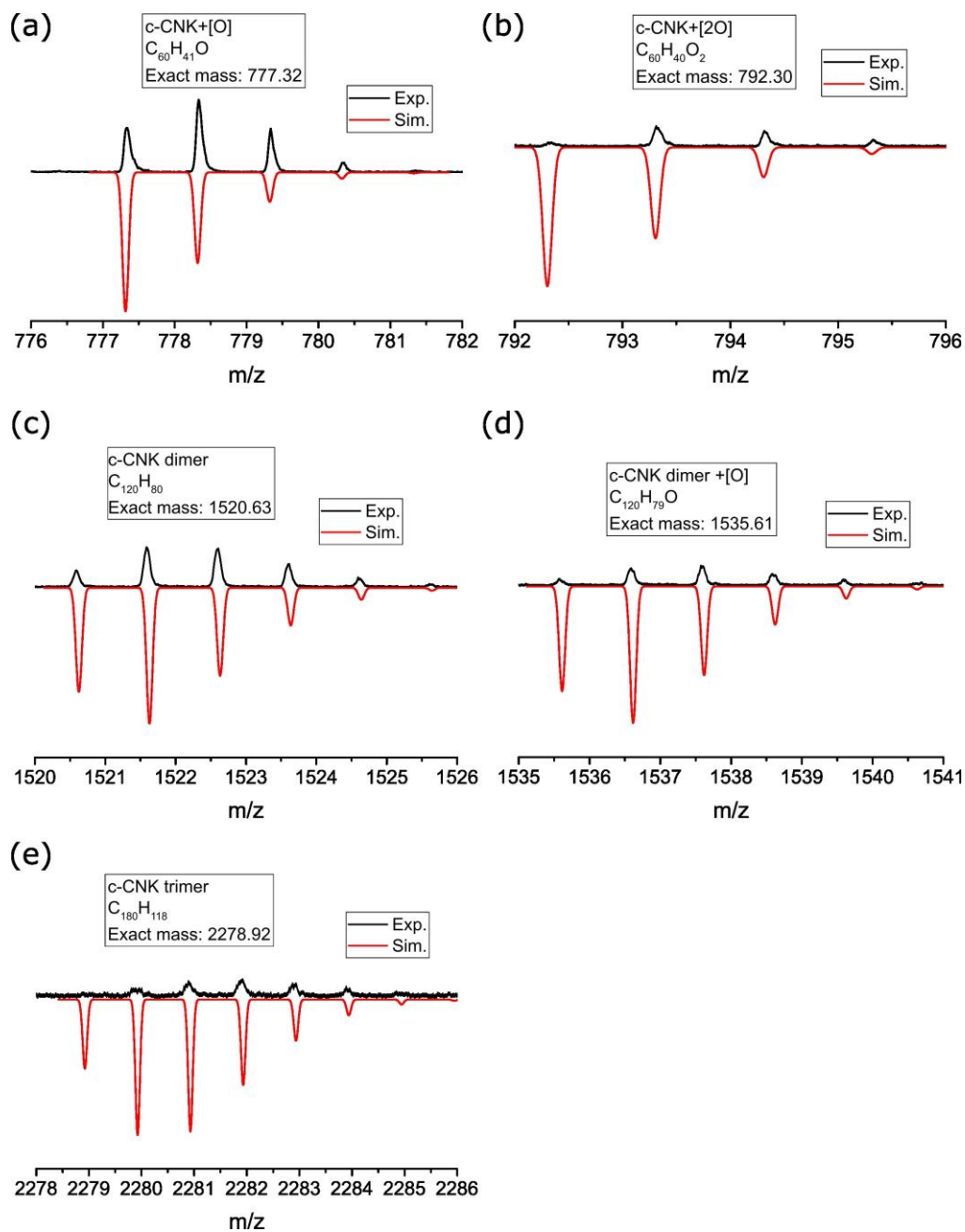


Figure S11. HR-MALDI-TOF mass spectrum of c-CNK.



**Figure S12.** MALDI-TOF mass spectrum of c-CNK shows the formation of c-CNK along with oxidized product (light pink), dimer formation (light green) and trimer formation (teal). There are also unidentifiable decomposition products as well.



**Figure S13.** Comparison between experimental and simulated mass spectra of (a) c-CNK+[1O] (b) c-CNK+2O (c) c-CNK dimer (d) c-CNK dimer+[1O] and (e) c-CNK trimer.

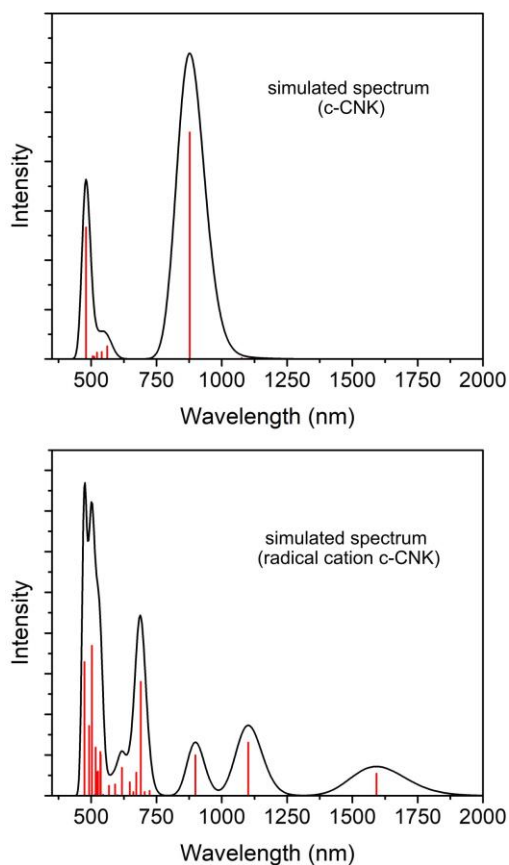
## VIII. DFT Calculations

DFT calculations were performed with the Gaussian09 suite of programs. [S2] The input files were generated from Gaussview 5.0.8. Ground and first triplet excited state geometries were optimized in Gaussian09 using the density functional b3lyp with a 6-31+g(d) basis set. Frequency calculations were performed to confirm the presence of local minima (only positive frequencies).

**Table S3**

*Calculated energy of different energy states of compound c-CNK.*

Parameters	Spin Multiplicity		
	Singlet open-shell	Triplet	Singlet closed-shell
Energy (Hartrees)	-2312.107714	-2312.107044	-2312.082207
$\Delta E_{S-T}$ (kcal, meV)	0.42 kcal/mol, 18.2 meV		
Biradical Yield ( $Y_0$ )	0.97		



**Figure S14.** Simulated UV-Vis-NIR spectrum of *c*-CNK and its radical cation using TD-DFT using basis set *ub3lyp/6-31g(d)* *scrf*=(solvent=dichloromethane).

## DFT optimized structural coordinates:

Singlet closed shell optimized geometry of **c-CNK** at rb3lyp/6-31G(d) level of theory.

C	0.80153500	1.64316200	0.08456700
C	0.83479100	4.06309900	0.61416300
C	1.53226200	2.84319800	0.38854000
C	2.96126000	2.78735400	0.50906500
C	1.53820900	5.15790700	1.11170900
C	1.49007400	0.48147000	-0.14416100
C	3.60480900	3.90688300	1.10043100
C	3.67130200	1.59762300	0.10959100
C	2.90439400	5.05611100	1.40211400
C	2.91520700	0.40405000	-0.10876400
C	-0.61051000	4.13979900	0.32482000
C	-0.66676400	1.67666600	0.08862800
C	-1.34089000	2.94748200	0.06658400
C	-2.75887000	2.98828800	-0.15276900
C	-1.42083400	0.53420100	0.16896400
C	-1.28925000	5.35706300	0.33163100
C	-3.48873000	1.76016800	-0.34243000
C	-3.40192600	4.24956700	-0.05526500
C	-2.84288700	0.54224200	0.03223000
C	-4.84801100	1.68248500	-0.83857000
C	-2.67807000	5.40348600	0.16377200
C	-5.60327500	0.49444200	-0.59021800
C	-4.99011200	-0.64630800	0.02750700
C	-3.58681900	-0.63555000	0.26323000
C	-6.97986900	0.42602300	-0.97842900
C	-7.73500400	-0.73057800	-0.65929500
C	-7.14639100	-1.79889600	0.00035100
C	-5.79315500	-1.76930800	0.33373800
C	-5.44601100	2.69080200	-1.62313700
C	-6.77800600	2.60146000	-2.03555900
C	-7.55223500	1.50854100	-1.68906100
C	5.90721000	2.68116900	-0.33907200
C	7.29554500	2.58799700	-0.46549500
C	7.93114500	1.36195000	-0.38906300
C	7.16995600	0.17422900	-0.27492000
C	7.78769800	-1.10186200	-0.29090800
C	7.02353900	-2.25861600	-0.26056000
C	5.63182000	-2.18735200	-0.23775500
C	5.10593500	1.54235400	-0.10929300
C	5.74386000	0.26393600	-0.17714800
C	4.96585400	-0.94014900	-0.20861700

C	3.54954300	-0.84670400	-0.27629100
C	2.74910500	-2.07313000	-0.55566200
C	2.67625600	-2.55441200	-1.88030900
C	1.94545800	-3.71374200	-2.14287800
C	1.28819700	-4.41454000	-1.12779600
C	1.36894300	-3.91997300	0.17439000
C	2.08184800	-2.75631100	0.47828400
C	2.12515900	-2.24542200	1.89798100
C	3.37623300	-1.82735700	-3.00306900
C	0.50067000	-5.66197600	-1.44425500
C	-2.92480300	-1.85031100	0.81774700
C	-2.56118700	-1.88728900	2.18161900
C	-1.99696100	-3.05272600	2.70340500
C	-1.79100200	-4.18806900	1.91477600
C	-2.14072600	-4.12543400	0.56542700
C	-2.69633400	-2.97416100	0.00045800
C	-3.03876100	-2.94154200	-1.46910200
C	-2.78598500	-0.69247700	3.07686300
C	-1.21705000	-5.44795200	2.51617700
H	1.02456600	6.08468300	1.33682600
H	0.95333500	-0.42811600	-0.37994100
H	4.64836700	3.83710600	1.37506200
H	3.41527100	5.88955800	1.87575500
H	-0.94641300	-0.42605800	0.32954800
H	-0.75168200	6.28417500	0.49037000
H	-4.48150000	4.30230800	-0.09171600
H	-3.19416500	6.35653100	0.23762100
H	-8.78297200	-0.76562500	-0.94377300
H	-7.73873200	-2.67545100	0.24756600
H	-5.33539300	-2.61989800	0.82575800
H	-4.85088500	3.53207700	-1.95344000
H	-7.20230500	3.40032300	-2.63721400
H	-8.59556400	1.44978100	-1.98668600
H	5.43881300	3.64743700	-0.46644300
H	7.87437500	3.49209400	-0.63219800
H	9.01270400	1.28989100	-0.46379500
H	8.87157700	-1.15641800	-0.34235700
H	7.50998800	-3.22993000	-0.27406200
H	5.03810900	-3.09439500	-0.24960900
H	1.89021000	-4.08024600	-3.16607000
H	0.86522300	-4.44864300	0.97685100
H	3.15185600	-2.03905400	2.21965200
H	1.56587300	-1.30739700	1.99945600
H	1.68321600	-2.97097300	2.58713700
H	4.46596200	-1.88696400	-2.89892100
H	3.11751600	-0.76280900	-3.01080200



H	3.10463500	-2.25398000	-3.97318200
H	0.27592900	-6.23332400	-0.53835100
H	-0.45475600	-5.41639800	-1.92589000
H	1.04783800	-6.31739800	-2.13126200
H	-1.72491300	-3.07864500	3.75674000
H	-1.97419500	-4.99257800	-0.06758400
H	-4.12334300	-2.92021300	-1.62836500
H	-2.63012300	-2.04680000	-1.95103600
H	-2.63785800	-3.82066100	-1.98262900
H	-2.62240000	-0.95592900	4.12598000
H	-3.80395500	-0.30200100	2.97329100
H	-2.10504400	0.12897400	2.82467600
H	-0.97598500	-6.18569100	1.74440700
H	-0.30175600	-5.24179200	3.08397400
H	-1.92576900	-5.91589800	3.21117900

Energy: -2312.082207 Hartree

Dipole moment: 0.557528 Debye

Singlet open shell optimized geometry of **c-CNK** at ub3lyp/6-31G(d) level of theory.

C	-7.57472900	0.75958100	0.33585800
C	-9.92188300	0.72456800	1.12455500
C	-8.74760800	1.45725600	0.78680100
C	-8.70412000	2.87972300	0.95032900
C	-10.96021300	1.38664800	1.77702900
C	-6.45490900	1.48094000	0.00611000
C	-9.75497300	3.47845100	1.68996300
C	-7.57586200	3.62905400	0.43766100
C	-10.84941500	2.74284000	2.10086900
C	-6.40756600	2.90390800	0.06196000
C	-10.00698000	-0.70984800	0.78766900
C	-7.58215400	-0.70715600	0.29902900
C	-8.83612100	-1.40799100	0.37946100
C	-8.87532000	-2.81622000	0.11739400
C	-6.42391800	-1.44227700	0.24388900
C	-11.20593700	-1.41421600	0.89292800
C	-7.65497400	-3.51400600	-0.22896900
C	-10.10398400	-3.48876900	0.32608200
C	-6.42261400	-2.85364600	0.04140400

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C	-7.60376800	-4.84895200	-0.78842100
C	-11.24428300	-2.79604500	0.68598600
C	-6.37671400	-5.57909800	-0.71666900
C	-5.18565000	-4.96166100	-0.20599400
C	-5.20373600	-3.57804200	0.10414100
C	-6.31926900	-6.93307600	-1.17815000
C	-5.11142800	-7.66554500	-1.03768800
C	-3.98410500	-7.07462500	-0.48474200
C	-4.00853500	-5.74107600	-0.08176000
C	-8.68405400	-5.44445600	-1.47652100
C	-8.61001600	-6.75193800	-1.95980800
C	-7.46223000	-7.50673900	-1.78257300
C	-8.74729300	5.85315600	0.19537500
C	-8.69557300	7.24440700	0.09431900
C	-7.47973500	7.90384800	0.03013000
C	-6.27536900	7.16515300	-0.02831800
C	-5.02241100	7.81129300	-0.19482400
C	-3.85681900	7.07244700	-0.33915600
C	-3.89864500	5.68002400	-0.34326700
C	-7.57323200	5.06901500	0.25642000
C	-6.32577200	5.73575700	0.04415300
C	-5.12060600	4.98515800	-0.16179900
C	-5.19389200	3.57241300	-0.24796900
C	-3.99728900	2.80428000	-0.70094500
C	-3.73476000	2.70411000	-2.08311900
C	-2.59629200	2.01983800	-2.51031200
C	-1.70531800	1.43814500	-1.60355700
C	-1.98876300	1.54027600	-0.24127200
C	-3.12563700	2.20683500	0.22666800
C	-3.41067700	2.27808500	1.70703500
C	-4.66990900	3.33241800	-3.08779100
C	-0.47632800	0.71412400	-2.09611100
C	-3.95618100	-2.90115400	0.56239100
C	-3.75896700	-2.66765900	1.93994700
C	-2.57316400	-2.06598600	2.36367000
C	-1.57318000	-1.69518000	1.45982600
C	-1.79268900	-1.92562400	0.10156800
C	-2.97153500	-2.51506000	-0.36467900
C	-3.18477600	-2.72454500	-1.84394800
C	-4.81166200	-3.06395500	2.94691100
C	-0.29364200	-1.06116200	1.94864900
H	-11.84303300	0.84377300	2.09346800
H	-5.56431900	0.97025500	-0.33709600
H	-9.67302800	4.51374700	1.99079300
H	-11.62965900	3.22012700	2.68678700
H	-5.46157400	-0.95415900	0.33733600

H	-12.12131600	-0.90004700	1.16142000
H	-10.14166800	-4.56739400	0.25846500
H	-12.17566300	-3.33451200	0.83640700
H	-5.08483100	-8.69762300	-1.37625000
H	-3.06851800	-7.64962300	-0.37800400
H	-3.11690300	-5.27647700	0.32392500
H	-9.57364900	-4.86212400	-1.67717900
H	-9.46318200	-7.17397000	-2.48345800
H	-7.41211600	-8.53290600	-2.13631500
H	-9.71355800	5.36834700	0.17895900
H	-9.62339600	7.80842200	0.05852300
H	-7.43694200	8.98812700	-0.02593600
H	-4.99591100	8.89709500	-0.22416200
H	-2.90559400	7.58073800	-0.46987100
H	-2.99121000	5.10605800	-0.49303900
H	-2.39613600	1.94554900	-3.57741500
H	-1.31027800	1.09350700	0.47856200
H	-3.55631700	3.31231000	2.03869600
H	-4.32694000	1.73130700	1.96005300
H	-2.59082800	1.84122700	2.28484400
H	-4.68268700	4.42433200	-2.99116200
H	-5.70052800	2.99021200	-2.94100400
H	-4.36921000	3.08503000	-4.11015000
H	0.20508700	0.47805400	-1.27297100
H	-0.74057400	-0.22963900	-2.59044600
H	0.07523500	1.31513800	-2.82835700
H	-2.42275700	-1.89110400	3.42717900
H	-1.03036500	-1.63816000	-0.61654900
H	-3.22276700	-3.79051000	-2.09720300
H	-4.13382300	-2.28624300	-2.17240200
H	-2.37907900	-2.26489500	-2.42409000
H	-4.44046900	-2.94133900	3.96865500
H	-5.11816300	-4.10729600	2.81440800
H	-5.71530600	-2.45252700	2.83917200
H	0.38035500	-0.82989100	1.11787700
H	-0.49063200	-0.12751800	2.49052800
H	0.24267500	-1.72343300	2.63918700

Energy: -2312.107714 Hartree

Dipole moment: 0.593747 Debye

Triplet open shell optimized geometry of **c-CNK** at ub3lyp/6-31G(d) level of theory.

C	0.78508500	1.64536800	0.11069200
C	0.80943900	4.06609400	0.63214400
C	1.51388200	2.84832800	0.40679500
C	2.93961900	2.79747900	0.53205300
C	1.50612200	5.15755000	1.14576600
C	1.47798600	0.48393700	-0.11396100
C	3.57661800	3.91299500	1.13200600
C	3.65561200	1.60518400	0.12691200
C	2.87023700	5.05884700	1.44033300
C	2.90205200	0.41703300	-0.09509500
C	-0.63364800	4.13983100	0.32746100
C	-0.68351300	1.67572600	0.11822500
C	-1.36207500	2.94382000	0.07482100
C	-2.77662700	2.97951400	-0.14897800
C	-1.43668000	0.53385900	0.21853100
C	-1.31524300	5.35572800	0.31532900
C	-3.50362700	1.74050200	-0.33254100
C	-3.42333900	4.23637500	-0.06212400
C	-2.85449700	0.53595100	0.05794300
C	-4.85614200	1.65089600	-0.84295400
C	-2.70229100	5.39660400	0.14517100
C	-5.60140300	0.45325700	-0.61180200
C	-4.98595800	-0.68355900	0.01249600
C	-3.59442000	-0.65495400	0.27963500
C	-6.96967400	0.36819200	-1.02490600
C	-7.71473800	-0.80311400	-0.72804600
C	-7.12334200	-1.87177000	-0.06868700
C	-5.77832200	-1.82592400	0.29077100
C	-5.45683900	2.65742900	-1.63165700
C	-6.77917900	2.55271000	-2.06550800
C	-7.54486900	1.44568400	-1.73781400
C	5.88930200	2.70089000	-0.30781400
C	7.27554400	2.61213300	-0.44279200
C	7.91392300	1.38430200	-0.39034200
C	7.15538900	0.19515600	-0.29314200
C	7.77651700	-1.08055100	-0.33784900
C	7.01546800	-2.24107500	-0.33029800
C	5.62471900	-2.17396700	-0.29880900
C	5.08927100	1.55554000	-0.09383500
C	5.72968400	0.28022500	-0.18535200

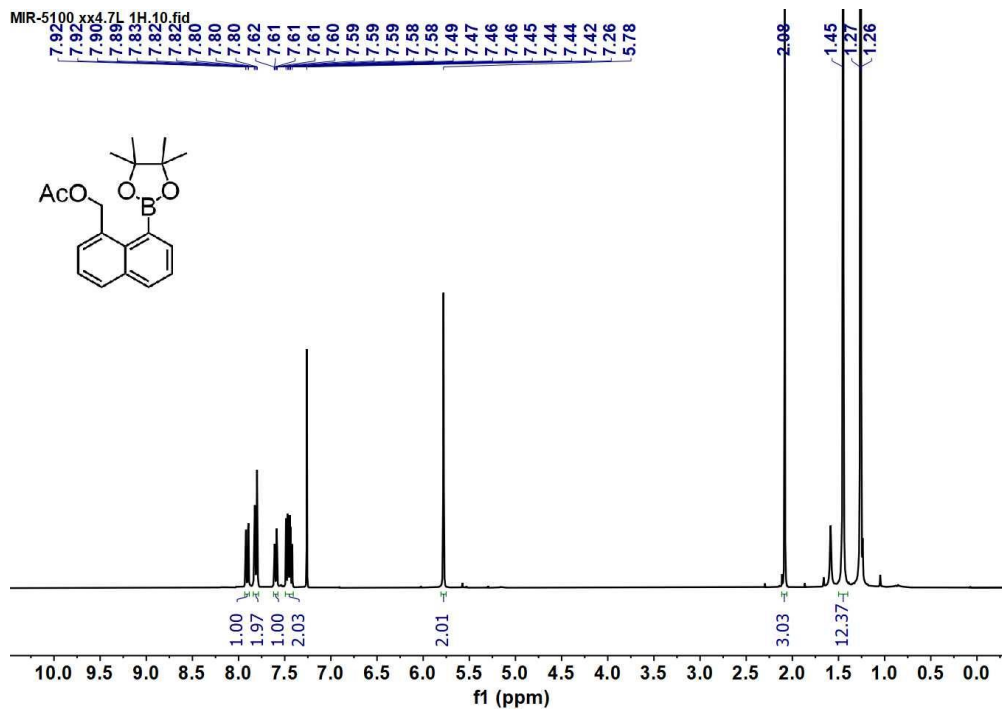
C	4.95443600	-0.92606000	-0.23440900
C	3.54178400	-0.83618400	-0.28725000
C	2.74134600	-2.06106500	-0.58050900
C	2.59193700	-2.47301000	-1.92113200
C	1.87791100	-3.63946000	-2.19757800
C	1.31418900	-4.41439900	-1.17965700
C	1.46524800	-3.98385300	0.13884700
C	2.16246500	-2.81393200	0.45644000
C	2.28700300	-2.36795800	1.89287400
C	3.20022400	-1.66612300	-3.04252800
C	0.55735200	-5.67760200	-1.50943700
C	-2.92178000	-1.85326600	0.85941300
C	-2.65802100	-1.89822100	2.24479900
C	-2.05918100	-3.03706200	2.78530700
C	-1.71985100	-4.13633900	1.99101100
C	-1.98075100	-4.06736100	0.62231000
C	-2.56852900	-2.94037600	0.04017900
C	-2.80997100	-2.89037100	-1.44870900
C	-3.01952500	-0.73416900	3.13554600
C	-1.08464600	-5.36004700	2.60514900
H	0.98634900	6.07966300	1.37771300
H	0.94375000	-0.42983900	-0.34067500
H	4.61957900	3.84653300	1.40921000
H	3.37670600	5.89040900	1.92186500
H	-0.96078700	-0.42087500	0.40621100
H	-0.77890200	6.28572200	0.46331900
H	-4.50281000	4.28660000	-0.10200300
H	-3.22123700	6.34910100	0.20418600
H	-8.75694300	-0.84932500	-1.03164000
H	-7.70799100	-2.75929000	0.15674700
H	-5.31430000	-2.67442900	0.78082900
H	-4.86802600	3.50794700	-1.94886400
H	-7.20466500	3.34867900	-2.67016600
H	-8.58196100	1.37438700	-2.05407200
H	5.41912200	3.66822900	-0.41784600
H	7.85251300	3.51944500	-0.59816400
H	8.99516300	1.31529400	-0.47274400
H	8.86035100	-1.13063300	-0.39533000
H	7.50486900	-3.21023700	-0.36897600
H	5.03233100	-3.08139200	-0.32968900
H	1.76560600	-3.95510100	-3.23297700
H	1.03360500	-4.57103500	0.94325700
H	3.33415100	-2.21099100	2.17524700
H	1.76750800	-1.41646900	2.05799000
H	1.85242700	-3.10784800	2.57150600
H	4.29477900	-1.66202100	-2.98169000

H	2.87760700	-0.61970100	-3.00084100
H	2.91536000	-2.07378400	-4.01695500
H	0.33876100	-6.25904700	-0.60845000
H	-0.39825400	-5.45351900	-2.00087100
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H	-1.86084600	-3.06995400	3.85480600
H	-1.71912800	-4.90912800	-0.01201500
H	-3.88062400	-2.85273000	-1.68116400
H	-2.35700400	-1.99662000	-1.89245900
H	-2.38416800	-3.76828800	-1.94361200
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H	-4.06403500	-0.43449100	2.99655700
H	-2.40518100	0.14532600	2.90954500
H	-0.90436800	-6.13585400	1.85442200
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H	-1.72148300	-5.79234000	3.38643700

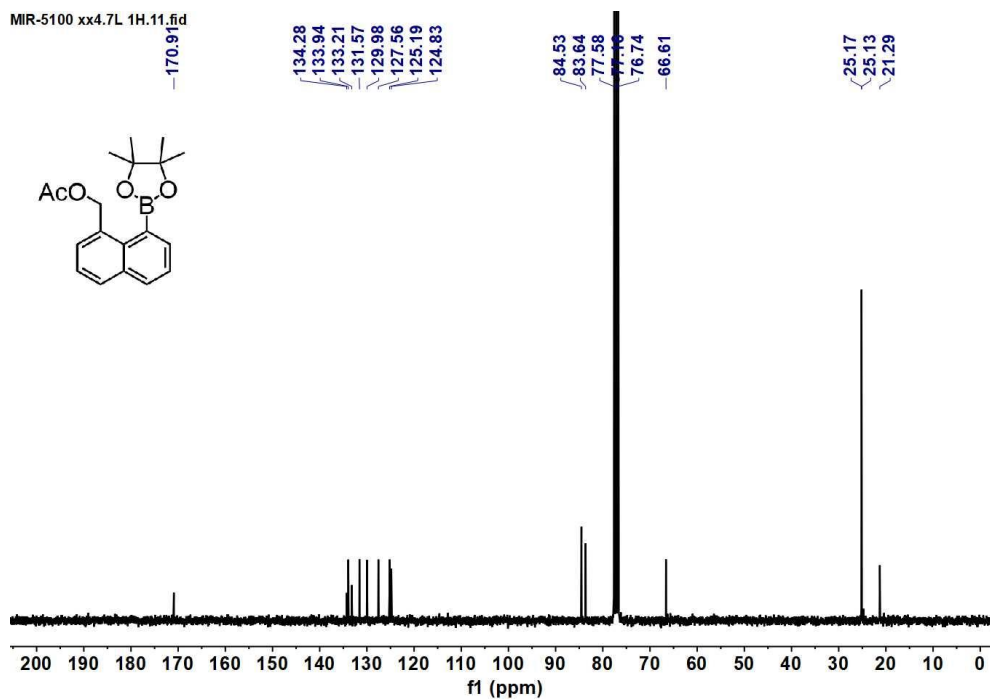
Energy: -2312.107044 Hartree

Dipole moment: 0.592197 Debye

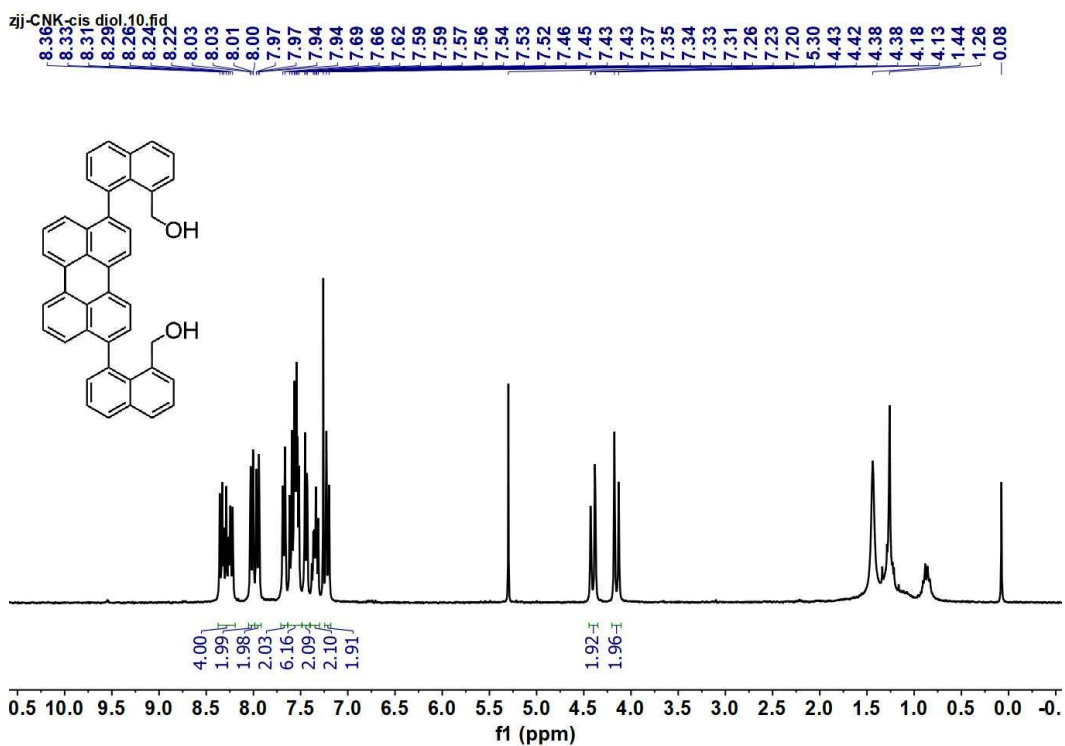
## IX. NMR Spectra



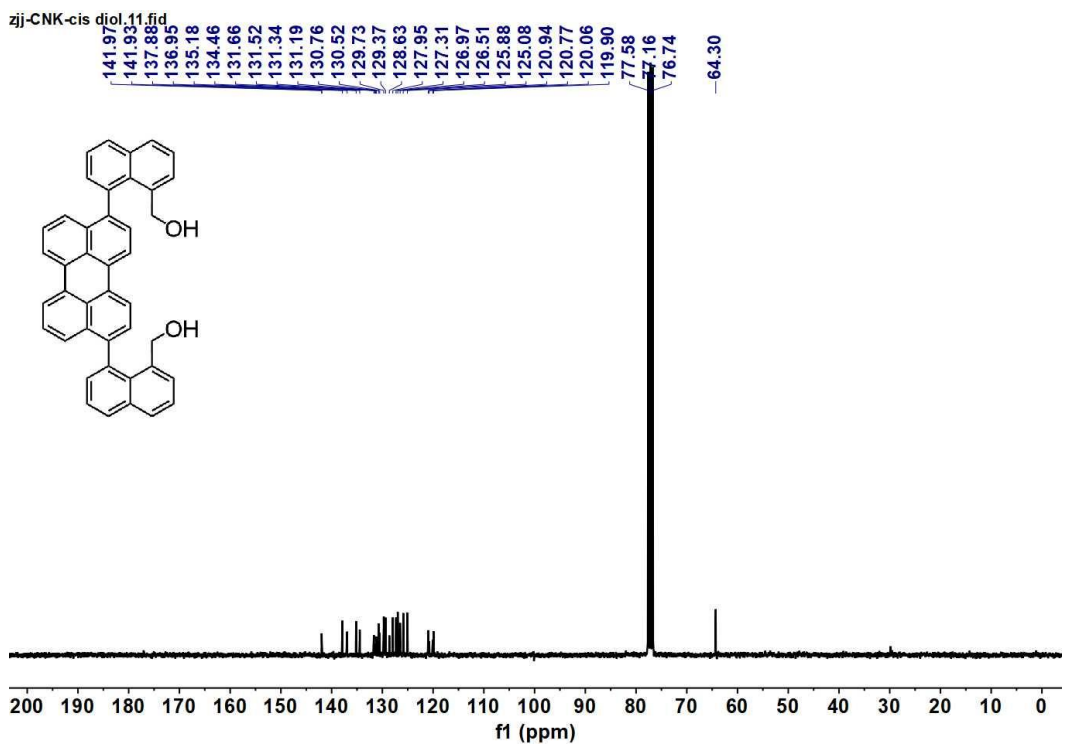
$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of compound 4.



$^{13}\text{C}$  NMR spectrum (75 MHz,  $\text{CDCl}_3$ ) of compound 4.

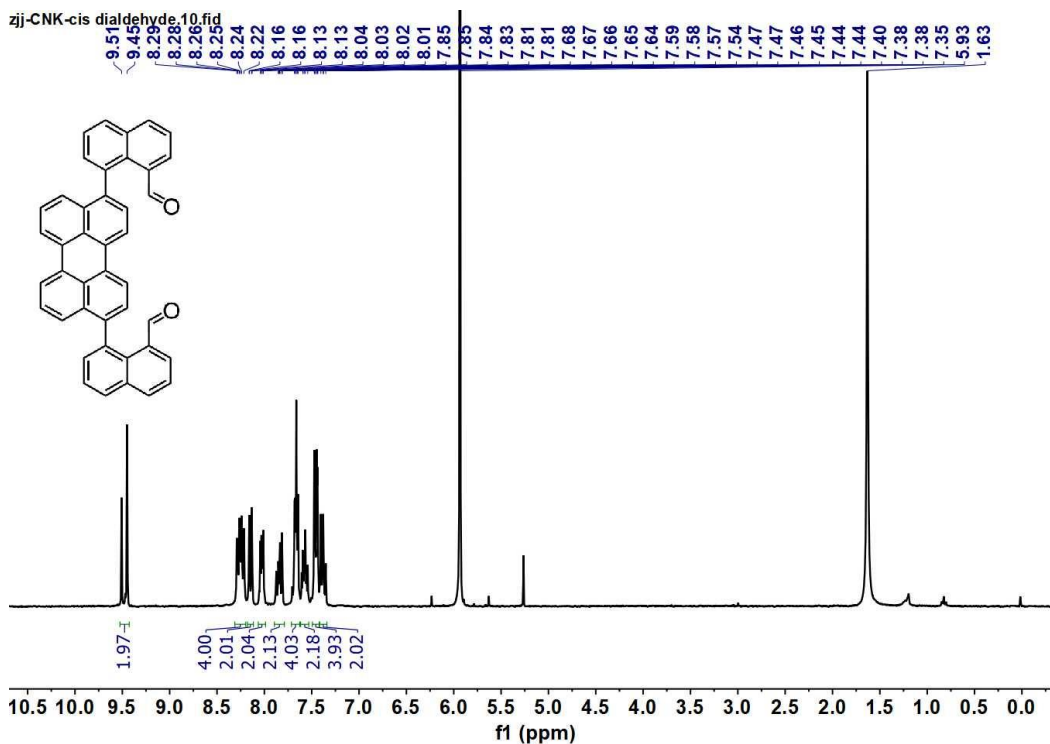


$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ ) of compound **6**.

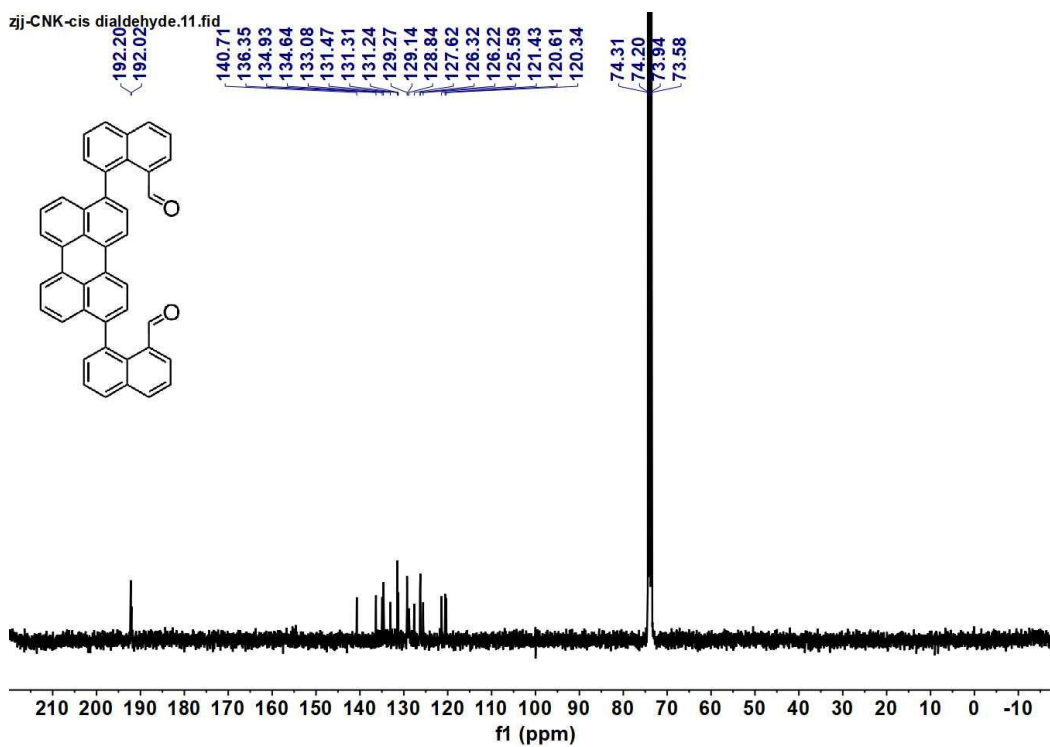


$^{13}\text{C}$  NMR spectrum (75 MHz,  $\text{CDCl}_3$ ) of compound **6**.

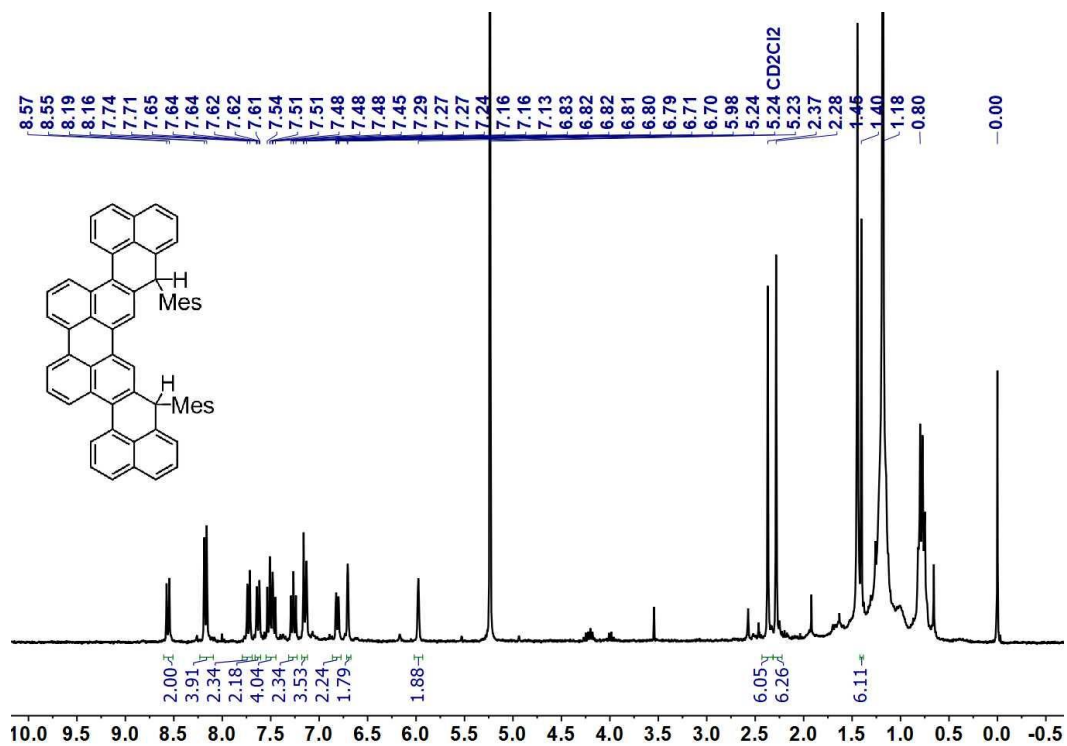




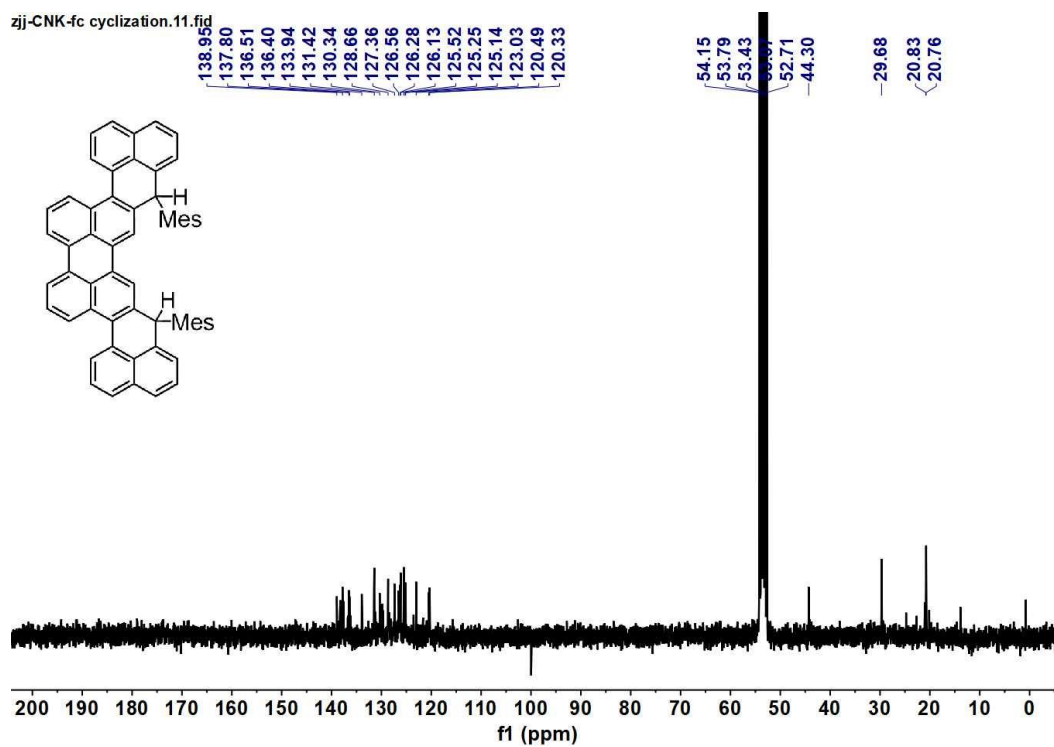
$^1\text{H}$  NMR spectrum (300 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of compound 7.



$^{13}\text{C}$  NMR spectrum (75 MHz,  $\text{C}_2\text{D}_2\text{Cl}_4$ ) of compound 7.



<sup>1</sup>H NMR spectrum (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound **2H-c-CNK**.



<sup>13</sup>C NMR spectrum (75 MHz, CD<sub>2</sub>Cl<sub>2</sub>) of compound **2H-c-CNK**.

## X. References

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S2. Gaussian 09, Revision A.02, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2016.