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Supplementary Information

On-surface synthesis of nitrogen-doped nanographenes with 5-7 membered rings

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Chemical synthesis of the precursor

General Information

Unless otherwise stated, the commercially available reagents and dry solvents were used without further purification. The reactions were performed using standard vacuum-line and Schlenk techniques, work and purification of all compounds were performed under air and with reagent-grade solvents. Column chromatography was done with silica gel (particle size 0.063-0.2 mmm from VWR) and silica coated aluminum sheets with fluorescence indicator from Merck were used for thin layer chromatography.

NMR Data were recorded on a Bruker AV-III 600 spectrometer operating at 600 MHz for ^{1}H and 151 MHz for ^{13}C with standard Bruker puls programs at room temperature. Chemical shifts δ are given in ppm relative to TMS, coupling constants J are given in Hertz. $C_2D_2Cl_4$ ($\delta(^1H)$ = 5.91 ppm, $\delta(^{13}C)$ = 74.2 ppm) was used as solvent, lock and internal standard.

HR-MALDI-TOF MS spectra were recorded on a Bruker Autoflex Speed MALDI-TOF MS (Bruker Daltonics, Bremen, Germany) with *trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB) as the matrix. The preparation for all samples was performed in solid state.

Thermogravimetric Analysis (TGA) measurement was recorded on Mettler-Toledo TGA 1 SF 1100 with a 70 ml AlOx crucible under nitrogen atmosphere.

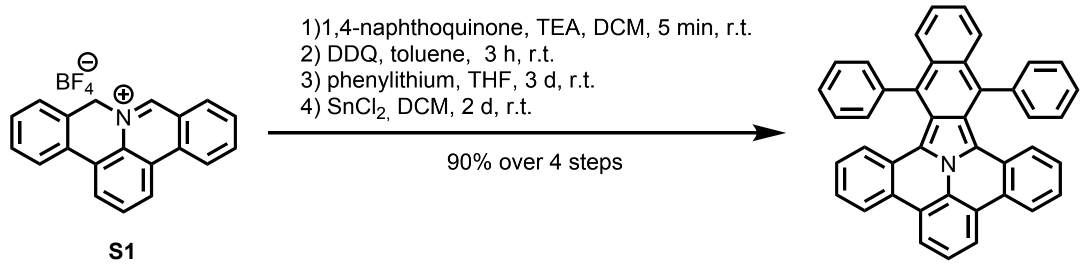
Experimental Section

The synthesis and the analytical data of 8*H*-isochinolino[4,3,2-*de*]phenantridinium tetrafluororborate (**S1**) was reported in our previous work.[1] The used chemicals can be found in the table.

Table S1. List of the chemicals inclusive suppliers and purity.

Chemical Name	Suppliers	Purity
1,4-Naphthoquinone	Sigma-Aldrich	97%
Triethylamine	Sigma-Aldrich	>99% (anhydrous)
2,3-Dichloro-5,6-dicyano-p-benzoquinone	Sigma-Aldrich	98%
Phenyllithium in dibutyl ether	Sigma-Aldrich	1.9 M
Tin(II)chloride	ACROS Organics	98% (anhydrous)

Synthesis of 5,17-diphenylbenzo[7,8]naphtho[2',3':1,2]indolizino[6,5,4,3-*def*]phenanthridine (1)

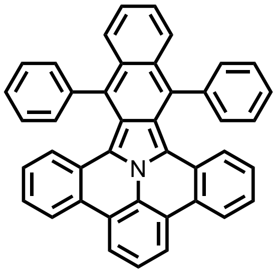


S1

1

In a dry and inert Schlenk flask 8*H*-isochinolino[4,3,2-*de*]phenantridinium tetrafluoroborate (**S1**, 200 mg, 563 µmol, 1.0 eq.) and 1,4-napthoquinone (115 mg, 732 µmol, 1.3 eq.) was suspended in anhydrous dichloromethane (DCM, 20 ml). Triethylamine (TEA, 683 mg, 7.76 mmol, 12.0 eq.) was added to the mixture in one portion. After five minutes the reaction mixture was transferred into a round bottle flask and the solvent as well as the residual triethylamine was removed under reduced pressure. After the addition of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 230 mg, 1.0 mmol, 1.8 eq.) to the crude mixture, the reaction mixture was sealed with a septum and purged with argon for five minutes. After the addition of toluene (20 ml), the reaction was stirred for three hours at room temperature. The reaction mixture was quenched with water, filtered and washed with ethanol (100 ml). Afterwards, the crude product was suspended in anhydrous tetrahydrofuran (THF, 10 ml) in a dry and inert flask. Phenyllithium (1.9 M in dibutylether, 2.96 ml, 5.63 mmol, 10.0 eq.) was added dropwise to the reaction mixture at room temperature. The addition of phenyllithium was repeated after 24h and 48 hours. After further stirring overnight, the reaction mixture was quenched with water and extracted with DCM (15ml) three times. The combined organic layers were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure and the residue was purified by filtration over a silica pad in *i*-hexane/ ethyl acetate mixture with a ration 5:1. Afterwards, the solvent was removed under reduced pressure. To the solid residue, anhydrous $SnCl_2$ (747 mg, 3.94 mmol, 7.0 eq.) and anhydrous DCM (5 ml) was added in a dry and inert Schlenk flask. The reaction mixture was stirred over two days at room temperature. Afterwards, the reaction mixture was precipitated in cold methanol (70 ml) as well as filtered under argon purging. Furthermore, the red solid was washed with methanol (20 ml), ethanol (15 ml) and acetonitrile (10 ml). The target compound was observed as dark red solid in 90% yield over 4 steps.

5,17-diphenylbenzo[7,8]naphtho[2',3':1,2]indolizino[6,5,4,3-*def*]phenanthridine



1

^{1}H-NMR (600 MHz, $C_2D_2Cl_4$): δ 8.26 (d, J = 8.0 Hz, 2H), 8.17 – 8.00 (m, 4H), 7.66 (t, J = 7.9 Hz, 1H), 7.58 (d, J = 7.0 Hz, 4H), 7.40 (t, J = 7.4 Hz, 4H), 7.36 (t, J = 7.4 Hz, 2H), 7.24 (dd, J = 7.0, 3.2 Hz, 2H), 7.09 (dd, J = 16.0, 7.8 Hz, 4H), 6.73 (t, J = 7.4 Hz, 2H).
The ^{1}H-NMR spectra of **1** showed broad signals in the aromatic region at room temperature. After the addition of the reducing agent hydrazine to quench radical impurities, sharp signals were observed in NMR spectra in$C_2D_2Cl_4$.

^{13}C-NMR (151 MHz, $C_2D_2Cl_4$): δ 141.0, 132.3, 129.9, 128.9, 127.7, 127.0, 125.9, 125.7, 124.3, 123.9, 121.9, 119.6, 115.3.

Due to the low solubility in $C_2D_2Cl_4$ chemical shifts of 13-C nuclei were derived from the HMBC experiment. Unfortunately, not all carbon atoms could be detected.

HR-MS (MALDI-TOF): m/z = 543.1987, calcd. for $C_{42}H_{25}N$: m/z = 543.1986; error = 0.18 ppm.

HR-MALDI-TOF MS gave the exact mass of **1** and showed an additional peak plus m/z = 17 (OH-group). This can be attributed to partial oxidation during the MALDI-TOF measurement.

HR-MALDI-TOF MS

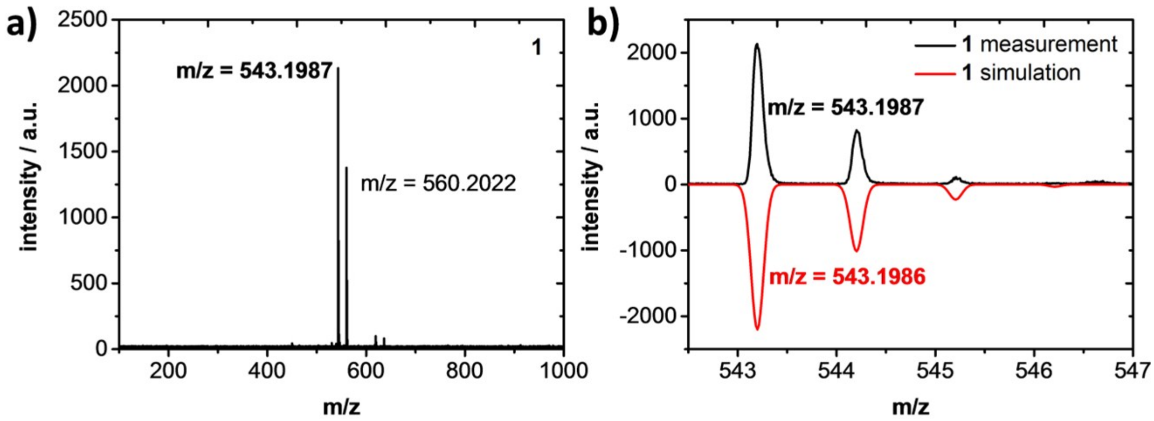


Fig. S1 a) HR-MALDI-TOF spectrum of **1**. b) HR-MALDI-TOF measurement of **1** (black line) is in agreement to the expected isotopic distribution pattern (red line).

Thermogravimetric Analysis (TGA)

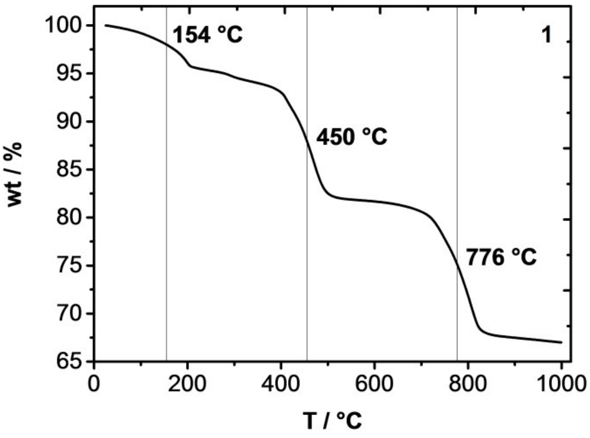


Fig. S2 TGA spectrum of **1** with a heat rate of 10 K/min under nitrogen atmosphere.

NMR Spectroscopy

The ^{1}H-NMR spectra of **1** showed broad signals in the aromatic region at room temperature. After the addition of the reducing agent hydrazine to quench radical impurities, sharp signals were observed in NMR spectra in $C_2D_2Cl_4$. The ^{13}C- and 2D-NMR spectra (correlation spectroscopy (COSY), heteronuclear single quantum coherence (HSQC), heteronuclear multiple-bond correlation (HMBC) and nuclear Overhauser effect spectroscopy (NOESY)) were further measured after addition of hydrazine.

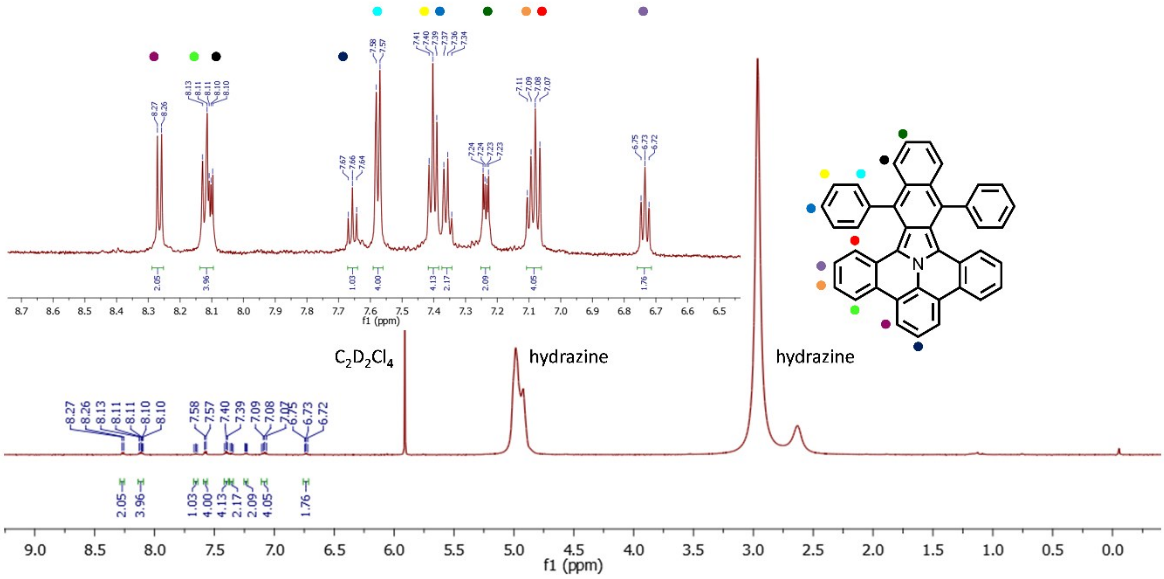


Fig. S3 ^{1}H-NMR (600 MHz) spectrum of **1** at 298 K in $C_2D_2Cl_4$ and hydrazine.

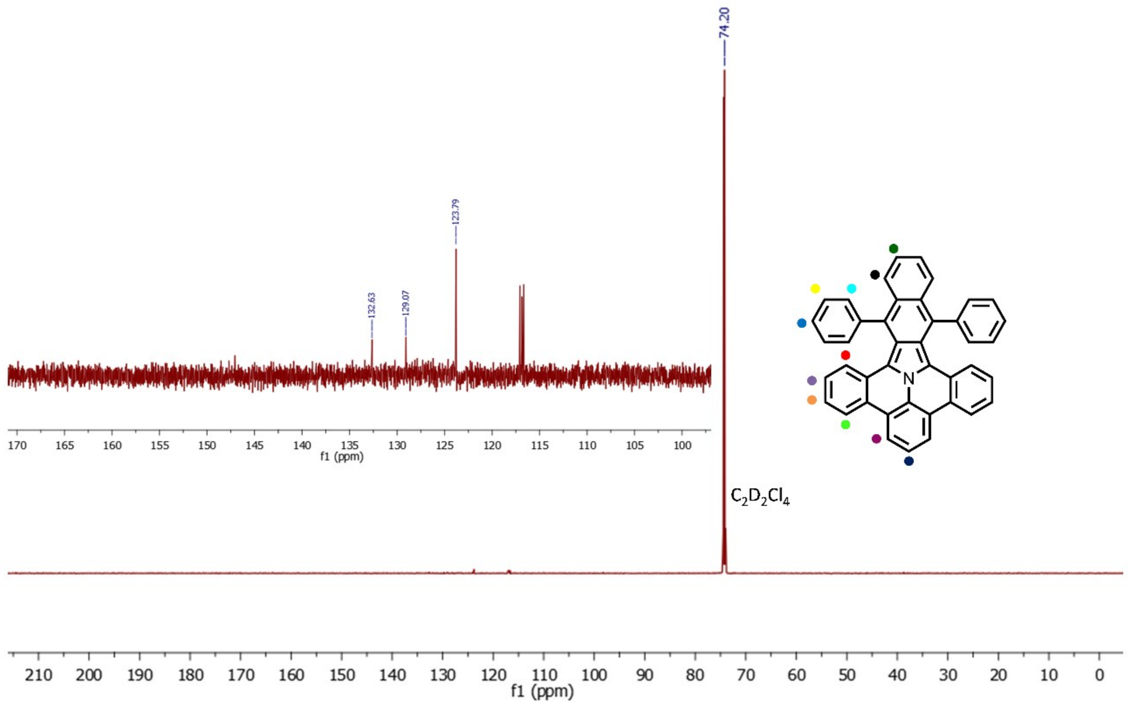


Fig. S4 ^{13}C-NMR (151 MHz) spectrum of **1** at 298 K in $C_2D_2Cl_4$ and hydrazine.

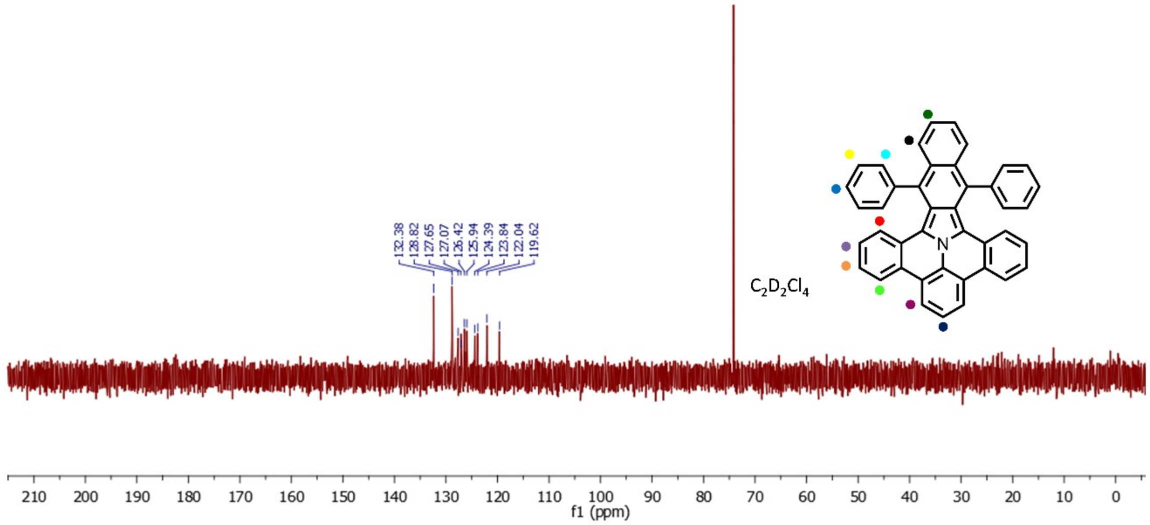


Fig. S5 ^{13}C- distortionless enhancement by polarization transfer (DEPT)-NMR (151 MHz) spectrum of **1** at 298 K in $C_2D_2Cl_4$ and hydrazine.

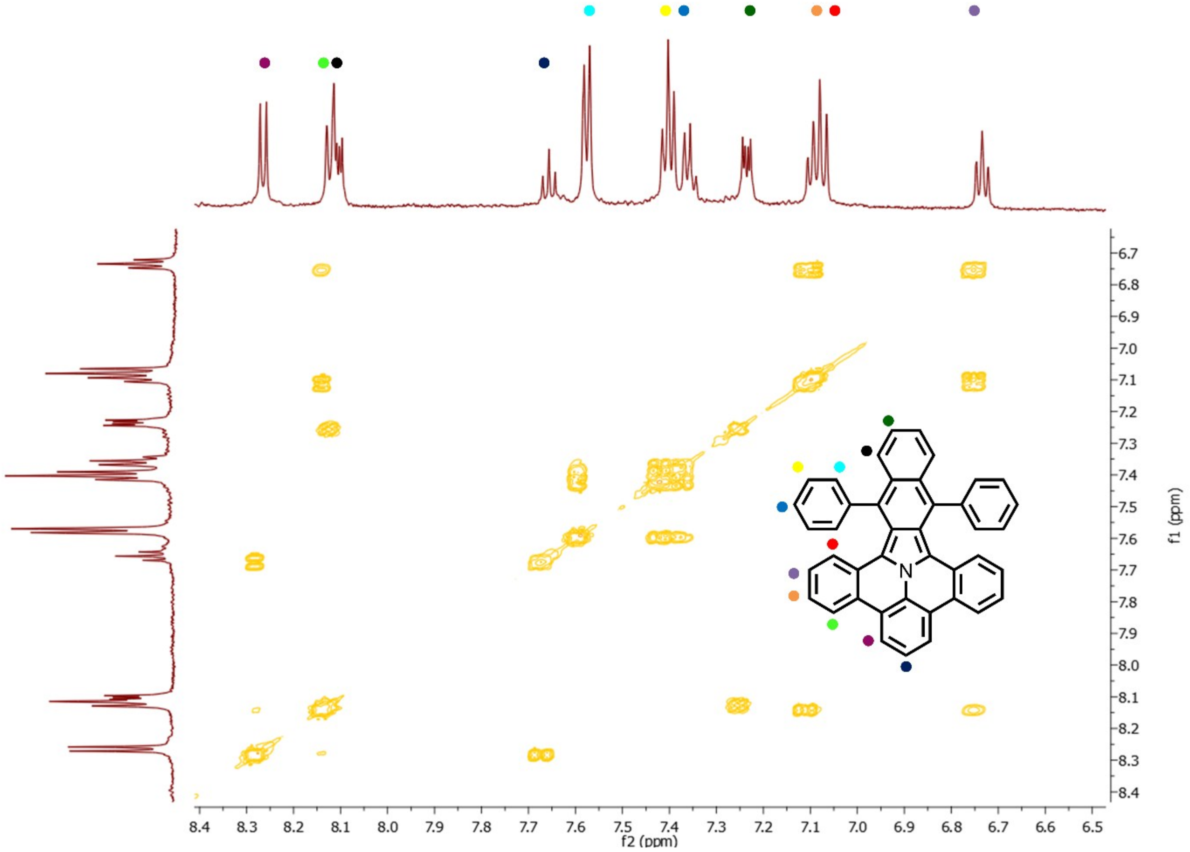


Fig. S6 COSY-2D-NMR spectrum of **1** at 298 K in $C_2D_2Cl_4$ and hydrazine.

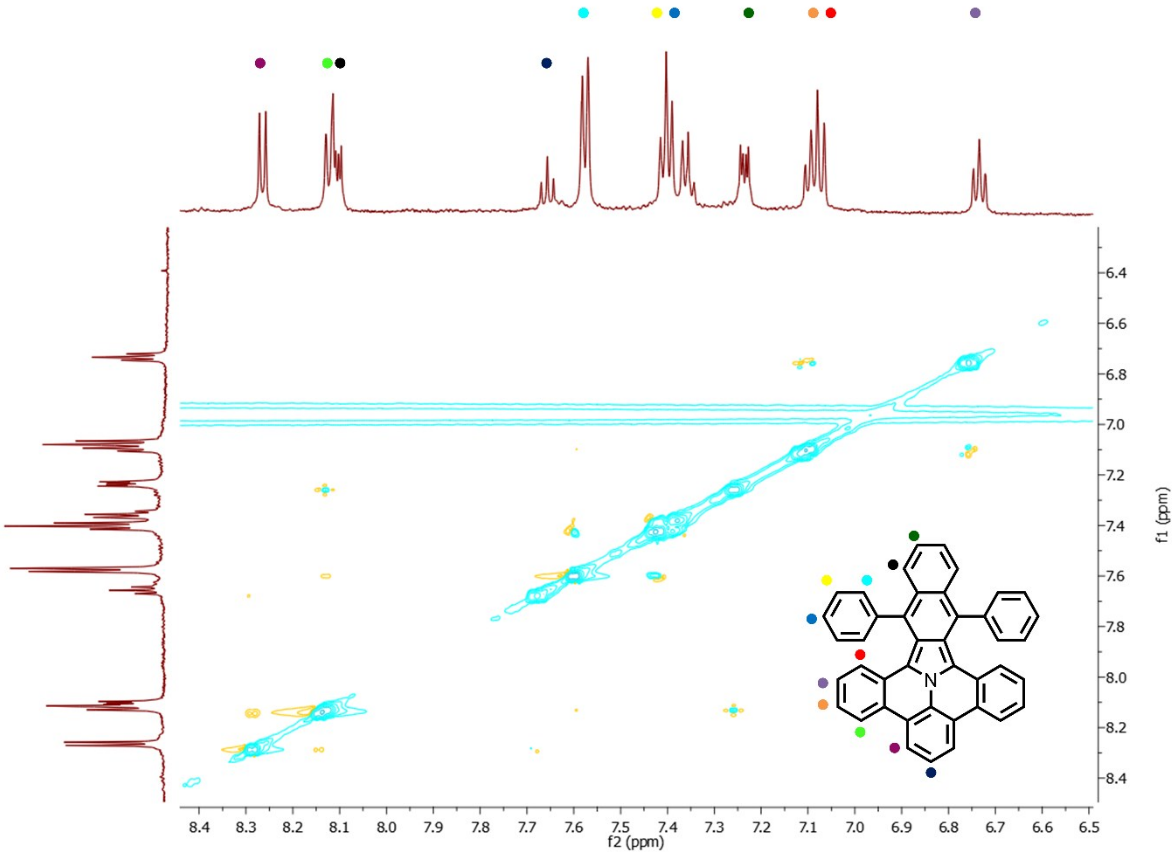


Fig. S7 NOESY-2D-NMR spectrum of **1** at 298 K in $C_2D_2Cl_4$ and hydrazine.

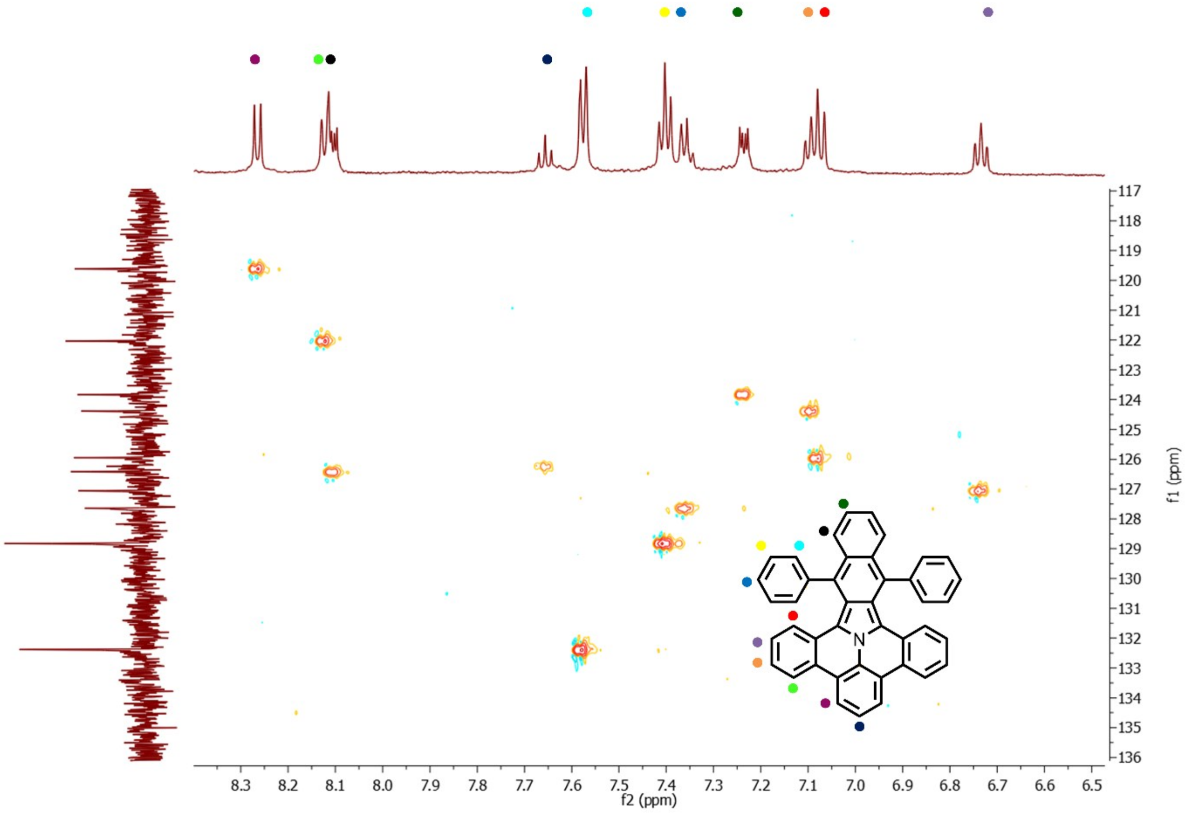


Fig. S8 HSQC-2D-NMR spectrum of **1** at 298 K in $C_2D_2Cl_4$ and hydrazine.

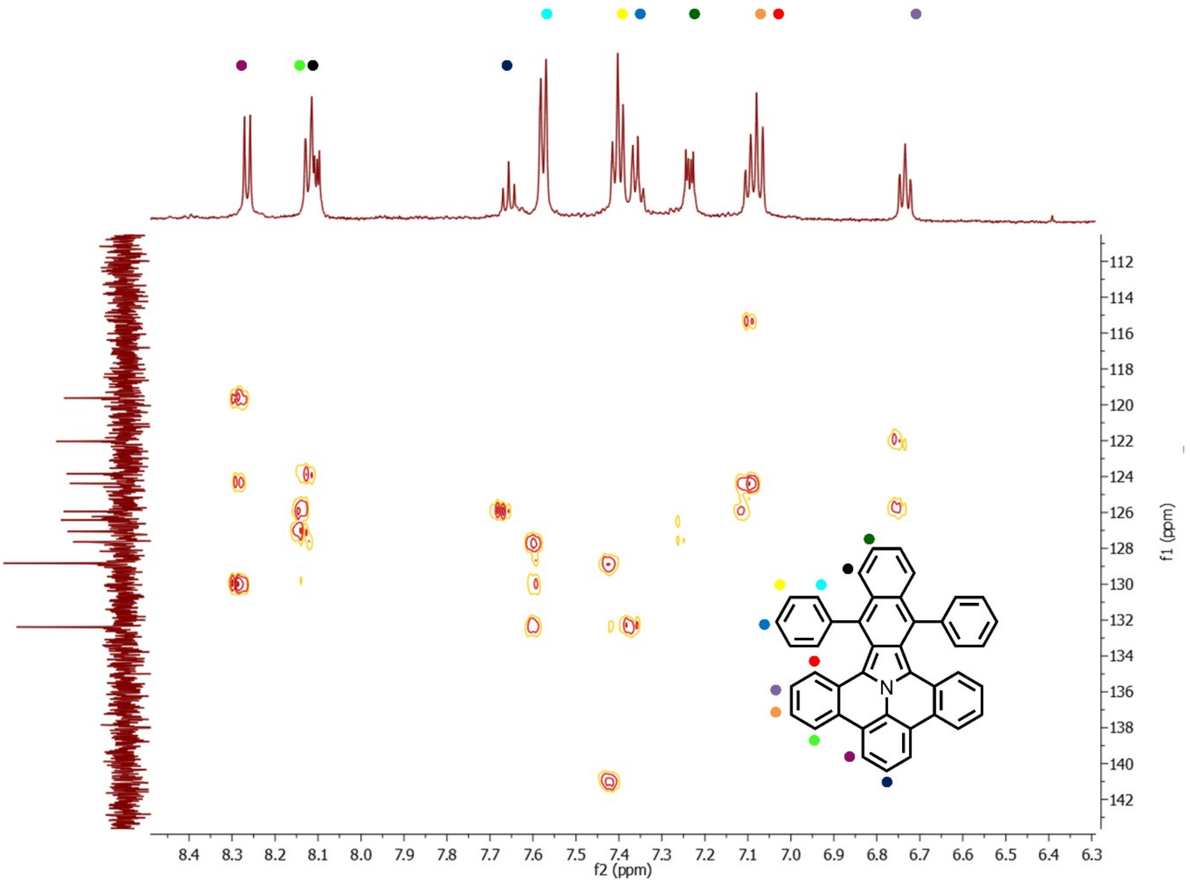


Fig. S9 HMBC-2D-NMR spectrum of **1** at 298 K in $C_2D_2Cl_4$ and hydrazine.

Additional STM images

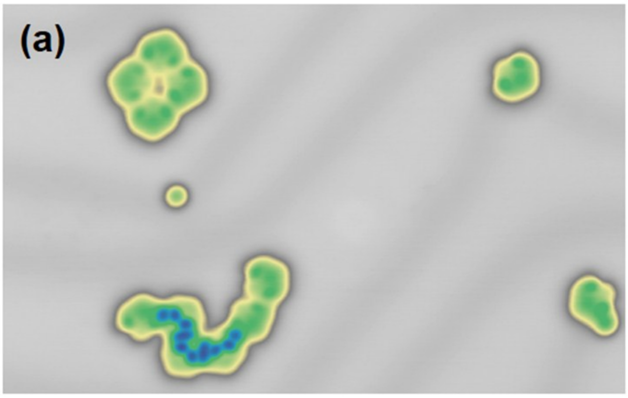


Fig. S10 Overview STM image of precursor **1** after sublimation on the Au(111) surface held at room temperature showing the adsorption of single molecules on the elbow sites and the formation of small supramolecular structures. Imaging parameters: U = 0.5 V, I = 100 pA, 20 nm x 12.5 nm.

We deposited the molecular precursor **1** on an atomically clean Au(111) surface held at room temperature in a sub-monolayer coverage. Adsorbed mostly at the elbow sites of the surface reconstruction, they possess a characteristic shape with two bright features located on both sides of the symmetry axis of the molecule. These features correspond to the phenyl rings, which lead to the non-flat adsorption geometry. On a supramolecular scale, the non-planarity resulted in the formation of chain-like and tetrameric structures, stabilized by non-covalent interactions. (see Figure S10)

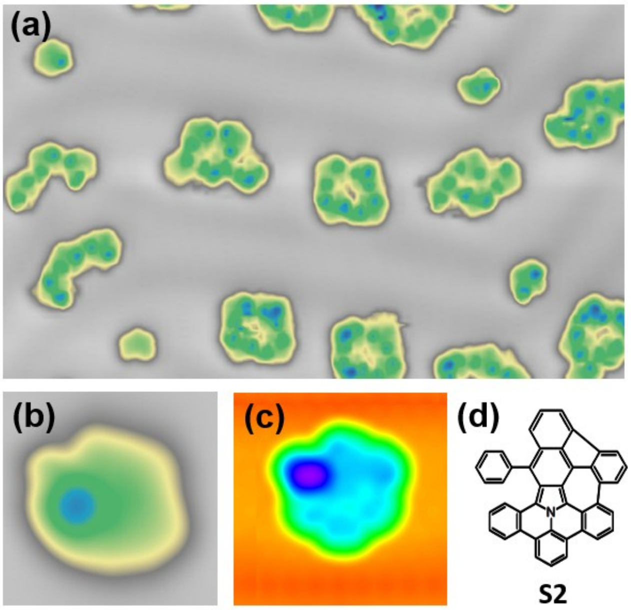
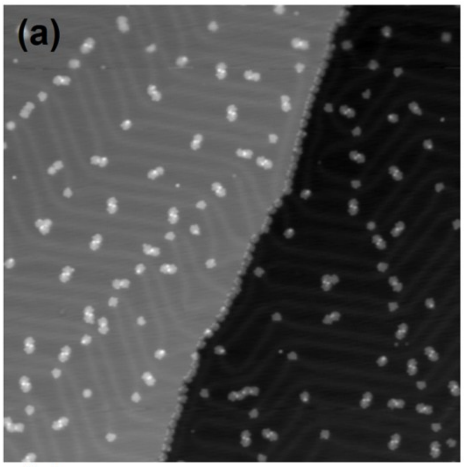


Fig. S11 Annealing the sample to 250 ˚C leads to the partial reaction of molecules. (a) Overview STM image. Imaging parameters: U = 0.5 V, I = 50 pA, 25 nm x 15 nm. (b) STM image of a single half-reacted molecule (-0.5 V, 100 pA, 2.5 nm x 2.5 nm). (c) Calculated STM image of this species (the same size). (d) Chemical structure of the half-reacted species **S2**.

The first structural changes started to appear after annealing to 250 ˚C (Figure S11). Although the majority of the precursor **1** remained unchanged at this step, there is a significant portion of the species with changed topography. Among them, we could identify mainly intermediates that resembles the appearance of an unreacted molecule on one side, but is flat on the other side, suggesting the successful cyclodehydrogenation (Figure S11b). Therefore, we assign this to the half-reacted species **S2**, which is supported by the calculated STM image (Figure S11c).



(b)

Molecule	Counts	Proportion
Nanographene 3	8	10%
Nanographene 4	19	25%
Nanographene 5	51	65%

Fig. S12 (a) Overview STM image after annealing the sample to 300 °C with the different reacted species (Imaging parameters: U = -0.5 V, I = 100 pA, 80 nm x 80 nm). (b) Table of the proportion of the different reacted nanographenes 3, 4 and 5 after annealing to 300 °C.

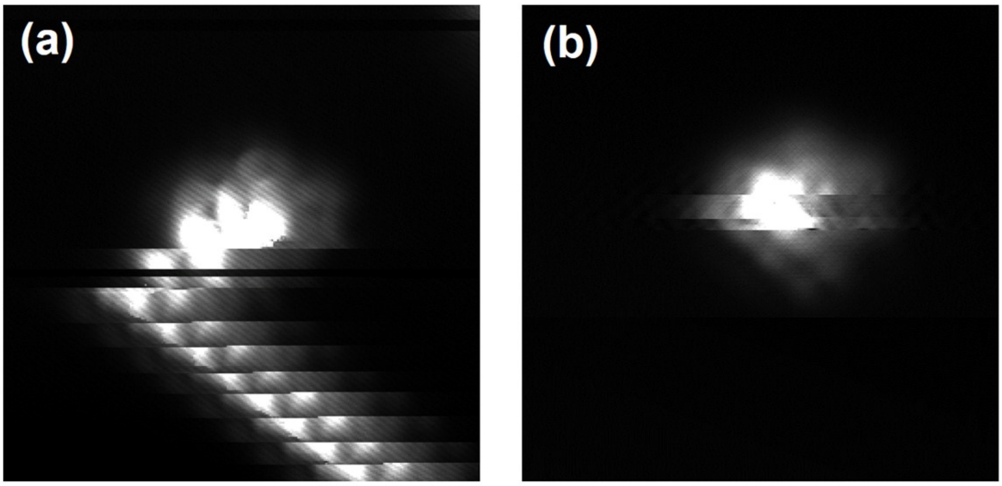


Fig. S13 Constant-height images of nanographenes **3** with a CO-functionalized tip. (a) Constant height image leading to the movement of the nanographenes during imaging (set-point: U = -0.5 V, I = 100 pA; imaging conditions at const. height: U = 10 mV; Z-Offset = +0.8 Å). (b) No inner structure visible and still movement after retracting the tip by 0.6 Å as compared to (a). (image sizes: 3.5 nm x 3.5 nm)

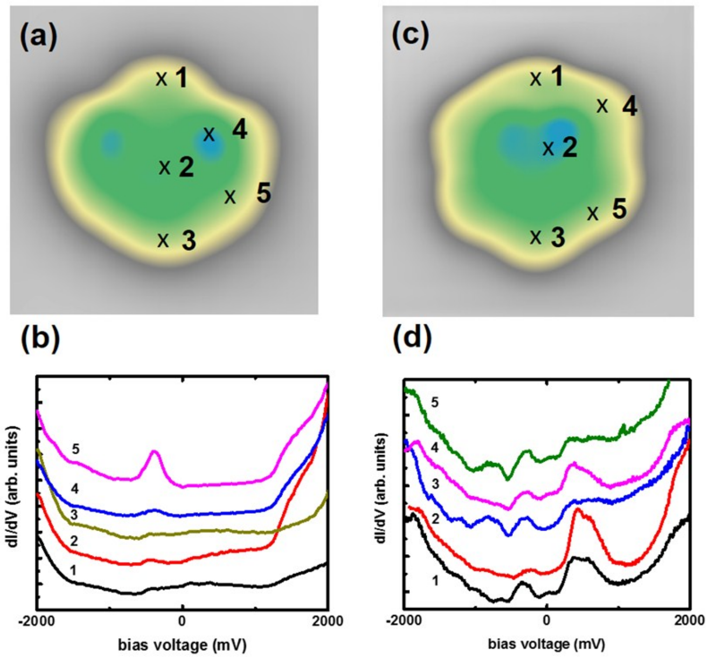


Fig. S14 (a) Precursor molecule **1** after deposition on the Au(111) surface. Imaging parameters: U = 0.5 V, I = 100 pA, 2.5 nm x 2.5 nm. (b) Collected dI/dV spectra acquired on the molecule at the positions shown by the crosses and numbered as in the inset in (a) (a) Nanographene **3** on the Au(111) surface. Imaging parameters: U = 0.5 V, I = 100 pA, 2.5 nm x 2.5 nm. (b) Collected dI/dV spectra acquired on the molecule at the positions shown by the crosses and numbered as in the inset in (c).

References

1. X.-Y. Wang, M. Richter, Y. He, J. Björk, A. Riss, R. Rajesh, M. Garnica, F. Hennersdorf, J. J. Weigand, A. Narita, R. Berger, X. Feng, W. Auwärter, J. V. Barth,C.-A. Palma and K. Müllen, *Nature Communications*, 2017, **8**, 1948.