Nanographenes, namely polycyclic aromatic hydrocarbons (PAHs) with nanoscale dimensions (>1 nm), are atomically precise cutouts from graphene. They represent prime models to enhance the scope of chemical and physical properties of graphene through structural modulation and functionalization. Defined nitrogen doping in nanographenes is particularly attractive due to its potential for increasing the number of $\pi$-electrons, with the possibility of introducing localized antiaromatic ring elements. Herein we present azomethine ylide homocoupling as a strategy to afford internally nitrogen-doped, non-planar PAH in solution and planar nanographene on surfaces, with central pyrazine rings. Localized antiaromaticity of the central ring is indicated by optical absorption spectroscopy in conjunction with theoretical calculations. Our strategy opens up methods for chemically tailoring graphene and nanographenes, modified by antiaromatic dopants.
Together with the advent of graphene science, an important chapter in organic chemistry has opened exploring the synthesis of extended polyenic aromatic hydrocarbon (PAH) systems. Large PAHs, as represented by hexa-peri-hexabenzocoronene (HBC, 1) with π-conjugated structures extending over 1 nm, can be regarded as structurally defined, nanoscale cutouts of graphene, designated nanographene molecules1–3. Such systems can serve as platforms both for investigating the physical and chemical properties of graphene upon heteroatom-doping, as well as for the development of semiconducting materials (see Fig. 1). Doped nanographenes are similarly relevant for the study of aromaticity and antiaromaticity, which are fundamental concepts of organic chemistry4–6. As proposed by Hückel6 and later by Frost and Musulin7, as well as Breslow8, while cycles with [4n]π-electrons show aromatic character with strong stabilization, cycles with [4n + 2]π-electrons are antiaromatic and destabilized. Despite a few theoretical suggestions on local antiaromatic “defects”, or “dopants”, in graphene9,10 and rapidly increasing variety of nanographene molecules, well-defined nanographene molecules with a pronounced antiaromatic ring, i.e., a local antiaromatic element, remain challenging targets to be explored.

Nitrogen (N)-doped nanographenes have attracted considerable attention due to promising electronic and magnetic properties11 offering potential applications in metal-free catalysis12,13 and sensing14,15. However, the existing synthetic protocols do not allow the precise control of the doping level and heteroatom positioning. The chemical nature of nitrogen dopants (i.e., pyridinic, pyrrolic, and “graphitic” N atoms) remains largely undefined16, restricting the fine-tuning of the resulting properties as well as reliable structure-property relationship elucidation. In this regard, structurally well-defined N-doped nanographene molecules offer an opportunity to accurately investigate N-doping effects. Notwithstanding, N-doping of defined nanographenes has been predominantly limited to pyridinic17–19 (e.g., compound 219 in Fig. 1) and pyrrolic (e.g., compounds 320 and 421,22) N atoms, which only resulted in replacing benzene rings with other N-containing π aromatic rings, such as pyrimidines and pyrroles.

To develop nanographenes with strong antiaromatic ring dopants, we consider the possibility of incorporating a pyrazine structure inside the aromatic core, which employs two “graphitic” N atoms in the framework, thus providing additional π-electrons when compared to a benzene ring. 1,4-Disubstituted pyrazine entails intriguing chemistry, expressing π antiaromatic (neutral), 7π non-aromatic (cationic), or 6π aromatic (dicaticionic) properties, depending on its oxidation state. Thus, a pyrazine ring embedded in a carbonaceous hexagonal structure serves as a localized antiaromatic ring dopant, influencing ring and perimeter currents23,24 with the potential to give rise to new types of 2D materials with unconventional semiconducting properties.

Here, we report in situ solution synthesis and spectroscopy of the partially fused, pyrazine-incorporated hexabenzoperylene (HBP) derivative 6a as well as on-surface synthesis of the diaza-HBC 7c with a completely embedded pyrazine core. N-doped HBP 6a features an 8π antiaromatic core structure, as documented by 1H NMR and UV–vis absorption spectroscopy together with density functional theory (DFT) calculations. Notably, the solution chemistry of polycyclic aromatic azomethine ylides (PAMys)26 can be successfully adapted on the Ag(111) surface, achieving the synthesis of 7c through surface-assisted homocoupling of the dibenzo-η6-azaphenalene (DBAP) salt 5c and concomitant cyclohydrogenation. High-resolution scanning
tunneling microscopy (STM) and frequency-modulated atomic force microscopy (FM-AFM)\textsuperscript{27} unambiguously elucidate the chemical structure of diaza-HBC 7c. Moreover, computational modeling using DFT indicates that 7c conserves its $8\pi$ character on the Ag(111) surface. Nucleus-independent chemical shift (NICS)\textsuperscript{28} calculations on 6a and 7c reveal high positive values at the center and 1 Å above the center of the central pyrazine rings (NICS(0) and NICS(1) values, respectively), indicative of anti-

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Fig. 3 Structural characterizations of the in situ generated diaza-HBP 6a. a $^1$H NMR spectra of 8a and 6a together with their structural assignments (C$_2$HDCl$_2$). Compared to precursor 8a, the signals of 6a were down-field shifted, corroborating the extension of the $\pi$-conjugation. b Aromatic region of the $^1$H-$^1$H COSY spectrum of 6a in C$_2$D$_2$Cl$_4$. c Aromatic region of the $^1$H-$^1$H NOESY spectrum of 6a in C$_2$D$_2$Cl$_4$. d High-resolution MALDI-TOF MS spectrum of 6a, with an inset showing its experimental (black line) and simulated isotopic distributions (red line).

Fig. 4 Photophysical investigations. a Experimental and b TDDFT-simulated absorption spectra of 6a and its precursor 8a. The simulated spectra of 6a showed the appearance of a new band at 577 nm, in accordance with the experimental observation. c X-ray single-crystal structure of 8c. d DFT-optimized structure of 8a. e DFT-optimized structure of 6a.
aromaticity. These results demonstrate the antiaromatic nature of pyrazine-doped nanographene molecules and provide an on-surface synthesis route to N-doping nanographene materials.

Results

Solution synthesis and characterizations. The synthesis of pyrazine-embedded HBP 6a (Fig. 2) was carried out based on the chemistry of DBAP, which has been employed to construct N-doped PAHs such as dibenzo[cd]ulazulenes and 6b2-azapentabenzo[bc,efhi,k]corannulenes22,26,29,30. DBAP salts 5a-c with different substituents were first synthesized according to our previous method26. They were then dimerized to form precursors 8a–c (Fig. 2) by treatment with a large excess of tributylamine in dry dimethyl sulfoxide (DMSO) under argon at 190 °C. Oxidation of 8a with excess 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) in dry C6D6Cl4 afforded diaza-HBP 6a, as characterized by 1H NMR and mass spectroscopy (MS) analyses (Fig. 3). Diaza-HBP 6a turned out to be extremely unstable probably because of the antiaromatic pyrazine core, and thus the oxidation step was performed in situ in a sealed NMR tube under exclusion of air. Oxidation of other precursors 8b and 8c were also attempted with the same method, but failed to provide corresponding diaza-HBP derivatives according to 1H NMR analysis, suggesting that the electron-donating methoxy groups of 8a played an important role in the reaction31. As shown in Fig. 3a, the disappearance of the characteristic signal from H2 of (5.13 ppm) of 8a indicated complete conversion of the starting material. All the signals in the aromatic region of 6a were down-field shifted compared to those of 8a, in agreement with the extension of the π-conjugation upon dehydrogenation. Notably, proton H2 of 8a is above the neighboring benzene plane according to the optimized geometry by DFT (Fig. 4) and thus is strongly shielded. In contrast, after dehydrogenation of 8a via DDQ, the proton H2 of 6a is shifted away from the neighboring benzene into its deshielding region, in accordance with a down-field shift of H2 in the 1H NMR spectrum. Moreover, 2H–1H correlation spectroscopy (COSY) and 1H–1H nuclear Overhauser effect spectroscopy (NOESY) analyses (Fig. 3b, c) allowed unambiguous assignments of the proton signals of 6a. The structure was further characterized by 1H–13C heteronuclear single-quantum correlation (HSQC) and 1H–13C heteronuclear multiple-bond correlation (HMBC) spectroscopies. The chemical identity of 6a was confirmed by high-resolution matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) MS, which showed a matching isotopic pattern starting at m/z = 590.1980, in agreement with the theoretical value of 590.1994 (Fig. 3d).

To investigate the photophysical properties of 6a, we prepared diaza-HBP 6a in situ by carrying out the oxidation reaction in a sealed quartz cell and recorded the absorption and photoluminescence spectra. As shown in Fig. 4a, dimer precursor 8a exhibited an absorption maximum at λmax = 390 nm, and an absorption onset at ≈500 nm. After dehydrogenation, the absorption maximum barely changed, but a new band emerged in the range of 500 to 630 nm, suggesting an extended π-conjugation. To further understand the photophysical properties, DFT calculations were performed on both 8a and 6a. In order to determine the exact molecular geometry of 8a, growth of single crystals of 8a–c was pursued and a single crystal of 8c suitable for X-ray analysis was successfully obtained, revealing an anti-folded structure (Fig. 4c). Thus, the anti-folded geometry was employed as input geometry for the DFT optimization of similar precursors (Fig. 4d). DFT studies on dehydrogenated 6a indicate that the anti-folded conformation (Fig. 4e) is energetically preferred compared to the twisted one. Time-dependent DFT (TDDFT) calculations of 6a and 8a indicated that the emerging absorption band of 6a can be attributed to the HOMO→LUMO + 2 transition (Fig. 4b and Supplementary Tables 1–3). The HOMO→LUMO transition of 6a is symmetry forbidden, and 6a is non-emissive, in agreement with previous reports on antiaromatic systems32,33.

On-surface synthesis of 7c. Despite generation of diaza-HBP 6a through solution synthesis, further characterization of 6a was restricted by its low stability. In addition, attempts to oxidize intermediate product 8a–c directly to diaza-HBC derivatives resulted in insoluble solids, which could not be characterized.

Fig. 5 On-surface homocoupling of precursor 5c yields fully planar and neutral diaza-HBC 7c on Ag(111). a Scanning tunneling microscopy (STM) overview of reaction product and unreacted species on Ag(111). Vt = 30 mV, It = 10 pA. b Constant-height STM data of diaza-HBC with partially superposed molecular model. Vt = 5 mV. c Frequency-modulated atomic force microscopy (FM-AFM) and d Laplace-filtered FM-AFM data reveal details in the molecular structure. Apparent C–C distance 1.5 Å (black), N–C 1.8 Å (blue). For simulation parameters see Methods. g–n Constant-height STM data of diaza-HBC with partially superposed molecular structure. Apparent C–C distance 1.3 Å (black), N–C 1.5 Å (blue). For simulation parameters see Methods. e–f g–i k–l m–n

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This led us to adapt the solution chemistry of PAMys to on-surface synthesis\textsuperscript{34–37}, which offers today a new approach to organic chemistry. We thus deposited 5c on Ag(111) by molecular beam evaporation (Methods section and Supplementary Fig. 2). Upon annealing to 270 °C, small quantities of diaza-HBC 7c were detected as displayed in Fig. 5a. Unlike solution synthesis (Fig. 2), no intermediate product 8c was identified after annealing the deposited 5c in several ultra-high vacuum (UHV) preparations on Ag(111), Ag(100), Cu(111), and boron nitride (BN) on Cu(111), suggesting that homocoupling and dehydrogenation occur synergistically at the employed reaction temperatures. Notably, 7c was detected on BN/Cu(111) templates\textsuperscript{38} at similar annealing temperatures in trace-quantities (Supplementary Fig. 3), indicating that the on-surface coupling strategy proceeds in a metal-free fashion, further motivating studies on reaction mechanisms and on-surface synthesis on insulators.

High-resolution, constant height STM (Fig. 5b) and FM-AFM (Fig. 5c, d), using CO-functionalized tips, confirmed 7c on Ag (111). In FM-AFM data on Ag(111), the central pyrazine ring of 7c (Fig. 5d) appears distorted. Observation of a $D_{2h}$ symmetry points toward the nitrogen atoms sitting at the positions indicated by white arrows. Note that the predicted DFT C=C bond length of the central pyrazine ring is 1.40 Å vs. 1.42 Å for the N–C bond, and the molecule remains planar ($z \pm 0.05$ Å) for calculated adsorption sites on Ag(111) (Supplementary Fig. 4). Bond lengths in AFM data typically undergo distortions\textsuperscript{27,39–41} especially under the influence of electrostatic interactions with the CO tip\textsuperscript{42–46}. This causes a distorted appearance of the central pyrazine ring. Quantitative evidence of these combined effects is summarized in the AFM frequency shift simulation including a DFT-derived electrostatic potential (Fig. 5e, f, see Methods section). Note how the apparent C=C bond length in the simulated image (1.3 Å) appears shorter than the apparent N–C bond length (1.9 Å, Fig. 5f), in good agreement with the experimental data (1.0 and 1.8 Å, respectively). When a neutral tip is employed for the AFM simulation the central pyrazine ring is fully symmetric, with apparent N–Ca n dC=C lengths of 1.5 Å (Fig. 5e), confirming that the distortions in the FM-AFM data originate mostly from electrostatic effects.

Combined scanning probe data and theoretical investigations indicate that 7c remains neutral (conserving its pyrazine $8\pi$ state) on the surface, which is a requirement for antiaromaticity. Bader charge analysis was employed to assess molecule-substrate charge transfer. As shown by NICS calculations on isolated molecules, a neutral species of 7c implies an $8\pi$ pyrazine unit, which is antiaromatic in the isolated state. Upon oxidation, a positively

![Fig. 6 DFT electronic structure comparison of the isolated and Ag(111)-supported diaza-HBC 7c. a Projected $p_z$ contributions to the density of states of isolated 7c (blue) and on Ag(111). The Fermi energy ($E_F$) of the isolated molecule has been arbitrarily defined for comparison. b, c Contribution of the highest occupied molecular orbital H$_{ad}$ (at $-0.32$ eV in a) and (H-1)$_{ad}$ to 7c on Ag(111). d Electron density difference between 7c on Ag(111) and the isolated molecule plus isolated substrate. Red regions represent electron density depletion, whilst blue electron density gain. Atoms are rendered translucent. e, f Highest occupied molecular orbital H and H-1 of isolated 7c. These results suggest that antiaromatic character is preserved on Ag(111).](image)
charged “7π” radical cation state of the diaza-HBC 7c displays significantly reduced antiaromaticity and a “6π” dication species exhibits an aromatic character (Supplementary Fig. 1). On Ag (111), theoretical charge analysis finds only marginal electron transfer to the substrate (the molecule is charged positively by less than + 0.14e for all calculated molecular configurations on Ag (111), Supplementary Fig. 4). Moreover, when trying to enforce molecular charging by removing electrons from the calculated system, the charge at the molecule was only increased to about + 0.8e, when the whole 29 Å × 25 Å × 22 Å unit cell was charged by + 10e. These theoretical analyses indicate that 7c remains in the neutral “8π” state on Ag(111). The good correlation of the STM experimental data with Tersoff-Hamann simulations supports the validity of the theoretical conclusions (Fig. 5g, n and see Supplementary Fig. 5 for extended comparisons). It should be noted how at negative energies (voltages), the symmetry of the tunneling image follows the diaza-HBC 7c hexagonal frame (marked by a white arrow, Fig. 5g, h). At high positive biases (between 0.9 and 2.1 eV, see Supplementary Fig. 5) the symmetry of the tunneling data is rotated (blue arrows, Fig. 5k, l) with respect to the diaza-HBC hexagonal frame, that is, tunneling is enhanced between the bay regions in the periphery of diaza-HBC. Notably, between ~0.5 and 0.5 eV (Fig. 5i, j, m, n), both experiment and simulation follow the hexagonal symmetry of 7c on Ag(111).

Having identified a neutral state of 7c on Ag(111), comparison between 7c on Ag(111) and the isolated antiaromatic species provides evidence on the preserved antiaromatic character of 7c on Ag(111). Figure 6 depicts the site-projected density of states (PDOS) as well as plots for the individual Kohn-Sham orbitals. Only marginal hybridization resulting in mid-gap states is observed when the isolated molecule interacts with Ag(111) (Fig. 6a, red line). The mid-gap states do not appear to significantly influence the antiaromatic character of the adsorbed molecule: the HOMO (H) and HOMO-1 (H-1) signatures of isolated 7c are reflected undisturbed at the surface (compare Fig. 4b, c, e, f). Instead, the electronic density difference plot (Fig. 6d) shows that the mid-gap states originate from homogeneous orbital contributions, including the role of rings which are considered to be aromatic (Supplementary Fig. 1). Note that scanning tunneling spectroscopy follows the major theoretical LDOS features including a pronounced broadening (Supplementary Fig. 6).

Discussion

In summary, we have demonstrated the chemical synthesis of a partially fused PAH in solution and the on-surface synthesis of a fully planarized nanographene molecule with antiaromatic pyrazine dopants. Diazah-BHP 6a has been achieved in solution and investigated by NMR, high-resolution MALDI-TOF MS and UV-vis absorption spectroscopy, while the fully cyclized diaza-HBC 7c has been successfully fabricated on Ag(111) and characterized by STM and FM-AFM. We suggest that pyrazine rings are potential candidates to be included in 2D materials to spawn novel functional properties induced by breaking the conjugated lattice via antiaromatic ring dopants. Importantly, the chemistry of on-surface azomethine ylide homocoupling reported here opens up a new route to novel nanographene materials, especially graphene nanoribbons, on a large variety of substrates.

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Methods

Procedure for the in situ preparation of 6a. Inside an argon-filled glovebox, precursor 8a (2.0 mg, 1.0 eq.), DDQ (15 mg, 20 eq.) and C2D2Cl4 (0.6 mL) were added sequentially to a scalable NMR tube. The mixture was heated at 100 °C for 1 min and cooled down to room temperature, and then analyzed by NMR spectroscopy. Synthetic procedures and characterization data of 8a–c and 6a are provided in the Supplementary Methods and Supplementary Figs. 7–45.

STM and FM-AFM measurements. Precursor 5c was sublimated between 200 °C and 220 °C at 10–12 mbar. Data was acquired in situ using a CreaTest STM-AFM (5.5 K) under ultra-high vacuum (10–10 mbar). AFM data were taken in constant height mode at 0.0 V bias, using a PtPlus sensor (resonance frequency ~22 kHz, oscillation amplitude: 70 pm to 100 pm). The tungsten tip was prepared by focused-ion beam processing and in situ tip forming. For subsequent tip functionalization, carbon monoxide (CO) was dosed on the cold sample and transferred to the tip. The images were processed using the Gwyddion software package42.
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