Electronic Supplementary Material (ESI) for ChemComm. This journal is © The Royal Society of Chemistry 2020

# **Electronic supplementary information**

## **On-surface synthesis of super-heptazethrene**

Shantanu Mishra, Jason Melidonie, Kristjan Eimre, Sebastian Obermann, Oliver Gröning, Carlo A. Pignedoli, Pascal Ruffieux, Xinliang Feng and Roman Fasel

#### Table of contents:

1. Experimental and theoretical methods	2
2. Additional STM/STS data and calculations	3
3. Synthetic procedures	6
4. NMR spectra	8
5. References	17

#### 1. Experimental and theoretical methods

**1.1 Sample preparation and STM/STS measurements.** STM measurements were performed with a Scienta Omicron low-temperature STM operating at 4.5 K and base pressure below  $5 \times 10^{-11}$  mbar. Au(111) single crystal surfaces were prepared by Ar<sup>+</sup> sputtering and annealing cycles. Precursor molecule **2** was contained in a quartz crucible in powder form and deposited from a home-built evaporator at 508 K on Au(111) held at room temperature. STM images and dI/dV maps were acquired in constant-current mode. Unless noted otherwise, gold-coated tungsten tips were used for imaging and spectroscopy. Indicated tunneling biases are provided with respect to the sample. dI/dV spectra and maps were acquired with a lock-in amplifier operating at a frequency of 860 Hz. Modulation voltage (root mean square amplitude,  $V_{\rm rms}$ ) for each measurement is provided in the respective figure captions. Ultrahigh-resolution STM images were acquired with CO-functionalized tips, where the molecules are scanned in constant-height mode, and the current channel is displayed. Open feedback parameters, and subsequent tip approach distance ( $\Delta z$ ) for each measurement is provided in the respective figure captions. The data shown in this study were processed and analyzed with WaveMetrics Igor Pro or WSxM software.<sup>1</sup>

**1.2. TB and MFH calculations.** The tight-binding calculations were performed by numerically solving the mean-field Hubbard Hamiltonian with nearest neighbor hopping:

$$\widehat{H}_{MFH} = -t \sum_{\langle \alpha,\beta\rangle,\sigma} c^{\dagger}_{\alpha,\sigma} c_{\beta,\sigma} + U \sum_{\alpha,\sigma} \langle n_{\alpha,\sigma} \rangle n_{\alpha,\overline{\sigma}} - U \sum_{\alpha} \langle n_{\alpha,\uparrow} \rangle \langle n_{\alpha,\downarrow} \rangle,$$
(S1)

Here,  $c_{\alpha,\sigma}^{\dagger}$  and  $c_{\beta,\sigma}$  denote the spin selective ( $\sigma \in \{\uparrow,\downarrow\}$  with  $\bar{\sigma} \in \{\downarrow,\uparrow\}$ ) creation and annihilation operator at neighboring sites  $\alpha$  and  $\beta$ , t is the nearest neighbor hopping parameter (with t = 2.7 eV used), Uis the on-site Coulomb repulsion,  $n_{\alpha,\sigma}$  is the number operator and  $\langle n_{\alpha,\sigma} \rangle$  is the mean occupation number at site  $\alpha$ . Orbital electron densities,  $\rho$ , of the  $n^{\text{th}}$ -eigenstate with energy  $E_n$  have been simulated from the corresponding state vector  $a_{n,i,\sigma}$  by:

$$\rho_{n,\sigma}(\vec{r}) = \left| \sum_{i} a_{n,i,\sigma} \phi_{2p_z}(\vec{r} - \vec{r}_i) \right|^2, \tag{S2}$$

where *i* denotes the atomic site index, and  $\phi_{2p_z}$  denotes the Slater  $2p_z$  orbital for carbon.

**1.3. DFT and GW calculations.** DFT, GW and image charge (IC) correction calculations were performed with the CP2K code.<sup>2</sup> Due to the IC correction depending on the adsorption details, all the presented orbital energy levels were calculated on the gas-phase molecule in the adsorption conformation on Au(111).

For the adsorption geometry, the surface/adsorbate system was modeled within the repeated slab scheme,<sup>3</sup> with a simulation cell containing four atomic layers of Au along the [111] direction and a layer of hydrogen atoms to passivate one side of the slab in order to suppress one of the two Au(111) surface states. 40 Å of vacuum was included in the simulation cell to decouple the system from its periodic replicas in the direction perpendicular to the surface. The electronic states were expanded with a TZV2P Gaussian basis set<sup>4</sup> for C and H species and a DZVP basis set for Au species. A cutoff of 600 Ry was used for the plane wave basis set. Norm-conserving Goedecker-Teter-Hutter pseudopotentials<sup>5</sup> were used to represent the frozen core electrons of the atoms. We used the PBE parameterization for the generalized gradient approximation of the exchange correlation functional.<sup>6</sup> To account for van der Waals interactions, we used the D3 scheme proposed by Grimme.<sup>7</sup> The Au surface was modeled by a supercell of 41.27×40.85 Å<sup>2</sup> corresponding to 224 surface units. To obtain the equilibrium geometries, we kept the atomic positions of the bottom two layers of the slab fixed to the ideal bulk positions, and all other atoms were relaxed until forces were lower than 0.005 eV/Å.

The gas-phase DFT orbital energies were calculated within the restricted Kohn-Sham (RKS, for the closed-shell configuration) and unrestricted Kohn-Sham (UKS, for the open-shell singlet and tripletcon-figurations) formalisms. The non-periodic cell of  $25 \times 30 \times 16$  Å<sup>3</sup> was used together with the Martyna-Tuckerman Poisson solver, while other inputs were kept equivalent to the slab calculation.

The eigenvalue self-consistent GW and IC correction calculations were also performed within the RKS and UKS formalism based on the DFT PBE wavefunctions. We employed the GTH pseudopotentials and analytic continuation with a two-pole model. The aug-DZVP basis set from Wilhelm et al.<sup>8</sup> was

used. The IC correction accounting for the screening by the metal surface was applied according to Neaton et al.<sup>9</sup> To determine the image plane position with respect to the molecular geometry, we used a distance of 1.42 Å between the image plane and the first surface layer, as reported by Kharche et al.<sup>10</sup>

1.4. Solution synthesis, general aspects. Unless otherwise stated, commercially available starting materials, catalysts, reagents, and dry solvents were used without further purification. Reactions were performed using standard vacuum-line and Schlenk techniques. All starting materials were obtained from Sigma Aldrich, TCI, abcr, Alfa Aesar, Acros Organics, Sigma Aldrich or chemPUR. Catalysts were purchased from Strem. Column chromatography was performed on silica (SiO<sub>2</sub>, particle size 0.063-0.200 mm, purchased from VWR) or aluminum oxide (Al<sub>2</sub>O<sub>3</sub>, Alox 90 active neutral, activity stage I, purchased from Merck KGaA). Silica-coated aluminum sheets with a fluorescence indicator (TLC silica gel 60  $F_{254}$ , purchased from Merck KGaA) were used for thin-layer chromatography. MALDI-TOF spectra were recorded on a Bruker Autoflex Speed MALDI-TOF MS (Bruker Daltonics, Bremen, Germany). All samples were prepared by mixing the analyte and the matrix, 1,8-dihydroxyanthracen-9(10H)-one (dithranol, purchased from Fluka Analytical, purity >98%) or trans-2-[3-(4-tertbutylphenyl)-2-methyl-2-propenylidene]malononitrile (DCTB, purchased from Sigma Aldrich, purity >99%) in the solid state. High-resolution ESI and APCI mass spectra were recorded with an Agilent 6538 UHD accurate-mass O-TOF LC-MS system using the positive and negative mode. NMR data were recorded on a Bruker Ascend 300 spectrometer operating at 300 MHz for <sup>1</sup>H and 76 MHz for <sup>13</sup>C with standard Bruker pulse programs at room temperature (296 K). Chemical shifts were referenced to  $\delta_{TMS}$ = 0.00 ppm (<sup>1</sup>H, <sup>13</sup>C). Chemical shifts ( $\delta$ ) are reported in ppm. Coupling constants (J) are reported in Hz. Dichloromethane-d<sub>2</sub> ( $\delta$ (<sup>1</sup>H) = 5.32 ppm,  $\delta$ (<sup>13</sup>C) = 53.8 ppm) was used as solvent. The following abbreviations are used to describe peak patterns as appropriate: s = singlet, d = doublet, and m = multiplet. Dichloromethane-d<sub>2</sub> (99.9 atom% D) was purchased from Eurisotop. Melting points were determined on a Büchi Melting Point M-560 in a range of 50-400 °C with a temperature rate of 10 °Cmin<sup>-1</sup>. FTIR spectrometry was carried out on a Bruker Tensor II with an ATR crystal at room temperature.

#### 2. Additional STM/STS data and calculations



Fig. S1 (a and b) High-resolution (a) and ultrahigh-resolution (b) STM images of four 1 molecules. The three molecules toward the bottom and the one at the top left corner are enantiomers. (c) Ultrahigh-resolution STM image of 1, whose Laplace-filtered version is shown in Fig. 2c. Scanning parameters: (a) V = -1 V, I = 100 pA; (b and c) V = -5 mV, I = 50 pA,  $\Delta z = -0.7$  Å.



**Fig. S2** (a) TB wave functions of the HOMO-1 to LUMO+1 of **1**. Red/green isosurfaces denote opposite signs of the wave function. (b) MFH spin-polarized wave functions of the SOMOs and SUMOs of **1** in the open-shell singlet state. Also shown is the spin polarization plot of **1**, where blue/red isosurfaces denote mean population of spin up/spin down electrons. The numbers denote the largest mean populations of spin up electrons at the upper terminus of **1**. (c) MFH energy spectrum, spin-polarized wave functions of the SOMOs and SUMOs, and spin polarization plot of **1** in the open-shell triplet state. (d) Overview STM image after annealing **2** on Au(111) at 280 °C. **1** and **1'** molecules are highlighted. (e and f) High-resolution STM image and chemical structure of **1'**. The uncyclized methyl group is highlighted with a dashed oval. (g) TB energy spectrum of **1'**, along with the calculated wave function of the zero-energy state. To compute the electronic structure of **1'** with the TB model, we consider the structure where the methyl group, highlighted by the thick solid line, is replaced with a hydrogen atom, amounting to the carbon atom belonging to the methyl group as being out of conjugation with the rest of the molecular system. (h) dI/dV spectroscopy on **1'** in the vicinity of the Fermi energy revealing a Kondo resonance (filled circles), with the corresponding fit with the Frota function (solid line). Scanning parameters: (a) V = -10 mV, I = 100 pA; (b) V = -200 mV, I = 100 pA. Open feedback parameters for dI/dV spectroscopy: V = -50 mV, I = 500 pA;  $V_{\rm rms} = 400$  µV.

The electronic structure of diradicaloids such as 1 is chemically depicted as a resonance between closed-shell Kekulé and open-shell non-Kekulé forms (Fig. 1a), with the equivalent physical picture being the competition

between the electronic hybridization energy (leading to the formation of HOMO and LUMO, and a closed-shell ground state; Fig S2a) and the electrostatic Coulomb repulsion between valence electrons (resulting in the formation of SOMOs, and an open-shell ground state; Fig S2b and c). The closed-shell ground state of 1 on Au(111) entails the dominance of the former mechanism, where the edge-localized states hybridize to form the conventional HOMO and LUMO. However, provided the edge-localized states at one of the termini of 1 can be suppressed, the hybridization energy can then be effectively removed. The experimental realization of this scenario is depicted in Fig. S2d, where annealing 2 on Au(111) at a lower temperature of 280  $^{\circ}$ C leads to the formation of 1 with low yields, with the majority of molecules on the surface exhibiting varying degrees of partial cyclization reactions. Fig. S2e and f present the high-resolution STM image and the chemical structure, respectively, of species 1', which contains one uncyclized methyl group. This leads to incomplete formation of zigzag edges at the lower terminus of the molecule, thus suppressing the edge state. Therefore, 1' consists of an odd number of  $\pi$ -electrons and cannot be described by a classical Kekulé structure without leaving an unpaired electron (Fig. S2f). Accordingly, the TB energy spectrum of 1' reveals a single non-bonding zero-energy state occupied by one electron, localized at the upper end of the molecule (Fig. S2g). Such zero-energy states are known to become spin-polarized at infinitesimally small values of Coulomb repulsion, which, in the present case, should lead to 1' being a spin-1/2 system. dI/dV spectroscopy on 1' in the vicinity of the Fermi energy reveals a sharp and pronounced zero-bias peak (Fig. S2h), which we attribute to a Kondo resonance<sup>11</sup> arising from the screening of a localized spin by a delocalized electron gas. Kondo resonances have been previously detected in organic molecules on metal surfaces,<sup>12-14</sup> and its detection in the present case proves the spin-1/2 character of 1'. The spectrum can be accurately modeled with a Frota function, <sup>15,16</sup> and from the fit we obtain a half width at half-maximum  $\Gamma \approx 7$  meV, corresponding to a Kondo temperature  $T_{\rm K} \approx \Gamma / k_{\rm B} = 81$  K.



**Fig. S3** (a) Calculated singlet-triplet gap of 1 within the MFH model, as a function of U (scaled here with respect to t = 2.7 eV). The singlet-triplet gap is calculated as the mean-field energy difference between the converged electronic structures of the open-shell triplet and the open-shell singlet configurations. Over the entire range of U considered here, the antiferromagnetic (AFM), open-shell singlet state is lower in energy than the ferromagnetic (FM), open-shell triplet state. (b) Total magnetic moment of the open-shell singlet state of 1 as a function of U. 1 is driven into an open-shell singlet state for  $U \ge 1.62 \text{ eV}$ .



**Fig. S4** (a –c) Energy spectrum of the open-shell singlet (a), open-shell triplet (b) and closed-shell (c) electronic configurations of **1** in the gas-phase from spin-polarized DFT calculations. The energies of the three configurations are in the order:  $E_{open-shell singlet} < E_{open-shell triplet} < E_{closed-shell}$ . (d) Energies of the HOMO–1 to LUMO+1 resonances of **1** on Au(111) from GW+IC calculations of the open-shell singlet and closed-shell states, and STS. The electronic gap for each case is indicated. Energies of the calculated and experimental levels are aligned at HOMO/SUMO (corresponding to zero energy).



**Fig. S5** (a and b) Constant-height dI/dV maps at the HOMO (a) and LUMO (b) resonances of 1, acquired with a CO-functionalized tip. (c and d) Corresponding Laplace-filtered images for better visibility of the LDOS features. Clearly, the dI/dV maps exhibit different shapes and symmetries, which indicates that they correspond to hybridized states. Open feedback parameters for dI/dV maps: (a) V = -110 mV, I = 300 pA; (b) V = +120 mV, I = 300 pA;  $V_{\rm rms} = 24$  mV.

#### 3. Synthetic procedures

#### 3.1. Synthesis of 1,5-dibromo-2,6-dimethylnaphthalene (4)<sup>17</sup>



In a 100 ml two-necked flask, 2,6-dimethylnaphthalene (10.00 g, 64.01 mmol, 1.00 eq) was dissolved in dichloromethane (30 ml) and cooled down to 0 °C. Bromine (7.21 ml, 140.82 mmol, 2.20 eq) in dichloromethane (20 ml) was added in one hour via dropping funnel. The reaction mixture was stirred at room temperature for 3 h and quenched with a saturated aqueous  $Na_2S_2O_3$  solution (30 ml). The aqueous phase was extracted three times with chloroform (100 ml) and the combined organic layers were dried over MgSO<sub>4</sub>, filtered and all volatiles were evaporated under reduced pressure. The residue was washed with methanol (100 ml) and 1,5-dibromo-2,6-dimethylnaphthalene (18.60 g, 59.23 mmol) was obtained as a white solid in a yield of 93%.

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 8.18 (d, *J* = 8.6 Hz, 2H), 7.43 (d, *J* = 8.6 Hz, 2H), 2.61 (s, 6H) ppm.

<sup>13</sup>C NMR (76 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 136.4, 132.2, 130.2, 126.6, 124.2, 24.1 ppm.

HR-MS (APCI, pos) *m/z*: [M<sup>+</sup>] calculated for C<sub>12</sub>H<sub>10</sub>Br<sub>2</sub>: 311.9144, found: 311.9143, error: -0.32 ppm.

Rf: 0.73 (iso-hexane).

# **3.2.** Synthesis of 2,2'-(2,6-dimethylnaphthalene-1,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaboro-lane) (5)<sup>18</sup>



In a 25 ml pressure tube, 1,5-dibromo-2,6-dimethylnaphthalene (0.70 g, 2.23 mmol, 1.00 eq), potassium acetate (1.75 g, 17.83 mmol, 8.00 eq) and 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (2.26 g, 8.91 mmol, 4.00 eq) were suspended in dimethyl sulfoxide (7 ml) and bubbled with argon for 45 min. The catalyst [1,1'-bis(diphenylphosphino)ferrocene]dichloropalladium(II) (0.33 g, 0.45 mmol, 0.20 eq) was added and the reaction mixture was heated to 80 °C overnight. After cooling down to room temperature, water (20 ml) was added and the aqueous phase was extracted three times with dichloromethane (30 ml). The combined organic layers were dried over MgSO<sub>4</sub>, filtered and all volatiles were evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, dichloromethane) and further washed with hexane. 2,2'-(2,6-dimethylnaphthalene-1,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (0.30 g, 0.74 mmol) was obtained as white solid in a yield of 33%.

mp: 301 °C.

ATR-IR (cm<sup>-1</sup>) v: 2977, 2928, 1503, 1411, 1377, 1332, 1300, 1213, 1166, 1134, 1107, 1031, 963, 862, 839, 812, 699, 664, 603, 577, 508.

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 8.00 (d, *J* = 8.5 Hz, 2H), 7.25 (d, *J* = 8.6 Hz, 2H), 2.56 (s, 6H), 1.46 (s, 24H) ppm.

<sup>13</sup>C NMR (76 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 140.3, 134.7, 129.5, 128.9, 84.4, 25.3, 22.5 ppm.

HR-MS (MALDI-TOF, DCTB) m/z: [M<sup>+</sup>] calculated for C<sub>24</sub>H<sub>34</sub>B<sub>2</sub>O<sub>4</sub>: 408.2638, found: 408.2625, error = -3.18 ppm.

R<sub>f</sub>: 0.47 (dichloromethane).

#### **3.3.** Synthesis of 9,9'-(2,6-dimethylnaphthalene-1,5-diyl)dianthracene (2)<sup>19</sup>



In a 25 ml pressure tube, 2,2'-(2,6-dimethylnaphthalene-1,5-diyl)bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (70 mg, 172 µmol, 1.00 eq), 9-bromoanthracene (0.53 g, 2.06 mmol, 12.00 eq) and K<sub>3</sub>PO<sub>4</sub> (0.87 g, 4.12 mmol, 24.00 eq) were dissolved in toluene (5 ml), ethanol (1 ml) and water (1 ml) and bubbled with argon for 45 min. Pd<sub>2</sub>(dba)<sub>3</sub> (110 mg, 120 µmol, 0.70 eq) and DPEPhos (129 mg, 240 µmol, 1.40 eq) were added and the reaction mixture was heated to 110 °C for 4 d. After cooling down to room temperature, water (10 ml) was added and the aqueous phase was extracted three times with dichloromethane (30 ml). The combined organic layers were dried over MgSO<sub>4</sub>, filtered and all volatiles were evaporated under reduced pressure. The residue was purified by column chromatography (silica gel, *iso*hexane to *iso*-hexane:chloroform = 9:1) and 9,9'-(2,6-dimethylnaphthalene-1,5-diyl)dianthracene (19 mg, 37 µmol) was obtained as white solid in a yield of 22%.

mp: 390 °C.

ATR-IR (cm<sup>-1</sup>) *v*: 3053, 2953, 2922, 2853, 1440, 1378, 1336, 1316, 1260, 1222, 1100, 1008, 976, 957, 889, 854, 841, 809, 791, 754, 733, 700, 666, 657, 638, 611, 595, 558, 531, 491, 474, 407.

<sup>1</sup>H NMR (300 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 8.66 (s, 2H), 8.18 (d, *J* = 8.5 Hz, 4H), 7.56 – 7.49 (m, 4H), 7.44 (d, *J* = 7.9 Hz, 4H), 7.35 (ddd, *J* = 8.8, 6.3, 1.2 Hz, 4H), 7.22 (d, *J* = 8.6 Hz, 2H), 6.93 (d, *J* = 8.5 Hz, 2H), 1.86 (s, 6H) ppm.

<sup>13</sup>C NMR (76 MHz, CD<sub>2</sub>Cl<sub>2</sub>)  $\delta$  = 135.0, 134.9, 134.5, 132.8, 132.1, 131.1, 129.2, 129.1, 127.1, 126.8, 126.4, 126.2, 125.8, 20.0 ppm.

HR-MS (MALDI-TOF, DCTB) m/z: [M<sup>+</sup>] calculated for C<sub>40</sub>H<sub>28</sub>: 508.2186, found: 508.2198, error = +2.36 ppm.

 $R_{f}$ : 0.27 (*iso*-hexane:dichloromethane = 5:1).

## 4. NMR spectra



Fig. S4 <sup>1</sup>H-NMR of 4 dissolved in dichloromethane-d2, 300 MHz, room temperature. \* marks impurities.



**Fig. S5** <sup>13</sup>C-NMR of **4** dissolved in dichloromethane-d2, 76 MHz, room temperature. \* marks impurities.



**Fig. S6** <sup>13</sup>C-DEPT-NMR of **4** dissolved in dichloromethane-d2, 76 MHz, room temperature. \* marks impurities.



Fig. S7 <sup>1</sup>H-NMR of 5 dissolved in dichloromethane-d2, 300 MHz, room temperature.



Fig. S8 <sup>13</sup>C-NMR of 5 dissolved in dichloromethane-d2, 76 MHz, room temperature.



Fig. S9 <sup>13</sup>C-DEPT-NMR of 5 dissolved in dichloromethane-d2, 76 MHz, room temperature.



Fig. S10 <sup>1</sup>H-NMR of 2 dissolved in dichloromethane-d2, 300 MHz, room temperature.



Fig. S11 <sup>13</sup>C-NMR of 2 dissolved in dichloromethane-d2, 76 MHz, room temperature.



Fig. S12 <sup>13</sup>C-DEPT-NMR of 2 dissolved in dichloromethane-d2, 76 MHz, room temperature.

#### 5. References

- 1 I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero and A. M. Baro, *Rev. Sci. Instrum.*, 2007, **78**, 013705.
- 2 J. Hutter, M. Iannuzzi, F. Schiffmann and J. VandeVondele, *Wiley Interdiscip. Rev. Comput. Mol. Sci.*, 2014, **4**, 15–25.
- 3 W. E. Pickett, Comput. Phys. Rep., 1989, 9, 115-197.
- 4 J. VandeVondele and J. Hutter, J. Chem. Phys., 2007, 127, 114105.
- 5 S. Goedecker, M. Teter and J. Hutter, Phys. Rev. B, 1996, 54, 1703–1710.
- 6 J. P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 1996, 77, 3865.
- 7 S. Grimme, J. Antony, S. Ehrlich and H. Krieg, J. Chem. Phys., 2010, 132, 154104.
- 8 J. Wilhelm, M. Del Ben and J. Hutter, J. Chem. Theory Comput., 2016, 12, 3623-3635.
- 9 J. B. Neaton, M. S. Hybertsen and S. G. Louie, Phys. Rev. Lett., 2006, 97, 216405.
- 10 N. Kharche and V. Meunier, J. Phys. Chem. Lett., 2016, 7, 1526-1533.
- 11 M. Ternes, A. J. Heinrich and W.-D. Schneider, J. Phys.: Condens. Matter, 2008, 21, 053001.
- 12 J. Li, S. Sanz, M. Corso, D. J. Choi, D. Peña, T. Frederiksen and J. I. Pascual, *Nat. Commun.*, 2019, 10, 200.
- 13 S. Mishra, D. Beyer, K. Eimre, S. Kezilebieke, R. Berger, O. Gröning, C. A. Pignedoli, K. Müllen, P. Liljeroth, P. Ruffieux, X. Feng and R. Fasel, *Nat. Nanotechnol.*, 2020, **15**, 22–28.
- 14 S. Mishra, D. Beyer, R. Berger, J. Liu, O. Gröning, J. I. Urgel, K. Müllen, P. Ruffieux, X. Feng and R. Fasel, *J. Am. Chem. Soc.*, 2020, **142**, 1147–1152.
- 15 H. O. Frota, Phys. Rev. B, 1992, 45, 1096–1099.
- 16 H. Prüser, P. E. Dargel, M. Bouhassoune, R. G. Ulbrich, T. Pruschke, S. Lounis and M. Wenderoth, *Nat. Commun.*, 2014, **5**, 5417.
- 17 K. Liu, F. Qiu, C. Yang, R. Tang, Y. Fu, S. Han, X. Zhuang, Y. Mai, F. Zhang and X. Feng, *Cryst. Growth Des*, 2015, **15**, 3332–3338.
- 18 K. Xu, Y. Fu, Y. Zhou, F. Hennersdorf, P. Machata, I. Vincon, J. J. Weigand, A. A. Popov, R. Berger and X. Feng, *Angew. Chem. Int. Ed.*, 2017, **56**, 15876–15881.
- 19 Y. Gu, X. Wu, T. Y. Gopalakrishna, H. Phan and J. Wu, Angew. Chem. Int. Ed., 2018, 57, 6541–6545.