Supporting Information: On-Surface Synthesis of BN-Substituted Heteroaromatic Networks

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Chemical synthesis

Synthesis of monomer **1**:

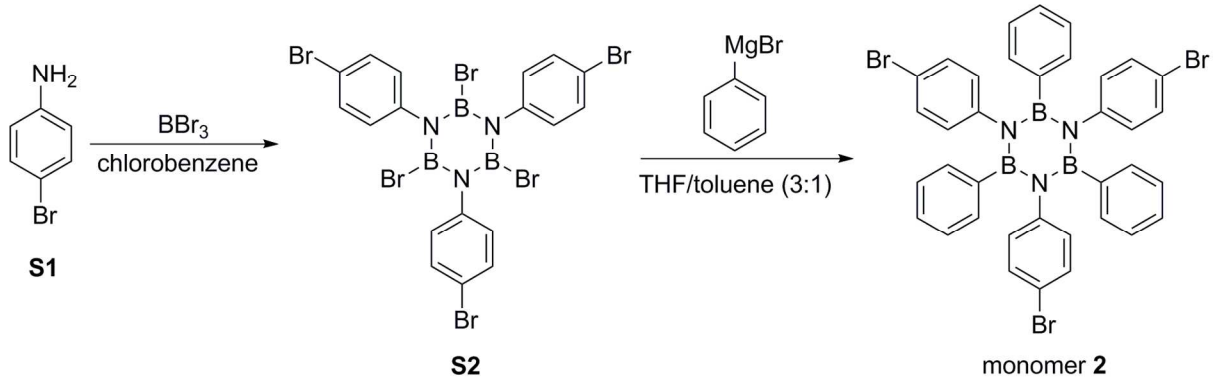
Monomer (**1**) was synthesized as described previously.[23]

Synthesis of monomer **2**:

All experiments were performed under anhydrous conditions in Schlenk apparatus using argon as protective gas. 4-Bromoaniline (**S1**), boron tribromide and bromobenzene were purchased from Sigma Aldrich and used as received. Dried chlorobenzene, tetrahydrofuran (THF), diethyl ether and toluene were purchased from Acros Chemicals and used as received. Deuterated solvents, benzene-d_6 and chloroform-d, were obtained from Sigma Aldrich and were distilled from calcium hydride and phosphorus pentoxide, respectively. Chlorotrimethylsilane (TMSCl) was purchased from Sigma Aldrich and distilled before NMR experiments. Mg-turnings were purchased from Alfa Aesar.

Phenylmagnesium bromide was prepared by dropwise addition of diluted bromobenzene in diethyl ether onto Mg-turning and its concentration was determined by titration with TMSCl. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 300. ^{11}B NMR spectra were recorded on a Bruker AVANCE III 500. The chemical shifts were reported as the delta scale in ppm relative to its internal reference from residual undeuterated solvent molecules: ^{1}H (δ = 7.26 ppm in $CDCl_3$; δ = 7.16 ppm in benzene-d_6) and from 1 M boron trifluoride diethyl etherate for ^{11}B (δ = 0.00 ppm). Matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) mass spectra were obtained from a Bruker Reflex II TOF using tetracyanoquinodimethane (TCNQ) as matrix.

Monomer **2** was synthesized in two steps:



Scheme 1 Synthesis of monomer **2**

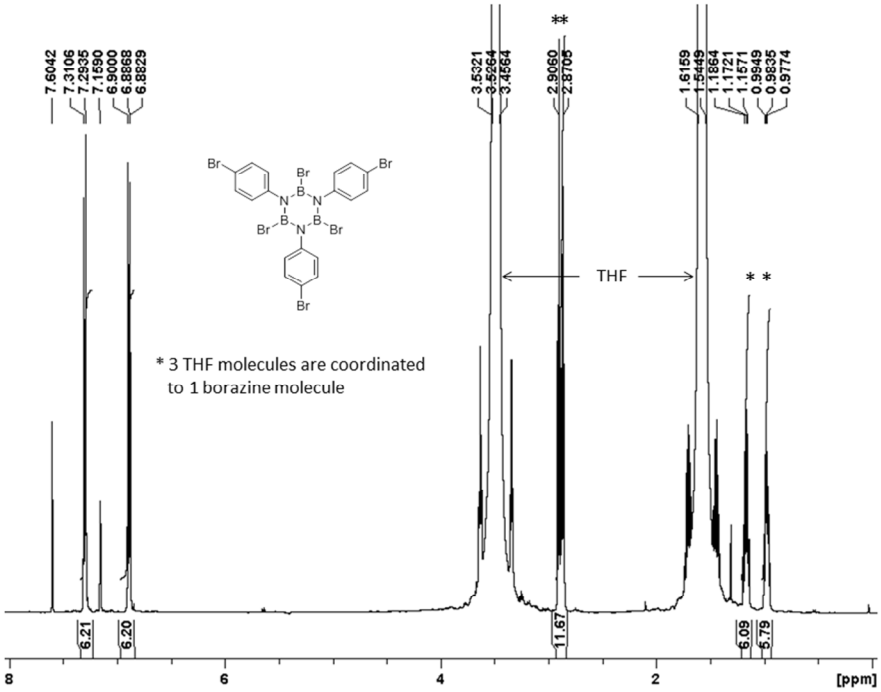
Synthesis of 2,4,6-tribromo-1,3,5-tris(4-bromophenyl)-borazine (S2):

To a solution of 4-bromoaniline (**S1**) (25.0 g, 145 mmol) in 140 ml chlorobenzene was slowly added a mixture of 20 ml chlorobenzene and 15.2 ml borontribromide (160 mmol) at 130 °C under vigorous stirring. The formed precipitate was dissolved after heating the mixture to reflux. After 20 h the reaction mixture was cooled to room temperature and approximately 50 ml of the solvent was removed by vacuum evaporation. The precipitate was collected by filtration, and then recrystallized twice from chloroform to obtain the title compound as a slightly grey microcrystalline powder (22.0 g, 58% yield). ^{1}H NMR (500 MHz, THF/C_6D_6): δ = 7.31-7.29 (m, 6H), 6.90-6.88 (m, 6H) ppm. ^{11}B NMR (160 MHz, THF/C_6D_6): δ = 24.1 ppm (FWHM = 1417 Hz); ^{13}C NMR (75 MHz, THF/C_6D_6): δ = 143.9, 131.7, 131.4, 118.7 ppm. NMR spectra were recorded in dry THF to avoid the hydrolysis of the title compound by trace amounts of water in standard deuterated solvents. As lock compound a small amount of benzene-d_6 was used. MS analysis failed because of the spontaneous hydrolysis of the title compound.

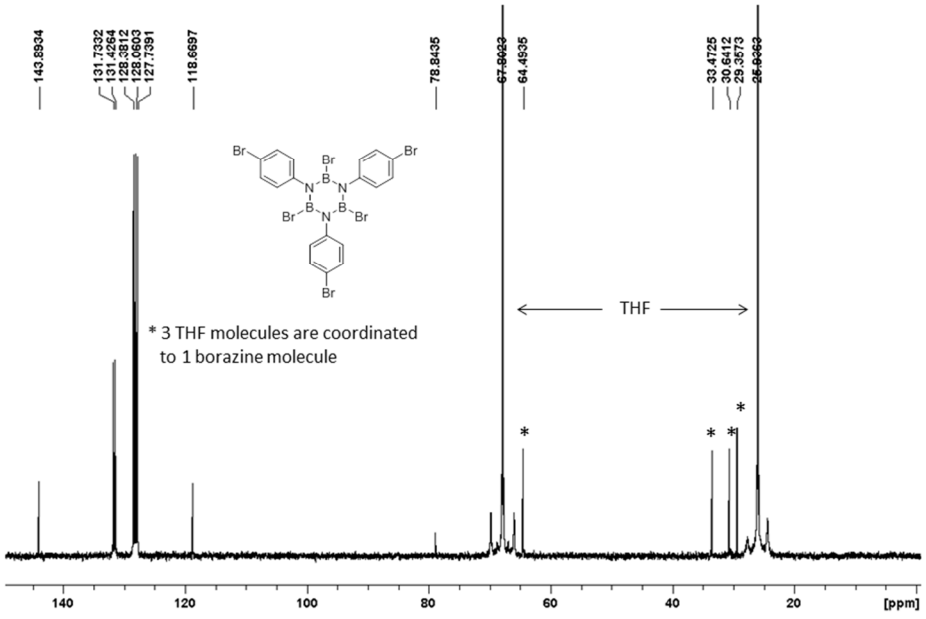
Synthesis of 1,3,5-tri(4-bromophenyl)-2,4,6-triphenylborazine (monomer 2):

2,4,6-tribromo-1,3,5-tris(4-bromophenyl)-borazine (**S2**) (8.23 g, 10.5 mmol) was dissolved in a mixture of 180 ml THF and 60 ml toluene. To the solution was slowly added a 1.1 M phenylmagnesium bromide solution in diethyl ether (35 ml, 39 mmol) at room temperature, and then the reaction mixture was refluxed for 1 h. After cooling to room temperature the solvents were partially removed in vacuo and the precipitated Mg-salt was removed by filtration. Then, the solvents were removed completely and the resulting brownish solid was recrystallized twice from chloroform at –20 °C to afford the title compound as colorless crystals (2.0 g, 25% yield). For UHV experiments the compound was further purified by sublimation at 300 °C and 10^{-2} bar. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.96-6.94 (m, 6H), 6.92-6.85 (m, 9H), 6.81-6.79 (m, 6H), 6.61-6.59 (m, 6H) ppm; ^{11}B NMR (160 MHz, $CDCl_3$): δ = 36.1 ppm (FWHM = 1624 Hz); ^{13}C NMR (75 MHz in $CDCl_3$): δ = 145.7, 137.5, 132.3, 131.1, 130.6, 126.9, 126.8, 117.8 ppm; MALDI-TOF MS (TCNQ as matrix): *m*/*z* (%) – calculated for $C_{36}H_{27}B_3Br_3N_3$ $[M]^+$ 773.00 (100), 774.99 (98), 772.00 (74), 774.00 (72), 776.00 (38), 771.00 (34), 776.99 (32), 770.00 (25), 771.00 (18)778.00 (12), 769.01 (6), found 772.92 (100), 774.91 (94), 773.94 (85), 771.95 (72), 775.97 (53), 770.98 (46), 776.95 (45), 769.96 (22), 777.98 (15), 786.95 (7).

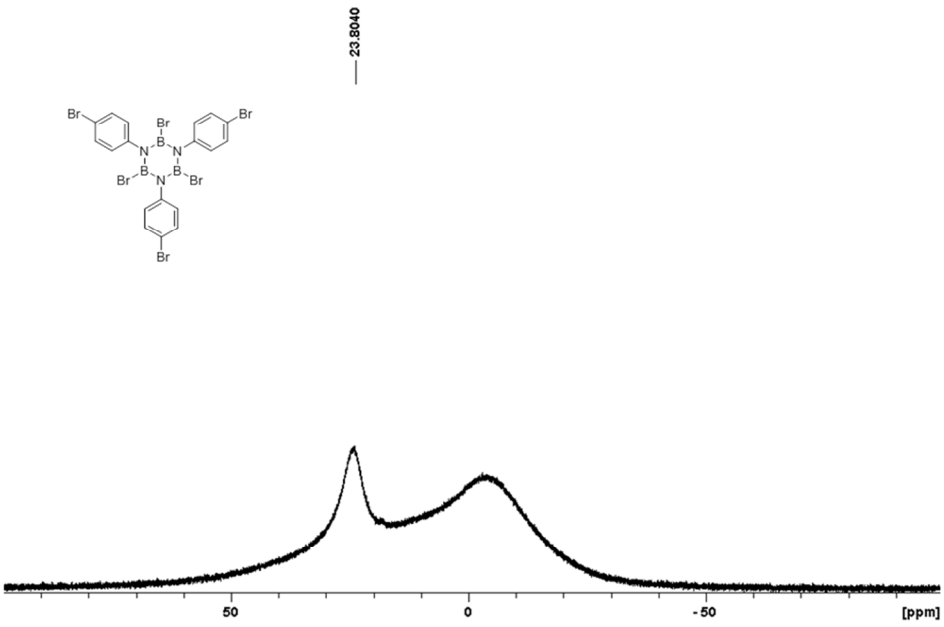
^{1}H, ^{13}C and ^{11}B spectra



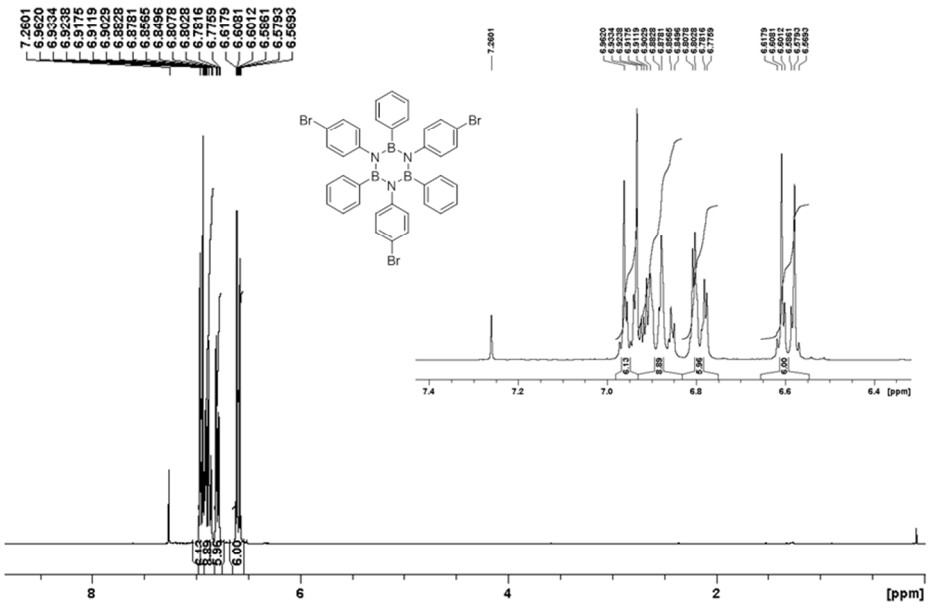
^{1}H NMR spectrum of compound **S2** (500 MHz, THF/C_6D_6).



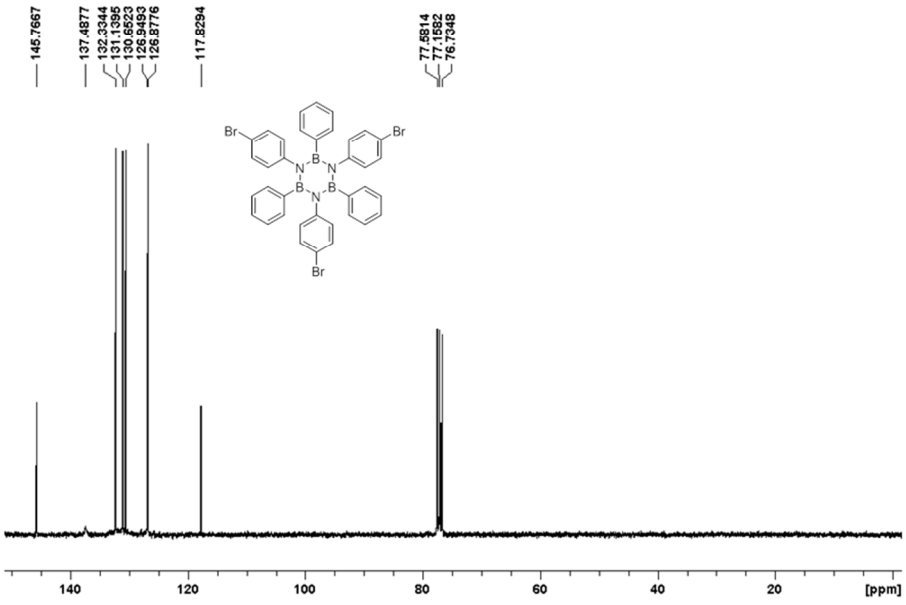
^{13}C NMR spectrum of compound **S2** (75 MHz, THF/C_6D_6).



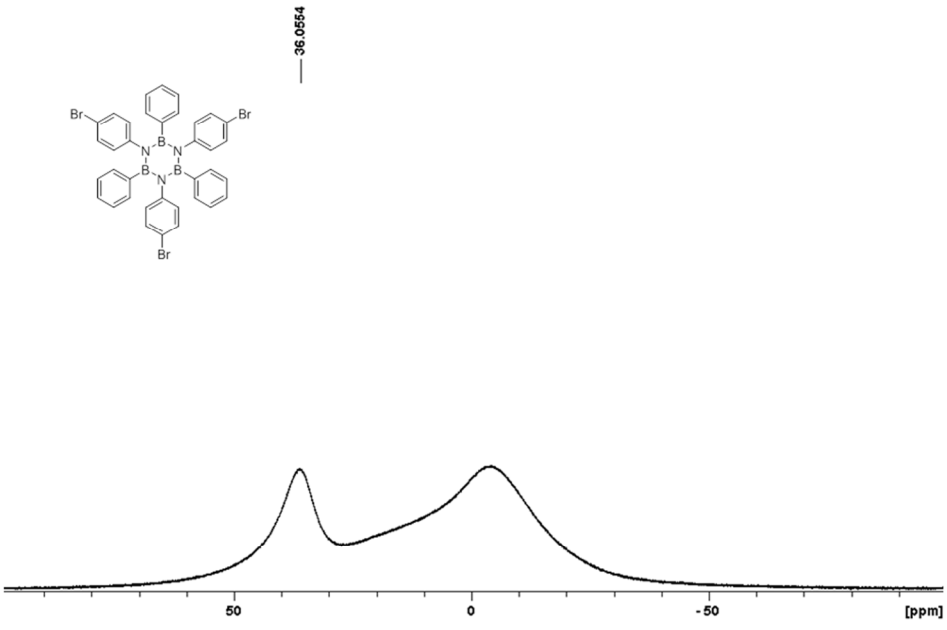
^{11}B NMR spectrum of compound **S2** (160 MHz, THF/C_6D_6).



^{1}H NMR spectrum of monomer **2** (300 MHz, $CDCl_3$).



^{13}C NMR spectrum of monomer **2** (75 MHz in $CDCl_3$).



^{11}B NMR spectrum of monomer **2** (160 MHz, $CDCl_3$).

Determination of the presence and orientation of the BN core

High-resolution STM images of the unoccupied states of the fully cyclodehydrogenated network can be used to confirm the presence of the borazine ring as well as its orientation within the molecular network. According to the design of both molecular precursors shown in Figure 1, the nitrogen atoms in the borazine ring are facing the bromine atoms at the periphery of the molecule, and should therefore also face the intermolecular bonds in the network. Figure S1a shows a high-resolution STM image of the unoccupied states of the fully cyclodehydrogenated network. A radical change in the appearance of the network when probing unoccupied or occupied states is observed. At 2.5 V, the network looks much more homogeneous and its building blocks cannot be easily distinguished. On the other hand, new intramolecular features arise (highlighted in red), in particular, three maxima forming a triangle within the molecule and two maxima flanking the intermolecular bond. These features are reproduced by the STM simulations shown in Figure S1b, where the three maxima arise from the B-C bonds whilst the other two maxima are associated with the intermolecular C-C bond. This comparison univocally confirms that the orientation of the borazine ring within the molecular precursors is indeed as designed.

For STM simulations, the geometry and electronic structure of the freestanding molecular network was calculated within the framework of DFT using the Quantum ESPRESSO package.[1] We have used the PBE ex-change-correlation functional,[2] 100 Ry plane-wave cutoff and 24 non-equivalent k-points in the first Brillouin zone of the network unit cell. STM simulations were carried out on a plane 3.0 Å above the atoms in the Tersoff-Hamann approximation.[3]

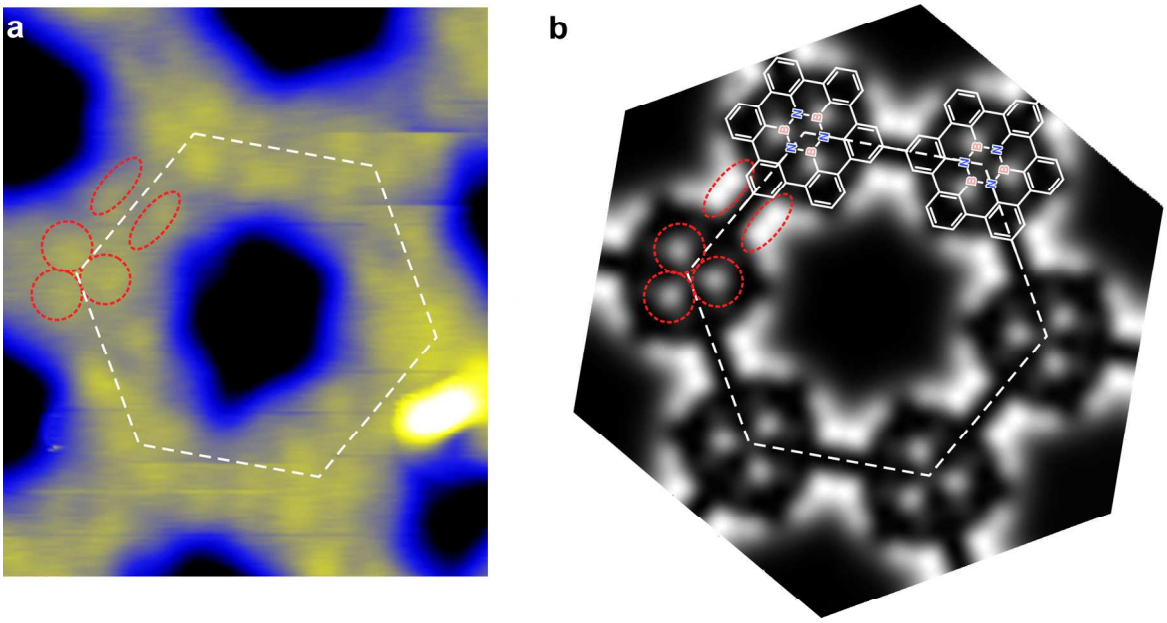


Figure S1.- a) High-resolution STM image of the fully cyclodehydrogenated network (obtained from monomer **1**). It is possible to distinguish the main internal features, which have been highlighted in red for the sake of clarity. (34 Å x 39 Å) I = 500 pA, U = 2.8 V. **b)** Simulated STM image (constant height mode, U = 0.7 eV above the onset of the conduction band) of the fully cyclodehydrogenated network. The schematic molecular model is superimposed, making possible to assign the three internal lobes to the B-C bonds. These features are highlighted in red.

Substrate influence on network quality

As explained in the manuscript, monomer flexibility plays a critical role on the final network quality. However, this is not the unique parameter involved. Another crucial aspect is the surface as it acts as the catalytic support where both reactions, namely dehalogenation and cyclodehydrogenation, take place. The substrate importance clearly manifests in Figure S2. Panel **a** shows a STM image of monomer **1** deposited on the Au(111) surface held at 200°C, temperature at which dehalogenation and covalent coupling – and consequently defining the final network quality – among activated monomers is expected. As we can see, mainly disordered structures are formed, with just some small patches where the characteristic flower-like structure can be observed (see, for example, green arrows). On the other hand, panel **b** shows the equivalent STM image for the network grown on Ag(111). In this later case, a clear prevalence of the characteristic six-membered rings is observed. Although some ill-formed areas close to step-edges are found, there is a good long range order. For the bottom-up fabrication of BN-substituted heteroaromatic networks

we thus find an important role of the substrate, which sensitively influences molecule-substrate interactions and the related network formation kinetics. This is in line with earlier investigations of polyaromatic hydrocarbons on metal substrates, where a pronounced dependence between network quality and strength of molecule-substrate interaction[4] on one hand as well as relative coupling and diffusion probabilities[5] on the other hand has been revealed.

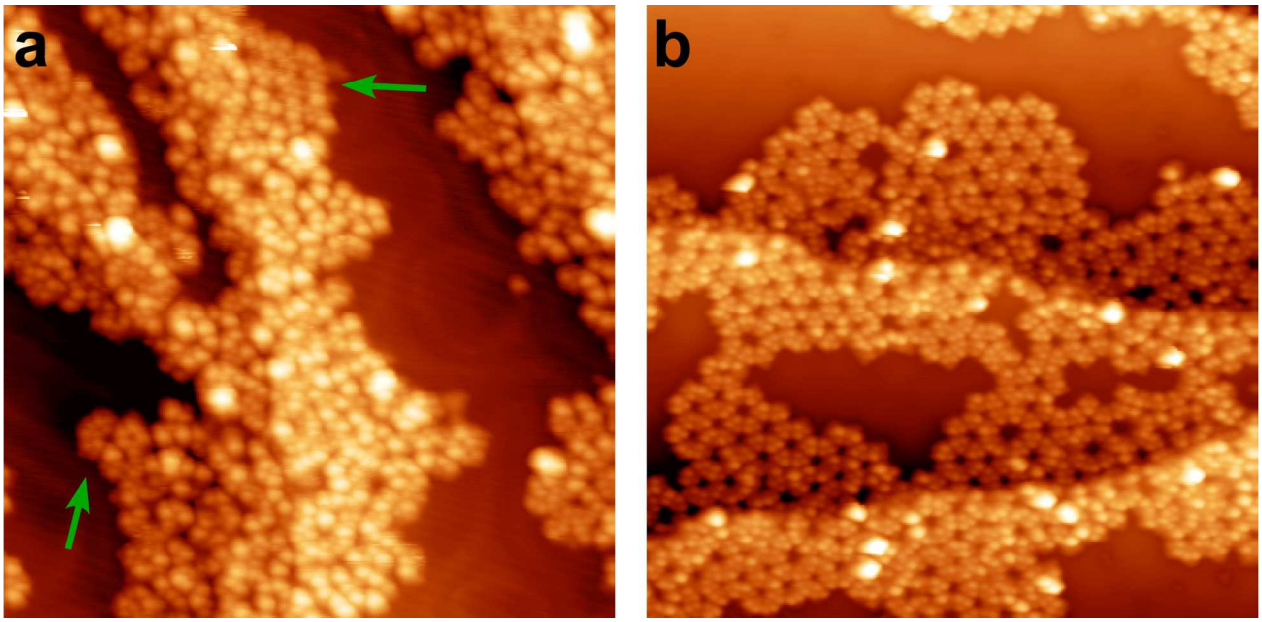


Figure S2.- STM images of the covalent network formed upon deposition of monomer **1** at 200°C on Au(111) and Ag(111). **a)** Network on Au(111). Mainly disordered structures are formed. (500 Å x 500 Å) I = 50 pA, U = -1.5 V. **b)** Network on Ag(111). Ordered patches are formed. (500 Å x 500 Å) I = 150 pA, U = -1.0 V

References (Supporting Information)

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