Electronic Supplementary Information for

Binary supramolecular networks of bridged triphenylamines with different substituents and identical scaffolds

Christian Steiner,a Zechao Yang,a Bettina D. Gliemann,b Ute Meinhardt,b Martin Gurrath,c Maximilian Ammon,a Bernd Meyer,*c Milan Kivala*b and Sabine Maier*a

a Department of Physics, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erwin-Rommel-Straße 1, D-91058 Erlangen, Germany
b Department of Chemistry and Pharmacy, Friedrich-Alexander-Universität Erlangen-Nürnberg, Nikolaus-Fiebiger-Straße 10, D-91058 Erlangen, Germany
c Interdisciplinary Center for Molecular Materials (ICMM) and Computer-Chemistry-Center (CCC), Friedrich-Alexander-Universität Erlangen-Nürnberg, Nägelsbachstraße 25, D-91052 Erlangen, Germany

Corresponding authors:
Sabine Maier:  sabine.maier@fau.de
Milan Kivala:  milan.kivala@fau.de
Bernd Meyer:  bernd.meyer@fau.de

Table of contents

1. Experimental details  2
2. Computational details  2
3. High-resolution and overview STM images of the porous networks  4
4. Structure of the H-bonded mixed ADTPA+CDTPA network  5
5. Intermolecular binding energies: A DFT comparison  6
6. Properties of the mixed ADTPA+CDTPA network on Au(111)  7
7. Organisational chirality of the H-bonded networks  10
8. Defects in the binary ADTPA+CDTPA network  11
9. STS of the DTPA frontier orbitals  13
10. Wavefunction plots of the CDTPA and ADTPA monomers and dimers  15
11. Charge density difference plots  17
12. References  17
1. Experimental details

The experiments were performed using a low-temperature STM/nc-AFM (Omicron Nanotechnology GmbH) operated in ultra-high vacuum (UHV) at 4.7 K/77.8 K. The instrument is housed in a two-chamber UHV system that is equipped with a separate preparation chamber (base pressure below $1 \cdot 10^{-10}$ mbar). All STM topography images were acquired in constant current mode using Pt-Ir tips, which were prepared by mechanical cutting followed by controlled indentation into the bare Au(111) substrate. For the STM/STS measurements, the bias voltage is applied to the tip. The bias voltages in the manuscript and the ESI refer to a grounded tip. The STM/STS data were analysed and processed using the WSxM software.\(^1\)

In the scanning tunneling spectroscopy (STS) experiments, the differential conductance $dI/dV$ was measured using conventional lock-in technique (typical modulation parameters: 687.0 Hz and 8 mV$_{rms}$). The $dI/dV$ spectra were recorded in constant-height STS for the HOMO and constant-current STS for the LUMO, respectively. The $dI/dV$ maps were acquired in constant current mode.

The Au(111) crystal was cleaned by subsequent cycles of Ar$^+$ ion sputtering (1 kV at $3 \cdot 10^{-6}$ mbar) and annealing at 700 K, respectively. The carboxyl-substituted triphenylamine derivative (CDTPA) and the dianinotriazine-substituted triphenylamine derivative (ADTPA) were thermally evaporated simultaneously from quartz crucibles that were heated to about 600 K and 500 K, respectively, in a commercial evaporator (Kentax GmbH). The sample was kept at room temperature during evaporation. A quartz-crystal microbalance was used to calibrate a constant deposition rate of around 0.3 ML/min. The overall molecular coverage was in all preparations around 0.6 ML. The molecules were thoroughly degassed prior to deposition.

Details about the synthesis of the CDTPA ($(4,4,8,8,12,12\text{-hexamethyl-8,12-dihydro-4H-benzo}[9,1]\text{quinolizino}[3,4,5,6,7\text{-defg}])\text{acridine-2,6,10-tricarboxylic acid}$) and the ADTPA $(6,6',6''\text{-}(4,4,8,8,12,12\text{-hexamethyl-8,12-dihydro-4H-benzo}[9,1]\text{quinolizino}[3,4,5,6,7\text{-defg}]\text{acridine-2,6,10-triyl})\text{tris}(1,3,5\text{-triazine-2,4-diamine})$ are found elsewhere.\(^2\)

2. Computational details

Periodic density functional theory (DFT) calculations were performed with the plane wave code PWscf of the Quantum Espresso software package\(^3\) using the gradient-corrected Perdew-Burke-Ernzerhof (PBE) functional,\(^4\) Vanderbilt ultrasoft pseudopotentials,\(^5\) and a plane wave kinetic energy cutoff of 30 Ry. The structure of gas phase DTPA monomers, dimers, and monolayers were optimized either by PBE only or in combination with the D3 dispersion correction by Grimme et al.\(^6\) using the Becke-Johnson damping function\(^7\) (PBE+D3). Structures were assumed to be relaxed when a force convergence threshold of 3 meV/Å was reached. The stress tensor turned out to be not reliable enough to allow determination of the lattice parameters of the periodic gas phase monolayer structures. Instead, atomic relaxations were performed for sets of 10-14 values of each lattice parameter and the energy minimum was calculated from a fit of the total energies to a polynomial function.

The CDTPA monomer, dimer, and monolayer maintain a strictly planar configuration in the gas phase geometry optimization. Also, the mixed ADTPA+CDTPA dimer and monolayer remain basically planar. Only the hydrogen atoms of the terminating amino groups which are not involved in the H-bonding are slightly tilted out of the molecular plane. For each of the three ADTPA dimers (with tip-to-tip, tip-to-side, and side-to-side bonding motif), however, we find two different relaxed structures. One is also almost planar. This configuration
is obtained when the geometry optimization is started from a flat structure in which the hydrogen atoms of the H-bonds are initially placed within the molecular plane. The almost planar structures, however, are only metastable. The global energy minima are twisted, 3-dimensional configurations due to the preferred out-of-plane tilt of the amino groups (see Ref. [8] for details). In Table S1 we refer to the two structural alternatives as “planar” and “twisted”. As building block for the ADTPA monolayers, which are meant to represent the planar conformation of the adsorbed molecules on the Au(111) surface, we considered only the almost planar ADTPA dimer motifs.

The charge density difference plots of Fig. 3 and Fig. S12 were obtained by subtracting the charge densities of the individual molecules, which were determined by separate DFT calculations for isolated molecules, however, using the same atomic positions as within the relaxed monolayer, from the charge density of the periodic monolayer.

For a more reliable description of the electronic structure of DTPA gas phase monomers and dimers (HOMO and LUMO energy levels), calculations were repeated with the ORCA code using the B3LYP hybrid functional and the triple-zeta def2-TZVP basis set. Structures were re-optimized by including Grimme D3 dispersion corrections (B3LYP+D3).

Finally, geometry optimizations for the mixed ADTPA+CDTPA network on the Au(111) surface were performed using the PBE+D3 functional. The Grimme D3 parameters for Au were adjusted according to a recently developed scheme in order to reduce the inherent overbinding of adsorbates on Au surfaces in the original Grimme method. The Au surface was represented by a periodically repeated slab with a thickness of four atomic layers. The atoms in the bottom two layers were kept fixed at their bulk positions and only the upper two layers together with the molecular network were allowed to relax in the geometry optimizations. The PBE+D3 optimized Au lattice constant (with the modified D3 parameters) of 4.118 Å was used for the lateral extension of the slab. The lattice vectors of the hexagonal mixed molecular network are aligned along the $\langle 11\bar{2}\rangle$-directions of the Au(111) surface. In the gas phase, the mixed monolayer has a lattice constant of 30.20 Å (see Table 1). This matches perfectly a $(6\sqrt{3} \times 6\sqrt{3})$ unit cell of the Au substrate. This unit cell has a lateral dimension of 30.26 Å and each atomic layer contains 108 atoms. Together with the 152 atoms of a unit of the mixed monolayer we arrive at 584 atoms (5200 electrons) for the overall supercell. The geometry relaxations and the total energy calculations were done with a $(2,2,1)$ Monkhorst-Pack $k$-point grid (for a detailed evaluation of the required $k$-point density in a similar system, see Ref. [12]). The $k$-point density was increased to $(4,4,1)$ in the density-of-states (DOS) calculation.
3. High-resolution and overview STM images of the porous networks

In Fig. S1, we compare high-resolution STM images of (a-b) homomolecular ADTPA, (c-d) homomolecular CDTPA and (e-f) mixed ADTPA+CDTPA (1:1) networks. The relative orientation of the molecules within the networks and the bonding motifs are visualized best by the three protrusions (green triangles) that correspond to the dimethylmethylene groups. In the ADTPA network with the tip-to-side bonding motif, the triangle apexes are directed towards each other with a small lateral offset. In contrast, in the homomolecular CDTPA and the intermixed ADTPA+CDTPA self-assemblies with the tip-to-tip bonding motif, the sides of the triangles face each other. Thus, the self-assembly of the binary ADTPA+CDTPA network is topologically related to that of the homomolecular CDTPA, and topologically distinct from that of the homomolecular ADTPA.

![Fig. S1](image_url)

**Fig. S1** High-resolution STM topographies of the (a-b) homomolecular ADTPA, (c-d) homomolecular CDTPA, and (e-f) binary ADTPA+CDTPA network composed of both ADTPA and CDTPA. The green triangles indicate the position of the dimethylmethylene groups. The overview STM image in (g) reveals a typical domain size of the mixed ADTPA+CDTPA network. STM parameters: (a) 77.8 K, -850 mV, 550 pA, (b) 77.8 K, -800 mV, 150 pA, (c) 4.7 K, -50 mV, 600 pA, (d) 4.7 K, -80 mV, 1.5 nA, (e-f) 4.7 K, -50 mV, 600 pA, and (g) 4.7 K, -200 mV, 10 pA.

In the STM images, the diaminotriazine (DAT) moieties have a paddle-shaped structure (blue arrow in b), while the carboxyl groups appear as straight connections between the molecules (red arrow in d). We observe a similar imaging contrast of the end groups also in the binary network (green arrow in f). A cross-section (Fig. 1b) along the axis of the mixed dimer shows an asymmetry along the bonding region, which stems from the paddle-shaped contrast of the DAT groups connecting via a tip-to-tip bonding motif to a carboxyl group. Thus, an identification of the molecules is possible in high-resolution STM topographies that reveal the structure of the functional groups.

The overview STM image in Fig. S1g reveals a typical domain size of the mixed ADTPA+CDTPA network. We note that these domains might show interstitial defects of ADTPA and CDTPA incorporated into the honeycomb lattice (see Section 8), which can only be identified in zoom images or dI/dV maps. Additional overview images of the homomolecular ADTPA and CDTPA network can be found in Ref. [8].
4. Structure of the H-bonded mixed ADTPA+CDTPA network

Fig. S2a shows the DFT-optimized structure of the periodic binary ADTPA+CDTPA network in detail. We note that the molecular scaffolds remain basically planar in the geometry relaxation. Only one of the two amino groups per DAT unit is involved in the hydrogen bonding. The calculated N···O distances are 2.605 Å and 2.838 Å for the N_triazine···H-O and N_amino-H·O bonds, respectively. The N_triazine···H and O···H hydrogen bond lengths are 1.546 Å and 1.810 Å, respectively. The H-bond lengths are slightly longer than those for the pure CDTPA network (1.526 Å) and shorter than those for the pure ADTPA network (1.948 Å and 1.966 Å for the monolayer with tip-to-side and 1.926 Å for the monolayer with tip-to-tip bonding motif). Fig. S2b shows a side view of the binary network. Both the molecular scaffolds as well as the DAT and carboxyl groups are confined within one plane, while the dimethymethylene groups stick out of that plane.

![DFT-optimized geometry (PBE+D3) of the binary ADTPA+CDTPA self-assembly in the gas phase. (a) A zoom on the ADTPA-CDTPA contact between DAT and carboxyl group. (b) A side view of the binary network, showing the planar configuration of the molecular scaffolds and the bonding groups.](image-url)
5. Intermolecular binding energies: A DFT comparison

As a test for the reliability of our plane wave PBE calculations and to check how sensitive results depend on the chosen basis set and energy functional we calculated ADTPA and CDTPA dimer binding energies using the plane-wave-based PWscf and the Gaussian-based ORCA code together with the PBE and B3LYP functional. Table S1 shows excellent agreement between the plane wave (PWscf) and the Gaussian (ORCA) calculations. All binding energies have significant van der Waals contributions as reflected in the D3 corrections of about 100 and 450 meV for the tip-to-tip and tip-to-side bonding motif, respectively. The B3LYP hybrid functional gives slightly lower binding energies than PBE, but all trends for the relative stability of different dimers and bonding motifs remain the same.

Table S1 DFT-calculated binding energies $E_B$ for ADTPA and CDTPA dimers using different basis sets and functionals. The results for the monolayers from Table 1 in the manuscript are added for comparison. The geometry optimization for the ADTPA dimers yields two local energy minima: a metastable, almost planar structure and a twisted nonplanar configuration as global minimum.

<table>
<thead>
<tr>
<th>Molecules, bonding motif</th>
<th>$E_B$ in eV - Dimer</th>
<th>$E_B$ in eV - Monolayer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>PWscf</td>
<td>ORCA</td>
</tr>
<tr>
<td></td>
<td>PBE</td>
<td>PBE+D3</td>
</tr>
<tr>
<td>ADTPA, tip-to-side</td>
<td>planar (twisted)</td>
<td>-0.57</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ADTPA, tip-to-tip</td>
<td>planar (twisted)</td>
<td>-0.40</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CDTPA, tip-to-tip</td>
<td>planar</td>
<td>-0.81</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mixed, tip-to-tip</td>
<td>planar</td>
<td>-0.71</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6. Properties of the mixed ADTPA+CDTPA network on Au(111)

First, we determined the lateral position of the mixed network on the Au(111) surface. The relative position of the network with respect to the Au(111) substrate will be given by specifying the location of the central N atoms of the DTPA molecules above the surface. This notation does not imply that the interaction of these N atoms with the substrate is of any specific importance for the preferred lateral position of the network. In the unit cell of the mixed monolayer, the two central N atoms of the ADTPA and the CDTPA molecule are separated by 1/3 of the sum of the two hexagonal lattice vectors. Thus, in a \((6\sqrt{3} \times 6\sqrt{3})\) supercell both N atoms always sit above the same Au surface site. The lowest energy is found for the hcp hollow position of the N atoms (see Fig. S3). A shift to the fcc hollow site and the top site increases the energy by 0.14 eV and 0.49 eV per DTPA pair, respectively. When geometry optimizations were started from bridge sites, the whole layer shifted until the central N atoms had moved back to one of the hollow positions.

![Fig S3](image)

**Fig S3** Side and top view of the DFT-optimized structure (PBE+D3) of the binary ADTPA+CDTPA network on the Au(111) surface. The central N atoms of the DTPA molecules sit above hcp hollow sites. The hexagonal unit cell is indicated by dashed black lines. Au, C, N, O, and H are shown in yellow, black, blue, red and white, respectively.
These results show that the potential energy surface for the DTPA molecules is rather flat. The DTPA molecules can easily diffuse, which is a pre-requisite for the formation of highly ordered molecular structures. Note that only the mixed molecular layer is commensurate with the Au(111) substrate. In the homomolecular networks, molecules will always have to adopt less favorable adsorption sites. Though the corrugation of the potential energy landscape is rather small, the commensurability might be an additional factor that drives the formation of the mixed network and prevents phase separation.

Fig. S3 shows that the DTPA molecules undergo strong distortions upon adsorption. In the gas phase, the two methyl groups of the dimethylmethylene units are mirror-symmetric with respect to the molecular plane (see Fig. S2). In contrast, on the Au(111) surface the dimethylmethylene units tilt so that one methyl group becomes almost perpendicular to the molecular plane and the other group is oriented almost parallel to the substrate with one H atom pointing down. When this methyl group is rotated by 60° (i.e., two H atoms are now pointing down and the third one is pointing up), the structure relaxes back to the original orientation in a geometry optimization. The energy cost for these deformations, which optimize the interaction of the network with the Au substrate, is rather moderate. When the molecular network is lifted from the substrate and a DFT calculation is performed without changing the atomic positions, the energy is higher by only 0.37 eV per DTPA pair compared to the fully relaxed gas phase monolayer.

The structural change of the DTPA molecules on the Au(111) surface, however, might lead to a modification of the molecule-molecule interactions compared to our results for the gas phase conformations given in Table 1 of the manuscript and Table S1. To exclude this possibility, we made the following test calculations: We took the fully relaxed structures of the DTPA molecules on Au(111) as shown in Fig. S3. The positions of the atoms within the molecular scaffold were kept fixed and only the carboxyl and the DAT groups were allowed to relax in the subsequent optimization. We then recalculated the monolayer binding energies in the gas phase (including optimization of the lattice parameters) for the monomolecular and the mixed networks. The results deviate by not more than 0.02 eV from the values given in Table 1 and Table S1.

![Projected DOS of selected atoms in the mixed ADTPA+CDTPA monolayer on Au(111). The Fermi level is at 0 eV and is indicated by a vertical solid black line.](image)

**Fig S4** Projected DOS of selected atoms in the mixed ADTPA+CDTPA monolayer on Au(111). The Fermi level is at 0 eV and is indicated by a vertical solid black line.
To give a further quantification of the charge transfer in the mixed molecular network, we performed a Bader charge analysis. For the gas phase monolayer, we find, as expected, that about 0.27 of an electron has moved from ADTPA to CDTPA. On Au(111), both molecules lose charge to the substrate. The electron gain of CDTPA is reduced to 0.12 and ADTPA becomes more positively charged with a Bader charge of +0.49.

In the final step, we analyzed the electronic structure by calculation of density-of-states (DOS). Because of the size of the supercell (584 atoms), these calculations could only be performed in the generalized-gradient approximation (GGA) with the PBE functional. The results for the HOMO and LUMO level alignment with respect to the substrate and the HOMO-LUMO gap are therefore hampered by the well-known deficiency of GGA functionals. Nevertheless, we find a good quantitative agreement with experiment. Fig. S4 shows the projected DOS for the C atoms (averaged over all C atoms in the scaffold) and the central N atoms of the ADTPA and CDTPA molecules. The HOMO and HOMO-1 are exclusively located at ADTPA and CDTPA, respectively, as it is also found in the gas phase calculations (see Fig. S10 in Section 10) and as it is expected for a charge donor-acceptor system. For the splitting of the two levels, we obtain about 0.2 eV, which closely matches the experimental value. Only the absolute position of the two levels is predicted slightly too close to the Fermi level in GGA (PBE: -0.82 and -0.64 eV, experiment: -1.38 and -1.15 eV, see Fig. 2 in the manuscript).
7. Organisational chirality of the H-bonded networks

Although ADTPA molecules are achiral, their self-assembled honeycomb network is chiral. The *tip-to-side* bonding motif of the DAT head group has two bonding options, which leads to an organisational chirality, where homochiral domains with left-handed and right-handed chirality were observed. In contrast, the homomolecular CDTPA network is symmetric. However, the binary ADTPA+CDTPA network also bears the possibility of organisational chirality, since it has an asymmetric *tip-to-tip* bonding motif, see Fig. S5 for the corresponding structural models. The effect of the organisational chirality in the binary ADTPA+CDTPA network is difficult to unambiguously determine experimentally, since the H-bonding groups are imaged only weakly in STM. We note that a few pores deviate from a perfect hexagonal shape, which might be attributed to deviations from homochiral pores.

---

**Fig. S5** Organisational chirality in the binary ADTPA+CDTPA (left) and homomolecular ADTPA (right) network. In contrast, the homomolecular CDTPA network (centre) is not chiral. Structural model of homochiral domains with right-handed (upper row) and left-handed chirality (lower row).
8. Defects in the binary ADTPA+CDTPA network

Preparations with an unequal ratio of both building blocks are analyzed in order to investigate the selectivity of the binding motifs in the binary ADTPA+CDTPA network. Fig. S6a shows a preparation, where the evaporation rate of the ADTPA was slightly reduced to 0.25 ML/min compared to the rate of CDTPA, which was kept at 0.3 ML/min. Accordingly, we find more CDTPAs on the surface than for the preparation shown in the main manuscript, where both rates were calibrated equally around 0.3 ML/min (see Figs. 1c and S6b). In the case of ADTPA < CDTPA, we find a homogeneously formed porous network with occasional interstitial defects incorporated into the honeycomb lattice and irregularly shaped pores (Fig. S6a and S7). Since the molecule-molecule distance is a fingerprint of the dimers in the network (see Table 1 in the main text), we identify in a distance analysis of next-neighbors both, CDTPA dimers (d_{NN,DFT} = 1.524 nm) and mixed ADTPA+CDTPA dimers (d_{NN,DFT} = 1.744 nm), see the histogram in Fig. S6c. Both dimer motifs connect via a tip-to-tip geometry. In the case of ADTPA ≈ CDTPA, the network is homogeneous and has regularly formed pores throughout the whole network (Fig. S6b). The next-neighbor distance is for most dimers the same, which corresponds to the mixed ADTPA+CDTPA dimer (histogram in Fig. S6d). Furthermore, the amount of interstitial defects (both ADTPA and CDTPA) is increased in intact pores (green arrow in Fig. S6b), which is reflected in a next-neighbor distance of around 1.3 ± 0.05 nm. Though this length is close to d_{NN,DFT} = 1.290 nm for ADTPA tip-to-side dimers, their formation can be ruled out by the orientation of the molecules in the pores. ADTPA tip-to-tip dimers (d_{NN,DFT} = 1.994 nm) within the binary ADTPA+CDTPA network as well as separated homomolecular domains are never observed in both preparations.

![Fig. S6 Comparison between preparations with an unequal local ratio of molecules: (a) In the case of CDTPA > ADTPA, CDTPA dimers (DFT-calculated centre-to-centre distance: 1.524 nm) coexist with mixed ADTPA+CDTPA dimers (DFT-calculated centre-to-centre distance: 1.744 nm) in a homogeneous network, whereas in the case (b) ADTPA ≈ CDTPA, mostly mixed ADTPA+CDTPA dimers are observed besides some interstitial defects in the network (see Fig. S7) and in the pore (see blue arrow). STM parameters: T = 4.7 K, (a) -1.1 V, 50 pA, (b) -200 mV, 700 pA.](image-url)
The formation of the binary ADTPA+CDTPA network is possible because ADTPA offers a *tip-to-tip* bonding geometry, which fits the bonding geometry of CDTPA. The strongly bound ADTPA *tip-to-side* dimer cannot be incorporated into a homogeneous intermixed network without introducing defective structures yielding open H-bonds. Only resorting to a mutual bonding motif, the *tip-to-tip* contact, facilitates a maximized number of H-bonds and increases the net amount of H-bonds between both types of molecules. The maximization of the overall number of H-bonds is also supported by the observation of interstitial defects incorporated in the honeycomb lattice instead of vacancies, which would yield open H-bonds at locations where the intermixing is not perfect. Annealing could eventually reduce the number of such defects. Interstitial defects can be visualized by $dI/dV$ mapping, which allows differentiating between ADTPA and CDTPA molecules as described in Fig. 1. Fig. S7 shows an example of interstitial ADTPA and CDTPA in the mixed ADTPA+CDTPA network.

![Topography and corresponding $dI/dV$ maps reveal interstitial ADTPA and CDTPA defects in areas of the mixed honeycomb network where the ADTPA+CDTPA are not perfectly intermixed. The HOMO of the ADTPA is roughly located at -1.1 eV, therefore they appear pronounced compared to the CDTPA in $dI/dV$ maps at -1.1 V. In $dI/dV$ maps at -1.6 V both the ADTPA and CDTPA are visible. The intensity of individual molecules in the $dI/dV$ maps varies due to the underlying herringbone reconstruction. STS parameters: $T = 4.7 \text{ K}$, open feedback at 450 pA.](image-url)
9. **STS of the DTPA frontier orbitals**

Scanning tunneling spectroscopy (STS) measurements were conducted in order to measure the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals in the two homomolecular (labelled "ADTPA" and "CDTPA", respectively) and the mixed ADTPA+CDTPA network (labelled "mixed"). The surface state of Au(111) was measured before each experiment to verify that the tip is metallic and clean of adsorbates and is plotted as a reference, see grey curves in Fig. S8.

As discussed in the main text (Fig. 2 and Table 1), the HOMO of the DTPA networks are observed in constant height STS around 1.1-1.4 eV below the Fermi level and are measured at the centre of the molecules. Above the Fermi level, constant height STS resolves features around 1.6-2 eV that are measured at the junction between two molecules. We attribute them to the LUMO energies of the DTPAs. However, we manipulate the molecules at these energies, which prohibits reproducible STS measurements even with low feedback resistance. In order to minimize tip-molecule interactions, constant current STS measurements were conducted, where the feedback is active during the bias sweep to prevent high current densities in the tunnel junction.

Constant current STS spectra for the homomolecular and binary networks are shown in Fig. S8b. The unfilled states are more pronounced in the bonding region than at the centre of the DTPA backbone. This agrees well with the calculated density of states by DFT presented in Fig. S10/S11, where LUMO to LUMO+3 show a node at the central N-atom. The approximate energy values for the LUMOs that correspond to the onset of the increase in the differential conductance in the constant current STS curves are summarized in Table S2. The relative alignment of the experimentally determined LUMO with respect to the Fermi level is consistent with DFT. We note that for the binary network we cannot distinguish any longer between CDTPA and ADTPA since the LUMO is measured in the bonding region of both molecules.

The HOMO-LUMO gaps we can experimentally only approximate qualitatively in the three networks since different techniques were applied. The HOMO-LUMO gaps are about 2.82 eV for the mixed, 3.31 eV for the ADTPA, and 2.99 eV for the CDTPA network, which agrees with the typical HOMO-LUMO gap of DTPA derivatives between 3-4 eV.²,¹³

<table>
<thead>
<tr>
<th>LUMO</th>
<th>constant current STS</th>
<th>DFT/B3LYP</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADTPA</td>
<td>2.05 ± 0.07 V</td>
<td>-1.49 eV</td>
</tr>
<tr>
<td>CDTPA</td>
<td>1.61 ± 0.07 V</td>
<td>-1.91 eV</td>
</tr>
<tr>
<td>mixed</td>
<td>1.67 ± 0.07 V</td>
<td>-1.77 eV</td>
</tr>
</tbody>
</table>

Table S2: Measured and calculated LUMO energies in the DTPA networks. Constant current STS spectra recorded at the intermolecular junctions of the homomolecular and binary networks were used to determine the LUMO experimentally. The LUMO energies calculated at the B3LYP level refer with respect to the vacuum level.
**Fig. S8** STS measurements of the DTPA networks. (a) Constant height STS of the HOMO recorded at the centre of ADTPA (blue) and CDTPA (red) in homomolecular (dashed lines) and binary (solid lines) networks. (b) Constant current STS of the LUMO taken at the head groups of ADTPA (dark blue line), CDTPA (dark red line) and binary ADTPA+CDTPA (green line) networks. The relative positions, where the spectra were recorded, are indicated with colored crosses in panels (c)-(e). STM parameters: Scale bar 1 nm; (c) 0.3 V, 100 pA; (d) -2 V, 100 pA; (e) 0.3 V, 80 pA. STS parameters: (a) -2 V, 100 pA (open feedback); (b) 100 pA (closed feedback).

Fig. S9 shows constant height $dI/dV$ maps for additional bias voltages. At -1.3 V the CDTPAs are pronounced, while at -1.1 V the ADTPAs show a higher differential conductance. At positive bias voltages, also in the junction a measurable density of states is observed.

**Fig. S9** Topography and constant height $dI/dV$ maps of the mixed ADTPA+CDTPA network. In the topography images of the ADTPA+CDTPA network, the ADTPAs are highlighted in blue and the CDTPAs in red. STS parameters: opened feedback above ADTPA with -1V, 50 pA.
10. Wavefunction plots of the CDTPA and ADTPA monomers and dimers

**Fig. S10** Wavefunction isosurface plots of the HOMO and LUMO states of the CDTPA (left) and ADTPA (right) monomer and the mixed CDTPA+ADTPA dimer (centre). Calculations were done with the ORCA code and the B3LYP functional for the B3LYP+D3-optimized geometries.
Fig. S11 Wavefunction isosurface plots of the HOMO and LUMO states of the CDTPA (left) and ADTPA (right) dimer. Calculations were done with the ORCA code and the B3LYP functional for the B3LYP+D3-optimized geometries.
11. Charge density difference plots

![Charge density difference plots: CDTPA, CDTPA+ADTPA, ADTPA](image)

**Fig. S12** Charge density difference plots of the three DTPA networks: CDTPA (left), mixed ADTPA+CDTPA (centre), and ADTPA (right). Calculations were done with PWscf for the PBE+D3 monolayer geometries. (a) Isosurface of 0.01 $e/\text{bohr}^3$. (b) Isosurface of $10^{-5} e/\text{bohr}^3$. A small charge transfer between CDTPA and ADTPA in the mixed ADTPA+CDTPA monolayer is visible.

**References**