Supporting Information

On-Surface Synthesis of Two-dimensional Imine Polymers with Tunable Band Gap: a Combined STM, DFT and Monte Carlo Investigation

1. Extra STM images

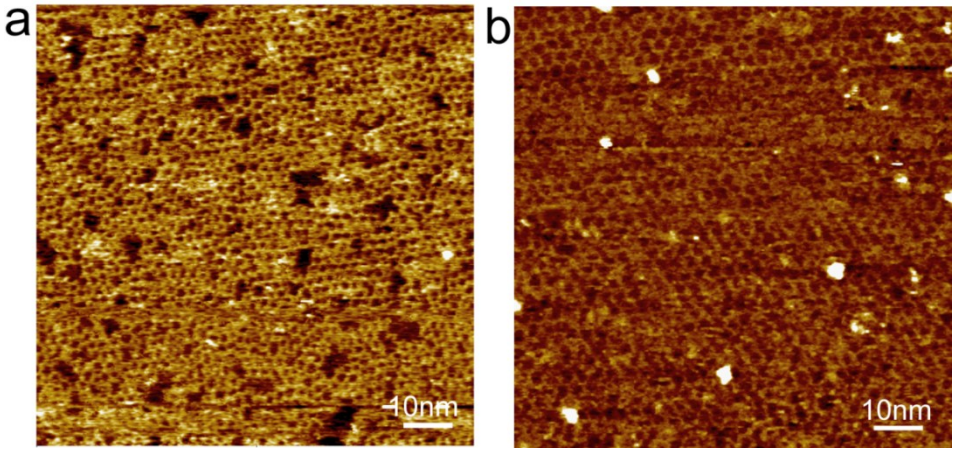


Figure S1. STM images of $2DP_{BTA\text{-}PDA}$ and $2DP_{BTA\text{-}DAB}$ obtained by annealing at 140 °C under low vacuum.

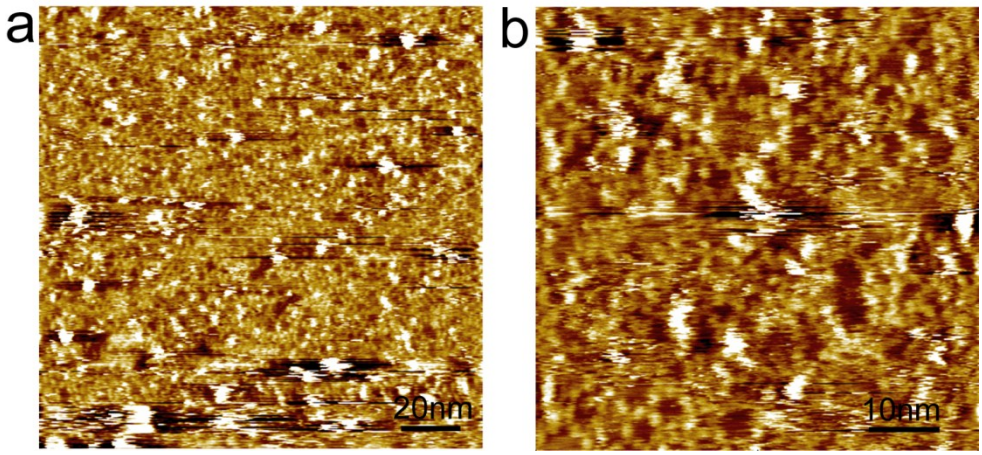


Figure S2. STM images of $2DP_{BTA\text{-}AABA}$ obtained with total monomer concentration of 0.01 mg/g in DMSO, after annealing at 200 °C for 30 min under low vacuum.

2. UV-Vis spectra of 2DPs

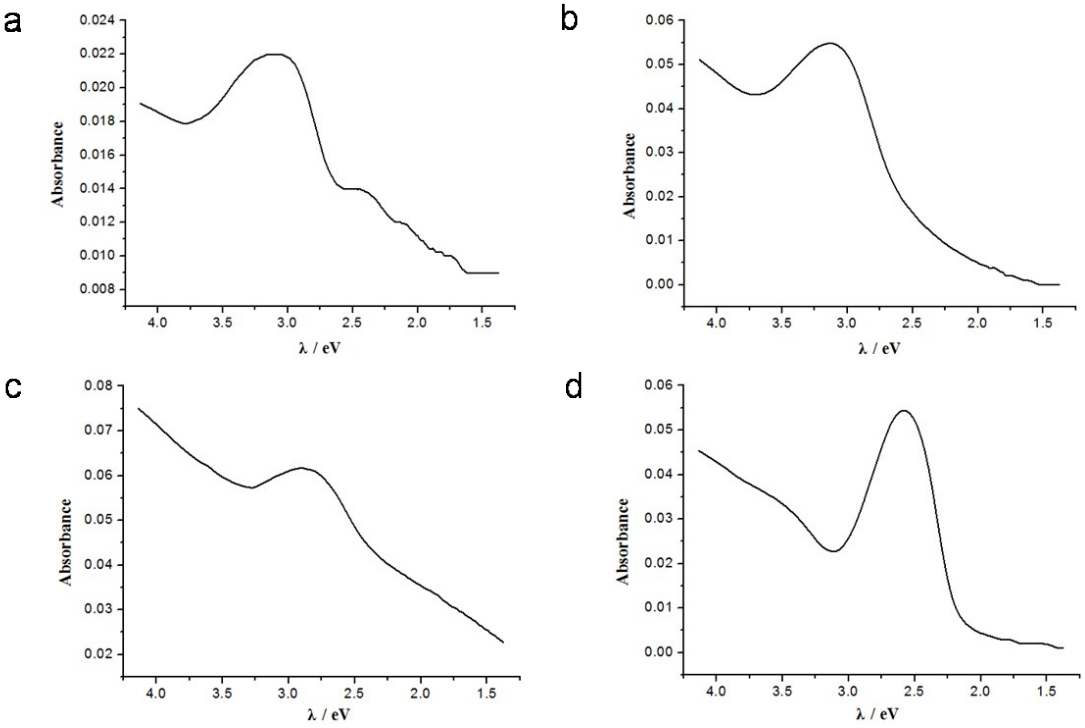


Figure S3. UV-Via spectra of $2DP_{BTA\text{-}PDA}$ (a), 2DPBTA-DAB (b), 2DPBTA-DAN (c), 2DPBTA-ABBA, the absorption maximum of these 2DPs are determined to be 400 nm, 303 nm, 428 nm and 480 nm, respectively.

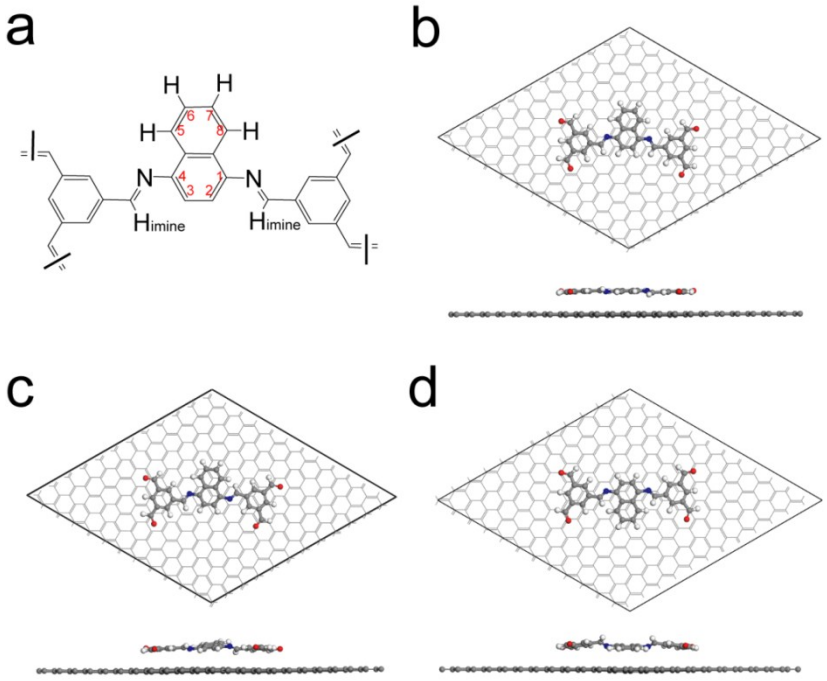


Figure S4. Different conformations of the imine moiety in $2DP_{BTA\text{-}DAN}$ optimized by DFT method. (a) Chemical structure of the imine moiety, DFT optimized (b) *cis-egzo*,

(c) *trans*, (d) *cis-endo* conformation, top and side views. As illustrated in the optimized structural model, due to the rotation of single bonds in the imine moiety different conformations exist, which can be defined as *cis-egzo*, *trans* and *cis-endo*, respectively. The planarity of the fragment with *cis-egzo* conformation is the best and there is basically no repulsion between H_{imine} and H2, H3 atoms in the naphthalene ring. However, the repulsion between the H_{imine} and H5, H8 atoms in the *trans* and *cis-endo* conformation, breaking the planarity of the molecules. However, the DFT simulation indicates the energy difference is not so large between these conformations, thus coexistence of these three conformations is expected, which may be the cause of decreased regularity of $2DP_{BTA-DAN}$, which will be discussed in more detail later.

3. Details of the Monte Carlo model and simulation

To simulate the mixed self-assembly of amine (DAN) and dialdehyde (BTA) molecules we used the simplified lattice Monte Carlo model whose successful application to a wide class of 2D supramolecular systems was demonstrated in the previous works.[1-3] Accordingly, the interacting species were treated as rigid flat structures composed of interconnected segments, each of which occupied one lattice on a triangular lattice. The segments were arranged in a way to reproduce both shape and distribution of interaction centers in the molecules of DAN and BTA. These simplified structures are shown in Figure S3.

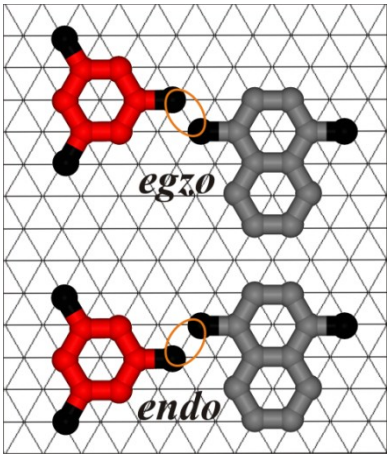


Figure S5. Schematic structure of the bimolecular amine(grey)-aldehyde(red)

configurations, called *egzo* and *endo*, differing in the relative position of the interacting species. The black segments denote molecular parts able to interact and to stabilize the heterogeneous DAN-BTA connections encircled in orange. The interaction energies for each of the configurations are denoted by ε_{egzo} and ε_{endo}.

The molecules of DAN and BTA were assumed to be able to interact with each other only when their active segments (-OH and -NH_2 groups marked in black in Figure S5) occupied nearest neighbor sites on the lattice and when these molecules were in one of the configurations *egzo* and *endo* shown in Figure S4. According to the DFT calculations the configurations were assigned potential energies fulfilling the condition $\varepsilon_{egzo} < \varepsilon_{endo}$. All of the remaining interactions between molecular segments (including DAN- DAN and BTA-BTA) were neglected. The elementary energies ε_{egzo} and ε_{endo} were used to calculate the energies of the trimolecular complexes shown in Figures 6 and 7. Specifically these energies were equal: $E_{cis\_egzo} = 2\varepsilon_{egzo}$, $E_{cis\_endo} = 2\varepsilon_{endo}$ and $E_{trans} = \varepsilon_{egzo} + \varepsilon_{endo}$. In most of the calculations we used two sets of parameters, that is we fixed $\varepsilon_{egzo} = -1.00$ and run the simulations for ε_{endo}= –0.95 and ε_{endo}= –0.90 (see Figure 5 and Figure S6 and S7). Moreover, to assess the individual role of the different trimolecular configurations in the structure formation we performed additional calculations in which some of these configurations were excluded. This refers to the three extreme cases from Figure 6 in which only the *cis egzo* (a), both *trans* (b) and *trans L* (c) configuration were allowed. In these cases we assumed that the energy of each of these configurations is equal to -2 and the other configurations do not occur in the corresponding adsorbed overlayer. Finally, we carried out also test simulations in which all of the configurations from Figure 5a had the same energy, that is we assumed $\varepsilon_{egzo} = \varepsilon_{endo} = -1.00$, which means no preference in the formation of any type of intermolecular connections.

The simulations were performed on a 200×200 triangular lattice using the canonical Monte Carlo method with Metropolis sampling.[1-3] To eliminate edge

effects periodic boundary conditions in both planar directions were imposed. In all of the simulations we used dimensionless parameters, so that energy values are given in the units of $|\varepsilon|$ and temperature in the units of $|\varepsilon|/k$ where k is the Boltzmann constant. Solvent molecules were neglected in the simulations. In the calculations we used 450 amine molecules and 300 aldehyde molecules (DAN:BTA = 3:2). To minimize the risk of trapping the simulated systems in metastable states we additionally applied the annealing procedure, in which the overlayer was slowly cooled down from $T=0.5$ to the target temperature $T=0.1$ in a linear fashion within 400 intervals of equal length. In each temperature interval 2×10^5 MC steps per molecule were performed where one MC step involved a random displacement and in-plane rotation of an adsorbed molecule. Then the exemplary snapshots from Figures 5 , 6 and S6 were taken.

4. Additional results from the simulations

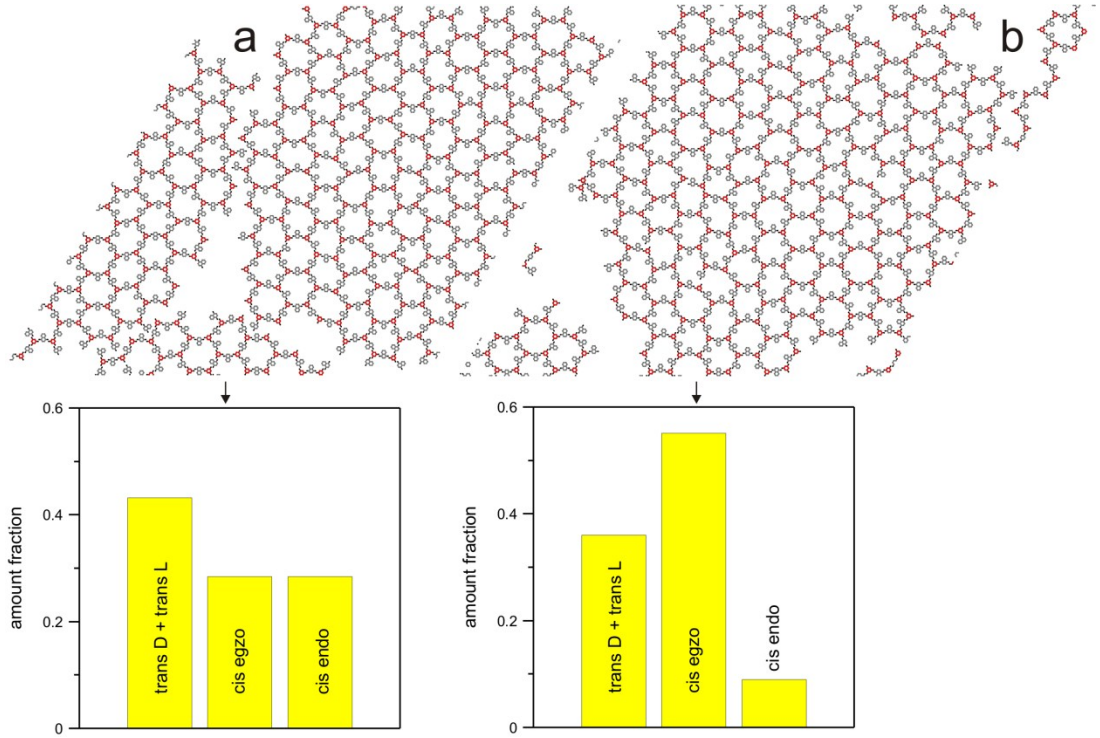


Figure S6. Exemplary snapshots of the adsorbed structures comprising 450 amine molecules and 300 aldehyde molecules simulated for $\varepsilon_{egzo} = \varepsilon_{endo} = -1.00$ (a) and $\varepsilon_{egzo} = -1.00$ $\varepsilon_{endo} = -0.90$ (b). The plots in the bottom part show the corresponding relative populations of the trimolecular configurations. These data are normalized with respect to the total number of trimolecular configurations in the adsorbed phase.

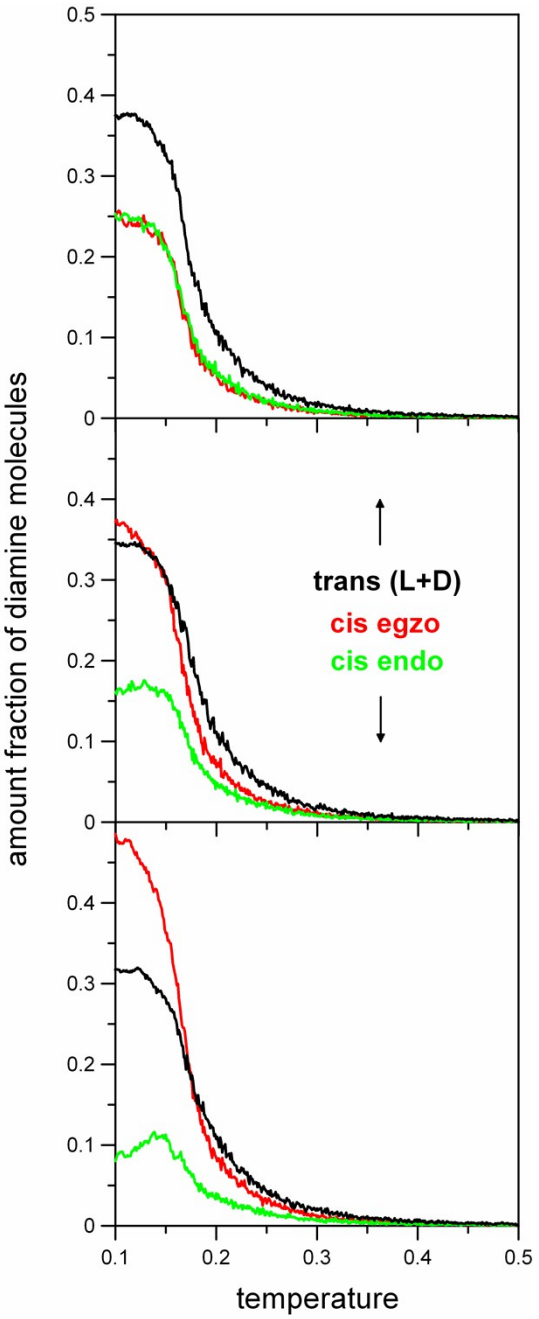
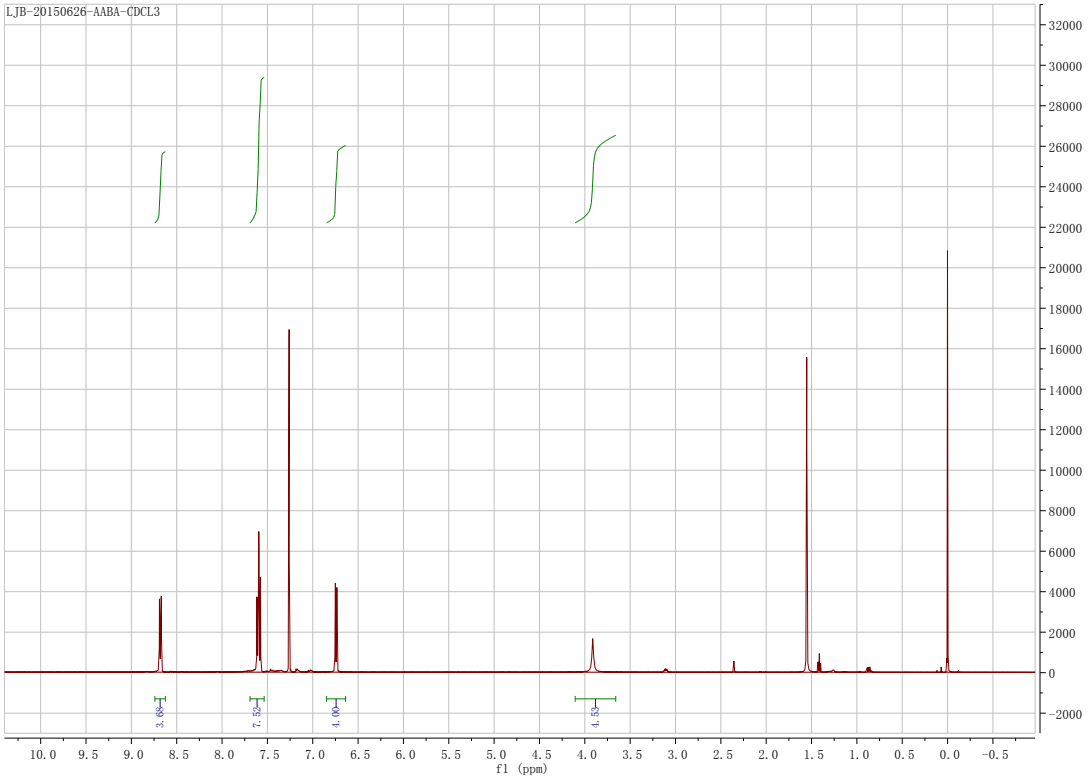
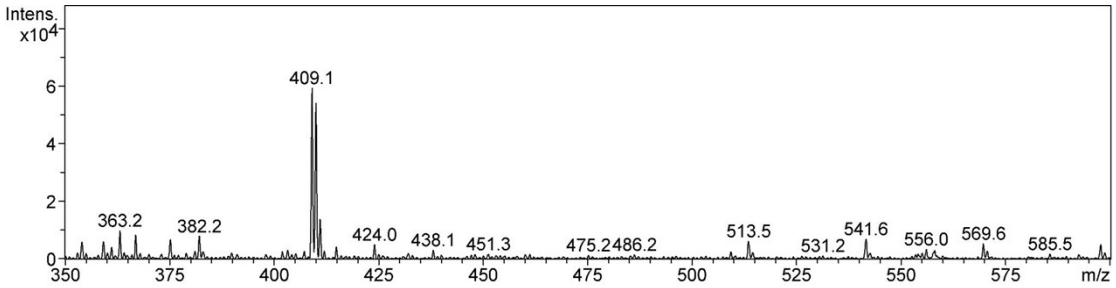


Figure S7. Influence of temperature on the relative amount of diamine molecules in the configurations listed in the figure. These data are normalized with respect to all diamine molecules, including those unbound and bound to one aldehyde molecule. The curves from the top, middle and bottom part correspond to $\varepsilon_{egzo} = -1.00$ and ε_{endo} equal to -1.00, -0.95 and -0.90 respectively.

5. [1]HNMR and MS of AABA



^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 – 8.67 (m, 4H), 7.62 – 7.57 (m, 8H), 6.74 (d, *J* = 8.5 Hz, 4H), 3.91 (s, 4H).



MS(ESI) m/z 409.1 [M^+]

References:

1. Szabelski, P.; De Feyter, S.; Drach, M.; Lei, S. B. Computer Simulation of Chiral Nanoporous Networks on Solid Surfaces. *Langmuir* **2010**, *26*, 9506–9515.

2. Lei, S.; Tahara, K.; Müllen, K.; Szabelski, P.; Tobe, Y.; De Feyter S. Mixing behavior of Alkoxylated Dehydrobenzo(12)annulenes at the Solid-Liquid Interface: Scanning Tunneling Microscopy and Monte Carlo Simulations. *ACS Nano*, **2011**, *5*, 4145–4157.

3. Szabelski, P.; Rżysko, W.; Pańczyk, T.; Ghijsens, E.; Tahara, K.; Tobe, Y.; De Feyter S.

Self-assembly of Molecular Tripods in Two Dimensions: Structure and Thermodynamics from Computer Simulations. *RSC Advances*, **2013**, *3*, 25159-25165