Electronic Supplementary Information

Peculiar adsorbed phase behaviour of binary mixtures of oligopyridines and extension to a ternary mixture in a host-guest system

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Experimental part

STM

Solutions of 2,4'-BTP, 2,3'-BTP, and 3,3'-BTP, respectively, in 1,2,4-trichlorobenzene (TCB) (Aldrich, >99%) were prepared within a concentration interval of 0.025 mg mL^{-1} ($4 \cdot 10^{-6}$ mol L^{-1}) and 0.50 mg mL^{-1} ($8 \cdot 10^{-5}$ mol L^{-1}).

2 µL of the (mixed) solutions were deposited on a freshly cleaved surface of highly ordered pyrolytic graphite (HOPG) with the mechanically sharpened tip (80/20 Pt/Ir) in tunnel contact. Before the desired measurements, the tip has been tested by imaging the HOPG surface. After successful imaging of the oligopyridine network with the STM (SPM1000, RHK) at ambient conditions in a 75 nm x 75 nm area containing ca. $2 \cdot 10^3$ molecules the tip-position was moved to a completely different area of the HOPG surface. At the new tip position another image was taken and the measurement was repeated until at least 20 images at different places of a certain mixing ratio were achieved. Images were obtained within 20 to 30 min of solvent deposition as so not to have any significant loss of solvent. The raw STM images were smoothed, the heights were compensated using the program XPMPro™ (RHK). The observed surface coverage was evaluated by a home made software.

There were done sample experiments for the proof of thermodynamic control of the adlayer formation as following. 2 µL of the 1:1 mixture at total concentrations of 0.05 mg mL^{-1} of the combination 2,3'-BTP/2,4'-BTP and 3,3'-BTP/2,4'-BTP, respectively, were deposited on freshly cleaved HOPG and imaged by STM showing the 1:1 adlayer composition. After that, excess (4 µL of 0.2 mg mL^{-1} (for 3,3'-BTP) and 0.4 mg mL^{-1} (for 2,3'-BTP and 2,4'-BTP), respectively) of one of the compounds from the mixture was added leading almost exclusively to the monolayers of the added compound in all cases corresponding to the S shape curve reported in ref. 1. Similarly, starting with the adlayer of a pure compound (2 µL, 0.05 mg mL^{-1}) and adding the other oligopyridine in excess showed the disappearance of the 2D structure of the first oligopyridine and the emergence of the monolayer of the subsequently added oligopyridine.

Starting with a pure compound (1 µL, 0.05 mg mL^{-1}) and adding the other oligopyridine (1 µL, 0.05 mg mL^{-1}) led to the corresponding surface coverage as obtained by the simultaneous adlayer preparation with the already mixed solution.

The statistical evaluation of the adlayer composition was performed as described in our previous paper by assigning the phases via the symmetry and the lattice parameters. Intermixing of the molecules could be ruled out because of energetic reasons as shown by calculations.[1]

The ternary system containing 2,4'-BTP, 3,3'-BTP, and copper phthalocyanine was prepared by the following method. First, 2 µL of a 3,3'-BTP solution ($8 \cdot 10^{-5}$ mol L^{-1}) and 2 µL of a copper phthalocyanine solution ($9 \cdot 10^{-5}$ mol L^{-1}) were dropped on HOPG to obtain a hexagonal pattern of the 3,3'-BTP with partly incorporated copper phthalocyanine molecules in the cavities of the oligopyridine lattice. Then 2 µL of a 2,4'-BTP solution ($8 \cdot 10^{-5}$ mol L^{-1}) was added. The same result can be obtained by adding the

oligopyridine mixture (2,4'-BTP and 3,3'-BTP) first and then a copper phthalocyanine solution or by dropping a mixture of all three compounds onto the surface.

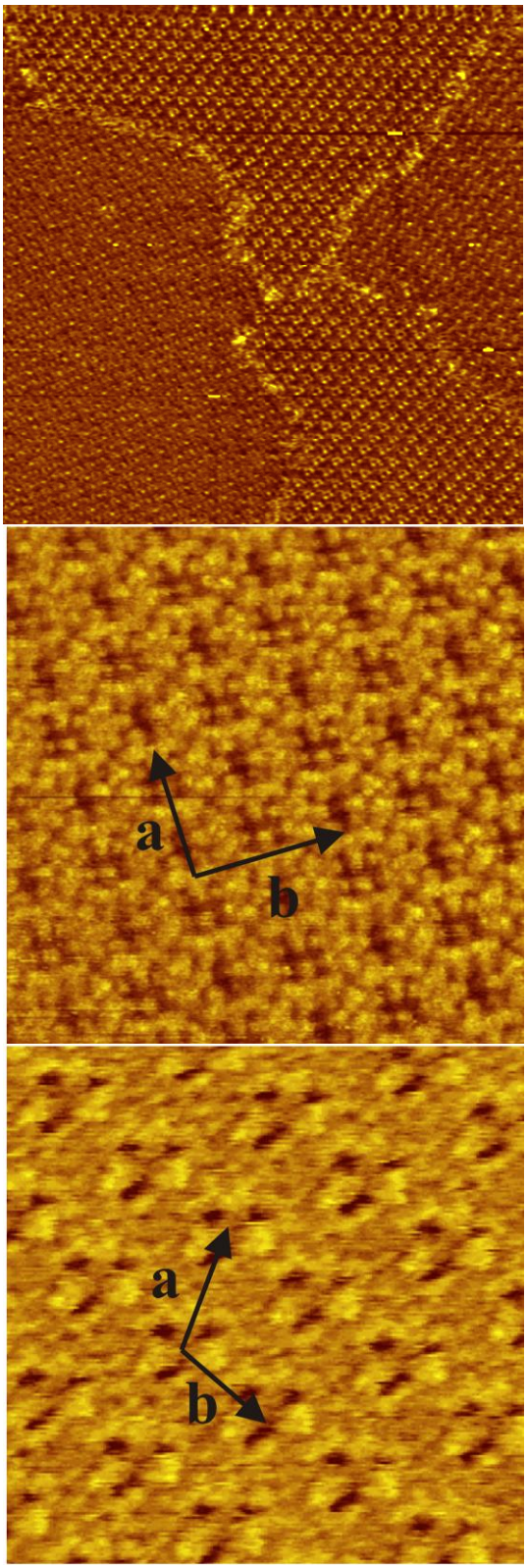

Fig. 1S Representative STM images of the binary system 2,4'-BTP/2,3'-BTP. Top: 1:1 mixture with the 2,4'-BTP phase left and right and the 2,3'-BTP phase in the middle, total concentration 0.40 mg mL^{-1}, scan area: 75 nm x 75 nm, V_{set} = - 0.67 V, I_{set} = 20.0 pA; middle:[1] magnified area of 2,4'-BTP phase with unit cell: $a = b$ = 3.1 nm ± 0.2, $\angle_{a,b}$ = 90° ± 1°, I_{set} = 82 pA, V_{set} = -1.00 V; bottom:[1]

magnified area of 2,3'-BTP phase with unit cell: a = 2.9 nm ± 0.2 nm, b = 2.6 nm ± 0.2 nm, $\angle_{a,b}$ = 120° ± 1°, I_{set} = 1.0 nA, V_{set} = -0.60 V.

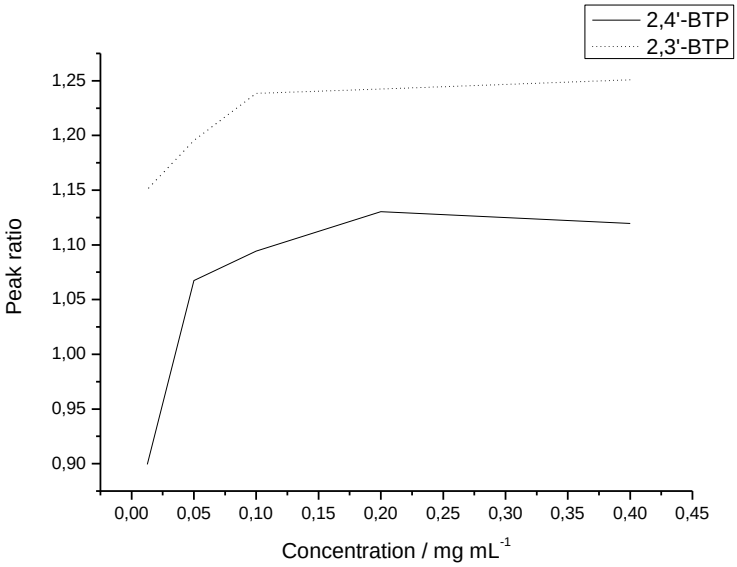

Fig. 2S Concentration dependent intensity ratio of the peaks at ca. 440 nm and 420 nm in the emission spectra of 2,4'-BTP (bottom) and 2,3'-BTP (top).

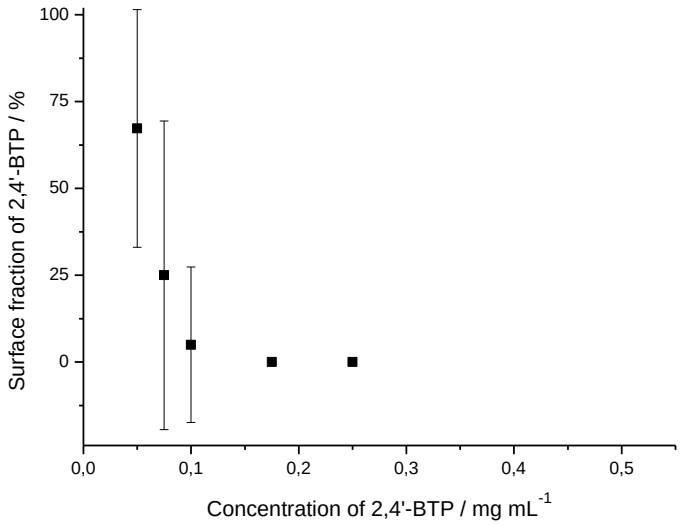

Fig. 3S Concentration dependent surface coverage of 2,4'-BTP at a 1:1 ratio of 2,4'-BTP/3,3'-BTP.

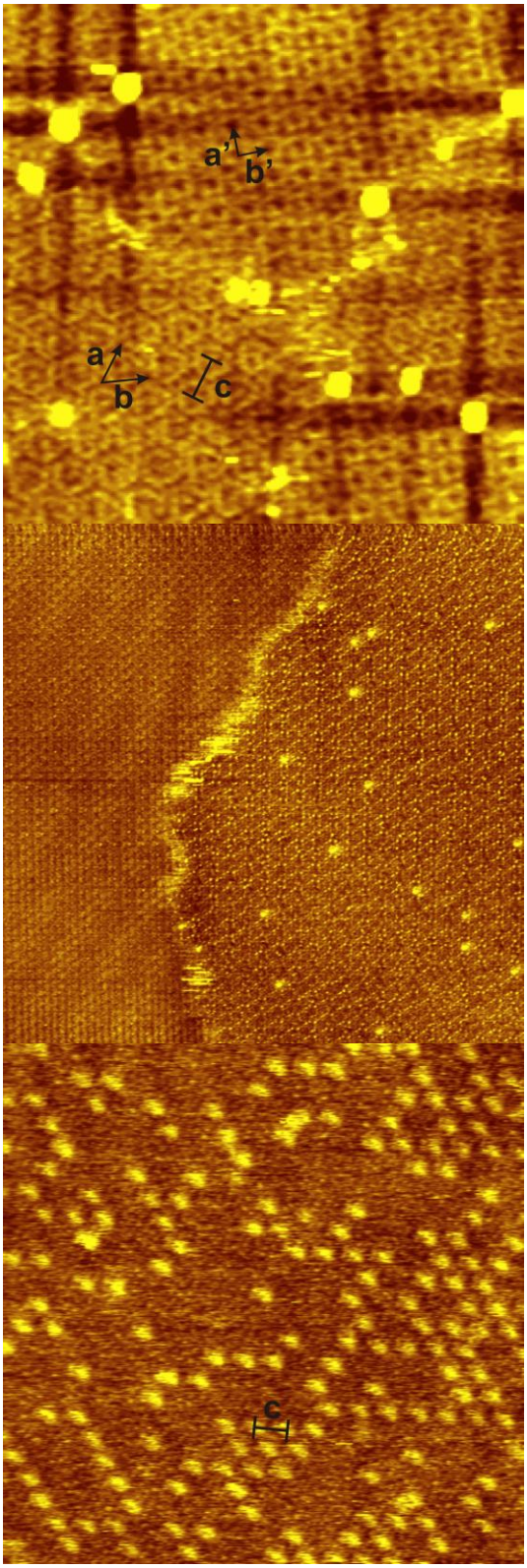

Fig. 4S STM images of the ternary system 2,4'-BTP / 3,3'-BTP / CuPc. Top: 50 nm x 50 nm (I_{set} = -0.60 V, V_{set} = 1.32 nA). a = b = 4.4 nm ± 0.2 nm. $\angle_{a,b}$ = 60 ± 1°. Distance c = 4.4 nm ± 0.2 nm between two cavities of the hexagonal 3,3'-BTP pattern. a' = b' = 3.1 nm ± 0.2 nm. $\angle_{a',b'}$ = 90° ± 1°. Middle: 110 nm x 110 nm (I_{set} = 1.50 nA, V_{set} = -0.62 V). Left: 2,4'-BTP phase. Right: 3,3'-BTP phase with CuPc in some cavities. Bottom: 75 nm x 75 nm (I_{set} = -0.62 V, V_{set} = 1.50 nA). Distance c = 4.4 nm ± 0.2 nm between two with CuPc filled cavities of the hexagonal 3,3'-BTP pattern.

References

1 D. Caterbow; M. Roos; H. E. Hoster; R. J. Behm; K. Landfester and U. Ziener, *Chem.-Eur. J.* 2011, **17**, 7831-7836.

Electronic Supplementary Material (ESI) for Chemical Communications