Tunable symmetry and periodicity in binary supramolecular nanostructures

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We present a route to change the “compositional” order of highly crystalline binary layers comprising diindenoperylene and copper-phthalocyanines from two- into one-dimensional periodicity. This is achieved exchanging fluorine by hydrogen atoms in the phthalocyanines, thereby reducing the C-F...H-C interactions and allowing the interplay of long-range electrostatic interactions in mesoscopic phases. Linear patterns are thus obtained, whose periodicity can be additionally tuned by an appropriate stoichiometry of the components.

Molecular electronics is envisioned as one of the possible breakthroughs in electronics and information technology. Progress in the control of supramolecular self-assembly is expected to make it possible, paving the way towards tailored synthesis of functional molecular nanostructures. However, the assembly of appropriate molecules into well ordered arrays on technologically relevant surfaces is a challenge that demands the control of system interactions at different length scales. At the nanoscopic level, the process is determined by a complex interplay between intermolecular and molecule-substrate interactions. Several routes have been exploited to steer those interactions. A handle on molecule-substrate interactions is provided by the use of nanostructured surfaces. This has been demonstrated with surface superstructures or stepped surfaces, which can, for example, define preferential adsorption sites.¹⁻⁵ In turn, the use of appropriate molecules with complementary functional groups allows the formation of strong intermolecular interactions. These include hydrogen bonds,⁵⁻¹⁰ or even chemical reactions,^{11,12} both of whose directionality provides an additional control parameter in the design of molecular arrays.

Ideally, long-range ordered molecular arrays with tunable symmetry and periodicity are desired. A beautiful example thereof recently reported are molecular gratings made of methionine stripes on silver surfaces,¹³ which have been used as templates for the subsequent growth of atomic strings.¹⁴ Their tunable periodicity (via methionine coverage), together with their behavior as one-dimensional electron resonators, allows tailoring the characteristics of quantum-well states.¹⁵ Supramolecular self-assembly of two- (or multi-) component systems has been repeatedly used for successful synthesis of highly ordered nanostructured layers with diverse crystalline structures. Most examples report the formation of well ordered two-dimensional molecular mixtures.^{5,6,7,8,16-31} A lesser number reports the formation of crystalline structures with each of the molecular components arranged in separate rows and therefore leading to one-dimensional

“compositional” order.^{28,35} Only few of the aforementioned examples show tunable properties of their symmetry (changing e.g. between one- and two-dimensional structures) or periodicity, which is achieved either by adjusting the molecular ratio^{9,16,25,30,31} or by annealing treatments.^{26,29,32} In this letter, we demonstrate the formation of supramolecular nanostructures with tunable properties of both their symmetry and periodicity, by means of adjustment of the intermolecular interactions and of the binary layer stoichiometry of copper-phthalocyanines and diindenoperylene (DIP, Fig. 1a).

The complementary functionalities of fluorinated copper-phthalocyanines (F₁₆CuPc, Fig. 1a) and DIP give rise to rather strong intermolecular interactions via C-H...F-C bonds.^{36,37} As a consequence, in order to maximize them, growth of binary layers in a 1:1 ratio on Au(111) and Cu(111) surfaces leads to the formation of highly crystalline two-dimensional structures with the molecules arranged in such a way that each molecule is surrounded by the opposite species (Fig. 1b). However C-H...F-C interactions can be eliminated by exchanging F₁₆CuPc by its homeomorphic non-fluorinated counterpart CuPc (Fig. 1a), whose combination with DIP in binary layers is therefore expected to present a much lower 2D cohesive energy.

Our results show that indeed, in DIP-CuPc binary layers, the molecules do not surround themselves by the opposite specie. In contrast, they arrange into alternating molecular rows, finally producing well ordered layers with one-dimensional compositional periodicity (Fig. 1c) and domains of up to several tens of nanometers (Fig. S1).

Such findings apply to different substrates, demonstrated here with Au(111) and Cu(111). Figure 2 shows small scale STM images of 1:1 binary layers on both substrates. The similarity among the structures obtained on either surface is evident, and the main difference is related to their symmetry.

In the case of Au(111) we find two different molecular orientations within the rows of each molecular specie. The two azimuthal orientations of each molecule are related by a mirror plane directed along the molecular rows, evidencing their alignment with the high symmetry directions of the substrate. In particular, the rows have been found to align along the Au [1-10] and equivalent directions, giving rise to three discrete row orientations separated by 60°, each of them additionally displaying two equivalent mirror domains. The frequent changes in molecular orientation associated to the two mirror domains indicate the low energy associated to such domain boundaries.

In contrast, on Cu(111) DIP and CuPc molecules present a

Fig. 1 (a) Schematic representation of F₁₆CuPc, DIP and CuPc molecules. (b) 12×12 nm² STM image of a binary layer combining DIP with F₁₆CuPc on Au(111) in a 1:1 ratio. (c) The same as (b) combining DIP with CuPc.

Fig. 2 10×10 nm² STM images of the CuPc:DIP 1:1 crystalline structures on Au(111) and Cu(111) surfaces (top) together with the corresponding epitaxial models (bottom). For the model on Au(111), the herringbone reconstruction has been neglected in spite of its experimental observation. Consequently, lattice mismatches of up to 4 % may occur in dependence of the reconstruction domain orientation. The inclusion of such effect into the model is hindered by the extension of the molecular domains throughout multiple rotational domains of the substrate reconstruction.

interactions may play an important role, the latter resulting either from intrinsic molecular dipoles or from absorption-induced surface dipoles. Such surface dipoles are responsible for the commonly observed work function changes of metal surfaces upon molecular adsorption and may largely vary from molecule to molecule, being specific to each molecule-substrate interface.⁴⁰ According to previous works, energy minimization by dipole-dipole interactions in binary systems (with stoichiometries in the range of those used for the present experiments) leads to segregation into striped phases.^{41,42}

Thus, although other aspects such as epitaxial relations with the substrate may play additional important roles in the resulting film structure (as discussed above), it seems plausible to ascribe a decisive role in the linear molecular arrangements of these binary layers to long-range dipole-dipole interactions. In this context, the shortest possible periodicity (alternating, single molecular rows) points to very low phase boundary energies allowing for maximized dipole-dipole interactions.

However, most important is the fact that a controlled reduction of the intermolecular interactions simply exchanging fluorine by hydrogen atoms, yields remarkable changes from two- to one-dimensional periodicities in the crystalline structures.

It is worth noting that a similar attempt was reported on binary layers combining nickel-tetraphenylporphyrin (NiTPP) with the fluorinated (F₁₆CoPc) and non-fluorinated (CoPc) cobalt-phthalocyanines.²⁴ However, the experiment failed to find a tunability of the crystalline properties of such layers, given the disordered nature of the NiTPP-CoPc mixture.

Table 1 Structural parameters of the 1:1 crystalline phases on Au(111) and Cu(111) from experiment and epitaxial models.

		a	b	γ	χ	ϕ	Matrix
Au(111)	Exp.	25.4±0.9	14.3±0.4	83±3	24±4	34±4	a
	Model	25.1	14.4	83.4	26	33	
Cu(111)	Exp.	24.4±1	13.8±0.5	83±3	24±4	33±4	
	Model	24.7	13.5	83.8	25	33	

^a This matrix is only approximate, as deviations arising due to the surface reconstruction are neglected.

Fig. 3 14×14 nm² STM images of the resulting structures for binary layers combining DIP with CuPc with varying ratios on Au(111) and Cu(111) surfaces. For better resolution in the 2:1 structure image on Cu(111), an image of the pure DIP region is shown, and we refer to the 1:1 structure in the binary regions. Marked with grey lines are those systems leading to periodic linear patterns.

The structures obtained modifying the CuPc:DIP stoichiometry on either surface are further summarized in Figure 3. Being already published previous works on single component CuPc or DIP on both surfaces,⁴⁷⁻⁴⁹ we only focus on binary layers with molecular ratios of 2:1 and 1:2. Most

interestingly, we find that the periodicity of the one-dimensional structures can be tuned via the stoichiometry. For the CuPc:DIP 2:1 ratio we find the following. On Au(111) we either observe phase separation into pure CuPc and binary 1:1 regions, or a disordered mixture (alternating double, triple, or higher multiplicity CuPc rows with those of DIP). However, on Cu(111) the binary layer keeps an ordered arrangement of alternating molecular rows, now featuring double rows for the CuPc. The result is thus a highly regular linear pattern comparable to the 1:1 structure but with an increased periodicity.

A comparable scenario appears for the 2:1 ratio, though in this case it is on the Cu(111) where we observe phase separation into pure DIP and binary regions, both of them highly ordered.⁴⁸ Segregation of pure DIP beyond the 1:1 stoichiometry and the absence of disordered mixtures with alternating molecular rows of randomly varying multiplicity points to the DIP structure as a particularly low energy phase, which alters the mesoscopic balance of dipole-dipole and phase boundary energies. In contrast, on Au(111) the one-dimensional compositional order is maintained. Now it is the DIP which features double molecular rows alternating with those of CuPc. The presence of single DIP rows in the STM image is related to a slightly deviated stoichiometry, but the absence of disorder or phase separated regions points to potentially highly periodic linear patterns upon a more precise stoichiometric deposition.

The differences in the 1D ordering for different stoichiometries of the CuPc:Dip mixtures on Au(111) and Cu(111) reveal the pronounced interplay between the intermolecular interactions (including short-ranged steric effects, medium ranged van-der-Waals and longer ranged electrostatic interactions) and those between molecule and substrate. However, most importantly we have found that the linear nature of the molecular arrays can be obtained for different stoichiometries and its lateral periodicity can thus be varied in a controlled way.

In conclusion, we have shown how control of the intermolecular interactions in binary supramolecular layers of homeomorphic components can change the symmetry of their highly crystalline nanostructures. An exchange of fluorine and hydrogen atoms within a molecule can inhibit the formation of hydrogen bonds and change the structure of the binary layers from having a two- to a one-dimensional compositional periodicity. In addition, by changing the stoichiometry of the deposition we can tune the periodicity of the binary structures. This has been proved for molecular ratios between 2:1 and 1:2, but controllability of the periodicity over a larger range might be equally possible going to more disparate

stoichiometries. Altogether, this letter reports on supramolecular self-assembly in which we obtain molecular templates with tunable symmetry and periodicity, a landmark in organic self-assembly of potential use for subsequent synthesis of tailored functional molecular nanostructures.

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Notes and references

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- ¹ H. L. Zhang, W. Chen, L. Chen, H. Huang, X. S. Wang, J. Yuhara, A. T. S. Wee, *Small* 2007, **3**, 2015
- ² S. Berner, M. Corso, R. Widmer, O. Groening, R. Laskowski, P. Blaha, K. Schwarz, A. Goriachko, H. Over, S. Gsell, M. Schreck, H. Sachdev, T. Greber, J. Osterwalder, *Angew. Chem. Int. Ed.* 2007, **46**, 5115
- ³ N. Neel, J. Kröger, R. Berndt, *Adv. Mater.* 2006, **18**, 174
- ⁴ R. Otero, Y. Naitoh, F. Rosei, P. Jiang, P. Thosttrup, A. Gourdon, E. Lægsgaard, I. Stensgaard, C. Joachim, F. Besenbacher, *Angew. Chem. Int. Ed.* 2004, **43**, 2092
- ⁵ F. Silly, A. Q. Shaw, K. Porfyrakis, G. A. D. Briggs, M. R. Castell, *Appl. Phys. Lett.* 2007, **91**, 253109
- ⁶ J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness, P. H. Beton, *Nature* 2003, **424**, 1029
- ⁷ M. E. Cañas-Ventura, W. Xiao, D. Wasserfallen, K. Müllen, H. Brune, J. V. Barth, R. Fasel, *Angew. Chem. Int. Ed.* 2007, **46**, 1814.
- ⁸ M. Ruiz-Oses, N. Gonzalez-Lakunza, I. Silanes, A. Gourdon, A. Arnau, J. E. Ortega, *J. Phys. Chem. B* 2006, **110**, 25573
- ⁹ M. Treier, M.-T. Nguyen, N. V. Richardson, C. Pignedoli, D. Passerone, R. Fasel, *Nano Lett.* 2009, **9**, 126
- ¹⁰ S. De Feyter, F. C. De Schryver, *Chem. Soc. Rev.* 2003, **32**, 139
- ¹¹ L. Grill, M. Dyer, L. Lafferentz, M. Persson, M. V. Peter, S. Hecht, *Nat. Nanotech.* 2007, **2**, 687
- ¹² R. Gutzler, H. Walch, G. Eder, S. Kloft, W. M. Hecklab, M. Lackinger, *Chem. Commun.* 2009, 4456
- ¹³ A. Schiffrin, A. Riemann, W. Auwaerter, Y. Pennec, A. Weber-Bargioni, D. Cvetko, A. Cossaro, A. Morgante, J. V. Barth, *Proc. Nat. Acad. Sci.* 2007, **104**, 5279
- ¹⁴ A. Schiffrin, J. Reichert, W. Auwärter, G. Jahnz, Y. Pennec, A. Weber-Bargioni, V. S. Stepanyuk, L. Niebergall, P. Bruno, J. V. Barth, *Phys. Rev. B* 2008, **78**, 035424.
- ¹⁵ Y. Pennec, W. Auwärter, A. Schiffrin, A. Weber-Bargioni, A. Riemann, J. V. Barth, *Nat. Nanotech.* 2007, **2**, 99
- ¹⁶ E. Barrena, D. G. de Oteyza, H. Dosch, Y. Wakayama, *ChemPhysChem* 2007, **8**, 1915
- ¹⁷ M. Ruiz-Oses, D. G. de Oteyza, I. Fernandez-Torrente, N. Gonzalez-Lakunza, P. M. Schmidt-Weber, T. Kampen, K. Horn, A. Gourdon, A. Arnau, J. E. Ortega, *ChemPhysChem* 2009, **10**, 896
- ¹⁸ T. N. Krauss, E. Barrena, H. Dosch, Y. Wakayama, *ChemPhysChem* 2009, **10**, 2445
- ¹⁹ C. Bobisch, Th. Wagner, A. Bannani, R. Möller, *J. Chem. Phys.* 2003, **119**, 9804
- ²⁰ W. Chen, H. Li, H. Huang, Y. Fu, H. L. Zhang, J. Ma, A. T. S. Wee, *J. Am. Chem. Soc.* 2008, **130**, 12285
- ²¹ K. J. Franke, G. Schulze, N. Henningsen, I. Fernandez-Torrente, J. I. Pascual, S. Zarwell, K. Rück-Braun, M. Cobian, N. Lorente, *Phys. Rev. Lett.* 2008, **100**, 036807
- ²² K. W. Hipps, L. Scudiero, D. E. Barlow, M. P. Cooke, *J. Am. Chem. Soc.* 2002, **124**, 2126
- ²³ B. Xu, C. Tao, W. G. Cullen, J. E. Reutt-Robey, E. D. Williams, *Nano Lett.* 2005, **5**, 2207
- ²⁴ L. Scudiero, K. W. Hipps, D. E. Barlow, *J. Phys. Chem. B* 2003, **107**, 2903
- ²⁵ Y. Wakayama, D. G. de Oteyza, J. M. Garcia-Lastra, D. J. Mowbray, *ACS Nano* DOI: 10.1021/nn102887x
- ²⁶ F. Silly, U. K. Weber, A. Q. Shaw, V. M. Burlakov, M. R. Castell, G. A. D. Briggs, D. G. Pettifor, *Phys. Rev. B* 2008, **77**, 201408
- ²⁷ P. Samori, N. Severin, C. D. Simpson, Klaus Mullen, J. P. Rabe, *J. Am. Chem. Soc.* 2002, **124**, 9454
- ²⁸ M. de Wild, S. Berner, H. Suzuki, H. Yanagi, D. Schlettwein, S. Ivan, A. Barattoff, H.-J. Guentherodt, T. A. Jung, *ChemPhysChem* 2002, **10**, 881
- ²⁹ B. Calmettes, S. Nagarajan, A. Gourdon, M. Abel, L. Porte, R. Coratger, *Angew. Chem. Int. Ed.* 2008, **47**, 6994
- ³⁰ Y. L. Huang, W. Chen, H. Li, J. Ma, J. Pflaum, A. T. S. Wee, *Small* 2010, **6**, 70
- ³¹ X. Sun, H. T. Jonkman, F. Silly, *Nanotech.* 2010, **21**, 165602
- ³² W. Chen, H. L. Zhang, H. Huang, L. Chen, A. T. S. Wee, *Appl. Phys. Lett.* 2008, **92**, 193301
- ³³ N. Gonzalez-Lakunza, I. Fernandez-Torrente, K. J. Franke, N. Lorente, A. Arnau, J. I. Pascual, *Phys. Rev. Lett.* 2008, **100**, 156805
- ³⁴ K. Suto, S. Yoshimoto, K. Itaya, *J. Am. Chem. Soc.* 2003, **125**, 14976
- ³⁵ L. Chen, W. Chen, H. Huang, H. L. Zhang, J. Yuhara, A. T. S. Wee, *Adv. Mater.* 2008, **20**, 484
- ³⁶ D. G. de Oteyza, J. M. García-Lastra, M. Corso, B. P. Doyle, L. Floreano, A. Morgante, Y. Wakayama, A. Rubio, J. E. Ortega, *Adv. Funct. Mater.* 2009, **19**, 3567
- ³⁷ D. G. de Oteyza, I. Silanes, M. Ruiz-Oses, E. Barrena, B. P. Doyle, A. Arnau, H. Dosch, Y. Wakayama, J. E. Ortega, *Adv. Funct. Mater.* 2009, **19**, 259
- ³⁸ D. E. Hooks, T. Fritz, M. D. Ward, *Adv. Mater.* 2001, **13**, 227
- ³⁹ H. Huang, Y. Huang, J. Pflaum, A. T. S. Wee, W. Chen, *Appl. Phys. Lett.* 2009, **95**, 263309
- ⁴⁰ H. Ishii, K. Sugiyama, E. Ito, K. Seki, *Adv. Mater.* 1999, **11**, 605
- ⁴¹ D. Vanderbilt, *Surf. Sci. Lett.* 1992, **268**, L300
- ⁴² K.-O. Ng, D. Vanderbilt, *Phys. Rev. B* 1995, **52**, 2177
- ⁴³ D. G. de Oteyza, A. El-Sayed, J. M. Garcia-Lastra, E. Goiri, T. N. Krauss, A. Turak, E. Barrena, H. Dosch, J. Zegenhagen, A. Rubio, Y. Wakayama, J. E. Ortega, *J. Chem. Phys.* 2010, **133**, 214703
- ⁴⁴ I. Chizhov, G. Scoles, A. Kahn, *Langmuir* 2000, **16**, 4358
- ⁴⁵ D. G. de Oteyza, E. Barrena, H. Dosch, Y. Wakayama, *Phys. Chem. Chem. Phys.* 2009, **11**, 8741
- ⁴⁶ D. G. de Oteyza, E. Barrena, M. Ruiz-Oses, I. Silanes, B. P. Doyle, J. E. Ortega, A. Arnau, H. Dosch, Y. Wakayama *J. Phys. Chem. C* 2008, **112**, 7168
- ⁴⁷ H. Karakuban, M. Lange, J. Schaffert, O. Weingart, Th. Wagner, R. Möller, *Surf. Sci.* 2009, **603**, L39
- ⁴⁸ The phase separated DIP regions do not show the same structure as on the bare Cu(111), but the structure observed for DIP on Cu(111) subject to confinement in terraces of widths below 15 nm [ref. 47]. The reason why this structure now extends to distances far above 15 nm remains unclear, but is unambiguously related to the presence of CuPc.