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Title

Controlling the Self-Metalation Rate of Tetraphenylporphyrins on Cu(111) via Cyano Functionalization

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Controlling the Self-Metalation Rate of Tetraphenylporphyrins on Cu(111) via Cyano Functionalization

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The great self-metalation race

4 x CN

2 x CN

1 x CN

0 x CN
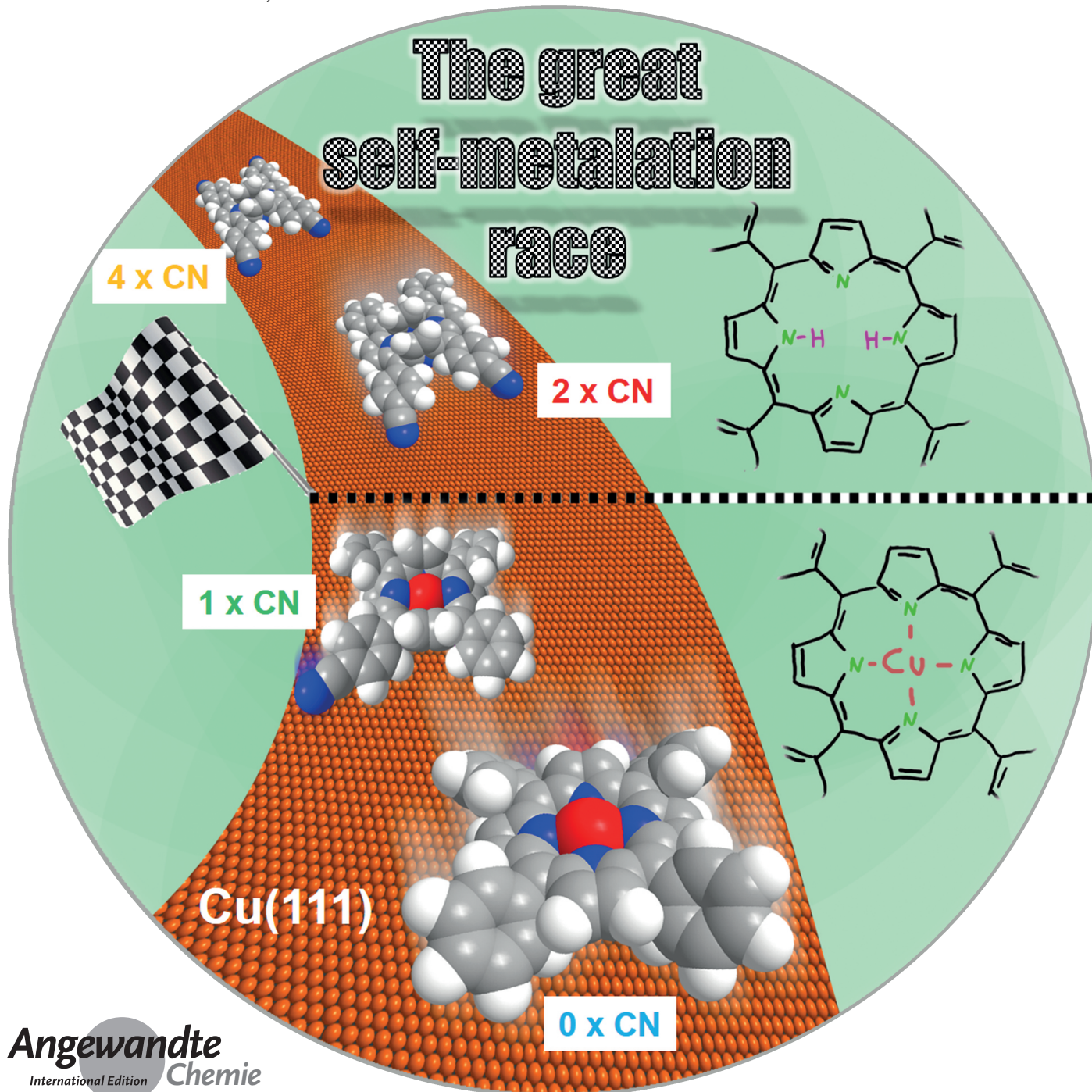
Cu(111)

Abstract: *The reaction rate of the self-metalation of free-base tetraphenylporphyrins (TPPs) on Cu(111) increases with the number of cyano groups (n = 0, 1, 2, 4) attached at the para positions of the phenyl rings. The findings are based on isothermal scanning tunneling microscopy (STM) measurements. At room temperature, all investigated free-base TPP derivatives adsorb as individual molecules and are aligned with respect to densely packed Cu substrate rows. Annealing at 400 K leads to the formation of linear dimers and/or multimers via CN-Cu-CN bonds, accompanied by self-metalation of the free-base porphyrins following a first-order rate equation. When comparing the non-cyano-functionalized and the tetra-cyano-functionalized molecules, we find a decrease of the reaction rate by a factor of more than 20, corresponding to an increase of the activation energy from 1.48 to 1.59 eV. Density functional theory (DFT) calculations give insights into the influence of the peripheral electron-withdrawing cyano groups and explain the experimentally observed effects.*

The ultimate goal of the controlled bottom-up fabrication of novel molecular-based devices has stimulated lively research activity in the field of functional molecules on surfaces. Porphyrins certainly belong to the most promising candidates in that regard.[1] Important examples of porphyrins as main functional building blocks can be found in nature, for example iron–porphyrin in heme and magnesium–porphyrin in chlorophyll, demonstrating the crucial role of the metal center. Therefore, the investigation of different aspects of the role of the central metal atom in the porphyrin macrocycle has received increasing attention in surface science.[2] In particular in situ metalation of free-base porphyrins with metal atoms from the substrate or with pre- and post-deposited material presents a flexible approach for tailoring functional nanomaterials. This approach has been demonstrated and discussed in numerous studies.[2b,3]

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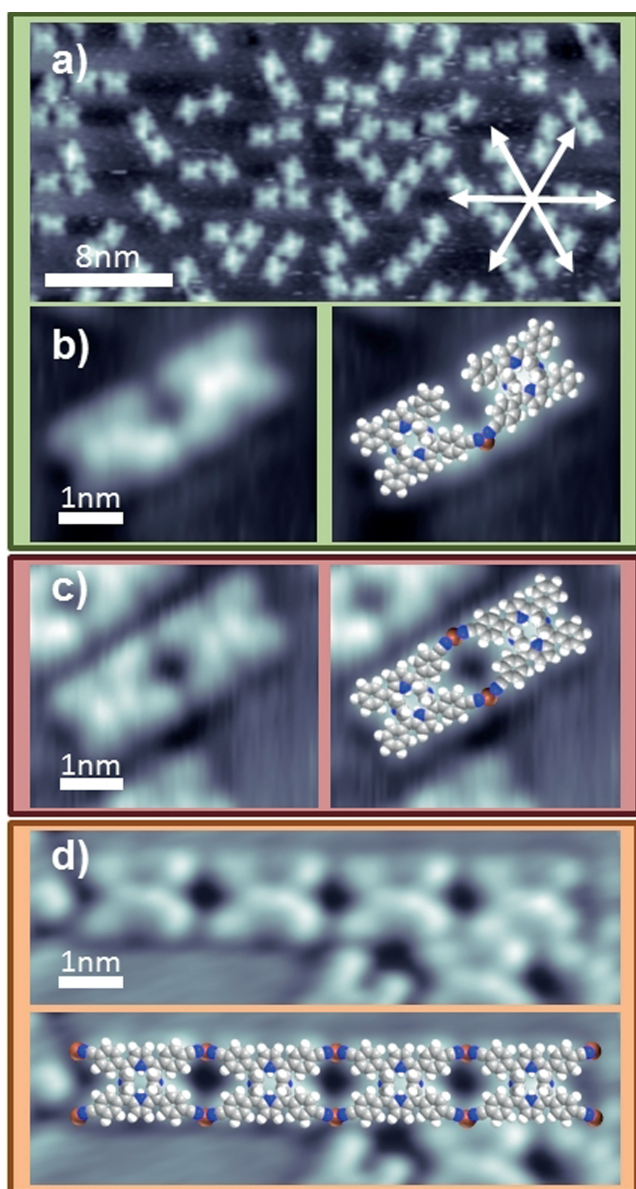https://doi.org/10.1002/anie.201803601.

Herein we present evidence that the peripheral functionalization of porphyrins with cyano groups is not only suitable to modify its adsorption behavior but also can significantly influence the self-metalation rate of a free-base porphyrin on Cu(111). Up to now, functionalization of the porphyrin periphery or the macrocycle has been reported with a focus on the adsorption behavior of the corresponding porphyrin derivatives and the possible formation of two-dimensional networks.[1a,2a,3a,4] In particular, the functionalization or modification of the peripheral phenyl groups of tetraphenylporphyrin (TPP) molecules was largely explored, for example, by the attachment of *tert*-butyl groups[4a,f] and Br atoms,[3a] or by replacement of the phenyls with pyridyls.[4e] Very recently we already expanded these substituents to cyano groups.[5] It was demonstrated that the corresponding modifications significantly alter the adsorption behavior in comparison to that of the pristine TPP molecules. In particular, the functionalization with Br can be used to fabricate covalently linked supramolecular porphyrin architectures via Ullmann coupling.[2a,4c]

In our approach, we start with the 2*H*-tetraphenylporphyrin (2HTPP) which we functionalize with cyano groups. The nonfunctionalized 2HTPP was intensively investigated on Cu(111) in the past. It had been shown that it adsorbs, even at room temperature (RT), as individual molecules oriented along one of the main crystallographic directions in a peculiar "inverted" configuration due to a strong site-specific interactions with the substrate.[2a,6] Subsequent annealing leads to chemical modifications, including self-metalation to CuTPP,[2b,3d,e,7] which is followed by dehydrogenation and subsequent formation of intramolecular C−C bonds.[3c] The metalation reaction lowers the aforementioned strong attractive interaction with the substrate drastically, that is, the CuTPP molecules become very mobile at RT, and a 2D gas phase was observed in STM instead of stationary molecules. The corresponding self-metalation reaction of 2HTPP to CuTPP with Cu atoms from the substrate was monitored by STM, and also by TPD and XPS.[3c,d] Ditze et al. presented a detailed study revealing the reaction kinetics and activation barrier of this self-metalation reaction by Arrhenius analysis.[3e] Furthermore, Röckert et al. demonstrated that the rate of the self-metalation reaction of 2HTPP on Cu(111) depends on the coverage. With increasing coverage, in particular with the formation of the so-called checkerboard structure, the metalation rate of 2HTPP on Cu(111) significantly increases.[7]

However, further information on how to influence or even control the self-metalation rate of free-base porphyrins is missing. In this regard, we explored how the functionalization of 2HTPP with an increasing number of cyano groups (n = 0, 1, 2, 4) at the *para* positions of the respective phenyl legs (see molecular models in Figure 1) influences the self-metalation process. From the literature, the functionalization of organic molecules adsorbed on metal substrates with cyano groups is known to promote different binding motifs, namely H-bonding, dipolar coupling, and the formation of organometallic bonds.[8] In a recent study, we determined the latter as the dominant interaction of the fourfold-functionalized 5,10,15,20-tetrakis(*para*-cyanophenyl)porphyrin

Figure 1. a) Overview image of 2HMCNPP on Cu(111). The main crystallographic directions are indicated by the white arrows. b)–d) The linear binding motif for 2HMCNPP, 2HcisDCNPP, and 2HTCNPP. As indicated, the stabilization of molecules in the linear motif is via a CN-Cu-CN bond. Tunneling parameters can be found in the Supporting Information.

(2HTCNPP), resulting in the formation of one-dimensional molecular chains.[5] However, the adsorption behavior of the cyanoporphyrins with fewer cyano groups and in particular the corresponding dynamics of the self-metalation behavior of cyanoporphyrins in general has not yet been reported. In the following, the monocyano-functionalized 5-(*para*-cyano-phenyl)-10,15,20-trisphenylporphyrin will be abbreviated as 2HMCNPP ("monocyanoporphyrin"), while the difunction-alized 5,10-bis(*para*-cyanophenyl)-15,20-bisphenylporphyrin will be referred to as 2HcisDCNPP ("di-*cis*-cyanopor-phyrin").

Figure 1 a shows an overview image of a low coverage (0.013 ML) of 2HMCNPP (monofunctionalized 2HTPP) on

Cu(111) at RT. The general adsorption behavior is quite similar to that of 2HTCNPP (fourfold-functionalized 2HTPP) on Cu(111), which has been described and discussed in detail in a recent study.[5] All investigated free-base porphyrins in our study exhibited a similar adsorption behavior in two main regards: Firstly, the molecules are exclusively aligned along one of the three directions of the densely packed Cu substrate, that is, the ⟨110⟩ directions, as exemplarily depicted for 2HTCNPP in Figure 1 a. This orientation is due to a strong attractive site-specific interaction between the iminic nitro-gens of the macrocycle and the Cu atoms of the Cu(111) substrate.[3d,5,6] Due to this strong chemical interaction, isolated molecules can be imaged in STM at RT. Secondly, for all investigated free-base porphyrins the intramolecular conformation of cyanoporphyrins can be described by the so-called "inverted" structure with two vertically oriented pyrrole rings.[6b,9] This structure leads to the bright central protrusions in the submolecularly resolved images in Fig-ure 1 b, as illustrated by the scaled overlaid models.

However, in contrast to 2HTPP, the cyano-functionalized free-base porphyrins tend to form linear motifs by the linking of cyano groups of neighboring molecules via Cu adatoms on Cu(111).[5] While the mono- and difunctionalized 2HMCNPP and 2HcisDCNPP tend to form dimers (cf. Figure 1 b,c and Figure 2 b,f), the fourfold-functionalized 2HTCNPP arranges to 1D molecular chains without crosslinking (cf. Figure 2 j).[5]

For all cyanoporphyrins, annealing at 400 K for 10 min leads to incorporation of the majority of molecules into linear arrangements, as observable in Figure 2. For all three cyanoporphyrins we have studied the changes upon extended annealing at 400 K (100 and 160 min). Figure 2 c,d illustrates that extended annealing of 2HMCNPP at 400 K does not lead to a clear trend towards increased formation of linear dimers, in contrast to the situation for 2HcisDCNPP (Figure 2 g,h) and 2HTCNPP (Figure 2 k,l). For 2HcisDCNPP we observe a transition to almost exclusively linear dimers, and for 2HTCNPP almost all visible molecules are incorporated in the linear chains.

However, a significant change is a pronounced decrease in the number of individual cyanoporphyrins on the surface accompanied by the observation of striped features in between the molecules. This is obvious for the mono- and difunctionalized porphyrins, e.g., by comparing Figures 2 a and d as well as Figures 2 e and h. This observation indicates the formation of a new, very mobile species by consumption of the stationary free-base porphyrins. The mobile molecules cannot be imaged by STM at RT. A very similar observation for 2HTPP on Cu (111) was attributed to the self-metalation reaction of 2HTPP to CuTPP via surface Cu atoms, as unequivocally verified by XPS, TPD, and STM.[3c–e] We conclude that a similar self-metalation reaction of free-base cyanoporphyrins to Cu–cyanoporphyrins occurs here. Since the Cu atom inserted in the macrocycle coordinates to all four central nitrogens atoms, the site-specific interaction with the Cu substrate is lifted; thus the formed Cu-cyanoporphyrin has a weaker interaction with the surface than the free-base analogue. This yields fast diffusing molecules which can only be observed as striped features at RT.[3e] We also performed control experiments with the corresponding metal species, for
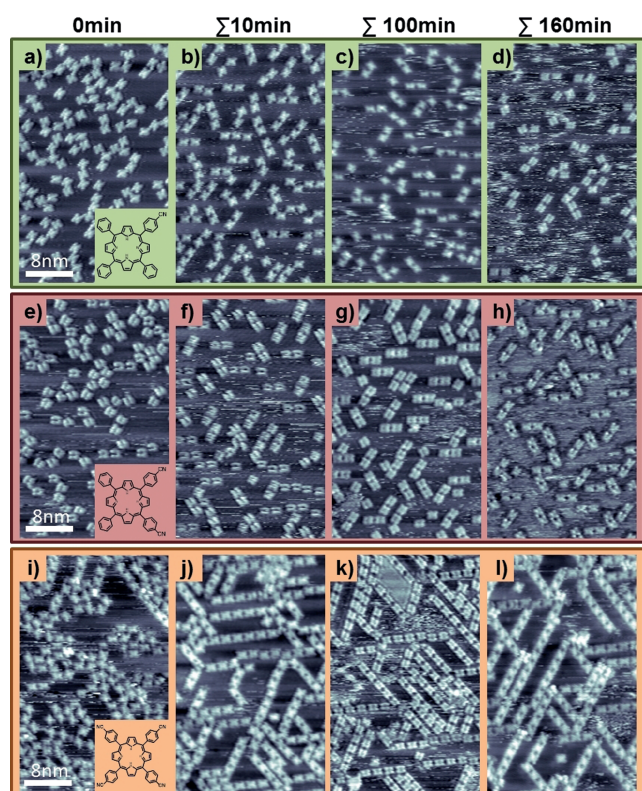
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Figure 2. STM images of 2HMCNPP (a–d), 2HcisDCNPP (e–h), and 2HTCNPP (i–l) acquired at RT, after annealing at 400 K. The formation of the 2D gas phase and the decrease in stationary free-base porphyrins, which can be understood as due to a self-metalation reaction, is most evident for 2HMCNPP (a–d) and 2HcisDCNPP (e–h). Tunneling parameters can be found in the Supporting Information.

Figure 3. Plots depicting the development of normalized coverage of free-base porphyrin (reactant) with the annealing time at 400 K (a) on a linear and (b) on a logarithmic scale from which the metalation rate can be deduced: 2HMCNPP (green), 2HcisDCNPP (red), and 2HTCNPP (yellow) compared with 2HTPP (blue).

example, CuTCNPP, and observed that the molecular appearance of the Cu porphyrins is significantly different, i.e., these never appear with a central protrusion in STM in contrast to the free-base species. This is important to note, since it rules out that "stationary" molecules in dimers or chains, which presumably mutually stabilize each other to some extent, are metalated species. In addition, it is well established that porphyrins do not desorb from the Cu(111) surface at 400 K.

In order to gain further insight into this on-surface reaction, we counted the remaining "stationary" free-base porphyrins after each annealing step for all three cyanoporphyrins and compared this number to the situation before annealing. The corresponding data sets are plotted versus time on a linear scale in Figure 3a and on a logarithmic scale in Figure 3b (for each annealing series 15000–20000 molecules were counted). A similar analysis was performed by Ditze et al. for 2HTPP to deduce the self-metalation rate of 2HTPP on Cu(111).[3e,6c] As already mentioned above, the self-metalation rate for 2HTPP increases suddenly at an increased coverage close to 0.36 molecules nm^{-2}.[7] We therefore compared the metalation of cyanoporphyrins at low starting coverages at around 0.16 molecules nm^{-2}, where coverage-dependent effects can be ruled out.

The decrease in the number of molecules with increasing annealing time is systematically different for the three cyanoporphyrins. As evident in Figures 2 and 3, the decrease
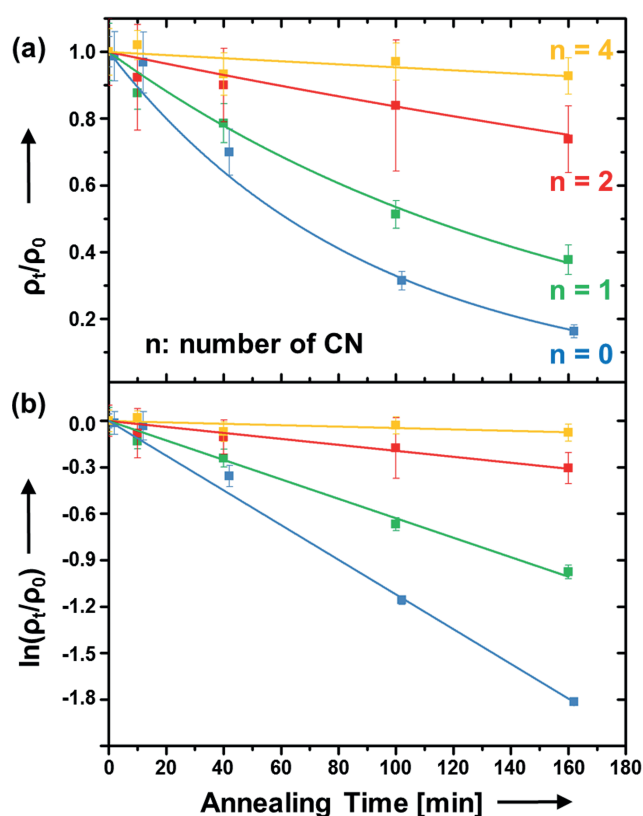
of the free-base species is strongest for 2HMCNPP and becomes less pronounced with an increasing number of cyano groups for 2HcisDCNPP and 2HTCNPP. As mentioned above, for the latter two molecules annealing leads to incorporation of the majority of molecules in linear dimers or linear multimers.

We now quantitatively analyze the data for the three cyanoporphyrins together with the data of the nonfunctionalized 2HTPP determined by Ditze et al.[3e] Figure 3a shows the normalized free-base porphyrin coverage versus the annealing time at 400 K: after 160 minutes, roughly 85% of the 2HTPP molecules (blue) are metalated. For 2HMCNPP (green), only 60% metalation is determined after the same annealing time. An even lower metalation rate is found for 2HcisDCNPP (red) with an approximate metalation yield of 25%. For the fourfold-functionalized 2HTCNPP (yellow), a single-digit metalation yield of 8% is deduced. These results reveal a pronounced trend towards lower self-metalation rates through the introduction of more cyano groups per tetraphenylporphyrin molecule; the decrease relative to the rate of the non-cyano-functionalized 2HTPP is a factor of 22 for 2HTCNPP, 6 for 2HcisDCNPP, and 2 for 2HMCNPP.

In addition to the data points (symbols), we have also included the fit of the data of each porphyrin with an exponential decay curve. In all cases, we obtain a very good

agreement, which is particularly evident from the linear fitting curve in the logarithmic plot in Figure 3b. This exponential decay indicates pseudo first-order reaction behavior for all 2*H*-cyanoporphyrins and for 2HTPP. Ditze et al. performed such measurements for 2HTPP at various temperatures and could derive an activation energy of 1.48 eV and a pre-exponential factor of 1×10^{15} s^{-1}. While such an extensive analysis is beyond the scope of the present paper, we can perform two simple considerations: If we attribute the rate decrease solely to an increase of the activation energy (with a fixed pre-exponential factor), we obtain a value of 1.59 eV for 2HTCNPP, which shows the lowest reaction rate. This makes an energy difference of the corresponding activation energies of 0.11 eV. Alternatively, if we attribute the lower rate solely to a decrease of the pre-exponential factor (with a fixed activation energy), we obtain a value of 5×10^{13} s^{-1}.

From the data in Figure 3 and the numbers given above, it is evident that the self-metalation rate strongly decreases with an increasing number of cyano groups. Density functional theory (DFT) calculations were performed to understand why the cyano groups alter the self-metalation rate. It is well known that the functionalization with electron-withdrawing cyano groups strongly change the redox potential of porphyrins.[10] This is reflected in the significant increase in the calculated ionization potential and electron affinity of the porphyrins with an increasing number of cyano groups (see the Supporting Information (SI), Table S1). At first glance, one might speculate that this changes the relative stability of free-base and metalated porphyrins. However, for the gas-phase molecules in their relaxed equilibrium saddle-shape configuration, this is not the case. The calculated overall energy change for the metalation of gas-phase free-base porphyrins [Eq. (1)] by a Cu adatom from the Cu(111) surface under release of a H$_2$ molecule is basically independent of the number n of attached cyano groups (see SI, Table S2).

$$2 \text{ HTPP-}n\text{CN } + \text{ Cu}_{\text{ad}} \ \rightarrow \ \text{CuTPP-}n\text{CN } + \text{ H}_2 \qquad (1)$$

This changes when we take into account that on the Cu(111) surface the free-base porphyrins do not adopt the saddle-shape but the inverted conformation.[5,6b,9] The cyano groups reduce the energy cost for converting the saddle-shape into the inverted geometry (see SI, Table S3). This can be understood by the enhanced conjugation between all phenyl rings and two of the pyrrole units in the rather flat inverted configuration. Overall, the metalation of the inverted 2HTCNPP with four cyano groups (assuming a simplified gas-phase model structure, see the Supporting Information) becomes less favorable by 0.07 eV compared to 2HTPP, which captures already a significant portion of the experimentally estimated value of 0.11 eV discussed above. In addition, the higher electron affinity of the free-base porphyrins with attached cyano groups gives rise to larger charge transfers from the Cu(111) surface to the molecules (see SI, Table S4). This interface polarization leads to a further stabilization of the cyano-functionalized free-base porphyrins on the surface and contributes to the decrease of the metalation rate. Altogether, we identify the enhanced electron affinity by

the electron-withdrawing cyano groups and the inverted porphyrin structure as the key factors for the reduction of the metalation rate with an increasing number of attached cyano groups.

Notably, also other factors might influence the metalation rate. For 2HTPP (no cyano group), no dimers but only isolated molecules are formed. In the direct comparison of the two unilateral-functionalized 2HMCNPP and 2HcisDCNPP, the increased number of two cyano groups per molecule apparently leads to more stable linear dimers. Possibly, this reduction of the degrees of freedom can act as an obstacle to overcome for the correct alignment of the free-base porphyrins on the surface for the self-metalation process. In this context, one should also keep in mind that for self-metalation to occur, Cu adatoms have to be able to diffuse on the surface and access the reaction site of the porphyrin macrocycle. For 2HTCNPP, two sides of the molecule are already occupied and "shielded" by the neighboring molecules in the wire, which potentially leads to a hindered reaction site access of diffusing Cu adatoms. Another kinetic reason might simply be the lower number of available Cu adatoms on the surface for the self-metalation reaction due to the linking of the free-base porphyrins through CN-Cu-CN bonds. This is, however, unlikely, because we assume the Cu atom concentration to be dominated by thermodynamics rather than by kinetics.

In conclusion, we present evidence for the modification of the self-metalation rate of tetraphenylporphyrins on Cu(111) by attachment of an increasing number of cyano groups ($n = 0, 1, 2, 4$) at the *para* positions of peripheral phenyl groups. In general, all investigated free-base cyanoporphyrins adsorb as individual molecules at RT, in alignment with the densely packed Cu substrate rows. However, annealing at 400 K leads to incorporation of the cyanoporphyrins in linear dimers and/or multimers coupled via CN-Cu-CN bonds. In addition, the annealing process leads to a pronounced decrease in the number of free-base porphyrins on the surface accompanied by observation of a 2D gas phase, which can be understood by the self-metalation reaction of the free-base species via Cu surface atoms following a first-order rate equation. Comparison of the non-cyano-functionalized and the tetracyano-functionalized molecules shows a significant decrease of the metalation rate by a factor of more than 20, correlating to an increase of the activation energy from 1.48 to 1.59 eV assuming a fixed preexponential factor. Gas-phase DFT calculations indicate electron-transfer processes to the CN groups as crucial for the observed peculiar effect. Our study presents a notable step towards controlled fabrication of nanostructures and the control of their reactions.

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Conflict of interest

The authors declare no conflict of interest.

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