

Self Assembly of Acetylene-Appended Porphyrin on Au(111) and cycloaddition of 7,7,8,8-Tetracyano-p-quinodimethane (TCNQ) visualized by Scanning Tunneling Microscopy

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The formation of covalently interlinked two-dimensional structures on surfaces is highly desirable because they feature higher thermal stability and robustness than their self-assembled analogues.^[1] These structures can be equipped with functionalities to provide technologically interesting properties like specific electronic conductivity^[2] or high third-order optical nonlinearities.^[3] This benefits future applications in nanodevices.

Scanning tunneling microscopy (STM) can be used to study the outcome of chemical reactions which occur on single-crystal metal supports with submolecular resolution. Only a few reactions have been observed by STM on metal surfaces, mainly in closed-packed arrangements.^[4]

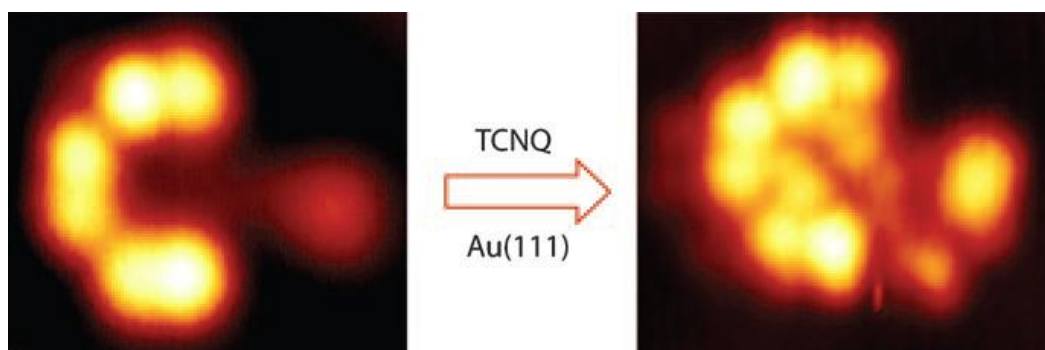
The tetra (di-tertiary butyl-phenyl) porphyrin module has been functionalized with electron rich alkyne substituents as functional groups and has been deposited onto atomically clean Au(111) substrates. In detailed STM studies the self organization of these molecules in different 2D phases and structures has been observed to be of characteristic difference from previously observed cases for molecules with other porphyrin based bi-functional architectures. This phenomenon emerges from the complex interplay between the electrophilic and nucleophilic substituents with conformational adaptation. In combination with X-ray photoelectron spectroscopy (XPS) studies, the applicability of a formal [2+2] cycloaddition between electron rich alkynes and electron-deficient TCNQ on an atomically clean Au(111) surface was demonstrated. At low coverage, monomeric and self assembled dimeric species of the initial compounds as well as of the reaction product, a TCNQ-conjugated porphyrin, could be visualized.^[5]

References

- [1] Recent reviews: a) J.A.A.W. Elemans, S.B. Lei, S. De Feyter, *Angew. Chem.*, **121** (2009), 7434-7469; *Angew. Chem. Int. Ed.* **48** (2009), 7298-7332; b) J.V. Barth, *Annu. Rev. Phys. Chem.*, **58** (2007), 375-407; c) T. Kudernac, S.B. Lei, J.A.A.W. Elemans, S. De Feyter, *Chem. Soc. Rev.* **38** (2009), 402-421.
- [2] D.F. Perepichka, F. Rosei, *Science* **323** (2009), 216-217.
- [3] a) C. Koos, P. Vorreau, T. Vallaitis, P. Dumon, W. Bogaerts, R. Beats, B. Esembeson, I. Biaggio, T. Michinobu, F. Diederich, W. Freude, J. Leuthold, *Nat. Photonics*, **3** (2009), 216-219; b) G. de La Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, *Chem. Rev.*, **104** (2004), 3723-3750.
- [4] Recent reviews: a) A. Gordon, *Angew. Chem.*, **120** (2008), 7056-7059; *Angew. Chem. Int. Ed.* **47** (2008), 6950-6953; b) J. Sakamoto, J. van Heijst, O. Lukin, A.D. Schluter, *Angew. Chem.*, **121** (2009), 1048-1089; *Angew. Chem. Int. Ed.*, **48** (2009), 1030-1069.

[5] P. Fesser, C. Iacovita, C. Wäckerlin, S. Vijayaraghavan, N. Ballav, K. Howes, J. P. Gisselbrecht, M. Crobu, C. Boudon, M. Stöhr, T. Jung, F. Diederich, *Chem. Eur. J.*, **17** (2011) 5246-5250

Figure



Reaction of Acetylene-Appended Porphyrin molecules with TCNQ on Au(111). The STM zoom depicts the starting material on the left and the reaction product on the right.