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Chemisorption-Induced Double Hydrogen Bonding, Self-Assembly, and Stereoselection**

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By carefully choosing molecular components, it is possible to design supramolecular assemblies on metal surfaces for a variety of applications ranging from templating to asymmetric catalysis.[1–3] The choice of molecular building blocks is based on the fundamental chemical concept of functional groups; hydrogen-bond donor–acceptor pairs have proven exceptionally useful for self-assembly.[4–6] Hence, it is crucial to recognize that associative chemisorption can generate hydrogen-bond donor functionality in molecules for which hydrogen bonding is negligible in the gas or solution-phase.[7,8]

Herein, we report that nonsubstituted arenes form strong C–H···O hydrogen bonds to co-adsorbed esters and ketoesters on Pt(111) surfaces. Scanning tunneling microscopy (STM) imaging is used to isolate well-defined aryl–carbonyl assemblies at 150–300 K and to identify the interaction that binds them as double hydrogen bonding. In this way, chemisorption-activated arenes are found to combine two powerful properties for 2D self-assembly: planarity and double hydrogen bonding. Furthermore, the direct observation of aryl–carbonyl C–H···O interactions supports a new mechanism for the stereoselective hydrogenation of ketoesters on cinchona-modified platinum.[7] In turn, the observation also suggests that aryl C–H···X bonding, where X is a hydrogen-bond acceptor, should be explicitly considered in the design of metal–arene chiral catalysts.

STM images of a single chemisorbed pyrene molecule surrounded by 10 molecules of ethyl formate, one for each aryl C–H bond, are shown in Figure 1 A,B. These crownlike structures are observed over the entire Pt(111) surface (Figure 1 D). Pyrene is imaged as an oval-shaped protrusion with a long and a short axis, in keeping with its molecular structure. The long axis is collinear with two C–H bonds, whereas the short axis lies between C–H bonds (Figure 1 C). The docking of ethyl formate to pyrene occurs along the short axis, but not along the long axis (Figure 1 A), revealing that each interadsorbate interaction involves a pair of adjacent C–

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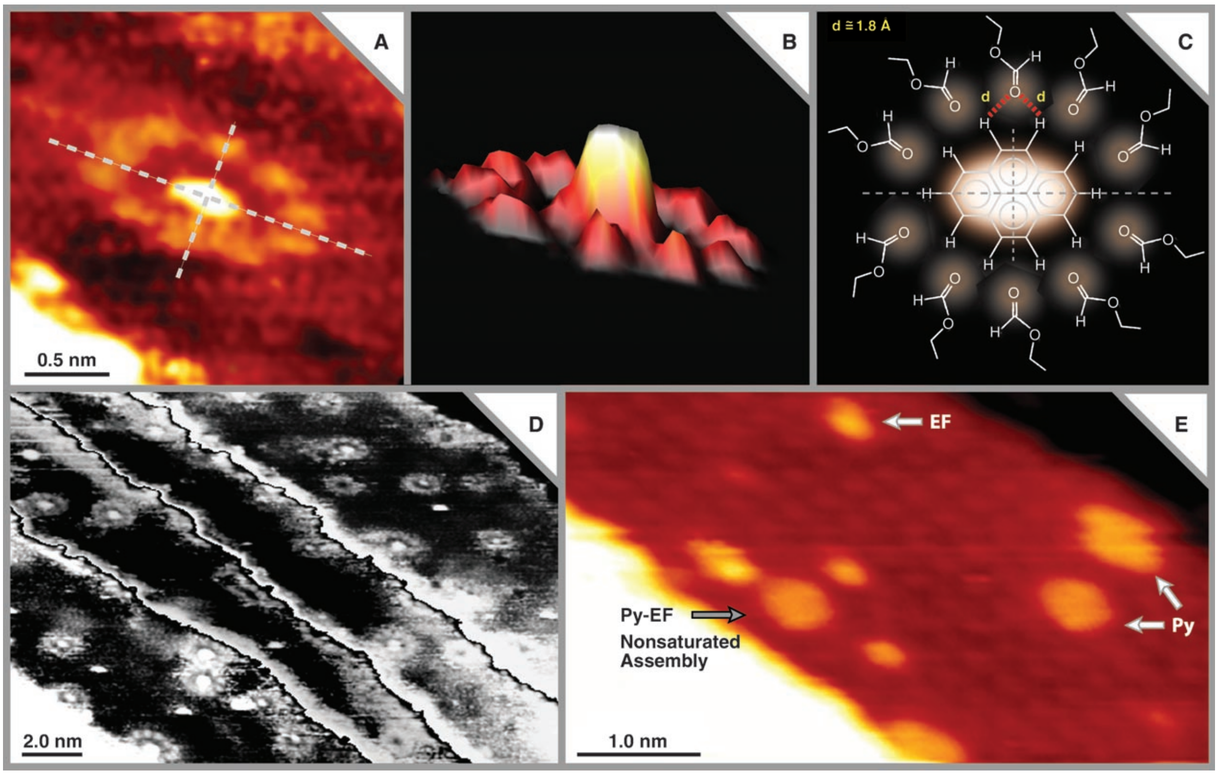

Figure 1. STM images of pyrene (Py) and ethyl formate (EF) co-adsorbed on a Pt(111) surface at 150 K. A) and B) An assembly of 10 molecules of ethyl formate around a single pyrene molecule. C) Illustration of the assembly. D) Assemblies located on terraces over the entire surface. E) A nonsaturated assembly of three molecules of ethyl formate around a single pyrene molecule.

H bonds. The strong directionality of the interaction indicates that the aromatic molecule serves as a double hydrogen-bond donor to ethyl formate, forming one C–H···O bond per lone pair of electrons on the carbonyl oxygen atoms. Saturated complexes containing one carbonyl group per C–H bond are observed at low coverages of pyrene and moderate coverages of ethyl formate. The ethyl formate protrusions are not equally distant from the aromatic molecule in unsaturated assemblies (Figure 1 E). The more well-defined structure of the saturated assemblies suggests a cooperative hydrogen-bonding process.

Aryl C–H···O bonding is known to play a role in self-assembly on noble-metal surfaces in cases where an aromatic donor is activated by an electron-withdrawing nitro or carboxylate group.[9–11] The carboxylate groups serve, in turn, as charge-bearing hydrogen-bond acceptors, and it is known that appropriately substituted aromatic molecules can form strong hydrogen bonds to anion acceptors.[12] In contrast, the interaction between pyrene and ethyl formate on the Pt(111) surface is due to the chemisorption-induced polarization of an otherwise non-activated aromatic molecule. Computational studies have shown that the chemisorption of aromatic molecules on Group VIII metals results in an unequal elongation of the C–C bonds, a movement of the hydrogen atoms out of the molecular plane by approximately 20°, an increased positive charge on the hydrogen atoms, and an increased negative charge on the carbon atoms.[13–15] These effects translate into enhanced acidity for the aromatic molecule, thereby, enabling C–H···O bonding to nonresonant carbonyl groups. A related phenomenon was reported by Ho and co-workers.[16,17] They found that O_2 molecules adsorbed on a Ag(111) surface serve as hydrogen-bond acceptors in interactions with co-adsorbed ethylene and acetylene molecules.

The hydrogen-bond lengths in the crownlike assemblies were deduced by averaging hundreds of peak-to-peak distances between pyrene and ethyl formate protrusions. The model illustrated in Figure 1 C and reference distances determined from atomically resolved images of the Pt(111) surface (Figure 1 E) were used to estimate the O···H distances as $d = (1.8 \pm 0.1)$ Å. For this distance estimation, the dimensions of gas-phase pyrene were used, with the exception that the C–H bonds were assumed to tilt away from the surface by 20°; adsorbate–metal distances were not taken into account; and the protrusions observed for ethyl formate were assumed to be centered over the carbonyl oxygen atom.

The strength and, hence, the number of C–H···O interactions may be tuned by substitution on the aromatic molecule. As shown in the STM images in Figure 2, ethyl formate preferentially assembles at one ring of methylnaphthalene molecules adsorbed on a Pt(111) surface. The images show two, three, or rarely four ethyl formate molecules located at one side of the substituted aromatic molecule, whereas nonsubstituted naphthalene molecules adsorbed on Pt(111) may be completely surrounded by ethyl formate molecules. The methyl group of the methylnaphthalene

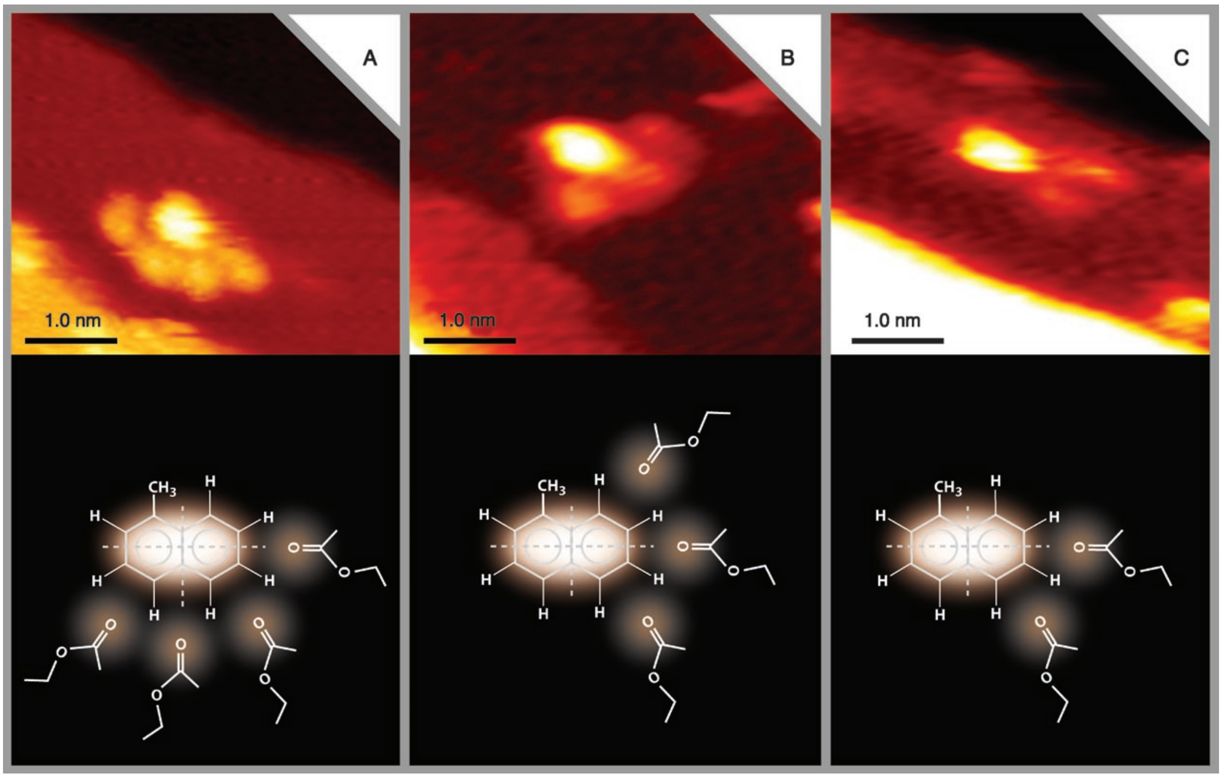

Figure 2. A)–C) STM images of methylnaphthalene and ethyl formate co-adsorbed on a Pt(111) surface at 150 K. The assemblies of ethyl formate and methylnaphthalene molecules are illustrated in the lower panels.

molecule weakens the interaction of one aromatic ring with the metal surface, leading to the effective activation of only the nonsubstituted ring.

Figure 3A displays an STM image (measured at room temperature) of an assembly of 10 molecules of methyl pyruvate around a single pyrene molecule on a Pt(111) surface. This manifestation of metal-activated C–H···O bonding is of particular relevance to the enantioselective hydrogenation of α-ketoesters on chirally modified platinum catalysts.[18,19] The reaction is performed at room temperature using a range of modifier–substrate pairs with the following characteristics.[7] All modifiers (for example, cinchonidine) are anchored to the platinum surface by a multiple-ring aromatic group and all have a conventional hydrogen-bonding group, which is held away from the surface. All substrates (for example, methyl pyruvate) contain both an activated prochiral ketocarbonyl and a second group capable of conventional hydrogen bonding. Hence, if platinum-activated aryl C–H···O bonding is taken into account, all modifier–substrate pairs can simultaneously form two distinct hydrogen-bonding interactions, as illustrated in Figure 3B. An energetic inequivalence of approximately 2–3 kcal mol^{-1} is required for the observed levels of enantioselection (ca. 95% *ee*). Hence, we assume that the strength of the double C–H···O bond is at least 2–3 kcal mol^{-1}. This hypothesis is consistent with calculations and experimental data showing that polarized aromatic molecules, such as tetrafluorobenzene, can form relatively strong C–H···O bonds.[20] The observation that the substituted ring of methylnaphthalene is not strongly activated towards C–H···O bonding is consistent with the fact that all effective modifiers for the Orito reaction contain multiple-ring aromatic groups.

The significance of metal-activated aryl–carbonyl C–H···O bonding extends to homogeneous chiral catalysis with planar-chiral and double hydrogen-bond donor catalysts. Planar-chiral catalysts are based on arene–metal complexes.[21] As with the activation of aromatic molecules on the platinum surface, the aromatic groups of the planar-chiral catalysts display enhanced acidity because of their activation by the metal.[22] It is instructive to consider the unexpected antiperiplanar conformation observed for formyl ligands in metal–cyclopentadiene complexes.[23] In the antiperiplanar geometry, the formyl oxygen atom points towards the arene ring, consistent with C–H···O bond formation to the metal-activated cyclopentadienyl group.[24] In contrast, the synperiplanar orientation, in which the carbonyl oxygen atom points away from the arene, is observed for the pentamethylcyclopentadienyl (Cp*) complex [Cp*Ru(CO)(PPhMe$_2$)HCO],[25] presumably because of the absence of aryl C–H bonds. Indeed, evidence for intermolecular C–H···O bonding is found in the crystal structures of metal–arene complexes.[26] Hence, our work indicates that a stereodirecting role for C–H···X bonding in planar-chiral catalysis should be considered. The ability to directly image aryl–carbonyl bonding is also important in the context of asymmetric catalysis activated by double hydrogen-bond donors.[27–29] Aromatic systems combine a high density of donor pairs with skeletal rigidity, well-defined planar shapes, and the opportunity to tune the C–H···X interaction through judicious substitution.

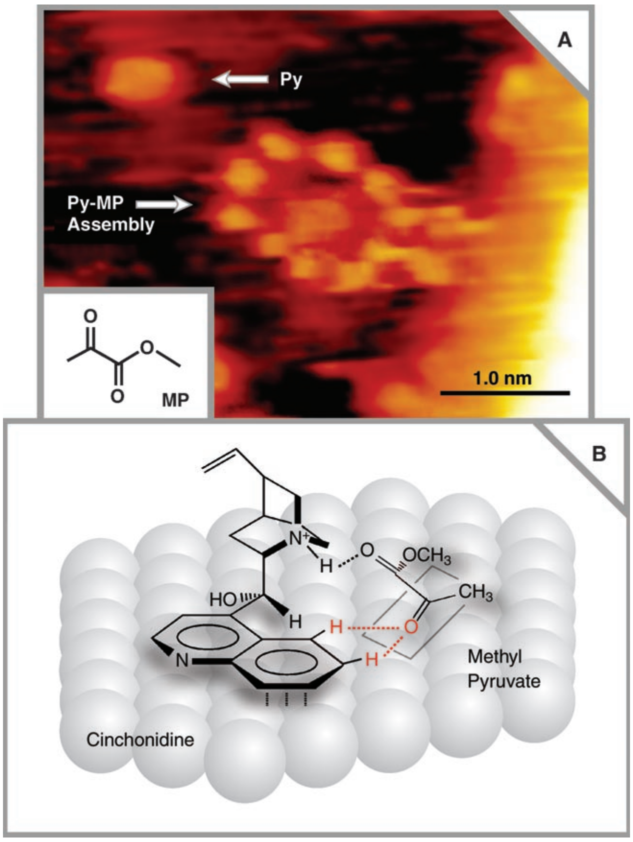

Figure 3. A) STM image of pyrene (Py) and methyl pyruvate (MP) co-adsorbed on a Pt(111) surface. Adsorption was carried out at 150 K and images were recorded at room temperature. B) Illustration of the role of aryl–carbonyl C–H···O bonding in the formation of a prochiral complex between cinchonidine and methyl pyruvate co-adsorbed on platinum.

In summary, we have shown that nonsubstituted aromatic molecules chemisorbed on a platinum surface form double C–H···O bonds to co-adsorbed esters and ketoesters. The hydrogen-bond strength is sufficient to form well-defined assemblies at 150–300 K and may be tuned by substitution on the aromatic molecule. The C–H···O interaction is key to understanding the asymmetric hydrogenation of α-ketoesters on cinchona-modified platinum catalysts and may also be relevant to catalysis by metal–arene complexes. We anticipate that double hydrogen bonding involving aromatic molecules will play an increasingly important role in the rational design of both chiral catalysts and 2D supramolecular structures.

Experimental Section

Variable-temperature STM measurements were carried out on clean polished Pt(111) surfaces under ultrahigh vacuum. A tunneling current of $I_t = 0.96$ nA and tunneling voltages of $V = -0.84$ to -0.99 V were used.

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[1] S. M. Barlow, R. Raval, *Surf. Sci. Rep.* **2003**, *50*, 201.
[2] J. V. Barth, G. Costantini, K. Kern, *Nature* **2005**, *437*, 671.
[3] R. Fasel, M. Parschau, K. H. Ernst, *Nature* **2006**, *439*, 449.
[4] Q. Chen, N. V. Richardson, *Nat. Mater.* **2003**, *2*, 324.
[5] L. J. Prins, F. De Jong, P. Timmerman, D. N. Reinhoudt, *Nature* **2000**, *408*, 181.
[6] K. G. Nath, O. Ivasenko, J. A. Miwa, H. Dang, J. D. Wuest, A. Nanci, D. F. Perepichka, F. Rosei, *J. Am. Chem. Soc.* **2006**, *128*, 4212.
[7] S. Lavoie, M.-A. Laliberté, I. Temprano, P. H. McBreen, *J. Am. Chem. Soc.* **2006**, *128*, 7588.
[8] S. Lavoie, P. H. McBreen, *J. Phys. Chem. B* **2005**, *109*, 11986.
[9] M. Bohringer, K. Morgenstern, W. D. Schneider, R. Berndt, F. Mauri, A. De Vita, R. Car, *Phys. Rev. Lett.* **1999**, *83*, 324.
[10] F. Vidal, E. Delvigne, S. Stepanow, N. Lin, J. V. Barth, K. Kern, *J. Am. Chem. Soc.* **2005**, *127*, 10101.
[11] S. Stepanow, N. Lin, F. Vidal, A. Landa, M. Ruben, J. V. Barth, K. Kern, *Nano Lett.* **2005**, *5*, 901.
[12] V. S. Bryantsev, B. P. Hay, *Org. Lett.* **2005**, *7*, 5031.
[13] C. Morin, D. Simon, P. Sautet, *J. Phys. Chem. B* **2004**, *108*, 12084.
[14] G. Held, W. Braun, H. R. Steinruck, S. Yamagishi, S. J. Jenkins, D. A. King, *Phys. Rev. Lett.* **2001**, *87*, 216102.
[15] Y. P. Tan, S. Khatua, S. J. Jenkins, J.-Q. Yu, J. B. Spencer, D. A. King, *Surf. Sci.* **2005**, *589*, 173.
[16] S. W. Gao, J. R. Hahn, W. Ho, *J. Chem. Phys.* **2003**, *119*, 6232.
[17] J. R. Hahn, W. Ho, *J. Phys. Chem. B* **2005**, *109*, 20350.
[18] Y. Orito, S. Imai, S. Niwa, *J. Chem. Soc. Jpn.* **1979**, *8*, 1118.
[19] C. J. Baddeley, *Top. Catal.* **2003**, *25*, 17.
[20] V. Venkatesan, A. Fujii, N. Mikami, *Chem. Phys. Lett.* **2005**, *409*, 57.
[21] G. C. Fu, *Acc. Chem. Res.* **2000**, *33*, 412.
[22] F. Mathey, A. Sevin, *Molecular Chemistry of the Transition Elements: An Introductory Course*, Wiley, New York, **1996**.
[23] S. Shambayati, W. E. Crowe, S. L. Schreiber, *Angew. Chem.* **1990**, *102*, 273; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 256.
[24] W.-K. Wong, W. Tam, C. E. Strouse, J. A. Gladysz, *J. Chem. Soc. Chem. Commun.* **1979**, 530.
[25] G. O. Nelson, C. E. Sumner, *Organometallics* **1986**, *5*, 1983.
[26] D. Braga, F. Grepioni, *Acc. Chem. Res.* **2000**, *33*, 601.
[27] M. S. Taylor, E. N. Jacobsen, *Angew. Chem.* **2006**, *118*, 1550; *Angew. Chem. Int. Ed.* **2006**, *45*, 1520.
[28] P. M. Pihko, *Angew. Chem.* **2004**, *116*, 2110; *Angew. Chem. Int. Ed.* **2004**, *43*, 2062.
[29] Y. Huang, A. K. Unni, A. N. Thadani, V. H. Rawal, *Nature* **2003**, *424*, 146.