Angewandte
International Edition Chemie

DOI: 10.1002/anie.201303745

Tailored 2D Pores

Tailoring Surface-Confined Nanopores with Photoresponsive Groups**

Kazukuni Tahara, Koji Inukai, Jinne Adisoejoso, Hiroyuki Yamaga, Tatyana Balandina, Matthew O. Blunt, Steven De Feyter,* and Yoshito Tobe**

Recently, the construction of two-dimensional (2D) porous patterns on solid surfaces using molecular self-assembly has become a subject of interest because of potential applications in nanoscience and nanotechnology, for nanoreactors and catalysts that may function cooperatively with substrate surfaces and for molecular wires and 2D polymers generated by surface-controlled reactions.[1] Surface-confined pores within the 2D porous molecular networks can be used as a host space to immobilize guest molecules at the surface.[2] These molecular networks are typically observed by means of scanning tunneling microscopy (STM) under ultrahigh vacuum (UHV) conditions or at the liquid–solid interface.

One of the significant challenges in the design of 2D porous system is physical (i.e. size and shape) or chemical (i.e. electrostatic properties) modification of the interior space of porous networks to construct tailored functional pores. There are only a few studies which have investigated the influence that chemical modification of the pore structure has on guest co-adsorption.[3] However, none of them achieved specific recognition of guest molecule(s) by shape and size complementarities between the guest and modified pore. Herein, we report the construction of tailored 2D pores, which exhibit a tight stoichiometric binding selectivity toward a guest molecule. These pores are formed by self-assembly at the liquid–solid interface of designer molecular building blocks bearing photo-responsive groups. Moreover, the size of the pores is reversibly altered by irradiation with light of different wavelengths as demonstrated by a change in the number of co-adsorbed guest molecules. This is, to our knowledge, the first example of the construction of 2D pores which respond to external stimuli in a specific manner.[4]

Among the various molecular building blocks, alkoxylated dehydrobenzo[12]annulene (DBA) derivatives are chosen because of their strong tendency to form porous honeycomb patterns by the interdigitation of alkyl chains at the liquid–solid interface,[5] tunability of pore size by varying alkyl chain length, and their synthetic versatility in chemical modification of the alkyl chains.[6] The design to tailor pore environments is based on the introduction of functional groups at the end of three of the DBAs six alkyl chains, in an alternating fashion (Figure S1 in the Supporting Information). Molecular modeling suggests that such DBAs form a honeycomb structure in which the functional groups are located inside the pores. By selection of functional groups we can modify the physical and chemical environments of the pores. In this case, photoresponsive azobenzene is chosen as the functional group. In addition, two carboxy groups are introduced to the azobenzene units to achieve high guest selectivity by creating a confined space within a hydrogen-bonded hexamer of dicarboxyazobenzene units: a cyclic hexamer of isophthalic acid can immobilize one coronene (COR) molecule on surfaces by size and shape recognition (Figure 1 a,b).[6] To locate the cyclic hexamer of the dicarboxyazobenzene units in the pore, the azobenzene units are connected by *meta*-phenylene linkers at the end of shorter C_{12} chains. Moreover, taking into account the established photoisomerization of azobenzene derivatives at surfaces[7] and the structural difference between a planar *trans*-configuration and kinked 3D *cis*-configuration, the azobenzene units can change the pore size and shape upon photoisomerization (Figure 1 c). This change in pore geometry also leads to a change in the number of adsorbed COR guest molecules.

The synthesis of azobenzene-functionalized DBAs **1** and **2** is described in Supporting information (Scheme S1 and S2). DBAs **1** and **2** reveal very similar spectroscopic properties in solution. A 1-octanoic acid solution of all-*trans* **1** has an absorption band at 315 nm arising from π–π* absorptions of the DBA core and the azobenzene units and a weak band (435 nm) corresponding to an n–π* transition of the azobenzene chromophore (Figure S2).[8] Upon irradiation with UV light (313 nm) of a solution of all-*trans* **1** in $[D_8]$THF, a photostationary state containing 57 % of the *cis*-azobenzene unit was achieved within a few minutes as indicated by ^{1}H NMR spectroscopy. If we assume all the azobenzene units in **1** exhibit identical photoisomerization efficiency, the distribution of **1** with one, two, and three *cis*-azobenzene unit(s) becomes 31.6 %, 41.9 %, and 18.5 %, respectively, and

---

[*] Dr. K. Tahara, K. Inukai, H. Yamaga, Prof. Dr. Y. Tobe
Division of Frontier Materials Science
Graduate School of Engineering Science, Osaka University
1-3 Machikaneyama, Toyonaka, Osaka 560-8531 (Japan)
E-mail: tahara@chem.es.osaka-u.ac.jp
tobe@chem.es.osaka-u.ac.jp

Dr. J. Adisoejoso, Dr. T. Balandina, Dr. M. O. Blunt, Prof. S. De Feyter
Department of Chemistry
Division of Molecular Imaging and Photonics, Laboratory of Photochemistry and Spectroscopy, KU Leuven
Celestijnenlaan 200 F, 3001 Leuven (Belgium)
E-mail: Steven.DeFeyter@chem.kuleuven.be

[**] This work is supported by Grant-in-Aid for Scientific Research from the Ministry of Education, Culture, Sports, Science, and Technology (Japan), the Fund of Scientific Research—Flanders (FWO), K.U.Leuven (GOA), the Belgian Federal Science Policy Office through IAP, NMP4-SL-2008-214340 and JSPS and FWO under the Japan–Belgium Research Cooperative Program. J.A. is grateful to the Agency for Innovation by Science and Technology in Flanders (IWT). We thank Prof. F. C. De Schryver for fruitful discussion.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201303745.

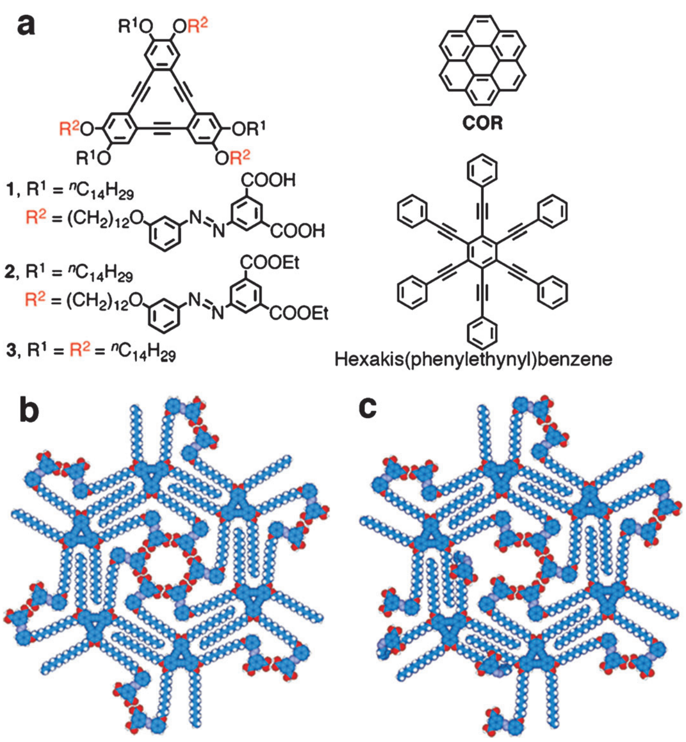

Figure 1. a) Structural formula of DBAs, *trans*-**1**, *trans*-**2** and **3**, coronene (COR), and hexakis(phenylethynyl)benzene. b) Molecular models of a honeycomb structure formed by self-assembly of *trans*-**1** with all-*trans*-azobenzene units (*trans*-**1**) in which a hydrogen-bonded hexamer of dicarboxyazobenzene units creates a size and shape confined space. c) The same pore as (b) with one of the dicarboxyazobenzene units adopting a *cis* configuration. Note that there is no space to accommodate more than one COR, except if the COR molecules are adsorbed on top of the first layer or if the not all azobenzene units are adsorbed.

the remaining 8.0% is all-*trans* **1** (Figure S3). We abbreviate such a mixture at the photostationary state of **1** as *PS*-**1** hereafter. Upon irradiation of visible light (> 400 nm) to the solution of *PS*-**1** or heating it at 55 °C, the *cis*-azobenzene units were transformed back to all-*trans* **1**. *PS*-**1** was stable thermally and its half-life time at room temperature was two days. Virtually identical results were obtained with all-*trans* **2** in solution leading to *PS*-**2** (Figure S4).

To form a nanostructured 2D layer, a 1-octanoic acid solution of *trans*-**1** (1.0×10^{-5} M) was drop cast on graphite and the resulting self-assembled monolayer was observed by means of STM. Bright triangular features correspond to the DBA π-cores as a result of their higher tunneling efficiency. The large apparent height of these features relates to the higher tunneling efficiency of the aromatic part of the molecule.[9] The interdigitated alkyl chains were also imaged clearly (Figure 2a and S5), revealing the formation of a honeycomb network of all-*trans* **1**. Moreover, nearly all the azobenzene units directed towards the center of the nanowell were visualized, suggesting the formation of a cyclic hexamer of the dicarboxyazobenzene units in the honeycomb pore by hydrogen-bonding interactions.

Prior to any irradiation, the guest-binding capability of the hexagonal pores formed by *trans*-**1** toward COR was investigated by using a premixed sample of *trans*-**1** (3.0×10^{-6} M) and COR (5.5×10^{-4} M) in 1:1 volumetric ratio. As a result, we observed one COR molecule immobilized in most of the pores formed by *trans*-**1** (Figure 2b and S6). Statistical analysis revealed that 96.5% of the pores were filled with one COR molecule, whereas only 3.0 and 0.5% of the pores accommodated two and three COR molecules, respectively (Figure 3, *trans*-**1** premixed with COR). Moreover, by using a premixed sample of *trans*-**1** (1.9×10^{-5} M), hexakis(phenylethynyl)benzene (Figure 1a, 3.7×10^{-6} M) and COR (5.0×10^{-6} M) in 1:1:1 volumetric ratio, only COR was immobilized within the pores even in the presence of hexakis(phenylethynyl)benzene which has larger affinity to graphite (Figure S7). In addition, note that the pore honeycomb network formed by DBA **3** bearing only C_{14} alkyl chains (without azobenzene groups) host an undefined number of COR molecules in the nanopore (Figure S8).[10] In the latter case, the pores are imaged as fuzzy bright features. These results demonstrate that the nanopores can be tailored by the functional groups attached to the terminal of the alkyl chains of DBA and can exhibit high selectivity to host a specific guest molecule.

The effect of the photoisomerization of the azobenzene units was studied. A solution of *PS*-**1** containing 57% of *cis*-azobenzene moieties (2.0×10^{-6} M) formed mostly disordered structures though with some small honeycomb domains (Figure S9). In the honeycomb domains, six azobenzene units were clearly observed in the pores, indicating that the honeycomb structure must consist of solely *trans*-azobenzene units. This implies that larger adsorption affinity of the *trans*-azobenzene unit[11] and the hydrogen bonding between the dicarboxy groups in the *trans*-azobenzene units stabilizes the honeycomb structure of **1**. However, because *PS*-**1** containing *cis*-azobenzene units did not form large domains of the honeycomb structure, **2** was also investigated to gather statistically relevant data. Contrary to *PS*-**1**, the formation of honeycomb domains of comparable size to those of *trans*-**2** was also confirmed for the sample in the *PS* state of **2** (Figure S10 and S11). However, the number of observed azobenzene units in the monolayer formed by *PS*-**2** decreased from 91.9% for the non-irradiated solution to 68.9%. We attribute these unobserved azobenzene units mainly to the *cis*-isomer.

The guest-binding capability was explored by in situ irradiation of the already formed honeycomb structure of *trans*-**1** at the 1-octanoic acid/graphite interface. To avoid UV light absorption by the COR molecules we chose a sequential addition method: a saturated solution of COR in 1-octanoic acid (5.5×10^{-4} M) was drop cast after irradiation. First, the difference resulting from the preparation method was investigated. The proportion of pores with different numbers of COR molecules before light irradiation was as follows: one COR 86.2%, two CORs 4.0%, three CORs 0.5%, and fuzzy feature 9.2% (Figure 3, sequential addition of COR). The proportion of the pores displaying fuzzy features increases compared with that formed from the premixed sample. At the liquid–solid interface different preparation methods can sometimes produce different outcomes because kinetic factors can influence the self-assembly process.[12] By irradiation

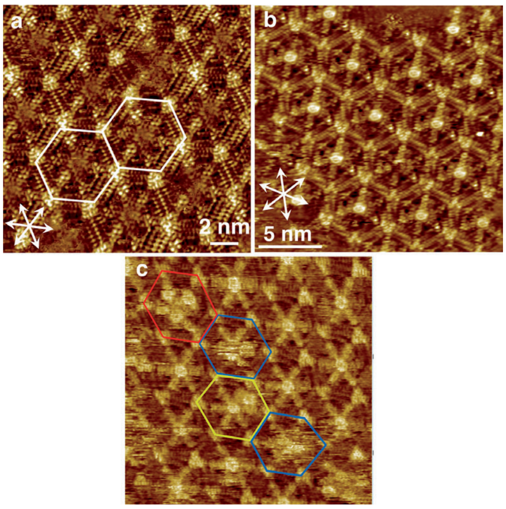

Figure 2. a) A honeycomb structure formed by *trans*-**1** at the 1-octanoic acid/graphite interface (concentration; 1.0×10^{-5} M, tunneling conditions; $I_{set}=0.26$ nA, $V_{set}=-0.20$ V). Statistical analysis shows 97% of azobenzene units were visualized. b) A self-assembled monolayer formed from a mixture of *trans*-**1** and COR at the 1-octanoic acid/graphite interface (concentrations of original solutions; 3.0×10^{-6} M for **1** and 5.5×10^{-4} M for COR, tunneling conditions; $I_{set}=0.27$ nA, $V_{set}=-0.13$ V). c) A self-assembled monolayer formed by in situ UV irradiation of *trans*-**1** followed by addition of COR (concentrations of original solutions; 1.0×10^{-5} M for **1** and 5.5×10^{-4} M for COR, $I_{set}=0.10$ nA, $V_{set}=-0.20$ V). The white arrows correspond to the main symmetric axes of graphite. The colored hexagons indicate the pores containing four CORs (red), two CORs (yellow), and those with fuzzy images (blue).

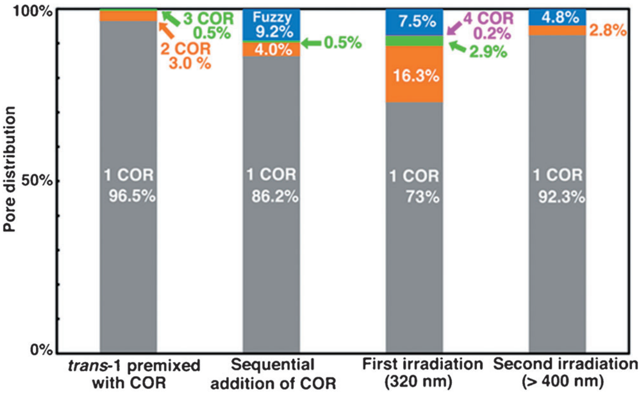

Figure 3. Percentage distributions of the number of adsorbed COR in the pore formed by DBA **1**. from left to right: premixed sample of *trans*-**1** and COR; sequential addition of COR for pre-formed honeycomb structure of *trans*-**1**; after first irradiation of light (320 nm); after second irradiation of light (>400 nm).

of (320±10) nm light for 10 min followed by drop casting a saturated solution of COR, the number of the pores containing more than two COR molecules increased (Figure 2c and S12). Statistical analysis revealed the following distribution: one COR, 73.0%; two CORs, 16.3%; three CORs, 2.9%; four CORs, 0.2%; fuzzy feature, 7.5% (Figure 3, first irradiation (320 nm)). Molecular modeling indicates that the *trans*-to-*cis* isomerization followed by desorption of one azobenzene unit generates enough space to accommodate an additional COR molecule (Figure S13). These results indicate that isomerization of one or two *trans*-azobenzene unit(s) took place to leave free space in the pore, affecting the distribution in the number of guest molecules within the pores. Similarly, the number of COR molecules co-adsorbed in the pores of *PS*-**2** was larger than that for *trans*-**2** (Figure S14 and S15), though the stoichiometric selectivity was not as strict as that observed for **1** owing to the absence of a hydrogen-bonding network in the pores formed by **2**.

To demonstrate the reversibility of this process the enlarged pore size was shrunk to the initial size by *cis*-to-*trans* isomerization of the azobenzene units. The network formed from all-*trans*-**1** was irradiated with 320 nm light and a solution containing COR was added as above. This mixture was then irradiated with long-wavelength light ($\lambda > 400$ nm) for 10 min. Note, in this case, COR would not interfere with the absorption of the visible light by the *cis*-azobenzene unit of **1**. The distribution of the number of COR molecules changed as follows: one COR, 92.3%; two CORs, 2.8%; fuzzy features, 4.8% (Figure 3 second irradiation (>400 nm)). No pores containing three or four CORs were detected. The recovery of the stoichiometric selectivity is attributed to the reduction of the pore size by *cis*-to-*trans* isomerization of the azobenzene units. This process causes excess COR molecules to be desorbed from the pore. Co-adsorption of the guest was thus controlled reversibly by light irradiation.

The question remains where the in situ photo-induced reaction takes place, on the surface or in solution? It is established that the presence of surfaces might quench the photo-isomerization reaction.[7a–e,13] Therefore, we performed an experiment in which half of the sample area was protected from the light irradiation, by placing an aluminum foil a few mm above the graphite substrate. Statistical analysis of three different experiments showed the distribution in the number of adsorbed COR molecules in the masked area was virtually identical to that after sequential addition of COR, except for the distribution of fuzzy pores. On the other hand, the distribution in the unmasked area was comparable with that obtained in the other illumination experiments (Figure S16 and Table S1). These results render the rapid diffusion and adsorption–desorption dynamics of DBA **1** at the interface unlikely, and support the view that photoisomerization of the azobenzene units of **1** occurs while they are adsorbed on the graphite surface.

We have shown that tailored nanopores in 2D molecular networks constructed from designer molecular building blocks can host a specific guest molecule with high selectivity. We have also demonstrated that the size of the pores can be reversibly altered by irradiation with light of different wavelengths as shown by the change of the number of co-adsorbed guest molecules. These insights may provide opportunities for the creation of novel functional molecular self-assemblies on surfaces.

Received: May 2, 2013

Keywords: annulenes · photochemistry · porous materials · scanning tunneling microscopy · self-assembly

---

[1] a) J. V. Barth, *Annu. Rev. Phys. Chem.* **2007**, *58*, 375 – 407; b) L. Bartels, *Nat. Chem.* **2010**, *2*, 87 – 95; c) J. V. Barth, G. Costantini, K. Kern, *Nature* **2005**, *437*, 671 – 679; d) J. A. A. W. Elemans, S. Lei, S. De Feyter, *Angew. Chem.* **2009**, *121*, 7434 – 7469; *Angew. Chem. Int. Ed.* **2009**, *48*, 7298 – 7332; e) M. Bieri, M. Treier, J. Cai, K. Aït-Mansour, P. Ruffieux, O. Gröning, P. Gröning, M. Kastler, R. Rieger, X. Feng, K. Müllen, R. Fasel, *Chem. Commun.* **2009**, 6919 – 6921; f) X. Zhang, Y. Shen, S. Wang, Y. Guo, K. Deng, C. Wang, Q. Zeng, *Sci. Rep.* **2012**, *2*, 742; g) J. Cai, P. Ruffieux, R. Jaafar, M. Bieri, T. Braun, S. Blankenburg, M. Muoth, A. P. Seitsonen, M. Saleh, X. Feng, K. Müllen, R. Fasel, *Nature* **2010**, *466*, 470 – 473.

[2] a) D. Bonifazi, S. Mohnani, A. Llanes-Pallas, *Chem. Eur. J.* **2009**, *15*, 7004 – 7025; b) J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness, P. H. Beton, *Nature* **2003**, *424*, 1029 – 1031.

[3] a) A. G. Phillips, L. M. A. Perdigão, P. H. Beton, N. R. Champness, *Chem. Commun.* **2010**, *46*, 2775 – 2777; b) S. Stepanow, M. Lingenfelder, A. Dmitriev, H. Spillmann, E. Delvigne, N. Lin, X. Deng, C. Cai, J. V. Barth, K. Kern, *Nat. Mater.* **2004**, *3*, 229 – 233; c) M. T. Räisänen, A. G. Slater (née Phillips), N. R. Champness, M. Buck, *Chem. Sci.* **2012**, *3*, 84 – 92.

[4] W. R. Browne, B. L. Feringa, *Annu. Rev. Phys. Chem.* **2009**, *60*, 407 – 428.

[5] a) K. Tahara, S. Furukawa, H. Uji-i, T. Uchino, T. Ichikawa, J. Zhang, W. Mamdouh, M. Sonoda, F. C. De Schryver, S. De Feyter, Y. Tobe, *J. Am. Chem. Soc.* **2006**, *128*, 16613 – 16625; b) K. Tahara, S. Lei, J. Adisoejoso, S. De Feyter, Y. Tobe, *Chem. Commun.* **2010**, *46*, 8507 – 8525; c) K. Tahara, H. Yamaga, E. Ghijsens, K. Inukai, J. Adisoejoso, M. O. Blunt, S. De Feyter, Y. Tobe, *Nat. Chem.* **2011**, *3*, 714 – 719.

[6] a) S. Lei, M. Surin, K. Tahara, J. Adisoejoso, R. Lazzaroni, Y. Tobe, S. De Feyter, *Nano Lett.* **2008**, *8*, 2541 – 2546; b) M. Lackinger, W. M. Heckl, *Langmuir* **2009**, *25*, 11307 – 11321; c) Y.-T. Shen, M. Li, Y.-Y. Guo, K. Deng, Q.-D. Zeng, C. Wang, *Chem. Asian J.* **2010**, *5*, 787 – 790.

[7] a) C. Dri, M. V. Peters, J. Schwarz, S. Hecht, L. Grill, *Nat. Nanotechnol.* **2008**, *3*, 649 – 653; b) M. Alemani, M. V. Peters, S. Hecht, K.-H. Rieder, F. Moresco, L. Grill, *J. Am. Chem. Soc.* **2006**, *128*, 14446 – 14447; c) P. Vanoppen, P. C. M. Grim, M. Rücker, S. De Feyter, G. Moessner, S. Valiyaveettil, K. Müllen, F. C. De Schryver, *J. Phys. Chem.* **1996**, *100*, 19636 – 19641; d) X. Zhang, S. Xu, M. Li, Y. Shen, Z. Wei, S. Wang, Q. Zeng, C. Wang, *J. Phys. Chem. C* **2012**, *116*, 8950 – 8955; e) X. Zhang, S. Wang, Y. Shen, Y. Guo, Q. Zeng, C. Wang, *Nanoscale* **2012**, *4*, 5039 – 5042; f) D. Bléger, A. Ciesielski, P. Samorì, S. Hecht, *Chem. Eur. J.* **2010**, *16*, 14256 – 14260.

[8] N. Tamai, H. Miyasaka, *Chem. Rev.* **2000**, *100*, 1875 – 1890.

[9] R. Lazzaroni, A. Calderone, G. Lambin, J. P. Rabe, J. L. Brédas, *Synth. Met.* **1991**, *41*, 525 – 528.

[10] S. Furukawa, K. Tahara, F. C. De Schryver, M. Van der Auweraer, Y. Tobe, S. De Feyter, *Angew. Chem.* **2007**, *119*, 2889 – 2892; *Angew. Chem. Int. Ed.* **2007**, *46*, 2831 – 2834.

[11] B.-Y. Choi, S.-J. Kahng, S. Kim, K. Kim, H. W. Kim, Y. J. Song, J. Ihm, Y. Kuk, *Phys. Rev. Lett.* **2006**, *96*, 156106.

[12] A. Bellec, C. Arrigoni, G. Schull, L. Douillard, C. Fiorini-Debuisschert, F. Mathevet, D. Kreher, A.-J. Attias, F. Charra, *J. Chem. Phys.* **2011**, *134*, 124702.

[13] a) M. J. Comstock, N. Levy, A. Kirakosian, J. Cho, F. Lauterwasser, J. H. Harvey, D. A. Strubbe, J. M. J. Fréchet, D. Trauner, S. G. Louie, M. F. Crommie, *Phys. Rev. Lett.* **2007**, *99*, 038301; b) R. Arai, S. Uemura, M. Irie, K. Matsuda, *J. Am. Chem. Soc.* **2008**, *130*, 9371 – 9379.