A rigid sublimable naphthalenediimide cyclophane as model compound for UHV STM experiments†

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The design, synthesis and characterization of a rigid naphthalenediimide cyclophane as a model compound for ultrahigh vacuum (UHV) STM experiments are described together with first self-assembly investigations on an Au(111) substrate displaying the formation of densely packed parallel rows of molecules.

Since Pellegrin synthesized [2.2]metacyclophane in 1899,[1] cyclophanes have attracted considerable attention due to both their structural beauty and their intrinsic physical properties.[2,3] While the synthetic challenge, the extent of aromaticity of strained cyclic compounds[4] and the electronic interactions of interlinked aromatic systems[5] were initially the driving force for cyclophane chemistry, their supramolecular host properties have been investigated more recently.[6,7] The considerable stability of the resulting supramolecular complexes even made mechanically interlinked supermolecules, like catenanes and rotaxanes, synthetically accessible.[8]

Our interest in cyclophanes results from scanning probe investigations of π-systems on metallic substrates. While cyclophanes have already been investigated by STM either at the solid/liquid interface[9,10] or after deposition from solution,[11] high resolution ultrahigh vacuum (UHV) investigations are missing so far due to the poor sublimability of the macromolecular cyclophanes under investigation.[11] As displayed by UHV-STM investigations, delocalized planar π-systems usually form well ordered surface patterns on flat substrates.[12] However, optical properties of these immobilized chromophores are affected by the electronic states of the underlying substrate. To decouple the chromophore from the substrate either multilayers of molecules[13] or thin insulating salt layers have been investigated.[14] In cyclophanes, which consist of two parallel π-systems, adsorption with only one π-system appears likely, while the second chromophore would be lifted and hence partially decoupled from the surface's electronic states. A first important step towards the investigation of this concept would be the design and synthesis of rigid, stable and sublimable cyclophanes comprising two chromophores. Naphthalene diimides (NDIs) have already been used successfully as building blocks for cyclophanes with interesting host/guest properties[7] and as subunits of mechanically interlinked supermolecules.[8] Furthermore, NDIs display physical properties ideally suited for the envisaged experiments like the tuneability of the electronic properties by its core-substituents[15] and a rather low molecular weight, providing the sublimability of NDI derivatives required for UHV surface experiments.

Here we report the synthesis, characterization and first UHV-STM investigations on an Au(111) surface of the cyclophane **1** (Scheme 1). To fix both NDI chromophores as tight as possible, a rigid *meta*-methylenebenzene spacer has been chosen.

To meet both requirements, solubility for chemical processing and sublimability for UHV-investigations, the spacer has been functionalized with an additional bulky *tert*-butyl group.

The assembly of the cyclophane **1** is displayed in Scheme 1.† Starting from commercially available 1-*tert*-butyl-3,5-dimethylbenzene (**2**), bromination followed by a Gabriel synthesis provided the rather labile diamine **5** after cleavage with hydrazine. A variety of reaction conditions, including microwave irradiation,[16] have been investigated to obtain the cyclophane **1** in a single reaction step by condensing **5** and **6**. However, the isolated yields of **1** did not exceed 4%. Interestingly, the best isolated yield of 3.4% for the cyclophane assembly in a single step was obtained from a reaction mixture comprising a large excess of the dianhydride **6** (36 mM) in a mixture of dimethylformamide and acetic acid at 120 °C to which the dissolved diamine **5** had been added over a period of 1 h. In a typical 1 : 1 entry, a 36 mM solution of both **5** and **6** in *iso*-propanol, containing triethylamine as a base, was refluxed for 3 days. After column chromatography, the desired cyclophane **1** was isolated as a white solid in only 1.2% yield. To further improve the yield of the desired cyclophane, a sequential assembly strategy was investigated. Thus, one of the two amine functions of **5** was protected with a *tert*-butoxycarbonyl group (BOC) to provide the amine **7**. Condensation of 2 equiv. of **7** with the dianhydride **6** gave the doubly BOC protected naphthyldiimide **8** in a yield of 44%, which was deprotected to the diamine **9** quantitatively. Subsequent condensation of the diamine **9** with the dianhydride **6** provided the desired cyclophane **1** in 40% yield after column chromatography.

Compound **1** and its precursors have been fully characterized by ^{1}H- and ^{13}C-NMR spectroscopy, mass spectrometry

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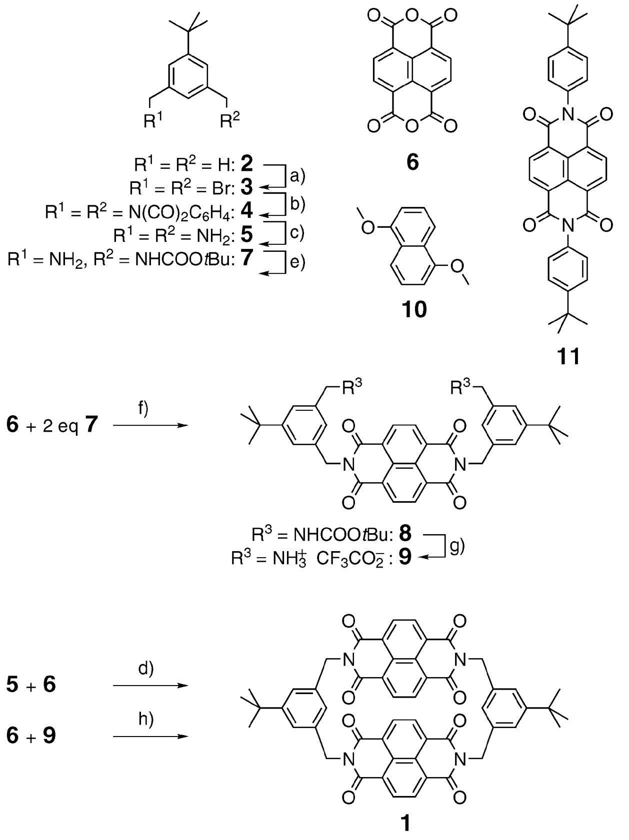
† Electronic supplementary information (ESI) available: Synthetic protocols, analytical data and NMR spectra of the compounds **1**, **3–5**, **7–9** and **11**; X-ray structures of cyclophane **1** with different solvent molecules; UHV STM pictures of monolayers of **1** and **11** on Au(111). Crystallographic data in CIF format: CCDC 673653–673654. See DOI: 10.1039/b719796a



Scheme 1 Synthesis of the macrocycle **1** and its precursors.† Molecular structures of the compounds **10** and **11**. (a) NBS, AIBN, CHOOCH$_3$, *hν*, 4.5 h, 48%; (b) $C_6H_4(CO)_2NK$, K_2CO_3, CH_3CN, reflux, 5 h, 86%; (c) N_2H_4, MeOH, reflux, 2 h, 82%; (d) Et_3N, *i*-PrOH, reflux, 3 d, 2–3%; (e) BOC$_2$O, CHCl$_3$, 0 °C, 5 h, 47%; (f) Et_3N, *i*-PrOH, reflux, 3 d, 44%; (g) CF$_3$COOH, CH$_2$Cl$_2$, rt, 2 h, 100%; (h) Et_3N, *i*-PrOH, reflux, 3 d, 40%.

and elemental analysis.† Furthermore, single crystals suitable for X-ray analysis have been obtained by slow evaporation of solutions of **1** in CH_2Cl_2 or xylene.‡

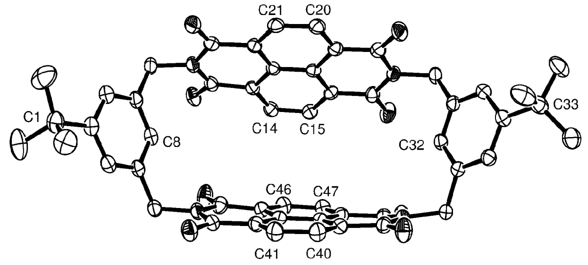


Fig. 1 Solid state structure of the cyclophane **1** obtained by evaporation of a CH_2Cl_2 solution. The partially penetrating CH_2Cl_2 molecule is omitted for clarity. ORTEP representation; thermal ellipsoids are set at the 50% probability level.

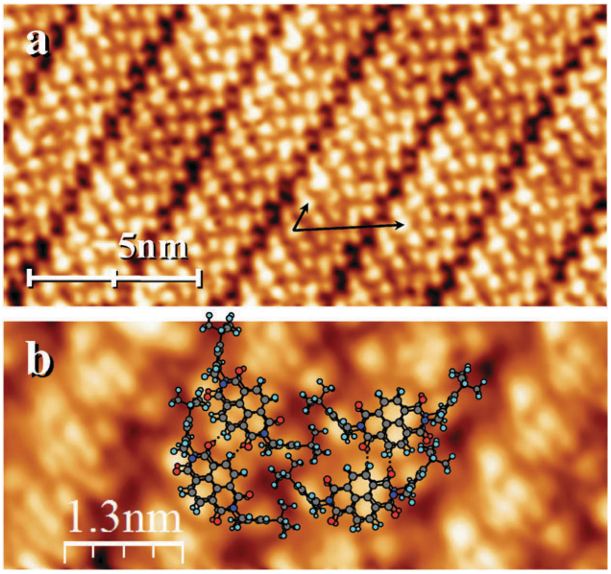


Fig. 2 (a) Large scale STM image of a cluster of self-assembled cyclophanes **1** on Au(111) and (b) enlarged stripe-region with the structure of **1** overlaid. Arrows in (a) represent unit cell vectors of the 2D molecular organisation. Dotted lines in (b) indicate stabilizing hydrogen bonds.

In spite of the molecule's symmetry, the cyclophane **1** does not crystallize with an inversion centre, but opens a minute cavity by tilting both NDI planes with respect to each other (Fig. 1). The inter NDI C–C distances are with 0.71 nm between C20 and C40 doubled at the front rim compared with the values of 0.36 nm observed in the back (C14–C46). Furthermore, the interlinking *tert*-butylphenyl spacers both point towards the open side with a distance between C1 and C33 of 1.59 nm. In the solid state structure, a CH_2Cl_2 solvent molecule is partially penetrating the cavity of **1**. A very comparable solid state structure has been obtained from technical grade xylene with a *para*-xylene molecule partially penetrating the cavity of **1**.[17]

Due to the short rigid spacers of **1**, the tiny cavity between the two NDIs should not allow for complexation of electron rich aromatic systems. The cyclophane **1** was still to some extent able to quench the fluorescence of the electron rich guest 1,5-dimethoxynaphthalene **10**. Assuming a 1 : 1 complex **10** ⊂ **1**, a moderate binding constant of 81 M^{-1} has been determined. As a control experiment, the model compound **11** displayed comparable quenching properties with an association constant of the same order, 106 M^{-1}, pointing to association of **10** to the outer surface as a quenching mechanism.[18]

Of particular interest was the suitability of **1** for UHV experiments and its self-assembly properties on metal surfaces. Thus, the cyclophane **1** was deposited on Au(111) samples in a UHV chamber by sublimation.[19a] Subsequent investigation of the sample surface by STM at 6 K revealed large islands consisting of parallel stripes with a regular periodicity of about 2.7 ± 0.2 nm (Fig. 2a). The high resolution of the STM pictures of the monolayers formed by **1** together with the comparison with monolayers obtained from the NDI model compound **11**,[19b] made it possible to identify individual cyclophanes as the building blocks of the stripes (Fig. 2b)[19c] and demonstrated the sublimation of cyclophane molecules without degradation. The bent crescent-like shape of the immobile cyclophane **1** corresponds to its solid state structure. As illustrated by the added model, the stripes consist of two rows of intercalated cyclophane molecules which are rotated by about 120° with respect to each other. Each row is stabilized by a pair of intermolecular hydrogen bonds, formed between the carbonyl oxygens and the naphthalene hydrogens of the surface immobilized NDI chromophores (dotted lines in Fig. 2b). Similar hydrogen bonds have been found to stabilize the formation of supramolecular nanotubes of amino acid functionalized NDIs.[20]

The intercalation of both rows as well as the densely packed arrangement of the parallel stripes seems to be driven by maximisation of the surface coverage. The two vectors defining the 2D unit cell have lengths of 3.5 ± 0.2 and 0.9 ± 0.1 nm, respectively and open an angle of 50 ± 3°.

The reconstruction of the underlying Au surface can still be observed (see contents entry image) which is indicative of a weak interaction between molecule and substrate.[21] More importantly, this image shows that the molecules are attached to the Au with one chromophore, while the other remains separated from the substrate. The structural analogy of immobilized **1** with its solid state structure suggests a comparable spacing of approximately 0.7 nm from the surface for the upper chromophore. While the conservation of the spatial separation of both chromophores in these surface immobilized cyclophanes and the predominant interaction of the metal surface with only one of the two π-systems are promising results on the way towards surface decoupled chromophores, the parallel arrangement of the main axis of both NDI subunits may be less favourable considering Förster energy transfer as a potential quenching mechanism for the decoupled chromophore.[22] However, the synthesis described here is ideally suited for the assembly of cyclophanes consisting of two differently functionalized NDI subunits. Through sterically demanding core substituents the intramolecular spatial arrangement of both chromophores of the cyclophane may become tuneable. Furthermore, the optical properties of both NDIs can be tailored by these substituents.[15]

In conclusion, the design, synthesis and characterization of a new rigid NDI cyclophane are reported. Its immobilization and self-assembly on Au(111) are discussed. The cyclophane is perfectly sublimable and self-assembles to ordered patterns driven by hydrogen bonds. Moreover the molecules adopt a staged configuration on the surface with one chromophore over the other. This system may be regarded as a model for the design of separated platforms. Related cyclophane structures are currently under investigation. Such systems are of great interest for single molecule fluorescence studies using STM.

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Notes and references

‡ Crystal data and structure refinement for **1-CH$_2$Cl$_2$** and **1-xylene**: The crystals were measured on a Nonius KappaCCD diffractometer at 173 K using graphite-monochromated Mo K$_\alpha$-radiation with λ = 0.71073 Å. **1-CH$_2$Cl$_2$** formula $C_{53}H_{42}Cl_2N_4O_8$, M = 933.84, F(000) = 972, colourless plate, size 0.09 × 0.14 × 0.30 mm^3, triclinic, space group $P\bar{1}$, Z = 2, a = 11.2478(2) Å, b = 13.9007(2) Å, c = 14.9298(3) Å, α = 90.3583(11)°, β = 110.9346(11)°, γ = 90.1421(12)°, V = 2180.15(7) Å^3, $D_{\text{calc.}}$ = 1.422 Mg m^{-3}. Minimal/maximal transmission 0.97/0.98, μ = 0.214 mm^{-1}. The COLLECT suite has been used for data collection and integration. From a total of 20 283 reflections ($\Theta_{\max}$ = 27.871°), 10 386 were independent (merging r = 0.041). From these, 6267 were considered as observed ($I > 1.0\sigma(I)$) and were used to refine 622 parameters. The structure was solved by direct methods using the program SIR92. Least-squares refinement against F was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0662 (observed data), wR = 0.1089 (all data), GOF = 1.1417. Minimal/maximal residual electron density = −1.09/0.43 e Å^{-3}. Chebychev polynomial weights were used to complete the refinement. Plots were produced using ORTEP3. **1-xylene** formula $C_{68.60}H_{61.20}N_4O_8$, M = 1069.66, F(000) = 2259.200, colourless block, size 0.32 × 0.34 × 0.44 mm^3, monoclinic, space group $P2_1/c$, Z = 4, a = 17.7349(2) Å, b = 16.9022(2) Å, c = 19.1495(2) Å, α = 90°, β = 92.6081(6)°, γ = 90°, V = 5734.29(11) Å^3, $D_{\text{calc.}}$ = 1.239 Mg m^{-3}. Minimal/maximal transmission 0.97/0.97, μ = 0.081 mm^{-1}. The COLLECT suite has been used for data collection and integration. From a total of 50 388 reflections ($\Theta_{\max}$ = 27.858°), 13 631 were independent (merging r = 0.033). From these, 9239 were considered as observed ($I > 3.0\sigma(I)$) and were used to refine 802 parameters. The structure was solved by direct methods using the program SIR92. Least-squares refinement against F was carried out on all non-hydrogen atoms using the program CRYSTALS. R = 0.0839 (observed data), wR = 0.0867 (all data), GOF = 1.0531. Minimal/maximal residual electron density = −0.46/1.12 e Å^{-3}. Chebychev polynomial weights were used to complete the refinement. Restraints have been used to control the refinement of the disordered solvent molecules and one *tert*-butyl group in the case of the single crystal obtained from technical xylene. Plots were produced using ORTEP3.

1 M. M. Pellegrin, *Recl. Trav. Chim. Pays-Bas*, 1899, **18**, 457.
2 F. Vögtle, *Cyclophane-Chemistry*, Teubner, Stuttgart, 1990.
3 *Modern Cyclophane Chemistry*, ed. R. Gleiter and H. Henning, Wiley-VCH, Weinheim, 2004.
4 D. J. Cram and J. M. Cram, *Acc. Chem. Res.*, 1971, **4**, 204.
5 T. Kawashima, T. Otsubo, Y. Sakata and S. Misumi, *Tetrahedron Lett.*, 1978, **51**, 5115.
6 (*a*) S. I. Pascu, T. Jarrosson, C. Naumann, S. Otto, G. Kaiser and J. K. M. Sanders, *New J. Chem.*, 2005, **29**, 80; (*b*) K. D. Johnstone, K. Yamaguchi and M. J. Gunter, *Org. Biomol. Chem.*, 2005, **3**, 3008.
7 A. J. Blacker, J. Jazwinski, J.-M. Lehn, M. Cesario, J. Guilhem and C. Pascard, *Tetrahedron Lett.*, 1987, **28**, 6057.
8 (*a*) G. D. Fallon, M. A.-P. Lee, S. J. Langford and P. J. Nichols, *Org. Lett.*, 2004, **6**, 655; (*b*) J. G. Hansen, N. Feeder, D. G. Hailton, M. J. Gunter, J. Becher and J. K. M. Sanders, *Org. Lett.*, 2000, **2**, 449; (*c*) T. Iijima, S. A. Vignon, H. R. Tseng, T. Jarrosson, J. K. M. Sanders, F. Marchioni, M. Venturi, E. Apostoli, V. Balzani and J. F. Stoddart, *Chem.–Eur. J.*, 2004, **10**, 6375.
9 F. Jäckel, M. D. Watson, K. Müllen and J. P. Rabe, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2006, **73**, 045423.
10 M. D. Watson, F. Jäckel, N. Severin, J. P. Rabe and K. Müllen, *J. Am. Chem. Soc.*, 2004, **126**, 1402.
11 R. E. Palmer and Q. Guo, *Phys. Chem. Chem. Phys.*, 2002, **4**, 4275.
12 J. V. Barth, *Annu. Rev. Phys. Chem.*, 2007, **58**, 375.
13 (*a*) H. Kuhn, *Pure Appl. Chem.*, 1965, **11**, 345; (*b*) K. H. Drexhage, M. Fleck, F. P. Schäfer and W. Sperling, *Ber. Bunsen-Ges. Phys. Chem.*, 1966, **72**, 1179; (*c*) X. H. Qiu, G. V. Nazin and W. Ho, *Science*, 2003, **299**, 542; (*d*) Z.-C. Dong, X.-L. Guo, A. S. Trifonov, P. S. Dorozhkin, K. Miki, K. Kimura, S. Yokoyama and S. Mashiko, *Phys. Rev. Lett.*, 2004, **92**, 086801; (*e*) E. Ćavar, M.-C. Blüm, M. Pivetta, F. Patthey, M. Chergui and W.-D. Schneider, *Phys. Rev. Lett.*, 2005, **95**, 196102.
14 (*a*) R. Berndt, R. Gaisch, J. K. Gimzewski, B. Reihl, R. R. Schlittler, W.-D. Schneider and M. Tschudy, *Science*, 1993, **262**, 1425; (*b*) G. Hoffmann, L. Libioulle and R. Berndt, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 212107.
15 (*a*) F. Würthner, S. Ahmed, C. Thalacker and T. Debaerdemaeker, *Chem.–Eur. J.*, 2002, **8**, 4742; (*b*) A. Błaszczyk, M. Fischer, C. von Hänisch and M. Mayor, *Helv. Chim. Acta*, 2006, **89**, 1986.
16 P. Pengo, G. D. Pantos, S. Otto and J. K. Sanders, *J. Org. Chem.*, 2006, **71**, 7063.
17 Further details concerning both X-ray structures of **1** are available in the electronic supporting information.
18 (*a*) J. J. Reczek, K. R. Villazor, V. Lynch, T. M. Swager and B. L. Iverson, *J. Am. Chem. Soc.*, 2006, **128**, 7995; (*b*) G. Kaiser, T. Jarrosson, S. Otto, Y.-F. Ng, A. D. Bond and J. K. M. Sanders, *Angew. Chem., Int. Ed.*, 2004, **43**, 1959; (*c*) S. Bhosale, A. L. Sisson, P. Talukdar, A. Fürstenberg, N. Banerji, E. Vauthey, G. Bollot, J. Mareda, C. Röger, F. Würthner, N. Sakai and S. Matile, *Science*, 2006, **313**, 84.
19 Further details concerning the UHV STM experiment together with additional pictures are displayed in the supporting information: (*a*) Experimental set-up and sublimation procedure; (*b*) STM pictures of **11**; (*c*) Details of STM pictures of **1**; (*d*) Au(111) reconstruction.
20 G. Dan Pantos, P. Pengo and J. K. M. Sanders, *Angew. Chem., Int. Ed.*, 2007, **46**, 194.
21 F. Vonau, D. Aubel, L. Bouteiller, G. Reiter and L. Simon, *Phys. Rev. Lett.*, 2007, **99**, 086103.
22 *Principles of Fluorescence Spectroscopy*, ed. J. R. Lakowicz, Springer, New York, 2006, ch. 13, p. 443.