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Nanostructures

Cyclic Self-Assembled Structures of Chlorophyll Dyes on HOPG by the Dendron Wedge Effect**

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Dedicated to Professor Alfred Holzwarth on the occasion of his 60th birthday

The construction of self-assembled cyclic nanostructures, especially those based on chromophores, has become an attractive research field, not only because of the artistic structural beauty of cyclic dye assemblies, but also from the viewpoint of mimicking the functions of their natural archetypes. Chromophoric circular arrays are of pivotal importance for natural light harvesting (LH). For instance, light-harvesting complexes LH1 and LH2 in purple bacterial photosynthetic membranes contain cyclic bacteriochlorophyll dye arrays embedded in a protein matrix for efficient collection of sunlight and subsequent energy transfer to the reaction centers.[1] The cyclic topology of these arrays, as well as their two-dimensional packing in the photosynthetic membranes, have been confirmed by AFM.[2] Notably, a cyclic arrangement of bacteriochlorophyll dyes prevails in tubular assemblies, even in natural LH systems that lack a protein matrix, that is, chlorosomes of green bacteria.[3] In recent years, scanning tunneling microscopy (STM) has become an important tool for the investigation of cyclic structures.[4] A broad variety of macrocyclic molecules have been synthesized and their structural features have been explored by STM with submolecular resolution.[5,6] In particular, bioinspired light-harvesting systems that consist of porphyrins have been extensively studied with regard to their structural organization and efficient photochemical properties.[5] Furthermore, several self-assembled dye structures, including macrocycles, have been created on substrates and investigated by STM.[7,8] Various nanostructures such as honeycomb networks have been constructed on surfaces by supramolecular interactions, in particular hydrogen bonding and metal-ion coordination, under ambient conditions.[8] However, to date, self-assembled cyclic structures of semisynthetic zinc chlorins, which are appropriate model systems for natural (bacterio)chlorophyll dyes,[3,9] and their two-dimensional organization on surfaces, reminiscent of that found in natural photosynthetic membranes, have not been realized. To bridge this knowledge gap, we have designed new zinc chlorin dyes that contain second-generation dendrons (see Scheme 1). We report herein that, depending on the size of the dendritic wedges, these zinc chlorins self-assemble on highly oriented pyrolytic graphite (HOPG) surfaces into cyclic structures that resemble dye arrays in photosynthetic membranes, as revealed by scanning probe microscopy (SPM) studies.

Our strategy for the construction of self-assembled cyclic structures of zinc chlorins is based on the "dendron wedge" approach pioneered by Percec and co-workers.[10] In this technique, different self-assembled structures, including rows, columns, and spheres, can be constructed, depending on the generation number and size of peripheral dendritic wedges. Self-assembly of such dendrons has also been investigated by STM.[11] The construction of 2D self-assembled architectures, either cyclic or linear, can be controlled by molecular structures and by variation of the solvents used for STM measurements. By considering the size of a zinc chlorin unit as the focal point for the creation of 2D structures, we have synthesized the dendritic zinc chlorins **1**–**3** (with 4, 6, and 9 alkyl chains in the dendrons, respectively; Scheme 1).[9,12]

We initially investigated the self-assembly of **1**–**3** on HOPG by AFM (Figure 1). For all three compounds, no large aggregates could be observed on the whole surface, but layers with interesting structural features were created. For **1**, which bears four alkyl chains in the dendron, linearly ordered striations with a width of (4.8 ± 0.3) nm are observed in the layers (Figure 1a). In contrast, **3**, which bears nine alkyl chains in the dendron, did not form any ordered structures within the layers (Figure 1c). Pleasingly, **2**, which has a dendron of size between that of **1** and **3**, was found to form highly ordered cyclic structures with a center-to-center distance of (7.6 ± 0.3) nm between neighboring circular arrays (Figure 1b). These results clearly indicate that the 2D packing behavior of these zinc chlorins on HOPG is dependent on the nature of the dendron wedges. The dendron of **1**, which has the smallest wedge in this series, leads to the formation of linearly ordered structures. In **2**, the dendron group acts as an effective wedge for the formation of cyclic self-assembled structures, and both wedges in **1** and **2** can adopt planar orientations that lead to better interaction of the aromatic chlorin core with the graphite surface, thus enabling their visualization as layers by AFM. In contrast, **3** might have a conical shape, as schematically illustrated in Figure 1f, owing to the large number of alkyl chains on the periphery.

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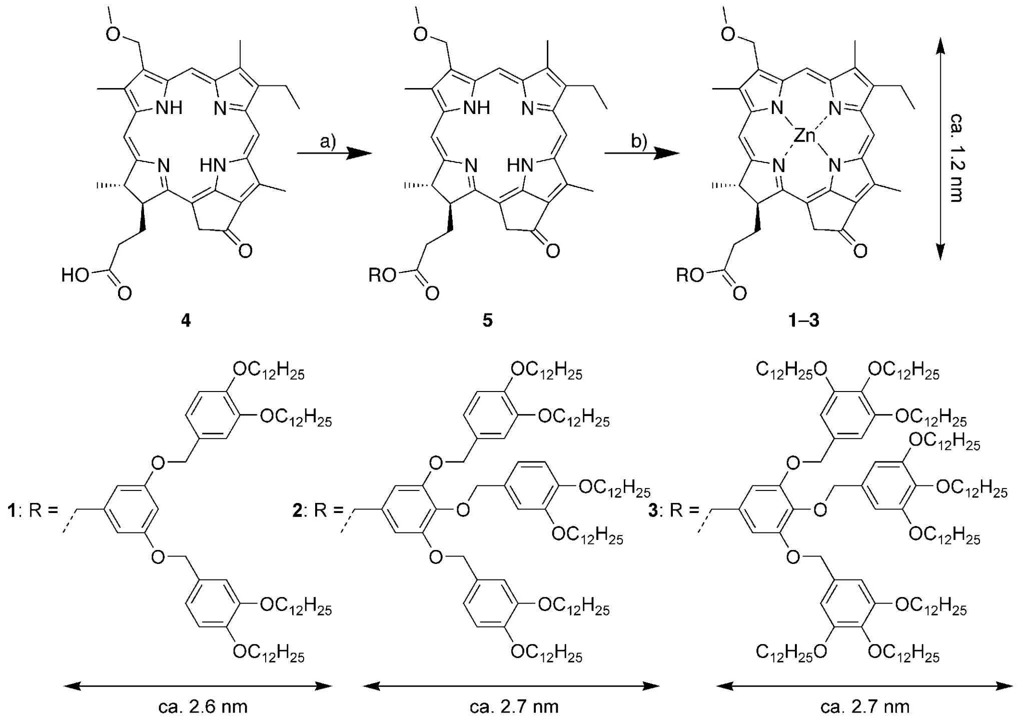

Scheme 1. Synthesis of **1**–**3**: a) DCC, DMAP, DPTS, *N*,*N*-ethyldiisopropylamine, CH_2Cl_2, room temperature, 3–4 h, ROH; b) $Zn(OAc)_2$, MeOH, THF, room temperature, 3 h. Molecular dimensions of the zinc chlorin core and dendritic wedges are indicated along the structures. DCC = dicyclohexylcarbodiimide, DMAP = 4-dimethylaminopyridine, DPTS = dimethylaminopyridinium-*p*-toluenesulfonate.

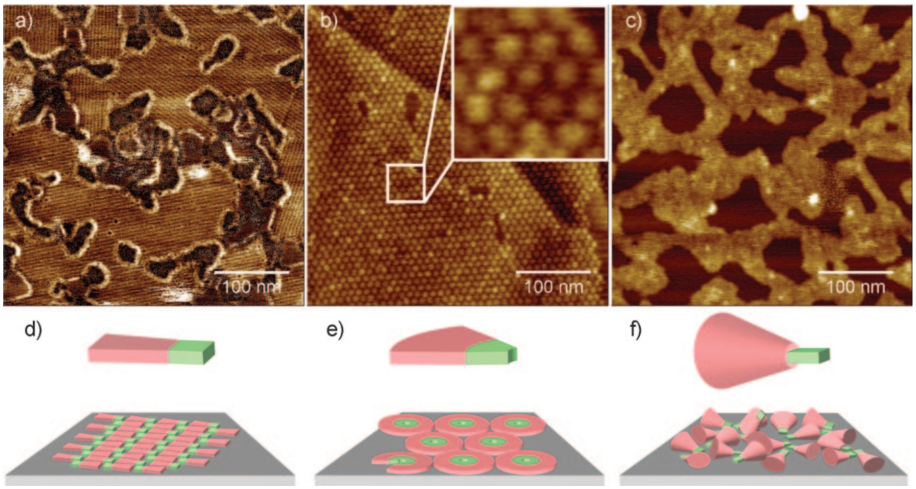

Figure 1. AFM images of **1**–**3** on HOPG spincoated from solutions in THF at approximately 5×10^{-5} M. a) Phase image of **1**; b,c) height images of **2** and **3**, respectively. The inset shows a section magnification. d–f) Schematic illustrations of **1**–**3** and their self-assembled structures on surfaces.

This feature is apparently disadvantageous for planarization on graphite surfaces and thus leads to disordered structures.

To obtain more insight into the molecular ordering of dye molecules on HOPG surfaces, we performed STM investigations with the zinc chlorin derivatives.[13] For **1**, lamellar structures are observed at the phenyloctane–HOPG interface (Figure 2a). Closer examination of the high-resolution STM image reveals that both circular brighter spots (indicated by green circles) ordered in a zigzag fashion and feeble bright areas (indicated by pink ellipses) are present in the lamellae. In the dark areas, striations with six lines in a repeat unit are observed (see Figure S1 in Supporting Information). Generally, aromatic moieties in STM images are detected at higher tunneling currents than the alkyl chains; therefore, the images of aromatic units are much brighter than those of alkyl groups.[14] Thus, in the STM image of **1**, the brighter spots could be attributed to the chlorin cores, the feeble bright areas to the phenyl rings of the dendron, and the striations in the dark trough to the alkyl chains of the dendron. Accordingly, a tentative model for the molecular arrangement of **1** in the lamellae is illustrated in Figure 2b. The unit cell parameters of this arrangement (marked in Figure 2a) are $a=(2.65\pm0.10)$ nm, $b=(9.40\pm0.19)$ nm, and $\alpha=(92\pm2)°$. Notably, chlorin dyes may adopt two different molecular orientations, namely "face-on" and "edge-on", on the surfaces.[12a,15] As well as chlorin dyes, other planar aromatic compounds, particularly phthalocyanine and porphyrin derivatives, can orient to the surface in both fashions.[16] Based on the above-mentioned STM investigations, we propose that the "face-on" orientation prevails for **1**, the chlorin cores adopt an offset arrangement, and the

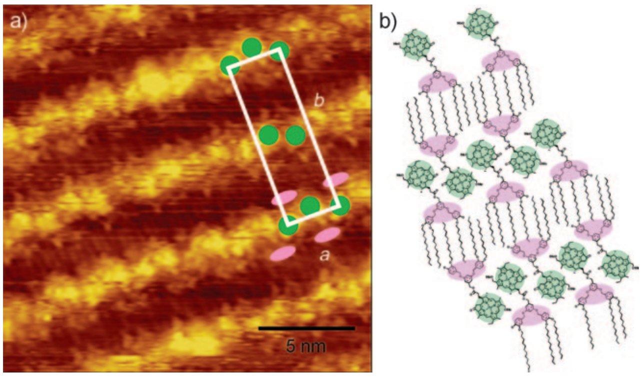

Figure 2. a) STM image of the self-assembly of **1** at the 1-phenyloctane–HOPG interface; $V_{bias}=-0.9$ V and $I=50$ pA. b) A tentative model for the molecular arrangement of **1** in lamellar structures.

dendrons of neighboring zinc chlorins are oriented in opposite directions (Figure 2b). The alkyl chains of **1** molecules of the neighboring rows are interdigitated at the dark trough, and three out of four alkyl chains of each zinc chlorin molecule are in contact with graphite surface, as revealed by the six lines observed for the repeat unit in STM current image of **1** (see Figure S1 in the Supporting Information). This observation implies that some of the alkyl chains are directed toward the supernatant solution.[17]

For **2**, which contains six alkyl chains in the dendron, two different self-assembled structures are observed at the solution–HOPG interface, depending on the concentration of the solution (Figure 3, see also Figure S2 in the Supporting Information). STM images of a 1×10^{-5} M solution of **2** in 1-phenyloctane/octanoic acid (1:1) on HOPG show highly ordered cyclic structures with hexagonal packing (Figure 3a), which are similar to those observed by AFM for **2** (see Figure 1b). The center-to-center distance between the neighboring cyclic structures is 7.4 nm, which is in good agreement with the value ((7.6 ± 0.3) nm) observed for cyclic structures of **2** on HOPG in air by AFM. Moreover, a single cyclic structure is composed of six molecules of **2**, as six brighter spots that correspond to the chlorin cores can be seen in the STM image (Figure 3a, inset). The structural order of cyclic arrays of **2** is shown schematically in Figure 3c. A unit cell with the parameters $a=b=(7.37\pm0.08)$ nm and $\alpha=(60\pm5)°$, which are in good agreement with hexagonal packing, is marked in Figure 3a. In addition, the centers of the hexameric cyclic structures appear to possess holes since the alkyl chains of the dendrons surround the chlorin cores, as indicated by the dark areas in the STM image (Figure 3a). As the chlorin core does not possess any additional functional groups such as hydroxy groups, which can stabilize 2D structures, it is reasonable that these cyclic structures are established by the steric hindrance imposed by the dendron wedge that bears a large number of alkyl chains and leads to nanosegregation. Therefore, the chlorin cores tend to stay near the center and the side chains at the periphery of the structure.

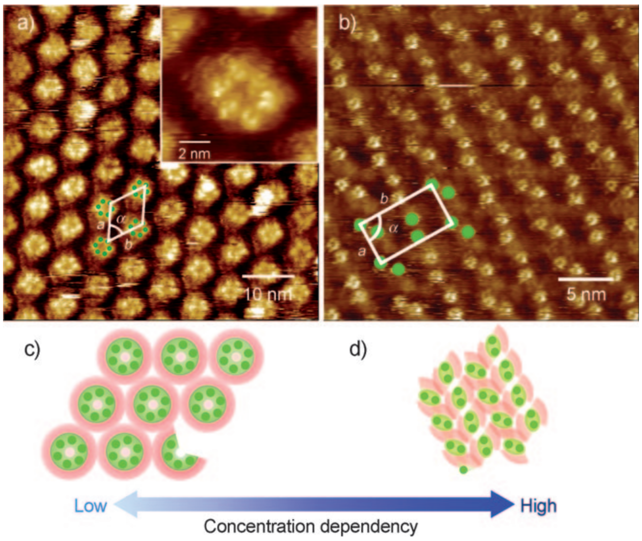

Figure 3. STM images of self-assembly of **2** at different concentrations in 1-phenyloctane/octanoic acid (1:1). a) 1×10^{-5} M solution (STM conditions: $V_{bias}=-1.8$ V and $I=5$ pA). The inset shows a magnified image of the cyclic structure. b) 2×10^{-5} M solution (STM conditions: $V_{bias}=-1.5$ V and $I=6$ pA). c, d) Schematic illustrations of the corresponding molecular arrangements in (a) and (b).

At higher concentrations (2×10^{-5}–5×10^{-5} M) of **2** in 1-phenyloctane/octanoic acid (1:1), linear structures are observed at the solution–HOPG interface. From the high-resolution image in Figure 3b, it is evident that the bright rows are composed of dimeric units of **2** in two orientations, and that the dimers are alternately aligned in the neighboring linear structures (Figure 3d). The center-to-center distance in the dimers is approximately 1.4 nm. A unit cell with the parameters $a=(3.9\pm0.2)$ nm, $b=(7.2\pm0.1)$ nm, and $\alpha=(85\pm5)°$ is marked in Figure 3b.

The concentration-dependent formation of two different types of self-assembled structures of dendritic zinc chlorin **2** may be explained in terms of molecular packing at the interface by considering the areas of the molecules in the unit cells. The unit cell areas divided by the number of molecules per unit cell in linear structures and in cyclic structures can be estimated to be 7.0 nm^2 and 7.8 nm^2, respectively. The linear structures have a slightly smaller area per molecule than that of the cyclic structures, thus implying that the molecular packing density is higher in the former case. Therefore, the molecular packing change at the interface can occur through concentration control. At low concentrations of **2**, cyclic structures with a “face-on” molecular orientation are formed. Upon increasing the concentration of the solution, **2** adopts a dimeric linear structure because of increasing adsorbate concentration at the interface. However, the transition from cyclic to linear structures has not been observed at any concentration, therefore indicating that the phenomenon is not kinetically driven. Recently, De Feyter and co-workers have reported such concentration-dependent behavior for self-assembled structures at the solution–solid interface.[18] This behavior shows that the balance of interactions between solvent, molecule, and substrate is very important for supramolecular 2D structures at the interface.

In summary, the self-assembly of zinc chlorins **1**–**3** that bear second-generation dendrons has been investigated by SPM on HOPG. The formation of self-assembled structures can be controlled by the dendron wedge effect, and **2** forms cyclic structures without common intermolecular interactions such as hydrogen bonding, but by steric hindrance of the dendron with an appropriate wedge. The cyclic arrays of **2** possess holes at the center, which provide further opportunities for the incorporation of other functional molecules. This cyclic arrangement of zinc chlorins with dendron wedges is reminiscent of the light-harvesting systems LH1 and LH2 in nature, hence the present results might provide a promising path toward the realization of light harvesting with such semiartificial systems.

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[1] a) G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell, N. W. Isaacs, *Nature* **1995**, *374*, 517 – 521; b) T. Pullerits, V. Sundström, *Acc. Chem. Res.* **1996**, *29*, 381 – 389.

[2] a) S. Scheuring, J. N. Sturgis, V. Prima, A. Bernadac, D. Lévy, J.-L. Rigaud, *Proc. Natl. Acad. Sci. USA* **2004**, *101*, 11293 – 11297; b) S. Bahatyrova, R. N. Frese, C. A. Siebert, J. D. Olsen, K. O. Van der Wert, R. Van Grondelle, R. A. Niederman, P. A. Bullough, C. Otto, C. N. Hunter, *Nature* **2004**, *430*, 1058 – 1062; c) S. Scheuring, *Curr. Opin. Chem. Biol.* **2006**, *10*, 387 – 393.

[3] a) T. S. Balaban, H. Tamiaki, A. R. Holzwarth, *Top. Curr. Chem.* **2005**, *258*, 1 – 38; b) V. Huber, M. Katterle, M. Lysetska, F. Würthner, *Angew. Chem.* **2005**, *117*, 3208 – 3212; *Angew. Chem. Int. Ed.* **2005**, *44*, 3147 – 3151.

[4] T. Kudernac, S. Lei, J. A. A. W. Elemans, S. De Feyter, *Chem. Soc. Rev.* **2009**, *38*, 402 – 421.

[5] a) J. A. A. W. Elemans, M. C. Lensen, J. W. Gerritsen, H. van Kempen, S. Speller, R. J. M. Nolte, A. E. Rowan, *Adv. Mater.* **2003**, *15*, 2070 – 2073; b) X. Peng, N. Aratani, K. Takagi, T. Matsumoto, T. Kawai, I.-W. Hwang, T. K. Ahn, D. Kim, A. Osuka, *J. Am. Chem. Soc.* **2004**, *126*, 4468 – 4469; c) O. Shoji, H. Tanaka, T. Kawai, Y. Kobuke, *J. Am. Chem. Soc.* **2005**, *127*, 8598 – 8599; d) W.-S. Li, K. S. Kim, D.-L. Jiang, H. Tanaka, T. Kawai, J. H. Kwan, D. Kim, T. Aida, *J. Am. Chem. Soc.* **2006**, *128*, 10527 – 10532.

[6] a) S. Höger, K. Bonrad, A. Mourran, U. Beginn, M. Möller, *J. Am. Chem. Soc.* **2001**, *123*, 5651 – 5659; b) C. Grave, D. Lentz, A. Schäfer, P. Samorì, J. P. Rabe, P. Franke, A. D. Schlüter, *J. Am. Chem. Soc.* **2003**, *125*, 6907 – 6918; c) E. Mena-Osteritz, P. Bäuerle, *Adv. Mater.* **2006**, *18*, 447 – 451; d) B. Schmaltz, A. Rouhanipour, H. J. Räder, W. Pisula, K. Müllen, *Angew. Chem.* **2009**, *121*, 734 – 738; *Angew. Chem. Int. Ed.* **2009**, *48*, 720 – 724; e) S.-S. Li, B. H. Northrop, Q.-H. Yuan, L.-J. Wan, P. J. Stang, *Acc. Chem. Res.* **2009**, *42*, 249 – 259.

[7] a) S. De Feyter, F. De Schryver, *Top. Curr. Chem.* **2005**, *258*, 205 – 255; b) J. A. Theobald, N. S. Oxtoby, M. A. Phillips, N. R. Champness, P. H. Beton, *Nature* **2003**, *424*, 1029 – 1031; c) M. Stöhr, M. Wahl, C. H. Galka, T. Riehm, T. A. Jung, L. H. Gade, *Angew. Chem.* **2005**, *117*, 7560 – 7564; *Angew. Chem. Int. Ed.* **2005**, *44*, 7394 – 7398; d) N. Wintjes, J. Hornung, J. Lobo-Checa, T. Voigt, T. Samuely, C. Thilgen, M. Stöhr, F. Diederich, T. A. Jung, *Chem. Eur. J.* **2008**, *14*, 5794 – 5802.

[8] a) R. Madueno, M. T. Räisänen, C. Silien, M. Buck, *Nature* **2008**, *454*, 618 – 621; b) M. O. Blunt, J. C. Russell, M. del Carmen Giménez-López, J. P. Garrahan, X. Lin, M. Schröder, N. R. Champness, P. H. Beton, *Science* **2008**, *322*, 1077 – 1081; c) I. De Cat, C. Röger, C. C. Lee, F. J. M. Hoeben, M. J. Pouderoijen, A. P. H. J. Schenning, F. Würthner, S. De Feyter, *Chem. Commun.* **2008**, 5496 – 5498; d) F. J. M. Hoeben, J. Zhang, C. C. Lee, M. J. Pouderoijen, M. Wolffs, F. Würthner, A. P. H. J. Schenning, E. W. Meijer, S. De Feyter, *Chem. Eur. J.* **2008**, *14*, 8579 – 8589; e) A. Llanes-Pallas, C.-A. Palma, L. Piot, A. Belbakra, A. Listorti, M. Prato, P. Samorì, N. Armaroli, D. Bonifazi, *J. Am. Chem. Soc.* **2009**, *131*, 509 – 520.

[9] a) H. Tamiaki, M. Amakawa, Y. Shimono, R. Tanikaga, A. R. Holzwarth, K. Schaffner, *Photochem. Photobiol.* **1996**, *63*, 92 – 99; b) T. S. Balaban, *Acc. Chem. Res.* **2005**, *38*, 612 – 623.

[10] a) S. D. Hudson, H.-T. Jung, V. Percec, W.-D. Cho, G. Johansson, G. Ungar, V. S. K. Balagurusamy, *Science* **1997**, *278*, 449 – 452; b) V. Percec, C.-H. Ahn, G. Ungar, D. J. P. Yeardley, M. Möller, S. S. Sheiko, *Nature* **1998**, *391*, 161 – 164; c) V. Percec, W.-D. Cho, P. E. Mosier, G. Ungar, D. J. P. Yeardley, *J. Am. Chem. Soc.* **1998**, *120*, 11061 – 11070; d) V. Percec, W.-D. Cho, G. Ungar, D. J. P. Yeardley, *Chem. Eur. J.* **2002**, *8*, 2011 – 2025.

[11] a) S. A. Prokhorova, S. S. Sheiko, A. Mourran, R. Azumi, U. Beginn, G. Zipp, C.-H. Ahn, M. N. Holerca, V. Percec, M. Möller, *Langmuir* **2000**, *16*, 6862 – 6867; b) P. Wu, Q. Fan, Q. Zeng, C. Wang, G. Deng, C. Bai, *ChemPhysChem* **2002**, *3*, 633 – 637; c) J.-R. Gong, S.-B. Lei, L.-J. Wan, G.-J. Deng, Q.-H. Fan, C.-L. Bai, *Chem. Mater.* **2003**, *15*, 3098 – 3104; d) A. Mourran, U. Beginn, G. Zipp, M. Möller, *Langmuir* **2004**, *20*, 673 – 679; e) L. Merz, H.-J. Güntherodt, L. J. Scherer, E. C. Constable, C. E. Housecroft, M. Neuberger, B. A. Hermann, *Chem. Eur. J.* **2005**, *11*, 2307 – 2318; f) W. Mamdouh, H. Uji-i, J. S. Ladislaw, A. E. Dulcey, V. Percec, F. C. De Schryver, S. De Feyter, *J. Am. Chem. Soc.* **2006**, *128*, 317 – 325.

[12] a) V. Huber, M. Lysetska, F. Würthner, *Small* **2007**, *3*, 1007 – 1014; b) V. Huber, S. Sengupta, F. Würthner, *Chem. Eur. J.* **2008**, *14*, 7791 – 7807.

[13] Note that no self-assembled structures of **3** could be observed by STM. Presumably, the layers on HOPG are amorphous and the molecule–molecule and molecule–substrate interactions of **3** are too weak to observe the molecular feature by STM.

[14] R. Lazzaroni, A. Calderone, G. Lambin, J. P. Rabe, J. L. Brédas, *Synth. Met.* **1991**, *41–43*, 525 – 528.

[15] a) S. Boussaad, A. Tazi, R. M. Leblanc, *Proc. Natl. Acad. Sci. USA* **1997**, *94*, 3504 – 3506; b) H. Möltgen, K. Kleinermanns, A. Jesorka, K. Schaffner, A. R. Holzwarth, *Photochem. Photobiol.* **2002**, *75*, 619 – 626; c) Q.-M. Xu, L.-J. Wan, S.-X. Yin, C. Wang, C.-L. Bai, T. Ishii, K. Uehara, Z.-Y. Wang, T. Nozawa, *J. Phys. Chem. B* **2002**, *106*, 3037 – 3040; d) V. Iancu, S.-W. Hla, *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 13718 – 13721.

[16] a) P. Samorí, H. Engelkamp, P. De Witte, A. E. Rowan, R. J. M. Nolte, J. P. Rabe, *Angew. Chem.* **2001**, *113*, 2410 – 2412; *Angew. Chem. Int. Ed.* **2001**, *40*, 2348 – 2350; b) C. B. France, P. G. Schroeder, B. A. Parkinson, *Nano Lett.* **2002**, *2*, 693 – 696; c) Y. Zhou, B. Wang, M. Zhu, J. G. Hou, *Chem. Phys. Lett.* **2005**, *403*, 140 – 145; d) L. Piot, C. Marie, X. Feng, K. Müllen, D. Fichou, *Adv. Mater.* **2008**, *20*, 3854 – 3858; e) S. Maier, L.-A. Fendt, L. Zimmerli, T. Glatzel, O. Pfeiffer, F. Diederich, E. Meyer, *Small* **2008**, *4*, 1115 – 1118.

[17] Y. Kaneda, M. E. Stawasz, D. L. Sampson, B. A. Parkinson, *Langmuir* **2001**, *17*, 6185 – 6195.

[18] S. Lei, K. Tahara, F. C. De Schryver, M. Van der Auweraer, Y. Tobe, S. De Feyter, *Angew. Chem.* **2008**, *120*, 3006 – 3010; *Angew. Chem. Int. Ed.* **2008**, *47*, 2964 – 2968.