## Perylene bisimide macrocycles and their self-assembly on HOPG surfaces<sup>†</sup>

Felix Schlosser, Vladimir Stepanenko and Frank Würthner\*

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Acetylene-linked macrocycles incorporating multiple perylene tetracarboxylic acid bisimide (PBI) chromophores have been synthesised and separated by recycling GPC. The very first example of such macrocycles, *i.e.*, cyclic trimer 5, containing three PBI dyes self-assembles into highly ordered donut-shaped unique hexagonal nanopatterns on HOPG surfaces as revealed by atomic force microscopy (AFM).

Macrocyclic compounds have always been attractive targets due to the challenges involved in their synthesis and the prospects arising from their distinct molecular shape and geometry. In the field of  $\pi$ -conjugated systems, acetylenebased macrocycles occupy a prominent standing.<sup>1</sup> The concept of acetylene and acetylenephenylene linkage has indeed provided large-sized macrocyclic scaffolds with highly defined molecular shapes and properties that are quite distinctive from conformationally flexible open-chain analogues.<sup>2</sup> In extension of fundamental work on the synthesis of acetylene-based macrocycles, the successful incorporation of different chromophores and electrophores such as oligothiophenes,<sup>3</sup> tetrathiafulvalenes,<sup>4</sup> carbazoles,<sup>5</sup> salphens,<sup>6</sup> or porphyrins<sup>7-9</sup> in such macrocyclic scaffolds has been demonstrated. Many of these macrocycles are rigid, planar architectures that facilitated fascinating investigations of their self-organisation on surfaces by scanning tunneling microscopy (STM).<sup>10,11</sup>

Embedding of chromophores into rigid macrocyclic scaffolds in a precise arrangement is of great significance to ensure defined electronic and excitonic coupling patterns that are otherwise difficult to attain in synthetic molecular scaffolds, but such photophysical functions are common in natural light-harvesting complexes, where protein matrices ensure the desired fixation of circular dye arrays.<sup>12</sup> Inspired by the cyclic organisation of chlorophyll dyes in natural lightharvesting systems, appreciable number of acetylene- and phenylene-linked macrocycles containing up to 32 porphyrin units have been synthesised by the groups of Sanders,<sup>7</sup> Lindsey,<sup>8</sup> and Osuka.<sup>9</sup> It is however surprising, keeping in mind the modest fluorescence and exciton transport properties of porphyrins, that related macrocyclic systems based on outstanding fluorophores such as perylene bisimides<sup>13-16</sup> are still unprecedented.

Herein, we report the first example of a rigid acetylenelinked perylene bisimide (PBI) macrocycle 5 (Scheme 1) that



Scheme 1 Synthesis of PBI macrocycle 5. (a) Imidazole, 120 °C, 30 min, 99%; (b) Pd(PPh\_3)\_2Cl\_2, CuI, THF, HN<sup>*i*</sup>Pr\_2, 50 °C, 1 h, 99%; (c) *n*Bu<sub>4</sub>NF, THF, rt, 2 min, 90%; (d) Pd(PPh\_3)\_2Cl\_2, CuI, CH<sub>2</sub>Cl\_2, HN<sup>*i*</sup>Pr\_2, -30 °C, 3 d, 46% yield of crude macrocyclic products; TIPS = triisopropylsilyl.

could be synthesised in remarkably high yield, and show that this cyclic trimer self-assembles into highly ordered twodimensional (2D) nanopatterns on highly ordered pyrolytic graphite (HOPG) surface.

The synthesis of macrocycle 5 was accomplished in four straightforward steps as depicted in Scheme 1, starting with the condensation of perylene tetracarboxylic acid bisanhydride (PBA) 1 with 3-iodoaniline in imidazole at 120 °C to give the corresponding PBI chromophore 2. The latter was then reacted with triisopropylsilylacetylene in a Sonogashira coupling reaction to obtain PBI 3. Removal of the protecting groups with tetrabutylammoniumfluoride afforded the building block PBI 4 containing terminal acetylene groups at the imide positions. The subsequent macrocyclisation of 4 was performed by palladium-catalysed oxidative homocoupling under high dilution conditions. For this purpose, the precursor 4 and the catalysts were dissolved in CH<sub>2</sub>Cl<sub>2</sub>/HN<sup>i</sup>Pr<sub>2</sub> (9:1 vol%, ca. 0.2 mM) under ambient atmosphere and the reaction mixture was stored in a freezer at -30 °C for three days. Afterwards, the solvent was removed under reduced pressure and the crude mixture was filtered over a silica gel pad with CH<sub>2</sub>Cl<sub>2</sub> to remove residual reagents and polymeric side products. The product mixture obtained after filtration does not contain any terminal acetylene groups as revealed by <sup>1</sup>H NMR, indicating that the product mixture consists of only macrocycles. MALDI-TOF analysis reveals that cyclic trimer (n = 3) is the major product, although higher cyclic oligomers up to the octamer could be detected (Fig. 1). It is remarkable

Universität Würzburg, Institut für Organische Chemie, Am Hubland, 97074 Würzburg, Germany.

*E-mail: wuerthner@chemie.uni-wuerzburg.de;* 

*Fax:* +49 (0)931 31 84756; *Tel:* +49 (0)931 31 85340 † Electronic supplementary information (ESI) available: Synthetic

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Fig. 1 MALDI-TOF mass spectrum of macrocyclic product mixture.

that the overall yield for the three steps from PBA 1 to precursor molecule 4 is almost 90% and that the macrocyclisation step affords 46% of macrocyclic products,<sup>17</sup> hence an easy access to this new class of PBI-based macrocycles is worked out.

The mixture of macrocycles was then further purified by recycling GPC (JAIGEL 2H + 2.5H columns; CHCl<sub>3</sub>, 3.5 mL min<sup>-1</sup>). The separation is illustrated in Fig. 2 wherein the peak of the cyclic trimer (n = 3: 5) is marked with an asterisk. Macrocycles larger than the hexamer were cut off during the purification procedure to avoid overlapping of the peaks. After six cycles, the pure trimeric macrocycle 5 was obtained in a yield of 18%. The molecular structure of macrocycle 5 was confirmed by NMR spectroscopy and mass spectrometry. The optical and electrochemical properties of 5 have been studied by UV-vis and fluorescence spectroscopy, and cyclic voltammetry (CV) (see ESI<sup>†</sup>).

The optical properties of the monomeric building block PBI 4 and macrocycle 5 have been characterised by UV-vis absorption and fluorescence emission measurements. For both monomer 4 and cyclic trimer 5, an absorption maximum at 582 nm is



**Fig. 2** Recycling GPC traces of the mixture of macrocycles (JAIGEL 2H + 2.5H columns; CHCl<sub>3</sub>, 3.5 mL min<sup>-1</sup>; UV-vis detection at 500 nm). The peak of the trimer **5** is marked with an asterisk; to the left of this peak follow the peaks for tetramer, pentamer, and so on.

observed in  $CH_2Cl_2$  with an absorption coefficient of 49 200 M<sup>-1</sup> cm<sup>-1</sup> and 139 500 M<sup>-1</sup> cm<sup>-1</sup>, respectively. The absorption coefficient of trimer **5** is nearly three times higher than that for the monomer **4** but otherwise both spectra are of same shape,‡ indicating that the electronic interaction between the chromophores in macrocycle **5** is negligible in the ground state. The emission spectra for **4** and **5** are both almost the mirror image of the corresponding absorption spectra with maxima at 611 nm and 614 nm, respectively. The fluorescence quantum yield of monomer **4** is 95% and for the cyclic trimer **5** with 91% is surprisingly high, which is to our knowledge unprecedented among multichromophoric macrocycles.

The electrochemical properties of **4** and **5** have been investigated by CV, revealing two reversible reductions and one reversible oxidation for each of them that resemble the electrochemical characteristics of similar PBI chromophores.<sup>13</sup> The redox potentials of monomer **4** and cyclic trimer **5** are very similar, indicating that neither the circular arrangement of the chromophores nor the dialkyne bridge has an influence on the redox properties of **5** (for CV data and cyclovoltammograms, see ESI<sup>†</sup>).

The capability of the cyclic trimer **5** to self-assemble into 2D nanopatterns on HOPG was investigated by AFM. A dilute solution of **5** in a THF/MCH mixture (7 : 93 vol%) was spin-coated onto HOPG under 4000 rpm. As shown in Fig. 3, macrocycle **5** self-assembles into 2D donut-like structures in a unique hexagonal arrangement.



Fig. 3 AFM height images of a monolayer of 5  $(5.25 \times 10^{-6} \text{ M})$  obtained by spin-coating from THF/MCH solution onto HOPG. (a–c) Topographic images with *z*-scale of 0.8 nm (a) and 0.6 nm (b, c); inset in (b) is cross-section analysis along the yellow line 1-1'; (c) zoomed unit of the hexagonal domains and proposed model (Hyperchem) for the molecular arrangement of cyclic trimer 5 in donut-like structures (the distance between the centres of the donuts and the width of a donut ring are indicated by yellow arrows, and the average values are 8.2–8.6 nm and 1.6–1.8 nm, respectively); (d) an expanded section of the model shown in (c).

From the size and the shape of the hexagonal nanopattern, it is most likely that six cyclic trimers constitute one hexagon (molecular donut). In Fig. 3c, we show the proposed arrangement of the chromophores modelled with Hyperchem. In this model, the dialkyne edges are laying next to each other and the bulky substituents of the pervlene core are pointing outside, building a donut-like structure out of six trimers in the sterically most favourable arrangement. These molecular donuts are hierarchically organised in even bigger patterned domains. The distances proposed in this model are in excellent agreement with those determined for the 2D structure by AFM. The distance between two donut holes is estimated to be 8.2-8.6 nm by AFM and 8.6-8.8 nm in the model. The width of a donut ring that corresponds to the diameter of the macrocycle is determined to be 1.6-1.8 nm in average, which is quite close to that in the model (1.7–1.9 nm). The height was estimated from the cross-section analysis to be  $0.20 \pm 0.03$  nm (see inset in Fig. 3b), indicating a monolayer.

To conclude, we have reported here the first synthesis of acetylene-linked macrocycles incorporating multiple perylene bisimide chromophores. The obtained cyclic trimer **5** exhibits a fluorescence quantum yield of 91%, which is to the best of our knowledge unprecedented for macrocyclic multichromophoric arrays. Macrocycle **5** self-assembles on HOPG surfaces into a unique well-ordered hexagonal nanopattern with donut-like structure. In our future work, the organisational and functional properties of macrocyle **5** and its higher homologues will be approached. This new class of macrocycles is highly promising for future exploration of exciton and charge transport phenomena on the nanoscale that can be addressed by a broad variety of spectroscopic and microscopic techniques as they possess outstanding fluorescent and redox properties.

## Notes and references

<sup>‡</sup> Note that in the trimer spectrum two absorption bands at 310 nm and 332 nm are present, which are assigned to the absorption of the dialkyne units.

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