ADVANCED MATERIALS

COMMUNICATION

DOI: 10.1002/adma.200802019

A Macrocyclic Model Dodecamer for Polyfluorenes**

By *Sascha C. Simon, Bruno Schmaltz, Ali Rouhanipour, Hans J. Räder,* and *Klaus Müllen**

Polyfluorenes are a class of conjugated polymers that have received great attention due to their attractive properties as the active layer in thin film devices, such as organic light-emitting diodes (OLEDs)[1] and organic photovoltaics (OPVs).[2] Polyfluorenes show high thermal and oxidative stability, high photoluminescence (PL) quantum yields, and are easily processable due to their good solubility in common organic solvents.[3] The study of oligomers can be helpful in understanding structure–property relationships.[4] Several groups synthesized series of pure linear fluorene oligomers[5] by Yamamoto[6] and/or Suzuki coupling.[7] The drawbacks of polydispersity or keto-defects are not evident in these well-defined structures.[8] Recently, Hogen-Esch and Fomina described the one-pot synthesis of various cyclic 3,6-polyfluorene structures.[9] However, the presence of the 3,6-linkage interrupts an extended π-conjugation and changes the optical properties. Therefore, we decided to focus on the fluorene-2,7-diyl structures, allowing extended π-conjugation.

In this paper, we present the first synthesis and characterization of a monodisperse cyclododeca-2,7-fluorene. This new model compound consists of exactly 12 fluorene units. In comparison to linear oligofluorenes, the fluorene macrocycle can be regarded in principle as a model for an infinite π-conjugated chain, since there is no influence from different end groups.[10] This large ring system is also similar to the ideal structure of a poly(*para*-phenylene) (PPP) macrocycle. Theoretical investigations of such cycles using Hückel theory were performed by Wennerström and coworkers.[11] The formation of a ring with only a small number of phenylenes linked in their *para*-positions is hampered by strong steric strain, and becomes feasible due to bending within the fluorene units.

Large cyclic systems can be obtained either by a geometry-driven or by a templated approach.[12] Only a few of these lead to extended π-conjugations and persistent shapes.[13] We have recently demonstrated that a meso-tetra(4-carboxyphenyl) porphyrin can be used as template in order to obtain a 2,7-carbazole-based macrocyclic dodecamer.[13a] Since the geometries of 2,7-carbazole and 2,7-fluorene are similar, this concept could also be successful in the synthesis of a large cyclododeca-2,7-fluorene.

Building block **1**, consisting of three fluorene units, has been designed as follows: i) the anchor group has to be attached to the central unit, which in further steps connects the porphyrin with the template; ii) the solubility of the whole block and the target molecule is controlled by two alkyl chains attached to the 9-position of the outer fluorenes. A chloro substituent is present on both sides of the building block, allowing the Yamamoto coupling ring-closure of **3**. The complete synthetic procedure to obtain the trimer **1** is reported in the Supporting Information. Scheme 1 shows the last four steps of the synthesis of macrocycle **4**. In a Mitsunobu esterification, four equivalents of **1** were attached to the *meso*-tetra(4-carboxyphenyl)porphyrin (**2**, 65%), which was subsequently complexed with zinc (**3**, 97%) in order to avoid any other metal insertion in the further steps. The ring-closure of **3** was performed by a Ni^0-mediated Yamamoto coupling reaction under high-dilution conditions (10^{-5} mol L^{-1}; microwave reaction).[13a] Finally, the porphyrin template was removed from the cavity of the macrocycle by a simple hydrolysis. Knowing that the elution volumes of the linear and the cyclic dodecamer are different, the purification of the target molecule was possible by preparative gel-permeation chromatography (GPC) in chloroform. The completely π-conjugated dodeca-2,7-fluorene macrocycle **4** was obtained in 1.5% yield (calculated for the last two reactions). It is important to mention that the yield is in the same range compared to the previously reported 2,7-carbazole macrocycle.[13a] Even if the yield of the cyclization is not high, the use of a porphyrin template makes the cyclododeca-2,7-fluorene accessible. In fact, without the utilization of the template, a Yamamoto coupling reaction of an ester of **1** leads exclusively to linear oligomers.

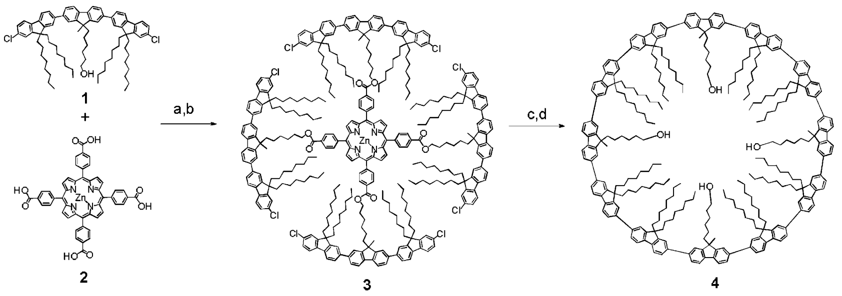
Macrocycle **4** was characterized by UV-vis and fluorescence spectroscopy, mass spectrometry (MS), scanning tunnelling microscopy (STM), and ^{1}H NMR spectroscopy measurements. The matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectrum is shown in Figure 1a. It exhibits one intense signal, corresponding to the calculated mass of **4**. The experimental isotopic distribution (black curve) matches the calculated one (red curve, see Fig. 1b). ^{1}H NMR spectroscopy confirms the ring formation, showing only three singlets and six doublets in the aromatic region, characteristic of the high symmetry of the cycle (see Supporting Information).

The absorption spectra of molecule **4**, its linear subunits (trimer **5**, hexamer **6**, nonamer **7**, and dodecamer **8**), and poly(9,9′-dioctylfluorene-2,7-diyl) **9** (M_n 126 600, M_w 322 700, PPP standard, see Fig. 2) as linear model compounds in

---

[*] Prof. K. Müllen, S. C. Simon, Dr. B. Schmaltz, A. Rouhanipour, Dr. H. J. Räder
Max Planck Institute for Polymer Research
Ackermannweg 10, Mainz 55128 (Germany)
E-mail: muellen@mpip-mainz.mpg.de

[**] This work was financially supported by the German Science Foundation "Elementarprozesse der organischen Photovoltaik" Mu 334/31-1. The authors also acknowledge the German Science Foundation (Korean–German IRTG). Supporting Information is available online from Wiley InterScience or from the authors.



Scheme 1. Synthesis of fluorene macrocycle **4**. a) PPh_3, diethyl azodicarboxylate, THF, 40 °C, 48 h, 65%. b) $Zn(OAc)_2 \cdot 2H_2O$, dichloromethane, methanol, 40 °C, 48 h, 97%. c) bis(1,5-cyclooctadiene)-nickel(0), cyclooctadiene, 2,2′-bipyridine, toluene, DMF, 70 °C for 3 h, 80 °C for 3 h, 100 °C for 8 h. d) KOH, H_2O, methanol, THF, 70 °C, 24 h, 1.5%.

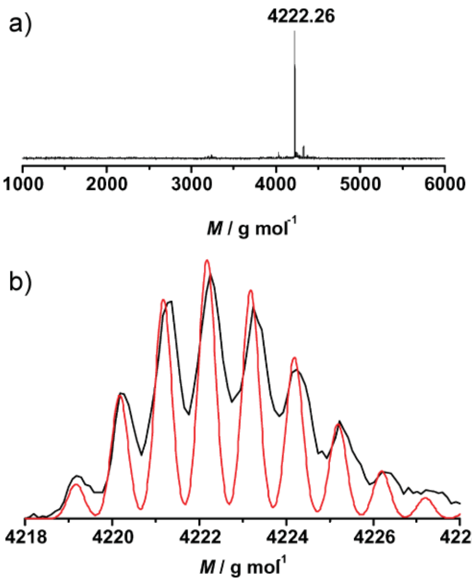


Figure 1. a) MALDI-TOF measurement of compound **4**. b) Expanded view of the molecular-ion region of the experimental (black curve) and simulated (red curve) spectra.

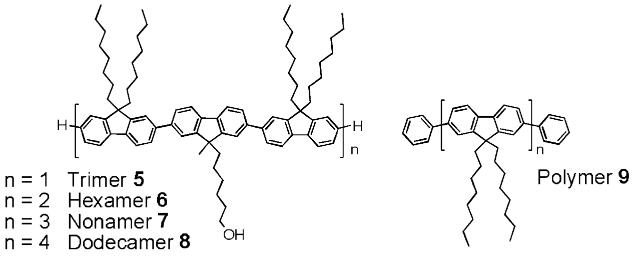


Figure 2. Chemical formula of the linear model compounds used in the UV-vis and PL studies: linear tris-, hexa-, nona-, dodeca-fluorene **5–8**, and poly(9,9′-dioctylfluorene-2,7-diyl) **9** (M_n 126 600, M_w 322 700, PPP standard).

chloroform are shown in Figure 3a. The linear oligofluorenes were obtained as side products from the Yamamoto coupling reaction, and could be isolated by preparative GPC. Compounds **5–8** no longer contain Cl atoms, since they were removed during the nickel-mediated reaction. The absorption maximum of the linear oligofluorenes is red-shifted when the number of fluorene units increases (**5**, 353 nm; **6**, 376 nm; **7**, 378 nm; **8**, 381 nm) corresponding to an increase in the conjugation length.[5] This trend is consistent with recent publications concerning monodisperse oligofluorenes.[5] Geng et al. reported nearly identical maximum absorption wavelengths for their oligomers up to the dodecamer.[5d] Compound **4** shows an absorption maximum at 369 nm. Compared to the linear dodecamer **8**, the maximum value is blue-shifted by 12 nm, indicating a smaller conjugation length. The absorption maximum lies between that of the hexamer (376 nm) and that of the pentamer (366 nm) as described by Geng.[5d] From these data, we can estimate the conjugation length to be between 5 and 6 fluorene units. This shift is attributed to a stronger twist between successive fluorene units, since they are all arranged in a *cis* fashion in the macrocycle. The molar extinction coefficient ε, deduced from the absorption spectra, increases from trimer **5** to dodecamer **8**.[5e] Compared to the linear analogs, macrocycle **4** shows the highest ε value (391 100 L mol^{-1} cm^{-1}). This behavior has already been observed in a previous comparison between linear and cyclic compounds.[14] The emission spectra of **4** and its linear oligofluorenes are shown in Figure 3b. Three well-resolved fluorescence bands for all investigated structures are observed, and can be assigned to the 0–0, 0–1, and 0–2 intrachain singlet transitions.[15] Unlike the absorption maxima, the emission maxima are almost identical for all linear oligofluorenes (starting with the hexamer **6**), polymer **9**, and the macrocycle **4,** indicating similar excited-state geometries.[13a] The emission maximum for each was observed at 417 nm, in good agreement with the values reported in the literature.[5d,e]

The 2D organization of **4** was investigated by STM on a graphite substrate (tunneling current: 1.8 pA, bias voltage: 800 mV). A monolayer of **4** was achieved by spin-coating a dilute THF solution on a freshly cleaved, highly oriented pyrolytic graphite (HOPG) surface. Figure 4 confirms the

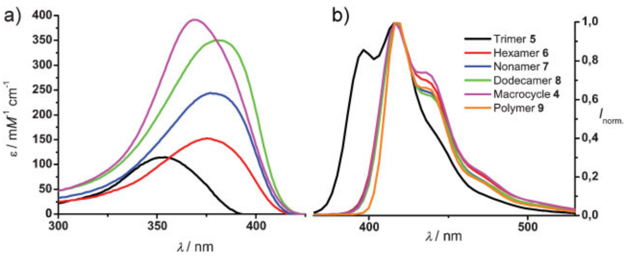


Figure 3. a) Absorption and b) emission spectra of trimer **5** (black), hexamer **6** (red), nonamer **7** (blue), dodecamer **8** (green), macrocycle **4** (magenta), and poly(9,9′-dioctylfluorene-2,7-diyl) **9** (orange) in $CHCl_3$ with a concentration of 10^{-6} mol L^{-1}. The molar extinction coefficients (ε) for structures **4–8** in L mol^{-1} cm^{-1} are 391 100, 112 600, 153 000, 237 000, and 347 800, respectively.

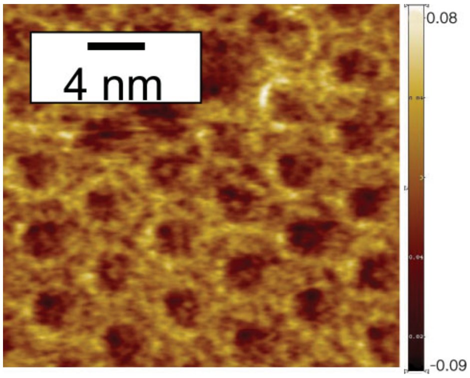


Figure 4. STM image of a 2D monolayer of molecule **4** on an HOPG surface at the solid/air interface (tunneling current: 1.8 pA, bias voltage: 800 mV), showing self-assembled hexagonal packing.

formation of conjugated ring-shape structures, and shows that the cycles self-arrange in a dense hexagonal packing. The average diameter of the macrocycles was estimated at approximately 4.0 nm, in good agreement with simulation (3.4 nm, force field calculations (mmFF)). Moreover, as expected due to the comparable substructures of fluorene and carbazole, the size of the cyclododeca-2,7-fluorene ring is similar to that of the previously reported cyclododeca-2,7-carbazole.[13a]

In conclusion, we have presented the first synthesis of a monodisperse, completely π-conjugated, cyclododeca-2,7-fluorene macrocycle. It is a model compound for an idealized infinite polymer chain without end-groups. MALDI-TOF, ^{1}H NMR, and STM measurements evidenced the formation of the ring structure. The optical properties of **4** were compared with those of its linear analogs. The conjugation length was estimated to be approximately 5–6 fluorene units. The emission maximum is almost identical for all investigated compounds. STM measurements indicate that molecule **4** self-organizes on HOPG, forming a well-defined hexagonal pattern. This macrocycle opens way for a new family of 2,7-polyfluorenes, which are no longer restricted to linear structures. This new ring-shaped macromolecule also brings polymer scientists closer to their vision of synthesizing poly(*para*-phenylene) cyclic structures.

Received: July 16, 2008
Revised: August 22, 2008
Published online:

---

[1] a) M. Gross, D. D. Müller, H.-G. Nothofer, U. Scherf, D. Neher, C. Bräuchle, K. Meerholz, *Nature* **2000**, *405*, 661. b) A. W. Grice, D. D. C. Bradley, M. T. Bernius, M. Inbasekaran, W. W. Wu, E. P. Woo, *Appl. Phys. Lett.* **1998**, *73*, 629. c) R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos-Santos, J. L. Bredas, M. Lögdlund, W. R. Salaneck, *Nature* **1999**, *397*, 121. d) Q. Pei, Y. Yang, *J. Am. Chem. Soc.* **1996**, *118*, 7416.

[2] a) X. Wang, E. Perzon, J. L. Delgado, P. de la Cruz, F. Zhang, F. Langa, M. Andersson, O. Inganäs, *Appl. Phys. Lett.* **2004**, *85*, 5081. b) M. Chen, E. Perzon, K. M. Jönsson, M. R. Andersson, M. Fahlmann, M. Berggren, *Appl. Phys. Lett.* **2004**, *84*, 3570. c) F. Zhang, W. Mammo, L. M. Andersson, S. Admassie, M. R. Andersson, O. Inganäs, *Adv. Mater.* **2006**, *18*, 2169.

[3] a) D. Neher, *Macromol. Rapid Commun.* **2001**, *22*, 1365. b) U. Scherf, E. J. W. List, *Adv. Mater.* **2002**, *14*, 477.

[4] a) R. E. Martin, F. Diederich, *Angew. Chem. Int. Ed.* **1999**, *38*, 1350. b) *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, Germany **1998**.

[5] a) G. Klaerner, R. D. Miller, *Macromolecules* **1998**, *31*, 2007. b) S. H. Lee, T. Tsutsui, *Thin Solid Films* **2000**, *363*, 76. c) R. Anemian, J.-C. Mulatier, C. Andrault, O. Stephan, J.-C. Vial, *Chem. Commun.* **2002**, 1608. d) Y. Geng, A. Traykovska, D. Katsis, J. D. Ou, S. W. Culligan, S. H. Chen, *J. Am. Chem. Soc.* **2002**, *124*, 8337. e) J. Jo, C. Chi, S. Höger, G. Wegner, D. Y. Yoon, *Chem. Eur. J.* **2004**, *10*, 2681.

[6] T Yamamoto,, A. Morita, Y. Miyazaki, T. Maruyama, H. Wakayama, Z. Zhou, Y. Nakamura, T. Kanbara, S. Sasaki, K. Kubota, *Macromolecules* **1992**, *25*, 1214.

[7] N. Miyaura, A. Suzuki, *Chem. Rev.* **1999**, *576*, 147.

[8] a) J. M. Lupton, M. R. Craig, E. W. Meijer, *Appl. Phys. Lett.* **2002**, *80*, 4489. b) U. Scherf, E. W. J. List, *Adv. Mater.* **2002**, *14*, 477. c) E. W. J. List, P. Guentner, P. Scanducci de Freitas, U. Scherf, *Adv. Mater.* **2002**, *14*, 374. d) A. C. Grimsdale, K. Müllen, *Macromol. Rapid Commun.* **2007**, *28*, 1676.

[9] N. Fomina, T. E. Hogen-Esch, *Macromolecules* **2008**, *41*, 3765.

[10] X. Chen, H. E. Tseng, J. L. Liao, S. A. Chen, *J. Phys. Chem. B* **2005**, *109*, 17496.

[11] a) U. Norinder, O. Wennerström, *Tetrahedron Lett.* **1984**, *13*, 1397. b) U. Norinder, O. Wennerström, *Tetrahedron* **1985**, *4*, 713.

[12] a) S. Höger, A. D. Meckenstock, S. Müller, *Chem. Eur. J.* **1998**, *4*, 2423. b) S. Höger, *Chem. Eur. J.* **2004**, *10*, 1320. c) D. H. Zhao, J. S. Moore, *Chem. Commun.* **2003**, *807*. d) S. Höger, *J. Polym. Sci., Part A* **1999**, *37*, 2685.

[13] a) S.-H. Jung, W. Pisula, A. Rouhanipour, H. J. Räder, J. Jacob, K. Müllen, *Angew. Chem. Int. Ed.* **2006**, *45*, 4685. b) J. Krömer, I. Rios-Carreras, G. Fuhrmann, C. Musch, T. Wunderlin, T. Debaerdemaeker, E. Mena-Osteritz, P. Bäuerle, *Angew. Chem. Int. Ed.* **2000**, *39*, 3481. c) G. Fuhrmann, J. Krömer, P. Bäuerle, *Synth. Met.* **2001**, *119*, 125.

[14] P. Bäuerle, M. Ammann, M. Wilde, G. Günther, E. Mena-Osteritz, A. Rang, C. A. Schalley, *Angew. Chem. Int. Ed.* **2007**, *46*, 363.

[15] M. Fukuda, K. Sawada, K. Yoshino, *J. Polym. Sci. Part A: Polym. Chem.* **1993**, *31*, 2465.