ORGANIC
LETTERS

2008
Vol. 10, No. 11
2123−2126

Shape-Persistent Elliptic Macrocycles Composed of Polycyclic Aromatic Hydrocarbons: Synthesis and Photophysical Properties

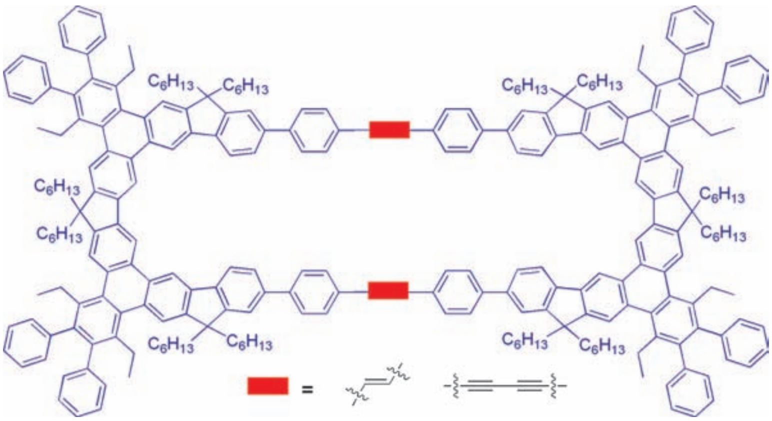
Wen-Jun Liu, Yan Zhou, Qi-Feng Zhou, Yuguo Ma,* and Jian Pei*

The Key Laboratory of Bioorganic Chemistry and Molecular Engineering of Ministry of Education and the Key Laboratory of Polymer Chemistry and Physics of Ministry of Education, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, China

jianpei@pku.edu.cn

Received March 6, 2008

ABSTRACT



Bimolecular coupling/unimolecular cyclization strategies, including McMurry- and Glaser-type homocoupling reactions, were utilized to synthesize two shape-persistent elliptic macrocycles, which consist of polycyclic aromatic hydrocarbon units. The identity and purity of both macrocycles MC1 and MC2 were verified by ^1H and ^{13}C NMR, elemental analysis, as well as MALDI-TOF MS. The photophysical properties of MC1 and MC2 in dilute solution were also investigated.

Considerable attention has recently been devoted to shape-persistent macrocycles, not only for their aesthetic appearance but also for their potential applications in supramolecular and material chemistry.[1] A diversity of supramolecular assemblies, including host−guest complexes,[2a] discotic liquid crystals,[2b] extended tubular channels,[2c] and organic porous solids,[2d] were realized by shape-persistent macrocycles possessing rigid cyclic backbones. The noncollapsible scaffolds and the resultant well-defined cavities were exploited to reinforce the intermolecular interaction, thus facilitating

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10.1021/ol800505y CCC: $40.75

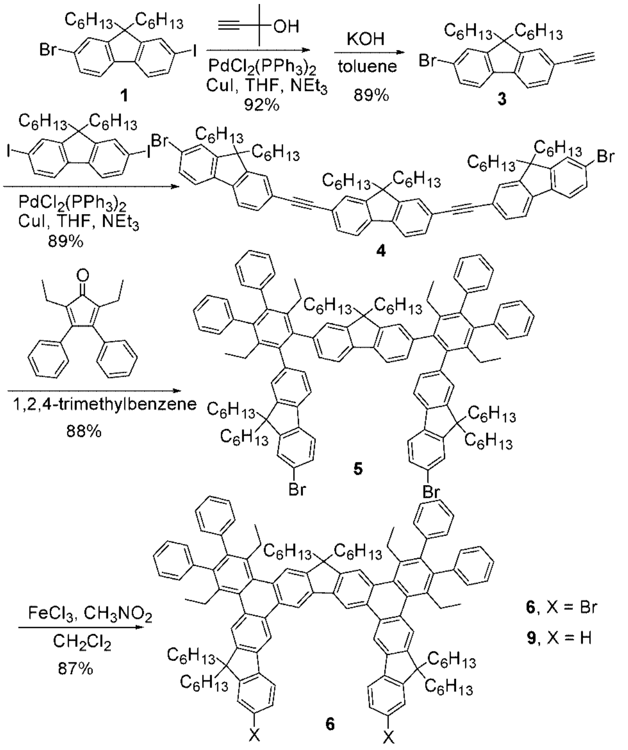
the formation of these highly ordered rigid structures. Polycyclic aromatic hydrocarbons (PAHs) are ideal building blocks for the preparation of cofacially stacked supramolecular structures and display various attractive optoelectronic properties.[3]However, the synthesis of rigid macrocycles is still a great challenge. The desired cyclic structure has to compete against the statistic distribution of various linear/cyclic oligomers/polymers of different chain lengths in reaction, resulting in poor reaction yields,[1e] although many different methodologies have been developed to overcome such problems.[1]

In this contribution, we incorporate polycyclic aromatic hydrocarbon moieties into the shape-persistent marocycles in order to take advantages of the features of both polycyclic aromatic hydrocarbons and macrocycles. The strategy of bimolecular coupling followed by intramolecular cyclization, as illustrated in Figure 1, which can achieve a better balance between the number of synthetic steps and the overall reaction yield,[4] was utilized to approach the shape-persistent macrocycles from geometrically appropriate polycyclic aromatic hydrocarbons.

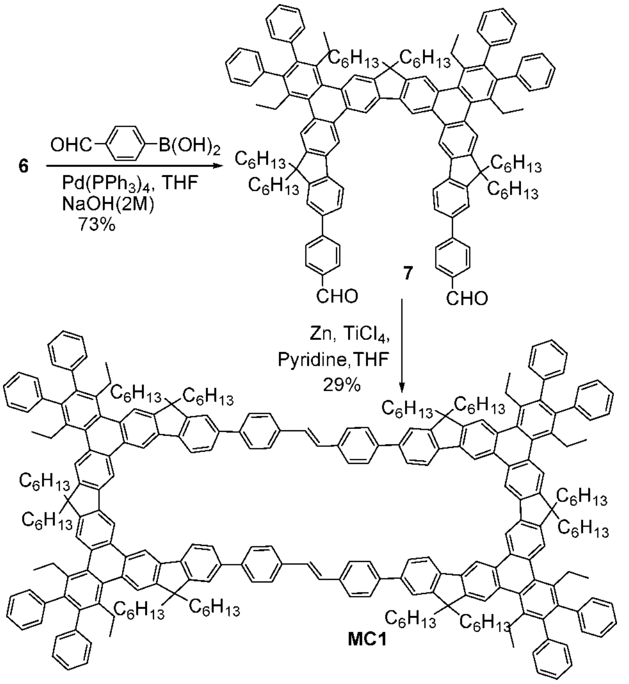
Figure 1. Schematic representation of bimolecular coupling/unimolecular cyclization strategy.

Scheme 1 illustrates the synthetic route to polycyclic aromatic hydrocarbon **6**. In order to differentiate the reactivities of two positions in fluorene undergoing the Sonogashira cross-coupling reaction, 9,9-dihexyl-2-bromo-7-iodofluorene (**1**) was chosen as the starting material, which was easily prepared through the iodination in high yield followed by the bromination from commercially available 9,9-dihexylfluorene. Selective Sonogashira cross-coupling reaction at room temperature between **1** and 2-methyl-3-butyn-2-ol and subsequent deprotection of tertiary alcohol with KOH furnished **3**, which was then carried on a Sonogashira cross-coupling reaction with 9,9-dihexyl-2,7-diiodofluorene to afford **4** in 89% yield. The relatively unreactive aryl bromides flanking **4** could be further functionalized in the following steps. The Diels−Alder reaction between **4** and 2,5-diethyl-3,4-diphenylcyclopentadienone followed by decarbonylation in refluxed 1,2,4-trimethylbenzene produced **5** in 88% yield. The FeCl$_3$-promoted oxidative cyclization condition was applied to generate polycyclic aromatic hydrocarbon **6** in 87% yield.[5] This oxidative cyclization reaction proceeded effectively despite the presence of two electron-withdrawing bromide groups, presumably due to the negligible inductive effect of bromide groups relative to the extended π-conjugated reactant.

Scheme 1. Synthetic Route to **6**



Scheme 2. Synthetic Route to **MC1**



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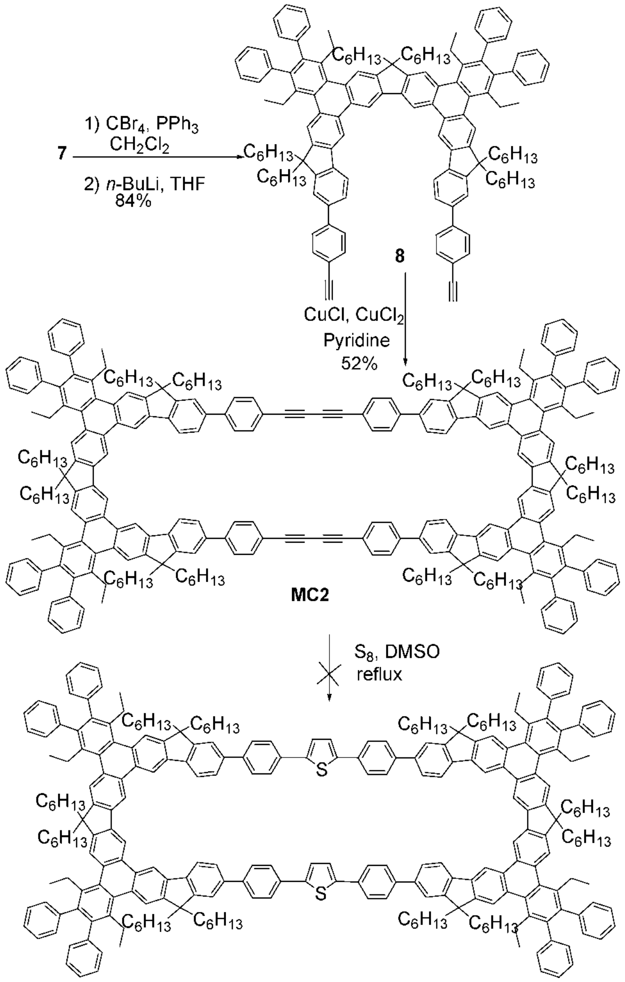
After the bimolecular coupling, the intramolecular cyclization methodology to shape-persistent macrocycles is outlined in Scheme 2. From polycyclic aromatic hydrocarbon **6**, a Suzuki coupling reaction with 4-formylphenylboronic acid afforded **7** with two aldehyde functionalities in 73% yield. The precursor **7** was then subjected to McMurry[6] homocoupling reaction to afford **MC1** in 29% yields.

As shown in Scheme 3, **7** was further converted to terminal ethynyl groups to produce **8** in 84% yield through a Corey-Fuchs reaction. The precursor **8** was then subjected Glaser-type homocoupling reactions[7] to afford **MC2** in 52% yields. We also tried to convert butadiynylene groups to the thiophene ring by addition of sulfur; unfortunately, due to the rigidity of this macrocycle, we did not obtain the target molecules.

Scheme 3. Synthetic Route to **MC2**



MC1 and **MC2** as slightly yellow solids were readily soluble in common organic solvents, such as dichloromethane, chloroform, tetrahydrofuran, and toluene. The identity and purity of **MC1** and **MC2** were verified by ^{1}H and ^{13}C NMR, MALDI-TOF MS, and elemental analysis. Comparing the ^{1}H NMR spectra between the precursors and the macrocycles, we observed the singlet at 10.1 ppm in **7** (Figure 2a) and the singlet at 3.19 ppm in **8** (Figure 2b) belonging to the protons of aldehyde in **7** and ethynyl in **8**, respectively, vanished after the corresponding cyclization, which clearly indicates the cyclization rather than oligomerization of the precursors took place. From the ^{1}H NMR spectrum of **MC1**, we also observed that the double bonds predominately exist as the *E*-isomer.[8] Furthermore, as shown in Figure 3, the signals at 3482 Da (100%) for **MC1** and at 3524 Da (100%) for **MC2** (see the Supporting Information) exhibited on the MALDI-TOF MS spectra unambiguously

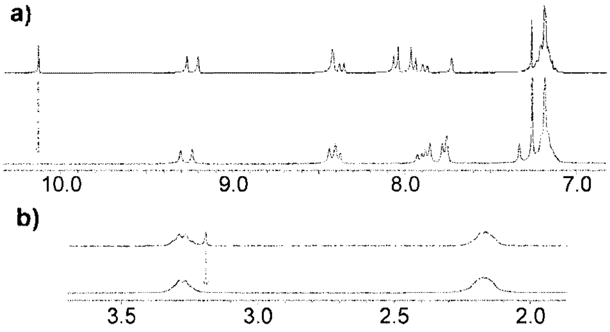


Figure 2. (a) ^{1}H NMR spectra of **7** (black) and **MC1** (blue) from 7.0−11.0 ppm. (b) ^{1}H NMR spectra of **8** (black) and **MC2** (blue) from 2.0−3.5 ppm.

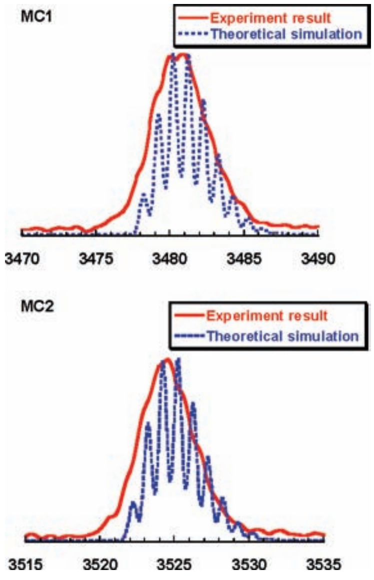


Figure 3. Measured and simulated MALDI-TOF MS spectra of **MC1** and **MC2**.

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demonstrated that their structures containing two polycyclic aromatic hydrocarbons were linked by different spacers. We can still recognize the similar isotopic distributions between measured and simulated results regardless of the sensitivity of the facility.

Figure 4 illustrates the photophysical behaviors of the shape-persistent macrocycles **MC1** and **MC2** in dilute THF solution (10^{-5} M), and their photophysical properties are summarized in Table 1. The absorption of **MC1** show a maximum at 382 nm, which red-shifted by 11 nm in comparison with **MC2** (λ_{max} = 371 nm). The emission of **MC2** peaked at 426 nm while **MC1** exhibit emission maximum at 435 nm with a small shoulder at 459 nm.

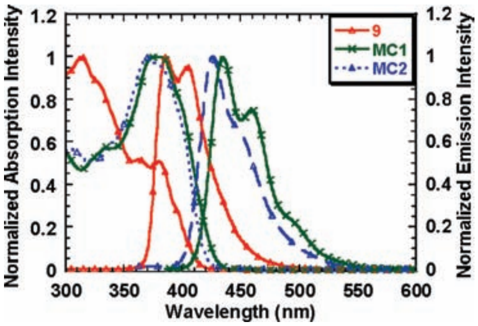

Figure 4. Absorption and emission spectra of **9**, **MC1**, and **MC2** in dilute THF solution (10^{-5} M). Emission spectra were obtained upon excitation at absorption maximum.

Table 1. Photophysical Properties of Macrocycles **MC1** and **MC2** in Dilute THF Solution

macrocycles	ϵ (M^{-1} cm^{-1})	λ_{max} abs (nm)	λ_{max} PL (nm)
MC1	6.5×10^5	382	435, 459
MC2	5.4×10^5	371	426

The emission maximum of **MC1** red-shifted by 9 nm relative to that of **MC2**. Such red shifts in both absorption and emission spectra of **MC1** implied that ethylene unit is superior in extending the effective conjugation length than the diacetylene unit.[9] Furthermore, we compared the macrocycles with compound **9**,[5a] which has been investigated in our previous work (see the Supporting Information).[6] The absorption peak has been significantly red-shifted by 68 and 57 nm in comparison to compound **9** for **MC1** and **MC2**, respectively. Such red shift shows the conjugation length of the molecules have been extended after the macrocyclization. The emission spectrum showed the same trend. The maximum emission peak was red-shifted by 48 and 39 nm from 387 nm for **MC1** and **MC2**, respectively. The vibration emission peak of **9** turned to be a shoulder peak in **MC1** and **MC2**. More specifically, the Stokes shift decreased from 72 to 53 nm after the cyclization, indicating that the rigidity of the molecule enhanced after the cyclization. The fluorescence quantum yields (ΦF) of **MC1** and **MC2** in dilute THF solution were 0.94 and 0.82, respectively, using 9,10-diphenylanthracene as the standard.

In summary, two shape-persistent elliptic macrocycles composed of polycyclic aromatic hydrocarbons (**MC1** and **MC2**) have been designed and synthesized in a relatively straightforward manner. $FeCl_3$-promoted oxidative cyclization and bimolecular coupling followed by unimolecular cyclization strategy are adopted to construct the polycyclic aromatic hydrocarbons and shape-persistent macrocycles, respectively. Geometrical conformation of the precursors is demonstrated to play a key role in the formation of the desired macrocycles. The investigation of the synthetic route and the photophysical behaviors of **MC1** and **MC2** gives insight into the rational design of rigid macromolecules, as well as the fine-tuning of their photophysical properties.

Acknowledgment. This work was supported by the National Basic Research Program (No. 2006CB921602 and 2007CB808000) from the Ministry of Science and Technology, and National Natural Science Foundation of China (NSFC 20425207, 50473016, 20521202, and 20604001).

Supporting Information Available: Experimental procedures and ^{1}H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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