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Synthesis and Characterization of Macrocyclic Poly(fluorene-3,6-diyl)

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A number of reports have appeared recently on the synthesis and characterization of chromophore-containing macrocycles.[1–5] Macrocycles, in general, are interesting in that they tend to be shape-persistent and may self-assemble into highly ordered supramolecular structures, such as extended channels,[5] metal-coordinated frameworks,[6] and host−guest complexes.[7] Macrocyclic vinyl aromatic polymers have been shown to have interesting optical, thermal, and other properties that differ from their linear analogues.[8,9] For instance, they have been shown to emit light with greater quantum yields compared with the linear polymers of the same MW.[8]

Polyfluorenes have attracted much attention in the past decade as efficient blue-light-emitting materials.[10–16] A large number of polyfluorene copolymers have also been reported.[16–26] However, all of these had the fluorene-2,7-diyl structure and had emission maxima at around 420 nm. The presence of the 3,6-linkage in polyfluorenes is expected to change its conformation, leading to the formation of more highly bent conformations than in poly(9,9-dialkylfluorene-2,7-diyl) and hence to modify its optical properties. The introduction of a meta-linkage in conjugated polyaromatic poly(*p*-phenylenevinylene) (PPV) and similar polymers or copolymers has been shown to reduce their effective conjugation lengths and increase the optical bandgaps.[27–29] Thus, there is a potential for energy transfer to chromophores giving emissions at shorter wavelengths.

The properties of macrocyclic polyfluorenes are of interest because of the absence of end-group defects that have been proposed to contribute to an undesirable green emission.[30] Furthermore, because of their shape persistence, the availability of such polymers also could contribute to new knowledge with regard to intramolecular exciton transfer.

Here we report for the first time the synthesis by Yamamoto coupling of macrocyclic polyfluorene tetramer and analogous low-MW cyclic oligomers linked through the 3- and 6- positions (macrocyclic poly(9,9-dihexylfluorene-3,6-diyl) (36PDHF)). Although the synthesis of the linear 36PDHF has been reported,[31] to the best of our knowledge the synthesis of a pure cyclic polyfluorene of any structure is unprecedented.

The tetra(9,9-dihexyfluorene-3,6-diyl) macrocycle is isolated as the *major* low-MW component in the polymerization mixture. Surprisingly we did not find the corresponding *low-MW linear* polymers. Furthermore, in contrast to the formation of most macrocycles from linear precursors, the formation of the cyclic tetramer does not appear to depend on the chain end concentration.[8,9] The formation of conjugated macrocyclic species may have occurred in other polymerizations as well but may not have been recognized as low-MW fractions are frequently removed by fractionation.

The synthesis of 3,6-dibromo-9,9-dihexylfluorene differs from that published earlier (Scheme 1).[31] Since substitution/halogenation at the 3- and 6-positions in fluorene or fluorenone is problematic, it was decided to synthesize 3,6-dibromofluorene (**6**) from commercially available phenanthrenequinone (**1**). Bromination of **1** was carried out according to Bhatt's procedure,[32] and 3,6-dibromophenanthrenequinone (**2**) was obtained in 79% isolated yield. A one-pot rearrangement of **2** into 3,6-dibromofluorenone (**3**) via 3,6-dibromo-9-hydroxy-9*H*-fluorene-9-carboxylic acid gave a 70% yield. The direct reduction of **3** under basic conditions to give **6** was found unsuitable due to formation of fluorenyl anions that undergo side reactions. However, a reduction−halogenation of **3** gave 3,6-dibromo-9-chlorofluorene (**5**) that was reduced under acidic conditions to give **6** in 76% yield. Alkylation of **6** with 1-bromohexane using LDA as a base gave 3,6-dibromo-9,9-dihexylfluorene (**7**) in 65% yield. The overall yield of **7** from **1** was 27%.

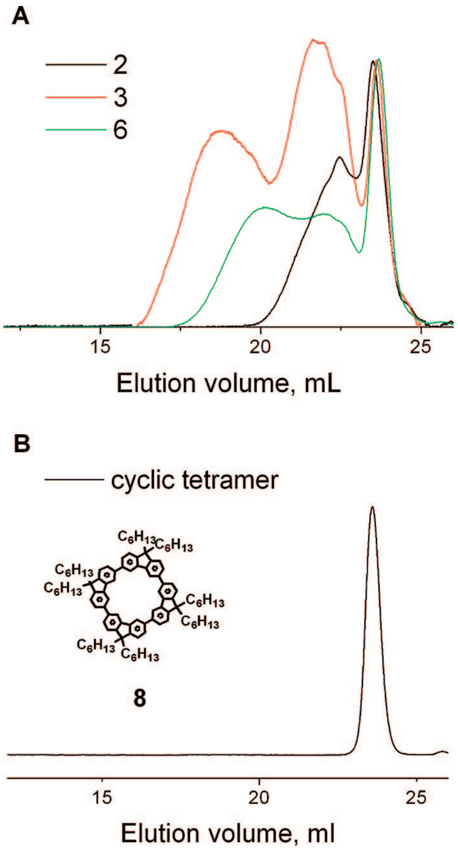

Figure 1. SEC curves of 36PDHF's (A) and isolated cyclic tetramer **8** (B) obtained with refractive index detector.

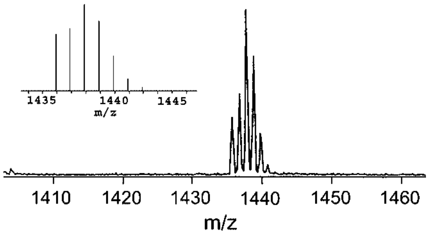

Figure 2. MALDI-TOF spectrum of [M^+ + Ag] of **8**. Inset: simulated isotope distribution of the cyclic tetramer.

Monomer **7** was polymerized using standard Yamamoto conditions (Scheme 2).[33] Molecular weights varying from 2400 to 33 000 (determined by SEC/light scattering) were obtained

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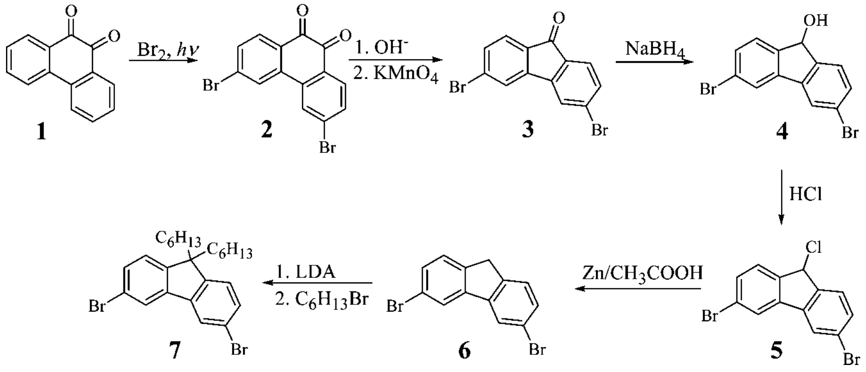
Scheme 1. Synthesis of 9,9-Dihexyl-3,6-dibromofluorene



Scheme 2. Polymerization of 7 by Yamamoto Coupling

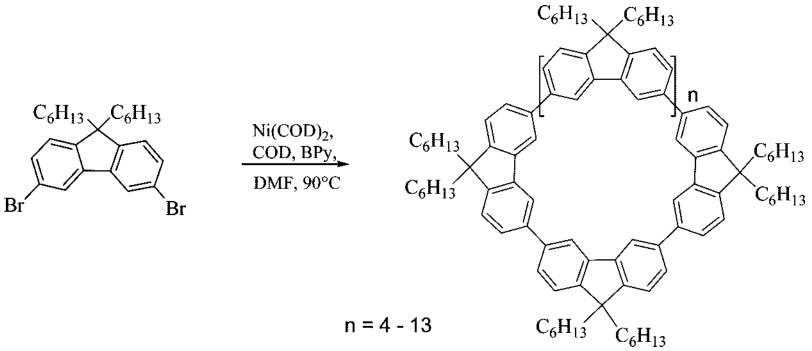


Table 1. Polymerization of Monomer 7 in Toluene/DMF Solutions

entry no.	[**7**], mol/L	[Ni(COD)$_2$]:[**7**]	Tol:DMF	M_w, LS	yield,[a] %	% **8**[b]	% **8**[c]
1	0.01	1.1:1	1:1	2 400	56	12	14
2	0.01	2.2:1	0:1	4 600	83	37	38
3	0.1	2.2:1	0:1	33 000	76	16	15
4	0.1	2.2:1	1:1	18 400	83	24	23
5	0.1	2.2:1	1:4	12 400	82	27	28
6	0.1	2.2:1	4:1	14 500	57	35	33

[a] Isolated yield. [b] Mass percentage of cyclic tetramer **8** in polymer calculated from ^{1}H NMR. [c] Mass percentage of **8** calculated by SEC.

by changing the concentration of **7**, the Ni(COD)$_2$/**7** ratio, and solvent composition (Table 1). ^{1}H and ^{13}C NMR, MADLI-TOF MS, and elemental analysis confirmed the structure and composition of the polymers. As shown in Table 1, the molecular weights of the polymers increase with monomer concentration at a constant Ni(COD)$_2$/**7** ratio. At monomer concentration of 0.01 M (entries 1 and 2, Table 1) mostly oligomers are formed as shown by SEC (Figure 1A). At higher monomer concentrations (entries 3–6, Table 1) higher molecular weight polymers are formed. However, large fractions of oligomers are always present. In particular, a distinct peak is present at an elution volume of 24.5 mL attributable to the cyclic tetramer, **8** (see below). This is usually not the case for polymerization of 2,7-dibromofluorenes, but similar behavior has been observed in polymerization of 3,6-dibromocarbazoles.[34] The MALDI-TOF mass spectrum of a low-MW polymer (entry 2, Table 1) showed an intense signal at *m/z* 1244 and a number of smaller peaks up to *m/z* 4766 (Supporting Information). Higher molecular weights cannot be detected presumably due to lower volatilities. The peaks at *m/z* 1244 and 1436 match the molecular weight of the *macrocyclic* tetramer, **8**, corresponding to [$M^+ - C_6H_{13}$] and [$M^+ + Ag$], respectively. The peaks at 1576–4766 *m/z* are assigned to higher *cyclic* oligomers ($n = 5-13$) as the distance between the adjacent [$M^+ + Ag$] peaks matches the molecular mass of the repeat unit. This shows the presence of macrocycles with degrees of polymerization ranging from $n = 4$ to at least $n = 13$, the cyclic tetramer being the major low-MW product. The formation of higher MW cycles seems plausible, but detection by MALDI-TOF does not allow verifying this.

The efficient formation of the cycles, especially **8**, is consistent with the angles between adjacent fluorene units being close to 90°. The formation of cycles is also consistent with the SEC elution volumes of the oligomers not decreasing with increasing monomer conversions. Furthermore, their fractions remain high (Figure 1A). Interestingly, no low-MW linear chains were detected by MALDI-TOF presumably because of the predominance of the cyclization reactions. However, the presence of higher MW linear polymers cannot be ruled out and seems plausible at higher monomer concentrations.

The cyclic tetramer, **8**, was isolated from the mixture of oligomers by preparative TLC with hexane as eluent. As shown in Figure 1B, the SEC of **8** shows a single peak with an elution volume at 24.5 mL. MALDI-TOF analysis confirmed the composition of **8** (Figure 2). As shown in the figure, the [$M^+ + Ag$] signal of **8** and simulated isotope distribution for the cyclic tetra(9,9-dihexylfluorene-3,6-diyl) (generated with Chem-SW software) match very well.

The ^{1}H NMR of **8** (Figure 3) shows three peaks of equal intensity at 7.44, 7.65, and 8.29 ppm corresponding to the fluorene 1-, 2-, and 4-protons, respectively. In contrast, the ^{1}H NMR of the high-MW unfractionated polymer (entry 4, Table

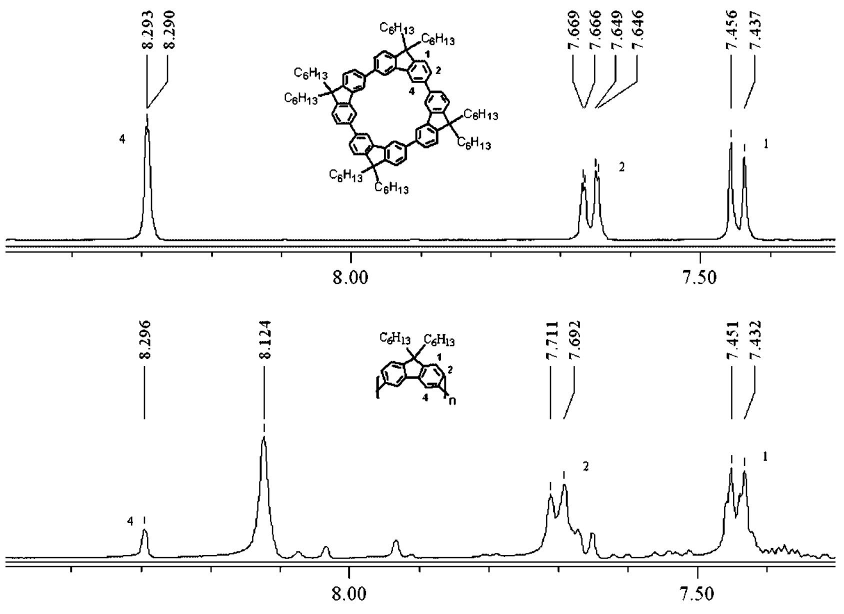


Figure 3. ^{1}H NMR of cyclic tetramer **8** and unfractionated 36PDHF (entry 4, Table 1) in $CDCl_3$.

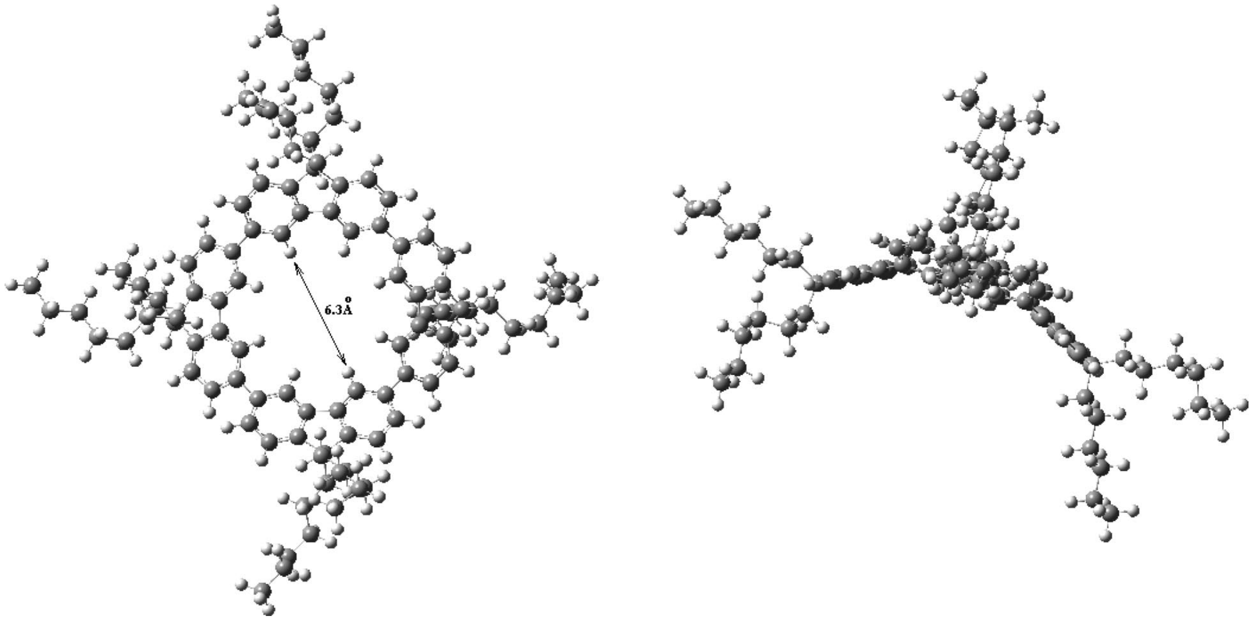


Figure 4. Conformation of **8** obtained by geometry optimization using a B3LYP 6-31G* DFT method.

1) shows three major signals at 7.44, 7.70, and 8.12 ppm and a distinct peak at 8.29 ppm corresponding to the 4-protons of **8** (Figure 3). The downfield shift (0.17 ppm) of the 4-protons of **8** relative to that of the other oligomers/polymers (8.12 ppm) is apparently due to its unique conformation giving deshielding of the 4-protons by the neighboring fluorene groups (consistent with the DFT calculations; see below).This allows the determination of the fractions of **8** in the various polymer mixtures by ^{1}H NMR (between 12 and 37%) (Table 1). The determination of the mass fractions of **8** by SEC is excellent agreement with the NMR data (Table 1). The ^{13}C NMR of **8** is similar to that of higher MW 36PDHF (see Supporting Information).

It should be pointed out that the fraction of tetramer is not especially dependent on chain end concentrations and that of the Ni catalyst. The corresponding oligomerization of 9,9-dihexyl-2,7-dibromofluorene does not appear to form oligomers at all under the above conditions. This is unusual for cyclization reactions.[9]

A geometry optimization of **8** was carried out using a DFT B3LYP method with a 6-31G* basis set as the most widely used method for conformational modeling and for predicting NMR properties.[35–37] Figure 4 shows that **8** is symmetrical (D_{2d} point group) and "saddle"-shaped with alternating positive and negative torsion angles of ±39.55° between adjacent fluorene units. The diameter of the inner cavity is about 6.3 Å. The calculated ^{1}H chemical shifts are in good agreement with the experimental results (Table 2).

Table 2. Calculated and Experimental Chemical Shifts of the Aromatic Protons of 8[38]

proton no.	DFT	expt
1	7.86	7.44
2	7.72	7.65
4	8.36	8.29

All of the 36PDHF's have two absorption bands with the maxima at 262 and 321 nm, irrespective of MW. Interestingly, the extinction coefficient of 36PDHF in DCM solution was determined to be 43 400 L mol^{-1} cm^{-1} per monomer unit—value that is much higher than that of poly-2,7-dihexylfluorene (30 300

L mol^{-1} cm^{-1}).[39] The photoluminescence spectra of 36PDHF's show an emission maxima at 347 nm and a shoulder at 358 nm.[31]

In conclusion, macrocyclic tetra(9,9-dihexylfluorene-3,6-diyl), **8**, and higher MW cyclic homologues with up to 13 fluorene units were synthesized for the first time. The cyclic tetramer was isolated from the 36PDHF polymers as the major low-MW component and characterized by NMR and MALDI-TOF MS. No low-MW linear polymers were detected. This synthesis is unusual in that the fraction of cyclic tetramer in the polymeric products was found to be independent of chain end concentration. The corresponding oligomerization of 9,9-dihexyl-2,7-dibromofluorene shows no such cyclization. Further work will be focused on photochemical and electrochemical properties of **8** and higher MW macrocyclic 36PDHFs and their linear analogues.

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Supporting Information Available: All experimental procedures for monomer synthesis and polymerization; ^{1}H and ^{13}C NMR spectra of compounds **2**−**8** and 36PDHF and MALDI-TOF spectra of **8** and 36PDHF. This material is available free of charge via the Internet at http://pubs.acs.org.

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