



## Synthesis and properties of cyclic ethylene-bridged 3,6-fluorene dimer and its linear analogues

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### ABSTRACT

Three oligomers of ethylene-bridged 3,6-fluorene were synthesized starting from phenanthrenequinone. McMurry reaction was applied to synthesize the cyclic compound. Horner–Emmons reaction was used to synthesize the linear compounds with all-trans configuration. The crystal structure of the cyclic compound was described. The optical and electronic properties of these compounds were fully characterized and compared.

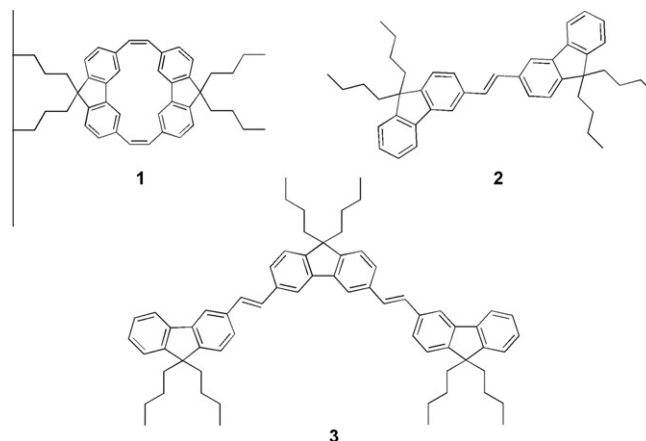
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Recently, conjugated cyclic oligomers have become a topic of growing interest in several fields of research, such as supramolecular chemistry, organic material science, and nanotechnology.<sup>1</sup> The cyclic structure of these compounds represents a defect-free and well-defined  $\pi$ -conjugated chain, which ideally combines an infinite polymer with the structural features of a well-defined oligomer, but without any perturbing end-effects.<sup>2</sup> Our group has focused on the cyclic compounds containing chromophores such as triphenylamine, carbazole, and thiophene.<sup>3</sup> Compared with linear compounds, they always have special electrical and optical properties. The structure–property relationships reveal that the cyclic conformation significantly affects the molecular ordering in the solid state. Importantly, we found that the cyclic compounds always had a reduced reorganization energy compared with the linear compounds.<sup>3</sup> Therefore these results provided useful information for molecular design in the development of novel molecular materials, and also promoted us to design and synthesize more cyclic oligomers and compare the properties with their linear oligomers.

Fluorene-based materials have attracted much attention due to their attractive properties as the active layer in thin film devices, such as organic light-emitting diodes (OLEDs)<sup>4</sup> and organic field effect transistors (OFETs).<sup>5</sup> However, most molecules are based on the fluorene-2,7-diyl structure. Though it is thought that the presence of the 3,6-linkage interrupts an extended  $\pi$ -conjugation and changes the optical properties, there are some new properties in fluorene-3,6-diyl structures. For example, the presence of the 3,6-linkage in polyfluorenes is expected to change its conformation, leading to the formation of more highly bended conformations than in poly(9,9-dialkylfluorene-2,7-diyl) and hence to modify its optical properties.<sup>6</sup> Meanwhile, there are only a few reports on the cyclic compounds based on fluorene units.<sup>7</sup> Furthermore, the

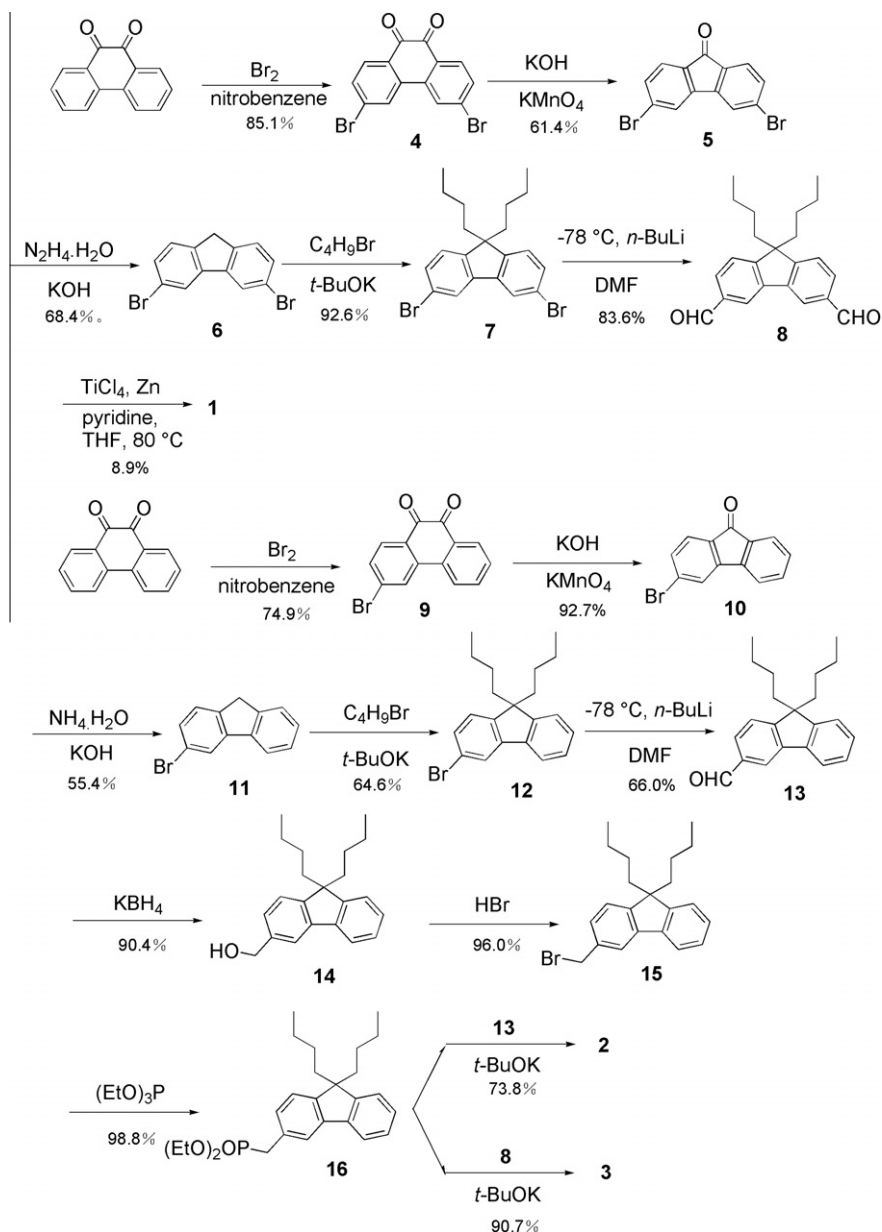
fluorenes were all linked directly in these studies. To the best of our knowledge, ethylene-bridged oligofluorenes are rare.

In this Letter, we presented the synthesis of ethylene-bridged 3,6-fluorene dimer (**1**) and its linear analogues (**2** and **3**). The synthetic strategy for the target compounds is outlined in Scheme 1. McMurry reaction was applied to synthesize the cyclic dimer. Horner–Emmons reaction was used to synthesize the linear compound with all-trans configuration.



It is known that substitution/halogenation at the 3- and 6-positions in fluorene or fluorenone is problematic, because fluorene will be substituted at 2- and 7-positions during direct substitution. It was reported that 3,6-dichlorofluorene can be synthesized from 2,2'-dibromo-5,5' dichlorobiphenylene,<sup>6</sup> but this route was long and complicated. We decided to synthesize 3,6-substituted fluorene from commercially available phenanthrenequinone. Bromination of phenanthrenequinone was carried out according to the reported procedure,<sup>8</sup> and 3,6-dibromophenanthrenequinone (**4**) was obtained in 85.1% isolated yield. Then **4** was converted

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Scheme 1. Synthesis of the target molecules.

to 3,6-dibromofluorenone by  $\text{KMnO}_4$ . It was found that 3,6-dibromofluorenone had very low solubility in common organic solvents, and it was difficult to be purified by column chromatography according to the literature. We found that the crude fluorenone could be used in the next reducing step without further purification, and the fluorene **6** was got in good yield. Alkylation of **6** with 1-bromo-*n*-butane using  $\text{KOtBu}$  as a base gave 3,6-dibromo-9,9-dibutylfluorene in 92.6% yield. Then it was followed by lithiation and reaction with DMF, which afforded the diformyl compound **8** in 83.6% yield. The reaction of 9,9-dibutylfluorene-3,6-dicarbaldehyde with  $\text{TiCl}_4$ , Zn powder, and pyridine in THF at reflux under nitrogen gave **1** in yield of 8.9%.

9,9-Dibutylfluorene-3-carbaldehyde was synthesized by a similar way of compound **8**. In order to prevent cis isomers of linear oligomers, we have synthesized **2** and **3** via Horner–Emmons coupling reactions.<sup>9</sup> It is well known that the Horner–Emmons reaction can form the all-*trans* configuration. The 9,9-dibutylfluorene-3-carbaldehyde was reduced by  $\text{KBH}_4$  to afford compound

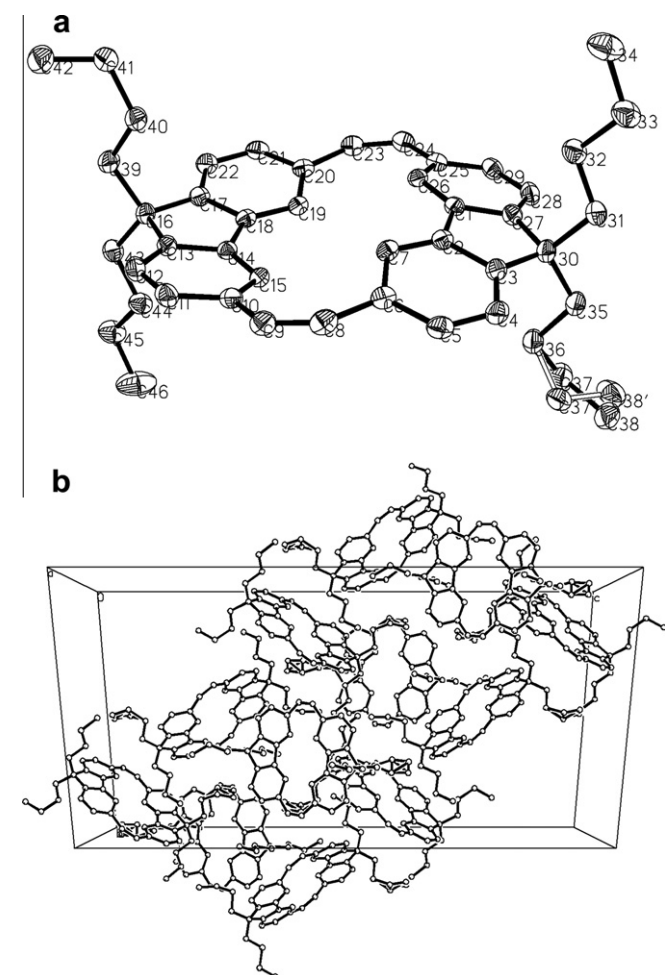
**14**, which was transformed into the bromomethyl derivative using HBr. The Michaelis–Arbuzov reaction of **15** with triethylphosphite yielded 3-ethylphosphonate-9,9-dibutylfluorene. Synthesis of the target compounds **2** and **3** was achieved by reacting compound **16** with aldehydes in the presence of an excess of potassium *tert*-butoxide in tetrahydrofuran at room temperature. The three targeted compounds were all white solids. Compounds **2** and **3** were well soluble in chlorinated solvents and THF, while cyclic compound **1** was less soluble. Their chemical structures were confirmed by  $^1\text{H}$ ,  $^{13}\text{C}$  NMR, and high resolution mass spectrometry (HRMS) analysis.<sup>10</sup>

Single crystals of **1** suitable for X-ray analysis were obtained by slow evaporation of its toluene solution. The crystal belongs to trigonal crystal system and R-3:H space group with unit-cell parameters of  $a = 22.214(5)$ ,  $b = 22.214(5)$ , and  $c = 38.879(9)$  Å. As shown in Figure 1,<sup>11</sup> the asymmetric unit contains one molecule of compound **1**. The main skeleton is not completely coplanar, but in a chair conformation. Because of the powerful tensile force in the

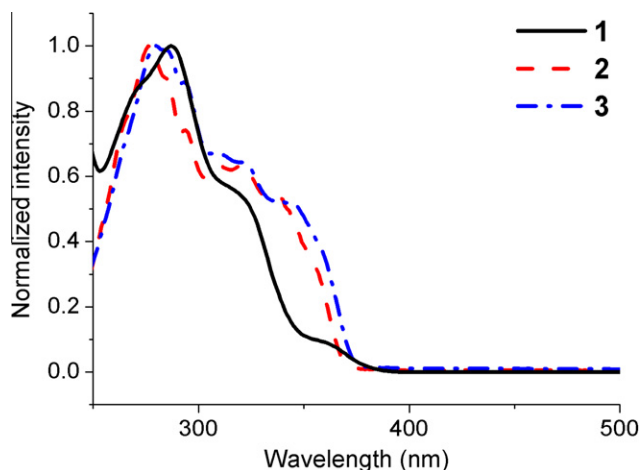
cycle, the fluorene units are even slightly distorted into a non-planar structure. 4-*n*-butyl carbon chains are almost perpendicular to the fluorene plane. From its crystal packing diagram we can see that its crystal packing is more disordered than the triphenylamine and carbazole cyclic dimer we have reported,<sup>3</sup> and there are no  $\pi$  interactions between the adjacent molecules.

The UV–vis spectra of **1–3** in CH<sub>2</sub>Cl<sub>2</sub> solutions are depicted in Figure 2. Their spectra show absorption peaks at 287, 276, and 279 nm, respectively. The absorption peak of cyclic compound **1** is a little red-shifted compared with the linear compound **2**. While their maximum absorption wavelengths (<300 nm) are all less than 2,7-substituted fluorene vinylene oligomers (>350 nm).<sup>12</sup> For the linear compounds, as the number of repeat units increases, the maximum absorption peak shows slightly red-shifted, which is consistent with 2,7-substituted fluorene vinylene dimer and trimer.<sup>12</sup> Like the absorption spectra, the emission band of the cyclic compound compared with linear compounds is red-shifted (Fig. 3).

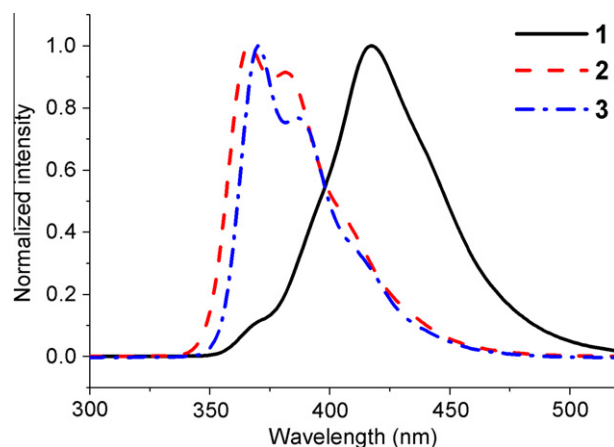
Cyclic voltammetric measurements have been carried out on these compounds (Fig. 4). We used a conventional three-electrode cell with Pt working electrodes, a platinum wire counter electrode, and an Ag/AgCl reference electrode at room temperature. The experiments were calibrated with the ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox system. The HOMO levels could be estimated by using the equation  $\text{HOMO} = -(E_{\text{ox}}^{\text{onset}} + 4.4)$  eV.<sup>13</sup> Therefore, the HOMO levels of **1–3** were estimated by using the oxidation onsets (1.32, 1.26, and 1.24 V for **1**, **2**, and **3**, respectively) and were found to be  $-5.72$ ,  $-5.66$ , and  $-5.64$  eV, respectively. These values were



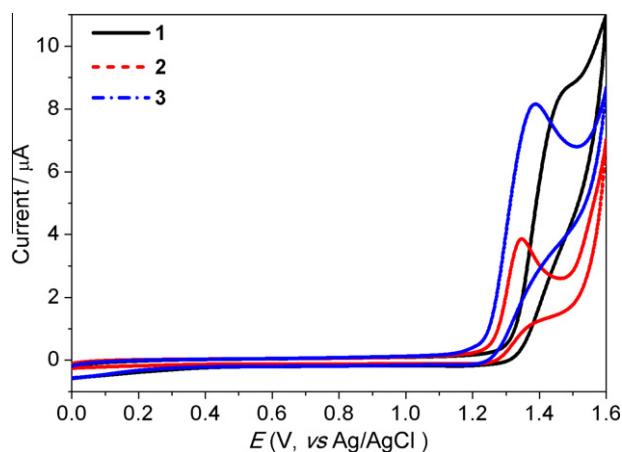
**Figure 1.** (a) Molecular structure of compound **1**. (b) Stacking pattern of **1** in the crystal viewed along the *a*-axis (hydrogen atoms were omitted for clarity).



**Figure 2.** Absorption spectra of **1**, **2**, and **3** in dichloromethane with a concentration of  $10^{-6}$  mol L<sup>-1</sup>.



**Figure 3.** Emission spectra of **1**, **2**, and **3** in dichloromethane with a concentration of  $10^{-6}$  mol L<sup>-1</sup>.



**Figure 4.** Cyclic voltammograms of **1–3** in dichloromethane at room temperature (scan rate =  $50$  mV s<sup>-1</sup>).

all very low, which implies high oxidative stability. Cyclic compound possessed the slight lower HOMO energy level than the linear compounds **2** and **3**.

In conclusion, we have presented a convenient and efficient method for the synthesis of three ethylene-bridged 3,6-fluorene

derivatives using phenanthrenequinone as raw materials. McMurry coupling reaction was used to synthesize a cyclic ethylene-bridged 3,6-fluorene dimer **1**. Horner–Emmons reaction was used for the synthesis of vinyl-fluorene linear oligomers **2** and **3** with all-trans configuration. They were fully characterized by NMR and MS. Single crystals of the cyclic compound **1** were got by solution evaporation method and its structure was analyzed. Their UV–vis absorption spectra, fluorescence spectra, and cyclic voltammetry measurements have been carried out, and all the properties were compared. We believe that the results presented here can provide a lot of opportunities to develop new cyclic compounds, and also find wide applications in new functional materials. The test of their potential use in OFET and OLED is in progress.

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## Supplementary data

Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.tetlet.2010.07.064](https://doi.org/10.1016/j.tetlet.2010.07.064).

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- See Supplementary data.
- X-ray crystal data for **1**. C<sub>46</sub>H<sub>52</sub>, M<sub>r</sub> = 604.88, crystal size: 0.24 × 0.22 × 0.18 mm, trigonal, space group R-3:H, a = 22.214(5) Å, b = 22.214(5) Å, c = 38.879(9) Å, V = 16615(7) Å<sup>3</sup>, Z = 18, T = 113(2) K. 62016 reflections collected, 7282 independent (R<sub>int</sub> = 0.0551), GOF = 1.122; R<sub>1</sub> = 0.0739, wR<sub>2</sub> = 0.1559 (for all reflections). CCDC 774642 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk](http://www.ccdc.cam.ac.uk).
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