Giant Extended π-Conjugated Dendrimers Containing the 10,15-Dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene Chromophore: Synthesis, NMR Behaviors, Optical Properties, and Electroluminescence

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This paper reports the facile synthetic strategy of a series of novel π-conjugated dendrimers (G0 and G1) based on 10,15-dihydro-5H-diindeno[1,2-a;1',2'-c]fluorene (truxene) in which the benzene cores are generated “in-situ” from acetyl aromatics by the acid-promoted cyclotrimerizations. The unique NMR behaviors, physical properties, and electroluminescence device applications are also presented. Besides the purity, the structure, and the confirmation of the successful formation and isolation of desired compounds by clear assignments of every molecule by 1H and 13C and 2D NMR characterizations, several astonishing NMR behaviors have been observed in various solvents. For 1, chemical shift values belonging to H-2′ of hexyl substituents move to the most upfield; however, such chemical shift values move from 0.48 to 0.85 ppm when pyridine-d5 or benzene-d6 is used as solvent. Our dendrimers as the emissive layers in organic light-emitting diodes gave blue-green light with an external quantum efficiency up to 0.16% both for G0 and for G1 in nitrogen, respectively, which exhibit unique electroluminescence spectra in comparison with their corresponding photoluminescence ones.

Introduction

Triggered by their well-defined, unique macromolecular structures and fascinating properties, considerable interest has been devoted recently to the design and synthesis of novel dendrimers and star-shaped molecules.1 In particular, extended π-conjugated dendrimers and star-shaped molecules with definite nanometer sizes and intrinsic stiff nature have been proven to exhibit interesting electrical, optical, nonlinear optical, and electroluminescent properties for applications in electronic and photoelectronic devices including organic light-emitting diodes (OLEDs).2 One of the important challenging goals of dendrimer chemistry is to develop new families of π-conjugated dendrimers with novel branches and cores, to investigate their physical and chemical properties, and to understand the structure–property relationship within such structures.

The convergent approach to these dendritic molecules provides greater structural control, a lower number of reactions at each growth step, and more structural purity and synthetic versatility than their divergent counterparts.1h Recently, several synthetic strategies have been used to construct extended π-conjugated dendrimers.3 However, such methodologies employ the repetition of activation and coupling steps to access target molecules iteratively, which not only requires a massive excess of...
one reactant but also inevitably generates partially substituted byproducts, making the purification troublesome. Moreover, the preparation of giant dendrimers is easily complicated by steric inhibition, resulting in sharply decreased yields. The cyclotrimerization reactions have provided a powerful strategy for the construction of a 1,3,5-trisubstituted benzene moiety or hexasubstituted (tris-annulated) benzenes, which have become important building blocks for the synthesis of bowl-shaped polycyclic aromatic hydrocarbons and the rational synthesis of C60, starburst or star-shaped molecules, shaped polycyclic aromatic hydrocarbons and the ratio-derivatives have been exhibited unique fluroene), oligo(9,9-dialkylfluroene), and ladder-poly(p-phenylene) (LPPP) derivatives have been exhibited unique chemical and physical properties and emerged as the most promising light-emitting materials for organic light-emitting diodes (OLEDs). Recently, we chose 10,15-dihydro-5H-diinden[1,2-a;1′,2′-c]fluorene (truxene) as building block for novel \(\pi\)-conjugated star-shaped molecules and dendrimers (Chart 1). Three fluroene moieties are annulated to afford a unique three-dimensional symmetric truxene moiety by sharing a central benzene ring (Chart 2). Investigation of their photophysical properties would give insight into the effect of delocalization through the benzene core in dendrimers and star-shaped molecules based on polycyclic aromatics. The synthesis and properties of star-shaped oligothiophenes-functionalized truxene derivatives was recently reported. These molecules represented oligothiophenes and were interesting in that they provided a model of interchromophore contacts not only in main-chain polychromophores such as polythiophenes but also in star-shaped \(\pi\)-conjugated molecules. However, a fundamental importance for dendrimers constructed by polycyclic aromatics with \(C_3\) tripods concerns the extent of delocalization for the inter-ring space, since it plays a key role in determining the frequency and efficiency of emission and because it reflects the ability of large fragments to delocalize through the small core.

In this paper, we first investigate the effects of various conditions, such as the concentration of hydrogen chlo-

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Results and Discussion

Reaction Conditions Investigation. Our first strategy was to investigate the effect of the intrinsic solubility of all molecules on the reactions as shown in Scheme 1. In Table 1, the poor solubility of reactants and products resulted in relatively low yields, large amounts of starting materials, and tedious purification procedures (entries 1–6). In contrast, the introduction of two hexyl groups in the fluorene moiety not only greatly elevated the yield of the desired product but also significantly facilitated the isolation procedure (entry 7). Therefore, it provided a strategy to access functional organic materials (especially like polycyclic aromatic hydrocarbons assembly) efficiently and conveniently. We deemed it constructive to extend our studies to a larger moiety with a polycyclic aromatic hydrocarbon framework. The heptacyclic polycyclic truxene moiety, by virtue of its unique three-dimensional topology, is an attractive building motif for use as a potential dendrimer building block. However, the poor solubility and the large steric hindrance rendered the synthesis of these types of dendrimers a challenge. With the strategy presented above, we introduced six hexyl groups onto the C-5, C-10, and C-15 positions of the truxene moiety, which greatly enhanced the solubility and made the subsequent modification at C-2, C-7, C-12 positions by aromatic electrophilic substitution more facile.

However, the cyclotrimerizations of G0 met severe difficulties due to the steric hindrance of the giant truxene moiety at first, which naturally forced us to further study the reaction. Table 2 summarizes the results under the various conditions. Initially, we attempted to afford G0 by literature procedures (entries 1 and 2). Although the addition of toluene could increase the yields of cyclotrimerizations (entry 3), it is far from enough for some target molecules with giant substituted aromatic groups since good intrinsic solubility is a required criteria for both acquiring them and processing them into organic photoelectronic devices.

However, it reminded us that the solubility was not the most significant driving force to get across the steric hindrance barrier. We noticed the TiCl4-dichlorobenzene system developed by Scott, which turned out to be the most powerful strategy to convert 2 into G0 molecule. However, we failed to exclude the dark black impurities from our products by all means of methods (entry 4). We also found it to be a temperature-dependent reaction. When the temperature decreased from 180 to 140 °C, the yield dropped dramatically from quantitative to none, and even the β-methylchalcone was not formed at this temperature (entry 5). It seems that such TiCl4-dichlorobenzene system is more practical to those molecules with poor solubility.

Entry 7 revealed that the concentration of hydrogen chloride played a pivotal role in this reaction. No target compound was obtained when Et3N was added; instead, quite a lot of β-methylchalcone was formed under this condition. Although the synthesis of β-methylchalcone with small aromatic substituents by using 1 equiv of SiCl4 has been reported before, we developed an alternative method to prepare such compounds with giant aromatic substituents efficiently by both increasing the amount.

**TABLE 1. Acid-Promoted Cyclotrimerization of Acetyl Aromatics**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ar</th>
<th>Yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td></td>
<td>32 %a</td>
</tr>
<tr>
<td>2</td>
<td></td>
<td>49 %a</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>49 %a</td>
</tr>
<tr>
<td>4</td>
<td></td>
<td>&lt; 10 %a</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>&lt; 10 %a</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>55 %a</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>87 %a</td>
</tr>
</tbody>
</table>

a After recrystallization. b After flash chromatography. c 5 equiv of SiCl4.

**TABLE 2. Comparison with Conditions of Cyclotrimerizations to Dendrimer G0**

<table>
<thead>
<tr>
<th>Entry</th>
<th>Conditions</th>
<th>Yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HOAc–HCl, 120 °C</td>
<td>NR</td>
</tr>
<tr>
<td>2</td>
<td>SiCl4 (5 equiv), EtOH, reflux</td>
<td>&lt;1</td>
</tr>
<tr>
<td>3</td>
<td>SiCl4 (20 equiv), EtOH-Tol, reflux</td>
<td>23</td>
</tr>
<tr>
<td>4</td>
<td>TiCl4 (1.5 equiv), o-C6H4Cl2, 180 °C</td>
<td>100%</td>
</tr>
<tr>
<td>5</td>
<td>TiCl4 (1.5 equiv), o-C6H4Cl2, 140 °C</td>
<td>NR</td>
</tr>
<tr>
<td>6</td>
<td>SiCl4 (30 equiv), (HOC2H4)2O-Tol, 160 °C</td>
<td>12</td>
</tr>
<tr>
<td>7</td>
<td>SiCl4 (20 equiv), EtOH-Tol, Et3N, reflux</td>
<td>d</td>
</tr>
<tr>
<td>8</td>
<td>SiCl4 (30 equiv), EtOH-Tol, reflux</td>
<td>91</td>
</tr>
</tbody>
</table>

a 24 h. b After purification. c Conversion. d A β-methylchalcone dimer was formed.
of SiCl₄ and addition of Et₃N to eliminate the hydrogen chloride in the system, which forced the reaction staying in the β-methylchalcone intermediate. Finally, we varied the amount of SiCl₄ from 20 to 30 equiv (entry 8), and the yields increased dramatically under this tendency. Encouraged by such results, we decided to expand the scope of this strategy to a more ambitious level. With increasing the amount of SiCl₄ to 100 equiv, we even found astonishing behavior and to better understand the aromaticity, the effective conjugation length, the conformation, and structure of dendrimers, we carried out a more detailed investigation by employing ¹H and ¹³C and 2D NMR techniques. For the purpose of discussion, the carbon atoms and the corresponding hydrogen atoms were numbered the same. The aromatic framework (truxene, fluorene, and benzene moieties) and hexyl side chains were labeled in two numbering systems, starting from 1 and 1′, respectively (as shown in Chart 3).

The truxene and fluorene moieties (1 and 6) were served as models to understand the structure of the dendrimers (Figure 1). It is obvious that chemical shift values belonging to protons of one methylene group for both 1 and 6 moved more upfield. Distinct difference in resonance signals of H-1 was also observed for these two compounds: only one group of multiplet peaks appeared in the structure of some dendrimers, which could be used to help establish the purity of dendrimers as well as to provide an extremely related structural information. In our previous report, we reported that ¹H NMR spectra of 1 and its oligothiophenes-functionalized derivatives in CDCl₃ did not exhibit any change with an increase of the concentration, indicating that the stretching long substituents effectively reduced self-association by arene π–π stacking. More surprisingly, the chemical shifts belonging to methylene groups moved more upfield than those of methyl groups, the values (about 0.5–0.6 ppm!) were considerably lower than those of methyl and other methylene groups. What is more, when we turned to a more extended scope, we found this astonishing behavior has actually also been existed in the extensively investigated 9,9-dialkylfluorene moiety. By contrast with the extensive NMR investigation toward annulenes, these perspective building blocks in materials science receive fairly little attention in this aspect. To shed light on such astonishing behavior and to better understand the aromaticity, the effective conjugation length, the conformation, and structure of dendrimers, we carried out a more detailed investigation by employing ¹H and ¹³C and 2D NMR techniques. For the purpose of discussion, the carbon atoms and the corresponding hydrogen atoms were numbered the same. The aromatic framework (truxene, fluorene, and benzene moieties) and hexyl side chains were labeled in two numbering systems, starting from 1 and 1′, respectively (as shown in Chart 3).

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**NMR Behaviors and Molecular Modeling.** The monodispersity and high symmetry associated with dendrimers have presented numbers of interesting characterization traits and obtained an unprecedented amount of the structural information utilizing advanced characterization techniques. ¹H and ¹³C NMR spectra allowed the identification of every unique proton or carbon atom

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**REFERENCES**


at 1.95 ppm for 6, however, two groups of multiplet peaks exhibited at about 2.97 and 2.05 ppm for 1, respectively. All chemical shift values of H\(^2\)–H\(^6\) in 1 moved to upfield in comparison with those of 6. Meantime, as in G0 and G1, the corresponding values continued slightly moving to downfield and the peaks became broad with the increase of the generation of dendrimers. 2D \(^1\)H–\(^1\)H COSY, \(^1\)H–\(^13\)C HSQC, \(^1\)H–\(^1\)H ROESY, and \(^1\)H–\(^1\)C HMBC results also demonstrated the same results (see the Supporting Information).

To better elucidate these interesting behaviors, the energy-minimized structures of 1 and 6 have been obtained employing the MM2 (MM+) force field optimization, as implemented in HyperChem Pro. 7.0 (Hypercube Inc.) (as shown in Figure 2). Due to the prohibitively large number of atoms in the subsequent dendrimers, a force field method was favored rather than quantum mechanics methods. The conformation of the resulting fluorene moiety (6) is in good agreement with that of the reported crystal structure analysis, in which the all-anti alkyl side chains in 9,9-dialkyfluorene are orthogonally stretched to the fluorene ring plane.\(^{13b-0}\) As a result, it would be safely to assume that the calculated structures of its three-direction analogue truxene moiety (1) and dendrimers (G0 and G1) are as good an approximation as the fluorene model is. The substituted truxene moiety displayed similar side chains conformation as the fluorene segment from the view of the lowest-energy structure calculation. The optimized structure of 1 was also employed to build up its dendrimer derivatives G0, and then the energy-minimized structure of G0 was employed to build up larger dendrimer G1. After rotation around the three bonds connecting the truxene moiety (or the G0 subunit) and central benzene, several conformations were obtained. The conformations with lowest energy for the dendrimers G0 and G1 were shown in Figure 3.

The above \(^1\)H NMR behaviors could be interpreted by traditional ring current model based on the “Pauling–Lonsdale–London \(\pi\)–model”.\(^{15}\) The shielding and deshielding regions are inside or outside the anisotropic cones induced by the intramolecular ring currents in our aromatic frameworks, either the truxene moiety or the fluorene moiety. The shielding effect vanishes with increasing distance from the ring along the molecular axis. As shown in Figure 2, all hexyl substituents in 1 and 6 are almost perpendicularly attached to the aromatic ring plane, and the H-2′ suffered the most severe upfield shift because they were situated in the shielding cone of the aromatic ring. Since the shielding effect decreased with increasing distance from the ring along the molecular axis, the H-4′ signals shifted downfield in comparison with those of H-2′. Likewise, due to the shielding effect difference between their locations, the H-2′, H-4′, and H-6′ were more shielded than corresponding H-1′, H-3′, and H-5′, respectively. The different H-1′ signals of 1 and 6 could be ascribed to the different chemical environment surrounding them.

With these data in hand, to further understand the relationship between the NMR and the structure and also to investigate the effect of the hexyl substituents on the conformation of the whole molecule, we investigated the \(^1\)H and \(^13\)C NMR behaviors by varying the solvents. When the solvent was changed from CDCl\(_3\) to pyridine-d\(_5\) or benzene-d\(_6\), we observed that chemical shift values of all protons at hexyl substituents moved to downfield, especially abnormal chemical shift ones of H-2′ moved to the downfield from 0.48 to 0.75 ppm, and chemical shift ones of methyl groups also moved about 0.05 ppm. Figure 7 presents the comparison of the \(^1\)H NMR spectra of 1 in different solvents (as shown in Figure 4). The similar behavior was also observed for the \(^1\)H NMR spectra of 6 (see the Supporting Information).

Although the polar CDCl\(_3\) molecule can have electrostatic interactions with a polar substrate, it can only interact with nonpolar molecules 1 or 6 through van der Waals forces and had a minimal effect on the chemical shift value. On the other hand, the disklike benzene or pyridine molecule possessed large diamagnetic anisotropy, hence resulting in an upfield shift (decrease of chemical shift value). We assumed that the disklike

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**FIGURE 1.** \(^1\)H NMR spectra of (A) 6, (B) 1, (C) G0, and (D) G1 at aliphatic regions in CDCl\(_3\).
aromatic solvent molecules interacted with the substrate by \( \pi-\pi \) stacking. As a consequence, the H-2' and some other protons were exposed to the deshielding regions of the solvent molecules, which would attenuate the shielding effect from the substrate aromatic frameworks. It is well-known that the accidentally overlapping resonance

**FIGURE 2.** Lowest energy calculated structures of the front (a) and side view (b) for 1 and of the front view for 6 (c).

**FIGURE 3.** Lowest energy calculated structure for G0 (a) and G1 (b).
of chemically different nuclei is usually separated by using a different solvent.

Optical Properties. The absorption spectra for 1, G0, and G1 in THF solutions are shown in Figure 5. Normally, \( \pi \)-conjugated dendrimers show a very strong \( \pi-\pi^* \) electron absorption band in the UV-vis region, which progressively red-shifted with increase of effective conjugation length. From absorption spectra in Figure 5, we observed that absorption \( \lambda_{\text{max}} \) (309 nm for G0 and 310 nm for G1, respectively) exhibited a small red-shift with the increase of the truxene moiety and of the generation of the dendrimer in comparison with that of 1 (307 nm) by virtue of the large molar extinction coefficients \( (\varepsilon > 10^5 \text{ M}^{-1} \text{ cm}^{-1}) \). However, absorption spectra showed very strong shoulder peaks at 320 nm for G0 and 330 nm for G1, respectively, while the intensity of such peak of G1 was higher than that of G0.

We also observed that onsets of absorption spectra were obviously red-shifted from 1 to G1. The absorption \( \lambda_{\text{max}} \) for these compounds might belong to the \( \pi-\pi^* \) electron absorption band of the truxene skeleton, and we did not observe the very obvious \( \pi-\pi^* \) delocalization with the increase of the truxene moiety, which was owing to the large torsion angle between the benzene ring and the truxene system caused by three giant truxene skeletons at one smaller benzene ring. However, the intensity of shoulder peaks augmented from G0 to G1, which suggested that the relative delocalization might be promoted with an increase of the generation of dendrimers.

The optical absorptions of 1, G0, and G1 in the solid states are shown in Figure 6. The structured absorption bands observed in solution were also exhibited in the solid states. However, absorption peaks on the solid state were slightly red-shifted to their corresponding ones in solution. The similarity of absorption spectra shape on the solution and the solid state in these molecules suggested that there was a slight increase in conjugation length in the solid state, which indicated that the \( \pi \)-stacking in solid state was significantly reduced due to the giant truxene moiety and also because of the large torsion angle between the truxene group and the phenyl group. The intensity of shoulder peaks augmented from
G0 to G1, which suggested that the relative delocalization might be promoted with an increase of the generation of dendrimers. The photoluminescence (PL) spectra of G0, G1, and G2 in dilute solution (5 x 10^-5 M) are also shown in Figure 5. All compounds have structured emission peaks. If the 0-0 transitions in the emission and corresponding absorption peaks were considered, the Stoke shift is small for these three compounds. In dilute solutions, no emission light was observed because the emission light of these three compounds was in the UV range. The PL spectra of G0, G1, and G2 in solid states are shown in Figure 6. In addition of their broad featureless characteristics, the emission spectra of these three compounds in the solid states slightly red-shifted from the dilute solution ones, which also indicated the decreased ð-stacking in these molecules.

Organic Light-Emitting Properties. Some conjugated dendrimers have been used successively as charge-transporting layer in OLEDs due to their good charge-transporting characteristics and the fact that they can form stable amorphous films. We fabricated organic light-emitting diodes (OLEDs) from G0 and G1 as the emissive layer. Preliminary results on intrinsic electroluminescence (EL) of these dendrimers is first presented and discussed. Device configuration was: ITO/PEDOT/G0 or G1/Ba/Al. Both the dendrimers emitted blue-green color at a forward bias (ITO wired positively) above 8 V. A typical curve of light intensity versus bias (L-V) is given in Figure 7. The external quantum efficiencies for G1 and G2 are compared in Figure 8. The external quantum efficiency (QE) was measure to be 0.16% at 27 V for G0 and 0.16% at 13 V for G1, respectively. The EL spectra are also illustrated in Figure 9. In comparison with PL spectra in solid states (in Figure 6), it is obvious that EL emission is significantly red-shifted compared to that of PL spectra due to the formation of ketonic defects in the device processing. The further improvement of the LED efficiency of these dendrimers can be achieved by modification of dendrimer/electrode interface in order to enhance and balance the electron and hole injection. The corresponding studies are in progress.

Conclusions
In conclusion, we have demonstrated a convenient and highly efficient convergent approach for the synthesis of a new family of large-size and precisely well-defined dendrimers and star-shaped molecules via “in-situ” generation of benzene core from aryl methyl ketones by acid-promoted cyclotrimerization reactions. We also have investigated their photophysical and electroluminescence. We have developed a platform to synthesize a new family of dendrimers utilizing giant polycyclic aromatics, further investigation toward the formation of hexasubstituted (briannulated) benzenoids using this strategy to create novel nonalternant polycyclic aromatic hydrocarbons containing alternating five- and six-membered rings are in progress. The unique NMR behaviors have exhibited

that the chemical shifts of the H-2′ of hexyl substituents move to the most upfield (0.48 ppm). The lowest energy calculations of the structure have proved that this methylene group is on the top of the shielding cone of polycyclic aromatic rings. The photoproperties of such dendrimers indicate that the large torsion angle between the giant truxene moiety and the benzene ring might affect full π-delocalization of the whole molecule. We have developed a platform to synthesize a new family of dendrimers utilizing giant polycyclic aromatics and to understand photophysical and electroluminescence properties of polycyclic dendrimers through the investigation of such dendrimers. The basic investigations with these macromolecules would provide novel insights and directions for the uses of novel extend π-conjugated dendrimers based on truxene in organic materials science. We expect that further investigation could also be devoted to the synthesis and characterization of nonalternating polycyclic aromatics.

Experimental Section

Basic Characterization. The NMR spectra were recorded at 298 K on a spectrometer operating at frequencies of 499.89 MHz (1H) and 125.71 MHz (13C) in CDCl3, pyridine-d5, and benzene-d6 with concentrations of ~15 mg per 600 ìL of solvent. Chemical shifts δ (ppm) were referenced to internal Me4Si (TMS) for 1H and solvent peaks for 13C. Two-dimensional gradient-selected COSY (homonuclear correlated spectroscopy), HSQC (heteronuclear single quantum coherence), HMBC (heteronuclear multiple bond coherence), and ROESY (rotational NOE spectroscopy) experiments were performed using standard pulse sequences.

Device Fabrication and Characterization. LED was fabricated on pre-patterned indium–tin oxide (ITO) with sheet resistance 10–20Ωsq. The substrate was ultrasonically cleaned with acetone, detergent, deionized water, and 2-propanol. Oxygen plasma treatment was made for 10 min as the final step of substrate cleaning.

External quantum efficiency was verified by the measurement of the integrating sphere, and luminance was calibrated after the encapsulation of devices with UV-curing epoxy and thin cover glass.

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Supporting Information Available: Complete experimental procedures; full characterization of all new compounds; NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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