Synthesis of Novel Carbazole Dendrimers Having a Metal Coordination Site

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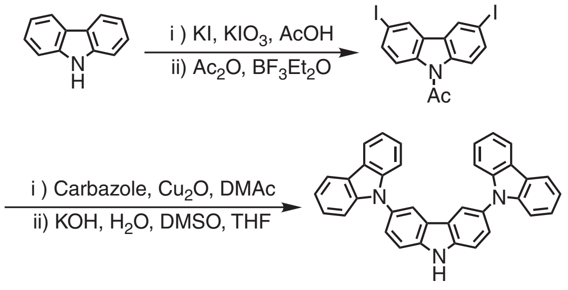
(Received April 11, 2003; CL-030313)

We have synthesized novel carbazole dendrimers via cyclotrimerization. This synthetic procedure to prepare the dendrimers, especially with a higher generation, via the cyclization reaction was found to be an extremely effective method. These dendrimers have the ability to assemble metal ions such as Sn^{2+} and Eu^{3+}, resulting in a change in its fluorescence property.

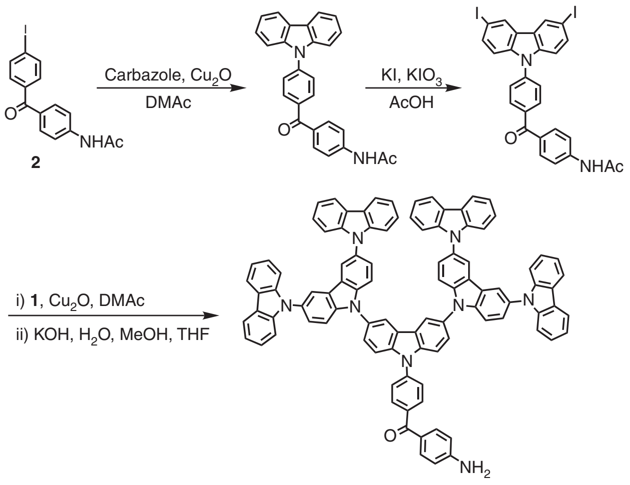
Discrete triphenylamine arrays based on linear,[1] cyclic,[2] and dendritic[3–5] systems with a conjugated backbone have attractive magnetic and electronic properties. Also, acting as hole-transport materials in various electro-optical applications, for example, electroluminescent devices[6] and photocells,[7] branched and dendritic structures exhibit a better amorphous property and high solubility because of the geometry of these molecules without close packing. From a synthetic viewpoint, carbazole analogous to the triphenylamine backbone can be easily functionalized at its 3-, 6-, and 9-positions and covalently linked to other molecular moieties.[8] As a result of its special photo, electrical, and chemical properties, carbazole has been used as a functional building block in the fabrication of organic photoconductors, nonlinear optical materials, and photorefractive materials. Azomethines, imines, or Schiff bases are well-known to be a strong coordination site for various metal assembling which results in electrochemical and/or photochemical properties as well as polyaniline. We now report the synthesis of novel carbazole dendrimers via the cyclotrimerization. These dendrimers have a phenylazomethine core as the metal coordination site, and the spectral change results in change in the degree of energy transfer.

The G2 dendron, that is, the carbazole trimer was obtained by the combination of the iodination,[9] acetylation, and the modified Ullmann condensation[10] (Scheme 1). We adopted the acetyl group for protection of the amines. This is due to the high thermal stability of the amide bond compared with the Boc (*tert*-butoxycarbonyl) group that is a traditional protecting group of amines. The cyclization monomers were obtained from 4-acetylamino-4′-iodobenzophenone **2** using the same reactions. The G1 and G2 monomers were simply synthesized from **2**, and carbazole or **1** via the Ullmann condensation. However, the synthesis of the G3 monomer was carried out with a route like a double stage convergent method as shown in Scheme 2. This is due to the decreased reactivity of the amine site at the G3 dendron, which can be synthesized by the same reactions as the G2 dendron.



1, G2 Dendron

Scheme 1. Synthesis of the G2 dendron.



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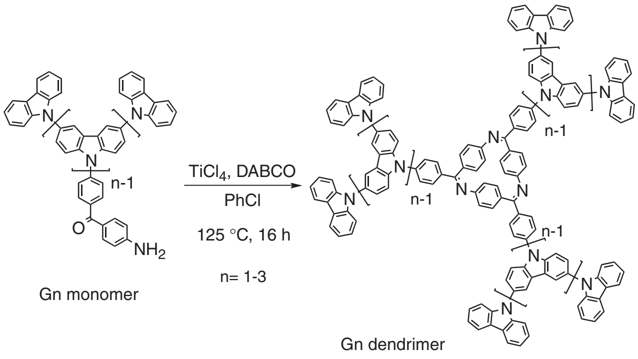
G3 Monomer

Scheme 2. Synthesis of the G3 monomer.

The G1, G2, and G3 carbazole dendrimers were synthesized via the cyclotrimerization of the corresponding monomers in the presence of titanium (IV) tetrachloride (0.75 equiv.) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (1.5 equiv.) in 30, 56, and 95% yields, respectively (Scheme 3).[11] As a conventional synthetic technique to prepare the dendrimers, the convergent



Scheme 3. Synthesis of the dendrimers via the cyclotrimerization.

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method results in a lower conversion yield with increasing the generation due to their steric hindrance of the bulky dendrons with a small core.[12] We developed a useful synthetic method for preparative dendrimer formation in which the core is generated from a dendritic precursor by a cyclization reaction.[13] We have already reported that aminophenylketones such as 4-aminoacetophenone produce only the corresponding linear polymer; however, the reaction of the 4-aminobenzophenone derivatives provides the formation of cyclic phenylazomethines in high yield owing to the steric hindrance of the bulky α-phenyl ring in the monomer.[14] Thus, this synthetic procedure to prepare dendrimers, especially with a higher generation, via the cyclization reaction was found to be an extremely effective method.

The UV–vis spectra of the dendrimers show the absorption bands at 300–425 nm (λ_{max}; 343 nm) attributed to the π-π* transition of the cyclic phenylazomethine unit at the core and at 225–350 nm (λ_{max}; 294 nm) of the dendritic polycarbazole moiety. No significant red shifts in the absorption were observed. This means that the degree of π delocalization is limited.[15] The absorption attributed to the carbazole unit proportionally intensifies as the number of carbazole units with the growth of their generation number, even though the absorption attributed to their core unit does not change. This localization is caused by the loss of coplanarity of the aromatic systems due to the twists in the polycarbazole dendrons at the 3 and 6 positions. The MM2 calculation also supported the fact that they are twisted by 36.3 degrees between the carbazole units. These dendrimers are expected to come close to the sphere-like structure with higher generations.

The dendrimers have 3 C=N units as a core. With the addition of $SnCl_2$ or $Eu(OTf)_3$ to the dichloromethane–acetonitrile (4:1) solution of the dendrimer (G3), the yellow solution (λ_{max}; 343 nm) changed to light orange (λ_{max}; 425 nm) based on the complexation. The UV spectrum changed with an isosbestic point at 371 nm (Figure 1, Scheme 4). The complexation proceeds at random and the imine groups act as an excellent coordination site.[16] The equilibrium constants of the formation of 1:1 complexes with $SnCl_2$ on the imine sites were estimated to be $K = 5 \times 10^5$ (M^{-1}) which was not influenced by the generations. Similar complexations with $Eu(OTf)_3$ were confirmed. These results indicate that these dendrimers have the ability to assemble metal ions with no steric effects among the carbazole dendrons and the HOMO and LUMO energy levels change by the complexation, which results in the red shift of the spectra.

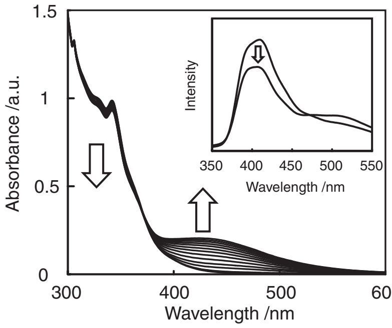
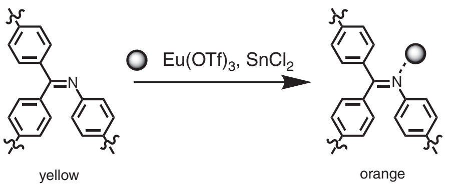


Figure 1. UV-visible spectra of G3 dendrimer during complexation with $SnCl_2$ (4:1 dichloromethane–acetonitrile, at room temperature). The inset shows the change of the fluorescence spectra by the complexation.



Scheme 4. Formation of the imine-metal complex.

The photoluminescence spectra showed emission from the carbazole moieties that were quenched by the Förster type energy transfer to the imine unit. When complexing with metals, a lower fluorescence intensity was observed on the basis of the change of the UV–vis spectra. The larger spectral overlap between fluorescence from the dendrimer and the absorption attributed to the π-π* transition at 400–500 nm (λ_{max}; 425 nm) of the phenylazomethine–metal unit resulted in a higher quenching and less fluorescence at 370–500 nm (λ_{em}; 408 nm) (Figure 1, inset). This phenomenon suggests that a spectral overlap and the degree of energy transfer can be controlled by the complexation.

In summary, we have synthesized novel carbazole dendrimers via cyclotrimerization. These dendrimers have the ability to trap metal ions such as Sn^{2+} and Eu^{3+} and their complexation results in a spectral overlap. The degree of energy transfer can be controlled by the complexation. A development study about hole-transport in organic electroluminescence devices is now in progress.

This work was supported by a Kanagawa Academy Science and Technology Research Grant (project No. 23) and Grant-in-Aid for the 21st Century COE program "KEIO Life Conjugate Chemistry" from the Ministry of Education, Culture, Sports, Science, and Technology, Japan.

References and Notes

1 F. E. Goodson, S. I. Hauck, and J. F. Hartwig, *J. Am. Chem. Soc.*, **121**, 7527 (1999).
2 T. D. Selby and S. C. Blackstock, *Org. Lett.*, **1**, 2053 (1999).
3 J. Louie and J. F. Hartwig, *J. Am. Chem. Soc.*, **119**, 11695 (1997).
4 T. D. Selby and S. C. Blackstock, *J. Am. Chem. Soc.*, **120**, 12155 (1998).
5 M. I. Ranasinghe, O. P. Varnavski, J. Pawlas, S. I. Hauck, J. Louie, J. F. Hartwig, and T. Goodson, III, *J. Am. Chem. Soc.*, **124**, 6520 (2002).
6 C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, **51**, 913 (1987).
7 U. Bach, D. Lupo, P. Comte, J. E. Moser, F. Weissörtel, J. Salbeck, H. Spreitzer, and M. Grätzel, *Nature*, **395**, 583 (1998).
8 J. A. Joule, *Adv. Heterocycl. Chem.*, **35**, 83 (1984).
9 S. H. Tucker, *J. Chem. Soc.*, **1926**, 546.
10 R. G. R. Bacon and D. J. Maitland, *J. Chem. Soc. C*, **1970**, 1973.
11 G3 dendrimer; ^1H NMR (400 MHz, $CDCl_3$, TMS standard, 30 °C, ppm): δ 8.52 (m, 168H), 6.75 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$, TMS standard, 30 °C, ppm): δ 170.15, 152.72, 141.64, 141.40, 140.63, 140.35, 139.47, 137.74, 135.60, 131.16, 130.18, 130.01, 129.46, 128.13, 126.46, 126.22, 125.78, 125.43, 124.34, 123.69, 123.60, 123.01, 120.21, 119.60, 111.71, 111.13, 109.57. TOF-MS: 4009.6 ($[M + H]^+$ calcd for $C_{291}H_{174}N_{24}$: 4003.4). UV(chloroform) λ_{max}, nm(ε): 294 (12100), 343 (13200).
12 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, **112**, 7638 (1990).
13 M. Higuchi, H. Kanazawa, M. Tsuruta, and K. Yamamoto, *Macromolecules*, **34**, 8847 (2001).
14 M. Higuchi, A. Kimoto, S. Shiki, and K. Yamamoto, *J. Org. Chem.*, **65**, 5680 (2000).
15 Z. Zhu and J. S. Moore, *J. Org. Chem.*, **65**, 116 (2000).
16 K. Yamamoto, M. Higuchi, S. Shiki, M. Tsuruta, and H. Chiba, *Nature*, **415**, 509 (2002).

Published on the web (Advance View) July 7, 2003; DOI 10.1246/cl.2003.674