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Highly luminescent glycocluster: silole-core carbosilane dendrimer having peripheral globotriaose

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Abstract—A novel glycocluster periphery functionalized by globotriaose (Galα1–4Galβ1–4Glcβ1–) possessing a silole moiety as a luminophor was synthesized. The photoluminescence spectrum of the glycocluster in pure water showed extremely strong emission at 475 nm. Analogous intense emission of the silole dendrimer was also observed in a lower water fraction of water/acetone mixture. The water fraction of the silole dendrimer solution strongly affected the emission intensity; however, these luminescences were constantly detected at around 475 nm.

Carbohydrate–protein interactions are of paramount importance in the cell adhesion process. It is known that the clustering effect of carbohydrates increases the individual interactions between carbohydrates and proteins.[1] Today, the effect has been often applied for the molecular design of artificial inhibitors of toxins, bacteria, and viruses, and several forms of glycoclusters have been developed.[2] We recently reported syntheses of glycoclusters in which carbosilane dendrimers were employed as the scaffolds of carbohydrates[3] and the biological activities of some of these glycoclusters.[4] For example, a carbosilane dendrimer having peripheral globotriaose (Gb_3: Galα1–4 Galβ1–4Glcβ1–) neutralized Vero toxins produced by *Escherichia coli* O157:H7 with high affinity in in vivo experiments using mice.[5] In the course of our investigation on glycoclusters, we became interested in the synthesis of a novel carbohydrate scaffold possessing a luminophor.

Much interest has recently been shown in siloles (silacyclopentadienes) because of their unique optical and electronic properties and their potential applications in organic electroluminescent devices.[6] These properties can be attributed to the low-lying LUMO level associated with the σ^*–π^* conjugation arising from the interaction between the σ^* orbital of the silicon atom and π^* orbital of the butadiene moiety.[7] In this Letter, we report the first synthesis of a luminescent glycocluster containing a silole moiety as a luminophor and its unique optical properties in aqueous solution.

The silole core **2**, 1,1-diallyl-2,3,4,5-tetraphenylsilole, was synthesized via a known intermediate **1**[8] in 50% overall yield from 1,2-diphenylacetylene as shown in Scheme 1. Hydrosilation of **2** with trichlorosilane using $H_2PtCl_6 \cdot 6H_2O$ as a catalyst and the succeeding Grignard reaction with allyl magnesium bromide provided the first generation of silole-core dendrimer **3** in 74% yield. The resulting dendrimer **3** was treated with dicyclohexylborane followed by hydrolysis with hydrogen peroxide in alkaline solution to afford a hexahydroxy derivative **4** (64%), which further underwent successively O-mesylation and replacement with bromo anions, giving **5** in 67% yield (2 steps). Although hydrosilation and hydroboration of the butadiene moieties in **2** and **3**, respectively, were suspected in this synthetic strategy, these reactions regioselectively took place at the expected terminal olefins under such reaction conditions Scheme 2.

Coupling reaction between the silole-core dendrimer **5** and a peracetylated globotriaose derivative **6**[3f] was

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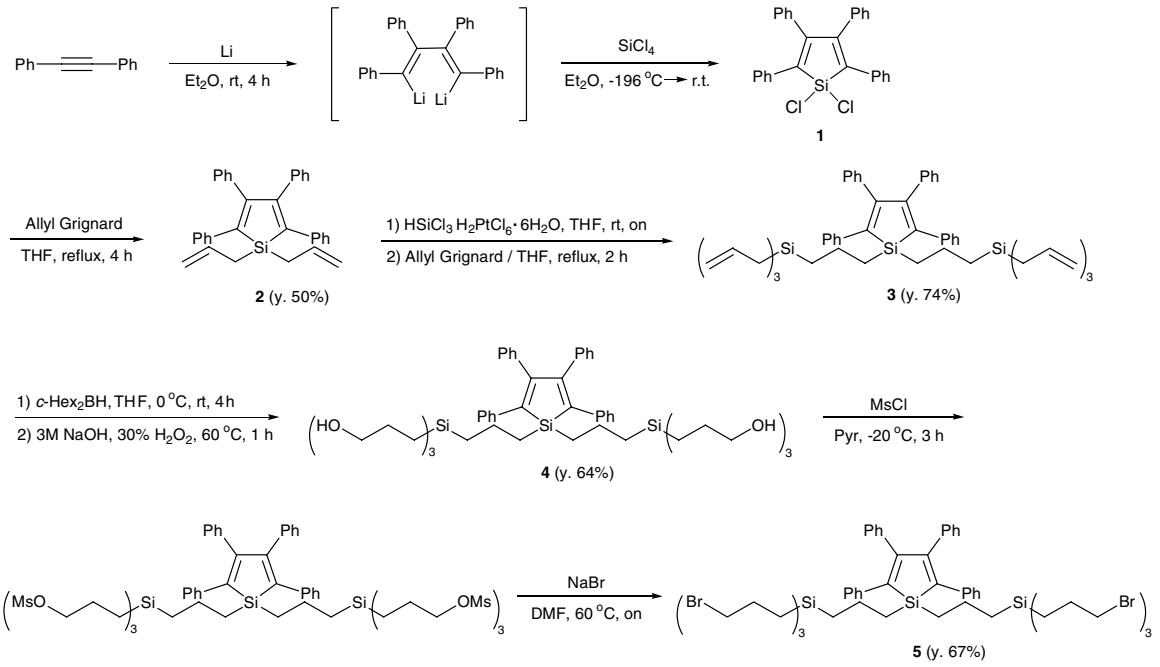
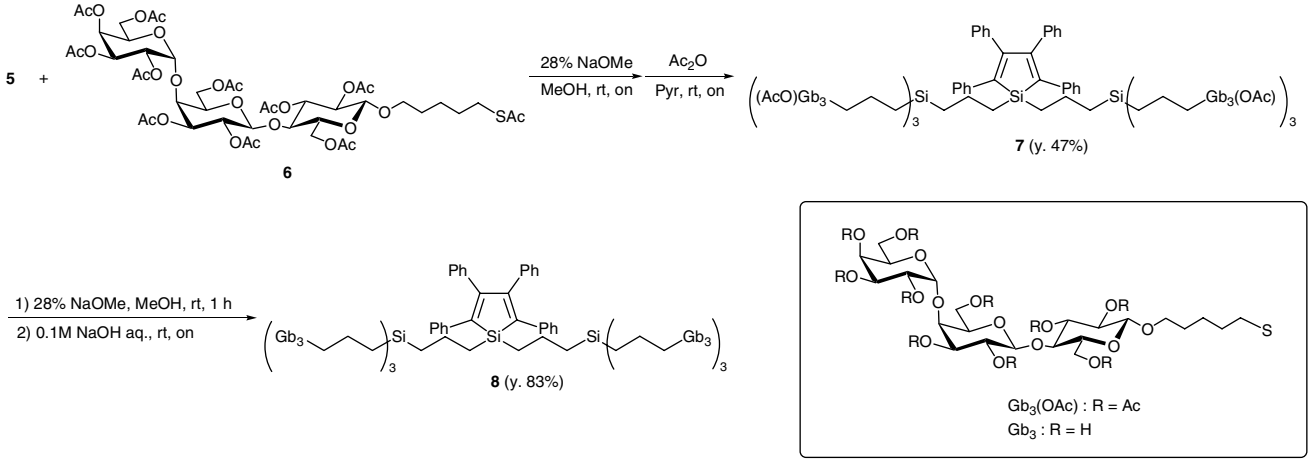


Scheme 1.



Scheme 2.

achieved by nucleophilic substitution of the terminal bromide on the dendrimer **5** with a thiolate anion generated from **6** by treatment with sodium methoxide in methanol.[9] Since a part of the acetyl protecting group was deprotected under such reaction conditions, the resulting products were re-protected by the reaction with acetic anhydride in pyridine for purification. After purification by means of recycling GPC, the silole-core glycocluster **7** fully substituted by globotriaose was obtained in 47% yield. Then the glycocluster **7** was deprotected by a combination of Zemplén's condition and saponification to afford the corresponding silole-core dendrimer **8** (83%), the structure of which was confirmed by NMR, UV–vis, and PL spectra, and MALDI-TOF mass spectrometry.[10] It should be noted that the glycocluster **8** obtained is not only the first glycocluster possessing a luminophor but also the first hydrophilic silole derivative.[11]

A photoluminescence spectrum of the synthesized silole-dendrimer **8** measured in water is shown in Figure 1 together with photoluminescence spectra of representative hydrophobic silole-dendrimers **5** and **7** for comparison. Although all of these silole dendrimers have an emission band at around 475 nm from the silole moieties, the hydrophilic dendrimer **8** displayed remarkably strong emission in sharp contrast to hydrophobic dendrimers **5** and **7** measured in chloroform. Extremely bright blue luminescence from dendrimer **8** in water is shown in Figure 2. The difference between the emission intensity of hydrophilic dendrimer **8** and emission intensities of hydrophobic dendrimers **5** and **7** might be attributable

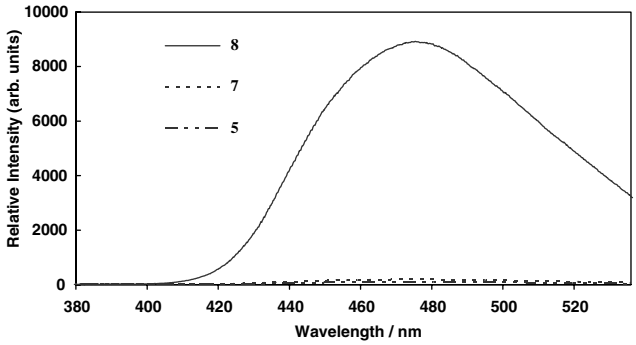


Figure 1. PL spectra of silole-dendrimers **5** and **7** (in chloroform), and **8** (in water) at room temperature. Concentration: 10 μM; excitation: 360 nm.

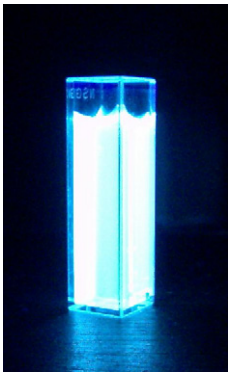


Figure 2. Photoluminescence of silole-dendrimer **8** in pure water at room temperature. Concentration: 1 mM; excitation: 360 nm.

to their molecular aggregation form in each solvent. Tang and co-workers recently reported aggregation-induced emission (AIE) phenomena of a hydrophobic simple silole molecule in an ethanol/water mixture whose emission intensity was significantly enhanced by increasing the water fraction above 50%.[12] Analogous AIE phenomena of some hydrophobic siloles also have been observed in aqueous solutions.[13]

Next, we examined the dependence of the emission intensity of the hydrophilic dendrimer **8** on solvent composition using water/acetone mixture. The PL spectra of **8** are shown in Figure 3a (water fractions of 100–70%) and Figure 3b (20–1%), and these emission intensities vs water fraction in the solutions are plotted in Figure 4. In the range of 70 to 100% of water fraction, emission intensity was enhanced by increasing the water fraction in analogy with cases of previously reported hydrophobic siloles (Fig. 3a). Surprisingly, similar strong emission from **8** was also observed in the case of water fraction of less than 20%, and the intensity increased in inverse proportion to the water content in the solution as shown in Figure 3b. Consequently, silole **8** showed extremely intense emission in 100 and 1% water fractions, the highest and lowest water contents under the experimental conditions (Fig. 4). The fluorescence quantum yields (Φ_{FL}) in 100%, 50%, and 2% water fractions were estimated to be 0.65, 0.059, and 0.37, respectively. These results reveal that the water fraction of the solution has a significant

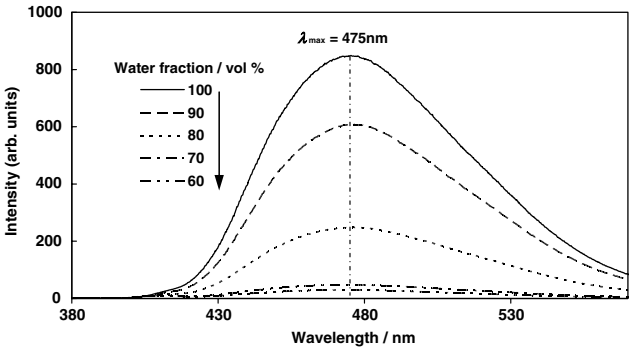


Figure 3a. PL spectra of silole-dendrimer **8** in water and water/acetone mixture with 90%, 80%, 70%, and 60% water fractions. Concentration: 1 μM; excitation: 360 nm.

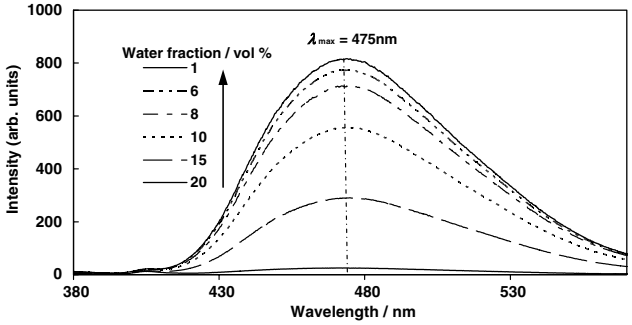


Figure 3b. PL spectra of silole-dendrimer **8** in water/acetone mixture with 1%, 6%, 8%, 10%, 15%, and 20% water fractions. Concentration: 1 μM; excitation: 360 nm.

influence on the emission intensity of **8**. Interestingly, however, the water fraction had little effect on luminescence wavelength from silole **8**, and PL spectra of silole **8** were constantly detected at around 475 nm (Fig. 3a and 3b). The hydrophilic silole **8** in water/acetone mixture showed different emission behavior than the behavior of hydrophobic siloles previously reported AIE effect.[12,13]

In the ^{1}H NMR spectrum of **8** in D_2O at 298 K broad signals were observed, whereas in a mixture of D_2O/acetone-d_8 (50/50) the relatively sharp signals compared with the signals in D_2O were detected at the same temperature. In general, NMR spectrum of a compound aggregated in a solution shows broadening signal due to sluggish exchange on NMR time scale and increasing

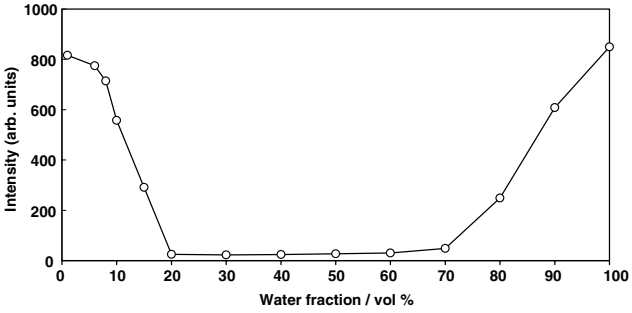


Figure 4. Emission intensity of **8** vs solvent composition of the water/acetone mixture.

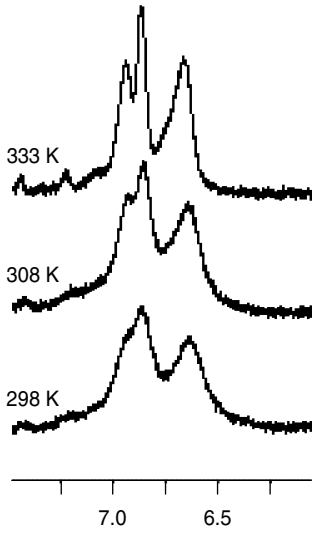


Figure 5. Variable temperature ^{1}H NMR spectra of **8** in D_2O.

of the measurement temperature transform the peak shape from broad to sharp.

The aromatic proton signals of **8** measured in D_2O at between 298 K and 333 K are shown in Figure 5. The broadening signals observed at 298 K progressively lead to sharp signals with increasing of the temperature. These NMR studies reveal that faster exchange of silole-dendrimer **8** in the state of aggregation is caused by raising temperature. Analogous NMR experiment of **8** in lower water fraction of D_2O/acetone-d_8 (2/98) mixture failed because of the poor solubility.

Although account for the intense emission of **8** in the lower water fraction solutions has remained uncertain so far, we speculate that the silole moieties of **8** aggregate in a solution with the higher water fractions from the results of variable temperature ^{1}H NMR studies. Further investigations on elucidation of intense luminescence of **8** in the lower water fractions and the application to a visualization of pathogens are currently in progress.

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10. Silole-core dendrimer **8**; δ_H (400 MHz; D_2O; HDO) 0.20–0.75(br, 16H, 8 × SiCH_2), 1.18–1.89 (br, 56H, 2 × SiCH_2-CH_2, 6 × SiCH$_2$CH_2, 6 × SCH$_2$CH_2CH_2CH_2), 2.22–2.71 (br, 24H, 6 × CH_2SCH_2), 3.28–3.31 (br, 6H, 6 × H-2), 3.57–4.49 (br, 124H, 6 × CH_2O, 6 × H-1, 6 × H-3, 6 × H-4, 6 × H-5, 6 × H-6ab, 6 × H-1′, 6 × H-2′, 6 × H-3′, 6 × H-4′, 6 × H-5′, 6 × H-6′ ab, 6 × H-2″, 6 × H-3″, 6 × H-4″, 6 × H-5″, 6 × H-6″ ab) 4.91 (br s, 6 H, 6 × H-1″), 6.38–7.32 (br, 20 H, Ph); λ_{max} (H_2O)/nm 361 (ε/dm^3 mol^{-1} cm^{-1} 6 960); ν_{max} (KBr)/cm^{-1} 3361, 2922, 1151, 1074, 1049 and 1028; $[\alpha]_D^{30}$ +41.0 (*c* 0.80 in H_2O); *m/z* (MALDI-TOF) ([M+ Na]$^+$ 4432.84 $C_{310}H_{434}O_{156}S_6Si_3$ requires 4432.73).
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