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Original article

Hierarchical self-assembly of triangular metallodendrimers into the ordered nanostructures

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ABSTRACT

We designed and constructed a new family of 60° dendritic dipyridyl donors, from which two novel triangular metallodendrimers were successfully prepared *via* coordination-driven self-assembly. Inspired by the existence of multiple intermolecular interactions (*e.g.*, π–π stacking and CH–π interactions) imposed by the DMIP-functionalized poly(benzyl ether) dendrons, their hierarchical self-assembly behaviors were studied in various mixed solvents by using scanning electron microscopy (SEM). Interestingly, it was found that the morphologies of the obtained metallodendrimers were highly depended on the dendron generation. For example, the first-generation metallodendrimer was able to hierarchically self-assemble into the spherical nanostructures in various mixed solvents. However, the nanofibers were observed for the second-generation metallodendrimer under the similar conditions. Furthermore, the driven force for the formation of such ordered nanostructures was investigated by using ^{1}H NMR and fluorescence spectroscopy.

1. Introduction

During the past few decades, dendrimers have received increasing attention not only for their aesthetic attributes but also because of their wide range of applications in nanomedicine, molecular electronics, and catalysis [1–4]. Among them, metallodendrimers represents an important class of dendrimers because the incorporation of metals provides the resulting metallodendrimers with the wider applications such as biological mimetics, supramolecular redox sensors, and light-harvesting antennae [5–8]. Coordination-driven self-assembly [9–25], which is based on metal–ligand coordination interaction, has provided a particularly powerful strategy for construction of supramolecular metallodendrimers with well-defined shapes and sizes. Although a variety of metallodendrimers have been prepared *via* coordination-driven self-assembly, most of them have been limited to the rhomboidal or hexagonal ones. The successful examples of triangular metallodendrimers have been relatively few, presumably due to the difficulty in finding the appropriate corner unit. Moreover, the triangular metallacycles sometimes suffer from the noticeable equilibrium with the molecular squares when the flexible building blocks are employed [26–28]. Thus, the construction of triangular metallodendrimers with well-defined shape and size is still a challenge [29]. Moreover, the hierarchical self-assembly behaviors of triangular metallodendrimers have been relatively unexplored.

Herein, we successfully synthesized two discrete peripherally dimethyl isophthalate (DMIP) functionalized poly(benzyl ether) metallodendrimers featuring a well-defined triangular cavity at their cores *via* coordination-driven self-assembly (Scheme 1). Interestingly, it was found that the dendron generation played an important role in hierarchical self-assembly behaviors of the obtained triangular metallodendrimers. For example, the first-generation of metallodendrimer was able to hierarchically self-assemble into the spherical nanostructures in various mixed solvents. However, the nanofibers were observed for the second-generation of metallodendrimer under the similar conditions. Furthermore, the ^{1}H NMR and fluorescence spectroscopy studies revealed that the formation of ordered nanostructures was mainly driven by intermolecular π–π stacking interaction imposed by the poly(benzyl ether) dendrons.

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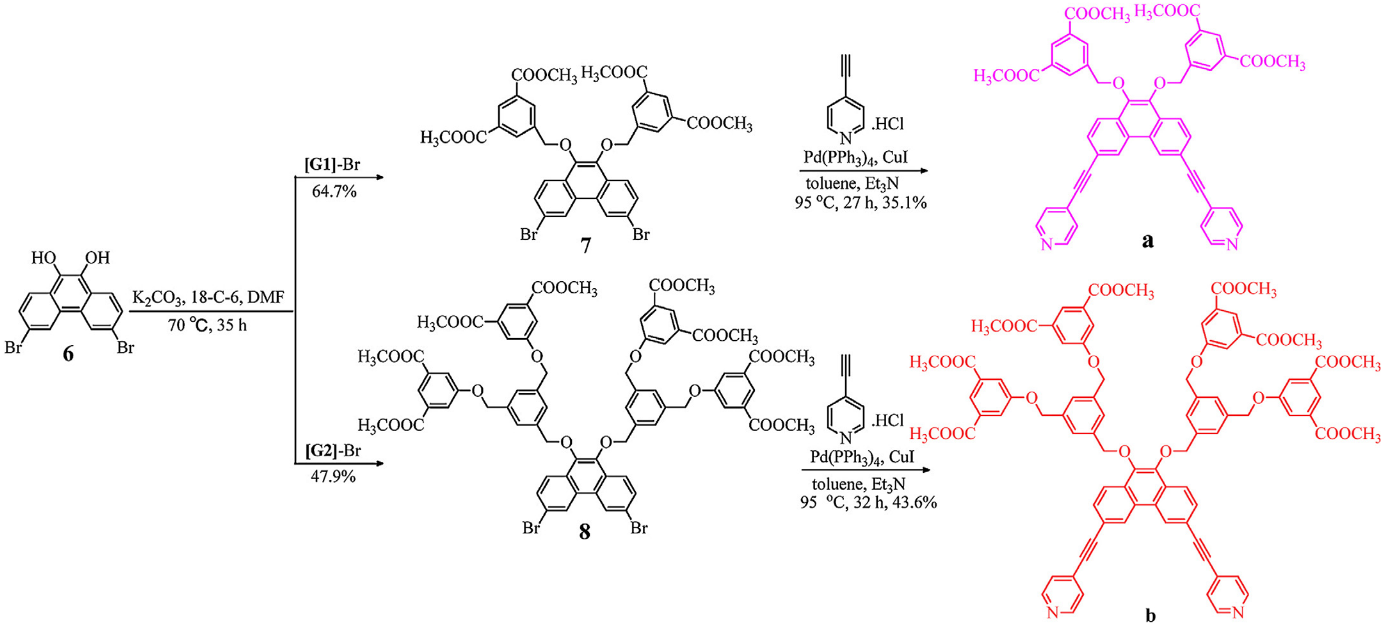

Scheme 1. Synthetic routes of dendrimer ligands **a** and **b**.

2. Experimental

2.1. Synthesis of the ligand *a*

Under an atmosphere of nitrogen, 5.0 mL of toluene and 2.0 mL of Et_3N were added to a mixture of 4-ethynylpyridine hydrochloride (180.0 mg, 1.29 mmol), compound **7** (250.0 mg, 0.32 mmol), CuI (15 mg, 0.08 mmol), and $Pd(PPh_3)_4$ (75 mg, 0.06 mmol). The mixture was stirred at 95 °C for 27 h. Then the solvents were removed *in vacuo*, and the residue was purified by column chromatography on silica gel (dichloromethane/methanol = 20/1) to give **a** (93 mg, 35.1%) as a yellow solid. R_f = 0.6 (dichloromethane/methanol = 20/1). M.p. 232 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.93 (s, 2H), 8.64 (d, 4H, J = 6.0 Hz), 8.55 (s, 2H), 8.29 (d, 2H, J = 8.4 Hz), 8.27 (s, 4H), 7.83 (d, 2H, J = 8.8 Hz), 7.50 (d, 4H, J = 6.0 Hz), 5.35 (s, 4H), 3.91 (s, 12H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 150.3, 144.6, 138.6, 133.0, 131.4, 131.3, 130.5, 130.4, 129.8, 128.5, 127.3, 125.8, 123.2, 120.6, 94.2, 88.1, 75.0, 52.7. ESI-MS: 825.55(M + H$^+$).

2.2. Synthesis of the ligand *b*

Following the procedure for the preparation of **a**. Compound **8** (220.0 mg, 0.15 mmol), 4-ethynylpyridine hydrochloride (110.0 mg, 0.79 mmol), CuI (15 mg, 0.08 mmol), $Pd(PPh_3)_4$ (40 mg, 0.035 mmol), toluene (3.0 mL) and Et_3N (2.0 mL) yielded **b** (100.0 mg, 43.6%) as a yellow solid after purification by column chromatography (dichloromethane/methanol = 20/1). R_f = 0.4 (dichloromethane/methanol = 20/1). M.p. 180 °C. ^1H NMR ($CDCl_3$, 400 MHz): δ 8.92 (s, 2H), 8.64 (d, 4H, J = 4.0 Hz), 8.33 (d, 2H, J = 8.0 Hz), 8.167 (s, 4H), 7.82 (d, 2H, J = 8.4 Hz), 7.73 (s, 8H), 7.60 (s, 4H), 7.57 (s, 2H), 7.50 (d, 4H, J = 4.4 Hz), 5.35 (s, 4H) 5.08 (s, 8H), 3.88 (s, 24H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 166.1, 159.0, 150.3, 144.8, 138.7, 137.7, 132.3, 131.5, 130.5, 130.1, 128.5, 127.3, 127.1, 126.6, 125.9, 123.3, 120.1, 94.33, 88.0, 75.6, 70.3, 52.7, 30.1. MALDI-TOF MS of **b**: calcd. for $C_{86}H_{68}N_2O_{22}$ [M + 2H$^+$]$^{2+}$: 1482.43, found: 1482.36.

2.3. Synthesis of the triangular metallodendrimer *A*

The dipyridyl donor ligand **a** (10.04 mg, 12.2 μmol) and the organoplatinum 180° acceptor **10** (12.88 mg, 12.2 μmol) were weighed accurately into a glass vial. To the vial was added 1.2 mL of acetone and 0.2 mL of H_2O, and the reaction solution was then stirred at 55 °C for 15 h to yield a homogeneous orange solution. Then acetone (3.0 mL) was added, followed by the addition of a saturated aqueous solution of KPF_6 into the bottle with continuous stirring (5 min) to precipitate the product (Scheme 2). The reaction mixture was centrifuged, washed three times with water, and dried. The pare-yellow product **A** (22.5 mg, 98%) was collected and redissolved in CD_2Cl_2 for NMR analysis. ^1H NMR (CD_2Cl_2, 400 MHz): δ 9.15 (s, 6H), 8.70 (d, 12H, J = 5.6 Hz), 8.57 (s, 6H), 8.34 (d, 6H, J = 8.4 Hz), 8.29 (s, 12H), 7.88–7.92 (m, 18H), 7.09 (s, 12H), 5.38 (s, 12H), 3.93 (s, 36H), 1.38 (m, 72H), 1.20 (s, 108H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 12.95 ($^1J_{Pt-P}$ = 2716.7 Hz). CSI-TOF-MS of **A**, [M–3PF$_6^-$]$^{3+}$: 1908.53, found: 1908.62; [M–4PF$_6^-$]$^{4+}$: 1395.16, found: 1395.20; [M–5PF$_6^-$]$^{5+}$: 1087.13, found: 1087.19.

2.4. Synthesis of the triangular metallodendrimer *B*

Following the procedure for the preparation of **A**. Compound **b** (15.09 mg, 10.19 μmol), **10** (10.83 mg, 10.19 μmol), acetone (1.8 mL), water (0.3 mL) yielded **B** (25.6 mg, 99%) as a pare-yellow solid. ^1H NMR (CD_2Cl_2, 400 MHz): δ 9.15 (s, 6H), 8.70 (d, 12H, J = 5.6 Hz), 8.40 (d, 6H, J = 8.4 Hz), 8.18 (s, 12H), 7.85–7.91 (m, 18H), 7.75 (s, 24H), 7.61 (s, 12H), 7.59 (s, 6H), 7.09 (s, 12H), 5.38 (s, 12H), 5.10 (s, 24H), 3.89 (s, 72H), 1.38 (m, 72H), 1.18 (s, 108H). ^{31}P NMR (CD_2Cl_2, 161.9 MHz): δ 12.96 ($^1J_{Pt-P}$ = 2723.2 Hz). CSI-TOF-MS of **B**, [M–4PF$_6^-$]$^{4+}$: 1887.5, found: 1887.5; [M–5PF$_6^-$]$^{5+}$: 1481.0, found: 1481.2.

3. Results and discussion

The newly designed 60° dendritic dipyridyl donors **a** and **b** were synthesized through a two-step sequence as shown in Schemes S3 in Supporting information. The DMIP-functionalized poly(benzyl ether) dendrons were introduced by an etherification reaction of compound **6** with the corresponding dendritic bromides. The subsequent Sonogashira coupling of **7** or **8** with 4-ethynylpyridine hydrochloride yielded 60° donor ligands **a** or **b** in the presence of $Pd(PPh_3)_4$ and CuI as catalysts.

The metallacycles **A** and **B** were well characterized by multiple nuclear (^1H and ^{31}P) NMR spectroscopy, which revealed the