JOC*Note*

Self-Assembly of Interlocked Supramolecular Dendrimers

Kyu-Sung Jeong* and Eun-Jin Park

Center for Bioactive Molecular Hybrids and Department of Chemistry, Yonsei University, Seoul 120-749, Korea

ksjeong@yonsei.ac.kr

Received December 9, 2003

Abstract: Interlocked supramolecular dendrimers were spontaneously self-assembled from molecular components, metallocycles, and dumbbells bearing benzyl ether repeating units. Here, the metallocycles were in situ self-assembled from L-shaped ligands with dendritic branches, 2,3-dimethyl-2-butene and osmium tetraoxide. The supramolecular dendrimers were stabilized by hydrogen-bonding interactions between the pyridine-2,6-dicarboxamide unit in the metallocycle and the adipamide unit in the dumbbell.

Self-assembly processes have been proven a powerful tool for construction of supramolecular dendrimers with structural diversity over the past decade.[1] Owing to the directionality and strength, hydrogen bonds are particularly useful for the self-assembly of smaller molecular components to form the supramolecular dendrimers in a programmed way. Since the pioneering work reported by Zimmerman,[2] several examples of the self-assembled supramolecular dendrimers mediated by hydrogen-bonding interactions have been reported to date.[3−5] Here, we report on the preparation and kinetic and thermodynamic stabilities of rotaxane-type dendrimers[5,6] that were spontaneously assembled by combination of osmylation, coordination, and hydrogen bonding between four different components, 2,3-dimethyl-2-butene, osmium tetraoxide, bispyridyl ligands **1a**−**c**, and dumbbell-shaped molecules **2a**−**c**, of which the last two components possess dendritic branches of benzyl ether repeating units (Scheme 1).

Rotaxanes can be divided into two distinct molecules, a macrocycle and a dumbbell, having complementary binding sites inside. As reported previously,[7] the rotaxanes can be self-assembled in solution when metallocycles with reversible coordinative bonds are used. The metallocycles can be also prepared using various self-assembling motifs, that is, combinations of transition metals and ligands.[8] With this in mind, we prepared bispyridyl ligands **1a**−**c** and dumbbells **2a**−**c** for synthesis of interlocked supramolecular dendrimers. Syntheses of **1a**−**c** and **2a**−**c** are outlined in Schemes 2 and 3, respectively. The benzyl ether dendritic branches were prepared following a literature procedure[9] and attached to the positions remote from the internal hydrogen-bonding sites, the 4-position of the pyridine in **1a**−**c** and the ends of **2a**−**c**, to minimize possible steric crowding upon their assembly.

Here, the interlocked dendrimers were assembled in two different ways: *direct self-assembly* from the ligand, olefin, OsO_4, and the dumbbell in one pot and *stepwise assembly*, self-assembly of the metallocycle first, followed by the rotaxane.

The direct self-assembly was investigated using ^{1}H NMR spectroscopy (Figure 1a−d). When a ligand **1a** and 2,3-dimethylbut-2-ene were added to a $CDCl_3$ solution of a dumbbell **2a**, the ^{1}H NMR spectral change of each compound was negligible (Figure 1c), implying that there is no appreciable aggregation between these components. However, two sets of new signals spontaneously appeared when osmium tetraoxide was added to the above solution (Figure 1d). One originates from the metallocycle **3a**, self-

* To whom correspondence should be addressed. Fax: (+) 82-2-364-7050. Tel: (+) 82-2-2123-2643.

(1) For reviews, see: (a) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681−1712. (b) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26−34. (c) Narayanan, V. V.; Newkome, G. R. *Top. Curr. Chem.* **1998**, *197*, 19−77. (d) Fischer, M.; Vögtle, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 884−905. (e) Smith, D. K.; Diederich, F. *Top. Curr. Chem.* **2000**, *210*, 183−227. (f) Dykes, G. M. *J. Chem. Technol. Biotechnol.* **2001**, *76*, 903−918. (g) Grayson, S. M.; Fréchet, J. M. J. *Chem. Rev.* **2001**, *101*, 3819−3867. (h) Zimmerman, S. C.; Lawless, L. J. *Top. Curr. Chem.* **2001**, *217*, 95−120.

(2) Zimmerman, S. C.; Zeng, F.; Reichert, D. E. C.; Kolotuchin, S. V. *Science* **1996**, *271*, 1095−1098.

(3) (a) Wang, Y.; Zeng, F.; Zimmerman, S. C. *Tetrahedron Lett.* **1997**, *38*, 5459−5462. (b) Kraft, A.; Osterod, F.; Fröhlich, R. *J. Org. Chem.* **1999**, *64*, 6425−6433. (c) Corbin, P. S.; Lawless, L. J.; Li, Z.; Ma, Y.; Witmer, M. J.; Zimmerman, S. C. *Proc. Nat. Acad. Sci. U.S.A.* **2002**, *99*, 5099−5104. (d) Goh, S. L.; Francis, M. B.; Fréchet, J. M. J. *Chem. Commun.* **2002**, 2954−2955. (e) Ma, Y.; Kolotuchin, S. V.; Zimmerman, S. C. *J. Am. Chem. Soc.* **2002**, *124*, 13757−13769.

(4) For other supramolecular dendrimers, see: (a) Enomoto, M.; Aida, T. *J. Am. Chem. Soc.* **1999**, *121*, 874−875. (b) Percec, V.; Cho, W.-D. Ungar, G.; Yeardley, D. J. P. *J. Am. Chem. Soc.* **2001**, *123*, 1302−1315. (c) Percec, V.; Holerca, M. N.; Uchida, S.; Cho, W.-D.; Ungar, G.; Lee, Y.; Yeardley, D. J. P. *Chem. Eur. J.* **2002**, *8*, 1106−1117. (d) Percec, V.; Glodde, M.; Johansson, G.; Balagurusamy, V. S. K.; Heiney, P. A. *Angew. Chem., Int. Ed.* **2003**, *42*, 4338−4342.

(5) For pseudorotaxane-based supramolecular dendrimers, see: (a) Yamaguchi, N.; Hamilton, L. M.; Gibson, H. W. *Angew. Chem., Int. Ed.* **1998**, *37*, 3275−3279. (b) Gibson, H. W.; Hamilton, L., Yamaguchi, N. *Polym. Adv. Technol.* **2000**, *11*, 791−797. (c) Gibson, H. W.; Yamaguchi, N.; Hamilton, L.; Jones, J. W. *Am. Chem. Soc.* **2002**, *124*, 4653−4665. (d) Elizarov, A. M.; Chang, T.; Chiu, S.-H.; Stoddart, J. F. *Org. Lett.* **2002**, *4*, 3565−3568. (e) Dykes, G. M.; Smith, D. K.; Seeley, G. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 3254−3257. (f) Jones, J. W.; Bryant, W. S.; Bosman, A. W.; Janssen, R. A. J.; Meijer, E. W.; Gibson, H. W. *J. Org. Chem.* **2003**, *68*, 2385−2389. Also see: (g) Kenda, B.; Diederich, F. *Angew. Chem., Int. Ed.* **1998**, *37*, 3154−3158. (h) Lee, J. W.; Ko, Y. H.; Park, S.-H.; Yamaguchi, K.; Kim, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 746−749.

(6) For rotaxanes bearing dendritic branches, see: (a) Amabilino, D. B.; Ashton, P. R.; Balzani V.; Brown, C. L.; Credi, A.; Fréchet, J. M. J.; Leon, J. W.; Raymo, F. M.; Spencer, N.; Stoddart, J. F.; Venturi, M. *J. Am. Chem. Soc.* **1996**, *118*, 12012−12020. (b) Hübner, G. M.; Nachtsheim, G.; Li, Q. Y.; Seel, C.; Vögtle, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 1269−1272. (c) Reuter, C.; Pawlitzki, G.; Wörsdörfer, U.; Plevoets, M.; Mohry, A.; Kubota, T.; Okamoto, Y.; Vögtle, F. *Eur. J. Org. Chem.* **2000**, 3059−3067. (d) Elizarov, A. M.; Chiu, S.-H.; Glink, P. T., Stoddart, J. F. *Org. Lett.* **2002**, *4*, 679−682.

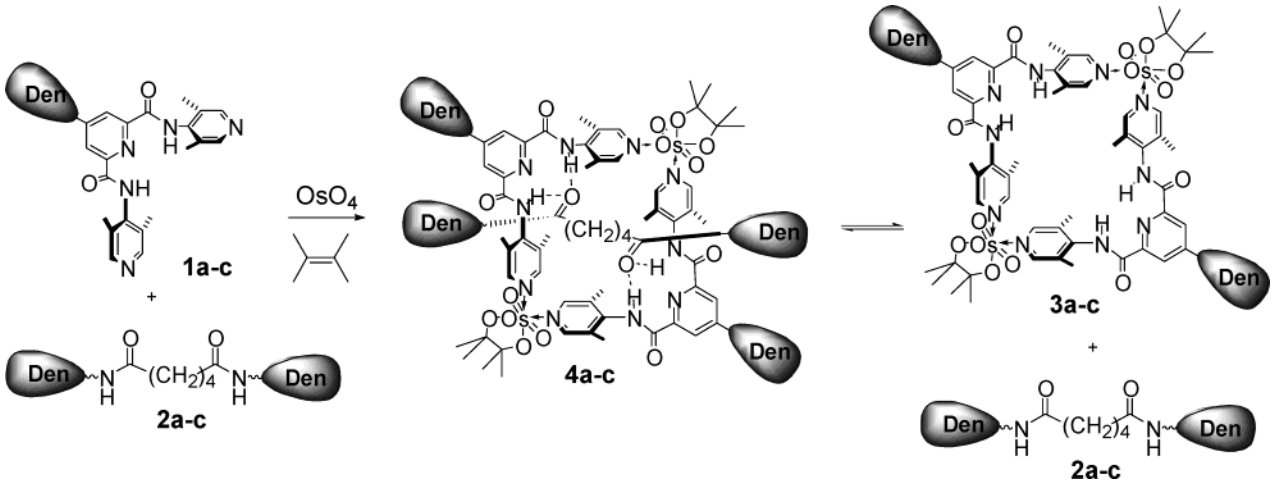
(7) (a) Jeong, K.-S.; Choi, J. S.; Chang, S.-Y.; Chang, H.-Y. *Angew. Chem., Int. Ed.* **2000**, *39*, 1692−1695. (b) Chang, S.-Y.; Choi, J. S.; Jeong, K.-S. *Chem. Eur. J.* **2001**, *7*, 2687−2697. (c) Chang, S.-Y.; Jang, H.-Y.; Jeong, K.-S. *Chem. Eur. J.* **2003**, *9*, 1535−1541. (d) Chang, S.-Y.; Jeong, K.-S. *J. Org. Chem.* **2003**, *68*, 4014−4019. (e) Hunter, C. A.; Low, C. M. R.; Packer, M. J.; Spey, S. E.; Vinter, J. G.; Vysotsky, M. O.; Zonta, C. *Angew. Chem., Int. Ed.* **2001**, *40*, 2678−2682.

(8) For recent reviews, see: (a) Leininger, S.; Olenyuk, B.; Stang, P. J. *Chem. Rev.* **2000**, *100*, 853−908. (b) Holliday, B. J.; Mirkin, C. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 2022−2043. (c) Sun, S.-S.; Lees, A. J. *Coord. Chem. Rev.* **2002**, *230*, 171−192.

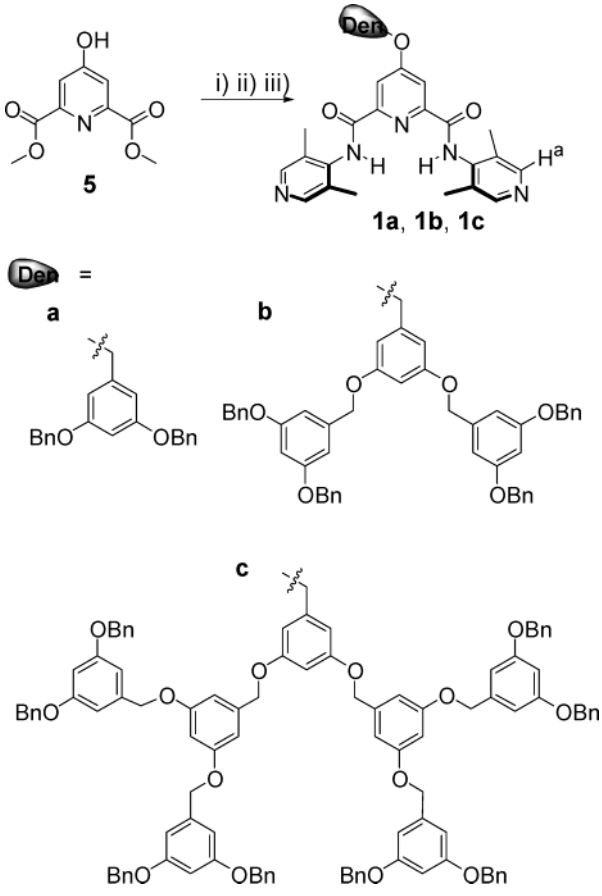
(9) (a) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638−7647. (b) Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010−1013.

10.1021/jo035798u CCC: $27.50
Published on Web 03/03/2004

SCHEME 1. Synthesis of Rotaxane-Type Dendrimers

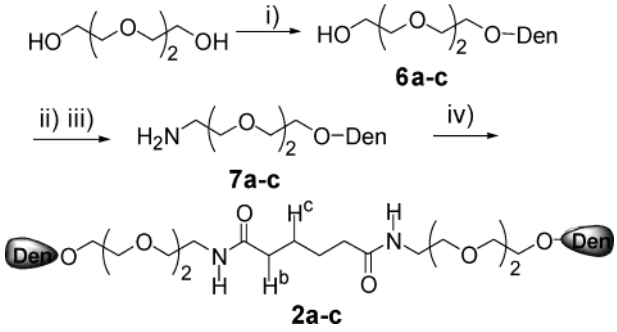


SCHEME 2. Synthesis of Bispyridyl Ligands 1a−c[a]



[a] Reaction conditions: (i) Den-Br **a**−**c**, K_2CO_3, acetone, 18-crown-6, reflux, 75−93%; (ii) LiOH, THF, H_2O, reflux, 90−95%; (iii) $(COCl)_2$, DMF, CH_2Cl_2, rt, argon, then 4-amino-3,5-lutidine, DIPEA, CH_2Cl_2, rt, argon, 50−83%.

SCHEME 3. Synthesis of Dumbbells 2a−c[a]



[a] Reaction conditions: (i) Den-Br **a**−**c**, NaH, THF, reflux, 80−86%; (ii) CBr_4, PPh_3, THF, rt, 68−72%; (iii) phthalimide, K_2CO_3, DMF, 60−70 °C, then NH_2NH_2, EtOH, reflux, 75−85%; (iv) adipoyl chloride, DIPEA, CH_2Cl_2, rt, 50−82%.

assembled in situ from osmium tetraoxide, 2,3-dimethylbut-2-ene, and the ligand **1a**. This was confirmed by comparison of the ^{1}H NMR spectrum of an authentic sample prepared independently (Figure 1e).[10] The other corresponds to the interlocked dendrimer **4a** stabilized by hydrogen-bonding interactions[11] between **2a** and **3a** as shown in Scheme 1. Evidence is as follows. First, the NH signal in the metallocycle is considerably downfield shifted ($\Delta\delta$ = 1.5 ppm) relative to those of the free **3a**, indicative of hydrogen-bond formation. Second, the signals for the methylene units $-(CH_2)_4-$ of the adipamide stations appear at 0.9 and 0.3 ppm, while those in the free **2a** resonance at 2.1 and 1.3 ppm. These large upfield shifts are clear evidence for insertion of the adipamide part into the cavity surrounded by four pyridyl rings. These observations are consistent with those seen in the metallocycle-based rotaxanes studied previously in our laboratory.[7a−d]

On the other hand, the dendrimer **4a** can be prepared by the stepwise assembly using the preassembled metallocycle **3a** and the dumbbell **2a**. When two components were mixed in component in $CDCl_3$ at 24 °C, the complex **4a** was immediately formed by hydrogen-bond interactions (Figure 1f). The ^{1}H NMR spectrum (Figure 1f) is identical to that (Figure 1d) obtained from the direct self-

(10) (a) Jeong, K.-S.; Cho, Y. L.; Song, J. U.; Chang, H.-Y.; Choi, M.-G. *J. Am. Chem. Soc.* **1998**, *120*, 10982−10983. (b) Jeong, K. S.; Cho, Y. L.; Chang, S.-Y.; Park, T.-Y.; Song, J. U. *J. Org. Chem.* **1999**, *64*, 9459−9466. (c) Cho, Y. L.; Uh, H.; Chang, S.-Y.; Chang, H.-Y.; Choi, M.-G.; Shin, I.; Jeong, K.-S. *J. Am. Chem. Soc.* **2001**, *123*, 1258−1259.

(11) For hydrogen bond-based rotaxanes derived from covalent tetralactams, see: (a) Schalley, C. A.; Beizai, K.; Vögtle, F. *Acc. Chem. Res.* **2001**, *34*, 465−476. (b) Gatti, F. G.; Leigh, D. A.; Nepogodiev, S. A.; Slawin, A. M. Z. Teat, S. J.; Wong, J. K. Y. *J. Am. Chem. Soc.* **2001**, *123*, 5983−5989. (c) Altieri, A.; Gatti, F. G.; Kay, E. R.; Leigh, D. A.; Martel, D.; Paolucci, F.; Slawin, A. M. Z.; Wong, J. K. Y. *J. Am. Chem. Soc.* **2003**, *1253*, 8644−8654 and references are therein.

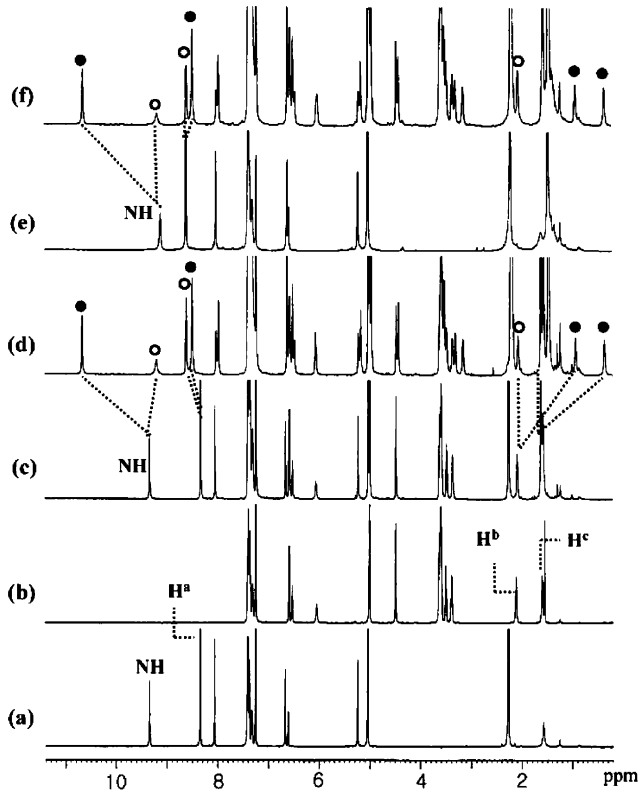


FIGURE 1. ^{1}H NMR spectra (500 MHz, $CDCl_3$, 24 °C) of (a) ligand **1a**, (b) dumbbell **2a**, (c) **1a** + **2a** + 2,3-dimethylbut-2-ene, (d) **1a** + **2a** + 2,3-dimethylbut-2-ene + OsO_4, (e) metallocycle **3a**, (f) **3a** + **2a**. ●: complex **4a**. ○: Free **2a** and **3a**.

TABLE 1. Association Constants (K_a, M^{-1}) and Activation Energy ($\Delta G^{\ddagger}$, kcal mol^{-1}) of the Interlocked Dendrimers 4a, 4b, and 4c at 24 ± 1 °C in $CDCl_3$

dendrimer (molar mass)	association constant (K_a, M^{-1})	activation energy ($\Delta G^{\ddagger}$, kcal/mol)
4a (3047)	2800 ± 350	15.9
4b (4776)	1200 ± 150	16.2
4c (8172)	600 ± 50	16.8

assembly. The relative intensities of the signals corresponding to the complex and its components depend on concentrations of the components; the signals for the complex increase at higher concentrations, but they decrease at lower concentrations. The binding affinity between two components, **2a** and **3a**, was measured to be 2800 ± 350 M^{-1}, based on ^{1}H NMR integrations of five different stock solutions containing 1−5 mM of each component (see the Supporting Information).

The other interlocked dendrimers **4b** and **4c** with higher generations of dendritic branches were also self-assembled by two different processes from the corresponding components, respectively, and the spectral behaviors are exactly the same as those described above in the self-assembly of **4a** (see the Supporting Information). However, the binding affinities decrease as the generation of the branches increases, as summarized in Table 1. The reduction in the affinities is attributed to the increased steric crowding between dendritic branches in both the metallocycle and the dumbbell.

The kinetic stabilities of the self-assembled, supramolecular dendrimers **4a**−**c** were revealed with 2D-EXSY experiments.[12] The dendrimers **4a**−**c** all are reversibly converted into their components, a metallocycle and a dumbbell, at ambient temperature. The activation free energies of the interconversion were determined to be 15.9−16.8 kcal/mol (Table 1), based on diagonal and cross-peaks for the NH signals of the complex and the free metallocycle. The activation energies are slightly increased in the dendrimers with higher generations, probably due to an increased steric hindrance on the assembly and disassembly process. Overall, the magnitudes are comparable to that (15.5 kcal/mol) of the interlocked complexes reported previously.[7a−c]

In conclusion, we have demonstrated the self-assembly of interlocked dendrimers from smaller components by combination of osmylation, coordination, and hydrogen bonds. Considering that various processes for self-assembly of metallocycles are well-known, this approach can be applied to the preparation of supramolecular functional dendrimers that contain transition metals with diverse electrochemical or photochemical properties.

Experimental Section

Substituted benzyl bromides with different generations of benzyl ether dendritic branches were prepared according to literature procedures.[9] Ligands **1a**−**c** and dumbbells **2a**−**c** were prepared as shown in Schemes 2 and 3, and experimental details have been described in the Supporting Information.

1a: mp 118−120 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.79 (s, 2H, NH), 8.25 (s, 4H), 8.05 (s, 2H), 7.42−7.32 (m, 10H), 6.66 (s, 2H), 6.61 (s, 1H), 5.21 (s, 2H, $ArCH_2O$), 5.05 (s, 4H, $PhCH_2O$), 2.21 (s, 12H, Py-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.2, 161.7, 160.7, 150.8, 149.5, 142.6, 137.4, 136.9, 130.9, 129.0, 128.5, 127.9, 113.0, 106.7, 102.5, 71.0, 70.6, 15.9; IR (KBr) 3400−3200, 1686 cm^{-1}; MS (MALDI-TOF) *m/z* 694.3 $[M + H]^+$. Anal. Calcd for $C_{42}H_{39}N_5O_5$: C, 72.71; H, 5.67; N, 10.09. Found: C, 72.69; H, 5.60; N, 10.10.

1b: mp 112−114 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.57 (s, 2H, NH), 8.32 (s, 4H), 8.09 (s, 2H), 7.41−7.31 (m, 20H), 6.70 (br s, 4H), 6.67 (br s, 2H), 6.60 (br s, 3H), 5.25 (s, 2H, $ArCH_2O$), 5.05 (s, 8H, $PhCH_2O$), 5.00 (s, 4H, $ArCH_2O$), 2.26 (s, 12H, Py-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 161.0, 160.2 (two overlapped signals), 150.4, 149.1, 142.0, 138.9, 136.9, 136.7, 130.1, 128.5, 128.0, 127.5, 112.6, 106.3 (two overlapped signals), 102.1, 101.6, 70.7, 70.1 (two overlapped signals), 15.5; IR (KBr) 3400−3200, 1686 cm^{-1}; MS (MALDI-TOF) *m/z* 1118.5 $[M + H]^+$. Anal. Calcd for $C_{70}H_{63}N_5O_9$: C, 75.18; H, 5.68; N, 6.26. Found: C, 75.32; H, 5.65; N, 6.09.

1c: mp 96−98 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.49 (s, 2H, NH), 8.30 (s, 4H), 8.05 (s, 2H), 7.39−7.28 (m, 40H), 6.66−6.54 (m, 21H), 5.18 (s, 2H, $ArCH_2O$), 5.00 (s, 16H, $PhCH_2O$), 4.96 (s, 12H, $ArCH_2O$) 2.25 (s, 12H, Py-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.9, 160.9, 160.1 (two overlapped signals), 150.3, 149.2, 141.8, 139.1, 138.9, 136.7, 129.9, 128.5, 127.9, 127.5, 112.6, 106.3 (two overlapped signals), 101.5 (three overlapped signals), 70.1 (three overlapped signals), 15.5; IR (KBr) 3400−3200, 1686 cm^{-1}; MS (MALDI-TOF) *m/z* 1967.0 $[M + H]^+$. Anal. Calcd for $C_{126}H_{111}N_5O_{17}$: C, 76.93; H, 5.69; N, 3.56. Found: C, 76.92; H, 5.60; N, 3.30.

2a: mp 82−84 °C; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42−7.30 (m, 20H), 6.60 (s, 4H), 6.54 (s, 2H), 6.11 (s, 2H, NH), 5.02 (s, 8H, $PhCH_2O$), 4.50 (s, 4H, $ArCH_2O$), 3.64−3.62 (m, 16H), 3.52 (t, J = 8.7 Hz, 4H), 3.41 (t, J = 8.7 Hz, 4H), 2.14 (br s, 4H), 1.34 (br s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.7, 160.0, 140.6, 136.8, 128.5, 127.9, 127.5, 106.5, 101.2, 73.0, 70.5, 70.1, 70.0, 69.7, 69.3 (5 peaks of 6 expected between 69.3 and 70.5), 39.1,

(12) (a) Perrin, C. L.; Dwyer, T. J. *Chem. Rev.* **1990**, *90*, 935−967. (b) Pons, M.; Millet, O. *Prog. Nucl. Magn. Reson. Spectrosc.* **2001**, *38*, 267−324.

36.0, 25.0; IR (KBr) 3334, 1669 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1013.4 $[M + H]^+$. Anal. Calcd for $C_{60}H_{72}N_2O_{12}$: C, 71.12; H, 7.16; N, 2.76. Found: C, 71.13; H, 7.06; N, 2.66.

2b: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.42−7.32 (m, 40H), 6.68 (br s, 8H), 6.59(s, 4H), 6.52 (br s, 6H), 6.07 (s, 2H, NH), 5.03 (s, 16H, $PhCH_2O$), 4.96 (s, 8H, $ArCH_2O$), 4.50 (s, 4H, $ArCH_2O$), 3.64−3.61 (m, 16H), 3.51 (m, 4H), 3.40 (m, 4H), 2.12 (br s, 4H), 1.61 (br s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.6, 160.1, 159.9, 140.6, 139.2, 136.7, 128.5, 127.9, 127.5, 106.5, 106.3, 101.4, 101.2, 73.0, 70.5, 70.0, 69.9, 69.8, 69.3 (5 peaks of 7 expected between 69.3 and 70.5), 39.0, 36.0, 25.0; IR (film) 3354, 1664 cm^{-1}; MS (MALDI-TOF) *m*/*z* 1899.8 $[M + K]^+$. Anal. Calcd for $C_{116}H_{120}N_2O_{20}$: C, 74.82; H, 6.50; N, 1.50. Found: C, 74.89; H, 6.59; N, 1.49.

2c: colorless oil; ^1H NMR (500 MHz, $CDCl_3$) δ 7.37−7.26 (m, 80H), 6.65 (br s, 24H), 6.57−6.51 (m, 18H), 6.02 (s, 2H, NH), 5.06 (s, 32H, $PhCH_2O$), 4.99 (s, 24H, $ArCH_2O$), 4.46 (s, 4H, $ArCH_2O$), 3.57 (m, 16H), 3.47−3.45 (m, 4H), 3.39−3.35 (m, 4H), 2.10 (br s, 4H), 1.57 (br s, 4H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.1, 160.1 (two overlapped signals), 160.0, 140.7, 139.2 (two overlapped signals), 136.7, 128.5, 128.0, 127.5, 106.4 (three overlapped signals), 101.6 (two overlapped signals), 101.2, 73.0, 70.5, 70.1, 69.9, 69.6, 69.4 (5 peaks of 8 expected between 69.4 and 70.5), 39.3, 35.7, 24.9; IR (film) 3339, 1670 cm^{-1}; MS (MALDI-TOF) *m*/*z* 3583.0 $[M + K]^+$. Anal. Calcd for $C_{228}H_{216}N_2O_{36}$: C, 76.92; H, 6.12; N, 0.79. Found: C, 76.92; H, 6.26; N, 0.63.

General Procedure for Preparation of Metallocycles 3a−c. These compounds were all prepared by the same method, and synthesis of **3a** will be here described as a representative. Osmium tetraoxide (0.50 M in CH_2Cl_2, 360 μL, 0.18 mmol) was added to a CH_2Cl_2 solution of ligand **1a** (84 mg, 0.12 mmol) and 2,3-dimethylbut-2-ene (15 mg, 0.18 mmol). After the solution was stirred for 40 min at room temperature, the brown precipitate was collected, washed with diethyl ether, and dried under vacuum to give **3a** (110 mg, 92%) as a gray solid, which was slowly decomposed on heating: ^1H NMR (500 MHz, $CDCl_3$) δ 9.14 (s, 4H, NH), 8.64 (s, 8H), 8.05 (s, 4H), 7.41−7.33 (m, 20H), 6.64 (s, 4H), 6.61 (s, 2H), 5.24 (s, 4H, $ArCH_2O$), 5.05 (s, 8H, $PhCH_2O$), 2.24 (s, 24H, Py-CH_3), 1.49 (s, 24H, osmate-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 160.3, 160.0, 149.7, 148.0, 145.7, 136.6, 136.4, 131.0, 128.6, 128.1, 127.5, 112.9, 106.2, 102.1, 90.1, 70.8, 70.2, 24.5, 16.2; IR (KBr) 3283, 1694, 829 cm^{-1}. Anal. Calcd for $C_{96}H_{102}N_{10}O_{18}Os_2$: C, 55.85; H, 4.98; N, 6.79. Found: C, 55.89; H, 4.79; N, 6.83.

3b: ^1H NMR (500 MHz, $CDCl_3$) δ 9.13 (s, 4H, NH), 8.64 (s, 8H), 8.05 (s, 4H), 7.40−7.31 (m, 40H), 6.67 (br s, 8H), 6.61 (br s, 4H), 6.61 (br s, 6H), 5.23 (s, 4H, $ArCH_2O$), 5.03 (s, 16H, $PhCH_2O$), 4.99 (s, 8H, $ArCH_2O$), 2.23 (s, 24H, Py-CH_3), 1.50 (s, 24H, osmate-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.4, 161.0, 160.2 (two overlapped signals), 149.8, 148.0, 145.7, 139.0, 136.7, 131.0, 128.5, 128.0, 127.5, 112.9, 106.3 (two overlapped signals), 102.2, 101.7, 90.1, 70.1 (three overlapped signals), 24.5, 16.2; IR (KBr) 3304, 1695, 829 cm^{-1}. Anal. Calcd for $C_{152}H_{150}N_{10}O_{26}Os_2$: C, 62.66; H, 5.19; N, 4.81. Found: C, 62.68; H, 5.13; N, 4.74.

3c: ^1H NMR (500 MHz, $CDCl_3$) δ 9.09 (s, 4H, NH), 8.65 (s, 8H), 8.01 (s, 4H), 7.53−7.29 (m, 80H), 6.65−6.53 (m, 42H), 5.17 (s, 4H, $ArCH_2O$), 4.98−4.95 (m, 56 H, $ArCH_2O$ and $PhCH_2O$), 2.19 (s, 24H, Py-CH_3), 1.50 (s, 24H, osmate-CH_3); ^{13}C NMR (126 MHz, $CDCl_3$): δ 168.3, 160.1 (four overlapped signals), 149.6, 147.9, 145.7, 139.1, 138.9, 136.7 (two overlapped signals), 131.0, 128.5, 127.9, 127.5, 112.8, 106.4 (two overlapped signals), 106.2, 102.1, 101.5, 90.1, 70.0 (four overlapped signals), 24.5, 16.1; IR (KBr) 3314, 1694, 829 cm^{-1}. Anal. Calcd for $C_{264}H_{246}N_{10}O_{42}Os_2$: C, 68.76; H, 5.38; N, 3.04. Found: C, 68.96; H, 5.42; N, 2.92.

Acknowledgment. This work was financially supported by Korea Institute of Science & Technology Evaluation and Planning (M10213030001-02B1503-00310) and KOSEF-CBMH.

Supporting Information Available: Experimental procedures of **1a−c** and **2a−c**, physical properties and spectroscopic data of their intermediates, ^1H NMR studies on self-assembly of **4b** and **4c**, and determination of binding affinities and 2D-EXSY experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

JO035798U