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2,2′:6′,2″-Terpyridine and bis(2,2′:6′,2″-terpyridine)ruthenium(II) complex on the dendritic periphery

Chungkyun Kim *, Hyojeong Kim

Department of Chemistry, Dong-A University, Busan 604-714, South Korea

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Abstract

2,2′:6′,2″-Terpyridine end-functionalized dendrimers were prepared utilizing chlorinated siloxane dendrimer and 6-hydroxyhexa-4′-(2,2′:6′,2″-terpyridine) ether. The terpyridine groups on dendrimers accepted the ruthenium chloride ions on the mild condition that produced the paramagnetic ruthenium complex G*n*-*m*TPY-$RuCl_3$. The continual addition of 2,2′:6′,2″-terpyridine to the ruthenium–terpyridine complex on the dendritic periphery progressed to bis(2,2′:6′,2″-terpyridine)ruthenium(II) complex G*n*-*m*[TPY-Ru-TPY] ($n = 1$, $m = 4$; $n = 2$, $m = 8$; $n = 3$, $m = 16$) which revealed diamagnetic property.

Keywords: Dendrimer; Terpyridine; Carbosilane; Ruthenium; Siloxane

1. Introduction

During the last decade, dendrimers have been considered to be the prime impetus in nano-scale building blocks for material sciences and there have been versatile investigations for synthetic methodology and usability [1]. Many researchers developed the complex ability, photochemical properties and the supramolecular building block on the dendritic surface, etc. [2]. Dendritic carbosilanes [3] are of special interest as building blocks because they are chemically inert and fluid at high molecular weight in high generation [4]. Furthermore, 4′-functionalized 2,2′:6′,2″-terpyridine [5] as tridentate ligand on dendritic surfaces [6] are of special interest because of their photochemical property and increasing usability for the incorporation of the supramolecular chemistry and nanoscience [7,8]. The new approach to include terpyridine in carbosilane dendrimers makes possible the adaptation of metallic components to the dendritic periphery by the self-assembly coordinated methods [9]. We report here the preparative methods of dendrimers containing 2,2′:6′,2″-terpyridine on the periphery and the terpyridine ruthenium complex.

2. Results and discussion

The 6-hydroxyhexyl-4′-(2,2′:6′,2″-terpyridine)ether as a building block was prepared utilizing 4′-chloro-2,2′:6′,2″-terpyridine and 1,6-hexanediol in the excess of potassium hydroxide and DMSO as solvents [10]. Here we present the synthetic method of the different generations of the dendritic carbosilane that include 4-, 8- and 16-terpyridine on the periphery, and the metallo-supramolecular building blocks with ruthenium chloride and the bis(2,2′:6′,2″-terpyridine)ruthenium(II) complex on the dendritic periphery (Scheme 1).

The substitution of the terpyridine on the dendritic surface has been introduced by the reaction of Si–Cl bonded parent dendrimers (G*n*-*m*Cl; $n = 1$, $m = 4$; $n = 2$, $m = 8$; $n = 3$, $m = 16$, etc.) and 6-hydroxyhexyl-4′-(2,2′:6′,2″-terpyridine) ether in the presence of TMEDA as base. All end-functionalized terpyridine dendrimers (G*n*-*m*TPY; $n = 1$, $m = 4$; $n = 2$, $m = 8$; $n = 3$, $m = 16$) have to be monitored by NMR spectroscopy that revealed quantitative exchange to new chemical shifts. The new dendritic terpyridine groups showed at 7.36–7.39, 7.78–7.95, 8.00 and 8.55–8.75 ppm.

* Corresponding author. Tel.: +81-51-200-7247; fax: +81-51-200-7259.

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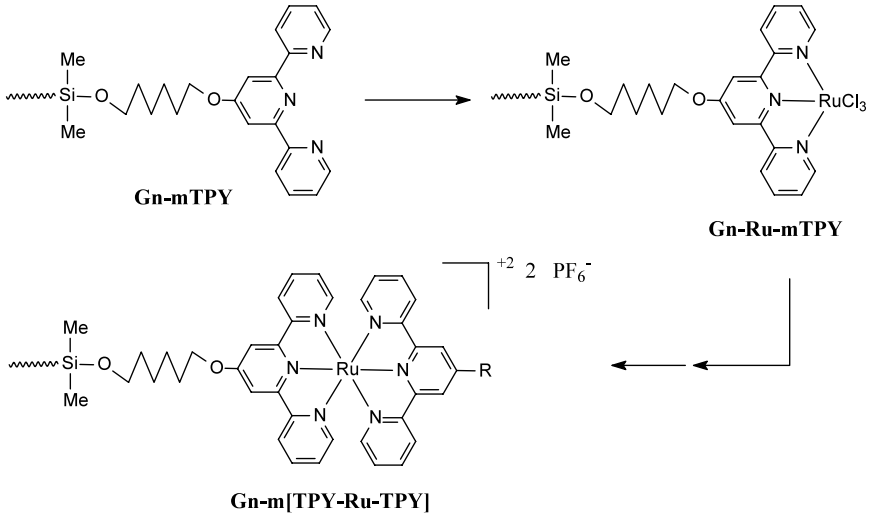


Scheme 1.

The products were isolated after flash chromatography by the use of a silica gel and nonpolar eluent such as toluene and chloroform. They revealed a white precipitate that is stable against moisture and air. The characterization of G*n*-*m*TPY dendrimers was carried out using NMR and UV, IR MALDI mass spectroscopy and EA. ^{1}H-NMR spectroscopy detected by characteristic signals for terpyridine rests and ^{13}C-NMR spectra viewed eight signals at 107.3, 121.3, 123.7, 136.7, 148.9, 156.1, 156.9 and 167.2, which were the same views for second and third generations G2-8TPY and G3-16TPY (Fig. 1). The MALDI mass spectroscopy of G1-4TPY ($M_w = 1974.8$) dendrimer was detected, but the second and third generational dendrimers did not produce the molecular peak (Fig. 2). The absorption maxima (λ_{max}) and molar absorption coefficient (ε) of all terpyridine dendrimer G*n*-*m*TPY ($n = 1$–3 and $m = 4$, 8, 16) showed two strong peaks at $\lambda_{max} = 241$ ($\varepsilon = 2.45 \times 10^5$ M^{-1} cm^{-1}) and 276 (2.34×10^5) which are collected in Table 1. In addition the absorption spectra of ruthenium containing dendrimers G*n*-*m*[TPY-Ru-TPY] are strongly shifted toward long wavelength (red shift) and showed four strong peaks at $\lambda_{max} = 241$ ($\varepsilon = 1.31 \times 10^5$ M^{-1} cm^{-1}), 269 (1.50×10^5), 305 (1.96×10^5), 480 (0.53×10^5) which are collected in Table 2. The molar absorption coefficient values for the dendrimers are increased according to increasing generation (Tables 1 and 2). Absorption band at 241 and 276 nm in G*n*-*m*TPY are assigned as π–π^* for the uncoordinated terpyridine ligands on dendritic periphery. The absorption band at 269 and 305 nm of G*n*-*m*[TPY-Ru-TPY] which are 29 nm shifted from 241 and

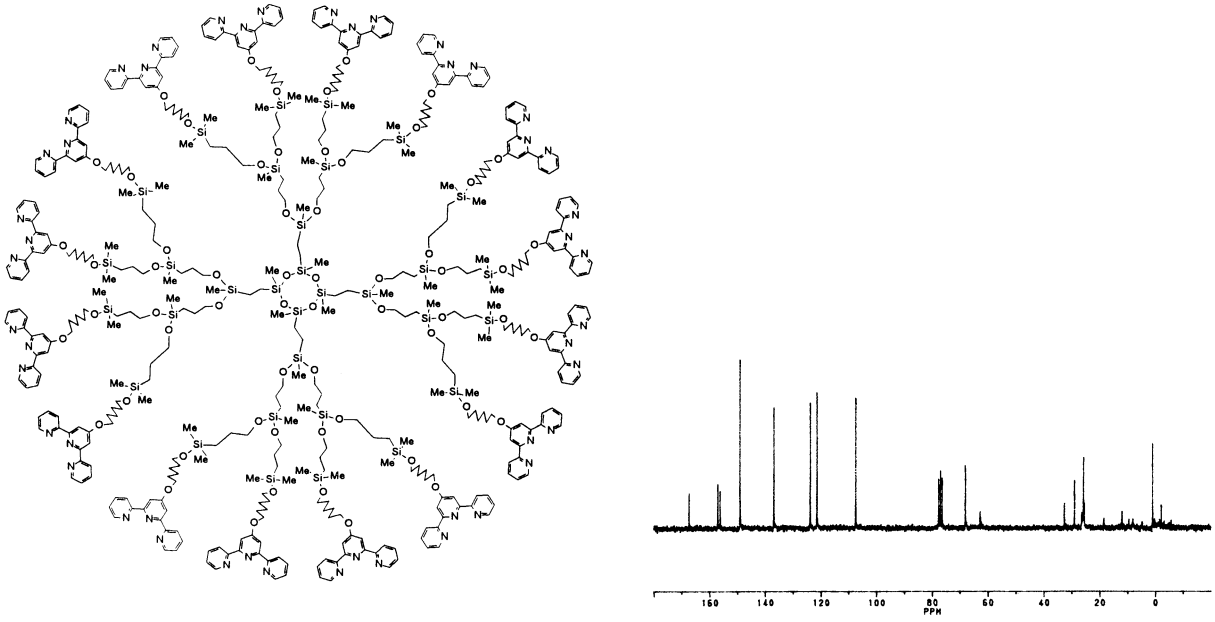


Fig. 1. Planar view and ^{13}C-NMR spectra of G3-16TPY type dendrimers.

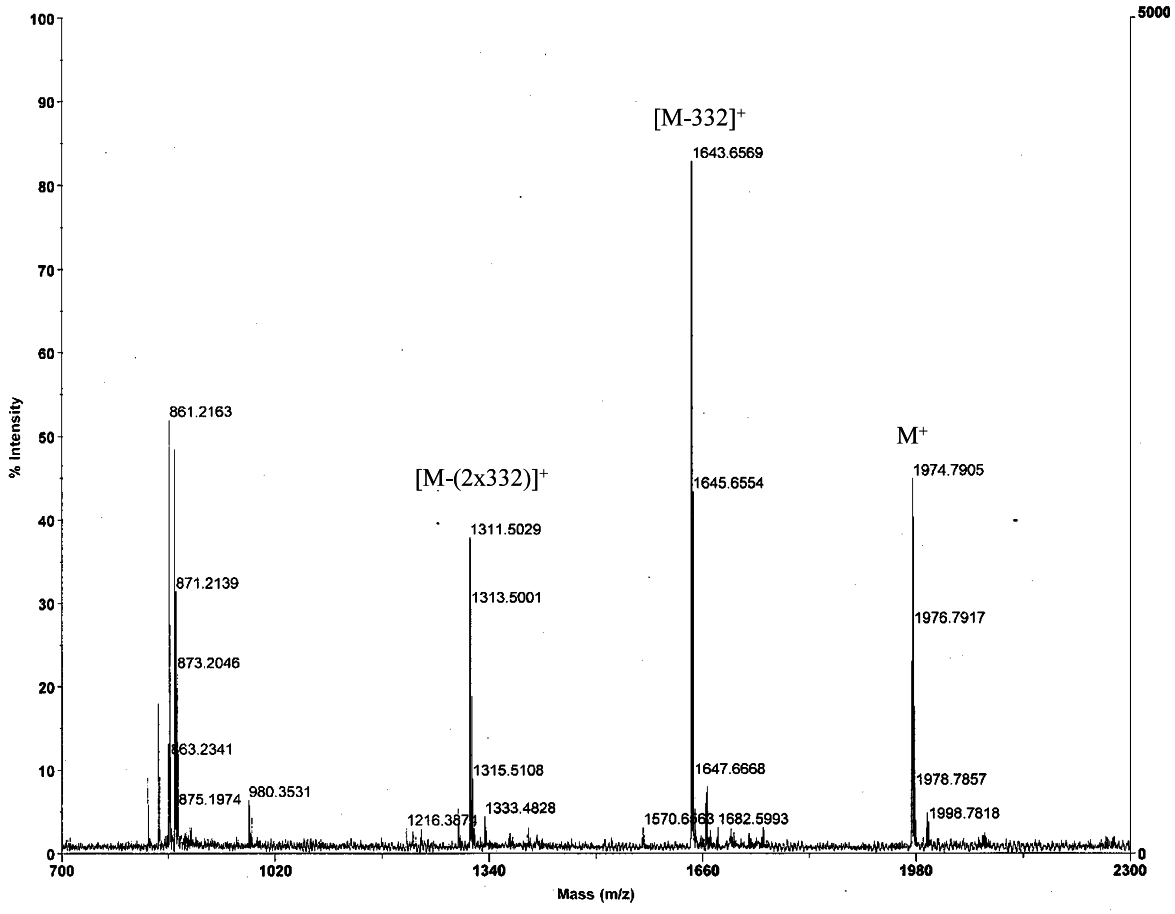


Fig. 2. MALDI-TOF mass spectrum of G1-4TPY.

Table 1
UV–vis data of G*n*-*m*TPY type dendrimers

λ_{max} (nm)	G1-4TPY	G2-8TPY	G3-16TPY
240	2.45×10^5	5.21×10^5	9.83×10^5
276	2.34×10^5	4.75×10^5	8.94×10^5

Table 2
UV–vis data of G*n*-*m*[TPY-Ru-TPY] type dendrimers

λ_{max} (nm)	G1-4[TPY-Ru-TPY]	G2-8[TPY-Ru-TPY]	G3-16[TPY-Ru-TPY]
241	1.31×10^5	3.07×10^5	6.36×10^5
269	1.50×10^5	3.56×10^5	7.39×10^5
305	1.96×10^5	4.55×10^5	9.38×10^5
480	0.53×10^5	1.25×10^5	2.61×10^5

269 nm of G*n*-*m*TPY type dendrimers, respectively. The broad feature with 480 nm is assigned as a metal (Ru^{2+}) to ligand (π* of terpyridine) charge transfer (Fig. 3 and Tables 1 and 2).

The terpyridine dendrimers G*n*-*m*TPY represent very interesting building blocks for direct use in metal complexation. As an example concerning complexation

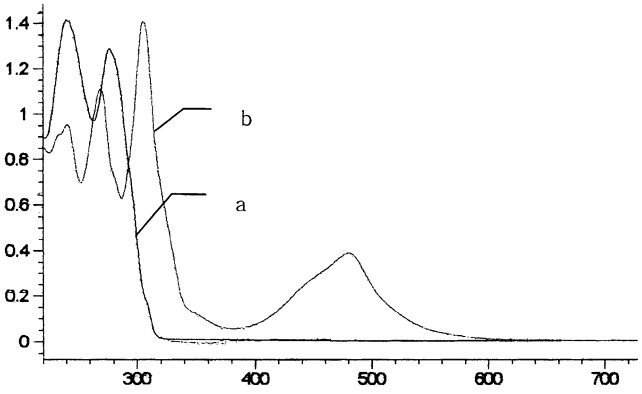


Fig. 3. UV–vis spectra of (a) G3-16TPY and (b) G3-16[TPY-Ru-TPR] in CH_3CN at room temperature.

in functionalized metallo-supramolecular units, we reacted G*n*-*m*TPY dendrimer with ruthenium chloride. The ruthenium metal complex on the dendritic periphery was formed in a methanol medium and could be isolated in very a high yield. Furthermore, the resulting dendrimers G*n*-*m*TPY-$RuCl_3$ were isolated by washing the red precipitate with distilled water, pentane and ether, in due order. ^{1}H-NMR spectroscopy of the red

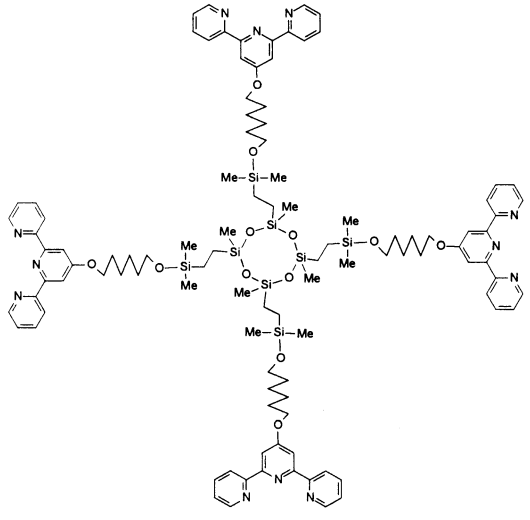
complex produced no signal at the resonance area absolutely, due to the paramagnetic properties of the complex. The solubility in organic solvents of the prepared dendritic ruthenium complex was very low. The bifunctionalized metallo-supramolecular terpyridine units on the dendritic periphery was formed by the reaction of terpyridine–ruthenium complex G*n*-*m*TPY-$RuCl_3$ and 2,2′:6′,2″-terpyridine in methanol by the reflux condition and it could be isolated in 75% yield after anion exchange utilizing the large excess of ammonium hexafluorphosphate. The excess 2,2′:6′,2″-terpyridine was removed by washing with pentane and excess salt was removed by washing with H_2O, pentane and Et_2O, in due order. The products were difficult to solve in polar solvents. In particular, the NMR spectrum was shown again because the product revealed diamagnetism. The characterization of the end-capped dendritic complex was carried out using NMR, UV–vis spectrometry as well as elemental analysis.

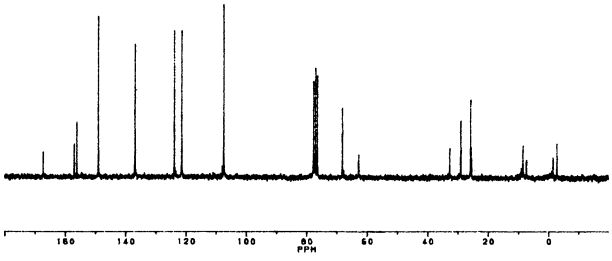
3. Experimental

The preparation of 6-hydroxyhexa-4′-(2,2′:6′,2″-terpyridine) ether (HOHTE) was made according to the Ref. [10] but the following may serve as an example: to a stirred suspension of powdered KOH (5.6 g, 100.4 mmol) in dried DMSO (50 ml) at 80 °C, hexanediol (2.55 g, 21.60 mmol) was added. After 30 min, 4′-chloro-(2,2′:6′,2″-terpyridine; 5.37 g, 21.60 mmol) was slowly added and the mixture was stirred for 4 h at 80 °C and poured into cold water. The water phase was extracted with a methylenechloride. The combined organic phase was dried with molecular sieve 4 Å. After the removal of the solvent, the product was chromatographed with a mixed solvent (chloroform and methanol: 6–4) yielding 5.50 g, 80% as a white solid. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = 1.34$–1.72, 1.72–2.00 (m, 8H, CH_2), 3.51–3.80, 4.12–4.34 (m, 4H, OCH_2), 7.36–7.39, 7.78–7.95, 8.00, 8.55–8.75 (terpyridine rest). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = 25.39$, 25.73, 28.89, 32.62 (CH_2), 62.77, 68.01, (OCH_2), 107.38, 121.33, 123.77, 136.75, 148.98, 156.14, 156.97 and 167.26 (terpyridine rest). GC Mass: Calc., 349.45. Found: 349.

3.1. G1-4TPY

To 0.42 g (0.59 mmol) of G1-4Cl dissolved in 15 ml of dried toluene were added the mixed reactants, 0.91 g (2.59 mmol) of terpyridine (HOHTE) and 0.30 g (2.59 mmol) of TMEDA in 15 ml of chloroform and then refluxed for 2 h. The salt was filtered off and the solvent was removed by reduced pressure. The pure G1-4TPY was obtained by flash chromatography with a silica gel and mixed eluent (THF:$CH_3Cl = 6$:5). The product (0.91 g, 78%) was a white solid. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = 0.09$ (s, 36H, SiMe (G0–G1)), 0.36–0.64, 1.34–1.72, 1.72–2.00 (m, 48H, CH_2 (G0–G1)), 3.51–3.80, 4.12–4.34 (m, 16H, OCH_2 (G1)), 7.36–7.39, 7.78–7.95, 7.95–8.14, 8.55–8.75 (terpyridine rest). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -2.80$ (SiMe (G1)), -1.49 (SiMe (G0)), 7.31, 8.43 (CH_2 (G0)), 25.73, 25.81, 28.89, 32.64 (CH_2), 62.66, 68.01 (OCH_2 (G1)), 107.37, 121.32, 123.75, 136.76, 136.79, 156.11, 156.97, 167.27 (terpyridine rest). EA for $C_{104}H_{140}Si_{18}O_{12}N_{12}$ ($M_W = 1973$): C, 63.28%, H, 7.09%, N, 8.86%. Found: C, 62.71%, H, 7.00%, N, 8.86%. UV–vis (nm, in CH_3CN): $\lambda_{max} = 241$ ($\varepsilon = 2.45 \times 10^5$), 276 ($2.34 \times 10^5$ M^{-1} cm^{-1}). MALDI-TOF Mass: Calc., 1973. Found: 1974.78.





G1-4TPY

3.2. G2-8TPY

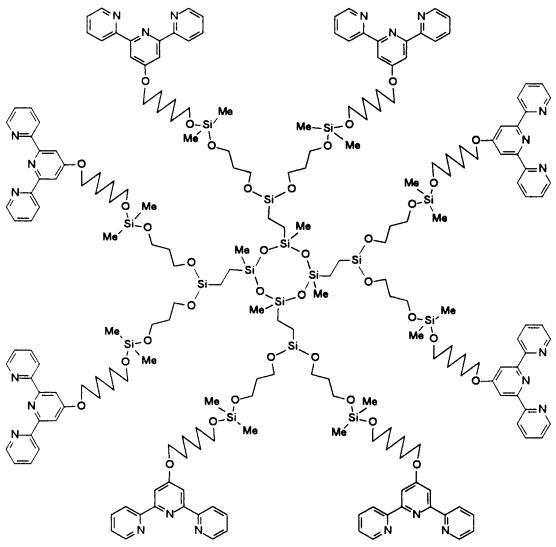
The same method as that of G1-4TPY was used in the reaction of G2-8Cl (0.43 g, 0.25 mmol), HOHTE (0.75 g, 2.16 mmol) and TMEDA (0.25 g, 2.16 mmol). Yield: 0.89 g (0.21 mmol, 92%) of a yellow gel. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = 0.06$ (s, 24H, SiMe (G0–G1)), 0.09 (s, 48H, SiMe (G2)), 0.42–0.72, 1.38–1.75, 1.75–2.00 (m, 112H, CH_2 (G0–G2)), 3.54–3.85, 4.15–4.32 (m, 48H, OCH_2 (G1–G2)), 7.28–7.39, 7.80–7.95, 7.95–8.18, 8.55–8.75 (terpyridine rest). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -2.17$ (SiMe (G2)), -0.36 (SiMe (G0–G1)), 7.31, 8.43 (CH_2 (G0)), 11.96, 25.40 (CH_2 (G1, G2)), 25.40, 25.75, 28.87, 32.60 (CH_2), 62.70, 68.01, (OCH_2 (G1)), 65.24 (OCH_2 (G2)), 107.39, 121.39, 123.31, 136.80, 136.85, 148.94, 156.09, 156.92, 167.27 (terpyridine rest). EA for $C_{224}H_{312}Si_{16}O_{28}N_{24}$ ($M_W = 4232$): C, 63.51%, H, 7.37%, N, 7.94%. Found: C, 62.87%, H, 7.37%, N, 6.85%. UV–vis (nm, in CH_3CN): $\lambda_{max} = 240$ ($\varepsilon = 5.12 \times 10^5$), 276 ($4.75 \times 10^5$ M^{-1} cm^{-1}).

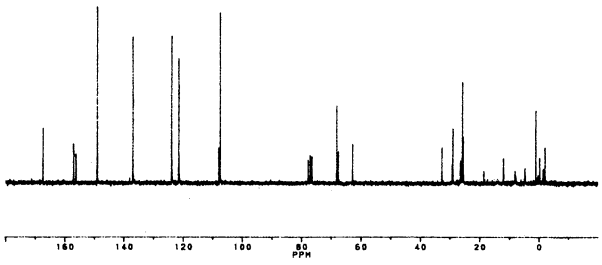
3.3. G3-16TPY

The same method as that of G1-4TPY was used in the reaction of G3-16Cl (0.45 g, 0.12 mmol), HOHTE (0.74 g, 2.11 mmol) and TMEDA (0.24 g, 2.11 mmol). Yield: 0.93 g (0.10 mmol, 88%) of a yellow gel. ^{1}H-NMR (ppm, $CDCl_3$): $\delta = 0.06$ (s, 36H, SiMe (G0–G2)), 0.09 (s, 96H, SiMe (G3)), 0.42–0.72, 1.35–1.75, 1.75–2.00 (m, 240H, CH_2 (G0–G2)), 3.54–3.80, 4.15–4.32 (m, 96H, OCH_2 (G1–G3)), 7.28–7.39, 7.80–7.95, 7.95–8.18, 8.55–8.75 (terpyridine rest). ^{13}C-NMR (ppm, $CDCl_3$): $\delta = -2.17$ (SiMe (G3)), -0.32 (SiMe (G0–G2)), 7.95, 9.43 (CH_2 (G0)), 14.77, 25.40 (CH_2 (G1–G3)), 25.40, 25.75, 28.87, 32.60 (CH_2), 62.70, 68.08 (OCH_2 (G1)), 65.24 (OCH_2 (G2–G3)), 107.39, 121.39, 123.31, 136.80, 136.85, 148.94, 156.09, 156.92, 167.27 (terpyridine rest). EA for $C_{464}H_{656}Si_{32}O_{60}N_{48}$ ($M_W = 8752$): C, 63.62%, H, 7.49%, N, 7.68%. Found: C, 63. 65%, H, 7.66%, N, 6.61%. UV–vis (nm, in CH_3CN): $\lambda_{max} = 240$ ($\varepsilon = 9.83 \times 10^5$), 276 ($8.94 \times 10^5$ M^{-1} cm^{-1}).

3.4. G1-4[TPY-Ru-TPY]

To the suspension of G1-TPY (0.21 g, 0.11 mmol) in methanol (25 ml), the methanol solution of $RuCl_3 \cdot 3H_2O$ (0.10 g, 0.51 mmol) was added and refluxed for 2 h. By ^{1}H-NMR spectroscopy, the product observed no signal because the product progressed to paramagnetic property. The solvent was removed from reaction medium and continually washed the red precipitate with distilled water, pentane and ether, in due order. Also to the suspension of the red precipitate (0.20 g, 0.07 mmol of G1-4(TPY-Ru)) in methanol (25 ml), 2,2′:6′,2″-terpyridine (0.08 g, 0.34 mmol) was added. The reaction mixture was refluxed for 2 h, cooled to room temperature and added NH_4PF_6 (40 times). The reaction





G2-8TPY

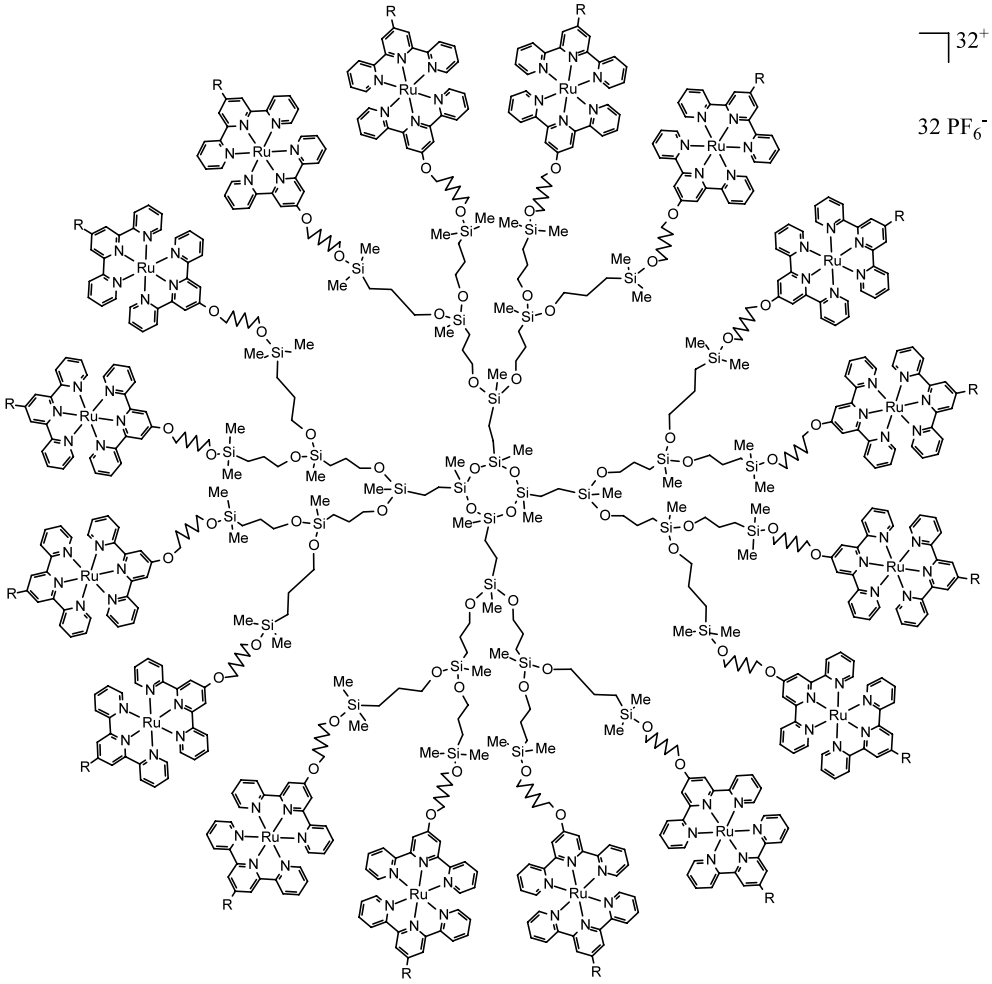
product was continually washed the reaction product with H_2O, pentane and Et_2O, in due order. Yield: 0.24g of red precipitate (0.054 mmol, 75%). ^{1}H-NMR (ppm, DMSO): $\delta = 0.00$ (s, 36H, SiMe (G0–G1)), 0.36–0.64, 1.34–1.72, 1.72–2.00 (m, 48H, CH_2 (G0–G1)), 3.12–3.70, 4.44–4.68 (m, 16H, OCH_2 (G1)), 7.00–7.40, 7.40–7.57, 7.80–8.10, 8.28–8.54, 8.54–9.10 (terpyridine rest). ^{13}C-NMR (ppm, DMSO): $\delta = -1.46$ (SiMe (G1)), -0.63 (SiMe (G0)), 8.30, 8.93 (CH_2 (G0)), 25.31, 25.49, 28.59, 32.52 (CH_2), 60.64, 69.86 (OCH (G1)), 111.33, 123.89, 124.42, 124.66, 127.71, 135.21, 137.90, 151.98, 152.25, 154.75, 155.28, 157.84, 157.93, 166.02 (terpyridine rest). EA for $C_{164}H_{184}Si_8O_{12}N_{24}Ru_4P_8F_{48}$ ($M_W = 4468$): C, 44.00%, H, 4.12%, N, 7.52%. Found: C, 43.15%, H, 4.10%, N, 7.25%. UV–vis (nm, in CH_3CN): $\lambda_{max} = 241$ ($\varepsilon = 1.31 \times 10^5$), 269 ($1.50 \times 10^5$), 305 ($1.96 \times 10^5$), 480 ($0.53 \times 10^5$ M^{-1} cm^{-1}).

3.5. G2-8[TPY-Ru-TPY]

The same method as that of G1-4[TPY-Ru-TPY] was used. ^{1}H-NMR (ppm, DMSO): $\delta = -0.03$ (s, 24H, SiMe (G0–G1)), 0.01 (s, 48H, SiMe (G2)), 0.30–0.52, 1.34–1.72, 1.75–2.10 (m, 112H, CH_2 (G0–G2)), 3.12–3.66, 4.32–4.68 (m, 48H, OCH_2 (G1–G2)), 7.10–7.48, 7.80–8.10, 8.28–8.55, 8.55–9.10 (terpyridine rest). ^{13}C-NMR (ppm, DMSO): $\delta = -1.32$ (SiMe (G0–G2)), 7.94, 8.30 (CH_2 (G0)), 13.57 (CH_2 (G1, G2)), 25.24, 25.41, 28.52, 32.44 (CH_2), 62.59, 69.79 (OCH_2), 64.51 (OCH_2 (G2)), 111.24, 123.80, 124.33, 124.56, 127.63, 135.13, 137.84, 151.90, 152.16, 155.23, 155.33, 157.83, 157.86, 165.97 (terpyridine rest). EA for $C_{344}H_{400}Si_{16}O_{28}N_{48}Ru_8P_{16}F_{96}$ ($M_W = 9224$): C, 44.75%, H, 4.34%, N, 7.28%. Found: C, 43.43%, H, 4.28%, N, 6.49%. UV–vis (nm, in CH_3CN): $\lambda_{max} = 241$ ($\varepsilon = 3.07 \times 10^5$), 269 ($3.56 \times 10^5$), 305 ($4.55 \times 10^5$), 480 ($1.25 \times 10^5$ M^{-1} cm^{-1}).

3.6. G3-16[TPY-Ru-TPY]

The same method as that of G1-4[TPY-Ru-TPY] was used. ^{1}H-NMR (ppm, DMSO): $\delta = -0.03$ (s, 36H, SiMe (G0–G2)), 0.03 (s, 96H, SiMe (G3)), 0.30–0.68, 1.25–1.79, 1.79–2.22 (m, 240H, CH_2 (G0–G3)), 3.02–



Scheme 2. G3-16[TPY-Ru-TPY].

3.80, 4.32–4.72 (m, 96H, OCH_2 (G1–G3)), 7.00–7.25, 7.25–7.62, 7.80–8.17, 8.35–8.57, 8.98–9.14 (terpyridine rest). ^{13}C-NMR (ppm, DMSO): $\delta = -1.13$ (SiMe (G0–G3)), 7.82 (CH_2 (G0)), 13.33 (CH_2 (G1–G3)), 25.25, 25.42, 28.54, 32.47 (CH_2), 60.62, 69.80 (OCH_2), 64.47 (OCH_2 (G2–G3)), 111.26, 123.81, 124.35, 124.57, 127.64, 135.15, 137.83, 151.91, 152.18, 155.25, 155.35, 157.84, 157.88, 165.99 (terpyridine rest). EA for $C_{704}H_{832}Si_{32}O_{60}N_{96}Ru_{16}P_{32}F_{192}$ ($M_W = 18\,666$): C, 44.26%, H, 4.46%, N, 7.20%. Found: C, 43.07%, H, 3.99%, N, 6.31%. UV–vis (nm, in CH_3CN): $\lambda_{max} = 241$ ($\varepsilon = 6.36 \times 10^5$), 269 ($7.39 \times 10^5$), 305 ($9.38 \times 10^5$), 480 ($2.61 \times 10^5 M^{-1}\ cm^{-1}$) (Scheme 2).

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