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Palladium-Mediated One-Step Coupling between Polypyridine Metal Complexes: Preparation of Rigid and Dendritic Nano-Sized Ruthenium Complexes

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Summary: The Pd-catalyzed one-step graft reaction of metallodendron units with a core coordination compound afforded polypyridine metal-based and stiff dendritic architecture which showed characteristics potentially useful for light-harvesting devices.

The recent rapid development of methodologies for constructing dendritic architectures has enabled the synthesis of a number of nanometer-sized molecular particles with well-defined composition.[1−3] Among modern trends to integrate various functionalities into nanosized molecules, those for potential light-harvesting devices have attracted interest.[4] Since artificial light harvest would require absorption of incident visible light by peripheral multiantenna components and efficient channeling of the excitation energy to a common focal component, an important factor to be considered, particularly for the basic research, appears to be the rigidity of the system.[5,6] When the geometry of the dendrimer is strictly defined, the photophysical results obtained can be compared with theoretical predictions more easily than can those of systems with flexible arms and undefined structures. Further, it is desirable for the number of antenna units at the periphery to be large in order to achieve high capture efficiency of photons. Good examples which satisfy these requirements are the metallodendrimers synthesized by Balzani's group[7] and others,[8,9] which consist of M(2,3-dpp) (M = Ru(II), Os(II); dpp = bis(2-pyridyl)pyrazine) or similar networks with an estimated particle size of 5 nm. As in these cases, Ru(II)−polypyridine type complexes are excellent candidates for chromophore components because of their outstanding excited-state characteristics in the visible region. Herein we describe a new strategy to construct rigid and octahedral dendritic molecules by grafting, in one step, the rods of metallodendron units to that of a core metallodendron unit.[10] With this method, the synthesis of a large-sized stiff metallodendrimer is feasible, and this is demonstrated by the formation of cationic complexes with 6, 12, and 18 peripheral Ru(II)−terpyridine units. The largest cationic compound prepared in this fashion has an estimated diameter of 9 nm with 38 positive charges and 1435 atoms. Preliminary photophysical data are also presented.

Our design comprises a tris(bipyridine)metal unit to be placed at the center of a large molecule from which (ethynylene-*p*-phenylene)$_n$ arms are extended from the 4,4′-positions of each bipy ligand, which is accomplished by a palladium-catalyzed cross-coupling reaction.[11] Aside from its relevance to a light-harvesting device, this type of tris(bipyridine)metal-centered three-dimensional conjugated array has the possibility of being a good octupolar NLO device[12] and, consequently, development of systematic synthesis is highly desired. Initial attempts to use (4,4′-Br_2-bipy)$_3$M(PF_6)$_2$ (M = Ni, Cu, Ru) as the starting core complex were unsuccessful because they decomposed readily to intractable material even at room temperature in the presence of large excess amine. Since the more reactive iodide analogue 4,4′-I_2-bipy was found to be difficult to prepare, we turned to the "graft-synthesis", which utilizes complex **1** (Scheme 1). Complex **1**(PF_6)$_2$[13] was easily prepared by the reaction of 4,4′-(IC_2-C_6H_4)$_2$-bipy with the appropriate metal salts (metal = Ni, Cu, Ru) and was found to undergo a smooth

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(10) For the syntheses of "soft" metallodendrimers based on Ru-(terpy)$_2$ units with flexible linkages between them, see for example: (a) Newkome, G.; Cardullo, F.; Constable, E. C.; Moorefield, C. N.; Thompson, A. M. W. C. *J. Chem. Soc., Chem. Commun.* **1993**, 925. (b) Marvaud, V.; Astruc, D. *Chem. Commun.* **1997**, 773. (c) Constable, E. C. *Chem. Commun.* **1997**, 1073.

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10.1021/om980864h CCC: $18.00
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Scheme 1

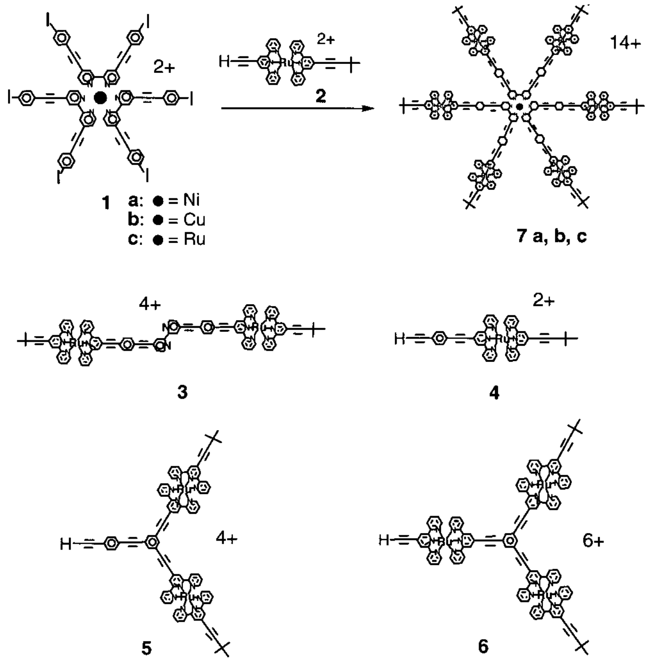
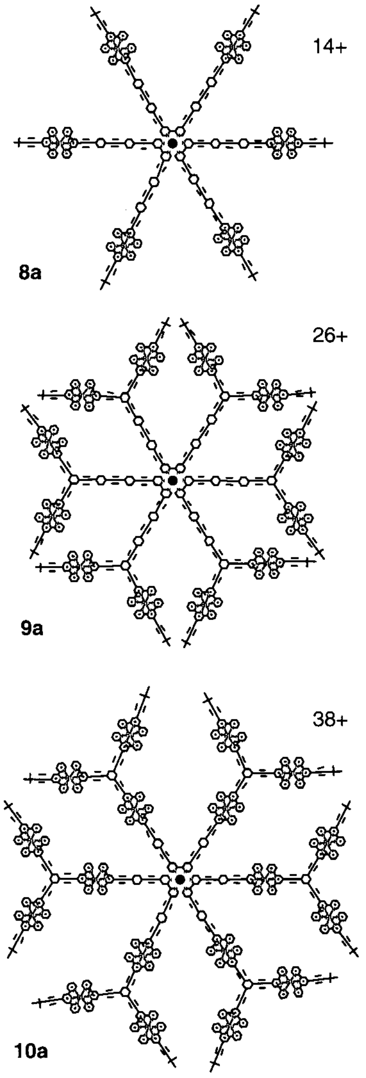


Chart 1



palladium-mediated cross-coupling reaction at room temperature with ca. 6.3 equiv of the (terpy)$_2$M derivative **2**$(PF_6)_2$,[15] having ethynyl terminal, to give **7a**–**c**$(PF_6)_{14}$.[16] The use of only a Pd complex as the catalyst is of key importance in this reaction. The often employed CuI cocatalyst[17,18] results in dominant formation of homocoupled **2**. The presence of the t-Bu groups at the outer terpy ligands is also crucial; without these substituents the complexes are hardly soluble in any solvent and the coupling reaction stops before completion. To the best of our knowledge, this reaction represents the first successful example for cross-coupling between two ligands which belong to different coordination compounds. Complexes **7a**–**c**$(PF_6)_{14}$ were fully characterized by elemental analyses, ^{1}H NMR spectra, and electrospray mass spectrometry (ESMS), in which clear peaks due to **7c**$(PF_6)_n$ ($n = 0$–9) were observed.[19] The molecular composition of **7a**–**c** was further confirmed by another synthetic route based on a convergent process; 3 equiv of **3** (Scheme 1) was reacted with MCl_2 (M = Ni, Cu) or $Ru(DMSO)_4Cl_2$ followed by addition of KPF_6. The convergent route, however, was extremely difficult when synthesis of analogous but larger complexes was attempted. Complexes **7a**–**c**$(PF_6)_{14}$ were obtained as dark red solids and are soluble in dichloromethane and acetonitrile.

Having established that the one-step multigraft reaction between the two metal complexes by means of Pd-mediated cross-coupling is highly efficient, we applied it to the synthesis of the larger dendritic molecules **8a**$(PF_6)_{14}$, **9a**$(PF_6)_{26}$, and **10a**$(PF_6)_{38}$ (Chart 1) by reacting **1a**$(PF_6)_2$ with ca. 6.3 equiv of **4**, **5**, and **6**, respectively. All the reactions proceeded smoothly and gave the desired products in good yields (67–78%). ESMS spectra of these complexes failed to give molecular ion peaks but showed fragment peaks due to dissociation of the central Ni–bipy bonds. The presence of the expected "grafted-bipy" units and absence of peaks due to unreacted bipy or (terpy)$_2$Ru fragments strongly suggest that the desired complexes have been successfully formed. ^{1}H NMR spectra of the complexes are also fully consistent with their formation.[20] Since molecule **10a** appears to be one of the largest (ca. 90 Å) transition-metal-containing and stiff-structured dendrimers yet known, it was further characterized by TEM (transmission electron microscopy) examination. As shown in

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[15] Osawa, M.; Sonoki, H.; Hoshino, M.; Wakatsuki, Y. *Chem. Lett.* **1998**, *11*, 1081.

[16] A typical experimental procedure is given for **7a**$(PF_6)_{14}$. To a degassed solution of **1a**$(PF_6)_2$ (0.059 g, 0.027 mmol) and $Pd(PPh_3)_4$ (0.020 g, 0.017 mmol) in DMF (10 mL)/THF (10 mL)/Et_3N (10 mL) was added solid **2**$(PF_6)_2$ (0.164 g, 0.170 mmol). After 3.5 h of ultrasonic agitation at room temperature, the crude reaction mixture was evaporated to dryness. The product **7a**$(PF_6)_{14}$ was obtained in 62% yield as an orange-red powder after size exclusion chromatography (Sephadex LH-20; eluent, CH_3CN). UV/vis (CH_3CN, nm): λ_{max} (ϵ) 497 (3.3×10^5). Anal. Calcd for $C_{306}H_{216}N_{42}F_{84}P_{14}Ni_1Ru_6$: C, 51.21; H, 3.03; N, 8.20; Ru, 8.46; Ni, 0.82. Found: C, 50.73; H, 3.13; N, 8.08; Ru, 7.98; Ni, 0.81. IR (KBr, cm^{-1}): ν(C≡C) 2213 (br). ESMS (m/z): 993.0 $[(M - Ni - 2PF_6)/3 - 2PF_6]^{2+}$, 613.8 $[(M - Ni - 2PF_6)/3 - 3PF_6]^{3+}$, 424.5 $[(M - Ni - 2PF_6)/3 - 4PF_6]^{4+}$.

[17] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

[18] Osakada, K.; Sakata, R.; Yamamoto, T. *Organometallics* **1997**, *16*, 5354.

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[20] The two aromatic protons next to the ethynyl group (HC≡C–) in **6** appear at δ 8.84, while the corresponding proton peak in **10a** is at δ 8.99. All other ^{1}H NMR peaks for **10a** were also reasonably assignable, and no extra peaks due to any impurities were observed.

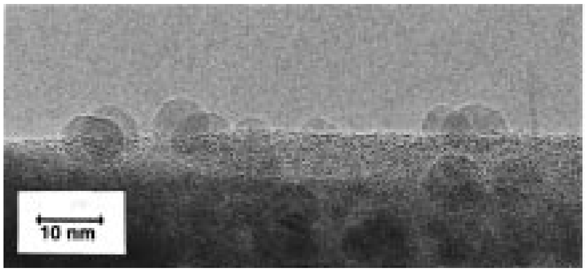

Figure 1. Electron micrograph (TEM) of molecules of **10a** supported on cellulose microcrystals.

Figure 1, individual molecules are clearly recognized and their sizes agree quite well with the value predicted for the dendritic cation. After ca. 15 min under the electron beam (820 kV), **10a** began to decompose and disappeared in a short time. In the cases of "soft" dendrimers, visualization by TEM[21−23] or scanning microscopy[24−26] has often caused problems such as aggregation, flattening, and other deformations.

The emission measurements were performed at 150 K in *n*-C_3H_7CN solution with laser excitation at 532 nm, where the absorption is by the ^{1}MLCT band of the $(terpy)_2Ru$ moiety, and the concentrations of all samples were adjusted so that the absorbency at 532 nm is 0.2. The emission peak positions are almost constant and are at 680−690 nm. Taking the emission intensity of **3** as the standard (1.0), the following intensity values were obtained: **7a** (0.44), **7b** (1.06), **8a** (0.41).[27] Likewise, when the bipy fragment of **9**, i.e., one-third of the whole ligand of **9**, is taken as the standard, **9a** was observed to emit with an intensity of 0.86. Though a standard complex for **10** could not be prepared, the quenching efficiency for **10a** was estimated to be approximately similar to that of **9a**. In contrast, Cu(II) in **7b** does not quench the MLCT state of the peripheral polypyridine−Ru units. These results suggest that the electronic energy transfer from the photoexcited Ru(II)−polypyridine periphery to the central focal point depends largely on the central metal and branching structure of the link units.

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Supporting Information Available: Text giving details of the experimental procedures for assembling steps (**3**−**10**) of dendrons (6 pages). Ordering information is given on any current masthead page.

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[27] The change of emission intensity on addition of various metal ions to a solution of $Ru(terpy)_2C_2$-substituted bipy ligand has recently been reported: Hissler, M.; El-ghayoury, A.; Harriman, A.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 1717.