Chiral Hybrid Metal–Organic Dendrimers
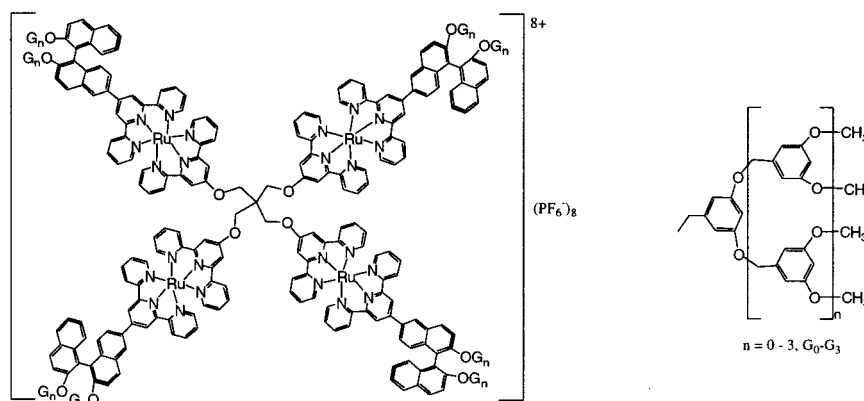
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ABSTRACT

New chiral terpyridines containing Frechét-type dendrons have been readily synthesized by coupling dendritic benzyl bromide and 4′-[6-(2,2′-dihydroxy-1,1′-binaphthyl)]-2,2′:6′2″-terpyridine. These chiral dendritic terpyridines were used to efficiently construct high molecular weight hybrid metal–organic dendrimers based on the Ru(II)–bis(terpy) linkage. Preliminary fluorescence measurements show generation-dependent fluorescence quenching behavior of 3,5-dimethoxybenzyl peripherals by the $[Ru(terpy)_2]^{2+}$ unit.

Metal-containing dendrimers are of great current interest because they can be used as catalysts or molecular carriers for catalysts[1,2] and synthetic light-harvesting antennae.[3] Moreover, metal−ligand coordination provides a facile pathway for the efficient assembly of highly branched dendritic architectures owing to the tunability of both metal−ligand bond strength and metal−ligand coordination geometry. Since the pioneering work by Newkome et al.[4] and Balzani et al.[5] a decade ago, numerous dendritic structures

based on metal−ligand ligation have been reported.[6] Owing to their monodisperse nature and the ability to control the positioning of their constituent building units, dendritic structures have been extensively explored as model systems for light-harvesting and energy transfer processes.[7] By placing light-collecting chromophores (dendrons) on their peripheries and an energy "sink" at the core, efficient energy transfer has been achieved in these dendritic structures. A variety of such dendritic structures have been designed as models for functional light-emitting diodes,[8] signal ampli-

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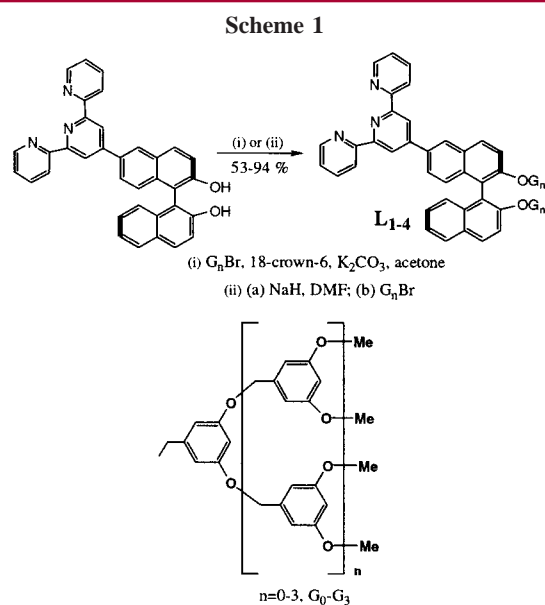
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fiers,[9] fluorescent sensors,[10] and other photonic devices.[11] We have recently become interested in the design and synthesis of robust chiral metal−organic dendritic structures for potential applications in asymmetric catalysis. Herein we report facile synthesis of high molecular weight chiral hybrid metal−organic dendrimers based on the Ru(II)−bis(terpy) linkage. These novel chiral hybrid metal−organic dendrimers exhibit interesting generation-dependent fluorescence quenching behavior of 3,5-dimethoxybenzyl peripherals by the [Ru(terpy)$_2$]$^{2+}$ unit.

Frechét-type benzyl bromide dendrons, G$_n$Br, were synthesized following the literature procedures.[12] Enantiopure dendritic terpyridine ligands L$_{1-4}$ were synthesized in good yields either by treating 4′-[6-(2,2′-dihydroxyl-1,1′-binaphthyl)]-2,2′:6′2′′-terpyridine, L,[13] with dendritic benzyl bromides G$_n$Br using the Fréchet conditions or by deprotonation of L with NaH followed by nucleophilic attack on dendritic benzyl bromides G$_n$Br (Scheme 1). All the ligands L$_{1-4}$ have

Scheme 1

(i) or (ii)
53-94 %

L$_{1-4}$

(i) G$_n$Br, 18-crown-6, K$_2$CO$_3$, acetone

(ii) (a) NaH, DMF; (b) G$_n$Br

n=0-3, G$_0$-G$_3$

been characterized by ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. L$_1$ and L$_2$ have also been characterized using high-resolution mass spectrometry, while L$_3$ and L$_4$ have been characterized by FAB-MS and MALDI-TOF-MS, respectively.

Ru(III) complexes Ru(L$_{1-4}$)Cl$_3$ were prepared in high yields (76−95%) by refluxing RuCl$_3$ and ligands L$_{1-4}$ in a mixture of acetone and ethanol overnight. Ru(III) complexes Ru(L$_{1-4}$)Cl$_3$ prepared in this manner were purified by preparative-scale thin-layer chromatography. Complexes Ru(L$_{1-4}$)Cl$_3$ were treated with tetrakis(2,2′:6′,2′′-terpyridinyl-4′-oxymethyl)methane in ethylene glycol with 4-ethylmor-

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pholine as the reducing agent at 120 °C to afford the crude products, whose chloride anions were metathesized with PF$_6^-$ to give more soluble chiral metallodendrimers 1a−d in 20−59% overall yields after purifications by repeated recrystallization from CH$_3$CN/MeOH (Scheme 2).[14] Compounds

Scheme 2

RuCl$_3$

L$_1$-L$_4$

HOCH$_2$CH$_2$OH 120 °C

NaPF$_6$

8+

(PF$_6$)$_8$

n=0-3, 1a-1d
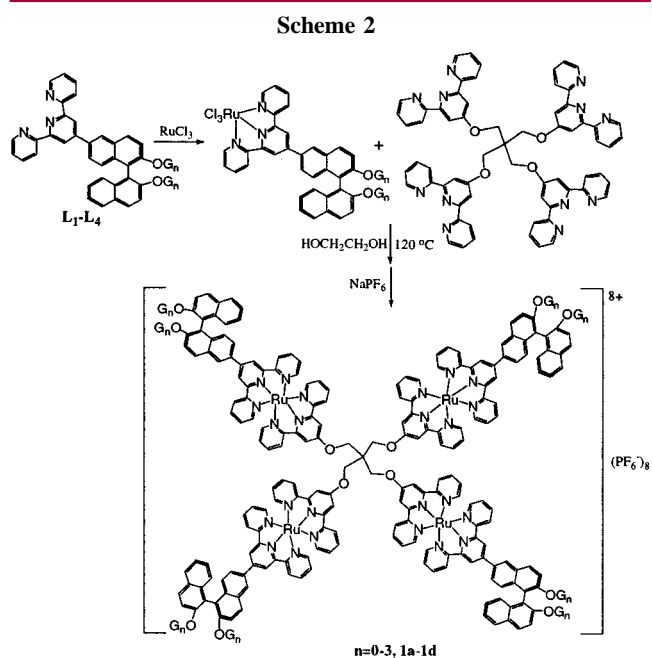
1a−d were characterized by ^{1}H and ^{13}C{^{1}H} NMR, COSY, ESI-MS, and MALDI-TOF-MS.

The proton signals of the ^{1}H NMR spectra of 1a−d are well separated into five groups: signals between 9.2 and 7.0 ppm are attributed to the aromatic protons of the terpyridyl and binaphthyl groups; signals between 6.7 and 6.2 ppm belong to protons of phenyl groups of benzyl aryl ethers; a broad singlet at ∼5.8 ppm is assigned to the methylene protons of the tetrakis(2,2′:6′,2′′-terpyridinyl-4′-oxymethyl)-methane ligand; signals between 5.5 and 4.6 ppm are attributed to methylene groups of the G$_0$−G$_3$ dendrons; and the peaks between 4.3 and 4.0 ppm are attributed to the peripheral methoxy groups. For lower generation dendrimers 1a and 1b, we were able to assign almost all of the proton signals on the basis of the ^{1}H NMR and COSY spectra (Figure 1). However, for higher generation dendrimers 1c and 1d, the signals for the aromatic protons due to the L and tetrakis(2,2′:6′,2′′-terpyridinyl-4′-oxymethyl)methane groups have become quite weak owing to the dominance of the peripheral dendrons. In addition, the aromatic proton signals for the third-generation dendrimers 1d have become very broad, a direct consequence of reduced tumbling for such high molecular weight dendrimers in solution (molecular weight of ∼21 kD for 1d). Detailed assignments of these proton signals have thus not been possible. Fortunately, the

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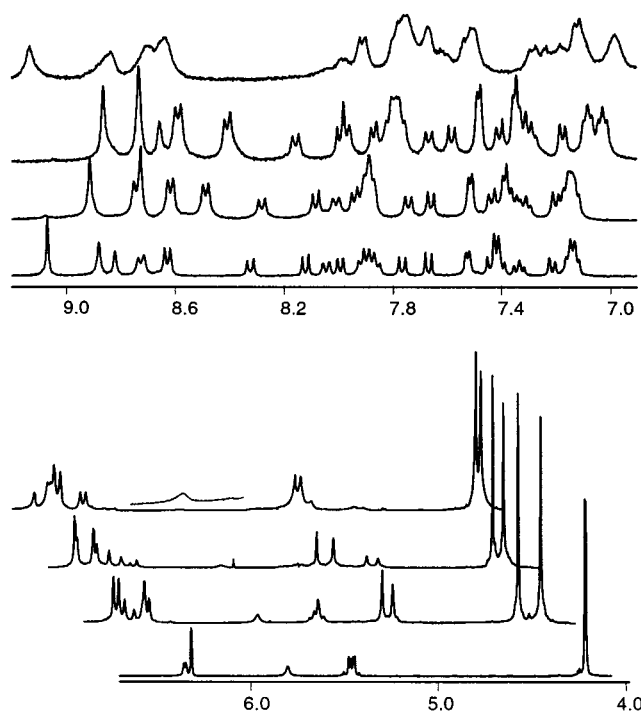**Figure 1.** ^{1}H NMR spectra for dendrimers **1a–d** (from bottom to top).

Figure 2. UV−vis spectra of **1a–d**.

purity of **1a–d** can be readily ascertained on the basis of two characteristics in their ^{1}H NMR spectra. First, there are only two sets of signals expected for the peripheral methyl protons in pure samples of **1a–d**. Second, the integration ratio of the signals due to terpyridyl and binaphthyl protons vs that of the methylene protons for the tetrakis(2,2′:6′,2″-terpyridinyl-4′-oxymethyl)methane group of 31:2 provides another excellent diagnostic for the purity of **1a–d**.

The UV−vis spectra of **1a–d** exhibit broad peaks around 496 nm due to metal-to-ligand charge transfer excitation, in addition to those bands assignable to the ligands **L₁₋₄** and tetrakis(2,2′:6′,2″-terpyridinyl-4′-oxymethyl)methane core. These ^{3}MLCT bands are slightly red-shifted from that of [Ru(terpy)$_2$]$^{2+}$ (cf. 476 nm), consistent with the presence of electron-donating groups in the 4′-positions of the modified terpy ligands.[15] It is interesting to note that the bands due to the phenyl ether units steadily grow in intensity as the generation grows, while the bands due to the terpyridyl and binaphthyl units and the metal-to-ligand charge transfer excitation remain essentially constant among the different generation of metallodendrimers. Compounds **1a–d** exhibit one reversible Ru^{II,III} oxidation process with $E_{1/2}$ values of 1.27, 1.26, 1.24, and 1.29 V in methylenechloride, respectively.

Although ligands **L₁₋₄** are highly luminescent to give a broad peak at ∼430 nm upon excitation at 330 nm, the lower

generation (G$_0$–G$_2$) chiral metallodendrimers **1a–c** are nonemissive in solution at room temperature (Figure 3). In contrast, **1d** exhibits a weak emission peak at ∼390 nm when excited at 340 nm.[16] It is well-established that low-lying metal-centered states can efficiently quench the luminescent ^{3}MLCT state in ruthenium(II) bis(terpyridine) complexes.[17] Moreover, we believe that the intersystem crossing from the π* bands of the peripheral 3,5-dimethoxybenzyl fluorophores to the ^{3}MLCT bands of the interior Ru(terpy)$^{2+}$ moieties is also highly efficient in **1a–c**. The Ru(terpy)$^{2+}$ moieties thus efficiently quench the luminescence of not only the terpy and binaphthyl fluorophores but also the peripheral 3,5-dimethoxybenzyl fluorophores. As a result, **1a–c** are non-emissive in solution at room temperature. A comparison of

Figure 3. Top: fluorescence spectra of **L₁₋₄**. Bottom: luminescence spectra of **1a–d**.

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(16) Luminescence quantum yield for **1d** is estimated to be 0.14 in acetonitrile with anthracene as the reference.

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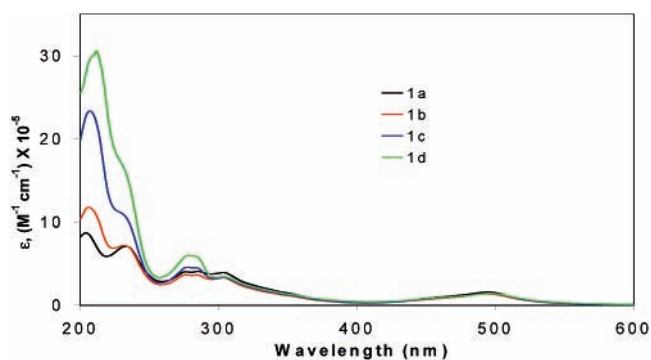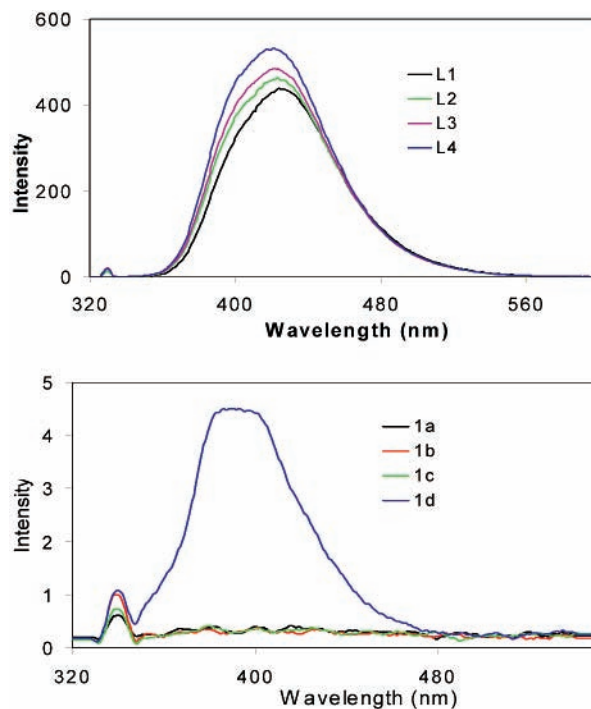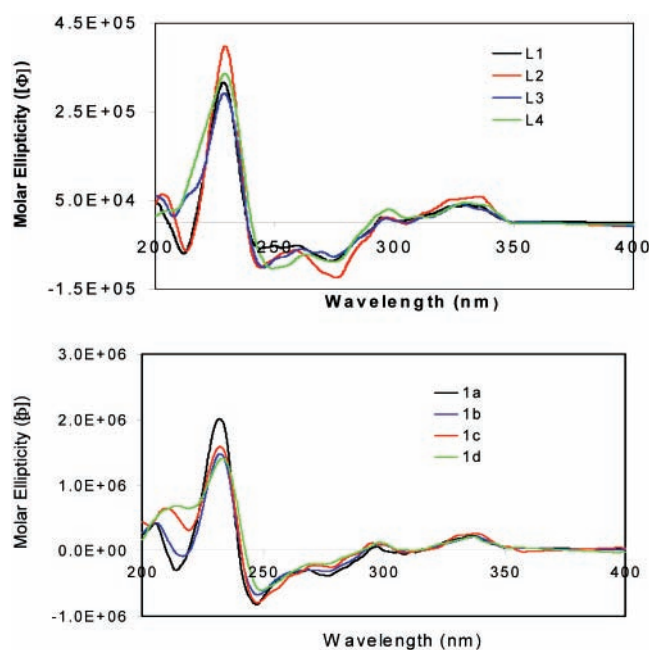
Figure 4. Top: circular dichroism spectra of **L₁₋₄**. Bottom: circular dichroism spectra of **1a−d**.

the fluorescence spectra of **L₁₋₄** shows that they exhibit a shoulder peak at ~390 nm (in addition to a major emission band at ~430 nm), whose intensity steadily increases as the generation increases. We therefore assign this shoulder emission peak at ~390 nm to the peripheral 3,5-dimethoxy-benzyl groups. This assignment has been further supported by the fluorescence spectrum of 3,5-dimethoxybenzyl alcohol, which exhibits a weak fluorescence peak at ~390 nm upon excitation at 330 nm. Taken together, we believe that the weak emission of **1d** at ~390 nm is due to the peripheral 3,5-dimethoxybenzyl groups whose fluorescence cannot be

completely quenched by the Ru(terpy)$^{2+}$ moieties as a result of larger separation between the peripheral 3,5-dimethoxy-benzyl groups and the Ru(terpy)$^{2+}$ moieties. The preliminary luminescence study thus places an upper limit of 27−33 Å[18] for efficient energy transfer between the π^* bands of the peripheral 3,5-dimethoxybenzyl fluorophores and the ^{3}MLCT bands of the interior Ru(terpy)$^{2+}$ moieties.

Circular dichroism (CD) spectra of chiral terpy ligands **L₁₋₄** exhibit three Cotton effects around 231, 275, and 335 nm, corresponding to the ^{1}B, ^{1}L$_a$, and ^{1}L transitions, respectively (Figure 4). The Cotton effects due to the ^{1}L$_a$ and ^{1}L$_b$ transitions are much more visible in comparison to the parent 1,1′-bi-2-naphthol. These bands have been previously observed in 1,1′-binaphthyl-based oligomers linked through their 6,6′-positions.[19] Chiral metallodendrimers **1a−d** exhibit CD signals similar to chiral terpy ligands **L₁₋₄**, indicating that no new chirality has resulted upon the formation of metallodendrimers.

In summary, chiral hybrid metal−organic dendrimers with high molecular weights have been readily synthesized, and interesting generation-dependent luminescent behavior was observed. Elucidation of the exact luminescence mechanisms using time-resolved spectroscopy is currently under investigation.

Supporting Information Available: Experimental procedures, analytical data, one table, and one figure. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) We estimate the exterior 3,5-dimethoxybenzyl groups to be ~27 Å away from the Ru(II) centers in **1c** and ~33 Å in **1d**.

(19) Ma, L.; White, P. S.; Lin, W. *J. Org. Chem.*, ASAP (JO0255680).