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Synthesis of fluorescent dendritic 8-hydroxyquinoline ligands and investigation on their coordinated Zn(II) complexes

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Abstract—A series of luminescent PAMAM dendrons emanating from 8-hydroxyquinoline have been synthesized and their coordination with Zn(II) was investigated for the first time. The obtained dendritic Zn(II) complexes were soluble in common organic solvents. It was found that the luminescence intensity of G2 dendron **6** was higher than that of G1 dendron **4**. Furthermore, when they were coordinated with Zn(II), red-shift was observed and the intensities of the coordinated Zn(II) complexes were higher than that of the corresponding ligands.

Dendrimers are highly ordered, globular monodisperse macro-molecules composed of repeated branch units emanating from a central core.[1] Their physical properties depend mainly on their ending groups. Dendrimers with an active site encapsulated inside, for example, the core as a ligand of coordination, are very interesting. Dendrimer, containing a photo- or/and an electro-active unit as a core, was expected to have significant enhancement in its photochemical and electrochemical properties, in comparison with its core molecule.[2,3]

8-Hydroxyquinoline and its derivatives are of the most extensively investigated ligands in the coordination chemistry.[4] They have been used in metallic ion detection,[5] chromatography[6] and especially in organic light-emitting diodes (OLEDs).[7,8] Most metallic complexes of 8-hydroxy-quinoline have poor solubility in organic solvents, so that tedious vacuum-grafting technique had to be applied to fabricate films for OLEDs. Therefore, to synthesize readily soluble metallic complexes of 8-hydroxyquinoline is of great importance.

Here, we report a convenient method for the preparation of a group of solvent-soluble dendrons emanating from 8-hydroxyquinoline. The protection and deprotection of hydroxyl group in 8-hydroxyquinoline was efficiently avoided. Furthermore, the coordination of ester-terminated dendrons **4** and **6** with Zn(II) in ethyl acetate was investigated for the first time. Enhanced green fluorescence emitting of the complexes was observed.

As shown in Scheme 1, 5-amino-8-hydroxyquinoline **1**, was acylated using 1.0 equiv of acryloyl chloride in the presence of 1.0 equiv of Et_3N.[9] The crude product was washed with CH_2Cl_2 to yield **2** (50%) as a white powder. The Michael reaction of **2** with ethylenediamine was carried out with a large excess of ethylenediamine in methanol, followed by chromatography of the crude product with CH_2Cl_2–CH_3OH (25:1 v/v), to yield **3** (80%) as a yellow powder. A further Michael reaction of **3** with methyl acrylate was carried out in methanol to give **4** as yellow oil in 75% yield after column chromatography (silica gel). The second generation of ester-terminated dendritic ligand **6** (50%), as yellow oil, was prepared from **4** by the previous method.[10] Their structures were assigned by ESI-MS, ^1H NMR, ^{13}C NMR, 2D ^{13}C–^1H COSY and IR spectra.[11] The experimental result showed that the ester-terminated ligands **4** and **6** have good solubility in most common organic solvent, such as CH_3OH, CH_2Cl_2, $CHCl_3$, THF, CH_3CN and EtOAc.

Dendritic complexes **Zn(4)$_2$** and **Zn(6)$_2$** were formed by treating dendron **4** and **6** (30 mL, 1.9×10^{-4} M, in ethyl

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Keywords: Synthesis; Dendritic; 8-Hydroxyquinoline; Luminescence.

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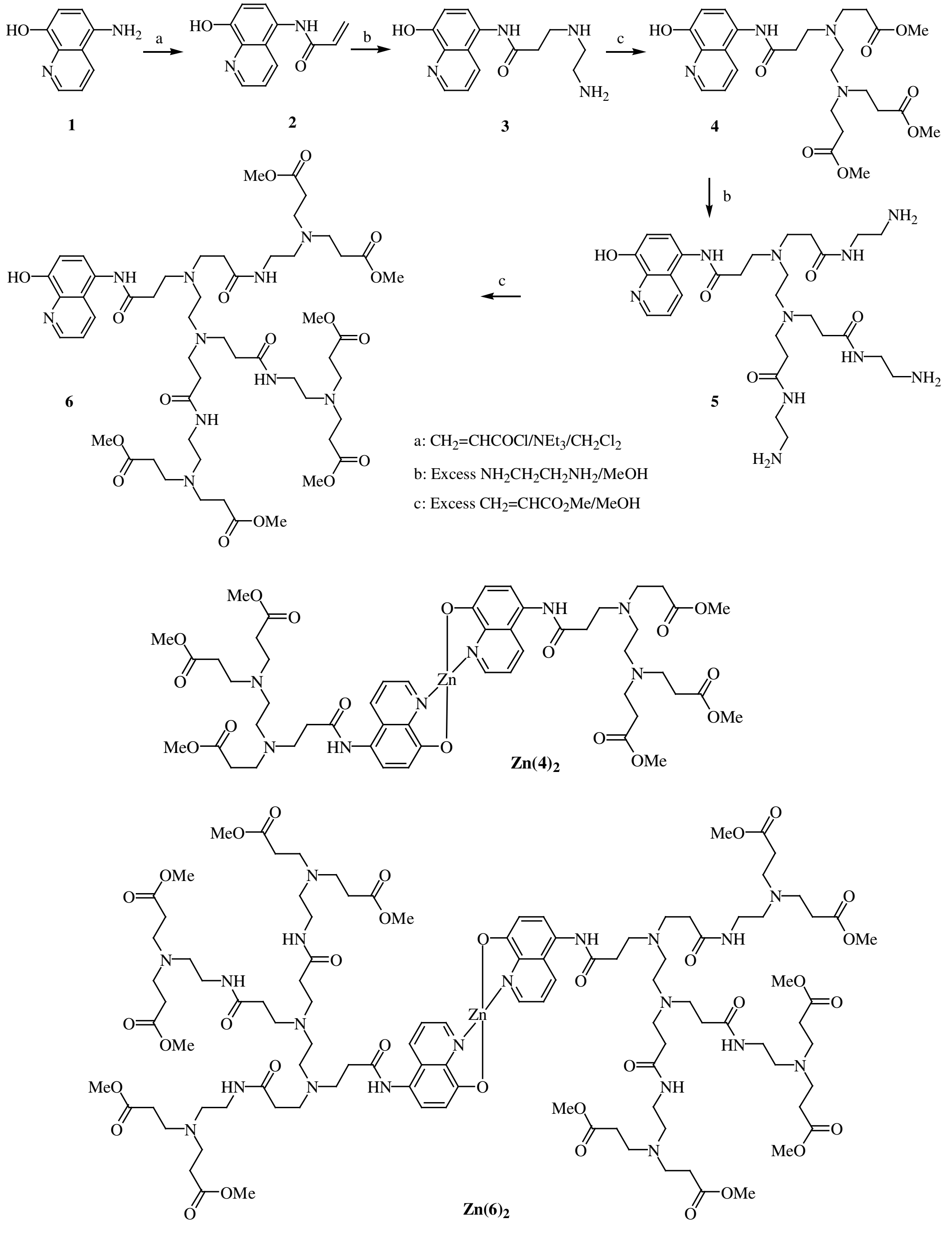

Scheme 1. Synthesis of dendritic 8-hydroxyquinoline ligands and their complexes with Zn(II).

acetate), respectively, with stoichiometric amounts of $Zn(OAc)_2$ in CH_3OH (0.50 mL). The resulting dendrimer complexes with Zn(II), $\mathbf{Zn(4)_2}$ and $\mathbf{Zn(6)_2}$, have been confirmed by ESI-MS spectrum. At the first generation, the mass spectrum of **4** exhibits an intense signal at *m/z* 533 corresponding to $[\mathbf{4}+H]^+$ and a weak signal at *m/z* 555 corresponding to $[\mathbf{4}+Na]^+$. The signal at *m/z* 533 almost disappears after addition of a stoichiometric amount of $Zn(OAc)_2$, whereas two intense signals at *m/z* 1128 and 1150 corresponding to $[\mathbf{Zn(4)_2}+H]^+$ and $[\mathbf{Zn(4)_2}+Na]^+$ were emerged. For the second generation, the mass spectrum of **6** exhibits an intense signal at *m/z* 1134 corresponding to $[\mathbf{6}+H]^+$. The signal almost disappears after addition of a stoichiometric amount of $Zn(OAc)_2$, whereas an intense signal at *m/z* 2351 corresponding to $[\mathbf{Zn(6)_2}+Na]^+$ appeared (Fig. 1).

The fluorescence spectra of the dendrons (**4** and **6**) and the dendrimer complexes $\mathbf{Zn(4)_2}$ and $\mathbf{Zn(6)_2}$ were shown in Figures 2 and 3. The intensity of **6** is higher than that of **4** at 520 nm. The dendrimer complexes show stronger fluorescent intensity and a red-shifted emission in

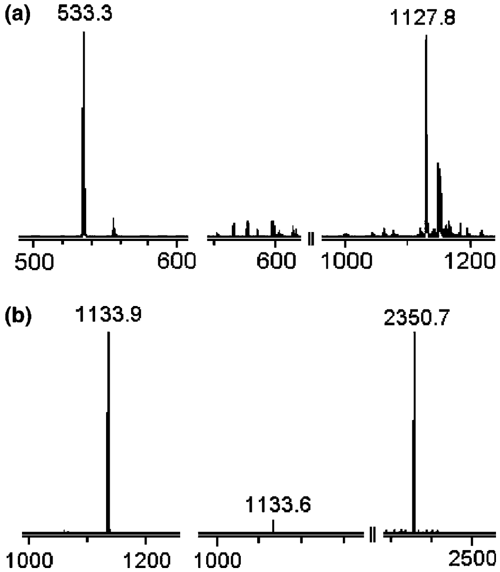

Figure 1. (a) ESI-MS spectrum of **4** (1.9×10^{-4} M, in ethyl acetate) before (left) and after (right) addition of a stoichiometric amount of $Zn(OAc)_2$; (b) ESI-MS spectrum of **6** (1.9×10^{-4} M, in ethyl acetate) before (left) and after (right) addition of a stoichiometric amount of $Zn(OAc)_2$.

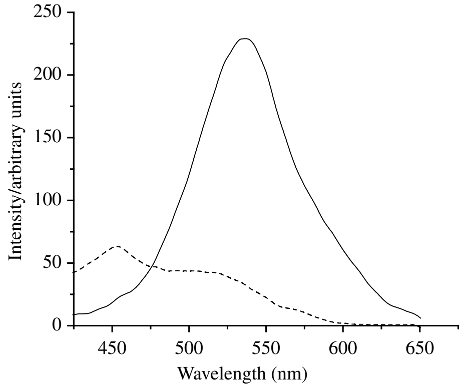

Figure 2. Luminescence of **4** (1.9×10^{-4} M, in ethyl acetate) before (dashed line) and after (full line, $\lambda_{max} = 536$ nm) addition of a stoichiometric amount of $Zn(OAc)_2$ on excitation at 400 nm (room temperature).

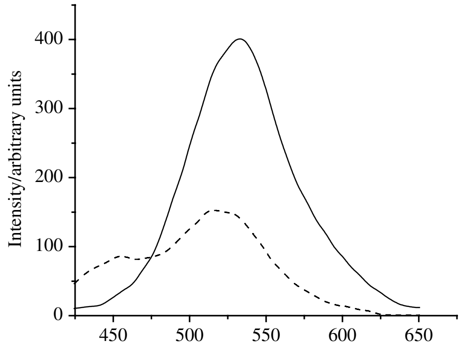

Figure 3. Luminescence of **6** (1.9×10^{-4} M, in ethyl acetate) before (dashed line) and after (full line, $\lambda_{max} = 533$ nm) addition of a stoichiometric amount of $Zn(OAc)_2$ on excitation at 400 nm (room temperature).

comparison with their dendrons. The dendrimer complexes **$Zn(4)_2$** and **$Zn(6)_2$** in ethyl acetate emit at 536 and 533 nm, respectively. The intensity of **$Zn(4)_2$** is higher than that of **4** and the intensity of **$Zn(6)_2$** is higher than that of **6**. From a spectroscopic and photophysical viewpoint, they could consist of a core of bis(8-hydroxyquinoline) zinc(II) (ZnQ_2) chromophoric unit. ZnQ_2 in CH_2Cl_2 emits at 535 nm.[12] The emission spectra in visible region for ZnQ_2, **$Zn(4)_2$** and **$Zn(6)_2$** are quite similar, indicating that the shape and chemical properties of the dendrimer branches do not substantially affect the ZnQ_2-based chromophoric core. Figures 2 and 3 show that the higher generation dendron or dendrimer complex exhibits stronger luminescence. All of the luminescence measurements were carried out in air-equilibrated solutions at room temperature with a Perkin–Elmer LS50B spectrofluorimeter.

In conclusion, an efficient divergent procedure for synthesizing novel dendritic 8-hydroxyquinoline ligands was described and their complexation with Zn(II) was investigated. The ester-terminated dendrimer Zn(II) complexes emit green fluorescence and have excellent solubility in a wide-range of organic solvents. Work is continuing in our laboratory to synthesize high generation of dendrons and their complexes with other metallic ions.

Acknowledgements

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11. Selected characterization data of the dendritic ligands. Compound **4**: IR 3263, 2952, 2833, 1735, 1682, 1657 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.68 (s, 1H, ArNHC=O), 8.79 (dd, 1H, $J = 4.2, 1.3$), 8.22 (dd, 1H, $J = 8.5, 1.3$), 8.21 (br s, 1H, ArOH), 7.56 (d, 1H, $J = 8.2$), 7.49 (dd, 1H, $J = 8.5, 4.2$), 7.15 (d, 1H, $J = 8.2$), 3.63 (s, 6H, –OCH_3), 3.42 (s, 3H, –OCH_3), 2.95 (t, 2H, –NCH_2–), 2.89 (t, 2H, –NCH_2–), 2.73 (t, 4H, –NCH_2–), 2.69 (t, 2H, –NCH_2–), 2.66 (t, 2H, –NCH_2–), 2.59 (t, 2H, –CH_2C=O), 2.56 (t, 2H, –CH_2C=O), 2.35 (t, 4H, –CH_2C=O); ^{13}C NMR (100 MHz, $CDCl_3$) δ 172.9, 172.8, 171.9, 150.6, 147.8, 138.2, 132.0, 124.2, 124.2, 124.1, 121.7, 109.4, 51.7, 51.5, 51.4, 50.8, 49.4, 49.3, 33.9, 32.0, 31.5; ESI-MS: calcd for $(M+H)^+$: 533. Found: *m/z* $(M+H)^+$: 533. Compound **6**: IR 3413, 2955, 2835, 1734, 1649 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.69 (s, 1H, ArNHC=O), 8.77 (dd, 1H, $J = 4.2, 1.4$), 8.39 (d, 1H, $J = 8.3$), 8.18 (br s, 1H, ArOH), 7.58 (d, 1H, $J = 8.2$), 7.49 (dd, 1H, $J = 8.6, 4.2$), 7.12 (d, 1H, $J = 8.2$), 7.02 (s, 2H, –NHC=O), 6.96 (s, 1H, –NHC=O), 3.65 (s, 12H, –OCH_3), 3.63 (s, 6H, –OCH_3), 3.26–3.22 (m, 4H, –CH_2NHC=O), 2.87 (br, 4H, –NCH_2–, 2H, –CH_2NHC=O), 2.77–2.70 (m, 4H, –NCH_2–), 2.73 (t, 8H, –NCH_2–), 2.64 (br, 4H, –NCH_2CH_2N–, 2H, –CH_2C=O), 2.56 (t, 4H, –NCH_2–), 2.49 (t, 4H, –NCH_2–), 2.41 (t, 12H, –CH_2COOCH_3), 2.30 (t, 6H, –CH_2CONH–), 2.16 (t, 2H, –NCH_2–); ^{13}C NMR (100 MHz, $CDCl_3$) δ 173.0, 172.6, 172.3, 150.3, 147.8, 138.1, 132.6, 124.8, 124.3, 124.0, 121.6, 109.2, 52.9, 52.4, 51.8, 51.6, 51.6, 51.4, 51.1, 50.1, 49.8, 49.2, 49.0, 37.1, 36.9, 34.8, 33.8, 33.6, 32.6; ESI-MS: calcd for $(M+H)^+$: 1133. Found: *m/z* $(M+H)^+$: 1133.
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