

Luminescence Enhancement of Tb³⁺ Ion in Assemblies of Amphiphilic Linear–Dendritic Block Copolymers: Antenna and Microenvironment Effects

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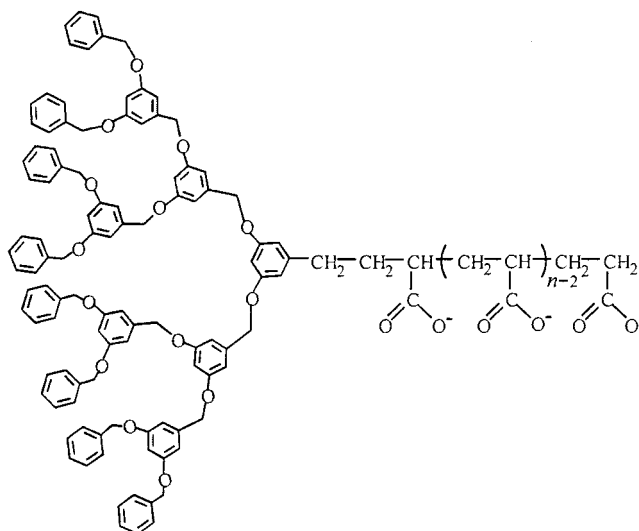
The luminescence enhancement of Tb³⁺ ion bound to amphiphilic linear–dendritic block copolymers [poly(acrylic acid)–dendritic polyether, PAA–Dendr.PE] was investigated. Tb³⁺ ion complexes with a PAA chain of block copolymer to form a supramolecular luminophore. The observed prominent enhancement in luminescence properties can be attributed to two important factors. The antenna effect, energy harvest and transfer from the dendritic polyether subunit to the ground state of the Tb³⁺ ion, leads to a remarkable increase of luminescence intensity of Tb³⁺ ion, which enlarges obviously with increasing generation of dendrimer. Furthermore, the unique microenvironment surrounding the Tb³⁺ ion that derives from multimolecular assembly of copolymer results in a large decrease of the number of water molecules coordinated to Tb³⁺ from 3.5 to 1.3, which is the other factor to greatly enhance the luminescence intensity of Tb³⁺ ion.

I. Introduction

Dendrimers are highly branched yet structurally perfect molecules with a large number of end groups that grow exponentially with their generation number.^{1–3} Their unique structure is expected to provide a broad range of possible applications; especially the treelike macromolecules are promising candidates as large single-molecule photonic antenna systems.^{4–10} The authors have recently developed a novel class of anionic linear–dendritic amphiphiles, PAA–Dendr.PE, with a linear poly(acrylic acid) chain and a dendritic polyether unit¹¹ (Scheme 1). The versatile copolymers combine a metal cation binding subunit (PAA) and an efficient ultraviolet light-harvesting dendron. Moreover, the amphiphilic copolymers derived from linear PAA as a hydrophilic block and polyether dendron as a hydrophobic block can self-assemble into micelle-like aggregates in aqueous solution.¹² Therefore, the molecular architecture of the linear–dendritic copolymer (PAA–Dendr.PE) provides a possibility to design an unusual supramolecular photoreaction device, where the energy harvested by appended aryl chromophores of the dendritic subunit permit migration along with the PAA chain to the reaction center to which active metal ions are bound.

Lanthanide metal ions such as Tb³⁺ and Eu³⁺ are known for their unique luminescence properties such as long, millisecond-order lifetime, narrow-width emission band, and hypersensitivity to coordinative environment. Due to these special characteristics, these lanthanide elements may be used as lasers, optical communication amplifiers, photophysical probes, etc.^{13–16} However, the fluorescence intensity of the ions is normally quite weak in aqueous solution. In an effort to obtain stronger fluorescence, one general approach involves the addition of a sensitizer chromophore to the solution, usually an organic ligand, which will absorb energy and transfer it to a rare earth ion. In this respect, intramolecular energy transfer from the lowest triplet state of the ligand molecules to the metal ion in lanthanide complexes is well-known.^{17–23} However, supramolecular sensitization is less studied and is mainly focused on micellar organization.^{24–28} Using sodium dodecanesulfonate micelles in

SCHEME 1



aqueous solution, Fendler²⁴ and co-workers showed energy transfer from micellar solubilized naphthalone to the terbium ion. In addition, a suitable change in coordinative environment and a decrease in coordinated water molecules serving as efficient quenchers of the emission are alternative methods to enhance the fluorescence of the lanthanide ions. Okamoto^{29,30} observed that the emission intensity of Tb³⁺ ion is enhanced upon binding to polycarboxylates. The results indicate Tb³⁺ ion was strongly bound to these polyanions in aqueous solution and that some of their inner coordinated water molecules were expelled upon binding.

Here we report the luminescence enhancement of Tb³⁺ ion in the assemblies of linear–dendritic block copolymers (PAA–Dendr.PE) in which Tb³⁺ ion was bound to PAA chains. Both the microenvironment and antenna effects provided by unique supramolecular systems have been investigated in detail.

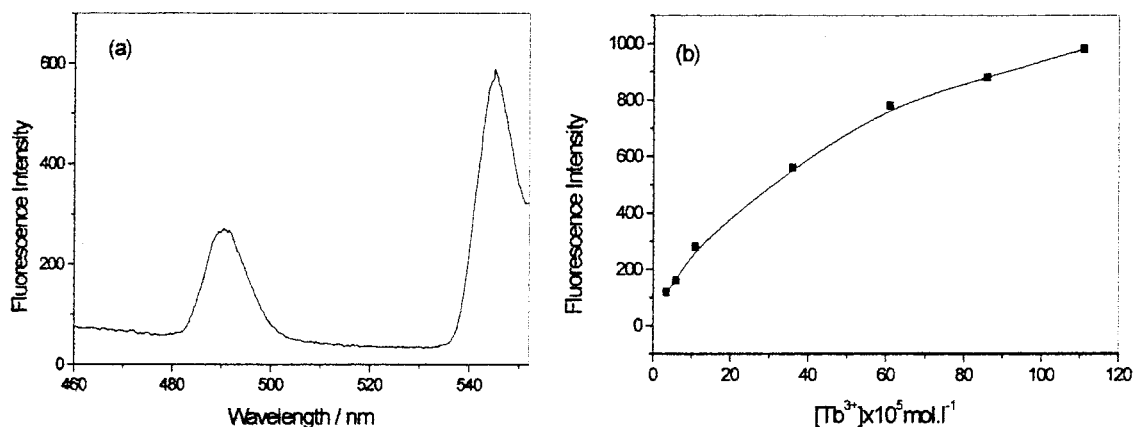


Figure 1. (a) Luminescence of Tb^{3+} ion in the presence of PAA-Dendr.PE in aqueous solution: $[\text{G}_3\text{-101}] 9.02 \times 10^{-6} \text{ mol}\cdot\text{L}^{-1}$; $[\text{Tb}^{3+}] 8 \times 10^{-4} \text{ mol}\cdot\text{L}^{-1}$; $\lambda_{\text{ex}} 288 \text{ nm}$. (b) Luminescence of $\text{G}_3\text{-101}/\text{Tb}^{3+}$ complex under different Tb^{3+} concentrations: $[\text{G}_3\text{-101}] 4.51 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $\lambda_{\text{em}} 545 \text{ nm}$; $\lambda_{\text{ex}} 288 \text{ nm}$.

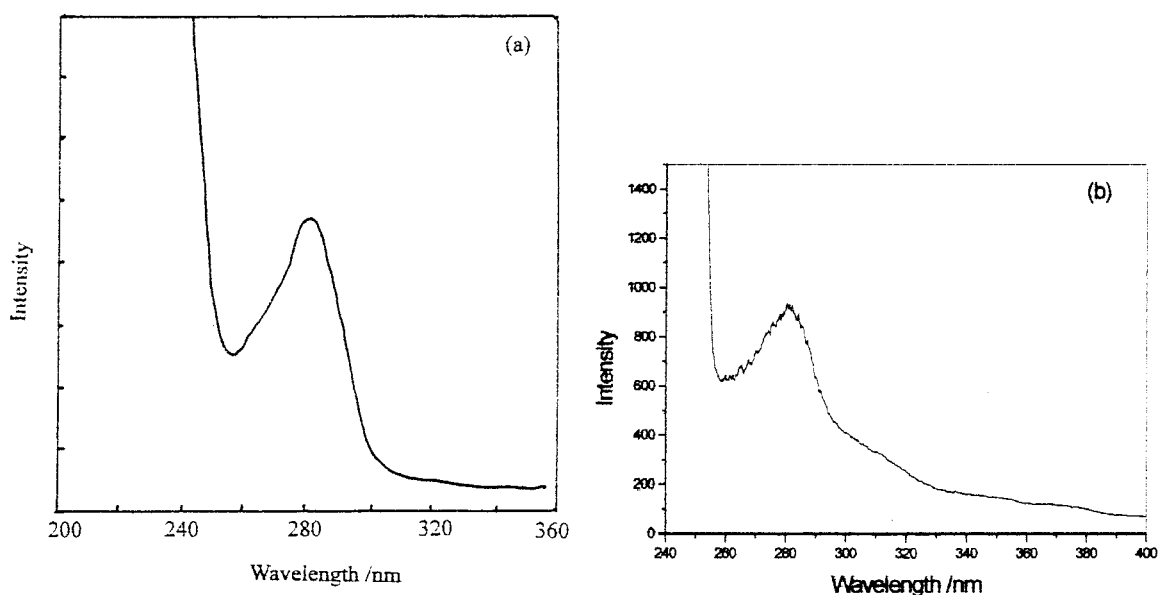


Figure 2. (a) Absorption spectra of $\text{G}_3\text{-101}$ in aqueous solution: $[\text{G}_3\text{-101}] 4.51 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$. (b) Excitation spectra of $\text{G}_3\text{-101}/\text{Tb}^{3+}$ complex: $[\text{G}_3\text{-101}] 4.51 \times 10^{-5} \text{ mol}\cdot\text{L}^{-1}$; $[\text{Tb}^{3+}] 1 \times 10^{-3} \text{ mol}\cdot\text{L}^{-1}$; $\lambda_{\text{em}} 490 \text{ nm}$.

II. Experimental Section

Materials. The block copolymers, PAA-Dendr.PE, were synthesized as described in ref 11. The molecular weight characteristics of the polymers used are summarized in Table 1. Terbium (Tb_2O_3) (99.99%) was purchased from Yue Long Chemical Factory, Shanghai, China. $\text{TbCl}_3\cdot 6\text{H}_2\text{O}$ was prepared by dissolving Tb_2O_3 in hydrochloric acid.

Fluorescence Measurement. The given amount of PAA-Dendr.PE was dissolved in deionized water. Aqueous solutions were quantitatively neutralized with NaOH to pH 8.52 and were then sonicated for 10 min at room temperature before the addition of Tb^{3+} ion. The mixture was stirred for 1/2 h. Fluorescence spectra were recorded on a Hitachi MPF-4500 instrument at ambient temperature.

III. Results and Discussion

Antenna Effect. The typical emission spectra of Tb^{3+} ion in the presence of PAA-Dendr.PE are shown in Figure 1a. The emission peaks at 490 and 545 nm correspond to the $^5\text{D}_4 \rightarrow ^7\text{F}_6$ and $^5\text{D}_4 \rightarrow ^7\text{F}_5$ transitions of Tb^{3+} ion, respectively. The fluorescence intensity of Tb^{3+} ion is remarkably enhanced in the presence of the polymer. Figure 1b shows that the

TABLE 1: Data of PAA-Dendr.PE with Different Generations and Chain Lengths

PAA-Dendr.PE	generation (G_i)	deg polymzn (n)	M_n (NMR)	M_w/M_n	CAC, $\text{mol}\cdot\text{L}^{-1}$
$\text{G}_1\text{-75}$	1	75	7 325		
$\text{G}_2\text{-85}$	2	85	8 734	1.21	3.58×10^{-6}
$\text{G}_3\text{-14}$	3	14	2 908	2.18	6.46×10^{-7}
$\text{G}_3\text{-42}$	3	42	5 540	1.38	
$\text{G}_3\text{-101}$	3	101	11 086	1.42	9.02×10^{-7}
$\text{G}_3\text{-217}$	3	217	21 990	1.47	4.54×10^{-6}

luminescence intensity obviously increases with increasing solution concentration of Tb^{3+} ion in the presence of PAA-Dendr.PE. These phenomena suggest the formation of the supramolecular complex of the trivalent Tb^{3+} ion with PAA-Dendr.PE. As shown in Figure 2, the excitation spectra of the same solution (using 490 nm as emission wavelength) are in excellent agreement with the observed absorption spectra of the aqueous solution of PAA-Dendr.PE. The absorption of PAA block is so weak³¹ in this area that only the strong absorption ($\lambda_{\text{max}} = 280 \text{ nm}$, $\epsilon = 6735$) of aryl chromophore in the dendritic subunit at the UV region exhibits at the observed absorption spectra of the aqueous solution of PAA-Dendr.PE (Figure 2a). Since aryl chromophore in the dendritic subunit does not emit

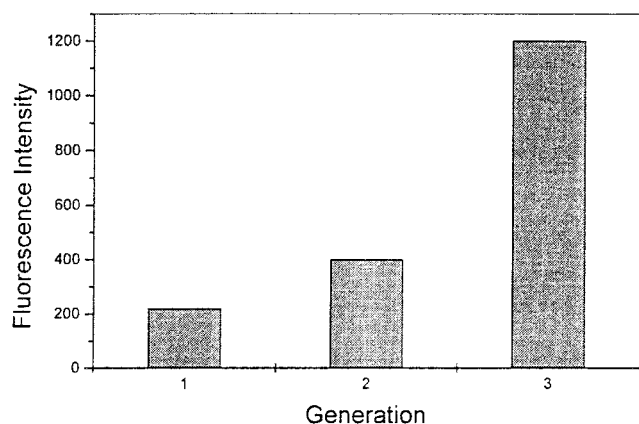


Figure 3. Highest fluorescence intensity (545 nm) of PAA-Dendr.PE/Tb³⁺ complexes with different generations: λ_{ex} 288 nm; [Tb³⁺] 1×10^{-3} mol·L⁻¹; [G₁-75] 6.83×10^{-4} mol·L⁻¹; [G₂-85] 1.14×10^{-4} mol·L⁻¹; [G₃-101] 4.51×10^{-5} mol·L⁻¹.

at the wavelength at which the excitation spectrum was analyzed (490 nm), these results are a clear manifestation of energy transfer from the light-harvesting dendritic subunit to the Tb³⁺ ion via the excited state. Furthermore, the generation number ($G_i = 1, 2, 3$) effects of PAA-Dendr.PE copolymers on the luminescence enhancement of Tb³⁺ ion were investigated. The obtained results (Figure 3) indicate that the luminescence intensity of Tb³⁺ ion further increases intensively with increasing dendrimer generation (G_i). Frechet and co-workers also observed the same phenomena.²³ Obviously, owing to the strong absorption of the aryl groups that increase exponentially with generation, the light-harvesting “antenna” acting by the dendritic subunit of copolymer is a significantly important factor for the great luminescence enhancement of Tb³⁺ ion.

To further demonstrate the energy transfer process from the dendritic subunit to Tb³⁺ ion in the block copolymer PAA-Dendr.PE/Tb³⁺ systems, the fluorescence quenching of polyether dendrimer by Tb³⁺ ion was measured. However, dendritic subunit fluorescence quenching by Tb³⁺ ion was not observed. Therefore, energy transfer from the sensitizer chromophore to the terbium cation is a triplet mechanism because of a singlet spin forbidden process.²⁸

Microenvironment Effect. The amphiphilic dendritic-linear block copolymers, PAA-Dendr.PE, which have unique molecular aggregation behaviors, can self-assemble into spherical micelle-like aggregates. Undoubtedly, these multimolecular assemblies will remarkably change the coordinative environment of Tb³⁺ ion bound to PAA block. Figure 4 shows the relationships between the emission intensity of Tb³⁺ ion and the concentration of copolymer G₃-101. At concentrations below the critical aggregation concentration (CAC) of PAA-Dendr.PE, the fluorescence intensity of Tb³⁺ ion is very weak. However, at concentrations above the CAC, a sharp increase in the fluorescence intensity of Tb³⁺ ion was observed; even the luminescence intensity increased to over 150 times as high as that in the initial state. These results indicate that aggregate formation leads to a significant change in the microenvironment surrounding the Tb³⁺ ion. The increment of the fluorescence intensity ratio I_3/I_1 (the ratio of the intensity of peak 3 to peak 1) of pyrene probe as shown in Figure 4 clearly demonstrates that the molecular aggregation effectively prevents the penetration of water, thereby resulting in a decrease of environmental polarity. Additionally, the high packing and favorable orientation of PAA chain in a micelle-like aggregate provide much a higher local concentration of carboxylate ligand compared with that in homo-PAA solution at equal concentration, which would

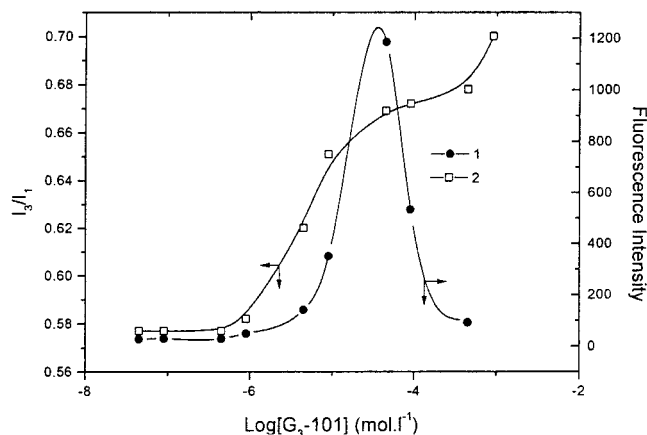


Figure 4. Effect of aggregation of copolymer on luminescence intensity of Tb³⁺ ion. Curve 1: luminescence intensity of Tb³⁺ ion as a function of G₃-101 concentration; [Tb³⁺] 1×10^{-3} mol·L⁻¹, λ_{ex} 288 nm. Curve 2: ratio of peak 3 to peak 1 (I_3/I_1) of pyrene probe as a function of G₃-101 concentration; [pyrene] 2×10^{-6} mol·L⁻¹; λ_{ex} 335 nm.

promote Tb³⁺ ion to preferentially complex with carboxylates in the PAA chain. Both further facilitate reduction of the number of coordinated water molecules for Tb³⁺ ion. Horrocks and Sundnick^{32,33} have developed that the number of coordinated water molecules, q , to Tb³⁺ ion is given by

$$q\tau_h = A(1 - \tau_h/\tau_d) \quad (1)$$

where A is constant (4.2); τ_h and τ_d are the experimental excited-state lifetimes in H₂O and D₂O solutions, respectively. As a first approximation,²³ I_h/I_d may be used instead of τ_h/τ_d , where I_h and I_d are the intensities of the stronger emission peaks in H₂O and D₂O solutions, respectively. Thus, eq 1 may be modified to

$$q\tau_h = A(1 - I_h/I_d) \quad (2)$$

Horrocks and Sudnick have also reported an experimental relationship between the variation in the decay constant, $\Delta K_{\text{obs}} = (1/\tau_h - 1/\tau_0)$, and the value q which may be expressed by

$$\Delta K_{\text{obs}} = 1/\tau_h - 1/\tau_0 = Bq \quad (3)$$

where B is constant (0.237) and τ_0 is the experimental excited-state lifetime for the nonhydrated Tb³⁺ ion. The value $1/\tau_0$ was reported^{32,33} as 0.83 ms^{-1} for Tb³⁺. Therefore eq 3 can be written as

$$q = q\tau_h(1/\tau_0)(1 - Bq\tau_h)^{-1} \quad (4)$$

Finally, using the experimental value I_h/I_d obtained from the luminescence intensity measurements, the hydration number q may be calculated from eq 4. The measured results show at PAA-Dendr.PE concentration above the CAC that the average number of water molecules bound to Tb³⁺ ion is further decreased abruptly from 2.8 ([PAA-Dendr.PE] = 4.51×10^{-7} mol·L⁻¹, below the CAC) to 1.3 ([PAA-Dendr.PE] = 4.51×10^{-5} mol·L⁻¹, above the CAC), which is much lower than that (3.5)²⁹ in homo-PAA/Tb³⁺ systems. This result demonstrates that the hydrophobic dendritic block in the PAA-Dendr.PE can afford a more hydrophobic microenvironment for the binding of Tb³⁺ ion. Especially, these microenvironment effects will be further remarkably strengthened after the amphiphilic block copolymer aggregates into ordered multimolecular assemblies due to more water expelled. However, it should be noted that

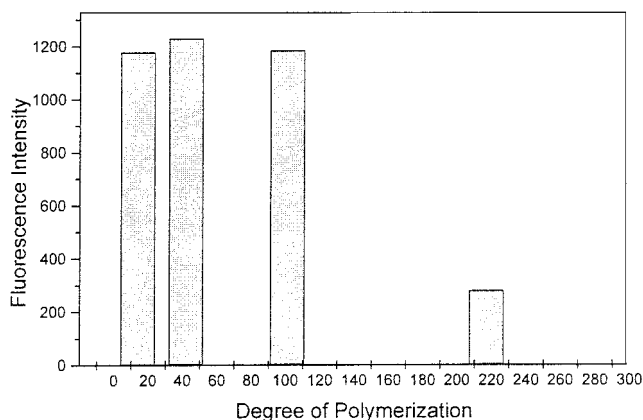


Figure 5. Highest fluorescence intensity (545 nm) of PAA-Dendr.PE/Tb³⁺ complexes with different chain lengths of PAA at equal generations of dendritic block ($G_i = 3$); λ_{ex} 288 nm; [Tb³⁺] 1×10^{-3} mol·L⁻¹; [G₃-14] 1.72×10^{-4} mol·L⁻¹; [G₃-42] 9.02×10^{-5} mol·L⁻¹; [G₃-101] 4.51×10^{-5} mol·L⁻¹; [G₃-217] 2.27×10^{-5} mol·L⁻¹.

as the PAA-Dendr.PE concentration is further above a limit and the micelle formation is complete, the luminescence intensity of Tb³⁺ ion decreases sharply. It is more likely that because of the more compact aggregates, as demonstrated by pyrene probe, the PAA near the aryl ether core is not deprotonated and the Tb³⁺ ion cannot approach the aryl groups, as is required for sensitization.

The effect of the chain length of PAA block (degree of polymerization, n) on the luminescence intensity of Tb³⁺ ion was also investigated at given generation number of dendritic subunit ($G_i = 3$) and concentration of Tb³⁺ ion. As Figure 5 shows, the chain length of PAA chain does not afford a pronounced influence on the luminescence properties in the extent of $n = 14$ –101. However, in the case of G₃-217, the luminescence intensity is sharply decreased by 5 times because no order aggregates were observed in aqueous solution for copolymer bearing a too long hydrophilic PAA chain.¹² Moreover, the length of PAA chain of G₃-217 may not permit Tb³⁺ ion bound to the polycarboxylates to be effective, folding back onto the aryl dendron and sensitizing by the dendritic subunit. Therefore, these results further demonstrate that the microenvironment effect provided by PAA-Dendr.PE multimolecular aggregates is alternatively an important factor for the great enhancement of luminescence intensity of Tb³⁺ ion.

IV. Conclusion

The amphiphilic hybrid block copolymers PAA-Dendr.PE, combining a dendritic polyether as the hydrophobic subunit and a linear PAA as the hydrophilic block, have characteristics of both dendrimer and linear polymer. These amphiphiles can easily self-assemble into micelle-like aggregates in very dilute aqueous solution (10^{-6} – 10^{-7} M). The combination of copolymer (PAA-Dendr.PE) with Tb³⁺ ion constructs a supramolecular luminophore. Their great enhancement in the luminescence intensity of Tb³⁺ ion was observed and can be attributed to two factors. The first one is the antenna effect, the energy harvest and transfer from the aryl dendritic framework to the bound

Tb³⁺ ion, and which obviously enlarges with increasing generation number of the dendritic block. The second one is the microenvironment effect of the multimolecular aggregates, which results in a decrease of the average number of coordinated water molecules to Tb³⁺ ion from 3.5 (in homo-PAA solution) to 1.3. These unique properties of amphiphilic block copolymer PAA-Dendr.PE may be of general applicability in the design of energy-harvesting devices and amplifiers for optics.

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References and Notes

- (1) Tomalia, D. A.; Naylor, A. M.; Goddard, W. A. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.
- (2) Frechet, J. M. J. *Science* **1994**, *263*, 1710.
- (3) Zeng, F.; Zimmerman, S. C. *Chem. Rev.* **1997**, *97*, 1681.
- (4) Gilat, S. L.; Adronov, A.; Frechet, J. M. J. *Angew. Chem., Int. Ed.* **1999**, *38*, 1422.
- (5) Bar-Haim, A.; Klafiter, J. *J. Phys. Chem. B* **1998**, *102*, 1662.
- (6) Jiang, D. L.; Aida, T. *Nature* **1997**, *388*, 454.
- (7) Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354.
- (8) Devadoss, C.; Bharathi, P.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9635.
- (9) Bar-Haim, A.; Klafiter, J.; Kopelman, R. *J. Am. Chem. Soc.* **1997**, *119*, 6197.
- (10) Balzani, V.; Campagna, S.; Denti, G.; Juris, A.; Serroni, S.; Venturi, M. *Acc. Chem. Res.* **1998**, *31*, 26.
- (11) Zhu, L. Y.; Tong, X. F.; Li, M. Z.; Wang, E. J. *J. Polym. Sci., Part A* **2000**, *38*, 4282.
- (12) Zhu, L. Y.; Li, M. Z.; Wang, E. J. *Acta Chimica Sinica* **2001**, *59*, 291.
- (13) Sabbatini, N.; Guardigli, M.; Lehn, J.-M. *Coord. Chem. Rev.* **1993**, *123*, 201.
- (14) Corllar-Walrand, C.; Binnemans, K. *Handbook on the Physics and Chemistry of Rare Earths*; Gschneidner, K. A., Eyring, L. R., Eds.; Elsevier: Amsterdam, 1998; Vol. 25, p 101.
- (15) Tang, B.; Jin, L. P.; Zheng, X. J.; Zhu, L. Y. *Spectrochim. Acta, Part A* **1999**, *55*, 1731.
- (16) Feig, A. L.; Scott, W. G.; Uhlenbeck, O. C. *Science* **1998**, *279*, 81.
- (17) Alpha, B.; Lehn, J.-M.; Mathis, G. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 266.
- (18) Dexter, D. L. *J. Chem. Phys.* **1953**, *21*, 836.
- (19) Watson, W. M.; Zenger, P. R.; Yardley, J. T.; Stucky, G. D. *Inorg. Chem.* **1975**, *14*, 2675.
- (20) Hayes, A. V.; Drickamer, H. E. *J. Chem. Phys.* **1982**, *76*, 114.
- (21) Steemers, F. J.; Verboom, W.; Reinhoudt, D. W.; van der Tol, E. B.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1995**, *115*, 9408.
- (22) Sohna, J. S.; Fages, F. *Tetrahedron Lett.* **1997**, *38*, 1381.
- (23) Kawa, M.; Frechet, J. M. J. *J. Chem. Mater.* **1998**, *10*, 286.
- (24) Escabi-Perez, J. R.; Name, F.; Fendler, J. H. *J. Am. Chem. Soc.* **1977**, *99*, 7749.
- (25) Correll, C. D.; Cheser, R. N.; Name, F.; Fendler, J. H. *J. Am. Chem. Soc.* **1978**, *100*, 1254.
- (26) Gelade, E.; De Schryver, F. C. *J. Am. Chem. Soc.* **1984**, *106*, 5871.
- (27) Almgren, M.; Greiser, F.; Thomas, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 2021.
- (28) Darwent, J. R.; Dong, W.; Flint, C. D.; Sharpe, N. W. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 873.
- (29) Kido, J.; Brittan, H. G.; Okamoto, Y. *Macromolecules* **1988**, *21*, 1872.
- (30) Okamoto, S.; Vyprachticky, D.; Furura, H.; Abe, A.; Okamoto, Y. *Macromolecules* **1996**, *29*, 3511.
- (31) Muller, G.; Laine, J. P.; Fenyo, J. C. *J. Polym. Sci., Polym. Chem. Ed.* **1979**, *17*, 659.
- (32) Horrocks, W. D.; Sudnick, D. R. *J. Am. Chem. Soc.* **1979**, *101*, 334.
- (33) Horrocks, W. D.; Sudnick, D. R. *Acc. Chem. Res.* **1981**, *14*, 384.