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A Facile One-pot Synthesis of Fluorescent Hyperbranched Polyesteramine (PEA) Architecture

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Summary:

One pot synthesis of hyperbranched polyester amine (PEA) **1 (G2)** with peripherally appended naphthyl units has been achieved and found to display strong fluorescence signaling towards Co(II) and Cu(II) ions.

Introduction:

The dendritic as well as the hyperbranched macromolecular architectures[1-4] have received tremendous research interest, principally owing to their well defined branched and compartmentalized structures featuring a densely packed exterior and a largely-meshed interior. In particular, the design of branched macromolecular assemblies[5-6] capable of modulating the luminescence properties in response to the chemical input has been a fascinating pursuit in recent years in the field of chemistry and biology.

Continuing our investigations in the field of dendritic macromolecules,[7] we report herein for the first time a new one-pot synthesis of novel hyperbranched polyester amine (PEA) **1** (G2) with peripherally appended naphthyl units exhibiting strong fluorescence signaling.

Experimental:

Characterization:

FTIR spectra were recorded with a Thermo – Nicolate Nexus- 870 FTIR spectrometer. NMR spectra were recorded on a Bruker AC200 spectrometer using $CDCl_3$ solvent. CHN-analysis was obtained from 2400 series II CHN-analyser, Perkin Elmer, USA, using helium as driving gas and oxygen as combustion gas. Thermogravimetric analysis (TGA) was conducted in argon atmosphere on a STA 625 STANTON-REDCROFT thermal analyzer at a heating rate of 10°C/min. Gel permeation chromatography (GPC) analysis was performed using polystyrene standards (2700, 5000, 9000). The molecular weight was calculated from the GPC data using DMF eluent and a calibration curve constructed from those linear polystyrene standards. For fluorescence measurements Shimadzu absorption spectrophotometer (UV-1601) and Spex-fluorolog-3 spectrofluorimeter (FL3-11) were used respectively. MALDI-TOF mass spectrum of **1** was obtained on a Biospectrometry Voyager-DE PROs instrument by using cinnanic acid matrix.

Synthesis of hyperbranched polyesteramine 1:

A 100 ml round bottomed flask equipped with a dean stark trap, was charged with N,N-bis(hydroxyethyl) glycine (0.5 g, 3.06 mmol), triethanolamine (0.05 g, 0.34 mmol) (in stoichiometric correspondence to a perfect generation of second generation), and p-toluene sulfonic acid (0.581 g, 3.06 mmol). The mixture was then refluxed with xylene. After refluxing for 4.5 h the terminal hydroxyl groups of hyperbranched dendrimer were endcapped by adding 1-naphthylacetic acid (0.887 g, 4.77 mmol) and refluxed for further 4.5 h. The xylene was then removed by vacuum distillation. The reaction mixture was then washed with aqueous 10% $NaHCO_3$ solution and extracted with $CHCl_3$ and dried by anh. Na_2SO_4 to afford the reddish brown gummy product. Yield (80-85%).
UV-vis (MeOH) λ_{max} = 280nm ($c=1.6x10^{-5}$). FT-IR (KBr): 3418, 1736, 1631, 1395, 1250, 1060, 785 cm^{-1}. 1H NMR (200MHz, $CDCl_3$) δ: 7.96- 7.77 (bm, 36H, Ar-H), 7.54- 7.33 (bm, 52H, Ar-H), 4.20 (t, 24H, J= 4Hz, H_h), 4.08 (s, 23H, naph-CH_2), 4.00 (t, J= 4Hz, H_eH_a), 3.97 (s, H_c), 3.81 (m, 16H, $C\underline{H}_2OH$, branching defect), 3.14 (s, 16H, H_f), 2.50 (t, 24H, J= 4Hz, H_g), 2.35 (m, 28H, H_dH_b). ^{13}C NMR (50 MHz, $CDCl_3$) δ: 171.2 ($ArCH_2\underline{C}OO$-), 166.9 (-CH_2-$\underline{C}OO$-), 133.7 (ArC), 131.9 (ArC), 130.3 (ArC), 128.7 (ArCH), 128.0 (ArCH), 126.3 (ArCH), 125.8 (ArCH), 125.7 (ArCH), 125.4 (ArCH), 123.6 (ArCH), 68.4 (-C_hH_2-), 63.0, 62.4, 61.6 [(-$C_{f, cH2}$-), unresolved], 55.5 (-$C_{e,a}H_2$), 55.1 (naph-$\underline{C}H_2$-), 48.3 (-C_bH_2-), 39.2 (-$C_{g,d}H_2$-, unresolved). Anal. calcd for $C_{204}H_{210}N_{10}O_{42}$: C, 70.54; H, 6.05; N, 4.03; found: C, 67.21; H, 5.63; N, 3.46. MALDI-TOF-MS: *m/z* calcd, 3806 [MH^+]; found 3675.08, 3746.02; GPC: $\overline{M}_n \approx 650$, $\overline{M}_w \approx 1600$, PD = 2.46; Intrinsic viscosity [η] = 0.68dl/g (c = 0.133g/dl, $CHCl_3$, (38 ±0.1) ^0C).

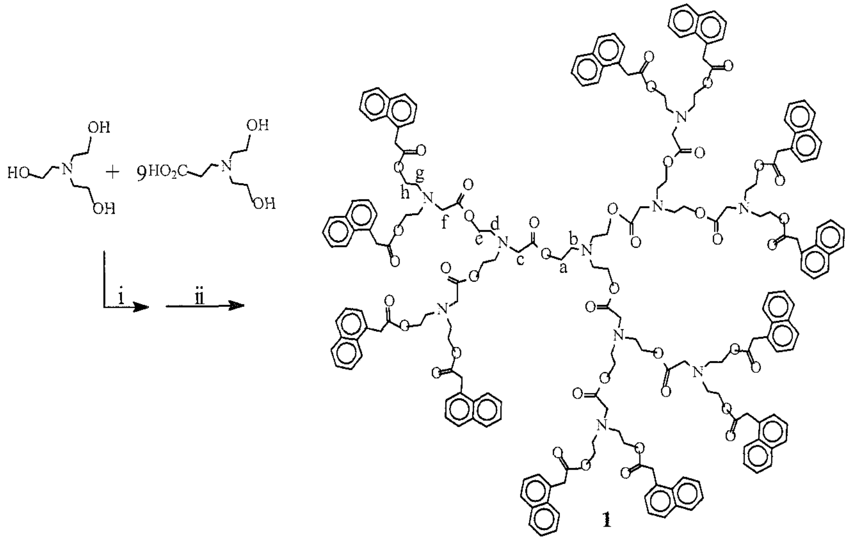
Viscosity Measurement:

The intrinsic viscosity of the **1** was determined in $CHCl_3$ using Ubbelohde viscometer thermostated at $38^\circ C$. In this study, the intrinsic viscosity [η] of the **1** was determined by using the equation derived by Raju *et.al* [8] as mentioned in our previous papers.[7]

Results and Discussion:

Synthesis and Characterization:

The synthesis commences (Scheme – 1) by a simple esterification of the corresponding N, N-bis (hydroxyethyl) glycine (AB_2 monomer) with triethanolamine as the core unit using p-toluene sulfonic acid (p-TSA) condensing agent followed by end-capping with 1-naphthyl acetic acid. PEA, **1**, which was gummy in nature, was characterized by means of UV, IR, NMR (^1H, ^{13}C), MALDI-TOF-MS and elemental analysis.



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Scheme 1. Reagents and conditions: (i) Xylene, p-TSA, Reflux, 4.5 hrs. (ii) 1- naphthyl acetic acid, Reflux, 4.5 h

In the ^{1}H NMR spectrum of **1** (figure 1) the resonances of CH_2 protons, assigned as H_f, of the outer glycine unit are significantly upfield from those of the inner CH_2, marked as H_c, indicate the shielding effect of the naphthyl units. The quoted number of protons corresponding to each resonance in ^{1}H NMR spectrum demonstrates the structural irregularity from its idealized structure **1**. The signal corresponding to the methylene protons of $-CH_2OH$ motifs was detected at δ 3.81, indicating the branching defects into the structure. Moreover, the resonances assigned to H_b and H_d (totaling 18H) have larger integral than the peak assigned to H_g (total 24H), arguing a significant divergence from the idealized structure **1**.

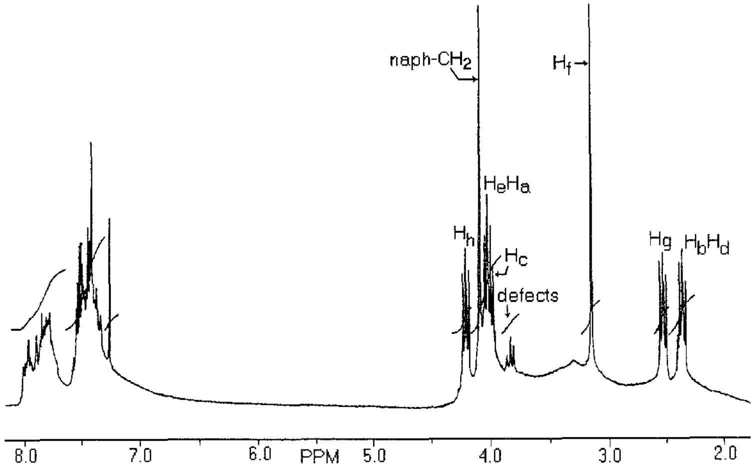

Figure 1. ^{1}H NMR spectrum of **1**

Structural regularity (s) of **1** was estimated from the ^{1}H NMR spectroscopy by comparing the integration of the peaks for the respective units according to the equation: $s = (x/y)_{expl} / (x/y)_{calc.}$; where, x = total number of protons of naphthyl units, y = total number of protons other than naphthyl units. $(x/y)_{calc}$ was obtained by considering the perfectly branched structure of **1** as represented in scheme 1. However, the estimated structural regularity (s) in the targeted system was found to be 0.70 reflecting good branching. These were further supported by elemental analysis, the data of which deviate slightly from the calculated ones (calculated by considering ideal dendritic architecture **1**). GPC measurement, calibrated with linear polystyrene, significantly underestimates the molecular weight distribution profile of this hyperbranched polymer ($\overline{M}_n \approx 650$, PD = 2.46) due to the difference of its hydrodynamic radius, R_h or radius of gyration, S from its linear counterparts of the same molar mass which was also evidenced in the literature.[9] But the molecular weight of **1** measured by MALDI-TOF MS is much higher than that obtained by GPC suggesting its highly branched nature. However, the masses of up to 3746 obtained from MALDI-MS probably indicate the mass of the polymer of highest $\overline{DP}$. The intrinsic viscosity for **1** is unique and exhibits a slight decrease on increasing the generations (examined upto 4th generation) indicating its dendrimer-like structure. The targeted polyester **1** possesses moderate thermal stability and its onset decomposition temperature is upto 198°C as observed by a TGA analysis under argon atmosphere at 10°C/min.

Fluorescence study:

System **1** exhibits strong absorption bands in the UV spectral region ([**1**] = ~1.7×10^{-5}M, λ_{max} = 240 - 280 nm) which change slightly with solvent polarity ($CHCl_3$, CH_3CN, CH_3OH; Fig. 2- inset) and on excitation at 280 nm results in the strong fluorescence (Fig. 2) at 332 nm (shoulder) and 341nm at 27°C, as well as a broad band, solvent dependent and thereby intermolecular excimer emission.[5b]

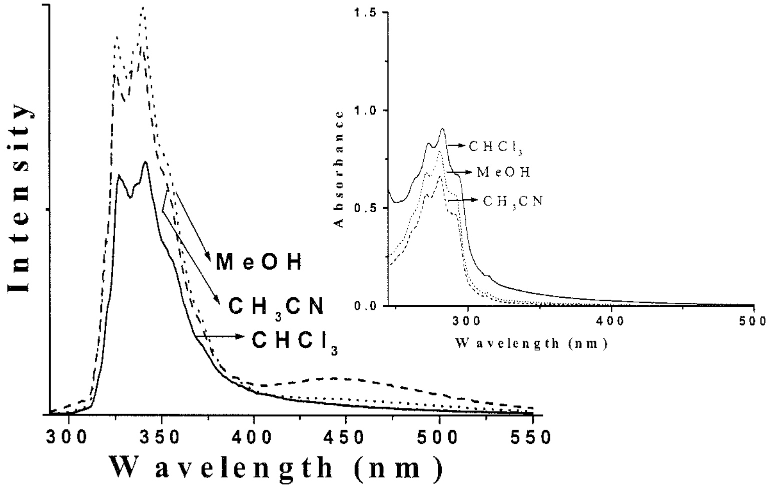

Figure 2. Fluorescence spectra of **1** in different solvents (λ_{exc} = 280 nm). Inset: corresponding UV-spectra.

Moreover, the study of fluorescence modulation in dendritic / hyperbranched systems[4] in presence of metal ions has recently attracted considerable interest because of their branched architectures as well as the presence of a greater number of coordinating sites in the interior. Although the methyl ester of napthylacetic acid reference compound does not show any change of fluorescence intensity upon addition of photophysically inactive Zn(II) ions, the marginal increase of emission intensity (fig. 3) of the methanolic solution of **1** upon addition of Zn(II) (upto 6.07×10^{-4} M, as $Zn(OAc)_2$, $2H_2O$), among other metal ions (Co(II), Cu(II)) under study, demonstrates the fact that the Zn(II) coordination with the amine –ester sites of **1** probably accounts the perturbations of excited naphthyl units.

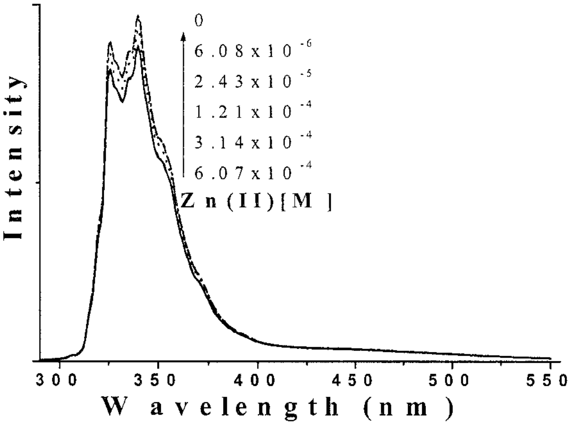

Figure 3. Fluorescence spectral change upon the addition of Zn^{+2} ions in MeOH (λ_{exc} = 280 nm).

On the contrary, strong fluorescence quenching in **1** upon addition of successive equivalents of photophysically active Cu(II) ions (upto 8.27×10^{-4} M, as $Cu(OAc)_2$, xH_2O) (fig 4) probably attributes to the energy transfer quenching between naphthyl excited state and Cu(II), complexed into the hyperbranched architectural interior.

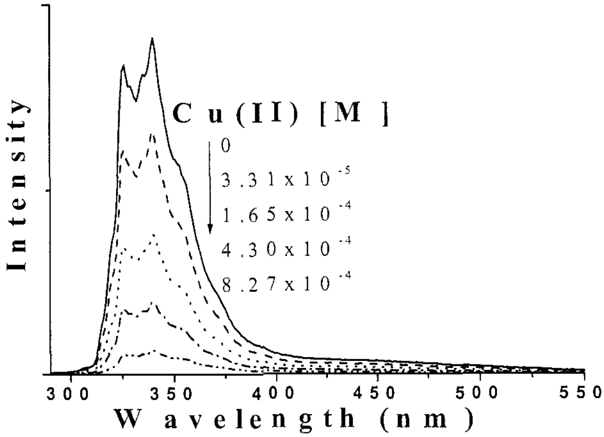

Figure 4. Fluorescence spectral change upon the addition of Cu^{+2} ions in MeOH ($\lambda_{exc} = 280$ nm).

Furthermore, addition of photophysically active Co(II) cations (upto $5.35x10^{-5}$M as $Co(OAc)_2$, $4H_2O$) exhibits moderate fluorescence quenching (fig. 5) of the appended naphthyl units. Although the methyl ester of naphthyl acetic acid model compound shows similar fluorescence quenching towards Cu(II), Co(II) ions, this hyperbranched system acts potential highly branched, compartmentalized macromolecular host for the guest metal ions under study and at the same time shows highly selective luminescence modulation for Cu(II) ions as evidenced from the Stern-Volmer plot (Fig. 5: Inset).

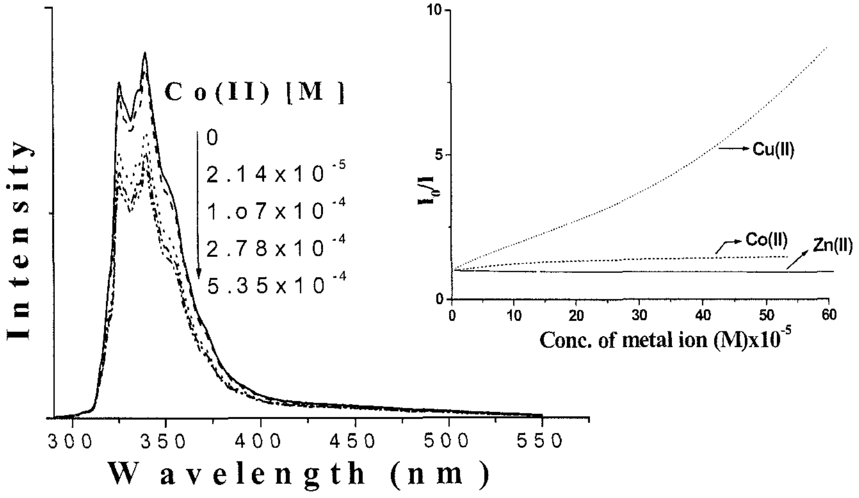

Figure 5. Fluorescence spectral change upon the addition of Co^{+2} ions in MeOH ($\lambda_{exc} = 280$ nm). Inset: Stern-Volmer plot.

Conclusion:

A straightforward method for the synthesis of system **1** representing a simple and hitherto unexplored class of luminescent supramolecular systems has been employed without using any protection / deprotection steps. We anticipate that fluorescent hyperbranched macromolecule of this type having remarkable solubility would be most welcome in the field of luminescence modulating extraction / detection processes with simultaneous hosting ability of the gallery of interior ester-amine functionalities. Further studies in our laboratory are in progress to explore the synthesis of higher generation hyperbranched macromolecular architectures and their fluorescent chemosensing events.

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