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Photophysical investigation of microenvironment in glycerol based dansylated polyether dendrons

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ABSTRACT

Photophysical studies of four generations of polyglycerol dendrons with isopropylidene end groups and dansyl moiety as a fluorophore attached at the focal point were carried out. All the four generations showed similar behaviour in their absorption transitions but the emission maximum for all generations of dendrons showed strong dependence on the solvent polarity. The solvatochromic shift of emission maximum showed linearity in the Lippert–Mataga plot, indicating the dominant importance of general solvent effect in all generations of dendrons. Photophysical parameters such as fluorescence quantum yield, fluorescence lifetime and radiative decay rate constant showed solvent polarity dependence. The detailed photophysical study reveals that due to the increased influence of the repeating dendron units of the higher order dendrons on the dansyl microenvironment, it becomes less and less influenced by the solvent.

1. Introduction

The possibility to modulate size, molecular weight, chemical functionalities, position and the number of functional groups in dendrimers makes them promising candidates for diverse applications in catalysis [1,2], MRI contrast agents [3,4] and in drug delivery [5–10]. In particular hyperbranched polyglycerols [11–18] and polyglycerol dendrimers [19–24] have engrossed much attention over the past few years due to their excellent water solubility and biocompatibility. Polyglycerol dendrimers have shown good transport capacities for poorly water soluble drugs *e.g.* hydrotropic solubilization of paclitaxel (PTX) in polyglycerol dendrimers resulted in 3 orders of magnitude higher than that in pure water [25]. A 20-fold increase in aqueous solubility of 10-hydroxycamptothecin (10-HCPT) was achieved in the presence of carboxylated poly(glycerol succinic acid) dendrimers [26] and an anionic amphiphilic dendrimers composed of glycerol and succinic acid has shown cytotoxicological potency against prokaryotic cells [27]. In an effort to value addition to glycerol, glycerol based dansylated polyether dendrons and their aggregation properties have been recently reported by us [28]. In order to gain a better understanding of the microenvironment of the dendrimers created at the core and to have a better idea of the effect of the dendrimer branching on the core, we have carried out an extensive photophysical studies upto fourth generations of polyglycerol dendrons with isopropylidene end groups and dansyl moiety as a fluorophore attached at the focal point. *(Gn)-PGL-ipd*, where Gn specifies the generation number of the dendron (Fig. 1).

2. Experimental

2.1. Dendrimer synthesis

The detailed procedure for the synthesis of the dendrimers and characterization has been reported by us [28]. Up to fourth generation dendrons (azide as focal point) were synthesized through a divergent methodology, all these dendrons were converted into corresponding amine dendrons and subsequent dansylation with 5-(dimethylamino)naphthalene-1-sulfonyl chloride. The dansyl moiety attached at the focal point acts as a fluorescent reporter of the microenvironment in the dendrons.

2.2. Solutions for photophysical studies

The stock solutions (10^{-3} M) of the dendrimers were prepared in cyclohexane. The solutions in all other solvents were prepared by evaporating the cyclohexane from the desired amount of the stock

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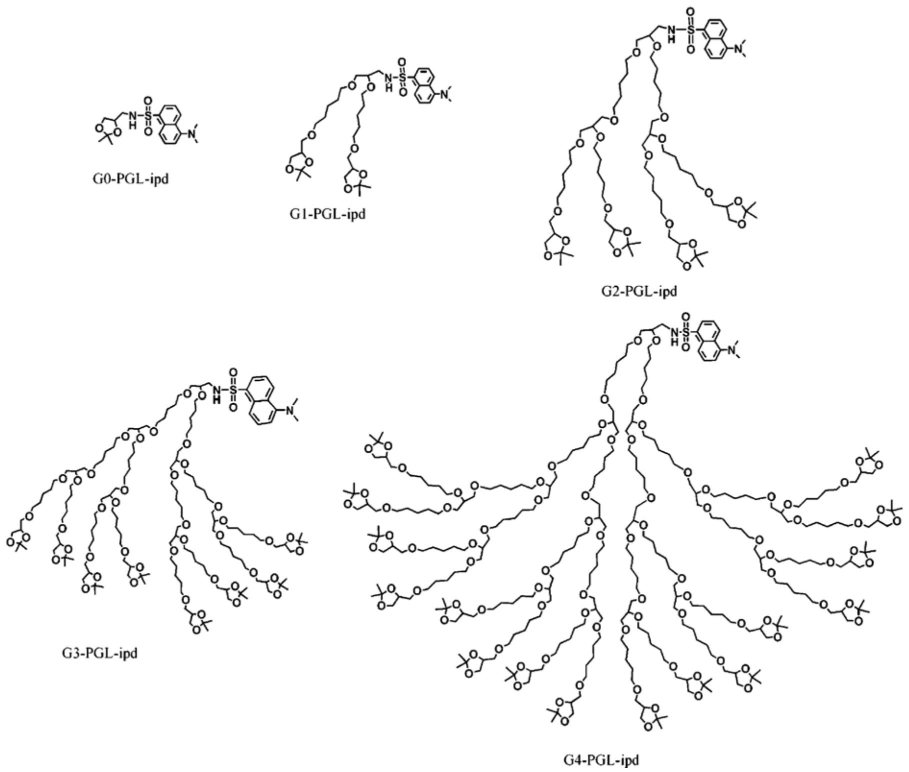

Fig. 1. Dansylated glycerol based polyether dendrons (G0–G4).

by gentle purging of nitrogen gas and then sonicating it with the solvent of interest. All the solvents used were of UV-spectroscopic grade and used without further purification.

2.3. Instrumentation

UV–visible spectra were measured on a Perkin Elmer Lambda 25 spectrophotometer. Fluorescence measurements were recorded on a Hitachi F-4500 spectrofluorimeter. Excitation and emission slits were set at 5/5 nm. Fluorescence lifetime (τ_f) measurements were carried out using Horiba Jobin Yvon TCSPC lifetime instrument in a time-correlated single-photon counting arrangement. A 340 nm nano LED was used as the light source. The pulse repetition rate was set to 1 MHz and the instrumental full width half maximum of the 340 nm LED, including the detector response is ∼800 ps. The instrument response function was collected using a dilute solution of a scatterer (Ludox AS40 colloidal silica). The decay data were analyzed using IBH software. A value of χ^2, $0.99 \leq \chi^2 \leq 1.4$ was considered as a good fit, which was further judged by the symmetrical distribution of the residuals.

2.4. Determination of fluorescence quantum yield (ϕ_f)

The fluorescence quantum yield of the dendrimers was measured in various solvents using quinine sulphate in 0.5 M aqueous solution of H_2SO_4 as standard [29] (quantum yield = 0.55). The excitation wavelength chosen was 326 nm. The following equation was used to determine the fluorescence quantum yield (ϕ_f)

$$\phi_f(\text{unknown}) = \phi_f(\text{standard}) \times \frac{F(\text{unknown})}{F(\text{standard})} \times \frac{A(\text{standard})}{A(\text{unknown})} \times \frac{\eta^2(\text{unknown})}{\eta^2(\text{standard})}$$

where, F's correspond to the integrated intensities under the corrected emission spectra, A's correspond to the absorbance of solutions, η's are refractive indices of the solvents used. The absorbance was less than 0.05 at the excitation wavelength to avoid effects like self-absorption, concentration quenching. The optical densities of the reference and the test samples were always adjusted to the same or comparable values. The measurements were performed in deaerated solutions by purging oxygen free argon and the temperature was maintained at 25 °C. The quantum yield values were calculated from the average of three sequential measurements of the same sample in all solvents, and it did not differ by more than 1% in the solvents studied. Three independent measurements of quantum yield were made and errors in the values of quantum yields are estimated to be no greater than 10%.

3. Results and discussion

3.1. UV–vis absorption studies

Fig. 2A represents the UV–vis absorption spectra of all the generations (G0–G4) of dendrons in cyclohexane. The absorption spectra in all the dendrons are broad and structureless. The absorption maxima and molar absorption coefficients are independent of the generation number, which essentially indicate that the microenvironment of the dansyl moiety is more or less the same for all generations of dendrons in the ground and Franck-condon excited states. In order to test out the effect of solvent polarity on the absorption characteristic of the dendrons, absorption studies were carried out in several solvents of varying polarity for all the generations. Fig. 2B depicts the UV–vis absorption spectra for G0 in all the solvents studied. There is not much change in the energy of transition in different solvents, which implies that the solvent stabilisation of the ground state species is not significant. The observed small broadening of the absorption spectral band with increasing solvent polarity (Fig. 2B) is often seen for molecules showing intra-molecular charge transfer. This is usually attributed to the fluctuations in the structure of the solvation shell surrounding the chromophore [30], and solvent-induced damping of molecular vibrations of the chromophore [31]. All the four generations

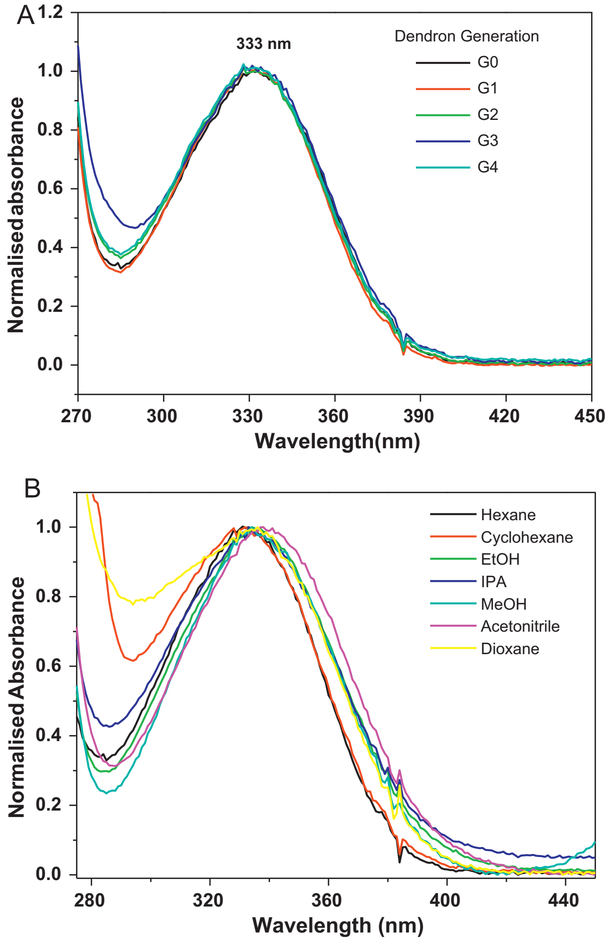

Fig. 2. (A) Normalised UV–vis absorption spectra of all the generations in n-hexane (G0–G4) and (B) normalised UV–vis absorption spectra for G0 in all the solvents studied.

showed similar behaviour like G0 indicating the similarity in the transition characteristic for G0–G4.

3.2. Fluorescence studies

The emission spectra for all the generations were measured in different solvents of varying polarity. Fig. 3 illustrates the normalised emission spectra of G0 in the solvents studied. The emission maximum shows strong dependence on the solvent polarity. There is almost a 70 nm bathochromic shift observed between nonpolar n-hexane and polar methanol, which is due to the stabilisation of the intra-molecular charge transfer excited state of dansyl moiety by polar solvents. Similar to G0, all generation dendrons showed solvatochromic shift in their emission maxima.

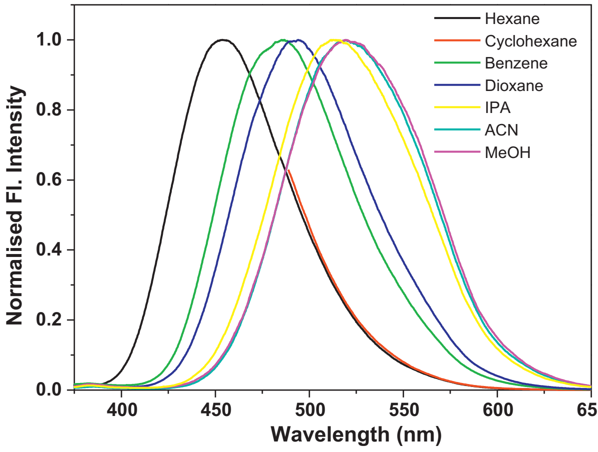

Fig. 3. Normalised emission spectra for G0 dendrons in different solvents of varying polarity (λ_{ex} = 340 nm).

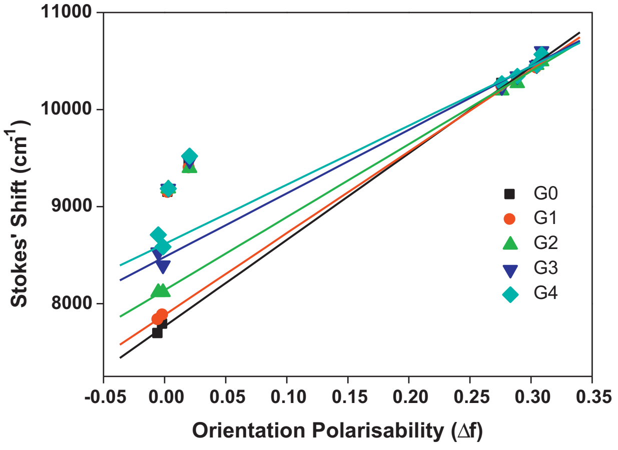

Fig. 4. Lippert–Mataga plots for all generations of dendrons (solvent-dependent spectral shifts).

3.3. Solvent dependence of emission and polarity scale

Solvent dependent spectral shifts are often interpreted in terms of the Lippert equation [32], which describes Stokes' shift in terms of the change in dipole moment of the fluorophore upon excitation and the dependence of energy of the dipole on the dielectric constant and refractive index of the solvent and is given as

$$\bar{\nu}_A - \bar{\nu}_F = \frac{2}{hc}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right)\frac{(\mu_E-\mu_G)^2}{a^3} + \text{constant}$$

where, $\bar{\nu}_A$ and $\bar{\nu}_F$ are the wavenumbers (cm^{-1}) of the absorption and emission, h is Planck's constant, c is the speed of light, a is the radius of the cavity in which the fluorophore resides, e is the dielectric constant of the medium, n is the refractive index of the solvent μ_E and μ_G are the dipole moments of the fluorophore in the excited state and the ground state, respectively and the term

$$\Delta f = \frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}$$

is the orientation polarisability, the resultant effect of both the mobility of electrons in the solvent and the dipole moment of the solvent.

A Lippert–Mataga plot, which is a plot of Stokes' shift *versus* orientation polarisability (Δf) of the solvent, provides a valuable framework for the consideration of solvent-dependent spectral shifts. Fig. 4 shows the Lippert–Mataga plots for all generations of dendrons. The data show a fairly linear correlation, with the exception of benzene and 1,4-dioxane. Due to their quadrapole moments, these two solvents are known to have better solvating ability than is revealed by their dielectric constants [33]. The linearity in Lippert–Mataga plot is often regarded as evidence for the dominant importance of general solvent effect. It is interesting to note that the slope of the Lippert–Mataga plot shows a decreasing trend on going from G0 to G4. The plots for all generations of dendrons converge on moving towards polar solvents. This is evident from the emission maxima for all generations of dendrons in the solvents studied (Table 1).

Table 1
Emission maximum in nanometer (nm) for all generations dendrons in various solvents.

Dendron	n-Hex	CH	Benz	Diox	ACN	IPA	EtOH	MeOH
G0	453	455	485	492	518	513	514	520
G1	456	457	485	491	517	512	514	519
G2	462	462	486	491	518	511	513	519
G3	471	468	486	493	518	512	515	522
G4	475	470	486	494	518	513	515	521

n-Hex—n-hexane; CH—cyclohexane; Benz—benzene; Diox—dioxane; ACN—acetonitrile; IPA—isopropyl alcohol; EtOH—ethanol; MeOH—methanol.

Table 2
Fluorescence quantum yield (ϕ_f) values for all generations dendrons in various solvents.

Dendron	n-Hex	CH	Benz	Diox	ACN	IPA	MeOH
G0	0.43	0.53	0.46	0.47	0.27	0.26	0.29
G1	0.43	0.54	0.49	0.44	0.26	0.26	0.29
G2	0.44	0.55	0.49	0.46	0.27	0.26	0.28
G3	0.45	0.56	0.47	0.47	0.27	0.27	0.30
G4	0.44	0.55	0.48	0.47	0.28	0.27	0.32

n-Hex—n-hexane; CH—cyclohexane; Benz—benzene; Diox—dioxane; ACN—acetonitrile; IPA—isopropyl alcohol; EtOH—ethanol; MeOH—methanol.

The emission maxima remain more or less constant for all generations in polar solvents and also in benzene. However, in n-hexane and cyclohexane the dendrons show a bathochromic shift in emission maximum with increasing dendron generation. Fig. 5A and B depicts the normalised emission spectra for all generation dendrons in n-hexane and cyclohexane, respectively. The insets show the plot of the emission energy (in cm^{-1}) against generation number of the dendron.

The emission energy shows a sigmoid variation with generation number and the maximum change in slope is observed between G1 and G3. Thus it appears that as the generation of the dendron increases from G1 to G3, the microenvironment of the dansyl moiety at the core becomes more and more polar. As observed from the chemical structure of the dendrons (Fig. 1), with increased dendron generation, more numbers of polar glycerol units are introduced in the proximity of dansyl moiety. This would enhance the local polarity surrounding the dansyl residue and thus the dansyl microenvironment would be less and less influenced by the solvent with increase in dendron generation number. The actual polarity felt by the fluorophore at the core is similar to a binary solvent mixture of the dendron and the solvent. When there is a considerable difference in polarity between the dendron and the solvent such as n-hexane and cyclohexane, the effect becomes more pronounced with the increased dendron generation and is manifested in the shift in emission maximum of the dansyl moiety. On the other hand if the polarity of the dendron and the solvent is comparable then the polarity felt by the fluorophore at the core is more or less similar for all generations of the dendron. Similar behaviour has also been observed in previous studies on polyether dendrimers and starburst dendrimers, the proposed reason being a structural change from an extended to a globular form for the higher order dendrimers [34]. This transition is known to be accompanied by a lowering of intrinsic viscosity of the dendrimer. In order to verify whether similar structural changes are taking place in the present case, fluorescence anisotropy values were measured for all generations of dendrons in all the solvents. Fluorescence anisotropy provides information about rotational diffusibility or the micro-viscosity experienced by the fluorophore. The anisotropy values were very small (0.003–0.004) and did not show any significant difference among the generations in all the solvents studied, which implies that, the dansyl moiety experiences almost similar micro-viscosity irrespective of the generation number and solvent medium. Hence, such a structural transition is not likely to be happening in the present case. An alternative explanation has been offered in order to explain the bathochromic shift observed in the transition energy of dansyl moiety attached at the focal point of Newkome type dendrimers, where the red shift of fluorescence with increasing generation is suggested due to the progressive raising of energy of the Franck Condon Ground (FCG) state as a result of the increased bulk of the dendrimer [35]. However, in absence of detailed structural studies or theoretical calculations it is difficult to rule out either possibility completely.

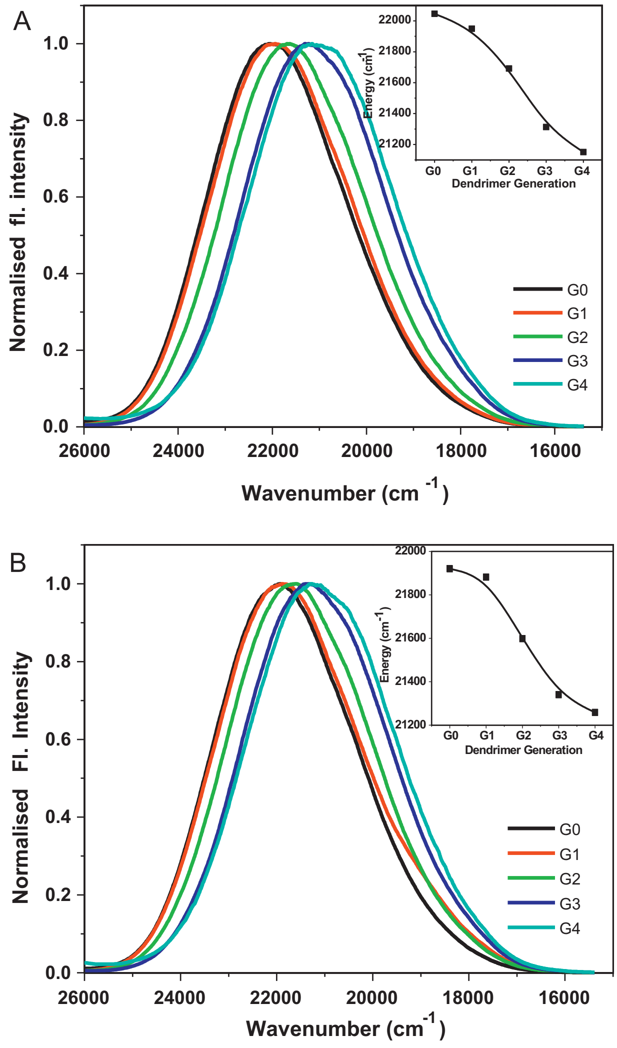

Fig. 5. (A) Normalised emission spectra for all generations of dendrons in n-hexane (λ_{ex} = 340 nm). Inset shows the plot of emission energy against generation number of the dendron in n-hexane and (B) normalised emission spectra for all generation dendrons in cyclohexane (λ_{ex} = 340 nm). Inset shows the plot of emission energy against generation number of the dendron in cyclohexane.

Table 3
Fluorescence lifetime (τ_f) values in nanoseconds (ns) for all generations dendrons in various solvents.

Dendron	CH	n-Hex	Benz	Diox	ACN	IPA	EtOH	MeOH
G0	9.2	6.7	11.3	15.5	12.6	14.1	12.7	11.7
G1	9.7	7.2	11.4	15.8	12.8	14.7	13.6	12.4
G2	10.8	8.4	11.7	16.4	13.6	15.2	14.0	13.0
G3	12.6	10.6	12.3	16.6	13.7	15.7	14.6	13.5
G4	13.3	11.9	12.5	16.8	14.2	15.7	14.6	13.5

n-Hex—n-hexane; CH—cyclohexane; Benz—benzene; Diox—dioxane; ACN—acetonitrile; IPA—isopropyl alcohol; EtOH—ethanol; MeOH—methanol.

Table 4
Radiative rate constant (k_r) and non-radiative rate constant (k_{nr}) values in ns^{-1} for all generations of dendrons in various solvents.

Dendron	CH		n-Hex		Benz		Diox		ACN		IPA		MeOH	
	k_r	k_{nr}	k_r	k_{nr}	k_r	k_{nr}	k_r	k_{nr}	k_r	k_{nr}	k_r	k_{nr}	k_r	k_{nr}
G0	5.76	5.11	6.42	8.51	4.07	4.78	3.03	3.42	2.14	5.79	1.84	5.25	2.48	6.07
G1	5.57	4.74	5.97	7.92	4.30	4.47	2.98	3.35	2.03	5.78	1.77	5.03	2.34	5.73
G2	5.09	4.17	5.24	6.67	4.19	4.36	2.81	3.29	1.99	5.37	1.71	4.87	2.15	5.54
G3	4.44	3.49	4.25	5.19	3.82	4.31	2.83	3.19	1.97	5.33	1.72	4.65	2.22	5.19
G4	4.14	3.38	3.70	4.71	3.84	4.16	2.80	3.16	1.97	5.07	1.72	4.65	2.37	5.04

n-Hex—n-hexane; CH—cyclohexane; Benz—benzene; Diox—dioxane; ACN—acetonitrile; IPA—isopropyl alcohol; EtOH—ethanol; MeOH—methanol.

3.4. *Fluorescence quantum yield*

Fluorescence quantum yields for G0–G4 generations of dendrons were measured in various solvents and the values are tabulated in Table 2. In general the quantum yields are reasonably high in all the solvents studied. In nonpolar solvents the values are higher than that in more polar solvents, which is expected for a fluorophore like dansyl that show intra-molecular charge transfer (ICT). For a particular solvent, the quantum yield values do not vary significantly with the generation of the dendron.

3.5. *Fluorescence lifetime study*

The fluorescence lifetime values for all generations (G0–G4) of dendrons in various solvents are given in Table 3. For all the four generations of dendron, the fluorescence showed monoexponential decay in all the solvents studied indicating the homogeneous nature of the dendron solutions. For a given generation of the dendron the fluorescence lifetime is relatively longer in polar solvents as compared to that in nonpolar solvents, which is generally expected for a molecule like dansyl showing ICT. Unlike fluorescence quantum yield, the fluorescence lifetime exhibits dependence on the dendron generation. In all the solvents studied the fluorescence lifetime shows an increasing trend with the increased generation of the dendron. In nonpolar solvents like n-hexane and cyclohexane the extent of change in lifetime with dendron generation is more pronounced as compared to that in polar solvents. It is interesting to note that with increasing generation number, the lifetime value in n-hexane and cyclohexane become comparable to that in polar solvents. This behaviour is analogous to the shift in the emission maximum seen earlier with increasing generation of the dendron, further supporting the proposition that as the generation number increases the microenvironment of the dansyl moiety becomes more polar.

It is interesting to note that for a particular solvent, τ_f values increase with increasing dendron generation, whereas the ϕ_f values are almost invariant even for nonpolar solvents like cyclohexane and n-hexane, implying a decrease in the radiative rate constant (k_r) with increasing dendron generation. Table 4 summarises the values of radiative (k_r) and non-radiative (k_{nr}) rate constants calculated from the ϕ_f and τ_f values for different generations of dendrons in all the solvents studied. The radiative decay rate constant shows solvent dependence *i.e.* k_r value is higher in nonpolar solvents as compared to that in polar solvents for all generations of dendrons. For a given solvent, however, the value decreases as the generation number increases, the magnitude of change being more for nonpolar solvents. The k_{nr} values do not show any particular trend with respect to the solvent polarity. But the variation of k_{nr} with generation number for a given solvent is very similar to that of k_r *i.e.* the k_{nr} value decreases with increased generation number. A proper rationalization of the trends of k_r and k_{nr} variations, however, would require independent evaluation of non-radiative deactivation processes.

4. Conclusion

Photophysical investigation on the microenvironment in four generations of polyglycerol dendrons with isopropylidene end group and having a dansyl moiety attached at the focal point has been carried out. All the four generations showed similar behaviour in their electronic absorption transitions. The similarity in their transition energy indicated that the solvent stabilisation of the ground state species is not significant. But unlike the absorption maxima, the emission maxima for all generations of dendrons showed strong dependence on solvent polarity. The solvatochromic shift of emission maximum showed linear Lippert–Mataga plots indicating the dominant importance of general solvent effect for all generations of dendrons. Photophysical parameters such as fluorescence quantum yield, fluorescence lifetime and radiative decay rate constant showed solvent polarity dependence. For a particular solvent, the quantum yield values do not vary significantly with the generation of the dendron but fluorescence lifetime values exhibit dependence on the dendron generation showing an increasing trend with the increased generation of the dendron. The detailed photophysical study revealed that because of the increased influence of the repeating dendron units of the higher order dendrons on the dansyl microenvironment, it becomes less and less influenced by the solvent.

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