Supramolecular Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

Toward a light-harvesting Hyperbranched Polyesteramine Host-guest Complex

Samaresh Ghosh[ab]; Ajit K. Banthia[a]
[a] Materials Science Centre, Indian Institute of Technology, Kharagpur, India [b] Department of Chemistry, Bankura Sammilani College, Kenduadihi, Bankura, WB, India

To cite this Article Ghosh, Samaresh and Banthia, Ajit K.(2005) 'Toward a light-harvesting Hyperbranched Polyesteramine Host-guest Complex', Supramolecular Chemistry, 17: 5, 409 — 414
To link to this Article: DOI: 10.1080/10610270500158639
URL: http://dx.doi.org/10.1080/10610270500158639

Supramolecular Chemistry, July–August 2005 VOL. 17 (5), pp. 409–414

Taylor & Francis
Taylor & Francis Group

Toward a light-harvesting Hyperbranched Polyesteramine Host–guest Complex

SAMARESH GHOSH[a,b] and AJIT K. BANTHIA[a,*]

[a]*Materials Science Centre, Indian Institute of Technology, Kharagpur 721302, India;* [b]*Department of Chemistry, Bankura Sammilani College, Kenduadihi, Bankura 722102, WB, India*

(Received (in Southampton, UK) 14 January 2005; Accepted 1 May 2005)

A novel hyperbranched polyesteramine (PEA) architecture 1 was found to display light-harvesting properties by hosting anthracene-9-carboxylic acid guest 3. The light-harvesting ability has been studied by means of fluorescence spectroscopy. The binding behaviour has also been described by FT-IR and ^{1}H NMR spectroscopic methods. Hyperbranched host 1 also acts as the photon-harvesting chemosensor of the anthracenyl guest over the benzoic acid guest. Furthermore, the host loaded with the anthracenyl guest also exhibited 'ON–OFF' switching on protonation of amine sub-units with HCl, thereby making it of potential use as a pH-assisted photon-harvesting material.

Keywords: Hyperbranched polyesteramine; Anthracene-9-carboxylic acid; Light-harvesting; Esteramine moieties

INTRODUCTION

The luminescent dendritic macrmolecular antenna, which exhibits light-harvesting properties [1–5], is of current interest. Another burgeoning topic in the arena of host–guest chemistry is the use of dendritic macromolecular hosts [6–8] because of their well-defined branched and compartmentalized structures featuring a densely packed exterior and a largely meshed interior. The utilization of branched macromolecular antennas capable of exhibiting light-harvesting properties in response to the luminescent chemical input has been a fascinating pursuit in recent years [4,9,10].

We have recently reported [11] the synthesis of a new easy-to-make hyperbranched polyesteramine macromolecular architecture (PEA) **1** (Second generation) with peripherally placed fluorophore motifs and investigated its luminescence properties. Therefore, continuing our investigations in the field of luminescent dendritic macromolecules [12,13], we now wish to explore herein the recognition and light-harvesting properties of our previously reported naphthalene based hyperbranched polyesteramine host **1** towards anthracene-based guests. This study is mainly based on our idea that the recognition events at the binding sites of the esteramine moieties of the hyperbranches would be efficiently communicated to the light-harvesting properties of the peripherally appended naphthalene unit to the hosted anthracene unit. We also wish to report herein the modulation of light-harvesting property through protonation of amine sub-units of dendritic host **1**.

RESULTS AND DISCUSSION

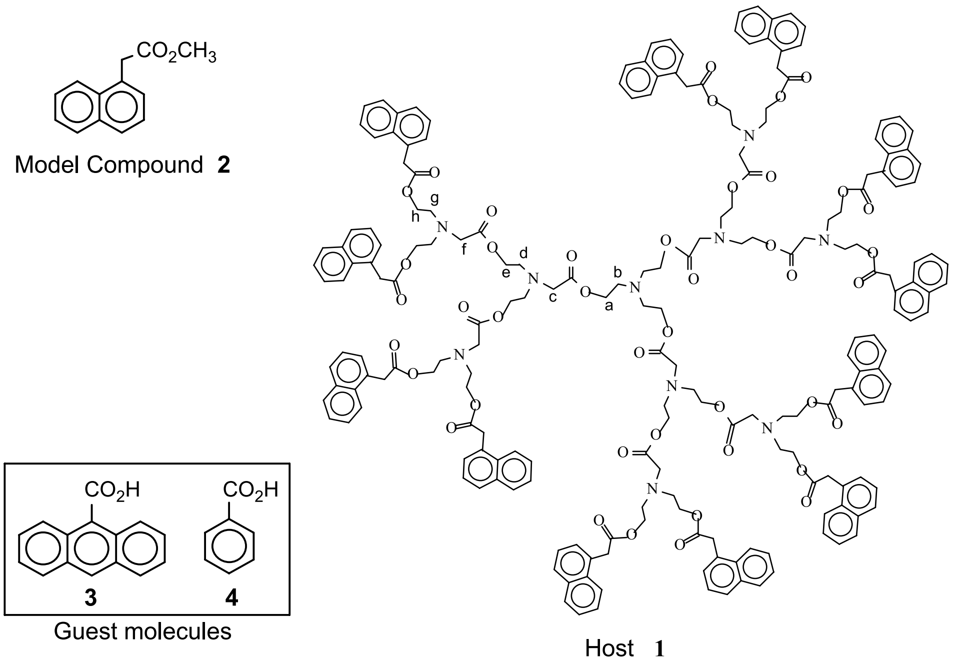
In our recent report [11], we have explored the one-pot synthetic strategy for the development of the novel peripherally appended naphthalene-based fluorescent hyperbranched polyesteramine **1** macromolecule as represented in the following by considering its idealized structure. The structural representation of the hyperbranched polymer is more difficult than for dendrimers because of the imperfections associated with their structures. Therefore, for the sake of simplicity, we have represented the structure of the hyperbranched poly (esteramine) (PEA) in a highly idealized way. Indeed, the hyperbranched polymer is structurally imperfect (see Scheme 1).

A large number of elaborations have been performed by several groups [14,15] for the development of naphthalene–anthracene-based

---

*Corresponding author. E-mail: ajitbanthia2000@yahoo.co.in

ISSN 1061-0278 print/ISSN 1029-0478 online © 2005 Taylor & Francis Group Ltd
DOI: 10.1080/10610270500158639



SCHEME 1 Hyperbranched polyesteramine (PEA) (Host 1: idealized representation), structure of model compound and guest molecules.

photon-harvesting systems where naphthalene acts as the energy donor and anthracene acts as the energy acceptor. Since the emission wavelength of naphthyl motif (donor) is almost overlapped by the absorption wavelength of anthracene motif (acceptor), binding of anthracene-9-carboxylic acid guest **3** into the hyperbranched host **1** fulfils the prerequisite for the occurrence of an efficient energy-transfer process in the dendritic antenna. Moreover, host **1** should have an excellent ability to bind the anthracene-9-carboxylic acid guest molecules because of the esteramine binding sites.

Figure 1 illustrates the fluorescence emission spectral properties of polymeric host **1**, guest **3** and host–guest complex. Targeted host **1** exhibits the naphthalene monomer fluorescence with maxima at 326, 340 and 352 nm on excitation at 280 nm. On the other hand, the emission spectrum of **3** exhibits its monomer fluorescence with maxima at 457 nm on excitation at 365 nm. Interestingly, the fluorescence intensity of guest differs from the guest, incorporated into the dendritic structure (Scheme 2) giving rise a stacked structure involving an energy-transfer process between naphthalene and anthracene units in their excited states. On the other hand, the absorption spectrum of the mixture of dendritic host **1** and guest **3** was essentially identical to the sum of the spectra of **1** and **3**, indicating the absence of interactions between naphthalene units of host and anthracenyl guests in their ground states.

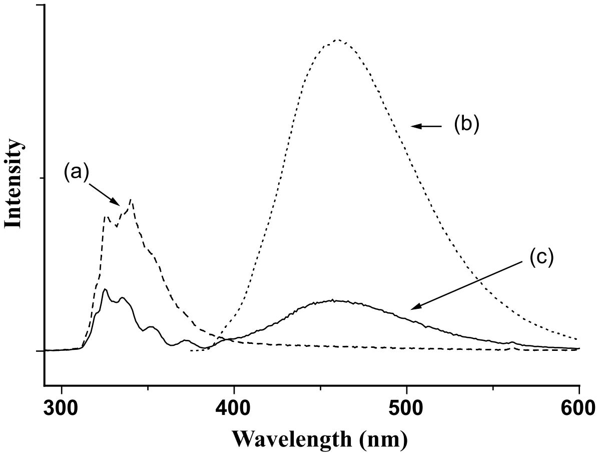


FIGURE 1 Fluorescence spectra of: (a) host 1 (8.5×10^{-6} M) ($\lambda_{exc} = 280$ nm, MeCN solution); (b) guest 3 (28.8×10^{-5} M) $\lambda_{exc} = 365$ nm, MeCN solution); (c) host (1): Guest (3) ($\lambda_{exc} = 280$ nm).

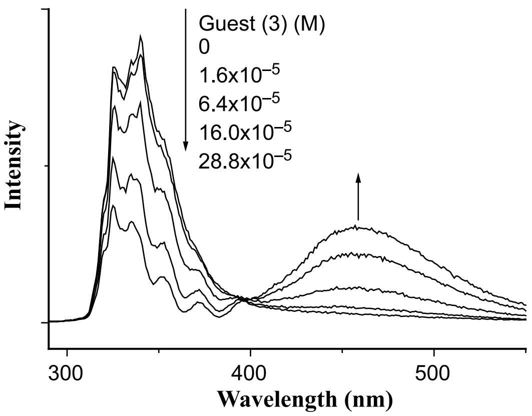


FIGURE 2 Fluorescence spectral changes in 1 (8.5×10^{-6} M) in MeCN (27°C, $\lambda_{exc} = 280$ nm) upon addition of guest (3).

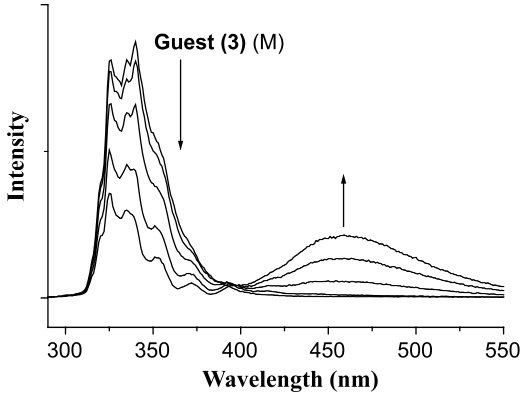


FIGURE 3 Fluorescence spectral changes in model compound 2 (9.6×10^{-5} M) in MeCN (27°C, $\lambda_{exc} = 280$ nm) upon addition of guest (3) (added up to 28.8×10^{-5} M).

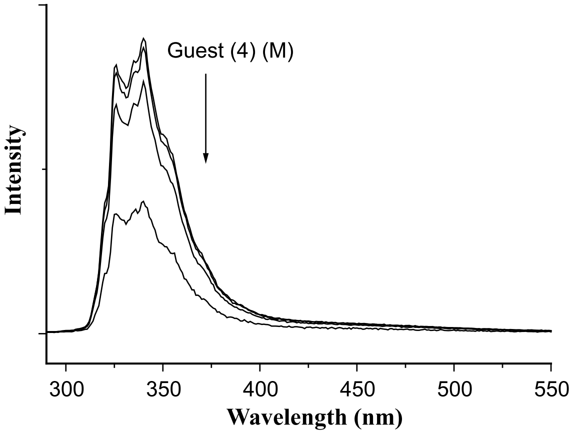


FIGURE 4 Fluorescence spectral changes in 1 (8.5×10^{-6} M) in MeCN (27°C, $\lambda_{exc} = 280$ nm) upon addition of guest (4) (added up to 39.24×10^{-5} M).

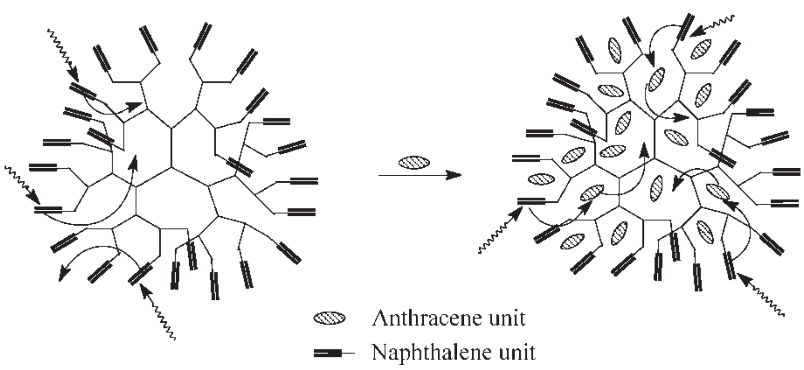
Titration of acetonitrile solution of **1** (8.5×10^{-6} M) with **3** (added up to 28.8×10^{-5} M) induces the gradual decrease in intensity of naphthyl monomer fluorescence with concomitant development of emission bands of **3** (Fig. 2) attributed to the energy transfer process between naphthyl and anthracenyl motifs. This spectral behaviour demonstrates that naphthyl units supply sufficient excitation pulse to the anthracene-9-carboxylic acid guest that fluoresces at 457 nm. It is also observed that the naphthalene emission spectral shape changes upon successive addition of guest and gradually shows the naphthalene monomeric emission with clear maxima at 323, 335, 352 and 372 nm as well as a guest emission band at 457 nm.

In this context, the quenching of naphthyl fluorescence on addition of anthracenyl guest occurred with a slight hypsochromic shift when compared with model compound (methyl ester of naphthyl acetic acid) **2** (Fig. 3), indicating the dendritic antenna effect in the energy-transfer process between the donor and acceptor units. Also, the internal cavities as well as esteramine-binding sites make the host **1** suited for the efficient loading of guest molecules.

This photon-harvesting scenario is represented in Scheme 2. The dendritic structure and the binding sites of **1** promote the hosting of anthracenyl guests that collect the excitation energy from the peripherally appended naphthyl units, thereby exhibiting the efficient light-harvesting properties.

The fluorescence-sensing ability for non-luminescent aromatic acids like benzoic acids was also examined. Progressive addition of the benzoic acid guest in the acetonitrile solution of **1** induces significant quenching of emission bands of host **1** as can be seen in Fig. 4. This might be due to the possible acid–base interactions between the guest carboxylic acids and the host tertiary amines as well as to some extent π—π stacking interactions between the aromatic rings of donor and acceptor units. Of particular note is the change of emission spectral shape of the naphthalene unit upon the input of benzoic acid guest **4**, which gradually becomes a broad featureless emission when comparing the same with the anthracenyl guest input.

The ability of the guest molecules to quench the fluorescence emission of naphthalene units has been estimated by the Stern-Volmer plot (Fig. 5). The plot shows more pronounced quenching with the anthracenyl guest than benzoic acid, demonstrating a better chemosensitivity of **1** for guest **3**. In this



SCHEME 2 Cartoon representation of the energy-transfer process (naphthyl units → anthracenyl units.

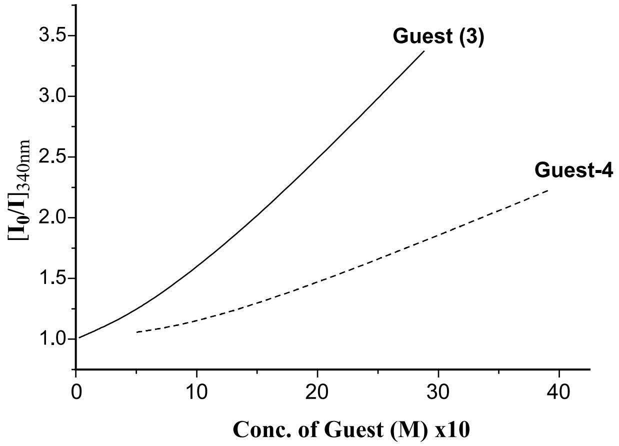


FIGURE 5 Stern-Volmer plot of I_0/I at 340 nm vs. concentration of guests for 1.

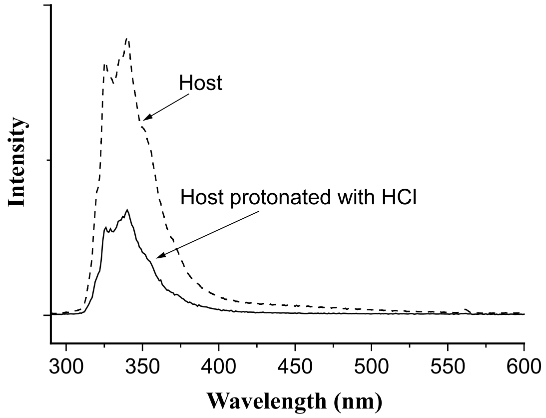


FIGURE 6 Fluorescence spectral changes of 1 (8.5×10^{-6} M) in MeCN (27°C, $\lambda_{exc} = 280$ nm) on passing HCl gas for 10 min.

context, this stronger quenching of naphthalene fluorescence was obviously due to the direct absorption of the anthracene chromophore at the emission wavelength of naphthalene units. This observation also suggests an energy-harvesting property providing selective recognition ability of **1** towards anthracene-9-carboxylic acid **3** compared with non-fluorescent aromatic carboxylic acids such as benzoic acid.

Another interesting feature is the sensitivity of the photon-harvesting property of the anthracenyl guest-loaded host towards acid because of the protonation of the tertiary amine sub-units of the dendritic skeleton. The fluorescence intensity of the host dramatically decreases on protonation of tertiary amine sub-units with HCl gas, as shown in Fig. 6.

This is probably attributed to the energy-transfer process involving protonated amine sub-units and naphthalene units (naphthyl units → protonated tertiary amine). After passing HCl gas for 10 min into the MeCN solution of **1** (8.5×10^{-6} M), irradiated at 280 nm, the host was titrated with a standard solution of the guest **3**.

Subsequently, successive addition of the guest induced a progressive decrease in the emission band of the naphthyl unit at 350 nm and the marginal development of anthracenyl emission band at 457 nm, indicating a weak sensitization of guest molecules as shown in Fig. 7. This probably reflects the occurrence of an energy-transfer process involving protonated amine, naphthyl units and anthracenyl units (naphthyl units → anthracenyl units → protonated tertiary amine). All these data clearly indicate that the anthracenyl guest-loaded hyperbranched polyesteramine architecture shows an efficient photon-harvesting property that can be modulated through protonation of amine sub-units, thereby making it useful for the development of a pH-assisted light-harvesting on–off switch.

To provide a full picture of the host–guest interaction between **1** and **3**, FT-IR and ^{1}H NMR spectroscopic data (Table I) were taken into account. FT-IR spectra were measured for the individual components, anthracene-9-carboxylic acid guest, dendritic host **1**, and a mixture of host and guest (1:5 molar ratio). The broad peak at 3440 cm^{-1} and the peaks in the region 2565–2660 cm^{-1} for guest **3** are associated with the contributing bands arising from the O—H stretching vibrations (both free and H-bonded) of the —CO·O—H group. Upon complexation of this guest with the host **1**, significant shifts in the O—H stretching bands ($\Delta\nu_1 = 32$ cm^{-1} at 3440 cm^{-1}; $\Delta\nu_2 = 30$ cm^{-1} at 2665 cm^{-1}) toward lower wavenumbers are observed. This result is indicative of participation of the binding sites of host **1** in forming the H-bonding complex with the carboxylic acid of the guest. Another important datum is the significant shift of C = O stretching of the —COOH group of the guest at 1679 cm^{-1} (sharp) toward a lower wavenumber 1636 cm^{-1} (broad and sharp) due to H-bonding (thus providing further evidence of its binding into the hyperbranched host **1**).

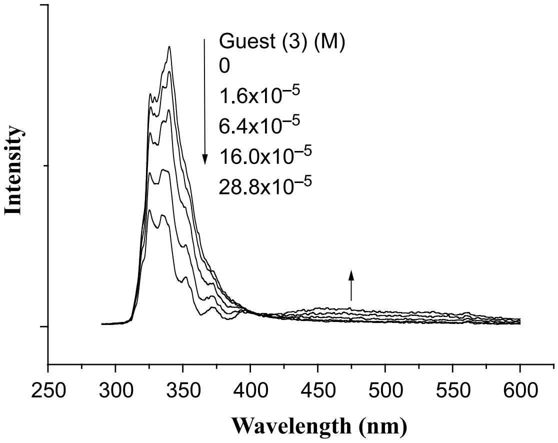


FIGURE 7 Fluorescence spectral changes in 1 (8.5×10^{-6} M) in MeCN (after passing HCl gas for 10 min) (27°C, $\lambda_{exc} = 280$ nm) upon addition of guest (3).

TABLE I FT-IR and ^{1}H NMR spectral data of the host (**1**)-guest (**3**) interaction

FT-IR spectral change		^{1}H NMR spectral change	
Wavenumber (ν) (cm^{-1})	Shift ($\Delta\nu$) (cm^{-1})	Chemical shift ($\Delta\delta$)	($\Delta\delta$)
3440 (O—H str.)	32	7.96–7.77 (naphthalene proton)	0.01
2565–2660 (O—H str.)	30	7.54–7.33 (naphthalene proton)	0.03
1679 (C=O str.)	43	4.20 (methylene H_h protons)	0.02
1254 (C—O str.)	08	3.97 (methylene H_c protons)	0.07
918 (O—H def.)	disappeared	2.50 (methylene H_g protons)	0.04
		2.35 (methylene $H_{d,b}$ protons)	0.02

The moderately strong band appearing at 1254 cm^{-1} due to C—O stretching of the —COOH group shifts to a lower wavenumber 1246 cm^{-1}, thus further corroborating the complexation between the host and guest.

Another noticeable change occurred at 918 cm^{-1} due to the *out-of-plane* deformation of the O—H bond of the —COOH group that disappeared on complexation with the dendritic host reflecting the involvement of acid—base interactions between the guest carboxylic acids and host tertiary amines. A binding property was also established from the ^{1}H NMR study (Table I). The signals corresponding to the methylene protons of dendritic skeleton show the downfield shifts ($\Delta\delta_{H(h)} = 0.02$ ppm, $\Delta\delta_{H(c)} = 0.07$ ppm, $\Delta\delta_{H(g)} = 0.04$ ppm, $\Delta\delta_{H(d,b)} = 0.02$ ppm) upon addition of the anthracene-9-carboxylic acid guest, indicating the participation of the —CO$_2$H group in H-bonding and acid–base interactions with the host.

Furthermore, the signals corresponding to the naphthalene protons showed slight downfield shifts ($\Delta\delta_{7.96-7.77} = 0.01$ ppm, $\Delta\delta_{7.54-7.33} = 0.03$ ppm) upon addition of the anthracenyl guest, suggesting that the naphthalene units of **1** and anthracene units are close to each other for π-stacking interaction upon complexation. Figure 8 shows the ^{1}H NMR spectra of the host and host–guest complex.

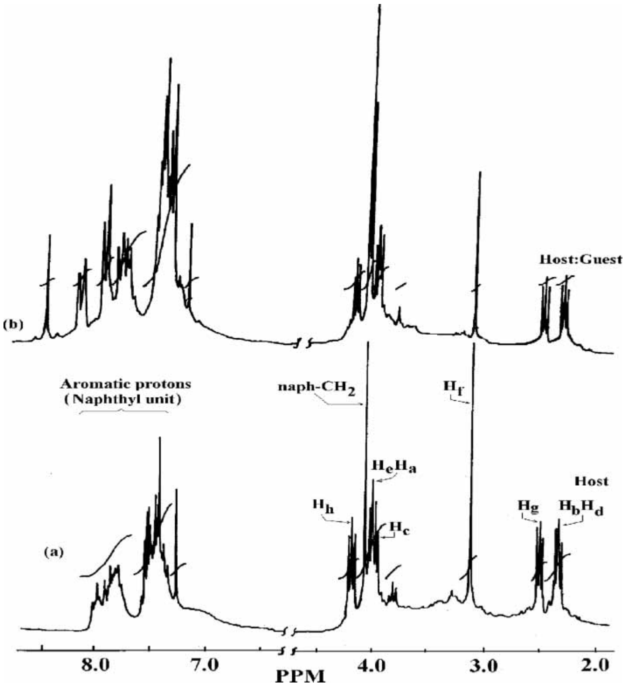


FIGURE 8 200 MHz ^{1}H NMR spectra of (a) host 1 and (b) host (1): guest (3) complex in CDCl$_3$.

EXPERIMENTAL

The peripherally appended naphthyl-unit-based hyperbranched polyesteramine (PEA) **1** (G2) architecture was synthesized following our one-pot synthetic strategy as described recently [11]. FT-IR spectroscopic measurements in KBr pellets were carried out using a Thermo-Nicolate Nexus-870-FT-IR spectrometer. NMR spectra were recorded on a Bruker AC200 spectrometer using CDCl$_3$ solvent. For fluorescence measurements, a Shimadzu absorption spectrophotometer (UV-1601) and Spex-fluorolog-3 spectrofluorimeter (FL3-11) were used. The photon-harvesting property was investigated by adding increasing amounts of guests (added up to 28.8×10^{-5} M for guest 3; added up to 39.24×10^{-5} M for guest **4**) into the MeCN solution of the hyperbranched host **1** (8.5×10^{-6} M).

CONCLUSION

Our results suggest that a hyperbranched artificial light-harvesting system can be achieved by hosting anthracene-9-carboxylic acid guest. Energy transfer occurs from the hyperbranched polymeric host to the anthracene-9-carboxylic acid guest because of the emission and absorption spectral overlap of the relevant donor/acceptor units. We anticipate that a fluorescent hyperbranched macromolecule of this type with a remarkable light-harvesting ability through hosting of anthracene-9-carboxylic acid would be most welcome in the development of photonic devices requiring an antenna effect. Moreover, this dendritic system acts as an efficient fluorosensor displaying a better photon-harvesting sensitivity towards the anthracenyl guest than benzoic acid. The photon-harvesting properties between the donor and acceptor units were affected by the protonation of the amine sub-units of the dendritic host, which is believed to play a major role in the pH-promoted ON–OFF light-harvesting switching. Further studies in our laboratory are in progress.

Acknowledgements

We like to thank CSIR, Government of India, for financial support.

References

[1] Stewart, G. M.; Fox, M. A. *J. Am. Chem. Soc.* **1996**, *118*, 4354.

[2] Adronov, A.; Robello, D. R.; Frechet, J. M. J. *J. Polym. Sci., Part A, Polym. Chem.* **2001**, *39*, 1366.

[3] Kobayashi, M.; Machida, S.; Takahasi, S.; Horie, K.; Yoshikawa, H.; Masuhara, H. *Chem. Lett.* **2002**, 394.

[4] Hahn, U.; Gorka, M.; Vogtle, F.; Vicinelli, V.; Ceroni, P.; Maestri, M.; Balzani, V. *Angew. Chem. Int. Ed.* **2002**, *41*, 3595.

[5] Frechet, J. M. J. *J. Polym. Sci. Part A, Polym. Chem.* **2003**, *41*, 3713.

[6] Zimmerman, S. C.; Lawless, L. J. *Top. Curr. Chem.* **2001**, *217*, 95.

[7] Boas, U.; Heegaard, P. H. M. *J. Chem. Soc. Rev.* **2004**, *33*, 43.

[8] Pittelkow, M.; Christensen, J. B.; Meijer, E. W. *J. Polym. Sci., Part A, Polym. Chem.* **2004**, *42*, 3792.

[9] Schenning, A. P. H. J.; Peeters, E.; Meijer, E. W. *J. Am. Chem. Soc.* **2000**, *122*, 4489.

[10] Balzani, V.; Ceroni, P.; Gestermann, S.; Gorka, M.; Kauffmann, C.; Vogtle, F. *Tetrahedron* **2002**, *58*, 629.

[11] Ghosh, S.; Banthia, A. K. *Polym. Bull.* **2004**, *52*, 243.

[12] Ghosh, S.; Banthia, A. K. *Tetrahedron Lett.* **2002**, *43*, 6459.

[13] Ghosh, S.; Banthia, A. K. *Supramol. Chem.* **2004**, *16*(7), 487.

[14] Bai, F.; Chang, C.-H.; Webber, S. E. *Macromolecules* **1986**, *19*, 2484.

[15] Zhao, C.-C.; Tong, Q.-X.; Li, Z.-T.; Wu, L.-Z.; Zhang, L.-P.; Tung, C.-H. *Tetrahedron* **2004**, *45*, 6807.