Multiple Chromophore Labeled Novel Bile Acid Dendrimers for Light Harvesting

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ABSTRACT: A facile synthesis of bile acid-based dendritic structures with multiple naproxen groups at the periphery and a single anthracenyl moiety on the side chain is described. The photophysical properties have been studied by both steady-state and time-resolved techniques. Absorption studies indicate that there are no ground-state interactions between the chromophores and the molar extinction coefficients increase linearly with increasing number of naproxen units. Upon excitation of the peripheral chromophores, there is efficient intramolecular energy transfer to the anthracenyl chromophore. These novel, non-conjugated dendrimers thus act as efficient molecular light harvesters.

Introduction

Photosynthesis is one of the most important natural phenomena and is vital for the survival of all life on earth. This process primarily involves the harvesting of solar energy and its subsequent conversion into useful chemical energy by supramolecular systems present in plants, photosynthetic bacteria, algae, and a few other microorganisms. The natural photosynthetic systems consist of a complex assembly of chromophores that function as antenna, absorbing photons from the sunlight and then transferring the energy with high efficiency to a reaction center where subsequent conversion to redox chemical energy takes place via charge separation.[1]

Of late there has been growing interest in the development of artificial systems that can mimic certain aspects of photosynthesis.[2] In this context, dendrimers[3] have proven to be excellent candidates for the design of artificial light-harvesting antennae, mainly due to their highly branched architecture and the presence of multiple functionalizable groups.[4] There have been essentially two approaches to dendrimer-based light-harvesting systems. In the first approach, the dendritic framework is designed to be photoactive. It functions as a light-absorbing antenna and transfers the energy to a central acceptor mainly via a through-bond mechanism.[5] The second strategy is to use the dendrimer backbone as a scaffold to hold the peripheral chromophores and the core chromophore together.[6] In such light-harvesting dendrimers, energy transfer from the peripheral donor chromophores to the core acceptor involves a through-space Förster-type interaction and is not affected by the dendritic backbone. To date, most work on such dendrimer-independent energy transfer systems has involved pol(aryl ether)-based dendrimers.[7] Using the second approach, we recently reported preliminary results on the synthesis and steady-state photophysical properties of a bile acid-based first-generation dendritic light harvesting system with peripheral naproxen units as donors and a single anthracenyl chromophore as the acceptor.[8] In this paper, the full synthetic details and extensive photophysical studies on the first and second-generation dendritic structures are reported.

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Synthesis and Characterization

The dendritic structures were synthesized using a combination of both convergent and divergent strategies and by exploiting the high reactivity of the chloroacetyl functionality. Per-(chloroacetylated) dendrons **1**, **4**, and **7** were synthesized from deoxycholic acid/cholic acid by a convergent route similar to reported procedures[9] (see Supporting Information for experimental details) and were subsequently hydrogenolyzed (Pd/C, dioxane, H_2) to yield dendrons **2** (90%), **5** (92%), and **8** (80%), respectively. Anthracenyl esters of the acids **2**, **5**, and **8** were prepared by forming the acid chlorides and coupling them with 9-anthracenemethanol to generate the anthracenyl-appended dendrons **3** (72%), **6** (70%), and **9** (62%), respectively (Scheme 1).

Trimers **1** and **3** were then reacted with an excess of the potassium salt of (*S*)-naproxen in DMSO to yield **10** (85%) and **11** (91%), respectively (Scheme 2). In an analogous manner, tetramers **4** and **6** were converted to the corresponding naproxen-terminated dendrimers **12** (84%) and **13** (80%), respectively (Scheme 2). The second-generation dendrimers **14** (62%) and **15** (60%) were also conveniently synthesized by following the same displacement strategy from the respective precursor heptamers, **7** and **9** (Scheme 3). For comparative studies with the dendritic structures, four monomeric analogues, **16**−**19** (Chart 1) were also prepared starting from lithocholic and cholic acid (Supporting Information). All the compounds were purified by column chromatography and characterized by ^{1}H NMR, ^{13}C NMR, IR, elemental analysis, and whenever possible, by ESI/MALDI-TOF MS. The homogenity of the compounds used for the photophysical studies were confirmed by reversed-phase HPLC.

^{1}H NMR spectral data were extremely useful in the characterization of the dendritic structures. Figure 1 shows the 400 MHz spectra for the dendritic structures **9** and **15** as representative examples. In the perchloroacetylated dendron **9**, the resonances of the methylene protons of the chloroacetyl group occur in the region 4.03−4.11 ppm. The 3β, 7β, and 12β H of the cholic acid units appeared between 4.6 and 5.21 ppm, the aromatic signals of the anthracenymethyl moiety appear at 7.46−8.50 ppm, and the methylene hydrogens appear as AB-quartet at 6.14−6.28 ppm. The observed ratios of the intensities of the signals are in good agreement with the expected values. For example, in heptamer **9**, there are twelve chloroacetyl

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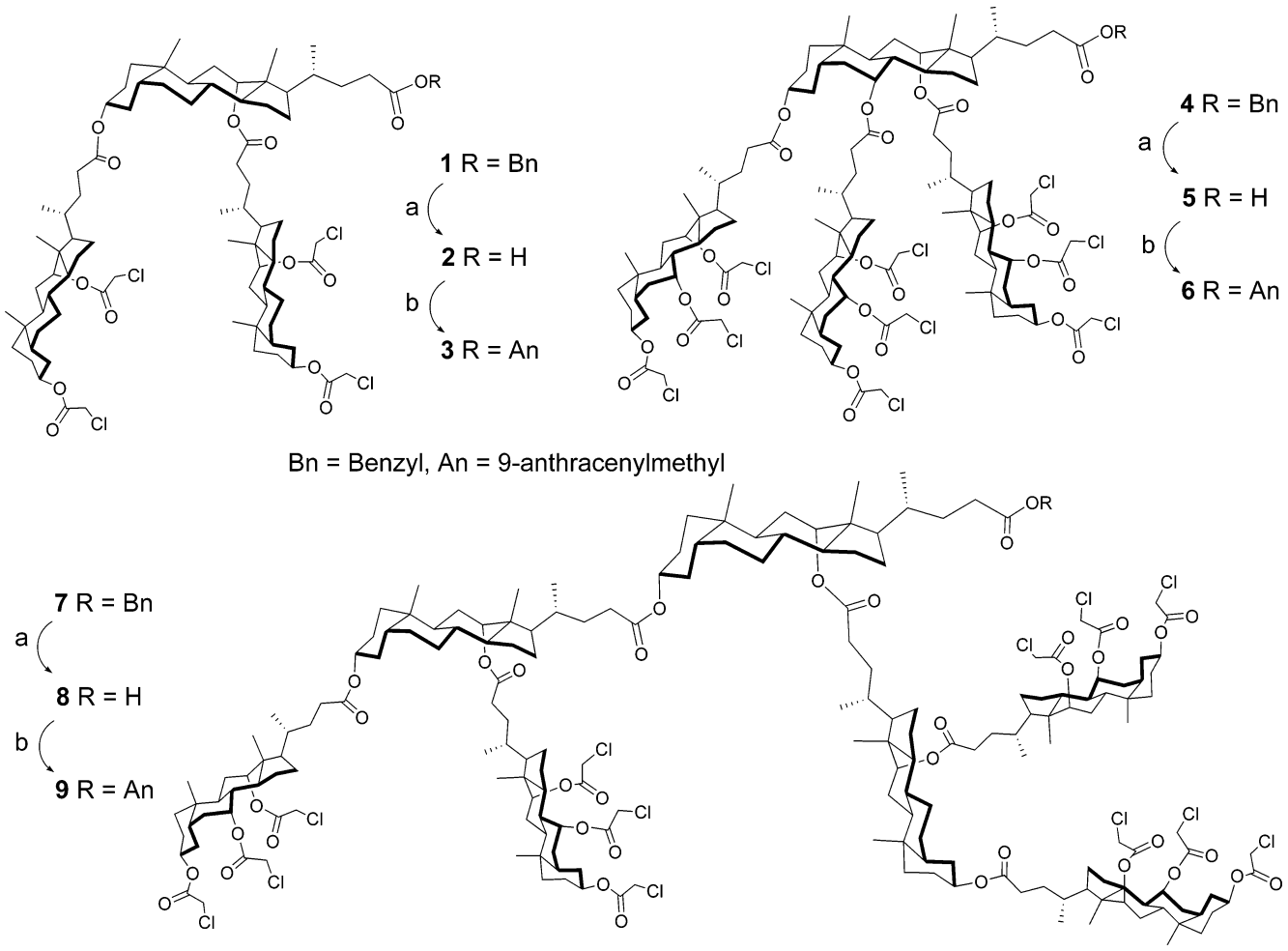
Scheme 1. Synthesis of Precursor Dendrons 3, 6, and 9



(a) Pd/C, dioxane, H_2 (b) (i) $(COCl)_2$, CH_2Cl_2, (ii) 9-anthracenemethanol, CaH_2, $PhCH_2Et_3N^+Cl^-$, toluene reflux, N_2.

groups, seven 3β H, four 7β H, and seven 12β H. As observed in Figure 1, the integration data are consistent with these values. After the naproxen units are linked to dendron **9** to form **15**, the methylene signals originally at 4.03−4.11 ppm shifted downfield to 4.33−4.69 ppm, while the other resonances remained almost unchanged. The complete absence of signals in the 4.03−4.11 region of **15** indicated that impurities due to incomplete reaction ("defects") were not present. In addition, the peripheral naproxen moieties in **15** gave rise to distinct sets of signals in the regions 3.84−3.98 (OCH_3, CH) and 7.04−7.66 (aromatic protons), with slight overlap with some of the aromatic protons of the anthracenyl moiety. The integration data also supported the presence of twelve naproxen moieties. Similar patterns were observed for all the other dendritic structures.

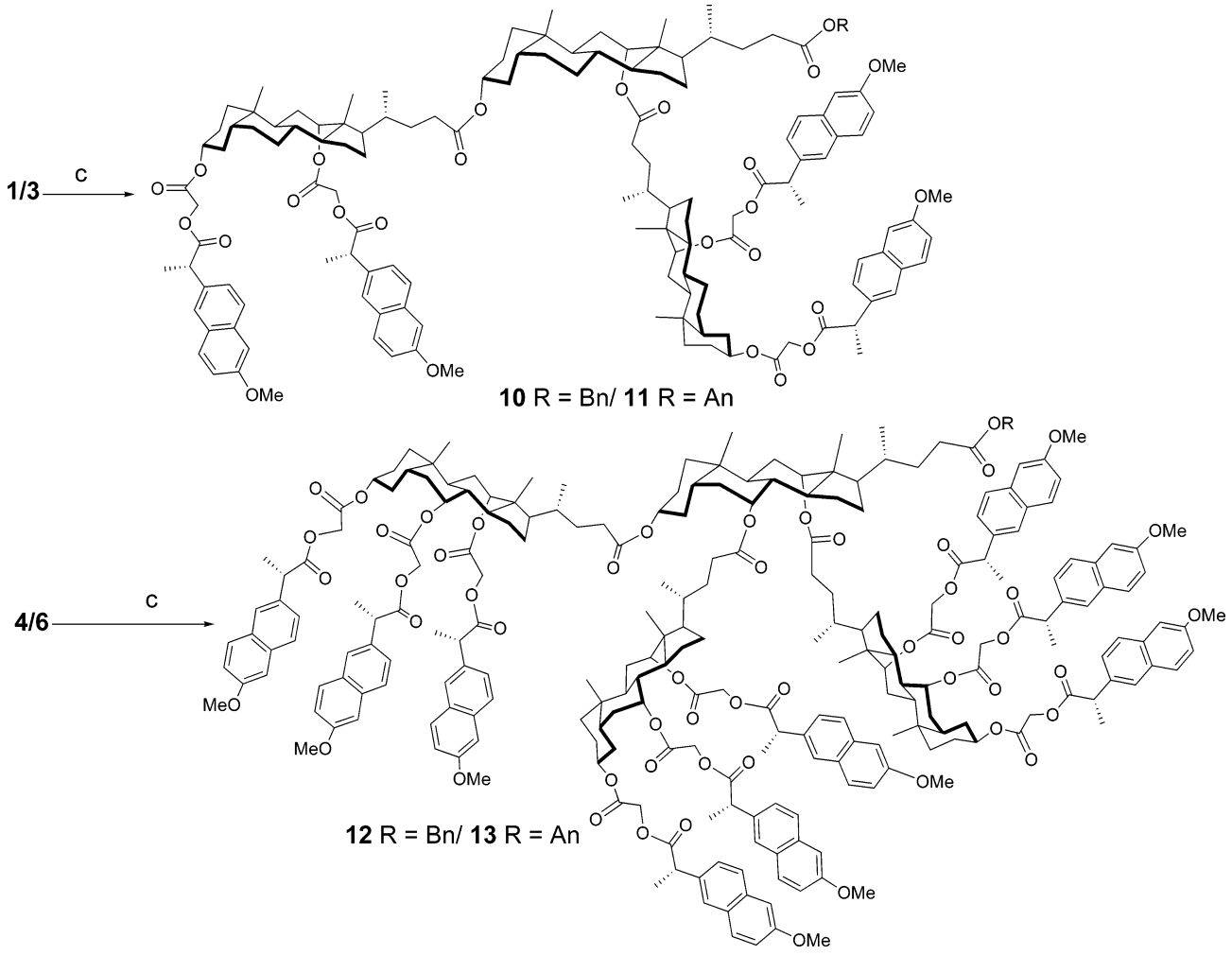
Absorption Spectroscopy Studies. The absorption, fluorescence spectra, and the fluorescence decay of all compounds were recorded in CH_3CN, except for **14** and **15,** which were recorded in 4% $CHCl_3$ in CH_3CN for complete solubilization under the experimental conditions.

The absorption spectra of dendrimers **10**, **12**, and **14** were characteristic of the naproxen chromophore similar to the monomeric analogues **16** and **18** (Figure 2). Also, the extinction coefficients increased linearly with increasing number of naproxen units from monomer **18** to heptamer **14**, which suggested the absence of ground-state interactions between the donor chromophores. Similarly, the dendritic structures **3**, **6**, and **9** showed typical anthracenyl absorption bands with no significant shift or change in absorption intensity in the series (inset, Figure 2).

In the series of compounds appended with naproxen *and* anthracenyl chromophores (**15**, **13**, **11**, **17**, and **19**), the absorption spectra closely matched the sum of the absorption of the naproxen chromophores and the 9-anthracenyl moieties. Moreover, the molar extinction extinction coefficients (corresponding to naproxen absorption) increased linearly with increasing number of naproxen units (Figure 3). These observations imply that the naproxen and anthracene units behave as *isolated chromophores* in the ground state in the monomers (**17** and **19**) and dendritic series (**11**, **13**, and **15**).

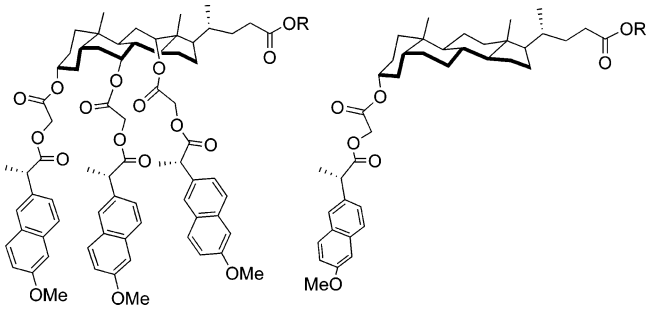
Steady-State Fluorescence Studies. To study the light harvesting and energy transfer properties of the donor−acceptor dendritic systems, we first examined their steady-state emission properties. Upon excitation at 360 nm, monomers **17** and **19** exhibited fluorescence characteristics typical of the anthracenyl chromophore with emission maxima at ∼390, ∼412, and ∼436 nm and a shoulder at ∼465 nm. In the case of the dendritic structures (**11**, **13**, and **15**), the spectra were similar to those of the monomers, with only **13** showing a slight decrease in the fluorescence intensity (Figure 4). The estimated quantum yields were 0.19 ± 0.01 for **11**, **15**, **17**, and **19** and 0.16 ± 0.01 for **13**. The dendritic structures **3**, **6**, and **9**, which are capped only with anthracene, can be used as model probes for studying the fluorescence characteristics of the anthracenyl chromophore in the absence of the peripheral naproxen moieties. The fluores-

Scheme 2. Synthesis of Multiple Naproxen Appended First-Generation Dendrimers 10, 11, 12, and 13



(c) Potassium salt of naproxen, DMSO, room temperature.

Chart 1

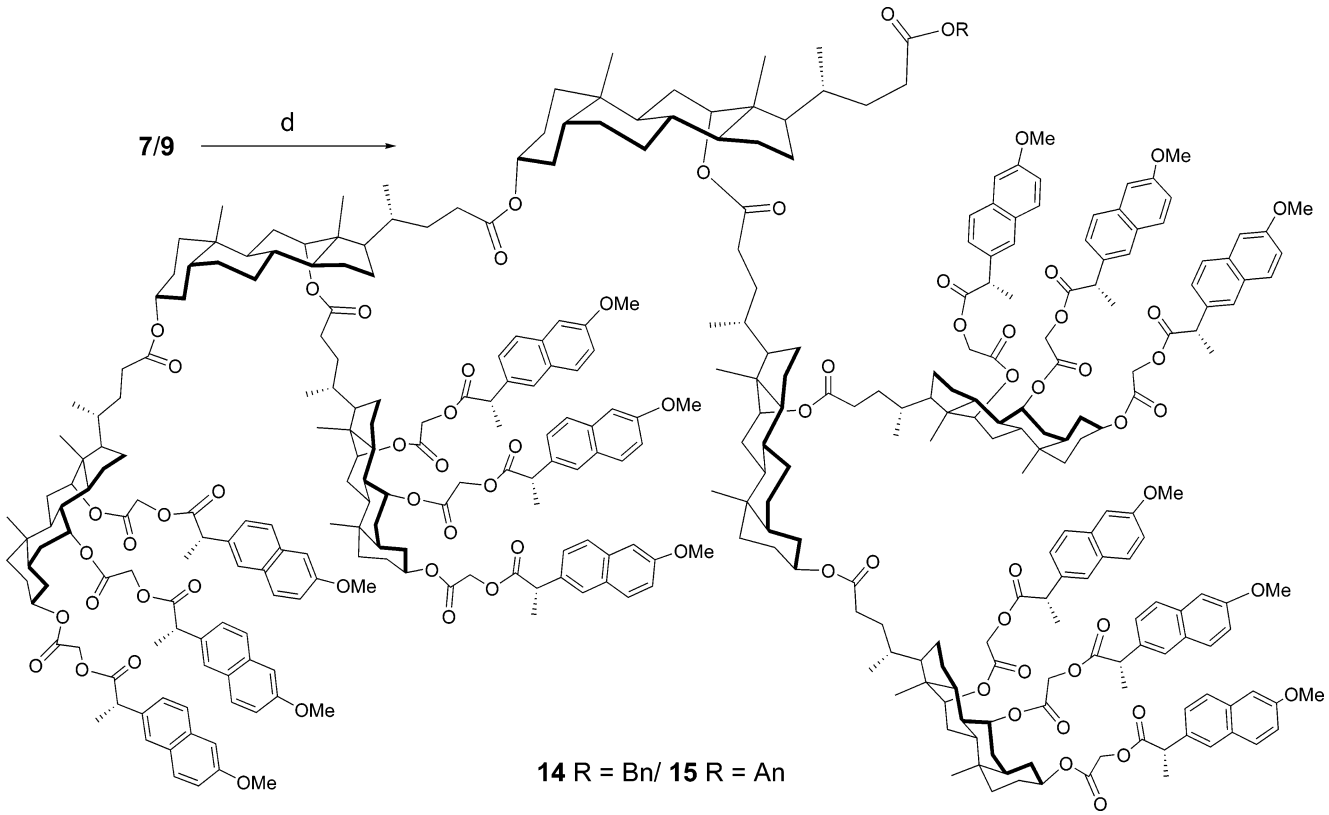


cence spectra of these compounds were similar to that of the above series at the same excitation wavelength ($\phi = 0.21 \pm 0.01$)[10] (inset, Figure 4). These results suggest that the steady state fluorescence properties of the anthracenyl moiety are mostly unaffected by the dendritic structure and by the presence of the naproxen chromophores.

The absorption studies suggested that the 275−290 nm region might be used to *selectively* excite the naproxen chromophore with minimal direct excitation of the anthracenyl moiety (Figure 2).[11] Compounds **10**, **12**, **14**, **16**, and **18** exhibited a strong fluorescence in acetonitrile ($\lambda_{ex} = 275$ nm) with maxima at ~353 nm (inset, Figure 5). The quantum yield was fairly constant ($\phi = 0.32 \pm 0.02$)[21] in the entire series, suggesting the absence of random quenching of the fluorescence due to the proximity of the naproxen units in the dendritic structures (**10**, **12**, and **14**). These observations along with the absorption spectral studies indicated that the light harvesting ability of the naproxen-capped series (donor series) increased steadily with increasing number of naproxens, which is indeed the desirable feature. Excitation of the monomers **17** and **19** at 275 nm resulted in emission chiefly from the anthracenyl moiety with very weak emission from the naproxen chromophore. This indicated energy transfer from naproxen (donor) to the anthracenyl chromophore (acceptor). Similarly, 275 nm excitation of the dendrimers (**11**, **13**, and **15**) resulted in intense emission from the acceptor with relatively weak emission from the donors. Moreover, the fluorescence intensity of the anthracene core increased from **11** to **15**, analogous to the monomers with increasing number of naproxens, but the residual emission of naproxen is also relatively higher, especially with **13** and **15** (Figure 5). The intramolecular nature of the energy transfer was confirmed by experiments on mixtures of naproxen and 9-anthracenemethanol that did not show any energy transfer from donor to acceptor in the same concentration range.

Time-Resolved Fluorescence Study. The fluorescence lifetimes of all the compounds were measured using the time-correlated single-photon counting method. The decay curves were analyzed using a nonlinear least-squares fitting procedure.[12] Figure 6 shows the fluorescence decay of dendron **11** as a representative example.

Scheme 3. Synthesis of Multiple Naproxen Appended Second-Generation Dendrimers 14 and 15



(d) Potassium salt of naproxen, DMSO, 45 °C.

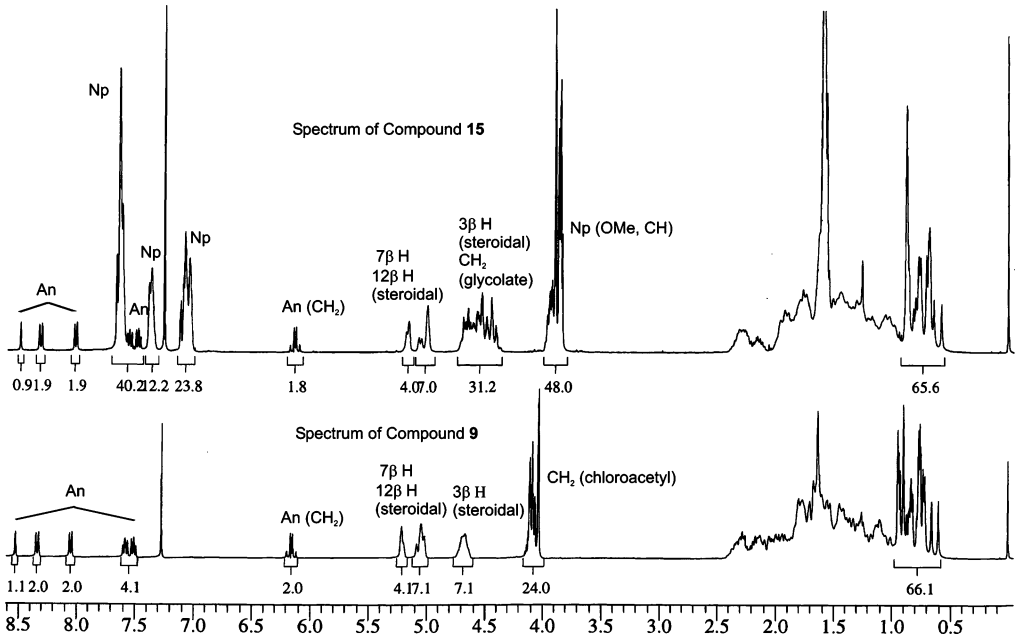


Figure 1. 400 MHz ^{1}H NMR spectra of compounds **9** and **15**. (Np = naproxen, An = anthracenylmethyl).

The lifetimes of the anthracene-capped dendrons (**3**, **6**, and **9**) and naproxen-terminated compounds, **10**, **12**, **14**, **16**, and **18** were first measured. The former series was excited at 369 nm and the fluorescence decay was monitored at 436 nm, while for the latter series, excitation was at 275 nm and emission wavelength was 350 nm. The anthracene-labeled compounds showed a single lifetime of 3.9−4.2 ns, which is similar to that of anthracene (∼4.1 ns) (Table 1).[13] In the donor series, all compounds except **14** exhibited single-exponential decay, with lifetimes ranging from 7.6 to 8.1 ns. These values are comparable to the lifetime of naproxen (7.2 ns) in acetonitrile, which suggest that there is no nonradiative quenching due to the proximity effect of the chromophores in the dendritic structures and in the monomer with three donors. Compound **14** alone showed a biexponential with an average lifetime of 7.5 ns. There was a minor amount of a shorter decay component of 4.6 ns due to slight quenching by $CHCl_3$, which was not present (as solvent component) in the other compounds.[14]

In the donor−acceptor series (**11**, **13**, **15**, **17**, and **19**), the fluorescence decay of the anthracenyl moiety on direct excitation

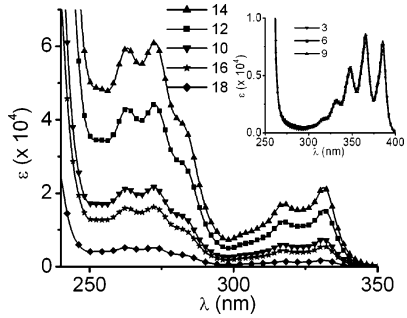


Figure 2. Absorption spectra (molar extinction coefficients as a function of wavelength) of compounds **10**, **12**, **16**, **18** in CH_3CN and **14** in 4% $CHCl_3/CH_3CN$ (concentration range − 10−50 μM). The inset shows the absorption spectra of dendrons **3**, **6** and **9** in CH_3CN.

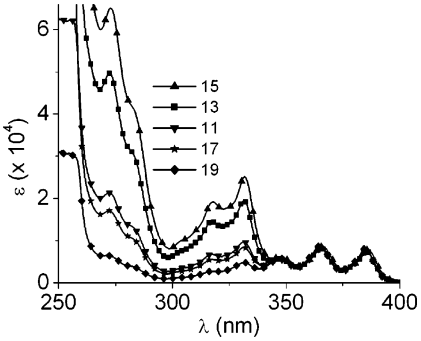


Figure 3. Absorption spectra of compounds **11**, **13**, **17**, **19** in CH_3CN and **15** in 4% $CHCl_3/CH_3CN$.

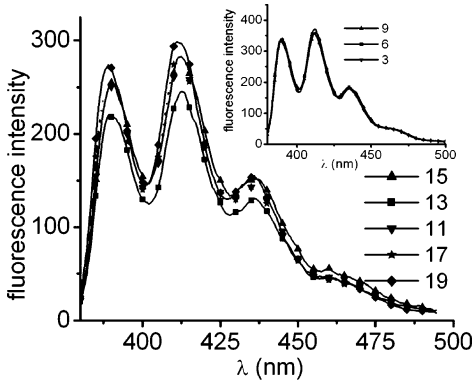


Figure 4. Emission spectra of compounds **11**, **13**, **17**, **19** in CH_3CN and **15** in 4% $CHCl_3/CH_3CN$ upon excitation at 360 nm,(concn = 2.5 μM). Inset shows the emission spectra of compounds **3**, **6** and **9** in CH_3CN upon excitation at 360 nm (concn = 2.5 μM).

(λ_{ex} = 369 nm) was found to be single exponential only in the case of the monomers (**17** and **19**). In the dendritic systems (**11**, **13**, **15**), the recovered decay curves were better fit with a biexponential decay function. These large structures are likely to have multiple conformations in solutions, and hence the anthracenyl moiety may experience different local environments that could lead to slight differences in the lifetimes.[6b] However, the *average lifetimes* in dendrimers **11** (τ_{avg} = 3.9 ns) and **13** (τ_{avg} = 4.0 ns) were similar to the values observed for the dendrons capped only with anthracene and with the lifetime of the monomers ($\tau = 3.8 \pm 0.1$ ns). Dendrimer **15** alone showed a slight increase in the lifetime (τ_{avg} = 4.5 ns).

The donor decays in the above series (λ_{ex} = 275 nm, λ_{em} = 350 nm) were all multiexponential. Monomers **17** and **19** showed biexponential decays with a short lifetime component and a minor amount of a long-lived component (Table 2). The long-lived fluorescence decay times were slightly lower in magnitude compared to that of the donor systems (**16** and **18**,

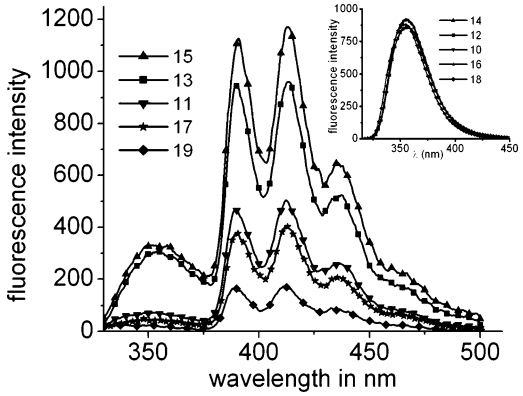


Figure 5. Emission spectra of compounds **11**, **13**, **17**, **19** in CH_3CN and **15** in 4% $CHCl_3/CH_3CN$ upon excitation at 275 nm (normalized to 1 μM). The inset shows the emission spectra of **10**, **12**, **16**, **18** in CH_3CN and **14** in 4% $CHCl_3/CH_3CN$ upon excitation at 275 nm at constant absorbance (0.1 OD).

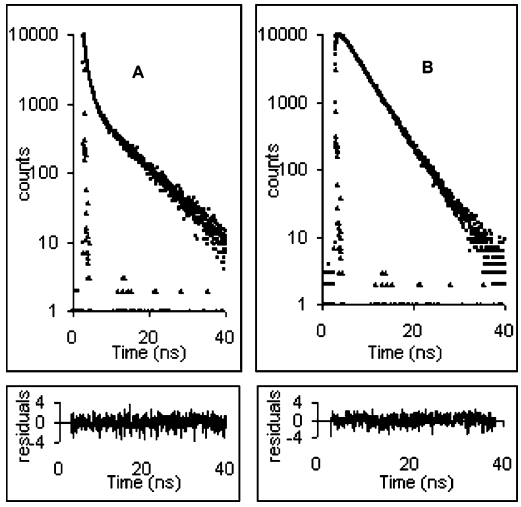


Figure 6. Fluoresence decays of donor (A) (λ_{em} = 350 nm) and sensitized acceptor (B) (λ_{em} = 436 nm) in compound **11**, (λ_{ex} = 275 nm).

Table 1. Fluorescence Lifetimes of Compounds 3, 6, 9 (anthracene-capped), and 10, 12, 14, 16, and 18 (naproxen-capped)

compound	τ (ns)
λ_{ex} = 369 nm, λ_{em} = 436 nm	
3	3.92
6	3.97
9	4.19
λ_{ex} = 275 nm, λ_{em} = 350 nm	
10	8.09
12	7.78
14	7.47[a]
16	7.59
18	7.70

[a] $\tau = \tau_{avg}$, τ_1 = 8.14 ns: B1 = 0.49 (80.5), τ_2 = 4.58 ns: B2 = 0.21 (19.5). "B" is the preexponential factor (amplitude). The values in parentheses are the relative amplitudes.

respectively). The presence of the fast decay component in the donor decays was due to energy transfer to the acceptor. This was further confirmed by monitoring the fluorescence dynamics of the sensitized acceptor[15] (λ_{ex} = 275 nm, λ_{em} = 436 nm). In monomers **17** and **19**, the anthracenyl chromophore exhibited rise times of 0.38 and 0.75 ns, respectively, which were comparable to the quenched donor lifetimes of 0.47 and 0.83 ns, respectively (Table 2).

In case of the dendritic structures **11**, **13**, and **15**, the donor decays could be best fit to a triexponential. There were two

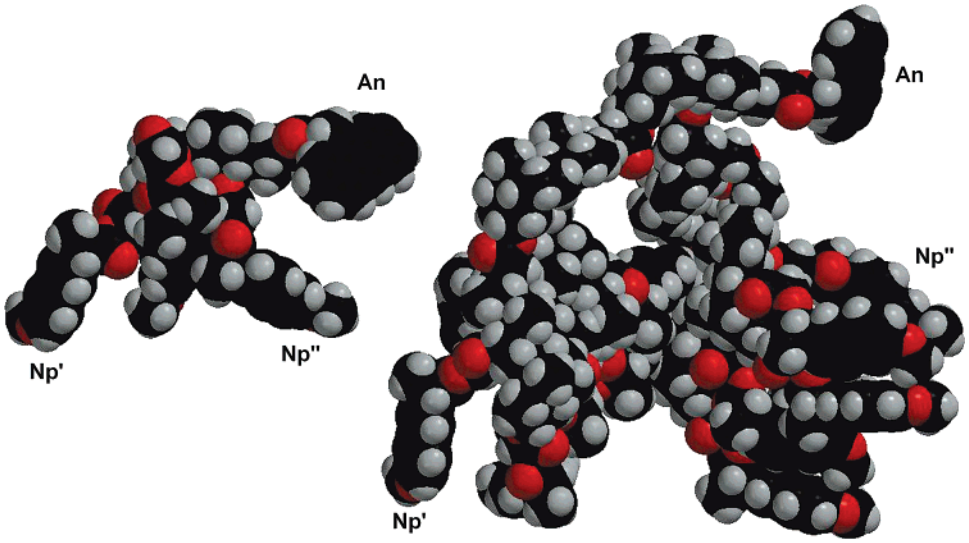


Figure 7. Space filling view of monomer **17** (Np′ − An: 23 Å; Np″ − An: 11 Å) and heptamer **15** (Np′ − An: 42 Å; Np″ − An: 16 Å) (Spartan ′04 minimized models in a vacuum).

Table 2. Fluorescence Lifetimes (τ), Preexponential Factors/Amplitude (B), and Relative Amplitudes (rel amp) of Compounds 11, 13, 15, 17, and 19 in CH_3CN

	λ_{ex} = 275 nm, λ_{em} = 350 nm			λ_{ex} = 369 nm, λ_{em} = 436 nm			λ_{ex} = 275 nm, λ_{em} = 436 nm		
compound	τ (ns)	B	rel amp (%)	τ (ns)	B	rel amp (%)	τ (ns)	B	rel amp (%)
11	0.55	0.67	28	2.95	0.25	27	0.57	−0.50	−8
	1.37	0.34	34	4.32	0.45	73	4.02	0.90	108
	7.88	0.07	38						
13	0.38	0.38	6	3.29	0.49	58	0.73	−0.61	−12
	1.52	0.36	32	5.09	0.23	42	4.23	1.02	112
	7.51	0.14	62						
15	0.35	0.28	6	3.01	0.20	34	0.93	−0.34	−13
	1.80	0.37	37	5.31	0.23	66	5.06	0.54	113
	7.05	0.15	57						
17	0.47	1.16	59				0.38	−0.30	−4
	7.35	0.05	41	3.72			3.63	0.81	104
19	0.83	1.11	85	3.80			0.75	−0.39	−12
	6.33	0.05	15				3.82	0.70	112

short-lifetime components and a small long-lived component, which was again comparable to that of the donor systems (**10**, **12**, and **14**, respectively) (Table 2). These bile acid-derived dendrimers are not symmetrical, and hence the donors are not equidistant from the acceptor, which could lead to different rates of energy transfer by the donors. This is probably why more than one fast decay component is observed. It is to be noted that, even in the monomers with two or three donors, the donor−acceptor distances are not same, but there is a greater degree of inhomogeneity (distance distribution) in the dendritic systems (Figure 7). The sensitized acceptor decays of the dendrimers showed a single rise time whose value lay between that of the shorter components of the corresponding donor decays, which suggests that probably it is the average rise time that was observed. For example, in compound **11**, the donor decay has two fast components of 0.55 and 1.37 ns, which corresponded to an average lifetime of 0.61 ns, and this value is comparable to the observed rise time of 0.57 ns. Moreover, the average rise time increased from the first to the second generation as the average distance of the donor from the acceptor increased. The lifetime of the sensitized acceptor remained unchanged (compared to direct excitation) in the monomers **17** and **19** (Table 2). In the case of the dendritic structures (**11**, **13** and **15**), single decay times were observed that were comparable to the average lifetimes on direct excitation.

The presence of the long-lived donor decay in both the monomers and dendrimers in the donor−acceptor series could be due to varied reasons and has been observed by others, too.[6b,7d] A possible explanation is that, since the donor and acceptor are linked to the bile acid backbone via highly flexible spacers, these molecules may adopt conformations in which donor−acceptor orientation is not favorable for energy transfer.[7d,16] Moreover, as the Förster's radius[17] is only 26 Å (28 Å under deaerated conditions), it is very likely that one or more donors may be at distances greater than 26 Å with a low energy transfer probability (Figure 7) in the dendritic structures due to their larger size and conformational flexibility. This could also be the reason for the increase in the amplitude of the long-lived component in the dendritic structures as compared to the monomers. The Förster's radius for self-transfer for the naproxen chromophore was estimated to be ∼13 Å.[16] The distance between the donor chromophores in a single bile acid unit calculated based on molecular modeling is ∼5−13 Å. Hence, it is also probable that the long-lived species could also be due to persistent energy migration between the naproxens.[18]

Energy-Transfer Estimation. The efficiency of energy transfer has been estimated both by steady state (E_S) and time-resolved measurements (E_T) using the donor-quenching method (Table 3).[19] It was observed that efficiencies calculated from time-resolved data were slightly lower compared to those estimated from the steady-state measurement, the reason for which is not clear. In the monomers (**17** and **19**), the efficiency is ∼92% based on steady state calculations. Although all the dendrimers exhibited slightly lower efficiencies compared to the monomers, there is an interesting pattern. It is observed that, in the first-generation dendritic systems, the efficiency decreased

Table 3. Energy Transfer Efficiencies Calculated by Donor Quenching Method

compound	E_S (%) ± 3	E_T (%) ± 2
11	88	84
13	80	75
15	76	68
17	92	90
19	93	86

with increasing number of branching units, **11** > **13**. One possible explanation is that, with increased branching to avoid steric crowding, the branches and chromophores are likely to adopt more extended conformations, which could lead to increase in distance between some of the donors and acceptor.

The second-generation dendritic structure (**15**) has lower energy transfer efficiency than the first generation (Table 3). Molecular modeling (in a vacuum) suggested that in **15** the distances varied from ~14−42 Å, with many of the donors exceeding the Förster's radius (26 Å), but the decrease in efficiency is not as much as might be expected (Figure 7). Because **15** is poorly soluble in CH_3CN as compared to the other compounds, it might adopt more compact conformations than extended forms, which could lead to reduced distance between the donors and acceptors and hence higher efficiencies. Also, rather than single-step Förster transfer to the acceptor, energy transfer may occur via energy hopping among donors.[18]

Conclusion

Novel bile acid-based dendritic light-harvesting systems with multiple peripheral naproxen units as donors and a single anthracene as an acceptor have been efficiently synthesized and their absorption, fluorescence, and energy-transfer properties investigated. The synthetic strategy we adopted also gave ready access to bile acid dendrimers, which either do not possess the anthracenyl chromophore or lack the peripheral naproxen units for comparison with compounds containing both the chromophores. It was observed that the photophysical properties of the naproxen chromophore were largely unaffected with an increasing number of naproxen units in the dendritic structure and also with an increase in the size of the dendrimer (in the absence of the anthracenyl chromophore). Similarly, the anthracenyl chromophore in dendrimers **3**, **6**, **9**, **11**, **13**, and **15** also did not show any significant change in the absorption spectra, quantum yield, or lifetime. Dendritic structures **11**, **13**, and **15** exhibited high energy transfer efficiencies, which have been estimated both by steady-state and time-dependent fluorescence spectroscopy.

Virtually any donor with a carboxylic acid group and any acceptor with a hydroxyl group can be assembled on the bile-dendritic structure using our methodology. The ease of synthesis of the bile oligomers and the modular nature of the construction of the donor−acceptor systems make these molecules attractive to design additional functional systems. Such systems are likely to extend and expand the possibilities envisaged for potential applications of synthetic light-harvesting molecules.

Experimental Section

Lithocholic acid, cholic acid, deoxycholic acid, chloroacetic anhydride, 9-anthracenemethanol, (*S*)-(+)-2-(6-methoxy-2-naphthyl)propanoic acid were purchased from Aldrich and were used without further purification. All solvents were laboratory grade and were distilled prior to use. DMF and DMSO were dried over BaO and toluene was dried with sodium. For column chromatography, silica gel (100−200 mesh) was used. ^{1}H and ^{13}C NMR were recorded on JEOL Lambda 300 MHz or Bruker AMX 400 MHz spectrometers. IR spectra were recorded on a Jasco-70 FT-IR spectrophotometer. For all compounds, IR (thin film) refers to a glassy film deposited on a NaCl plate from a chloroform solution. HPLC was recorded on a Shimadzu system using a 250 mm × 4.6 mm C-18 reversed-phase analytical column. MALDI-TOF MS were recorded on a Kompack Seq model (KRATOS Analytical, U.K) fitted with a nitrogen laser. ESI-QTOF MS was recorded on a Micromass Q-TOF micro (model).

All solvents used for absorption and fluorescence studies were spectroscopic grade, and nondegassed solutions were used for the fluorescence measurements. Absorption spectra were recorded on a Shimadzu UV−visible spectrophotometer. Steady-state fluorescence measurements were done in a Perkin-Elmer LS-50B spectrophotometer. Fluorescence decay measurements were carried out using the time-correlated single photon counting technique. The excitation source was a mode locked titanium sapphire laser (Spectra Physics) operating at 82 MHz and with a pulse width of <2 ps. The 369 second harmonic, and 275 third harmonic outputs were used for excitation, and a microchannel plate photomultiplier tube was used as the detector. The fluorescence photons were collected at right angles to the exciting beam. For recording the lamp profiles, a scatter was placed instead of the sample. The response time of the instrument was ~50 ps. The data analysis was carried out by software provided by IBH (DAS-6), which is based on the reconvolution technique using iterative nonlinear least-squares methods.

The synthesis of compounds **2**, **3**, **5**, **6**, **8**, **9**, and **10**−**15** are described below. Potassium salt of naproxen was synthesized following a reported procedure.[20] Synthesis of dendrons **1**, **4**, and **7** and monomers **16**−**19** are described in the Supporting Information.

Trimer (4Cl, acid) 2. To compound **1** (0.21 g, 0.13 mmol) dissolved in dioxane (10 mL), 10% Pd/C (0.040 g) was added and the mixture was stirred for 7 h under a H_2 atmosphere. The catalyst was filtered off using a Celite bed, and the crude product obtained after removal of the solvent was chromatographed on silica gel using 30% EtOAc/hexanes to yield 0.17 g (90%) of compound **2** as a white foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.20 (s, 2H), 5.08 (s, 1H), 4.80 (m, 2H), 4.69 (m, 1H), 4.08 (s, 4H), 4.04 (s, 4H), 2.34−2.20 (m), 1.88−1.01 (m), 0.93−0.73 (angular Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 179.4, 173.5, 173.3, 166.8, 166.53, 166.49, 78.0, 76.3, 75.7, 73.9, 49.5, 49.2, 47.6, 45.13, 45.06, 41.72, 41.66, 41.1, 35.54, 34.69, 34.61, 34.54, 34.4, 34.3, 34.0, 32.3, 31.9, 31.6, 31.4, 30.9, 30.7, 30.6, 27.31, 27.26, 26.8, 26.72, 26.65, 26.3, 25.8, 25.5, 23.4, 23.0, 22.9, 17.5, 17.4, 12.41, 12.36, 12.3. IR (thin film, cm^{-1}): 2947, 2870, 1732, 1294, 1009, 756. LRMS-ESI: Calcd for $C_{80}H_{120}Cl_4 + Na^+$: 1467.7; $C_{80}H_{120}Cl_4 + K^+$: 1484.4. Obsd: 1468, 1484. Anal. Calcd for $C_{80}H_{120}Cl_4$: C 66.38, H 8.36. Found: C 66.16, H 8.27. $[\alpha]^{25}_D$: +94.8 (1.16, $CHCl_3$).

Trimer (4Cl, An) 3. To a solution of **2** (0.145 g, 0.10 mmol) in dichloromethane (1 mL), oxalyl chloride (50 μL) was added and the mixture was stirred in the presence of 2 μL of DMF for 45 min. Volatiles were removed under reduced pressure, and the residue was dried under vacuum for 30 min. To the acid chloride, 9-anthracenemethanol (0.030 g, 0.14 mmol), CaH_2 (0.012 g, 0.29 mmol), $PhCH_2Et_3N^+Cl^-$ (0.009 g, 0.04 mmol), and toluene (1 mL) were added, and the reaction mixture was refluxed under N_2 for 6 h. The reaction mixture was then diluted with $CHCl_3$ (4 mL) and filtered through Celite. The evaporation of the organic layer yielded the crude product that was chromatographed on silica gel using 4% EtOAc/80% benzene/16% $CHCl_3$ to yield 0.12 g (72%) of compound **3** as a white foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.52 (s, 1H), 8.33 (d, 2H, J = 8.7 Hz), 8.05 (d, 2H, J = 8.1 Hz), 7.61−7.48 (m, 4H), 6.18 (d, 1H, J = 12.6 Hz), 6.14 (d, 1H, J = 12.6 Hz), 5.19 (s, 1H), 5.16 (s, 1H), 5.01 (s, 1H), 4.79 (m, 2H), 4.69 (m, 1H), 4.08 (s, 2H), 4.04 (s, 2H), 4.03 (s, 4H), 2.33−2.26 (m), 1.83−1.29 (m), 1.09−0.60 (angular Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.3, 173.5, 173.3, 166.79, 166.77, 166.6, 166.5, 131.3, 131.0, 129.12, 129.08, 126.7, 126.3, 125.1, 123.9, 78.03, 77.96, 77.2, 76.30, 76.28, 75.7, 73.9, 58.7, 49.5, 49.24, 49.21, 47.62, 47.55, 45.13, 45.08, 44.98, 41.74, 41.66, 41.20, 41.16, 41.1, 35.55, 35.51, 34.71, 34.65, 34.56, 34.4, 34.3, 34.0, 33.3, 31.9, 31.6, 31.4, 31.2,

30.9, 30.7, 27.33, 27.25, 26.8, 26.7, 26.6, 26.3, 25.8, 25.5, 23.4, 23.3, 23.0, 22.9, 17.5, 17.4, 12.4, 12.2. IR (thin film, cm^{-1}): 2945, 2866, 1731, 1180, 757. LRMS-ESI: *m/z* Calcd for $C_{95}H_{130}C_{l4}O_4 + Na^+$: 1658; $C_{95}H_{130}Cl_4O_4 + K^+$: 1673.8. Obsd: 1657.8, 1674. Anal. Calcd for $C_{95}H_{130}Cl_4O_4$: C 69.67, H 8.00. Found: C 70.03, H 8.17. $[\alpha]^{25}_D$: +95.3 (1.13, $CHCl_3$).

Trimer (4Naproxen, Bn) 10. To a solution of **1** (0.027 g, 0.02 mmol) in DMSO (0.5 mL), potassium (*S*)-2-(6-methoxy-2-naphthyl)propanoate (0.024 g, 0.089 mmol) was added and the reaction mixture stirred at room temperature for 5 h. The reaction mixture was poured in water (20 mL) and extracted with EtOAc (20 mL). The organic layer was washed with water (15 mL) and dried over anhyd Na_2SO_4. After removing the volatiles, the crude product was then chromatographed on silica gel using 4% EtOAc/toluene to yield 0.034 g (85%) of compound **10** as a white foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.71−7.65 (m, 12H), 7.44−7.40 (m, 4H), 7.36−7.30 (m, 5H), 7.15−7.07 (m, 8H), 5.15 (s, 2H), 5.09 (m, 3H), 4.74−4.45 (m, 11H), 3.99−3.92 (m, 4H), 3.90−3.84 (m, 12H), 2.33−2.06 (m), 1.82−1.24 (m), 0.90−0.67 (angular Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.0, 173.8, 173.7, 173.64, 173.61, 173.4, 167.3, 167.2, 167.1, 157.8, 157.7, 136.06, 135.08, 134.99, 134.96, 133.75, 133.73, 129.3, 128.89, 128.88, 128.5, 128.2, 128.19, 127.2, 127.1, 126.3, 126.20, 126.18, 126.1, 119.1, 119.01, 118.95, 105.6, 77.2, 75.7, 74.0, 66.1, 63.9, 61.2, 55.4, 55.3, 52.1, 49.5, 49.3, 47.74, 47.69, 45.08, 45.05, 45.03, 41.8, 37.0, 35.7, 35.53, 35.51, 34.8, 34.7, 34.5, 34.3, 34.08, 34.02, 33.99, 32.1, 31.8, 31.5, 31.3, 30.9, 30.8, 27.3, 26.9, 26.8, 26.3, 25.8, 25.7, 25.6, 23.4, 23.1, 23.0, 18.8, 18.6, 18.2, 17.5, 17.4, 17.3, 12.5, 12.41, 12.38. IR (thin film, cm^{-1}): 2941, 1740, 1606, 1454, 1159, 1025, 756. LRMS-ESI: *m/z* Calcd for $C_{143}H_{178}O_{26} + Na^+$: 2334.2. Obsd: 2334.3. Anal. Calcd for $C_{143}H_{178}O_{26}$: C 74.26, H 7.76. Found: C 73.98, H 7.88. $[\alpha]^{25}_D$: +100.4 (1.26, $CHCl_3$).

Trimer (4 Naproxen, An) 11. In an analogous manner, **3** (0.089 g, 0.054 mmol) yielded 0.12 g (91%) of compound **11** as a white foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.50 (s, 1H), 8.31 (d, 2H, J = 8.7 Hz), 8.02 (d, 2H, J = 8.1 Hz), 7.70−7.37 (m, 20H), 7.14−7.06 (m, 8H), 6.16 (d, 1H, J = 12.3 Hz), 6.12 (d, 1H, J = 12.3 Hz), 5.14 (s, 1H), 5.11 (s, 1H), 5.02 (s, 1H), 4.74−4.45 (m, 11H), 3.99−3.85 (m, 16H), 2.25−2.17 (m), 1.77−1.10 (m), 0.96−0.60 (angular Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.2, 174.0, 173.61, 173.58, 169.8, 167.2, 157.64, 157.60, 135.03, 134.97, 134.9, 133.7, 131.33, 131.0, 129.3, 129.2, 129.1, 128.9, 127.2, 127.1, 126.6, 126.30, 126.25, 126.1, 126.04, 125.05, 123.9, 119.0, 118.9, 105.59, 105.54, 105.49, 75.6, 74.5, 73.9, 61.2, 59.2, 58.6, 55.2, 49.2, 47.6, 47.1, 45.04, 45.01, 44.9, 41.7, 35.5, 34.8, 34.6, 34.2, 34.00, 33.95, 32.4, 32.0, 31.8, 31.4, 31.2, 30.8, 27.2, 26.8, 26.2, 25.7, 25.6, 23.3, 22.9, 22.4, 18.8, 18.6, 17.4, 12.3. IR (thin film, cm^{-1}): 2944, 2869, 1740, 1606, 1452, 1390, 1266, 1217, 1174, 755. LRMS-ESI: *m/z* Calcd for $C_{151}H_{182}O_{26} + Na^+$: 2434.3; $C_{151}H_{182}O_{26} + K^+$: 2450.3. Obsd: 2437, 2453. Anal. Calcd for $C_{151}H_{182}O_{26}$: C 75.16, H 7.60. Found: C 75.11, H, 7.53. $[\alpha]^{25}_D$: +97.1 (1.36, $CHCl_3$).

Tetramer (9Cl, Acid) 5. From **4** (0.22 g, 0.093 mmol), 0.19 g (92%) of the title compound was obtained as a white foamy solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.21 (s, 3H), 5.09 (s, 1H), 5.04 (s, 3H), 4.90 (s, 1H), 4.67 (m, 3H), 4.55 (m, 1H), 4.14−4.04 (m, 18H), 2.33−1.10 (m), 0.95−0.73 (angular Me). ^{13} C NMR (75 MHz, $CDCl_3$) δ: 173.4, 173.2, 173.0, 166.8, 166.53, 166.49, 166.32, 166.27, 166.22, 75.8, 75.2, 74.0, 73.1, 73.0, 70.5, 47.6, 47.4, 45.2, 45.13, 45.05, 43.3, 42.8, 41.1, 40.9, 40.5, 37.8, 34.5, 34.4, 34.3, 34.2, 31.6, 31.3, 31.23, 31.15, 30.7, 30.60, 30.5, 28.5, 27.1, 27.0, 26.4, 25.2, 22.84, 22.82, 22.5, 22.24, 17.5, 17.44, 17.41, 17.3, 12.2, 12.1, 12.04. IR (thin film, cm^{-1}): 2949, 2870, 1731, 1290, 1180, 1006. LRMS-ESI: *m/z* Calcd for $C_{114}H_{163}Cl_9O_{26} + Na^+$: 2285.9. Obsd: 2287. Anal. Calcd for $C_{114}H_{163}Cl_9O_{26}$: C 60.36, H 7.24. Found: C 60.12, H 7.20. $[\alpha]^{25}_D$: +78.7 (1.27, $CHCl_3$).

Tetramer (9Cl, An) 6. From **5** (0.147 g, 0.065 mmol) was obtained 0.12 g (70%) of the title compound. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.52 (s, 1H), 8.32 (d, 2H, J = 8.7 Hz), 8.05 (d, 2H, J = 8.4 Hz), 7.60−7.48 (m, 4H), 6.17 (d, 1H, J = 12.3 Hz), 6.13 (d, 1H, J = 12.3 Hz), 5.19 (s, 3H), 5.04−5.01 (4H), 4.89 (s, 1H), 4.67 (m, 3H), 4.54 (m, 1H), 4.10−4.03 (18H), 2.30−1.32 (m), 1.14−0.59 (angular Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.07, 173.36, 173.25, 173.06, 166.77, 166.55, 166.54, 166.50, 166.48, 166.22, 131.32, 130.96, 129.08, 126.61, 126.23, 125.09, 123.85, 75.82, 75.17, 74.02, 73.02, 70.49, 58.67, 47.62, 47.43, 47.27, 45.17, 45.14, 45.11, 44.99, 44.98, 43.30, 42.83, 42.76, 41.16, 40.87, 40.54, 37.83, 37.67, 34.97, 34.50 34.49, 34.42, 34.35, 34.30, 34.23, 31.53, 31.37, 31.16, 30.85, 30.66, 30.65, 30.61, 30.45, 28.82, 28.46, 27.1, 27.07, 26.99, 26.41, 25.40, 25.23, 25.21, 25.16, 22.88, 22.82, 22.79, 22.5, 22.3, 17.5, 17.4, 17.34, 17.30, 12.1, 12.0. IR (thin film, cm^{-1}): 2950, 2870, 1754, 1731, 1290, 1181, 1006, 967, 736. LRMS-ESI: *m/z* Calcd for $C_{129}H_{173}Cl_9O_{26} + Na^+$: 2475.9; $C_{151}H_{182}O_{26} + K^+$: 2491.9. Obsd: 2476.5, 2492.5. Anal. Calcd for $C_{129}H_{173}Cl_9O_{26}$: C 63.01, H 7.09. Found: C 63.18, H 7.23. $[\alpha]^{25}_D$: +77.1 (1.09, $CHCl_3$).

Tetramer (9 Naproxen, Bn) 12. The procedure for the synthesis of **10** was followed. From **4** (0.03 g, 0.013 mmol) was obtained 0.043 g (84%) of the title compound as a white foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.67−7.61 (m, 27H), 7.38−7.32 (m, 14H), 7.13−7.03 (m, 18H), 5.15 (s, 3H), 5.07 (s, 3H), 4.99 (s, 3H), 4.91 (s, 1H), 4.70−4.39 (m, 22H), 3.95−3.84 (m, 36H), 2.33−1.79 (m,), 1.6−1.56 (m), 1.44−1.02 (m), 0.90−0.68 (angular Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 174.0, 173.79, 173.76, 173.66, 173.46, 173.35, 173.2, 167.2, 167.1, 167.0, 157.6, 136.0, 135.0, 134.94, 134.92, 134.89, 133.7, 129.2, 128.8, 128.5, 128.21, 128.16, 127.17, 127.1, 126.2, 126.1, 118.9, 105.5, 75.2, 72.1, 70.4, 66.1, 61.2, 61.0, 55.2, 47.9, 47.7, 47.5, 45.3, 45.1, 45.0, 43.4, 41.0, 40.6, 37.7, 34.69, 34.66, 34.5, 34.40, 34.35, 34.21, 34.18, 31.8, 31.6, 31.4, 31.2, 31.1, 30.7, 30.6, 30.4, 29.9, 29.6, 29.0, 27.1, 26.5, 25.6, 22.7, 22.4, 18.70, 18.64, 18.57, 17.42, 17.35, 12.2. IR (thin film, cm^{-1}): 2947, 2871, 1741, 1606, 1391, 1173.5, 1149, 1030, 756. MALDI-TOF MS: *m/z* Calcd for $C_{247}H_{286}O_{53} + Na^+$: 4123. Obsd: 4122.98. Anal. Calcd for $C_{247}H_{286}O_{53}$: C 72.31, H 7.03. Found: C 72.63, H 7.37. $[\alpha]^{25}_D$: +98.3 (1.21, $CHCl_3$).

Tetramer (9 Naproxen, An) 13. In an analogous manner, **6** (0.042 g, 0.018 mmol) yielded 0.056 g (80%) of the title compound as a white foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 8.48 (s, 1H), 8.30 (d, 2H, J = 8.4 Hz), 8.01 (d, 2H, J = 8.4 Hz), 7.67−7.34 (40 H), 7.13−7.04 (m, 18 H), 6.14 (d, 1H, J = 12.6 Hz), 6.10 (d, 1H, J = 12.6 Hz), 5.15 (m, 3H), 4.99 (m, 4H), 4.89 (s, 1H), 4.68−4.40 (m, 22H), 3.96−3.83 (m, 36 H), 1.92−1.02 (m), 0.89−0.56 (angular Me). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 173.97, 173.76, 173.71, 173.44, 173.30, 173.21, 167.21, 167.18, 167.10, 166.93, 157.59, 157.57, 135.0, 134.92, 134.87, 133.65, 131.30, 130.94, 129.23, 129.20, 129.05, 128.82, 128.78, 127.16, 127.07, 126.58, 126.20, 126.12, 126.05, 125.07, 123.87, 118.88, 105.51, 77.20, 75.19, 74.01, 72.10, 70.37, 61.16, 61.13, 60.99, 58.61, 55.19, 47.88, 47.62, 47.46, 45.24, 45.20, 44.96, 43.33, 40.63, 37.64, 34.59, 34.40, 34.31, 34.20, 31.50, 31.14, 30.43, 28.95, 27.04, 26.53, 25.58, 22.57, 22.40, 18.72, 18.69, 18.62, 18.57, 17.32, 12.19, 12.11. IR (thin film, cm^{-1}): 2946, 1740, 1606, 1390, 1173, 1148, 754. MALDI-TOF MS: Calcd for $C_{255}H_{290}O_{53} + Na^+$: 4223. Obsd: 4221.9. Anal. Calcd for $C_{255}H_{290}O_{53}$: C 72.87, H 6.95. Found: C 72.58, H 6.86. $[\alpha]^{25}_D$: +98.2 (1.13, $CHCl_3$).

Heptamer (12 Cl, Acid) 8. From **7** (0.075 g, 0.02 mmol) was obtained 0.06 g (80%) of compound **8** as a white foam. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 5.22 (s, 4H), 5.08−5.04 (m, 7H), 4.67 (m, 7H), 4.11−4.03 (m, 24H) 2.28−1.01 (m), 0.95−0.72 (angular Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 177.02, 173.41, 173.38, 173.17, 166.80, 166.61, 166.57, 166.53, 166.49, 166.34, 166.31, 166.26, 166.25, 77.20, 75.85, 75.75, 75.68, 73.99, 73.94, 73.12, 73.07, 49.56, 48.04, 47.80, 47.63, 47.55, 47.46, 47.44, 45.23, 45.19, 45.14, 45.11, 42.86, 41.79, 41.18, 41.17, 41.14, 40.59, 37.93, 35.67, 35.05, 34.70, 34.60, 34.45, 34.37, 34.27, 34.04, 34.03, 34.0, 32.33, 32.05, 31.71, 31.49, 31.19, 30.87, 30.74, 30.61, 28.50, 27.37, 27.12, 26.86, 26.71, 26.43, 25.91, 25.59, 25.19, 23.47, 23.05, 22.88, 22.29, 22.27, 17.53, 17.48, 12.53, 12.43, 12.39, 12.16, 12.07. IR (thin film, cm^{-1}): 2949, 2870, 1734, 1290, 1179, 1006, 737. MALDI-TOF MS: *m/z* Calcd for $C_{192}H_{280}Cl_{12}O_{38} + K^+$: 3660.8. Obsd: 3661.4. Anal. Calcd for $C_{192}H_{280}Cl_{12}O_{38}$: C 63.67, H 7.79. Found: C 63.42, H 7.93. $[\alpha]^{25}_D$: +84.8 (0.92, $CHCl_3$).

Heptamer (12Cl, An) 9. From **8** (0.051 g, 0.014 mmol) was obtained 0.033 g (62%) of compound **9** as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (s, 1H), 8.33 (d, 2H, J = 8.7 Hz), 8.04 (d, 2H, J = 8.7 Hz), 7.60−7.49 (m, 4H), 6.18 (d 1H, J = 12.6 Hz), 6.14 (d, 1H, J = 12.6 Hz), 5.21−5.19 (m, 4H), 5.08−5.01 (m, 7H), 4.67, (m, 7H), 4.11−4.03, (m, 24H), 2.28−1.00 (m), 0.95−0.60 (angular Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.19, 173.40, 173.17, 173.08, 166.79, 166.53, 166.49, 166.45, 166.24, 131.38, 131.02, 129.10, 128.86, 126.59, 126.35, 125.09, 123.92, 77.20, 75.84, 75.77, 75.68, 73.98, 73.06, 58.69, 49.53, 49.48, 48.06, 47.87, 47.70, 47.55, 47.47, 45.19, 45.14, 45.07, 45.03, 42.86, 41.79, 41.15, 40.59, 37.94, 35.65, 35.03, 34.83, 34.69, 34.62, 34.45, 34.37, 34.27, 34.03, 32.34, 32.04, 31.76, 31.50, 31.27, 31.19, 30.96, 30.86, 30.70, 29.65, 28.50, 27.46, 27.26, 27.13, 26.87, 26.71, 26.43, 25.89, 25.59, 25.18, 23.51, 23.41, 23.07, 22.88, 22.65, 22.27, 17.54, 17.48, 17.42, 12.44, 12.26, 12.17, 12.14, 12.08. IR (thin film, cm^{-1}): 3024, 2949, 2870, 1730, 1379, 13556, 1184, 1007, 756. Anal. Calcd for $C_{207}H_{290}Cl_{12}O_{38}$: C 65.22, H 7.67. Found: C 65.24, H 7.83. $[\alpha]^{25}_D$: +85.3 (1.16, $CHCl_3$).

Heptamer (12 Naproxen, Bn) 14: To a solution of **7** (0.050 g, 0.013 mmol) in DMSO (0.5 mL), potassium (*S*)-2-(6-methoxy-2-naphthyl)propanoate (0.06 g, 0.22 mmol) was added and the reaction mixture was stirred at 45 °C for 5 h. The reaction mixture was poured into water (15 mL) and extracted with EtOAc (20 mL). The organic layer was washed with water (10 mL) and dried over anhyd Na_2SO_4. After removing volatiles, the crude product was chromatographed on silica gel using 8% EtOAc/32% $CHCl_3$/60% toluene to yield 0.05 g (62%) of compound **14** as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.66−7.61 (m, 36H), 7.39−7.30 (m, 17H), 7.12−7.04 (m, 24H), 5.18−5.16 (m, 4H), 5.10−5.06 (m, 5H), 5.0 (s, 4H), 4.69−4.40 (m, 31H), 3.98−3.85 (m, 48H), 1.93−1.26 (m), 0.88−0.68 (angular Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.0, 173.79, 173.76, 173.75, 173.4, 173.2, 167.20, 167.17, 167.0, 157.7, 136.10, 135.06, 135.0, 133.7, 129.28, 129.26, 128.9, 128.54, 128.53, 128.20, 128.17, 127.2, 127.1, 126.3, 126.2, 126.10, 126.07, 118.95, 118.93, 118.91, 105.59, 105.56, 75.7, 75.2, 73.9, 72.2, 66.1, 61.2, 61.13, 61.06, 55.28, 55.25, 49.4, 47.90, 47.79, 45.36, 45.30, 45.14, 45.13, 45.02, 43.43, 41.84, 40.71, 37.76, 35.74, 34.95, 34.73, 34.67, 34.46, 34.27, 34.06, 32.42, 31.77, 31.19, 30.92, 30.62, 29.68, 28.99, 27.14, 26.93, 26.76, 26.56, 25.94, 25.62, 23.52, 23.10, 22.71, 22.48, 18.75, 18.66, 18.62, 17.59, 17.51, 17.41, 17.33, 12.55, 12.47, 12.40, 12.33, 12.23. IR (thin film, cm^{-1}): 2941, 2872, 1741, 1606, 1149, 1029, 754. MALDI-TOF MS: *m*/*z* Calcd for $C_{367}H_{442}O_{74}$ + K^+: 6076.5. Obsd: 6076.3. Anal. Calcd for $C_{367}H_{442}O_{74}$: C 73.01, H 7.38. Found: C 73.04, H 7.40. $[\alpha]^{25}_D$: +93.5 (0.8, $CHCl_3$).

Heptamer (12 Naproxen, An) 15. In an analogous manner **9** (0.022 g, 0.005 mmol) yielded 0.021 g (60%) of the title compound as a white foam. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (s, 1H), 8.32 (d, 2H, J = 8.8 Hz), 8.01 (d, 2H, J = 8.6 Hz), 7.66−7.46 (40H), 7.39−7.37 (m, 12H), 7.12−7.04 (m, 24 H), 6.16 (d, 1H, J = 12.4 Hz), 6.12 (d, 1H, J = 12.4 Hz), 5.18−5.15 (m, 4H), 5.07−5.0 (m, 7 H), 4.69−4.33 (m, 31H), 3.98−3.84 (m, 48 H), 2.35−0.98 (m), 0.86−0.58 (angular Me). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 174.2, 174.0, 173.79, 173.75, 173.43, 173.36, 173.2, 173.1, 167.20, 167.17, 167.12, 167.08, 167.0, 157.7, 135.1, 135.0, 134.94, 134.93, 133.7, 131.4, 131.0, 129.28, 129.26, 129.1, 128.88, 128.86, 127.2, 127.1, 126.6, 126.4, 126.3, 126.2, 126.10, 126.07, 125.1, 123.9, 118.93, 118.91, 105.6, 77.2, 75.63, 75.57, 75.2, 73.9, 72.1, 61.2, 61.1, 61.0, 58.7, 55.3, 55.2, 49.4, 47.9, 47.8, 47.7, 45.34, 45.30, 45.1, 45.0, 43.4, 41.9, 40.7, 37.8, 35.7, 35.1, 34.8, 34.7, 34.5, 34.3, 34.1, 34.03, 32.4, 31.9, 31.76, 31.7, 31.3, 31.2, 30.6, 29.7, 29.0, 27.5, 27.1, 26.9, 26.7, 26.6, 25.9, 25.6, 23.9, 23.4, 23.10, 23.09, 22.70, 22.66, 22.5, 18.74, 18.65, 18.62, 17.6, 17.5, 17.4, 17.3, 12.5, 12.33, 12.30, 12.2. IR (thin film, cm^{-1}): 2945, 2871, 1741, 1606, 1174, 1149, 755. MALDI-TOF MS: *m*/*z* Calcd for $C_{375}H_{446}O_{74}$ + Na^+: 6160.5. Obsd: 6166.2. Anal. Calcd for $C_{375}H_{446}O_{74}$: C 73.39, H 7.32. Found: C 73.24, H 7.44. $[\alpha]^{25}_D$: +88 (0.83, $CHCl_3$).

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Supporting Information Available: Synthetic details for compounds **1**, **4**, **7**, and **16**−**19**. This material is available free of charge via Internet at http://pubs.acs.org.

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(14) This was confirmed by recording the lifetime of 14 only in $CHCl_3$ wherein a single-exponential decay was observed with a lifetime of ∼2.8 ns. Also it is to be noted that we do not see any visible effect on the steady-state fluorescence intensity. This is because the quenching is negligible and the average lifetime is still >7 ns.

(15) In the case of energy transfer, the acceptor decay kinetics (upon excitation at donor absorption wavelength) exhibits the characteristics

of an excited-state reaction with a rise time in the decay and a negative preexponential factor in the multiexponential analysis. The rise is on a time scale comparable to the quenched donor decay.

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(21) The quantum yields were measured using naproxen as standard in acetonitrile ($\phi = 0.47$ under deaerated conditions).

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