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Synthesis and characterization of anthracene-clustering dendrimers: observation of fluorescence resonance energy transfer in the multichromophoric system

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Abstract—A series of anthracene-clustering dendrimers bearing various aliphatic substituents at the terminal positions were synthesized using a direct coupling strategy. A remarkable effect of the side chains was imparted to chemical properties of the dendrimers such as drastically increased solubility. Although the multibranched anthracene arrays in the dendritic architectures exhibited no cooperativity in terms of the absorption feature and behaved as single chromophoric systems, investigations focusing on fluorescence properties revealed that a type of cooperativity was present as expressed in the reduced quantum yields of fluorescence. An alternative approach utilizing time-resolved fluorescence decay measurements clearly demonstrated that the most reasonable mechanism of the cooperative action should involve two discernible channels of intramolecular fluorescence resonance energy transfer (FRET) occurring from one chromophore to the others within and across junctions of the branching units.

1. Introduction

Nature has developed the most sophisticated solar energy storage systems in photosynthetic organisms, which contain large numbers of porphyrins held in particular three-dimensional arrays.[1,2] These complex assemblies capture photons at the light-harvesting antenna pigments and transport them into reaction centers for initiation of the photosynthetic reaction cascades. Based on this fact, a considerable effort has been devoted to mimic the natural light-harvesting system in order to create artificial photosynthetic models.[3–8] Since it has been shown that aromatic dendrimers exhibited the collective phenomena from light-harvesting peripheral units into molecular centers of their globular structures, there is much current interest in the study directed towards designing and synthesizing effective light-harvesting dendrimers capable of converting solar energy into useable photonic power.[9–12] Accordingly, ensuing search for effective light-collecting antennae may offer versatile solutions to produce more potential photonic system since the light-harvesting step is the first critical event in the natural photosynthetic processes.[13] In this regard, anthracene is envisaged as a potentially functionalized candidate for use in the light-harvesting dendrimers due to its high absorption coefficient as well as its high fluorescence quantum yield. Recently, we have reported that a primitive type of anthracene-clustering dendrimer **1** (R = H in Fig. 1), which represents an aggregated form of anthracene chromophores immobilized in a dendritic framework, exhibited an energy transport property within the supramolecular framework.[14] Although this property has been shown to be of direct relevance to practical fabrication of fluorescence resonance dendritic antennae, the resulting dendrimer exhibited poor solubility in common organic solvents and certain structural modification should therefore be given to establish more practical molecular systems. As part of our continuing efforts in synthesis and investigation of the designed molecules, we report here a convenient and general protocol for the preparation of anthracene-clustering dendrimers bearing various aliphatic side chains at their peripheral positions. During the course of studying effects of the substituents on physical and chemical properties of the dendrimers, we found that the presence of aliphatic auxiliaries markedly affected the solubility in a wide range of organic solvents without

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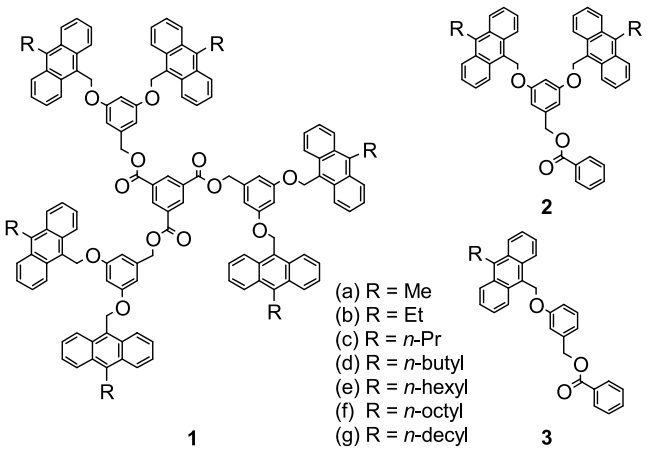
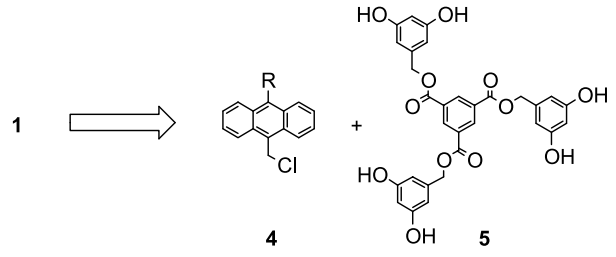


Figure 1. Structures of dendrimer **1** and its structurally simplified analogues **2** and **3**.

altering their own photophysical properties. One of the most remarkable findings in this context is that the aggregated chromophoric groups exhibited pronounced cooperative actions of energy transfer from one dendritic branch to the others as expressed in reduced quantum yields as well as faster transient decay profiles of their fluorescence signals relative to monomeric anthracene analogues.

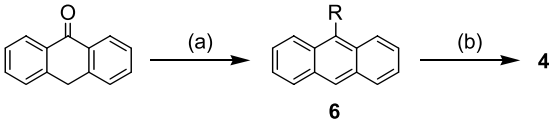
2. Results and discussion

Our previous report has shown that a successive convergent strategy can be used to construct a multichromophoric array of anthracenes in the dendritic framework. In this manner, synthetic route was established in several steps involving ether bond formation and subsequent esterification to connect all structural components of the dendritic architecture.[14] Despite the noteworthy synthetic achievement with high yields (75–98%) in all steps, the proposed synthetic strategy employed a multistep sequence of bond-forming events resulting in low yield recovery of the final product. To gain convenient access to the functionalized dendrimers, we decided to pursue an alternative approach of in situ coupling between anthracene units **4** and a dendritic backbone **5** as a useful and practical protocol (Scheme 1).

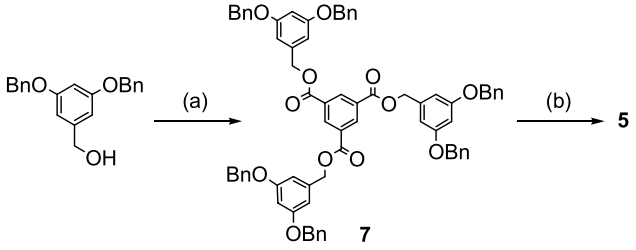


Scheme 1. Retrosynthetic analysis of **1**.

All 10-alkyl-substituted 9-anthryl chlorides **4** were prepared from anthrone according to an established literature procedure used for preparation of 9-chloromethyl-10-methylanthracene **4a**, which involved nucleophilic addition of the corresponding Grignard reagents to the carbonyl group of anthrone, aromatization after acidic dehydration of the resulting benzhydrol intermediate giving rise to a series of 9-alkylanthracenes **6**, and subsequent chloromethylation to form the corresponding **4** (Scheme 2).[15,16] Alternatively, one could synthesize the dendritic backbone **5** via catalytic hydrogenolysis of the Fréchet type dendrimer **7** in methanolic solvent, which could be prepared by esterification of commercially available 3,5-bis(benzyloxy)benzyl alcohol with trimesoyl chloride under the basic condition (Scheme 3).[17] All these structural components of the dendritic architectures were purified by recrystallization of the crude materials prior to their reactions.

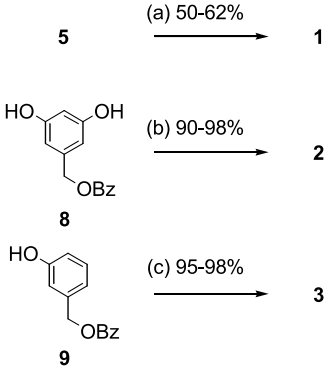


Scheme 2. Synthesis of **4**. Conditions: (a) RMgX (X=Br or I)/ether, benzene (1:1), reflux; (b) $(CH_2O)_n$/HClaq, AcOH, rt.



Scheme 3. Synthesis of **5**. Conditions: (a) Trimesoyl chloride, Et_3N/benzene, rt; (b) cat. Pd–C, $H_2/CHCl_3$, CH_3OH (1:1).

With two components in hand, a series of dendrimers **1a–g** were synthesized by a straightforward way carrying out the reaction of **5** with an excess of the corresponding anthryl chlorides **4**. As a result, nucleophilic attacks of phenolate ions onto **4** preferentially occurred at the multiple reaction sites of **5**, giving rise to the variously substituted dendrimers **1a–g** in predominant yields (50–62%) for all cases (Scheme 4). These dendrimers were purified by recrystallization from chloroform–methanol solutions and were fully characterized by elemental analyses and a range of



Scheme 4. Syntheses of **1**, **2**, and **3**. Conditions: (a) **4** (8.0 equiv), K_2CO_3 (8.0 equiv), 18-Crown-6 (3.0 equiv)/DMF, 55 °C; (b) **4** (2.5 equiv), K_2CO_3 (2.5 equiv), 18-Crown-6 (1.0 equiv)/DMF, 55 °C; (c) **4** (1.5 equiv), K_2CO_3 (1.5 equiv), 18-Crown-6 (0.15 equiv)/DMF, 55 °C.

Table 1. Size exclusion chromatography (SEC) results and side chain effects on solubilities of dendrimers **1**

Entry	Formula	M_w/M_n[a]	Nominal M_w	M_w[a]	[**1**] (mmol/mL)[b]
1a	$C_{126}H_{96}O_{12}$	1.006	1801	1385	0.6
1b	$C_{132}H_{108}O_{12}$	1.003	1885	1497	3.7
1c	$C_{138}H_{120}O_{12}$	1.003	1969	1666	5.9
1d	$C_{144}H_{132}O_{12}$	1.002	2053	1799	6.6
1e	$C_{156}H_{156}O_{12}$	1.004	2221	2074	10.0
1f	$C_{168}H_{180}O_{12}$	1.003	2389	2307	37.7
1g	$C_{180}H_{204}O_{12}$	1.003	2558	2567	44.5

[a] Calibrated with narrow-dispersity polystyrene standards.
[b] Maximum concentrations dissolved in chloroform at 20 °C.

spectroscopies. In terms of structural details, structural homogeneity of the products was well confirmed by observation of simplicity in the ^1H and ^{13}C NMR spectra due to their highly symmetric nature, wherein all the building components should be equivalent as previously demonstrated.[14] Consequently, this direct synthetic protocol provides an important strategic advantage over the previous methodology in accessing higher generation dendritic systems since this method has simplicity of synthesis allowing us to form highly ordered symmetric arrays of the molecular units rapidly. On the other hand, this synthetic strategy can be applied in the construction of structurally simpler analogous systems **2** and **3** that possess a small number of anthracenes, employing the corresponding phenolic backbones **8** and **9**, respectively, instead of **5**. These reactions worked well with less molar equivalents of **4** and gave rise to the mono- and bichromophoric products in excellent yields (90–98%) as confirmed by complete characterization data (Scheme 4).

Size effects of the external functional groups on the dendritic shell can be inferred from comparison of retention volumes on the size exclusion chromatography (SEC). This demonstrated each dendrimer gave a sharp and symmetrical peak in chloroform with a polydispersity index (PDI) $M_w/M_n < 1.01$ that should be in the range typically found for unified dendrimers (Table 1).[17] Figure 2 shows correlation diagrams for a series of polystyrene standards, indicating that retention volumes of the polystyrenes exhibited a linear dependence on logarithmic number of their averaged molecular weights following reverse order paralleling the molecular sizes. Such a trend was observed for the dendritic system (**1a**–**g**), giving the monomodal distribution, albeit

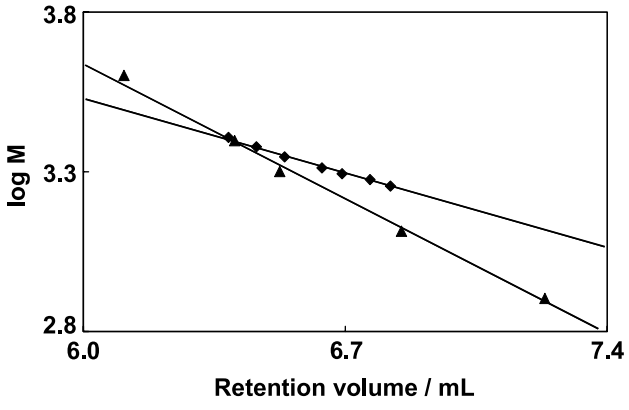


Figure 2. Semilogarithmic plot of average molecular weight versus SEC retention volumes for polystyrene standards (▲) and dendrimers (♦).

with a less steep downward slope as seen in Figure 2. It has been well recognized in this context that dendritic structures should be denser and more compact than linear polymers, giving underestimated values when determining the molecular weights by calibration with the linear polymers.[18] Thus, this rule also seems to be applicable to our macromolecular system functionalized with a range of alkyl groups at the surfaces of the commonly used dendritic motif. Table 1 summarizes the molecular weights of the dendrimers (M_w) determined by SEC calibrated with the polystyrene standards. As can be surveyed in Table 1, the estimated data for the longer chained homologues **1f**–**g** are close to the nominal molecular weights, whereas those for the smaller-sized dendrimers should be extremely deviated from the theoretical values with up to 23% weight loss. These observations indicate that the longer chained molecules were behaving as flexible spheres like linear polymers, which could change substantially in size or shape through the efficient interaction with solvent molecules. This correlation may exist only if relative contribution of the longer alkyl moieties to the macromolecular properties should be much larger than that of the rigid dendritic shell.

In this regard, degree of solvation is suggested to be more important in interpreting concomitant influence of the external alkyl groups on the lipophilic nature of dendrimers. It can be obviously seen that increasing chain length of the alkyl groups markedly enhanced the relative solubility of dendrimers in common organic solvents such as chloroform, THF, and toluene. Table 1 also includes maximum solubilities of the dendrimers, which were determined by dissolving the samples in chloroform and measuring their UV absorption maxima around 380 nm. From these data, significant difference was observed in the solubility among the dendrimer derivatives, where the critical concentrations ranged from 0.6 to 44.5 mmol/L. As a consequence, the structural modification significantly improved these values showing the maximum difference to be as large as nearly 74-fold. These results can be explained on the basis of a change in hydrodynamic radius of the dendrimers in the organic solvents.[18] In general, flexible dendrimers have mobile structures displaying large changes in hydrodynamic radii in various solvent systems, whereas rigid dendrimers are intuitively much more shape persistent and thus show little change in hydrodynamic radii as a function of solvent.[19] The experimental results of our preliminary studies are in good agreement with this theoretical proposal, which clearly demonstrates the local structural alteration at the external surfaces of dendrimers gives the larger

hydrodynamic radii and thus renders the resulting molecules soluble in a wide range of solvents.

As part of our continuing interest in the fundamental aspects of the multichromophoric dendrimer system, we focused attention on some of their photophysical properties in order to gain insight into the electronic details of polyaromatic aggregates. Figure 3 shows representative absorption and fluorescence spectra for constituent members of ethyl side chain analogues **1b–3b** composed of one to six anthracene groups, where all signals were normalized with respect to the corresponding absorption maxima and optical densities of the chromophoric units, respectively. As shown in Figure 3, three discrete spectra of **1b–3b** exhibited a closely overlapping feature around three typical absorption maxima at 359, 378, and 399 nm attributed to π,π^* transitions of the anthracene excitation, while the corresponding molar absorption coefficients were found to be approximately proportional to the number of the anthracene units. These results suggest that the anthracene groups of **1b** and **2b** behave like monomeric species and thus the contribution of each chromophoric unit to the absorption character is virtually the same in the ground-state, providing little or no intramolecular electronic interaction. However, pronounced differences were noticed in the fluorescence emission spectra of these systems. Figure 3 also illustrates the steady-state fluorescence spectra of **1b–3b** exhibiting the emission maxima at 407, 430, and 455 nm attributed to emission from the anthracene groups. It should be noted that three individual molecules showed markedly different intensity levels, whose quantum efficiencies (Φ_F) decreased with an increase in the number of chromophores. This can be rationalized by assuming that the relative contribution of each fluorescent unit in the multichromophoric systems such as **1** and **2** to the emission behavior clearly changed as expressed in the reduced quantum yields of fluorescence. Table 2 summarizes estimated values of fluorescence quantum yields for all dendrimers and their related analogues. In agreement with the above result, the other members also showed similar trends of their fluorescence quantum efficiencies following the order **3**>**2**>**1** throughout the whole given series of molecules. Additionally, the bi- and multichromophoric systems **1–2** did not produce photoproducts in any significant quantities during all measurements, and neither showed any sign of aggregate and excimer formation when all these solutions were dilute enough that intermolecular interactions should be negligible. While these processes causing a serious decrease in fluorescence quantum yields can be discounted, intramolecular energy transfer mechanism from one branch to the others provides a plausible rationale for the systematic decrease of quantum yields. Besides, it was found that a specific geometrical bias of the methyl group at the C10-position on the anthracene rings was also attributed to significant decrease in the quantum yields, where the methyl-substituted series **1a–3a** exhibited the markedly lowered quantum efficiencies of fluorescence in comparison to the other series. The interpretation of this effect was that rotational motion of the methyl group should lead to effective free rotor radiationless deactivation over the others as a result of less steric constraints.

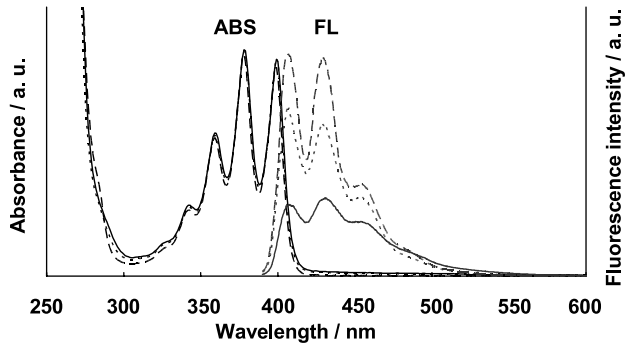


Figure 3. Absorption (ABS) and steady-state fluorescence spectra (FL) of a series of **1b** (solid line), **2b** (dotted line), and **3b** (dashed line) in chloroform solutions. The absorption spectra are normalized at the anthracene maxima (378 nm). The fluorescence spectra were obtained by excitation at 387 nm and are normalized to the same optical density at the excitation wavelength. All measurements were conducted in sufficiently low concentrations (10^{-8}–10^{-6} mol/mL) of the analytes to exclude the possibilities of intermolecular interactions.

Table 2. Fluorescence quantum yields (Φ_F) of **1–3**[a]

Entry	1	2	3
a	0.09	0.26	0.36
b	0.17	0.32	0.41
c	0.20	0.33	0.42
d	0.20	0.34	0.43
e	0.20	0.36	0.44
f	0.20	0.38	0.44
g	0.19	0.38	0.44

[a] Determined by referring to the value of anthracene as a standard.[20]

In our efforts to address a question as to how the multichromophoric molecular frameworks affect the fluorescence efficiencies, we explored an alternative approach utilizing time-resolved fluorescence decay measurements, which allow us to gain some further insights into photodynamic characters during the fluorescence emission processes. The measurements were performed on the ethyl-substituted anthracene series **1b–3b**, where the samples were dissolved in THF solutions and the fluorescence decay traces were recorded at excitation wavelengths of 355 nm as depicted in Figure 4. The decay traces for the monochromophoric system **3b** followed a simple

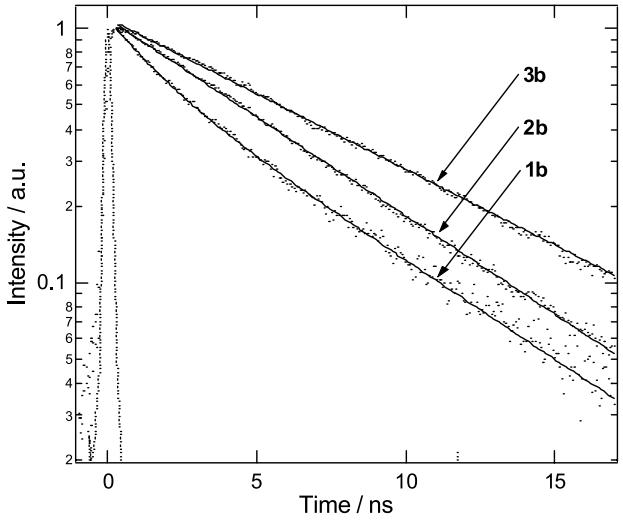


Figure 4. Fluorescence decay profiles of **1b–3b** in THF solutions at the excitation wavelength of 355 nm.

monoexponential decrease with a lifetime of 7.3 ns, which is close to the values reported for 9,10-disubstituted anthracenes.[21] Under identical conditions, the bichromophoric system **2b** behaved similarly attending a monoexponential mode of action but with a significantly short lifetime decay of 5.6 ns. The observation of reduced lifetime for **2b** suggests strongly that a type of cooperativity, which may be interpreted in terms of intramolecular energy migration from one chromophore to another, is present in this molecular system. As a matter of fact, the feasibility of intramolecular energy transfer step depends to a large extent upon accessible orientation of neighboring nonbonded chromophores in the multichromophoric systems. The structural description of **2b** guarantees that two anthracenes are immobilized in close proximity to interact as confirmed previously by X-ray structural analysis and molecular modeling study.[14] Therefore, it appears that the origin of energy delocalization responsible for the fast fluorescence decay can be a result of structurally unique disposal of the chromophoric groups. In contrast to the relative behavior of these two examples, the dendritic system **1b** showed a remarkable difference in the decay profile, which follows a double exponential curve with a much faster decay rate. The decay curve was well fitted with a double exponential function, which provides two product distributions classified into a longer-lived component (5.6 ns, 66%) and a short-lived component (1.6 ns, 34%). The decay time of the longer-lived component is in good agreement with that of **2b** and is therefore assigned to originate from the bichromophoric character of interactions between closely disposed chromophores within the branching units. From this, it can be deduced that the presence of the faster decay component should be explained on the basis of another radiationless deactivation channel emerging from chromophore-clustering domains in the three-dimensional molecular framework. As a consequence of these considerations, we can draw a speculative conclusion that the short-lived component is attributed to a fluorescence emission involving interactions from one bichromophoric unit to the other chromophores. On the other hand, strength of the Förster-type energy transfer interactions may depend largely on the amount of spectral overlap between absorption spectra of chromophoric acceptors and emission profiles of chromophoric donors.[22–25] In this context, all three series of compounds **1**–**3** showed a considerable degree of spectral overlap between the absorption and fluorescence spectra attributed to the anthracene groups, where the absorption tails extend over the region of the emission bands beyond 400 nm (Fig. 3). This spectroscopic feature may offer an opportunity for the fluorescence resonance energy transfer (FRET), which ultimately provides the energy transport character of the multichromophoric systems. We therefore conclude that the multichromophoric dendrimer systems offer a number of opportunities for the intramolecular FRET pathways available to the efficient energy transport of captured photons within the nanoscopic dimension of molecular architectures.

3. Conclusion

In conclusion, we have developed a new synthetic approach to the anthracene-clustering dendrimers employing a general and simple methodology. This synthetic procedure is beneficial and gives many practical and potential applications for the construction of a variety of higher generation dendrimer systems composed of anthracene residues as a functional repeat unit. Investigations of the physical and chemical properties of the dendrimer derivatives revealed that functionalization of the surface groups of the dendritic architectures should play critical roles in the solubility in common organic solvents. Furthermore, we have demonstrated that these dendrimers exhibited intriguing photophysical properties in terms of the intramolecular FRET between the peripheral chromophoric units. This photophysical outcome was noticed in the reduced quantum yields of fluorescence, the emission spectra, and the more complex time-dependent behavior due to the chromophore-clustering nature of the dendritic system. A detailed investigation of this property based on the time-resolved transient emission measurements revealed unambiguously that the dendrimer system offered two discrete channels for the FRET processes occurring from one chromophore to the others within and across the junctions of branching units. The results of our preliminary studies of the dendrimers indicate that this supramolecular system may act as a potential mediator for energy transport of absorbed photons and thus offer many advantages for applications in design and synthesis of artificial light-harvesting nanostructured materials.

4. Experimental

4.1. General

All solvents and reagents were of reagent grade quality from Wako Pure Chemicals used without further purification. A series of polystyrene standards (molecular weights = 800, 1300, 2000, 2500, and 4000) were purchased from Pressure Chemical Co. and used without further purification. The ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra operating at the frequencies of 300 and 75 MHz, respectively, were recorded on a JEOL JNM-AL300 spectrometer in chloroform-*d* ($CDCl_3$) or acetone-d_6 ($(CD_3)_2CO$). Chemical shifts are reported in parts per million (ppm) relative to TMS and the solvent used as internal standards, and the coupling constants are reported in Hertz (Hz). Fourier transform infrared (FT-IR) spectra were recorded on a JASCO FT/IR-410 spectrometer as KBr disks. Absorption spectra were recorded on a JASCO model V-570 UV-VIS-NIR spectrophotometer. Fluorescence spectra were measured on a Hitachi F-4500 spectrofluorometer. Melting points were determined on a Yanaco MP-S3 melting point apparatus. Fast atom bombardment (FAB) mass spectra were determined by a JASCO JMS-HX110A using a 3-nitrobenzyl alcohol matrix. Elemental analyses were obtained from Perkin-Elmer-240 instrument. Size exclusion chromatography (SEC) was performed on a system consisting of a JASCO model 880-PU pump at a flow rate of 0.5 mL/min and JASCO 875-UV absorbance detector (254 nm) equipped with a Shodex K-802 column, where chloroform was used as mobile phase. Time-resolved fluorescence decay measurements were performed on a system consisting of a Hamamatsu C5094 imaging spectrograph and a B. M. Industries 5022 D. PS. DP.10

passively/actively mode-locked Nd:YAG laser employing the third harmonic at 355 nm. The decays were fitted with the least-squares (LS) method to evaluate the fluorescence lifetimes. The quality of the fits has been judged from the estimated values and residuals. Samples of 9-chloromethyl-10-methylanthracene **4a**,[16] 9-chloromethyl-10-ethylanthracene **4b**,[26] 9-chloromethyl-10-butylanthracene **4d**,[27] and a series of 9-alkylanthracenes **6a–g**[15,28–31] were prepared by the sequence of procedures reported in the literature. Their physical properties and spectroscopic data were in full agreement with those reported earlier. The fluorescence quantum yields of **1–3** were measured in comparison to anthracene in ethanol solution ($\Phi_F=0.27$) as a standard.[20]

4.2. General procedure for the synthesis of 1

All dendrimers **1** were prepared as described in the following typical procedure. For example, synthesis of **1a** was exemplified as follows.

4.2.1. Tris[3,5-bis((10-methyl-9-anthracenediyl)-methoxy)benzyl] benzene-1,3,5-tricarboxylate 1a. A solution containing **4a** (0.33 g, 1.39 mmol), **5** (0.10 g, 0.17 mmol), potassium carbonate (0.19 g, 1.39 mmol), and 18-crown-6 (0.14 g, 0.52 mmol) in DMF (5 mL) was heated at 55 °C with stirring under argon atmosphere. After 4 h, the reaction mixture was then precipitated in ice-cold diluted HCl solution (50 mL). The precipitate was collected by filtration, intensively washed with water, and dried in a vacuum to afford a pale yellow solid. After complete vacuum drying, the solid sample was purified by recrystallization from chloroform–methanol, affording **1a** (0.16 g, 50%) as a pale yellow powdery material; mp 192–193 °C; UV ($CHCl_3$) 359 nm (ε 40,200), 378 nm (ε 64,500), 399 nm (ε 60,900); IR (KBr) 1593 cm^{-1} (C=C), 1732 cm^{-1} (C=O); MS (FAB+) *m/z* 1801 (s*M*+), 1802 (*MH*+); ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 18H, C*H*$_3$), 5.42 (s, 6H, C*H*$_2$), 5.83 (s, 12H, C*H*$_2$), 6.8–6.9 (m, 9H, Ar*H*), 7.4–7.5 (m, 24H, Ar*H*), 8.2–8.3 (m, 24H, Ar*H*), 9.02 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 14.4 (*C*H$_3$), 63.0 (*C*H$_2$), 67.4 (*C*H$_2$), 102.2 (*C*H), 107.6 (*C*H), 124.5 (*C*H), 124.9 (*C*H), 125.3 (*C*H), 126.0 (*C*H), 129.9 (*C*), 130.7 (*C*), 132.7 (*C*), 135.1 (*C*H), 138.0 (*C*), 160.7 (*C*), 164.8 (*C*). Anal. Calcd for $C_{126}H_{96}O_{12}$: C, 83.98; H, 5.37; N, 0.00. Found: C, 83.89; H, 5.60; N, 0.00.

4.2.2. Tris[3,5-bis((10-ethyl-9-anthracenediyl)methoxy)-benzyl] benzene-1,3,5-tricarboxylate 1b. This compound was obtained (0.19 g, 60%) as a pale yellow powdery material from chloroform–methanol solution; mp 191–192 °C; UV ($CHCl_3$) 359 nm (ε 42,100), 378 nm (ε 66,600), 399 nm (ε 63,800); IR (KBr) 1593 cm^{-1} (C=C), 1729 cm^{-1} (C=O); MS (FAB+) *m/z* 1885 (*M*+), 1886 (*MH*+); ^{1}H NMR ($CDCl_3$) δ 1.41 (t, *J*=7.3 Hz, 18H, CH_2CH_3), 3.59 (q, *J*=7.3 Hz, 12H, CH_2CH_3), 5.41 (s, 6H, C*H*$_2$), 5.84 (s, 12H, C*H*$_2$), 6.8–6.9 (m, 9H, Ar*H*), 7.4–7.5 (m, 24H, Ar*H*), 8.2–8.3 (m, 24H, Ar*H*), 9.00 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 15.5 (*C*H$_3$), 21.4 (*C*H$_2$), 63.0 (*C*H$_2$), 67.3 (*C*H$_2$), 102.0 (*C*H), 107.5 (*C*H), 124.7 (*C*H), 124.9 (*C*H), 125.1 (*C*H), 126.0 (*C*H), 128.9 (*C*), 130.9 (*C*), 131.3 (*C*), 135.1 (*C*H), 138.1 (*C*), 139.1 (*C*), 160.7 (*C*), 164.8 (*C*). Anal. Calcd for $C_{132}H_{108}O_{12}$: C, 84.05; H, 5.77; N, 0.00. Found: C, 84.11; H, 5.52; N, 0.05.

4.2.3. Tris[3,5-bis((10-propyl-9-anthracenediyl)methoxy)-benzyl] benzene-1,3,5-tricarboxylate 1c. This compound was obtained (0.20 g, 59%) as a pale yellow powdery material from chloroform–methanol solution; mp 189–190 °C; UV ($CHCl_3$) 360 nm (ε 40,900), 379 nm (ε 66,000), 400 nm (ε 63,300); IR (KBr) 1594 cm^{-1} (C=C), 1728 cm^{-1} (C=O); MS (FAB+) *m/z* 1969 (*M*+), 1970 (*MH*+); ^{1}H NMR ($CDCl_3$) δ 1.14 (t, *J*=7.3 Hz, 18H, $CH_2CH_2CH_3$), 1.82 (sext, *J*=7.9 Hz, 12H, $CH_2CH_2CH_3$), 3.55 (t, *J*=8.0 Hz, 12H, $CH_2CH_2CH_3$), 5.41 (s, 6H, C*H*$_2$), 5.86 (s, 12H, C*H*$_2$), 6.8–6.9 (m, 9H, Ar*H*), 7.4–7.5 (m, 24H, Ar*H*), 8.2–8.3 (m, 24H, Ar*H*), 9.01 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 14.7 (*C*H$_3$), 24.6 (*C*H$_2$), 30.4 (*C*H$_2$), 63.0 (*C*H$_2$), 67.3 (*C*H$_2$), 102.0 (*C*H), 107.5 (*C*H), 124.6 (*C*H), 124.98 (*C*H), 125.04 (C), 125.1 (*C*), 125.2 (*C*H), 126.0 (*C*H), 129.4 (*C*), 130.9 (*C*), 133.3 (*C*), 135.1 (*C*H), 137.8 (*C*), 138.1 (*C*), 160.7 (*C*), 164.8 (*C*). Anal. Calcd for $C_{138}H_{120}O_{12}$: C, 84.12; H, 6.14; N, 0.00. Found: C, 84.01; H, 6.13; N, 0.02.

4.2.4. Tris[3,5-bis((10-butyl-9-anthracenediyl)methoxy)-benzyl] benzene-1,3,5-tricarboxylate 1d. This compound was obtained (0.20 g, 56%) as a pale yellow powdery material from chloroform–methanol solution; mp 187–188 °C; UV ($CHCl_3$) 360 nm (ε 39,600), 379 nm (ε 64,300), 400 nm (ε 61,700); IR (KBr) 1594 cm^{-1} (C=C), 1728 cm^{-1} (C=O); MS (FAB+) *m/z* 2053 (*M*+), 2054 (*MH*+); ^{1}H NMR ($CDCl_3$) δ 1.00 (t, *J*=7.3 Hz, 18H, $(CH_2)_3CH_3$), 1.57 (sext, *J*=7.3 Hz, 12H, $(CH_2)_2CH_2CH_3$), 1.7–1.8 (m, 12H, $CH_2CH_2CH_2CH_3$), 3.55 (t, *J*=7.9 Hz, 12H, $CH_2(CH_2)_2CH_3$), 5.40 (s, 6H, C*H*$_2$), 5.83 (s, 12H, C*H*$_2$), 6.8–6.9 (s, 9H, Ar*H*), 7.4–7.5 (m, 24H, Ar*H*), 8.2–8.3 (m, 24H, Ar*H*), 9.00 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 14.0 (*C*H$_3$), 23.4 (*C*H$_2$), 28.1 (*C*H$_2$), 33.5 (*C*H$_2$), 63.0 (*C*H$_2$), 67.3 (*C*H$_2$), 102.0 (*C*H), 107.5 (*C*H), 124.6 (*C*H), 125.0 (*C*H), 125.1 (*C*H), 126.0 (*C*H), 129.3 (*C*), 130.9 (*C*), 131.3 (*C*), 135.1 (*C*H), 138.0 (*C*), 138.1 (*C*), 160.7 (*C*), 164.8 (*C*). Anal. Calcd for $C_{144}H_{132}O_{12}$: C, 84.18; H, 6.48; N, 0.00. Found: C, 84.27; H, 6.33; N, 0.09.

4.2.5. Tris[3,5-bis((10-hexyl-9-anthracenediyl)methoxy)-benzyl] benzene-1,3,5-tricarboxylate 1e. This compound was obtained (0.20 g, 54%) as a pale yellow powdery material from chloroform–methanol solution; mp 184–185 °C; UV ($CHCl_3$) 360 nm (ε 40,600), 379 nm (ε 65,900), 400 nm (ε 63,300); IR (KBr) 1594 cm^{-1} (C=C), 1730 cm^{-1} (C=O); MS (FAB+) *m/z* 2221 (*M*+), 2222 (*MH*+); ^{1}H NMR ($CDCl_3$) δ 0.91 (t, *J*=7.3 Hz, 18H, $(CH_2)_5CH_3$), 1.3–1.4 (m, 24H, $(CH_2)_3(CH_2)_2CH_3$), 1.5–1.6 (m, 12H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.7–1.8 (m, 12H, $CH_2CH_2(CH_2)_3CH_3$), 3.55 (t, *J*=7.9 Hz, 12H, $CH_2(CH_2)_4CH_3$), 5.42 (s, 6H, C*H*$_2$), 5.85 (s, 12H, C*H*$_2$), 6.8–6.9 (s, 9H, Ar*H*), 7.4–7.5 (m, 24H, Ar*H*), 8.2–8.3 (m, 24H, Ar*H*), 9.02 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (*C*H$_3$), 22.7 (*C*H$_2$), 28.5 (*C*H$_2$), 30.1 (*C*H$_2$), 31.4 (*C*H$_2$), 31.8 (*C*H$_2$), 63.1 (*C*H$_2$), 67.4 (*C*H$_2$), 102.1 (*C*H), 107.5 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.1 (*C*H), 126.0 (*C*H), 129.3 (*C*), 130.9 (*C*), 131.4 (*C*), 135.4 (*C*H), 135.1 (C), 138.1 (*C*), 160.7 (*C*), 164.8 (*C*). Anal. Calcd for $C_{156}H_{156}O_{12}$: C, 84.29; H, 7.07; N, 0.00. Found: C, 84.29; H, 7.00; N, 0.06.

4.2.6. Tris[3,5-bis((10-octyl-9-anthracenediyl)methoxy)-benzyl] benzene-1,3,5-tricarboxylate 1f. This compound was obtained (0.25 g, 61%) as a pale yellow powdery

material from chloroform–methanol solution; mp 181–182 °C; UV ($CHCl_3$) 360 nm (ε 40,800), 379 nm (ε 66,200), 400 nm (ε 63,600); IR (KBr) 1595 cm^{-1} (C=C), 1731 cm^{-1} (C=O); MS (FAB+) *m/z* 2390 (*M*+), 2391 (*MH*+); ^1H NMR ($CDCl_3$) δ 0.88 (t, $J=6.8$ Hz, 18H, $(CH_2)_7CH_3$), 1.2–1.4 (m, 48H, $(CH_2)_3(CH_2)_4CH_3$), 1.5–1.6 (m, 12H, $(CH_2)_2CH_2(CH_2)_4CH_3$), 1.7–1.8 (m, 12H, $CH_2CH_2(CH_2)_5CH_3$), 3.54 (t, $J=8.0$ Hz, 12H, $CH_2(CH_2)_6CH_3$), 5.41 (s, 6H, CH_2), 5.84 (s, 12H, CH_2), 6.8–6.9 (m, 9H, Ar*H*), 7.4–7.5 (m, 24H, Ar*H*), 8.2–8.3 (m, 24H, Ar*H*), 9.01 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 28.4 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 30.4 (CH_2), 31.4 (CH_2), 31.9 (CH_2), 63.0 (CH_2), 67.3 (CH_2), 102.1 (*C*H), 107.5 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.1 (*C*H), 126.0 (*C*H), 129.3 (*C*), 130.9 (*C*), 131.3 (*C*), 135.1 (*C*H), 138.0 (*C*), 138.1 (*C*), 160.7 (*C*), 164.8 (*C*). Anal. Calcd for $C_{168}H_{180}O_{12}$: C, 84.38; H, 7.59; N, 0.00. Found: C, 84.09; H, 7.56; N, 0.03.

4.2.7. Tris[3,5-bis((10-decyl-9-anthracenediyl)methoxy)-benzyl] benzene-1,3,5-tricarboxylate 1g. This compound was obtained (0.27 g, 62%) as a pale yellow powdery material from chloroform–methanol solution; mp 174–175 °C; UV ($CHCl_3$) 360 nm (ε 41,300), 379 nm (ε 66,400), 400 nm (ε 64,000); IR (KBr) 1594 cm^{-1} (C=C), 1730 cm^{-1} (C=O); MS (FAB+) *m/z* 2558 (*M*+), 2559 (*MH*+); ^1H NMR ($CDCl_3$) δ 0.87 (t, $J=6.8$ Hz, 18H, $(CH_2)_9CH_3$), 1.2–1.4 (m, 72H, $(CH_2)_3(CH_2)_6CH_3$), 1.5–1.6 (m, 12H, $(CH_2)_2CH_2(CH_2)_6CH_3$), 1.7–1.8 (m, 12H, $CH_2CH_2(CH_2)_7CH_3$), 3.54 (t, $J=7.9$ Hz, 12H, $CH_2(CH_2)_8CH_3$), 5.41 (s, 6H, CH_2), 5.85 (s, 12H, CH_2), 6.8–6.9 (m, 9H, Ar*H*), 7.4–7.5 (m, 24H, Ar*H*), 8.2–8.3 (m, 24H, Ar*H*), 9.01 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 28.4 (CH_2), 29.3 (CH_2), 29.6 (CH_2), 29.65 (CH_2), 29.70 (CH_2), 30.4 (CH_2), 31.4 (CH_2), 31.9 (CH_2), 63.0 (CH_2), 67.4 (CH_2), 102.0 (*C*H), 107.5 (*C*H), 124.6 (*C*H), 124.9 (*C*), 125.0 (*C*H), 125.1 (*C*H), 126.0 (*C*H), 129.3 (*C*), 130.9 (*C*), 131.3 (*C*), 135.1 (*C*H), 138.1 (*C*), 160.7 (*C*), 164.8 (*C*). Anal. Calcd for $C_{180}H_{204}O_{12}$: C, 84.47; H, 8.03; N, 0.00. Found: C, 84.45; H, 7.97; N, 0.04.

4.3. General procedure for the synthesis of 2

All bichromophoric compounds **2** were prepared as described in the following typical procedure. For example, synthesis of **2a** was exemplified as follows.

4.3.1. 3,5-Bis[(10-methyl-9-anthracenediyl)methoxy]-benzyl benzoate 2a. A solution containing **4a** (0.25 g, 1.02 mmol), **8** (0.10 g, 0.41 mmol), potassium carbonate (0.14 g, 1.02 mmol), and 18-crown-6 (0.11 g, 0.41 mmol) in DMF (5 mL) was heated at 55 °C with stirring under argon atmosphere. After 3 h, the reaction mixture was then precipitated in ice-cold diluted HCl solution (50 mL). The precipitate was collected by filtration, intensively washed with water, and dried in a vacuum to afford a pale yellow solid. After complete vacuum drying, the solid sample was purified by recrystallization from chloroform–hexane solution, affording **2a** (0.24 g, 90%) as a pale yellow powdery material; mp 243–244 °C; UV ($CHCl_3$) 359 nm (ε 13,600), 378 nm (ε 21,700), 399 nm (ε 20,900); IR (KBr) 1595 cm^{-1} (C=C), 1719 cm^{-1} (C=O); MS (FAB+) *m/z* 653 (*M*+), 654 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{46}H_{36}O_4$: 652.2614, found 652.2594; ^1H NMR ($CDCl_3$) δ 3.13 (s, 6H, CH_3), 5.40 (s, 2H, CH_2), 5.93 (s, 4H, CH_2), 6.92 (s, 3H, Ar*H*), 7.4–7.6 (m, 11H, Ar*H*), 8.0–8.2 (m, 2H, Bz*H*), 8.2–8.4 (m, 8H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.5 (CH_3), 63.1 (CH_2), 66.5 (CH_2), 101.4 (*C*H), 107.1 (*C*H), 124.6 (*C*H), 125.0 (*C*H), 125.4 (*C*H), 126.1 (*C*H), 128.4 (*C*H), 129.8 (*C*H), 130.0 (*C*), 130.1 (*C*), 130.8 (*C*), 132.5 (*C*), 133.1 (*C*H), 138.7 (*C*), 160.7 (*C*), 166.4 (*C*).

4.3.2. 3,5-Bis[(10-ethyl-9-anthracenediyl)methoxy]-benzyl benzoate 2b. This compound was obtained (0.27 g, 95%) as a pale yellow powdery material from chloroform–hexane solution; mp 146–147 °C; UV ($CHCl_3$) 359 nm (ε 13,600), 378 nm (ε 21,800), 399 nm (ε 21,100); IR (KBr) 1594 cm^{-1} (C=C), 1719 cm^{-1} (C=O); MS (FAB+) *m/z* 681 (*M*+), 682 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{48}H_{40}O_4$: 680.2927, found 680.2955; ^1H NMR ($CDCl_3$) δ 1.45 (t, $J=7.5$ Hz, 6H, CH_2CH_3), 3.66 (q, $J=7.5$ Hz, 4H, CH_2CH_3), 5.41 (s, 2H, CH_2), 5.91 (s, 4H, CH_2), 6.92 (s, 3H, Ar*H*), 7.4–7.6 (m, 11H, Ar*H*), 8.09 (d, $J=8.4$ Hz, 2H, Bz*H*), 8.1–8.4 (m, 8H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 15.5 (CH_3), 21.5 (CH_2), 63.0 (CH_2), 66.5 (CH_2), 101.3 (*C*H), 107.0 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.1 (*C*H), 126.1 (*C*H), 128.4 (*C*H), 129.0 (*C*), 129.8 (*C*H), 130.0 (*C*), 130.9 (*C*), 133.1 (*C*H), 138.7 (*C*), 139.2 (C), 160.7 (*C*), 166.4 (*C*).

4.3.3. 3,5-Bis[(10-propyl-9-anthracenediyl)methoxy]-benzyl benzoate 2c. This compound was obtained (0.29 g, 91%) as a pale yellow powdery material from chloroform–hexane solution; mp 202–203 °C; UV ($CHCl_3$) 360 nm (ε 13,700), 379 nm (ε 22,200), 400 nm (ε 21,500); IR (KBr) 1593 cm^{-1} (C=C), 1726 cm^{-1} (C=O); MS (FAB+) *m/z* 709 (*M*+), 710 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{50}H_{44}O_4$: 708.3240, found 708.3250; ^1H NMR ($CDCl_3$) δ 1.16 (t, $J=7.3$ Hz, 6H, $(CH_2)_2CH_3$), 1.86 (sext, $J=7.7$ Hz, 4H, $CH_2CH_2CH_3$), 3.5–3.7 (m, $J=8.1$ Hz, 4H, $CH_2CH_2CH_3$), 5.41 (s, 2H, CH_2), 5.91 (s, 4H, CH_2), 6.92 (s, 3H, Ar*H*), 7.3–7.6 (m, 11H, Ar*H*), 8.0–8.2 (m, 2H, Bz*H*), 8.2–8.4 (m, 8H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.7 (CH_3), 24.7 (CH_2), 30.4 (CH_2), 63.1 (CH_2), 66.5 (CH_2), 101.4 (*C*H), 107.1 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.1 (*C*), 125.2 (*C*H), 126.1 (*C*H), 128.4 (*C*H), 129.4 (*C*), 129.8 (*C*H), 130.1 (*C*), 130.9 (*C*), 133.0 (*C*H), 137.9 (*C*), 138.7 (*C*), 160.7 (*C*), 166.4 (*C*).

4.3.4. 3,5-Bis[(10-butyl-9-anthracenediyl)methoxy]-benzyl benzoate 2d. This compound was obtained (0.30 g, 93%) as a pale yellow powdery material from chloroform–hexane solution; mp 189–190 °C; UV ($CHCl_3$) 360 nm (ε 13,400), 379 nm (ε 21,900), 400 nm (ε 21,200); IR (KBr) 1593 cm^{-1} (C=C), 1716 cm^{-1} (C=O); MS (FAB+) *m/z* 736 (*M*+), 737 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{52}H_{48}O_4$: 736.3553, found 736.3517; ^1H NMR ($CDCl_3$) δ 1.02 (t, $J=7.3$ Hz, 6H, $(CH_2)_3CH_3$), 1.60 (sext, $J=7.3$ Hz, 4H, $(CH_2)_2CH_2CH_3$), 1.7–1.9 (m, 4H, $CH_2CH_2CH_2CH_3$), 3.61 (t, $J=7.9$ Hz, 4H, $CH_2(CH_2)_2CH_3$), 5.41 (s, 2H, CH_2), 5.90 (s, 4H, CH_2), 6.92 (s, 3H, Ar*H*), 7.3–7.6 (m, 11H, Ar*H*), 8.0–8.2 (m, 2H, Bz*H*), 8.2–8.4 (m, 8H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.0 (CH_3), 23.4 (CH_2), 28.1 (CH_2), 33.5 (CH_2), 63.1 (CH_2), 66.5 (CH_2), 101.4 (*C*H), 107.1 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.2 (*C*H), 126.1 (*C*H), 128.4 (*C*H), 129.4 (*C*), 129.8 (*C*H), 130.1 (*C*), 130.9

(*C*), 131.0 (C), 133.0 (*C*H), 138.1 (*C*), 138.7 (*C*), 160.8 (*C*), 166.4 (*C*).

4.3.5. 3,5-Bis[(10-hexyl-9-anthracenediyl)methoxy]-benzyl benzoate 2e. This compound was obtained (0.31 g, 94%) as a pale yellow powdery material from chloroform–hexane solution; mp 136–137 °C; UV ($CHCl_3$) 360 nm (ε 13,500), 379 nm (ε 22,000), 400 nm (ε 21,300); IR (KBr) 1595 cm^{-1} (C=C), 1715 cm^{-1} (C=O); MS (FAB+) *m/z* 792 (*M*+), 793 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{56}H_{56}O_4$: 792.4179, found 792.4208; ^1H NMR ($CDCl_3$) δ 0.92 (t, J=7.0 Hz, 6H, $(CH_2)_5CH_3$), 1.3–1.5 (m, 8H, $(CH_2)_3(CH_2)_2CH_3$), 1.5–1.7 (m, 4H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.7–1.9 (m, 4H, $CH_2CH_2(CH_2)_3CH_3$), 3.61 (t, J=8.2 Hz, 4H, $CH_2(CH_2)_4CH_3$), 5.41 (s, 2H, CH_2), 5.91 (s, 4H, CH_2), 6.92 (s, 3H, Ar*H*), 7.3–7.6 (m, 11H, Ar*H*), 8.0–8.2 (m, 2H, Bz*H*), 8.2–8.4 (m, 8H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (*C*H_3), 22.7 (*C*H_2), 28.5 (*C*H_2), 30.0 (*C*H_2), 31.4 (*C*H_2), 31.8 (*C*H_2), 63.1 (*C*H_2), 66.5 (*C*H_2), 101.4 (*C*H), 107.1 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.2 (*C*H), 126.1 (*C*H), 128.4 (*C*H), 129.3 (*C*), 129.8 (*C*H), 130.1 (*C*), 130.9 (*C*), 133.0 (*C*H), 138.1 (*C*), 138.7 (*C*), 160.7 (*C*), 166.4 (*C*).

4.3.6. 3,5-Bis[(10-octyl-9-anthracenediyl)methoxy]-benzyl benzoate 2f. This compound was obtained (0.35 g, 98%) as a pale yellow powdery material from chloroform–hexane solution; mp 166–167 °C; UV ($CHCl_3$) 360 nm (ε 13,500), 379 nm (ε 22,100), 400 nm (ε 21,300); IR (KBr) 1594 cm^{-1} (C=C), 1724 cm^{-1} (C=O); MS (FAB+) *m/z* 848 (*M*+), 849 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{60}H_{64}O_4$: 848.4805, found 848.4846; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=6.8 Hz, 6H, $(CH_2)_7CH_3$), 1.2–1.5 (m, 16H, $(CH_2)_3(CH_2)_4CH_3$), 1.5–1.7 (m, 4H, $(CH_2)_2CH_2(CH_2)_4CH_3$), 1.7–1.9 (m, 4H, $CH_2CH_2(CH_2)_5CH_3$), 3.62 (t, J=8.2 Hz, 4H, $CH_2(CH_2)_6CH_3$), 5.41 (s, 2H, CH_2), 5.94 (s, 4H, CH_2), 6.93 (s, 3H, Ar*H*), 7.3–7.6 (m, 11H, Ar*H*), 8.0–8.2 (m, 2H, Bz*H*), 8.2–8.4 (m, 8H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (*C*H_3), 22.7 (*C*H_2), 28.5 (*C*H_2), 29.3 (*C*H_2), 29.5 (*C*H_2), 30.4 (*C*H_2), 31.4 (*C*H_2), 31.9 (*C*H_2), 63.1 (*C*H_2), 66.5 (*C*H_2), 101.4 (*C*H), 107.1 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.2 (*C*H), 126.1 (*C*H), 128.4 (*C*H), 129.4 (*C*), 129.8 (*C*H), 130.1 (*C*), 131.0 (*C*), 133.0 (*C*H), 138.2 (*C*), 138.7 (*C*), 160.8 (*C*), 166.4 (*C*).

4.3.7. 3,5-Bis[(10-decyl-9-anthracenediyl)methoxy]-benzyl benzoate 2g. This compound was obtained (0.36 g, 96%) as a pale yellow powdery material from chloroform–hexane solution; mp 130–131 °C; UV ($CHCl_3$) 360 nm (ε 13,500), 379 nm (ε 22,100), 400 nm (ε 21,400); IR (KBr) 1596 cm^{-1} (C=C), 1714 cm^{-1} (C=O); MS (FAB+) *m/z* 904 (*M*+), 905 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{64}H_{72}O_4$: 904.5431, found 904.5424; ^1H NMR ($CDCl_3$) δ 0.90 (t, J=7.0 Hz, 6H, $(CH_2)_9CH_3$), 1.2–1.5 (m, 24H, $(CH_2)_3(CH_2)_6CH_3$), 1.5–1.7 (m, 4H, $(CH_2)_2CH_2(CH_2)_6CH_3$), 1.7–1.9 (m, 4H, $CH_2CH_2(CH_2)_7CH_3$), 3.64 (t, J=7.9 Hz, 4H, $CH_2(CH_2)_8CH_3$), 5.44 (s, 2H, CH_2), 5.95 (s, 4H, CH_2), 6.95 (s, 3H, Ar*H*), 7.44 (t, J=7.2 Hz, 9H), 7.5–7.6 (m, 9H, Ar*H*), 8.13 (d, J=7.2 Hz, 2H, Bz*H*), 8.3–8.4 (m, 8H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (*C*H_3), 22.7 (*C*H_2), 28.5 (*C*H_2), 29.3 (*C*H_2), 29.57 (*C*H_2), 29.63 (*C*H_2), 29.7 (*C*H_2), 30.4 (*C*H_2), 31.4 (*C*H_2), 31.9 (*C*H_2), 63.0 (*C*H_2), 66.5 (*C*H_2), 101.3 (*C*H), 107.0 (*C*H), 124.6 (*C*H), 124.96 (*C*H), 125.04 (*C*H), 125.2 (*C*H), 126.1 (*C*H), 128.4 (*C*H), 129.3 (*C*H), 129.8 (*C*), 130.0 (*C*), 130.9 (*C*), 133.1 (*C*), 138.2 (*C*), 138.7 (*C*), 160.7 (*C*), 166.4 (*C*).

4.4. General procedure for the synthesis of 3

All monochromophoric compounds **3** were prepared as described in the following typical procedure. For example, synthesis of **3a** was exemplified as follows.

4.4.1. 3-[(10-Methyl-9-anthracenediyl)methoxy]benzyl benzoate 3a. A solution containing **4a** (0.32 g, 1.32 mmol), **9** (0.20 g, 0.88 mmol), potassium carbonate (0.18 g, 1.32 mmol), and 18-crown-6 (0.04 g, 0.13 mmol) in DMF (5 mL) was heated at 55 °C with stirring under argon atmosphere. After 3 h, the reaction mixture was then quenched by slow addition of 1.0 mol/L HCl. The resulting mixture was extracted with ethyl acetate, and the combined organic extracts were intensively washed with water, saturated $NaHCO_3$ solution, and brine. The organic layer was separated, dried over anhydrous Na_2SO_4, filtered, and concentrated under vacuum to give pale yellow oily residue. Purification of the residue by silica-gel column chromatography (50% chloroform, 50% hexane) gave **3a** as a pale yellow crystalline mass (0.36 g, 95%). Further purification was achieved by recrystallization from chloroform–methanol solution affording purely pale yellow needles; mp 148–149 °C; UV ($CHCl_3$) 359 nm (ε 7200), 378 nm (ε 11,100), 399 nm (ε 10,400); IR (KBr) 1584 cm^{-1} (C=C), 1714 cm^{-1} (C=O); MS (FAB+) *m/z* 432 (*M*+), 433 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{30}H_{24}O_3$: 432.1725, found 432.1710; ^1H NMR ($CDCl_3$) δ 3.12 (s, 3H, CH_3), 5.38 (s, 2H, CH_2), 5.93 (s, 2H, CH_2), 7.1–7.2 (m, 2H, Ar*H*), 7.22 (br s, 1H, Ar*H*), 7.3–7.6 (m, 8H, Ar*H*), 8.0–8.1 (m, 2H, Bz*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.5 (*C*H_3), 62.9 (*C*H_2), 66.5 (*C*H_2), 114.5 (*C*H), 114.6 (*C*H), 120.7 (*C*H), 124.6 (*C*H), 124.9 (*C*H), 125.1 (*C*), 125.4 (*C*H), 126.0 (*C*H), 128.4 (*C*H), 129.7 (*C*H), 129.8 (*C*H), 129.9 (*C*), 130.1 (*C*), 130.7 (*C*), 132.8 (*C*), 133.0 (*C*H), 137.8 (*C*), 159.5 (*C*), 166.4 (*C*).

4.4.2. 3-[(10-Ethyl-9-anthracenediyl)methoxy]benzyl benzoate 3b. This compound was obtained (0.38 g, 96%) as a pale yellow powdery material from chloroform–methanol solution; mp 140–141 °C; UV ($CHCl_3$) 359 nm (ε 7000), 378 nm (ε 11,100), 399 nm (ε 10,500); IR (KBr) 1583 cm^{-1} (C=C), 1720 cm^{-1} (C=O); MS (FAB+) *m/z* 446 (*M*+), 447 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{31}H_{26}O_3$: 446.1882, found 446.1875; ^1H NMR ($CDCl_3$) δ 1.46 (t, J=7.6 Hz, 3H, CH_3), 3.67 (q, J=7.6 Hz, 2H, CH_2), 5.39 (s, 2H, CH_2), 5.93 (s, 2H, CH_2), 7.1–7.2 (m, 2H, Ar*H*), 7.23 (br s, 1H, Ar*H*), 7.3–7.6 (m, 8H, Ar*H*), 8.0–8.1 (m, 2H, Bz*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 15.5 (*C*H_3), 21.5 (*C*H_2), 62.9 (*C*H_2), 66.5 (*C*H_2), 114.4 (*C*H), 114.5 (*C*H), 120.7 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.1 (*C*H), 125.2 (*C*), 126.0 (*C*H), 128.4 (*C*H), 129.0 (*C*), 129.7 (*C*H), 129.8 (*C*H), 130.1 (*C*), 131.0 (*C*), 133.0 (*C*H), 137.8 (*C*), 139.2 (*C*), 159.5 (*C*), 166.4 (*C*).

4.4.3. 3-[(10-Propyl-9-anthracenediyl)methoxy]benzyl benzoate 3c. This compound was obtained (0.38 g, 95%) as a pale yellow powdery material from chloroform–methanol solution; mp 130–131 °C; UV ($CHCl_3$) 360 nm (ε 7100), 379 nm (ε 11,400), 400 nm (ε 10,800); IR (KBr)

1585 cm^{-1} (C=C), 1715 cm^{-1} (C=O); MS (FAB+) *m/z* 460 (*M*+), 461 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{32}H_{28}O_3$: 460.2038, found 460.2053; ^1H NMR ($CDCl_3$) δ 1.17 (t, $J=7.4$ Hz, 3H, $(CH_2)_2CH_3$), 1.87 (sext, $J=7.7$ Hz, 2H, $CH_2CH_2CH_3$), 3.5–3.7 (m, 2H, $CH_2CH_2CH_3$), 5.39 (s, 2H, CH_2), 5.92 (s, 2H, CH_2), 7.1–7.2 (m, 2H, Ar*H*), 7.23 (br s, 1H, Ar*H*), 7.3–7.6 (m, 8H, Ar*H*), 8.0–8.1 (m, 2H, Bz*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.7 (*C*H_3), 24.7 (*C*H_2), 30.4 (*C*H_2), 63.0 (*C*H_2), 66.5 (*C*H_2), 114.4 (*C*H), 114.5 (*C*H), 120.7 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.2 (*C*H), 126.0 (*C*H), 128.4 (*C*H), 129.4 (*C*), 129.7 (*C*H), 129.8 (*C*H), 130.1 (*C*), 131.0 (*C*), 133.0 (*C*H), 137.8 (*C*), 137.9 (*C*), 159.5 (*C*), 166.4 (*C*).

4.4.4. 3-[(10-Butyl-9-anthracenediyl)methoxy)benzyl benzoate 3d. This compound was obtained (0.40 g, 96%) as a pale yellow powdery material from chloroform–methanol solution; mp 134–135 °C; UV ($CHCl_3$) 360 nm (ε 6900), 379 nm (ε 11,200), 400 nm (ε 10,600); IR (KBr) 1584 cm^{-1} (C=C), 1715 cm^{-1} (C=O); MS (FAB+) *m/z* 474 (*M*+), 475 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{33}H_{30}O_3$: 474.2195, found 474.2210; ^1H NMR ($CDCl_3$) δ 1.04 (t, $J=7.3$ Hz, 3H, $(CH_2)_3CH_3$), 1.61 (sext, $J=7.5$ Hz, 2H, $(CH_2)_2CH_2CH_3$), 1.7–1.9 (m, 2H, $CH_2CH_2CH_2CH_3$), 3.63 (t, $J=8.2$ Hz, 2H, $CH_2(CH_2)_2CH_3$), 5.39 (s, 2H, CH_2), 5.93 (s, 2H, CH_2), 7.1–7.2 (m, 2H, Ar*H*), 7.23 (br s, 1H, Ar*H*), 7.3–7.6 (m, 8H, Ar*H*), 8.0–8.1 (m, 2H, Bz*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.0 (*C*H_3), 23.4 (*C*H_2), 28.1 (*C*H_2), 33.5 (*C*H_2), 63.0 (*C*H_2), 66.5 (*C*H_2), 114.5 (*C*H), 114.6 (*C*H), 120.7 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.2 (*C*H), 126.0 (*C*H), 128.4 (*C*H), 129.4 (*C*), 129.7 (*C*H), 129.8 (*C*H), 130.1 (*C*), 131.0 (*C*), 133.0 (*C*H), 137.8 (*C*), 138.0 (*C*), 159.5 (*C*), 166.4 (*C*).

4.4.5. 3-[(10-Hexyl-9-anthracenediyl)methoxy)benzyl benzoate 3e. This compound was obtained (0.42 g, 95%) as a pale yellow powdery material from chloroform–methanol solution; mp 93–94 °C; UV ($CHCl_3$) 360 nm (ε 7000), 379 nm (ε 11,300), 400 nm (ε 10,700); IR (KBr) 1585 cm^{-1} (C=C), 1718 cm^{-1} (C=O); MS (FAB+) *m/z* 502 (*M*+), 503 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{35}H_{34}O_3$: 502.2508, found 502.2529; ^1H NMR ($CDCl_3$) δ 0.93 (t, $J=7.1$ Hz, 3H, $(CH_2)_5CH_3$), 1.3–1.5 (m, 4H, $(CH_2)_3(CH_2)_2CH_3$), 1.5–1.7 (m, 2H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.7–1.9 (m, 2H, $CH_2CH_2(CH_2)_3CH_3$), 3.61 (t, $J=8.3$ Hz, 2H, CH_2 $(CH_2)_4CH_3$), 5.39 (s, 2H, CH_2), 5.93 (s, 2H, CH_2), 7.1–7.2 (m, 2H, Ar*H*), 7.23 (br s, 1H, Ar*H*), 7.3–7.6 (m, 8H, Ar*H*), 8.0–8.1 (m, 2H, Bz*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (*C*H_3), 22.7 (*C*H_2), 28.5 (*C*H_2), 30.1 (*C*H_2), 31.4 (*C*H_2), 31.8 (*C*H_2), 63.0 (*C*H_2), 66.5 (*C*H_2), 114.4 (*C*H), 114.5 (*C*H), 120.7 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.2 (*C*), 126.0 (*C*H), 128.4 (*C*H), 129.3 (*C*), 129.7 (*C*H), 129.8 (*C*H), 130.1 (*C*), 130.9 (*C*), 133.0 (*C*H), 137.8 (*C*), 138.1 (*C*), 159.5 (*C*), 166.4 (*C*).

4.4.6. 3-[(10-Octyl-9-anthracenediyl)methoxy]benzyl benzoate 3f. This compound was obtained (0.46 g, 98%) as a pale yellow powdery material from chloroform–methanol solution; mp 98–99 °C; UV ($CHCl_3$) 360 nm (ε 6800), 379 nm (ε 11,000), 400 nm (ε 10,000); IR (KBr) 1584 cm^{-1} (C=C), 1714 cm^{-1} (C=O); MS (FAB+) *m/z* 530 (*M*+), 531 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{37}H_{38}O_3$: 530.2821, found 530.2795; ^1H NMR ($CDCl_3$) δ 0.90 (t, $J=6.8$ Hz, 3H, $(CH_2)_9CH_3$), 1.2–1.5 (m, 8H, $(CH_2)_3(CH_2)_4CH_3$), 1.59 (quint, $J=7.7$ Hz, 2H, $(CH_2)_2CH_2(CH_2)_4CH_3$), 1.82 (quint, $J=7.8$ Hz, 2H, $CH_2CH_2(CH_2)_5CH_3$), 3.61 (t, $J=8.2$ Hz, 2H, $CH_2(CH_2)_6CH_3$), 5.38 (s, 2H, CH_2), 5.92 (s, 2H, CH_2), 7.1–7.2 (m, 2H, Ar*H*), 7.22 (br s, 1H, Ar*H*), 7.3–7.6 (m, 8H, Ar*H*), 8.0–8.1 (m, 2H, Bz*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (*C*H_3), 22.7 (*C*H_2), 28.5 (*C*H_2), 29.3 (*C*H_2), 29.5 (*C*H_2), 30.4 (*C*H_2), 31.4 (*C*H_2), 31.9 (*C*H_2), 62.9 (*C*H_2), 66.5 (*C*H_2), 114.4 (*C*H), 114.5 (*C*H), 120.7 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.1 (*C*), 125.2 (*C*H), 126.0 (*C*H), 128.4 (*C*H), 129.3 (*C*), 129.7 (*C*H), 129.8 (*C*H), 130.1 (*C*), 130.9 (*C*), 133.0 (*C*H), 137.8 (*C*), 138.1 (*C*), 159.5 (*C*), 166.4 (*C*).

4.4.7. 3-[(10-Decyl-9-anthracenediyl)methoxy)benzyl benzoate 3g. This compound was obtained (0.48 g, 97%) as a pale yellow powdery material from chloroform–methanol solution; mp 93–94 °C; UV ($CHCl_3$) 360 nm (ε 6900), 379 nm (ε 11,200), 400 nm (ε 10,600); IR (KBr) 1583 cm^{-1} (C=C), 1714 cm^{-1} (C=O); MS (FAB+) *m/z* 558 (*M*+), 559 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{39}H_{42}O_3$: 558.3134, found 558.3121; ^1H NMR ($CDCl_3$) δ 0.89 (t, $J=6.5$ Hz, 3H, $(CH_2)_9CH_3$), 1.2–1.5 (m, 12H, $(CH_2)_3(CH_2)_6CH_3$), 1.5–1.7 (m, 2H, $(CH_2)_2CH_2(CH_2)_6CH_3$), 1.7–1.9 (m, 2H, $CH_2CH_2(CH_2)_7CH_3$), 3.61 (t, $J=8.2$ Hz, 2H, $CH_2(CH_2)_8CH_3$), 5.39 (s, 2H, CH_2), 5.92 (s, 2H, CH_2), 7.1–7.2 (m, 2H, Ar*H*), 7.23 (br s, 1H, Ar*H*), 7.3–7.6 (m, 8H, Ar*H*), 8.0–8.1 (m, 2H, Bz*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (*C*H_3), 22.7 (*C*H_2), 28.5 (*C*H_2), 29.3 (*C*H_2), 29.56 (*C*H_2), 29.63 (*C*H_2), 29.7 (*C*H_2), 30.4 (*C*H_2), 31.4 (*C*H_2), 31.9 (*C*H_2), 63.0 (*C*H_2), 66.5 (*C*H_2), 114.4 (*C*H), 114.5 (*C*H), 120.7 (*C*H), 124.7 (*C*H), 125.0 (*C*H), 125.2 (*C*H), 126.0 (*C*H), 128.4 (*C*H), 129.3 (*C*), 129.7 (*C*H), 129.8 (*C*H), 130.1 (*C*), 130.9 (*C*), 133.0 (*C*H), 137.8 (*C*), 138.1 (*C*), 159.5 (*C*), 166.4 (*C*).

4.5. General procedure for the synthesis of 4

All 10-alkyl-9-chloromethylanthracenes **4** were synthesized according to the established literature procedure used for preparation of **4a**. For example, synthesis of **4c** was exemplified as follows.

4.5.1. 9-Chloromethyl-10-propylanthracene 4c. A solution containing **6c** (1.0 g, 4.54 mmol), paraformaldehyde (1.0 g), and concd HCl (10 mL) in acetic acid (20 mL) was heated at room temperature with vigorous stirring. After 14 h, the reaction mixture was then precipitated in ice-cold (50 mL). The precipitate was collected by filtration, intensively washed with water, and dried in a vacuum to afford a pale yellow solid. After complete vacuum drying, the solid sample was purified by recrystallization from chloroform–hexane solution, affording **4c** (1.1 g, 92%) as a pale yellow powdery material; mp 123–124 °C; IR (KBr) 759, 1249, 1444, 1478 cm^{-1}; MS (FAB+) *m/z* 268 (*M*+), 269 (*MH*+); ^1H NMR ($CDCl_3$) δ 1.14 (t, $J=7.5$ Hz, 3H, $CH_2CH_2CH_3$), 1.82 (sext, $J=7.5$ Hz, 2H, $CH_2CH_2CH_3$), 3.5–3.6 (m, 2H, CH_2), 5.57 (s, 2H, CH_2), 7.4–7.6 (m, 4H, Ar*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.7 (*C*H_3), 24.7 (*C*H_2), 30.4 (*C*H_2), 39.5 (*C*H_2), 124.1 (*C*H), 125.1 (*C*H), 125.4 (*C*H), 126.2 (*C*), 126.3 (*C*H), 129.5 (*C*), 129.9 (*C*), 138.2 (*C*). Anal. Calcd for $C_{18}H_{17}Cl$: C, 80.43; H, 6.38; N, 0.00. Found: C, 80.51; H, 6.49; N, 0.05.

4.5.2. 9-Chloromethyl-10-hexylanthracene 4e. This compound was obtained (1.1 g, 89%) from **6e** (1.0 g, 3.82 mmol) as a pale yellow powdery material from chloroform–hexane solution; mp 114–115 °C; IR (KBr) 756, 1246, 1446, 1459, 1479 cm^{-1}; MS (FAB+) *m/z* 310 (*M*+), 311 (*MH*+); ^1H NMR ($CDCl_3$) δ 0.91 (t, *J*=7.0 Hz, 3H, $(CH_2)_5CH_3$), 1.3–1.5 (m, 4H, $(CH_2)_3(CH_2)_2CH_3$), 1.56 (quint, *J*=7.3 Hz, 2H, $(CH_2)_2CH_2(CH_2)_2CH_3$), 1.77 (quint, *J*=7.5 Hz, 2H, $CH_2CH_2(CH_2)_3CH_3$), 3.56 (t, *J*=8.2 Hz, 2H, $CH_2(CH_2)_4CH_3$), 5.56 (s, 2H, CH_2), 7.4–7.6 (m, 4H, Ar*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 28.5 (CH_2), 30.0 (CH_2), 31.4 (CH_2), 31.7 (CH_2), 39.5 (CH_2), 124.1 (*C*H), 125.2 (*C*H), 125.3 (*C*H), 126.1 (*C*), 126.30 (*C*H), 129.33 (*C*), 129.9 (*C*), 138.4 (*C*). Anal. Calcd for $C_{21}H_{23}Cl$: C, 81.14; H, 7.46; N, 0.00. Found: C, 81.25; H, 7.50; N, 0.00.

4.5.3. 9-Chloromethyl-10-octylanthracene 4f. This compound was obtained (0.99 g, 85%) from **6f** (1.0 g, 3.45 mmol) as a pale yellow powdery material from chloroform–hexane solution; mp 96–97 °C; IR (KBr) 760, 1248, 1445, 1459, 1479 cm^{-1}; MS (FAB+) *m/z* 338 (*M*+), 339 (*MH*+); ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=7.0 Hz, 3H, $(CH_2)_7CH_3$), 1.2–1.4 (m, 8H, $(CH_2)_3(CH_2)_4CH_3$), 1.56 (quint, *J*=7.6 Hz, 2H, $(CH_2)_2CH_2(CH_2)_4CH_3$), 1.79 (quint, *J*=7.7 Hz, 2H, $CH_2CH_2(CH_2)_5CH_3$), 3.58 (t, *J*=8.2 Hz, 2H, $CH_2(CH_2)_6CH_3$), 5.59 (s, 2H, CH_2), 7.4–7.6 (m, 4H, Ar*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 28.5 (CH_2), 29.3 (CH_2), 29.5 (CH_2), 30.4 (CH_2), 31.5 (CH_2), 31.9 (CH_2), 39.6 (CH_2), 124.1 (*C*H), 125.2 (*C*H), 125.4 (*C*H), 126.1 (*C*), 126.3 (*C*H), 129.4 (*C*), 129.9 (*C*), 138.5 (*C*). Anal. Calcd for $C_{23}H_{27}Cl$: C, 81.51; H, 8.03; N, 0.00. Found: C, 81.52; H, 8.21; N, 0.00.

4.5.4. 9-Chloromethyl-10-decylanthracene 4g. This compound was obtained (0.96 g, 83%) from **6g** (1.0 g, 3.14 mmol) as a pale yellow powdery material from chloroform–hexane solution; mp 95–96 °C; IR (KBr) 760, 1249, 1445, 1459, 1477 cm^{-1}; MS (FAB+) *m/z* 366 (*M*+), 367 (*MH*+); ^1H NMR ($CDCl_3$) δ 0.88 (t, *J*=7.0 Hz, 3H, $(CH_2)_9CH_3$), 1.2–1.4 (m, 12H, $(CH_2)_3(CH_2)_6CH_3$), 1.57 (quint, *J*=7.3 Hz, 2H, $(CH_2)_2CH_2(CH_2)_6CH_3$), 1.79 (quint, *J*=7.7 Hz, 2H, $CH_2CH_2(CH_2)_7CH_3$), 3.57 (t, *J*=8.2 Hz, 2H, $CH_2(CH_2)_8CH_3$), 5.57 (s, 2H, CH_2), 7.4–7.6 (m, 4H, Ar*H*), 8.2–8.4 (m, 4H, Ar*H*); ^{13}C NMR ($CDCl_3$) δ 14.1 (CH_3), 22.7 (CH_2), 28.5 (CH_2), 29.3 (CH_2), 29.55 (CH_2), 29.62 (CH_2), 29.7 (CH_2), 30.4 (CH_2), 31.5 (CH_2), 31.9 (CH_2), 39.5 (CH_2), 124.1 (*C*H), 125.2 (*C*H), 125.4 (*C*H), 126.1 (*C*), 126.3 (*C*H), 129.4 (*C*), 129.9 (*C*), 138.5 (*C*). Anal. Calcd for $C_{25}H_{31}Cl$: C, 81.82; H, 8.51; N, 0.00. Found: C, 82.04; H, 8.57; N, 0.02.

4.5.5. Preparation of tris(3,5-dihydroxybenzyl) benzene-1,3,5-tricarboxylate 5. The following synthetic procedure was also used for the sample preparations of benzoyl 3,5-dihydroxybenzylate **8** and benzoyl 3-hydroxybenzylate **9**. To a solution of **7** (1.26 g, 1.13 mmol) in a mixture of HPLC grade methanol (20 mL) and chloroform (20 mL) was added a catalytic amount of 10% Pd–C (0.1 g) in some portions at room temperature. The mixture was stirred under a hydrogen gas atmosphere at ambient temperature for 20 h. The catalyst was removed by filtration and the filtrate was then evaporated to dryness to obtain a colorless oily residue. Purification of the residue by column chromatography (67% ethyl acetate, 33% hexane) and recrystallization from hexane–ethyl acetate gave **5** (0.51 g, 78%) as a white powdery material; mp 219–220 °C; IR (KBr) 1608 cm^{-1} (C=C), 1714 cm^{-1} (C=O), 3391 cm^{-1} (OH); MS (FAB+) *m/z* 576 (*M*+), 578 (*MH*+); HRMS (FAB+) *m/z* calcd for $C_{30}H_{24}O_{12}$: 576.1268, found 576.1245; ^1H NMR (acetone-d_6) δ 5.31 (s, 6H, CH_2), 6.34 (t, *J*=2.1 Hz, 3H, Ph*H*), 6.49 (d, *J*=2.1 Hz, 6H, Ph*H*), 8.32 (s, 6H, O*H*), 8.85 (s, 3H, Bz*H*); ^{13}C NMR (acetone-d_6) δ 68.3 (CH_2), 103.5 (*C*H), 107.4 (*C*), 132.7 (*C*), 135.3 (*C*H), 139.3 (*C*), 159.8 (*C*), 166.0 (*C*).

4.5.6. Preparation of tris(3,5-bis(benzyloxy)benzyl) benzene-1,3,5-tricarboxylate 7. To a solution containing 3,5-bis(benzyloxy)benzyl alcohol (0.56 g, 1.75 mmol) and triethylamine (0.34 mL, 2.44 mmol) in anhydrous benzene (20 mL) was added dropwise to a solution trimesoyl chloride (0.15 g, 0.55 mmol) in anhydrous benzene (20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 12 h, quenched by slow addition of 1.0 mol/L HCl, and then extracted with an additional benzene (150 mL). The combined organic layers were washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo. Silica-gel column chromatography (50% chloroform, 50% hexane) of the crude sample furnished **7** (0.60 g, 98%) as a colorless crystalline mass. Further purification was achieved by recrystallization from chloroform–hexane giving a purely powdery material; mp 123–124 °C; IR (KBr) 1597 cm^{-1} (C=C), 1724 cm^{-1} (C=O); MS (FAB+) *m/z* 1117 (*M*+), 1118 (*MH*+); ^1H NMR ($CDCl_3$) δ 5.00 (s, 12H, CH_2), 5.33 (s, 6H, CH_2), 6.58 (t, *J*=2.2 Hz, 3H, Ph*H*), 6.67 (d, *J*=2.2 Hz, 6H, Ph*H*), 7.2–7.4 (m, 30H, Ar*H*), 8.90 (s, 3H, Bz*H*); ^{13}C NMR ($CDCl_3$) δ 67.2 (CH_2), 70.1 (CH_2), 102.0 (*C*H), 107.3 (*C*H), 127.5 (*C*H), 128.0 (*C*H), 128.6 (*C*H), 131.2 (*C*), 135.0 (*C*H), 136.7 (*C*), 137.7 (*C*), 160.2 (*C*), 164.7 (*C*). Anal. Calcd for $C_{72}H_{60}O_{12}$: C, 77.40; H, 5.41; N, 0.00. Found: C, 77.41; H, 5.27; N, 0.07.

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