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Synthesis of lipophilic bisanthracene fluorophores: versatile building blocks toward the synthesis of new light-harvesting dendrimers

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ABSTRACT

Lipophilic bisanthracene-based fluorophore and its derivatives were synthesized by the Suzuki–Miyaura cross-coupling reaction of 9-anthrylboronic acid with a substituted dibromobenzene. In addition to desirable fluorescent properties, these molecular systems were demonstrated to serve as versatile building blocks toward the synthesis of two types of new light-harvesting dendrimers due to their chemical stability.

1. Introduction

Highly fluorescent molecules, so-called fluorophores, have attracted a great deal of attention because of their versatility[1] not only as useful sensors for analytical[2] and biological imaging[3] studies, but also as efficient energy and/or electron transmitters for fabrication of photoelectric devices[4] such as light-harvesting dendrimers[5] and organogels.[6] From this basis, considerable effort has been devoted over the past decade to develop organic dye fluorophores bringing advantageous functionality for many uses as well as ideal performance with high extinction coefficient, high fluorescence quantum yield, and good chemical stability.[7] In this context, a number of polyaromatic hydrocarbons exhibit favorable and unique properties such as strongly fluorescent behavior and intrinsically high intercalative binding affinity with DNA due to their extensively π-conjugated and planar structures, making them multifunctional fluorescent probes for biological applications.[8] Among a variety of polyaromatic compounds, anthracene and its derivatives represent an important class of functional materials, which show blue-light emitting characteristics with high thermal stability, thus serving as excellent fluorophores suitable for the opto-electronic device fabrication.[9] Nevertheless, development of anthracene-based systems and their application in molecular engineering of new functional materials is substantially less advanced due to their poor solubility in a range of solvent systems and low synthetic flexibility in accessing diverse analogs. In this publication, we disclose a new type of bisanthracene-based molecular system,[10] which works as strongly emitting fluorophores and as versatile building blocks toward the synthesis of new light-harvesting dendrimers.

2. Results and discussion

For the construction of bisanthracene-based structures, we utilized the Suzuki–Miyaura cross-coupling reaction to connect two anthracene rings covalently to the 1,3-positions of benzene nucleus, where a substituted dibromobenzene **1** should be prerequisite for the synthesis (Scheme 1). Thus, our synthetic approach started with the preparation of **1** from commercially available 3,5-dibromo-4-benzaldehyde through a three-step sequence involving Williamson methylation, $NaBH_4$ reduction, and TBS protection (92% for three steps). Subsequently, 1,8-bis(2-ethylhexyl)anthracene **2** prepared according to published procedures[11] was brominated at the C10-position upon treatment with NBS to give **3** in 77% yield. After conversion of **3** to the corresponding boronic acid, this synthetic intermediate was subjected to the coupling with **1** under the typical conditions for this transformation,[12] followed by removal of TBS protective groups upon treatment with TBAF, to provide bisanthracene-substituted benzyl alcohol **4** in 38% for three steps.

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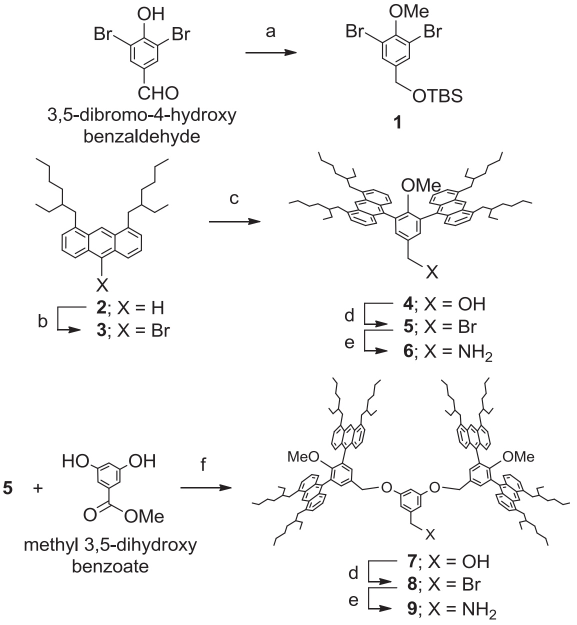


Scheme 1. Reagents and conditions: (a) (i) MeI, K_2CO_3, DMF, 55 °C, 3 h; 97%; (ii) $NaBH_4$, EtOH, rt, 5 h; 97%; (iii) TBSCl, imidazole, DMF, rt, 3 h; 98%; (b) NBS, DMF, rt, 5 h; 77%; (c) (i) *n*-BuLi, $B(OMe)_3$, THF, −78 °C for 30 min then rt for 1.5 h; 54%; (ii) **1**, $Pd(PPh_3)_4$, Na_2CO_{3aq}, toluene–EtOH (2:1), reflux, 4 h; (iii) TBAF, THF, 0 °C, 3 h; 71% (two steps); (d) CBr_4, PPh_3, THF, rt, 0.5 h; 95% for **5**, 91% for **8**; (e) (i) phthalimide, K_2CO_3, DMF, rt, 24 h; 94% for **6**, 73% for **9**; (ii) $(NH_2)_2 \cdot H_2O$, THF, reflux, 4 h; 98% for **6**, 80% for **9**; (f) (i) **5**, K_2CO_3, 18-crown-6, acetone, reflux, 5 h; 78%; (ii) LAH, THF, 0 °C, 12 h; 69%.

The success in the synthesis of this product was confirmed by a range of spectroscopies. In this structural system, the ^{1}H NMR spectrum clearly indicated that the two anthracene rings were oriented orthogonally to the benzene unit, as evidenced by the large upfield shift in the resonance for the methoxy protons relative to that of **1** (from δ_H 3.87 to 2.50 ppm) due to the aromatic ring currents.[13]

As a matter of fact, good chemical and thermal stability of this compound allowed facile derivatization with a variety of functional groups.[14] Appel bromination of **4** led to efficient production of **5** in 95% yield, which was converted to the corresponding amine **6** by the Gabriel synthesis in 92% (for two steps). Then **5** could be utilized to generate its dendronized derivative **7** via the Williamson reaction with methyl 3,5-dihydroxy benzoate and subsequent reduction with LAH (54% for two steps). A similar set of functional group transformations performed on **4** was also encountered with this product to afford the corresponding bromide **8** and amine **9** in 91% and 58% (two steps from **8**), respectively.

The bisanthracene-based fluorophores **4**–**9** showed good solubilities in a wide range of common organic solvents such as $CHCl_3$, THF, hexane, and MeOH, due to the lipophilic nature of 2-ethylhexyl moieties. Indeed, the absorption and fluorescence spectra of these compounds represented characteristic monomeric features, whose vibrational structures are similar but red-shifted by 10–15 nm relative to their building component **2** (Fig. 1 and S1–S7 in Supplementary data). Of particular interest in this context is that almost all of the bisanthracene-based systems are highly fluorescent with greater efficiencies (ϕ_F) than for **2** (Table 1), even though the covalent assemblage of chromophoric units on single molecular platforms would invoke attenuation of fluorescence quantum yield as observed in our earlier works.[14a–c] Further consideration of the high ϕ_F values for benzylamines **6** and **9** indicated that the presence of terminal amino substituents had no influence on fluorescence quantum yield, thereby excluding a possibility of electron-transfer quenching of the excited chromophores.[15]

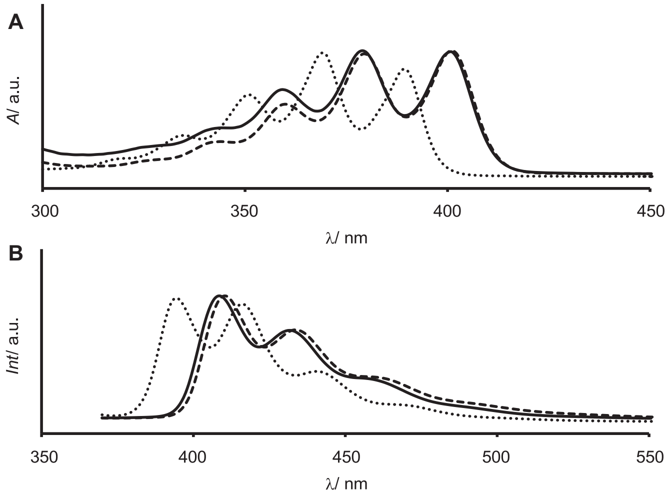


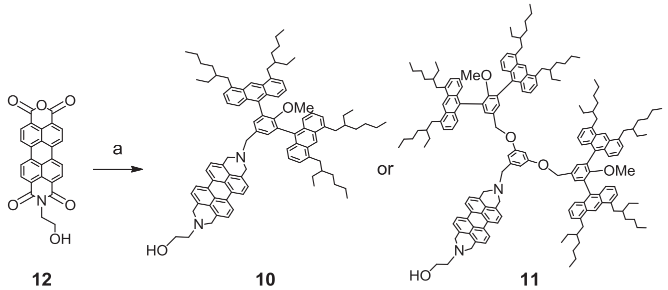
Fig. 1. Normalized (A) absorption and (B) fluorescence spectra (λ_{ex} 360 nm) of **2** (dotted line), **4** (solid line), and **7** (dashed line) in $CHCl_3$.

Table 1
Fluorescence quantum yields (ϕ_F) in various solvents[a]

Fluorophores	$CHCl_3$	THF	Hexane	MeOH
2	0.16	0.27	0.26	0.29
4	0.50	0.43	0.31	0.37
5	0.18	0.37	0.38	0.24
6	0.52	0.41	0.36	0.40
7	0.45	0.57	0.28	0.49
8	0.53	0.52	0.35	0.72
9	0.48	0.46	0.36	0.47

[a] Fluorescence quantum yields (ϕ_F) were determined by relative method employing a dilute solution of anthracene in cyclohexane (ϕ_F=0.36)[16] as a standard. The quantum yields for the fluorophores were averaged from the values obtained at three different excitation wavelengths (λ_{ex} 355, 360, and 365 nm).

The desirable combination of attractive photophysical characteristics, good solvent solubility, and functional group tolerance prompted us to undertake practical application of the bisanthracene-based systems as efficient antennae for light-harvesting materials. In our previous works, it has been demonstrated that perylene dyes can serve as a suitable acceptor to funnel energy from anthracene chromophores because of their high degree of spectral overlap between the donor emission and acceptor absorption profiles.[11b,17] Thus, we designed new model compounds **10** and **11**, containing the dendritic substituents at one side of the perylene nuclei (Scheme 2). The synthesis of these dendrimers employed a sequential imidation–reduction protocol to couple the bisanthracene and perylene units,[18] where requisite substrate **12** was prepared from commercially available



Scheme 2. Reagents and conditions: (i) **6** or **9**, NMP, 100 °C, 35 h; 57% for **10**, 28% for **11**; (ii) AlH_3, THF, 0 °C to rt, 4 h, 99% for **10** and 99% for **11**; (two steps).

3,4,9,10-peryl-enetetracarboxylic dianhydride according to published procedures.[19] Consequently, the dendrimers **10** and **11** could be readily obtained from **12** and two benzylamines **6** and **9** via the above synthetic sequences.

The photophysical properties of these dendrimers were characterized by steady-state absorption and fluorescence spectroscopic measurements (Fig. 2 and S8, S9 in Supplementary data). In the absorption spectra, all the samples displayed two series of vibronic fine-structures with spectrally resolved bands in the regions of 350–415 and 415–480 nm, whose intensities vary according to the number of anthracene and perylene groups embedded within the dendritic frameworks, respectively, indicative of independent behavior of these light absorbing chromophores (Fig. 2A and S8, S9A). Remarkably, the fluorescence measurements of these materials showed strong or moderate fluorescence quenching of the excited anthracene and appearance of significant fluorescence emissions arising from the perylene chromophores upon excitation at 360 nm, where direct excitation of the anthracene chromophores was most likely (Fig. 2B and S8, S9B). As described previously for other analogous systems,[11b] these observations could be adequately rationalized in terms of energy transfer from the anthracene antennae to the perylene cores, suggesting that the dendritic frameworks containing the densely arrayed donor (anthracene) and acceptor (perylene) units would give geometrical and electronic properties suitable for creating the unique light-harvesting antenna systems.

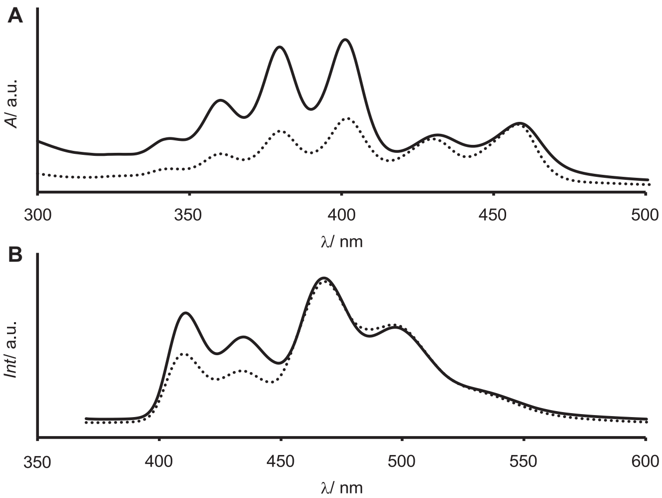


Fig. 2. Normalized (A) absorption and (B) fluorescence spectra (λ_{ex} 360 nm) of **10** (dotted line) and **11** (solid line) in $CHCl_3$.

Table 2 summarizes quantum yields for energy transfer (ϕ_{FT}) occurring in **10** and **11**, which were estimated by comparing quantum yields for the acceptor emissions obtained upon excitation of the donors (ϕ_{F1}) with those upon excitation of the acceptors (ϕ_{F2}).[20] From these data, it appears that the energy transfer occurs efficiently under all the solvent conditions with particularly high quantum yields for the chloroform solutions, but differences in the ϕ_{ET} values were noticed between the dendrimers bearing the less and more advanced antenna units. We believe that this can be simply explained by differences in average distances between the peripheral anthracene antennae and the perylene cores incorporated within individual dendrimer systems,[21] which primarily reflect the extent of their Coulombic interactions given by the Förster theory.[22]

Table 2

Averaged quantum yields for the core emissions (ϕ_{F1}) upon excitation of the donor groups,[a] quantum yields for the core emissions (ϕ_{F2}) upon excitation of the acceptor group,[a] and energy transfer efficiencies (ϕ_{ET})[b]

Dendrimer	Solvent	ϕ_{F1}[a]	ϕ_{F2}[a]	ϕ_{ET}[b]
10	$CHCl_3$	0.63	0.69	0.92
	THF	0.69	0.79	0.88
	Hexane	0.47	0.63	0.74
	MeOH	0.69	0.81	0.86
11	$CHCl_3$	0.41	0.50	0.82
	THF	0.54	0.83	0.65
	Hexane	0.15	0.25	0.60
	MeOH	0.42	0.65	0.65

[a] Quantum yields for the core emissions (ϕ_{F1} and ϕ_{F2}) were determined by relative method employing a dilute solution of perylene in cyclohexane (ϕ_F=0.94)[16] as a standard. The ϕ_{F1} values represent an average of measurements at three different excitation wavelengths (λ_{ex} 355, 360, and 365 nm) and the ϕ_{F2} values were obtained by measurements at λ_{ex} 420 nm.

[b] ϕ_{ET} values were given by ϕ_{F1}/ϕ_{F2}.

3. Conclusions

In conclusion, a new type of bisanthracene-based fluorophores was synthesized by the Suzuki–Miyaura cross-coupling reaction of 9-anthrylboronic acid with the substituted dibromobenzene. This aromatic system has been demonstrated to exhibit the desirable fluorescent properties as well as the remarkably high solubilities in a variety of organic solvents, serving as excellent fluorophores suitable for many applications. Furthermore, the high chemical stability of the molecular system allowed us to produce several synthetic intermediates, which were consequently applied as versatile building blocks for developing the efficient light-harvesting dendrimers. In addition, the present bisanthracene-based systems represent potentially superior functional materials that can be used to create novel sensors and opto-electronic devices. Further elaboration of the bisanthracene and dendrimer systems for the design and development of complex structures with advanced functionality will be presented in future publications.

4. Experimental section

4.1. General

All solvents and reagents were of reagent grade quality from Wako Pure Chemicals and Tokyo Chemical Industry (TCI) used without further purification. The ^1H 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* ($CDCl_3$). 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 (FTIR) spectra were recorded on a JASCO FT/IR-4100 spectrometer. UV–vis and fluorescence (excitation) spectra were recorded on a JASCO V-630 spectrophotometer and a JASCO FP-6200 spectrofluorometer, respectively. Melting points were measured with a Stanford Research Systems MPA100 automatic melting point apparatus. Elemental analysis of **3** was performed by JSL Model JM 10 instruments. Laser desorption ionization (LDI) or matrix-assisted laser desorption ionization (MALDI) mass spectra were obtained on a JEOL JMS-700/GI mass spectrometer, which performed low- and high-resolution mass spectrometry. For measuring the MALDI mass spectra, α-cyano-4-hydroxycinnamic acid (α-CHCA) matrix was used as a cationization agent.

4.2. Preparation and characterization of new compounds

4.2.1. Synthesis and characterization of ***1***. To a solution of 3,5-dibromo-4-hydroxybenzaldehyde (1.00 g, 3.57 mmol) and methyl iodide (MeI, 0.5 mL, 1.14 g, 8.03 mmol) in DMF (15 mL) was added anhydrous potassium carbonate (K_2CO_3, 0.992 g, 7.18 mmol). The reaction mixture was stirred at 55 °C for 3 h, cooled to room temperature, and quenched by addition of water (80 mL). The resultant white precipitate was filtered under vacuum, washed with water (40 mL), and dried to give the anisaldehyde intermediate (1.02 g, 3.47 mmol, 97%) as a white solid: mp 90–91 °C; IR (NaCl) 1688 cm^{-1} (C═O), 1546 cm^{-1} (C═C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.86 (s, 1H, C*H*O), 8.03 (s, 2H, Ar*H*), 3.97 (s, 3H, OC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 188.6 (*C*HO), 159.2 (*C*), 134.3 (*C*), 134.0 (*C*H), 119.3 (*C*), 60.8 (O*C*H$_3$). To a solution of this material (0.100 g, 0.340 mmol) in EtOH (3.5 mL) at 0 °C was added sodium borohydride ($NaBH_4$, 0.022 g, 0.592 mmol). The reaction mixture was stirred at room temperature for 5 h, quenched by addition of 3% aqueous HCl (5 mL), extracted with ethyl acetate (50 mL), washed with water (50 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to give the alcohol intermediate (0.098 g, 0.331 mmol, 97%) as a white solid: mp 38–39 °C; IR (NaCl) 3350 cm^{-1} (O–H), 1548 cm^{-1} (C═C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.51 (s, 2H, Ar*H*), 4.62 (s, 2H, ArC*H*$_2$), 3.88 (s, 3H, OC*H*$_3$), 1.90 (br s, 1H, O*H*); ^{13}C NMR (75 MHz, $CDCl_3$) δ 139.6 (*C*), 130.9 (*C*H), 118.1 (*C*), 63.3 (*C*H$_2$), 60.6 (O*C*H$_3$). To a solution of this material (0.387 g, 1.31 mmol) and imidazole (0.104 g, 1.53 mmol) in DMF (13 mL) at 0 °C was added *tert*-butyldimethylsilyl chloride (TBSCl, 0.116 g, 0.770 mmol). The reaction mixture was warmed to room temperature, stirred for 3 h, quenched by addition of water (20 mL), extracted with hexane (50 mL), washed with water (50 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 50:1) to yield **1** (0.527 g, 1.28 mmol, 98%) as a colorless oil: IR (NaCl) 1546 cm^{-1} (C═C); ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (s, 2H, Ar*H*), 4.64 (s, 2H, ArC*H*$_2$), 3.87 (s, 3H, OC*H*$_3$), 0.94 (s, 9H, C*H*$_3$), 0.11 (s, 6H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.9 (*C*), 140.2 (*C*), 130.2 (*C*H), 118.0 (*C*), 63.2 (*C*H$_2$), 60.6 (O*C*H$_3$), 25.8 (*C*H$_3$), 18.3 (*C*), −5.5 (*C*H$_3$).

4.2.2. Synthesis and characterization of ***3***. To a solution of 1,8-bis(2-ethylhexyl)anthracene (1.69 g, 4.20 mmol) in DMF (21 mL) was added *N*-bromosuccinimide (NBS, 0.895 g, 5.03 mmol) at room temperature. The reaction mixture was stirred for 5 h, quenched by addition of water (10 mL), extracted with hexane (50 mL), washed with water (50 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane) to yield **3** (1.56 g, 3.24 mmol, 77%) as a yellow solid: mp 43–44 °C; IR (NaCl) 2957 cm^{-1} (C–H), 2926 cm^{-1} (C–H), 2858 cm^{-1} (C–H); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.86 (s, 1H, Ar*H*), 8.42 (d, *J*=8.7 Hz, 2H, Ar*H*), 7.49 (dd, *J*=8.7, 6.6 Hz, 2H, Ar*H*), 7.31 (d, *J*=6.6 Hz, 2H, Ar*H*), 3.13 (d, *J*=7.2 Hz, 4H, ArC*H*$_2$), 1.92 (sept, *J*=7.2 Hz, 2H, C*H*), 1.54–1.26 (m, 16H, C*H*$_2$), 0.92 (t, *J*=7.5 Hz, 6H, C*H*$_3$), 0.86 (t, *J*=7.2 Hz, 6H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 138.4 (*C*), 131.0 (*C*), 130.8 (*C*), 126.7 (*C*H), 126.6 (*C*), 126.3 (*C*H), 124.0 (*C*H), 120.0 (*C*H), 39.9 (*C*H), 38.4 (*C*H$_2$), 32.7 (*C*H$_2$), 32.6 (*C*H$_2$), 28.6 (*C*H$_2$), 25.7 (*C*H$_2$), 25.6 (*C*H$_2$), 23.1 (*C*H$_2$), 14.0 (*C*H$_3$), 10.5 (*C*H$_3$). Anal. Calcd for $C_{30}H_{41}Br$: C, 74.83; H, 8.58. Found: C, 75.15; H, 8.23.

4.2.3. Synthesis and characterization of ***4***. An oven-dried round-bottom flask was purged with nitrogen, charged with a solution of **3** (1.00 g, 2.08 mmol) in dry THF (14.0 mL), and cooled to −78 °C. To this solution were sequentially added *n*-butyl lithium (*n*-BuLi, 3.0 mL, 4.95 mmol, 1.65 M solution in hexane) and trimethyl borate ($B(OMe)_3$, 2.3 mL, 2.14 g, 20.6 mmol) dropwise via syringe at this temperature. This mixture was stirred for 30 min at −78 °C, warmed to room temperature. After stirring for additional 1.5 h, it was quenched by addition of 3% aqueous HCl (5.0 mL), extracted with ethyl acetate (40 mL), washed with water (40 mL), saturated aqueous $NaHCO_3$ (30 mL), and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 30:1) to give the boronic acid intermediate (0.500 g, 1.12 mmol, 54%) as a dark yellow oil: IR (NaCl) 3401 cm^{-1} (O–H), 2957 cm^{-1} (C–H), 2927 cm^{-1} (C–H), 2858 cm^{-1} (C–H); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.79 (s, 1H, Ar*H*), 7.69 (d, *J*=8.7 Hz, 2H, Ar*H*), 7.35 (dd, *J*=8.7, 6.6 Hz, 2H, Ar*H*), 7.30 (d, *J*=6.6 Hz, 2H, Ar*H*), 6.16 (s, 2H, O*H*), 3.12 (d, *J*=7.2 Hz, 4H, ArC*H*$_2$), 1.94 (sept, *J*=7.2 Hz, 2H, C*H*), 1.43–1.21 (m, 16H, C*H*$_2$), 0.95–0.85 (m, 12H, C*H*$_3$). To an argon-purged solution of this material (0.239 g, 0.535 mmol) and **1** (0.0549 g, 0.134 mmol) in a mixture of toluene/EtOH (2:1, 13 mL) were sequentially added sodium carbonate (Na_2CO_3, 2.7 mL, 8.10 mmol, 3.0 M aqueous solution) and tetrakis(triphenylphosphine)palladium ($Pd(PPh_3)_4$, 0.023 g, 0.020 mmol) at room temperature. The reaction mixture was heated under reflux for 4 h, cooled to room temperature, filtrated through a pad of Celite followed by successive washings with hexane (30 mL), and extracted with hexane (50 mL). The extract was washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 50:1) to give a mixture of TBS-protected and deprotected bisanthracenes (0.151 g). To a solution of this material (0.151 g) in THF (5.0 mL) at 0 °C was added tetra-*n*-butylammonium fluoride (TBAF, 0.29 mL, 0.290 mmol, 1.0 M THF solution). The reaction mixture was stirred at 0 °C for 3 h, quenched by addition of saturated aqueous $NaHCO_3$ (5.0 mL), extracted with hexane (50 mL), washed with water (50 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 10:1) to yield **4** (0.0892 g, 0.0950 mmol, 71%, for two steps) as a pale yellow solid: mp 54–59 °C; IR (NaCl) 3582 cm^{-1} (O–H), 2957 cm^{-1} (C–H), 2926 cm^{-1} (C–H), 2857 cm^{-1} (C–H); MS (LDI) *m*/*z* 939 (M^+), 940 (MH^+); HRMS (LDI) *m*/*z* calcd for $C_{68}H_{90}O_2$: 938.6941, found 938.6927; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (s, 2H, Ar*H*), 7.77 (d, *J*=8.4 Hz, 4H, Ar*H*), 7.50 (s, 2H, Ar*H*), 7.38 (dd, *J*=8.4, 6.6 Hz, 4H, Ar*H*), 7.29 (d, *J*=6.6 Hz, 4H, Ar*H*), 4.83 (d, *J*=5.9 Hz, 2H, ArC*H*$_2$), 3.16 (br s, 8H, ArC*H*$_2$), 2.50 (s, 3H, OC*H*$_3$), 1.98 (br s, 4H, C*H*), 1.75 (t, *J*=5.9 Hz, 1H, O*H*), 1.41–1.27 (m, 32H, C*H*$_2$), 0.96–0.82 (m, 24H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 157.3 (*C*), 138.2 (*C*), 136.2 (*C*), 134.5 (*C*), 133.1 (*C*), 131.6 (*C*), 130.6 (*C*), 130.2 (*C*H), 126.1 (*C*H), 125.2 (*C*H), 125.1 (*C*H), 120.0 (*C*H), 64.9 (*C*H$_2$), 60.5 (O*C*H$_3$), 39.8 (*C*H), 38.4 (*C*H$_2$), 32.7 (*C*H$_2$), 32.6 (*C*H$_2$), 28.7 (*C*H$_2$), 25.8 (*C*H$_2$), 25.7 (*C*H$_2$), 23.1 (*C*H$_2$), 14.0 (*C*H$_3$), 10.6 (*C*H$_3$).

4.2.4. Synthesis and characterization of ***5***. To a mixture of **4** (91.0 mg, 0.0969 mmol), carbon tetrabromide (CBr_4, 80.3 mg, 0.242 mmol), and triphenylphosphine (PPh_3, 63.5 mg, 0.242 mmol) was added THF (0.54 mL) at room temperature. The reaction mixture was stirred at this temperature for 12 h, quenched by addition of water (50 mL), extracted with hexane (50 mL), washed with MeOH (30 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 30:1) to yield **5** (92.0 mg, 0.0918 mmol, 95%) as a pale yellow solid: mp 85–90 °C; IR (NaCl) 2957 cm^{-1} (C–H), 2926 cm^{-1} (C–H), 2857 cm^{-1} (C–H); HRMS (LDI, M^+) *m*/*z* calcd for $C_{68}H_{89}BrO$: 1000.6097, found 1000.6126; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.93 (s, 2H, Ar*H*), 7.75 (d, *J*=8.7 Hz, 4H, Ar*H*), 7.55 (s, 2H, Ar*H*), 7.40 (dd, *J*=8.7, 6.6 Hz, 4H, Ar*H*), 7.30 (d, *J*=6.6 Hz, 4H, Ar*H*), 4.62 (s, 2H, ArC*H*$_2$), 3.17 (br s, 8H, ArC*H*$_2$), 2.49 (s, 3H, OC*H*$_3$), 1.98 (br s, 4H, C*H*), 1.41–1.27 (m, 32H, C*H*$_2$), 0.97–0.82 (m, 24H, C*H*$_3$); ^{13}C NMR

(75 MHz, $CDCl_3$) δ 157.9 (*C*), 138.2 (*C*), 133.9 (*C*), 133.8 (*C*), 133.3 (*C*), 133.1 (*C*), 130.5 (*C*), 130.3 (*C*H), 126.1 (*C*H), 125.4 (*C*H), 124.9 (*C*H), 119.9 (*C*H), 60.4 (O*C*H$_3$), 39.8 (*C*H), 38.5 (*C*H$_2$), 38.4 (*C*H$_2$), 33.1 (*C*H$_2$), 32.7 (*C*H$_2$), 28.7 (*C*H$_2$), 25.8 (*C*H$_2$), 23.1 (*C*H$_2$), 14.0 (*C*H$_3$), 10.6 (*C*H$_3$).

4.2.5. Synthesis and characterization of ***6***. To a solution of **5** (28.0 mg, 0.0279 mmol) and phthalimide (16.4 mg, 0.112 mmol) in DMF (0.56 mL) was added anhydrous potassium carbonate (K_2CO_3, 22.6 mg, 0.164 mmol) at room temperature. The reaction mixture was stirred for 24 h, quenched by addition of saturated aqueous NH_4Cl (1.5 mL), filtrated through a pad of Celite followed by successive washings with hexane (20 mL). The filtrate was extracted with hexane (50 mL), washed with water (50 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 10:1) to give the phthalimide intermediate (28.0 mg, 0.0262 mmol, 94%) as a pale yellow solid: mp 55–60 °C; IR (NaCl) 2959 cm^{-1} (C–H), 2928 cm^{-1} (C–H), 2858 cm^{-1} (C–H), 1772 cm^{-1} (C=O), 1714 cm^{-1} (C=O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 2H, Ar*H*), 7.80 (q, J=2.7 Hz, 2H, Ar*H*), 7.73 (d, J=8.7 Hz, 4H, Ar*H*), 7.66 (q, J=2.7 Hz, 2H, Ar*H*), 7.52 (s, 2H, Ar*H*), 7.36 (dd, J=8.7, 6.6 Hz, 4H, Ar*H*), 7.27 (d, J=6.6 Hz, 4H, Ar*H*), 5.01 (s, 2H, ArC*H*$_2$), 3.15 (br s, 8H, ArC*H*$_2$), 2.44 (s, 3H, OC*H*$_3$), 1.97 (br s, 4H, C*H*), 1.40–1.26 (m, 32H, C*H*$_2$), 0.96–0.82 (m, 24H, C*H*$_3$). To a solution of this material (43.0 mg, 0.0402 mmol) in THF (3.0 mL) was added hydrazine monohydrate ($(NH_2)_2 \cdot H_2O$, 103 mg, 3.21 mmol). The reaction mixture was heated under reflux for 4 h, cooled to room temperature, quenched by addition of water (50 mL), extracted with hexane (50 mL), washed with brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to yield **6** (37.0 mg, 0.0394 mmol, 98%) as a pale yellow solid: mp 35–40 °C; HRMS (LDI, M$^+$) m/z calcd for $C_{68}H_{91}NO$: 937.7101, found 937.7105; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.92 (s, 2H, Ar*H*), 7.78 (d, J=8.7 Hz, 4H, Ar*H*), 7.42 (s, 2H, Ar*H*), 7.38 (dd, J=8.7, 6.6 Hz, 4H, Ar*H*), 7.29 (d, J=6.6 Hz, 4H, Ar*H*), 4.00 (br s, 2H, ArC*H*$_2$), 3.16 (br s, 8H, ArC*H*$_2$), 2.50 (s, 3H, OC*H*$_3$), 1.97 (br s, 4H, C*H*), 1.60 (br s, 2H, N*H*$_2$), 1.40–1.26 (m, 32H, C*H*$_2$), 0.96–0.82 (m, 24H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 156.6 (*C*), 138.2 (*C*), 134.7 (*C*), 133.0 (*C*), 131.4 (*C*) 130.6 (*C*), 130.3 (*C*), 130.3 (*C*H), 126.1 (*C*H), 125.1 (*C*H), 119.7 (*C*H), 60.5 (O*C*H$_3$), 39.8 (*C*H), 39.7 (*C*H$_2$), 38.4 (*C*H$_2$), 32.7 (*C*H$_2$), 28.7 (*C*H$_2$), 25.8 (*C*H$_2$), 23.1 (*C*H$_2$), 23.1 (*C*H$_2$), 14.0 (*C*H$_3$), 10.6 (*C*H$_3$).

4.2.6. Synthesis and characterization of ***7***. To a solution of **6** (99.0 mg, 0.105 mmol) and methyl 3,5-dihydroxybenzoate (7.4 mg, 0.0440 mmol) in acetone (0.73 mL) was added anhydrous potassium carbonate (K_2CO_3, 30.0 mg, 0.217 mmol) and 18-crown-6 (10.0 mg, 0.0367 mmol) at room temperature. The reaction mixture was heated under reflux for 5 h, quenched by addition of saturated aqueous NH_4Cl (2.0 mL), extracted with hexane (50 mL), washed with water (100 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 30:1) to give the benzoate intermediate (69.0 mg, 0.0343 mmol, 78%): mp 98–103 °C; IR (NaCl) 2958 cm^{-1} (C–H), 2927 cm^{-1} (C–H), 2858 cm^{-1} (C–H), 1725 cm^{-1} (C=O), 1161 cm^{-1} (C–O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 4H, Ar*H*), 7.74 (d, J=8.7 Hz, 8H, Ar*H*), 7.56 (s, 4H, Ar*H*), 7.37–7.24 (m, 18H, Ar*H*), 6.78 (t, J=2.3 Hz, 1H, Ar*H*), 5.17 (s, 4H, OC*H*$_2$), 3.79 (s, 3H, OC*H*$_3$), 3.15 (d, J=6.9 Hz, 16H, ArC*H*$_2$), 2.47 (s, 6H, OC*H*$_3$), 1.97 (br s, 8H, C*H*), 1.39–1.26 (m, 64H, C*H*$_2$), 0.95–0.81 (m, 48H, C*H*$_3$). To a solution of this material (25.0 mg, 0.0124 mmol) in THF (2.0 mL) at 0 °C was added lithium aluminum hydride (LAH, 3.0 mg, 0.079 mmol) in small portions. The reaction mixture was stirred at 0 °C for 12 h, quenched by addition of water (0.5 mL) and 3% aqueous HCl (3.0 mL), filtrated through a pad of Celite followed by successive washings with hexane (30 mL), extracted with hexane (100 mL), washed with water (100 mL), saturated aqueous $NaHCO_3$ (50 mL), and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 10:1) to yield **7** (17.0 mg, 0.00857 mmol, 69%) as a pale yellow solid: mp 48–53 °C; IR (NaCl) 3444 cm^{-1} (O–H), 2958 cm^{-1} (C–H), 2927 cm^{-1} (C–H), 2858 cm^{-1} (C–H), 1159 cm^{-1} (C–O); HRMS (LDI, MNa$^+$) m/z calcd for $C_{143}H_{184}NaO_5$: 2004.4041, found 2004.4024; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 4H, Ar*H*), 7.75 (d, J=8.4 Hz, 8H, Ar*H*), 7.55 (s, 4H, Ar*H*), 7.35 (dd, J=8.4, 6.9 Hz, 8H, Ar*H*), 7.24 (d, J=6.9 Hz, 8H, Ar*H*), 6.60 (d, J=2.1 Hz, 2H, Ar*H*), 6.54 (t, J=2.1 Hz, 1H, Ar*H*), 5.14 (s, 4H, OC*H*$_2$), 4.55 (d, J=6.0 Hz, 2H, C*H*$_2$OH), 3.14 (d, J=6.9 Hz, 16H, ArC*H*$_2$), 2.47 (s, 6H, OC*H*$_3$), 1.97 (br s, 8H, C*H*), 1.46–1.26 (m, 65H, C*H*$_2$ and O*H*), 0.95–0.81 (m, 48H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.2 (*C*), 157.5 (*C*), 143.4 (*C*), 138.1 (*C*), 134.2 (*C*), 133.1 (*C*), 132.3 (*C*), 130.6 (*C*), 130.2 (*C*H), 129.1 (*C*H), 128.3 (*C*H), 126.1 (*C*H), 125.2 (*C*H), 119.8 (*C*H), 106.5 (*C*H), 101.7 (*C*H), 69.8 (*C*H$_2$), 65.2 (*C*H$_2$), 60.3 (O*C*H$_3$), 39.7 (*C*H), 38.4 (*C*H$_2$), 32.7 (*C*H$_2$), 28.7 (*C*H$_2$), 25.7 (*C*H$_2$), 23.1 (*C*H$_2$), 14.0 (*C*H$_3$), 10.6 (*C*H$_3$).

4.2.7. Synthesis and characterization of ***8***. To a mixture of **7** (17.0 mg, 0.00857 mmol), carbon tetrabromide (CBr_4, 13.5 mg, 0.0407 mmol), and triphenylphosphine (PPh_3, 10.6 mg, 0.0404 mmol) was added THF (0.38 mL) at room temperature. The reaction mixture was stirred at this temperature for 12 h, quenched by addition of water (30 mL), extracted with hexane (50 mL), washed with MeOH (10 mL) and brine (30 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 50:1) to yield **8** (16.0 mg, 0.00782 mmol, 91%) as a pale yellow solid: mp 64–69 °C; IR (NaCl) 2957 cm^{-1} (C–H), 2927 cm^{-1} (C–H), 2858 cm^{-1} (C–H), 1161 cm^{-1} (C–O); HRMS (MALDI, MNa$^+$) m/z calcd for $C_{143}H_{183}O_4NaBr$: 2066.3198, found 2066.3205; ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 4H, Ar*H*), 7.74 (d, J=8.7 Hz, 8H, Ar*H*), 7.54 (s, 4H, Ar*H*), 7.35 (dd, J=8.7, 6.9 Hz, 8H, Ar*H*), 7.24 (d, J=6.9 Hz, 8H, Ar*H*), 6.61 (d, J=2.1 Hz, 2H, Ar*H*), 6.54 (t, J=2.1 Hz, 1H, Ar*H*), 5.14 (s, 4H, OC*H*$_2$), 4.35 (s, 2H, C*H*$_2$Br), 3.14 (d, J=7.2 Hz, 16H, ArC*H*$_2$), 2.47 (s, 6H, OC*H*$_3$), 1.97 (br s, 8H, C*H*), 1.39–1.26 (m, 64H, C*H*$_2$), 0.95–0.81 (m, 48H, C*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 160.1 (*C*), 157.6 (*C*), 139.7 (*C*), 138.1 (*C*), 134.3 (*C*), 133.2 (*C*), 132.2 (*C*), 130.6 (*C*), 130.3 (*C*H), 126.1 (*C*H), 125.2 (*C*H), 125.1 (*C*H), 119.8 (*C*H), 100.6 (*C*H), 93.0 (*C*H), 69.9 (*C*H$_2$), 60.5 (*C*H$_2$), 39.8 (*C*H), 38.4 (*C*H$_2$), 32.7 (*C*H$_2$), 31.5 (*C*H$_2$), 28.7 (*C*H$_2$), 25.7 (*C*H$_2$), 23.1 (*C*H$_2$), 14.0 (*C*H$_3$), 10.6 (*C*H$_3$).

4.2.8. Synthesis and characterization of ***9***. To a solution of **8** (16.0 mg, 0.00782 mmol) and phthalimide (11.9 mg, 0.0809 mmol) in DMF (0.5 mL) was added anhydrous potassium carbonate (K_2CO_3, 17.6 mg, 0.127 mmol) at room temperature. The reaction mixture was stirred at this temperature for 24 h, quenched by addition of saturated aqueous NH_4Cl (1.0 mL), filtrated through a pad of Celite followed by successive washings with hexane (20 mL). The filtrate was extracted with hexane (50 mL), washed with water (50 mL) and brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (eluent: hexane/ethyl acetate, 15:1) to give the phthalimide intermediate (12.0 mg, 0.00568 mmol, 73%) as a pale yellow solid: mp 51–56 °C; IR (NaCl) 2957 cm^{-1} (C–H), 2927 cm^{-1} (C–H), 2858 cm^{-1} (C–H), 1718 cm^{-1} (C=O), 1162 cm^{-1} (C–O); ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 4H, Ar*H*), 7.77–7.74 (m, 10H, Ar*H*), 7.63 (q, J=3.0 Hz, 2H, Ar*H*), 7.54 (s, 4H, Ar*H*), 7.34 (dd, J=8.7, 6.9 Hz, 8H, Ar*H*), 7.23 (d, J=6.9 Hz, 8H, Ar*H*), 6.66 (d, J=2.1 Hz, 2H, Ar*H*), 6.52 (t, J=2.1 Hz, 1H, Ar*H*), 5.09 (s, 4H, OC*H*$_2$), 4.71 (s, 2H, ArC*H*$_2$), 3.14 (d, J=7.2 Hz, 16H, ArC*H*$_2$), 2.46 (s, 6H, OC*H*$_3$), 1.96 (br s, 8H, C*H*), 1.39–1.26 (m, 64H, C*H*$_2$), 0.95–0.81 (m, 48H, C*H*$_3$). To a solution of this material (20.0 mg, 0.00947 mmol) in THF (2.0 mL) was added hydrazine monohydrate ($(NH_2)_2 \cdot H_2O$, 103 mg, 3.21 mmol). The reaction mixture was heated under reflux for 4 h, cooled to room temperature, quenched by addition of water (50 mL), extracted with hexane (50 mL), washed with brine (20 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to yield **9** (15.0 mg, 0.00757 mmol, 80%) as a pale yellow solid: mp 31–36 °C; HRMS (MALDI, MNa^+) *m*/*z* calcd for $C_{143}H_{185}NaNO_4$: 2003.4213, found 2003.4202; ^1H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 4H, Ar*H*), 7.75 (d, *J*=8.7 Hz, 8H, Ar*H*), 7.55 (s, 4H, Ar*H*), 7.34 (dd, *J*=8.7, 6.6 Hz, 8H, Ar*H*), 7.24 (d, *J*=6.6 Hz, 8H, Ar*H*), 6.54 (d, *J*=2.1 Hz, 2H, Ar*H*), 6.50 (t, *J*=2.1 Hz, 1H, Ar*H*), 5.14 (s, 4H, OCH_2), 3.73 (br s, 2H, ArCH_2), 3.14 (d, *J*=6.9 Hz, 16H, ArCH_2), 2.47 (s, 6H, OCH_3), 1.97 (br s, 8H, C*H*), 1.64 (br s, 2H, NH_2), 1.39–1.26 (m, 64H, CH_2), 0.95–0.81 (m, 48H, CH_3).

4.2.9. Synthesis and characterization of ***12***. The synthesis of **12** was achieved by the following modified procedure of the previously reported methods.[19,23,24] To a bulk solid of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCA, 242 mg, 0.617 mmol) was added an aqueous solution of KOH (5%, 7.0 mL). The reaction mixture was heated at 90 °C with stirring for 6 h, whereupon saturated aqueous H_3PO_4 (10%, 5.1 mL) was added and it was heated for additional 1 h to form a brown precipitate. After cooling to room temperature, this precipitate was filtered under vacuum, washed with water (50 mL) and MeOH (30 mL), and dried in vacuo to give a solid material (244 mg). To an aqueous solution of this material (244 mg, in 10 mL of water) was added 2-aminoethanol (316 mg, 5.17 mmol) at 0 °C. After stirring at this temperature for 1 h, the reaction mixture was heated under reflux for additional 4 h, cooled to room temperature, quenched by addition of 10% aqueous HCl (15 mL) to give a brown precipitate, whereupon aqueous sulfuric acid (2 mL, 24.0 mmol, 12 M solution) was added. It was heated at 90 °C for 30 min and cooled to room temperature to give a dark brown precipitate. The precipitate was filtered under vacuum, washed with water (50 mL) and MeOH (20 mL), and dried in vacuo to yield **12** (26.9 mg, 0.0618 mmol, 10% for two steps): mp >400 °C; IR (KBr) 1763 cm^{-1} (C=O), 1730 cm^{-1} (C=O), 1692 cm^{-1} (C=O), 1655 cm^{-1} (C=O).

4.2.10. Synthesis and characterization of ***10*** *and* ***11***. The synthesis of **10** was achieved by the following typical procedure.[18b] To a solution of **6** (24.4 mg, 0.0260 mmol) in *N*-methyl pyrrolidinone (NMP, 0.75 mL) was added **12** (17.0 mg, 0.0390 mmol). The reaction mixture was heated at 100 °C with stirring for 35 h, cooled to room temperature, and quenched by addition of water (5 mL). The resulting dark purple precipitate was extracted with hexane (30 mL), washed with water (100 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo. Purification of the residue by flash column chromatography on silica gel ($CHCl_3$/MeOH=40:1) gave the perylenebisimide intermediate (20.0 mg, 0.0148 mmol, 57%) as a red-purple solid: mp 130–135 °C; IR (NaCl) 3495 cm^{-1} (O–H), 2958 cm^{-1} (C–H), 2926 cm^{-1} (C–H), 2857 cm^{-1} (C–H), 1694 cm^{-1} (C=O), 1652 cm^{-1} (C=O); ^1H NMR (300 MHz, $CDCl_3$) δ 8.82 (s, 2H, Ar*H*), 8.37 (m, 4H, Ar*H*), 8.13 (br s, 4H, Ar*H*), 7.77 (d, *J*=8.4 Hz, 4H, Ar*H*), 7.66 (s, 2H, Ar*H*), 7.31 (dd, *J*=8.4, 6.9 Hz, 4H, Ar*H*), 7.20 (d, *J*=6.9 Hz, 4H, Ar*H*), 5.56 (s, 2H, CH_2), 4.42 (t, *J*=4.8 Hz, 2H, CH_2), 4.02 (t, *J*=4.8 Hz, 2H, CH_2), 3.08 (d, *J*=6.6 Hz, 8H, ArCH_2), 2.40 (s, 3H, OCH_3), 1.91 (br s, 4H, C*H*), 1.39–1.26 (m, 33H, CH_2 and O*H*), 0.94–0.77 (m, 24H, CH_3). To a solution of this material (20.0 mg, 0.0148 mmol) in THF (1.5 mL) at 0 °C was added a THF solution of aluminum hydride (AlH_3, 1.48 mmol), which was prepared by stirring a solution of aluminum chloride ($AlCl_3$, 197 mg, 1.48 mmol) and lithium aluminum hydride ($LiAlH_4$, 56.2 mg, 1.48 mmol) in anhydrous THF (1.5 mL) at 0 °C for 1 h. The reaction mixture was stirred at room temperature for 4 h, quenched with water (0.5 mL) and 3% aqueous HCl (3 mL) at 0 °C, treated with aqueous NaOH (10 mL, 10.0 mmol, 1.0 M solution), and filtrated through a pad of Celite followed by successive washings with hexane (50 mL). The filtrate was extracted with hexane (50 mL), washed with water (100 mL) and brine (50 mL), dried over Na_2SO_4, filtered, and concentrated in vacuo to yield **10** (19.0 mg, 0.0146 mmol, 99%) as a yellow solid: mp 55 °C; HRMS (LDI, M^+) *m*/*z* calcd for $C_{94}H_{110}N_2O_2$: 1298.8567, found 1298.8609; ^1H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 2H, Ar*H*), 8.00 (d, *J*=6.6 Hz, 4H, Ar*H*), 7.81 (d, *J*=8.4 Hz, 4H, Ar*H*), 7.53 (s, 2H, Ar*H*), 7.40 (dd, *J*=8.4, 6.9 Hz, 4H, Ar*H*), 7.28 (d, *J*=6.9 Hz, 4H, Ar*H*), 7.16 (d, *J*=7.8 Hz, 4H, Ar*H*), 4.05 (s, 2H, CH_2), 3.99 (s, 4H, CH_2), 3.97 (s, 4H, CH_2), 3.78 (t, *J*=4.8 Hz, 2H, CH_2), 3.16 (br s, 8H, ArCH_2), 2.81 (t, *J*=4.8 Hz, 2H, CH_2), 2.53 (s, 3H, OCH_3), 1.97 (br s, 4H, C*H*), 1.40–1.26 (m, 33H, CH_2 and O*H*), 0.94–0.81 (m, 24H, CH_3). Following the above procedures with **9** (15.0 mg, 0.00757 mmol) and **12** (9.9 mg, 0.023 mmol) afforded the corresponding perylene bisimide (5.0 mg, 0.0021 mmol, 28%) as a red-purple solid: mp 175–180 °C; ^1H NMR (300 MHz, $CDCl_3$) δ 8.90 (s, 4H, Ar*H*), 8.42–8.36 (m, 4H, Ar*H*), 8.19 (br s, 4H, Ar*H*), 7.80 (d, *J*=8.4 Hz, 8H, Ar*H*), 7.60 (s, 4H, Ar*H*), 7.35 (dd, *J*=8.4, 6.9 Hz, 8H, Ar*H*), 7.24 (d, *J*=6.9 Hz, 8H, Ar*H*), 6.89 (br s, 2H, Ar*H*), 6.63 (br s, 1H, Ar*H*), 5.55 (s, 2H, ArCH_2), 5.26 (s, 4H, OCH_2), 4.39 (br s, 2H, CH_2), 4.04 (br s, 2H, CH_2), 3.13 (br s, 16H, ArCH_2), 2.44 (s, 6H, OCH_3), 1.96 (br s, 8H, C*H*), 1.36–1.25 (m, 65H, CH_2 and O*H*), 0.90–0.75 (m, 48H, CH_3). The AlH_3 reduction of this material (3.5 mg, 0.00146 mmol) provided **11** (3.4 mg, 0.00144 mmol, 99%) as a viscous yellow syrup: HRMS (MALDI, MH^+) *m*/*z* calcd for $C_{169}H_{205}N_2O_5$: 2342.5849, found 2342.5817; ^1H NMR (300 MHz, $CDCl_3$) δ 8.90 (br s, 4H, Ar*H*), 8.04 (br s, 4H, Ar*H*), 7.76 (br s, 8H, Ar*H*), 7.55 (s, 4H, Ar*H*), 7.36–7.30 (m, 16H, Ar*H*), 7.13 (br s, 4H, Ar*H*), 6.69 (br s, 3H, Ar*H*), 5.14 (br s, 4H, OCH_2), 3.92 (br s, 10H, CH_2), 3.64 (t, *J*=6.0 Hz, 2H, CH_2), 3.15 (br s, 16H, ArCH_2), 2.77 (br s, 2H, CH_2), 2.46 (s, 6H, OCH_3), 1.96 (br s, 8H, C*H*), 1.43–1.25 (m, 65H, CH_2 and O*H*), 0.90–0.83 (m, 48H, CH_3).

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Supplementary data

Absorption and fluorescence spectra for all the fluorophores and dendrimers in all the organic solvents tried. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2011.10.021.

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