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Synthesis and Two-Photon Absorption Properties of Star-Shaped Chromophores Derived from Functionalized Fluorene Units

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A set of small star-shaped chromophores composed of three fluorene-based congeners have been synthesized and shown experimentally to possess strong and widely dispersed twophoton absorptivities in the visible to near-IR region under the irradiation of femtosecond and nanosecond laser pulses. In addition, the number of electron-donating fluorenyl units incorporated in the final structure was closely connected to the molecular two-photon activities of these model com-

Introduction

A two-photon absorption (2PA) process occurs when a molecule is promoted from the ground state to an excited state through the simultaneous absorption of two photons. The theory of this nonlinear optical phenomenon was predicted by Maria Göppert-Mayer in 1931,^[1] and the experimental evidence for it came out about thirty years later, when scientists observed the upconverted emission from media under the irradiation of laser light with wavelengths far from the linear absorption bands of the studied media.^[2] In the past fifteen years, the availability of stable and high peak power lasers has triggered the momentum to explore two-photon technologies. Many potential applications based on 2PA in the emerging field of photonics and biophotonics have been proposed and explored including optical power-limiting applications, frequency upconverted lasing, 3D data storage, 3D microfabrication, nondestructive bioimaging and tracking, and two-photon-assisted photodynamic therapy.^[3] Organic compounds that exhibit a large 2PA within the desired spectral region are of use in these applications and, consequently, are in great demand. So far, it has been realized that a molecular 2PA is related

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pounds. Effective optical power attenuation and stabilization behaviors of these dye molecules in the nanosecond time domain were also investigated. The results indicate that such a structural motif could be useful in the molecular design of strong two-photon absorbing material systems for quick-responding and broadband optical suppressing-related applications, particularly for laser pulses with long durations in the near-IR region.

to a combination of several structural parameters such as intramolecular charge-transfer efficiency and the effective size of the π -conjugated domain within a molecule.^[4–10] Depending on the application, photophysical properties in addition to a strong molecular 2PA may also be required of designed molecules. For instance, to be utilized as an optical power limiter that operates in a nanosecond regime, compounds that have an extended excited-state lifetime may be beneficial to the apparent nonlinear absorption because of a two-photon-assisted excited-state absorption (2PA-assisted ESA),^[11] and, therefore, the effective optical power attenuation would be enhanced. In searching for the connection between structural parameters and nonlinear absorption properties in conjugated systems, we have been interested in exploring the influence of the arrangement of building units and the manner of substitution on the molecular 2PA, as we construct multibranched π frameworks. Herein, we present the synthesis of a new series of starshaped two-photon-active model chromophores 1-3, which are derived from functionalized fluorene moieties, as well as the initial investigations of their 2PA properties in the femtosecond and nanosecond time domains.

Results and Discussion

The chemical structures and synthetic routes for the studied model compounds are illustrated in Figure 1 and Schemes 1 and 2, respectively. This model compound set contains three multibranched congeners with the same generic structure, which has a nitrogen atom as the central point of ramification to connect three electron-donating branches of various sizes in their π framework. Compound

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1 is the smallest model chromophore, which uses (diphenylamino)fluorene moieties as the branches, whereas compound 2 utilizes three fluorene units to form the inner circle and incorporates six (diphenylamino)fluorene units at the peripheries. On the basis of the same concept of structural expansion, compound 3 represents the largest model chromophore and incorporates a total of nine fluorene units in the inner circles and twelve (diphenylamino)fluorene moieties at the peripheral positions. The molecular design of these chromophores originated from a simple attempt to tentatively construct a set of symmetrically-substituted π frameworks with various numbers of attached electron-donating units. Therefore, upon light excitation, the resulting fluorophores may possess a different extent of charge transfer/redistribution, which in turn may be connected to the molecular 2PA. Furthermore, it would be



Figure 1. Molecular structures of the studied model chromophores.

interesting to analyze the relationship between the molecular 2PA and the π electrons added during the enlargement of chromophore structure. Thus, we may elucidate either a



Scheme 1. Synthesis for the central and peripheral parts of the final model compounds.

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beneficial or deleterious arrangement of each structural unit. On the other hand, the pendent alkyl chains on all fluorenyl moieties in these model chromophores are expected to enhance the solubility in common organic solvents, and this is an important parameter to be considered in the molecular design from either the aspect of experiments or applications. The synthetic procedures for these model dye molecules are relatively straightforward and mainly involve consecutive functionalizations of the fluorene moiety and a Buchwald–Hartwig-type amination to prepare the key intermediates and the final model compounds (see Schemes 1 and 2). The syntheses for these key intermediates and the final model compounds are described in detail in the Exp. Sect.



Scheme 2. Synthetic procedures toward target model chromo-phores.

Figure 2 illustrates the linear absorption and fluorescence spectra of the studied dye molecules in solution phase using THF (tetrahydrofuran) as the solvent. The intense one-photon absorption (1PA) for these compounds was found at approximately 400 nm (with $\varepsilon_{\rm max} \approx 1.15 \times 10^5 \, {\rm cm}^{-1} {\rm M}^{-1}$ for 1, $\varepsilon_{\rm max} \approx 3.00 \times 10^5 \, {\rm cm}^{-1} {\rm M}^{-1}$ for 2, and $\varepsilon_{\rm max} \approx 6.12 \times 10^5 \, {\rm cm}^{-1} {\rm M}^{-1}$ for 3). The model chromophore solutions also exhibited a strong two-photon-excited upconverted emission of purple-blue in color, which was readily seen by the naked eye, even under the illumination of an unfocused femtosecond laser beam at a low intensity level ($\lambda \approx 790$ nm). Figure 3 illustrates the 2PA-induced fluorescence spectra of compounds 1–3, and each inset



Figure 2. (a) Linear absorption and (b) fluorescence spectra of compounds 1–3 in solution phase $(1 \times 10^{-6} \text{ M in THF})$.



Figure 3. Two-photon-excited fluorescence spectra of the studied model chromophores. Insets: logarithmic plots of the power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity of these compounds in THF.

curve in Figure 3 confirms that the 2PA process is the major cause, in all cases, for the detected upconverted emission. To investigate and compare the dispersion of the 2PA behavior of these dye molecules as a function of wavelength, we conducted the degenerate two-photon-excited fluorescence (2PEF) measurement in the near-IR regime (720–890 nm) using fluorescein (ca. 80 μ M; in NaOH solution, pH = 11) as the standard.^[12,13] Figure 4 shows the measured degenerate two-photon absorption spectra of these model compounds in THF, and the combined photophysical data are summarized in Table 1.



Figure 4. Measured degenerate two-photon absorption spectra of model chromophores 1–3 (1×10^{-4} M in THF) by 2PEF method (with experimental error about 15%).



Using compound 1 as a reference point, Figure 4 shows that all of these model chromophores not only exhibit nearly identical dispersion patterns of their two-photon activities, but also show an ascending overall magnitude of the 2PA from compounds 1 to 3. This feature indicates that the gradual expansion of the π domain by attaching additional electron-donating units to the original trigonal scaffold in compound 1 enhances the molecular 2PA without shifting the major 2PA band of the dye system. Molecules with this property could be very beneficial to particular applications, when large multiphoton absorptivities within a specific spectral region are required. Furthermore, the observed increasing two-photon absorptivities within the short wavelength region implies that for these compounds the most accessible two-photon states are higher in energy than those of the lowest allowed one-photon states. Similar trends have been observed and reported previously for other chromophore systems.^[5a-5f,5i-5k,6a-6c,7d,8b,9c,10a-10f] Additionally, for these model chromophores, analyzing the relative increment of the observed overall magnitude of the 2PA within the studied spectral region has revealed that extending the size of the π system from compounds 1 to 2 leads to a larger promotion of the overall molecular 2PA. However, further expansion of the π domain from compounds 2 to 3 results in a comparatively smaller enhancement of the overall 2PA. This feature indeed parallels the trend of the relative incremental increase in the effective π electron numbers^[14] of these model chromophores (see Figure 4 and Table 1), which indicates that during the molecular structure expansion from compounds 2 to 3, the simultaneously added π electrons are not being utilized in their full potential to promote a molecular 2PA. Therefore, monotonically increasing the number of fluorene units and using tertiary nitrogen atoms as the linkages in a molecule, as demonstrated in this work, may not be the best methodology to enhance the molecular 2PA at the same level in this dye system.

It is notable that the excited-state lifetimes of the studied model chromophores are in the nanosecond range, which implies that a significant excited-state population is retained and, consequently, excited-state absorptions are possessed during excitation by longer laser pulses. This is particularly desirable with regards to optical power-limiting applica-

Table 1. Photophysical properties of the studied model compounds 1-3 in solution phase.

	$\lambda_{\rm max}^{\rm abs}/{ m nm}^{\rm [b]}$	$\log \varepsilon_{\max}$	$\lambda_{\max}^{em}/nm^{[c]}$	$\Phi_{\scriptscriptstyle F}{}^{[d]}$	$ au_{\mathrm{1PA-FL}}/\mathrm{ns}$ [e]	$\delta^{\text{max}}_2/\text{GM}^{[f]}$	$N_{\pi}^{\mathrm{eff}\;[\mathrm{g}]}$	$\delta_2^{ ext{max}} ig/ N_\pi^{ ext{eff}}$
1	399	1.15	426	0.53	1.62	~50	25.5	~1.96
2	401	3.00	437	0.64	1.21	~380	41.6	~9.13
3	403	6.12	440	0.62	1.17	~1320	63.1	~20.9

^[a]Concentration was 1×10^{-6} M and 1×10^{-4} M for 1PA-related and 2PA-related measurements, respectively.^[b]One-photon absorption maximum.^[c]1PA-induced fluorescence emission maximum.^[d]Fluorescence quantum efficiency.^[e]1PA-induced fluorescence lifetime. ^[f]Maximum 2PA cross-section value (with experimental error ca. ±15%); 1GM = 1×10^{-50} cm⁴ s/photon-molecule.^[g]Effective π -electron number.

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tions in the nanosecond regime on the basis of 2PA-induced excited-state absorptions (2PA-induced ESA), because the effective three-photon absorption coefficient increases significantly with the excited-state lifetime.^[11f,11g] For this investigation, to study the effective power-limiting performance based on these model compounds, we utilized nanosecond laser pulses at 720 nm as the representative probing wavelength for the demonstration, because these model chromophores possess a comparatively stronger 2PA and are theoretically expected to show better power-limiting properties at this wavelength. In our experiment, the nonlinear absorbing medium was a 1 cm path length solution of the studied dye in THF with concentration of 0.01 M. A tunable nanosecond laser system (an integrated Q-switched Nd:YAG laser and OPO NT 342/3 from Ekspla) was employed as an excitation laser light source to provide ca. 6 ns laser pulses with a controlled average pulse energy in the range from ca. 0.02 to ca. 2 mJ and repetition rate of 10 Hz. The laser beam was slightly focused onto the center of the sample solution to obtain a nearly uniform laser beam radius within the whole cell path length, and the transmitted laser beam from the sample cell was detected by an optical power (energy) meter with a large detection area of ca. 25 mm in diameter. Figure 5 illustrates the measured power attenuation performance based on these chromophore solutions at ca. 720 nm. In this set of model compounds, compound 3 displays a superior power restriction property at 720 nm in comparison to the other two analogues, and this initial finding demonstrates the potential of using this model fluorophore for broadband power-suppressing-related applications in the nanosecond regime.



Figure 5. Measured optical power-attenuation curves based on the sample solutions of compounds 1-3 under the excitation of nanose-cond laser pulses at ca. 720 nm.

On the other hand, the output/input curve shown in Figure 5 represents a characteristic type of optical control that is ideal for use in optical power (or intensity) stabilization. The principle of this type of optical stabilization is based on the fact that a huge magnitude change in the input signal leads to only a small variation of output level.^[15] This means that a larger input power (or intensity) fluctuation leads to a much smaller output fluctuation by passing through a nonlinear absorptive medium such as the solution of model chromophore 3. The experimental results for the optical stabilization study based on the solution of compound 3 are shown in Figure 6. The curves in parts a and b of this graphic are the instantaneous pulse energy changes in the input and output laser pulses at 720 nm, respectively. For the purpose of comparison, the average levels for both the input and output signals were normalized to the same value. The input pulses possess a relatively larger energy fluctuation as shown in Figure 6 (a), and after passing through the solution of compound 3, a reduced fluctuation in the pulse energy is observed for the output signal as illustrated in Figure 6 (b).



Figure 6. (a) Measured instantaneous pulse energy fluctuations in the input laser pulses and (b) measured instantaneous pulse energy fluctuations in the output laser pulses. The repetition rate of the laser pulses was 10 Hz, and the average input pulse energy level was ca. 0.7 mJ.

Conclusions

In summary, we have synthesized a new multipolar set of chromophores composed of three analogues with gradually enlarged star-shaped skeletons containing functionalized fluorene moieties. The initial experimental results indicate that these model fluorophores manifest strong and widely dispersed two-photon absorptivities in the near IR-region. Tentative analysis of this model compound system for the correlation between molecular structure and the observed



overall 2PA behavior reveals that consecutively expanding the size of π domain has a positive contribution on the enhancement of the 2PA. However, the first step of the structural expansion (from 1 to 2) offers a larger increment of change in the overall molecular 2PA in comparison to the second step of expansion in the π framework (from 2 to 3). This resembles the trend in the incremental increase in effective π electron numbers upon the molecular size enlargement. We also found that these model chromophores possess a strong nonlinear attenuation under the irradiation of laser pulses working in the nanosecond regime, which indicates that these compounds may have strong two-photon-assisted excited state absorptions within the studied spectral region. The effective optical power-limiting/stabilization behaviors of these dendritic fluorophores also show that such dye molecules are potential materials for broadband and quick-responding optical limiters/stabilizers against laser lights with longer pulses.

Experimental Section

General Methods: All commercially available reagents for the preparation of the intermediates and targeted chromophores were obtained from Aldrich Chemical Co. and, unless stated otherwise, were used as received. THF was distilled from sodium benzophenone ketyl. ¹H and ¹³C NMR spectroscopic data were recorded with either a 200 or 300 MHz spectrometer and were referenced to TMS or the residual CHCl₃. For the NMR signal assignments, the representative numbering schemes for the carbon and hydrogen atoms in each intermediate and model chromophore are systematized and illustrated in the Supporting Information. High resolution mass spectroscopy was conducted with a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS spectra were obtained with a Voyager DE-PRO mass spectrometer (Applied Biosystem, Houston, USA). For the syntheses of the key intermediates and the targeted model compounds, a series of functionalization steps starting from purchased compound 4 were conducted.

2,7-Dibromo-9,9-dihexyl-9H-fluorene (5): Fluorene (4, 30 g, 0.18 mol) and zinc chloride (28.3 g, 0.21 mol) were dissolved in acetic acid (200 mL), and then benzyltrimethylammonium tribromide (BTMABr₃, 73.8 g, 0.189 mol) was added. The resulting solution was heated at reflux and stirred for 6 h. After the completion of reaction, NaHSO3 (aqueous) was added to neutralize the excess amount of BTMABr₃. The mixture was extracted with ethyl acetate (300 mL) and then washed with brine (2×300 mL). The organic layer was filtered and dried with MgSO₄. After filtration, the solvent was removed in vacuo. The crude product was recrystallized from ethyl acetate (EA)/methanol to afford the desired product (50.3 g, 86%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.623–7.620 (d, J = 0.9 Hz, 2 H, H^F), 7.560–7.533 (d, J = 8.1 Hz, 2 H, H^C), 7.481–7.450 (dd, $J_1 = 0.9$ Hz, $J_2 = 8.1$ Hz, 2 H, H^B), 3.802 (s, 2 H, NH₂) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 144.68 (C^E), 139.56 (C^D), 130.02 (C^F), 128.17 (C^C), 121.07 (C^B), 120.84 (C^A), 36.45 (C^a, sp³-hybridized carbon) ppm. HRMS (FAB): calcd. for $C_{13}H_8Br_2$ [M]⁺ 321.8993; found 321.8994 $[(^{79}Br)(^{79}Br)M]^+$, 323.8980 $[(^{79}Br)(^{81}Br)M]^+$, 325.8968 $[(^{81}Br)(^{81}Br) M^{+}$.

2,7-Dibromo-9,9-dihexyl-9H-fluorene (6): Compound **5** (50.0 g, 0.2 mol) and NaOtBu (76.9 g, 0.8 mol) were combined with THF

(200 mL) in a 500 mL three-neck flask. The resulting solution was stirred and heated at reflux for 1 h. The entire system was then cooled to room temp., and *n*-hexyl bromide (86.32 g, 0.52 mol) was added. The reaction mixture was stirred and heated at reflux overnight. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate and then washed with brine $(2\times)$. The combined organic layers were dried with anhydrous MgSO4 and filtered, and then the solvent was removed by evaporation. The crude product was purified by column chromatography on silica gel (hexane) to afford the desired product (66.1 g, 87%) as a white solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.55–7.50 (d, J = 1.5 Hz, 2 H, H^F), 7.502–7.501 (d, J = 8.4 Hz, 2 H, H^C), 7.46–7.42 (dd, J_1 = 1.5 Hz, J_2 = 8.4 Hz, 2 H, H^B), 1.937–1.882 (m, 4 H, H^b), 1.133– 1.032 (m, 12 H, H^e, H^d, H^c), 0.799-0.753 (t, 6 H, H^g), 0.631-0.602 (m, 4 H, H^f) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 152.50 (C^E), 139.01 (C^D), 130.12 (C^F), 126.15 (C^C), 121.47 (C^A), 121.05 (C^B), 55.63 (C^a), 40.15 (C^b), 31.40 (C^e), 29.53 (C^d), 23.61 (C^c), 22.53 (C^f), 13.95 (C^g) ppm. HRMS (FAB): calcd. for $C_{25}H_{32}Br_2$ [M]⁺ 490.0871; found 490.0870 [(⁷⁹Br)(⁷⁹Br)M]⁺, 492.0866 [(⁷⁹Br)(⁸¹Br)- $M]^+$, 494.0850 [(⁸¹Br)(⁸¹Br)M]⁺.

7-Bromo-9,9-dihexyl-N,N-diphenyl-9H-fluoren-2-amine (7): A mixture of compound 6 (50 g, 0.1015 mol), diphenylamine (18.9 g, 0.1118 mol), $Pd_2(dba)_3$ [0.93 g, 1.03 mmol, (dba = dibenzylideneacetone)], 2,2'-bis(diphenylphosphanyl)-1,1'-binaphthyl (BINAP, 1.895 g, 3.05 mmol), NaOtBu (13.65 g, 0.1421 mol), and toluene (330 mL) was stirred and heated at 80 °C under nitrogen for 12 h. The mixture was cooled to room temp. and then extracted with brine/EA. The organic extract was dried and then concentrated by a rotary evaporator. The residual brown oil (59 g) was transferred to a column with silica gel (600 g, hexane) to afford the desired compound 7 (31.78 g, 54%). ¹H NMR (300 MHz, CDCl₃): δ = 7.45–7.42 (d, J = 8.1 Hz, 1 H, H³), 7.418–7.368 (m, 3 H, H², H⁸, H¹¹), 7.230–7.178 (m, 3 H, H⁹, H¹⁶), 7.128–7.083 (m, 5 H), 7.025– 6.940 (m, 4 H, H¹⁴), 1.86–1.80 (m, 4 H, H^b), 1.15–1.05 (m, 12 H, H^{c} , H^{d} , H^{e}), 0.81–0.76 (t, J = 6.6 Hz, 6 H, H^{g}), 0.69–0.66 (m, 4 H, H^f) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 152.76 (C⁵), 151.67 (C¹²), 147.82 (C¹³), 147.49 (C¹⁰), 139.87 (C⁴), 135.00 (C⁷), 129.88 (C⁶), 129.13 (C¹⁵), 125.84 (C³), 123.84 (C¹⁴), 123.39 (C⁸), 122.58 (C^{16}) , 120.43 (C^2) , 120.35 (C^1) , 120.16 (C^{11}) , 118.99 (C^9) , 55.25 (Ca), 40.10 (Cb), 31.44 (Ce), 29.51 (Cd), 23.66 (Cc), 22.50 (Cf), 14.03 (C^g) ppm. HRMS (FAB): calcd. for C₃₇H₄₂BrN [M]⁺ 579.2501; found 579.2501 [(79Br)M]+, 581.2507 [(81Br)M]+.

9,9-Dihexvl-N², N²-diphenvl-9H-fluorene-2,7-diamine (8): Compound 7 (20 g, 0.0344 mol), CuI (8.2 g, 0.0344 mmol), and potassium phthalimide (7.95 g, 0.0344 mmol) were combined with dimethylacetamide (DMAc, 400 mL) in a 1000 mL three-neck flask, and the resulting mixture was heated at reflux and stirred overnight. After completion of reaction, the DMAc was removed in vacuo first, and the resulting mixture was extracted $(2\times)$ with a mixture of ethyl acetate (250 mL)/brine (250 mL)/aqueous NH₄OH (100 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated in vacuo to obtain a dark yellow oil. To this crude product were added hydrazine hydrate (1.25 g, 21.5 mmol) and methanol (100 mL), and the resulting solution was heated at reflux and stirred for 6 h. After the completion of reaction, the solvent was removed in vacuo, and the reaction mixture was filtered to remove the white impurities. The filtrate was then concentrated, and the resulting residue was purified by a short silica gel column (EA/hexane, 1:6) to obtain the target compound (11.6 g, 65%) as a yellow oil. ¹H NMR (300 MHz, CDCl₃): $\delta =$ 7.438-7.386 (m, 2 H, H³, H⁸), 7.326-7.196 (m, 4 H, H¹⁴, H¹¹), 7.114-7.06 (m, 5 H, H², H¹¹), 6.991-6.944 (m, 3 H, H⁶, H¹⁶), 6.616.59 (m, 2 H, H², H⁹), 3.728 (s, 2 H, NH₂), 1.817–1.763 (m, 4 H, H^b), 1.116–1.049 (m, 12 H, H^c, H^d, H^e), 0.863–0.795 (t, J = 6.6 Hz, 6 H, H^g), 0.64 (m, 4 H, H^f) ppm. ¹³C NMR (300 MHz, CDCl₃): $\delta = 152.56$ (C¹²), 151.14 (C⁵), 148.11 (C¹³), 145.42 (C¹⁰), 145.38 (C¹), 137.26 (C⁷), 132.24 (C⁴), 129.01 (C¹⁵), 124.07 (C¹), 123.26 (C¹⁶), 121.97 (C¹⁴), 119.99 (C⁶), 119.94 (C⁹), 118.95 (C⁸), 113.92 (C²), 109.76 (C³), 54.77 (C^a), 40.48 (C^b), 31.53 (C^e), 29.65 (C^d), 23.69 (C^c), 22.56 (C^f), 14.05 (C^g) ppm. HRMS (FAB): calcd. for C₃₇H₄₄N₂ [M + H]⁺ 516.3504; found 516.3505.

9,9-Dihexyl-9H-fluorene (9): Fluorene (4, 15.0 g, 0.09 mol), potassium iodide (14.9 mg, 0.9 mmol), and NaOtBu (34.6 g, 0.36 mol) were combined with THF (200 mL) in a 500 mL three-neck flask. The resulting mixture was stirred and heated at reflux for 1 h. The entire system was then cooled to room temp., and n-hexyl bromide (38.8 g, 0.23 mol) was added. The mixture was stirred and heated at reflux overnight. After cooling to room temperature, the reaction mixture was diluted with ethyl acetate (250 mL), and the resulting solution was washed with brine $(2 \times 250 \text{ mL})$. The organic layer was dried with anhydrous MgSO4 and filtered, and the solvent was removed in vacuo. The crude product was then purified by column chromatography on silica gel (hexane) to afford the desired product (17.4 g, 60%) as a pale yellow liquid. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.709 - 7.678$ (m, 2 H, H^F), 7.350 - 7.234 (m, 6 H, H^A, H^B, H^C), 1.979-1.924 (m, 4 H, H^b), 1.110-1.015, (m, 12 H, H^c, H^d, H^e), 0.774-0.728 (t, J = 6.6 Hz, 6 H, H^g), 0.629-0.607 (m, 4 H, H^f) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 150.63 (C^E), 1141.05 (C^D), 126.94 (C^F), 126.63 (C^C), 122.78 (C^B), 119.59 (C^A), 54.95 (C^a), 40.38 (C^b), 31.48 (Ce), 29.71 (Cd), 23.68 (Cc), 22.58 (Cf), 14.01 (Cg) ppm. HRMS (FAB): calcd. for C₂₅H₃₄ [M]⁺ 334.2661; found 334.2665.

9,9-Dihexyl-2-nitro-9*H*-fluorene (10): Compound 9 (15 g. 0.015 mol) was dissolved in acetic acid (200 mL). The resulting solution was cooled to 10 °C over 10 min, and then nitric acid (15 mL, 0.045 mmol) was added dropwise. After the addition, the resulting solution was stirred at 10 °C for 15 min. NaOH (1 м aqueous solution, 100 mL) was added to neutralized the excess amount of nitric acid. The mixture was diluted with ethyl acetate (200 mL), and the resulting solution was washed with brine (2×200 mL). The organic layer was dried with anhydrous MgSO₄ and then filtered, and the solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (hexane/dichloromethane, 10:1) to afford the desired product (11.11 g, 71%) as a pale yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 8.280–8.245 (dd, J₁) = 2.1 Hz, J_2 = 8.4 Hz, 1 H, H^E), 8.206–8.199 (d, J = 2.1 Hz, 1 H, H^{F}) 7.807–7.779 (d, J = 8.4 Hz, 1 H, H^{C}) 7.798–7.772 (m, 1 H, H^H), 7.440–7.368 (m, 3 H, H^I, H^J, H^K), 1979–1.924 (m, 4 H, H^b), 1.110-1.015, (m, 12 H, H^c, H^d, H^e), 0.774-0.727 (t, 6 H, H^g), 0.629-0.607 (m, 4 H, H^f) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 152.17 (C^D), 151.84 (C^L), 147.55 (C^A), 147.00 (C^D), 138.60 (C^F), 129.16 (C^C), 127.27 (C^K), 123.15(C^H), 123.07 (C^J), 121.09 (C^I), 119.67 (C^F), 118.09 (C^B), 55.54 (C^a), 39.97 (C^b), 31.33 (C^e), 29.44 (C^d), 23.60 (C^c), 22.43 (C^f), 13.86 (C^g) ppm. HRMS (FAB): calcd. for $C_{25}H_{34}O_2N [M + H]^+$ 380.2590; found 380.2589.

2-Bromo-9,9-dihexyl-7-nitro-9*H***-fluorene (11):** Compound **10** (11 g, 0.029 mol) and zinc chloride (9.09 g, 0.067 mol) were combined with acetic acid (150 mL) in a 500 mL three-neck flask, and then BTMABr₃ (23.8 g, 0.061 mmol) was added. The resulting mixture was heated at reflux and stirred for 6 h. After completion of reaction, NaHSO₃ (aqueous solution, 200 mL) was added to quench the excess amount of BTMABr₃. The mixture was extracted with ethyl acetate (200 mL) and washed with brine (2×200 mL). The organic layer was dried with MgSO₄ and then filtered, and the solvent was removed by evaporation. The crude product was purified

by column chromatography on silica gel (hexane/dichloromethane, 10:1) to afford the desired product (11.96 g, 90%) as a pale yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 8.300–8.266 (dd, J_1 = 2.1 Hz, J_2 = 8.1 Hz, 1 H, H^B), 8.241–8.234 (d, J = 2.1 Hz, 1 H, H^F,) 7.809–7.782 (d, J = 8.1 Hz, 1 H, H^C) 7.683–7.656 (d, J = 8.1 Hz, 1 H, H^H), 7.575–7.569 (d, J = 1.8 Hz, 1 H, H^K) 7.555–7.523 (dd, J_1 = 1.8 Hz, J_2 = 8.1 Hz, 1 H, H^I), 2.1–1.8 (m, 4 H, H^b), 1.2–0.9 (m, 12 H, H^c, H^d, H^e), 0.8–0.7 (t, 6 H, H^g), 0.7–0.5 (m, 4 H, H^f) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 154.28 (C^A), 151.51 (C^E), 147.33 (C^L), 146.33 (C^D), 137.64 (C^G), 130.62 (C^C), 126.47 (C^F), 123.60 (C^K), 123.31 (C^H), 122.38 (C^B), 119.86 (C^J), 118.18 (H^I), 54.99 (C^a), 40.45 (C^b), 31.45 (C^e), 29.59 (C^d), 23.51 (C^c), 22.50, (C^f), 13.97 (C^g) ppm. HRMS (FAB): calcd. for C₂₅H₃₄O₂N [M + H]⁺ 458.1695; found 458.1690.

7-Bromo-9,9-dihexyl-9H-fluoren-2-amine (12): Compound 11 (3 g, 6.54 mmol) was dissolved in ethyl acetate (40 mL), and then SnCl₂·2H₂O (14.78 g, 65.4 mmol) was added. The mixture was heated at reflux and stirred for 6 h. After completion of reaction, NaHCO₃ (aqueous solution, 200 mL) was added to quench the excess amount of SnCl₂·2H₂O. The mixture was diluted with ethyl acetate (200 mL), and the resulting solution was washed with brine $(2 \times 200 \text{ mL})$. The organic layer was dried with MgSO₄ and then filtered. The solvent was removed by evaporation. The crude product was purified by column chromatography on silica gel (hexane/ EA, 8:1) to afford the desired product (1.99 g, 71%) as a pale yellow solid. ¹H NMR (300 MHz, CDCl₃): δ = 7.418–7.359 (m, 4 H, H^C, H^I, H^K), 6.606–6.583 (m, 2 H, H^B, H^F), 3.654 (s, 2 H, NH₂), 1.890-1.827 (m, 4 H, H^b), 1.2-0.9 (m, 12 H, H^c, H^d, H^e), 0.8-0.7 (t, J = 6.6 Hz, 6 H, H^g), 0.7–0.5 (m, 4 H, H^f) ppm. ¹³C NMR $(75 \text{ MHz}, \text{CDCl}_3)$: $\delta = 52.19 (\text{C}^{\text{E}}), 151.97 (\text{C}^{\text{A}}), 146.28 (\text{C}^{\text{L}}), 131.10$ (C^D), 129.56 (C^G), 125.68 (C^C), 120.52 (C^K), 119.54 (C^J), 118.90 (C^I), 113.94 (C^F), 109.43 (C^B), 54.99 (C^a), 40.46 (C^b), 31.42 (C^e), 29.62 (C^d), 23.56 (C^c), 22.53, (C^f), 13.94 (C^g) ppm. HRMS (FAB): calcd. for C₂₅H₃₄BrN [M + H]⁺ 428.4482; found 428.4361.

2-Bromo-9,9-dihexyl-7-iodo-9H-fluorene (13): A mixture of compound 12 (7 g, 16.3 mmol), HCl (12 N solution, 120 mL), water (480 mL), and NaNO₂ (2.24 g, 0.033 mol) in a 1000 mL three-neck round-bottom flask was stirred at 0 °C for 1 h. A solution of potassium iodide (10.8 g, 65.2 mmol) in water (30 mL) was added, and then the entire system was stirred at room temperature overnight. After completion of reaction, a saturated aqueous solution of NaHSO₃ (100 mL) was added, and the resulting mixture was extracted with ethyl acetate (180 mL) and washed with brine $(2 \times 100 \text{ mL})$. The organic phase was dried with anhydrous MgSO₄, and the solvent was removed in vacuo. The crude product was then purified by column chromatography on silica gel (hexane) to afford the desired product (4.48 g, 51%) as a white solid. ¹H NMR (300 MHz, CDCl₃): 7.65-7.63 (m, 2 H), 7.52-7.50 (m, 1 H), 7.45-7.38 (m, 3 H), 1.93-1.87 (m, 4 H), 1.15-1.03 (m, 12 H), 0.80-0.75 (m, 6 H), 0.60–0.53 (m, 4 H) ppm. 13 C NMR (75 MHz, CDCl₃): δ $= 152.56 (C^{L}), 152.20 (C^{E}), 139.54 (C^{G}), 138.98 (C^{D}), 135.95 (C^{K}),$ 131.96 (C^F), 130.05 (C^H), 126.03 (C^C), 121.56 (C^J), 121.34 (C^I), 121.05 (C^B), 93.04 (C^A), 55.48 (C^a), 40.0 (C^b), 31.34 (C^e), 29.50 (C^d), 23.57 (C^b), 22.5 (C^f), 13.9 (C^g) ppm. HRMS (FAB): calcd. for $C_{25}H_{32}BrI [M + H]^+ 428.4482$; found 428.4361.

Tris(7-bromo-9,9-dihexyl-9*H*-fluoren-2-yl)amine (14): A mixture of compound 12 (1.30 g, 4.11 mmol), compound 13 (3.85 g, 9.02 mmol), CuI (380 mg, 2.00 mmol), 1,10-phenanthroline (360 mg, 2.00 mmol), and KOH (2.30 g, 40.99 mmol) in *o*-xylene (10 mL) was added to a 250 mL three-neck flask, and the resulting mixture was heated at 130 °C for 24 h under argon. The solution was cooled to room temp. and then extracted (3×) with a mixture



of EA (100 mL)/brine (100 mL)/NH₄OH (50 mL). The combined organic layers were dried with anhydrous MgSO₄. The solvent was removed in vacuo by a rotary evaporator. The resulting residue was purified by column chromatography on silica gel (hexane/CH₂Cl₂, 15:1) to provide compound 14 (2.14 g, 41.4%) as a yellow solid. 1 H NMR (300 MHz, CDCl₃): δ = 7.520–7.469 (d, J = 8.4 Hz, 3 H, H^C), 7.479–7.451 (d, J = 8, 4 Hz, 3 H, H^H) 7.469–7.418 (m, 6 H, H^{I} , H^{K}) 7.220–7.213 (d, J = 2.1 Hz, 3 H, H^{F}) 7.023–6.989 (dd, J_{1} = 2.1 Hz, J₂ = 8.1 Hz, 3 H) 1.941–1.789 (m, 12 H, H^b), 1.171–1.076 (m, 36 H, H^e, H^d, H^c), 0.859-0.906 (t, J = 6.6 Hz, 18 H, H^g), 0.721-0.597 (m, 12 H, H^f) ppm. ¹³C NMR (75 MHz, CDCl₃): δ = 152.61 (C^L), 151.67 (C^E), 147.18 (C^A), 139.99 (C^G), 135.04 (C^D), 129.94 (C^K), 125.98 (C^H), 123.02 (C^I), 120.47 (C^C), 120.35 (C^F), 120.19 (C^J), 118.04 (C^B), 55.36 (C^a), 40.24 (C^b), 31.63 (C^e), 29.64 (C^d), 23.83 (C^c), 22.59 (C^f), 14.07 (C^g) ppm. HRMS (FAB): calcd. for $C_{75}H_{96}Br_3N [M + H]^+$ 1247.5093; found 1247.6011.

N²-[7-(Diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl]-9,9-dihexyl- N^7 , N^7 -diphenyl-9*H*-fluorene-2, 7-diamine (15): Compound 7 (15 g, 29 mmol), compound 8 (16.9 g, 29 mmol), and NaOtBu (3.3 g) were first combined with dry toluene (100 mL) in a 500 mL threeneck flask, and to this were quickly added Pd₂(dba)₃ (133 mg, 0.145 mol) and P(tBu)₃ (59 mg, 0.29 mmol). The resulting mixture was stirred and heated at reflux for 4 h under argon. After completion of reaction, the entire system was cooled to room temp. and diluted with EA (200 mL). The resulting mixture was washed with brine $(2 \times 200 \text{ mL})$. The organic layer was collected and dried with MgSO₄. After filtration, the solvent was removed by rotary evaporation, and the crude residue was purified by column chromatography (THF/hexane, 1:20) to obtain 15 (21.1 g, 69%) as a brown solid. ¹H NMR (300 MHz, [D₆]acetone): δ = 7.631–7.604 (d, J = 8.1 Hz, 2 H, H⁸), 7.613–7.586 (d, J = 8.1 Hz, 2H, H³), 7.319–7.313 $(d, J = 1.8 \text{ Hz}, 2 \text{ H}, \text{H}^{11}), 7.301-7.248 \text{ (m}, 8 \text{ H}, \text{H}^{15}), 7.154-7.148$ (d, J = 1.8 Hz, 2 H, H⁶), 7.089–7.033 (m, 8 H, H¹⁴), 7.008–6.964 (m, 8 H, H¹⁶, H³, H⁶), 1.963–1.889 (m, 8 H, H^b), 1.203–1.117 (m, 24 H, H^c, H^d, H^e), 0.820–0.774 (t, J = 6.6 Hz, 12 H, H^g), 0.744– 0.720 (m, 8 H, H^f) ppm. ¹³C NMR (75 MHz, [D₆]acetone): δ = 52.71 (C¹²), 152.22 (C⁵), 149.11 (C¹³), 146.82 (C¹⁰), 143.78 (C⁷), 138.32 (C¹), 134.43 (C⁴), 130.13 (C¹⁵), 125.00 (C⁸), 124.22 (C¹⁴), 123.25 (C¹⁶), 121.26 (C³), 120.86 (C¹¹), 120.35 (C⁶), 117.80 (C⁹), 111.58 (C²), 55.74 (C^a), 41.36 (C^b), 32.47 (C^e), 29.68 (C^d), 24.79 (C^c), 23.33 (C^f), 14.43 (C^g) ppm. HRMS (FAB): calcd. for $C_{74}H_{85}N_3 [M + H]^+$ 1015.6743; found 1015.6738.

N²-(7-Bromo-9,9-dihexyl-9H-fluoren-2-yl)-N²-[7-(diphenylamino)-9,9dihexyl-9H-fluoren-2-yl]-9,9-dihexyl-N⁷,N⁷-diphenyl-9H-fluorene-2,7diamine (16): Compound 6 (1.76 g, 3.56 mmol), compound 15 (4.0 g, 3.94 mmol), and NaOtBu (0.48 g, 5.0 mmol) were combined with dry toluene (48 mL) in a 250 mL three-neck flask. Pd₂-(dba)₃ (32.3 mg, 39.4 µmol) and 1,1'-bis(diphenylphosphanyl)ferrocene (dppf, 16.4 mg, 0.107 mmol] were then added, and the resulting mixture was stirred and heated at reflux for 12 h under argon. After completion of reaction, the entire system was cooled to room temp. and then diluted with EA (200 mL). The resulting solution was washed with brine $(2 \times 200 \text{ mL})$. The organic layer was collected and dried with MgSO₄. After filtration, the solvent was removed by rotary evaporation, and the crude residue was purified by column chromatography (CH₂Cl₂/hexane, 1:5) to afford 16 (3.05 g, 60.1%) as a yellow powder. ¹H NMR (300 MHz, [D₆]acetone): δ = 7.726–7.699 (d, J = 8.1 Hz, 1 H), 7.670–7.638 (m, 6 H), 7.512–7.479 (dd, $J_1 = 1.8$ Hz, $J_2 = 8.1$ Hz, 1 H), 7.324–7.272 (m, 11 H), 7.194–7.188 (d, J = 1.8 Hz, 2 H), 7.117–7.007 (m, 16 H), 1.915–1.862 (m, 12 H, H^b, H^{b'}), 1.126–1.111 (m, 36 H, H^c, H^{c'}, H^d, H^{d'}, H^e, H^{e'}), 0.899–0.785 (m, 30 H, H^g, H^{g'}, H^f, H^{f'}) ppm. ¹³C NMR (75 MHz, [D₆]acetone): δ = 152.44 (C^L), 151.46 (C⁵, C¹²), 151.17 (C^E), 147.68 (C¹³), 147.45 (C¹⁷), 146.28 (C¹⁰), 146.19 (C¹), 139.96 (C^G), 136.09 (C⁷), 135.86 (C⁴), 134.26 (C^D), 129.62 (C^I), 128.85 (C¹⁵), 125.62 (C⁸), 123.45 (C³), 123.11 (C¹⁴), 122.98 (C⁶), 122.27 (C¹⁹), 122.14 (C¹⁶), 120.42 (C^H), 120.30 (C^K), 119.75 (C^F), 119.67 (C¹¹), 119.34 (C^J), 119.17 (C⁹), 117.99 (C²), 117.14 (C^B), 54.95 (C^{a'}), 54.57 (C^a), 39.63 (C^b, C^{b'}), 31.34 (C^e), 29.10 (C^d), 23.48 (C^c), 21.96 (C^f), 13.16 (C^g) ppm. HRMS (FAB): theoretical average calcd. for C₉₉H₁₁₆BrN₃ [M + H]⁺ 1428.9495; found 1428.9543.

N²-(9,9-Dihexyl-7-nitro-9*H*-fluoren-2-yl)-N²-[7-(diphenylamino)-9,9dihexyl-9H-fluoren-2-yl]-9,9-dihexyl-N7,N7-diphenyl-9H-fluorene-2,7-diamine (17): Compound 11 (1.71 g, 3.74 mmol), compound 15 (3.8 g, 3.74 mmol), and NaOtBu (0.50 g, 5.24 mmol) were combined with dry toluene (50 mL) in a 250 mL three-neck flask. To the solution were quickly added Pd₂(dba)₃ (34.3 mg, 0.037 mol) and $P(tBu)_3$ (15.1 mg, 0.075 mmol). The resulting mixture was stirred and heated at reflux for 4 h under argon. After completion of reaction, the entire system was cooled to room temp. and diluted with EA (100 mL), and the resulting mixture was washed with brine (2×100 mL). The organic layer was collected and dried with MgSO₄. After filtration, the solvent was removed by rotary evaporation, and the crude mixture was purified by column chromatography (CH₂Cl₂/hexane, 1:5) to afford 17 (3.59 g, 69%) as a yellow powder. ¹H NMR (300 MHz, [D₆]acetone): $\delta = 8.299-8.293$ (d, J = 1.8 Hz, 1 H, H^K), 8.260–8.226 (dd, J_1 = 1.8 Hz, J_2 = 8.1 Hz, 1 H, H^I), 7.875–7.829 (d, J = 8.1 Hz, 1 H, H^H), 7.847–7.801 (d, J =8.1 Hz, 1 H, H^C), 7.675–7.621 (m, 4 H, H³, H⁸), 7.373–7.181 (m, 12 H, H^B, H^F, H¹¹, H¹⁵), 7.111-7.001 (d, 18 H, H², H⁶, H⁹, H¹⁴, H¹⁶), 2.232–2.144 (m, 4 H, H^{b'}), 2.192–1.862 (m, 8 H, H^b), 1.126– 1.118 (m, 36 H, H^e, H^{e'}, H^d, H^{d'}, H^c, H^{c'}), 0.884-0.760 (m, 30 H, H^g, H^{g'}, H^f, H^{f'}) ppm. ¹³C NMR (75 MHz, $[D_6]$ acetone): δ = 153.36 (C^J), 151.56 (C⁵), 151.50 (C¹²), 150.97 (C^G), 149.03 (C^L), 147.60 (C¹³), 147.37 (C^E), 146.43 (C¹⁰), 145.89 (C^A), 145.67 (C¹), 136.53 (C⁷), 135.77 (C⁴), 132.14 (C^D), 128.81 (C¹⁵), 123.71 (C⁸), 123.32 (C³), 123.15 (C14), 132.01 (C⁶), 122.16 (C¹⁶), 121.89 (C^H), 121.22 (C^C), 119.80 (C¹¹, C^K), 119.01 (C⁹), 118.82 (C²), 118.58 (C^F), 117.60 (C^B), 115.53 (C^I), 55.08 (C^{a'}), 54.57 (C^a), 39.56 (C^b), 39.25 (C^{b'}), 31.10 (C^e, C^{e'}), 29.32 (C^d, C^{d'}), 23.47 (C^c), 23.36 (C^{c'}), 21.92 (Cf), 13.15 (Cg) ppm. HRMS (FAB): calcd. for C₉₉H₁₁₆N₄O₂ [M + H]⁺ 1393.9177; found 1393.9221.

N²-(7-Amino-9,9-dihexyl-9H-fluoren-2-yl)-N²-[7-(diphenylamino)-9,9dihexyl-9H-fluoren-2-yl]-9,9-dihexyl-N⁷,N⁷-diphenyl-9H-fluorene-2,7-diamine (18): Compound 17 (2.0 g, 1.43 mmol) and SnCl₂·2H₂O (3.23 g, 14.3 mmol) were dissolved in EA (15 mL), and the resulting solution was stirred and heated at reflux for 6 h. To the mixture was added a saturated aqueous solution of NaHCO₃ (30 mL) to quench the excess amount of SnCl₂·2H₂O. The reaction mixture was filtered, and the filtrate was then extracted $(2\times)$ with a mixture of EA (90 mL)/brine (200 mL). The combined organic layers were dried with MgSO₄. After filtration and removal of solvent in vacuo, the crude product was purified by column chromatography (EA/hexane, 1:8) to obtain 18 (1.37 g, 70%) as a yellow solid. ¹H NMR (300 MHz, [D₆]acetone): $\delta = 7.648-7.620$ (d, J = 8.4 Hz, 2 H, H³), 7.631–7.604 (d, J = 8.1 Hz, 2 H, H⁸), 7.523–7.496 (d, J = 8.1 Hz, 1 H, H^C), 7.442–7.416 (d, J = 8.1 Hz, 1 H, H^H), 7.323–7.295 (m, 8 H, H¹⁵), 7.244–7.237 (d, J = 2.1 Hz, 2 H, H⁶), 7.185–7.179 (d, J = 1.8 Hz, 2 H, H¹¹), 7.119–7.008 (m, 16 H, H², H⁹, H¹⁴, H¹⁶, H^B, H^F), 6.756–6.750 (d, J = 1.8 Hz, 1 H, H^K), 6.688–6.655 (dd, $J_1 = 1.8$ Hz, $J_2 = 8.1$ Hz, 1 H, H^I), 4.746 (s, 1 H, NH₂), 2.011–1.798 (m, 12 H, H^b, H^{b'}), 1.224–1.132 (m, 36 H, He, He', Hd, Hd', Hc, Hc'), 0.891-0.791 (m, 30 H, Hg, Hg', Hf, H^{f'}) ppm. ¹³C NMR (75 MHz, [D₆]acetone): δ = 151.72 (C^L), 151.40 (C⁵, C¹²), 150.41 (C^E), 147.78 (C¹³), 147.69 (C^J), 146.72 (C¹⁰), 146.10 (C¹), 144.77 (C^A), 137.65 (C^D), 136.40 (C⁷), 135.11 (C⁴), 130.02 (C^G), 128.90 (C¹⁵), 123.59 (C³, C⁸), 123.44 (C^C), 123.14 (C¹⁴), 122.14 (C¹⁶), 119.67 (C¹¹), 119.62 (C⁶), 119.56 (C¹¹), 118.85 (C^F), 118.35 (C^B), 117.09 (C⁹), 113.01 (C^I), 54.60 (C^a), 54.22 (C^{a'}), 40.23 (C^{b'}), 39.79 (C^b), 31.32 (C^e, C^{c'}), 29.46 (C^d, C^{d'}), 23.58 (C^c, C^{c'}), 22.11 (C^f, C^{f'}), 14.02 (C^g, C^{g'}) ppm. HRMS (FAB): theoretical average calcd. for $C_{99}H_{118}N_4$ [M + H]⁺ 1365.0584; found 1365.0741.

N²-{7-[(7-{Bis[7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl]amino}-9,9-dihexyl-9H-fluoren-2-yl)amino]-9,9-dihexyl-9H-fluoren-2-yl}-N2-[7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl]-9,9-dihexyl-N7,N7-diphenyl-9H-fluorene-2,7-diamine (19): Compound 16 (1.2 g, 0.84 mmol), compound 18 (1.26 g, 0.92 mmol), NaOtBu (0.112 g, 1.17 mmol), Pd₂(dba)₃ (4 mg, 4.4 µmol), and P(tBu)₃ (2 mg, 8.4 µmol) were combined with dry toluene (15 mL) in a 100 mL brown three-neck flask. The resulting mixture was heated at reflux and stirred for 6 h. After completion of reaction, the mixture was washed with brine (50 mL) and then extracted with ethyl acetate (50 mL). The organic layer was dried with MgSO₄ and then filtered. The solvent was removed in vacuo. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1:15) to give the final purified product (1.54 g, ca. 67%). ¹H NMR (300 MHz, C₆D₆): δ = 7.662–7.633 (dd, J_1 = 1.5 Hz, J_2 = 8.1 Hz, 6 H, H^C, H⁶), 7.588–7.561 (d, J = 8.1 Hz, 2 H, H^H) 7.541– 7.514 (d, J = 8.1 Hz, 2 H, H^F), 7.531–7.504 (d, J = 8.1 Hz, 4 H, H³), 7.412–7.385 (d, J = 8.1 Hz, 4 H, H⁸), 7.349–7.316 (dd, $J_1 =$ 2.1 Hz, $J_2 = 8.1$ Hz, 10 H, H¹⁶, H^K), 7.270–7.215 (m, 20 H, H¹¹, H¹⁵), 7.135–7.083 (m, 18 H, H¹⁴, H^B), 6.886–6.839 (m, 10 H, H², H⁹, H^I), 5.356 (s, 1 H, amino hydrogen), 2.000-1.978 (m, 8 H, H^{b'}), 1.858-1.766 (m, 16 H, H^b), 1.247-1.086 (m, 72 H, H^c, H^c, H^d, H^{d'}, He, He'), 0.866–0.835 (m, 60 H, Hf, Hf', Hg, Hg') ppm. ¹³C NMR (75 MHz, C_6D_6): $\delta = 152.61$ (C⁵), 152.48 (C¹², C^E), 152.00 (C^L), 148.72 (C¹³), 147.78 (C¹⁰), 147.11 (C¹), 146.92 (C^A), 142.65 (C^J), 137.30 (C^D), 136.97 (C⁷), 136.44 (C⁴), 134.89 (C^G), 129.61 (C¹⁵), 128.10 (C⁸), 124.29 (C¹⁴), 124.10 (C^C), 123.47 (C³), 122.86 (C¹⁶), 120.56 (C¹¹), 120.47 (C⁶) 120.40 (C^K), 120.04 (C^H), 119.96 (C²), 119.38 (C⁹), 118.63 (C^F), 117.54 (C^B), 112.29 (C^I), 55.56 (C^{a'}), 55.51 (Ca), 41.20 (Cb'), 40.56 (Cb), 32.16 (Ce'), 32.06 (Ce), 30.42 (Cd'), 30.17 (Cd), 24.70 (Cc'), 24.57 (Cc), 23.12 (Cf'), 23.06 (Cf), 14.4 (C^g) ppm. HRMS (MALDI-TOF): calcd. for $C_{198}H_{233}N_7$ [M]⁺ 2708.8447; found 2708.8523.

Compound 1: Compound 7 (0.95 g, 1.63 mmol), compound 15 (1.5 g, 1.48 mmol), and NaOtBu (0.199 g, 2.07 mmol) were combined with dry toluene (10 mL) in a 50 mL three-neck flask. To the solution were added Pd₂(dba)₃ (13.6 mg, 14.8 µmol) and P(tBu)₃ (6.0 mg, 29.6 mmol), and the resulting mixture was stirred and heated at reflux for 4 h under argon. After completion of reaction, the entire system was cooled to room temperature, washed with brine (50 mL), and extracted with ethyl acetate (2×50 mL). The combined organic layers were dried with MgSO₄ and then filtered. The crude mixture was purified by column chromatography (THF/ hexane, 1:20) to afford pure compound 1 (1.55 g, 69%) as a yellow powder. ¹H NMR (300 MHz, [D₆]acetone): δ = 7.656–7.629 (d, J = 8.1 Hz, 6 H, H³, H⁸), 7.303-7.250 (m, 15 H, H⁹, H¹⁵), 7.165-7.159 (d, J = 1.8 Hz, 3 H, H⁶), 7.095–6.984 (m, 21 H, H², H¹⁴, H16), 1.920-1.797 (m, 12 H, Hb), 1.196-1.019 (m, 36 H, Hc, Hd, H^e), 0.8–0.7 (t, J = 5.7 Hz, 18 H, H^g), 0.798–0.701 (m, 12 H, H^f) ppm. ¹³C NMR (75 MHz, [D₆]acetone): δ = 151.83 (C¹²), 148.10 (C⁵), 146.79 (C¹³, C¹⁰), 146.59 (C¹), 136.59 (C⁷), 135.96 (C⁴), 129.25 (C¹⁵), 123.88 (C³), 123.50 (C¹⁶), 123.08 (C⁶), 122.52 (C¹⁴), 120.10 (C⁸), 120.02 (C⁹), 119.62 (C²), 118.11 (C¹¹), 54.96 (C^a), 40.06 (C^b), 31.56 (C^e), 29.43 (C^d), 23.91 (C^c), 22.37 (C^f), 13.58 (C^g) ppm.

HRMS (MALDI-TOF): calcd. for $C_{111}H_{126}N_4$ [M]⁺ 1514.9983; found 1515.0012.

Compound 2: Compound 14 (0.32 g, 0.26 mmol), compound 15 (0.861 g, 0.84 mmol), and NaOtBu (0.1 g, 1.08 mmol) were combined with dry toluene (8 mL) in a high pressure tube. Then, Pd₂(dba)₃ (3.51 mg, 3.84 µmol) and P(*t*Bu)₃ (1.6 mg, 7.7 µmol) were added, and the reaction vessel was purged with argon and sealed tightly. The resulting mixture was stirred and heated at reflux for 12 h. After completion of reaction, the entire system was cooled to room temperature. The reaction mixture was diluted with EA (50 mL), and the resulting solution was washed with brine $(2 \times 50 \text{ mL})$. The organic layer was dried with MgSO₄ and then filtered. The crude mixture was purified by column chromatography CH₂Cl₂/hexane, 1:5) to afford pure compound 2 (0.301 g, 28.8%) as a yellow powder. ¹H NMR (300 MHz, C_6D_6): $\delta = 7.656-$ 7.608 (m, 12 H, H⁹, H¹¹), 7.592–7.564 (d, J = 8.4 Hz, 3 H, H^H) 7.575–7.548 (d, J = 8.4 Hz, 3 H, H^C) 7.532–7.504 (d, J = 8.4 Hz, 6 H, H³), 7.408–7.381 (d, J = 8.4 Hz, 6 H, H⁸), 7.331–7.310 (m, 18 H, H⁶, H¹⁶), 7.240-7.208 (m, 24 H, H¹⁵), 7.133-7.080 (m, 30 H, H14, H2), 6.886-6.838 (m 12 H, H18, HB, HF, HI), 1.918-1. 761H (m, 36 H, H^{b'}, H^b), 1.265–0.837 (m, 198 H, H^{c'}, H^c, H^d, H^{d'}, H^e, $H^{e'}$, $H^{f'}$, H^{f} , H^{g} , $H^{g'}$) ppm. ¹³C NMR (75 MHz, C_6D_6): $\delta = 152.57$ (C⁵), 152.43 (C¹², C²¹, C²⁸), 148.65 (C¹³), 147.32 (C¹, C^A, C^J), 147.09 (C¹⁰), 136.84 (C^D, C^G), 136.62 (C⁷), 136.51 (C⁴), 129.55 (C¹⁵), 128.10 (C⁸), 124.24 (C¹⁴), 123.80 (C^H), 123.69 (C^H), 123.54 (C³), 122.82 (C¹⁶), 120.37 (C⁶, C^F, C^K), 119.87 (C¹¹), 119.03 (C^I), 118.92 (C^B), 118.74 (C⁹) ppm. HRMS (MALDI-TOF): theoretical average calcd. for C₂₉₇H₃₄₈N₁₀ [M]⁺ 4058.1201; found 4058.1387.

Compound 3: Compound 14 (0.189 g, 0.152 mmol), compound 19 (1.398 g, 0.516 mmol), NaOtBu (62.3 mg, 0.638 mmol), Pd₂(dba)₃ (5.7 mg, 6.22 µmol), and P(tBu)₃ (2.0 mg, 9.9 µmol) with dry toluene (6 mL) were added to a high pressure tube. The reaction vessel was purged with argon and sealed tightly. The entire system was stirred at -110 °C for 12 h. After completion of reaction, the mixture was cooled to room temperature and extracted $(2\times)$ with a mixture of brine (50 mL)/ethyl acetate (50 mL). The combined organic layers were dried with MgSO4 and then filtered. After removal of the solvent, the crude residue was purified by column chromatography on silica gel (CH₂Cl₂/hexane, 1:3) to give the final purified product (0.402 g, 29%). ¹H NMR (300 MHz, C_6D_6): $\delta =$ 7.659–7.611 (m, 24 H, H⁹, H¹¹), 7.595–7.568 (d, J = 8.1 Hz, 9 H, $H^{C'}$, H^{H}), 7.575–7.548 (d, J = 8.1 Hz, 9 H, $H^{H'}$, H^{C}) 7.532–7.505 $(d, J = 8.1 \text{ Hz}, 12 \text{ H}, \text{H}^3)$, 7.408–7.381 $(d, J = 8.1 \text{ Hz}, 12 \text{ H}, \text{H}^8)$, 7.475-7.437 (m, 3 H, HK'), 7.354-7.278 (m, 36 H, H¹⁶, H⁶), 7.237-7.210 (m, 48 H, H¹⁵), 7.133-7.081 (m, 60 H, H², H¹⁴), 7.042-7.015 (m, 6 H, H^{B'}, H^{F'}), 6.953–6.773, (m, 27 H, H^I, H^I, H^F, H^K, H^B) 1.915-1.764 (m, 84 H, H^b, H^{b'}, H^{b''}), 1.263-0.838 (m, 462 H, H^c, $H^{c'},\ H^{c''},\ H^{d},\ H^{d'},\ H^{d''},\ H^{e},\ H^{e'},\ H^{e''},\ H^{f},\ H^{f'},\ H^{f''},\ H^{g},\ H^{g'},$ $H^{g''}$) ppm. ¹³C NMR (75 MHz, C₆D₆): δ = 152.64 (C⁵, C^E), 152.56 (C^L, C^{E'}), 152.51 (C¹²), 148.72 (C¹³), 147.40 (C¹, C^J, C^{J'}, C^A, C^{A'}), 147.17 (C¹⁰), 136.91 (C⁴, C^{G'}), 136.69 (C^{D'}, C^G), 136.59 (C⁷, C^{D'}), 129.62 (C¹⁵), 128.10 (C⁸), 124.32 (C¹⁴), 123.86 (C^C, C^{C'}), 123.80 (C^H, C^{H'}), 123.61 (C³), 122.89 (C¹⁶), 120.44 (C⁶), 119.94 (C¹¹), 119.11 (C^I, C^{I'}), 119.04 (C^B, C^{B'}), 118.94 (C²), 118.82 (C⁹), 55.67 (Ca''), 55.52 (Ca, Ca'), 40.79 (Cb''), 40.56 (Cb, Cb'). 32.24 (Ce''), 32.07 (Ce, Ce'). 30.30 (Cd''), 30.17 (Cd, Cd'), 24.81 (Cc''), 24.57 (Cc, C^{c'}), 23.14(C^{f''}), 23.06 (C^f, C^{f'}), 14.49 (C^{g''}), 14.41 (C^g, C^{g'}) ppm. HRMS (MALDI-TOF): theoretical average calcd. for C₆₆₉H₇₉₂N₂₂ $[M + H]^+$ 9142.8896; found 9142.8555.

Supporting Information (see footnote on the first page of this article): Representative numbering of carbon and hydrogen atoms for various structural units and optical experiment details.

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