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Synthesis and Two-Photon Properties of Multi-Branched Fluorophores Composed of Ladder-Type Conjugated Cores and Functionalized Diquinoxalinylamino Peripheries

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Two multipolar fluorophores using ladder-type oligo-(*p*-phenylene) units as the central π-bridges and functionalized diquinoxalinylamino moieties as the peripheral groups have been synthesized and experimentally shown to manifest strong two-photon absorption (2PA) and medium-high up-converted emission properties in the near-IR (NIR) spectral region under the irradiation of femtosecond laser pulses. Tentative analysis of the structure–2PA property revealed that in the presented structural combination, diquinoxalinylamino units are useful 2PA-enhancing subunits when properly incorporated. The π-conjugation length of the central oligo-(*p*-phenylene) components was also found to be one of the key parameters that relates to the magnitude of the overall molecular 2PA properties in the studied molecular system, and this structural motif provides access to highly efficient two-photon absorbers with large two-photon action cross-section values.

Introduction

For the past two decades, much effort has been made toward the development of organic molecules that possess intense two-photon absorption (2PA) properties because of their potential for many applications in the emerging field of photonics and biophotonics, including optical power-limiting, frequency up-converted lasing, 3-D data storage, 3-D microfabrication, nondestructive bio-imaging/tracking, and two-photon photodynamic therapy.[1] The accumulated experiences and knowledge based on these efforts have realized the close connection between molecular 2PA properties and various structural parameters, such as intramolecular charge-transfer efficiency, effective size of π-conjugation domain within a molecule, molecular symmetry and molecular dimensionality.[2–9] This relationship, in turn, can serve as a guideline for the molecular design, engineering, and optimization of highly active 2PA chromophores. Depending on the application, other photophysical properties in addition to strong molecular 2PA may also be required for the designed molecules. For example, to be utilized as an effective frequency up-converter, molecules that simultaneously possess large 2PA values and high fluorescence quantum yields are very desirable, because a sufficient two-photon action cross-section value (i.e., quantum yield × two-photon absorption cross-section = $\Phi_F\delta_2$) can be obtained for practical uses.[1a,1d,2] In addition, knowing how to control the spectral dispersion of 2PA by tuning the molecular structure is another important issue, because in many cases, enhanced 2PA, either at a specific wavelength or within a particular spectral region, is required. In searching structural parameters for 2PA optimization in conjugated systems, we are interested in exploring the influence of the structural arrangements and the electronic natures of the selected building units on the molecular 2PA properties of a multi-branched dye system. In this paper, we present two newly synthesized two-photon-active model chromophores (**1–2**) with molecular structures composed of ladder-type oligo-(*p*-phenylenes) as the π-bridges in the center and functionalized diquinoxalinylamino moieties as the peripheral parts of the whole structure, as well as the initial investigations of their 2PA-related properties in the femtosecond regime.

Results and Discussion

I. Model Molecules and Syntheses

This model compound set contains two structural congeners that possess a common donor-π-donor (D-π-D) motif using oligo-(*p*-phenylenes) with different conjugation lengths as the central π-bridges to connect two identical

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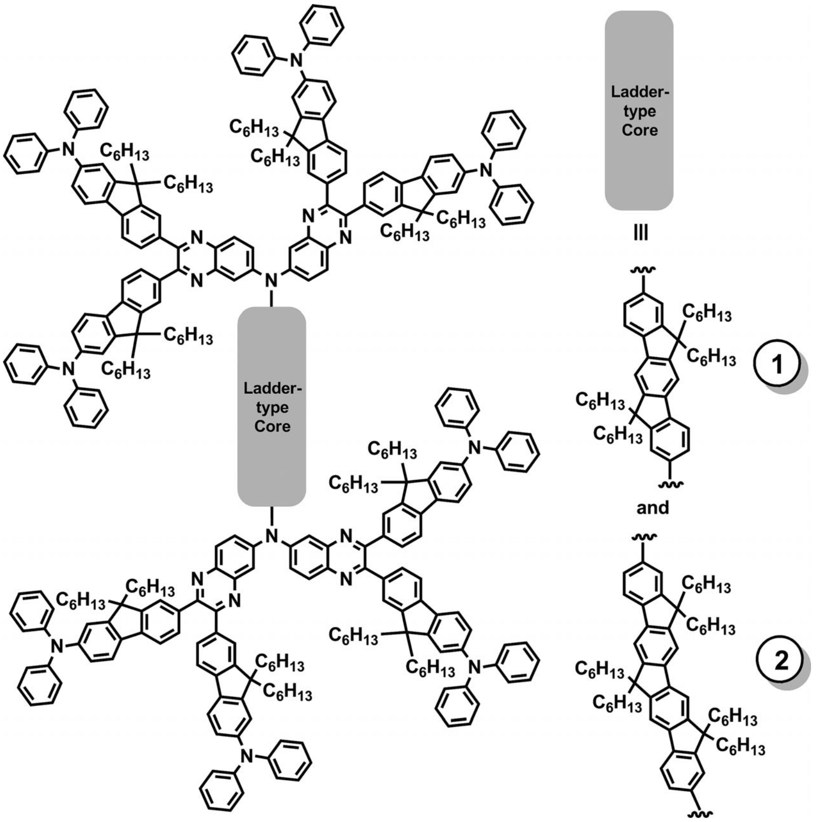

Figure 1. Chemical structures of the model chromophores.

functionalized diquinoxalinylamino units, to form multibranched skeletons. The molecular structures and the synthetic procedures of these model compounds are illustrated in Figure 1 and Scheme 1, respectively. The original molecular design strategies of these chromophores stem from the concept of incorporating both electron-withdrawing heterocyclic ring complexes and oligo-(*p*-phenylenes) into the branched molecular structure so that the electronic properties of the resulting fluorophores may be different from the all-carbon analogues due to the involvement of heteroatoms, and the whole molecule will possess an extended π-domain, as well as more pronounced multi-polar characters. Because the solubility of the resulting model structure in common organic solvents is crucial for both experiments and applications, long alkyl chains were intentionally attached to each fluorenyl unit of the studied compounds for this purpose. For the syntheses of the target model compounds, the brominated oligo-(*p*-phenylenes) (i.e. compounds **9** and **11** in Scheme 1) and a secondary amine with a quinoxaline ring complex structure (i.e. compound **10**) were employed as the major synthons for the Buchwald–Hartwig type amination toward the final fluorophores. Both compounds **10** and **11** were prepared by following the established procedures,[9a,9e] while the synthesis of compound **9** was accomplished through the same synthetic methodology as **11** by using compound **3** as the starting material. The detailed syntheses, including the preparation of the key intermediates and the final catalytic coupling reactions to afford the targeted model fluorophores, are described in the Experimental Section.

II. Optical Property Characterizations

Figure 2 shows the linear absorption and fluorescence spectra of chromophores **1** and **2** in THF. These two fluorophores exhibited very similar linear absorption patterns, accompanied by three distinct intense absorption peaks in the range of 300–450 nm. Moreover, both chromophore solutions manifested strong fluorescence emission under the irradiation of a common laboratory UV lamp, and the fluorescence quantum yields were determined to be $\Phi_F = 0.53$ and 0.55 for **1** and **2**, respectively. All the photophysical data are collected in Table 1.

Figure 3(a) illustrates the normalized 2PA-induced fluorescence spectrum of compounds **1** and **2**. In this experiment, a wavelength-tunable mode-locked Ti:Sapphire laser (Tsunami pumped with a Millennia 10W, Spectra-Physics) which delivers ≈120 fs pulses with the repetition rate of 80 MHz, and a beam diameter of 2 mm was utilized as the excitation light source. The intensity level of the excitation beam was carefully controlled to avoid the saturation of absorption and photodegradation of the samples during the experiments. Also, the relative position of excitation beam was adjusted to be as close as possible to the wall of the quartz cell (10 mm × 10 mm cuvette) so that only the emis-

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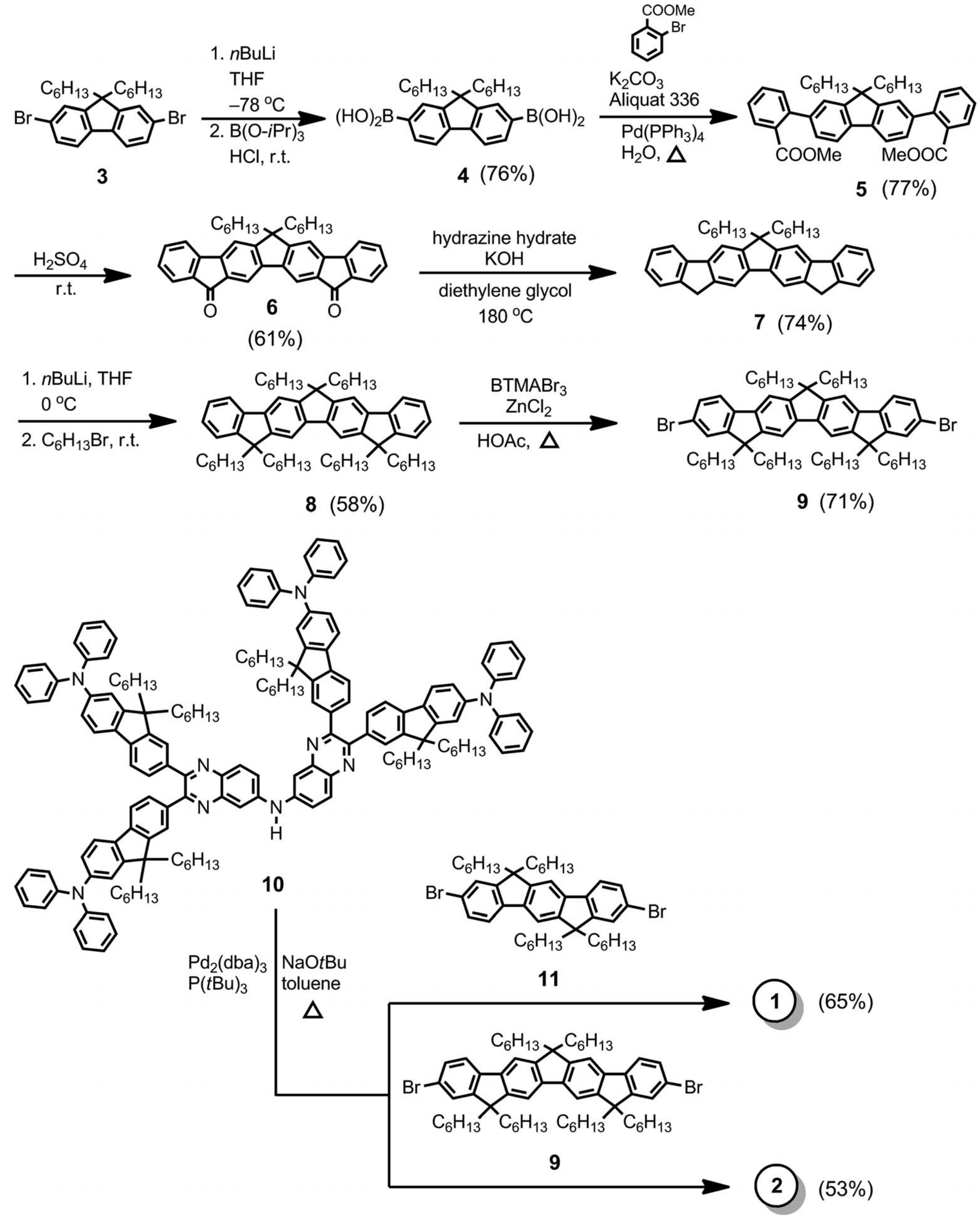

Scheme 1. Synthesis of the key intermediates and final compounds.

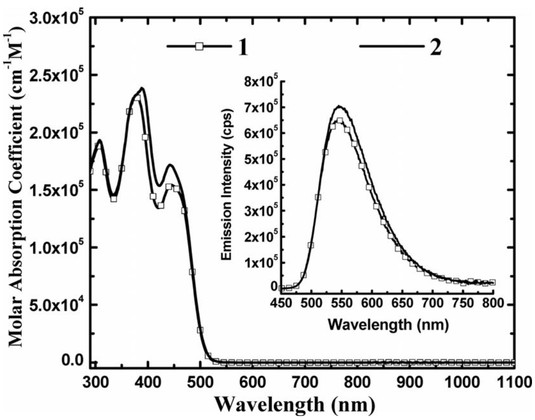

Figure 2. Linear absorption and fluorescence spectra of compounds **1** and **2** in THF.

Table 1. Photophysical properties of model chromophores **1**–**2** in THF.[a]

	$\lambda_{\max}^{\text{abs}}$/ nm[b]	$\log \varepsilon$[c]	$\lambda_{\max}^{\text{em}}$/ nm[d]	Φ_{F}[e]	$\delta_2^{\max}$/ GM[f]	$\Phi_{\mathrm{F}}\delta_2^{\max}$/ GM[g]
1	308 376 445	5.19	545	0.53	≈ 6380	≈ 3380
2	308 390 445	5.23	545	0.55	≈ 10200	≈ 5600

[a] Concentrations were 1×10^{-6} M and 1×10^{-4} M for 1PA-related and 2PA-related measurements, respectively. [b] One-photon absorption maximum. [c] Molar absorption coefficient of the lowest-energy absorption peak. [d] 1PA-induced fluorescence emission maximum. [e] Fluorescence quantum efficiency. [f] Maximum 2PA cross-section value (with experimental error ca. ±15%); 1 GM = 1×10^{-50} cm^4 s/photon-molecule. [g] Two-photon action cross-section value.

sion from the front-surface of the sample was recorded in order to minimize the re-absorption or inner-filter effect.

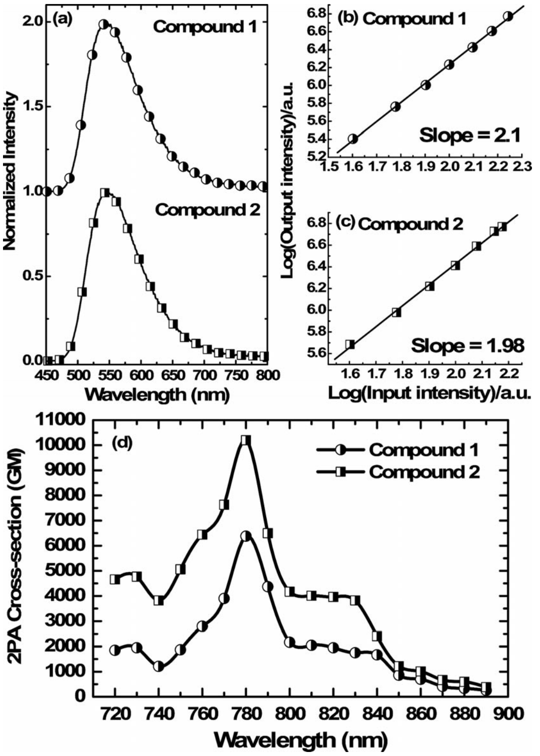

Figure 3. 2PA-related photophysical properties of **1** and **2** in THF: (a) normalized 2PA-induced fluorescence spectra; (b) and (c) logarithmic plots of the power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity; (d) 2PA spectra in toluene.

The quadratic dependence of the up-converted emission intensity on the incident light intensity was also examined, as illustrated in Figure 3 (b) and (c). The results (i.e. slope ≈ 2) validate that the observed up-converted fluorescence emissions from these two model chromophores were mainly caused by 2PA process in all cases.

In order to investigate and compare the dispersion of 2PA behaviors of these dye molecules as a function of wavelength, the degenerate two-photon-excited fluorescence (2PEF) measurement was conducted in the near-IR regime using Fluorescein (ca. 80 μM in pH = 11 NaOH solution) as the standard.[10] Figure 3 (d) shows the measured two-photon absorption spectra of these model compounds in THF. From Figure 3 (d), one can see that both compounds **1** and **2** possess large 2PA values (≥700 GM) across the entire probing range (i.e. 720–860 nm) with both of their local 2PA maxima located at 780 nm (i.e. $\delta_2^{\max}$ = 6380 GM for **1** and $\delta_2^{\max}$ = 10200 GM for **2**), suggesting that the electron-donor-decorated quinoxaline and ladder-type oligo-(*p*-phenylene) moieties are useful building units for the construction of strong 2PA dyes. It should be noted that the aforementioned quinoxaline unit has been previously utilized to construct a simple trigonal π-system using a nitrogen atom as the ramification center, and that structure was found to manifest larger maximum 2PA values than that of compound **1** studied in this work.[9e] This may suggest that a trigonal skeleton based on the motif of a symmetrically substituted tertiary amine may provide more effective access toward a large 2PA cross-section value. Compared to other multi-branched systems of similar size and effective π-electron numbers, these two model compounds exhibit comparable maximum two-photon cross-section and two-photon-action cross-section ($\Phi_F\delta_2^{\max}$) values,[1a,2a,11] and this property implies that the selected building blocks and their structural arrangement in the presented chromophore system may provide a useful approach to build efficient frequency up-converters. Moreover, it is notable from Figure 3 (d) that all these model chromophores not only exhibit nearly identical dispersion pattern of their two-photon activities but also show ascending overall magnitude of 2PA from compound **1** to compound **2**. These features indicate that elongating the π-length of the central core can further promote the molecular 2PA without dramatic shift of the 2PA band position in this molecular system. Molecules with this kind of property could be very beneficial for some particular applications when large multi-photon absorptivities within a specific spectral region or at a particular wavelength are required. If one compares the measured one-photon absorption (1PA) and 2PA spectra of these compounds in THF solution (see Figures 2 and 3, d), it is notable that both model chromophores exhibit either detectable or strong 2PA at wavelengths equal to twice the wavelengths in the ultraviolet–visible region where they possess intense 1PA. A probable reason for this is that those one-photon allowed states in this branched dye system are coincidentally located near the two-photon allowed states, so that they are energetically accessible by both excitation modes.

Finally, from the standpoint of the subunits, both of these compounds contain 2,3-diaryl quinoxaline moieties in their structures, and such subchromophores can be assumed to possess strong dipolar character because of the substitution pattern. If these subchromophores act independently in the grafted structures of **1** and **2**, the photophysical properties of the whole molecule may be dominantly controlled by these subunits. On the other hand, in such a large dendritic molecular system, it is also possible that the dynamic conformation change between conformers has led to imperfect cancellation of transition probability. These are interesting issues to investigate in multi-chromophoric systems with similar structural arrangement to the presented model compounds. Such work is being undertaken currently, and will be reported in due course.

Conclusions

In summary, we have synthesized a multipolar chromophore set composed of two analogues using various ladder-type oligo-(*p*-phenylene) units as the central cores and functionalized diquinoxalinylamine moieties as the peripheral groups. It was found that the presented structural arrangement led to large molecular 2PA values. Also, extending the length of the central π-bridge further promoted the molecular 2PA in this model compound system. Combined with the medium level fluorescence quantum yields, these two model chromophores possess fairly good two-photon action cross-sections, which may suggest these model architectures as potential frequency up-converters for photonic applications.

Experimental Section

General: All commercially available reagents for the preparation of the intermediates and targeted chromophores were purchased from Acros Organics or Alfa Aesar, and were used as received unless stated otherwise. ^{1}H NMR and ^{13}C NMR spectra were recorded with a 300 MHz spectrometer and referenced to TMS or residual $CHCl_3$. The numbering of carbon and hydrogen atoms on each intermediate and model chromophore for the NMR signal assignment is systematized and illustrated in the Supporting Information. High-resolution mass spectroscopy (HRMS) was conducted by using a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS spectra were obtained with a Voyager DE-PRO mass spectrometer (Applied Biosystem, Houston, USA).

Photophysical Methods: All the linear optical properties of compounds **1** and **2** were measured by corresponding spectrometers. The detailed experimental conditions and the optical setups for nonlinear optical property investigations are described in the Supporting Information.

Synthesis: In Scheme 1, compounds **9**–**11** were the major synthons for the synthesis of the final model chromophores. Compounds **10** and **11** were obtained by following established procedures.[9a,9e] For the synthesis of other key intermediates (compounds **4**–**9**) and the targeted model compounds (**1** and **2**), a series of functionalization steps starting from compounds **3** have been conducted and are presented as follows:

(9,9-Dihexyl-9*H*-fluorene-2,7-diyl)diboronic Acid (4): To a solution of compound **3** (5 g, 10.1 mmol) in dry THF (100 mL) was added an *n*-butyllithium solution (1.6 M in hexane, 25.4 mL, 40.6 mmol) in dropwise fashion at –78 °C. The resulting mixture was stirred at –78 °C under argon for 1 h. Triisopropylborate (6.8 mL, 60.9 mmol) was added quickly at –78 °C, and the mixture was stirred overnight, allowing the temperature to rise gradually to 20 °C. Aqueous HCl (2 N, 100 mL) was added to the white suspension, and the mixture was stirred at 20 °C for 4 h. The resulting solution was extracted with diethyl ether (30 mL × 3). The organic layer was collected and dried with $MgSO_4$ (s). After removing the solvent, the crude product was obtained as a white solid, which was recrystallized from hexane to give white crystals with yield of 76% (3.25 g). ^{1}H NMR (300 MHz, [D$_6$]DMSO): δ = 8.00 (s, 4 H), 7.84 (s, 2 H, H^2), 7.79–7.73 (m, 4 H, H^4, H^5), 1.97–1.92 (m, 4 H, H^f), 1.04–0.97 (m, 12 H, H^c, H^d, H^e), 0.72–0.67 (t, J = 6.6 Hz, 6 H, H^a), 0.48 (s, 4 H, H^b) ppm. ^{13}C NMR (75 MHz, [D$_6$]DMSO): δ = 149.39 (C^1), 142.33 (C^6), 132.91 (C^2), 128.39 (C^4), 119.00 (C^5), 54.17 (C^g), 39.94 (C^f), 30.92 (C^e), 29.00 (C^d), 23.42 (C^c), 21.93 (C^b), 13.76 (C^a) ppm. HRMS-FAB: [M + H]$^+$ calcd. for $C_{25}H_{36}B_2O_4$ 423.3015; found 423.3028.

Dimethyl 2,2′-(9,9-Dihexyl-9*H*-fluorene-2,7-diyl)dibenzoate (5): To a three-neck flask was added compound **4** (3.25 g, 7.7 mmol), methyl 2-bromobenzoate (3.64 g, 16.9 mmol) in toluene/H_2O (2:1, 30 mL), aliquat 336 (0.8 g, 1.98 mmol) and K_2CO_3 (5.32 g, 38.5 mmol). $Pd(PPh_3)_4$ (17.8 mg, 0.0154 mmol) was added, and the resulting mixture was heated to reflux under argon for 24 h. At this point, 50 mL of water was added to quench the reaction. The reaction mixture was extracted with ethyl acetate (30 mL × 3). The organic layer was separated, dried with $MgSO_4$ (s), and the solvents were evaporated under vacuum. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1:100) as the eluent to give a colorless oil in 76.6% yield (3.55 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.89–7.86 (d, J = 7.5 Hz, 2 H, H^2), 7.80–7.77 (d, J = 7.8 Hz, 2 H, H^5), 7.62–7.57 (m, 2 H, H^3), 7.51–7.44 (m, 4 H, H^4, H^8), 7.36–7.33 (d, J = 7.8 Hz, 2 H, H^7), 7.32 (s, 2 H, H^{11}), 3.65 (s, 6 H, H^{14}), 2.05–1.99 (m, 4 H, H^f), 1.17–1.11 (m, 12 H, H^c, H^d, H^e), 0.82–0.75 (m, 10 H, H^a, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.42 (C^{13}), 150.80 (C^{10}), 142.79 (C^9), 140.29 (C^{12}), 139.96 (C^6), 131.20 (C^4), 131.11 (C^2), 130.75 (C^8), 127.11 (C^3), 127.00 (C^5), 122.90 (C^{11}), 119.42 (C^7), 55.19 (C^g), 51.78 (C^{14}), 40.53 (C^f), 31.54 (C^e), 29.72 (C^d), 23.70 (C^c), 22.55 (C^b), 13.95 (C^a) ppm. HRMS-FAB: [M]$^+$ calcd. for $C_{41}H_{46}O_4$ 602.3396; found 602.3398.

6,6-Dihexyl-6*H*-cyclopenta[1,2-*b*:5,4-*b*′]difluorene-12,15-dione (6): Compound **5** (3.55 g, 5.89 mmol) in H_2SO_4 (60 mL) was stirred at room temperature for 3 h. The green reaction mixture was then poured into ice and filtered to the collect orange crystals, which were then washed with water (100 mL). The collected product was dissolved in dichloromethane (90 mL) and washed with a sodium hydrogen carbonate solution (50 mL). The organic layer was collected and dried with $MgSO_4$ (s). After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel, using THF/hexane (1:10) as the eluent to give a yellow solid in 61% yield (1.93 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.00 (s, 2 H, H^8), 7.68–7.66 (d, J = 7.2 Hz, 2 H, H^2), 7.61–7.58 (d, J = 7.2 Hz, 2 H, H^5), 7.52 (m, 2 H, H^4), 7.49 (s, 2 H, H^{11}), 7.31–7.26 (t, 2 H, H^3), 2.12–2.07 (m, 4 H, H^f), 1.07 (m, 12 H, H^c, H^d, H^e), 0.74–0.72 (m, 10 H, H^a, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 193.18 (C^{13}), 158.32 (C^{10}), 144.56 (C^{12}), 144.34 (C^6), 141.28 (C^9), 134.90 (C^1), 134.57 (C^4), 134.11 (C^7), 128.94 (C^2), 124.26 (C^8), 120.20 (C^3), 115.95 (C^5), 114.70 (C^{11}), 56.20 (C^g), 40.32 (C^f), 31.39 (C^e), 29.59 (C^d), 23.79 (C^c), 22.47 (C^b), 13.88 (C^a) ppm. HRMS-FAB: [M + H]$^+$ calcd. for $C_{39}H_{38}O_2$ 539.2872; found 539.2961.

6,6-Dihexyl-12,15-dihydro-6*H*-cyclopenta[1,2-*b*:5,4-*b*′]difluorene (7): To a mixture of compound **6** (1.93 g, 3.58 mmol) and KOH (85%, 5.86 g, 88.8 mmol) in diethylene glycol (100 mL) was added hydrazine monohydrate (98%, 5.62 mL, 110.2 mmol), and the resulting mixture was heated at 180 °C for 48 h. When the reaction was completed (monitored by TLC), the hot solution was poured into crushed ice and was neutralized by 1 N HCl (aq). The orange precipitate was filtered and washed with water (100 mL). The collected product was then extracted with dichloromethane (30 mL × 3) and dried with $MgSO_4$ (s). After filtration and solvent evaporation, the crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1:5) as the eluent to afford an orange solid in 74.3% yield (1.36 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.86 (s, 2 H, H^8), 7.84 (s, 2 H, H^{11}), 7.74–7.72 (d, J = 4.5 Hz, 2 H, H^2), 7.55–7.53 (d, J = 7.2 Hz, 2 H, H^5), 7.43–7.37 (td, J_1 = 7.2, J_2 = 3.3 Hz, 2 H, H^4), 7.31–7.27 (m, 2 H, H^3), 3.95 (s, 4 H, H^{13}), 2.13–2.06 (m, 4 H, H^f), 1.06–1.04 (m, 12 H, H^c, H^d, H^e), 0.75–0.69 (m, 10 H, H^a, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 150.39 (C^{10}), 143.74 (C^6), 142.36 (C^1), 142.11 (C^{12}), 140.88 (C^7), 140.60 (C^9), 126.71 (C^4), 126.31 (C^2), 125.05 (C^8), 119.60 (C^3), 115.95 (C^5), 114.11 (C^{11}), 54.50 (C^g), 41.13 (C^f), 36.81 (C^{13}), 31.54 (C^e), 29.81 (C^d), 23.79 (C^c), 22.60 (C^b), 13.97 (C^a) ppm. HRMS-FAB: [M + H]$^+$ calcd. for $C_{39}H_{42}$ 511.3287; found 511.3365.

6,6,12,12,15,15-Hexahexyl-12,15-dihydro-6*H*-cyclopenta[1,2-*b*:5,4-*b*′]difluorene (8): To compound **7** (1.36 g, 2.66 mmol) in dry THF

(20 mL) under nitrogen, *n*-butyllithium (1.6 M in hexane, 5.0 mL, 7.98 mmol) was added dropwise at 0 °C. During the addition of *n*-butyllithium, the initial orange solid gradually dissolved, and the color of solution turned to dark brown. The whole system was stirred at room temperature for 30 min, and then 1-bromohexane (1.12 mL, 7.98 mmol) was added. After the reaction mixture was stirred for 4 h, the second portion of *n*-butyllithium (1.6 M in hexane, 5.0 mL, 7.98 mmol) was added dropwise at 0 °C. After another 30 min, the second portion of 1-bromohexane (1.12 mL; 7.98 mmol) was added at room temperature. After the completion of addition, the resulting mixture was stirred at room temperature for 12 h, and the reaction was quenched with aqueous ammonium chloride. The resulting mixture was extracted with ethyl acetate (30 mL × 3). The organic layer was separated, dried with MgSO$_4$ (s), and the solvents were evaporated under vacuum. The crude product was purified by column chromatography on silica gel, using hexane as the eluent to give white solid in 58% yield (1.3 g). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.75–7.73 (d, *J* = 7.2 Hz, 2 H, H^{2}), 7.67 (s, 2 H, H^{8}), 7.63 (s, 2 H, H^{11}), 7.35–7.26 (m, 6 H, H^{5}, H^{4}, H^{3}), 2.08–2.03 (m, 12 H, H^{f}, H$^{f'}$), 1.06 (m, 36 H, H^{c}, H^{d}, H^{e}, H$^{c'}$, H$^{d'}$, H$^{e'}$), 0.72–0.70 (m, 30 H, H^{a}, H^{b}, H$^{a'}$, H$^{b'}$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 151.03 (C^{1}), 150.45 (C^{10}), 150.04 (C^{7}), 141.64 (C^{6}), 141.08 (C^{12}), 140.25 (C^{9}), 126.64 (C^{4}), 126.51 (C^{2}), 122.87 (C^{8}), 119.33 (C^{3}), 113.86 (C^{5}), 113.56 (C^{11}), 54.73 (C^{13}), 54.36 (C^{g}), 41.03 (C^{f}), 40.61 (C$^{f'}$), 31.58 (C^{e}), 31.46 (C$^{e'}$), 29.70 (C^{d}, C$^{d'}$), 23.74 (C^{c}), 23.67 (C$^{c'}$), 22.52 (C^{b}, C$^{b'}$), 13.97 (C^{a}, C$^{a'}$) ppm. HRMS-FAB: [M + H]$^+$ calcd. for $C_{63}H_{90}$ 847.7043; found 847.7121.

2,10-Dibromo-6,6,12,12,15,15-hexahexyl-12,15-dihydro-6*H*-cyclopenta[1,2-*b*:5,4-*b*′]difluorene (9): A mixture of compound **8** (1.3 g, 1.53 mmol), zinc chloride (0.48 g, 3.52 mmol), and BTMABr$_3$ (1.26 g, 3.21 mmol) in acetic acid (20 mL) was stirred at 70 °C for 12 h under nitrogen. After cooling to room temperature, saturated NaHSO$_3$ (aq, 50 mL) was added to the reaction mixture and stirred for 1 h. After filtration, the crude solid product was collected and recrystallized from methanol. The purified product was obtained as a pale pink solid in 71.2% yield (1.1 g). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 7.62 (s, 2 H, H^{8}), 7.61–7.59 (d, *J* = 8.4 Hz, 2 H, H^{5}), 7.57 (s, 2 H, H^{11}), 7.48–7.45 (m, 4 H, H^{2}, H^{4}), 2.07–1.99 (m, 12 H, H^{f}, H$^{f'}$), 1.05 (m, 36 H, H^{c}, H^{d}, H^{e}, H$^{c'}$, H$^{d'}$, H$^{e'}$), 0.75–0.67 (m, 30 H, H^{a}, H^{b}, H$^{a'}$, H$^{b'}$) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 153.29 (C^{1}), 150.70 (C^{10}), 149.77 (C^{7}), 141.26 (C^{9}), 140.58 (C^{12}), 139.28 (C^{6}), 129.78 (C^{4}), 126.13 (C^{2}), 120.74 (C^{5}), 120.45 (C^{3}), 113.96 (C^{11}), 113.65 (C^{8}), 55.09 (C^{13}), 54.41 (C^{g}), 40.86 (C^{f}), 40.43 (C$^{f'}$), 31.50 (C$^{e'}$), 31.39 (C^{e}), 29.63 (C$^{d'}$), 29.57 (C^{d}), 23.59 (C^{c}, C$^{c'}$), 22.47 (C^{b}, C$^{b'}$), 13.93 (C^{a}, C$^{a'}$) ppm. HRMS-FAB: [M]$^+$ calcd. for $C_{63}H_{88}Br_2$ 1005.1808; found 1005.2076.

Compound 1: A mixture of compound **10** (2.21 g, 0.976 mmol), compound **11** (0.365 g, 0.488 mmol), Pd$_2$(dba)$_3$ (17.9 mg, 0.0195 mmol), sodium *tert*-butoxide (0.113 g, 1.17 mmol), and P(*t*Bu)$_3$ (8 mg, 0.039 mmol) in dry toluene (15 mL) was loaded into a high-pressure tube (from ACE Glass) and stirred at 110 °C under Ar for 24 h. After cooling to room temperature, the solution was extracted with ethyl acetate (30 mL × 3), and the organic layer was collected and dried with MgSO$_4$ (s). After removing the solvent, the crude product was purified by column chromatography on silica gel using THF/hexane (1:8) as the eluent to give a dark yellow powder in 64.8% yield (1.62 g). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.10–8.07 (d, *J* = 9.3 Hz, 4 H, H^{22}), 7.95–7.94 (d, *J* = 2.1 Hz, 4 H, H^{19}), 7.80–7.78 (d, *J* = 8.4 Hz, 2 H, H$^{4'}$), 7.70–7.66 (dd, J_1 = 9.3, J_2 = 2.1 Hz, 4 H, H^{21}), 7.63 (s, 2 H, H$^{5'}$), 7.55–7.47 (m, 32 H, H^{9}, H^{12}, H^{13}, H^{15}), 7.34–7.31 (d, *J* = 8.4 Hz, 2 H, H$^{3'}$), 7.26 (s, 2 H, H$^{1'}$), 7.24–7.19 (m, 32 H, H^{2}), 7.12–7.08 (m, 40 H, H^{3}, H^{6}), 7.02–6.96 (m, 24 H, H^{1}, H^{8}), 1.96 (m, 8 H, H$^{f'}$), 1.72–1.70 (m, 32 H, H^{f}), 1.10–0.98 (m, 120 H, H^{c}, H^{d}, H^{e}, H$^{c'}$, H$^{d'}$, H$^{e'}$), 0.81–0.72 (m, 68 H, H^{a}, H$^{a'}$, H$^{b'}$), 0.62 (m, 32 H, H^{b}) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 154.34 (C^{17}), 153.31 (C$^{7'}$), 152.62 (C^{18}), 152.40 (C^{5}), 150.55 (C^{16}), 148.38 (C$^{10'}$), 147.93 (C^{4}), 147.37 (C^{11}), 145.32 (C^{19}), 142.41 (C^{10}), 141.55 (C^{22}), 141.36 (C^{9}), 139.80 (C$^{8'}$), 138.80 (C$^{9'}$), 138.37 (C^{24}), 137.56 (C^{23}), 137.38 (C^{7}), 135.63 (C^{15}), 129.91 (C^{12}), 129.13 (C^{2}), 128.86 (C$^{3'}$), 127.43 (C$^{2'}$), 125.18 (C$^{1'}$), 124.35 (C^{13}), 123.84 (C^{3}), 123.40 (C^{14}), 122.51 (C^{1}), 120.80 (C^{6}), 120.04 (C$^{4'}$), 119.14 (C^{8}), 118.85 (C^{21}), 118.24 (C$^{5'}$), 113.85 (C^{20}), 55.05 (C^{g}, C$^{6'}$), 40.08 (C^{f}, C$^{f'}$), 31.52 (C^{e}, C$^{e'}$), 29.59 (C^{d}, C$^{d'}$), 23.84 (C^{c}, C$^{c'}$), 22.58 (C^{b}, C$^{b'}$), 14.07 (C^{a}, C$^{a'}$) ppm. MALDI-TOF: [M + H]$^+$ calcd. for $C_{372}H_{408}N_{18}$ 5132.3405; found 5132.4873.

Compound 2: Compound **9** (0.42 g, 0.418 mmol), compound **10** (1.9 g, 0.836 mmol), Pd$_2$(dba)$_3$ (15.3 mg, 0.0167 mmol), sodium *tert*-butoxide (0.096 g, 1.003 mmol), P(*t*Bu)$_3$ (7 mg, 0.034 mmol), and dry toluene (15 mL) were charged into a high-pressure tube, and the whole system was stirred at 110 °C under Ar for 24 h. After cooling to room temperature, the solution was extracted with ethyl acetate (30 mL × 3) and then dried with MgSO$_4$ (s). After removing the solvent, the crude product was purified by column chromatography on silica gel using THF/hexane (1:6) as the eluent to give a dark-yellow powder in 53.3% yield (1.2 g). ^{1}H NMR (300 MHz, CDCl$_3$): δ = 8.11–8.08 (d, *J* = 9.3 Hz, 4 H, H^{22}), 7.95–7.94 (d, *J* = 1.8 Hz, 4 H, H^{19}), 7.82–7.80 (d, *J* = 8.1 Hz, 2 H, H$^{5'}$), 7.71–7.64 (m, 8 H, H^{21}, H$^{8'}$, H$^{11'}$), 7.56–7.48 (m, 32 H, H^{9}, H^{12}, H^{13}, H^{15}), 7.34–7.32 (m, 4 H, H$^{2'}$, H$^{4'}$), 7.23–7.19 (m, 32 H, H^{2}), 7.12–7.07 (m, 40 H, H^{3}, H^{6}), 7.02–6.96 (m, 24 H, H^{1}, H^{8}), 2.08–1.99 (m, 12 H, H$^{f'}$, H$^{f''}$), 1.70 (m, 32 H, H^{f}), 1.10–1.00 (m, 132 H, H^{c}, H^{d}, H^{e}, H$^{c'}$, H$^{d'}$, H$^{e'}$, H$^{c''}$, H$^{d''}$, H$^{e''}$), 0.76–0.72 (m, 78 H, H^{a}, H$^{a'}$, H$^{b'}$, H$^{a''}$, H$^{b''}$), 0.62 (m, 32 H, H^{b}) ppm. ^{13}C NMR (75 MHz, CDCl$_3$): δ = 154.32 (C^{17}), 153.22 (C$^{1'}$), 152.61 (C^{18}), 152.36 (C^{5}), 150.77 (C$^{10'}$), 150.50 (C^{16}), 148.40 (C$^{7'}$), 147.91 (C^{4}), 147.36 (C^{11}), 145.15 (C^{19}), 142.41 (C^{10}), 141.54 (C^{22}), 141.35 (C^{9}), 140.95 (C$^{9'}$), 139.50 (C$^{12'}$), 139.06 (C$^{6'}$), 138.33 (C^{24}), 137.57 (C^{23}), 137.38 (C^{7}), 135.56 (C^{15}), 129.89 (C^{12}), 129.12 (C^{2}), 128.86 (C$^{4'}$), 127.38 (C$^{3'}$), 125.28 (C$^{2'}$), 124.34 (C^{13}), 123.82 (C^{3}), 123.38 (C^{14}), 122.49 (C^{1}), 121.40 (C$^{5'}$), 120.78 (C^{6}), 119.92 (C^{20}), 119.11 (C^{8}), 118.95 (C^{21}), 113.77 (C$^{11'}$), 113.65 (C$^{8'}$), 55.04 (C^{g}, C$^{g'}$, C$^{13'}$), 40.07 (C^{f}, C$^{f'}$, C$^{f''}$), 31.52 (C^{e}, C$^{e'}$, C$^{e''}$), 29.54 (C^{d}, C$^{d'}$, C$^{d''}$), 23.81 (C^{c}, $C^{c'}$, $C^{c''}$), 22.57 (C^{b}, C$^{b'}$, C$^{b''}$), 14.05 (C^{a}, C$^{a'}$, C$^{a''}$) ppm. MALDI-TOF(*m*/*z*): [M + H]$^+$ calcd. for $C_{391}H_{436}N_{18}$, 5388.7661, found 5388.9204.

Supporting Information (see footnote on the first page of this article): Numbering of carbons and hydrogens on various structural units and optical experiment details.

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