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Synthesis and characterization of a highly two-photon active dendrimer derived from 2,3,8-trifunctionalized indenoquinoxaline units†

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A dendritic chromophore derived from 2,3,8-trifunctionalized indenoquinoxaline units was synthesized and experimentally shown to manifest very strong and widely-dispersed two-photon absorption (2PA) across the dynamic tuning range of a Ti:sapphire laser. The maximum 2PA of the studied chromophore was found to reach ≈31 700 GM, indicating that 2,3,8-trifuctionalized indenoquinoxaline units are useful building moieties for the construction of highly active 2PA-dyes. In addition, this dendritic structure was also demonstrated to effectively regulate the optical power of femtosecond laser pulses at 800 nm.

1. Introduction

The momentum of developing materials with highly efficient two-photon absorption (2PA) properties is greatly incited not only by the availability of powerful ultra-fast lasers but also by the potentiality of using these materials in many photonic and biophotonic applications such as optical power-limiting, frequency up-converted lasing, 3-D data storage, nondestructive bioimaging/tracking, and two-photon-assisted photodynamic therapy.[1] For the past fifteen years great endeavors have been devoted to 2PA optimization *via* molecular design and engineering, leading to the investigation of a range of π-conjugated molecules with various archetypes including quasi-linear, multi-branched, and dendritic geometries. So far, it has been realized that the combination of several structural parameters such as intramolecular charge-transfer efficiency, effective size of π-conjugation domain, and molecular dimensionality of a molecule is closely related to the molecular 2PA.[2–10] In other words, the arrangement of the selected composing units within a molecule is a hinge for the molecular design toward highly active 2PA-chromophores. Among the studied π-systems, multi-branched and dendritic chromophores have been experimentally shown to manifest highly efficient multi-photon absorption.[4a–c,5,6c,7a,b,d,8d–f,9a–d,10–12] From the standpoint of molecular design, branched and dendritic skeletons offer an approach to incorporate numbers of 2PA-enhancing parameters into a single dye system so that it is accessible for materials chemists to optimize a single molecule that simultaneously combines desired characteristics for different purposes. In searching for design strategies to achieve highly efficient 2PA materials at a molecular level, we are interested in exploring the 2PA properties of multi-branched or dendritic organic structures composed of various π-conjugated frameworks with heterocyclic moieties incorporated because the involvement of hetero-atoms is expected to alter the electronic nature of the resulting chromophores and may consequently bring impact on the molecular 2PA. Following this concept and our continuous efforts in developing multi-branched π-derivatives based on fluorene units, in this paper we report the synthesis of a new model fluorophore (**1**) using tri-functionalized indenoquinoxaline as the major building block to construct a dendritic scaffold and the initial investigations of its 2PA properties in the femtosecond time domain.

2. Results and discussions

I. Molecular structure and synthesis of the dendrimer

As illustrated in Fig. 1, the structure of compound **1** is constructed by using a nitrogen atom as the electron-donating ramification center to connect three identical large branches, each one of which possesses two consecutive inner-layers of indenoquinoxaline moieties and four diphenylaminofluorene units at the outermost positions. Hence the resulting dendrimer contains totally nine heterocyclic ring complexes as the interior circles and twelve electron-pushing π-units as the peripheries. As for the synthesis of this dendrimer, the originally designed convergent method attempting to directly accomplish the final structure through a two-fold Buchwald amination process by using compounds **11** and **12** (see Scheme 1) as the precursors was unsuccessful. Instead, another approach based on a strategy starting from the diamine (**2**) to prepare the central core (**6**) and the large diketone (**10**) as the

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major synthons for the final coupling reaction to afford compound **1** was found to be rather efficient. As shown in Scheme 1, the formation of a fused [1,2,5]thiazole ring was employed to protect the diamine functional groups during the synthetic course from compound **2** toward the tertiary amine (**5**) and the diamine functional groups can be easily recovered by using $LiAlH_4$ (LAH) as the reducing agent to furnish the central trigonal core (**6**) for the final coupling. Besides, we have attached alkyl chains at the C9 positions of all the fluorenyl units in order to enhance the solubility of the target dendrimer in common solvents, which is another important issue to be considered in the molecular design from both the aspects of experiments and applications.

II. Linear and nonlinear optical properties

One-photon absorption (1PA) and fluorescence spectra. Linear absorption and fluorescence spectra of the studied model compound (**1**) in solution phase were recorded by a Shimadzu 3501 PC spectrophotometer and a Jobin-Yvon FluoroMax-4 spectrometer, respectively. Compound **1** exhibits intense linear absorption ranging from 300 nm to 450 nm and strong fluorescence emission in various solvents as illustrated in Fig. 2. Despite its symmetric substitution nature, this dye molecule manifests salient solvent effect on the fluorescence colors and life-times as shown in Fig. 2 and summarized in Table 1, respectively. Similar properties have been observed in other multi-polar chromophore systems and the symmetry-breaking phenomenon caused by electron–vibration coupling and dipolar solvation effects were proposed to account for this behavior.[13,14]

Two-photon-excited fluorescence property studies. In these experiments, a mode-locked Ti:Sapphire laser (Chameleon Ultra II, Coherent) which delivers ~140 fs pulses with a repetition rate of 80 MHz and a beam diameter of 2 mm was employed as the probing light source. The intensity level of the excitation beam was carefully controlled in order to avoid the saturation of absorption and photodegradation. Besides, the relative position of the excitation beam was adjusted as close as possible to the wall of the quartz cell (10 mm × 10 mm cuvette) so that only the emission from the front-surface of the sample was recorded in order to minimize the re-absorption or inner-filter effect. It is found that the same solvato-fluorochromic behavior can also be observed from **1** under two-photon excitation conditions as illustrated in Fig. 3(a) and (b), suggesting that the final emissive state accessed by the two-photon process of this molecule is strongly dipolar and sensitive to the polarity of the environment as well. The power-squared dependence of the 2PA-induced fluorescence intensity on the excitation intensity of **1** was also examined and since the linear fitting slopes in the logarithmic plots (Fig. 3(c)–(e)) of the measured data are close to 2, it validates that a 2PA process is responsible for the observed up-converted emissions in all cases.

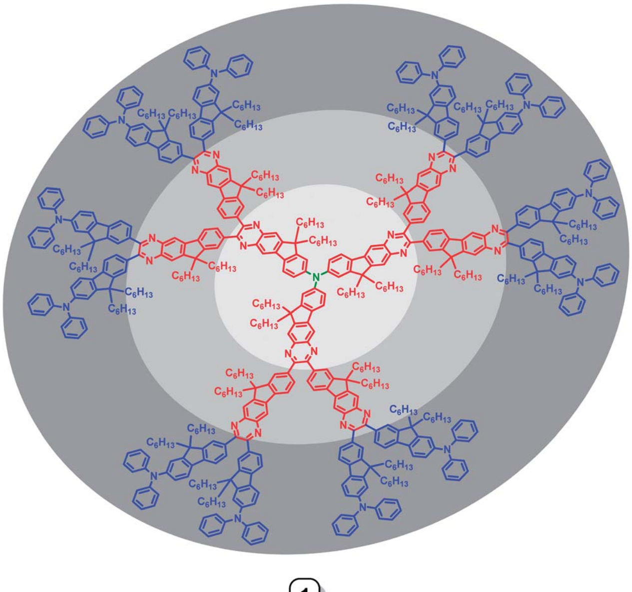

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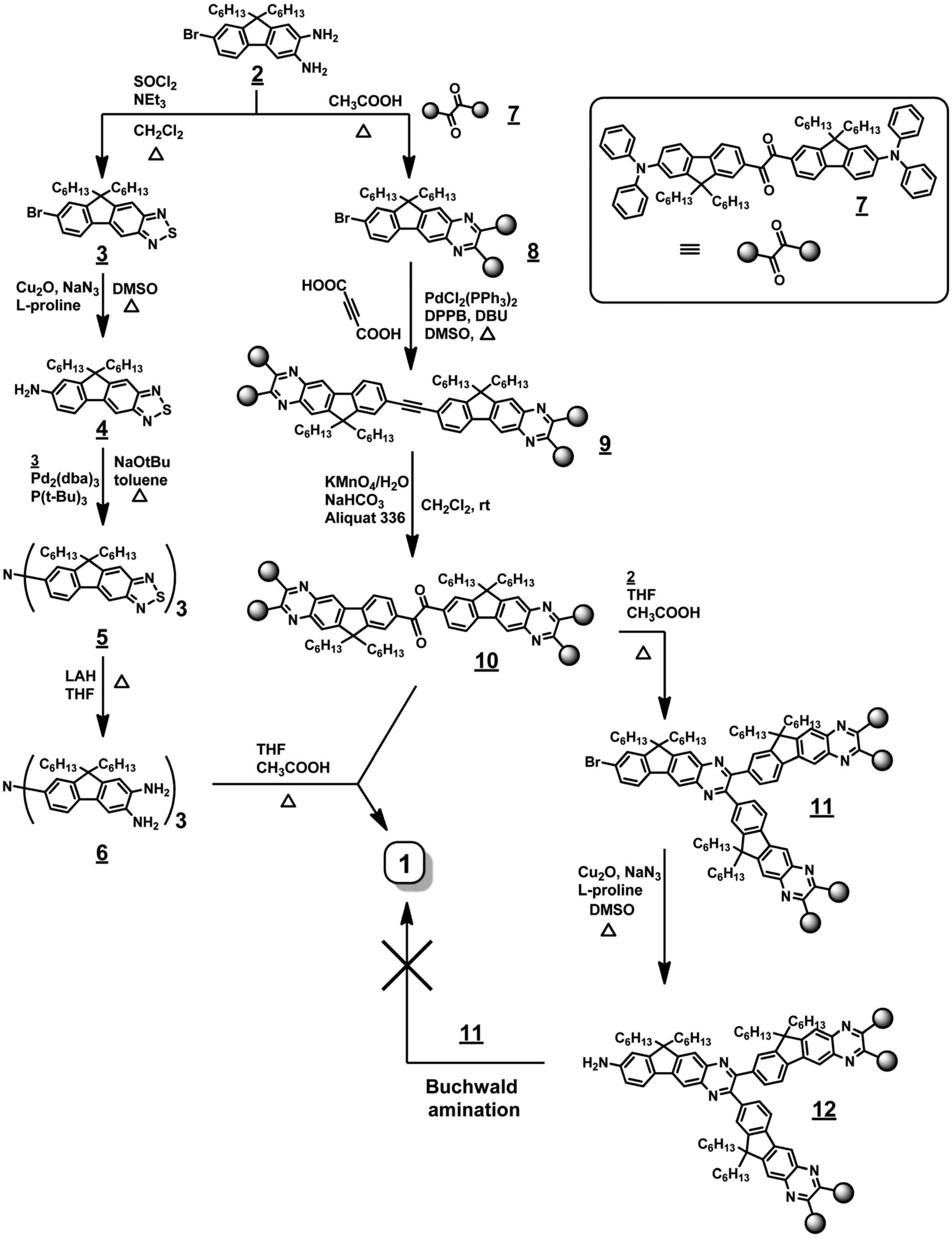
Fig. 1 The molecular structure of dendrimer **1**.

Degenerate two-photon absorption spectrum measurement. The degenerate 2PA-spectrum of **1** in toluene was measured *via* a two-photon-excited fluorescence (2PEF) technique[15,16] utilizing the aforementioned femtosecond laser system as the probing tool and the result is illustrated in Fig. 4. It is notable that this dendritic dye compound exhibits widely dispersed and strong 2PA ($\delta_2 \geq 5000$ GM) across most of the effective tuning range of a Ti:sapphire oscillator accompanied by a local 2PA maximum around 740 nm ($\delta_2 \sim 31\,700$ GM). From the view point of molecular structure, this dendrimer can be expected to manifest unsymmetrical charge-redistribution upon light excitation since it possesses different structural units with unequal electron-donating strengths in the center and at the peripheral positions. Multi-branched chromophores with similar structural arrangement have been experimentally observed to show strong molecular 2PA.[5c,7d,9b,c,10] On the other hand, it is also revealed that the incorporation of indenoquinoxaline moieties as the mediating layers in this dendritic scaffold did not inflict a deleterious effect on the molecular 2PA; instead, indenoquinoxaline could be an effective building unit for the construction of highly active 2PA-dyes when properly integrated. Besides, the widely dispersed and intense 2PA as well as medium-high fluorescence quantum yield has made this dendritic chromophore a promising candidate for 2PA-based applications such as broadband optical-limiters and fluorescence up-converters.

III. Optical-power limiting performance against femtosecond pulses

It is well known that an ideal optical-limiter is expected to possess an intensity-dependent transmission feature so that the output intensity is always below a certain maximum value, which makes optical-limiters useful for protecting human eyes and sensors against damaging sources of light. This power restriction phenomenon is also important for the optical dynamic range compression in optical signal processing and



Scheme 1 Synthetic procedure for dendrimer **1**.

nonlinear ultra-fast filtering/reshaping of optical fiber signals. To evaluate the power-limiting performance of this dendritic fluorophore, we have utilized ultrafast laser pulses (∼30 fs, from a femtosecond regenerative amplifier system) at ∼800 nm to probe their 2PA-based optical power suppressing properties. The sample solution for this study was prepared in toluene with a concentration of 0.01 M and the experimental setup for this measurement is described in detail in the ESI.† Fig. 5 illustrates the measured data for the dependence of output power on the input power of the probing laser beam. As presented in Fig. 5, the measured input–output curve starts to deviate from the linear transmission (diagonal dotted line) at a low level of pumping power, and rapidly approaches larger values of this deviation while the excitation power increases. To be more specific, when the input power increased from ∼54 mW to ∼660 mW (∼12-fold increase), the transmitted output only shifts from ∼40 mW to ∼210 mW (∼5.25-fold increase), which fits the theoretically predicted optical-limiting behavior (the solid-line) based on 2PA. Moreover, the 2PA cross-section value of this model compound was calculated to be ∼23 500

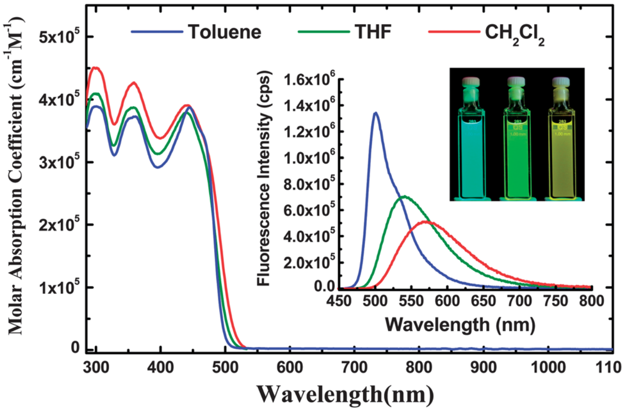


Fig. 2 Linear absorption and fluorescence spectra of **1** in various solvents. (Concentration: 1 × 10^{-6} M; inset photo: the distinct fluorescence color change of **1** in different solvents.)

GM from the performed optical-power-limiting experiment, which is very close to the result obtained from the 2PEF method within experimental uncertainty and this indicates that 2PA should be the major cause for the observed upconverted emission and optical power restriction in this dendrimer system.

3. Conclusion

In summary, a model dendritic structure composed of an electron-donating center, two generations of tri-functionalized indenoquinoxaline units, and twelve diphenylfluorenylamino moieties at peripheral positions has been synthesized through a carefully designed synthetic route and experimentally shown to manifest very strong and broadly dispersed molecular 2PA in the near-IR region. It is also demonstrated that the studied model compound possesses effective optical-control of the femtosecond laser pulses. These rudimentary results imply that the indenoquinoxaline unit could be a useful building unit for the construction of highly active 2PA-chromophores when properly functionalized and incorporated.

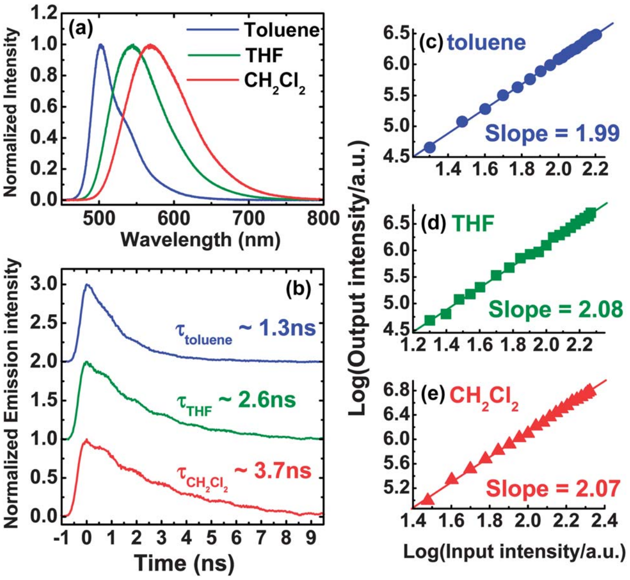


Fig. 3 2PA-related photophysical properties of **1** in various solvents: (a) normalized 2PA-induced fluorescence spectra; (b) 2PA-induced fluorescence decay curves; (c–e) logarithmic plots of power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity.

4. Experimental section

I. General

All commercially available reagents for the preparation of the intermediates and targeted chromophores were obtained from Acros Organics or Alfa Aesar and were used as received, unless stated otherwise. THF was distilled from sodium benzophenone ketyl. ^1H-NMR and ^{13}C-NMR spectra were recorded either on 200 or 300 MHz spectrometers and referenced to TMS or residual $CHCl_3$. The numbering of carbon and hydrogen atoms on each intermediate and the final chromophore for the NMR signal assignment are systematized and illustrated in the ESI.† High-resolution mass spectroscopy (HRMS) was conducted using a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS spectra were obtained on a Voyager DE-PRO mass spectrometer (Applied Biosystem, Houston, USA).

Table 1 Photophysical properties of **1** in solution phase[a]

	λ_{max}^{abs} [b]/nm	$\varepsilon^c/10^{-5}$ cm^{-1} M^{-1}	λ_{max}^{em} [d]/nm	$\Phi_F{}^e$	$\tau^{1PA\text{-}FL\ f}$/ns	$\tau^{2PA\text{-}FL\ g}$/ns	$\delta_2^{max\ h}$/GM
1 in toluene	301	3.89	501	0.60	~1.3	~1.3	~31 700
	358	3.73					
	445	3.87					
1 in THF	300	4.09	541	0.59	~2.6	~2.6	—
	358	3.87					
	440	3.80					
1 in CH_2Cl_2	301	4.50	571	0.52	~3.7	~3.7	—
	359	4.27					
	443	3.90					

[a] Concentrations were 1 × 10^{-6} M and 1 × 10^{-4} M for 1PA-related and 2PA-related measurements, respectively. [b] 1PA maximum. [c] Extinction coefficient. [d] 1PA-induced fluorescence emission maximum. [e] Fluorescence quantum efficiency. [f] 1PA-induced fluorescence lifetime. [g] 2PA-induced fluorescence lifetime. [h] Maximum 2PA cross-section value (with experimental error ~±15%); 1 GM = 1 × 10^{-50} cm^4 s per photon-molecule.

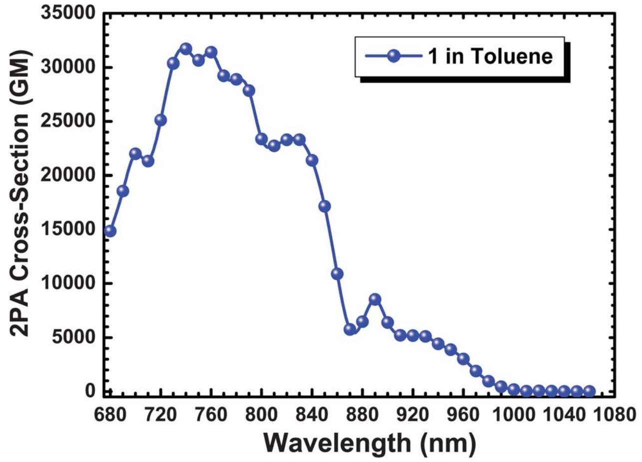


Fig. 4 2PA spectrum of dendrimer **1** in toluene.

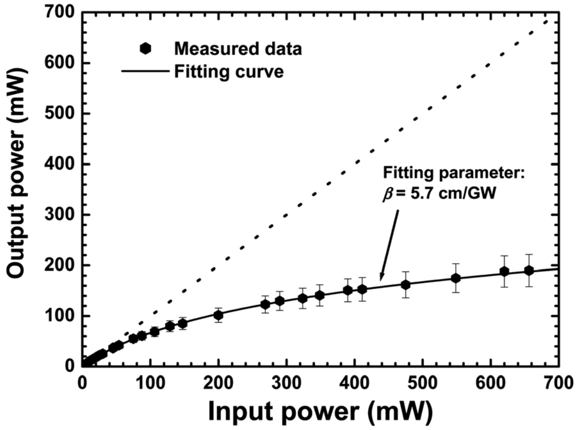


Fig. 5 Measured output energy *versus* input energy of ~30 fs laser pulses at ~800 nm based on a 1 cm path solution sample of **1** in toluene at 0.01 M. The solid curve is the theoretical data with a best-fit parameter of $\beta = 5.7$ cm GW^{-1}.

II. Photophysical methods

All the linear optical properties of the subject model compound were measured by corresponding spectrometers and the detailed experimental conditions as well as the optical set-ups for the nonlinear optical property investigations are described in the ESI.†

III. Synthesis

In Scheme 1, the preparation of compounds **2**, **7**, and **8** has been previously reported.[10c] For the synthesis of other key intermediates and the targeted model chromophore, a series of functionalization steps starting from compound **2** have been conducted and are presented as the following:

7-Bromo-9,9-dihexyl-9*H*-fluoreno[2,3-*c*][1,2,5]thiadiazole (3). To a mixture of compound **2** (0.65 g, 1.48 mmol) and triethylamine (0.60 g, 5.92 mmol) in CH_2Cl_2 (10 mL). Thionyl chloride (0.53 g, 4.44 mmol) was added slowly and the mixture was refluxed for 4 h. After cooling, the solvent was removed by a rotatory evaporator and 50 mL of water was added. Concentrated $HCl_{(aq)}$ was then added to adjust the final pH value of the solution to pH = 2. The above solution was extracted by CH_2Cl_2 (30 mL × 3) and the combined organic layer was dried over anhydrous $MgSO_{4(s)}$. After filtration and concentration, the residue was purified by column chromatography on silica gel (ethyl acetate : hexanes = 1 : 10 in v/v) to afford **3** (0.656 g, 1.48 mmol, 80%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 8.19–8.18 (d, J = 0.9 Hz, 1H, H_H), 7.89–7.88 (d, J = 0.9 Hz, 1H, H_K), 7.74–7.71 (d, J = 8.1 Hz, 1H, H_E), 7.54–7.53 (dd, J_1 = 8.1 Hz, J_2 = 1.8 Hz, 1H, H_D), 7.52–7.51 (d, J = 1.8 Hz, 1H, H_B), 2.08–2.00 (m, 4H, $H_{f'}$), 1.12–1.04 (m, 12H, $H_{c'}$, $H_{d'}$, $H_{e'}$), 0.75–0.63 (m, 10H, $H_{a'}$, $H_{b'}$); ^{13}C-NMR (75 MHz, $CDCl_3$, tentative assignment based on calculated values): δ = 155.32 (C_J), 155.23 (C_I), 153.79 (C_L), 153.23 (C_A), 143.67 (C_G), 137.57 (C_F), 130.68 (C_B), 126.50 (C_E), 123.77 (C_C), 122.47 (C_D), 114.41 (C_H), 110.17 (C_K), 54.70 ($C_{g'}$), 41.42 ($C_{f'}$), 31.32 ($C_{e'}$), 29.47 ($C_{d'}$), 23.81 ($C_{c'}$), 22.41 ($C_{b'}$), 13.84 ($C_{a'}$); HRMS-FAB: m/z calcd for $C_{25}H_{32}BrN_2S$: 471.1469 [M + H]$^+$; found: 471.1482.

9,9-Dihexyl-9*H*-fluoreno[2,3-*c*][1,2,5]thiadiazol-7-amine (4). A mixture of L-proline (69 mg, 0.60 mmol), NaN_3 (65 mg, 0.92 mmol), Cu_2O (65 mg, 0.46 mmol) and **3** (0.22 g, 0.46 mmol) in DMSO (4 mL) was heated in an oil bath at 100 °C for 2 h. The color of the reaction mixture turned from dark red to dark brown over the course of the reaction. The progress of the reaction was monitored by TLC and after completion of reaction, the dark reaction solution was cooled to room temperature, quenched by the addition of saturated $NH_4Cl_{(aq)}$ (5 mL) and ethyl acetate (5 mL). This biphasic mixture was stirred at room temperature for 30 min. The resulting dark green solution was filtered through a pad of Celite. Ethyl acetate (20 mL) and water (5 mL) was then added to the filtrate and the resulting mixture was transferred to a separation funnel, the aqueous phase was removed, and the organic phase was washed with saturated $NaHCO_{3(aq)}$ (15 mL × 1) and saturated $NaCl_{(aq)}$ (15 mL × 2). The organic phase was then collected and dried over anhydrous $MgSO_{4(s)}$. After filtration and concentration, the residue was purified by column chromatography on silica gel (ethyl acetate : hexanes = 1 : 5 in v/v) to afford **4** (0.133 g, 0.33 mmol, 70%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ = 7.95–7.94 (d, J = 0.9 Hz, 1H, H_H), 7.77–7.76 (d, J = 0.9 Hz, 1H, H_K), 7.65–7.62 (d, J = 8.1 Hz, 1H, H_E), 6.73–6.69 (dd, J_1 = 8.1 Hz, J_2 = 2.1 Hz, 1H, H_D), 6.63–6.62 (d, J = 2.1 Hz, 1H, H_B), 3.98 (s, 2H, NH_2), 2.06–1.89 (m, 4H, $H_{f'}$), 1.13–1.02 (m, 12H, $H_{c'}$, $H_{d'}$, $H_{e'}$), 0.79–0.71 (m, 10H, $H_{a'}$, $H_{b'}$); ^{13}C-NMR (75 MHz, $CDCl_3$, tentative assignment based on calculated values): δ = 155.86 (C_J), 155.04 (C_I), 154.95 (C_L), 153.40 (C_A), 148.47 (C_G), 145.64 (C_F), 129.54 (C_C), 122.50 (C_K), 114.83 (C_H), 113.84 (C_E), 108.99 (C_B), 107.20 (C_D), 54.24 ($C_{g'}$), 41.76 ($C_{f'}$), 31.52 ($C_{e'}$), 29.71 ($C_{d'}$), 23.91 ($C_{c'}$), 22.59 ($C_{b'}$), 13.98 ($C_{a'}$); HRMS-FAB: m/z calcd for $C_{25}H_{33}N_3S$: 408.2473 [M + H]$^+$; found: 408.2485.

Tris(9,9-dihexyl-9*H*-fluoreno[2,3-*c*][1,2,5]thiadiazol-7-yl)amine (5). Compound **3** (0.338 g, 0.717 mmol), compound **4** (0.13 g, 0.33 mmol), NaO*t*Bu (76 mg, 0.78 mmol), P(tBu)$_3$ (1.5 mg, 0.006 mmol) and $Pd_2(dba)_3$ (3 mg, 0.003 mmol) were mixed in dry toluene (5 mL). The whole system was then heated to reflux for 12 h. After cooling to room temperature, the solution was poured into water and was extracted with CH_2Cl_2 (15 mL × 2). The organic phase was collected and dried over anhydrous $MgSO_{4(s)}$. After filtration and concentration, the residue was purified by column chromatography on silica gel (ethyl acetate : hexanes = 1 : 20 in v/v) to afford **5** (0.31 g, 0.26 mmol, 81%). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 8.10$ (s, 3H, H_H), 7.86 (s, 3H, H_K), 7.79–7.76 (d, $J = 8.1$ Hz, 3H, H_E), 7.30–7.29 (d, $J = 1.8$ Hz, 3H, H_B), 7.18–7.14 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.8$ Hz, 3H, H_D), 2.11–1.94 (m, 12H, $H_{f'}$), 1.26–1.12 (m, 36H, $H_{c'}$, $H_{d'}$, $H_{e'}$), 0.88–0.76 (m, 30H, $H_{a'}$, $H_{b'}$); ^{13}C-NMR (75 MHz, $CDCl_3$, tentative assignment based on calculated values): $\delta = 155.64$ (C_J), 155.25 (C_I), 154.63 (C_L), 152.90 (C_A), 148.53 (C_G), 144.48 (C_F), 134.20 (C_C), 123.92 (C_K), 122.34 (C_H), 118.25 (C_E), 114.33 (C_B), 108.99 (C_D), 54.62 ($C_{g'}$), 41.53 ($C_{f'}$), 31.66 ($C_{e'}$), 29.68 ($C_{d'}$), 24.20 ($C_{c'}$), 22.58 ($C_{b'}$), 14.04 ($C_{a'}$); MALDI-TOF: *m/z* calcd for $C_{75}H_{93}N_7S_3$: 1187.6655 $[M + H]^+$; found: 1187.6692.

***N*7,*N*7-Bis(6,7-diamino-9,9-dihexyl-9*H*-fluoren-2-yl)-9,9-dihexyl-9*H*-fluorene-2,3,7-triamine (6).** Compound **5** (0.31 g, 0.264 mmol) was dissolved in deaerated THF (45 mL). Then lithium aluminum hydride (0.12 g, 3.17 mmol) was added under an argon atmosphere. The mixture was heated to 60 °C for overnight. After cooling to room temperature, the reaction mixture was quenched with 2 N $NaOH_{(aq)}$ (10 mL). The above solution was filtered through a pad of Celite and the filtrate was extracted with ethyl acetate (25 mL × 3). The combined organic layers were collected and dried over anhydrous $MgSO_{4(s)}$, filtered, and concentrated to dryness. Compound **6** was used directly for the next step without further purification. ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 7.33$–7.30 (d, $J = 8.1$ Hz, 3H, H_E), 7.18–7.17 (d, $J = 1.5$ Hz, 3H, H_B), 6.96 (s, 3H, H_K), 6.94–6.90 (dd, $J_1 = 8.1$ Hz, $J_2 = 1.5$ Hz, 3H, H_D), 6.64 (s, 3H, H_H), 3.37 (s, 12H, NH_2), 1.80–1.75 (m, 12H, $H_{f'}$), 1.17–1.07 (m, 36H, $H_{c'}$, $H_{d'}$, $H_{e'}$), 0.83–0.71 (m, 30H, $H_{a'}$, $H_{b'}$); ^{13}C-NMR (75 MHz, $CDCl_3$, tentative assignment based on calculated values): $\delta = 151.54$ (C_A), 146.01 (C_L), 143.25 (C_F), 136.25 (C_G), 133.92 (C_C), 133.78 (C_J), 133.45 (C_I), 122.50 (C_B), 118.71 (C_D), 117.91 (C_E), 111.30 (C_K), 107.76 (C_H), 54.46 ($C_{g'}$), 40.66 ($C_{f'}$), 31.75 ($C_{e'}$), 29.85 ($C_{d'}$), 23.90 ($C_{c'}$), 22.68 ($C_{b'}$), 14.11 ($C_{a'}$); HRMS-FAB: *m/z* calcd for $C_{75}H_{105}N_7$: 1103.8431 $[M]^+$; found: 1103.8434.

7-(8-(2-(2,3-Bis(2-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-7-yl)-10,10-dihexyl-10*H*-indeno[2,1-*g*]quinoxalin-8-yl)ethynyl)-3-(2-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-7-yl)-10,10-dihexyl-10*H*-indeno[2,1-*g*]quinoxalin-2-yl)-9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (9). To a mixture of compound **8** (5.64 g, 3.85 mmol) and acetylenedicarboxylic acid (0.22 g, 0.1.93 mmol) in DMSO (8 mL) was added 1,4-bis(diphenylphosphino)butane (0.17 mg, 0.386 mmol), DBU (1.18 g, 7.72 mmol) and $PdCl_2(PPh_3)_2$ (0.14 g, 0.193 mmol). The resulting mixture was stirred at 110 °C under an Ar atmosphere for 8 h. After cooling to room temperature, ∼100 mL of H_2O was added to the reaction mixture. The above solution was then extracted with CH_2Cl_2 (30 mL × 3). The organic phase was dried over anhydrous $MgSO_{4(s)}$. After filtration and concentration, the residue was purified by column chromatography on silica gel (THF : hexanes = 1 : 15 in v/v) to afford **9** (3.31 g, 1.19 mmol, 62%). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 8.47$ (s, 1H, H_H), 8.13 (s, 1H, H_K), 7.96–7.93 (d, $J = 7.8$ Hz, 1H, H_D), 7.70–7.52 (m, 8H, H_9, H_{12}, H_{13}, H_{15}, H_E, H_B), 7.27–7.21 (m, 8H, H_2), 7.14–7.11 (m, 10H, H_3, H_6), 7.03–6.98 (m, 6H, H_1, H_8), 2.27–2.04 (m, 4H, H_f), 1.77–1.73 (m, 8H, $H_{f'}$), 1.13–1.06 (m, 36H, H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.83–0.56 (m, 30H, H_a, $H_{a'}$, H_b, $H_{b'}$); ^{13}C-NMR (75 MHz, $CDCl_3$, tentative assignment based on calculated values): $\delta = 153.47$ (C_5, C_N), 153.04 (C_M), 152.59 (C_{16}), 151.49 (C_L), 150.59 (C_F), 150.50 (C_A), 147.90 (C_4), 147.41 (C_{11}), 143.19 (C_G), 141.50 (C_J), 141.41 (C_I), 139.98 (C_7), 137.53 (C_K), 137.45 (C_H), 135.53 (C_{10}), 131.12 (C_B), 129.12 (C_2), 126.26 (C_{12}), 128.28 (C_{15}), 126.30 (C_E), 124.42 (C_{14}), 123.89 (C_3), 123.42 (C_{13}), 122.57 (C_1), 122.36 (C_D), 120.87 (C_6), 119.16 (C_9), 118.74 (C_8), 118.18 (C_C), 91.29 (acetylene carbon), 55.35 (C_g), 55.11 ($C_{g'}$), 41.51 (C_f), 40.16 ($C_{f'}$), 31.60 (C_e), 30.34 ($C_{e'}$), 29.73 (C_d), 29.65 ($C_{d'}$), 23.89 (C_c, $C_{c'}$), 22.67 (C_b, $C_{b'}$), 14.13 (C_a), 14.02 ($C_{a'}$); MALDI-TOF: *m/z* calcd for $C_{204}H_{230}N_8$: 2795.0626 $[M + 1]^+$; found: 2795.1472.

1,2-Bis(2,3-bis(7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)-10,10-dihexyl-10*H*-indeno[1,2-*g*]quinoxalin-8-yl)ethane-1,2-dione (10). To a solution of compound **9** (3.33 g, 1.19 mmol) in CH_2Cl_2 (15 mL) was added $KMnO_4$ (1.50 g, 9.54 mmol), $NaHCO_3$ (1.00 g, 1.193 mmol), Aliquat 336 (0.01 g), and H_2O (15 mL). The resulting mixture was stirred at room temperature for 24 hours. Then, saturated $NaHSO_{3(aq)}$ (20 mL) and 1 N HCl (15 mL) were added into the reaction mixture. The above solution was then extracted with CH_2Cl_2 (30 mL × 3). The organic phase was dried over anhydrous $MgSO_{4(s)}$. After filtration and concentration, the residue was purified by column chromatography on silica gel (THF : hexanes = 1 : 15 in v/v) to afford **10** (2.46 g, 0.87 mmol, 73%). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 8.57$ (s, 2H, H_H), 8.22–8.16 (m, 4H, H_D, H_E), 8.04 (s, 4H, H_K, H_B), 7.63–7.51 (m, 16H, H_9, H_{12}, H_{13}, H_{15}), 7.27–7.22 (m, 16H, H_2), 7.13–7.08 (m, 20H, H_3, H_6), 7.01–6.98 (m, 12H, H_1, H_8), 2.20–2.14 (m, 8H, H_f), 1.71–1.68 (m, 16H, $H_{f'}$), 1.10–1.03 (m, 72H, H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.80–0.67 (m, 60H, H_a, $H_{a'}$, H_b, $H_{b'}$); ^{13}C-NMR (75 MHz, $CDCl_3$, tentative assignment based on calculated values): $\delta = 194.71$ (carbonyl carbon), 153.90 (C_{16}), 153.82 (C_M), 152.66 (C_5), 152.38 (C_N), 150.64 (C_A, C_L), 147.95 (C_4), 147.57 (C_F), 146.38 (C_G), 141.97 (C_M), 141.85 (C_{11}), 141.75 ($C_{11'}$), 141.04 (C_N), 137.32 (C_{14}), 137.25 ($C_{14'}$), 135.48 (C_{10}), 133.18 (C_E), 130.87 (C_B), 129.02 (C_2, C_{12}), 125.68 (C_{15}), 124.42 (C_3), 123.93 (C_{13}), 123.42 (C_D), 122.62 (C_1), 121.32 (C_K), 120.94 (C_6), 120.51 (C_H), 119.09 (C_9, C_8), 55.66 (C_g), 55.13 ($C_{g'}$), 41.22 (C_f), 40.18 ($C_{f'}$), 31.60 (C_e, $C_{e'}$), 29.65 (C_d, $C_{d'}$), 24.05 (C_c), 23.90 ($C_{c'}$), 22.67 (C_b), 22.59 ($C_{b'}$), 14.13 (C_a), 14.01 ($C_{a'}$); MALDI-TOF: *m/z* calcd for $C_{204}H_{230}N_8O_2$: 2827.1468 $[M + 1]^+$; found: 2827.1572.

Compound 1. To a mixture of compound **6** (0.29 g; 0.264 mmol) and compound **10** (2.46 g; 0.871 mmol) in THF (10 mL) was added CH_3COOH (2 mL) and the resulting mixture was refluxed under a N_2 atmosphere for 12 hours. After cooling to room temperature, the reaction mixture was then extracted with CH_2Cl_2 (30 mL × 3). The organic phase was collected and dried over anhydrous $MgSO_{4(s)}$. After filtration and concentration, the residue was purified by column chromatography on silica gel (THF : hexane = 1 : 15 in v/v) to afford compound **1** (1.00 g, 0.106 mmol, 40%). ^{1}H-NMR (300 MHz, $CDCl_3$): $\delta = 8.45$ (s, 9H, H_H, $H_{H'}$), 8.17 (s, 3H, $H_{K'}$), 8.09 (s, 6H, H_K), 7.98–7.54 (m, 75H, H_9, H_{12}, H_{13}, H_{15}, H_B, $H_{B'}$, H_D, $H_{D'}$, H_E, $H_{E'}$), 7.27–7.22 (m, 48H, H_2), 7.13–7.10 (m, 60H, H_3, H_6), 7.03–6.99 (m, 36H, H_1, H_8), 2.16–1.74 (m, 84H, H_f, $H_{f'}$, $H_{f''}$), 1.11–1.03 (m, 252H, H_c, $H_{c'}$, $H_{c''}$, H_d, $H_{d'}$, $H_{d''}$, H_e, $H_{e'}$, $H_{e''}$), 0.80–0.64 (m, 210H, H_a, $H_{a'}$, $H_{a''}$, H_b, $H_{b'}$, $H_{b''}$); ^{13}C-NMR (75 MHz, $CDCl_3$, tentative assignment based on calculated values): $\delta = 154.09$ (C_N), 153.67 (C_5), 153.46 (C_M), 153.04 ($C_{N'}$), 152.78 ($C_{M'}$), 152.66 (C_{16}), 151.96 (C_L, $C_{L'}$), 151.55 (C_A, $C_{A'}$), 150.60 (C_F, $C_{F'}$), 148.38 (C_4), 147.97 (C_{11}), 147.78 ($C_{G'}$), 147.44 (C_G), 144.20 ($C_{J'}$), 143.29 (C_J), 141.82 (C_I), 141.55 ($C_{I'}$), 141.49 (C_E), 141.41 ($C_{E'}$), 141.29 (C_C), 140.30 (C_K, $C_{K'}$), 137.65 (C_H, $C_{H'}$), 137.58 ($C_{C'}$), 135.65 (C_7), 135.09 (C_{10}), 129.60 (C_B), 129.19 (C_2), 125.00 (C_{12}), 124.43 (C_{15}), 123.89 ($C_{B'}$), 123.46 (C_{14}), 122.57 (C_3), 120.88 (C_{13}), 119.18 (C_1), 118.98 (C_6), 118.38 (C_9), 117.41 (C_8), 55.43 ($C_{g''}$), 55.33 ($C_{g'}$), 55.11 (C_g), 41.43 ($C_{f''}$), 40.18 (C_f, $C_{f'}$), 31.85 ($C_{e''}$), 31.60 ($C_{e'}$, C_e), 29.94 ($C_{d''}$), 29.65 ($C_{d'}$, C_d), 24.30 ($C_{c''}$), 23.90 ($C_{c'}$, C_c), 22.76 ($C_{b''}$), 22.67 ($C_{b'}$, C_b), 14.13 ($C_{a''}$, $C_{a'}$, C_a). MALDI-TOF: *m*/*z* calcd for $C_{687}H_{783}N_{31}$: 9475.0332 $[M]^+$; found: 9475.0781.

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