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Two-photon absorption and effective broadband optical power limiting properties of a multi-branched chromophore containing 2,3-diarylquinoxalinyl moieties as the electron-pulling units

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ABSTRACT

A novel multi-branched chromophore containing 2,3-diarylquinoxalinyl units as the electron-acceptors had been synthesized and its nonlinear optical properties were characterized in the femtosecond and nanosecond regime. The experimental results show that the studied fluorophore possesses strong and wide-dispersed two-photon absorption in near infrared (NIR) region. It is demonstrated that the incorporation of 2,3-disubstituted quinoxaline moieties as a part of π -conjugation in a dye molecule could be a useful approach toward large molecular two-photon absorptivities within the studied spectral region. Effective optical-power-attenuation behaviors in the nanosecond time domain of this compound were also investigated and the results indicate that such dye molecule can be a potential material as a broadband and quick-responsive optical limiter especially when against those laser lights with longer pulses.

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1. Introduction

Although two-photon absorption (2PA) was theoretically predicted by Maria Göppert-Mayer in 1931,¹ the first experimental observation of this nonlinear optical phenomenon was realized about 30 years later when Kaiser and Garret observed two-photon induced up-converted fluorescence emission from a CaF₂:Eu²⁺ inorganic crystal in 1961.² With the advent of high peak-power laser systems, numerous 2PA-based photonic and biophotonic applications have been explored and demonstrated including optical power limiting, frequency up-converted lasing, 3-D data storage, 3-D microfabrication, nondestructive bio-imaging and tracking, and two-photon-assisted photodynamic therapy.³ To be of use in these applications, organic compounds that manifest strong 2PA within specific spectral region are consequently in great demand. The accumulated knowledge and experience based on enormous efforts to understand the connections between molecular structure and 2PA property by testing and modeling various dye systems ever since mid-1990s have revealed that large 2PA can be achieved by judicious control of the intramolecular charge-transfer efficiency and/or effective size of π -conjugation domain within a molecule.⁴⁻¹⁰ Among the investigated dye systems, it has been experimentally shown that octupolar chromophores could lead to highly efficient multi-photon absorption^{5d-f,i,6,7d,8a,b,f,9c,e-h,11,12} while maintaining linear transparency over wide spectral range¹³ and this is a beneficial feature especially for the broadband optical limiting applications based on 2PA. In general, fluorophores with octupolar and/or higher-polar characters are composed of branched or dendritic backbones. From the viewpoint of structural motif, branched architecture not only provides an access to incorporating several 2PA-enhancing parameters into a single molecular system but also allows material chemists to possibly optimize a dye molecule that can simultaneously combine various expected characteristics for different specific applications. Besides, branched skeletons are potential building blocks for constructing dendritic and/or supermolecular structures, which are suggested as probable approaches to pursue the fundamental limits of molecular 2PA.¹⁴ In searching for effective strategies toward highly efficient 2PA materials, we have been interested in exploring the 2PA properties of multi-branched or dendritic organic structures with various types of π -conjugation frameworks. In this paper, we report our studies of degenerate twophoton absorption, up-converted emission and effective optical power limiting properties of a newly synthesized multi-branched model chromophore by using high peak power IR laser pulses working in the femtosecond and nanosecond regimes as the probing tools.

2. Results and discussion

2.1. Molecular structures and syntheses

The chemical structure and the synthetic procedure of the studied model chromophore (1) in the present work are illustrated





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in Scheme 1. The scaffold of compound **1** is constructed by placing an electron-donating core (i.e., triphenylamine) in the center, which is connected to three 2,3-diarylquinoxalinyl units via vinylene groups to form a six-branched dendritic structure. Recently, electro-deficient quinoxaline moiety has been actively used as the acceptor to produce highly efficient bipolar luminescent materials due to its great diversity of tunable electronic properties resulting from the manner of aromatic substitution, where the systematic alteration is mainly carried out by incorporating electron-donating groups to the 2,3-or 5,8-position of the quinoxaline moiety.¹⁵ Other than the light-emitting materials, so far only limited reports on 2PA and/or χ^3 materials can be found that containing quinoxalinyl moieties.¹⁶ Therefore, it might be worthy to explore more about the usage of quinoxaline units in design and synthesis of two-photon active materials. Our original molecular design of this model compound in the present work was based on a simple intention which is to use quinoxaline moiety as an electron-withdrawing unit and attach various electron-donating units to the 2, 3, and 6 positions of each quinoxaline moiety so that the resulting fluorophore may have overall expanded π -domain and possess larger multipolar characters. Furthermore, the pendent alkyl chains on all fluorenyl moieties in this model chromophore are expected to enhance its solubility in common organic solvents, which is another important parameter to be considered in the molecular design from either the aspect of experiments or applications. The synthesis of this model compound is relatively straightforward as outlined in Scheme 1. We have used 2-bromo-7-diphenylaminofluorene (**2**) as the starting material and followed the established protocols for the consecutive chemical alteration to accomplish compound (**4**), which was then coupled with (**2**) under Sonogashira



Scheme 1. Synthetic procedure for the studied model compound 1. Reagents and conditions: (a) 2 (1 equiv), PdCl₂(PPh₃)₂ (0.06 equiv), Cul (0.1 equiv), *i*-Pr₂NH (6 equiv), trime-thylsilyl acetylene (1.05 equiv) in benzene, 80 °C, 18 h (80%); (b) 3 (1 equiv), K₂CO₃ (2 equiv) in ethyl ether–methanol, rt, 4 h (94%); (c) 4 (1 equiv), 2 (1.1 equiv), Pd(PPh₃)₄ (0.05 equiv), Cul (0.1 equiv), *i*-Pr₂NH (1.5 equiv) in THF, 70 °C, 24 h (39%); (d) 5 (1 equiv), KMnO₄ (4 equiv), NaHCO₃ (1 equiv), Aliquat 336 (0.05 equiv) in CH₂Cl₂–H₂O, rt, 12 h (71%); (e) 6 (1 equiv), 7 (1.1 equiv) in CH₃COOH, reflux, 6 h (70%); (f) Heck reaction: 8 (3.3 equiv), 9 (1 equiv), Pd(OAc)₂ (0.06 equiv), P(o-tolyl)₃ (0.36 equiv) in NEt₃–MeCN, 110 °C, 48 h (66%). The numbering manners of carbons and hydrogens for the representative structures apply to all other compounds in this work.

reaction condition to form compound (**5**) in 39% yield. Compound (**5**) was oxidized by KMnO₄ to afford its diketone derivative (**6**), which is the major synthon for the synthesis of the 2,3,6-trisubstituted quinoxaline (**8**). By following the Heck reaction method, the targeted model chromophore was accomplished in 66% yield. The detailed syntheses including the preparation of the key intermediates (**3–6**, **8**) and the final catalytic coupling reaction toward the targeted model compound are described in the Experimental section.

2.2. Optical properties characterization

2.2.1. One-photon absorption (1PA) and fluorescence spectra measurement. Linear absorption and fluorescence spectra of the studied model compound (**1**) in THF solution (with concentration of 1×10^{-5} M) are shown in Figure 1. The 1PA spectra were recorded



Figure 1. Linear absorption and fluorescence spectra (see the inset) of compound 1 in solution phase (concentration was controlled at 1×10^{-5} M in all cases). The excitation wavelength was fixed at 450 nm for the fluorescence spectra measurements.

through a Shimadzu 3501 PC spectrophotometer and the 1PA-induced fluorescence spectra were measured utilizing a Jobin-Yvon FluoroMax-3 spectrometer. Compound (1) was found to show strong and broad 1PA within the spectral range of 300–475 nm. Under the irradiation of common UV-lamp, this model compound also exhibits solvent dependent photoluminescence and the measured emission spectra of this model fluorophore in different solvents are illustrated in the inset of Figure 1.

2.2.2. Two-photon-excited fluorescence (2PEF) emission properties. The studied model chromophore manifests intense two-photon-excited upconversion emission which can be easily observed by naked eyes even under the illumination of an ~790 nm unfocused femtosecond laser beam. Figure 2(a) illustrates the 2PA-induced fluorescence spectra of the model chromophore **1** in solution phase. The sample solutions were freshly prepared at concentration of 1×10^{-4} M in various organic solvents for this measurement and the excitation source utilized for this two-photon induced fluorescence study is from a mode-locked Ti: Sapphire laser (Tsunami pumped with a Millennia 10 W, Spectra-Physics), which delivers ~80 fs pulses with the repetition rate of 80 MHz and the beam diameter of 2 mm. The intensity level of the excitation beam was carefully controlled in order to avoid the saturation of absorption and photodegradation. To minimize the effect of re-absorption due to the relatively high concentration of the sample solution used in this measurement, we have focused the excitation beam as close as possible to the wall of the quartz cell (5 mm \times 5 mm cuvette) so that only the emission from the surface of the sample was recorded. It can be seen in Figure 2(a) that for the model chromophore the shape and spectral position of each measured 2PA-induced emission is basically identical to its corresponding 1PA-induced fluorescence band shown in Figure 1. This result implies that in our dye system the radiative relaxation processes occurred within the studied samples are from the same final excited states regardless of the excitation method.

The power-squared dependence of the 2PA-induced fluorescence intensity on the excitation intensity of the studied



Figure 2. (a) Normalized two-photon-excited upconversion spectra of fluorophore 1 in various solvent at 1×10^{-4} M; (b), (c) and (d) are the logarithmic plots of power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity of compound 1 in different solvents. ((b): in toluene; (c): in THF; (d): in DMF).

fluorophore was also examined. Figure 2(b)–(d) are logarithmic plots of the measured data and the results confirm that 2PA process is responsible for the observed up-converted fluorescence emissions in all cases.

The temporal behavior and lifetime of 1PA- and 2PA-induced fluorescence of the same sample solutions were also probed based on the time-correlated single photon counting (TCSPC) technique using a highly sensitive photomultiplier equipped with accumulating real-time processor as the detection system (PMA-182 and TimeHarp 200, PicoQuant). The same Ti: sapphire laser system (vide supra) was employed for this experiment. The measured fluorescence decay curves of the studied compound solutions are depicted in Figure 3 on a 10-ns full scale for one- and two-photon excitation (in the femtosecond regime). Theoretical fitting of each decay curve

We have used fluorescein (~80 μ M in pH=11 NaOH solution) as the standard for this experiment.¹⁷ Figure 4 shows the measured degenerate two-photon absorption spectra of this model compound in THF (at the concentration of 1×10^{-4} M) and the combined photophysical data are summarized in Table 1. It is notable that this model chromophore exhibits strong 2PA ($\delta_2 \ge 650$ GM) from 700–850 nm with an absorption maximum located around 830 nm ($\delta_2 \sim 3100$ GM).

2.3. Discussion of results

From the measured photophysical properties of the studied model compound in the present work, some features are notable:



Figure 3. Normalized fluorescence decay curves of the studied model compound solutions excited by one-photon absorption (at \sim 395 nm) and two-photon absorption (at \sim 790 nm): (a) in toluene; (b) in THF.

Table 1

Photophysical properties of compound 1 in toluene and THF

Compound	$\lambda_{max}^{1PA}/nm^{a,b}$		$\log \epsilon_{\max}^{c}$	$\lambda_{max}^{1PA-FL}/nm^{b,d}$		$\Phi_{\rm F}{}^{\rm c,e}$	$\tau^{1\text{PA}-\text{FL}}/\text{ns}^{\text{c,f}}$	2PA-related properties		
	Toluene	THF		Toluene	THF			$\delta_2^{\max}/{ m GM}^{ m c,g}$	$\lambda_{max}^{2PA-FL}/nm^{c,h}$	$\tau^{2PA-FL}/ns^{c,i}$
1	450	452	5.25	505	570	0.56	3.1	~3100	571	3.1

^a One-photon absorption maximum.

^b The concentration was 1×10^{-5} M.

^c In THF.

^d Spectral position of 1PA-induced fluorescence emission maximum.

^e Fluorescence quantum efficiency.

^f 1PA-induced fluorescence lifetime.

^g The concentration was 1×10^{-4} M for 2PEF measurements; δ_2^{max} : the maximum 2PA cross-section value (with experimental error=±15%); 1GM=1×10^{-50} cm⁴ s/photon-molecule.

^h Spectral position of 2PA-induced fluorescence emission maximum.

ⁱ 2PA-induced fluorescence lifetime.

by single-exponential dependence has revealed that for each chromophore solution identical 1PA-/2PA-induced fluorescence lifetime were observed and this phenomenon is independent of the excitation process. The measured 1PA-/2PA-induced fluorescence lifetime values for each model compound solution are listed in Table 1.

2.2.3. Degenerate two-photon absorption spectra measurement. The 2PA behaviors of the studied dye molecule as a function of wavelength was explored in the spectral region of 700–850 nm by the degenerate two-photon-excited fluorescence (2PEF) technique based on a set-up very similar to that reported by Xu and Webb.¹⁷ (1) If one compares the measured 1PA and 2PA spectra of this compound in THF solution (See Figs. 1 and 2), it can be readily found that this model chromophore exhibits detectable 2PA at wavelengths equal to twice of those wavelengths in ultraviolet–visible (UV–vis) region where it possesses strong 1PA. This indicates that many excited states of this model dye molecule are energetically accessible by both one-photon and two-photon transitions. Besides, the widely dispersed two-photon activities in near-IR spectral regime suggests that this model chromophore could be a potential candidate as a broadband optical power limiter when against ultra-short laser pulses.



Figure 4. Measured degenerate two-photon absorption spectra of model chromophore **1** by 2PEF method in THF solution at 1×10^{-4} M (with experimental error $\sim \pm 15\%$).

- (2) Based on the fact that the measured fluorescence emission spectra (shown in Figs. 1 and 2) and the fluorescence lifetimes (depicted in Fig. 3) for each sample solution are nearly the same for one- and two-photon excitations, one may conclude that in these cases, each fluorescence emissions is predominantly from the same singlet state of this model chromophore.¹⁸ On the other hand, the medium-high quantum yield observed from compound 1 also indicates that it could be an efficient frequency upconverter for the biophotonic applications such as two-photon-excited fluorescence microscopy.
- (3) The excited-state lifetime of this model compound is found to be solvent dependent and can be tuned when dissolved in different organic solvents with various polarity. (e.g., $\tau_1 \sim 1.6$ ns in toluene and $\tau_1 \sim 3.1$ in THF). This feature is particularly desirable with regards to optical power limiting applications in the nanosecond regime based on 2PA-induced excited-state absorption (2PA-induced ESA) since the effective three-photon absorption coefficient increases significantly with the excitedstate lifetime.¹⁹

3. Effective optical power limiting behaviors in nanosecond regime

It is well known that an ideal optical-limiter is expected to show an intensity-dependent transmission feature so that the output intensity always below a certain maximum value, which makes optical-limiters useful for protecting human eyes and sensors against damaging sources of light. Additionally, this power limiting phenomenon is also important for optical dynamic range compression and noise suppression in signal processing as well as nonlinear ultra-fast filtering/reshaping of optical fiber signals. Compared to other mechanisms of optical power limiting such as reverse saturable absorption and nonlinear scattering,²⁰ the 2PA mechanism provides several promising features includes: (1) high initial transmission (ca. ~ 100%) for weak optical signals; (2) quick response to a change of the intensity or peak power of the incident optical signal; and (3) retention of optical quality of the input beam after passing through the nonlinear absorption medium.

Recently, many researchers have posited that the intensity-dependent 2PA-induced excited-state absorption plays an essential role for the observed large 2PA in various organic systems under the irradiation of nanosecond laser pulses,²¹ and for this reason the term 'effective 2PA' is used to describe the apparent 2PA parameter measured in nanosecond time domain.^{9b,21b}From the viewpoint of application, any medium that exhibits strong apparent nonlinear absorption covering wide spectral range could be very useful optical-power-attenuators against the laser pulses working in nanosecond time domain. $^{\rm 3c,22}$

It is noted that the excited-state lifetime of the studied model chromophore in the present work are in the nanosecond range, which indicates that significant excited-state population may be retained and may consequently possess excited-state absorption during the excitation by longer laser pulses. In order to study the *effective* power limiting performance of this model chromophore (**1**). we have utilized nanosecond laser pulses for this investigation. In our experiment, the nonlinear absorbing medium was a 1-cm pathlength solution of 1 in THF with concentration of 0.02 M. As an excitation laser light source, a tunable nanosecond laser system (an integrated Q-switched Nd:YAG laser and OPO: NT 342/3 from Ekspla) was employed to provide ~ 6 ns laser pulses with controlled average pulse energy of ~ 1 mJ and repetition rate of 10 Hz for this study. The laser beam was slightly focused onto the center of the sample solution in order to obtain a nearly uniform laser beam radius within the whole cell path-length. The transmitted laser beam from the sample cell was detected by an optical power (energy) meter with a large detection area of ~ 25 mm in diameter. Figure 5 shows the measured average transmittance in the spectral range of 700–1000 nm. Although the entire dispersion of ESA as a function of wavelength (i.e., ESA spectra) is not yet revealed at current stage, it is noted that under our experimental conditions this model compound can attenuate nanosecond laser pulses within a broad spectral region especially around 800 nm. The attenuation of the incident laser pulses based on this sample solution can be presented in another way as shown in the inset of Figure 5. In this experiment, the local intensity within this sample solution was tuned by a set of neutraldensity filter. Three representative wavelengths have been selected for this demonstration of power restriction efficiency. One can see that compound **1** displays the best power restriction properties at 800 nm. This initial finding suggests the potentiality of using this model fluorophore for broadband power-suppressing-related applications in the nanosecond regime.



Figure 5. Measured transmission spectrum based on a 1-cm path solution sample of compound **1** in THF at 0.02 M. The energy of the input laser pulses was controlled at $\sim 1 \text{mJ}$ for every data point. Inset: Measured optical-power-attenuation curves at various wavelengths based on the same sample solution.

4. Conclusion

We have synthesized a novel octupolar chromophore with 2,3diarylquinoxalinyl units as the molecular termini and characterized its nonlinear optical properties in the femtosecond and nanosecond regime. The experimental results show that the subject compound manifests wide-dispersed and strong two-photon absorption in near infrared region. It is demonstrated that the incorporation of 2,3-disubstituted quinoxaline moieties as a part of π -framework in a dye molecule could provide an access toward large molecular two-photon absoptivities within the studied spectral region. Effective optical-power-attenuation behaviors in the nanosecond time domain of this model chromophore were also investigated and the results suggest that such dye compound can be a potential material as a broad-band and agile optical limiter especially when against those laser lights with longer pulses.

5. Experimental

5.1. General

All commercially available reagents for the preparation of the intermediates and targeted chromophores were purchased from Aldrich Chemical Co. and were used as received, unless stated otherwise. ¹H NMR and ¹³C NMR spectra were recorded either at 200 or 300 MHz spectrometers and referenced to TMS or residual CHCl₃. High-resolution mass spectroscopy (HRMS) was conducted by using a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS spectrum was obtained on a Voyager DE-PRO mass spectrometer (Applied Biosystem, Houston, USA). Elemental analysis was performed utilizing a Perkin Elmer series II CHNS/O Analyzer 2400.

5.2. 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 nonlinear optical property investigations are described in the Supplementary Data.

5.3. Synthesis

In Scheme 1, compounds 2 and 9 were synthesized by following the established literature processes^{23,24} with overall yields of ~45% for compound 2 and ~35% for compound 9. The synthesis of model chromophore 1 was accomplished via the well-known Heck coupling reaction using compounds 8 and 9 as the major synthons and was obtained in the yield of ~66%. The experimental details for the syntheses of these compounds are presented as the following:

5.3.1. 9,9-Dihexyl-N,N-diphenyl-7-(2-(trimethylsilyl)ethynyl)-9H*fluoren-2-amine* (**3**). To a solution of compound **2** (6 g; 0.0103 mol) in benzene (45 mL) was added of PdCl₂(PPh₃)₂ (0.435 g; 0.62 mmol), CuI (0.197 g; 1.033 mmol), i-Pr₂NH (6.273 g; 0.062 mol), and trimethylsilyl acetylene (1.066 g; 0.01085 mol) was stirred at 80 °C under Ar atmosphere for 18 h. After cooling to the room temperature. ~50 mL of saturated NH₄Cl solution was added into the reaction mixture and the resultant solution was stirred at room temperature for 0.5 h. The above solution was then extracted with ethyl acetate (30 mL×3) and then dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using hexane as the eluent to give the final purified product as pale-yellow oil with yield of $\sim 80\%$ (4.94 g). ¹H NMR(300 MHz, CDCl₃) δ: 7.59–7.55 (m, 2H, ArH), 7.51– 7.48 (d, 2H, ArH), 7.32-7.27 (dd, 4H, H₃), 7.20-7.17 (m, 5H, ArH), 7.09–7.03 (m, 3H, ArH), 1.93–1.90 (t, H_a, 4H), 1.20–1.12 (m, H_b, H_c, H_d 12H), 0.89–0.85 (m, 6H, H_f), 0.71 (br, m, 4H, H_e), 0.35 (s, -Si(CH₃)₃, 9H); ¹³C NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ: 152.42 (C₁₆), 150.41 (C₁₇), 147.83 (C₁), 147.58 (C₆), 141.45 (C₁₅), 135.37 (C₁₄), 131.18 (C₁₂), 129.14 (C₃), 126.02 (C₁₀), 123.88 (C₂), 123.35 (C₈), 122.62 (C₄), 120.72 (C₉), 120.34 (C₇), 118.95 (C₅), 118.82 (C₁₁), 106.42 (Ar-C≡C-Si(CH₃)₃), 93.55 (Ar-C≡C-Si(CH₃)₃), 55.03 (C₁₃), 40.20 (C_a), 31.51 (C_b), 29.58 (C_c), 23.67 (C_d),

22.54 (C_e), 14.04 (C_f), 0.08 (-Si(CH₃)₃). Anal. calcd for C₄₂H₅₁NSi: C, 84.36; H, 8.60; N, 2.34; Si, 4.70; found: C, 84.45; H, 8.55; N, 2.35.

5.3.2. 7-Ethynyl-9,9-dihexyl-N,N-diphenyl-9H-fluoren-2-amine (4). A mixture of compound 3 (4.33 g; 0.00724 mol), ethyl ether (20 mL), potassium carbonate (2 g; 0.014 mol), and methanol (20 mL) was stirred at room temperature for 4 h. Then, \sim 50 mL of saturated NH₄Cl solution was added into the reaction mixture and the resultant solution was stirred at room temperature for 0.5 h. The above solution was then extracted with ethyl acetate $(30 \text{ mL} \times 3)$ and then dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using hexane as the eluent to give the final purified product as pale-yellow oil with yield of $\sim 94\%$ (3.58 g). ¹H NMR(300 MHz, CDCl₃) δ: 7.60–7.57 (m, 2H, ArH), 7.52–7.49 (m, 2H, ArH), 7.33-7.28 (dd, 4H, H₃), 7.21-7.18 (m, 5H, ArH), 7.11-7.04 (m, 3H, ArH), 3.14 (s, Ar-C≡C-H, 1H), 2.00–1.84 (m, 4H, H_a), 1.23–1.12 $(m, 12H, H_b, H_c, H_d), 0.89-0.84 (t, 6H, H_f), 0.74-0.72 (m, 4H, H_e); {}^{13}C$ NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ: 152.42 (C₁₆), 150.51 (C₁₇), 147.81 (C₁), 147.65 (C₆), 141.68 (C₁₅), 135.19 (C₁₄), 131.17 (C₁₂), 129.16 (C₃), 126.25 (C₁₀), 123.93 (C₂), 123.29 (C₈), 122.64 (C₄), 120.75 (C₇, C₉), 119.28 (C₅), 118.89 (C₁₁), 84.80 (Ar-C≡C-H), 76.83, (Ar-C≡C-H), 55.01 (C₁₃), 40.13 (C_a), 31.47 (C_b), 29.55 (C_c), 23.67 (C_d), 22.52 (C_e), 14.02 (C_f). HRMS-FAB(*m*/*z*): M⁺ calcd for C₃₉H₄₃N, 525.3396; found, 525.3402. Anal. calcd for C₃₉H₄₃N: C, 89.09; H, 8.24; N, 2.66; found: C, 89.12; H, 8.26: N. 2.62.

5.3.3. 7-(2-(7-(Diphenvlamino)-9.9-dihexvl-9H-fluoren-2-vl)ethvnvl)-9,9-dihexyl-N,N-diphenyl-9H-fluoren-2-amine (5). To a solution of compound 2 (3.64 g; 0.00627 mol) and 4 (3 g; 0.0057 mol) in THF (35 mL) was added of Pd(PPh₃)₄ (0.33 g; 0.285 mmol), CuI (0.1087 g; 0.57 mmol), and *i*-Pr₂NH (0.87 g; 0.00856 mol) was stirred at 70 °C under N₂ for 24 h. After cooling to the room temperature, ~ 50 mL of saturated NH₄Cl solution was added into the reaction mixture and the resultant solution was stirred at room temperature for 0.5 h. The above solution was then extracted with ethyl acetate (30 mL \times 3) and then dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate-hexane (1:60) as the eluent and recrystallized from methanol/hexane. The purified product was obtained as yellow powder with yield of $\sim 39\%$ (2.29 g). ¹H NMR(300 MHz, CDCl₃) δ: 7.60–7.49 (m, 8H, ArH), 7.27– 7.22 (dd, 8H, H₃), 7.13-7.11 (d, 10H, ArH), 7.04-6.99 (m, 6H, ArH), 1.95-1.78 (m, 8H, H_a), 1.16-1.06 (m, 24H, H_b, H_c, H_d), 0.82-0.77 (t, 12H, H_f), 0.65 (br, m, 8H, H_e); ¹³C NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ : 152.43 (C_{16}), 150.63 (C₁₇), 147.86 (C₁), 147.49 (C₆), 141.10 (C₁₅), 135.51 (C₁₄), 130.60 (C₁₂), 129.16 (C₃), 125.69 (C₁₀), 123.88 (C₂), 123.40 (C₈), 122.59 (C₄), 120.64 (C₇, C₉), 119.01 (C₅, C₁₁), 90.49 (internal acetylene carbons), 55.08 (C₁₃), 40.28 (C_a), 31.54 (C_b), 29.63 (C_c), 23.73 (C_d), 22.57 (C_e), 14.04 (C_f); HRMS-FAB(*m*/*z*): M⁺ calcd for C₇₆H₈₄N₂, 1024.6635; found, 1024.6639. Anal. calcd for C76H84N2: C, 89.01; H, 8.26; N, 2.73; found: C, 88.98; H, 8.25; N, 2.77.

5.3.4. 1,2-Bis(7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl)ethane-1,2-dione (**6**). To a solution of compound **5** (2.25 g; 0.00219 mol) in CH₂Cl₂ (20 mL) was added KMnO₄ (1.387 g; 0.00877 mol), NaHCO₃(0.184 g; 0.00219 mol), Aliquat 336(0.045 g; 0.1097 mmol), and H₂O (10 mL) was stirred at room temperature for 12 h. Then, ~50 mL of saturated NaHSO₃ and 1 N HCl solutions were added into the reaction mixture. The above solution was then extracted with dichloromethane (30 mL×3) and then dried over MgSO₄(_S). After removing the solvent, the crude product was purified by column chromatography on silica gel using dichloromethane–hexane (1:4) to give the final purified product as saffron-yellow powder with yield of \sim 71% (1.64 g). 1 H NMR(300 MHz, CDCl₃) δ : 8.04 (s, 2H, H₁₂), 7.88–7.85 (d, *J*=7.8 Hz, 2H, H₉), 7.65–7.62 (d, *J*=7.8 Hz, 2H, H₁₀), 7.61–7.58 (d, 2H, H₈), 7.29–7.24 (dd, 8H, H₃), 7.15–7.11 (m, 10H, ArH), 7.07–7.01 (m, 6H, ArH), 1.98–1.79 (m, 8H, H_a), 1.15–1.04 (m, 24H, H_b, H_c, H_d), 0.82–0.77 (t, 12H, H_f), 0.64 (br, m, 8H, H_e); 13 C NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ : 195.15 (carbonyl carbon), 153.83 (C₁₆), 151.27 (C₁₇), 149.02 (C₁₅), 147.79 (C₁), 147.55 (C₆), 133.78 (C₁₄), 130.92 (C₁₂), 129.27 (C₃), 124.42 (C₂), 123.16 (C₄), 122.70 (C₈), 121.82 (C₁₀, C₁₁), 118.84 (C₅), 118.02 (C₇), 55.27 (C₁₃), 39.91 (C_a), 31.44 (C_b), 29.49 (C_c), 23.73 (C_d), 22.51 (C_e), 14.01 (C_f). HRMS-FAB(*m*/*z*): M⁺ calcd for C₇₆H₈₄N₂O₂: C, 86.32; H, 8.01; N, 2.65; O, 3.03; found: C, 86.25; H, 8.06; N, 2.68.

5.3.5. 7-(6-Bromo-3-(7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2yl)quinoxalin-2-yl)-9,9-dihexyl-N,N-diphenyl-9H-fluoren-2-amine (8). A mixture of compound 6 (1.2 g; 0.001134 mol) and 7 (0.233 g; 0.00125 mol) in CH₃COOH (30 mL) was refluxed under N₂ atmosphere for 6 h. After cooling to the room temperature, \sim 50 mL of H₂O was added to the reaction mixture. After filtration, the crude solid product was collected and recrystallized from methanol. The purified product was obtained as green-brownish powder with yield of ~88% (1.21 g).¹H NMR (300 MHz, CDCl₃) δ: 8.37 (s, 1H, H_C), 8.05-8.02 (d, J=9 Hz, 1H, H_F), 7.83-7.79 (d, J=9 Hz, 1H, H_E), 7.58-7.50 (m, 8H, ArH), 7.26-7.21 (m, 8H, H₃), 7.12-7.08 (m, 10H, ArH), 7.03-6.98 (m, 6H, ArH), 1.74-1.72 (m, 8H, H_a), 1.10-1.02 (m, 24H, H_b, H_c , H_d), 0.80–0.76 (t, 12H, H_e), 0.64–0.62(m, 8H, H_f); ¹³C NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ: 154.78 (C_A), 154.30 (C_B), 152.63 (C₁₆), 150.62 (C₁₇), 147.89 (C₁), 147.57 (C₁₄), 141.95 (C_H), 141.88 (C_G), 141.66 (C₆), 139.82 (C₁₅), 136.95 (C_F), 136.85 (C_C), 135.33 (C_E), 133.04 (C₁₂), 131.36 (C₈), 130.39 (C₉), 129.15 (C₃), 124.33 (C₁₀), 123.90 (C₂), 123.34 (C₁₁), 122.59 (C₄), 120.89 (C₅), 119.02 (C₇), 118.89 (C_D), 55.09 (C₁₃), 40.09 (C_a), 31.53 (C_b), 29.57 (C_c), 23.83 (C_d), 22.60 (C_e), 14.07 (C_f); HRMS-FAB(*m*/*z*): M⁺ calcd for C₈₂H₈₇BrN₄, 1206.6114; found, 1206.6104. Anal. calcd for C₈₂H₈₇BrN₄: C, 81.50; H, 7.26; Br, 6.61; N, 4.64; found: C, 81.52; H, 7.23; N, 4.65.

5.3.6. 7-(6-((E)-2-(4-(Bis(4-((E)-2-(2,3-bis(7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl)quinoxalin-6-yl)vinyl)phenyl)amino)phenyl)vinyl)-3-(7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl)quinoxalin-2-yl)-9,9-dihexyl-N,N-diphenyl-9H-fluoren-2-amine(1). A mixture of compound 8 (1.1 g; 0.918 mmol), tris(4-vinylphenyl)amine (9, 0.09 g; 0.278 mmol), Pd(OAc)₂ (0.0037 g; 0.0167 mmol), P(o-tolyl)₃ (0.03 g; 0.1 mmol), triethylamine (5 mL), and acetonitrile (10 mL) was loaded into a heavy-wall high pressure reaction tube equipped with a magnetic stirrer and a rigid Teflon cap. The reaction mixture was heated up to 110 °C under N2 atmosphere and kept at this temperature by means of an oil bath or a heating mantle for 48 h. The targeted compound was obtained as orange powder in 66% (0.68 g) via column chromatography (SiO₂; eluent: hexane/ethyl acetate=10/1). ¹H NMR(300 MHz, CDCl₃) δ: 8.21 (s, 3H, H_C), 8.17– 8.14 (d, J=9 Hz, 3H, H_F), 8.01-7.98 (d, J=9 Hz, 3H, H_F), 7.55-7.50 (m, 36H, ArH on fluorene and central triphenylamine units), 7.39-7.34 (d, J=15 Hz, 3H, ethylene protons), 7.29-7.24 (d, J=15 Hz, 3H, ethylene protons), 7.26-7.19 (m, 24H, H₃), 7.12-7.07 (m, 30H, ArH), 7.03–6.98 (m, 18H, ArH), 1.73 (br, m, 24H, H_a), 1.13–1.02 (m, 72H, H_b, H_c , H_d), 0.80–0.76 (t, 36H, H_f), 0.64 (br, m, 24H, H_e); ¹³C NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ: 154.36 (C_A), 153.31 (C_B), 152.39 (C₁₆), 150.52 (C₁₇), 148.30 (C₁), 147.88 (C14), 147.41 (CH), 146.97 (CG), 141.56 (C6), 140.88 (carbons on central triphenylamine unit), 138.90 (C₁₅), 137.38 (C_C and C_F), 135.50 (C_E), 131.95 (C₈), 130.39 (C₉), 129.86 (carbons on central triphenylamine unit), 129.12 (C₂), 128.21 (ethylene carbons), 127.89 (ethylene carbons), 126.61 (carbons on central triphenylamine unit), 126.30 (carbons on central triphenylamine unit), 124.36 (C₁₀), 123.83 (C₂), 123.37 (C₁₁), 122.51 (C₄), 120.83 (C₅), 119.78 (C₇), 119.07 (C₆'), 55.04 (C₁₃), 40.09 (C_a), 31.52 (C_b), 29.57 (C_c), 23.83 (C_d), 22.60 (C_e), 14.08 (C_f); MALDI-TOF MS: $[M+H]^+$ calcd for C₂₇₀H₂₇₉N₁₃, 3707.1914; found, 3707.1974. Anal. calcd for C₂₇₀H₂₇₉N₁₃: C, 87.50; H, 7.59; N, 4.91; found: C, 87.45; H, 7.62; N, 4.93.

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Supplementary data

Supplementary data associated with this article can be found in online version at doi:10.1016/j.tet.2009.11.109.

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