CHEMISTRY
A EUROPEAN JOURNAL

FULL PAPER

DOI: 10.1002/chem.201202178

Synthesis and Two-Photon Absorption Property Characterizations of Small Dendritic Chromophores Containing Functionalized Quinoxaliniod Heterocycles

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Abstract: A series of star-shaped multipolar chromophores (compounds **1**–**3**) containing functionalized quinoxaline and quinoxalinoid (indenoquinoxaline and pyridopyrazine) units has been synthesized and characterized for their two-photon absorption (2PA) properties both in the femtosecond and the nanosecond time domain. Under our experimental conditions, these model fluorophores are found to manifest strong and wide-dispersed two-photon absorption in the near-infrared region. It is demonstrated that molecular structures with multi-branched π frameworks incorporating properly functionalized quinoxalinoid units would possess large molecular nonlinear absorptivities within the studied spectral range. Effective optical-power attenuation and stabilization behaviors in the nanosecond time domain of a selected representative dye molecule (i.e., compound **2**) from this model compound set were also investigated and the results indicate that such structural motif could be a useful approach for the molecular design toward strong two-photon-absorbing material systems for quick-responsive and broadband optical-suppressing-related applications, particularly to confront long laser pulses.

Keywords: absorption · amination · chromophores · heterocycles · nonlinear optics

Introduction

A two-photon absorption (2PA) process occurs when a molecule is promoted from the ground state to an excited state through simultaneous absorption of two photons. Although the theory of this nonlinear optical phenomenon was predicted by Göppert-Mayer in 1931,[1] its experimental evidence came out about thirty years later when scientists observed upconverted emission from media under irradiation of laser light with wavelengths far from the linear absorption bands of the studied media.[2] In the past fifteen years, the availability of high-peak power lasers has incited the momentum to explore the two-photon technologies. Many promising applications in the emerging field of photonics and biophotonics based on a 2PA have been proposed including optical power limiting, frequency upconverted lasing, 3D data storage, 3D microfabrication, nondestructive bioimaging and tracking, and two-photon-assisted photodynamic therapy.[3] Because the commercially available materials do not provide sufficiently large 2PA to be of practical use in these applications, the need to develop new organic compounds that exhibit a strong 2PA within a specific spectral region is consequently escalating. In the recent decade researchers have put enormous efforts in exploring the connection between the molecular structure and the 2PA by investigating various molecular systems with different archetypes, including quasi-linear, multi-branched, and dendritic geometries. The accumulated knowledge and experience has revealed that molecular 2PA is closely related to both the intramolecular charge-transfer efficiency and the effective size of the π-conjugation domain within a molecule.[4–10] Among the aforementioned molecular architectures, it has been experimentally revealed that chromophores with branched π frameworks could manifest strong multi-photon absorption[5d–f,i,6,7d,8a,b,f,9c,e–g,10–12] while retaining the linear transparency over a wide spectral range[13] and this is a beneficial feature especially for the broadband optical-control applications based on 2PA. On the other hand, a branched structure also provides an access to incorporate several 2PA-enhancing parameters into a single molecular system and allows material chemists to optimize a dye molecule that simultaneously combines various expected characteristics for different specific applications. Moreover, branched skeletons are potential building blocks for con-

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201202178.

structing dendritic and/or supramolecular structures, which are suggested as probable approaches to pursue fundamental limits of molecular 2PAs.[14] Following our continuous efforts in searching new strategies toward highly efficient 2PA materials, we have been interested in developing multibranched or dendritic organic structures with expanded π systems that contains various types of heterocyclic moieties and in exploring the structural parameters that may have impacts on the 2PA properties.

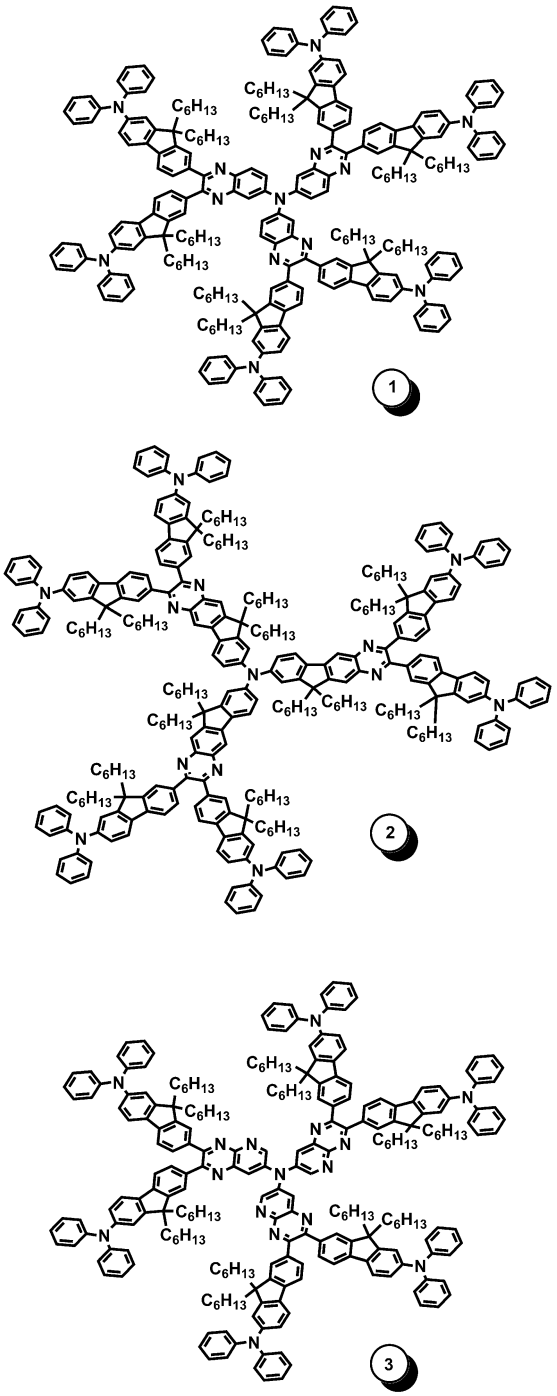
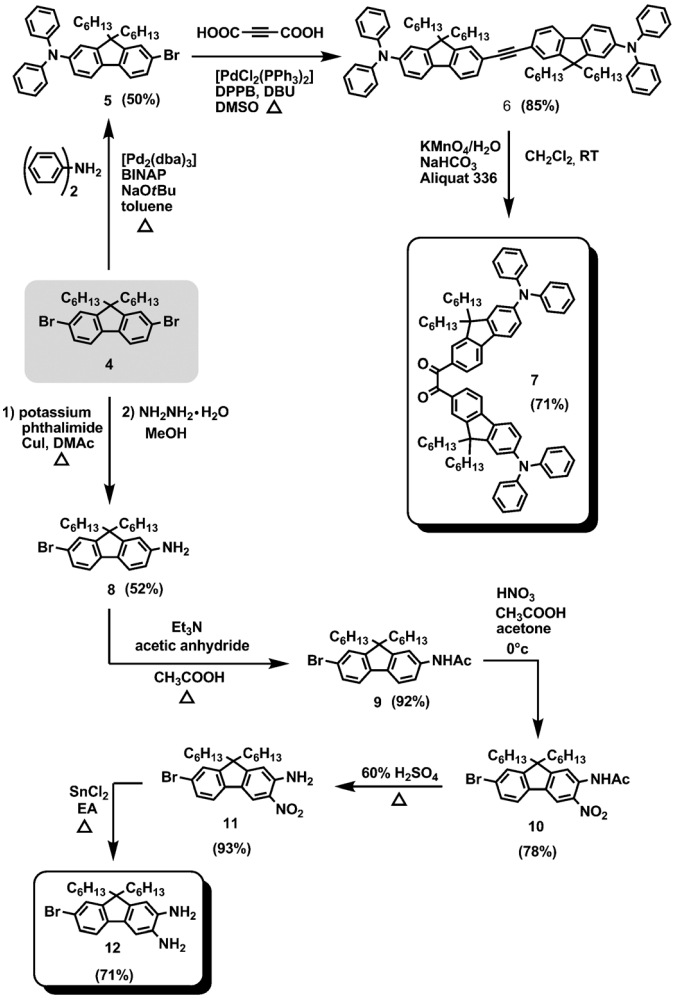


Figure 1. Molecular structures of the studied model chromophores **1**–**3**.

In this paper, we report our studies of degenerate two-photon absorption, upconverted emission, and effective optical power-limiting properties of a newly synthesized multibranched model chromophore set by using high-peak power IR laser pulses working in the femtosecond and nanosecond time domain as the probing tools.

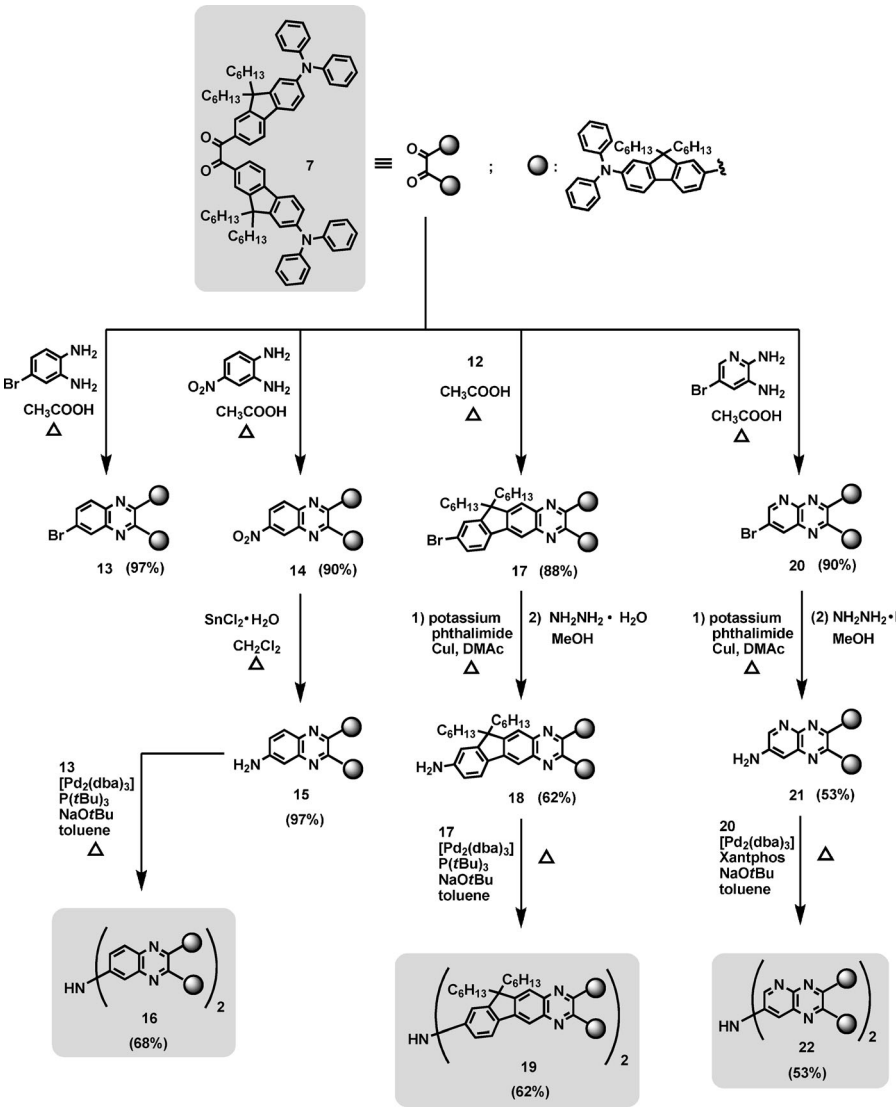
Results

Molecular structures and syntheses: The chemical structures of the studied model compounds in the present work are illustrated in Figure 1. Compound **1** is basically a three-branched chromophore that uses a nitrogen atom as an electron-donating ramification center for the connection of three identical 2,3-diphenylaminofluorenyl quinoxaline units to construct a dendritic π framework. Compared with compound **1**, model compound **2** can be conceptually considered

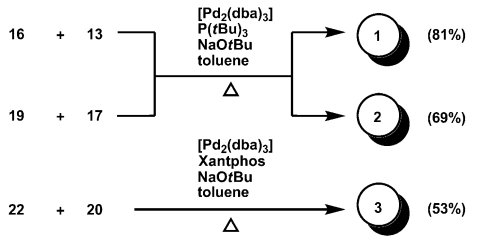


Scheme 1. Synthetic routes toward key intermediates **7** and **12** (the yield for each compound is indicated in parenthesis). DPPB = 1,4-bis(diphenylphosphino)butane; DBU = 1,5-diazabicyclo[5.4.0]undec-5-ene; dba = dibenzylideneacetone; BINAP = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl; DMAc = *N*,*N*-dimethylacetamide; EA = ethyl acetate.

as an expanded version of compound **1** because the "elongated" heterocyclic units (i.e., indenoquinoxaline moieties) were employed as the peripheral parts in this chromophore. Differently, the structure of compound **3** is built based on a motif that uses pyridopyrazine units to replace the benzopyrazine moieties (i.e., quinoxaline units) in model compound **1** so that the resulting structure can be expected to possess more heterocyclic characters and may be an interesting subject to explore the connection between this type of structural arrangement and the molecular 2PA behavior. The original molecular design strategies of these chromophores were based on the idea of incorporating electron-pulling heterocyclic units into the branched molecular structure so that the electronic properties of the resulting fluorophores may be altered and tuned due to the existence of heteroatoms and the whole molecule will possess an extended π domain as well as more pronounced multipolar characters. Furthermore, the pendent alkyl chains of all fluorenyl moieties in these model chromophores are expected to enhance the solubility in common organic solvents, which is another important issue to be considered in the molecular design from both the aspect of experiments and applications. The syntheses of the target model compounds are relatively straightforward as illustrated in Schemes 1–3, which mainly involve the preparation of the primary intermediates with the quinoxalinoid ring complex structures (i.e., compounds **13**, **14**, **17**, and **20**) followed by a series of appropriate functional group conversions to provide the primary amines (i.e., compounds **15**, **18**, and **21**) for the consecutive Buchwald–Hartwig-type amination toward the final chromophores. For the construction of each heterocyclic ring complex, the corresponding diamines and diaryldiketone **7** are employed as the major synthons. Among the selected diamines in this work, compound **12** is not commercially available so that this key intermediate has to be synthesized starting from compound **4** as outlined in Scheme 1. As for the synthesis of compound **7**, instead of using our previous methodology to synthesize the diarylacetylene precursor **6**,[10d] we have employed a recently developed one-step Sonogashira reaction protocol[15] to accomplish this precursor with saliently improved yield and then utilized $KMnO_4$ as the major oxidant to furnish the targeted diketone **7**. Once compounds **13**, **14**, **17**, and **20** become available, a series of functional group transformations are



Scheme 2. Synthetic procedures for the preparation of the primary intermediates with functionalized quinoxalinoid ring complexes (the yield for each compound is indicated in parenthesis).



Scheme 3. Final coupling processes toward the target model chromophores (the yield for each compound is indicated in parenthesis).

performed to prepare the primary amines (i.e., compounds **15**, **18**, and **21** in Scheme 2) for the first-step Buchwald–Hartwig amination to afford the secondary amines (i.e., compounds **16**, **19**, and **22** in Scheme 2). These secondary amines are in turn used as the starting materials for the second-step amination to prepare the tertiary amines (i.e., compounds **1**–**3**) as the final model chromophores. It is worthy to note that a different combination of the catalytic system (i.e., $[Pd_2(dba)_3]$–Xantphos) was employed for the syntheses of compounds **3** and **22** in order to obtain higher yields in our case. The detailed syntheses including the preparation of the key intermediates and the final two-step catalytic coupling reactions toward the targeted model fluorophores are described in the Experimental Section.

Characterization of the optical properties

One-photon absorption (1PA) and fluorescence spectra measurement: Linear absorption and fluorescence spectra of the studied compounds in toluene (with a concentration of 1×10^{-6} M) are shown in Figure 2. The 1PA spectra were recorded by using a Shimadzu 3501 PC spectrophotometer and the 1PA-induced fluorescence spectra were measured by utilizing a Jobin–Yvon FluoroMax-4 spectrometer. All these chromophores exhibit intense linear absorption in the UV/Vis region with the lowest-energy peaks located at $\lambda=$ 452 ($\varepsilon\approx1.25\times10^5\,cm^{-1}M^{-1}$), 469 ($\varepsilon\approx2.91\times10^5\,cm^{-1}M^{-1}$), and 471 nm ($\varepsilon\approx1.30\times10^5\,cm^{-1}M^{-1}$) for compounds **1**–**3**, respectively. The solutions of these compounds also emit intense fluorescence under the irradiation of a common UV lamp with blue-greenish color for compounds **1** and **2** and green-yellowish color for compound **3**, which is in agreement with the measured emission spectra (see Figure 2, inset). From the view point of the molecular structure, chromophores **1**–**3** possess symmetrical substitution patterns so that they are intuitionally expected to show very limited solvatochromic characters. Interestingly, these model fluorophores indeed illustrate a strong solvent effect on their fluorescence properties including band positions and lifetimes as illustrated in Figure 3 by using compound **2** as a representative for this behavior. Similar properties have been observed from 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.[5c,16]

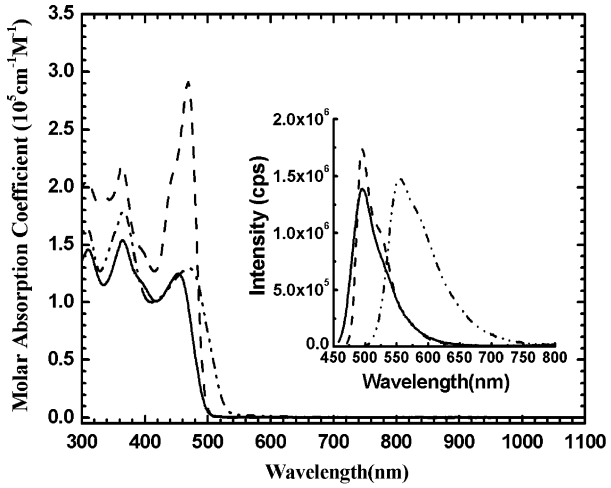


Figure 2. Linear absorption and fluorescence spectra (inset) of compounds **1**–**3** in toluene (concentration of the sample in solution $=1\times10^{-6}$ M; ——$=$**1**, -----$=$**2**, – · · $=$**3**).

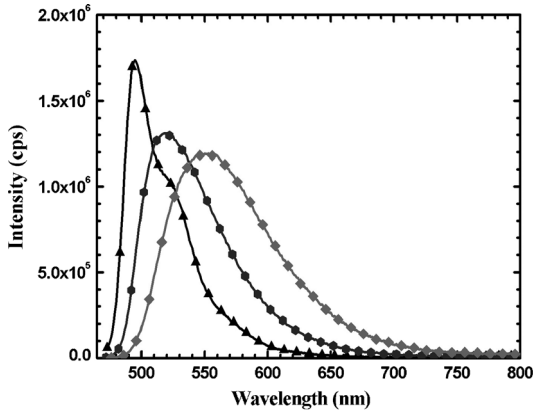


Figure 3. Fluorescence spectra of compound **2** in various solvents (▲= toluene, ●=THF, ◆=CH_2Cl_2); The color version of the spectra with a photo that illustrates the distinct color change of compound **2** in the different solvents can be found in the Supporting Information ($\tau_{1PA\text{-}FL}$=fluorescence lifetime, $\tau_{1PA\text{-}FL}=1.22$, 2.02, 3.01 ns in toluene, THF, CH_2Cl_2, respectively; concentration of compound **2** $=1\times10^{-6}$ M for all cases).

Two-photon-excited fluorescence (2PEF) emission properties: The studied model chromophores manifest strong two-photon-excited upconversion emission, which can be easily observed by naked eyes even under the illumination of a $\lambda\approx790$ nm unfocused femtosecond laser beam. Figure 4a illustrates the 2PA-induced fluorescence spectra of the model chromophores **1**–**3**. Solutions of the samples in toluene were freshly prepared at a concentration of 1×10^{-4} M for this measurement and the excitation source utilized for this two-photon-induced fluorescence study was obtained from a mode-locked Ti:sapphire laser (Tsunami pumped with a Millennia 10 W, Spectra-Physics) which delivers approximately 100 fs pulses with a repetition rate of 82 MHz and a beam diameter of 2 mm. The intensity level of the excitation beam was carefully controlled in order to avoid saturation of the absorption and photodegradation. To minimize the effect of re-absorption due to the relatively high concentration of the solutions used in this measurement, we have focused the excitation beam as close as possible to the wall of the quartz cell (10 mm×10 mm cuvette) so that only the emission from the surface of the sample was recorded. It can be seen in Figure 4a that for each model chromophore the shape and spectral position of the measured 2PA-induced emission is identical to its corresponding 1PA-induced

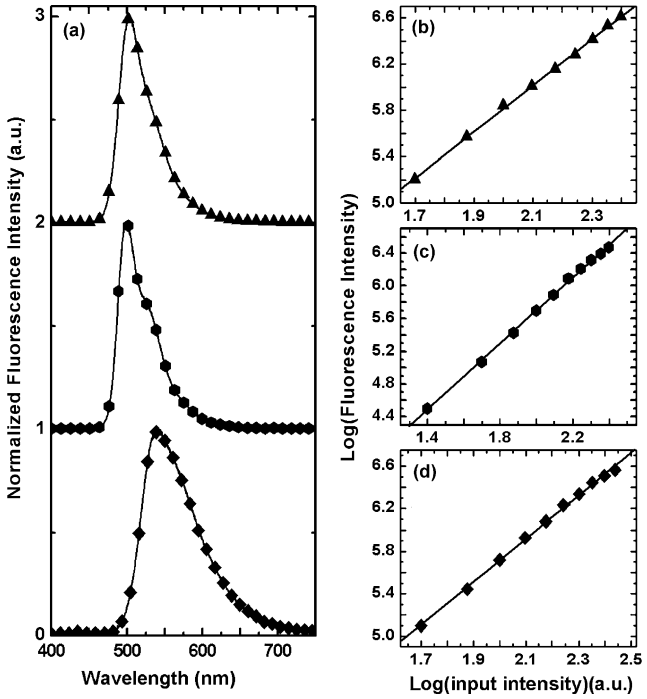


Figure 4. a) Normalized two-photon-excited upconversion spectra of fluorophores **1**–**3** in toluene at a concentration of 1×10^{-4} M; b)–d) are the logarithmic plots of the power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity of these compounds in toluene (▲=**1**, slope=2.00 (b); ●=**2**, slope=2.01 (c); and ◆=**3**, slope=2.02 (d))

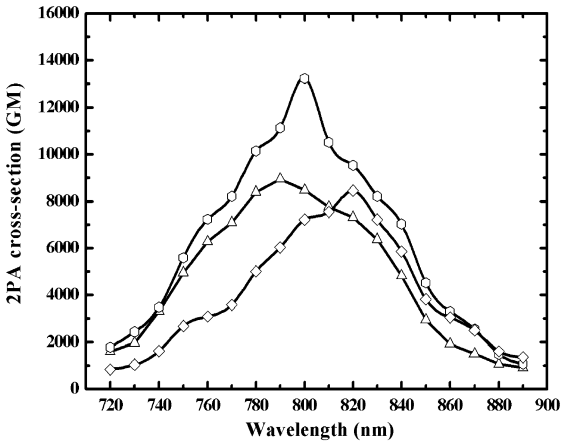


Figure 5. Measured degenerate two-photon absorption spectra of model chromophores **1**–**3** by the 2PEF method in toluene at a concentration of 1×10^{-4} M (with an experimental error of ~15%; △=**1**, ○=**2**, ◇=**3**).

Table 1. Photophysical properties of the studied model chromophores **1**–**3** in toluene.[a]

	λ_{max}^{abs} [nm][b]	ε[c] [10^5 cm^{-1} M^{-1}]	λ_{max}^{em} [nm][d]	Φ_F[e]	$\tau_{1PA\text{-}FL}$ [ns][f]	δ_2^{max} [GM][g]
1	310, 365, 452	1.25	498	0.42	1.84	ca. 8950
2	310, 364, 469	2.91	495	0.80	1.22	ca. 13230
3	308, 366, 471	1.30	534	0.48	2.78	ca. 8500

[a] The concentration was 1×10^{-6} and 1×10^{-4} M for the 1PA-related and the 2PA-related measurements, respectively. [b] One-photon absorption maximum. [c] Molar absorption coefficient. [d] 1PA-Induced fluorescence emission maximum. [e] Fluorescence quantum efficiency. [f] 1PA-Induced fluorescence lifetime. [g] Maximum 2PA cross-section value (with an experimental error of approximately ±15%); 1 GM=1×10^{-50} cm^{4}s per photon molecule.

fluorescence band, which is shown in Figure 1. This result implies that in our dye system the radiative relaxation processes that 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 fluorophores was also examined. Figures 4 b–d are logarithmic plots of the measured data and the results confirmed that a 2PA process is responsible for the observed upconverted fluorescence emissions in all cases.

Degenerate two-photon absorption spectra measurement: The distribution of the 2PA activities of the studied dye molecules as a function of the wavelength was delineated in the spectral region of $\lambda=720$–890 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] (see the Supporting Information). We have used fluorescein (ca. 80 μM in aqueous NaOH solution, pH 11) as standard for this experiment.[17,18] Figure 5 shows the measured degenerate two-photon absorption spectra of the three model compounds in toluene (at a concentration of 1×10^{-4} M) and the combined photophysical data are summarized in Table 1. It is notable that all the studied compounds exhibit strong 2PA ($\delta_2\geq800$ GM) within the entire investigated spectral region. Besides, each studied chromophore also possesses an individual local 2PA maximum at different wavelengths with 2PA cross-section values of approximately 8950 GM at $\lambda=$ 790 nm for compound **1**, approximately 13230 GM at $\lambda=$ 800 nm for compound **2**, and approximately 8500 GM at $\lambda=$ 820 nm for compound **3**.

Discussion

From the measured photophysical properties of the studied compounds in the present work, some features are notable.

1) Based on the observed linear absorption behaviors of the studied chromophores and by using compound **1** as a reference point, it can be noted that compound **2** exhibits a saliently promoted linear absorption, although it remains nearly the identical shape and spectral position to those of compound **1**, whereas compound **3** shows comparatively smaller enhancement of the linear absorption and a red-shifted lowest-energy band. These results imply that the incorporation of fluorene units into this molecular system (as in the case of compound **2**) is an effective approach to enhance the linear absorptivity without major shifting of the absorption band, whereas the utilization of pyridine moie-

ties for the construction of the ring complexes (as in the case of compound **3**) is useful for broadening the linear absorption spectral range by bathochromically pushing the lowest-energy band. Besides, the observed solvatochromic behaviors (see Table 1) suggest that the (relaxed) excited states of these chromophores are highly dipolar.

2) The dispersion manner and relative magnitudes of the 2PA activities of the studied model chromophores within the investigated spectral range follow similar pattern as they possess in the linear absorption, that is, compound **2** possesses a distinctly hyperchromic and slightly bathochromic 2PA band, whereas compound **3** manifests a saliently red-shifted 2PA band when compared with that of compound **1**. On the other hand, if one compares the measured 1PA and 2PA spectra of these fluorophores (see Figures 2 and 5), it can be readily found that the peak positions of the two-photon absorption maxima of the studied model chromophores in Figure 5 are monotonically blue shifted (or at significantly shorter wavelengths) compared to the wavelength position of twice of their lowest-energy linear absorption peak (i.e., $\lambda_{max}^{2PA} < 2\lambda_{max}^{1PA}$ for each studied compound). This implies that the most accessible two-photon states are higher in energy than those of the lowest allowed one-photon state of these compounds. A similar observation has been reported for many other multi-branched systems.[5a–f,i–k,6a–c,7d,8b,9c,g,10a–f] Besides, the widely dispersed two-photon activities in the near-IR spectral regime suggests that these model chromophores could be potential candidate as broadband optical power limiters when used against ultra-short laser pulses.

3) Compared with compound **1**, the larger overall 2PA accompanied by an approximately 50% increased 2PA cross-section (i.e., $\delta_2^{max}(2)/\delta_2^{max}(1) \approx 1.48$) observed for compound **2** may indicate that expanding the size of the π-conjugation domain accomplished by elongating the π length of the heterocyclic ring complexes (i.e., from the quinoxaline units in compound **1** to the indenoquinoxaline units in compound **2**) could be an effective approach toward enhanced molecular nonlinear absorptivities in this molecular system. On the other hand, the replacement of a carbon atom by a nitrogen atom in the original quinoxaline moiety to form the pyridopyrazine unit (as in the case of compound **3**) seems to provide an efficient access to shift the molecular 2PA band toward a longer wavelengths region without major diminishing of the 2PA magnitude. These features are particularly useful for the molecular design when either large 2PA at a specific spectral range or a red-shifted 2PA band with a fixed cross-section level is required for various applications.

4) From the molecular structures of model chromophores **1**–**3**, it can be reasonably assumed that the π framework of each compound may permit unsymmetrical charge transfer/charge redistribution between the molecular termini and the central part of the molecule under the excitation of light because all these π systems connect different electron-donating units (at peripheral and central positions) with uneven electron-pushing strengths by various electron-deficient quinoxalinoid rings within one molecule. Although at current stage there is no clear understanding about how the structural arrangement in the case of this model compound set connects to the molecular two-photon activities, our preliminary results show that such structural combination may help to promote the molecular 2PA. Another interesting issue that needs to be further studied with respect to this multi-branched model compound set is the importance of structural coplanarity on the molecular 2PA behaviors and therefore, efforts toward realization of the structure–nonlinear absorption properties by using quantum-mechanical analysis of this chromophore system are needed, and such work is underway currently.

5) Based on the fact that the measured fluorescence emission spectra (shown in Figures 2 and 4) for each individual model compound are nearly the same for one- and two-photon excitations, one may conclude that in these cases, the fluorescence emission is predominantly from the same singlet state of each model chromophore.[19] On the other hand, the medium-high quantum yield observed for compound **2** also indicates that it could be an efficient frequency upconverter for the biophotonic applications such as two-photon-excited fluorescence microscopy.

Effective optical power-limiting and stabilization performances in nanosecond regime: It is well known that an ideal optical limiter is expected to show an intensity-dependent transmission feature so that it can act like a transparent medium when the incident intensity of light stays low and once the input intensity rises up, the medium starts to regulate the transmitted output intensity to be always below a certain maximum value before any optical saturation or damage occurs. This feature makes optical limiters useful for protecting human eyes and sensors against hazardous 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 ultrafast filtering/reshaping of optical fiber signals.

Recently, many researchers have realized that the intensity-dependent 2PA-induced excited-state absorption plays an essential role for the observed large 2PA in various organic systems under irradiation of nanosecond laser pulses,[20] and the term "effective 2PA" is consequently used to describe the apparent 2PA parameter measured in the nanosecond time domain.[9b,20b] From the viewpoint of application, any medium that exhibits strong apparent nonlinear absorption by covering a wide spectral range could be very useful optical power attenuators against the laser pulses working in the nanosecond time regime.[21]

In order to study the effective power-limiting performance based on these model compounds, we have utilized nanosecond laser pulses for this investigation. As an example, we select chromophore **2** as a representative for the demonstration because this model compound possesses a very strong 2PA around $\lambda = 800$ nm and is theoretically expected to show a good power-limiting property at this wavelength. In our experiment, the nonlinear absorbing medium was a solution of the studied dye in toluene with a path length of 1 cm and a concentration of 0.02 M. A tunable nanosecond

laser system (an integrated Q-switched Nd/YAG laser and OPO/NT 342/3 from Ekspla) was employed as an excitation laser light source to provide approximately 6 ns laser pulses with a controlled average pulse energy in the range of approximately 0.02 to about 2 mJ and a 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 and the transmitted laser beam from the sample cell was detected by an optical power (energy) meter with a large detection area with a diameter of approximately 25 mm. Figure 6

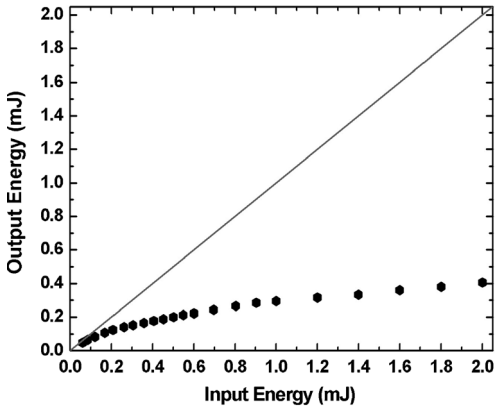


Figure 6. Measured optical power attenuation curve based on the sample solution of compound **2** under the excitation of a nanosecond laser pulses at $\lambda \approx 800$ nm.

illustrates the measured power-attenuation performance at $\lambda \approx 800$ nm based on this chromophore solution. One can see that compound **2** displays the superior power restriction property at $\lambda = 800$ nm and this initial finding suggests the potentiality of using this model fluorophore for broadband power-suppressing-related applications in the nanosecond regime.

On the other hand, the output/input curve shown in Figure 6 represents a characteristic type of optical control, which is ideal for the use in optical power (or intensity) stabilization. The principle of this type of optical stabilization is based on the fact that a huge magnitude change of the input signal will lead to only a small variation of output level.[22] This means that a larger input power (or intensity) fluctuation will lead to a much smaller output fluctuation by passing through a nonlinear absorptive medium such as the solution of model chromophore **2**. The experimental results for the optical stabilization study based on the same sample solution are shown in Figure 7. The curves in Figures 7a and b are the instantaneous pulse energy changes of the input and output laser pulses at $\lambda = 800$ nm. For the purpose of comparison, the average levels for both the input and the output signals were normalized to the same value. One can see that the input pulses possess a relatively larger energy fluctuation as shown in Figure 7a and after passing through the solution of compound **2**, a reduced fluctuation of the

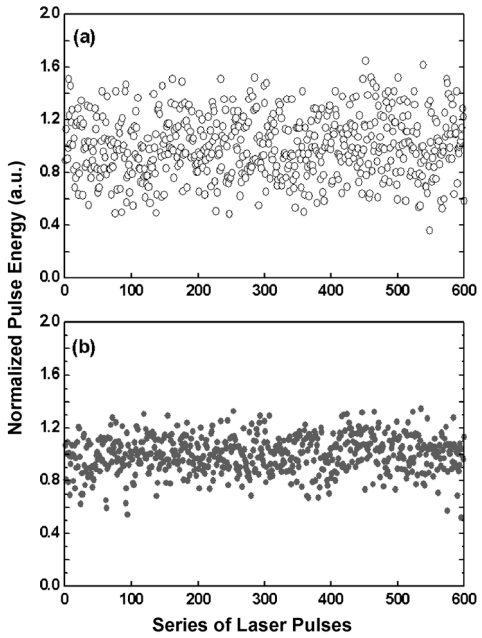


Figure 7. a) Measured instantaneous pulse energy fluctuation of the input laser pulses and b) measured instantaneous pulse energy fluctuation of the output laser pulses. The repetition rate of the laser pulses was 10 Hz and the average input pulse energy level was approximately 0.7 mJ.

pulse energy is observed for the output signal as illustrated in Figure 7b.

Conclusion

We have characterized the degenerate two-photon-absorption-related properties both in the femtosecond and nanosecond regime of a newly synthesized multi-polar model chromophore set with dendritic molecular structures based on multi-substituted quinoxalinoid heterocyclic skeletons by using two-photon-excited fluorescence and nonlinear transmission techniques as probing tools. It is demonstrated that chromophores with a branched skeleton based on the structural motif of a multi-substituted quinoxalinoid ring complex can possess strong molecular 2PA in a specific spectral region. In the present work it is also observed that model compound **2** exhibits both an intense upconverted emission when excited by a two-photon process and an effective optical power limiting/power stabilization against nanosecond laser pulses. These observations may suggest that the quinoxalinoid ring complexes utilized in this work could be useful structural units for the construction of highly active 2PA chromophores for potential applications.

Experimental Section

General: All commercially available reagents for the preparation of the intermediates and targeted chromophores were purchased from Aldrich Chemical Co. or Alfa Aesar and were used as received, unless stated oth-

erwise. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz spectrometer and referenced to TMS or residual $CHCl_3$. The representative numbering of the carbon and hydrogen atoms of each intermediate and the model chromophores for the NMR signal assignment are systematized and illustrated in the Supporting Information. High-resolution mass spectrometry (HRMS) was conducted by 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).

Photophysical methods: All 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 Supporting Information.

Synthesis: In Scheme 1, compounds **4** and **5** are shown to be the major starting materials for the synthesis of the backbones of each intermediates and the model chromophores. These two compounds were obtained in yields of approximately 80% for compound **4** and about 50% for compound **5** by following established procedures.[9a] For the synthesis of other key intermediates (compounds **6**–**22**) and the targeted model compounds (compounds **1**–**3**), a series of functionalization steps starting from compounds **4** and **5** has been conducted and is presented as the following:

7,7′-(Ethyne-1,2-diyl)bis(9,9-dihexyl-*N,N*-diphenyl-9*H*-fluoren-2-amine) (6): 1,4-Bis(diphenylphosphino) butane (0.58 g, 1.37 mmol), and $[PdCl_2(PPh_3)_2]$ (0.05 g, 0.07 mmol) were added to a mixture of compound **5** (8 g, 0.013 mol) and acetylenedicarboxylic acid (0.76 g, 6.66 mmol) in DMSO (15 mL). The resulting mixture was stirred at 110°C under an Ar atmosphere for 8 h. After cooling the reaction mixture to the room temperature, methanol (ca. 5 mL) and cold hexane (ca. 5 mL) were added, the solution was then stirred at 0°C. After filtration, the crude solid product was collected and recrystallized from methanol. The purified product was obtained as yellow powder (6.04 g, ca. 85%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.61 (d, J = 8.1 Hz, 2H; H_{15}), 7.59–7.51 (m, 6H; H_{12}, H_9, H_{14}), 7.28 (t, J = 7.2 Hz, 8H; H_2), 7.16–7.13 (m, 10H; H_{10}, H_3), 7.07–7.04 (m, 6H; H_6, H_1), 1.95–1.86 (m, 8H; H_f), 1.15–1.10 (m, 24H; H_c, H_d, H_e), 0.88–0.85 (t, J = 7.2 Hz, 12H; H_a), 0.62 ppm (s, 8H; H_b); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.43 (C_{16}), 150.63 (C_5), 147.86 (C_4), 147.49 (C_7), 141.10 (C_{11}), 135.51 (C_{10}), 130.60 (C_{15}), 129.16 (C_2), 125.69 (C_9), 123.88 (C_3), 123.40 (C_{12}), 122.59 (C_1), 120.64 (C_6), 120.56 (C_8), 119.01 (C_{13}, C_{14}), 99.49 (ethynyl carbon), 55.08 (C_g), 40.28 (C_f), 31.54 (C_e), 29.63 (C_d), 23.73 (C_c), 22.57 (C_b), 14.04 ppm (C_a); HRMS-FAB: m/z calcd for $C_{76}H_{84}N_2$: 1024.6635 $[M]^+$; found: 1024.6639.

1,2-Bis(7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl)ethane-1,2-dione (7): $KMnO_4$ (3.08 g, 0.195 mmol), $NaHCO_3$ (0.41 g, 4.88 mmol), Aliquat 336 (0.045 g, 0.22 mmol), and H_2O (20 mL) were added to a solution of compound **6** (5 g, 4.88 mmol) in CH_2Cl_2 (25 mL). The resulting mixture was stirred at room temperature for 12 h. Then, saturated aqueous solution of $NaHSO_3$ (50 mL) and HCl (1 N, 20 mL) were added. The solution was then extracted with dichloromethane (50 mL) and the collected organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using dichloromethane/hexane (1:4) to give the final product as saffron-yellow powder (3.64 g, ca. 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.03 (d, J = 1.2 Hz, 2H; H_{12}), 7.86 (dd, J^1 = 8.1 Hz, J^2 = 1.2 Hz, 2H; H_{15}), 7.64 (d, J = 8.1 Hz, 2H; H_{14}), 7.63 (d, J = 8.1 Hz, 2H; H_9), 7.30–7.25 (m, 8H; H_2), 7.12–7.10 (m, 10H; H_{10}, H_3), 7.05–7.01 (m, 6H; H_6, H_1), 2.01–1.78 (m, 8H; H_f), 1.11–1.05 (m, 24H; H_c, H_d, H_e), 0.86–0.83 (m, 12H; H_a), 0.77 ppm (s, 8H; H_b); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.19 (C_{17}), 153.89 (C_{11}), 151.34 (C_7), 149.08 (C_{16}), 147.83 (C_5), 147.62 (C_4), 133.85 (C_{13}), 131.01 (C_8), 130.99 (C_9), 129.32 (C_2), 124.48 (C_3), 123.21 (C_1), 122.77 (C_{15}, C_{12}), 121.86 (C_{14}), 118.89 (C_6), 118.11 (C_{10}), 55.33 (C_g), 39.96 (C_f), 31.49 (C_e), 29.54 (C_d), 23.79 (C_c), 22.55 (C_b), 14.04 ppm (C_a); HRMS-FAB: m/z calcd for $C_{76}H_{84}N_2O_2$: 1056.6533 $[M]^+$; found: 1056.6627.

7-Bromo-9,9-dihexyl-9*H*-fluoren-2-amine (8): Two-step reaction: 1) Potassium phthalimide (3.76 g, 20.3 mmol) and CuI (3.76 g, 20.3 mmol) were added to a solution of compound **4** (10 g, 20.3 mmol) in DMAc (160 mL). The resulting solution was stirred and heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was extracted with diethyl ether (40 mL) and the collected organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was obtained as dark brown solid. 2) $NH_2NH_2{\cdot}H_2O$ (1.18 g, 20.3 mmol) was added to a solution of the crude product from the first step in methanol (80 mL). The resulting solution was stirred and heated to reflux for 6 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using dichloromethane/hexane (1:10) as eluent to give the final product as brown powder (4.53 g, ca. 52%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.42–7.36 (m, 4H; H_B, H_E, H_D, H_G), 6.61–6.58 (m, 4H; H_K, H_I), 3.68 (s, 2H; NH_2), 1.88–1.83 (m, 4H; H_f), 1.04–1.03 (m, 12H; H_c, H_d, H_e), 0.76 (t, J = 7.2 Hz, 6H; H_a), 0.60 ppm (s, 4H; H_b). ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.36 (C_A), 152.14 (C_L), 146.45 (C_J), 140.71 (C_F), 131.27 (C_G), 129.73 (C_E), 125.84 (C_H), 120.69 (C_D), 119.70 (C_B), 119.08 (C_C), 114.10 (C_K), 109.59 (C_I), 55.15 ($C_{g'}$), 40.63 ($C_{f'}$), 31.59 ($C_{e'}$), 29.79 ($C_{d'}$), 23.73 ($C_{c'}$), 22.70 ($C_{b'}$), 14.11 ppm ($C_{a'}$); HRMS-FAB: m/z calcd for $C_{25}H_{34}BrN$: 428.4482 $[M+H]^+$; found: 428.4361.

***N*-(7-Bromo-9,9-dihexyl-9*H*-fluoren-2-yl)acetamide (9)**: Triethylamine (1.2 g, 11.8 mmol), and acetic anhydride (1.2 g, 11.8 mmol) were added to a solution of compound **8** (4.1 g, 9.8 mmol) in CH_2Cl_2 (30 mL). The resulting mixture was stirred at room temperature for 4 h. The reaction mixture was then extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using ethyl acetate/hexane (1:5) as the eluent to give the final product as white powder (4.05 g, ca. 92%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.02 (s, 1H; NH), 7.63 (s, 1H; H_2), 7.56 (d, J = 8.1 Hz, 1H; H_5), 7.45–7.40 (m, 4H; H_4, H_8, H_{11}, H_9), 2.21 (s, 3H; H_{14}), 1.93–1.88 (m, 4H; H_f), 1.03–1.01 (m, 12H; H_c, H_d, H_e), 0.75 (t, J = 7.2 Hz, 6H; H_a), 0.59 ppm (s, 4H; H_b); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.59 (sp^2 carbon atom of the Ac group), 152.87 (C_A), 151.50 (C_L), 139.76 (C_J), 137.80 (C_F), 136.23 (C_G), 129.93 (C_E), 126.06 (C_H), 120.63 (C_D), 120.54 (C_B), 120.12 (C_C), 118.65 (C_I), 114.36 (C_K), 55.53 ($C_{g'}$), 40.34 (C_F), 31.51 ($C_{e'}$), 29.66 ($C_{d'}$), 24.69 (sp^3 carbon atom of the Ac group), 23.72 ($C_{c'}$), 22.59 ($C_{b'}$), 14.00 ppm ($C_{a'}$); HRMS-FAB: m/z calcd for $C_{27}H_{35}BrNO$: 470.4848 $[M+H]^+$; found: 470.2022.

***N*-(7-Bromo-9,9-dihexyl-3-nitro-9*H*-fluoren-2-yl)acetamide (10)**: HNO_3 (4 g, 63.6 mmol) was added dropwise to a solution of compound **9** (3 g, 6.36 mmol) in acetone (10 mL) and acetic acid (30 mL). The resulting mixture was stirred at 5°C for 10 min. The reaction mixture was then extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using ethyl acetate/hexane (1:10) as the eluent to give the final product as yellow powder (2.6 g, ca. 78%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 10.61 (s, 1H; NH), 8.81 (s, 1H; H_8), 8.47 (s, 1H; H_{11}), 7.58 (d, J = 8.1 Hz, 1H; H_4), 7.51–7.48 (m, 2H; H_5, H_2), 2.33 (s, 3H; H_{14}), 2.02–1.94 (m, 4H; H_f), 1.05–1.04 (m, 12H; H_c, H_d, H_e), 0.77 (t, J = 7.2 Hz, 6H; H_a), 0.58–0.56 ppm (m, 4H; H_b); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 169.06 (sp^2 carbon atom of the Ac group), 159.41 (C_L), 152.77 (C_A), 137.55 (C_I), 135.79 (C_J), 135.66 (C_F), 134.71 (C_G), 130.62 (C_E), 126.42 (C_H), 122.41 (C_D), 121.40 (C_B), 116.63 (C_C), 116.18 (C_K), 55.56 ($C_{g'}$), 40.17 (C_F), 31.41 ($C_{e'}$), 29.48 ($C_{d'}$), 25.83 (sp^3 carbon atom of the Ac group), 23.77 ($C_{c'}$), 22.52 ($C_{b'}$), 13.95 ppm ($C_{a'}$); HRMS-FAB: m/z calcd for $C_{27}H_{35}BrN_2O_3$: 516.4824 $[M+H]^+$; found: 516.1794.

7-Bromo-9,9-dihexyl-3-nitro-9*H*-fluoren-2-amine (11): Sulfuric acid (60%, 3.5 mL) was added to a solution of compound **10** (2.5 g, 4.85 mmol) in methanol (25 mL) and the resulting mixture was stirred at 80°C for 10 h. The reaction mixture was then extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using ethyl acetate/hexane (1:8) as the eluent to give the final product as yellow powder (2.14 g, ca. 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.38 (s, 1H; H_H), 7.50 (d, J = 7.8 Hz, 1H; H_E), 7.46 (dd, J^1 = 7.8 Hz, J^2 = 1.5 Hz, 1H; H_D), 7.39 (d, J = 1.5 Hz, 1H; H_B), 6.72 (s, 1H; H_K), 6.27 (s, 2H; NH_2), 1.92–1.85 (m, 4H; $H_{f'}$), 1.07–1.05 (m, 12H; $H_{c'}$, $H_{d'}$, $H_{e'}$), 0.78 (t, J = 7.2 Hz, 6H; $H_{a'}$), 0.63–0.59 ppm (m, 4H; $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 159.48 (C_L), 151.33 (C_A), 145.28 (C_J),

138.17 (C_I), 131.29 (C_F), 130.47 (C_G), 130.23 (C_E), 125.87 (C_H), 120.86 (C_D), 120.52 (C_B), 116.42 (C_C), 112.40 (C_K), 55.44 ($C_{g'}$), 40.61 ($C_{f'}$), 31.26 ($C_{e'}$), 29.39 ($C_{d'}$), 23.59 ($C_{c'}$), 22.37 ($C_{b'}$), 13.78 ppm ($C_{a'}$); HRMS-FAB: m/z calcd for $C_{25}H_{33}BrN_2O_2$: 474.4457 $[M+H]^+$; found: 474.1730.

7-Bromo-9,9-dihexyl-9*H*-fluorene-2,3-diamine (12): $SnCl_2{\cdot}2H_2O$ (9.5 g, 42.2 mmol) was added to a solution of compound **10** (2 g, 4.2 mmol) in ethyl acetate (40 mL) and stirred at 80 °C for 5 h. After cooling to room temperature, a saturated aqueous solution of $NaHCO_3$ (ca. 50 mL) was added to the reaction mixture. The solution was then extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using ethyl acetate/hexane (1:3) as the eluent to give the final product as yellow powder (1.33 g, ca. 71%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37 (d, J = 1.5 Hz, 1H; H_B), 7.33 (dd, J^1 = 7.8 Hz, J^2 = 1.5 Hz, 1H; H_D), 7.26 (d, J = 7.8 Hz, 1H; H_E), 6.92 (s, 1H; H_K), 6.60 (s, 1H; H_H), 3.44 (s, 4H; NH_2), 1.85–1.80 (m, 4H; $H_{f'}$), 1.03–1.01 (m, 12H; $H_{e'}$, $H_{d'}$, $H_{e'}$), 0.75 (t, J = 7.2 Hz, 6H; $H_{a'}$), 0.64–0.62 ppm (m, 4H; $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.59 (C_A), 142.93 (C_L), 140.62 (C_F), 135.19 (C_J), 133.41 (C_I), 132.02 (C_E), 129.37 (C_D), 125.50 (C_B), 119.39 (C_G), 118.82 (C_C), 110.61 (C_H), 108.08 (C_K), 54.52 ($C_{g'}$), 40.32 ($C_{f'}$), 31.34 ($C_{e'}$), 29.55 ($C_{d'}$), 23.52 ($C_{c'}$), 22.44 ($C_{b'}$), 13.85 ppm ($C_{a'}$).

7,7′-(6-Bromoquinoxaline-2,3-diyl)bis(9,9-dihexyl-*N,N*-diphenyl-9*H*-fluoren-2-amine) (13): A mixture of compound **7** (2 g, 1.9 mmol) and 4-bromobenzene-1,2-diamine (0.39 g, 2.1 mmol) in CH_3COOH (30 mL) was heated to reflux under a N_2 atmosphere for 6 h. After cooling to room temperature, H_2O (ca. 50 mL) 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 (2.3 g, 96.6%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.41 (d, J = 2.1 Hz, 1H; H_F), 8.12 (d, J = 8.7 Hz, 1H; H_C), 7.82 (dd, J^1 = 8.7 Hz, J^2 = 2.1 Hz, 1H; H_B), 7.56–7.45 (m, 8H; H_9, H_{12}, H_{13}, H_{15}), 7.25–7.20 (m, 8H; H_2), 7.10–7.05 (m, 10H; H_3, H_6), 7.02–6.96 (m, 6H; H_1, H_8), 1.71–1.68 (m, 8H; H_f), 1.01–0.99 (m, 24H; H_e, H_d, H_e), 0.76 (t, J = 7.2 Hz, 12H; H_a), 0.61 ppm (s, 8H; H_b). ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 154.78 (C_G), 154.30 (C_H), 152.63 (C_5), 150.62 (C_{16}), 147.89 (C_4), 147.57 (C_{11}), 141.95 (C_7), 141.88 (C_D), 141.66 (C_E), 139.82 (C_{10}), 136.95 (C_F), 136.85 (C_C), 135.33 (C_{15}), 133.04 (C_9), 131.36 (C_{12}), 130.39 (C_A), 129.15 (C_3), 124.33 (C_{13}), 123.90 (C_2), 123.34 (C_{14}), 122.59 (C_1), 120.89 (C_6), 119.02 (C_B), 118.89 (C_8), 55.09 (C_g), 40.09 (C_f), 31.53 (C_e), 29.57 (C_d), 23.83 (C_c), 22.60 (C_b), 14.07 ppm (C_a); HRMS-FAB: m/z calcd for $C_{82}H_{87}BrN_4$: 1206.6114 $[M]^+$; found: 1206.6104.

7,7′-(6-Nitroquinoxaline-2,3-diyl)bis(9,9-dihexyl-*N,N*-diphenyl-9*H*-fluoren-2-amine) (14): A mixture of compound **7** (2 g, 1.9 mmol) and 4-nitrobenzene-1,2-diamine (0.29 g, 2.1 mmol) in CH_3COOH (30 mL) was heated to reflux under a N_2 atmosphere for 6 h. After cooling to room temperature, H_2O (ca. 50 mL) 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 (2.01 g, ca. 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.09 (s, 1H; H_F), 8.51 (dd, J^1 = 8.7 Hz, J^2 = 2.1 Hz, 1H; H_B), 8.30 (d, J = 8.7 Hz, 1H; H_C), 7.65–7.52 (m, 8H; H_9, H_{12}, H_{13}, H_{15}), 7.28–7.22 (m, 8H; H_2), 7.13–7.09 (m, 10H; H_3, H_6), 7.04–6.99 (m, 6H; H_1, H_8), 1.79–1.74 (m, 8H; H_f), 1.11–0.95 (m, 24H; H_e, H_d, H_e), 0.79 (t, J = 7.2 Hz, 12H; H_a), 0.64–0.63 ppm (m, 8H; H_b); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 156.80 (C_G), 156.20 (C_H), 152.68 (C_5), 150.69 (C_{16}), 147.80 (C_4), 147.54 (C_{11}), 143.52 (C_7), 142.71 (C_D), 142.51 (C_E), 139.79 (C_{10}), 136.16 (C_F), 134.95 (C_C), 130.48 (C_{15}), 129.17 (C_9), 125.48 (C_{12}), 124.37 (C_A), 123.98 (C_3), 123.22 (C_{13}), 122.89 (C_2), 122.24 (C_{14}), 121.02 (C_1), 119.03 (C_6), 118.95 (C_B), 118.82 (C_8), 55.12 (C_g), 40.09 (C_f), 31.53 (C_e), 29.57 (C_d), 23.83 (C_c), 22.60 (C_b), 14.07 ppm (C_a).

7,7′-(6-Aminoquinoxaline-2,3-diyl)bis(9,9-dihexyl-*N,N*-diphenyl-9*H*-fluoren-2-amine) (15): $SnCl_2{\cdot}2H_2O$ (2.3 g, 10.2 mmol) was added to a solution of compound **14** (1.2 g, 1.02 mmol) in ethyl acetate (20 mL). The resulting mixture stirred at 80 °C for 5 h. After cooling to room temperature, a saturated aqueous solution of $NaHCO_3$ (ca. 30 mL) was added to the reaction mixture. The solution was then extracted with ethyl acetate (3× 30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using ethyl acetate/hexane (1:3) as the eluent to give the final product as yellow powder (1.15 g, ca. 97%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.98 (d, J = 8.7 Hz, 1H; H_C), 7.51–7.49 (m, 8H; H_9, H_{12}, H_{13}, H_{15}), 7.45 (d, J = 8.4 Hz, 1H; H_B), 7.27–7.19 (m, 8H; H_2), 7.17 (d, J = 2.7 Hz, 1H; H_F), 7.12–7.06 (m, 10H; H_3, H_6), 7.02–6.98 (m, 6H; H_1, H_8), 1.74–1.69 (m, 8H; H_f), 1.12–1.02 (m, 24H; H_e, H_d, H_e), 0.78 (t, J = 7.2 Hz, 12H; H_a), 0.63 ppm (s, 8H; H_b); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 153.71 (C_G), 152.62 (C_H), 152.55 (C_5), 150.47 (C_{16}), 120.21 (C_4), 147.94 (C_{11}), 142.91 (C_D), 141.27 (C_7), 140.91 (C_E), 137.82 (C_{10}), 136.15 (C_A), 135.73 (C_{14}), 130.08 (C_C), 129.09 (C_2), 129.89 (C_{15}), 124.25 (C_{12}), 123.76 (C_3), 123.39 (C_9), 122.34 (C_1), 122.71 (C_F), 120.79 (C_{13}), 119.18 (C_6), 118.82 (C_8), 107.85 (C_B), 55.03 (C_g), 40.08 (C_f), 31.53 (C_e), 29.58 (C_d), 23.82 (C_c), 22.60 (C_b), 14.07 ppm (C_a); HRMS-FAB: m/z calcd for $C_{82}H_{89}N_5$: 1143.7118 $[M]^+$; found: 1143.7111.

7,7′-[6-({2,3-Bis[7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]quinoxalin-6-yl}amino)quinoxaline-2,3-diyl]bis(9,9-dihexyl-*N,N*-diphenyl-9*H*-fluoren-2-amine) (16): $[Pd_2(dba)_3]$ (2 mg, 0.002 mmol), sodium *tert*-butoxide (0.05 g, 0.54 mmol), and $P(tBu)_3$ (0.9 mg, 0.0045 mmol) were added to a mixture of compounds **15** (0.51 g, 0.45 mmol), and **13** (0.54 g, 0.45 mmol) in dry toluene (8 mL). The resulting mixture was stirred at 90 °C under an Ar atmosphere for 12 h. After cooling to room temperature, H_2O (ca. 100 mL) was added to the reaction mixture. The solution was then extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified through column chromatography on silica gel by using THF/hexane (1:10) as the eluent to give the final product as gray power (0.7 g, ca. 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.16 (d, J = 8.7 Hz, 2H; H_C), 8.03 (s, 2H; H_F), 7.63 (d, J = 9 Hz, 2H; H_{22}), 7.55–7.50 (m, 16H; H_9, H_{12}, H_{13}, H_{15}), 7.26–7.22 (m, 16H; H_2), 7.12–7.09 (m, 20H; H_3, H_6), 7.03–6.98 (m, 12H; H_1, H_8), 6.58 (s, 1H; NH), 1.71–1.68 (m, 16H; H_f), 1.11–1.02 (m, 48H; H_e, H_d, H_e), 0.73 (t, J = 7.2 Hz, 24H; H_a), 0.64 ppm (s, 8H; H_b); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 154.39 (C_G), 152.59 (C_H), 151.73 (C_5), 150.56 (C_{16}), 147.91 (C_4), 147.33 (C_{11}), 142.93 (C_D), 142.50 (C_{10}), 141.66 (C_C), 141.29 (C_9), 137.75 (C_A), 136.45 (C_D), 137.33 (C_7), 135.54 (C_{15}), 130.36 (C_{12}), 129.12 (C_2), 124.43 (C_{13}), 123.82 (C_3), 123.38 (C_{14}), 122.49 (C_1), 120.80 (C_6), 119.13 (C_8), 118.91 (C_F), 112.11 (C_B), 55.06 (C_g), 40.09 (C_f), 31.53 (C_e), 29.57 (C_d), 23.83 (C_c), 22.60 (C_b), 14.07 ppm (C_a); HRMS-FAB: m/z calcd for $C_{82}H_{87}BrN_4$: 2271.3970 $[M]^+$; found: 2271.4028.

7,7′-(8-Bromo-10,10-dihexyl-10*H*-indeno[1,2-*g*]quinoxaline-2,3-diyl)-bis(9,9-dihexyl-*N,N*-diphenyl-9*H*-fluoren-2-amine) (17): A mixture of compound **7** (2 g, 1.9 mmol) and compound **12** (0.93 g, 2.1 mmol) in CH_3COOH (30 mL) was heated to reflux under a N_2 atmosphere for 12 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using THF/hexane (1:15) as the eluent to give the final product as yellow powder (2.44 g, ca. 88%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.44 (s, 1H; H_H), 8.10 (s, 1H; H_K), 7.93 (dd, J^1 = 3 Hz, J^2 = 1.8 Hz, 1H; H_D), 7.60–7.52 (m, 8H; H_9, H_{12}, H_{13}, H_{15}), 7.43–7.42 (m, 2H; H_E, H_B), 7.27–7.22 (m, 8H; H_2), 7.13–7.08 (m, 10H; H_3, H_6), 7.03–6.98 (m, 6H; H_1, H_8), 2.13–2.10 (m, 4H; H_f), 1.71–1.68 (m, 8H; $H_{f'}$), 1.10–1.04 (m, 36H; $H_{e'}$, $H_{e'}$, $H_{d'}$, $H_{d'}$, $H_{e'}$, $H_{e'}$), 0.81–0.66 ppm (m, 30H; H_a, $H_{a'}$, H_b, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 153.58 (C_{16}), 153.16 (C_N), 152.94 (C_M), 152.67 (C_5), 150.67 (C_A), 150.59 (C_L), 147.98 (C_4), 147.51 (C_F), 142.90 (C_J), 141.65 (C_I), 141.38 (C_G), 141.29 (C_{11}), 138.78 (C_7), 137.56 (C_{14}), 137.49 ($C_{14'}$), 135.60 (C_{10}), 130.70 (C_B), 129.42(C_E), 129.37(C_2), 129.22(C_{12}), 126.55 (C_{25}), 124.51 (C_{15}), 124.55 (C_3), 123.93 (C_K), 123.46 (C_C), 122.61 (C_1), 122.47 (C_{13}), 120.92 (C_6), 119.16 (C_9), 119.06 (C_8), 118.54 (C_H), 55.22 (C_g), 55.10 ($C_{g'}$), 41.44 (C_f), 40.16 ($C_{f'}$), 31.60 (C_e, $C_{e'}$), 29.77 (C_d), 29.65 ($C_{d'}$), 23.89 (C_c, $C_{c'}$), 22.68 (C_b), 22.61 ($C_{b'}$), 14.14 (C_a), 14.01 ppm ($C_{a'}$); MALDI-TOF: m/z calcd for $C_{101}H_{115}BrN_4$: 1463.8305 $[M+H]^+$; found: 1463.8384.

7,7′-(8-Amino-10,10-dihexyl-10*H*-indeno[1,2-*g*]quinoxaline-2,3-diyl)-bis(9,9-dihexyl-*N,N*-diphenyl-9*H*-fluoren-2-amine) (18): Two-step reaction: 1) Potassium phthalimide (0.25 g, 1.37 mmol) and CuI (0.26 g,

1.37 mmol) were added to a solution of compound **17** (2 g, 1.37 mmol) in DMAc (20 mL). The resulting solution was stirred and heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was extracted with ethyl ether (50 mL) and the collected organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was obtained as dark brown solid. 2) $NH_2NH_2{\cdot}H_2O$ (0.08 g, 1.37 mmol) was added to a solution of the crude product from the first step in methanol (60 mL). The resulting solution was stirred and heated to reflux for 6 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3×30 mL), and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using THF/hexane (1:6) as the eluent to give the final product as brown powder (1.2 g, ca. 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, 1H; H_H), 8.04 (s, 1H; H_K), 7.74 (d, J = 7.8 Hz, 1H; H_E), 7.60–7.54 (m, 8H; H_9, H_{12}, H_{13}, H_{15}), 7.31–7.25 (m, 8H; H_2), 7.17–7.12 (m, 10H; H_3, H_6), 7.07–7.02 (m, 6H; H_1, H_8), 6.79–6.73 (m, 2H; H_D, H_B), 3.97 (s, 2H; NH_2), 2.15–2.11 (m, 4H; H_f), 1.79–1.76 (m, 8H; $H_{f'}$), 1.14–1.03 (m, 36H; H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.83–0.71 ppm (m, 30H; H_a, $H_{a'}$, H_b, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 153.53 (C_{16}), 153.41 (C_N), 152.92 (C_M), 152.55 (C_5), 151.80 (C_{19}), 150.48 (C_A), 150.39 (C_L), 147.88 (C_4), 147.25 (C_{23}), 144.73 (C_C), 141.62 (C_I), 141.20 (C_G, C_{11}), 140.58 (C_7), 137.80 (C_{14}), 137.72 ($C_{14'}$), 135.65 (C_{10}), 130.62 (C_{12}), 129.09 (C_2), 125.46 (C_E), 124.36 (C_{15}), 123.76 (C_3), 123.37 (C_{13}), 123.76 (C_K), 122.44 (C_1), 121.71 (C_{13}), 120.74 (C_6), 119.12 (C_9), 118.92 (C_8), 115.66 (C_H), 114.55 (C_D), 109.10 (C_B), 54.99 (C_g), 54.83 ($C_{g'}$), 41.55 (C_f), 40.09 ($C_{f'}$), 31.52 (C_e, $C_{e'}$), 29.77 (C_d), 29.57($C_{d'}$), 23.82 (C_c, $C_{c'}$), 22.59 (C_b, $C_{b'}$), 14.06 (C_a), 13.96 ppm ($C_{a'}$);.

7,7′-[8-({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}amino)-10,10-dihexyl-10*H*-indeno[1,2-*g*]quinoxaline-2,3-diyl]bis(9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine) (19): $[Pd_2(dba)_3]$ (2.3 mg, 0.0025 mmol), sodium *tert*-butoxide (0.06 g, 0.6 mmol), and P(*t*Bu)$_3$ (1.1 mg, 0.05 mmol) were added to a mixture of compounds **18** (0.7 g, 0.5 mmol), and **17** (0.73 g, 0.5 mmol) in dry toluene (15 mL). The resulting mixture was stirred at 90°C under an Ar atmosphere for 12 h. After cooling to room temperature, H_2O (ca. 100 mL) was added to the reaction mixture. The solution was extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified through column chromatography on silica gel by using THF/hexane (1:10) as the eluent to give the final product as yellow powder (0.86 g, 62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.32 (s, 1H; H_H), 8.06 (s, 1H; H_K), 7.85 (d, J = 8.1 Hz, H_D), 7.64–7.51 (m, 8H; H_9, H_{12}, H_{13}, H_{15}), 7.27–7.22 (m, 8H; H_2), 7.13–7.09 (m, 12H; H_3, H_6, H_B, H_E), 7.03–6.99 (m, 6H; H_1, H_8), 6.32 (s, 2H; NH), 2.17–2.15 (m, 4H; H_f), 1.75–1.69 (m, 8H; $H_{f'}$), 1.13–1.04 (m, 36H; H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.79–0.65 ppm (m, 30H; H_a, $H_{a'}$, H_b, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 153.51 (C_N), 153.25 (C_{16}), 152.64 (C_5), 152.30 (C_M), 150.62 (C_A), 150.53 (C_L), 147.97 (C_4), 147.38 (C_F), 144.20 (C_C), 143.63 (C_J), 141.63(C_G), 141.40 (C_I,C_7), 140.90 (C_{11}), 137.76 (C_{14}), 137.68 ($C_{14'}$), 135.69 (C_{10}), 133.22 (C_E), 129.19 (C_2), 128.98 (C_{12}), 124.44 (C_{15}), 123.87 (C_3), 123.45 (C_K), 122.55 (C_1), 122.05 (C_{13}), 120.86 (C_6), 119.19 (C_9), 119.04 (C_8), 117.56 (C_H), 116.57 (C_D), 111.54 (C_B), 55.10 (C_g, $C_{g'}$), 41.67 (C_f), 40.18 ($C_{f'}$), 31.74 (C_e), 31.62 ($C_{e'}$), 29.93 (C_d), 29.66 ($C_{d'}$), 24.12 (C_c, $C_{c'}$), 22.69 (C_b), 22.61 ($C_{b'}$), 14.15 (C_a), 14.07 ppm ($C_{a'}$); MALDI-TOF: m/z calcd for $C_{202}H_{231}N_9$: 2782.8352 $[M+H]^+$; found: 2783.8430.

7,7′-(7-Bromopyrido[2,3-*b*]pyrazine-2,3-diyl)bis(9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine) (20): A mixture of compound **7** (2 g, 1.9 mmol) and 5-bromopyridine-2,3-diamine (0.29 g, 2.1 mmol) in CH_3COOH (30 mL) was heated to reflux under a N_2 atmosphere for 6 h. After cooling to room temperature, H_2O (ca. 50 mL) 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 (1.98 g, ca. 90%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.16 (d, J = 1.8 Hz, 1H; H_B), 8.72 (d, J = 1.8 Hz, 1H; H_E), 7.81 (s, 1H; H_{15}), 7.70 (d, J = 8.1 Hz, 1H; H_{12}), 7.63 (d, J = 7.8 Hz, 1H; $H_{12'}$), 7.59–7.48 (m, 5H; H_{13}, $H_{13'}$, H_9, $H_{9'}$, $H_{15'}$), 7.30–7.25 (m, 8H; H_2), 7.19–7.11 (m, 10H; H_3, H_6), 7.07–7.02 (m, 6H; H_1, H_8), 1.86–1.72 (m, 8H; H_f, $H_{f'}$), 1.15–1.06 (m, 24H; H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.79 (t, J = 7.2 Hz, 12H; H_a, $H_{a'}$), 0.65 ppm (s, 8H; H_b, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 157.20 (C_G), 156.13 (C_F), 154.57 (C_C), 152.80 (C_{16}), 152.70 ($C_{16'}$), 150.83 (C_5), 150.65 ($C_{5'}$), 148.28 (C_B), 147.88 (C_4), 142.66 (C_E), 142.55 (C_{11}), 139.31 (C_7), 136.31 (C_{14}), 136.25 ($C_{14'}$), 136.03 (C_D), 135.19 (C_{10}), 135.11 ($C_{10'}$), 129.72 (C_{12}), 129.22 (C_2), 129.00 ($C_{12'}$), 124.37 (C_{15}), 124.36 ($C_{15'}$), 124.01 (C_3), 123.33 (C_{13}), 122.72 (C_1), 121.04 (C_6), 120.44 (C_A), 119.23 (C_9), 118.90 (C_8), 118.68 ($C_{9'}$), 55.30 (C_g), 55.13 ($C_{g'}$), 40.23 (C_f), 40.11 ($C_{f'}$), 31.64 (C_e), 31.58 ($C_{e'}$), 29.61 (C_d, $C_{d'}$), 23.91 (C_c), 23.83 ($C_{c'}$), 22.66 (C_b, $C_{b'}$), 14.13 ppm (C_a, $C_{a'}$); HRMS-FAB: m/z calcd for $C_{81}H_{86}BrN_5$: 1210.4870 $[M]^+$; found: 1210.5282.

7,7′-(7-Aminopyrido[2,3-*b*]pyrazine-2,3-diyl)bis(9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine) (21): Two-step reaction: 1) Potassium phthalimide (0.15 g, 0.83 mmol) and CuI (0.16 g, 0.83 mmol) was added to a solution of compound **20** (1 g, 0.83 mmol) in DMAc (10 mL). The resulting solution was stirred and heated to reflux for 24 h. After cooling to room temperature, the reaction mixture was extracted with diethyl ether (50 mL) and dried over $MgSO_4$. After removing the solvent, the crude product was obtained as dark brown solid. 2) $NH_2NH_2{\cdot}H_2O$ (0.05 g, 0.83 mmol) was added to a solution of the crude product from the first step in methanol (50 mL). The resulting solution was stirred and heated to reflux for 6 h. After cooling to room temperature, the reaction mixture was extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified by column chromatography on silica gel by using THF/hexane (1:4) as the eluent to give the final product as brown powder (0.49 g, ca. 53%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.74 (d, J = 2.7 Hz, 1H; H_B), 7.79 (s, 1H; H_E), 7.71 (dd, J^1 = 7.8, J^2 = 0.9 Hz, 1H; H_{13}), 7.63 (d, J = 7.8 Hz, 1H; H_{12}), 7.56 (q, J = 2.7 Hz, 2H; H_9, $H_{9'}$), 7.50 (d, J = 8.1 Hz, 1H; $H_{12'}$), 7.51–7.48 (m, 3H; H_{13}, H_{15}, $H_{15'}$), 7.29–7.24 (m, 8H; H_2), 7.15–7.11 (m, 10H; H_3, H_6), 7.08–7.02 (m, 6H; H_1, H_8), 4.37 (s, 2H; NH_2), 1.87–1.72 (m, 8H; H_f, $H_{f'}$), 1.08–1.04 (m, 24H; H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.79 (t, J = 7.2 Hz, 12H; H_a, $H_{a'}$), 0.62 ppm (s, 8H; H_b, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 155.10 (C_G), 152.55 (C_C), 152.40 (C_F), 150.59 (C_{16}), 150.30 ($C_{16'}$), 147.83 (C_4), 147.42 (C_5), 147.32 ($C_{5'}$), 146.19 (C_B), 144.16 (C_A), 141.45 (C_D), 141.72 (C_{11}), 141.45 ($C_{11'}$), 137.32 (C_{14}), 137.13 ($C_{14'}$), 136.80 (C_7), 135.53 (C_{10}), 135.35 ($C_{10'}$), 129.42 (C_{12}), 129.22 (C_3), 128.80 ($C_{12'}$), 124.34 (C_{15}), 124.22 ($C_{15'}$), 123.79 (C_2), 123.31 (C_{13}), 122.49 (C_1), 120.79 (C_6), 119.12 (C_9), 118.99 (C_8), 118.38 ($C_{9'}$), 114.74 (C_E), 55.13 (C_g), 54.94 ($C_{g'}$), 40.18 (C_f), 40.00 ($C_{f'}$), 31.54 (C_e), 31.48 ($C_{e'}$), 29.58 (C_d, $C_{d'}$), 23.81 (C_c), 23.83 ($C_{c'}$), 22.66 (C_b, $C_{b'}$), 14.13 ppm (C_a, $C_{a'}$); MALDI-TOF: m/z calcd for $C_{81}H_{88}N_6$: 1145.6056 $[M]^+$; found: 1145.7183.

7,7′-[6-({2,3-Bis[7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]pyrido[2,3-*b*]pyrazin-7-yl}amino)quinoxaline-2,3-diyl]bis(9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine) (22): $[Pd_2(dba)_3]$ (1.82 mg, 0.002 mmol), sodium *tert*-butoxide (0.07 g, 0.68 mmol), Xantphos (5.2 mg, 0.009 mmol) were added to a mixture of compounds **21** (0.65 g, 0.57 mmol) and **20** (0.82 g, 0.68 mmol) in dry toluene (15 mL). The resulting solution was stirred at 90°C under an Ar atmosphere for 12 h. After cooling to room temperature, H_2O (ca. 100 mL) was added to the reaction mixture. The solution was extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified through column chromatography on silica gel by using THF/hexane (1:4) as the eluent to give the final product as orange powder (0.92 g, 71.4%). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 9.27 (s, 1H; H_B), 8.57 (d, J = 2.7 Hz, 1H; H_E), 7.81 (s, 1H; H_{15}), 7.74 (d, J = 8.4 Hz, 1H; H_{12}), 7.63 (d, J = 7.8 Hz, 1H; $H_{12'}$), 7.59–7.44 (m, 5H; H_{13}, $H_{13'}$, H_9, $H_{9'}$, $H_{15'}$), 7.32–7.25 (m, 8H; H_2), 7.18–7.11 (m, 10H; H_3, H_6), 7.07–7.02 (m, 7H; H_1, H_8, NH), 1.82–1.76 (m, 8H; H_f, $H_{f'}$), 1.06–1.04 (m, 24H; H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.81 (t, J = 7.2 Hz, 12H; H_a, $H_{a'}$), 0.48 ppm (s, 8H; H_b, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 155.77 (C_G), 154.11 (C_F), 152.59 (C_C), 150.66 (C_{16}), 150.48 ($C_{16'}$), 148.43 (C_B), 147.80 (C_4), 147.51 (C_5), 147.43 ($C_{5'}$), 145.64 (C_A), 142.05 (C_{11}), 141.87 ($C_{11'}$), 138.97 (C_7), 136.81 (C_{10}), 136.71 ($C_{10'}$), 136.40 (C_D), 135.34 (C_{14}), 135.30 ($C_{14'}$), 129.49 (C_{12}), 129.09 (C_3), 124.38 (C_{15}), 124.23 ($C_{15'}$), 123.81 (C_2), 123.27 (C_{13}), 122.50 (C_1), 120.84 (C_6), 119.23 (C_9), 118.92 (C_8), 118.57 ($C_{9'}$), 117.82 (C_E), 55.12 (C_g), 55.05 ($C_{g'}$), 40.11 (C_f), 40.01 ($C_{f'}$), 31.53 (C_e), 31.48 ($C_{e'}$), 29.52 (C_d, $C_{d'}$), 23.71 (C_c),

23.54 ($C_{c'}$), 22.66 (C_b, $C_{b'}$), 14.13 ppm (C_a, $C_{a'}$); MALDI-TOF: *m*/*z* calcd for $C_{163}H_{174}N_{10}$: 2274.1927 $[M]^+$; found: 2275.2559.

Compound 1: $[Pd_2(dba)_3]$ (1.41 mg, 0.0014 mmol), sodium *tert*-butoxide (0.035 g, 0.38 m mol), and P(*t*Bu)$_3$ (0.63 mg, 0.0032 mmol) were added to a mixture of compounds **16** (0.7 g, 0.31 mmol) and **13** (0.37 g, 0.31 mmol) in dry toluene (8 mL). The resulting solution was stirred at 90 °C under an Ar atmosphere for 12 h. After cooling to room temperature, of H_2O (ca. 100 mL) was added to the reaction mixture. The solution was extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified through column chromatography on silica gel by using THF/hexane (1:10) as the eluent to give the final product as yellow powder (0.84 g, ca. 81 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.20 (d, J = 9.3 Hz, 3H; H_C), 8.02 (d, J = 2.7 Hz, 3H; H_F), 7.76 (dd, J^1 = 9.3, J^2 = 2.7 Hz, 3H; H_B), 7.62–7.49 (m, 24H; H_9, H_{12}, H_{13}, H_{15}), 7.29–7.22 (m, 24H; H_2), 7.15–7.10 (m, 30H; H_3, H_6), 7.56–6.99 (m, 18H; H_1, H_8), 1.74 (s, 24H; H_f), 1.06–1.01 (m, 72H; H_c, H_d, H_e), 0.81–0.67 (m, 36H; H_a), 0.63 ppm (s, 24H; H_b); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 154.56 (C_G), 154.08 (C_H), 152.65 (C_5), 150.58 (C_{16}), 147.93 (C_4), 147.64 (C_A), 147.43 (C_{11}), 142.33 (C_7), 141.70 (C_D), 141.55 (C_E), 138.86 (C_{10}), 137.38 (C_F), 137.21 (C_C), 135.51 (C_{15}), 135.49 (C_9), 130.50 (C_{12}), 129.17 (C_3), 127.94 (C_B), 125.55 (C_{13}), 124.37 (C_2), 123.87 (C_{14}), 123.41 (C_1), 120.86 (C_6), 119.08 (C_8), 55.09 (C_g), 40.11 (C_f), 31.57 (C_e), 29.57 (C_d), 23.84 (C_c), 22.62 (C_b), 14.12 ppm (C_a); MALDI-TOF: *m*/*z* calcd for $C_{246}H_{261}N_{13}$: 3399.7916 $[M]^+$; found: 3399.8914.

Compound 2: $[Pd_2(dba)_3]$ (1.31 mg, 0.0013 mmol), sodium *tert*-butoxide (0.033 g, 0.34 m mol), and P(*t*Bu)$_3$ (0.58 mg, 0.0029 mmol) were added to a mixture of compounds **19** (0.8 g, 0.29 mmol) and **17** (0.42 g, 0.29 mmol) in dry toluene (10 mL). The resulting solution was stirred at 90 °C under an Ar atmosphere for 12 h. After cooling to room temperature, H_2O (ca. 100 mL) was added to the reaction mixture. The solution was extracted with ethyl acetate (3×30 mL) and the collected organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified through column chromatography on silica gel by using THF/hexane (1:10) as the eluent to give the final product as yellow power (0.87 g, ca. 69 %). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.45 (s, 1H; H_H), 8.18 (s, 3H; H_K), 7.92 (d, J = 8.1 Hz, 3H; H_D), 7.72–7.59 (m, 24H; H_9, H_{12}, H_{13}, H_{15}), 7.50–7.48 (m, 6H; H_E, H_B), 7.34–7.29 (m, 24H; H_2), 7.21–7.18 (m, 30H; H_3, H_6), 7.09–7.05 (m, 18H; H_1, H_8), 2.26–2.22 (m, 12H; H_f), 1.84–1.78 (m, 24H; $H_{f'}$), 1.21–1.04 (m, 108H; H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.81–0.75 ppm (m, 90H; H_a, $H_{a'}$, H_b, $H_{b'}$); ^{13}C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 153.60 (C_{16}), 153.41 (C_N), 153.03 (C_M), 152.68 (C_5), 150.67 (C_A), 150.59 (C_L), 148.25 (C_J), 148.01 (C_4), 147.47 (C_F), 143.79 (C_C), 141.52 (C_I), 141.13 (C_{11}, C_7), 137.75 (C_{14}), 137.68 ($C_{14'}$), 135.69 (C_{10}), 135.18 (C_E), 129.22 (C_2), 128.98 (C_{12}), 124.49 (C_{15}), 123.92 (C_3), 123.49 (C_K), 122.60 (C_1), 122.24 (C_{13}), 120.91 (C_6), 119.21 (C_9), 119.08 (C_8, C_H), 118.26 (C_D), 117.34 (C_B), 55.36 (C_g), 55.10 ($C_{g'}$), 41.49 (C_f), 40.23 ($C_{f'}$), 31.86 (C_e, $C_{e'}$), 29.89 (C_d), 29.65 ($C_{d'}$), 23.89 (C_c, $C_{c'}$), 22.68 (C_b), 22.61 ($C_{b'}$), 14.18 ppm (C_a, $C_{a'}$); MALDI-TOF: *m*/*z* calcd for $C_{303}H_{345}N_{13}$: 4170.0685 $[M]^+$; found: 4170.2090.

Compound 3: $[Pd_2(dba)_3]$ (1.27 mg, 0.0014 mmol), sodium *tert*-butoxide (0.05 g, 0.47 mmol), and Xantphos (3.8 mg, 0.0065 mmol) were added to a mixture of compounds **22** (0.9 g, 0.4 mmol) and **20** (0.57 g, 0.47 mmol) in dry toluene (15 mL). The resulting mixture stirred at 90 °C under an Ar atmosphere for 12 h. After cooling to room temperature, H_2O (ca. 100 mL) was added to the reaction mixture. The solution was extracted with ethyl acetate (3×30 mL) and the organic layer was dried over $MgSO_4$. After removing the solvent, the crude product was purified through column chromatography on silica gel by using THF/hexane (1:4) as the eluent to give the final product as orange powder (0.71 g, ca. 53 %). ^{1} H NMR (300 MHz, $CDCl_3$): δ = 9.20 (d, J = 3 Hz, 1H; H_B), 8.36 (d, J = 3 Hz, 1H; H_E), 7.78 (s, 1H; H_{15}), 7.66 (d, J = 8.1 Hz, 1H; H_{12}), 7.60 (d, J = 7.8 Hz, 1H; $H_{12'}$), 7.58–7.49 (m, 5H; H_{13}, $H_{13'}$, H_9, $H_{9'}$, $H_{15'}$), 7.30–7.23 (m, 8H; H_2), 7.16–7.09 (m, 10H; H_3, H_6), 7.08–7.01 (m, 6H; H_1, H_8), 1.82–1.68 (m, 8H; H_f, $H_{f'}$), 1.07–1.04 (m, 24H; H_c, $H_{c'}$, H_d, $H_{d'}$, H_e, $H_{e'}$), 0.70 (t, J = 7.2 Hz, 12H; H_a, $H_{a'}$), 0.62 ppm (s, 8H; H_b, $H_{b'}$); ^{13} C NMR (75 MHz, $CDCl_3$, tentative assignments based on calculates values): δ = 157.21 (C_G), 156.43 (C_F), 152.80 (C_{16}), 152.70 ($C_{16'}$), 150.73 (C_5), 150.67 (C_C), 150.54 ($C_{5'}$), 147.87 (C_4), 147.75 (C_C), 147.36 (C_7), 142.49 (C_{11}), 142.30 ($C_{11'}$), 136.39 (C_{10}), 136.30 (C_E), 136.19 ($C_{10'}$), 135.31 (C_{14}), 135.16 ($C_{14'}$), 129.69 (C_{12}), 129.20 (C_3), 129.00 (C_A), 124.40 (C_{15}), 123.97 (C_2), 123.31 (C_{13}), 122.67 (C_1), 121.03 (C_6), 119.11 (C_B), 118.92 (C_9), 118.76 (C_8), 118.68 ($C_{9'}$), 55.28 (C_g), 55.14 ($C_{g'}$), 40.24 (C_f), 40.08 ($C_{f'}$), 31.64 (C_e), 31.58 ($C_{e'}$), 29.56 (C_d, $C_{d'}$), 23.81 (C_c), 23.63 ($C_{c'}$), 22.62 (C_b, $C_{b'}$), 14.13 ppm (C_a, $C_{a'}$); MALDI-TOF: *m*/*z* calcd for $C_{245}H_{260}N_4$: 3401.7797 $[M]^+$; found: 3401.8647.

Acknowledgements

T.C.L. and group members acknowledge the financial support from the National Science Council of Taiwan (NSC) under Grant No. 99-2113M-006-MY2. J.H.L. and group members acknowledge the financial support from the National Science Council of Taiwan (NSC) under Grant No. NSC 99-2112M-027-001-MY3.

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Received: June 20, 2012
Revised: September 18, 2012
Published online: November 21, 2012

