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Synthesis and Two-Photon Absorption Properties of Symmetrical Chromophores Derived from 2,3,5-Trisubstituted Quinoxaline Units

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A set of symmetrically substituted multibranched chromophores composed of three quinoxaline-based congeners has been synthesized and experimentally shown to possess strong and widely dispersed two-photon absorptivities in the visible to near-IR region under the irradiation of femtosecond and nanosecond laser pulses. The electronic properties of the central π bridges incorporated into the final structures are closely connected to the molecular two-photon activities of these model compounds. Effective optical-power attenuation and stabilization behaviors in the nanosecond time domain of these dye molecules were also investigated. The structural motif of these compounds provides a useful approach for the molecular design of strong two-photon absorbing material systems with the potential for quick-responsive and broadband optical-control related applications, particularly for long-duration laser pulses in the near-IR region.

Introduction

Long after the first theoretical prediction of two-photon absorption by Göppert-Mayer in 1931,[1] the advent of lasers in the 1960s helped scientists to experimentally verify its existence through upconverted emission from substances under the irradiation of laser light with wavelengths far greater than the linear absorption bands of the substance.[2] In the past two decades, the availability of stable and high-peak-power lasers has further incited the momentum to explore two-photon-related technologies. Many potential 2PA-based applications in the emerging fields of photonics and biophotonics have been proposed and explored, including optical power limiting, frequency upconverted lasing, 3D data storage, 3D microfabrication, nondestructive bioimaging and tracking, and two-photon photodynamic therapy.[3] For these applications, the demand for rationally designed organic compounds that exhibit sufficiently large 2PA within the desired spectral region is consequently escalating. The combination of several structural parameters, such as the efficiency of intramolecular charge-transfer and/or the effective size of the π-conjugation domain within a molecule, is closely related to molecular 2PA.[4–10] In addition to strong 2PA, other photophysical properties may also be required for the designed molecules for various practical needs. For example, for use as optical power limiters in the nanosecond regime, compounds that possess longer excited-state lifetimes are believed to benefit from apparent nonlinear absorption because of two-photon-assisted excited-state absorption (2PA-assisted ESA),[11] so that the effective optical power attenuation will be enhanced. In our search for effective strategies to design highly active 2PA chromophores, we have continuously explored the influence of the incorporation of heterocyclic ring complexes and the electronic properties of the central conjugation bridge on molecular 2PA in multibranched π frameworks. Herein, we present the synthesis of a new series of multipolar two-photon-active model chromophores **1**–**3** derived from functionalized quinoxaline moieties connected by various π bridges as well as initial investigations of their 2PA properties in the femtosecond and nanosecond time domains.

Results and Discussion

I. Molecular Structures of Model Compounds

The chemical structures and the synthetic routes toward the studied model compounds are illustrated in Figure 1 and Scheme 1, respectively.

This model-compound set contains three multibranched congeners with various π linkers, namely, vinylene, fluorene, and dialkoxybenzene, to connect 2,3-difunctionalized quinoxaline units and form fluorophores with a common generic “donor–quinoxaline–π–quinoxaline–donor” (D–Q–π–Q–D) structure. Diphenylaminofluorene moieties are introduced as the peripheral electron-donating units in this model-compound system. The molecular design of these chromophores originates from a simple attempt to construct a set of symmetrically substituted π frameworks by using various π bridges with different electronic properties

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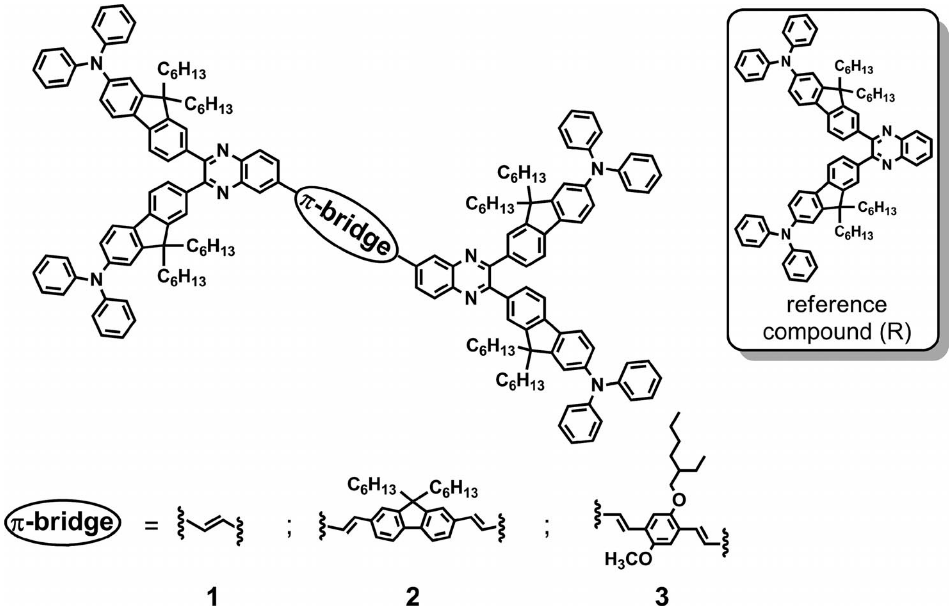
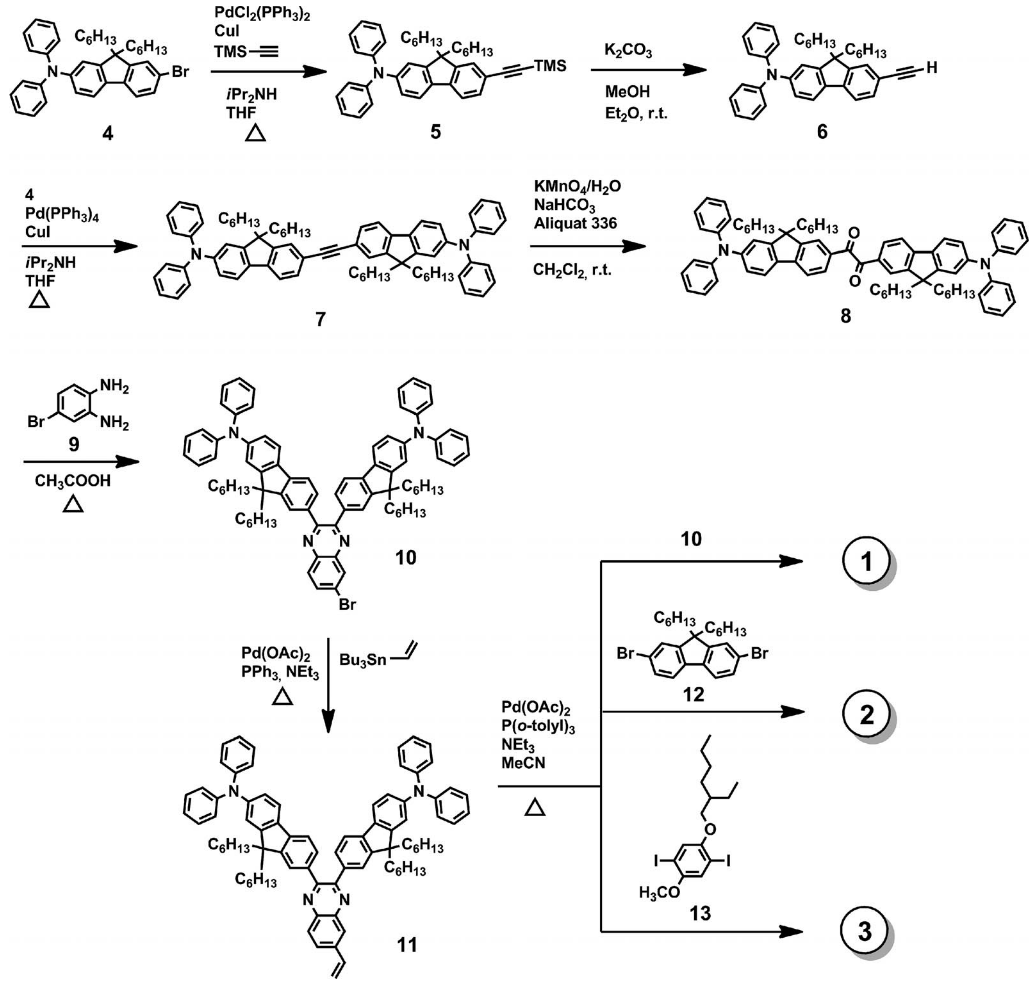


Figure 1. Molecular structures of the studied model chromophores.



Scheme 1. Synthetic procedures toward target model chromophores.

to connect two identical functionalized quinoxaline moieties. The extent of charge-transfer/redistribution upon light excitation of the resulting dye molecules may be different and this, in turn, is believed to correlate with molecular

2PA. Furthermore, it would be interesting to analyze the relationship between molecular 2PA and the arrangement of structural units in a chromophore, so that either the beneficial or deleterious effects caused by each structural unit may be elucidated. On the other hand, we have attached alkyl chains at the C-9 positions of all the fluorenyl units to enhance the molecular solubility in common organic solvents, which is another important issue to be considered in the molecular design from both an experimental and practical viewpoint. The synthetic procedures toward these model dye molecules mainly involve consecutive transformation of functional groups on the fluorene moieties, quinoxaline ring complex formation, and Heck coupling to prepare the key intermediates and the targeted model compounds as shown in Scheme 1. The details of the syntheses of these key intermediates and the final model chromophores are described in the Exp. Section. As shown in Figure 1, a previously reported compound[10c] that represents the "D–Q" components of the studied model compounds was selected as a reference compound (**R**) for comparison.

II. Linear and Nonlinear Optical Property Measurements

Figure 2 illustrates the linear absorption and fluorescence spectra of the studied dye molecules in toluene solution. Each of the studied model chromophores shows three distinct intense absorption peaks in the range 300–450 nm. These model-chromophore solutions also exhibit strong two-photon-excited blue to blue-green upconversion emission, which can be readily seen with the naked eye even under irradiation with a low-intensity unfocused femtosecond laser beam at ca. 790 nm. Figure 3 (a) illustrates the normalized 2PA-induced fluorescence spectra of **1**–**3**. As an excitation light source for this experiment, a wavelength-tunable mode-locked Ti:sapphire laser (Chameleon Ultra II, Coherent), which delivers ca. 140 fs pulses with a repetition rate of 80 MHz and a beam diameter of 2 mm was utilized. The intensity level of the excitation beam was carefully controlled to avoid the saturation of absorption and photodegradation of the samples during the experiments. Also, the relative position of the excitation beam was adjusted as close as possible to the wall of the quartz cell (10 × 10 mm cuvette), so that only emission from the front surface of the sample was recorded to minimize re-absorption and the inner-filter effect. From each inset logarithmic curve in Figure 3 (a), one can see that the results (i.e., slope ca. 2) validate that a 2PA process is the major cause of the observed upconverted fluorescence emissions in all cases.

The temporal behavior and lifetimes of the 2PA-induced fluorescence of the same sample solutions were also probed by the time-correlated single photon counting (TCSPC) technique by using a highly sensitive photomultiplier equipped with an accumulating real-time processor as the detection system (PMA-182 and TimeHarp 200, PicoQuant). The same femtosecond laser system (vide supra) was employed for this experiment. The measured fluorescence decay curves are depicted in Figure 3 (b). Theoretical fitting of each decay curve to a single-exponential dependence has revealed that these model chromophores possess fluorescence lifetimes of 1.2–1.6 ns, and these data are collected in Table 1.

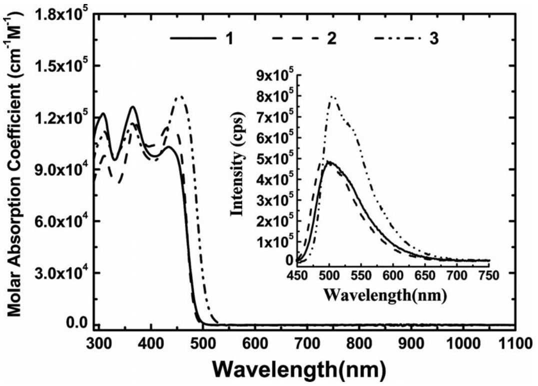


Figure 2. Linear absorption and fluorescence spectra (inset) of **1**–**3** in solution (1×10^{-6} M in toluene).

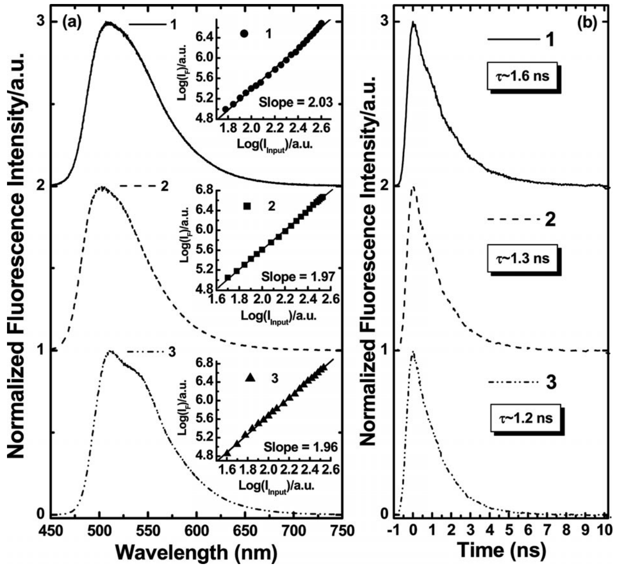


Figure 3. (a) Two-photon-excited fluorescence spectra of the studied model chromophores. Inset: logarithmic plots of the power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity of these compounds in toluene; (b) 2PA-induced fluorescence decay curves.

To investigate and compare the dispersion of 2PA behaviors of these dye molecules as a function of wavelength, the degenerate two-photon-excited fluorescence (2PEF) measurement was conducted in the near-IR regime (680–1000 nm) with fluorescein (ca. 80 μM in a pH 11 NaOH solution) as the standard.[12–13] Figure 4 shows the measured degenerate two-photon absorption spectra of **1**–**3** and **R** in toluene.

The reference compound **R** exhibits a relatively small but detectable 2PA with a local maximum at ca. 800 nm (Figure 4, $\delta_2^{max} \approx 180$ GM), whereas **1** exhibits a large 2PA ($\geq$ 500 GM) within the spectral range 720–860 nm, which implies that the use of a vinylene group to connect two units of **R** offers a useful approach to expand the π domain and

Table 1. Photophysical properties of **1**–**3** in solution.[a]

	$\lambda_{\max}^{\text{abs}}$ [nm][b]	$\lambda_{\max}^{\text{em}}$ [nm][c]	Φ_F[d]	$\tau_{\text{1PA–FL}}$ [ns][e]	$\delta_2^{\max}$ [GM][f]	$\tau_{\text{2PA–FL}}$ [ns][g]	N^{π}_{eff}[h]
1	308, 365, 434	502	0.57	1.6	ca. 1250	1.6	72.03
2	310, 370, 432	491	0.54	1.3	ca. 1680	1.3	85.70
3	310, 364, 454	505	0.77	1.2	ca. 2300	1.2	83.74
R	312, 394	501	0.50	2.3	ca. 180	2.3	36.06

[a] The concentrations were 1×10^{-5} and 1×10^{-4} M in toluene for 1PA-related and 2PA-related measurements, respectively. [b] One-photon absorption maximum. [c] 1PA-induced fluorescence emission maximum. [d] Fluorescence quantum efficiency. [e] 1PA-induced fluorescence lifetime. [f] Maximum 2PA cross-section value (with an experimental error of ca. ±15%); 1 GM = 1×10^{-50} $\text{cm}^4\,\text{s}\,\text{photon}^{-1}\,\text{molecule}^{-1}$. [g] 2PA-induced fluorescence lifetime. [h] Effective π-electron number.

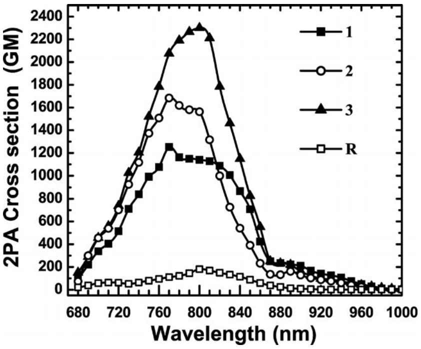


Figure 4. Degenerate two-photon absorption spectra of **1**–**3** (1×10^{-4} M) in toluene measured by the 2PEF method (experimental error ca. 15%).

leads to greatly enhanced molecular 2PA. On the other hand, if one uses **1** as a reference, it is notable that all these model chromophores not only exhibit a similar dispersion pattern of their two-photon activities but also show ascending overall magnitude of 2PA from **1** to **3** within the investigated spectral region (Figure 4). These features indicate that the insertion of aromatic rings, such as fluorene and dialkoxybenzene units, into the middle part of **1** (as is the case for **2** and **3**, respectively) further helps to promote the molecular 2PA without a dramatic shift of the 2PA band position. Molecules with this property could be very useful for some particular applications, in which large multiphoton absorptivities within a specific spectral region are desired. Additionally, the insertion of an electron-rich dialkoxybenzene moiety offers a larger increment of molecular 2PA compared to the insertion of a fluorene unit, which implies that the electronic properties of the central π bridge play an important role in the promotion of molecular 2PA in this dye system.

III. Effective Optical-Power-Limiting Properties in the Nanosecond Regime

The excited-state lifetimes of **1**–**3** are in the nanosecond range, which means that significant excited-state population may be retained and, therefore, the occurrence of excited-state absorption within the tested sample is possible during excitation by longer laser pulses. This, in turn, may lead to strong apparent optical attenuation.[11] Such a feature is particularly beneficial for optical-power-control applications in the nanosecond regime based on 2PA-induced excited-state absorption (2PA-induced ESA) because, from the application standpoint, any medium that possesses a large apparent nonlinear absorption over a wide spectral range could be a very useful optical power attenuator for long laser pulses.[14]

To study the effective power-limiting performance of these model compounds, we utilized nanosecond laser pulses. For example, we selected **3** as a representative compound to demonstrate the power-limiting properties of these fluorophores as it manifests very strong 2PA at 800 nm and is theoretically expected to show better optical power control at this wavelength. In our experiment, the nonlinear absorbing medium was a 1 cm path-length solution of the studied dye in toluene with a concentration of 0.02 M. A tunable nanosecond laser system [an integrated Q-switched Nd:YAG laser and optical parameter oscillator (OPO), model NT342/3 from Ekspla] was employed as an excitation source to provide ca. 6 ns laser pulses with a controlled average pulse energy in the range ca. 0.02–2 mJ and a repetition rate of 10 Hz. The laser beam was slightly focused onto the center of the sample solution to provide a nearly uniform laser beam radius within the whole cell path length, and the transmitted laser beam from the sample cell was detected by an optical power (energy) meter. Figure 5 illustrates the measured power-attenuation performance at 800 nm based on this chromophore solution. Compound **3** displays fairly good power-restriction properties at 800 nm, and this initial finding suggests the potential of this model fluorophore for broadband power-suppressing applications in the nanosecond regime.

In addition, the output/input curve shown in Figure 5 represents a characteristic type of optical compression, which is ideal for use in optical power (or intensity) stabilization because a huge magnitude change of the input signal will lead to only a small variation of the output level.[15] This means that a larger input-power (or intensity) fluctuation will lead to a much smaller output fluctuation when the pulse passes through a nonlinear absorptive medium, such as a solution of **3**. The results of an optical-stabilization study based on the solution of **3** are shown in Figure 5 (b) and (c). The curves in Figure 5 (b) and (c) are the instantaneous pulse energy changes of the input and output laser pulses at 800 nm, respectively. For comparison, the average levels for both the input and output signals were normalized to the same value. The input pulses possess a relatively large energy fluctuation as shown in Figure 5 (b), and after the pulse passes through the solution of **3**, a re-

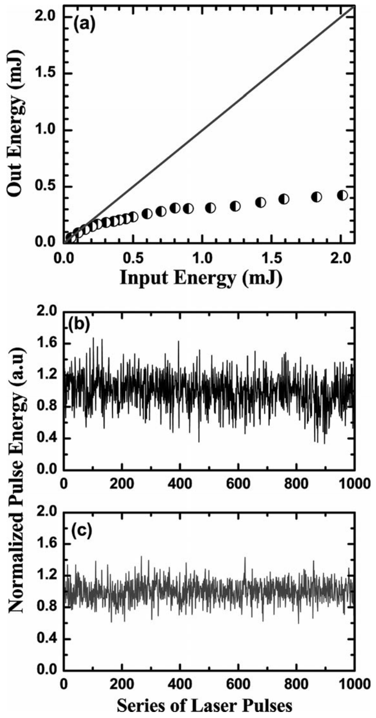


Figure 5. (a) Measured optical-power-attenuation curve based on a toluene solution of **3** under the excitation of nanosecond laser pulses at ca. 800 nm, (b) measured instantaneous pulse-energy fluctuation of the input laser pulses, and (c) measured instantaneous pulse-energy fluctuation of the output laser pulses. The repetition rate of the laser pulses was 10 Hz, and the average input pulse energy level was ca. 1 mJ.

duced fluctuation of pulse energy is observed for the output signal as illustrated in Figure 5 (c).

Conclusions

We have synthesized a new multipolar chromophore set composed of three analogues with various central π bridges and functionalized quinoxaline moieties as the major building units. The initial experimental results indicate that these model fluorophores manifest strong and widely dispersed two-photon absorption in the near-IR region. Tentative analysis of the correlation between the molecular structures and the observed overall 2PA behaviors reveals that expanding the size of the π domain through the insertion of different aromatic rings has a positive contribution to the promotion of 2PA in this compound system, and the insertion of the electron-rich dialkoxybenzene unit provides a larger increment of molecular 2PA. The model compound **3** exhibits both intense upconverted emission when excited by a two-photon process and effective optical power-limiting/stabilization properties for nanosecond laser pulses. These observations may suggest that the functionalized quinoxaline ring systems utilized in this work could be useful structural units for the construction of highly active 2PA chromophores for practical applications.

Experimental Section

General: All commercially available reagents for the preparation of the intermediates and targeted chromophores were obtained from the Aldrich Chemical Co. and were used as received, unless stated otherwise. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl. ^{1}H and ^{13}C NMR spectra were recorded with 200 or 300 MHz spectrometers and are referenced to tetramethylsilane (TMS) or residual $CHCl_3$. A representative numbering scheme for the assignment of the NMR signals of the C and H atoms of the intermediates and model chromophores is provided in the Supporting Information. HRMS was conducted by using a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS spectra were obtained with a Voyager DE-PRO mass spectrometer (Applied Biosystems, Houston, USA).

Synthesis: Compounds **4**, **12**, and **13** (Scheme 1) were obtained by following established procedures.[9a,16] For the synthesis of other key intermediates (**5**–**8**, **10**, and **11**) and the targeted model compounds (**1**–**3**), a series of functionalization steps starting from **4** were conducted and are presented below.

9,9-Dihexyl-*N*,*N*-diphenyl-7-[2-(trimethylsilyl)ethynyl]-9*H*-fluoren-2-amine (5): To a solution of **4** (8.4 g, 14.47 mmol) in THF (130 mL) was added $PdCl_2(PPh_3)_2$ (0.61 g, 0.87 mmol), CuI (0.28 g, 1.47 mmol), *i*Pr_2NH (8.8 g, 0.087 mol), and trimethylsilyl acetylene (1.5 g, 15.27 mmol), and the resulting solution was stirred at 80 °C under Ar for 18 h. The solution was cooled to room temp., and a saturated NH_4Cl solution (ca. 50 mL) was added. The mixture was stirred at room temp. for 0.5 h. and then extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel with hexane as the eluent to give the final purified product as pale yellow oil in a yield of 82.5% (13.83 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.65–7.60 (m, 2 H, H^{15}, H^{12}), 7.57–7.54 (d, *J* = 8.1 Hz, 2 H, H^9, H^{13}), 7.38–7.33 (t, 4 H, H^2), 7.26–7.24 (m, 5 H, H^8, H^3), 7.16–7.09 (m, 3 H, H^6, H^1), 2.06–1.90 (m, 4 H, H^f), 1.31–1.19 (m, 12 H, H^e, H^d, H^c), 1.02–0.91 (m, 6 H, H^a), 0.78 (br., m, 4 H, H^b), 0.35 (s, 9 H, TMS CH_3) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.42 (C^5), 150.41 (C^{16}), 147.84 (C^4), 147.60 (C^7), 141.45 (C^{11}), 135.38 (C^{10}), 131.18 (C^{15}), 129.15 (C^2), 126.02 (C^{13}), 123.90 (C^3), 123.35 (C^9), 122.63 (C^1), 120.73 (C^{12}), 120.39 (C^8), 118.95 (C^6), 118.83 (C^{14}), 106.44 (sp C), 93.54 (sp C), 55.03 (C^g), 40.20 (C^f), 31.50 (C^e), 29.58 (C^d), 23.68 (C^c), 22.53 (C^b), 14.03 (C^a), 0.08 (TMS CH_3) ppm. HRMS (FAB): calcd. for $C_{42}H_{51}NSi$ $[M]^+$ 597.3791; found 597.3796.

7-Ethynyl-9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (6): A mixture of **5** (12.85 g, 0.021 mol), diethyl ether (60 mL), and potassium carbonate (5.94 g, 0.043 mol) in methanol (60 mL) was stirred at room temperature for 4 h. A saturated NH_4Cl solution (ca. 90 mL) was then added, and the reaction mixture was stirred at room temperature for 0.5 h. The solution was then extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel with hexane as the eluent to give the final purified product as a pale yellow oil in a yield of ca. 100% (11.3 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56–7.53 (d, *J* = 8.1 Hz, 2 H, H^{15}, H^{12}), 7.48–7.46 (m, 2 H, H^9, H^{13}), 7.29–7.24 (t, *J* = 7.8 Hz, 4 H, H^2), 7.18–7.15 (m, 5 H, H^8, H^3), 7.08–7.00 (m, 3 H, H^6, H^1), 3.08 (s, 1 H, sp H), 1.93–1.89 (m, 4 H, H^f), 1.32–1.11 (m, 12 H, H^e, H^d, H^c), 0.86–0.81 (t, 6 H, H^a), 0.73–0.71 (m, 4 H, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.41 (C^5), 150.50 (C^{16}), 147.82 (C^4), 147.66 (C^7), 141.64 (C^{11}), 135.20 (C^{10}), 131.17 (C^{15}), 129.14 (C^2), 126.24 (C^{13}), 123.93 (C^3), 123.29 (C^9), 122.64 (C^1), 120.75 (C^8, C^{12}), 119.36 (C^6), 118.89 (C^{14}), 84.77 (sp C), 76.86 (sp C), 55.00 (C^g), 40.11 (C^f), 31.44 (C^e), 29.53 (C^d), 23.67 (C^c), 22.48 (C^b), 13.99 (C^a) ppm. HRMS (FAB): calcd. for $C_{39}H_{43}N$ $[M]^+$ 525.3396; found 525.3402.

7-{2-[7-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]ethynyl}-9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (7): To a solution of **4** (11.48 g, 19.8 mmol) and **6** (10.42 g, 19.8 mmol) in THF (60 mL) was added $Pd(PPh_3)_4$ (0.7 g, 0.61 mmol), CuI (0.38 g, 2.0 mmol), and $i\mathrm{Pr}_2\mathrm{NH}$ (3 g, 0.3 mol), and the resulting solution was stirred at 80 °C under N_2 for 18 h. The solution was cooled to room temp., and a saturated NH_4Cl solution (ca. 50 mL) was added into the reaction mixture, which was stirred at room temperature for 0.5 h. The solution was then extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel with hexane as the eluent and recrystallized from methanol/hexane. The purified product was obtained as a yellow powder in a yield of 52.5% (10.67 g). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.60–7.49 (m, 8 H, H^{15}, H^{12}, H^9, H^{13}), 7.27–7.22 (t, 8 H, H^2), 7.13–7.11 (d, J = 7.8 Hz, 10 H, H^6, H^3), 7.03–6.99 (m, 6 H, H^1, H^8), 1.96–1.79 (m, 8 H, H^f), 1.16–1.06 (m, 24 H, H^e, H^d, H^c), 0.87–0.78 (t, 12 H, H^a), 0.66 (br., m, 8 H, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.46 (C^5), 150.66 (C^{16}), 147.90 (C^4), 147.53 (C^7), 141.13 (C^{11}), 135.55 (C^{10}), 130.63 (C^{15}), 129.18 (C^2), 125.72 (C^{13}), 123.91 (C^3), 123.44 (C^9), 122.61 (C^1), 120.75 (C^8), 120.66 (C^{12}), 119.06 (C^6, C^{14}), 90.52 (sp C), 55.10 (C^g), 40.30 (C^f), 31.56 (C^e), 29.64 (C^d), 23.76 (C^c), 22.58 (C^b), 14.04 (C^a) ppm. HRMS (FAB): calcd. for $C_{76}H_{84}N_2$ $[M]^+$ 1024.6635; found 1024.6639.

1,2-Bis[7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]ethane-1,2-dione (8): To a solution of **7** (10 g, 9.75 mmol) in CH_2Cl_2 (50 mL) was added $KMnO_4$ (6.16 g, 39 mmol), $NaHCO_3$ (0.82 g, 9.76 mmol), Aliquat 336 (0.06 g), and H_2O (60 mL), and the resulting solution was stirred at room temperature for 12 h. A saturated $NaHSO_3$ solution (ca. 50 mL) and a 1 N HCl solution were added into the reaction mixture. The solution was then extracted with dichloromethane (3 × 30 mL). The combined organic layers were dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel with dichloromethane/hexane (1:8) to give the final purified product as a saffron-yellow powder in a yield of 65% (6.65 g). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.06 (s, 2 H, H^{15}), 7.89–7.87 (d, J = 7.2 Hz, 2 H, H^{12}), 7.65–7.62 (d, J = 8.4 Hz, 2 H, H^{13}), 7.61–7.58 (d, J = 8.1 Hz, 2 H, H^9), 7.25–7.23 (d, J = 5.1 Hz, 8 H, H^2), 7.15–7.13 (d, J = 5.4 Hz, 10 H, H^6, H^3), 7.07–7.01 (m, 6 H, H^1, H^8), 1.94–1.87 (m, 8 H, H^f), 1.27–1.06 (m, 24 H, H^e, H^d, H^c), 0.89–0.80 (m, 12 H, H^a), 0.67 (br., m, 8 H, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 195.00 (C=O), 153.71 (C^5), 151.14 (C^{16}), 148.94 (C^{11}), 147.68 (C^4), 147.43 (C^7), 133.65 (C^{10}), 130.84 (C^{15}, C^{12}), 129.16 (C^2), 124.31 (C^3), 123.07 (C^1), 122.59 (C^9), 121.73 (C^{13}, C^{14}), 118.76 (C^6), 117.89 (C^8), 55.15 (C^g), 39.79 (C^f), 31.32 (C^e), 29.37 (C^d), 23.62 (C^c), 22.38 (C^b), 13.89 (C^a) ppm. HRMS (FAB): calcd. for $C_{76}H_{84}N_2O_2$ $[M]^+$ 1056.6533; found 1056.6627.

7-{6-Bromo-3-[7-(diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]quinoxalin-2-yl}-9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (10): A mixture of **8** (4.2 g, 3.97 mmol) and **9** (0.82 g, 4.42 mmol) in CH_3COOH (65 mL) was heated to reflux under N_2 for 6 h. The solution was cooled to room temp, and H_2O (ca. 50 mL) was added to the reaction mixture. The crude solid product was collected by filtration and recrystallized from methanol. The purified product was obtained as a green-brown powder in a yield of 96.6% (4.83 g). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.37 (s, 1 H, H^F), 8.05–8.02 (d, J = 9 Hz, 1 H, H^C), 7.83–7.79 (d, J = 9 Hz, 1 H, H^B), 7.58–7.50 (m, 8 H, H^{12}, H^{15}, H^{13}, H^9), 7.26–7.21 (m, 8 H, H^2), 7.12–7.08 (m, 10 H, H^6, H^3), 7.03–6.98 (m, 6 H, H^1, H^8), 1.74–1.72 (m, 8 H, H^f), 1.10–1.02 (m, 24 H, H^e, H^d, H^c), 0.80–0.76 (t, J = 6.9 Hz, 12 H, H^a), 0.64–0.62 (m, 8 H, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.78 (C^G), 154.30 (C^H), 152.63 (C^5), 150.62 (C^{16}), 147.89 (C^4), 147.57 (C^{10}), 141.95 (C^E), 141.88 (C^D), 141.66 (C^7),139.82 (C^{11}), 136.95 (C^C), 136.85 (C^F), 135.33 (C^B), 133.04 (C^{15}), 131.36 (C^9), 130.39 (C^{12}), 129.15 (C^2), 124.33 (C^{13}), 123.90 (C^3), 123.34 (C^{14}), 122.59 (C^1), 120.89 (C^6), 119.02 (C^8), 118.89 (C^A), 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 (C^a) ppm. HRMS (FAB): calcd. for $C_{82}H_{87}BrN_4$ $[M]^+$ 1206.6114; found 1206.6104.

7-{3-[7-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-2-yl]-6-vinylquinoxalin-2-yl}-9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (11): Compound **10** (4 g, 3.3 mmol), $Pd(OAc)_2$ (0.038 g, 0.169 mmol), and PPh_3 (0.174 g, 0.648 mmol) were dissolved in NEt_3 (60 mL). Tributyl(vinyl)stannane (1.58 g, 4.98 mmol) was then added, and the resulting solution was stirred at 95 °C under N_2 for 24 h. The solution was cooled to room temp., and saturated NH_4Cl solution was added into the reaction mixture, which was stirred at room temp. for 1h. The solution was filtered, and the filtrate was then extracted with ethyl acetate (3 × 30 mL). The combined organic layers were dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:20) to give the final purified product as a yellow powder in a yield of 91.6% (3.5 g). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.14–8.12 (d, J = 8.4 Hz, 1 H, H^C), 8.12 (s, 1 H, H^F), 7.91–7.87 (dd, J_1 = 1.8 Hz, J_2 = 1.5 Hz, 1 H, H^B), 7.57–7.50 (m, 8 H, H^{12}, H^{15}, H^{13}, H^9), 7.26–7.21 (m, 8 H, H^2), 7.12–7.07 (m, 10 H, H^6, H^3), 7.03–6.98 (m, 6 H, H^1, H^8), 6.96–6.92 (d, J = 11.1 Hz, 1 H, vinyl H), 6.04–5.98 (d, J = 17.1 Hz, 1 H, vinyl H), 5.50–5.45 (d, J = 11.1 Hz, 1 H, vinyl H), 1.75–1.70 (m, 8 H, H^f), 1.12–0.98 (m, 24 H, H^e, H^d, H^c), 0.80–0.76 (t, J = 6.9 Hz, 12 H, H^a), 0.64–0.61 (m, 8 H, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.29 (C^H), 153.61 (C^G), 152.57 (C^5), 150.50 (C^{16}), 147.86 (C^4), 147.40 (C^{11}), 141.58 (C^E), 141.29 (C^D), 140.96 (C^7), 138.75 (C^C), 137.29 (C^{10}), 136.13 (C^{15}, C^B), 135.44 (vinyl C), 129.11 (C^{12}, C^9), 127.29 (C^2), 126.66 (C^F), 124.32 (C^A), 123.81 (C^{13}), 123.34 (C^3), 122.50 (C^{14}), 120.82 (C^1), 119.03 (C^6), 118.90 (C^8), 116.21 (vinyl C), 55.02 (C^g), 40.07 (C^f), 31.51 (C^e), 29.55 (C^d), 23.80 (C^c), 22.59 (C^b), 14.07 (C^a) ppm. HRMS (FAB): calcd. for $C_{84}H_{91}N_4$ $[M + H]^+$ 1155.7165; found 1155.7251.

Compound 1: A high-pressure tube was charged with $Pd(OAc)_2$ (1.98 mg, 0.00882 mmol), P(*o*-tolyl)$_3$ (16 mg, 0.053 mmol), **11** (0.51 g, 0.441 mmol), **10** (0.59 g, 0.488 mmol), NEt_3 (5 mL), MeCN (10 mL), and DMF (5 mL). The tube was sealed with a PTFE cap, and the mixture was stirred at 110 °C under N_2 for 24 h. The mixture was cooled to room temp., and dichloromethane was added. The resulting solution was stirred at room temp. for 10 min. and then extracted with H_2O (3 × 30 mL). The organic layer was dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10). The purified product was obtained as a yellow solid with yield of 72% (0.72 g) after recrystallization from methanol. ^1H NMR (300 MHz, $CDCl_3$): δ = 8.31 (s, 2 H, H^F), 8.22–8.19 (d, J = 8.7 Hz, 2 H, H^C), 8.10–8.07 (d, J = 9 Hz, 2 H, H^B), 7.59–7.51 (m, 16 H, H^{12}, H^{15}, H^{13}, H^9), 7.24–7.22 (m, 16 H, H^2), 7.12–7.08 (m, 20 H, H^6, H^3), 7.03–6.99 (m, 14 H, H^1, H^8, vinylene H), 1.76–1.71 (m, 16 H, H^f), 1.13–1.03 (m, 48 H, H^e, H^d, H^c), 0.81–0.77 (m, 24 H, H^a), 0.65–0.63 (m, 16 H, H^b) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.59 (C^H), 153.77 (C^G), 152.63 (C^5), 150.59 (C^{16}), 147.90 (C^4), 147.46 (C^{11}), 141.69 (C^E), 141.48

(C^{D}), 141.22 (C^{7}), 138.24 (C^{C}), 137.29 (C^{10}), 137.24 (C^{15}, C^{B}), 135.47 (vinylene C), 130.09 (C^{12}), 129.46 (C^{9}), 129.14 (C^{2}), 127.26 (C^{F}), 124.38 (C^{A}), 123.86 (C^{13}), 123.37 (C^{3}), 122.54 (C^{14}), 120.86 (C^{1}), 119.08 (C^{6}), 118.97 (C^{8}), 55.07 (C^{g}), 40.10 (C^{f}), 31.54 (C^{e}), 29.59 (C^{d}), 23.85 (C^{c}), 22.62 (C^{b}), 14.09 (C^{a}) ppm. HRMS (FAB): calcd. for $C_{166}H_{176}N_8$ [M]$^+$ 2281.4019; found 2281.4089.

Compound 2: A high-pressure tube was charged with Pd(OAc)$_2$ (1.71 mg, 0.0076 mmol), P(*o*-tolyl)$_3$ (13.87 mg, 0.0456 mmol), **11** (0.92 g, 0.796 mmol), **12** (0.187 g, 0.38 mmol), NEt$_3$ (5 mL), MeCN (10 mL), and DMF (5 mL). The tube was sealed with a PTFE cap, and the mixture was stirred at 110 °C under N_2 for 24 h. The mixture was cooled to room temperature, and dichloromethane was added. The resulting solution was stirred at room temperature for 10 min. and then extracted with H_2O (3 × 30 mL). The organic layer was dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) and recrystallized from methanol. The purified product was obtained as yellow solid in a yield of 66% (0.66 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.27 (s, 2 H, H^{F}), 8.19–8.16 (d, *J* = 8.7 Hz, 2 H, H^{C}), 8.07–8.03 (d, *J* = 8.7 Hz, 2 H, H^{B}), 7.79–7.74 (d, *J* = 8.1 Hz, 2 H, vinylene H), 7.62–7.44 (m, 22 H, H$^{B'}$, H$^{D'}$, H$^{E'}$, H$^{K'}$, H$^{H'}$, H$^{I'}$, H^{12}, H^{15}, H^{13}, H^{9}), 7.27–7.22 (m, 16 H, H^{2}), 7.13–7.09 (m, 20 H, H^{3}, H^{6}), 7.03–6.99 (m, 14 H, H^{1}, H^{8}, vinylene H), 1.75–1.73 (m, 20 H, H^{f}, H$^{f'}$), 1.10–1.04 (m, 60 H, H^{e}, H^{d}, H^{c}, H$^{e'}$, H$^{d'}$, H$^{c'}$), 0.81–0.77 (m, 30 H, H^{a}, H$^{a'}$), 0.65–0.63 (m, 20 H, H^{b}, H$^{b'}$) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 154.40 (C^{H}), 153.39 (C^{G}), 152.62 (C^{5}), 151.80 (C$^{L'}$, C$^{A'}$), 150.58 (C^{16}), 147.90 (C^{4}), 147.43 (C^{11}), 141.61 (C^{E}), 141.42 (C^{12}), 141.11 (C^{D}), 140.95 (C^{7}), 138.94 (C$^{G'}$, C$^{F'}$), 137.36 (C^{F}), 136.02 (C^{B}), 135.51 (C^{C}), 131.71 (C^{10}), 129.14 (C^{2}), 128.30 (C$^{K'}$, C$^{B'}$), 127.68 (C^{15}), 127.13 (C$^{I'}$, C$^{D'}$), 126.50 (vinylene C), 126.28 (vinylene C), 126.02 (C^{9}), 124.38 (C^{13}), 123.86 (C^{3}), 123.38 (C^{14}), 122.54 (C^{1}), 121.18 (C$^{H'}$, C$^{E'}$), 120.85 (C^{6}), 120.18 (C$^{J'}$, C$^{C'}$), 119.09 (C^{8}), 118.94 (C^{A}), 55.07 (C^{g}, C$^{g'}$), 40.12 (C^{f}, C$^{f'}$), 31.55 (C^{e}, C$^{e'}$), 29.74 (C$^{d'}$), 29.59 (C^{d}), 23.85 (C^{c}, C$^{c'}$), 22.62 (C^{b}, C$^{b'}$), 14.09 (C^{a}), 14.00 (C$^{a'}$) ppm. HRMS (FAB): calcd. for $C_{193}H_{211}N_8$ [M + H]$^+$ 2640.6758; found 2640.6841.

Compound 3: A high-pressure tube was charged with Pd(OAc)$_2$ (5.75 mg, 0.026 mmol), P(*o*-tolyl)$_3$ (46.9 mg, 0.15 mmol), **11** (1.63 g, 1.41 mmol), **13** (0.304 g, 0.62 mmol), NEt$_3$ (5 mL), MeCN (10 mL), and DMF (5 mL). The tube was sealed with a PTFE cap, and the reaction mixture was stirred at 110 °C under N_2 for 24 h. The mixture was cooled to room temp., and dichloromethane was added. The resulting solution was stirred at room temperature for 10 min. and then extracted with H_2O (3 × 30 mL). The organic layer was dried with $MgSO_4$. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel with ethyl acetate/hexane (1:10) and recrystallized from methanol. The purified product was obtained as a light orange solid in a yield of 43% (0.7 g). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.28 (s, 1 H, H^{F}), 8.23 (s, 1 H, H^{F}), 8.18–8.15 (d, *J* = 8.7 Hz, 2 H, H^{C}), 8.08–8.02 (dd, J_1 = 9 Hz, J_2 = 9 Hz, 2 H, H^{B}), 7.81–7.74 (dd, J_1 = 16.2 Hz, J_2 = 4.8 Hz, 2 H, vinylene H), 7.67–7.47 (m, 16 H, H^{12}, H^{15}, H^{13}, H^{9}), 7.42–7.36 (d, *J* = 16.8 Hz, 2 H, vinylene H), 7.27–7.22 (m, 18 H, H^{2}, H$^{B'}$, H$^{E'}$), 7.13–7.08 (m, 20 H, H^{3}, H^{6}), 7.03–6.99 (m, 12 H, H^{1}, H^{8}), 4.05–4.02 (d, *J* = 10.5 Hz, 2 H, H$^{f'}$), 3.95 (s, 3 H, H$^{i'}$), 1.96–1.86 (m, 1 H, H$^{e'}$), 1.75–1.60 (m, 18 H, H^{f}, H$^{g'}$), 1.51–1.42 (m, 6 H, H$^{b'}$, H$^{c'}$, H$^{d'}$), 1.11–0.94 (m, 54 H, H^{e}, H^{d}, H^{c}, H$^{a'}$, H$^{h'}$), 0.79–0.65 (t, *J* = 7.2 Hz, 24 H, H^{a}), 0.65 (br., 16 H, H^{b}) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 154.38 (C^{G}), 153.37 (C^{H}), 152.64 (C^{5}), 151.68 (C$^{D'}$), 150.57 (C^{16}), 147.94 (C^{4}), 147.45 (C^{10}), 141.59 (C^{E}), 141.00 (C^{D}), 139.38 (C^{7}), 137.39 (C^{11}), 135.55 (C^{B}), 129.15 (C^{2}), 129.00 (C$^{A'}$), 128.37 (C^{C}), 128.25 (C^{F}), 128.01 (C^{15}), 127.64 (C^{9}), 127.01 (C^{12}), 126.76 (vinylene C), 126.60 (vinylene C), 125.91 (C$^{F'}$), 125.66 (C$^{C'}$), 124.40 (C^{13}), 123.87 (C^{3}), 123.41 (C^{14}), 122.54 (C^{1}), 120.84 (C^{6}), 119.14 (C^{8}), 118.94 (C^{A}), 110.43 (C$^{B'}$), 109.54 (C$^{E'}$), 71.98 (C$^{f'}$), 56.38 (C$^{i'}$), 55.09 (C^{g}), 40.12 (C^{f}), 39.75 (C$^{e'}$), 31.56 (C^{e}), 31.02 (C$^{d'}$), 29.61 (C^{d}), 29.30 (C$^{c'}$), 24.30 (C$^{g'}$), 23.86 (C^{c}), 23.14 (C$^{b'}$), 22.62 (C^{b}), 14.16 (C^{a}), 14.08 (C$^{a'}$), 11.34 (C$^{h'}$) ppm. HRMS (FAB): calcd. for $C_{183}H_{200}N_8O_2$ [M + H]$^+$ 2542.5872; found 2542.5930.

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

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