DOI: 10.1002/ejoc.201001165

Synthesis and Characterization of Highly Soluble Two-Photon-Absorbing Chromophores with Multi-Branched and Dendritic Architectures

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Keywords: Chromophores / Dendrimers / Two-photon absorption / Optical power limiting

A set of novel multi-polar compounds composed of four fluorene-based derivatives with systematic alteration of the molecular structure was synthesized and their nonlinear optical properties in the femtosecond and nanosecond time domain were examined. Preliminary experimental results show that the two-photon activities of the model compounds are connected to structural parameters, such as the number of peripheral electron-donating groups and/or the size of the π-domain in a dye molecule. It is also found that these model chromophores possess large nonlinear attenuation under the irradiation of laser pulses working at nanosecond regimes, indicating that these compounds may have strong two-photon-assisted excited-state absorption within the studied spectral region. Effective optical-power-limiting behaviors of the dendritic fluorophores were also demonstrated to show that such dye molecules can be potential materials for use as broadband and rapid-responsive optical limiters, especially against laser lights with longer pulses.

1. Introduction

Two-photon absorption (2PA) processes occur 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 Maria Göppert-Mayer in 1931,[1] experimental evidence was obtained about thirty years later when up-converted emission from the media was observed under irradiation of laser light with wavelengths far from the linear absorption bands of the studied media.[2] Over the past fifteen years, the availability of high peak power lasers has created the momentum to explore two-photon technologies. Many promising applications in the emerging field of photonics and biophotonics based on 2PA have been proposed, including optical power limiting, frequency up-converted lasing, 3D data storage, 3D microfabrication, nondestructive bioimaging and tracking, and two-photon-assisted photodynamic therapy.[3] To be of use in these applications, organic compounds that manifest strong 2PA within a specific spectral region are consequently in great demand. The accumulated knowledge and experience of many research groups to understand the connections between molecular structure and 2PA properties by testing and modeling various dye systems since the mid-1990s have revealed that molecular 2PA is related to a combination of several structural parameters, such as intramolecular charge-transfer efficiency and/or the effective size of the π-conjugation domain within a molecule.[4–10] Recently, it has been experimentally shown that multipolar chromophores could lead to highly efficient multi-photon absorption,[5d–5f,5i,6,7d,8a–8b,8f,9c,9e–9h,11,12] while retaining linear transparency over a wide spectral range;[13] this is a desirable feature especially for the broadband optical limiting applications based on 2PA. In general, fluorophores with octupolar and/or higher-polar characters are composed of branched or dendritic backbones. From the viewpoint of molecular design, branched architecture not only provides a way to incorporate several 2PA-enhancing parameters into a single molecular system, but also allows material chemists to optimize a dye molecule to simultaneously combine various expected characteristics for specific purposes. Furthermore, branched skeletons are potential building blocks for constructing dendritic and/or supermolecular structures, which are suggested as possible ways to probe the fundamental limits of molecular 2PA.[14] In the search for well-defined strategies that can be used to generate highly efficient 2PA materials, we have been interested in exploring the 2PA properties of multi-branched and dendritic organic structures. In particular, we wanted to systematically vary the molecular structures so that the essential structural parameters governing the strength of molecular 2PA could be elucidated. In this paper, we report our studies on degenerate two-photon absorption, up-converted emission, and effective optical power limiting properties of a series of newly synthesized model chromophores with systematically varied structures by using high peak power IR laser pulses working in the femtosecond and nanosecond regimes as probing tools.

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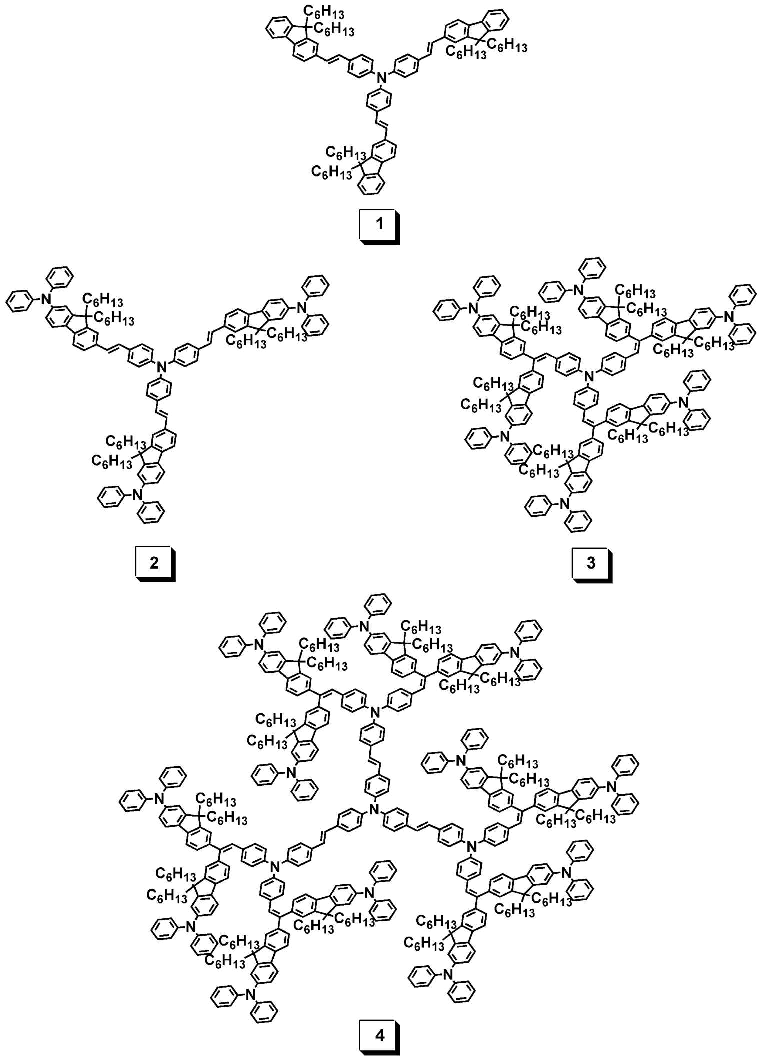
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201001165.

2. Results and Discussion

I. Molecular Structures and Syntheses

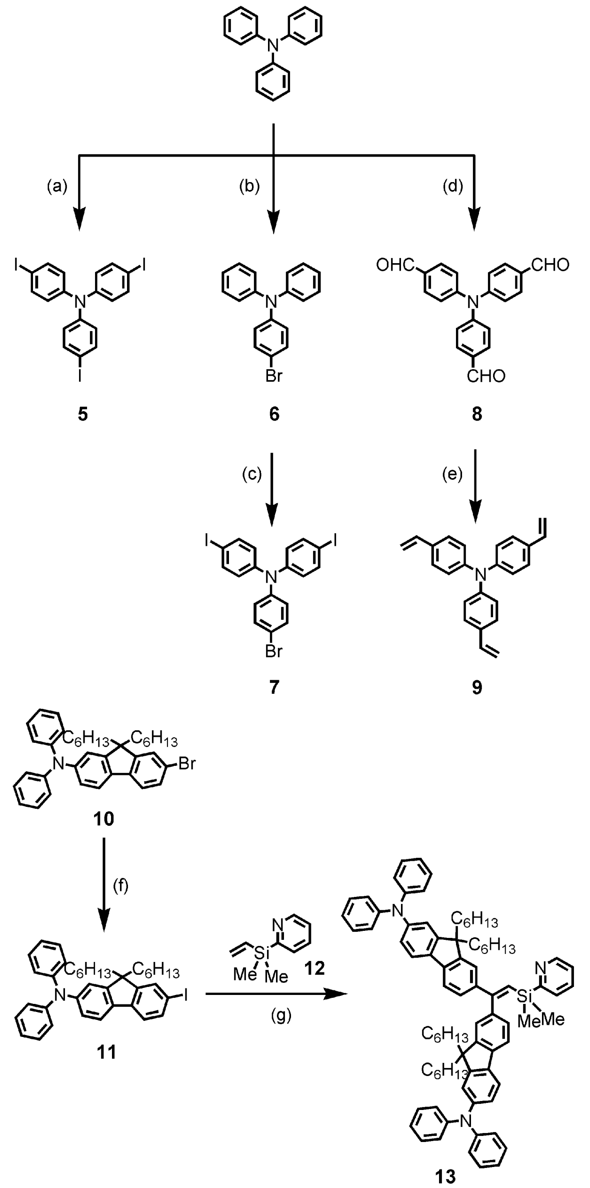
The chemical structures of the model chromophores studied in this work are presented in Scheme 1. This model compound set contains four multi-branched congeners and the frameworks of these four members are derived by incorporating fluorene and triphenylamine as the main building units. Among these models, compounds **1** and **2** are three-branched chromophores, whereas compounds **3** and **4** have dendritic architectures with six and twelve branches, respectively. Compound **1** is the smallest model, with triphenylamine as the central core surrounded by three fluorenyl arms and vinyl groups as the linkers. The generic structure of compound **2** is the same as that of **1** but end-capped by an electron-donating diphenylamino unit on each arm. Compared to compound **2**, compound **3** has three additional diphenylaminofluorenyl units attached to the central triphenylamine core to form a six-branched dendritic structure. The molecular structure of model compound **4** is based on a combination of four triphenylamine and twelve diphenoaminofluorenyl units, using vinyl groups as linkers to form the largest π-framework in this model compound set.

Many efforts have been made to study large two-photon-absorbing molecules with either conjugated or non-conjugated dendritic frameworks using fluorene and/or stibenoid units as the main building blocks.[15] The molecular design of the model compounds used in the present work originated from the simple idea of constructing a set of multi-branched and dendritic frameworks with systematically altered molecular structures based on a combination of fluorene and di-/tri-arylamine units so that the resulting fluorophores may possess consecutively expanded π-domains and increased multipolar characteristics. On the other hand, the pendent alkyl chains on the fluorenyl moieties in these model chromophores were expected to enhance their solubility in common organic solvents, which is another important parameter to be considered in the molecular design of compounds for use in experimental studies and in potential applications.

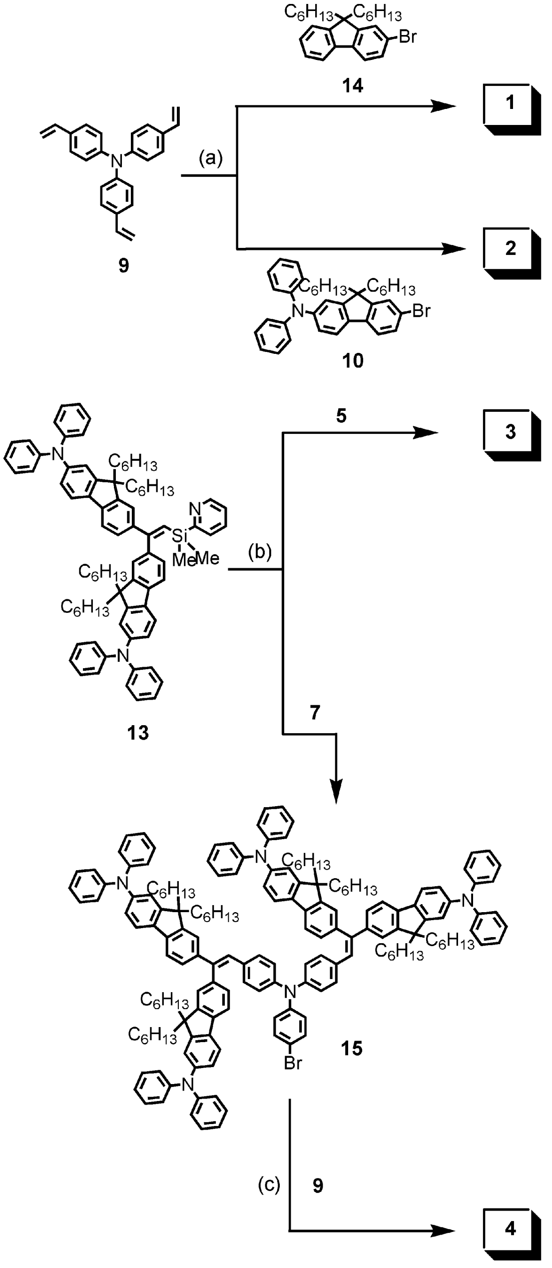


Scheme 1. Molecular structures of the studied model fluorophores.

The synthetic procedures used to prepare the model fluorophores are outlined in Schemes 2 and 3. To obtain the target chromophores, various synthetic protocols were followed to prepare key intermediates, which were subsequently combined in the final coupling reactions. Compounds **1** and **2** were both synthesized through threefold Heck reaction procedures using compounds **9**, **10**, and **14** as the major synthons and were obtained in yields of 50 and 40%, respectively. For the synthesis of compound **3**, instead of following the previously utilized one-pot synthetic strategy,[16] a two-step catalytic process (i.e.,



Scheme 2. Synthetic procedures for the key intermediates (**5**–**9**, **11**, and **13**). *Reagents and conditions*: (a) Triphenylamine (1 equiv.), KI (3 equiv.), KIO_3 (3 equiv.) in HOAc, 80 °C, 15 h (76%); (b) Triphenylamine (1 equiv.), tetrabutylammonium tribromide ($TBABr_3$) (1 equiv.) in CH_2Cl_2/MeOH, r.t., 24 h (84%); (c) **6** (1 equiv.), KI (1.35 equiv.), KIO_3 (0.67 equiv.) in HOAc, 85 °C, 12 h (80%); (d) triphenylamine (1 equiv.), $POCl_3$ (25 equiv.) in DMF (23 equiv.), 95 °C, 24 h (40%); (e) **8** (1 equiv.), NaH (6 equiv.), $CH_3PPh_3^+I^-$ (4 equiv.) in THF, reflux, 1 h (70%); (f) **10** (1 equiv.), CuI (0.05 equiv.), $(CH_3)_2NC_2H_4NH_2$ (0.1 equiv.), NaI (2 equiv.) in dioxane, 110 °C, 24 h (98%); (g) **11** (2 equiv.), **12** (1 equiv.), $[Pd_2(dba)_3]$ (0.03 equiv.), $P(tBut)_3$ (0.06 equiv.), NEt_3 (4 equiv.) in toluene, 90 °C, 12 h (52%).



Scheme 3. Synthetic procedures for model chromophores (**1**–**4**) and compound **15**. *Reagents and conditions*: (a) For the synthesis of compound **1**: **9** (1 equiv.), **14** (3.3 equiv.), $[Pd(OAc)_2]$ (0.06 equiv.), $P(o\text{-tolyl})_3$ (0.36 equiv.) in NEt_3/MeCN, 110 °C, 48 h (50%); For the synthesis of compound **2**: **9** (1 equiv.), **10** (3.3 equiv.), $[Pd(OAc)_2]$ (0.06 equiv.), $P(o\text{-tolyl})_3$ (0.36 equiv.) in NEt_3/MeCN, 110 °C, 48 h (40%); (b) For the synthesis of compound **3**: **5** (1 equiv.), **13** (3.3 equiv.), Bu_4NF (4.5 equiv.), $[PdCl_2(PhCN)_2]$ (0.15 equiv.) in toluene, 110 °C, 48 h (70%); For the synthesis of compound **15**: **7** (1 equiv.), **13** (2 equiv.), Bu_4NF (2 equiv.), $[PdCl_2(PhCN)_2]$ (0.1 equiv.) in toluene, 70 °C, 2 h (50%); (c) **9** (1 equiv.), **15** (3.3 equiv.), $[Pd(OAc)_2]$ (0.06 equiv.), $P(o\text{-tolyl})_3$ (0.36 equiv.) in NEt_3/MeCN, 110 °C, 48 h (25%).

11→**13**→**3**) that combined stepwise Heck and cross-coupling reactions, was adopted;[17] this model dye structure was obtained in an overall yield of 35%. The synthesis of model compound **4** started from the preparation of the key intermediate (i.e., compound **15**) through the same two-step catalytic protocol (i.e., **11**→**13**→**15**) followed by a threefold Heck reaction to construct the final dendritic scaffold. All the final model fluorophores were highly soluble in common organic solvents, such as hexane, toluene, dichloromethane and tetrahydrofuran (THF). The detailed syntheses, including the preparation of the key intermediates and the final catalytic coupling reactions toward the targeted model compounds, are described in the Exp. Section.

II. Optical Properties

One-Photon Absorption (1PA) and Fluorescence Spectra Measurement

Linear absorption and fluorescence spectra of the studied compounds in THF solutions (with concentrations of 1×10^{-5} M) are shown in Figure 1. The 1PA spectra were recorded with a Shimadzu 3501 PC spectrophotometer and the 1PA-induced fluorescence spectra were measured with a Jobin–Yvon FluoroMax-3 spectrometer. All these compounds were found to show strong 1PA within the spectral range of 400–425 nm with increasing absorption intensity (i.e., $\varepsilon \approx 0.82\times10^5$, 1.26×10^5, 2.04×10^5, and 2.78×10^5 cm^{-1} M^{-1} for **1**, **2**, **3**, and **4**, respectively). Moreover, the shape and spectral position of the absorption bands of compounds **2**–**4** were almost identical, which may be useful for the design of molecules that can enhance molecular nonlinear absorption without shifting the major absorption band. This feature could be important for applications for which large multi-photon absorbing strength in specific spectral regions are required. These compound solutions also emit intense blue-greenish fluorescence under the irradiation of a common UV-lamp, which is in agreement with the measured emission spectra (see the inset of Figure 2).

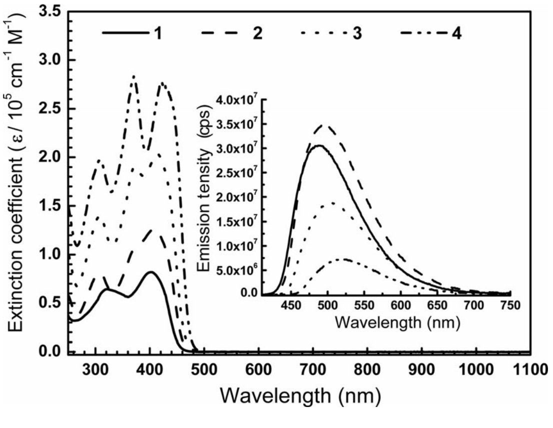


Figure 1. Linear absorption and fluorescence spectra (see the inset) of compounds **1**–**4** in the solution phase (concentration was 1×10^{-5} M in all cases; solvent: THF). The excitation wavelength was fixed at 400 nm for the fluorescence spectra measurements.

Two-Photon-Excited Fluorescence (2PEF) Emission Properties

The studied model chromophores manifest strong two-photon-excited up-conversion emission, which can be easily observed by the naked eye even under the illumination of a ca. 790 nm unfocused femtosecond laser beam. Figure 2 (a) illustrates the normalized 2PA-induced fluorescence spectra of these model chromophores. The sample solutions were freshly prepared at concentrations of 1×10^{-4} M in THF for this measurement, and the excitation source utilized for this two-photon induced fluorescence study was from a mode-locked Ti:Sapphire laser (Tsunami-pumped with a Millennia 10W, Spectra-Physics), which generates ca. 80 fs pulses with a repetition rate of 80 MHz and a beam diameter of 2 mm. The intensity level of the excitation beam was carefully controlled to avoid saturation of the absorption and photodegradation. To minimize the effect of re-absorption due to the relatively high concentration of the sample solution used in this measurement, we focused the excitation beam as close as possible to the wall of the quartz cell (5 × 5 mm cuvette) so that only the emission from the surface of the sample solution was collected. It can be seen in Figure 2 (a) that, for each model chromophore, the shape and spectral position of the measured 2PA-induced emission is basically identical to the corresponding 1PA-induced fluorescence band shown in Figure 1. This result indicates 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 process.

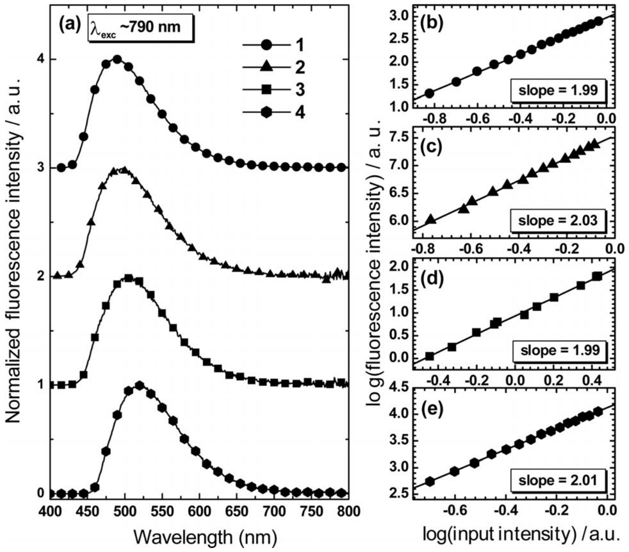


Figure 2. (a) Normalized two-photon excited up-conversion spectra of fluorophores **1**–**4** in THF at 1×10^{-4} M; (b–e) logarithmic plots of power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity of the model compounds in THF.

The power-squared dependence of the 2PA-induced fluorescence intensity on the excitation intensity of the studied fluorophores was also examined. Figure 2 (b–e) show the log–log plots of the measured data and the results (slopes ca. 2) confirm that a 2PA process is the major cause of the observed up-converted fluorescence emissions in all cases.

Table 1. Photophysical properties of the model chromophores in THF.[a]

	1PA-Related properties					2PA-Related properties			
	λ_{max}^{abs} [nm][b]	$\log \varepsilon_{max}$	λ_{max}^{em} [nm][c]	Φ_F[d]	τ_{2PA-FL} [ns][e]	λ_2^{max}/GM[f]	τ_{2PA-FL} [ns][g]	N_π^{eff}[h]	$\delta_2^{max}/N_\pi^{eff}$
1	402	4.91	489	0.52	1.58	ca. 725	1.58	34.6	ca. 21
2	408	5.10	497	0.76	1.32	ca. 1620	1.32	37.6	ca. 43
3	419	5.30	506	0.48	1.39	ca. 3500	1.39	59.2	ca. 61
4	423	5.44	519	0.36	1.60	ca. 9240	1.60	87.2	ca. 106

[a] Concentration was 1×10^{-5} M and 1×10^{-4} M 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 (experimental error ca. ±15%); 1 GM = 1×10^{-50} cm^4 s/photon. [g] 2PA-induced fluorescence lifetime. [h] Effective π-electron number.

The temporal behavior and lifetime of the 1PA- and 2PA-induced fluorescence of the same sample solutions were also probed by using the time-correlated single photon counting (TCSPC) technique with a highly sensitive photomultiplier equipped with an accumulating real-time processor as the detection system (PMA-182 and TimeHarp 200, PicoQuant). The same Ti: sapphire laser system (see above) was employed for this experiment. The measured fluorescence decay curves of the studied compound solutions are depicted in Figure 3 on a 10 ns full scale for one- and two-photon excitation (in the femtosecond regime). Theoretical fitting of each decay curve by single-exponential dependence revealed that, for each chromophore solution, identical 1PA-/2PA-induced fluorescence lifetimes were observed and that this phenomenon was independent of the excitation process. The measured 1PA/2PA-induced fluorescence lifetime values for each model compound solution are listed in Table 1.

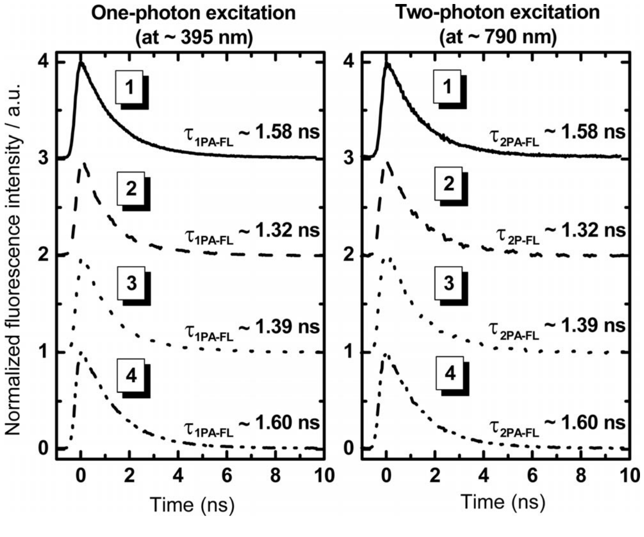


Figure 3. Normalized fluorescence decay curves of the studied model compound solutions excited by one-photon absorption (at 395 nm) and two-photon absorption (at 790 nm) in THF.

Degenerate Two-Photon Absorption Spectra Measurement

Changes in the 2PA behaviors of the studied dye molecules as a function of wavelength was explored in the spectral region 700–900 nm by using a degenerate two-photon-excited fluorescence (2PEF) technique based on a set-up very similar to that reported by Xu and Webb;[18] we used Fluorescein (ca. 80 μM in pH 11 NaOH solution) as the standard for this experiment.[18] Figure 4 shows the measured degenerate two-photon absorption spectra of these model compounds in THF (at concentrations of 1×10^{-4} M) and the combined photophysical data are summarized in Table 1. It is notable that all these model chromophores exhibit detectable 2PA within the investigated spectral range and possess an overall ascending capability of 2PA from compound **1** to compound **4**.

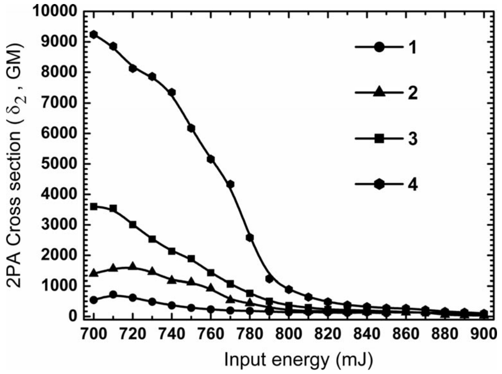


Figure 4. Measured degenerate two-photon absorption spectra of model chromophores **1**–**4** generated by the 2PEF method in THF solution at 1×10^{-4} M (error ca. ±15%).

III. Discussion of Results

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

(1) These chromophores exhibit very similar dispersion behaviors for the 2PA activities within the detection range, that is, the 2PA cross-section values for each compound approach higher values at short excitation wavelength ranges and drops down monotonically in the long excitation wavelength direction. The observed rising two-photon absorptivities in the short wavelength region implies that the most accessible two-photon states are higher in energy than those of the lowest one-photon allowed states of these compounds. Similar trends have been observed and reported previously for other chromophore systems.[4a–4b,5c,5e,6a,7e] Furthermore, the widely dispersed two-photon activities in near-IR spectral regime suggests that these model chromo-

phores could be potential candidates for broadband optical power limiters.

(2) It is observed that consecutive expansion of the molecular π-structures has led to ascending overall 2PA (from model chromophores **1**–**4**) as shown in Figure 3. We tentatively collect and discuss some potential structural parameters that may relate to the molecular 2PA as follows:

(a) Using compound **1** as the reference point, the incorporation of peripheral electron-donating groups seems to play an essential role in the promotion of two-photon activities. It is clear that the molecular 2PA rises for model compound **2** after the attachment of three additional diphenylamino groups to the terminal sites of model compound **1**.

(b) The structural motif of two identical electron-donating arms at the geminal positions of each olefinic unit to form a six-branched dendritic scaffold (as in compound **3**) provides an effective way to expand the π-domain of the molecule, which also leads to a doubling of the molecular two-photon absorptivity [i.e., $\delta_2^{\max}(\mathbf{3})/\delta_2^{\max}(\mathbf{2}) \approx 2.2$]. Further expansion of the π-framework from six-branched structure (compound **3**) to a twelve-branched dendritic skeleton (compound **4**) led to further enhanced two-photon activities [i.e., $\delta_2^{\max}(\mathbf{4})/\delta_2^{\max}(\mathbf{3}) \approx 2.6$]. Additionally, it is worth noting that when the size of the π-conjugation was expanded from compound **1** to compound **4**, both the effective π-electron number and multi-polar character of the dye molecule also increased simultaneously in this model chromophore set. The changes in these two properties are believed lie behind the enhanced molecular 2PA.[5d–5f,5i,6,7d,8a,8b,8f,9c,9e–9h,11,12,14]

(c) From the molecular structures of the model chromophores **2** and **3**, it can be reasonably assumed that the π-framework of each compound may permit unsymmetrical charge-transfer/redistribution from the molecular termini to the central part of each molecule under the excitation of light, because both π-systems combine different electron-donating units (at the peripheral and central positions) with uneven electron-pushing strengths within one molecule. Although at present there is no clear understanding of how this imbalance of electron-donating strength combines with the structural arrangement in the cases of compounds **2** and **3** to influence the molecular two-photon activities, our preliminary results show that such structural combinations may help to promote the molecular 2PA and, interestingly, both of these two model compounds were also found to possess medium to strong three-photon absorption (3PA) in the near-IR region.[12]

(d) As the size of π-system is enlarged further to construct the dendritic model compound **4**, no deterioration in the molecular 2PA was observed, which may suggest that the combination of the above-mentioned structural parameters in a dendrimeric framework with early generation could be a useful approach toward enhanced molecular 2PA in our dye system.

(e) Another interesting issue that requires further study with respect to this multi-branched/dendritic model compound set is the importance of structural coplanarity on the molecular 2PA behavior. Efforts towards delineating the structure–nonlinear absorption properties by using quantum-mechanical analysis of this chromophore system are needed, and such work is underway currently.

(3) Based on the fact that the measured fluorescence emission spectra (shown in Figures 1 and 2) and the fluorescence lifetimes (shown in Figure 3) for each model compound are nearly the same for one- and two-photon excitations, it may be concluded 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 yields observed from these model compounds also indicate that these dyes could be efficient frequency up-converters for biophotonic applications, such as two-photon-excited fluorescence microscopy.

Although the dynamic tuning range of the pumping source limits the spectral probing range at this stage, the studied model compounds may possess either higher magnitudes of 2PA or additional 2PA bands in the visible region (i.e., shorter than 700 nm). These are desirable features for some specific applications utilizing two-photon technologies within the visible regime, and further investigations on these aspects are needed.

3. Effective Optical Power-Limiting Behavior in the Nanosecond Regime

Ideal optical-limiters would be expected to show an intensity-dependent transmission feature so that it can act as a transparent medium when the incident intensity of light stays low and, once the input intensity is increased, the medium starts to regulate the transmitted output intensity so that it is maintained 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 in nonlinear ultra-fast filtering/reshaping of optical fiber signals. Compared to other mechanisms for optical power limiting, such as reverse saturable absorption and nonlinear scattering,[20] the 2PA-based mechanism provides several promising features, including: (1) high initial transmission (ca. 100 %) for weak optical signals; (2) rapid response to a change in the intensity or the peak power of the incident optical signal; and (3) retention of the optical quality of the input beam after passing through the nonlinear absorption medium.

Recently, it has been reported that the intensity-dependent 2PA-induced excited-state absorption (2PA-induced ESA) plays an essential role in the observed large 2PA in various organic systems under the irradiation of nanosecond laser pulses.[21] For this reason, the term "effective 2PA" is used to describe the apparent 2PA parameter measured in the nanosecond time domain.[9b,21b] From the viewpoint of applications, any medium that exhibits strong apparent nonlinear absorption covering a wide spectral range could be utilized as optical power-attenuators against laser beams with long pulse widths.[22]

It should be noted that the excited-state lifetimes of the model chromophore in the present work are in the nanosecond range, which implies that significant excited-state population may be retained and consequently undergo excited-state absorption during excitation by longer laser pulses. We have used nanosecond laser pulses to investigate the *effective* power-limiting performance of these model chromophores. In these experiments, the nonlinear absorbing medium was a 1-cm path-length solution of the studied model fluorophore in THF with a concentration of 0.02 M. For the probing laser light source, a tunable nanosecond laser system (an integrated Q-switched Nd:YAG laser and OPO: NT 342/3 from Ekspla) was employed to provide approximately 6 ns laser pulses with controlled average pulse energies of approximately 1 mJ and repetition rates of 10 Hz. The laser beam was only slightly focused onto the center of the sample solution to obtain a nearly uniform laser beam radius within the whole cell path length. The transmitted laser beam from the sample cell was detected by an optical power/energy meter with a large detection area of approximately 25 mm in diameter. Figure 5 (a) shows the measured average transmittance in the spectral range 700–1000 nm. Although the entire distribution of ESA as a function of wavelength (i.e., ESA spectra) has not yet been determined, it should be noted that, under our experimental conditions, these model compounds can attenuate nanosecond laser pulses within a broad spectral region, and especially around 700 nm.

The attenuation of the incident laser pulses based on these sample solutions can also be presented as shown in Figure 5 (b). In this experiment, the local intensity within this sample solution was adjusted by a set of neutral-density filters. Laser pulses with wavelengths at which each model compound possesses the greatest power-restriction were selected. It can be readily seen that, compared to other members of this model compound set, chromophore **4** exhibits the most rapid deviation from the linear attenuation behavior [designated by the diagonal line in Figure 5 (b)] and thus represents the best power-suppressing material. This initial finding demonstrates the potential for using this model fluorophore in broadband power-suppression applications that operate in the nanosecond time-scale.

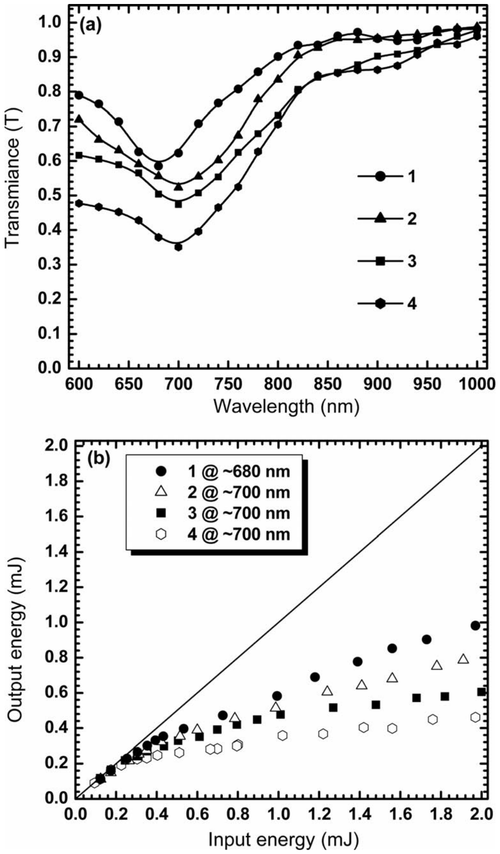


Figure 5. (a) Measured transmission spectra of the modal compounds as 0.02 M solutions in THF (1 cm path-length). The energy of the input laser pulses was controlled at ca. 1 mJ for every data point; (b) Measured optical-power-attenuation curves at wavelengths with best power-limiting performance based on the same sample solutions.

4. Conclusion

We have synthesized a novel, multi-polar model compound set composed of four fluorene-based chromophores with systematic structural modifications and characterized their nonlinear optical properties in the femtosecond and nanosecond regimes. The experimental results show that compounds with larger π-frameworks manifest widely dispersed and strong two-photon absorption in the near-infrared region. It was also found that these model chromophores possess strong nonlinear attenuation when exposed to irradiation of laser pulses working at the nanosecond regime, indicating that these model compounds may have strong two-photon-assisted excited-state absorption within the studied spectral region. Effective optical-power-limiting behaviors of the dendritic fluorophores also demonstrated that such dye molecules have the potential to be used as broadband, rapid-response optical limiters, especially when used with laser lights with longer pulses.

Experimental Section

General: All commercially available reagents were purchased from Aldrich Chemical Co. and were used as received, unless stated otherwise. ^1H NMR and ^{13}C NMR spectra were recorded with either 200 or 300 MHz spectrometers and were referenced to TMS or residual $CHCl_3$. High-resolution mass spectroscopy (HRMS) were conducted with a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS were obtained with a Voyager DE to PRO mass spectrometer (Applied Biosystem, Houston, USA).

Photophysical Methods: All the linear optical properties of the model compounds were measured with the spectrometers described above and the detailed experimental conditions as well as the optical set-up for nonlinear optical property investigations are described in the Supporting Information.

Synthesis: In Schemes 2 and 3, compounds **8**–**10**, **12**, and **14** were synthesized by following the established literature processes,[9a,23–27] with overall yields of approximately 35, 90, 40, 80, and 65% for compounds **8**, **9**, **10**, **12**, and **14**, respectively. The experimental details for the syntheses of other key intermediates **5**–**7**, **11**, **13**, and **15** and the model compounds **1**–**4** are presented here.

Tris(4-iodophenyl)amine (5): A mixture of triphenylamine (0.29 g, 0.0012 mol), KI (0.6 g, 0.0036 mol), and KIO_3 (0.77 g, 0.0036 mol) was stirred at 85 °C in HOAc for 15 h. After cooling to r.t., aq. $NaHSO_3$ (35mL) was added into the reaction mixture and stirred for 20 min. The solution was extracted with CH_2Cl_2 (3 × 50 mL), then the organic layer was collected and dried with $MgSO_4$. After removal of the solvent, the crude product was purified by recrystallization (CH_2Cl_2/MeOH) to give the purified product as a white solid (0.58 g, 78%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.55–7.52 (d, J = 8.7 Hz, 6 H), 6.82–6.79 (d, J = 8.7 Hz, 6 H) ppm. HRMS-FAB: calcd. for $C_{18}H_{12}NI_3$ $[M]^+$ 622.8104; found 622.8117.

***N*-(4-Bromophenyl)-*N*-phenylbenzenamine (6):** To a solution of triphenylamine (1.6 g, 0.0065 mol) in CH_2Cl_2 (50 mL) was added $TBABr_3$ (3.13 g, 0.0065 mol) and MeOH (20 mL), and the resulting solution was stirred at r.t. for 24 h. Another portion of MeOH (50 mL) was added and the reaction mixture was stirred for 25 min. The precipitate was filtered and collected, and the final purified product was obtained through recrystallization from MeOH as white solid (ca. 2.29 g, 78%). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.36–7.27 (m, 3 H), 7.26–7.21 (m, 3 H), 7.09–7.03 (m, 6 H), 6.98–6.91 (m, 2 H) ppm. HRMS-FAB: calcd. for $C_{18}H_{14}BrN$ $[M]^+$ 323.031; found 323.0295.

***N*-(4-Bromophenyl)-4-iodo-*N*-(4-iodophenyl)benzenamine (7):** A mixture of compound **6** (1.62 g, 0.005 mol), KI (1.12 g, 0.0068 mol), and KIO_3 (0.72 g, 0.00335 mol) was stirred at 85 °C in HOAc for 12 h. After cooling to r.t., aq. $NaHSO_3$ (50 mL) was added and the reaction mixture was stirred for 20 min. The solution was extracted with CH_2Cl_2 (3 × 50 mL), and the organic layer was dried with $MgSO_4$. After removal of the solvent, the crude product was purified through recrystallization (CH_2Cl_2/MeOH) to afford the target product as a white solid (2.29 g, 80%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.51 (d, J = 8.7 Hz, 4 H), 7.36–7.33 (d, J = 8.7 Hz, 2 H), 6.94–6.91 (d, J = 8.7 Hz, 2 H), 6.81–6.78 (d, J = 8.7 Hz, 4 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 146.57, 145.86, 138.39, 132.50, 125.86, 125.70, 116.26, 86.51 ppm. HRMS-FAB: calcd. for $C_{18}H_{12}BrI_2N$ $[M]^+$ 574.8242; found 572.8245.

9,9-Dihexyl-7-iodo-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (11): A mixture of **10** (3.0 g; 5.17 mmol), *N*,*N*-dimethylenediamine (0.068 g; 0.77 mmol), CuI (0.049 g; 0.258 mmol), and NaI (1.7 g; 0.0137 mmol) in dioxane (10 mL) was heated to 110 °C under argon for 24 h. After cooling, aq. NH_4OH (30 mL) was added to the reaction mixture, which was stirred for 20 min, poured into water (50 mL), and extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phase was dried, concentrated, and the residue was purified by flash chromatography on silica gel (*n*-hexane) to provide of the target product (3.15 g, 98%) as a colorless oil. ^1H NMR (200 MHz, $CDCl_3$): δ = 7.54–7.50 (m, 1 H), 7.50–7.44 (m, 1 H), 7.45–7.40 (m, 2 H), 7.30–7.22 (m, 4 H), 7.14–7.09 (m, 2 H), 7.14–7.09 (m, 2 H), 7.05–6.98 (m, 4 H), 1.87–1.79 (m, 4 H), 1.17–0.99 (m, 12 H), 0.81 (t, J = 6.9 Hz, 6 H), 0.64 (m, 4 H) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ = 152.95, 151.43, 147.79, 147.65, 140.49, 135.77, 135.01, 131.72, 129.12, 123.86, 123.62, 123.33, 122.58, 120.74, 120.49, 119.37, 118.86, 91.56, 55.17, 40.08, 31.54, 29.53, 23.65, 22.52, 14.04 ppm. HRMS-FAB: calcd. for $C_{37}H_{42}IN$ $[M]^+$ 627.6405; found 627.6423.

7-{1-[2-(Diphenylamino)-9,9-dihexyl-9*H*-fluoren-7-yl]-2-[dimethyl(pyridin-2-yl)silyl]vinyl}-9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-2-amine (13): To a solution of **12** (3.43 g, 0.021 mol) and **11** (26.36 g, 0.042 mol) in toluene (80 mL), was added $P(tBu)_3$ (0.255 g, 0.00126 mmol), $[Pd(dba)_3]$ (0.28 g, 0.3 mmol), and NEt_3 (4.1 g; 0.042 mol) and the resulting solution was stirred at 90 °C for 12 h. After cooling to r.t., the reaction mixture was filtered and the solution phase was collected and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1:20) to give the purified product as a transparent oil (12.79 g, 52%). ^1H NMR (300 MHz, $CDCl_3$): δ = 8.83–8.82 (d, J = 4.5 Hz, 1 H), 7.58–7.45 (m, 8 H), 7.35–6.95 (m, 27 H), 6.66 (s, 1 H), 1.84 (br., 8 H), 1.17–1.08 (br., 24 H), 0.86–0.72 (m, 20 H), 0.22 (s, 6 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 168.38, 159.85, 152.51, 152.12, 150.30, 150.12, 147.84, 147.05, 141.22, 141, 140.73, 140.31, 136.09, 135.80, 133.81, 129.03, 128.65, 126.72, 124, 123.60, 122.35, 121.41, 120.34, 119.35, 119.23, 118.53, 118.34, 55, 40.01, 31.42, 29.49, 23.66, 22.46, 14.01, –1.72 ppm. HRMS-FAB: calcd. for $C_{83}H_{95}N_3Si$ $[M]^+$ 1161.7295; found 1161.7278.

***N*,*N*-Bis{4-[2,2-bis(9,9-dihexyl-*N*,*N*-diphenyl-9*H*-fluoren-7-yl)-vinyl]phenyl}-4-bromobenzenamine (15):** A mixture of **7** (2.13 g, 0.0037 mol), **13** (8.6 g, 0.0074 mol), Bu_4NF (1.0 M in THF, 7.4 mL, 0.0074 mol), and $[PdCl_2(PhCN)_2]$ (0.142 g, 0.00037 mol) was stirred at 70 °C for 2 h. After cooling to r.t., CH_2Cl_2 (50 mL) was added and the reaction mixture was stirred at r.t. for 15 min. The resulting solution was filtered and the filtrate was concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1:40) to give the purified product as a yellow solid (4.39 g, 50%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.59–7.44 (m, 22 H), 7.28–7.20 (m, 16 H), 7.12–7.09 (m, 24 H), 7.00–6.96 (m, 10 H), 6.85–6.83 (m, 2 H), 6.74–6.71 (m, 4 H), 1.79 (br., 16 H), 1.15–0.98 (br., 48 H), 0.87–0.67 (m, 40 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.51, 152.25, 150.96, 150.63, 147.96, 147.14, 147.00, 145.29, 142.26, 141.77, 140.31, 138.97, 136.17, 136.00, 132.54, 132.11, 130.46, 129.12, 126.52, 125.99, 125.63, 124.55, 123.74, 123.31, 122.42, 121.51, 120.35, 119.64, 119.39, 118.64, 55.11, 40.08, 31.50, 29.59, 23.78, 22.53, 14.08 ppm. HRMS-FAB: calcd. for $C_{170}H_{182}BrN_5$ $[M + H]^+$ 2373.3579; found 2373.3565.

Model Compound 1: A mixture of compound **9** (0.47 g, 0.00146 mol), **14** (2 g, 0.00482 mol), $[Pd(OAc)_2]$ (0.0196 g, 0.000088 mol), and $P(o\text{-tolyl})_3$ (0.1067 g, 0.0003504 mol) in a mixed solvent system composed of NEt_3/MeCN (5 mL/10mL) was stirred in a sealed pressure tube at 110 °C for 48 h. After cooling to r.t., ethyl acetate (40 mL) was added and the reaction mixture was stirred for 20 min. The solution was extracted with water (50 mL) then the organic layer was collected and dried with $MgSO_4$. The resulting solution was filtered and the organic solution was concentrated by evaporation. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1:20) to give the final purified product as a yellow solid (1.0 g, 52%). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.53 (m, 12 H), 7.30–7.22 (m, 24 H), 7.15–7.02 (m, 30 H), 1.85 (br., 12 H), 1.08 (br., 36 H), 0.81–0.73 (m, 30 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 152.39, 151.17, 150.64, 147.99, 147.04, 136.10, 135.77, 129.13, 123.77, 122.44, 121.59, 120.34, 119.39, 118.65, 54.96, 54.79, 40.29, 31.59, 31.51, 29.63, 23.54, 22.54, 14.08 ppm. HRMS-FAB: calcd. for $C_{99}H_{117}N$ $[M]^+$ 1320.9240; found 1320.9264.

Model Compound 2: A mixture of compound **9** (0.44 g, 0.00137 mol), **10** (2.85 g, 0.00453 mol), $[Pd(OAc)_2]$ (0.0185 g, 0.000082 mol), and P(*o*-tolyl)$_3$ (0.1 g, 0.0003288 mol) in a mixed solvent system composed of NEt_3/MeCN (5 mL/10mL) was stirred in a sealed pressure tube at 110 °C for 48 h. After cooling to r.t., CH_2Cl_2 (50 mL) was added and the reaction mixture was stirred for 15 min. The resulting solution was filtered and the filtrate was concentrated by evaporation. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1:100) to give the final purified product as a yellow solid (1.0 g, 40%). ^1H NMR (200 MHz, $CDCl_3$): δ = 7.70–7.62 (m, 6 H), 7.57–7.46 (m, 6 H), 7.38–7.26 (m, 12 H), 7.24–7.04 (m, 9 H), 7.00–6.9 (m, 6 H), 1.95 (br., 12 H), 1.05 (br., 36 H), 0.76–0.73 (m, 30 H) ppm. ^{13}C NMR (50 MHz, $CDCl_3$): δ = 151.25, 151.11, 150.96, 140.83, 136.46, 132.43, 127.37, 126.95, 126.74, 125.36, 124.30, 123.43, 122.85, 120.61, 119.62, 119.23, 54.96, 40.47, 29.72, 23.74, 22.57, 12.03 ppm. ^{13}C NMR (200 MHz, $CDCl_3$): δ = 153.16, 150.87, 146.61, 139.84, 139.56, 136.92, 132.30, 132.25, 129.91, 127.82, 126.10, 125.53, 124.21, 55.31, 40.35, 31.51, 29.63, 23.69, 22.56, 13.99 ppm. HRMS-FAB: calcd. for $C_{135}H_{144}N_4$ $[M]^+$ 1821.1391; found 1821.1343.

Model Compound 3: A mixture of compound **5** (0.53 g, 0.00086 mol), **13** (3.3 g, 0.00284 mol), Bu_4NF (1.0 M in THF, 3.9 mL, 0.00387 mol), and $[PdCl_2(PhCN)_2]$ (0.05 g, 0.000129 mol) was stirred at 110 °C for 48 h. After cooling to r.t., CH_2Cl_2 (50 mL) was added and the reaction mixture was stirred for 20 min. The resulting solution was filtered and the organic solution was collected and concentrated by rotary evaporation. The crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1:40) to give the final purified product as a yellow solid (1.0 g, 35%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.54–7.49 (m, 12 H), 7.28–7.19 (m, 36 H), 7.12–7.08 (m, 32 H), 7.02–6.97 (m, 28 H), 6.72–6.69 (m, 3 H), 1.78 (br., 24 H), 1.15–0.98 (br., 72 H), 0.82–0.71 (br., 60 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.56, 152.32, 150.97, 150.65, 148.04, 147.16, 141.95, 140.24, 139.08, 136.25, 136.13, 132.26, 130.37, 129.15, 126.56, 124.62, 123.78, 123.04, 122.45, 121.56, 120.34, 119.61, 118.64, 54.98, 40.13, 31.83, 29.62, 23.82, 22.51, 14.09 ppm. MALDI-TOF: calcd. for $C_{246}H_{267}N_7$ $[M + H]^+$ 3322.80; found 3322.89.

Model Compound 4: A mixture of compound **9** (0.18 g, 0.00056 mol), **15** (4.35 g, 0.00185 mol), $[Pd(OAc)_2]$ (0.0076 g, 0.000034 mol), and P(*o*-tolyl)$_3$ (0.04 g, 0.000136 mol) in a mixed solvent system composed of NEt_3/MeCN (5 mL/10mL) was stirred in a sealed pressure tube at 110 °C for 48 h. After cooling to r.t., CH_2Cl_2 (70 mL) was added and the reaction mixture was stirred for 25 min. The resulting solution was filtered and the filtrate was concentrated by evaporation. After removing the solvent, the crude product was purified by column chromatography on silica gel (ethyl acetate/hexane, 1:10) to give the final purified product as a yellow solid (1.0 g, 25%). ^1H NMR (300 MHz, $CDCl_3$): δ = 7.57–7.48 (m, 24 H), 7.34–7.19 (m, 84 H), 7.15–6.99 (m, 72 H), 6.97–6.91 (m, 60 H), 6.75 (m, 12 H), 1.759 (br., 48 H), 1.13–0.983 (m, 144 H), 0.818–0.671 (m, 120 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 152.26, 152.03, 150.71, 150.36, 147.72, 146.84, 146.72, 146.03, 145.27, 141.78, 141.61, 139.98, 138.79, 135.97, 135.79, 132.01, 130.14, 128.85, 126.82, 126.26, 125.94, 124.35, 123.93, 123.48, 123.43, 123.07, 122.14, 121.26, 120.06, 119.37, 119.16, 119.37, 54.86, 40.00, 31.31, 29.33, 23.52, 22.26, 13.81 ppm. MALDI-TOF: calcd. for $C_{534}H_{564}N_{16}$ $[M + H]^+$ 7207.30; found 7207.51.

Supporting Information (see also the footnote on the first page of this article): Photophysical methods for the measurement of linear and nonlinear optical properties.

Acknowledgments

We thank the National Science Council (NSC), Taiwan for financial support.

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Received: August 18, 2010
Published Online: December 27, 2010