Accepted Manuscript

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PII: S0143-7208(14)00171-5

DOI: 10.1016/j.dyepig.2014.04.035

Reference: DYPI 4363

To appear in: Dyes and Pigments

Received Date: 26 February 2014

Revised Date: 17 April 2014

Accepted Date: 25 April 2014

Please cite this article as: Lin T-C, Liu Y-Y, Li M-H, Lee Y-H, Synthesis and Two-photon Property Studies of Symmetrically Substituted Bisarylacetylene Structures Using Functionalized Quinoxaliniod Units as the Aryl Substituents, *Dyes and Pigments* (2014), doi: 10.1016/j.dyepig.2014.04.035.

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Graphical Abstract for paper



Synthesis and Two-photon Property Studies of Symmetrically Substituted Bisarylacetylene Structures Using Functionalized Quinoxaliniod Units as the Aryl Substituents

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Abstract

A series of symmetrically substituted multi-polar chromophores (1-3) based on the skeleton of bisarylacetylene using functionalized quinoxaline, indenoquinoxaline, and pyridopyrazine moieties as the aryl substituents has been synthesized and characterized for their two-photon absorption properties using femtosecond laser pulses as the probing tool. Under our experimental conditions, these model fluorophores are found to manifest strong and wide dispersed two-photon absorption in the near infrared (NIR) region. It is demonstrated that molecular structures with multi-branched π -frameworks incorporating functionalized quinoxalinoid units would possess large molecular nonlinear absorptivities within the studied spectral range. Optical-power-limiting behavior in the femtosecond time domain of the indenoquinoxaline-derived dye molecule (2) from this model compound set was also investigated and the result indicates that such structural motif could be a useful approach for the molecular design towards strong two-photon absorbing material system for quick-responsive and broadband optical-control related applications.

Keywords: Two-photon absorption, Sonogashira reaction, quinoxaline, indenoquinoxaline, pyridopyrazine, optical power-limiting.

1. Introduction

Similar to the development path of many other science subjects, the theoretical prediction of two-photon absorption (2PA) made by Maria Göppert-Mayer in 1931 is far ahead of its experimental evidence.[1] After the advent of lasers in 1960, scientists started to have appropriate light sources to practically observe and study this nonlinear optical phenomenon.[2, 3] For the past two decades, the availability of high peak power lasers has triggered the momentum to explore the two-photon technologies and many potential applications in the emerging field of photonics and biophotonics based on 2PA have been demonstrated including optical power-limiting, frequency up-converted lasing, 3-D data storage, 3-D microfabrication, nondestructive bio-imaging and tracking, and two-photon photodynamic therapy.[4-9] In the course to develop two-photon technologies, the exploration of new materials with strong 2PA plays an equally important counterpart as the advancement of laser systems. Through rational molecular design, it is possible to construct organic chromophores that exhibit several orders of intensified 2PA with other desired molecular characteristics simultaneously incorporated, which greatly compensates for the relatively poor performance of commercialized dyes for the aforementioned applications. So far, it has been realized that the combination of several structural parameters such as intramolecular charge-transfer efficiency, effective size of π -conjugation domain, and molecular dimensionality of a molecule is closely related to the molecular 2PA.[10-32] In other words, the arrangement of the selected building units within a molecule is a hinge for the molecular design toward highly active 2PA-chromophores. In searching new strategies toward highly efficient 2PA materials, we have been interested in the exploration of effective building units and structural arrangement that may enhance the molecular 2PA. In this paper, we report our recent studies of degenerate two-photon absorption, up-converted emission and optical power-limiting properties of a series of newly synthesized quinoxalinoid chromophores by using ultafast IR laser pulses working in the femtosecond regime as the major probing tools.

2. Results and discussion

2.1 Molecular structures and syntheses

The chemical structures of the studied model compounds in this work are illustrated in Figure 1. These three structural congeners are constructed based on the scaffold of a bisarylacetylene by using electron-donor-functionalized quinoxalinoid units as the aryl substituents. We have selected pyrazine-containing ring complexes as the heterocyclic parts in this model compound system since the involvement of electron-withdrawing hetero-atoms is expected to alter the electronic nature of the resulting chromophores compared to the all-carbon analogues. From the standpoint of molecular structure, each functionalzed quinoxalinoind moiety of the studied model compound can be assumed to

be dipolar because of its push-pull nature and skeletal geometry. Therefore, the connection between the presented structural arrangement and molecular 2PA would be an interesting subject to study. Furthermore, we have attached alkyl chains at C9 positions of all the fluorenyl units in order to improve the molecular 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 Scheme 1, which mainly include the preparation of various precursors with appropriate functional groups for either conventional or modified Pd-catalyzed Sonogashira reactions to accomplish final chromophores. In brief, compound 1 was synthesized in one-step fashion by using a more reactive aryl iodide (5) and bis(methylsilyl)acetylene as the synthons while compound 2 was accomplished developed through another recently one-step coupling method that involves decarboxylative processes.[33] Differently, the typical multi-step Sonogashira reaction was finally found to be the most effective protocol to construct compound 3 instead of using either the aforementioned one-step cross-coupling conditions after several attempts. All the new dyes were obtained in acceptable yields and the details for the syntheses of these model compounds are presented in the Experimental section.

2.2 Optical properties characterization

2.2.1 One-photon absorption (1PA) and fluorescence-related measurements

Linear absorption and fluorescence spectra of the studied compounds in toluene solutions (with concentration of 1×10^{-6} M) are shown in Fig. 2 and the related photophysical data are collected in Table 1. The 1PA spectra were recorded through a Shimadzu 3501 PC spectrophotometer and the 1PA-induced fluorescence spectra were measured 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 428 nm for 1 (ε ~6.11×10⁴ cm⁻¹M⁻¹), 445 nm for 2 (ε ~1.50×10⁵ cm⁻¹M⁻¹), and 466 nm for 3 (ε ~6.83×10⁴cm⁻¹M⁻¹), respectively. These compound solutions also emit intense fluorescence under the irradiation of a common UV–lamp with blue-greenish color for 1 and 2 and green-yellowish color for 3, which is in agreement with the measured emission spectra as illustrated in Fig. 2(b).

The photostability of the studied dye compounds in solution phase was tentatively evaluated by continuously monitoring the decay of the fluorescence intensity during the course of UV-irradiation. We have utilized a set of UV-lamps as the excitation light source to provide ~350 nm radiation with total output of 120 W for this experiment. The detailed experimental arrangement is described in the Supporting Information. A commercialized laser dye, Coumarin 307, was selected as the reference and the results are illustrated in Fig 3. It can be seen that during the first 1-hour consecutive exposure of UV-light, both compounds 1 and 2 retain >97% of their original emission intensity while compound 3 exhibits an observable decline (~15%) of the original fluorescence intensity. Prolonged irradiation further deteriorates the emissive property of these model chromophore solutions and it is found that compound 3 shows a larger fluorescence intensity decrease (~55%) whilst those of 1 and 2 are kept within ~12% after 3 hours of UV-light exposure. On the other hand, it is also found that compounds 1 and 2 possess better photostability compared to Coumarin 307. Overall, model compounds 1 and 2 manifest fairly good resistance of photo-damage which is comparable to that of Coumarin 307 and is superior to that of compound 3 under our experimental condition. We suspect that the weak photo-resistance of compound 3 may be originated from the pyridine unit but the clarification of this issue is currently beyond the scope of this work.

2.2.2 Two-photon-excited fluorescence (2PEF) emission properties

The studied model chromophores manifest strong two-photon-excited upconversion emission which can be easily sighted even under low power of excitation by an unfocused femtosecond laser beam at ~ 800 nm. Fig. 4(a) illustrates the 2PA-induced fluorescence spectra of the model chromophores **1-3**. The sample solutions were freshly prepared at concentration of 1×10^{-4} M in toluene for this measurement and the excitation source utilized for this two-photon induced fluorescence study is from a mode-locked Ti:Sapphire laser (Chameleon Ultra II, Coherent) which delivers ~140 fs pulses with the repetition rate of 80 MHz and the beam diameter of 2 mm. The intensity level of the excitation beam was carefully controlled to avoid the saturation of absorption and photodegradation. Besides, the relative position of the excitation beam was adjusted to be as close as possible to the wall of the quartz cell (10mm×10mm cuvette) so that only the emission from the front-surface of the sample was recorded in order to minimize the re-absorption or inner-filter effect. It is noted from Fig. 4(a) that for each model chromophore the shape and spectral position of the measured 2PA-induced emission is basically identical to its corresponding 1PA-induced fluorescence band in Fig. 2(b), which implies that in our dye system the radiative relaxation processes occurred within the studied samples are from the same final excited states regardless of the excitation method.

The power-squared dependence of the 2PA-induced fluorescence intensity on the excitation intensity of the studied fluorophores was also examined. Figs. 4(b)-(d) are logarithmic plots of the measured data and the results (*i.e.* the fitting slope \approx 2) validate that 2PA process is responsible for the observed up-converted fluorescence emissions in all cases.

The temporal behavior and lifetime of 2PA-induced fluorescence of the same sample solutions were also probed through time-correlated single photon counting (TCSPC) technique and the same femtosecond laser system (*vide supra*) was employed as the

excitation light source for this experiment. The measured fluorescence decay curves of the studied compound solutions are depicted in Fig. 4(e). Theoretical fitting of each decay curve by single-exponential dependence has revealed that these model chromophores possess fluorescence lifetime ranging from 1.2 ns to 3.0 ns and these data are collected in Table 1.

2.2.3 Degenerate two-photon absorption spectra measurement

The 2PA spectra of the studied model chromophores was delineated in the spectral region of 700-1040 nm through degenerate two-photon-excited fluorescence (2PEF) technique using the aforementioned femtosecond laser system as the excitation light source.[34, 35] Fig. 5 shows the measured degenerate 2PA spectra of these three model compounds in toluene (at the 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 detectable 2PA within the entire dynamic tuning range of the employed Ti:sapphire oscillator. To be more specific, compound 1 exhibits a broad 2PA band with two local maxima located around 730 nm and 830 nm while compound 2 possesses very similar dispersion of 2PA but with prominently elevated magnitude of 2PA particularly around 730 nm in comparison to 1, which indicates that the incorporation of the indenoquinoxaline moiety into this dye system has a positive contribution on the molecular 2PA especially at shorter wavelength region. On the other hand, compound **3** also manifests widely dispersed 2PA and the local

maximum is located around 930 nm.

2.3 Discussion of results

From the measured photophysical properties of the studied model chromophores in the present work, some features can be noted:

(1) Based on the observed linear absorption behaviour of the studied model chromophores and use compound 1 as a reference, it is noted that compound 2 exhibits conspicuously promoted linear absorption with nearly identical spectral dispersion to those of compound 1 whereas compound 3 possesses relatively smaller enhancement of the linear absorption and a red-shifted lowest-energy band. These features imply that using a fluorene unit as a part of heterocyclic ring complex in this molecular system (as in the case of compound 2) provides an effective access to enhance the linear absorptivity without shifting of the absorption band while the utilization of a pyridine moiety for the construction of the ring complex (as in the case of compound 3) is useful for expanding the spectral range of linear absorption by pressing the lowest-energy band bathochromically.

(2) We originally expected that the acetylene unit utilized in this model chromophore system as the linkage could be photo-sensitive and consequently weaken the photo-resistance of these compounds but interestingly, the experimental results suggest that this functional group is fairly inert toward UV-radiation at ~350 nm. Among these three model compounds, **1** and **2** exhibit good photostability which is comparable to that of Coumarin 307 and this indicates that the structural units employed in these two compounds are suitable for the development of fluorescence probes that are required for long-term light-exposure.

(3) Compared to compound **1**, the distinctly hyperchromic 2PA of **2** and saliently red-shifted 2PA of **3** indicate that fluorene can be an effective unit to enhance molecular 2PA with roughly immobilized spectral position of 2PA band whereas the pyridine scaffold can work as an efficient red-shifter of 2PA without dramatic decrease of 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) It has been theoretically revealed that the molecular 2PA is correlated with the square of effective π -electron number of certain studied structures.[36] Although this approximation rule is not verified yet to be suitable for every class of molecules, we still can tentatively analyze our experimental results based on this scaling. It is found that the ratio between the maximum 2PA cross-section values of the studied model compounds $(\delta_2^{\max}(\mathbf{1}) : \delta_2^{\max}(\mathbf{2}) : \delta_2^{\max}(\mathbf{3}) = -\mathbf{1} : -\mathbf{1} \cdot \mathbf{5} : -\mathbf{1})$ is close to the ratio between the square of their calculated effective π -electron numbers (i.e. $N_{eff}^{\pi^2}$). This result implies that the π -electrons on these model dye compounds should adopt the same mode to contribute to the nonlinear

response. Since the major structural difference between these model compounds is the heterocyclic part of molecule, the compound with a ring complex that provides a larger number of π -electrons can be expected to exhibit higher maximum molecular 2PA. On the other hand, these chromophores are also found to possess a comparable magnitude of molecular 2PA among the reported highly two-photon active dyes with similar numbers of π -electrons.[36]

(5) Combining the medium-high fluorescence quantum yields and 2PA cross-section values, chromophores **1-3** exhibit comparable maximum two-photon action cross-section $(\Phi_F \delta_2^{max})$ [4-6, 10] and this property suggests that such structural motif could be a useful approach to build efficient frequency upconverter for imaging-related applications such as two-photon-excited fluorescence microscopy.

3. Optical power-limiting properties in femtosecond regime

An ideal optical-limiter is expected to possess an intensity-dependent transmission feature so that the output intensity is always below a certain maximum value, which makes optical-limiters useful for protecting human eyes and sensors against hazardous sources of light. This power-control phenomenon is also important for the optical dynamic range compression in optical-signal processing and nonlinear ultra-fast filtering/reshaping of optical fiber signals. To evaluate the power-limiting performance of the studied

fluorophores, we have selected compound 2 as a representative and utilized femtosecond laser pulses from a regenerative amplifier to probe its optical power-limiting property at ~ 800 nm. The sample solution for this study was prepared in toluene with a concentration of 0.06 M. Figure 6(a) shows the measured data (in open diamond) for nonlinear transmissivity, T_i , as a function of the laser input power. The influences from the windows of the cuvette and from the solvent were eliminated by subtracting the transmission data from a pure toluene-filled cuvette sample. One can see from figure 6(a) that the intensity-dependent nonlinear transmission of the sample dropped from ~0.91 to ~0.37 as the input intensity increased from ~24 mW to ~800 mW. In Figure 6(a), the solid-line represents the theoretical curve predicted by the basic 2PA theory[37, 38] with a best fitting parameter of $\beta = 1.6$ cm/GW, where β is the 2PA coefficient in the femtosecond regime of the sample solution. It will be more conceptually clear if this optical power-limiting behavior is presented in a different way based on the same set of experimental data as shown in Figure 6(b). In this figure the measured transmitted intensity data are presented by open circles, and the solid-line is the theoretical curve, with the same fitting parameter of $\beta = 1.6$ cm/GW. The diagonal dot-line shows the behavior for a medium without nonlinear absorption for comparison and one can see that the measured input-output curve starts to deviate from the linear transmission (diagonal dot-line) at low pumping power, and rapidly approach larger values of this deviation as the excitation power levels up. Moreover, the 2PA cross-section value of this model compound was calculated to be ~1100 GM from the performed optical-power-limiting experiment, which is very close to the result obtained from 2PEF method within experimental uncertainty and this validates that 2PA should be the major cause for the observed upconverted emission and optical-power restriction in this chromophore system.

4. Conclusion

A series of bisarylacetylene-based chromophores with functionalized quinoxalinoid units as the aryl substituents were synthesized and characterized for their two-photon-related properties in the femtosecond regime by using both two-photon-excited fluorescence and nonlinear transmission techniques as the probing tools. The experimental results have shown that these model molecules manifest strong and widely dispersed 2PA in the near-IR region. Tentative analysis of the structure-property relationship based on the structure of compound 1 has revealed that the involvement of the fluorene unit in the quinoxalinoid ring complex will enhance both linear absorptivity and molecular 2PA while the incorporation of **a** pyridine molety will result in bathochromic shift of 2PA band without deleterious effect on the magnitude of 2PA. Combined with the intrinsic medium-high quantum yields of fluorescence, these model fluorophores are found to possess comparable two-photon action cross-section values with chromophores of similar size. It is also observed that compounds 1 and 2 possess superior photostability against UV-radiation at a wavelength of \sim 350 nm. Furthermore, it is demonstrated that model compound 2 could be a potential optical power-limiter working in the near-IR region to confront ultra-short laser pulses.

4. Experimental section

4.1 General

All commercially available reagents for the preparation of the intermediates and targeted chromophores were obtained from Acros Organics or Alfa Aesar and were used as received, unless stated otherwise. THF was distilled from sodium benzophenone ketyl. ¹H-NMR and ¹³C-NMR spectra were recorded either at 200 or 300 MHz spectrometers and referenced to TMS or residual CHCl₃. The representative numbering of carbon and hydrogen atoms on each intermediate and model chromohopres for the NMR signal assignment are systematized and illustrated in the Supporting Information. High-resolution mass spectroscopy (HRMS) was conducted by using a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS spectrum was obtained on a Voyager DE-PRO mass spectrometer (Applied Biosystem, Houston, USA).

4.2 Synthesis

In Schemes 1, compounds 4, 6 and 7 were obtained by following established procedures.[39] For the synthesis of other key intermediates (compounds 5, 8 and 9) and the

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targeted model compounds (1-3), a series of functionalization steps starting from compounds 4, 6, and 7 have been conducted and are presented as the following:

4.2.1

7,7'-(6-Iodoquinoxaline-2,3-diyl)bis(9,9-dihexyl-*N*,*N*-diphenyl-9H-fluoren-2-amine) (5)

To a mixture of compound 4 (2 g; 1.05 mmol) in dry dioxane (8 mL) was added CuI (0.045 g; 0.25 mmol), NaI (0.54g; 3.64 mmol), and N,N-dimethylethylenediamine (0.54g; 0.74 mmol). The resulting mixture was stirred at 110°C under Ar atmosphere for 24 hours. After cooling to the room temperature, $NH_4OH_{(aq)}$ (~50mL) was added to the reaction mixture. The above solution was then extracted with ethyl acetate (30 mL×3) and the organic layer was collected and dried over MgSO4(S). After removing the solvent, the crude product was purified through column chromatography on silica gel using THF-hexane (1:10) as the eluent to give the final purified product as gray power with vield of 91.2% (1.89 g). ¹H-NMR (300 MHz, CDCl₃) δ : 8.64~8.63 (d, J = 1.8 Hz, 1H, H_F), $8.00 \sim 7.99$ (dd, $J_1 = 8.7$ Hz, $J_2 = 2.1$ Hz, 1H, H_B), $7.92 \sim 7.89$ (d, J = 8.7 Hz, 1H, H_C), 7.57~7.50 (m, 8H, H₉, H₁₂, H₁₃, H₁₅), 7.29~7.24 (m, 8H, H₂), 7.14~7.08 (m, 10H, H₃, H₆), 7.03~7.00 (m, 6H, H₁, H₈), 1.75~1.60 (m, 8H, H_f), 1.14~1.03 (m, 24H, H_c, H_d, H_e), 0.83~0.77(m, 12H, H_a), 0.64-0.62 (s, 8H, H_b) ¹³C-NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ: 154.44 (C_G), 154.34 (C_H), 152.55 (C₅), 150.52 $(C_{16}), 147.82 (C_4), 147.51(C_{11}), 141.80 (C_7), 141.53 (C_D), 141.04 (C_E), 140.15 (C_{10}), 140.15$ 136.90 (C_F), 136.82 (C_C), 135.43 (C₁₅) 135.27 (C₁₅), 130.26 (C₉), 129.49 (C₁₂), 129.08 (C₃), 124.26 (C₁₃), 123.83 (C₂), 123.29 (C₁₄), 122.53 (C₁), 120.84 (C₆), 118.94 (C₈, C_B), 95.09 (C_A), 55.01 (C_g), 40.03 (C_f), 31.46 (C_e), 29.50 (C_d), 23.77 (C_c), 22.53 (C_b), 14.01 (C_a) HRMS-FAB (m/z): M^+ calcd for C₈₂H₈₇IN₄ 1254.5975, found, 1254.5979.

4.2.2

7,7'-(7-((Trimethylsilyl)ethynyl)pyrido[2,3-b]pyrazine-2,3-diyl)bis(9,9-dihexyl-*N*,*N*-di phenyl-9H-fluoren-2-amine) (8)

To a mixture of compound 7 (1 g; 0.826 mmol) in dry THF (10 mL) was added PdCl₂(PPh₃)₂ (0.03 g; 0.049 mmol), CuI (0.02g; 0.083 mmol), trimethylsilyl acetylene (0.12 g; 1.24 mmole), and *i*-Pr₂NH (2.5 mL). The resulting solution was stirred at 90°C under Ar atmosphere for 12 hours. After cooling to the room temperature, H_2O (~100mL) was added to the reaction mixture. The above solution was then extracted with ethyl acetate (30 mL \times 3) and the organic layer was collected and dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using THF-hexane (1:15) as the eluent to give the final purified product as orange powder with yield of 91.1% (0.92 g). ¹H-NMR (300 MHz, CDCl₃) δ: 9.18~9.17 (d, J = 2.1 Hz, 1H, H_B), 8.61~8.60 (d, J = 2.1 Hz, 1H, H_E), 7.84 (s, 1H, H₁₅), 7.74~7.71 (d, J = 7.8 Hz, 1H, H_{12}), 7.65 (s, 1H, $H_{12'}$), 7.62~7.47 (m, 5H, H_{13} , $H_{13'}$, H_9 , $H_{9'}$, $H_{15'}$), 7.31~7.26 (m, 8H, H₂), 7.17~7.12 (m, 10H, H₃, H₆), 7.07~7.03 (m, 6H, H₁, H₈), 1.88~1.73 $(m, 8H, H_f, H_{f'}), 1.09 \sim 1.07 (m, 24H, H_c, H_{c'}, H_d, H_{d'}, H_e, H_{e'}), 0.85 \sim 0.82 (m, 12H, H_a, H_{a'}),$ $0.68 \sim 0.67$ (m, 8H, H_b, H_b[']), 0.38 (s, 9H, hydrogens of the TMS group); ¹³C-NMR (75) MHz, CDCl₃, tentative assignments based on calculated values) δ : 156.89 (C_G), 155.90 (C_F) , 155.69 (C_B) , 152.71 (C_{16}) , 152.58 $(C_{16'})$, 150.67 (C_5) , 150.51 $(C_{5'})$, 148.72 (C_C) , 147.79 (C₄), 142.51 (C₁₁), 142.29 (C₁₁), 139.93 (C₇), 136.45 (C₁₀), 136.05 (C₁₀), 135.16 (C_D) , 135.10 (C_{14}) , 134.93 $(C_{14'})$, 129.70 (C_{15}) , 129.12 (C_2) , 128.89 (C_E) , 124.43 (C_{12}) , 124.29 (C_{12'}), 123.89 (C₃), 123.25 (C₉), 122.60 (C₁), 121.16 (C_A), 120.98 (C₆), 120.91 $(C_{6'})$, 119.11 (C_{13}) , 118.83 (C_8) , 118.54 $(C_{13'})$, 100.97 (C_H) , 100.78 (C_I) , 55.20 (C_g) , 55.02 (Cg'), 40.17 (Cf), 40.03 (Cf'), 31.56 (Ce), 31.50 (Ce'), 29.52 (Cd, Cd'), 23.82 (Cc), 23.75 (C_c[']), 22.57 (C_b, C_b[']), 14.04 (C_a, C_a[']), -0.27 (carbons of the TMS group). MALDI-TOF (m/z): M⁺ calcd for C₈₆H₉₅N₅Si 1226.7935, found, 1226.8293.

4.2.3

7,7'-(7-Ethynylpyrido[2,3-b]pyrazine-2,3-diyl)bis(9,9-dihexyl-*N*,*N*-diphenyl-9H-fluor en-2-amine) (9)

To a mixture of compound 8 (0.9 g; 0.798 mmol) in THF/MeOH (10 mL/4 mL) was added KOH (0.08 g; 1.48 mmol), and the resulting solution was stirred at room temperature under Ar atmosphere for 4 hours. After cooling to the room temperature, H_2O (~100mL) was added to the reaction mixture. The above solution was then extracted with ethyl acetate ($30mL \times 3$) and the organic layer was collected and dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using THF-hexane (1:10) as the eluent to give the final purified product as orange powder with yield of 94.8% (0.79 g). ¹H-NMR (300 MHz, CDCl₃) δ: 9.16~9.15 (d, J = 2.1 Hz, 1H, H_B), 8.61~8.60 (d, J = 2.1 Hz, 1H, H_E), 7.81 (s, 1H, H₁₅), 7.71~7.69 (d, J= 7.8 Hz, 1H, H₁₂), 7.62~7.59 (d, J = 7.8 Hz, 1H, H₁₂), 7.56~7.43 (m, 5H, H₁₃, H₁₃', H₉, $H_{9'}, H_{15'}$, 7.27~7.22 (m, 8H, H₂), 7.13~7.07 (m, 10H, H₃, H₆), 7.04~6.99 (m, 6H, H₁, H₈), 3.42 (s, 1H, hydrogen on terminal alkyne; $-C \equiv H$), 1.84~1.68 (m, 8H, H_f, H_f), 1.12~1.02 (m, 24H, H_c, H_c', H_d, H_d', H_e, H_e'), 0.81~0.78(t, J = 7.2 Hz, 12H, H_a, H_a'), 0.64-0.62 (m, 8H, H_b , $H_{b'}$); ¹³C-NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ: 157.23 (C₆), 156.07 (C_F), 155.53 (C_B), 152.72 (C₁₆), 152.58 (C₁₆), 150.72 (C₅), 150.53 $(C_{5'})$, 148.95 (C_C) , 147.78 (C_4) , 147.71 $(C_{4'})$, 142.60 (C_{11}) , 142.37 $(C_{11'})$, 140.58 (C_7) , 136.33 (C_{10}), 135.93 (C_{10}), 135.09 (C_{14}), 134.80 (C_D), 129.71 (C_{15}), 129.13(C_2), $128.85(C_E)$, $124.42(C_{12})$, $124.26(C_{12'})$, $123.90(C_3)$, $123.25(C_9)$, $122.61(C_1)$, 121.00 (C_6) , 120.93 $(C_{6'})$, 120.07 (C_A) , 119.18 (C_{13}) , 118.82 (C_8) , 118.54 $(C_{13'})$, 82.57 (C_H) , 79.94 (C_{I}) , 55.21 (C_{g}) , 55.02 $(C_{g'})$, 40.15 (C_{f}) , 40.01 $(C_{f'})$, 31.55 (C_{e}) , 31.49 $(C_{e'})$, 29.52 $(C_{d}, C_{d'})$, 23.82 (C_c), 23.73 (C_c), 22.57 (C_b, C_b), 14.04 (C_a, C_a). HRMS-FAB (m/z): M^+ calcd for C₈₃H₈₇N₅ 1153.6961, found, 1153.6965

4.2.4 Compound 1

To a mixture of compound 5 (1.58 g; 1.256 mmol) and 1,2-bis(trimethylsilyl)ethyne (0.1 g; 0.59 mmol) in dry DMF (8 mL) was added CuCl (0.03 g; 0.299 mmol), and Pd(PPh₃)₄ (0.034 g; 0.0293 mmol). The resulting mixture was stirred at 110°C under Ar atmosphere for 8 hours. After cooling to the room temperature, H_2O (~100mL) was added to the reaction mixture. The above solution was then extracted with ethyl acetate (30 mL×3) and the organic layer was collected and dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using THF-hexane (1:20) as the eluent to give the final purified product as orange powder with yield of ~50.7% (0.69 g). ¹H-NMR (300 MHz, CDCl₃) δ : 8.48-8.47 (d , J = 3.0 Hz,2H, H_F), 8.23~8.20 (d, J = 9.0 Hz, 2H, H_C), 7.97~7.93 (dd, $J_1 = 3.0$ Hz, $J_2 = 9.0$ Hz, 2H, H_B), 7.62~7.54 (m, 16H, H₉, H₁₂, H₁₃, H₁₅), 7.30~7.25 (m, 16H, H₂), 7.15~7.11 (m, 20H, H₃, H₆), 7.06~7.01(m, 12H, H₁, H₈), 1.78~1.76 (m, 16H, H_f), 1.14~1.06 (m, 48H, H_c, H_d, H_e), 0.84~0.80(m, 24H, H_a), 0.66(s, 16H, H_b); ¹³C-NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ: 154.93 (C_G), 154.49 (C_H), 152.76 (C₅), 150.68 $(C_{16}), 148.00 (C_4), 147.68(C_{11}), 141.99 (C_7), 141.10 (C_D), 140.97 (C_E), 140.97 (C_{10}),$ 137.17 (C_F), 137.01 (C_C), 135.85 (C₁₅), 135.50 (C₁₅), 132.56 (C₉), 131.36 (C₁₂), 130.39 (C_A), 129.60 (C₃), 124.51 (C₁₃), 124.01 (C₂), 123.47 (C₁₄), 122.71 (C₁), 121.04 (C₆), 119.12 (C_BC₈), 91.61 (acetylene carbons), 55.20 (C_g), 40.24 (C_f), 31.66 (C_e), 30.43 (C_d), 23.97 (C_c), 22.73 (C_b), 14.22 (C_a); MALDI-TOF(m/z): M⁺ calcd for C₁₆₆H₁₇₄N₈ 2281.2732, found, 2281.2795.

4.2.5 Compound 2

To a mixture of compound **6** (1 g; 0.683 mmol) and acetylenedicarboxylic acid (0.04 g; 0.341 mmol) in DMSO (8 mL) was added 1,4-bis(diphenylphosphino) butane (2.9 mg; 0.068 mmol), and $PdCl_2(PPh_3)_2$ (2.4 mg; 0.034 mmol). The resulting mixture was stirred at

110°C under Ar atmosphere for 8 hours. After cooling to the room temperature, H₂O (~100mL) was added to the reaction mixture. The above solution was then extracted with ethyl acetate (30 mL \times 3) and the organic layer was collected and dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using THF-hexane (1:15) as the eluent to give the final purified product as orange powder with yield of ~67% (0.88 g). ¹H-NMR (300 MHz, CDCl₃) δ : 8.46 (s, 2H, H_H), 8.12(s, 2H, H_K), 7.95~7.90 (m, 2H, H_D), 7.67~7.51 (m, 16H, H₉, H₁₂, H₁₃, H₁₅, H_E, H_B), 7.27~7.24 (m, 16H, H₂), 7.13~7.09 (m, 20H, H₃, H₆), 7.03~6.98 (m, 12H, H₁, H₈), 2.19~2.16 (m, 8H, H_f), 1.76~1.74 (m, 16H, H_f), 1.11~1.05 $(m, 72H, H_c, H_{c'}, H_d, H_{d'}, H_e, H_{e'}), 0.82 \sim 0.68(m, 60H, H_a, H_{a'}, H_b, H_{b'}); {}^{13}C-NMR(75 MHz,$ CDCl₃, tentative assignments based on calculated values) δ: 153.49 (C₅, C_N), 153.05 (C_M), 152.59 (C₁₆), 151.48 (C_L), 150.59 (C_A), 150.51(C_F), 147.90 (C₄), 147.41 (C₁₁), 143.21 (C_G), 141.54 (C_J), 141.50 (C_I), 139.99 (C₇), 137.52 (C_K), 137.43(C_H), 135.53 (C₁₀), 131.12 (C_B),129.13 (C₂), 128.93(C₁₂), 126.25(C₁₅), 125.49 (C_E), 124.37 (C₁₄), 123.84 (C₃), 123.37 $(C_{13}), 122.52 (C_1), 122.32 (C_D), 121.13 (C_8), 120.83 (C_6), 119.09 (C_9), 118.69 (C_C), 91.24$ (acetylene carbons), $55.29(C_g)$, $55.06(C_{g'})$, $40.12(C_f)$, $31.55(C_e)$, $29.77(C_d)$, $29.59(C_{d'})$, 23.84 (C_c , $C_{c'}$), 22.62 (C_b , $C_{b'}$), 14.09 (C_a), 13.97($C_{a'}$); MALDI-TOF(m/z): [M+1]⁺ calcd for C₂₀₄H₂₃₀N₈ 2795.1472, found, 2795.1548

4.2.6 Compound 3

To a mixture of compound **7** (0.57 g; 0.476 mmol) and compound **9** (0.55 g; 0.476 mmol) in dry THF (10 mL) was added $PdCl_2(PPh_3)_2$ (0.02 g; 0.029 mmol), CuI (9.1 mg; 0.048 mmol), and *i*-Pr₂NH (2.5 mL). The resulting solution was stirred at 90°C under Ar atmosphere for 12 hours. After cooling to the room temperature, H₂O (~100mL) was added

to the reaction mixture. The above solution was then extracted with ethyl acetate (30 mL×3) and the organic layer was collected and dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using THF-hexane (1:5) as the eluent to give the final purified product as orange powder with yield of 72.2% (0.78 g). ¹H-NMR (300 MHz, CDCl₃) δ : 9.33~9.32 (d, J = 2.1 Hz, 2H, H_B), 8.75~8.75 (d, J = 2.1 Hz, 2H, H_E), 7.84 (s, 2H, H₁₅), 7.74~7.72 (dd, $J_1 = 7.8$ Hz, $J_2 = 1.2$ Hz, 2H, H₁₂), 7.63~7.46 (m, 12H, H₁₃, H₁₃', H₉, H₉', H₁₂', H₁₅'), 7.27~7.23 (m, 16H, H₂), 7.14~7.11 (m, 20H, H₃, H₆), 7.04~6.98 (m, 12H, H₁, H₈), 1.83~1.72 (m, 16H, H_f, H_f), 1.11~1.01 (m, 48H, H_c, H_c', H_d, H_d', H_e, H_e'), 0.80~0.77(m, 24H, H_a, H_a'), 0.64 (s, 16H, H_b, $H_{b'}$); ¹³C-NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ : 157.46 (C_G), 156.36 (C_F), 155.31 (C_B), 152.87 (C₁₆), 152.73 (C₁₆), 150.86 (C₅), 150.71 $(C_{5'})$, 149.23 (C_C) , 147.90 (C_4) , 142.82 (C_{11}) , 142.56 $(C_{11'})$, 140.15 (C_7) , 136.46 (C_{10}) , 136.06 (C_{10'}), 135.21 (C_D), 135.16 (C₁₄), 135.07 (C_{14'}), 129.87 (C₁₅), 129.24 (C₂), 125.56 (C_E) , 124.58 (C_{12}) , 124.41 $(C_{12'})$, 124.04 (C_3) , 123.36 (C_9) , 122.75 (C_1) , 121.07 (C_6) , 120.31 (C_A), 119.29 (C₁₃), 118.92 (C₈), 118.71 (C_{13'}), 90.99 (acetylene carbons), 55.34 (C_g), 55.17 (C_g[']), 40.28 (C_f), 40.16 (C_f[']), 31.67 (C_e), 31.61 (C_e[']), 29.64 (C_d, C_d[']), 23.95 (C_c), 23.88 ($C_{c'}$), 22.68 (C_{b} , $C_{b'}$), 14.15 (C_{a} , $C_{a'}$); MALDI-TOF(m/z): [M+1]⁺ calcd for C₁₆₅H₁₇₂N₁₀ 2284.2556, found, 2284.2629.

Acknowledgements

We acknowledge the financial support from National Science Council (NSC), Taiwan.

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Captions for Figures, Schemes, and Tables

Figure 1. Molecular structures of the studied model chromophores.

Scheme 1. Synthetic procedures for the precursors and final model chromophores.

Figure 2. Linear absorption and fluorescence spectra of the studied model compounds.

Figure 3. Tentative evaluation of photostability: Fluorescence intensity change of the studied chromophores and Coumarin 307 under consecutive irradiation of UV-light at ~350 nm.

Figure 4. (a) Normalized two-photon excited emission spectra of fluorophores **1-3** in toluene at 1×10^{-5} M; (b), (c), and (d) are the logarithmic plots of power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity of these compounds in toluene; (f) Normalized two-photon excited fluorescence decay curves of these chromophores in toluene.

Figure 5. Measured degenerate two-photon absorption spectra of model chromophores **1-3** by 2PEF method in toluene solution at 1×10^{-4} M (with experimental error ~15%).

Figure 6. (a) Measured nonlinear transmission of a 1-cm path-length compound **2** solution in toluene (0.04 M) as a function of the input intensity of the ~800 nm laser beam; (b) Measured output energy as a function of the input energy based on the same sample solution. The solid curves are the theoretical curve with a best fitting parameter of $\beta = 1.6$ cm/GW. (β is the 2PA coefficient)

 Table 1. Photophysical properties of the studied model chromophores 1-3 in toluene.

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	$\lambda_{ m max}^{ m abs}/ m nm^b$	$\log \epsilon^{c}$	$\lambda_{\max}^{\mathrm{em}}/\mathrm{nm}^d$	$\Phi_{\mathrm{F}}^{\; e}$	$ au^{ ext{2PA-FL}}/ ext{ns}^{f}$	$\delta^{\max}_2/{ m GM}^g$	$N_{\scriptscriptstyle e\!f\!f}^{\pi\ h}$	$\Phi_{\rm F} \delta_2^{\rm max}/{ m GM}^i$
1	305 363 428	4.79	507	0.56	1.8	~2000 (at 730 nm)	37.95	~1120
2	310 361 445	5.18	487	0.63	1.2	~3100 (at 750 nm)	46.48	~1950
3	299 367 466	4.83	569	0.70	3.2	~1900 (at 930 nm)	37.95	~1330

Table 1. Photophysical properties of the studied model chromophores 1-3 in toluene.^a

^{*a*}Concentration was 1×10^{-6} M and 1×10^{-4} M for 1PA-related and 2PA-related measurements, respectively; ^{*b*}One-photon absorption maximum; ^{*c*} Molar absorption coefficient of the lowest-energy absorption peak; ^{*d*}1PA-induced fluorescence emission maximum; ^{*e*}Fluorescence quantum efficiency; ^{*f*} 2PA-induced fluorescence lifetime; ^{*g*}Maximum 2PA cross-section value (with experimental error ~±15%); 1GM = 1 × 10⁻⁵⁰ cm⁴ s/photon-molecule; ^{*h*}Effective π -electron numbers (ref. 36); ^{*h*}Two-photon action cross-section value.

Critical Contraction of the second se



Figure 1. Molecular structures of the studied model chromophores.



Figure 2. Linear absorption and fluorescence spectra of the studied model compounds.



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Scheme 1. Synthetic procedures for the precursors and final model chromophores.

Highlights

[1] A series of symmetrically substituted multi-polar chromophores based on the skeleton of bisarylacetylene has been synthesized.

[2] These model fluorophores are found to manifest strong and wide dispersed two-photon absorption in the near infrared (NIR) region.

[3] Optical-power-limiting behavior a selected representative dye molecule is demonstrated

Synthesis and Two-photon Property Studies of Symmetrically Substituted Bisarylacetylene Structures Using Functionalized Quinoxaliniod Units as The Aryl Substituents

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♦ Numbering of C and H of the precursors and final chromophores



♦ Photophysical Methods ACCEPTED MANUSCRIPT

Linear absorption and emission spectra measurements

Linear absorption spectra were recorded on a Shimadzu 3150 PC spectrophotometer with freshly prepared sample solutions in various solvents. The same sample solutions were also used for the measurement of one-photon-induced fluorescence emission spectra by utilizing a Jobin-Yvon FluoroMax-4 spectrometer from Jobin-Yvon. Combining this fluorospectrometer and its integrated sphere accessories (Labsphere from Jobin-Yvon; diameter = 100 mm), the absolute fluorescence quantum yield of each model compound in solution phase at room temperature can be measured;^[1] Coumarin 153 ($\Phi_F = 0.38 \pm 5\%$ at $\lambda_{exc} = 423$ nm) was used as the standard for the calibration of the integrated sphere and the instrument.^[2, 3]

Photostability evaluation

The photostability of the studied model chromophores in solution phase was tentatively evaluated by consecutively monitoring the change of the fluorescence intensity during the course of UV-irradiation. We have utilized a home-made apparatus similar to a Rayonet-type photochemical reactor for the UV-light exposure in this experiment as illustrated in Figure S1. This multi-lamp apparatus is equipped with 15 lamps which are arranged in a circular fashion (40 cm diameter) and the room inside of the UV-lamp circle is to accommodate the vial in which the sample solution to be irradiated is contained. The sample is positioned on a rotating table that ensures the uniform illumination. A fan is also fitted in this apparatus in order to keep the temperature below 40°C during the experiment. Since all of our model chromophores exhibit medium-high absorptivity around 350 nm, we have selected phosphor-coated lamps as the excitation light source to provide ~350 nm UV-radiation and the total output power is 120 W. The sample solutions are freshly prepared in toluene at concentration of 1×10^{-5} M and the fluorescence spectra of the sample solutions after UV-light illumination are recorded by a Jobin-Yvon FluoroMax-4 spectrometer. A laser dye, Coumarin 307, is selected as a reference compound for comparison due to its excellent photostability.



Figure S1. The configuration of the home-made apparatus for photostability evaluation experiment in this work.

Two-photon-excited fluorescence (2PEF) measurements

Two-photon-excited fluorescence spectra of the studied model fluorophore in solution phase (concentration: 1×10^{-4} M) were measured according to the protocol established by Xu and Webb using Fluorescein (0.1N NaOH solution) as the standard.^[4] The experimental setup is illustrated in Figure S2. In brief, the excitation light source was a mode-locked Ti:Sapphire laser (Chameleon Ultra II, Coherent Inc.) which delivers ~80fs pulses with the repetition rate of 80MHz and the beam diameter of 2mm. The intensity level of the excitation beam was carefully controlled by a $\lambda/2$ wave plate in order to avoid the saturation of absorption and photodegradation. To minimize the effects of re-absorption, the excitation beam was focused as close as possible to the wall of the quartz cell (10mm×10mm cuvette) and the 2PEF emissions were collected and induced by a fiber bundle into a CCD imaging spectrometer (USB-4000, Ocean Optics) for the spectra recording. This optical system was also utilized for the characterization of the quadratic dependence of the 2PA-induced up-conversion emission intensity on the pumping intensity for every data point.



Figure S2. Optical setup for 2PEF-related experiments.

The 1PA- and 2PA-induced fluorescence lifetime of the same sample solutions were measured based on TCSPC technique by highly sensitive photomultiplier equipped with accumulating real-time processor as the detection system (PMA-182 and TimeHarp 200, PicoQuant). The optical setup for this experiment was very similar with the one shown in Figure S2, only differs in the detection system. The excitation light source for this measurement was the above-mentioned Ti: sapphire laser system to provide laser pulses at desired wavelength for the 2PA-induced fluorescence lifetime measurements and it can be used to pump a BBO crystal in order to generate frequency-doubled laser pulses for 1PA-induced fluorescence lifetime studies of the investigated samples.

Optical-power limiting property studyTED MANUSCRIPT

The optical-power limiting performance of the studied model compound (2) in solution phase (0.06M in toluene, light path-length = 1 cm) was probed at ~800nm using femtosecond laser pulses as the working tool. As shown in Figure S3, a regenerative amplifier system (CPA-2010, Clark-MXR) was employed as the excitation source to provide ~160 fs laser pulses with repetition rate of 1 KHz for this study. The laser beam was slightly focused onto the center of the sample solution in order to obtain a nearly uniform laser beam radius within the whole cell path-length. The local intensity within the sample solution was tuned by adjusting the incident laser power level with the aid of the combination of a half-wave plate and a polarizing beam splitter. In all cases, the incident and transmitted laser power were simultaneously acquired and recoded by a data acquisition card and a computer.



Figure S3. Experimental setup for the optical power-limiting behavior study.

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