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2PA fluorescence of the neat-film

## <u>Multi-photon Properties in Various Condensed Phases of Dendritic</u> <u>Chromophores Derived from Carbazole and Indenoquioxaline</u> <u>Units: Synthesis and Characterization</u>

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#### Abstract

We have used functionalized carbazoles and indenoquonoxalines as the main building units and enthynyl groups as the  $\pi$ -linkages to construct two novel dendritic fluorophores and studied their degenerate multi-photon absorption properties in both the solution phase and the neat-film state within femtosecond and nanosecond regions. In our experiments, these model compounds are found to manifest strong and widely dispersed two-photon absorption as well as effective power-limiting properties against ultra-short laser pulses in the near-IR region. In addition, both chromophores exhibit medium to strong three-photon-induced fluorescence, indicating such scaffold may serve as a reference structural motif for the development of three-photon materials.

**Keywords:** Two-photon absorption, three-photon absorption, Sonogashira reaction, carbazole, indenoqunoxaline.

### 1. Introduction

Conjugated molecules that exhibit strong two-photon absorption (2PA) property have drawn much attention in the past two decades owing to their potentiality for many

promising applications in photonics and biophotonics such as optical power-limiting, frequency up-converted lasing, optical data storage, nondestructive bio-imaging, and two-photon photodynamic therapy.[1-5] During the searching course of highly efficient 2PA materials, enormous efforts have being made in exploring the knowledge of 2PA molecular design and it is concluded that molecular 2PA can be affected by the combination of several structural parameters including efficiency of the intramolecular charge-transfer, effective size of the  $\pi$ -system and dimensionality of the molecule.[6-12] Among the studied molecular architectures, branched chromophores have been demonstrated to simultaneously possess strong multi-photon absorption and wide spectral window of linear transparency[13, 14] and such a feature is particularly favorable for the 2PA-based broadband optical-limiting applications. In addition, it has been posited that the 2PA cross section ( $\delta$ )-fluorescence quantum yield ( $\Phi_F$ ) product (*i.e.*  $\delta\Phi_F$ ) or the ratio of this product against photo-degradation quantum yield can be improved through rational optimization of branched structures, which are vitriol requirements for the 2PA-based imaging technologies.[1] Furthermore, branched scaffold provides an effective access for the material chemists to incorporate 2PA-promoting parameters with various other desired characteristics for specific purposes.

While much more attention was paid for the development of two-photon materials and technologies, comparatively fewer efforts were made in the systematic investigation of

organic materials that manifest strong three-photon absorption (3PA). Based on the multi-photon absorption theory, any medium that exhibits 2PA can be expected to possess detectable 3PA if appropriate experimental protocols are adopted. From the viewpoint of application, 3PA process is expected to provide more benefits for bio-imaging applications since near-infrared light with longer wavelength can be used and the light losses due to scattering as well as linear absorption within the living organism will be greatly reduced. On the other hand, a superior spatial confinement can be achieved because of the intrinsic cubic dependence of a 3PA process on the local optical intensity, which subsequently enhances the contrast and spatial resolution in the imaging-related applications. Besides, under the same level of nonlinear transmission this higher order nonlinear absorption process can offer promoted optical-limiting performance over broader spectral region. [15] Following our continuous efforts in exploring new strategies for the molecular design of highly efficient 2PA materials, we have focused our efforts on developing organic chromophores with branched or dendritic scaffolds using various heterocyclics as the building units and retrieving the structural parameters that may have either beneficial or adverse impacts on their 2PA properties. In this paper, we present the synthesis and 2PA-related properties in both solution and neat-film forms of two newly synthesized dendritic chromophores derived from carbazole and indenoquinoxaline moieties. In addition, the effective 3PA properties of these model chromophores were also investigated within the spectral range of 1100-1500 nm using our previously reported experimental condition in nanosecond regime, in order to explore the feasibility of such experimental protocol and the molecular design for the 3PA materials.

## 2. Results and discussion

#### 2.1 Molecular design and syntheses of the model chromophores

This model compound set contains two structural analogues as illustrated in Figure 1. We have utilized a carbazole unit as the central ramification core, which is bonded to either two or four peripheral lobes through ethynyl linkages to form model compound 1 and 2, respectively. For compound 1, the peripheral branches are connected at C3 and C6 whereas for compound 2, the four branches are attached at C1, C3, C6, and C8 of the central carbazole. Both diphenylaminocarbazole and indenoquinoxaline units are selected as the main building blocks to construct these novel outward branches. It is well-known that carbazole unit has been extensively utilized to construct various organic structures (i.e. small molecules, polymers, and copolymers) for electronic, optoelectronic and photonic applications including light-emitting diodes, [16] dye-sensitized solar cells, [17,18] photorefractive materials, [19] and fluorescent sensors. [20-22] In addition to these investigations, we have noticed that many carbazole-based small molecules were designed and synthesized for the study of their multi-photon absorption properties, [23-27] but in contrast, comparatively fewer carbazole-containing dendritic molecules[28, 29] were

made for such study. Therefore, we believe that it is worthy to deepen our knowledge about the nonlinear absorption behaviors of multi-branched or dendritic model structures built by carbazole units. Our original attempt for the molecular design is to combine various fused heterocyclic rings to form multi-branched polyarenes so that the final model structures can be expected to exhibit more polarizable characters compared to their all-carbon analogues and such feature is important for the enhancement of molecular multi-photon activities. The synthetic procedures for the key components and the designed model chromophores are depicted in Schemes 1 and 2. As shown in Scheme 1, the commercialized 9H-carbazole (3) was utilized as the prime starting material to prepare appropriately 3,6-difunctionalized and 1,3,6,8-tetrafunctionalized carbazoles (i.e. compounds 7 and 8) as the major synthons for the  $\pi$ -centers of these model chromophores through consecutive functional group transformation. On the other hand, since it is necessary to prepare the corresponding diketone (i.e. compound 15) and diamine (i.e. compound 16) for the synthesis of quinoxalinoid branch units, we have started from 4,4-dibromo-1,1-biphenyl (9) and performed nitration and triphenylphosphine-catalyzed ring closure reaction in sequence to accomplish the desired 2,7-dibromo-9*H*-carbazole (11) in the overall yield of 70%. Followed by the alkylation, amination, Pd-catalyzed decarboxylative coupling reaction, and oxidation, compound 15 can be obtained in an acceptable overall yield of 20% (from 11, four steps). Compound 15 was then coupled

with previously reported diamine (16)[11] to form the key quinoxalinoid precursor 17 in the yield of 86%. The same synthetic protocol used to transform the bromo functional groups of compound 5 to the ethynyl groups of compound 7 was also applied to compound 17 for the preparation of compound 19, another important quinoxalinoid precursor for the synthesis of targeted chromophores. Finally, the model compounds 1 and 2 were accomplished through a 2- and a 4-fold Pd-catalyzed Sonogashira coupling using the corresponding reactants and were obtained in the yields of 31% and 43%, respectively (See Scheme 2). Interestingly, the obtained higher yield of the final Sonogashira coupling for the preparation of compound 2 is contrary to our original expectation and we have conjectured that both the electronic nature and molecular size of the synthon units that bear either terminal alkyne (i.e. compounds 7 and 19) and bromo (i.e. compounds 8 and 17) functional groups may play important roles to affect their reactivities in this final Sonogashira reaction and lead to such results. All of the key intermediates and the final model chromophores were thoroughly purified and the structures were determined by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and HRMS. The detailed syntheses for the preparation of the aforementioned precursors and the targeted model fluorphores are described in the Experimental section.

#### 2.2 Optical properties characterization

#### 2.2.1 Linear absorption and fluorescence properties

Linear absorption (or one-photon absorption, 1PA) and fluorescence spectra of the studied compounds in solution phase are shown in Fig 2. These chromophores exhibit intense linear absorption in the UV-Vis region with their lowest-energy peaks located at 436 nm ( $\varepsilon$  ~9.59×10<sup>4</sup> cm<sup>-1</sup>M<sup>-1</sup>) and 448 nm ( $\varepsilon$  ~2.45×10<sup>5</sup> cm<sup>-1</sup>M<sup>-1</sup>), respectively. Strong yellow-green color of fluorescence from these two model compounds can be observed under the irradiation of UV light and their fluorescence spectra in toluene are shown in the inset of Fig. 2. All the photophysical data are collected in Table 1.

## 2.2.2 Two-photon-excited fluorescence properties in the femtosecond regime

2PA-induced fluorescence properties of these two chromophores were studied in the femtosecond regime and the results are shown in Fig. 3. In these experiments, a mode-locked wavelength-tunable Ti:Sapphire laser (Chameleon Ultra II, Coherent) was employed to deliver ~140 fs pulses with the repetition rate of 80 MHz and the beam diameter of 2 mm. The geometry of the optical setup for this experiment was carefully aligned to ensure that only the emission from the front surface of the sample was collected, which can minimize the inevitable inner filtering effect. The intensity of the excitation beam was also judiciously regulated to avoid the saturation of absorption and photodegradation. The same laser system and optical setup was also used for the

characterization of 2PA-related properties of the spin-coated neat-film prepared from compound **2** (*vide infra*).

In Fig 3(a), it is noted that the measured 2PA-induced emission spectrum for each model chromophore is basically identical to its corresponding 1PA-induced fluorescence spectra in the sense of the band shape and position (See the inset of Fig. 2), conveying that for each studied sample the observed radiative relaxations are from the same final emitting excited-states regardless of the excitation processes. A 2PA process is borne out to be the main cause for the measured up-converted emission since the power-squared dependence of the 2PA-induced fluorescence intensity on the excitation intensity was observed in all cases as shown in the Figs. 3(b) and 3(c).

The degenerate 2PA spectra of the studied compounds were probed from 680 nm to 1080 nm by two-photon-excited fluorescence (2PEF) technique[30] in the femtosecond regime as illustrated in Fig. 3(d). Both model chromophores exhibit strong two-photon activities within the most part of the investigated spectral region with ascending magnitude of the overall 2PA from compound **1** to compound **2**. It is noticed that there is an observable difference between the 2PA bands of these two compounds, that is, compound **1** possesses a single local 2PA maximum at 770 nm ( $\delta_2$ ~1950 GM) whereas compound **2** manifests multiple local 2PA maxima at 760 nm ( $\delta_2$ ~6100 GM), 830 nm ( $\delta_2$ ~2200 GM), 890 nm ( $\delta_2$ ~1600 GM), and 930 nm ( $\delta_2$ ~1300 GM), respectively.

From the measured one- and two-photon-related photophysical properties of the studied model compounds, some features are worthy to be discussed:

(1) The measured linear absorption spectra (Fig. 2) have revealed that both compounds 1 and 2 exhibit multi-maximum linear absorption bands covering virtually identical spectral region in the UV-Visible. Also, it is interesting to find that compound 1 shows descending molar absorption coefficients of its three local absorption maxima toward the lower-energy end of the spectrum while compound 2 exhibits a completely opposite tendency of it. The observed features indicate that expanding the  $\pi$ -conjugation of compound 1 by attaching two additional quinoxalinoid branches at C1 and C8 positions of the central carbazole to form compound 2 has enhanced the overall molecular linear absorptivity and the extent of such promotion is more favorable for the lower-energy absorption maxima. This behavior could be attributed to a fundamental difference in the molecular structures between these two model compounds, that is, although compounds 1 and 2 are structural analogues, yet the structure of compound 1 is not exactly equal to half a scaffold of compound 2 from the standpoint of molecular symmetry and the linking topology between the central carbazole-core and the peripheries. Therefore, it is reasonable to expect that these two model chromophores may possess distinct distribution pattern (either in the sense of intensity, position, and the shape) of their linear absorption spectra due to this intrinsic structural difference.

(2) Compared to compound 1, chromophore 2 shows promoted molar absorption coefficients and the maximal 2PA cross-section value as one can see from the measured linear absorption and 2PA spectra. Such promotion can be attributed to the increased number of the chromophoric units and the effective  $\pi$ -electrons while the molecular structure expands from 1 to 2. It is also noted that the aforementioned structural expansion exerts more extent of the enhancement on the molecular 2PA than on the linear absorptivities. In other words, for these two compounds the ratio of their maximal 2PA cross-section values (i.e.  $\delta_2^{\max}(2) / \delta_2^{\max}(1) \approx 3.13$ ) is larger than that of their molar coefficients absorption of the lowest-energy absorption peaks (i.e.  $\varepsilon_{\text{max}}(2 \text{ at } 448 \text{ nm}) / \varepsilon_{\text{max}}(1 \text{ at } 436 \text{ nm}) \approx 2.55)$ . Such feature may imply the existence of a 2PA cooperative enhancement in this multi-branched molecular system. Although many multi-branched molecules are reported to exhibit cooperative enhancement in their two-photon activities, however, it is indeed a fact that not every multi-branched structure possesses this kind of cooperative effect and since the general designing guide for such structural effect is still lacking, our model compounds may be appropriate to serve as a template for further study.

(3) The most accessible two-photon excited-states of these two chromophores should be energetically higher than those of the lowest one-photon-allowed excited-states since their major 2PA-bands are monotonically located at significantly shorter wavelength

region compared to the corresponding wavelength positions of twice of their lowest-energy linear absorption peaks (*i.e.*  $\lambda_{max}^{2PA} < 2\lambda_{max}^{1PA}$  for each case). Besides, appreciable two-photon activities aside from the main 2PA-band were observed at wavelengths that energetically correspond to the spectral positions where these dye molecules exhibit strong 1PA as well. All the above-mentioned features imply that although the 1PA and 2PA processes occurred within the studied chromophore system have followed different selection rules, there are many excited states of these model dye molecules accessible by both one-photon and two-photon transitions energetically.

(4) Using compound **1** as a reference point, the mode of structural expansion adopted on this compound has rendered not only an overall elevated molecular 2PA but also a broadened 2PA band as one can see from the measured 2PA spectra of compounds **1** and **2** in Fig. 3(d). This result indicates that these newly developed carbazole-containing indenoquinoxalinoid peripheries are beneficial units for the construction of highly active two-photon chromophores as long as they are incorporated appropriately. Moreover, any materials that possess widely distributed and strong 2PA may be useful for broadband optical power-limiting applications.

#### 2.2.3 Optical power-limiting in femtosecond regime

The quadratic dependence of 2PA on the input light intensity is the essential intrinsic

property that makes 2PA-materials to possess intensity-dependent transparency against incident light, which is applicable in optical power-limiting applications. With the increasing availability of hazardous light source especially those wavelength-tunable ultrashort laser systems, the need for optical power-limiters that work in wide spectral region with agile response are consequently very desirable. Since chromophore 2 manifests intense 2PA across a fairly wide spectral range, this compound is suitable to be as a representative for the demonstration of 2PA-based optical power-limiting property against femtosecond pulses. Figure 4(a) shows the measured data (in open triangle) of the nonlinear transmittance  $(T_i)$  versus input laser power at ~800 nm. It can be seen from Figure 4(a) that the intensity-dependent nonlinear transmission of the sample dropped from ~0.95 to ~0.42 as the incident intensity elevated from ~37.5 mW to ~1055 mW. The solid-line in Figure 4(a) represents the theoretical curve predicted by the basic 2PA theory [31, 32] using  $\beta = 1.7$  cm/GW (2PA coefficient of the sample solution) as the best fitting parameter. Based on the same set of data, Figure 4(b) illustrates an alternative way to conceptualize this optical-control behavior as transmitted intensity is plotted against input intensity. In this figure the theoretical fitting curve is presented by solid-line using the same fitting parameter of  $\beta = 1.7$  cm/GW and the diagonal dot-line represents the behavior for a medium without nonlinear absorption for comparison. It is noted from this measured input-output curve (open circles) that the transmitted intensity starts to be

suppressed at low pumping power, and such suppression rapidly approaches larger values as the excitation power levels up. In addition, the 2PA cross-section value of this model compound can be calculated to be ~2340 GM at 800 nm based on the performed optical-power-limiting experiment, which is in good agreement with the result obtained from 2PEF method and this verifies that 2PA is main cause for the observed optical-control and upconverted emission behaviors in this chromophore system.

#### 3. Two-photon properties of the neat-film fabricated from Compound 2

From the standpoint of application, it is important to gain knowledge about the optical properties of the developed 2PA chromophores especially in their solid states in order to further explore the applicability of these compounds for solid-state optical devices. As a starting point, we tentatively investigated the two-photon properties of a spin-coated neat-film prepared from compound **2** in the femtosecond regime based on 2PEF technique. The fabrication method and the basic photophysical data of the prepared neat-film are detailed in Supporting Information and summarized in Table 2, respectively. Figure 5 illustrates the normalized spectrum of two-photon excitation efficiency of the neat-film. One can see that although the spectral position of the major 2PA excitation efficiency band of the neat-film is roughly in good agreement with that of the measured 2PA spectrum of the solution, a notable shape difference between these two measured curves particularly

from 780 nm to 1000 nm is observed. We postulate that this behavior could be originated from the difference of the intramolecular interaction of this chromophore in its two distinct physical states because the significantly shorter intramolecular distance in solid state (i.e. neat-film case) may affect the molecular conformation and results in altered effective size of  $\pi$ -domain and charge-transfer efficiency and hence lead to partially altered spectral behavior. Nevertheless, it is a desirable property for the applications since a wider spectral window of 2PA activities is covered and the fabricated solid state device will consequently possess a broader active working range. In addition, the square dependence of the emission intensity on the excitation intensity (See Figure S3 has verified that a 2PA process is mainly responsible for the observed fluorescence. We wish to point out that it is important to evaluate the absolute two-photon strength of the neat-film within certain spectral range since it is an essential parameter for the future device design and fabrication. The development of such measurement is currently underway in our laboratory and will be reported in due course.

#### 4. Effective three-photon properties in nanosecond regime

One can imagine that 3PA would be much more difficult to be observed than 2PA since in theory the magnitude of 3PA is significantly smaller than that of 2PA for a given compound. Nevertheless, it is reasonable to select chromophores with intense 2PA as

model subjects for three-photon excitation (3PE) studies as such molecules have been experimentally validated to possess strong 3<sup>rd</sup>-order nonlinearity and can be anticipated to exhibit detectable higher-order nonlinearities. Moreover, it should be noted that the selection of appropriate range of excitation wavelength is important for achieving 3PE. We have previously demonstrated that under certain experimental condition some useful information regarding two- and three-photon excitation properties such as the order of absorption process (OAP) across a specific spectral region of a selected material can be retrieved by using a nanosecond laser.[33] At the same time, we are also curious about whether our experimental condition remains valid for other types of molecules. Therefore, experimental protocol intend to apply our on this newly developed we carbazole-containing system and explore the applicability of this method. In this investigation, the same experimental condition as previously reported by us has been followed to probe the three-photon-excited fluorescence (3PEF) intensities and OAP of these two compounds within the corresponding spectral range and the results are presented in Fig. 6.

When excited at 1400 nm, compound **2** exhibits an intensive green color emission with virtually identical spectrum of 2PA-induced fluorescence (see Fig. 3(a) and Fig. 6(a)). Since the excitation wavelength is significantly far away from the major 2PA band of this model chromophore and the observed emission intensity possesses a cubic-dependence on

the input intensity, it is corroborated that the measured fluorescence is induced by a 3PA process. The dispersion of three-photon-excitation efficiency of compounds **1** and **2** are presented in Fig. 6(b) and it is noted that in the studied spectral region these two compounds exhibit very similar dispersion pattern of their excitation efficiency with compound **2** manifests a saliently higher overall efficiency.

As illustrated in Fig. 6(c), the order of the absorption process (OAP) of compound 2 as a function of wavelength (i.e. OAP spectrum) can be delineated by monitoring the power-dependence of the up-converted emission intensity on the excitation intensity across different wavelengths. Agree to our anticipation, three major distinct OAP behaviors were found in the obtained spectrum and can be analyzed separately. In the region from 1160 to 1400 nm, the observed third-order dependence implies that all the transitions in this region are induced by 3PA. When the excitation wavelengths were tuned hyperchromically toward spectral region of 1000-1100 nm, intermediate values of OAP (i.e.  $\approx 2.3-2.7$ ) were obtained, indicating that 2PA and 3PA are coexistent and competing with each other within such spectral region. Therefore, for the excitation wavelengths which are close to the 1000 nm end, 2PA process would be dominant over 3PA because comparatively lower intensity is required to achieve 2PA and the obtained OAP is closer to 2 whereas if the excitation wavelengths near 1100 nm are utilized, the rising 3PA becomes competitive so that the obtained OAP value is closer to 3. Finally, in highly two-photon active spectral region (i.e. 760-950 nm) a quadratic dependence was held, which is in good agreement with the results measured by femtosecond laser.

Since there is no apparent distortion of the measured fluorescence properties based on the results shown in Fig. 6, it may suggest that our experimental protocol by using nanosecond laser to probe 3PA-induced fluorescence properties is suitable for different molecular systems.

#### 5. Conclusions

In summary, two new model chromophores using acetylene groups to connect a central carbazole core with either two or four peripheral diphenylaminocarbazole-substituted indenoquinoxalinoids were constructed and investigated for their multi-photon properties in both solution and neat-film states. These two model compounds are found to possess strong and wide dispersed two-photon activities in the near-IR region. The larger congener with four outward branches (i.e. compound **2**) was also demonstrated to exhibit efficient power-supressing property against femtosecond laser pulses at 800 nm. On the other hand, we have experimentally verified that our previously reported experimental protocol for studying three-photon-induced fluorescence properties and the order of absorption process (OAP) using nanosecond pulses is also applied to this model chromophore system, which may suggest that our experimental condition is reliable and can be commonly utilized for

such characterization. Besides, both chromophores are found to exhibit salient and detectable three-photon-induced fluorescence, indicating the designed scaffold may serve as a reference structural motif for the design of efficient three-photon materials.

#### 6. Experimental section

## 6.1 General

All the commercialized reagents for the preparation of the intermediates and targeted chromophores were purchased either from Acros Organics or Alfa Aesar and were used as received, unless stated otherwise. THF was distilled from sodium benzophenone ketyl. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded by a 300 MHz spectrometer and referenced to TMS or residual CHCl<sub>3</sub>. The numbering of carbon and hydrogen atoms on each intermediate and the final chromophore for the NMR signal assignment are systematized and illustrated in the ESI. 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).

## 6.2 Photophysical Methods and film fabrication

Linear optical properties including linear (one-photon) absorption spectra, fluorescence spectra, fluorescence quantum yields, and fluorescence lifetimes of the studied model compounds were recorded by the corresponding spectrometers. Two- and three-photon-related properties were measured using either a Ti:sapphire oscillator or a regenerative amplifier system as the probing tool. The detailed experimental conditions and the configuration of optical set-ups for nonlinear optical property investigations are described in the ESI.

### 6.3 Synthesis

The previously reported procedures were followed for the synthesis of compound **16** (See Scheme 1) [11] and the preparation of other key precursors and the final model chromophores are described in detail as the following:

#### 6.3.1

#### 9-Hexyl-9H-carbazole (4)

To a mixture of compound **3** (1.27 g, 0.07 mol) in THF (13 mL) was added KI (0.01 g, 0.08 mmol), sodium *tert*-butoxide (2.9 g, 0.030 mol), and 1-bromohexane (1.40 mL, 0.009 mol) stirred at 80 °C for 9 hours. Then the mixture was added pyridine (1 ml) and refluxed for 30 min. The above solution was cooled down to r.t. and quenched with 1N HCl to neutral then extracted with ethyl acetate (50 ml × 3) and then dried over MgSO<sub>4(S)</sub>. After filtration and removal the solvent, the crude product was purified with column chromatography on silica gel using hexane as eluent to afford the white solid with yield of 84.9 % (1.62 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.05-8.03 (d, *J* = 7.5Hz, 2H, H<sub>5</sub>), 7.41-7.29 (m, 4H, H<sub>2</sub>, H<sub>3</sub>), 7.19-7.14 (m, 2H, H<sub>4</sub>), 4.14-4.10 (m, 2H, H<sub>f</sub>), 1.76-1.72 (m, 2H, H<sub>e</sub>), 1.26-1.17 (m, 6H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.82-0.76 (m, 3H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.35 (C<sub>1</sub>), 125.48 (C<sub>3</sub>), 122.75 (C<sub>6</sub>), 120.25 (C<sub>5</sub>), 118.62 (C<sub>4</sub>), 108.58 (C<sub>2</sub>), 42.89 (C<sub>f</sub>), 31.51 (C<sub>e</sub>), 28.83 (C<sub>d</sub>), 26.88 (C<sub>c</sub>), 22.49 (C<sub>b</sub>), 13.97 (C<sub>a</sub>); HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>21</sub>N, 251.1674; found, 251.1673.

## 6.3.2

#### 3,6-Dibromo-9-hexyl-9H-carbazole (5)

A mixture of compound 4 (1.22 g, 4.84 mmol) and TBABr<sub>3</sub> (5.12 g, 10.63 mmol) in

CH<sub>2</sub>Cl<sub>2</sub> (49 mL) and MeOH (20 mL) was stirred at r.t. for 2 hours. Then the saturated NaHSO<sub>3(aq)</sub> (60 ml) was added into the reaction mixture and the resulting solution was extracted with dichloromethane (50 ml × 3). The organic layer was collected and dried over MgSO<sub>4(S)</sub>. After filtration and removal of the solvent, the crude solid product was collected and recrystallized from methanol. The purified product was obtained as green-brownish powder with yield of 74.7% (1.47 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14-8.13 (d, *J* = 1.8Hz, 2H, H<sub>5</sub>), 7.56-7.53 (dd, *J*<sub>1</sub> = 8.4Hz, *J*<sub>2</sub> = 1.8Hz, 2H, H<sub>3</sub>), 7.28-7.25 (d, *J* = 8.1Hz, 2H, H<sub>12</sub>), 4.26-4.21 (m, 2H, H<sub>f</sub>), 1.84-1.80 (m, 2H, H<sub>e</sub>), 1.33-1.26 (m, 6H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.88-0.83 (m, 3H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 139.26 (C<sub>1</sub>), 128.96 (C<sub>5</sub>), 123.39 (C<sub>6</sub>), 123.21 (C<sub>3</sub>), 111.89 (C<sub>4</sub>), 110.35 (C<sub>2</sub>), 43.31 (C<sub>f</sub>), 31.47 (C<sub>e</sub>), 28.79 (C<sub>d</sub>), 26.85 (C<sub>c</sub>), 22.48 (C<sub>b</sub>), 13.95 (C<sub>a</sub>); MALDI-TOF (m/z): [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>19</sub>Br<sub>2</sub>N, 409.1639; found, 409.1655.

## 9-Hexyl-3,6-bis((trimethylsilyl)ethynyl)-9*H*-carbazole (6)

To a solution of compound **5** (1.47 g, 3.59 mmol) in THF (12 mL) was added PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.31 g, 0.43 mmol), CuI (0.137 g, 7.18 mmol), trimethylsilyl acetylene (1.06 g, 10.78 mmol) and *i*-Pr<sub>2</sub>NH (3 mL) and the whole system was stirred at 90°C under N<sub>2</sub> for 24 hours. After cooling to the r.t., the above solution was then extracted with dichloromethane (30 mL × 3). The organic layer was collected and dried over MgSO<sub>4</sub>(s). After filtration and removal of the solvent, the crude product was purified through column chromatography on silica gel using hexane as the eluent to give the final product as pale-yellow oil with yield of 62.9% (1 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.23-8.22 (d, *J* = 0.9Hz, 2H, H<sub>5</sub>), 7.60-7.57 (dd, *J*<sub>1</sub> = 8.4Hz, *J*<sub>2</sub> = 1.0Hz, 2H, H<sub>3</sub>), 7.27-7.24 (d, *J* = 8.4Hz, 1H, H<sub>2</sub>), 4.19-4.15 (m, 2H, H<sub>f</sub>), 1.82-1.78 (m, 2H, H<sub>e</sub>), 1.29 (br, m, 6H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.90-0.86 (m, 3H, H<sub>a</sub>), 0.36 (s, 18H, hydrogens on the TMS group); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 140.40 (C<sub>1</sub>), 129.89 (C<sub>5</sub>), 124.55 (C<sub>3</sub>), 122.20 (C<sub>6</sub>), 113.69 (C<sub>4</sub>), 108.70 (C<sub>2</sub>), 106.40 (*sp*-carbon), 91.94 (*sp*-carbon), 43.12 (C<sub>f</sub>), 31.41 (C<sub>e</sub>), 28.76 (C<sub>d</sub>), 26.77 (C<sub>c</sub>), 22.45 (C<sub>b</sub>),13.91 (C<sub>a</sub>), 0.15 (methyl carbons on the TMS group).

## 6.3.3

## 3,6-Diethynyl-9-hexyl-9H-carbazole (7)

To a solution of compound **6** (1g, 2.44mmol) in THF/MeOH (10 mL/5 mL) was added KOH (1 g, 2.44 mmol) and H<sub>2</sub>O (2 mL) and the mixture was stirred at r.t. under N<sub>2</sub> for 6 hours. The above solution was then extracted with dichloromethane (30 mL × 3). The organic layer was collected and dried over MgSO<sub>4</sub>(s). After filtration and removal of the solvent, the crude product was purified through column chromatography on silica gel using hexane as the eluent to give the final product as pale-yellow oil with yield of 86% (0.37 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.14 (s, 2H, H<sub>5</sub>), 7.56-7.52 (dd,  $J_1$  = 8.4Hz,  $J_2$  = 1.5Hz, 2H, H<sub>3</sub>), 7.24-7.21 (d, J = 8.7Hz, 1H, H<sub>2</sub>), 4.14-4.09 (m, 2H, H<sub>f</sub>), 3.06 (s, 2H, *sp*-hydrogen), 1.76-1.72 (m, 2H, H<sub>e</sub>), 1.24 (br, m, 6H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.84-0.80 (m, 3H, H<sub>a</sub>);

<sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 140.51 (C<sub>1</sub>), 130.01 (C<sub>5</sub>), 124.62 (C<sub>3</sub>), 122.12 (C<sub>6</sub>), 112.60 (C<sub>4</sub>), 108.83 (C<sub>2</sub>), 84.73 (*sp*-carbon), 75.43 (*sp*-carbon), 43.13 (C<sub>f</sub>), 31.40 (C<sub>e</sub>), 28.76 (C<sub>d</sub>), 26.78 (C<sub>c</sub>), 22.43 (C<sub>b</sub>), 13.90 (C<sub>a</sub>).

## 6.3.4

#### 1,3,6,8-Tetrabromo-9-hexyl-9H-carbazole (8)

A solution composed of compound **4** (0.4 g, 1.57 mmol) and NBS (4.21 g, 23.65 mmol) in THF (20 mL) was stirred at r.t. for 24 hours. Then the saturated NaHSO<sub>3(aq)</sub> (20 ml) was added into the reaction mixture and the resulting solution was extracted with dichloromethane (50 ml × 3). After filtration, the organic solvent was removed by rotary evaporation to afford crude product which was then was purified by column chromatography on silica gel using hexane as eluent. The target compound was obtained as white solid with yield of 27.9 % (0.25 g). <sup>1</sup>H NMR ( 300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.018-8.011 (d, *J* = 2.1Hz, 2H, H<sub>5</sub>), 7.77-7.76 (d, *J* = 1.8Hz, 2H, H<sub>3</sub>), 5.09-5.03 (m, 2H, H<sub>f</sub>), 1.79-1.71 (m, 2H, H<sub>e</sub>), 1.35-1.25 (m, 6H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.89-0.75 (m, 3H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 136.64 (C<sub>1</sub>), 134.82 (C<sub>3</sub>), 125.88 (C<sub>6</sub>), 121.88 (C<sub>5</sub>), 112.64 (C<sub>4</sub>), 103.92 (C<sub>2</sub>), 44.62 (C<sub>f</sub>), 31.83 (C<sub>e</sub>), 31.35 (C<sub>d</sub>), 25.73 (C<sub>c</sub>), 22.57 (C<sub>b</sub>), 13.94 (C<sub>a</sub>); MALDI-TOF (m/z): [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>17</sub>Br<sub>4</sub>N, 566.9550; found, 566.9574.

## 6.3.5

## 4,4'-Dibromo-2-nitro-1,1'-biphenyl (10)

To a solution of compound 9 (24 g, 76.9 mmol) in acetic acid (360 ml) was added HNO<sub>3</sub> (112.78 ml, 2.70 mol) dropwisely. The resulting mixture was stirred at 100°C for 6 hours. The reaction mixture was then extracted with dichloromethane (50 ml  $\times$  3) and the organic layer was dried over  $MgSO_{4(S)}$ . After filtration and removal of the solvent, the crude purified by column chromatography product was on silica gel using dichloromethane-hexane (1:10) as the eluent to give the final purified product as yellow powder with yield of 87.6 % (24.13 g). <sup>1</sup>H NMR ( 300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.02-8.01 (d, J = 2.1Hz, 1H, H<sub>6</sub>), 7.76-7.73 (dd,  $J_1 = 8.4$ Hz,  $J_2 = 2.1$ Hz, 1H, H<sub>2</sub>), 7.56-7.53 (d, J = 8.7Hz, 2H, H<sub>9</sub>, H<sub>11</sub>), 7.29-7.26 (d, J = 8.1Hz, 1H, H<sub>3</sub>), 7.16-7.13 (d, J = 8.4Hz, 2H, H<sub>8</sub>, H<sub>12</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 149.20 (C<sub>5</sub>), 135.52 (C<sub>2</sub>), 135.25 (C<sub>4</sub>), 134.07 (C<sub>7</sub>), 132.98 (C<sub>3</sub>), 131.97 (C<sub>8</sub>, C<sub>12</sub>), 129.37 (C<sub>9</sub>, C<sub>11</sub>), 127.21 (C<sub>6</sub>), 123.02 (C<sub>10</sub>), 121.79 (C<sub>1</sub>); HRMS-EI (m/z):  $[M]^+$  calcd for  $C_{12}H_7Br_2NO_2$ , 354.8844; found 354.8850  $[(^{79}Br)(^{79}Br)M]^+$ , 356.8821  $[(^{79}Br)(^{81}Br)M]^+$ , 358.8803  $[(^{81}Br)(^{81}Br)M]^+$ .

## 6.3.6

#### 2,7-Dibromo-9*H*-carbazole (11)

A solution of compound 10 (24.13 g, 67.54 mmol) and PPh<sub>3</sub> (44.27 g, 168.88 mmol) in

*o*-dichlorobenzene (120 ml) was stirred at 180°C for 3 hours. After cooled down to r.t., the reaction mixture was purified by column chromatography on silica gel using dichloromethane-hexane (1:5) as the eluent to give the final purified product as white-off solids with yield of 82.5% (18.09 g). <sup>1</sup>H NMR (300 MHz,  $(CD_3)_2SO$ )  $\delta$ : 11.55 (s, 1H, -NH), 8.13-8.10 (d, J = 8.4Hz, 2H, H<sub>5</sub>), 7.75-7.74 (d, J = 1.5Hz, 2H, H<sub>2</sub>), 7.37-7.34 (dd,  $J_1 = 8.4Hz$ ,  $J_2 = 1.8Hz$ , 2H, H<sub>4</sub>); <sup>13</sup>C NMR (75 MHz,  $(CD_3)_2SO$ )  $\delta$ : 141.74 (C<sub>1</sub>), 123.05 (C<sub>4</sub>), 122.89 (C<sub>5</sub>), 121.95 (C<sub>6</sub>), 119.66 (C<sub>3</sub>), 114.81 (C<sub>2</sub>); HRMS-EI (m/z): [M]<sup>+</sup> calcd for C<sub>12</sub>H<sub>7</sub>Br<sub>2</sub>N, 322.8945; found 322.8938 [(<sup>79</sup>Br)(<sup>79</sup>Br)M]<sup>+</sup>, 324.8950 [(<sup>79</sup>Br)(<sup>81</sup>Br)M]<sup>+</sup>, 326.8954 [(<sup>81</sup>Br)(<sup>81</sup>Br)M]<sup>+</sup>.

## 6.3.7

#### 2,7-Hibromo-9-hexyl-9H-carbazole (12)

To a mixture of compound **11** (18.09 g, 0.053 mol) in THF (74 mL) was added KI (0.094 g, 0.53 mmol), sodium *tert*-butoxide (21.37 g, 0.221 mol) and 1-bromohexane (10.2 mL, 0.074 mole). The resulting solution was stirred at 80°C for 9 hours. Then pyridine (7.4 ml) was added and the whole system was refluxed for 30 min. The above solution was quenched with 1N HCl to neutral and then extracted with ethyl acetate (50 ml × 3). The organic layer was collected and dried over MgSO<sub>4(S)</sub>. After filtration and removal of the solvent, the crude product was purified with column chromatography on silica gel using hexane as eluent to afford the white solid with yield of 87.3 % (19.85 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.81-7.78 (d, *J* = 8.4Hz, 2H, H<sub>5</sub>), 7.467-7.462 (d, *J* = 1.5Hz, 2H, H<sub>2</sub>), 7.30-7.27 (dd, *J*<sub>1</sub> = 8.1Hz, *J*<sub>2</sub> = 1.5Hz, 2H, H<sub>4</sub>), 4.10-4.05 (m, 2H, H<sub>f</sub>), 1.79-1.74 (m, 2H, H<sub>e</sub>), 1.29 (m, 6H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.88-0.83 (m, 3H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 141.24 (C<sub>1</sub>), 122.43 (C<sub>4</sub>), 121.37 (C<sub>5</sub>), 121.18 (C<sub>6</sub>), 119.62 (C<sub>3</sub>), 111.89 (C<sub>2</sub>), 43.24 (C<sub>f</sub>), 31.44 (C<sub>e</sub>), 28.69 (C<sub>d</sub>), 26.79 (C<sub>c</sub>), 22.50 (C<sub>b</sub>), 13.96 (C<sub>a</sub>); MALDI-TOF (m/z): [M]<sup>+</sup> calcd for C<sub>18</sub>H<sub>19</sub>Br<sub>2</sub>N, 409.1639; found, 409.1652.

## 6.3.8

## 7-Bromo-9-hexyl-N,N-diphenyl-9H-carbazol-2-amine (13)

To a mixture of compound **12** (19.8 g, 48.36 mmol) and diphenylamine (8.17 g, 48.79 mmol) in toluene (98mL) was added BINAP (0.88 g, 1.43 mmol),  $Pd_2(dba)_3$  (0.440 g, 0.485 mmol), sodium *tert*-butoxide (2.68 g, 27.84 mmol) and the resulting solution stirred at 80°C under Ar atmosphere for 24 hours. After cooling to the r.t.,  $H_2O$  (100 mL) was added to the reaction mixture which was then extracted with ethyl acetate and the organic layer was dried over MgSO<sub>4(S)</sub>. After filtration and removal of the solvent, the crude product was purified through column chromatography on silica gel using hexane as eluent to give the final purified product as pale-yellow oil with yield of 51.2% (12.36 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.88-7.85 (d, *J* = 8.4Hz, 1H, H<sub>12</sub>), 7.82-7.79 (d, *J* = 8.1Hz, 1H, H<sub>13</sub>), 7.457-7.452 (d, *J* = 1.5Hz, 1H, H<sub>15</sub>), 7.29-7.25 (m, 5H, H<sub>2</sub>, H<sub>9</sub>), 7.24-7.22 (m, 2H,

H<sub>1</sub>), 7.15-7.14 (m, 1H, H<sub>8</sub>), 7.12-7.11 (m, 1H, H<sub>6</sub>), 7.07-6.98 (m, 4H, H<sub>3</sub>), 4.08-4.03 (m, 2H, H<sub>f</sub>), 1.74-1.69 (m, 2H, H<sub>e</sub>), 1.23-1.22 (m, 6H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.85-0.81 (m, 3H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 148.10 (C<sub>4</sub>), 146.59 (C<sub>7</sub>), 141.66 (C<sub>5</sub>), 141.55 (C<sub>16</sub>), 129.14 (C<sub>2</sub>), 123.94 (C<sub>3</sub>), 122.54 (C<sub>1</sub>), 121.98 (C<sub>12</sub>), 121.83 (C<sub>14</sub>), 120.87 (C<sub>13</sub>), 118.31 (C<sub>10</sub>), 117.98 (C<sub>11</sub>), 117.71 (C<sub>9</sub>), 117.32 (C<sub>15</sub>), 111.49 (C<sub>8</sub>), 104.82 (C<sub>6</sub>), 42.88 (C<sub>f</sub>), 31.40 (C<sub>e</sub>), 28.63 (C<sub>d</sub>), 26.68 (C<sub>c</sub>), 22.40 (C<sub>b</sub>), 13.96 (C<sub>a</sub>); MALDI-TOF (m/z): [M]<sup>+</sup> calcd for C<sub>30</sub>H<sub>29</sub>BrN<sub>2</sub>, 496.1514; found, 496.1527.

## 6.3.9

#### 7,7'-(Ethyne-1,2-diyl)bis(9-hexyl-*N*,*N*-diphenyl-9*H*-carbazol-2-amine) (14)

A mixture composed of compound **13** (12.36 g, 24.85 mmol), acetylenedicarboxylic acid (1.416g, 12.42mmol), 1,4-bis(diphenylphosphino) butane (1.06 g, 2.46 mmol) and PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.0872 g, 0.12 mmol) in DMSO (30.7 mL) was stirred at 110°C under Ar atmosphere for 8 hours. After cooling to the r.t., cold methanol (5 mL) and cold hexane (5 mL) was added to the reaction mixture and the whole system was stirred at 0°C for 30 min. After filtration, the crude solid product was collected and recrystallized from methanol. The purified product was obtained as yellow powder with yield of 68% (7.57 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 7.97-7.90 (m, 4H, H<sub>9</sub>, H<sub>12</sub>), 7.56 (s, 2H, H<sub>15</sub>), 7.44-7.42 (d, *J* = 8.1Hz, 2H, H<sub>13</sub>), 7.28-7.23 (m, 8H, H<sub>2</sub>), 7.16-7.14 (m, 8H, H<sub>3</sub>), 7.10-7.09 (m, 2H, H<sub>8</sub>), 7.04-6.95 (m, 6H, H<sub>1</sub>, H<sub>6</sub>), 4.16-4.11 (m, 4H, H<sub>f</sub>), 1.79-1.75 (m, 4H, H<sub>e</sub>), 1.26 (br, 12H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.86-0.82 (m, 6H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 148.17 (C<sub>4</sub>), 146.66 (C<sub>16</sub>), 142.26 (C<sub>7</sub>), 140.47 (C<sub>5</sub>), 129.16 (C<sub>2</sub>), 123.98 (C<sub>3</sub>), 122.88 (C<sub>11</sub>), 122.79 (C<sub>13</sub>), 122.55 (C<sub>1</sub>), 121.06 (C<sub>9</sub>), 119.61 (C<sub>12</sub>), 119.34 (C<sub>14</sub>), 118.34 (C<sub>10</sub>), 117.26 (C<sub>8</sub>), 111.64 (C<sub>15</sub>), 104.78 (C<sub>6</sub>), 90.46 (*sp*-carbon), 42.97 (C<sub>f</sub>), 31.52 (C<sub>e</sub>), 28.81 (C<sub>d</sub>), 26.82 (C<sub>c</sub>), 22.47 (C<sub>b</sub>), 14.00 (C<sub>a</sub>); MALDI-TOF (m/z): [M]<sup>+</sup> calcd for C<sub>62</sub>H<sub>58</sub>N<sub>4</sub>, 858.4661; found, 858.4682.

## 6.3.10

## 1,2-Bis(7-(diphenylamino)-9-hexyl-9H-carbazol-2-yl)ethane-1,2-dione (15)

To a solution of compound **14** (7.57 g; 8.84 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40mL) was added KMnO<sub>4</sub> (5.61 g; 35.39 mmol), NaHCO<sub>3</sub> (0.741 g; 8.84 mmol), Aliquat 336 (1.23 g), and H<sub>2</sub>O (20 mL) and the resulting solution was stirred at r.t. 18 hours before the addition of saturated NaHSO<sub>3</sub> (50 mL) and 1N HCl solutions. The above solution was then extracted with dichloromethane (50 mL×3). The organic layer was collected and dried over MgSO<sub>4</sub>(s). After filtration and removal of the solvent, the crude product was purified through column chromatography on silica gel using dichloromethane-hexane (1:3) as the eluent to give the final product as pale-orange powder with yield of 66.5% (5.24 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.10 (s, 2H, H<sub>15</sub>), 8.01-7.98 (d, *J* = 8.1Hz, 2H, H<sub>12</sub>), 7.93-7.91 (d, *J* = 8.7Hz, 2H, H<sub>9</sub>), 7.79-7.76 (dd, *J*<sub>1</sub> = 8.4Hz, *J*<sub>2</sub> = 1.2Hz, 2H, H<sub>13</sub>), 7.30-7.23 (m, 8H, H<sub>2</sub>), 7.18-7.15 (m, 8H, H<sub>3</sub>), 7.07-7.02 (m, 6H, H<sub>1</sub>, H<sub>6</sub>), 6.99-6.96 (dd, *J*<sub>1</sub> = 8.7Hz, *J*<sub>2</sub> = 1.8Hz, 2H, H<sub>8</sub>),

4.17-4.12 (m, 4H, H<sub>f</sub>), 1.75-1.70 (m, 4H, H<sub>e</sub>), 1.19 (br, m, 12H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>), 0.81-0.77 (m, 6H, H<sub>a</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 195.66 (carbonyl carbon), 148.38 (C<sub>16</sub>), 147.79 (C<sub>4</sub>), 143.65 (C<sub>7</sub>), 140.30 (C<sub>11</sub>), 129.44 (C<sub>14</sub>), 129.28 (C<sub>2</sub>), 128.43 (C<sub>5</sub>), 124.60 (C<sub>3</sub>), 123.18 (C<sub>1</sub>), 122.04 (C<sub>12</sub>), 121.63 (C<sub>9</sub>), 119.45 (C<sub>8</sub>), 117.03 (C<sub>10</sub>), 116.92 (C<sub>13</sub>), 109.80 (C<sub>15</sub>), 103.54 (C<sub>6</sub>), 42.98 (C<sub>f</sub>), 31.38 (C<sub>e</sub>), 28.80 (C<sub>d</sub>), 26.70 (C<sub>c</sub>), 22.38 (C<sub>b</sub>), 13.93 (C<sub>a</sub>); MALDI-TOF (m/z): [M]<sup>+</sup> calcd for C<sub>62</sub>H<sub>58</sub>N<sub>4</sub>O<sub>2</sub>, 890.4559; found, 890.4583.

## 6.3.11

# 7,7'-(8-Bromo-10,10-dihexyl-10*H*-indeno[1,2-g]quinoxaline-2,3-diyl)bis(9-hexyl-*N*,*N*-diphenyl-9*H*-carbazol-2-amine) (17)

To a solution of compound 16 (3.15 g, 7.2 mmol) and compound 15 (5.24 g, 5.89 mmol) in THF (20 ml) was added CH<sub>3</sub>COOH (2 mL). The resulting mixture was stirred at 80°C under Ar atmosphere for 12 hours. After cooling to the r.t., the reaction mixture was then extracted with ethyl acetate (30 mL  $\times$  3). The organic layer was collected and dried over MgSO<sub>4</sub>(s). After filtration and removal of the solvent, the crude product was purified through column chromatography on silica gel using dichloromethane-hexane (1:3) as the eluent to give the final product as yellow powder with yield of 86% (6.55 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ : 8.45 (s, 1H, H<sub>8</sub>), 8.13 (s, 1H, H<sub>11</sub>), 7.97-7.93 (dd,  $J_1 = 8.1$ Hz,  $J_2 = 100$ 1.8Hz, 2H, H<sub>18</sub>), 7.89-7.86 (dd,  $J_1 = 8.4$ Hz,  $J_2 = 0.9$ Hz, 2H, H<sub>19</sub>), 7.78-7.75 (d, J = 8.4Hz, 1H, H<sub>5</sub>), 7.58-7.53 (m, 3H, H<sub>2</sub>, H<sub>22</sub>), 7.48 (s, 2H, H<sub>16</sub>), 7.26-7.21 (m, 9H, H<sub>4</sub>, H<sub>28</sub>), 7.14-7.11 (m, 8H, H<sub>29</sub>), 7.02-6.93 (m, 10H, H<sub>23</sub>, H<sub>25</sub>, H<sub>27</sub>), 3.91-3.87 (m, 4H, H<sub>f1</sub>), 2.15-2.04 (m, 4H, H<sub>f</sub>), 1.32 (br, m, 4H, H<sub>e1</sub>), 1.09-1.06 (m, 16H, H<sub>c</sub>, H<sub>d</sub>, H<sub>d1</sub>, H<sub>e</sub>), 0.95-0.94 (m, 8H, H<sub>b1</sub>, H<sub>c1</sub>), 0.78-0.73 (m, 16H, H<sub>a1</sub>, H<sub>a</sub>, H<sub>b</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 154.07 (C<sub>13</sub>), 153.63 (C<sub>17</sub>), 153.54 (C<sub>17</sub>), 152.86 (C<sub>14</sub>), 148.15 (C<sub>30</sub>), 146.55 (C<sub>10</sub>), 142.79 (C<sub>1</sub>), 142.29 (C<sub>9</sub>), 141.30 (C<sub>15</sub>), 141.21 (C<sub>15</sub>), 140.31 (C<sub>7</sub>), 138.69 (C<sub>6</sub>), 136.00  $(C_{24}), 135.92$   $(C_{20}), 132.46$   $(C_{12}), 130.60$   $(C_2), 129.11$   $(C_{28}), 126.49$   $(C_5), 123.96$   $(C_{29}), 123.96$ 123.29 (C<sub>3</sub>), 123.05 (C<sub>26</sub>), 122.50 (C<sub>27</sub>), 121.15 (C<sub>4</sub>, C<sub>11</sub>), 120.93 (C<sub>8</sub>), 119.63 (C<sub>19</sub>, C<sub>22</sub>), 118.49 (C<sub>18</sub>), 118.17 (C<sub>21</sub>), 117.02 (C<sub>23</sub>), 110.58 (C<sub>16</sub>), 104.62 (C<sub>25</sub>), 55.46 (C<sub>g</sub>), 42.69 (C<sub>f1</sub>), 41.22 (C<sub>f</sub>), 31.49 (C<sub>e</sub>), 31.05 (C<sub>e1</sub>), 29.64 (C<sub>d</sub>), 28.37 (C<sub>d1</sub>), 26.47 (C<sub>c1</sub>), 23.91 (C<sub>c</sub>), 22.53 (C<sub>b</sub>), 22.34 (C<sub>b1</sub>), 13.94 (C<sub>a</sub>, C<sub>a1</sub>); MALDI-TOF (m/z): [M]<sup>+</sup> calcd for C<sub>87</sub>H<sub>89</sub>BrN<sub>6</sub>, 1296.6332; found, 1296.6370.

## 6.3.12

# 7,7'-(10,10-Dihexyl-8-((trimethylsilyl)ethynyl)-10*H*-indeno[1,2-g]quinoxaline-2,3-diyl )bis(9-hexyl-*N*,*N*-diphenyl-9*H*-carbazol-2-amine) (18)

To a solution of compound **17** (3.2 g, 2.46 mmol) in THF (15 mL) was added  $PdCl_2(PPh_3)_2$  (0.103 g, 0.147 mmol), CuI (0.047 g, 0.24 mmol), trimethylsilyl acetylene (0.36 g, 3.7 mmol) and *i*-Pr<sub>2</sub>NH (3.82 mL) and the resulting soluton was stirred at 90°C under N<sub>2</sub> for 24 hours. After cooling to the r.t., the reaction mixture was then extracted

with dichloromethane (30 mL  $\times$  3) and the organic layer was collected and dried over MgSO<sub>4</sub>(s). After filtration and removal of the solvent, the crude product was further purified through column chromatography on silica gel using THF-hexane (1:10) as the eluent to give the final product as yellow powder with yield of 87.8% (2.83 g). <sup>1</sup>H NMR  $(300 \text{ MHz}, \text{CDCl}_3) \delta$ : 8.44 (s, 1H, H<sub>8</sub>), 8.11 (s, 1H, H<sub>11</sub>), 7.6-7.92 (dd,  $J_1 = 7.8 \text{Hz}, J_2 =$ 2.1Hz, 2H, H<sub>18</sub>), 7.89-7.86 (dd,  $J_1 = 8.4$ Hz,  $J_2 = 8.4$ Hz, 2H, H<sub>23</sub>), 7.85-7.83 (d, J = 8.4Hz, 1H, H<sub>5</sub>), 7.55-7.51 (m, 3H, H<sub>2</sub>, H<sub>19</sub>), 7.47 (s, 2H, H<sub>16</sub>), 7.26-7.21 (m, 9H, H<sub>4</sub>, H<sub>28</sub>), 7.13-7.11 (m, 8H,  $H_{29}$ ), 7.02-6.92 (m, 10H,  $H_{22}$ ,  $H_{25}$ ,  $H_{27}$ ), 3.92-3.86 (m, 4H,  $H_{f1}$ ), 2.12-2.08 (m, 4H, H<sub>f</sub>), 1.32 (br, m, 4H, H<sub>el</sub>), 1.11-1.04 (m, 16H, H<sub>c</sub>, H<sub>d</sub>, H<sub>dl</sub>, H<sub>e</sub>), 0.95-0.93 (m, 8H, H<sub>b1</sub>, H<sub>c1</sub>), 0.77-0.67 (m, 16H, H<sub>a1</sub>, H<sub>a</sub>, H<sub>b</sub>), 0.36 (s, 9H, hydrogens on the TMS groups);  ${}^{13}$ C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 154.01 (C<sub>13</sub>), 153.59 (C<sub>14</sub>), 153.47 (C<sub>1</sub>), 151.30 (C<sub>17</sub>), 148.16 (C<sub>30</sub>), 146.55 (C<sub>10</sub>), 143.15 (C<sub>9</sub>), 142.29 (C<sub>6</sub>), 141.37 (C<sub>7</sub>), 141.21 (C<sub>12</sub>), 140.31 (C<sub>15</sub>), 140.06 (C<sub>24</sub>), 136.06 (C<sub>20</sub>), 135.96 (C<sub>26</sub>), 131.53 (C<sub>2</sub>), 129.10 (C<sub>28</sub>), 126.55 (C<sub>4</sub>), 123.96 (C<sub>29</sub>), 123.28 (C<sub>3</sub>), 122.49 (C<sub>27</sub>), 122.38 (C<sub>11</sub>), 121.14 (C<sub>5</sub>), 120.96  $(C_8)$ , 120.88  $(C_{22})$ , 119.61  $(C_{19})$ , 118.75  $(C_{18})$ , 118.19  $(C_{21})$ , 117.01  $(C_{23})$ , 110.60  $(C_{16})$ , 105.85 (C<sub>25</sub>), 104.62 (sp-carbon), 95.02 (sp-carbon), 55.23 (C<sub>g</sub>), 42.69 (C<sub>f1</sub>), 41.31 (C<sub>f</sub>), 31.52 (Ce), 31.04 (Ce1), 29.69 (Cd), 28.36 (Cd1), 26.46 (Cc1), 23.91 (Cc), 22.54 (Cb), 22.33  $(C_{b1})$ , 13.93  $(C_a, C_{a1})$ , 0.01 (methyl carbons on the TMS group); MALDI-TOF (m/z):  $[M]^+$ calcd for C<sub>92</sub>H<sub>98</sub>N<sub>6</sub>Si, 1314.7622; found, 1314.7651.

#### 6.3.13

## 7,7'-(8-Ethynyl-10,10-dihexyl-10*H*-indeno[1,2-g]quinoxaline-2,3-diyl)bis(9-hexyl-*N*,*N*-diphenyl-9*H*-carbazol-2-amine) (19)

To a solution of compound 18 (2.83 g, 2.15 mmol) in THF/MeOH (2 mL/7 mL) was added KOH (0.48 g, 8.59 mmol) and H<sub>2</sub>O (2.67 mL) and the resulting mixture was stirred at r.t. under N<sub>2</sub> for 6 hours. The reaction solution was then extracted with dichloromethane  $(30 \text{ mL} \times 3)$  and the organic layer was collected and dried over MgSO<sub>4</sub>(s). After filtration and removal of 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 product as yellow powder with yield of 91.5% (2.44 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.47 (s, 1H, H<sub>8</sub>), 8.14 (s, 1H, H<sub>11</sub>), 7.97-7.94 (dd,  $J_1 = 8.1$ Hz,  $J_2 = 2.1$ Hz, 2H, H<sub>18</sub>), 7.90-7.85 (m, 3H, H<sub>5</sub>, H<sub>23</sub>), 7.59-7.55 (m, 3H, H<sub>2</sub>, H<sub>19</sub>), 7.48 (s, 2H, H<sub>16</sub>), 7.26-7.20 (m, 9H, H<sub>4</sub>, H<sub>28</sub>), 7.14-7.11 (m, 8H, H<sub>29</sub>), 7.02-6.93 (m, 10H, H<sub>22</sub>, H<sub>25</sub>, H<sub>27</sub>), 3.91-3.87 (m, 4H, H<sub>f1</sub>), 3.18 (s, 2H, sp-hydrogen), 2.16-2.07 (m, 4H, H<sub>f</sub>), 1.34-1.30 (m, 4H, H<sub>e1</sub>), 1.11-1.05 (m, 16H, H<sub>c</sub>, H<sub>d</sub>, H<sub>d1</sub>, H<sub>e</sub>), 0.95-0.94 (m, 8H, H<sub>b1</sub>, H<sub>c1</sub>), 0.78-0.72 (m, 12H, H<sub>a1</sub>, H<sub>a</sub>), 0.70-0.67 (m, 4H, H<sub>b</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 154.05 (C<sub>13</sub>), 153.67 (C<sub>14</sub>), 153.40  $(C_1)$ , 151.40  $(C_{17})$ , 148.15  $(C_{30})$ , 146.55  $(C_{10})$ , 143.00  $(C_9)$ , 142.29  $(C_6)$ , 141.40  $(C_7)$ , 141.18 (C<sub>12</sub>), 140.32 (C<sub>15</sub>), 136.03 (C<sub>24</sub>), 135.93 (C<sub>20</sub>), 131.56 (C<sub>2</sub>), 129.10 (C<sub>28</sub>), 126.82 (C<sub>4</sub>, C<sub>11</sub>), 123.96 (C<sub>29</sub>), 123.30 (C<sub>26</sub>), 122.49 (C<sub>27</sub>), 122.16 (C<sub>3</sub>), 121.14 (C<sub>5</sub>), 120.96 (C<sub>8</sub>), 119.62 (C<sub>22</sub>), 118.86 (C<sub>18</sub>), 118.18 (C<sub>21</sub>), 117.02 (C<sub>23</sub>), 110.59 (C<sub>16</sub>), 104.61 (C<sub>25</sub>), 84.35 (*sp*-carbon), 77.92 (*sp*-carbon), 55.22 (C<sub>g</sub>), 42.68 (C<sub>f1</sub>), 41.25 (C<sub>f</sub>), 31.49 (C<sub>e</sub>), 31.04 (C<sub>e1</sub>), 29.66 (C<sub>d</sub>), 28.36 (C<sub>d1</sub>), 26.46 (C<sub>c1</sub>), 23.91 (C<sub>c</sub>), 22.52 (C<sub>b</sub>), 22.33 (C<sub>b1</sub>), 13.93 (C<sub>a</sub>, C<sub>a1</sub>); MALDI-TOF (m/z):  $[M]^+$  calcd for C<sub>89</sub>H<sub>90</sub>N<sub>6</sub>, 1242.7227; found, 1242.7267.

## 6.3.14

#### **Compound 1**

To a 3-neck round-bottom flask was charged compound 7 (0.35 g, 1.18 mmol), PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub> (0.098 g, 0.14 mmol), CuI (0.045 g, 0.235 mmol), compound **17** (3.35 g, 2.58 mmol), *i*-Pr<sub>2</sub>NH (7.5 mL) and THF (30mL). The above solution was stirred at 90°C under N<sub>2</sub> for 24 hours. The cooled reaction solution was then extracted with dichloromethane (30 mL  $\times$  3) and the organic layer was collected and dried over  $MgSO_4(s)$ . After filtration and removal of the solvent, the crude product was purified through column chromatography on silica gel using dichloromethane-hexane (1:3) as the eluent to give the final product as pale-yellow oil with yield of 31% (1.0 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.48 (s, 2H, H<sub>14</sub>), 8.38 (s, 2H, H<sub>5</sub>), 8.14 (s, 2H, H<sub>17</sub>), 7.96-7.93 (m, 4H, H<sub>24</sub>), 7.90-7.87 (m, 4H, H<sub>25</sub>), 7.75-7.72 (m, 2H, H<sub>11</sub>), 7.68-7.64 (m, 2H, H<sub>8</sub>), 7.57-7.53 (m, 4H, H<sub>28</sub>), 7.48 (s, 4H, H<sub>22</sub>), 7.44-7.41 (m, 2H, H<sub>3</sub>), 7.27-7.22 (m, 20H, H<sub>2</sub>, H<sub>10</sub>, H<sub>34</sub>), 7.14-7.11 (m, 16H, H<sub>35</sub>), 7.03-6.92 (m, 16H, H<sub>29</sub>, H<sub>31</sub>, H<sub>33</sub>), 4.33-4.32 (m, 2H, H<sub>f</sub>), 3.90 (br, m, 8H, H<sub>f2</sub>), 2.17-2.16 (m, 8H, H<sub>f1</sub>), 1.92-1.90 (m, 2H, H<sub>e</sub>), 1.33 (m, 14H, H<sub>b</sub>, H<sub>c</sub>, H<sub>d</sub>, H<sub>e2</sub>), 1.11-1.07 (m, 32H, H<sub>c1</sub>, H<sub>d1</sub>, H<sub>e1</sub>, H<sub>d2</sub>), 0.94 (br, m, 19H, H<sub>a</sub>, H<sub>b2</sub>, H<sub>c2</sub>), 0.78-0.73 (m, 32H, H<sub>a1</sub>, H<sub>a2</sub>, H<sub>b1</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ: 153.95 (C<sub>19</sub>), 153.58 (C<sub>23</sub>), 153.46 (C<sub>23</sub>), 151.48 (C<sub>20</sub>), 148.14 (C<sub>36</sub>), 146.50 (C<sub>16</sub>), 143.37 (C<sub>7</sub>), 142.26 (C<sub>15</sub>), 141.34 (C<sub>21</sub>), 141.28  $(C_{21'})$ , 140.72  $(C_{18})$ , 140.49  $(C_1)$ , 140.30  $(C_{13})$ , 139.43  $(C_{12})$ , 136.09  $(C_{30})$ , 135.99  $(C_{26})$ , 130.93 (C<sub>8</sub>), 129.09 (C<sub>34</sub>), 126.09 (C<sub>11</sub>), 124.20 (C<sub>5</sub>), 123.93 (C<sub>35</sub>), 123.24 (C<sub>32</sub>), 122.47  $(C_{33}), 122.36 (C_3), 121.12 (C_{10}, C_{17}), 120.96 (C_{14}), 119.60 (C_{25}), 118.52 (C_{28}), 118.18$  $(C_{24})$ , 117.00  $(C_{27})$ , 113.84  $(C_{29})$ , 112.54  $(C_{9})$ , 110.59  $(C_{22})$ , 109.08  $(C_{2})$ , 104.62  $(C_{31})$ , 99.11 (C<sub>6</sub>), 91.70 (C<sub>4</sub>), 88.83 (sp-carbon), 82.59 (sp-carbon), 55.23 (C<sub>g1</sub>), 43.34 (C<sub>f</sub>), 42.67 (C<sub>f2</sub>), 41.38 (C<sub>f1</sub>), 31.55 (C<sub>e1</sub>), 31.45 (C<sub>e</sub>), 31.03 (C<sub>e2</sub>), 29.74 (C<sub>d1</sub>), 29.65 (C<sub>d1</sub>), 28.87 (C<sub>d</sub>), 28.35 (C<sub>d2</sub>), 26.86 (C<sub>c</sub>), 26.45 (C<sub>c2</sub>), 23.99 (C<sub>c1</sub>), 22.56 (C<sub>b1</sub>), 22.48 (C<sub>b</sub>), 22.32 (C<sub>b2</sub>), 13.94 (C<sub>a</sub>, C<sub>a1</sub>, C<sub>a2</sub>); MALDI-TOF (m/z): [M]<sup>+</sup> calcd for C<sub>196</sub>H<sub>197</sub>N<sub>13</sub>, 2734.8210; found, 2734.8289.

#### 6.3.15

## Compound 2

To a solution of compound **8** (0.25 g, 0.44 mmol) in THF (27 mL) was added  $PdCl_2(PPh_3)_2$  (0.075 g, 0.11 mmol), CuI (0.033 g, 0.17 mmol), compound **19** (2.44 g, 1.96 mmol) and *i*-Pr<sub>2</sub>NH (6.67mL) and the resulting mixture was stirred at 90°C under N<sub>2</sub> for 24 hours. After cooling to the r.t., the above solution was then extracted with

dichloromethane (30 mL  $\times$  3) and the organic layer was collected and dried over  $MgSO_4(s)$ . After filtration and removal of the solvent, the crude product was purified through column chromatography on silica gel using dichloromethane-hexane (1:3) as the eluent to give the final product as pale-yellow oil with yield of 43% (1.0 g). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 8.50 (s, 4H, H<sub>14</sub>), 8.16 (s, 4H, H<sub>17</sub>), 7.96-7.93 (m, 8H, H<sub>24</sub>), 7.94 (s, 2H, H<sub>5</sub>), 7.91-7.86 (m, 8H, H<sub>25</sub>), 7.64 (br, m, 4H, H<sub>11</sub>), 7.61 (br, m, 4H, H<sub>8</sub>), 7.56-7.54 (m, 8H, H<sub>28</sub>), 7.52 (s, 2H, H<sub>3</sub>), 7.49 (br, m, 4H, H<sub>10</sub>), 7.27-7.22 (m, 40H, H<sub>22</sub>, H<sub>34</sub>), 7.14-7.11 (m, 32H, H<sub>35</sub>), 7.03-6.93 (m, 32H, H<sub>29</sub>, H<sub>31</sub>, H<sub>33</sub>), 3.90 (br, m, 18H, H<sub>f</sub>, H<sub>f2</sub>), 2.19-2.11 (m, 18H,  $H_e$ ,  $H_{f1}$ ), 1.33 (br, m, 22H,  $H_b$ ,  $H_c$ ,  $H_d$ ,  $H_{e2}$ ), 1.11-1.07 (m, 64H,  $H_{c1}$ ,  $H_{d1}$ ,  $H_{e1}$ ,  $H_{d2}$ ), 0.95-0.94 (m, 35H, H<sub>a</sub>, H<sub>b2</sub>, H<sub>c2</sub>), 0.78-0.73 (m, 64H, H<sub>a1</sub>, H<sub>a2</sub>, H<sub>b1</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ : 154.07 (C<sub>19</sub>), 153.73 (C<sub>23</sub>), 153.47 (C<sub>1</sub>), 151.51 (C<sub>20</sub>), 148.11 (C<sub>36</sub>), 146.56 (C<sub>16</sub>), 142.83 (C<sub>7</sub>), 142.28 (C<sub>15</sub>), 141.45 (C<sub>21</sub>), 141.13 (C<sub>13</sub>), 140.78 (C<sub>6</sub>), 140.29 (C<sub>12</sub>), 135.90 (C<sub>30</sub>), 135.80 (C<sub>26</sub>), 133.56 (C<sub>3</sub>), 133.34 (C<sub>3'</sub>), 132.90 (C<sub>18</sub>), 131.95 (C<sub>8</sub>), 129.49  $(C_4)$ , 129.45  $(C_{4'})$ , 129.08  $(C_{34})$ , 128.36  $(C_5)$ , 128.24  $(C_{5'})$ , 127.55  $(C_{11})$ , 127.22  $(C_2)$ , 123.94 (C<sub>35</sub>), 123.32 (C<sub>9</sub>), 122.48 (C<sub>33</sub>), 121.81 (C<sub>32</sub>), 121.14 (C<sub>10</sub>, C<sub>17</sub>), 120.90 (C<sub>14</sub>), 119.62 ( $C_{25}$ ,  $C_{28}$ ), 119.00 ( $C_{24}$ ), 118.12 ( $C_{27}$ ), 117.01 ( $C_{29}$ ), 110.52 ( $C_{22}$ ), 104.58 ( $C_{31}$ ), 83.19 (sp-carbon), 75.02 (sp-carbon), 55.26 (Cg1), 42.68 (Cf, Cf2), 41.20 (Cf1), 31.48 (Ce1), 31.02 (Ce, Ce2), 29.65 (Cd1), 28.35 (Cd, Cd2), 26.44 (Cc, Cc2), 23.94 (Cc1), 22.51 (Cb1), 22.31 (C<sub>b</sub>, C<sub>b2</sub>), 13.92 (C<sub>a</sub>, C<sub>a1</sub>, C<sub>a2</sub>); MALDI-TOF (m/z): [M+H]<sup>+</sup> calcd for C<sub>374</sub>H<sub>374</sub>N<sub>25</sub>, 5219.2773; found, 5219.2891.

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	$\lambda_{\max}^{Absb,c}$ (nm)	$\mathcal{E}_{max}$ (cm <sup>-1</sup> M <sup>-1</sup> )	$\lambda_{\max}^{\operatorname{Em} d}$ (nm)	$\Phi_{ extsf{F}}^{\ e}$	lifetime <sup>f</sup> $(\tau/ns)$	$\delta_2^{\max g}$ (GM <sup>g</sup> )
	316	122810	497	0.59	2.14	~1950
1	361	109500				
	436	95930				
	309	216070	507	0.69	2.29	~6100
2	366	231160				
	448	245000				

Table 1. Photophysical properties of the studied model compounds in solution phase.<sup>a</sup>

<sup>*a*</sup> All photophysical data were obtain in toluene as indicated. <sup>*b*</sup> The concentration was  $1 \times 10^{-6}$  M. <sup>*c*</sup> Linear absorption maxima. <sup>*d*</sup> One-photon-induced fluorescence emission maxima. <sup>*e*</sup> Fluorescence quantum efficiency. <sup>*f*</sup> Fluorescence lifetime; <sup>*g*</sup> Local maxima of two-photon absorption;  $1\text{GM} = 1 \times 10^{-50} \text{ cm}^4 \text{ s/photon-molecule.}$ 

	Film Thickness (nm)	$\lambda_{max}^{Abs}$ a (nm)	$\lambda_{max}^{Em}$ b (nm)	$\Phi_{F}^{c}$
1	109	317	561	0.15
		362		
		437		
2	107	309	538	0.21
		366		)
		448		

**Table 2.** Photophysical properties of the studied model compounds in neat-film state.

<sup>a</sup> Linear absorption maxima; <sup>b</sup> Fluorescence maximum; <sup>c</sup> Fluorescence quantum yield.



Figure 1. The molecular structures of the studied chromophores 1 and 2.



Figure 2. Linear absorption and fluorescence spectra (see the inset) of compounds 1 and 2 in toluene.



Figure 3. (a) 2PA-induced fluorescence emission spectra of **1** and **2** in toluene; (b)-(c) the log-log plots of power-squared dependence of the 2PA-induced fluorescence intensity on the input intensity of these compounds in toluene; (b) Degenerate 2PA spectra of **1** and **2** by 2PEF method in toluene solution at  $1 \times 10^{-4}$ M (with experimental error ~15%).



Figure 4. (a) Measured nonlinear transmission of a 1-cm path-length compound **2** solution in toluene (0.03 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  $\beta = 1.7$ cm/GW. ( $\beta$  is the 2PA coefficient)



Figure 5. Normalized two-photon excitation efficiency distribution of 2 the in neat-film state. For the purpose of comparison the 2PA spectrum of 2 in solution phase is included; inset photo: Close shot of the neat-film fabricated from compound 2 and the fluorescence spot under the irradiation of femtosecond laser pulses at ~800 nm.





Figure 6. (a) Normalized three-photon-excited fluorescence spectrum of compound **2** in toluene at  $2 \times 10^{-3}$ M. Inset curve: power dependence of the measured fluorescence intensity on the input intensity. Inset photo: three-photon-excited fluorescence; (b) Effective three-photon-excitation spectra of chromophores **1** and **2**; (c) Order of the absorption process (OAP) as a function of excitation wavelength.



Scheme 1. The synthetic procedures toward key precursors.



Scheme 2. Preparation methods of the targeted model compounds.

## Highlights

[1] Two dendritic chromophores derived from carbazole and indenoquinoxaline units have been synthesized and characterized.

[2] These fluorophores exhibit strong and wide dispersed two- and three-photon absorption in the near infrared (NIR) region.

[3] Two-photon-based optical-power-limiting of a representative dye molecule is demonstrated in the femtosecond regime.

[4] Two-photon-related properties of the spin-coated neat-film based on one of the model compound were studied.