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Two-photon absorption and effective optical power-limiting properties of small dendritic chromophores derived from functionalized fluorene/oxadiazole units

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ABSTRACT

A set of novel multi-branched chromophores composed of four analogues with generic skeletons of donor- π -acceptor (D- π -A) derived from functionalized fluorene/oxadiazole moieties has been synthe-sized and experimentally shown to possess strong and wide-dispersed two-photon absorptivities in near infrared (NIR) region under the irradiation of femtosecond laser pulses. It is demonstrated that structural parameters, such as the size of π -framework and the number of electron-donating units attached are closely connected to the molecular two-photon activities of these model compounds. Effective optical power-attenuation behaviors in the nanosecond time domain of the studied chromophores were also investigated and the results indicate that such dye molecules can be potential materials as broadband and quick-responsive optical-limiters especially against those laser lights with longer pulses.

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1. Introduction

Two-photon absorption (2PA) phenomenon was theoretically predicted by Maria Göppert-Mayer in 1931,¹ but its experimental evidence came out about thirty years later when scientists observed up-converted emission from the media under the irradiation of laser light with wavelengths far from the linear absorption bands of the studied media.² In conjunction with the intrinsic quadratic dependence of the incident light intensity in this nonlinear optical process, numerous 2PA-based photonic and biophotonic applications have been proposed and explored 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.³ In order to be applicable in these applications, organic compounds that exhibit large 2PA within desired spectral region are consequently in great demand. So far, it has been realized that molecular 2PA is related to the combination of several structural parameters, such as intramolecular charge-transfer efficiency and/or effective size of π conjugation domain within a molecule.^{4–9} Depending on the application, other photophysical properties in addition to strong molecular 2PA may also be required for the designed molecules because of various practical needs. For instance, in the case of optical power-limiting in nanosecond regime, compounds with extended excited-state lifetime may benefit the apparent nonlinear absorption due to two-photon-assisted excited-state absorption (2PA-assisted ESA)¹⁰ and can be used as optical power-limiters against long laser pulses. In searching the connection between structural parameters and two-photon absorption properties in conjugated systems, we are interested in exploring the influence that may be caused by the electronic properties of the selected building units and the number of π -branches on the molecular 2PA when constructing multi-branched π -frameworks. In this paper we present the synthesis of a new series of two-photon-active model chromophores (1-4) derived from functionalized fluorene and oxadiazole moieties as well as the initial investigations of their 2PArelated properties both in the femtosecond and nanosecond time domains.

2. Results and discussion

2.1. Molecular structures and syntheses

The chemical structures and the synthetic routes toward the studied model compounds are illustrated in Fig. 1 and Schemes 1-3. This model compound set contains four structural congeners with one possessing quasi-linear type structure (compound **1**) and



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Fig. 1. Molecular structures of the studied chromophores in this work.

other three having multi-branched skeleton (compounds 2-4). All these compounds are with generic structure of donor- π -acceptor $(D-\pi-A)$ using functionalized fluorene and oxadiazole units to construct their unsymmetric backbones with different numbers of π -branches. The original design concept of these model compounds is to tentatively construct a set of structurally unsymmetric π -frameworks with various numbers of electron-donating units attached so that the resulting fluorophores may possess multipolar character and different manners of charge-transfer/ redistribution upon light excitation. On the other hand, the pendent alkyl chains on all fluorenyl moieties in these chromophores are expected to enhance their solubility in common organic solvents and this is indeed another important parameter to be considered in the molecular design from either the aspect of experiments or applications. The synthetic procedures toward these model dye molecules are relatively straightforward, which majorly involve consecutive functionalization processes on the fluorene moiety and Buchwald–Hartwig type amination to prepare the key intermediates and the final model compounds as shown in Schemes 1–3. The detailed syntheses including the preparation of the key intermediates (8, 10, 13, 16, 21, and 22) and the final catalytic coupling reactions to accomplish the targeted compounds are described in the Experimental section.

2.2. Optical properties characterization

2.2.1. One-photon absorption (1PA) and fluorescence spectra measurement. Fig. 2 presents the linear absorption and fluorescence spectra of the studied dye molecules in solution phase using THF as the solvent. Intense one-photon absorption (1PA) was found around 385 nm for compound **1** (with $\varepsilon_{max} \sim 5.1 \times 10^4 \text{ cm}^{-1} \text{ M}^{-1}$) and 400 nm for compounds **2–4** (with $\varepsilon_{max} \sim 1.01 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ for **2**, $\varepsilon_{max} \sim 2.17 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ for **3**, and $\varepsilon_{max} \sim 3.77 \times 10^5 \text{ cm}^{-1} \text{ M}^{-1}$ for **4**). All the studied chromophore solutions emit visible fluorescence under the irradiation of a common UV-lamp with blue color for compound **1** and greenish-blue for compounds **2–4**.

2.2.2. Two-photon-excited fluorescence (2PEF) emission properties. The studied model chromophores also manifest intense twophoton-excited upconversion emission which can be easily observed by naked eyes even under the illumination of an ~790 nm unfocused femtosecond laser beam at low intensity level. Fig. 3(a) illustrates the 2PA-induced fluorescence spectra of these model chromophores in solution phase. The sample solutions were freshly prepared at concentration of 1×10^{-4} M in THF for this measurement and the excitation source utilized for this two-photon induced fluorescence study is from a mode-locked Ti:Sapphire laser (Tsunami



Scheme 1. The synthetic routes toward each electron-donating intermediate for the construction of the studied chromophores.

pumped with a Millennia 10W, Spectra-Physics), which delivers ~80 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 in order to avoid the saturation of absorption and photodegradation. To minimize the effect of re-absorption due to the relatively high concentration of the sample solution used in this measurement, we have focused the excitation beam as close as possible to the wall of the quartz cell (5 mm×5 mm cuvette) so that only the emission from the surface of the sample was recorded. It can be seen in Fig. 3(a) that for each studied chromophore the shape and spectral position of measured 2PA-induced emission is basically identical to its corresponding 1PA-induced fluorescence band shown in Fig. 1. This result 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 were also examined. Fig. 3(b)-(e) are logarithmic plots of the measured data and the results confirm 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 based on the timecorrelated single photon counting (TCSPC) technique using a highly sensitive photomultiplier equipped with accumulating real-time processor as the detection system (PMA-182 and TimeHarp 200, PicoQuant). The same Ti:Sapphire laser system (vide supra) was employed for this experiment. The measured 2PA-induced fluorescence decay curves of the studied compound solutions are depicted in Fig. 3(f). Theoretical fitting of each decay curve by single-exponential dependence has revealed that these fluorophores exhibit fluorescence lifetime ranging from 2.2 ns to 3.3 ns and these data are collected in Table 1.

2.2.3. Degenerate two-photon absorption spectra measurement. In order to probe and compare the dispersion of 2PA behaviors of



Scheme 2. The synthesis of the major electron-pulling π -bridges.



Scheme 3. Coupling reactions toward targeted fluorophores.

these dye molecules across the wavelengths, we have conducted the degenerate two-photon-excited fluorescence (2PEF) measurement in the near-IR regime (700–850 nm) using Fluorescein (~80 μ M in pH=11 NaOH solution) as the standard.¹¹ Fig. 4 shows the measured degenerate two-photon absorption spectra of these model compounds in THF (at the concentration of 1×10^{-4} M) and the combined photophysical data are summarized in Table 1. It is notable that all these model chromophores exhibit detectable 2PA within the investigated spectral range and possess an overall ascending capability of 2PA from compound **1** to compound **4**.

2.3. Discussion of results

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

(1) Using compound **1** as a reference point, the observed ascending 2PA from compound **1** to compound **4** suggests that



Fig. 2. Linear absorption and fluorescence spectra (see the inset) of compounds 1–4 in solution phase $(1 \times 10^{-5} \text{ M in THF})$.

simultaneously extending the size of π -domain by increasing the number of electron-donating branches attached to the original D- π -A framework of compound **1** could be an effective approach toward strong molecular 2PA. Besides, it can be seen from Fig. 4 that chromophores **2–4** exhibit nearly identical dispersion manner of 2PA with a common local maximum positioned around 830 nm and this feature reveals that continuous expansion of the π -conjugation of this molecular system under the aforementioned construction concept seems to provide a beneficial access to enhance the molecular 2PA without shifting the major 2PA band, which could be very useful for some particular applications when large multiphoton absorptivities in a specific spectral region is required.

(2) Based on the fact that the measured fluorescence emission spectra (shown in Figs. 1 and 2) for each sample solution are



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

Table 1Photophysical properties of the studied model chromophores $1-4^a$

	λ_{max}^{abs}/nm^b	$log \epsilon_{max}$	λ_{max}^{em}/nm^c	$\Phi_F{}^{\mathbf{d}}$	$\tau_{\text{2PA}-\text{FL}}/\text{ns}^{\text{e}}$	δ_2^{max}/GM^f	$N_{\pi}^{e\!f\!fg}$	$\delta_2^{\rm max}/N_\pi^{\rm eff}$
1	386	4.71	454	0.59	2.2	~185	23.6	7.8
2	396	5.00	518	0.40	3.3	~675	30.3	22.3
3	397	5.34	519	0.43	3.3	~1350	40.4	33.4
4	398	5.58	520	0.43	2.2	~2990	55.5	53.9

 a Concentration was $1{\times}10^{-5}$ M and $1{\times}10^{-4}$ M for 1PA-related and 2PA-related measurements, respectively.

^b One-photon absorption maximum.

^c 1PA-induced fluorescence emission maximum.

^d Fluorescence quantum efficiency.

e 2PA-indueced fluorescence lifetime.

 f Maximum 2PA cross-section value (with experimental error ~±15%); 1 GM=1×10^{-50} cm^4 s/photon-molecule.

^g Effective π -electron number.

nearly the same for one- and two-photon excitations, one can conclude that in these cases, the fluorescence emission is predominantly from the same relaxed excited-state of each model chromophore.¹² On the other hand, the observed medium-level quantum yields from these compounds also indicates that these chromophores could be utilized as frequency upconverters for the biophotonic applications, such as two-photon-excited fluorescence microscopy.

(3) It is notable that the excited-state lifetimes of the studied model chromophores in the present work are in the nanosecond range, which implies that significant excited-state population may be retained and consequently possessess excited-state absorption during the excitation by longer laser pulses. This feature is particularly desirable with regards to optical power-limiting applications in the nanosecond regime based on 2PA-induced excited-state absorption (2PAinduced ESA) since the effective three-photon absorption coefficient increases significantly with the excited-state lifetime.^{10f}



Fig. 4. Measured degenerate two-photon absorption spectra of model chromophores **1–4** by 2PEF method in THF solution at 1×10^{-4} M (with experimental error $\sim \pm 15\%$).

3. Effective optical power-limiting behaviors in nanosecond regime

It is well known that an ideal optical-limiter is expected to show an intensity-dependent transmission feature so that the output intensity always below a certain maximum value, which makes optical-limiters applicable for automatic protection of human eyes and sensors against intense laser radiation. Additionally, this power-limiting phenomenon is also important for optical dynamic range compression and noise suppression in signal processing as well as nonlinear ultra-fast filtering/reshaping of optical fiber signals. Compared to other mechanisms of optical power-limiting, such as reverse saturable absorption and nonlinear scattering,¹³ the 2PA mechanism provides several promising advantages includes: (1) Negligible linear absorption loss for weak optical signals; (2) quick temporal response to the intensity or power change of the incident optical signal; and (3) retention of optical quality for the input beam after passing through the nonlinear absorption medium.

Recently, many researchers have realized that the intensitydependent 2PA-induced excited-state absorption plays an essential role for the observed large 2PA in various organic systems under the irradiation of nanosecond laser pulses,¹⁰ and the term '*effective* 2PA' is consequently used to describe the apparent 2PA parameter measured in nanosecond time domain.^{9b,10b} From the viewpoint of application, any medium that exhibits strong apparent nonlinear absorption covering wide spectral range could be very useful optical power-attenuators against the laser pulses working in nanosecond time domain.^{3c,14}

In order to study the effective power-limiting performance of these model chromophores, we have utilized nanosecond laser pulses for this investigation. In our experiment, the nonlinear absorbing medium was a 1-cm path-length solution of each studied dye in THF with concentration of 0.02 M. A tunable nanosecond laser system (an integrated Q-switched Nd:YAG laser and OPO: NT 342/3 from Ekspla) was employed as an excitation laser light source to provide ~ 6 ns laser pulses with controlled average pulse energy in the range of \sim 0.02–2 mJ and repetition rate of 10 Hz for this study. The laser beam was slightly focused onto the center of the sample solution in order to obtain a nearly uniform laser beam radius within the whole cell path-length and the transmitted laser beam from the sample cell was detected by an optical power (energy) meter with a large detection area of ~ 25 mm in diameter. Fig. 5 illustrates the measured power-attenuation performance at \sim 800 nm based on these chromophore solutions. One can see that compound **4** displays the superior power restriction property at 800 nm compared to the other congeners. This initial finding suggests the potentiality of using this model fluorophore for broadband power-suppressing-related applications in the nanosecond regime.



Fig. 5. Measured optical power-attenuation curves at ${\sim}800$ nm based on the studied chromophore solutions at 0.02 M.

4. Conclusion

We have synthesized a novel multi-polar chromophore set composed of four members of analogues with unsymmetric substituted skeletons using functionalized fluorene and oxadiazole moieties as the major building units. The initial experimental results indicate that these model fluorophores manifest strong and wide-dispersed two-photon absorptivities in the near IR-region. Tentative analysis of the correlation between molecular structure and the observed overall 2PA reveals that repeatedly increase the number of electron-donating branches while extending the size of π -domain based on a D- π -A skeleton will enhance the molecular 2PA without shifting the major 2PA band in this dye system. Moreover, effective optical power-limiting behaviors of the dendritic fluorophores were also demonstrated to show that such dye molecules can be potential materials as broadband and quick-responsive optical-limiters especially against those laser lights with longer pulses.

5. Experimental

5.1. General

All commercially available reagents for the preparation of the intermediates and targeted chromophores were purchased from Aldrich Chemical Co. and were used as received, unless stated otherwise. ¹H NMR and ¹³C NMR spectra were recorded either at 200 or 300 MHz spectrometers and referenced to TMS or residual CHCl₃. High-resolution mass spectroscopy (HRMS) was conducted by using a Waters LCT ESI-TOF mass spectrometer. MALDI-TOF MS spectra were obtained on a Voyager DE-PRO mass spectrometer (Applied Biosystem, Houston, USA). IR spectra were measured by a Fourier transform infrared spectrometer (Jasco, FT/IR 4100).

5.2. Photophysical methods

All the linear optical properties of the subject model compound were measured by corresponding spectrometers and the detailed experimental conditions as well as the optical set-ups for nonlinear optical property investigations are described in the Supplementary data.

5.3. Synthesis

In Schemes 1 and 2, compound **5** (2,7-dibromo-9,9-dihexyl-9*H*-fluorene) is the major starting material for the synthesis of the backbones of each intermediates and model chromophores. This compound was obtained in a total yield of ~80% by applying bromination and then alkylation on a fluorene unit.¹⁵ For the synthesis of other key intermediates (compounds **6**–**22**) and the targeted model compounds (**1**–**4**), a series of functionalization steps starting from compound **5** have been conducted and are presented as the following:

5.3.1. 7-Bromo-9,9-dihexyl-N,N-diphenyl-9H-fluoren-2-amine (6). To a mixture of compound 5 (30 g; 0.06 mol) and diphenylamine (11.34 g; 0.067 mol) in toluene (120 mL) was added of BINAP (1.14 g; 1.8 mmol), Pd₂(dba)₃ (0.56 g; 0.6 mmol), sodium *tert*-butoxide (8.2 g; 0.084 mol) and stirred at 80 °C under Ar atmosphere for 24 h. After cooling to the room temperature, ~ 100 mL of H₂O was added to the reaction mixture. The above solution was then extracted with ethyl acetate and then dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using hexane as the eluent to give the final purified product as pale-yellow oil with yield of ~55% (19.44 g). IR (KBr, cm^{-1}): 3063, 3033 (C(*sp*²)–H stretching absorptions), 2954, 2925, 2853 (C(*sp*³)–H stretching absorptions), 1608, 1482 (stretching absorptions of benzene rings), 1466 (CH₂ bending absorption), 1375 (CH₃ bending absorption), 1300 (Ar-N stretching absorption). ¹H NMR (200 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.54–7.50 (d, *J*=8.1 Hz, 1H, ArH on the fluorene unit), 7.50–7.44 (d, *J*=8.1 Hz, 1H, ArH on the fluorene unit), 7.45–7.40 (dd, *J*₁=8.1 Hz, *J*₂=3 Hz, 2H, ArH on the fluorene unit), 7.30-7.22 (m, 4H, ArH on the diphenylamino group), 7.14–7.11 (dd, J₁=8.1 Hz, J₂=3 Hz, 2H, ArH on the diphenylamino group), 7.10–7.07 (m, 4H, ArH on the diphenylamino group), 7.05-6.98 (m, 2H, ArH on the fluorene unit), 1.87-1.79 (m, 4H, CH₂CH₃), 0.81 (t, J=7.04 Hz, 6H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.64 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 152.79 (aromatic carbon on the fluorene unit), 151.67 (aromatic carbon on the fluorene unit), 147.82 (aromatic carbon on the diphenylamino group), 147.49 (aromatic carbon on the fluorene unit), 139.88 (aromatic carbon on the fluorene unit), 135.00 (aromatic carbon on the fluorene unit), 129.87 (aromatic carbon on the diphenylamino group), 129.13 (aromatic carbon on the fluorene unit), 125.89 (aromatic carbon on the fluorene unit), 123.41 (aromatic carbon on the fluorene unit), 122.85 (aromatic carbon on the fluorene unit), 120.41 (aromatic carbon on the fluorene unit), 122.58 (aromatic carbon on the diphenylamino group), 120.43 (aromatic carbon on the fluorene unit), 120.36 (aromatic carbon on the diphenylamino group), 120.14 (aromatic carbon on the fluorene unit), 119.01 (aromatic carbon on the fluorene unit), 55.26 (sp³-carbon on the fluorene unit), 40.10 (carbon on the alkyl chain), 31.44 (carbon on the alkyl chain), 29.51 (carbon on the alkyl chain), 23.66 (carbon on the alkyl chain), 22.50 (carbon on the alkyl chain), 14.03 (carbon on the alkyl chain); HRMS-FAB(m/z): $[M+H]^+$ calcd for C₃₇H₄₂BrN, 579.2501, found $[(^{79}Br)M+H]^+=579.2507; [(^{81}Br)M+H]^+=281.2483.$

5.3.2. 7-(Diphenylamino)-9,9-dihexyl-9H-fluorene-2-carbonitrile (7). To a mixture of compound **6**(8 g: 13.8 mmol) in dry DMF(50 mL) was added CuCN (2.48 g; 27.4 mmol), then stirred and under reflux for 12 h. After cooling to the room temperature, the reaction was poured into NH₄OH_(aq) (\sim 100 mL) and stirred for 1 h. The above solution was then extracted with ethyl acetate and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using ether/hexane (1:20) as the eluent to give the final purified product as orange powder with yield of 87.5% (6.81 g). Mp: 79.9–82.1. IR (KBr, cm⁻¹): 3071, 3034 (C(*sp*²)–H stretching absorptions), 2958, 2927, 2854 (C(sp³)–H stretching absorptions), 2220 (C≡N stretching absorption), 1592, 1472 (stretching absorptions of benzene rings), 1463 (CH₂ bending absorption), 1376 (CH₃ bending absorption), 1312 (Ar–N stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.64–7.61 (m, 2H, ArH on the fluorene unit), 7.59-7.57 (m, 1H, ArH on the fluorene unit), 7.56–7.53 (d, J=7.5 Hz, 1H, ArH on the fluorene unit), 7.29–7.24 (t, *J*=7.2 Hz, 4H, ArH on the diphenylamino group), 7.14 (s, 1H), 7.11–7.09 (m, 2H, ArH on the diphenylamino group), 7.07–7.05 (dd, *J*₁=7.2 Hz, *J*₂=1.2 Hz, 1H, ArH on the fluorene unit), 7.07–7.05 (m, 4H, ArH on the diphenylamino group), 1.91-1.79 (m, 4H, CH₂CH₃), 0.82-0.77 (t, 6H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.64-0.59(d, 4H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 152.75 (aromatic carbon on the fluorene unit), 151.06 (aromatic carbon on the fluorene unit), 148.85 (aromatic carbon on the fluorene unit), 147.47 (aromatic carbon on the diphenylamino group), 145.46 (aromatic carbon on the fluorene unit), 133.44 (aromatic carbon on the fluorene unit), 131.27 (aromatic carbon on the fluorene unit), 129.20 (aromatic carbon on the diphenylamino group), 126.03 (aromatic carbon on the fluorene unit), 124.31 (aromatic carbon on the fluorene unit), 123.09 (aromatic carbon on the diphenylamino group), 122.68 (aromatic carbon on the diphenylamino group), 121.44 (aromatic carbon on the fluorene unit), 119.89 (aromatic carbon on the fluorene unit), 119.26 (aromatic carbon on the fluorene unit), 117.90 (carbon on the cyano group), 108.62 (aromatic carbon on the fluorene unit), 55.24 (*sp*³-carbon on the fluorene unit), 39.82 (carbon on the alkyl chain), 31.33 (carbon on the alkyl chain), 29.36 (carbon on the alkyl chain), 23.59 (carbon on the alkyl chain), 22.39 (carbon on the alkyl chain), 13.91 (carbon on the alkyl chain); HRMS-FAB(*m*/*z*): M⁺ calcd for C₃₈H₄₂N₂, 526.3348, found, 526.3342.

5.3.3. 9,9-Dihexyl-N,N-diphenyl-7-(1H-tetrazol-5-yl)-9H-fluoren-2*amine* (8). To a mixture of compound 7 (6 g; 11.4 mmol), and NaN_3 (0.88 g; 13.7 mmol) in toluene (20 mL) was added (n-Bu)₃SnCl (3.7 mL: 13.7 mmol), then stirred and refluxed in Ar for 24 h. After cooling to the room temperature, the above solution was then extracted with CH_2Cl_2 and the organic layer was dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:1) as the eluent to give the yellow purified product with yield of 80.2% (5.2 g). IR (KBr, cm⁻¹): 3061, 3036 ($C(sp^2)$ –H stretching absorptions), 2926, 2856 ($C(sp^3)$ –H stretching absorptions), 1610, 1488 (stretching absorptions of benzene rings), 1585 (N=N stretching absorption) 1469 (CH₂ bending absorption), 1376 (CH₃ bending absorption), 1340 (Ar–N stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.27 (s, 1H, ArH on the fluorene unit), 8.25–8.22 (dd, J₁=8.1 Hz, J₂=1.2 Hz, 1H, ArH on the fluorene unit), 7.77–7.74 (d, *J*=8.1 Hz, 1H, ArH on the fluorene unit), 7.59, 7.56 (d, J=8.1 Hz, 1H, ArH on the fluorene unit), 7.27–7.22 (t, J=7.2 Hz, 4H, ArH on the diphenylamino group), 7.12–7.10 (m, 6H, ArH on the diphenylamino group), 7.04–6.99 (m, 2H, ArH on the fluorene unit), 2.12–1.70 (m, 4H, -CH₂CH₂CH₂CH₂CH₂ CH₂CH₃), 1.09–0.98 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.73–0.69 $-CH_2CH_2CH_2CH_2CH_2CH_3$), 0.64–0.62 (m, 6H. 4H. (t, -CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 156.89 (carbon on tetrazole unit), 152.91 (aromatic carbon on the fluorene unit), 152.03 (aromatic carbon on the fluorene unit), 148.39 (aromatic carbon on the fluorene unit), 147.75 (aromatic carbon on the diphenylamino group), 144.82 (aromatic carbon on the fluorene unit), 134.49 (aromatic carbon on the fluorene unit), 129.22 (aromatic carbon on the diphenylamino group), 126.73 (aromatic carbon on the fluorene unit), 124.16 (aromatic carbon on the diphenylamino group), 123.13 (aromatic carbon on the fluorene unit), 122.89 (aromatic carbon on the diphenylamino group), 121.95 (aromatic carbon on the fluorene unit), 121.20 (aromatic carbon on the fluorene unit), 120.53 (aromatic carbon on the fluorene unit), 119.88 (aromatic carbon on the fluorene unit), 118.62 (aromatic carbon on the fluorene unit), 55.54 (sp³-carbon on the fluorene unit), 40.06 (carbon on the alkyl chain), 31.45 (carbon on the alkyl chain), 29.50 (carbon on the alkyl chain), 23.78 (carbon on the alkyl chain), 22.46 (carbon on the alkyl chain), 13.96 (carbon on the alkyl chain); HRMS-FAB(m/z): M⁺ calcd for C₃₈H₄₃N₅, 569.3518, found, 569.3525.

5.3.4. 9,9-Dihexyl-N²,N²-diphenyl-9H-fluorene-2,7-diamine (9). Two-step reaction: (i) To a solution of compound 6 (15 g; 0.258 mol) in DMAc (135 mL) was added potassium phthalimide (4.77 g; 0.258 mol), and CuI (4.92 g; 0.258 mol). The resulting solution was stirred and refluxed for 24 h. After cooling to the room temperature, the reaction mixture was then extracted with ether and then dried over MgSO_{4(S)}. After removing the solvent, the crude product was obtained as dark brown solid. (ii) To a solution of the crude product from first step in ethanol (150 mL) was added of NH₂NH₂·H₂O (1.293 g; 0.258 mol). The resulting solution was stirred and refluxed for 6 h. After cooling to the room temperature, the reaction mixture was then extracted with ethyl acetate (30mL×3), and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified by column chromatography on silica gel using ether/hexane (1:10) as the eluent to give the final purified product as brown powder with yield of \sim 62% (8.31 g). Mp: 117.1–119.2. IR (KBr, cm⁻¹): 3458, 3426 (N–H stretching absorptions), 3214 (C(*sp*²)–H stretching absorption), 2954, 2926, 2854 $(C(sp^3)$ —H stretching absorptions), 1630 (NH₂ bending absorption), 1610, 1468 (stretching absorptions of benzene rings), 1456 (CH₂ bending absorption), 1375 (CH₃ bending absorption), 1098 (Ar-N stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.43–7.40 (t, J=8.4 Hz, 2H, ArH on the fluorene unit), 7.23–7.18 (t, J=8.4 Hz, 4H, ArH on the diphenylamino group), 7.11-7.09 (m, 4H, ArH on the diphenylamino group), 7.08–7.07 (s, 1H, ArH on the fluorene unit), 7.00–6.97 (m, 1H, ArH on the diphenvlamino group), 6.96–6.92 (m. 2H. ArH on the fluorene unit), 6.61-6.59 (m, 2H, ArH on the fluorene unit). 3.689-3.66 (s, 2H, NH₂ on the amino group), 1.87-1.79 (m, 4H, CH₃), 0.81 (t, *J*=8.4 Hz, 6H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.64 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 152.51 (aromatic carbon on the fluorene unit), 151.09 (aromatic carbon on the fluorene unit), 148.08 (aromatic carbon on the diphenylamino group), 145.38 (aromatic carbon on the fluorene unit), 137.25 (aromatic carbon on the fluorene unit), 132.15 (aromatic carbon on the fluorene unit), 128.96 (aromatic carbon on the diphenylamino group), 124.03 (aromatic carbon on the fluorene unit), 123.22 (aromatic carbon on the diphenylamino group), 121.93 (aromatic carbon on the diphenylamino group), 119.97 (aromatic carbon on the fluorene unit), 119.89 (aromatic carbon on the fluorene unit), 118.89 (aromatic carbon on the fluorene unit), 113.87 (aromatic carbon on the fluorene unit), 109.68 (aromatic carbon on the fluorene unit), 54.72 (sp^3 -carbon on the fluorene unit), 40.42 (carbon on the alkyl chain), 31.46 (carbon on the alkyl chain), 29.60 (carbon on the alkyl chain), 23.65 (carbon on the alkyl chain), 22.49 (carbon on the alkyl chain), 13.97 (carbon on the alkyl chain); HRMS-FAB(m/z): M⁺ calcd for C₃₇H₄₄N₂, 516.3504. found. 516.3505.

5.3.5. N²-(7-(Diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl)-9,9*dihexyl-N⁷,N⁷-diphenyl-9H-fluorene-2,7-diamine (10).* To a mixture of compound 9 (8.3 g; 0.161 mol), and 6 (9.3 g; 0.161 mol) in dry toluene (15 mL) was added Pd₂(dba)₃ (0.073 g; 0.0803 mmol), sodium *tert*-butoxide (1.852 g; 0.193 mol), P(*t*-Bu)₃ (0.0322 g; 0.161 mmol) and stirred at 90 °C under Ar atmosphere for 12 h. After cooling to the room temperature, $\sim 100 \text{ mL of H}_20$ was added to the reaction mixture. The above solution was then extracted with ethyl acetate (30mL×3) and the organic layer was dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using ether/ hexane (1:20) as the eluent to give the final purified product as gray power with yield of ~60.2% (4.91 g). Mp: 129.9-132.3. IR (KBr, cm⁻¹): 3392 (N–H stretching absorption), 3061, 3033 (C(*sp*²)–H stretching absorptions), 2953, 2925, 2854 (C(*sp*³)–H stretching absorptions), 1597, 1473 (stretching absorptions of benzene rings), 1464 (CH₂ bending absorption), 1378 (CH₃ bending absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.52–7.48 (m, 4H, ArH on the fluorene unit), 7.36–7.32 (m, 4H, ArH on the fluorene unit), 7.30-7.22 (m, 4H, ArH on the diphenylamino group), 7.26-7.20 (t, J=8.1 Hz, 8H, ArH on the diphenylamino group), 7.12-7.10 (t, J=8.1 Hz, 12H, ArH on the diphenylamino group), 7.02–6.95 (m, 4H, ArH on the fluorene unit), 6.42 (s, 1H, NH on the amino group), 1.84-1.79 (m, 8H, $-CH_2CH_2CH_2CH_2CH_3),$ 1.15-1.08 24H, (m. CH₂CH₃), 0.64 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 152.62 (aromatic carbon on the fluorene unit), 150.47 (aromatic carbon on the fluorene unit), 148.06 (aromatic carbon on the diphenylamino group), 147.49 (aromatic carbon on the fluorene unit), 132.46 (aromatic carbon on the fluorene unit), 131.23 (aromatic carbon on the fluorene unit), 129.03 (aromatic carbon on the diphenylamino group), 127.06 (aromatic carbon on the fluorene unit), 125.89 (aromatic carbon on the fluorene unit), 123.83 (aromatic carbon on the fluorene unit), 122.85 (aromatic carbon on the fluorene unit), 121.66 (aromatic carbon on the fluorene unit), 120.98 (aromatic carbon on the diphenylamino group), 120.43 (aromatic carbon on the fluorene unit), 120.05 (aromatic carbon on the diphenylamino group), 118.14 (aromatic carbon on the fluorene unit), 112.01 (aromatic carbon on the fluorene unit), 54.93 (sp^3 -carbon on the fluorene unit), 40.47 (carbon on the alkyl chain), 31.60 (carbon on the alkyl chain), 23.84 (carbon on the alkyl chain), 22.60 (carbon on the alkyl chain), 14.05 (carbon on the alkyl chain); HRMS (m/z): M⁺ calcd for C₇₄H₈₅N₃ 1015.6743, found, 1015.6738.

5.3.6. 7-Bromo-9,9-(dihexyl-9H-fluoren-2-yl)trimethylsilane (11). n-Butyllithium in hexane (26.9 mL, 1.6 M, 0.043 mol) was added to a solution of 5 (20 g, 0.041 mol) in dry ether (150 mL) at -78 °C under N₂ atmosphere, and stirred for 1 h. Then chlorotrimethylsilane (6 mL, 0.0462 mol) was added slowly at -78 °C and the reaction was allowed to slowly warm to room temperature and stirred overnight. The reaction mixture was quenched with saturated brine and the resulting solution was extracted by diethyl ether. The organic layer was washed with brine and H₂O for three times and dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through chromatography on silica with hexane as eluent to give final purified product as a colorless oil (19.16 g, 97%). IR (KBr, cm⁻¹): 3201 (C(*sp*²)–H stretching absorption), 2954, 2925, 2853 (C(sp³)-H stretching absorptions), 1609, 1482 (stretching absorptions of benzene rings), 1455 (CH₂ bending absorption), 1376 (CH₃ bending absorption), 1305 (Ar–N stretching absorption), 1246 (Si–C stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.85–7.84 (d, J=7.8 Hz, 1H, ArH on the fluorene unit), 7.77–7.73 (m, 2H, ArH on the fluorene unit), 7.63-7.61 (m, 2H, ArH on the fluorene unit), 7.54–7.52 (d, J=7.8 Hz, 1H, ArH on the fluorene unit), 2.13-2.12 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃), 1.20-1.19 (m, 12H, CH₂CH₃), 0.64 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.46 (s, 9H, CH₃ on the TMS unit); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 153.07 (aromatic carbon on the fluorene unit), 149.17 (aromatic carbon on the fluorene unit), 140.68 (aromatic carbon on the fluorene unit), 139.96 (aromatic carbon on the fluorene unit), 139.71 (aromatic carbon on the fluorene unit), 132.09 (aromatic carbon on the fluorene unit), 129.89 (aromatic carbon on the fluorene unit), 127.41 (aromatic carbon on the fluorene unit), 126.19 (aromatic carbon on the fluorene unit), 121.44 (aromatic carbon on the fluorene unit), 121.07 (aromatic carbon on the fluorene unit), 119.06 (aromatic carbon on the fluorene unit), 55.20 (*sp*³-carbon on the fluorene unit), 40.03 (carbon on the alkyl chain), 31.30 (carbon on the alkyl chain), 29.50 (carbon on the alkyl chain), 23.57 (carbon on the alkyl chain), 22.45 (carbon on the alkyl chain), 14.00 (carbon on the alkyl chain), -0.89 (carbon on the TMS unit); HRMS-FAB(m/z): $[M+H]^+$ calcd for C₂₈H₄₁BrSi, 484.2161, found $[(^{79}Br)M+H]^+=484.2150; [(^{81}Br)M+H]^+=486.2150.$

5.3.7. 9,9-Dihexyl-7-(trimethylsilyl)-9H-fluoren-2-amine (**12**). Twostep reaction: (i) To a solution of compound **11** (19 g; 0.039 mol) in DMAc (45 mL) was added of potassium phthalimide (7.26 g; 0.039 mol), and Cul (7.44 g; 0.039 mol) was stirred and heated to reflux for 24 h. After cooling to the room temperature, the reaction mixture was then extracted with ether, dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was obtained as brown solid. (ii) To a solution of the crude product from first step in ethanol (300 mL) was added of $NH_2NH_2 \cdot H_2O$ (2.46 g; 0.039 mol) and the resulting solution was stirred and refluxed for 6 h. After cooling to room temperature, the reaction mixture was then extracted with ethyl acetate (30mL×3) and the collected organic layer was dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified by column chromatography on silica gel using ether/

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hexane (1:10) as the eluent to give the final purified product as white powder as pale-yellow oil with yield of 70.5% (11.62 g); IR (KBr, cm⁻¹): 3468, 3398 (N–H stretching absorptions), 3206 (C(*sp*²)–H stretching absorption), 2953, 2925, 2856 (C(*sp*³)–H stretching absorptions), 1624 (NH₂ bending absorption), 1609, 1482 (stretching absorptions of benzene rings), 1455 (CH₂ bending absorption), 1376 (CH₃ bending absorption), 1305 (Ar–N stretching absorption), 1246 (Si–C stretching absorption), ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.66–7.63 (d, J=7.5 Hz, 1H, ArH on the fluorene unit), 7.66–7.63 (d, *I*=7.5 Hz, 1H, ArH on the fluorene unit), 7.58–7.52 (m, 2H, ArH on the fluorene unit), 7.38–7.36 (d, J=7.5 Hz, 1H, ArH on the fluorene unit), 6.74–6.69 (m, 2H, ArH on the fluorene unit), 3.72 (s, 2H, NH₂ on on the amino group), 2.12 - 2.02(m, 4H. CH₃), 0.89–0.85 (m, 6H, –CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.78 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_3$), 0.41 (s, 9H, CH₃ on the TMS unit); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 152.44 (aromatic carbon on the fluorene unit), 149.62 (aromatic carbon on the fluorene unit), 145.86 (aromatic carbon on the fluorene unit), 141.49 (aromatic carbon on the fluorene unit), 132.27 (aromatic carbon on the fluorene unit), 131.62 (aromatic carbon on the fluorene unit), 126.48 (aromatic carbon on the fluorene unit), 125.21 (aromatic carbon on the fluorene unit), 122.42 (aromatic carbon on the fluorene unit), 120.32 (aromatic carbon on the fluorene unit), 118.20 (aromatic carbon on the fluorene unit), 113.78 (aromatic carbon on the fluorene unit), 109.59 (aromatic carbon on the fluorene unit), 54.65 (sp³-carbon on the fluorene unit), 40.61 (carbon on the alkyl chain), 31.47 (carbon on the alkyl chain), 29.73 (carbon on the alkyl chain), 23.61 (carbon on the alkyl chain), 22.55 (carbon on the alkyl chain), 13.94 (carbon on the alkyl chain), -0.90 (1° carbon on the TMS unit) HRMS-FAB (m/z): M⁺ calcd for C₂₈H₄₃NSi 421.3165, found, 421.7332.

5.3.8. Bis(9,9-dihexyl-7-(trimethylsilyl)-9H-fluoren-2-yl)amine (13). To a mixture of compound 12 (9 g; 0.0213 mol), and 11 (10.36 g; 0.0213 mol) in dry toluene (60 mL) was added Pd₂(dba)₃ (0.0976 g; 0.1064 mmol), sodium tert-butoxide (2.48 g; 0.256 mol), P(t-Bu)₃ (0.044 g; 0.2132 mmol) and stirred at 90 °C under Ar atmosphere for 12 h. After cooling to the room temperature, \sim 100 mL of H₂O was added to the reaction mixture. The above solution was then extracted with ethyl acetate (30mL×3) and the organic layer was over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:40) as the eluent to give the final purified product with yield of 55.6% (4.9 g). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.59-7.56 (m, 6H, ArH on the fluorene unit), 7.47-7.43 (m, 6H, ArH on the fluorene unit), 2.02–2.01 (m, 8H, –*CH*₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.14-1.12 (m, 24H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.79-0.75 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.65 (m, 8H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.30 (s, 18H, CH₃ on the TMS unit); IR (KBr, cm⁻¹): 3392 (N–H stretching absorptions), 3206 ($C(sp^2)$ –H stretching absorption), 2956, 2927, 2857 (C(sp³)-H stretching absorptions), 1597, 1473 (stretching absorptions of benzene rings), 1464 (CH₂ bending absorption), 1363 (CH₃ bending absorption). 1307 (Ar-N stretching absorption), 1247 (Si-C stretching absorption). ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 152.44 (aromatic carbon on the fluorene unit), 152.14 (aromatic carbon on the fluorene unit), 149.21 (aromatic carbon on the fluorene unit), 141.93 (aromatic carbon on the fluorene unit), 137.35 (aromatic carbon on the fluorene unit), 134.38 (aromatic carbon on the fluorene unit), 131.82 (aromatic carbon on the fluorene unit), 127.31 (aromatic carbon on the fluorene unit), 120.70 (aromatic carbon on the fluorene unit), 118.05 (aromatic carbon on the fluorene unit), 116.85 (aromatic carbon on the fluorene unit), 111.64 (aromatic carbon on the fluorene unit), 54.88 (sp^3 -carbon on the fluorene unit), 40.45 (carbon on the alkyl chain), 31.46 (carbon on the alkyl chain), 29.71 (carbon on the alkyl chain), 23.73 (carbon on the alkyl chain), 22.55 (carbon on the alkyl chain), 14.01 (carbon on the alkyl chain), -0.83 (1° carbon on the TMS unit); HRMS (m/z): M⁺ calcd for C₅₆H₈₃NSi₂ 825.6064, found, 825.6063.

5.3.9. Bis(9.9-dihexyl-7-(trimethylsilyl)-9H-fluoren-2-yl)carbamate (14). To a mixture of compound 13 (4.9 g; 6 mmol) in dry THF (45 mL) was added (Boc)₂O (2.59 g; 0.012 mol), 4-DMAP (0.362 g; 0.003 mmol) and stirred at 90 °C under N₂ atmosphere for 12 h. After cooling to the room temperature, the reaction mixture was then extracted with ethyl acetate and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:50) as the eluent to give the final purified product with yield of ~81% (4.45 g). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.69–7.64 (t, J=7.2 Hz, 4H, ArH on the fluorene unit), 7.54–7.52 (d, J=8.1 Hz, 4H ArH on the fluorene unit), 7.29-7.28 (d, J=8.1 Hz, 2H ArH on the fluorene unit), 7.24–7.21 (d, J=7.8 Hz, 2H ArH on the fluorene unit), 2.02-1.95 (m, 8H, -CH2CH2CH2CH2CH2CH3), 1.11-1.16 (m, 24H, -CH₂CH₂CH₂CH₂CH₂CH₃), 1.53 (s, 9H, CH₃ on the Boc group), 0.85-0.76 (m, 12H, -CH2CH2CH2CH2CH2CH3), 0.68 (m, 8H, $-CH_2CH_2CH_2CH_2CH_2CH_3$), 0.36 (s, 18H, CH₃ on the TMS group); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 153.75 (*sp*²-carbon on the Boc group), 151.27 (aromatic carbon on the fluorene unit), 149.98(aromatic carbon on the fluorene unit), 142.64 (aromatic carbon on the fluorene unit), 141.20 (aromatic carbon on the fluorene unit), 138.65 (aromatic carbon on the fluorene unit), 138.33 (aromatic carbon on the fluorene unit), 131.79 (aromatic carbon on the fluorene unit), 127.35 (aromatic carbon on the fluorene unit), 125.16 (aromatic carbon on the fluorene unit), 121.75 (aromatic carbon on the fluorene unit), 119.79 (aromatic carbon on the fluorene unit), 118.82 (aromatic carbon on the fluorene unit), 80.86 (4° carbon on the Boc group), 54.93 (sp^3 carbon on the fluorene unit), 40.12 (carbon on the alkyl chain), 31.38 (carbon on the alkyl chain), 29.55 (carbon on the alkyl chain), 28.28 (1° carbon on the Boc group), 23.62 (carbon on the alkyl chain), 22.46 (carbon on the alkyl chain), 13.98 (carbon on the alkyl chain), $-0.91(1^{\circ} \text{ carbon on the TMS unit})$; HRMS (*m*/*z*): M⁺ calcd for C₅₆H₈₃NSi₂ 925.6588, found, 925.6487.

5.3.10. tert-Butyl-bis(9,9-dihexyl-7-iodo-9H-fluoren-2-yl)carbamate (15). To a solution of compound 14 (4.45 g; 0.048 mol) in CH_2Cl_2 (20 mL) was added iodine monochloride (1.64 g; 0.01 mol) at 0 °C, then warm to room temperature and stirred for 4 h. ~50 mL of saturated NaHSO₃ solutions was added into the reaction mixture. The above solution was then extracted with dichloromethane $(30mL \times 3)$ and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1:40) to give the final purified product of \sim 75% (3.72 g). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.68–7.62 (t, J=7.5 Hz, 4H, ArH on the fluorene unit), 7.52–7.51 (d, J=8.1 Hz 4H, ArH on the fluorene unit), 7.29–7.28 (d, J=8.1 Hz, 2H, ArH on the fluorene unit), 7.24-7.22 (d, J=7.2 Hz, 2H, ArH on the fluorene unit), 1.81–1.78 (m, 8H, –CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.51 (s, 9H, CH₃ on the Boc group) 1.10–1.05 (m, 24H, $-CH_2CH_2CH_2CH_2CH_3),$ 0.84-0.76 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.65 (m, 8H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 152.75 (*sp*²-carbon on the Boc group), 151.11 (aromatic carbon on the fluorene unit), 150.87 (aromatic carbon on the fluorene unit), 149.87 (aromatic carbon on the fluorene unit), 141.54 (aromatic carbon on the fluorene unit), 141.10 (aromatic carbon on the fluorene unit), 138.95 (aromatic carbon on the fluorene unit), 137.25 (aromatic carbon on the fluorene unit), 130.24 (aromatic carbon on the fluorene unit), 128.91 (aromatic carbon on the fluorene unit), 128.95 (aromatic carbon on the fluorene unit), 120.25 (aromatic carbon on the fluorene unit), 118.59 (aromatic carbon on the fluorene unit), 118.26 (aromatic carbon on the fluorene unit), 92.18 (aromatic carbon on the fluorene unit), 80.88 (4° carbon on the Boc group), 54.89 (sp^3 -carbon on the fluorene unit), 39.84 (carbon on the alkyl chain), 31.26 (carbon on the alkyl chain), 29.48 (carbon on the alkyl chain), 21.83 (carbon on the Boc group), 22.89 (carbon on the alkyl chain), 21.83 (carbon on the alkyl chain), 12.85 (carbon on the alkyl chain), HRMS (m/z): M⁺ calcd for C₅₅H₇₃I₂NO₂ 1033.3731, found, 1033.8998.

5.3.11. N²-(7-(7-(Bis(7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2vl)amino)-9,9-dihexyl-9H-fluoren-2-ylamino)-9,9-dihexyl-9H-fluoren-2-yl)-N²-(7-(diphenylamino)-9,9-dihexyl-9H-fluoren-2-yl)-9,9dihexyl-N⁷,N⁷-diphenyl-9H-fluorene-2,7-diamine (**16**). Two-step reaction: (i) To a mixture of compound 15 (2.4 g; 2.321 mol), and 10 (4.718 g; 4.642 mol) in dry toluene (15 mL) was added Pd₂(dba)₃ (0.085 g; 0.093 mmol), sodium *tert*-butoxide (0.468 g; 4.874 mmol), P(t-Bu)₃ (0.038 g; 0.186 mmol) and stirred at 90 °C under Ar atmosphere for 12 h. After cooling to the room temperature, ~ 100 mL of H₂O was added to the reaction mixture. The above solution was then extracted with ethyl acetate (30mL×3) and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:20) as the eluent to give the final purified product with vield of ~78% (5.08 g). HRMS (m/z): M⁺ calcd for C₂₀₃H₂₄₁N₇O 2811.1313, found, 2812.8954. (ii) To a solution of compound from the first step in CH₂Cl₂ (30 mL) was added TFA (1.44 g; 0.013 mol), and stirred at room temperature under for 2 h. Then, ~ 50 mL of NaOH_(aq) was added into the reaction mixture, and the above solution was then extracted with dichloromethane ($30mL \times 3$) and then dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate/hexane (1:20) to give the final purified product as gray powder with yield of 84.6% (4.17 g). IR (KBr, cm⁻¹): 3395 (N–H stretching absorption), 3062, 3033 ($C(sp^2)$ –H stretching absorptions), 2953, 2926, 2855 ($C(sp^3)$ – H stretching absorptions), 1586, 1493 (stretching absorptions of benzene rings), 1465 (CH₂ bending absorption), 1377 (CH₃ bending absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.52–7.49 (m, 12H, ArH on the fluorene unit), 7.27-7.25 (m, 4H, ArH on the fluorene unit), 7.25-7.20 (m, 16H, ArH on the diphenylamino group), 7.13–7.10 (d, *J*=8.4 Hz, 24H, ArH on the diphenylamino group), 7.01-6.95 (m, 20H, ArH on the fluorene unit), 5.98 (s, 1H, NH on the amino group), 2.04-1.82 (m, 24H $-CH_2CH_2CH_2CH_2CH_3),$ 1.25 - 1.23(m. 72H. $-CH_2CH_2CH_2CH_2CH_3),$ 0.80 - 0.78(m. 36H. -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.65 (m, 24H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 152.83 (aromatic carbon on the fluorene unit), 151.89 (aromatic carbon on the fluorene unit), 147.21 (aromatic carbon on the diphenylamino group), 147.05 (aromatic carbon on the fluorene unit), 139.22 (aromatic carbon on the fluorene unit), 138.38 (aromatic carbon on the fluorene unit), 137.85 (aromatic carbon on the fluorene unit), 135.28 (aromatic carbon on the fluorene unit), 130.85 (aromatic carbon on the fluorene unit), 129.83 (aromatic carbon on the diphenylamino group), 126.79 (aromatic carbon on the fluorene unit), 124.81 (aromatic carbon on the fluorene unit), 123.41 (aromatic carbon on the diphenylamino group), 122.85 (aromatic carbon on the fluorene unit), 122.37 (aromatic carbon on the fluorene unit), 121.69 (aromatic carbon on the diphenylamino group), 120.51 (aromatic carbon on the fluorene unit), 120.36 (aromatic carbon on the fluorene unit), 120.29 (aromatic carbon on the fluorene unit), 120.14 (aromatic carbon on the fluorene unit), 119.01 (aromatic carbon on the fluorene unit), 117.20 (aromatic carbon on the fluorene unit), 55.26 (sp^3 -carbon on the fluorene unit), 40.10 (carbon on the alkyl chain), 31.44 (carbon on the alkyl chain), 29.51 (carbon on the alkyl chain), 23.66 (carbon on the alkyl chain), 22.50 (carbon on the alkyl chain), 14.03 (carbon on the alkyl chain); HRMS (m/z): M⁺ calcd for C₁₉₈H₂₃₃N₇ 2711.0155, found, 2712.0996.

5.3.12. 7-Bromo-9,9-dihexyl-9H-fluorene-2-carbonitrile (17). To a mixture of compound 5 (8 g; 0.016 mol) in dry DMF (50 mL) was added CuCN (1.3 g; 14.6 mmol), and stirred at 110 °C for 24 h. After cooling to the room temperature, $\sim 50 \text{ mL of NaOH}_{(aq)}$ was added to the reaction mixture. The above solution was then extracted with ethyl acetate and the organic layer was dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:20) as the eluent to give the final purified product as orange powder with yield of ~45% (3.21 g). Mp: 74.3–76.7. IR (KBr, cm^{-1}): 3068, 3051 (C(*sp*²)–H stretching absorptions), 2947, 2922, 2853 (C(*sp*³)–H stretching absorptions), 2224 (C=N stretching absorption), 1608, 1454 (stretching absorptions of benzene rings), 1463 (CH₂ bending absorption), 1376 (CH₃ bending absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 7.75–7.72 (dd, *J*₁=8.1 Hz, *J*₂=0.6 Hz, 1H, ArH on the fluorene unit), 7.65–7.58 (m, 3H, ArH on the fluorene unit), 7.52–7.49 (m, 2H, ArH on the fluorene unit), 2.00–1.90 (t, *I*=8.4 Hz, 4H, -*CH*₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.15-1.03 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.88-0.75 (t, J=8.4 Hz, *CH*₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 153.46 (aromatic carbon on the fluorene unit), 150.99 (aromatic carbon on the fluorene unit), 144.51 (aromatic carbon on the fluorene unit), 138.08 (aromatic carbon on the fluorene unit), 131.40 (aromatic carbon on the fluorene unit), 130.51 (aromatic carbon on the fluorene unit), 126.44 (aromatic carbon on the fluorene unit), 126.38 (aromatic carbon on the fluorene unit), 123.17 (aromatic carbon on the fluorene unit), 122.09 (aromatic carbon on the fluorene unit), 120.29 (aromatic carbon on the fluorene unit), 119.59 (carbon on the cyano group), 110.34 (aromatic carbon on the fluorene unit), $55.75 (sp^3$ -carbon on the fluorene unit), 39.95 (carbon on the alkyl chain), 31.36 (carbon on the alkyl chain), 29.42 (carbon on the alkyl chain), 23.60 (carbon on the alkyl chain), 22.46 (carbon on the alkyl chain), 13.90 (carbon on the alkyl chain); HRMS (m/z): $[M+H]^+$ calcd for C₂₆H₃₂BrN, 437.1718, found $[(^{79}Br)]$ $M+H]^+=438.1794; [(^{81}Br)M+H]^+=440.1794.$

5.3.13. 7-Bromo-9,9-dihexyl-9H-fluorene-2-carboxylic acid (18). To a mixture of compound 17 (2.7 g; 0.006 mol) in CH₃COOH (6 mL), H₂SO₄ (6 mL), and H₂O (6 mL) was stirred and refluxed for 24 h. After cooling to the room temperature, ~ 50 mL of NaOH_(aq) was added to the reaction mixture. The above solution was then extracted with ethyl acetate and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:1) as the eluent to give the final purified product as white powder with yield of ~97% (2.73 g). IR (KBr, cm⁻¹): 2952, 2928, 2856 ($C(sp^3)$ -H stretching absorptions), 1881 (C=O stretching absorption) 1609, 1478 (stretching absorptions of benzene rings), 1485 (CH₂ bending absorption), 1377 (CH₃ bending absorption). Mp: 86.2–87.5. ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.17–8.14 (d, J=7.8 Hz, 1H, ArH on the fluorene unit), 8.10 (s, 1H, ArH on the fluorene unit), 7.77–7.74 (d, J=7.5 Hz, 1H, ArH on the fluorene unit), 7.64–7.61 (d, J=8.1 Hz, 1H, ArH on the fluorene unit), 7.52–7.48 (m, 2H, ArH on the fluorene unit), 2.16–1.91 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.14–1.05 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.78–0.74 (t, J=6.6 Hz, 6H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.59 (m, 4H,

-CH₂CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 172.68 (*sp*²-carbon on the carbonyl acid), 154.10 (aromatic carbon on the fluorene unit), 150.51 (aromatic carbon on the fluorene unit), 145.61 (aromatic carbon on the fluorene unit)138.74 (aromatic carbon on the fluorene unit). 130.31 (aromatic carbon on the fluorene unit), 129.75 (aromatic carbon on the fluorene unit). 128.10 (aromatic carbon on the fluorene unit), 126.39 (aromatic carbon on the fluorene unit), 124.60 (aromatic carbon on the fluorene unit), 122.77 (aromatic carbon on the fluorene unit), 122.06 (aromatic carbon on the fluorene unit), 119.62 (aromatic carbon on the fluorene unit), 55.61 (sp^3 -carbon on the fluorene unit), 40.08 (carbon on the alkyl chain), 31.43 (carbon on the alkyl chain), 29.54 (carbon on the alkyl chain), 23.68 (carbon on the alkyl chain), 22.52 (carbon on the alkyl chain), 13.95 (carbon on the alkyl chain); HRMS (m/z): $[M+H]^+$ calcd for C₂₆H₃₃BrO₂, 457.1742, found $[(^{79}Br)M+H]^+=457.1751; [(^{81}Br)M+H]^+=459.1799.$

5.3.14. 4-Methyl-7-bromo-9,9-dihexyl-9H-fluorene-2-carboxylate (19). To a mixture of compound 18 (2.6 g; 5.6 mmol) in methanol (20 mL), and H₂SO₄ (4 mL), was stirred and refluxed for 6 h. After cooling to the room temperature, ~ 50 mL of NaOH_(aq) was added to the reaction mixture. The above solution was then extracted with ethyl acetate and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:20) as the eluent to give the final purified product as white powder with yield of ~93% (2.49 g). Mp: 73.8–75.1. IR (KBr, cm^{-1}): 2952, 2926, 2856 ($C(sp^3)$)–H stretching absorptions), 1719 (C=O stretching absorption) 1605, 1474 (stretching absorptions of benzene rings), 1465 (CH₂ bending absorption), 1375 (CH₃ bending absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.06–8.02 (dd, I_1 =7.8 Hz, I_2 =1.2 Hz, 1H, ArH on the fluorene unit), 7.99 (s, 1H, ArH on the fluorene unit), 7.71–7.68 (d, J=7.8 Hz, 1H, ArH on the fluorene unit), 7.61–7.58 (d, J=7.8 Hz, 1H, ArH on the fluorene unit), 7.49–7.46 (m, 2H, ArH on the fluorene unit), 3.95 (s, 3H, CH₃ on the COOMe group), 2.06-1.88 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_3$), 1.13-1.01 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.78-0.73 (t, J=6.9 Hz, 6H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.61-0.51 (m, 4H, -CH₂CH₂ CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 167.31(*sp*²-carbon on the COOMe group), 153.91 (aromatic carbon on the fluorene unit), 150.35 (aromatic carbon on the fluorene unit), 144.61 (aromatic carbon on the fluorene unit), 138.86 (aromatic carbon on the fluorene unit), 130.17 (aromatic carbon on the fluorene unit), 128.90 (aromatic carbon on the fluorene unit), 126.30 (aromatic carbon on the fluorene unit), 123.99 (aromatic carbon on the fluorene unit), 122.40 (aromatic carbon on the fluorene unit), 121.83 (aromatic carbon on the fluorene unit), 119.42 (aromatic carbon on the fluorene unit), 55.53 (sp^3 carbon on the fluorene unit), 52.03 (1° carbon on the COOMe group), 40.05 (carbon on the alkyl chain), 31.37 (carbon on the alkyl chain), 29.48 (carbon on the alkyl chain), 23.60 (carbon on the alkyl chain), 22.45 (carbon on the alkyl chain), 13.86 (carbon on the alkyl chain); HRMS (m/z): $[M+H]^+$ calcd for C₂₇H₃₅BrO₂, 470.1820, found $[(^{79}Br)]$ $M+H]^+=471.1900; [(^{81}Br)M+H]^+=473.1900.$

5.3.15. 7-Bromo-9,9-dihexyl-9H-fluorene-2-carbohydrazide (**20**). To a mixture of compound **19** (2.4 g; 5.1 mmol) in methanol (20 mL), was added hydrazine monohydrate (0.637 g; 0.01 mol), then stirred and refluxed for 24 h. The reaction mixture was then extracted with dichloromethane (30mL×3) and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate/ hexane (1:1) to give the final purified product as white powder with yield of 91.6% (2.28 g). Mp: 155.3–157.1. IR (KBr, cm⁻¹): 3293 (N–H stretching absorption), 3066 ($C(sp^2)$ –H stretching absorption), 2955, 2925, 2854 ($C(sp^3)$ –H stretching absorptions),

16,651,881 (C=O stretching absorption), 1612, 1483 (stretching absorptions of benzene rings), 1455 (CH₂ bending absorption), 1376 (CH₃ bending absorption), 1133 (C–N stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.05 (s, 1H, ArH on the fluorene unit), 7.84–7.74 (m, 2H, ArH on the fluorene unit), 7.70-7.67 (d, I=7.8 Hz, 1H, ArH on the fluorene unit). 7.59–7.56 (d. *I*=7.8 Hz. 1H. ArH on the fluorene unit). 7.49 (s. 1H. ArH on the fluorene unit), 4.24 (s. 3H. NH on the carbohydrazide unit), 2.10-1.86 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.12-1.01 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.77-0.72 (t, *I*=6.6 Hz, 6H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.65-0.51(m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ :168.79 (*sp*²-carbon on the carbohydrazide unit), 153.56 (aromatic carbon on the fluorene unit), 150.83 (aromatic carbon on the fluorene unit), 143.69 (aromatic carbon on the fluorene unit), 138.76 (aromatic carbon on the fluorene unit), 131.30 (aromatic carbon on the fluorene unit), 130.17 (aromatic carbon on the fluorene unit), 126.26 (aromatic carbon on the fluorene unit), 125.76 (aromatic carbon on the fluorene unit), 122.27 (aromatic carbon on the fluorene unit), 121.74 (aromatic carbon on the fluorene unit), 121.66 (aromatic carbon on the fluorene unit), 119.68 (aromatic carbon on the fluorene unit), 55.60 (sp³-carbon on the fluorene unit), 40.09 (carbon on the alkyl chain), 31.37 (carbon on the alkyl chain), 29.48 (carbon on the alkyl chain), 23.62 (carbon on the alkyl chain), 22.45 (carbon on the alkyl chain), 13.87 (carbon on the alkyl chain); HRMS (m/z): $[M+H]^+$ calcd for $C_{26}H_{35}BrN_2O$, 470.1933, found $[(^{79}Br)M+H]^+=470.1931$; $[(^{81}Br)$ $M+Hl^+=472.1906.$

5.3.16. 2-(7-Bromo-9,9-dihexyl-9H-fluoren-2-yl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (21). Two-step reaction: (i) To a mixture of compound 20 (2.25 g; 4.7 mmol) in THF (60 mL) was added 4-tertbutylbenzoyl chloride (1.03 g; 5.2mmole), pyridine (3 mL). The resulting solution was then heated and stirred for 12 h. After cooling to the room temperature, the solvent was removed and the crude solid product was collected and recrystallized from hexane. The purified product was obtained as white powder with yield of 90.3% (2.72 g). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 10.16–10.14 (d, J=5.4 Hz, 1H, NH on the carbohydrazide unit), 9.81–9.79 (d, J=5.4 Hz, 1H, NH on the carbohydrazide unit), 7.96-7.92 (m, 2H, ArH on the fluorene unit), 7.85–7.82 (d, J=8.1 Hz, 2H, ArH on the phenyl group), 7.69–7.66 (d, *J*=8.1 Hz, 1H, ArH on the fluorene unit), 7.57–7.54 (d, *J*=8.4 Hz, 1H, ArH on the fluorene unit), 7.48-7.45 (m, 2H, ArH on the fluorene unit), 7.44-7.42 (d, J=8.1 Hz, 2H, ArH on the phenyl group), 1.95–1.89 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃), 1.32 (s, 9H, CH₃ on the tert-butyl group), 1.11-0.93 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.74-0.68 (t, J=6.9 Hz, 6H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.50 (m, 4H, $-CH_2CH_2CH_2CH_2CH_2CH_3)$; ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ :164.73 (sp²-carbon on the carbohydrazide unit), 164.36 (*sp*²-carbon on the carbohydrazide unit), 156.09 (aromatic carbon on the fluorene unit), 153.77 (aromatic carbon on the phenyl group), 150.87 (aromatic carbon on the fluorene unit), 144.26 (aromatic carbon on the fluorene unit), 138.80 (aromatic carbon on the fluorene unit), 130.22 (aromatic carbon on the phenyl group), 130.14 (aromatic carbon on the fluorene unit), 128.44 (aromatic carbon on the fluorene unit), 127.17 (aromatic carbon on the phenyl group), 126.91 (aromatic carbon on the fluorene unit), 126.33 (aromatic carbon on the fluorene unit), 125.70 (aromatic carbon on the phenyl group), 122.43 (aromatic carbon on the fluorene unit), 121.84 (aromatic carbon on the fluorene unit), 121.79 (aromatic carbon on the fluorene unit), 119.84 (aromatic carbon on the fluorene unit), 55.72 (sp³-carbon on the fluorene unit), 40.12 (carbon on the alkyl chain), 35.02 (4° carbon on the tert-butyl group), 31.45 (carbon on the alkyl chain), 31.09 (1° carbon on the tert-butyl group), 29.52 (carbon on the alkyl chain),

23.70 (carbon on the alkyl chain), 22.52 (carbon on the alkyl chain), 13.93 (carbon on the alkyl chain); HRMS (*m*/*z*): HRMS (*m*/*z*): [M+H]⁺ calcd for $C_{37}H_{47}BrN_2O_2$, 631.6853, found [({79}Br) M+H]⁺=631.2908; [({81}Br)M+H]⁺=633.2892.

(ii) The compound from the previous step was suspended in POCl₃ (45 mL) and heated to reflux for 6 h. After cooling to the room temperature. 50 mL of ice water was added to the reaction mixture. After filtration, the crude solid product was collected and recrystallized from methanol. The purified product was obtained as white powder with yield of ~79% (2.09 g). Mp: 99.8-103.3. IR (KBr, cm⁻¹): 3066 (C(*sp*²)–H stretching absorption), 2954, 2928, 2856 (C(sp³)–H stretching absorptions), 1614, 1468 (stretching absorptions of benzene rings), 1581 (C=N stretching absorption), 1461 (CH₂ bending absorption), 1364 (CH₃ bending absorption), 1300 (Ar–N stretching absorption), 1268 (C–O–C stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.14–8.12 (m, 2H, ArH on the fluorene unit), 8.11–8.09 (d, J=8.1 Hz, 2H, ArH on the phenyl group), 7.80–7.78 (d, J=8.1 Hz, 1H, ArH on the fluorene unit), 7.62-7.52 (m, 3H, ArH on the fluorene unit), 7.50–7.47 (d, J=8.1 Hz, 2H, ArH on the phenyl group), 2.13-1.94 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃), 1.37 (s, 9H, CH₃ on the tert-butyl group), 1.14–1.05 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 0.77-0.72 (t, J=7.2 Hz, 6H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.65-0.60 (m, 4H, -CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 164.76 (aromatic carbon on the oxadiazole group), 164.49 (aromatic carbon on the oxadiazole group), 155.18 (aromatic carbon on the fluorene unit), 153.47 (aromatic carbon on the fluorene unit), 151.13 (aromatic carbon on the phenyl group), 143.43 (aromatic carbon on the fluorene unit), 138.80 (aromatic carbon on the fluorene unit), 130.23 (aromatic carbon on the fluorene unit), 126.70 (aromatic carbon on the phenyl group), 126.24 (aromatic carbon on the fluorene unit), 126.02 (aromatic carbon on the fluorene unit), 125.94 (aromatic carbon on the phenyl group), 122.72 (aromatic carbon on the phenyl group), 122.35 (aromatic carbon on the fluorene unit), 121.65 (aromatic carbon on the fluorene unit), 121.19 (aromatic carbon on the fluorene unit), 121.07 (aromatic carbon on the fluorene unit), 120.20 (aromatic carbon on the fluorene unit), 55.69 (sp³-carbon on the fluorene unit), 40.12 (carbon on the alkyl chain), 34.97 (4° carbon on the tert-butyl group), 31.37 (carbon on the alkyl chain), 31.02 (1° carbon on the *tert*-butyl group), 29.46 (carbon on the alkyl chain), 23.63 (carbon on the alkyl chain), 22.44 (carbon on the alkyl chain), 13.87 (carbon on the alkyl chain); HRMS (m/z): HRMS (m/z): $[M+H]^+$ calcd for C₃₇H₄₅BrN₂O, 612.2715, found $[(^{79}Br)M+H]^+=612.2719; [(^{81}Br)M+H]^+=614.2722.$

5.3.17. N-(7-(5-(4-tert-Butylphenyl)-1,3,4-oxadiazol-2-yl)-9,9dihexyl-9H-fluoren-2-yl)-N-(9,9-dihexyl-7-iodo-9H-fluoren-2-yl)-9,9-dihexyl-7-iodo-9H-fluoren-2-amine (22). Two-step reaction: (i) To a mixture of compound **21** (0.37 g; 0.603 mmol), and **13** (0.5 g; 0.603 mmol) in dry toluene (15 mL) was added $Pd_2(dba)_3$ (1.1 mg; 0.012 mmol), sodium tert-butoxide (0.069 g; 0.724 mmol), P(t-Bu)₃ (4.9 mg; 0.024 mmol) and stirred at 90 °C under Ar atmosphere for 12 h. After cooling to the room temperature, ~ 100 mL of H₂O was added to the reaction mixture. The above solution was then extracted with ethyl acetate and the organic layer was dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:20) as the eluent to give the final purified product as light yellow powder with yield of 75.6% (0.62 g). Mp: 101.1–102.3. IR (KBr, cm⁻¹): 3040, 3014 (C(*sp*²)–H stretching absorptions), 2954, 2927, 2856 (C(sp³)–H stretching absorptions), 1603, 1483 (stretching absorptions of benzene rings), 1577 (C=N stretching absorption), 1462 (CH₂ bending absorption), 1376 (CH₃ bending absorption), 1329 (Ar-N stretching absorption), 1266 (C-O-C stretching absorption), 1247(Si-C stretching absorption).

¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ: 8.12–8.08 (m, 4H, ArH on the fluorene unit), 7.74–7.71 (d, ArH on the fluorene unit 1H, ArH on the fluorene unit), 7.62-7.55 (m, 7H, ArH on the fluorene unit), 7.49-7.44 (m, 4H, ArH on the phenyl group), 7.30-7.28 (m, 3H, ArH on the fluorene unit), 7.09-7.03 (m. 3H. ArH on the fluorene unit). 2.08-1.82 (m. 12H. $-CH_2CH_2CH_2CH_2CH_3$, 1.38 (s, 9H, CH₃ on the *tert*-butyl group), 1.17–1.09 (m. 36H. –CH₂CH₂CH₂CH₂CH₂CH₂CH₂), 0.90–0.78 (m. 30H. -CH₂CH₂CH₂CH₂CH₂CH₃), 0.31 (s, 18H, CH₃ on the TMS unit); ¹³C NMR (75 MHz, CDCl₃, tentative assignments based on calculated values) δ : 165.16 (aromatic carbon on the oxadiazole group), 164.38 (aromatic carbon on the oxadiazole group), 155.11 (aromatic carbon on the fluorene unit), 152.77 (aromatic carbon on the fluorene unit), 152.23 (aromatic carbon on the fluorene unit), 151.18 (aromatic carbon on the fluorene unit), 149.57 (aromatic carbon on the fluorene unit), 148.30 (aromatic carbon on the phenyl group), 146.87 (aromatic carbon on the fluorene unit), 144.72 (aromatic carbon on the fluorene unit), 141.49 (aromatic carbon on the fluorene unit), 138.14 (aromatic carbon on the fluorene unit), 136.44 (aromatic carbon on the fluorene unit), 134.19 (aromatic carbon on the fluorene unit), 131.85 (aromatic carbon on the fluorene unit), 127.38 (aromatic carbon on the phenyl group), 126.7 (aromatic carbon on the fluorene unit)5, 126.15 (aromatic carbon on the fluorene unit), 126.00 (aromatic carbon on the phenyl group), 123.28 (aromatic carbon on the phenyl group), 122.44 (aromatic carbon on the fluorene unit), 121.30 (aromatic carbon on the fluorene unit), 121.08 (aromatic carbon on the fluorene unit), 120.47 (aromatic carbon on the fluorene unit). 119.27 (aromatic carbon on the fluorene unit). 118.65 (aromatic carbon on the fluorene unit), 118.36 (aromatic carbon on the fluorene unit), 117.20 (aromatic carbon on the fluorene unit), 55.41 (sp^3 -carbon on the fluorene unit), 55.01 (sp^3 -carbon on the fluorene unit), 40.31 (carbon on the alkyl chain), 40.12 (carbon on the alkyl chain), 35.04 (4° carbon on the tert-butyl group), 31.66 (1° carbon on the *tert*-butyl group), 31.51 (carbon on the alkyl chain), 31.11 (carbon on the alkyl chain), 29.67 (carbon on the alkyl chain), 29.59 (carbon on the alkyl chain), 23.85 (carbon on the alkyl chain), 23.78 (carbon on the alkyl chain), 22.58 (carbon on the alkyl chain), 22.51 (carbon on the alkyl chain), 14.05 (carbon on the alkyl chain), -0.88 (1° carbon on the TMS unit); HRMS (m/z): M⁺ calcd for C₉₃H₁₂₇N₃OSi₂ 1357.9518, found 1360.2367.

(ii) To a solution of compound from the first step (0.62 g; 0.46 mmol) in CH₂Cl₂ (10 mL) was added iodine monochloride (0.16 g; 0.96mmole) at 0 °C, then warmed to room temperature and stirred for 4 h. ~30 mL of saturated NaHSO₃ solutions was added into the reaction mixture. The above solution was then extracted with dichloromethane (30mL×3) and the organic layer was dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified by column chromatography on silica gel using ethyl acetate/ hexane (1:20) to give the final purified product as yellow powder with yield of ~91% (0.61 g). Mp: 103.1–105.4. IR (KBr, cm^{-1}): 3062, 3035 (C(sp²)-H stretching absorptions), 2953, 2925, 2854 (C(sp³)-H stretching absorptions), 1604, 1483 (stretching absorptions of benzene rings), 1576 (C=N stretching absorption) 1456 (CH₂ bending absorption), 1375 (CH₃ bending absorption), 1340 (Ar–N stretching absorption), 1268 (C–O–C stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ: 8.12–8.08 (m, 4H, ArH on the fluorene unit), 7.74–7.71 (dd, J_1 =8.4 Hz, J_2 =2.1 Hz, 1H, ArH on the fluorene unit), 7.64–7.55 (m, 7H, ArH on the fluorene unit), 7.54–7.51 (d, J=8.4 Hz, 2H, ArH on the phenyl group), 7.37–7.34 (dd, J₁=8.4 Hz, J₂=2.1 Hz, 2H, ArH on the phenyl group), 7.26-7.22 (m, 4H, ArH on the fluorene unit), 7.05–7.01 (dd, J₁=8.1 Hz, J₂=2.1 Hz, 2H, ArH on the fluorene unit), 2.07-1.79 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃), 1.38 (s, 9H, CH₃ on the tert-butyl group), 1.17-1.08(m, 36H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.84-0.76(m, 18H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.68 (br, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 165.00 (aromatic carbon on the oxadiazole group), 164.31 (aromatic carbon on the oxadiazole group), 155.01 (aromatic carbon on the fluorene unit), 152.77 (aromatic carbon on the fluorene unit), 152.00 (aromatic carbon on the fluorene unit), 151.47 (aromatic carbon on the fluorene unit), 151.10 (aromatic carbon on the phenyl group), 147.86 (aromatic carbon on the fluorene unit), 147.14 (aromatic carbon on the fluorene unit), 144.42 (aromatic carbon on the fluorene unit), 140.38 (aromatic carbon on the fluorene unit), 135.81 (aromatic carbon on the fluorene unit), 135.32 (aromatic carbon on the fluorene unit), 134.58 (aromatic carbon on the fluorene unit), 131.80 (aromatic carbon on the fluorene unit), 126.67 (aromatic carbon on the phenyl group), 125.92 (aromatic carbon on the phenyl group), 123.26 (aromatic carbon on the fluorene unit), 122.66 (aromatic carbon on the phenyl group), 121.44 (aromatic carbon on the fluorene unit), 121.19 (aromatic carbon on the fluorene unit), 120.72 (aromatic carbon on the fluorene unit), 120.54 (aromatic carbon on the fluorene unit), 119.33 (aromatic carbon on the fluorene unit), 118.25 (aromatic carbon on the fluorene unit), 117.46 (aromatic carbon on the fluorene unit), 91.66 (aromatic carbon on the fluorene unit), 55.35 (sp^3 -carbon on the fluorene unit), 55.23 (sp^3 -carbon on the fluorene unit), 40.13 (carbon on the alkyl chain), 34.95 (4° carbon on the tert-butyl group), 31.55 (1° carbon on the tert-butyl group), 31.05 (carbon on the alkyl chain), 29.56 (carbon on the alkyl chain), 23.77 (carbon on the alkyl chain), 22.51 (carbon on the alkyl chain), 14.03 (carbon on the alkyl chain); HRMS (*m*/*z*): M⁺ calcd for C₈₇H₁₀₉I₂N₃O 1465.666, found, 1467.6660.

5.3.18. Compound 1. To a mixture of compound 8 (0.5 g: 0.88 mmol) in dry pyridine (12 mL) was added 4-tert-butylbenzoyl chloride (0.2 g; 1.05 mmol), then stirred and refluxed under Ar atmosphere for 4 h. After cooling to the room temperature, the reaction mixture was extracted with ethyl acetate and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:10) as the eluent to give the final light yellow powder with yield of 91% (0.56 g). Mp: 117.1–118.0. IR (KBr, cm⁻¹): 3060, 3033 (C(sp²)–H stretching absorptions), 2952, 2925, 2853 (C(sp³)–H stretching absorptions), 1610, 1492 (stretching absorptions of benzene rings), 1541 (C=N stretching absorption), 1461 (CH₂ bending absorption), 1384 (CH₃ bending absorption), 1300 (Ar-N stretching absorption), 1271 (C–O–C stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.12 (s, 1H, ArH on the fluorene unit), 8.09-8.06 (m, 2H, ArH on the fluorene unit), 7.75–7.72 (d, J=8.4 Hz, 2H, ArH on the fluorene unit), 7.63–7.60 (d, J=8.4 Hz, 1H, ArH on the fluorene unit), 7.59–7.55 (dd, J₁=8.4 Hz, $I_2=2.1$ Hz, 2H, ArH on the phenyl group), 7.30(s, 1H, ArH on the fluorene unit), 7.27–7.24 (m, 4H, ArH on the diphenylamino group), 7.15–7.11 (m, 2H, ArH on the diphenylamino group), 7.11–7.09 (m, 2H, ArH on the phenyl group), 7.07-7.01 (m, 4H, ArH on the diphenylamino group), 2.04-1.83 4H, (m. $-CH_2CH_2CH_2CH_2CH_2CH_3$), 1.38 (s, 9H, CH₃ on the *tert*-butyl group), 1.17-1.06 (m, 12H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.81-0.76 (t, 6H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.66 (br, 4H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ :164.88 (aromatic carbon on the oxadiazole group), 164.15 (aromatic carbon on the oxadiazole group), 154.85 (aromatic carbon on the fluorene unit), 152.68 (aromatic carbon on the fluorene unit), 151.22 (aromatic carbon on the phenyl group), 148.16 (aromatic carbon on the fluorene unit), 147.55 (aromatic carbon on the diphenylamino group), 144.39 (aromatic carbon on the fluorene unit), 134.43 (aromatic carbon on the fluorene unit), 129.04 (aromatic carbon on the diphenylamino group), 126.55 (aromatic carbon on the phenyl group), 125.89 (aromatic carbon on the phenyl group), 125.77 (aromatic carbon on the fluorene unit), 123.97 (aromatic carbon on the diphenylamino group), 122.94 (aromatic carbon on the diphenylamino group), 122.73 (aromatic carbon on the phenyl group), 121.27 (aromatic carbon on the fluorene unit), 121.09 (aromatic carbon on the fluorene unit), 121.00 (aromatic carbon on the fluorene unit), 120.89 (aromatic carbon on the fluorene unit), 119.25 (aromatic carbon on the fluorene unit), 118.40 (aromatic carbon on the fluorene unit), 55.17 (sp^3 -carbon on the fluorene unit), 39.95 (carbon on the alkyl chain), 34.79 (4° carbon on the *tert*-butyl group), 31.30 (carbon on the alkyl chain), 30.90 (1° carbon on the *tert*-butyl group), 29.36 (carbon on the alkyl chain), 23.60 (carbon on the alkyl chain), 22.31 (carbon on the alkyl chain), 13.82 (carbon on the alkyl chain); HRMS (m/z): M⁺ calcd for C₄₉H₅₅N₃O, 701.4345, found, 701.4351.

5.3.19. Compound 2. To a mixture of compound 21 (0.32 g; 0.521 mmol), and **10** (0.53 g; 0.521 mmol) in dry toluene (15 mL) was added Pd₂(dba)₃ (9.55 mg; 0.011 mmol), sodium tert-butoxide (0.06 g; 0.626 mmol), P(t-Bu)₃ (4.2 mg; 0.021 mmol) and stirred at 90 °C under Ar atmosphere for 12 h. After cooling to the room temperature, $\sim 100 \text{ mL of H}_2\text{O}$ was added to the reaction mixture. The above solution was then extracted with ethyl acetate and the organic layer was dried over MgSO_{4(S)}. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:10) as the eluent to give the final purified product as yellow powder with yield of 80.6% (0.65 g). Mp: 103.3–105.7. IR (KBr, cm⁻¹): 3066 (C(sp²)–H stretching absorption), 2953, 2925, 2856 (C(sp³)-H stretching absorptions), 1598, 1482 (stretching absorptions of benzene rings), 1593 (C=N stretching absorption) 1454 (CH₂ bending absorption). 1384 (CH₃ bending absorption), 1312 (Ar–N stretching absorption), 1270 (C–O–C stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.11–8.06 (m, 4H, ArH on the fluorene unit), 7.73–7.70 (d, J=7.8 Hz, 1H, ArH on the fluorene unit), 7.59-7.54 (m, 3H, ArH on the fluorene unit), 7.50–7.47 (d, J=7.8 Hz, 4H, ArH on the phenyl group), 7.26–7.21 (m, 12H, ArH on the diphenylamino group and ArH on the fluorene unit), 7.12–7.09 (d, *J*=7.8 Hz 10H, ArH on the diphenylamino group and ArH on the fluorene unit), 7.06-6.96 (m, 8H, ArH on the diphenylamino group), 2.06 - 1.76(m, 12H. -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.38 (s, 9H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.19-1.07 (m, 36H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.84-0.71 (m, 30H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ :165.16 (aromatic carbon on the oxadiazole group), 164.38 (aromatic carbon on the oxadiazole group), 155.14 (aromatic carbon on the fluorene unit), 152.74 (aromatic carbon on the fluorene unit), 151.94 (aromatic carbon on the fluorene unit), 151.86 (aromatic carbon on the fluorene unit), 151.15 (aromatic carbon on the phenyl group), 148.32 (aromatic carbon on the fluorene unit), 148.00 (aromatic carbon on the diphenylamino group), 146.49 (aromatic carbon on the fluorene unit), 146.16 (aromatic carbon on the fluorene unit), 144.73 (aromatic carbon on the fluorene unit), 136.26 (aromatic carbon on the fluorene unit), 136.21 (aromatic carbon on the fluorene unit), 133.99 (aromatic carbon on the fluorene unit), 129.10 (aromatic carbon on the diphenylamino group), 126.75 (aromatic carbon on the phenyl group), 126.00 (aromatic carbon on the phenyl group), 123.81 (aromatic carbon on the fluorene unit), 123.61 (aromatic carbon on the fluorene unit), 123.41 (aromatic carbon on the diphenylamino group), 122.32 (aromatic carbon on the phenyl group), 122.22 (aromatic carbon on the diphenylamino group), 121.12 (aromatic carbon on the fluorene unit), 121.04 (aromatic carbon on the fluorene unit), 119.74 (aromatic carbon on the fluorene unit), 119.54 (aromatic carbon on the fluorene unit), 119.22 (aromatic carbon on the fluorene unit), 118.61 (aromatic carbon on the fluorene unit), 116.93 (aromatic carbon on the fluorene unit), 115.11 (aromatic carbon on the fluorene unit), 55.06 (sp^3 -carbon on the fluorene unit), 40.18 (carbon on the alkyl chain), 35.06(4° carbon on the *tert*-butyl group), 31.66 (carbon on the alkyl chain), 31.12(1° carbon on the *tert*-butyl group), 29.65 (carbon on the alkyl chain), 23.92 (carbon on the alkyl chain), 22.57 (carbon on the alkyl chain), 14.09; HRMS (*m*/*z*): M⁺ calcd for C₁₁₁H₁₂₉N₅O 1548.0197, found, 1548.0194.

5.3.20. Compound **3**. To a mixture of compound **21** (0.1 g: 0.163 mmol), and **16** (0.44 g: 0.163 mmol) in drv toluene (15 mL) was added Pd₂(dba)₃ (3 mg; 0.003 mmol), sodium *tert*-butoxide (0.018 g; 0.1955 mmol), P(t-Bu)₃ (1.3 mg; 0.006518 mmol) and stirred at 90 °C under Ar atmosphere for 12 h. After cooling to the room temperature, \sim 100 mL of H₂O was added to the reaction mixture. The above solution was then extracted with ethyl acetate and the organic layer was dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:15) as the eluent to give the final purified product as yellow powder with yield of 73.1% (0.386 g). Mp: 100.1–102.3. IR (KBr, cm⁻¹): 3059, 3034 (C(sp²)–H stretching absorptions), 2954, 2926, 2855 (C(sp³)–H stretching absorptions), 1600, 1483 (stretching absorptions of benzene rings), 1541 (C=N stretching absorption) 1464 (CH₂ bending absorption), 1376 (CH₃ bending absorption), 1311 (Ar-N stretching absorption), 1270 (C-O-C stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.11–8.07 (m, 8H, ArH on the fluorene unit), 7.73–7.70 (d, J=8.1 Hz, 2H, ArH on the fluorene unit), 7.60–7.55 (m, 8H, ArH on the fluorene unit), 7.51–7.48 (d, J=8.1 Hz, 4H, ArH on the phenyl group), 7.27-7.22 (m, 28H, ArH on the diphenylamino group and ArH on the fluorene unit), 7.13-7.10 (m, 18H, ArH on the diphenvlamino group and ArH on the fluorene unit), 7.07–6.97 (m. 16H, ArH on the diphenylamino group), 2.06-1.77 (m, 28H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.38 (s, 9H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₂CH₃), 1.17-1.08 (m, 84H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.85-0.75 (m, 70H, -CH₂CH₂CH₂CH₂CH₂CH₂CH₃); C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 165.13 (aromatic carbon on the oxadiazole group), 164.33 (aromatic carbon on the oxadiazole group), 155.09 (aromatic carbon on the fluorene unit), 152.70 (aromatic carbon on the fluorene unit), 151.90 (aromatic carbon on the fluorene unit), 151.81 (aromatic carbon on the fluorene unit), 151.10 (aromatic carbon on the phenyl group), 148.28 (aromatic carbon on the fluorene unit), 147.95 (aromatic carbon on the diphenylamino group), 146.45 (aromatic carbon on the fluorene unit), 146.11 (aromatic carbon on the fluorene unit), 144.70 (aromatic carbon on the fluorene unit), 136.22 (aromatic carbon on the fluorene unit), 136.16 (aromatic carbon on the fluorene unit), 135.65 (aromatic carbon on the fluorene unit), 133.95 (aromatic carbon on the fluorene unit), 129.65 (aromatic carbon on the fluorene unit), 129.06 (aromatic carbon on the diphenylamino group), 126.71 (aromatic carbon on the phenyl group), 125.97 (aromatic carbon on the phenyl group), 123.75 (aromatic carbon on the fluorene unit), 123.57 (aromatic carbon on the diphenylamino group), 122.28 (aromatic carbon on the diphenylamino group), 121.20 (aromatic carbon on the phenyl group), 121.02 (aromatic carbon on the fluorene unit), 119.76 (aromatic carbon on the fluorene unit), 119.49 (aromatic carbon on the fluorene unit), 119.20 (aromatic carbon on the fluorene unit), 118.56 (aromatic carbon on the fluorene unit), 116.87 (aromatic carbon on the fluorene unit), 55.02 (*sp*³-carbon on the fluorene unit), 40.15 (carbon on the alkyl chain), 35.02 (4° carbon on the tert-butyl group), 31.62 (carbon on the alkyl chain), 31.08 (1° carbon on the *tert*-butyl group), 29.62 (carbon on the alkyl chain), 23.88 (carbon on the alkyl chain), 22.54 (carbon on the alkyl chain), 14.06 (carbon on the alkyl chain); HRMS (m/z): M⁺ calcd for C₂₃₅H₂₇₇N₉O 3243.77, found, 3244.8767.

5.3.21. Compound **4**. To a mixture of compound **22** (0.12 g; 0.082 mmol), and **16** (0.44 g; 0.163 mmol) in dry toluene (15 mL) was added $Pd_2(dba)_3$ (3 mg; 0.003 mmol), sodium *tert*-butoxide (0.019 g; 0.196 mmol), P(*t*-Bu)_3 (1.3 mg; 0.0065 mmol) and stirred at 90 °C

under Ar atmosphere for 12 h. After cooling to the room temperature, ~ 100 mL of H₂O was added to the reaction mixture. The above solution was then extracted with ethyl acetate and the organic layer was dried over $MgSO_{4(S)}$. After removing the solvent, the crude product was purified through column chromatography on silica gel using ethyl acetate/hexane (1:30) as the eluent to give the final purified product as vellow powder with vield of 50% (0.27 g). Mp: 98.6–99.4. IR (KBr, cm⁻¹): 3061, 3033 (C(sp²)–H stretching absorptions), 2953, 2925, 2854 (C(sp³)–H stretching absorptions), 1603, 1482 (stretching absorptions of benzene rings), 1588 (C=N stretching absorption) 1464 (CH₂ bending absorption), 1376 (CH₃ bending absorption), 1310 (Ar-N stretching absorption), 1269 (C–O–C stretching absorption). ¹H NMR (300 MHz, CDCl₃, tentative assignment based on calculated values) δ : 8.12–8.07 (m, 8H, ArH on the fluorene unit), 7.74–7.71 (d, J=8.1 Hz, 4H, ArH on the fluorene unit), 7.60–7.55 (m, 4H, ArH on the phenyl group), 7.51–7.45 (m, 20H, ArH on the fluorene unit), 7.26-7.21 (m, 56H, ArH on the diphenylamino group and ArH on the fluorene unit), 7.13–7.10 (d, J=8.4 Hz, 42H, ArH on the diphenylamino group and ArH on the fluorene unit), 7.06–6.96, (m, 38H, ArH on the diphenylamino group and ArH on the fluorene unit), 2.31–2.17 (m, 4H 56H, $-CH_2CH_2CH_2CH_2CH_2CH_3),$ 1.81-1.78 (m. $-CH_2CH_2CH_2CH_2CH_2CH_3$), 1.38 (s, 9H, CH₃ on the *tert*-butyl group), 1.25-1.08 (m, 180H, -CH₂CH₂CH₂CH₂CH₂CH₃), 0.88-0.75 (m, 150H, -CH₂CH₂CH₂CH₂CH₂CH₃); ¹³C NMR (75 MHz, CDCl₃, tentative assignment based on calculated values) δ : 165.15 (aromatic carbon on the oxadiazole group), 164.35 (aromatic carbon on the oxadiazole group), 155.08 (aromatic carbon on the fluorene unit). 152.76 (aromatic carbon on the fluorene unit). 151.83 (aromatic carbon on the fluorene unit), 151.79 (aromatic carbon on the fluorene unit), 151.13 (aromatic carbon on the phenyl group), 148.38 (aromatic carbon on the fluorene unit), 148.00 (aromatic carbon on the diphenylamino group), 146.65 (aromatic carbon on the fluorene unit), 146.53 (aromatic carbon on the fluorene unit), 146.32 (aromatic carbon on the fluorene unit), 146.10 (aromatic carbon on the fluorene unit), 144.74 (aromatic carbon on the fluorene unit), 136.39 (aromatic carbon on the fluorene unit), 135.69 (aromatic carbon on the fluorene unit), 133.88 (aromatic carbon on the fluorene unit), 129.07 (aromatic carbon on the diphenylamino group), 128.43 (aromatic carbon on the fluorene unit), 126.74 (aromatic carbon on the phenyl group), 126.00 (aromatic carbon on the phenyl group), 123.86 (aromatic carbon on the fluorene unit), 123.55 (aromatic carbon on the diphenylamino group), 123.03 (aromatic carbon on the fluorene unit), 122.82 (aromatic carbon on the diphenylamino group), 122.26 (aromatic carbon on the phenyl group), 121.26 (aromatic carbon on the fluorene unit), 121.06 (aromatic carbon on the fluorene unit), 119.64 (aromatic carbon on the fluorene unit), 118.84 (aromatic carbon on the fluorene unit), 117.99 (aromatic carbon on the fluorene unit), 116.70 (aromatic carbon on the fluorene unit), 112.60 (aromatic carbon on the fluorene unit), $55.02 (sp^3$ -carbon on the fluorene unit), 40.21 (carbon on the alkyl chain), 35.05(4° carbon on the tert-butyl group), 31.65 (carbon on the alkyl chain), 31.11(1° carbon on the tertbutyl group), 29.76 (carbon on the alkyl chain), 23.91 (carbon on the alkyl chain), 22.56 (carbon on the alkyl chain), 14.09 (carbon on the alkyl chain); HRMS (m/z): M⁺ calcd for HRMS (m/z): M⁺ calcd for C₄₈₃H₅₇₃N₁₇O 6627.5309, found, 6627.0708.

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Supplementary data

Supplementary data related to this article can be found online at doi:10.1016/j.tet.2012.04.073.

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