Chapter – 3

Design and Synthesis of bis (carbazole fluorene ethynyl) arene derivatives as promising candidates for Two Photon Absorption
Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives

3.1 Introduction

The development of organic materials displaying high two-photon absorption (TPA) [1, 2] has attracted great interest in the past decade due to a variety of potential applications in photonics and optoelectronics, such as three-dimensional optical data storage, fluorescence imaging, nonlinear optics, microfabrication, two-photon optical power limiting, photodynamic therapy etc [3]. All these TPA-based applications benefit mainly from the following attributes of the two-photon absorption process: (a) the activation of high-energy photophysical properties by low-energy near-IR excitation (simultaneous absorption of two photons of half the excitation energy by a single molecule), resulting in larger material penetration compared to excitations by visible or UV light, and (b) quadratic dependence of the two-photon absorption on the intensity of light, which allows for more control and higher spatial resolution. In view of biological applications, such as invivo imaging, these advantages play an important role as they lead to a finer resolution and a better in-depth tissue penetration, combined with reduced cell damage. As a consequence, the two-photon microscopy experiences an increasing popularity. [4]

To fully exploit the great potential of the TPA process, research focused on the design and synthesis of molecules exhibiting large δTPA is still ongoing. [5-8] Apart from the large TPA absorption, high two-photon excited fluorescence (TPEF) quantum yields, good photo stability, appreciable solubility, and proper response wavelengths are also required to meet practical application needs in fields such as fluorescence microscopy or up converted lasing.[9]

It is important to understand the nature of the relationship between the molecular structure and the TPA property to provide guidelines for the development of materials with large TPA cross-sections. In particular, extended π-conjugated systems symmetrically substituted with electron-donating (D) and/or electron-accepting (A) functionalities have been revealed as efficient TPA dyes. Subsequently, a number of compounds including D–A–D, [10, 11] D–π–A, [12–15] A–D–A, [16–18] D–π–D type molecules, [19–21] macro cycles, [22] multi-branched molecules, [23–28] and organo metallic complexes [29] were synthesized. On the basis of this general setting, many factors play an important role in increasing δ
Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives.....

TPA, such as the efficiency of intramolecular charge transfer (ICT), the conjugation length, the planarity of molecule, the dimensionality of the charge-transfer network, and the donating and withdrawing abilities of the electron donor and acceptor. [30]

It is well-established that TPA increases with the extent of the charge transfer. Although the C=C bond is an excellent conjugation bridge for the intramolecular charge transfer (ICT) from the donor to the acceptor, it readily undergoes trans to cis photo isomerization. Because the TPA materials are photo excited by the two-photon process, such possibility always exists and may hamper the efficiency and the lifetime of the materials. This problem could be avoided if one uses triple bonds as the conjugation bridge. However, only few reports are present about the TPA materials containing the triple bond (C≡C). This has prompted us to design the TPA materials containing the triple bond (C≡C) which exhibit enhanced TPA cross sections along with specific features depending on the desired application.

Particularly interesting would be structures with the D-π-A-π-D constitution where a 2-fold intramolecular charge transfer between the end and the center of the molecule could take place.

Here, in this chapter the synthesis and characterization, the linear optical absorption and fluorescence properties, electrochemistry as well as the theoretically calculated TPA properties of five novel fluorene-carbazole derived dyes possessing a general D-π-A-π-D-type quadrupolar structure are reported. All the studied compounds C1–C5 (Scheme 3.1) composed of electron-donating carbazole moiety as donor group and benzene (compound C1) or anthracene (compound C2) or fluorene (compound C3) or thiophene (compound C4) or benzothiadiazole (compound C5) as the acceptor part, through fluorenylethynyl conjugated bridge. In particular, we incorporated the coplanar fluorene linker, since the coplanar fluorenes are beneficial for facilitating D-A electronic coupling and coplanar fluorene derivatives usually exhibit excellent TPA properties. [31] In addition, the 9-position of fluorene was alkylated by hexyl group to enhance the solubility. The acceptor capacity of different arene molecules was compared and the influence of them on photo physical properties and TPA properties was
examined. The experimental and theoretical results have been analyzed to establish a structure–property correlation.

Scheme 3.1: Structures of the bis (carbazole fluorene ethynyl) arene derivatives C1–C5.

3.2 Experimental section

3.2.1 Materials and Instruments

All the reagents were of Analytical Reagent grade and used without further purification except for DMF, which was distilled from molecular sieves BaO and CaH₂, respectively. ¹H-NMR spectra were recorded on a Bruker Avance (300 MHz) spectrometer in CDCl₃ and ¹³C-NMR spectra on a Bruker Avance (75 MHz) spectrometer in CDCl₃ with TMS as internal standard in both cases. Mass spectra were obtained by using electron ionization recorded on VG70-70H mass spectrometry and mass spectra also recorded in MALDI-TOF TOF with an Applied Biosystems, USA 4800 spectrometer using α-cyano-4-hydroxycinnamic acid as the matrix. UV-Visible absorption spectra were measured on a Jasco V-550 spectrophotometer. Steady state fluorescence spectra were recorded using a Spex model Fluorolog-3 spectrofluorometer. The fluorescence quantum yields (Φ) were estimated by using 9, 10-diphenylanthracene (DPA) as the standard [32]. Perkin-
Elmer Spectrum BX spectrophotometer was used to obtain IR spectra of the sensitizers at a resolution of 4 cm\(^{-1}\), where all the samples were pressed into KBr pellets. TGA was performed using TGA/SDTA 851e (METLER TOLEDO). Cyclic voltammetric measurements were performed on a PC-controlled CH instruments model CHI 62 °C electrochemical analyzer, using 1 mM dye solution in dichloromethane (DCM) at a scan rate of 100 mV/s using 0.1 M tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. The glassy carbon, standard calomel electrode (SCE) and platinum wire were used as working, reference and auxiliary electrodes respectively.

### 3.2.2 Synthesis and Characterization

We report the synthesis and characterization of five new derivatives, compounds C1–C5 namely 1,4-bis((7-(9H-carbazol-9-yl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)benzene (C1), 9,10-bis((7-(9H-carbazol-9-yl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)anthracene (C2), 9,9′-(7,7′-(9,9-dibutyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(9,9-dihexyl-9H-fluorene-7,2-diyl))bis(9H-carbazole) (C3), 2,5-bis((7-(9H-carbazol-9-yl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)thiophene (C4), 4,7-bis((7-(9H-carbazol-9-yl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)benzo[c][1,2,5]thiadiazole (C5), were synthesized by Sonogashira coupling reaction of bromo or iodo arenes with 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole. Synthesis of key starting materials is described below.

The synthesis of the key intermediate 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole is shown in scheme 3.2. 2,7-Dibromo fluorene 2 was synthesized by the bromination of fluorene 1 in presence of Fe catalyst [33]. 2, 7-dibromo 9,9-dihexyl fluorene 3 is prepared from 2 by the alkylation using n-hexyl bromide in presence of potassium tertiary butoxide as a base. A classic Ullmann coupling was used to build up C-N bond by reacting carbazole and 2, 7-dibromo 9, 9-dihexyl fluorene by modified procedure of Cul/proline catalyzed N-arylation reported by Deng et al [34] to get 9-(7-bromo-9,9-dihetyl-9H-fluoren-2-yl)-9H-carbazole 4. Commercially available 2-methyl-3-butyn-2-ol has been used to generate ethynyl spacer for the compound 4. 2-Methyl-3-butyn-2-ol and 4 compound were coupled by applying Sonogashira reaction [35] to afford alkynol
compound 5, which was then deprotected using KOH in isopropanol to afford 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole compound 6.

Scheme 3.2: Reagents and conditions: (a) Br₂ (2.1 eq.), Fe (0.015 eq.), 5 °C, 2 h. (b) (CH₃)₃COK (3 eq.), n-HexylBr (2.5 eq.), 0 °C-rt, 8 h. (c) 20 mol% CuI, 20 mol% L-proline, carbazole (1 eq.), compound 3 (1.5 eq.), 2.5 eq. K₂CO₃, DMF, reflux, 24 h. (d) 2-methyl-3-butyn-2-ol (2 equiv), 2 mol% Pd(PPh₃)₂Cl₂, 2 mol% CuI, toluene/Et₃N, 70 °C, 12 h. (e) KOH, i-PrOH, reflux, 3 h. Where Hex= n-hexyl

Dibromobenzene (7), dibromoanthracene (8), dibromothiophene (9) were used as purchased. Dibromobenzothiadiazole (10) was synthesized based on the previous report. [36] 9,9-dibutyl-2,7-diiodo-9H-fluorene 12 was prepared by the alkylation of diiodofluorene 11 which obtained by the iodination of fluorene 1 (scheme 3.3).

Scheme 3.3: Reagents and conditions: (a) Fluorene (1 eq), periodic acid dihydrate (0.7 eq.), iodine (0.7 eq.), 60-65 °C (b) (CH₃)₃COK (3 eq.), n-BuBr (2.5 eq), 0 °C-rt, 8 h. Where Bu= n-butyl

The synthesis of C₁—C₅ compounds is outlined in Scheme 3.4. A Pd/Cu-catalyzed Sonogashira coupling reaction of bromo or iodo arenes with 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole is used as a key reaction to construct these acetylene-linked compounds (C₁—C₅). All compounds C₁—C₅ were readily soluble in common organic solvents such as toluene, dichloromethane, chloroform and THF. All the compounds isolated were solids and easily purified by silica gel column chromatography. All the intermediates and final molecules were well characterized by NMR, mass and IR spectroscopy.
Compounds C1-C5 are thermally stable, and their initial decomposition temperatures were found by thermal gravimetric analysis (TGA) under nitrogen.

Scheme 3.4: Reagents and conditions: (a) 1,4-dibromobenzene (1 eq.), 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole (2.1 eq.), 2 mol% Pd(PPh₃)₂Cl₂, 2 mol% CuI, toluene/Et₃N, 70 °C, 12 h. (b) 9,10-dibromoanthracene (1 eq.), 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole (2.1 eq.), 2 mol% Pd(PPh₃)₂Cl₂, 4 mol% CuI, toluene/Et₃N, 70 °C, 1.5 h. (c) 2,7-diiodo-9,9-dibutyl-9H-fluorene (1 eq.), 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole (2.2 eq.), 2 mol% Pd(PPh₃)₂Cl₂, 2 mol% CuI, toluene/Et₃N, rt, 2 h. (d) 1,4-dibromothiophene (1 eq.), 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole (2.3 eq.), 2 mol% Pd(PPh₃)₂Cl₂, 2 mol% CuI, toluene/Et₃N, 80 °C, 12 h. (e) 4,7-dibromobenzo[c][1,2,5]thiadiazole (1 eq.), 9-(7-ethynyl-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole (2 eq.), 2 mol% Pd(PPh₃)₂Cl₂, 2 mol% CuI, toluene/diisopropyl amine, 80 °C, 12 h.

Synthesis of 2,7-dibromo-9H-fluorene (2): Bromine (50 g, 0.315 mol) in 100 mL of chloroform was added dropwise into a suspension solution containing fluorene 1.
(25 g, 0.154 mol), iron powder (0.13 g, 0.0023 mol) in a catalytic amount and 250 mL of chloroform. The flask was cooled by ice water, wrapped with aluminium foil and the temperature was controlled under 5 °C. The reaction was allowed to stand for 2 h. The product was filtered and recrystallized with chloroform, giving white crystal (44 g, 90% yield).

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{, 300 MHz)} : & \delta 3.84 (s, 2H), 7.44-7.49 (d, J = 8.31 \text{ Hz}, 2H), 7.53-7.59 (d, J = 8.31 \text{ Hz}, 2H), 7.63 (s, 2H). \\
\text{MS - EI} : & \text{m/z 324 } [\text{M}+2]^+ 
\end{align*}
\]

**2,7-dibromo-9,9-dihexyl-9H-fluorene (3):** To a stirred solution of 2 (40 g, 0.124 mol) in 250 mL THF under nitrogen was added potassium tertiary butoxide (41.66 g, 0.372 mol) in 100 mL THF slowly at 0 °C. After 1 h n-hexyl bromide (52.08 g, 0.31 mol) was added to the reaction mixture and stirred at room temperature for 8 h. The reaction mixture was filtered and the organic layer was concentrated under reduced pressure. The oily residue was purified by flash column chromatography (silica gel, hexane) to afford white solid (52.23 g, 92% yield).

\[
\begin{align*}
\text{1H NMR (CDCl}_3\text{, 300 MHz)} : & \delta 0.52-0.64 (m, 4H), 0.74-0.83 (t, J = 6.99 \text{ Hz}, 6H), 0.99-1.19 (m, 12H), 1.85-1.95 (m, 4H), 7.37-7.51 (m, 6H). \\
\text{MS - EI} : & \text{m/z 490 } [\text{M}]^+ 
\end{align*}
\]

**9-(7-bromo-9,9-dihexyl-9H-fluoren-2-yl)-9H-carbazole (4):** A mixture of 3 (49.2 g, 0.1 mol), carbazole (11.32 g, 0.067 mol), crushed anhydrous K$_2$CO$_3$ (23.18 g, 0.168 mol), CuI (2.55 g, 0.0134 mol), L-proline (1.54 g, 0.0134 mol) were taken in
100 mL of dry DMF and refluxed under nitrogen atmosphere for 24 h. Then cooled to rt and DMF was removed under reduced pressure. The resulting mixture was then diluted with ethyl acetate and filtered through a small pad of silica gel. The filtrate was concentrated and the residue was purified by column chromatography (silica gel, hexane) to afford the 9-(7-bromo-9,9-dibutyl-9H-fluoren-2-yl)-9H-carbazole 4 as a white solid (34.7 g, 60%).

$^1$H NMR (CDCl$_3$, 300 MHz): δ 0.68-0.83 (m, 10H), 1.02-1.21 (m, 12H), 1.92-2.01 (m, 4H), 7.26-7.33 (m, 2H), 7.4-7.44 (m, 4H), 7.47-7.54 (m, 4H), 7.58-7.62 (d, d $J = 0.57$ Hz, $J = 7.93$ Hz, 1H), 7.82-7.86 (d, d $J = 2.64$ Hz, $J = 8.69$ Hz, 1H), 8.14-8.18 (t, d $J = 0.94$ Hz, $J = 7.74$ Hz, 2H).

MS-EI: m/z 577 [M]$^+$

4-(9,9-dihexyl-7-(9H-carbazol-9-yl)-9H-fluoren-2-yl)-2-methylbut-3-yn-2-ol (5): A solution of 4 (34 g, 0.0589 mol), 2-methylbut-3-yn-2-ol (9.41 g, 0.112 mol) and Pd(PPh$_3$)$_2$Cl$_2$ (0.827 mg, 0.0012 mol) in 50 mL of toluene/Et$_3$N (5/1) was degassed with nitrogen for 30 min. Then CuI (0.224 g, 0.0012 mol) was added at once and deaeration was continued for 10 min, stirring was continued at 70 °C for 12 h. The solvent was removed under reduced pressure and the reaction mixture diluted with ethyl acetate. The resulting solution was filtered through celite. The filtrate was concentrated and the crude product was purified by column chromatography (silica gel, hexane 95%, ethyl acetate 5%) to afford a white solid. (32.8 g, 96.6% yield).
Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives......

$^1$H NMR (CDCl$_3$, 300 MHz) : $\delta$ 0.65-0.84 (m, 10H), 1.04-1.21 (m, 12H), 1.66 (s, 6 H), 1.93-2.04 (m, 4H), 7.21-7.28 (m, 2H), 7.32-7.40 (m, 5H), 7.41-7.45 (dd, $J = 1.13$ Hz, $J = 7.93$ Hz, 1H), 7.50-7.56 (m, 2H), 7.65-7.69 (d, $J = 7.74$ Hz, 1H), 7.84-7.88 (d, $J = 7.93$ Hz, 1H), 8.09-8.13 (d, $J = 7.74$ Hz, 2H).

MS-EI : m/z 581 [M]$^+$

9-(9,9-dihexyl-7-ethynyl-9H-fluorene-2-yl)-9H-carbazole (6): A mixture of 5 (30 g, 0.062 mol) and potassium hydroxide (10.42 g, 0.186 mol) in 100 mL of isopropanol was heated at reflux under nitrogen with vigorous stirring for 2 h. The solvent was then removed and the crude product was purified by column chromatography (silica gel, hexane) to afford white solid (24.3 g, 90% yield).

$^1$H NMR (CDCl$_3$, 300 MHz) : $\delta$ 0.67-0.84 (m, 10H), 1.03-1.23 (m, 12H), 1.94-2.04 (m, 4H), 3.09 (s, 1H), 7.21-7.28 (m, 2H), 7.32-7.41 (m, 4H), 7.45-7.57 (m, 4H), 7.67-7.71 (d, $J = 7.74$ Hz, 1H), 7.85-7.89 (d, $J = 7.93$ Hz, 1H), 8.09-8.13 (d, $J = 7.74$ Hz, 2H).

MS-EI : m/z 523 [M]$^+$

2,7-diiodo-9H-fluorene (11): Fluorene 1 (1.0 g, 6 mmol) was dissolved in 10 mL of the boiling solvent (CH$_3$COOH: H$_2$O:H$_2$SO$_4$ = 10: 2: 0.3), followed by cooling to 60-65 °C, adding periodic acid dihydrate (0.96 g, 4.2 mmol) and iodine (1.7 g, 4.2 mmol). After 4 h, the reaction mixture was cooled and the precipitate obtained was filtered, washed with 2 N aqueous Na$_2$CO$_3$ and water. The crude product was recrystallized from hexane to give pale yellow solid (1.71 g, 68% yield).

77
Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives

1H NMR (CDCl$_3$, 300 MHz) : $\delta$ 3.83 (s, 2H), 7.43-7.50 ($d, J = 8.12 \text{ Hz}, 2H$), 7.66-7.70 ($d, J = 7.93 \text{ Hz}, 2H$), 7.84 (s, 2H).

MS-EI : m/z 418 [M]$^+$

2,7-diiodo-9,9-dibutyl-9H-fluorene (12): To a stirred solution of 11 (1.6 g, 3.8 mmol) in 10 mL THF under nitrogen was added potassium tertiary butoxide (1.28 g, 1.14 mmol) in 10 mL THF slowly at 0 °C. After 1 h n-butyl bromide (1.56 g, 1.14 mmol) in 5 mL THF was added to the reaction mixture slowly and stirred at room temperature for 8 h. The reaction mixture was filtered and the organic layer was concentrated under reduced pressure. The crude product was purified by flash column chromatography (silica gel, hexane) to afford white solid (1.9 g, 89% yield).

1H NMR (CDCl$_3$, 300 MHz) : $\delta$ 0.49-0.63 (m, 4H), 0.66-0.75 ($t, J = 7.36 \text{ Hz}, 6H$), 1.03-1.17 (m, 4H), 1.85-1.94 (m, 4H), 7.35-7.41 ($d, J = 7.93 \text{ Hz}, 2H$), 7.58-7.66 (m, 4H).

MS-EI : m/z 530 [M]$^+$

1,4-bis((7-(9H-carbazol-9-yl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)benzene (C1):

1,4-dibromo benzene 7 (472 mg, 2 mmol), PdCl$_2$(PPh$_3$)$_2$ (28 mg, 0.04 mmol), Cul (7.6 mg, 0.04 mmol), were added to a degassed solution of Et$_3$N (5 mL) and Toluene (10 mL) under N$_2$. 9-(9,9-dihexyl-7-ethynyl-9H-fluoren-2-yl)-9H-carbazole 6 (2.2 g, 4.2 mmol) in toluene (5 mL) was added slowly. After the mixture was stirred at 70 °C for 12 h, the solvent was removed under reduced pressure and the reaction mixture diluted with ethyl acetate. The resulting solution was filtered through celite. The filtrate was concentrated and the crude product was purified by
column chromatography (silica gel, hexane) to afford a pale green color solid (0.85 g, 76% yield).

\[ \text{1H NMR (CDCl}_3\text{, 300 MHz): } \delta 0.74-0.83 (m, 20H), 1.08-1.21 (m, 24H), 1.99-2.06 (m, 8H), 7.23-7.28 (m, 4H), 7.34-7.41 (m, 8H), 7.51-7.60 (m, 12H), 7.72-7.76 (d, J = 7.37 Hz, 2H), 7.87-7.91 (d, J = 7.37 Hz, 2H), 8.09-8.14 (d, J = 7.37 Hz, 4H). \]

\[ \text{13C NMR (CDCl}_3\text{, 75 MHz): } \delta 14.0, 22.6, 23.9, 29.6, 31.5, 40.2, 55.5, 83.1, 92.4, 109.8, 119.9, 120.0, 120.3, 120.4, 121.2, 121.4, 121.6, 121.8, 123.4, 125.9, 127.0, 130.9, 131.6, 136.9, 138.6, 140.8, 140.9, 151.2, 153.0. \]

IR (KBr) in cm\(^{-1}\): 720, 746, 825, 1227, 1355, 1455, 1492, 1601, 2197, 2852, 2923, 3051.

MALDI-TOF-MS: (m/z) 1120.7046 [M]\(^+\).

Mp: 98 °C

**9,10-bis((7-(9H-carbazol-9-yl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)anthracene (C2):** 9-(9,9-dihexyl-7-ethynyl-9H-fluoren-2-yl)-9H-carbazole 6 (2.2 g, 4.2 mmol) in toluene (3 mL) was added slowly to a degassed solution of 9,10-dibromo anthracene 8 (672 mg, 2 mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (28 mg, 0.04 mmol), CuI (15 mg, 0.08 mmol), in Et\(_3\)N (5 mL) and Toluene (10 mL) under N\(_2\). After the mixture was stirred at 70 °C for 1.5 h, the solvent was removed under reduced pressure and the reaction mixture diluted with ethyl acetate. The resulting solution was filtered through celite. The filtrate was concentrated and the crude product was purified by column chromatography (silica gel, CHCl\(_3\)-Hexane 5/95 v/v) to afford a yellow color.
solid. This solid was further purified by crystallization of the compound from 1:1 mixture CHCl₃/MeOH. Isolated yield (1.63 g, 67%).

\[\text{C}2\]

$^1$H NMR (CDCl₃, 300 MHz) : $\delta$ 0.75-0.92 (m, 20H), 1.09-1.28 (m, 24H), 2.04-2.17 (m, 8H), 7.24-7.31 (m, 4H), 7.35-7.45 (m, 8H), 7.57-7.63 (m, 4H), 7.66-7.75 (m, 6H), 7.84 (s, 4H), 7.94-7.98 (d, $J = 7.55$ Hz, 2H), 8.11-8.16 (d, $J = 7.55$ Hz, 4H), 8.74-8.81 (m, 4H).

$^{13}$C NMR (CDCl₃, 75 MHz) : $\delta$ 14.03, 22.6, 23.9, 29.6, 31.5, 40.3, 55.6, 87.04, 103.6, 118.6, 119.9, 120.1, 120.4, 121.3, 121.8, 122.03, 123.4, 125.9, 126.9, 127.4, 131.2, 132.2, 136.9, 139.6, 140.97, 141.02, 151.4, 153.

IR (KBr) in cm$^{-1}$ : 723, 754, 819, 1228, 1310, 1360, 1462, 1601, 2192, 2854, 2924, 3053.

MALDI-TOF-MS : ($m/z$) 1221.7 [M]$^+$. 

mp : 244 °C

9,9’-(7,7’-(9,9-dibutyl-9H-fluorene-2,7-diyl)bis(ethyne-2,1-diyl)bis(9,9-dihexyl-9H-fluorene-7,2-diyl))bis(9H-carbazole) (C3): 9-(9,9-dihexyl-7-ethynyl-9H-fluoren-2-yl)-9H-carbazole 6 (575 mg, 1.1 mmol) in toluene (2 mL) was added slowly to a degassed solution of 2,7-diiodo-9,9-dibutyl-9H-fluorene 12 (265 mg, 0.5 mmol), PdCl$_2$(PPh$_3$)$_2$ (7 mg, 0.01 mmol), Cul (2 mg, 0.01 mmol), in Et$_3$N (5 mL) and Toluene (10 mL) under N$_2$. After the mixture was stirred at room temperature for 2 h, the solvent was removed under reduced pressure and the reaction mixture diluted with ethyl acetate. The resulting solution was filtered through celite. The filtrate was concentrated and the crude product was purified by column...
chromatography (silica gel, Hexane) to afford a pale yellow color solid (0.620 g, 94% yield).

\[ \text{C3} \]

$^1$H NMR (CDCl$_3$, 300 MHz) : $\delta$ 0.56-0.92 (m, 32H), 1.04-1.23 (m, 28H), 1.95-2.09 (m, 10H), 7.22-7.31 (m, 5H), 7.33-7.43 (m, 8H), 7.52-7.63 (m, 11H), 7.67-7.77 (m, 4H), 7.87-7.92 (d, $J = 7.55$ Hz, 2H), 8.09-8.15 (d, $J = 7.55$ Hz, 4H).

$^{13}$C NMR (CDCl$_3$, 75 MHz) : $\delta$ 13.9, 14.01, 22.6, 23.1, 23.9, 25.9, 29.7, 31.6, 40.4, 55.2, 55.5, 90.8, 100.7, 109.8, 119.9, 120.02, 120.4, 121.2, 121.8, 121.9, 122.02, 123.4, 125.87, 125.92, 126.02, 130.8, 130.9, 136.8, 137.1, 139.3, 139.7, 140.6, 140.7, 140.97, 151.1, 152.9.

IR (KBr) in cm$^{-1}$ : 721, 747, 819, 1119, 1228, 1335, 1462, 1602, 2186, 2853, 2923, 3052.

MALDI-TOF-MS : (m/z) 1320.7631 [M$^+$].

mp : 120 °C

2,5-bis((7-(9H-carbazol-9-yl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)thiophene (C4): 1,4-dibromo thiophene 9 (242 mg, 1mmol), PdCl$_2$(PPh$_3$)$_2$ (28 mg, 0.04 mmol), Cul (7.6 mg, 0.04 mmol), were added to a degassed solution of Et$_3$N (5 mL) and Toluene (5 mL) under N$_2$. 9-(9,9-dihexyl-7-ethynyl-9H-fluoren-2-yl)-9H-carbazole 6 (1.2 g, 2.3 mmol) in toluene (2 mL) was added slowly. After the mixture was stirred at 80 °C for 12 h, the solvent was removed under reduced pressure and the reaction mixture diluted with ethyl acetate. The resulting solution was filtered through celite. The filtrate was concentrated and the crude product
was purified by column chromatography (silica gel, hexane) to afford a pale yellow color solid (0.957 g, 85% yield).

\[
\begin{align*}
1^H \text{NMR (CDCl}_3, 300 \text{ MHz)} &: \delta 0.70-0.90 \text{ (m, 20H)}, 1.05-1.24 \text{ (m, 24H)}, 1.96-2.08 \text{ (m, 8H)}, 7.20 \text{ (s, 1H)}, 7.22-7.29 \text{ (m, 5H)}, 7.33-7.42 \text{ (m, 8H)}, 7.51-7.60 \text{ (m, 8H)}, 7.71-7.76 \text{ (dd, } J = 3.59 \text{ Hz, } J = 7.74 \text{ Hz, 2H)}, 7.87-7.91 \text{ (d, } J = 7.93 \text{ Hz, 2H)}, 8.09-8.15 \text{ (d, } J = 7.74 \text{ Hz, 4H)}.
\end{align*}
\]

\[
\begin{align*}
13^C \text{NMR (CDCl}_3, 75 \text{ MHz)} &: \delta 14.1, 22.6, 23.9, 29.7, 31.6, 40.3, 55.6, 82.8, 95.2, 109.8, 119.99, 120.4, 121.2, 121.3, 121.4, 121.8, 123.5, 125.97, 127.1, 130.9, 131.9, 136.97, 137.1, 139.5, 139.7, 141.0, 151.1, 151.2, 153.0, 153.1, 153.2.
\end{align*}
\]

IR (KBr) in cm\(^{-1}\) : 439, 813, 1011, 1225, 1322, 1453, 1598, 2203, 2852, 2921, 3051.

MALDI-TOF-MS : (\text{m/z}) 1126.6299 [M]^+.

mp : 140 °C

**4,7-bis((7-(9H-carbazol-9-yl)-9,9-dihexyl-9H-fluoren-2-yl)ethynyl)benzo[c][1,2,5]thiadiazole (C5):** 4,7-dibromobenzo [1,2,5] thiadiazole 10 (294 mg, 1mmol), PdCl\(_2\)(PPh\(_3\))\(_2\) (14 mg, 0.02 mmol), Cul (3.8 mg, 0.02 mmol), were added to a degassed solution of diisopropylamine (10 mL) under N\(_2\). 9-(9,9-dihexyl-7-ethynyl-9H-fluoren-2-yl)-9H-carbazole 6 (1.05 g, 2.0 mmol) in toluene (2 mL) was added slowly. After the mixture was stirred at 80 °C for 12 h, the solvent was removed under reduced pressure and the reaction mixture diluted with ethyl acetate. The
resulting solution was filtered through celite. The filtrate was concentrated and the crude product was purified by column chromatography (silica gel, hexane) to afford an orange red color solid (0.153 g, 13% yield).

![Chemical Structure](image)

$^{1}$H NMR (CDCl$_3$, 300 MHz) : δ 0.74-0.85 (m, 20H), 1.09-1.24 (m, 24H), 2.02-2.11 (m, 8H), 7.24-7.30 (3, 4H), 7.37-7.43 (m, 8H), 7.56-7.61 (m, 4H), 7.67 (s, 2H), 7.71-7.74 (d, J = 8.08 Hz, 2H), 7.78-7.82 (d, J = 8.08 Hz, 2H), 7.86 (s, 2H), 7.91-7.94 (d, J = 8.08 Hz, 2H), 8.12-8.16 (d, J = 7.07 Hz, 4H).

$^{13}$C NMR (CDCl$_3$, 75 MHz) : δ 14.1, 22.6, 23.9, 29.7, 31.6, 40.4, 55.7, 85.8, 98.7 109.8, 117.3, 119.99, 120.4, 121.03, 121.4, 121.8, 123.41, 123.45, 125.9, 126.4, 131.5, 132.6, 137.03, 139.50, 139.52, 140.9, 140.97, 141.4, 141.5, 151.15, 151.21, 153.08.

IR (KBr) in cm$^{-1}$ : 746, 822, 1227, 1347, 1453, 1602, 1735, 2200, 2853, 2922, 3051.

MALDI-TOF-MS : (m/z) 1178.5658 [M]$^+$.

mp : 261 °C

3.2.3 Computational Studies

In this study, all the calculations have been carried out using Gaussian09 ab initio/DFT quantum chemical package [37]. Minimum energy conformational search for all the molecules have been carried out at DFT-B3LYP with $C_2$ symmetry constraint and with a default integration grid as implements in the
Gaussian program [37]. For the sake of simplicity, hexyl solubilizing chains have been replaced by methyl groups. The optimized geometry have been confirmed to be real minima by the real frequencies through the vibrational frequency calculations. The minimum energy conformation geometry is then subjected to SACCI calculations to obtain the vertical electronic absorption properties. A 6-31G** basis set is employed in all the calculations. The two-photon cross sections have been calculated with the use of truncated three-state model approach by using the data obtained from the SACCI method.

3.3 Results and Discussion

3.3.1 Solid state properties

At room temperature, all the molecules obtained from the synthesis are solids. Hence the solid-state properties of these molecules such as melting point, thermal stabilities of C1–C5 were investigated by thermo gravimetric analysis (TGA), as shown in Table 3.1. The results reveal that the onset decomposition temperatures of the compounds are all around 355-490 °C under a nitrogen atmosphere, which indicates that they are quite thermally stable in the incident laser environment, i.e., there will not be any damage to the material by the impact of the laser light.

Table 3.1: Solid state properties for the molecule C1- C5.

<table>
<thead>
<tr>
<th>Molecule</th>
<th>mp °C</th>
<th>Td °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>98</td>
<td>355</td>
</tr>
<tr>
<td>C2</td>
<td>244</td>
<td>490</td>
</tr>
<tr>
<td>C3</td>
<td>120</td>
<td>380</td>
</tr>
<tr>
<td>C4</td>
<td>140</td>
<td>390</td>
</tr>
<tr>
<td>C5</td>
<td>261</td>
<td>440</td>
</tr>
</tbody>
</table>

3.3.2 Photo physical properties

The absorption and emission spectra of compounds C1–C5 were measured in chloroform, and the relevant data are presented in Table 3.2. The absorption spectra of C1–C5 compounds show intensive transitions in the UV
region, with moderately strong absorption bands in the range 200–300 nm (Figure 3.1, Table 3.2). The bands at about 247, 275, and 290 nm for these compounds are assigned to carbazole-centered transitions. Peaks at 300–450 nm in case of C1, C3, C4 with characteristic vibronic patterns are attributed to the $\pi-\pi^*$ transition of fluorene moiety, and also may be from the central core. Whereas the absorption features of C2 and C5 at wavelengths in the 300–380 nm region show strong absorbances, which are assigned to the $\pi-\pi^*$ absorption band of anthracene (C2) and benzothiadiazole (C5). Apart from the characteristic absorptions of the donors and acceptors, the solution spectra of C2, C5 show new broad bands at a longer wavelength of 380–550 nm, which depends on their effective conjugation lengths. In this case, anthracene, benzothiadiazole compounds C2 and C5 shows longer wavelengths than those of C1, C3 and C4, indicating longer effective conjugation lengths and smaller HOMO–LUMO gaps of C2 and C5 than those of C1, C3 and C4, respectively. The order of $\lambda_{\text{max}}$ of five compounds is $C1 < C3 < C4 < C5 < C2$. Among the five compounds C1—C5, C1 exhibits the lowest wavelength and thus has the shortest effective conjugation length along the molecule, whereas the longest effective conjugation length is observed for C2 from its onset absorption in the ground state may be due to the coplanar conformation of the anthracene and ethynylene groups, indicating a greater delocalization of electrons in C2.

![Absorbance vs Wavelength](image)

Figure 3.1: Absorption spectra of compounds C1–C5 in chloroform measured at 5×10⁻⁶ M concentration.
To gain further insight into the photophysical process within these compounds, we investigated their absorption behaviors in different solvents. The absorption spectra in different solvents are nearly independent of solvent polarity, which indicates a negligible intramolecular charge-transfer process between donor and acceptor chromophores in the ground states, shown in table 3.3, figure 3.2.

Figure 3.2: Normalized absorption spectra of compounds C1-C5 in different solvents
The fluorescence spectra of C1–C5 measured at the concentration of 1.0×10^{-6} M in chloroform are shown in Figure 3.3. The maximum emission wavelengths λ_{max} in chloroform for C1–C5 are 428, 543, 433, 455 and 548 nm, respectively. Red shifts in the fluorescence spectra were observed in the order of C1 < C3 < C4 < C2 < C5. These spectra have multiple peaks and they have two vibronically resolved peaks and C5 shows structure less broad spectra. The peak positions in the fluorescence spectra are summarized in Table 3.2. As already noted in the absorption spectra, the fluorescence spectra exhibit a monotonous bathochromic shift with increasing acceptor strength. All compounds show large Stokes shifts ranging from 54 to 98 nm (Table 3.2). As expected, the fluorescence Stokes shift increases as the acceptor strength increases. This means that the energy gap between the ground and the excited states decreases monotonically in the order, C1 > C3 > C4 > C2 > C5 (Table 3.2). As the acceptor strength increases, the charge-transfer character of the excited electronic state increases. This leads to the prediction that the salvation energy of the excited electronic state becomes large and the fluorescence Stokes shift will increase too.

![Figure 3.3: Fluorescence spectra of compounds C1–C5 in chloroform at 1.0×10^{-6} M concentration, excited at their corresponding λ_{max} wavelengths.](image-url)
Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives......

Fluorescence spectra for C1–C5 were measured in various solvents from nonpolar to polar media for verifying the influence of solvent polarity on their emission peaks, shown in figure 3.5 and tabulated in table 3.3. Compounds from C1–C4 shows negligible solvatochromism, with two resolved vibronically coupled peaks, indicating no intramolecular charge transfer in the excited state.

![Figure 3.4: Normalized fluorescence spectra of compounds C1–C4 in all solvents at 1.0×10^{-6} M concentration excited at their corresponding \( \lambda_{\text{max}} \) wavelengths.](image)

Compound C5 display a strong emission solvatochromism that is reflected by a large bathochromic shift of their fluorescence emission maxima with increasing solvent polarity. In contrast the absorption is not much shifted. This solvatochromic behavior, which results from the stabilization of the highly polar emitting state by polar solvents, is typical for compounds presenting an internal charge transfer upon excitation and has been fully documented for fluorophores containing donor (carbazole) acceptor(bezothiadiazole) units. The rotation of the donor part of the molecule with respect to the acceptor part is allowed, which
results a twisted intramolecular charge transfer (TICT) excited states and luminescence for C5. This is true and supported by the following results: (i) The large Stoke shifts of 98 nm for C5. (ii) The broad featureless shape of the emission spectra. (iii) The solvent dependence of the emission spectra, as shown in Figure 3.5 for compound C5. The emission spectra of compound C5 was recorded in various solvents from nonpolar to polar media. The maximum emission wavelength of C5 is red shifted by 45 nm from hexane (523 nm) to acetonitrile (568 nm). Interestingly in apolar media (hexane) the vibronic structure is restored likely due to the decrease of polarity in the solvation shell and hence a better vibronic coupling. The solvatochromic behavior is accompanied by a decrease of the fluorescence quantum yield when the polarity of the solvent increases. The origin of this quenching phenomenon is attributed to the lowered energies of the ICT states. All the compounds give relatively high fluorescence quantum yields.

![Graph showing emission spectra of C5 in different solvents](image)

**Figure 3.5:** Emission spectra of compound C5 in Hexane, Toluene, Tetrahydrofuran, Chloroform, and Acetonitrile at $1.0 \times 10^{-6}$ M concentration, excited at their corresponding $\lambda_{\text{max}}$ wavelengths.
Table 3.2: Absorption, molar extinction coefficient, Emission, quantum yield, stokes shift data of compounds C1—C5 measured in CHCl₃.

<table>
<thead>
<tr>
<th>Compound</th>
<th>λ&lt;sub&gt;max&lt;/sub&gt; (ε, M⁻¹ Cm⁻¹)&lt;sup&gt;a&lt;/sup&gt;</th>
<th>λ&lt;sub&gt;emi&lt;/sub&gt;&lt;sup&gt;b&lt;/sup&gt;</th>
<th>Φ&lt;sup&gt;c&lt;/sup&gt;</th>
<th>Stokes shift in cm⁻¹ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>247 (91244), 290 (57928), 365 (92896)</td>
<td>408, 430</td>
<td>0.34</td>
<td>4033 (63)</td>
</tr>
<tr>
<td>C2</td>
<td>248 (98012), 275 (112294), 344 (63232), 468 (76738), 489 (68028)</td>
<td>510, 543</td>
<td>0.43</td>
<td>2034 (54)</td>
</tr>
<tr>
<td>C3</td>
<td>247 (102276), 290 (56502), 376 (153274)</td>
<td>410, 433</td>
<td>0.38</td>
<td>3501 (57)</td>
</tr>
<tr>
<td>C4</td>
<td>247 (88706), 290 (53092), 333 (103054)</td>
<td>431, 455</td>
<td>0.36</td>
<td>4132 (72)</td>
</tr>
<tr>
<td>C5</td>
<td>247 (86500), 292 (50918), 342 (91166), 450 (53002)</td>
<td>548</td>
<td>0.19</td>
<td>3974 (98)</td>
</tr>
</tbody>
</table>

<sup>a</sup>λ<sub>max</sub> of the one-photon absorption spectra in nm and molar extinction coefficients in brackets measured at 5×10⁻⁶ M concentration. <sup>b</sup>λ<sub>max</sub> of the one-photon fluorescence spectra in nm measured at 1×10⁻⁶ M concentration. <sup>c</sup>Fluorescence quantum yield measured by taking diphenylanthracene (0.9 Φ in cyclohexane) as standard with a deviation of ± 10%.

To have a deeper understanding of the observed spectra, computational studies have been carried out at the SACKI level with 240 active orbitals which include 60 occupied and 180 unoccupied orbitals with 20 states for each irreducible representaions which provides a total of 40 excited states. The obtained theoretical values are presented in Table 3.4. From the table it reveals that the calculated values as well as the trends are in good agreement with the experimental values. The dominat transitions occuring in these molecules are in between HOMO-1 to LUMO by 80-90 % as shown in Figure 3.5. The charge density in the HOMO-1 is localized on the donor substituents (mainly on carbazole) where as in the case of HOMO, the charge is delocalized over the entire molecule. In the excited state LUMO, the charge density is shifted to the central core. The transition moments are also very high which ranges from 10-16 Debye. The difference in permanent dipole moments (Δμ<sub>ge</sub>) in C1-C4 are negligible indicating that there is no charge transfer in the ground state indicating the weak acceptors of the benzene, anthracene, fluorene and thiophene in C1, C2, C3 and C4. For C5, (Δμ<sub>ge</sub>) is considerably large 4.24 Debye indicating the charge transfer from the donor carbazole moiety. This is due to the strong accepting nature of the benzothiadiazole group in C5.
Table 3.4: Calculated one-photon absorption wavelength (OPA in nm), Oscillator strengths ($f$), ground to first excited state transition dipole moments, ground, excited states permanent dipole moments and the difference in the state dipole moments ($\mu_{ge}$, $\mu_g$, $\mu_e$ and $\Delta \mu_{ge}$ in Debye) and the $|\psi_i|$ contribution to the wavefunction.

| Molecule | $\lambda_{\text{exp}}$ (eV) | OPA$^a$ | $f$ | $\mu_{ge}$ | $\mu_g$ | $\mu_e$ | $\Delta \mu_{ge}$ | $|\psi_i|$ contribution |
|----------|-----------------|--------|-----|------------|--------|--------|-----------------|------------------|
| C1       | 365 (4.00)      | 337 (3.68) | 3.353 | 15.48     | 0.02   | 0.04   | 0.01            | HOMO-1→LUMO (76%) |
| C2       | 489 (2.54)      | 421 (2.95) | 1.881 | 12.96     | 0.06   | 0.07   | 0.01            | HOMO-1→LUMO (92%) |
| C3       | 376 (3.30)      | 343 (3.62) | 3.880 | 16.80     | 0.26   | 0.21   | 0.05            | HOMO-1→LUMO (77%) |
| C4       | 383 (3.24)      | 372 (3.34) | 2.622 | 14.38     | 3.07   | 2.82   | 0.25            | HOMO-1→LUMO (82%) |
| C5       | 450 (2.76)      | 476 (2.60) | 1.021 | 10.16     | 5.37   | 9.61   | 4.24            | HOMO-1→LUMO (85%) |

$^a$The values given in the parenthesis corresponds to the one-photon absorption energies in eV obtained from SACCI- method.
Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives....

C2

HOMO-1

HOMO

LUMO

C3

HOMO-1

HOMO

LUMO
Figure 3.5: The HOMO-1, HOMO, and LUMO Molecular orbitals pictures of C1–C5 molecules obtained at the B3LYP/6-31G(d,p) level. The orbitals are generated at an isovalue of 0.002 a.u.
3.3.3 Electrochemical Properties

To evaluate electrochemical properties of C1–C5, cyclic voltammetry studies were performed under N\textsubscript{2} in 0.1M CH\textsubscript{2}Cl\textsubscript{2}/tetra butyl ammonium perchlorate solutions with scan rates of 100 mV/s and a scan range between -2.0 and 2.0 V. Figure 3.6 shows representative voltammograms. The electrochemical properties as well as the energy level parameters of C1–C5 are listed in Table 3.5. It can be observed from Figure 3.6 that the first onset oxidation potentials (E\textsubscript{onset\ ox}) of C1–C5 were 1.22, 0.97, 1.15, 1.14, and 0.97 V, respectively. Therefore, the ground state oxidation potential corresponding to the HOMO energy levels are -5.62, -5.37, -5.55, -5.54 and -5.37 eV (vs vacuum), respectively, according to the equation HOMO = -e(E\textsubscript{onset\ ox} + 4.4) eV [38]. The first onset reduction potentials (E\textsubscript{onset\ red}) of C1–C5 were -1.26, -1.34, -1.27, -1.34, -1.41 V, respectively. Therefore, the ground state reduction potential corresponding to the LUMO energy levels are -3.14, -3.06, -3.13, -3.06 and -2.99 eV (vs vacuum), respectively, according to the equation LUMO = -e(E\textsubscript{onset\ red} + 4.4) eV. [38]
Oxidation and reduction potentials give information on the relative positions of the HOMO and LUMO. The band gaps for these compounds could be calculated from the first reduction and oxidation onset potentials. This was in good agreement with the determined optical band gap ($E_{0-0}$) obtained from the intercept of the normalized absorbance and fluorescence spectra, shown in Table 3.5. From the HOMO-LUMO gap and also from the optical band gap it is observed that from C2 and C5 are with low band gap. It indicates the absorption maximum is more for anthracene and benzothiadiazole centered molecules.

Table 3.5: Electrochemical properties and calculated energy differences of C1–C5.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_{ox,\text{onset}}^{c}$</th>
<th>HOMO</th>
<th>$E_{red,\text{onset}}^{d}$</th>
<th>LUMO</th>
<th>$E_{el,\text{gap}}^{e}$</th>
<th>$E_{op,\text{gap}}^{g}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>1.22</td>
<td>-5.62</td>
<td>-1.26</td>
<td>-3.14</td>
<td>2.48</td>
<td>3.12</td>
</tr>
<tr>
<td>C2</td>
<td>0.97</td>
<td>-5.37</td>
<td>-1.34</td>
<td>-3.06</td>
<td>2.31</td>
<td>2.48</td>
</tr>
<tr>
<td>C3</td>
<td>1.15</td>
<td>-5.55</td>
<td>-1.27</td>
<td>-3.13</td>
<td>2.42</td>
<td>3.08</td>
</tr>
<tr>
<td>C4</td>
<td>1.14</td>
<td>-5.54</td>
<td>-1.34</td>
<td>-3.06</td>
<td>2.48</td>
<td>2.98</td>
</tr>
<tr>
<td>C5</td>
<td>0.97</td>
<td>-5.37</td>
<td>-1.41</td>
<td>-2.99</td>
<td>2.38</td>
<td>2.49</td>
</tr>
</tbody>
</table>

$^{a}$Determined by cyclic voltammetry in CH$_2$Cl$_2$ with SCE as a reference electrode. Scan rate of 100 mVs$^{-1}$. $^{b}$onset oxidation potential. $^{c}$HOMO = $(E_{ox,\text{onset}}^{c} + 4.4)$ eV. $^{d}$onset reduction potential. $^{e}$LUMO = $(E_{red,\text{onset}}^{d} + 4.4)$ eV. $^{f}$Cyclic voltammetric HOMO–LUMO gap derived from the difference between HOMO and LUMO energy levels. $^{g}$energy of the optical band gap obtained from the intercept of the normalized absorption and emission spectra.

3.4 Two-Photon Absorption

The TPA cross-sections have been calculated based on the equations as mentioned in the section 1.7.3 in the Chapter 1. Excited-state electronic structure analysis is performed for 40 singlet excited states for dipoles. To stimulate the
finite spectra from theory, a damping factor \( \Gamma \) is introduced in the equation. In many theoretical calculations this factor has been fixed at 0.1 eV. The choice of this specific value is somewhat arbitrary as it corresponds to the one observed experimentally for the series of chromophores for which it was originally used. The error introduced by an inadequate bandwidth on the two-photon absorption cross section scales approximately as \( 1/\Gamma \) as can be simply inferred from expressions derived within effective two- (Equation 1.14) and three-state (Equation 1.15) models. For the different chromophores investigated in this chapter, the experimental half-bandwidth at half-maximum amounts to \( \Gamma_{\text{gau}} = 0.20 \pm 0.25 \) eV, with bands of roughly Gaussian shape. Thus the damping factor used in all calculations is fixed to \( \Gamma_{\text{lor}} = 0.17 \) eV and hence we have used \( \Gamma_{\text{lor}} = 0.1 \) eV is used in all our calculations. In all of our calculations, we have considered the two-photon state which is strongly electronically coupled to the one-photon state with a large transition moments between the one-photon and the two-photon state as shown in Table 3.6 and compared with the reference molecule R1 with the N,N-dimethyl amino benzene substitution on pyrene with a triple bond. [39] Similarly, the simulated TPA spectra along with the one-photon spectra are shown in Figure 3.7. The reference molecule R1 showed a \( \delta \) of 53 GM, which is equivalent to the experimental one (55 GM). This shows the reliability of our three-state model approximation to SOS. For C1 and C3, the TPA state is strongly coupled by an excited state transition moment by 18.65 and 20.69 Debye which also showed a large TPA cross-section of 4579 GM and 5882 GM with a benzene and fluorene centered compounds respectively. In the case of, C4 and C5, the TPA is relatively weakly coupled to the one-photon state by 11.66 and 14.55 Debye of excited state transition moments. Excited state transition dipole moment for compound C2 is very less 7.84 Debye, it indicates that incorporation of an anthracene moiety is not appropriate in order to accomplish large \( \delta \) for these type of quadrupolar D-A-D type chromophores and showed less \( \delta \). The \( \delta \) values also show the same trend as with the excited state transition moments in all cases. This infers that the magnitude of \( \delta \) will increase as the strength of the electronic coupling between the one-photon and the TPA state increases. The order of TPA for these compounds is C3 > C1 > C5 > C4 > C2. The TPA laser wavelength which is half of the TPA energy is always below the one-photon transition energy. The detuning factor \( \Delta \) which is defined as the difference between the one-photon transition energy and the TPA
laser wavelength is considerably large (0.86 – 1.35 eV) indicated that there is no pre-resonance which will further enhances the magnitude of $\delta$.

Table 3.6: Calculated one-photon absorption wavelength (OPA in nm), two-photon absorption laser wavelength (TPA in nm), detuning factor ($\Delta f$ in eV), transition dipole moments from the first excited sate to the lowest allowed TPA state ($\mu_{ee'}$ in Debye) and TPA cross-section ($\delta_{TPA}$ in GM).

<table>
<thead>
<tr>
<th>Molecule</th>
<th>$\lambda_{exp}$ max (eV)</th>
<th>OPA$^a$ (nm)</th>
<th>TPA$^a$ (nm)</th>
<th>$\Delta f$ (eV)</th>
<th>$\mu_{ee'}$ Debye</th>
<th>$\delta_{TPA}$ GM</th>
</tr>
</thead>
<tbody>
<tr>
<td>R$^b$</td>
<td>396 (3.13)</td>
<td>345 (3.59)</td>
<td>552 (2.24)</td>
<td>1.35</td>
<td>3.77</td>
<td>53</td>
</tr>
<tr>
<td>C1</td>
<td>365 (4.00)</td>
<td>337 (3.68)</td>
<td>529 (2.35)</td>
<td>1.34</td>
<td>18.65</td>
<td>4579</td>
</tr>
<tr>
<td>C2</td>
<td>489 (2.54)</td>
<td>421 (2.95)</td>
<td>672 (1.85)</td>
<td>1.10</td>
<td>7.84</td>
<td>728</td>
</tr>
<tr>
<td>C3</td>
<td>376 (3.30)</td>
<td>343 (3.62)</td>
<td>532 (2.33)</td>
<td>1.29</td>
<td>20.69</td>
<td>5882</td>
</tr>
<tr>
<td>C4</td>
<td>383 (3.24)</td>
<td>372 (3.34)</td>
<td>620 (2.00)</td>
<td>1.34</td>
<td>11.66</td>
<td>1061</td>
</tr>
<tr>
<td>C5</td>
<td>450 (2.76)</td>
<td>476 (2.60)</td>
<td>713 (1.74)</td>
<td>0.86</td>
<td>14.55</td>
<td>1857</td>
</tr>
</tbody>
</table>

$^a$The values given in the parenthesis corresponds to the one-photon absorption energies in eV. $^b$ The standard compound for comparision is taken from the reference [39]
Figure 3.7: Simulated one-photon and TPA spectra obtained at the SACCI/6-31G** and convoluted to get a unit Gaussian at the FWHM.
Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives.....

3.5 Conclusion

A series of donor–acceptor compounds featuring carbazole moieties as the electron-donating units have been successfully prepared by Sonogashira cross-coupling reactions. The absorption, emission, electrochemical properties, of these quadrupolar compounds are significantly affected by the different acceptors. Theoretical calculations provided further evidence for the observed electronic properties. Their linear and nonlinear optical properties were investigated theoretically. Depending on the degree on effective π conjugation, acceptor strength of compounds C1–C5 show red shifted optoelectronic properties, particularly the π-bridges, the HOMO–LUMO gaps of these molecules could be tuned in a controlled way. The significant solvent effect observed for C5 clearly indicates that charge separation in the excited state. All compounds showed good fluorescence quantum yields in all solvents.

We have theoretically analyzed the one photon and two photon properties of these five newly synthesized compounds by using SACC method. The maximal one-photon absorption intensities for these compounds appear in the first excited state. It reveals that these are HOMO-1 to LUMO transitions. The electron density in the HOMO-1 is mainly located in the carbazole moiety for all compounds and the LUMO is localized on the central arene core. The successful increase in δ values demonstrates the key of fluorene carbazole linkers in TPA chromophores to achieve a greater degree of excitation. The order of TPA cross-section for these compounds is C3 > C1 > C5 > C4 > C2 which follow the same trend with that of excited transition dipole moments. All compounds except C2 showed good TPA cross-section values theoretically, demonstrates that these compounds are attractive candidates for applications associated with Two Photon Absorption. Both large TPA and efficient fluorescence make these materials interesting for imaging applications.
3.6 References


Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives


Chapter 3: Design and synthesis of bis carbazole fluorene ethynyl arene derivatives.


$^1$H NMR spectrum of compound 2

$^1$H NMR spectrum of compound 3
$^1$H NMR spectrum of compound 4

$^1$H NMR spectrum of compound 5
$^1$H NMR spectrum of compound 6

$^1$H NMR spectrum of compound 12
$^1$H and $^{13}$CNMR spectrum of compound C1
$^1$H and $^{13}$CNMR spectrum of compound C2
$^1$H and $^{13}$CNMR spectrum of compound C3
$^1$H and $^{13}$C NMR spectrum of compound C4
$^1$H and $^{13}$CNMR spectrum of compound C5
EI mass spectrum of compound 2

EI mass spectrum of compound 3

EI mass spectrum of compound 4
EI mass spectrum of compound 5

EI mass spectrum of compound 6
MALDI-mass spectrum of compound C1

MALDI-mass spectrum of compound C2
MALDI-mass spectrum of compound C3

MALDI-mass spectrum of compound C4
MALDI-mass spectrum of compound C5

TGA thermogram of compound C1
TGA thermogram of compound C5