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# Aggregation induced emissive carbazole-based push pull NLOphores: Synthesis, photophysical properties and DFT studies

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ABSTRACT

2-Alkoxy-9-methyl-9*H*-carbazole-3-carbaldehyde based push pull chromophore were efficiently synthesized by a multi-step reaction starting from 9*H*-carbazole-2-ol. The fluorescence properties of these D–π–A chromophores were investigated in various solvents of varying polarities and in mixed solvent solutions of DMF and $H_2O$. They exhibited low fluorescent intensity in solution but a high fluorescent intensity in aggregate forms and in their solid state due to the promising aggregation-induced emission enhancement characteristics. These dyes were fully characterized by FT-IR, $^1$H NMR and HRMS spectra. The ratio of ground to excited state dipole moment of the novel push pull chromophore were calculated by Bakhshiev and Bilot–Kawski correlations. All the four dyes show more or less twisted intramolecular charge transfer (TICT) characteristics. They show a large first hyperpolarizability value ranging from 189–721 × $10^{-30}$ esu by theoretical method and 73–330 × $10^{-30}$ esu by experimental method.



## 1. Introduction

Designing and synthesizing organic fluorophore with excellent optical and electronic properties have long been topics of interest of many researchers [1]. However when organic fluorophores are to be used in their solid states in which the molecules form aggregates, their emissions suffer from the "aggregation-caused quenching" (ACQ) effect due to strong π–π stacking interactions in extended π-conjugated systems and dipole–dipole interactions in photoinduced D–A charge transfer systems as exemplified by fluorescein [2]. The photophysical behaviour of the molecule is mainly affected by the structure property relationships such as planarity and rotatability, intramolecular restriction, intermolecular interactions, weak excimer formation and ACQ-to-AIE (Aggregation Induced Emission) transformation [3]. ACQ is theoretically well understood phenomenon but it is a harmful photophysical effect in terms of practical applications. There has been huge efforts directed to solve the ACQ problem by impeding chromophore aggregation, but it ended with limited success. The first report on Aggregation Induced Emission (AIE) which is totally contrary to the ACQ phenomenon by Tang's group appeared in 2001 [4]. The important observation for the compounds showing aggregation induced emission enhancement (AIEE) characteristics that they exhibit weak luminescence or have almost no emissions in molecularly dissolved states, but their emission can be switched on when these molecules aggregate in concentrated solutions/solid states [4]. AIE based dyes are successfully utilized for a number of practical applications such as chemical sensors [5,6], fluorescent probes [7,8], live cell bioimaging [9–11] and OLEDs [12,13].

Number of fluorescent organic dyes showing AIE properties are well known, and they include arylethene derivatives [14], siloles [15–18], thienylazulene [19], pentacenequinone [20], salicylaldehyde azine derivatives [21], BODIPY dyes [22–24], ESIPT dyes [25,26] and isophorone based dyes [27]. However, in spite of the remarkable progress made in the synthesis of AIE molecules over the last decades, the D–π–A based AIEE dyes are still less developed. Therefore exploration of new AIEE fluorophores is an exciting field to a synthetic chemist. Heterocycles can be used to enhance the stability of conjugated molecules. So after screening of several known fluorescent dyes, in this work we have investigated 2-methoxy/2-ethoxy carbazole based push–pull AIE dyes. Carbazole is common heterocyclic compound containing electron donor nitrogen atom with interesting photo- and electro-chemistries and large number of derivatives can be synthesized by simple modification at 3, 6 and 9 positions on the carbazole core.

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Carbazole derivatives have attracted much attention because of their interesting photochemical properties such as high fluorescence quantum yield, excellent photostability and sharp absorption and emission spectra. Carbazole derivatives have high triplet energy, excellent hole transporting ability, high luminescence efficiency and due to the rigid framework are oftenly used in organic light emitting diodes [28–30], dye sensitized solar cells [31–33], liquid crystals [34,35] and laser dyes [36]. Due to the promising photophysical properties of carbazole, several carbazole derivatives containing AIE luminogens with high thermal stability have been developed [37–39]. Studies on AIE emissive carbazole derivative with large third order nonlinear optical properties are reported by Yuliang Li and coworkers [40]. AIE carbazole derivatives have garnered much attention from many research groups because of their fundamental importance and practical applications in optoelectronic devices such as organic light-emitting diodes (OLEDs) [41], field effect transistors, live-cell imaging and fluorescent sensors [1,42,43].

In this paper we have synthesized N-alkyl carbazole derivatives with 2 methoxy/2-ethoxy substituents. This 2 alkoxy substituted carbazole moiety were used as a donor and cyano group at terminal position as an acceptor which can exhibit high values of dipole moment and hyperpolarizability. They are desired attributes for nonlinear optics and luminescent chromophores. Due to introduction of methoxy/ethoxy group in ortho-position towards the π-bridge can more effectively conjugate with the π-system with the donation of lone pair electrons. The molecular design strategy is based on the structural changes like surrounding electron-donor and acceptor group position manipulation and its capability of effective intermolecular charge transfer (ICT) characteristics [44,45]. In addition, electron transfer or electron separation between the electron donor carbazole group and the accepting group like 2-(1-phenylethylidene)malononitrile and 2-(3,5,5-trimethylcyclohex-2-enylidene)malononitrile provides this class of compounds highly anisotropic structures and results in interesting photophysical properties [46].

## 2. Experimental

### 2.1. Computational strategy

All the computations were performed with Gaussian 09 package [47]. DFT method was used for the ground state optimization, while for the excited state optimization, time-dependent density functional theory (TD-DFT) was employed. The hybrid functional namely B3LYP (Becke3-Lee-Yang-Parr hybrid functional) [48–51] was used. The 6-31G(d) basis set was used for all atoms and later was ascertained in the literature [52]. The Polarizable Continuum Model (PCM) [53] was used to optimize the ground and excited state geometries in solvent environments. The excitation energies, oscillator strengths and orbital contribution for the lowest 10 singlet–singlet transitions at the optimized geometry in the ground state were obtained by TD-DFT calculations using the same basis set as for the geometry minimization. The solvents used were toluene, tetrahydrofuran (THF), chloroform ($CHCl_3$), dichloromethane (DCM), ethyl acetate (EtOAc), ethanol (EtOH), acetonitrile (ACN), *N,N*-dimethyl formamide (DMF), dimethyl sulfoxide (DMSO).

### 2.2. Materials and equipments

All the reagents were obtained from S. D. Fine Chemicals (India), Sigma Aldrich and used as supplied without any further purification. All the solvents were of spectroscopic grade. The active methylene intermediates 2-(1-phenylethylidene)malononitrile (**4a**) and 2-(3,5,5-trimethylcyclohex-2-enylidene)- malononitrile (**4b**) was prepared by the reported methods [54,55]. The reaction was monitored by thin layered chromatography (TLC) using 0.25 mm E-Merck silica gel 60 $F_{254}$ precoated plates, which were visualized under UV light. Melting points were measured on standard melting point apparatus from Sunder industrial product, Mumbai and are uncorrected. The FT-IR spectra were recorded on Perkins–Elmer 257 spectrometer using KBr discs. $^1$H NMR and $^{13}$C NMR spectra were recorded on VARIAN 500-MHz instrument (USA) using $CDCl_3$ as solvent. The chemical shifts were reported in parts per million (ppm) relative to internal standard tetramethyl silane (TMS) (0 ppm) and coupling constants in Hz. Splitting patterns are described as singlet (s), doublet (d), triplet (t), quartet (q), or multiplet (m). Mass spectrometry was performed on a quadrupole/time-of-flight tandem mass spectrometer (ESI) and recorded on Waters mass spectrometer. The visible absorption spectra of the dyes were recorded on a Perkin–Elmer Lambda 25 UV–Visible spectrophotometer. The quantum yields of dyes **5** and **6** in different solvents of varying polarities were calculated using Rhodamine 6G as reference standard ($\phi = 0.94$ in ethanol, $\lambda_{exc} = 488$ nm) [56].

### 2.3. Synthesis and characterization

#### 2.3.1. Synthesis of intermediates *2a*, *2b* and *3a*

The detailed experimental procedures for the synthesis of reported intermediates **2a**, **2b** and **3a** are provided in the supporting information.

#### 2.3.2. 2-ethoxy-9-ethyl-9H-carbazole-3-carbaldehyde (*3b*)

$POCl_3$ (4.9 mL, 52.00 mmol) was added drop wise to DMF (17 mL, 219.53 mmol) at 0–5 °C, and stirred for 30 min maintaining the temperature 0–5 °C. 2-ethoxy-9-ethyl-9*H*-carbazole (11.24 g, 47.00 mmol) was dissolved in 20 mL DMF was added dropwise within 30 min maintaining temperature between 0 and 5 °C. Stirring was continued for next 20–30 min, reaction mixture was then brought to room temperature and heated at 70–75 °C for 1 h. Completion of the reaction was monitored by TLC. The obtained reaction mass was poured into crushed ice stirred well and neutralized with sodium bicarbonate. The precipitate obtained was filtered off and dried. The crude product was purified by column chromatography on silica 100–200 mesh and using toluene as eluent. Yield 8.78 g (70%) m. p. 138–140 °C (recrystallized in ethanol).

$^1$H NMR ($CDCl_3$, 500 MHz) = δ 9.66 (s, 1H), 8.53 (s, 1H), 8.14 (d, 1H, $J = 7.5$ Hz), 7.83–7.85 (t, 2H, $J = 7.5$ & 8 Hz), 7.39 (d, $J = 8.0$ Hz, 1H), 7.00 (s, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 4.11 (q, $J = 6.9$ Hz, 2H), 1.38 (t, $J = 6.9$ Hz, 3H), 1.32 (t, $J = 7.2$ Hz, 3H).

HRMS *m/z* [M + H]+ Calcd for $C_{17}H_{18}NO_2$: 268.1338. Found: 268.1372.

#### 2.3.3. (E)-2-(3-(2-Methoxy-9-methyl-9H-carbazol-3-yl)-1-phenylallylide)malononitrile (*5a*)

Under nitrogen atmosphere, 2-methoxy-9-methyl-9*H*-carbazole-3-carbaldehyde (2.39 g, 10 mmol) and 2-(1-phenylethylidene) malononitrile (1.68 g, 10 mmol) were dissolved in absolute ethanol (100 mL). 0.1 mL of piperidine was added, and the solution was stirred at reflux temperature for 24 h. After cooling the reaction mixture, the red solid was filtered, washed with methanol and dried. The crude product was further purified by column chromatography (Petroleum Ether: Ethyl Acetate (80:20): yield (2.91 g, 75%), 260–262 °C.

$^1$H NMR (500 MHz, $CDCl_3$) δ 3.81 (s, 3H, $NCH_3$), 3.97 (s, 3H, $OCH_3$), 6.74 (s, 1H, ArH), 7.29 (d, $J = 7.8$ Hz, 1H, ArH), 7.35 (d, $J = 6.2$ Hz, 1H, ArH), 7.38–7.37 (m, 1H, ArH), 7.48–7.41 (m, 3H, ArH), 7.61–7.53 (m, 3H, ArH), 7.88 (d, $J = 15.5$ Hz, 1H, =CH), 8.02 (d, $J = 7.7$ Hz, 1H), 8.18 (s, 1H, ArH). $^{13}$C NMR (126 MHz, $CDCl_3$) 29.4,