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Graphical Abstract



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Quinoxaline based amines as Blue-orange emitters: Effect of modulating

donor system on Optoelectrochemical and theoretical properties

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Abstract

A series of eight novel donor-acceptor based quinoxaline-amine derivatives 2-9 were prepared by modulating donor species on quinoxaline core with Buchwald–Hartwig coupling amination reaction. The synthesized molecules were fully characterized and studied for impact of D-A interaction on optoelectrochemical properties of derivatives. Absorption spectra of 2-9 display intramolecular charge transfer (ICT) transitions in the range of 377–456 nm. Dyes 2–9 show positive solvatochromism in emission and emit in blue–orange region with emission maxima 472-592 nm on excitation at their respective ICT maxima in toluene, chloroform, DCM and neat solid film. Herein, dyes 2, 3 and 7 which possess intense emission in solid state were further studied for Aggregation Induced Emission (AIE) effect. The HOMO and LUMO energy level for compound 2-9 obtained by CV were found in the range of -5.23 to -5.83 eV and -3.55 to -3.74 eV. Theoretical studies of molecules were also carried out by using TD-DFT calculations. The comparable HOMO and LUMO energy level of 2-9 with reported ambipolar materials and efficient solid state emission make synthesized compounds potential candidate for solid state emissive, ambipolar materials in organic electronics.

Keywords: Donor–Acceptor (D–A) architecture, Quinoxaline–amines, Intramolecular charge transfer (ICT) transitions, Aggregation Induced Emission (AIE) effect, HOMO and LUMO energy levels, Ambipolar materials.

1. Introduction

The development in the field of organic semiconductors is of immense interest for researchers due to its widespread applications in organic light emitting diodes (OLEDs) [1,2], organic field effect transistors (OFETs) [3], dye sensitized solar cells (DSSCs) [4-6], sensors [7,8], etc. Organic materials are designed and synthesized with incorporation of Donor-Acceptor (D-A) system offers the unique properties such as well-defined structures, ease of purification, solubility in wide range of organic solvents, tuneable photophysical and electrochemical properties, thermal stability and low cost solution processing techniques [9]. This D-A design approach give choice of suitable D/A unit to obtain required luminescence and charge transporting properties in molecule. In the past, variety of D-A type of molecules having combination of electron deficient core like quinoxaline [10,11], indoloquinoxaline [12], pyarazine [13], phenazine [14,15], pyrazino-phenazine [16] and electron rich triarylamine/heterocyclic amines have been synthesized and explored in optoelectronic devices. The luminescence in such D-A system mainly arises due to ICT and can be tuned by structure modification. It has observed that efficient luminescence in dilute solutions obtained for many fluorophores is generally weakened or quenched in aggregation/ solid state leads to aggregation-caused quenching (ACQ) due to non-radiative relaxation taking place in the molecule [17–20]. However, organic materials with efficient solid state emission are essential for various optoelectronic applications. Hence, there is need to govern the factors which cause ACQ in order to obtain solid state emissive materials. In 2001, Tang et.al discovered propeller-shaped, non-planar luminogen that were almost nonfluorescent in solution, became highly fluorescent on aggregation. This phenomenon of enhanced emission on aggregation is known as aggregation-induced emission (AIE) [21]. The use of AIE active groups in

conventional ACQ building block has been effective approach to increase solid state emission [22].

At same time, literature witnessed successful development of hole transporting (ptype) materials (HTM) whereas the development of n-type and ambipolar materials is still lagging behind due to their difficult synthesis and instability under ambient conditions. However, electron transporting materials are indispensable component of integrated circuit and has huge requirement in optoelectronic applications. According to reports, p-type materials can be converted to n-type by introducing N-atom in structural core of molecule or by introducing electron withdrawing groups such as -F, -CN, -Cl, $-NO_2$, -COOH, etc [23]. On the other hand, there is great demand for ambipolar materials to achieve high performance optoelectronic device, as it facilitates both (p-channel) hole and (n-channel) electron transport, thus improves recombination frequency of excitons. Since, the charge transfer process in the small molecule is chain of redox processes, dependant on embedded electron donating and withdrawing moieties in the system. The incorporation of appropriate donor and acceptor moiety in the same molecule can help to build ambipolar transporting materials [24,25].

With this clues of ambipolar and AIE properties dependency on D–A architecture, we have chosen electron deficient 2,3-bis(4-bromophenyl)quinoxalin-6-yl(phenyl)methanone (1) having quinoxaline core as an acceptor. It has outstanding electron accepting properties due to presence of two 'N' atoms in ring and one electron withdrawing benzoyl group attached to this quinoxaline ring. Along with optoelectronic properties, quinoxaline is also well known for broad range of biological and pharmaceutical activities such as antibacterial [26], antiinflammetry [27], anticancer [28,29], antimicrobial [30], etc. Considering the importance of structure–property relationship, electron deficient quinoxaline incorporated with different donor moieties in order to study changes occurring in photophysical, electrochemical and

thermal properties of derivatives. Thus, we have designed and synthesized derivatives 2-9 by incorporating a Buchwald–Hartwig coupling amination [31,32] reaction between electron deficient **1** and various electron donating diarylamines/heterocyclic amines and aliphatic











Figure 1. Molecular structure of compounds 2–9.

amine morpholine. Further, the effect of various diarylamine substituted with electron donating $(-OCH_3)$ and withdrawing $(-NO_2, aza)$ group on their optoelectrochemical properties such as intramolecular charge transfer transition (ICT), HOMO–LUMO energy levels and band gap has been studied and discussed.

2. Experimental Section

2.1 Chemicals and materials

All the starting materials and reagents were purchased from commercial sources (Sigma Aldrich and Alfa Aesar) and were used without any further treatment and purification unless otherwise mentioned. The organic solvents were of HPLC and spectroscopic grade and were dried and freshly distilled using the standard procedures and handled in a moisture-free atmosphere. Column chromatography was carried out using SD-fine silica gel (60–120 mesh), eluting with n-hexane and chloroform. The progress of the reaction and the purity of the compound were checked by thin layer chromatography (TLC) on silica-gel-coated glass plates, in which the spots were visualized with UV light (365 nm) and in an iodine chamber.

2.2 Synthesis and Characterization

Compound **1** is prepared according to the reported procedure and confirmed by ¹H and ¹³C NMR. Compounds **2–9** were obtained by Buchwald-Hartwig coupling of **1** with the corresponding diarylamines/heterocyclic amines in the presence of $Pd_2(dba)_3$ catalyst, SPhos ligand and t-BuONa as strong base in toluene. The synthesized compounds **2–9** were obtained in moderate 42%–77% yield as yellow–green solids soluble in common organic solvents including toluene, dichloromethane (DCM), chloroform, Tetrahydrofuran (THF), dimethyl sulfoxide (DMSO). However, they are completely insoluble in water. The identity and purity of all the target compounds were confirmed by FT–IR, ¹H, ¹³C–NMR spectroscopy, MALDI–TOF mass spectrometry and elemental analysis. The synthetic route of compound **2–9** is shown in **Scheme 1**.



Scheme 1. Synthetic route of 2–9.

2.2.1 Synthesis of (2,3-bis(4-bromophenyl)quinoxalin-6-yl)(phenyl)methanone (1)

A mixture of 3,4-diaminobenzophenone (0.8 g, 3.77 mmol) and 4,4'-dibromobenzil (1.38 g, 3.77 mmol) was dissolved in 25 mL of glacial acetic acid and refluxed for 5 hours. The reaction mixture was allowed to cool and then poured over crushed ice to obtain white coloured solid. The obtained solid was then dried under vacuum and purified using column chromatography (eluent: n-hexane:chloroform ratio as 90:10), white solid, yield 1.84 g (90%); mp 200 0 C.

¹H NMR (300 MHz, CDCl₃): δ 8.50 (s, 1H), 8.26 (s, 2H), 7.89 (d, *J* = 7.1 Hz, 2H), 7.72–7.33 (m, 11H); ¹³C NMR (75 MHz, CDCl₃): δ 195.54 (C=O), 153.53, 153.00, 142.87, 140.20, 138.67, 137.20, 137.17, 137.02, 132.92, 132.47, 132.25, 131.77, 131.45, 131.34, 130.26, 130.11, 129.67, 128.54, 124.26, 124.09.

MALDI-TOF: mass calcd for $C_{27}H_{16}Br_2N_2O$ [M⁺]: 543.96, found: 543.96; FT–IR, (KBr, v_{max} cm⁻¹): 3054, 1650, 1575, 1072, 713; elemental anal. calcd for $C_{27}H_{16}Br_2N_2O$: C 59.59, H 2.96, Br 29.36, N 5.15, O 2.94. found: C 59.07, H 3.28, Br 29.46, N 5.33, O 2.86.

2.2.2 (2,3-bis(4-(diphenylamino)phenyl)quinoxalin-6-yl)(phenyl)methanone (2)

A mixture of compound **1** (0.2 g, 0.37 mmol) and diphenylamine (0.125 g, 0.74 mmol) was dissolved in anhydrous toluene (50 mL). To this solution $Pd_2(dba)_3$ (20 mg, 0.02 mmol), SPhos (25 mg, 0.048 mmol) and t-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100 0 C for 15 hours. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n–hexane:chloroform ratio as 80:20); yellow solid; 129 mg (48%); mp 254 0 C.

¹H NMR (300 MHz, CDCl₃): δ 8.47 (s, 1H), 8.22 (d, *J* = 1.1 Hz, 2H), 7.90 (d, *J* = 7.1 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.56–7.42 (m, 6H), 7.31–7.25 (m, 9H) (1H extra due to residual CHCl₃ in CDCl₃), 7.16–7.04 (m,16H); ¹³C NMR (75 MHz, CDCl₃): δ 195.91 (C=O), 154.82, 154.30, 149.02, 148.84, 147.18, 147.14, 142.99, 142.93, 139.97, 137.83, 137.35, 132.70, 132.35, 131.94, 131.74, 130.89, 130.69, 130.12, 129.48, 129.42, 129.39, 128.48, 125.20, 125.11, 123.72, 123.62, 121.93, 121.72.

MALDI-TOF: mass calcd for $C_{51}H_{36}N_4O$ [M⁺]: 720.29, found: 720.31; FT–IR (KBr, v_{max} cm⁻¹): 3034, 2921, 1658, 1586, 1278, 692; elemental anal. calcd for $C_{51}H_{36}N_4O$: C 84.97, H 5.03, N 7.77, O 2.22 found: C 85.02, H 4.97, N 7.82, O 2.19.

2.2.3 (2,3-bis(4-(naphthalen-1-yl(phenyl)amino)phenyl)quinoxalin-6-yl)(phenyl)methanone(3)

A mixture of compound 1 (0.2 g, 0.37 mmol) and N-Phenyl-1-napthylamine (0.169 g, 0.74 mmol) was dissolved in anhydrous toluene (50 mL). To this solution Pd₂(dba)₃ (20 mg, 0.02 mmol), SPhos (20 mg, 0.048 mmol) and t-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100 °C for 15 hours. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n-hexane:chloroform ratio as 80:20); yellow solid; 157 mg (51%); mp 160 0 C.

¹H NMR (300 MHz, CDCl₃): δ 8.44 (s, 1H), 8.19 (s, 2H), 7.94–7.75 (m, 7H), 7.63–6.96 (m, 26H), 6.89 (d, J = 6.8 Hz, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 196.07 (C=O), 154.97, 154.43, 149.51, 149.34, 147.56, 147.49, 142.92, 142.90, 142.87, 139.91, 137.68, 137.35, 135.29, 132.64, 132.31, 131.54, 131.04, 130.87, 130.66, 130.09, 129.41, 129.27, 129.25, 128.44, 127.35, 127.31, 126.91, 126.85, 126.49, 126.45, 126.30, 126.25, 124.09, 123.28, 123.17, 122.95, 122.84, 119.94, 119.75.

MALDI-TOF: mass calcd for $C_{59}H_{40}N_4O$ [M⁺]: 820.32, found: 820.55; FT–IR (KBr, v_{max} cm⁻¹): 3045, 2973, 1658, 1586, 1267, 692; elemental anal. calcd for $C_{59}H_{40}N_4O$: C 86.32, H 4.91, N 6.82, O 1.95 found: C 86.12, H 5.04, N 6.98, O 1.86.

2.2.4 (2,3-bis(4-(bis(4-methoxyphenyl)amino)phenyl)quinoxalin-6-yl)(phenyl)methanone(4)

A mixture of compound **1** (0.2 g, 0.37 mmol) and 4,4 -Dimethoxydiphenylamine (0.169 g, 0.74 mmol) was dissolved in anhydrous toluene (50 ml). To this solution $Pd_2(dba)_3$ (20 mg, 0.02 mmol), SPhos (20 mg, 0.048 mmol) and t-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100 $^{\circ}$ C for 15 hours. Reaction mixture was then cooled to room temperature and extracted with

chloroform. The solid thus obtained was then purified by column chromatography (eluent: n-hexane:chloroform ratio as 70:30); red solid; 162 mg (52%); mp 154 0 C.

¹H NMR (300 MHz, CDCl₃): δ 8.44 (s, 1H), 8.18 (d, *J* = 0.8 Hz, 2H), 7.89 (d, *J* = 7.1 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55–7.37 (m, 6H), 7.14–7.04 (m, 8H), 6.91–6.81 (m, 12H), 3.81 (s, 12H, –OCH₃); ¹³C NMR (75 MHz, CDCl₃): δ 196.00 (C=O), 156.39, 156.31, 154.95, 154.44, 149.78, 149.60, 142.90, 140.24, 140.16, 139.86, 137.50, 137.44, 132.62, 132.33, 130.76, 130.53, 130.19, 130.11, 129.98, 129.36, 129.13, 128.44, 127.22, 127.13, 118.96, 118.75, 114.78, 114.76, 55.49 (–OCH₃).

MALDI-TOF: mass calcd for $C_{55}H_{44}N_4O_5$ [M⁺]: 840.33, found: 840.79; FT–IR (KBr, v_{max} cm⁻¹): 2931, 1658, 1596, 1503, 1237, 1021, 815; elemental anal. calcd for $C_{55}H_{44}N_4O_5$: C 78.55, H 5.27, N 6.66, O 9.51 found: C 77.98, H 5.47, N 6.74, O 9.81.

2.2.5 (2,3-bis(4-((4-nitrophenyl)(phenyl)amino)phenyl)quinoxalin-6-yl)(phenyl)methanone(5)

A mixture of compound **1** (0.2 g, 0.37 mmol) and 4-Nitrodiphenylamine (0.157 g, 0.74 mmol) was dissolved in anhydrous toluene (50 mL). To this solution $Pd_2(dba)_3$ (20 mg, 0.02 mmol), SPhos (20 mg, 0.048 mmol) and t-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100 0 C for 15 hours. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n–hexane:chloroform ratio as 70:30); yellow solid; 158 mg (53%); mp 160 0 C.

¹H NMR (300 MHz, CDCl₃): δ 8.52 (s, 1H), 8.28 (d, *J* = 1.0 Hz, 2H), 8.05 (dd, *J* = 9.2, 3.9 Hz, 4H), 7.96–7.87 (m, 2H), 7.73–7.48 (m, 7H), 7.44–7.34 (m, 4H), 7.33–7.24 (m, 3H) (1H extra due to residual CHCl₃ in CDCl₃), 7.23–7.14 (m, 7H), 7.02 (dd, *J* = 9.2, 5.3 Hz, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 195.77 (C=O), 154.12, 153.49, 152.85, 147.08, 146.93, 145.38, 142.94, 141.04, 140.99, 140.19, 138.54, 137.10, 134.97, 134.84, 132.83,

132.27, 131.47, 131.32, 130.13, 129.64, 128.56, 126.75, 126.71, 126.26, 126.22, 125.45, 125.11, 124.99, 119.64, 119.54.

MALDI-TOF: mass calcd for $C_{51}H_{34}N_6O_5$ [M⁺]: 810.26, found: 810.36; FT–IR (KBr, v_{max} cm⁻¹): 3404, 1647, 1575, 1483, 1288, 1103, 692; elemental anal. calcd for $C_{51}H_{34}N_6O_5$: C 75.54, H 4.23, N 10.36, O 9.87 found: C 75.27, H 4.25, N 10.41, O 10.07. 2.2.6 (2,3-bis(4-(phenyl(4-((E)-phenyldiazenyl)phenyl)amino)phenyl)quinoxalin-6yl)(phenyl)methanone (**6**)

A mixture of compound **1** (0.2 g, 0.37 mmol) and 4-(Phenylazo)diphenylamine (0.202 g, 0.74 mmol) was dissolved in anhydrous toluene (50 mL). To this solution $Pd_2(dba)_3$ (20 mg, 0.02 mmol), SPhos (20 mg, 0.048 mmol) and t-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100 0 C for 15 hours. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n–hexane:chloroform ratio as 80:20); yellow solid; 147 mg (43%); mp 254 0 C.

¹H NMR (300 MHz, CDCl₃): δ 8.51 (s, 1H), 8.26 (s, 2H), 7.95–7.80 (m, 10H), 7.67–7.30 (m, 17H), 7.28–7.13 (m, 15H) (1H extra due to residual CHCl₃ in CDCl₃); ¹³C NMR (75 MHz, CDCl₃): ¹³C NMR (75 MHz, CDCl₃) δ 195.84 (C=O), 154.03, 152.87, 149.84, 148.28, 148.11, 147.99, 147.93, 146.51, 142.96, 140.07, 138.13, 137.27, 133.28, 133.11, 132.79, 132.34, 131.13, 130.96, 130.45, 130.13, 129.73, 129.04, 128.52, 126.07, 124.85, 124.79, 124.29, 123.56, 123.39, 123.16, 123.05, 122.62.

MALDI-TOF: mass calcd for $C_{63}H_{44}N_8O$ [M⁺]: 928.36, found: 928.97; FT–IR (KBr, v_{max} cm⁻¹): 3054, 2921, 1658, 1586, 1483, 1257, 692; elemental anal. calcd for $C_{63}H_{44}N_8O$: C 81.44, H 4.77, N 12.06, O 1.72 found: C 81.57, H 4.72, N 11.97, O 1.74. 2.2.7 (2,3-bis(4-(9H-carbazol-9-yl)phenyl)quinoxalin-6-yl)(phenyl)methanone (**7**).

A mixture of compound **1** (0.2 g, 0.37 mmol) and carbazole (0.123 g, 0.74 mmol) was dissolved in anhydrous toluene (50 mL). To this solution $Pd_2(dba)_3$ (20 mg, 0.02 mmol), SPhos (20 mg, 0.048 mmol) and t-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100 $^{\circ}$ C for 15 hours. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n–hexane:chloroform ratio as 80:20); yellow–green solid; 178 mg (68%); mp > 280 $^{\circ}$ C.

¹H NMR (300 MHz, CDCl₃): δ 8.61 (s, 1H), 8.41–8.30 (m, 2H), 8.14 (d, J = 7.7 Hz, 4H), 7.98–7.83 (m, 6H), 7.75–7.62 (m, 5H), 7.61–7.35 (m, 10H), 7.31–7.29 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 195.69 (C=O), 154.16, 153.59, 143.08, 140.44, 140.37, 139.03, 138.90, 138.75, 137.27, 137.20, 137.10, 132.94,131.61, 131.48, 130.16, 129.79, 128.58, 126.81, 126.76, 126.17, 123.68, 123.66, 120.43, 120.39, 120.36, 109.62.

MALDI-TOF: mass calcd for $C_{51}H_{32}N_4O$ [M⁺]: 716.26 found: 716.39; FT–IR (KBr, v_{max} cm⁻¹): 3065, 2921, 1658, 1596, 1452, 1237, 713; elemental anal. calcd for $C_{51}H_{32}N_4O$: C 85.45, H 4.50, N 7.82, O 2.23 found: C 85.54, H 4.63, N 7.92, O 1.91. 2.2.8 (2,3-bis(4-(10H-phenothiazin-10-yl)phenyl)quinoxalin-6-yl)(phenyl)methanone (**8**)

A mixture of compound **1** (0.2 g, 0.37 mmol) and phenothiazine (0.147 g, 0.74 mmol) was dissolved in anhydrous toluene (50 mL). To this solution $Pd_2(dba)_3$ (20 mg, 0.02 mmol), SPhos (20 mg, 0.048 mmol) and t-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100 0 C for 15 hours. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n–hexane:chloroform ratio as 80:20); brown solid, yield: 121 mg (42%); mp 151 0 C.

¹H NMR (300 MHz, CDCl₃): δ 8.58 (s, 1H), 8.33 (s, 2H), 7.93 (d, *J* = 7.0 Hz, 2H), 7.77–7.57 (m, 5H), 7.56–7.51 (m, 2H), 7.35 (d, *J* = 8.4 Hz, 4H), 7.15–7.09 (m, 4H), 6.91–

6.82 (m, 8H), 6.52–6.42 (m, 4H); ¹³C NMR (75 MHz, CDCl₃): δ 195.66 (C=O), 154.44, 153.91, 143.36, 143.29, 143.27, 143.09, 142.99, 140.31, 138.64, 137.13, 136.94, 136.58, 132.93, 132.40, 132.12, 132.01, 130.24, 130.16, 129.77, 128.58, 127.83, 127.34, 127.25, 127.24, 127.02, 126.99, 123.74, 123.52, 123.38, 123.23, 118.59, 118.19.

MALDI-TOF: mass calcd for $C_{51}H_{32}N_4OS_2$ [M⁺]: 780.20 found: 780.17; FT–IR (KBr, v_{max} cm⁻¹): 3053, 2921, 1658, 1575, 1452, 1257, 740; elemental anal. calcd for $C_{51}H_{32}N_4OS_2$: C 78.44, H 4.13, N 7.17, O 2.05, S 8.21 found C 78.34, H 4.18, N 7.27, O 2.03, S 8.18.

2.2.9 (2,3-bis(4-morpholinophenyl)quinoxalin-6-yl)(phenyl)methanone (9).

A mixture of compound **1** (0.2 g, 0.37 mmol) and morpholine (0.064 g, 0.74 mmol) was dissolved in anhydrous toluene (50 mL). To this solution $Pd_2(dba)_3$ (20 mg, 0.02 mmol), SPhos (25 mg, 0.048 mmol) and t-BuONa (75 mg, 0.75 mmol) were added. The reaction mixture was continuously stirred under nitrogen atmosphere at 100 0 C for 15 hours. Reaction mixture was then cooled to room temperature and extracted with chloroform. The solid thus obtained was then purified by column chromatography (eluent: n–hexane:chloroform ratio as 60:40); brown solid, yield: 157 mg (77%); mp 162 0 C.

¹H NMR (300 MHz, CDCl₃): δ 8.45 (s, 1H), 8.19 (s, 2H), 7.89 (d, *J* = 7.2 Hz, 2H), 7.72–7.27 (m, 10H), 3.86 (m, 8H, –OCH₂), 3.24 (m, 8H, –NCH₂); ¹³C NMR (75 MHz, CDCl₃): δ 195.97 (C=O), 154.67, 154.14, 151.78, 151.66, 142.88, 139.89, 137.58, 137.41, 132.65, 132.32, 131.07, 130.86, 130.12, 130.00, 129.83, 129.36, 129.19, 128.45, 114.71, 114.60, 66.73(–O(CH₂)₂), 48.50 (–N(CH₂)₂).

MALDI-TOF: mass calcd for $C_{35}H_{32}N_4O_3$ [M⁺]: 556.25, found: 556.25; FT–IR (KBr, v_{max} cm⁻¹): 2921, 1647, 1596, 1237, 1123, 928, 692; elemental anal. calcd for $C_{35}H_{32}N_4O_3$: C 75.52, H 5.79, N 10.06, O 8.62 found: C 75.68, H 5.88, N 10.44, O 8.00.

2.3 Instrumentation and methods

UV-visible spectra were recorded in 10^{-6} mol L⁻¹ solutions in a 1 cm path length quartz cuvette as well as the neat solid films on a SHIMADZU UV-2401PC instrument at room temperature. The neat solid films of compounds 2–9 were prepared by using a spin coater HO-TH-05) at 1000 rpm for 2 min ~ 6 mg mL⁻¹ of the sample in (Holmarc chloroform. Quartz plates were used for the neat solid film studies. The excitation and emission spectra were carried out on a Perkin Elmer LS 55 Fluorescence spectrophotometer. Cyclic voltammetry studies were carried out on a computer-controlled Palmsens3 potentiostat. Typically, a three-electrode cell equipped with a glassy carbon working electrode, a Ag/AgCl (non-aqueous) reference electrode, and platinum (Pt) wire as the counter electrode was employed. The measurements were carried at room temperature in anhydrous dichloromethane with tetra-butyl ammonium hexafluorophosphate solution (0.1 M) as the supporting electrolyte with a scan rate of 100 mVs^{-1} . The potential of the Ag/AgCl reference electrode was calibrated by using a ferrocene/ferrocenium redox couple, which has the known oxidation potential of +5.1 eV. The thermogravimetric analysis (TGA) were performed using a Metler Toledo instrument (TG) under nitrogen atmosphere. ¹H NMR spectra and ¹³C NMR spectra were recorded using CDCl₃ on Varian 300 MHz Ultrashield spectrometer with tetramethylsilane (TMS) as internal reference at working frequency 300 MHz and 75 MHz respectively. Fourier trans-form infrared (FT-IR) spectra were recorded on a Perkin Elmer Frontier 91579. Mass spectrometric measurements were recorded using MALDI-TOF (Bruker) and elemental analysis was carried out on EA Euro-elemental analysis instrument. To confirm formation of nanoparticle in AIE studies, sample of synthesized dye subjected to field emission gun scanning electron microscopy (JEOL JSM-7600F FEG-SEM).

2.4 Preparation of Nanoaggregates

Stock THF solution of the dyes **2**, **3** and **7** with concentration 10^{-4} M were prepared. Aliquots of stock solution were transferred to 5 mL volumetric flask. After appropriate amount of THF were added, water was added drop wise under vigorous shaking to obtain 10^{-5} M solution with different water contents (0–100 vol %). The photoluminescence (PL) measurement of resultant solution were recorded. Also, size and morphology of nanoparticles of dye **2** was observed by field emission scanning electron microscopy (FEG–SEM).

2.5 Theoretical Calculation

DFT and time dependant density functional theoretical (TD–DFT) calculations were performed using Gaussian 03 software package using B3LYP as exchange correlation functional at 6-311G, $6-311G + G^*$ and $6-311G + G^{**}$ basis set.

3. Results and Discussion

3.1 Photophysical Studies

Absorption and photoluminescence (PL) spectra of synthesized molecules were recorded in increasing polarity of solvents (toluene, chloroform, dichloromethane, and dimethyl sulphoxide) to compare their photophysical properties. The UV–Vis absorption spectra of compounds 2–9 in toluene and chloroform are presented in Figure 2 while pertinent data summarized in Table 1.



Figure 2. UV–Vis absorption spectra of compounds 2–9 in toluene (a) and chloroform (b)

(for other solvents and neat solid film see supporting information).

optical properties of 2–9 with the On comparison of parent 2,3-bis(4bromophenyl)quinoxalin-6-yl)phenyl methanone (1) (see supporting information for absorption spectra of 1) have observed that in case of compound 1 absorption peaks at 279overlapping of $n-\pi^*$ and $\pi-\pi^*$ transitions whereas absorption 334 nm arises due to maxima at 360–364 nm could be attributed to inbuilt D-A system where phenyl rings joined by single bond to quinoxaline core.

Table 1. Absorption data of 1–9.

Compd		$\lambda_{\mathrm{abs}}^{ \mathrm{a}}$			
F	Toluene	CHCl ₃	DCM	DMSO	Solid Film
1	278 (5.02), 293 (4.99), 364 (4.94)	259 (5.73), 364 (5.23)	259 (5.28) 361 (4.78),	256 (5.64), 331(5.04), 360 (5.18)	262, 373
2	286 (5.73), 431 (5.00)	256 (5.48), 305 (5.51), 441 (5.17)	259 (5.33), 296 (5.35), 434 (4.95)	251 (5.30), 305 (5.29), 435 (4.92)	327, 480
3	286 (5.65), 337 (5.05), 430 (4.93)	238 (5.59), 260 (5.60), 436 (5.14)	260 (5.22), 427 (4.80)	252 (5.51), 312 (5.29), 427 (5.06)	273, 377, 487
4	243 (5.08), 291 (5.32), 446 (4.94)	259 (5.53), 292 (5.54), 456 (5.18)	258 (5.14), 288 (5.12), 447 (4.73)	251 (5.53), 294 (5.47), 453 (5.12)	361, 501
5	288 (5.40), 332 (4.93), 411 (5.29)	239 (5.39), 257 (5.35), 416 (5.32)	259 (5.23), 417 (5.19)	251 (5.15), 314 (4.62), 412 (5.11)	260, 460
6	279 (5.25), 306 (5.21), 435 (5.36)	264 (5.46), 296 (5.39), 442(5.41)	230 (5.41), 306 (5.27), 439 (5.31)	258 (5.22), 306 (5.18), 441 (5.22)	269, 485
7	287 (5.94), 339 (5.05), 390 (4.94)	243 (6.07), 291 (5.80), 389 (5.29)	274 (6.20), 339 (5.11), 385 (5.00)	252 (5.36), 293 (5.14), 377 (4.92)	296, 386
8	232 (4.78), 289 (5.22), 408 (4.50)	258 (6.27), 410 (5.07)	258 (5.64), 397 (4.41)	251 (6.03), 307 (5.28), 402 (4.41)	274, 371, 447

9	285 (5.79), 418 (4.79)	238 (5.42), 261 (5.48), 415 (5.92)	259 (5.40), 416 (5.01)	251 (5.51), 377 (5.03),	263, 434	
,	418 (4.79)	415 (5.03)	416 (5.01)	425 (5.09)	,	

^aRecorded in10⁻⁶ M solution

Similarly, the absorption spectra of 2–9 show high absorption band between 232–339 nm in different polarity of solvents corresponds to $n-\pi^*$, $\pi-\pi^*$ transitions. These high energy transitions obtained due to entire molecule. The lower energy transition band found in the range of 377–456 nm attributed to intramolecular charge transfer (ICT) transition from electron donating triarylamine, heterocyclic and aliphatic amines to electron accepting quinoxaline core. These ICT transitions show considerable red shift for derivatives 2–9 due to modified D–A architecture as compared to 1.

Almost all the synthesized molecules in different solvents show similar pattern of absorption spectra with varying intensities and display better absorption and high molar absorptivity. The absorption spectra show that lowest intensity ICT band are more sensitive to donor moiety [33]. The bathochromic shift of 16–26 nm in ICT transition has observed in case of **4** attributed to presence of electron donating $-OCH_3$ group on triarylamine whereas the blue shift of around 19–25 nm in **5** corresponds to presence of electron withdrawing – NO₂ group on triarlyamine moiety. However, heterocyclic amine like carbazole, phenothiazine and morpholine show hypsochromic shift of 39–58 nm in **7**, 22–37 nm in **8** and 10–26 nm in **9** in ICT transitions compared to triphenylamine derivatives. In all the solvents, dye **7** display more blue shifted ICT band than **8** could be due to the weak electron donating strength of carbazole as compared to phenothiazine. This confirm the fact that extra sulfur atom present in the phenothiazine ring makes it strong electron donating moiety than carbazole [34]. Further, the absorption of **2–9** in neat solid film showed significant red shift of 9–60 nm in absorption maxima with broadening of peaks attributed to the molecular aggregation in molecules [35].

The other photophysical factors such as emission data, optical band gap, stokes shift and quantum yield were calculated and summarized in **Table 2**. Compound **2–9** emit in blue– orange region with emission maxima 472–592 nm on excitation at their respective ICT maxima in toluene, chloroform, DCM and neat solid film. (**Figure 3**)

Compound 2–9 display blue–green fluorescence with emission maxima (λ_{Emax}) of 472–552 nm in toluene. The occurrence of positive solvatochromism on using polar protic solvents such



Figure 3. Emission spectra of 2–9 in toluene (a), neat solid film (b) (for other solvents and

neat solid film of 1 see supporting information).

as chloroform and DCM witnessed by red shift of 5–53 nm and 21–68 nm in emission correspondingly drawn fluorescence to yellow–orange region in polar solvents (**Figure 4**).



Figure 4. Fluorescence image of **1–9** in toluene and Chloroform (10⁻⁶ M) under 365 nm UV illumination.

This noteworthy solvatochromism, in the emission spectra attributed to polarized excited state. The enhanced dipole moment of the polarized excited states due to charge transfer transitions stabilized with reorientation of solvent molecule. This process of reorientation helps solvent molecule to achieve high dipole moment, thereby reduces energy of system leading to bathochromic shift in emission [36].

The emission spectra presented in Figure 3 (a), show compound 4 in toluene own bathochromic shift of 41 nm due to presence of electron donating $-OCH_3$ group on triarlyamine moiety. On the other hand, it has observed that molecule 7 having carbazole as a weak donor unit display fluorescence with blue shift of 39–58 nm in toluene, chloroform and DCM. No emission was observed for compound 6 and 8 in all of the solvents. Such non-radiative relaxation in 6 could be due to presence of electron withdrawing diazene moiety whereas as quenching of emission in 8 could be attributed to photo induced electron transfer (PET) from strong donor phenothiazine to acceptor quinoxaline core leading to charge

separated state [37,38]. The possibility of photo induced electron transfer in 8 were further validated by density functional theory in theoretical discussion. However, dye 4 and 5 bearing polar functional group show quenching in emission in more polar solvents like chloroform and DCM. Furthermore, dyes 2–9 does not emit in DMSO. Such quenching of luminescence in polar solvent indicates manifestation of nonradiative relaxation from excited state to ground state [39].

The larger stokes shift in 2-9 indicates that the origin of emission is mainly based on intramolecular charge transfer between donor and acceptor unit and ensures that there is no reabsorption of the emitted photons. Further increase in stokes shift in more polar solvent like chloroform and DCM suggest interaction between charge transfer complex and polar solvents [40]. The lone pair of electrons in non-bonding orbitals of species like carbonyl and amines in dye molecules interact strongly with polar solvents, leads to stabilization of polarized excited state by polar solvent. Owing to this decrease in band gap for 2-9 has observed on increase in polarity of solvent from toluene (2.17–1.94 eV) to chloroform and DCM (2.06–1.83 eV).

The quantum yield of **2–9** were calculated using fluorescein ($\Phi = 0.79$ in 0.1 N NaOH) as reference and are presented in **Table 2**. The quantum yield of these dyes are in the range 0.15–0.52 in toluene and were found to be decreased due to presence of electron donating (– OCH₃)

Compd	λ_{emi}^{a} , nm, (E_{g}^{opt} , eV) ^b			Thin Film	Stokes shift, cm ⁻¹ , $(\phi_{\rm F})^{\rm c}$			Solid Film
	Toluene	CHCl ₃	DCM		Toluene	CHCl ₃	DCM	
1	-	_	—	_	-	_	_	_
2	515 (2.09)	559 (1.91)	575 (1.88)	541	3784 (0.46)	4786 (0.20)	5650 (0.06)	2349

Table 2. Emission data, Stokes shift, Optical band gap and Quantum yield of 1–9.

3	511	554	562	542	3686	4883	5625	2083
	(2.09)	(1.92)	(1.91)		(0.50)	(0.19)	(0.03)	
1	552	557	-	592	4336	3976	_	3068
4	(1.94)	(1.90)			(0.17)	(0.08)	(0.01)	
5	518	_	_	547	5025	_	5427	3457
5	(1.99)				(0.15)		(0.01)	
6			_	_		_	_	_
0	—	_			—			
7	472	525	540	480	4454	6650	7446	5073
1	(2.17)	(2.06)	(2.00)	_	(0.52)	(0.42)	(0.38)	
0			_	588	—	_		4765
ð	—	_						
0	521	548	559	554	3585	5850	6141	4990
9	(2.07)	(1.07)	(1.83)		(0.35)	(0.16)	(0.06)	

^aRecorded in 10⁻⁶ M solution, ^bOptical band gap (in parentheses) estimated using emission and excitation spectra $\left(\mathbf{E}_{g}^{opt} = \frac{1240.8}{\lambda_{optedge}}\right) \mathbf{eV}$. ^cQuantum yield (in parentheses) with reference to fluorescein ($\phi = 0.79$ in 0.1 M NaOH).

or withdrawing $(-NO_2)$ groups on diarylamine moiety in 4 and 5 respectively. Further, compound 2–9 showed red shift in emission with decrease in quantum yields on increase in solvent polarity can be explained by energy gap law, which says that, internal conversion efficiency of excited state and luminescence is reduced with decrease in energy gap between ground and excited states.

Almost all the compounds showed more or less intense emission in neat solid film except **6**. This quenching in emission of **6** could be due to aggregation-based quenching (ACQ) in solid state by fast interchain electron transfer from donor to acceptor subunit via close spatial contact [41]. However, the bathochromic shift in emission of around 8–40 nm for other derivatives in neat solid film was observed as compared to toluene. It could be attributed to intermolecular aggregation in the solid state. Amazingly, some of the derivatives (**2**, **3**, **5** and **7**) emits intensely in the neat solid film. These results revealed the existence of aggregation induced emission (AIE) effect [42]. Hence, we have studied AIE properties of some dyes in detail for better understanding.

3.2 AIE Phenomenon

To evaluate AIE characteristic, we chose molecule **2**, **3** and **7** which show intense emission in neat solid film. Figure 5 show fluorescent image of **2**, **3** and **7** dissolved in different THF/water mixtures (0–100%). The photoluminscence (PL) spectra of these molecules were recorded in different THF/water fractions for the comparision of PL intensities and presented in Figure 6. The synthesized molecules are highly soluble in THF but insoluble in water. Hence, we prepared nanoaggregates of luminophores **2**, **3** and **7** by increasing percentage of water in THF solution of molecules. This is the simple precipitation method reported to prepare nanoparticles without surfactants [43].

All the three luminophores show emission in 100% THF due to intramolecular charge transfer from the donor amines to acceptor quinoxaline moiety. The more or less intensity of fluorescence in pure THF is attributed to chromophores attached as donor unit in D–A system. It has observed that, luminophore **3** and **7** show large intensity in 100% THF whereas luminophore **2** possess comparatively less fluorescence in pure THF which rapidly increases on aggregation formation. This phenomenon could be explained on the basis of conformational stability of the molecule. The presence of bulky group like napthyl phenyl and closed ring in



Figure 5. Photograph of 2 (a), 3 (b) and 7 (c) in THF–water mixture with subsequently increasing water fractions (10⁻⁵ M) by 10% under UV–Visible light.

carbazole hinders the intramolecular rotations, making luminophore **3** and **7** intrinsically fluorescent in the solution state while the less fluorescence of **2** in pure THF could be attributed to intramolecular twisting by rotatable phenyl ring in diphenyl amine [44]. Later,



on addition

Figure 6. Fluorescence spectra of 2 (a), 3 (b) and 7 (c) (10⁻⁵ M) in THF–water mixture with increasing water fractions (f_w) and 2 (A), 3 (B) and 7 (C) plots of PL intensity and peak wavelength versus f_w.

of water in THF solutions of luminophores 2, 3 and 7, quenching in emission has found for mixtures with gradual increase of water up to 50% water content (f_w) due to insolubility of luminophores in water. The improved PL intensity of luminogen after 50% (f_w) validate formation of nanoaggregates. In the aggregate form originated restricted intramolecular rotation (RIR), owing to physical constraint blocks the non-radiative pathway and activate radiative channel, enabling the molecules to emit strongly [45]. Thus, molecules 2, 3 and 7 emits strongly in aggregate form. Luminophore 2 and 3 emits yellow–green fluorescence whereas luminophore 7 displays blue–green fluorescence in 60 to 90 % of water fraction (f_w) . This distinct red shift or blue shift in aggregates due to different conformations and packing modes [46].

The AIE behavior of **2**, **3** and **7** were further explored using absorption spectroscopy. The level of tails at longer wavelength of absorption spectra of luminophores above 50% f_w in THF/water mixture was caused due to Mie effect or light scattering by the nanoparticles formed during aggregation. This verifies presence of AIE activity in molecules [47]. Thus, molecules **2**, **3** and **7** can also termed as AIEgen. (for Absorption spectra see supporting information)

Further, the size and morphology of nanoparticles of luminophore 2 formed with non-solvent water in THF determined by field emission scanning electron microscopy (FEG-SEM). Figure 7 show that nanoparticles of luminophore 2 obtained in 70% water fraction (f_w) are spherical in shape with a mean diameter of around 30–50 nm. The nanoparticle suspension of 2, 3 and 7 formed on increasing water fraction after 60% f_w are

transparent and stable for longer period without precipitation. Similarly, the past reports have witnessed long period stability of many organic nanoparticles bearing carbonyl group in surfactant free water mixtures. This outstanding stability of organic nanoparticle suspension accredited to polar groups such as carbonyl which induces electronic repulsion and apparently prevents flocculation/coalescence of nanoparticles in water [48].



Figure 7: SEM image of nanoparticles of 2 obtained in nanoparticle suspension containing 70% volume fraction of water (f_w) in THF.

3.3 Electrochemical Properties

The HOMO-LUMO energy levels and electrochemical band gap are the important aspects of organic molecules for their application in organic electronics. Hence, the electrochemical behaviour of parent 1 and its derivatives 2-9 investigated by cyclic voltammetry in DCM with ferrocene as an internal standard to calibrate the redox potential and the pertinent data

preserved in **Table 3**. The cyclic voltammogram of **4** and **5** are presented in **Figure 8** (for other compounds see supporting information).



Figure 8. Cyclic voltammogram (full scan) of compound 4 and 5 measured in anhydrous dichloromethane (for other compounds see supporting information).

On anodic sweep, for parent **1** no oxidation peak was observed. Further, the substitution with different chromophoric group as a donor in **2–9** extends the D–A interaction and improves the oxidation peaks. In cyclic voltammogram of **2–9** all the dyes exhibited two quasi reversible oxidation wave except dye **4**, **8** and **9**. Dye **4** and **8** display one reversible and one quasireversible oxidation wave. These two oxidation peak in **2–8** attributed to oxidation of triarylamine moiety in **2–6** and oxidation of carbazole and phenothiazine moiety in **7** and **8** respectively corresponds to two electron processes while a single quasireversible wave was observe for dye **9** assigned to oxidation of aliphatic morpholine. It has found that the oxidation potential is sensitive to nature of donor group and E_{oxi} potential of **2–9** decreases on increasing donor strength (**4** > **8** > **2** > **9** > **3** > **7** > **6** > **5**).

Further, on cathodic sweep all the derivatives along with parent **1** predominately show two quasi reversible waves corresponding to reduction of quinoxaline core and carbonyl group present in acceptor unit of designed D–A system. Beside this, compound **5** and **6** display one

additional reduction peak could be assigned to reduction of $-NO_2$ group and diazene segment attached to triarylamine moiety respectively.

	noale	noalti	TIONO	L TIP COL	-FCe	m (la)f
Compd	E _{ovi}	E ^{peakb}	HOMO	LUMO"	Egev	$T_d(C)^2$
	UXI	leu				
		1.00 1.00		0.71		074 (010)
1	_	-1.02, -1.39	_	-3./1	-	274 (312)
2	0.92 1.12	-1 16 -1 46	-5 45	-3 55	1 90	432 (480)
-	0.92, 1.12	1110, 1110	5.15	5.55	1.50	152 (100)
3	1.12, 1.31	-1.05, -1.45	-5.63	-3.68	1.95	223 (487)
4	0.82 1.44	-1.02 -1.51	-5 30	-3.72	1 58	432 (505)
-	0.02, 1.11	1.02, 1.51	5.50	5.72	1.50	152 (505)
5	1.35, 1.44	-1.00, -1.26, -1.54	-5.83	-3.74	2.09	200 (401)
6	1 14 1 65	-1 04 -1 24 -1 49	-5.66	-3.68	1 98	258 (370)
U	1.14, 1.05	1.07, 1.27, 1.79	5.00	5.00	1.70	250 (570)
				Y		
7	1.11, 1.45	-1.12, -1.43	-5.56	-3.64	1.92	451 (510)
8	0.81 1.53	-1.05 -1.37	-5.23	_3 72	1 51	225 (398)
0	0.01, 1.55	1.05, 1.57	5.45	5.12	1.51	223 (370)
			Y			
9	1.08	-1.06, -1.51	-5.58	-3.70	1.88	242 (305)

Table 3. Electrochemical and thermal data of 1–9.

^a E_{oxi}^{peak} oxidation peak potential (V). ^b E_{red}^{peak} reduction peak potential (V). ^cHOMO energy level calculated from $E_{HOMO} = -[E_{oxi}^{peak} - E_{redox}(Fc/Fc^{+}) + 5.1] eV.$ ^dLUMO energy level calculated from $E_{LUMO} = -[E_{red}^{peak} - E_{redox}(Fc/Fc^{+}) + 5.1] eV.$ ^e E_{g}^{EC} calculated from $E_{g}^{EC} = [HOMO - LUMO] eV.$ ^fDecomposition temperature at 5% and 10% (in parentheses) weight loss derived by TGA.

The first potential of this oxidation and reduction waves was used to calculate HOMO and LUMO energy levels of **1–9** respectively. The HOMO energy level found in the range of -5.23 to -5.83 eV whereas LUMO energy level lies is in the range of -3.55 to -3.74 eV for compound **2–9**. According to previous reports on charge transporting properties of molecules, ambipolar transport arises when molecules have HOMO energy level below or equal to -5.0 eV and LUMO levels less than -3.15 eV [49,50]. Also, the HOMO and LUMO values reported for ambipolar materials in literature for small molecules are 6,13-bis(triisopropylsilylethynyl)-1,4,8,11-tetraazapentacene (TIPS-PEN) (HOMO = -5.49 eV; LUMO = -3.68 eV) [51], 2,2'-bis{5-[2,5-(2-ethylhexyl)-6-(5-cyano-thiophene-2-yl)pyrrolo[3,4-c]pyrrole-1,4-dione-3 yl]thiophene} (HOMO = -5.45 eV; LUMO = -3.74 eV) [52], and for polymers such as Poly[2-methoxy-5'3'7'dimethyloctyloxyl)-1,4phenylenevinylene) (MDMO- PPV) (HOMO = -5.4 eV; LUMO = -3.2 eV) [53], Poly[2,6(4,4-bis-2-ethylhexyl)-4*H*-cyclopenta-[2,1-b-3,4-b]dithiophene-alt-

4,7(2,1,3benzothiadazole) (PCPDTBT) (HOMO = -5.3 eV; LUMO = -3.55 eV) [54]; Dithienocoronenedimide (DTCDI)-bithiophene copolymer (HOMO = -5.56 eV; LUMO = -3.70 eV) [55]. The comparable HOMO and LUMO energy levels of **2**–**9** with these reported ambipolar materials, indicates that derivatives **2**–**9** have the ability of bipolar charge transfer and could be used as ambipolar materials. The electrochemical band gap of **2**–**9** are in the range of 1.51–2.09 eV. The increase in band gap was observed in compound **5** (2.09 eV) and **6** (1.98 eV) indicate impact of electron withdrawing $-NO_2$ group and diazene segment on diarlyamine respectively. On the other hand, a strong electron donating ability of electron rich methoxy substituted triphenylamine and phenothiazine is responsible for the small band gap 1.58 eV in **4** and 1.51 eV in **8** [56,57]. It is noteworthy that electrochemical band gap of derivatives is close to optical band gap obtained in DCM, indicating that the absorption peak obtained at higher wavelength region (i.e. ICT peak) represents electronic transitions from HOMO level to LUMO level [58]. This show that the charge transfers in the molecule is greatly influenced by D–A architecture.

3.4 **Theoretical Properties**

To further verify structure–property relationship at molecular level, we have performed time dependent density–functional (TD–DFT) calculations within the B3LYP hybrid functional as implemented in a Gaussian 03 program [59]. The molecular orbital levels and electrical properties of molecules 1-9 calculated theoretically by using the $6-311++G^{**}$ basis set.

Further, the electronic structures and photophysical properties obtained for **1–9** were comparatively studied for effect of different donor moieties attached to **1**.

The electronic distribution in the frontier molecular orbitals of 2 and 7 are displayed in Figure 9 (for other compounds see supporting information). In compound 1, the HOMO and LUMO is spread over the entire molecule. However, in case of its triarylamine derivatives 2–6 the HOMO is mainly located on triphenvlamine segment due to its good electron donating and hole transporting properties and extended to central benzene of quinoxaline unit. On the other hand, in heterocyclic derivative 7 HOMO is particularly located on donor carbazole moiety while in dye 8 the HOMO is located on only one of the phenothiazine moiety unambiguously. The HOMO in dye 9 having aliphatic morpholine as donor unit is extended from peripheral morpholine to quinoxaline. Further, the LUMOs of 2–9 are completely localized on electron deficient benzoyl substituted quinoxaline core. The presence of HOMO and LUMO on electron donating triarylamine/heterocyclic amines and electron deficient benzoyl substituted quinoxaline segment respectively verifies presence of D-A architecture in 2-9. This clearly signifies that HOMO-LUMO transitions occurring from electron donating triarylamine/heterocyclic amine unit to quinoxaline core. Such feature is characteristics to the ICT. Moreover, the HOMO and LUMO hardly overlapped in 7 due to twisted conformation of carbazole confirms weak D-A interaction in 7 while complete separation of HOMO and LUMO in 8 supports the electronic decoupling in donor and acceptor in ground state. Therefore, charge separation by PET may eventually possible with lower HOMO-LUMO gap in 8 [60,61]. In addition to this, in derivatives 2-9 has observed good oscillator strength even for charge transfer transition which are generally forbidden.

The computationally calculated energies of the HOMO–LUMO levels, HOMO–LUMO gap, vertical ionization potential, electron affinity and the ground state dipole moment for all molecules are given in **Table 4.** The HOMO and LUMO energy of **2–9** are in the range of

-5.01 to -6.56 eV and -2.15 to -2.92 eV respectively. These HOMO values shows close agreement with electrochemically calculated HOMO values while theoretically computed LUMO values show slight deviation with experimentally calculated data.



Figure 9. Optimized structures and Frontier molecular orbitals of 2 and 7 (for other compounds see supporting information).

Theoretical results show similar changing patterns of electronic properties on modulation of donor moiety on **1** as observed in experimentally calculated results. The band gap computed for the derivatives **2–9** is in the range of 2.45–3.93 eV and found to be decrease on attaching donor moiety like aromatic amines while it found to be increase in case of dye **9** having aliphatic morpholine as donor unit. Likewise, electrochemical studies the small band gap has obtained computationally for dye **4** and **8** due to electron rich methoxy substituted triphenylamine and phenothiazine respectively.

The first vertical ionization potential (IP) and the electron affinity (EA) were calculated computationally as the difference in the total energies of neutral and cationic/anionic species respectively. The ground state dipole moment of molecules 2-9 calculated were in the range of 2.28–5.77 Debye. Further, the optical properties were evaluated by TD–DFT in implicit water using $6-311++G^{**}$ basis set and simulated electronic transition of 1-9 in implicit water is presented in **Figure 10**. The transition energies, oscillator strength and assignment for the most relevant singlet excited states in each of the molecules are given in **Table 4** and other assignment are given in supporting information.

Further, the pattern of computed absorption spectra matches well with experimentally observed absorption spectra. Transitions observed at high energy below 350 nm for all molecules corresponds to $n-\pi^*$ and $\pi-\pi^*$ transitions while transition above 400 nm corresponds to ICT transitions. As simulated absorption spectra computed in implicit water, it exhibit red shift as compared to experimental one.

Compd	E _a (eV)	I _p (eV)	λ _{max} (nm)	F	Assignments	E _{HOMO} (eV)	E _{LUMO} (eV)	Eg(eV)	Dipole (debye)
1	1.61	7.82	387	0.6637	HOMO →LUMO (97 %)	-6.65	-2.85	3.80	2.3
			322	0.3287	HOMO→LUMO+1 (88%)				
2	1.37	6.27	540	0.3956	HOMO →LUMO (98 %)	-5.34	-2.15	2.84	5.37
			510	0.1323	HOMO–1→LUMO (98%)				
			433	0.8581	HOMO \rightarrow LUMO+1 (94%))			
3	1.34	6.27	525	0.4276	HOMO →LUMO (98 %)	-5.36	-2.44	2.92	5.77
			492	0.1262	HOMO $-1 \rightarrow$ LUMO (97%)				
			423	0.2543	HOMO \rightarrow LUMO+1 (91%)				
4	1.24	5.90	596	0.3992	HOMO \rightarrow LUMO (98 %)	-5.01	-2.36	2.65	5.63
			562	0.1431	HOMO $-1 \rightarrow$ LUMO (98%)				
			467	0.2551	HOMO \rightarrow LUMO+1 (95%)				
5	2.01	6.91	498	0.6462	HOMO →LUMO (84%)	-6.01	-2.92	3.09	2.97
			488	0.7798	HOMO→LUMO+1 (72%)				
			449	0.0880	HOMO $-1 \rightarrow$ LUMO+1 (62%)				
6	1.86	6.28	539	0.6744	HOMO →LUMO (88%)	-5.47	-2.66	2.81	3.99
			523	1.2707	HOMO \rightarrow LUMO+1 (49%)				
			463	0.2116	HOMO-1 \rightarrow LUMO+2 (83%)				
7	1.64	6.27	470	0.2721	HOMO →LUMO (97%)	-5.77	-2.81	2.96	2.28
			460	0.0377	HOMO–1 \rightarrow LUMO (97%)				
			388	0.1988	HOMO \rightarrow LUMO+1 (82%)				
8	1.70	6.34	544	0.0012	HOMO–1 \rightarrow LUMO (99%)	-5.34	-2.89	2.45	2.74
			371	0.6018	HOMO-4 \rightarrow LUMO (92%)				
9	1.24	6.69	504	0.5197	HOMO →LUMO (98%)	-6.56	-2.63	3.93	3.95
			405	0.2075	HOMO \rightarrow LUMO+1 (96%)				
			366	0.3065	HOMO-1 \rightarrow LUMO+1 (82%)				

Table 4. Computed Ionization potentials, Electron affinities, Wavelengths, Oscillator strengths, main vertical electronic transition in gas phase,Orbital energies and Dipole moments of 1–9.

Similarly, bathochromic shift in ICT tansitions observed for compound **4** attributed to electron donating –OCH₃ group attached to diphenylamine moiety whereas hypsochromic



shift

Figure 10. Simulated absorption spectra of compounds 1–9 in implicit water.

in ICT transitions of compound **5** and **7** corresponds to presence of electron withdrawing – NO₂ group on diphenylamine and weak electron donor carbazole respectively.

3.5 Thermal Properties

The thermal stability of **1–9** were studied by thermogravimetric analysis (TGA) and melting points determined by open capillary method.



Figure 11. TGA thermogram **2–9** under nitrogen atmosphere at normal pressure. Heating rate, 10 ⁰C/min.

The TGA thermograms of **2–9** are displayed in **Figure 11** (For TGA thermogram of **1** see supporting information).

TGA thermogram show compounds 2–9 exhibit good thermal stability. The decomposition temperature corresponds to 5% and 10% weight losses are found in the range 200–451 0 C and 305–510 0 C respectively (**Table 3**). The order of thermal stability in derivatives 2–9 is 7 > 4 > 2 > 6 > 9 > 3 > 8 > 5.

3. Conclusion

Novel D-A based dyes 2-9 were synthesized and studied for their photophysical, electrochemical and theoretical properties. The designed D-A structure in 2-9 generates ICT transition in absorption spectrum that significantly influenced by the nature of donor moiety. Dyes 2-9 emit in blue-orange region in toluene, chloroform, DCM and neat solid film and exhibit positive solvatochromism in emission spectra ranging from 472 to 575 nm. AIE properties of luminophores 2, 3 and 7 reveal that AIE dominates emission at higher water percentage due to formation of nanoparticles. The formation of nanoparticles at higher water percentage were confirmed by FEG-SEM studies of 2 which show nanoparticles formed are spherical in nature with mean diameter of 30–50 nm. The HOMO and LUMO energy level of compounds measured by CV are found in the range of -5.23 to -5.83 eV and -3.55 to -3.74eV respectively and comparable with reported ambipolar materials. DFT and TD-DFT studies show that HOMO and LUMO are mainly localized on electron rich amines and electron deficient quinoxaline core respectively and verifies presence of D-A architecture in molecules. Thermal studies reveal good thermal stability of all the derivatives. Thus, on the basis of these results of 2–9, we believe that these dyes could be used as ambipolar charge transporting material and emitter in various optoelectronic applications.

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Highlights:

- ➢ Novel Donor−Acceptor (D−A) based dyes are synthesized
- > Modulation of donor moiety affects Characteristic ICT transitions
- Dyes exhibit solvatofluorochromism and broad scale of fluorescence from "Blue to Orange" region in solution and solid state
- Some dyes holds excellent AIE properties and stability of nanoparticle suspension (30– 50 nm) for longer period
- Dyes offers small electrochemical band gap (1.51–2.09 eV) and ambipolar charge transfer