

Amino substituted 4-pyridylbutadienes: Synthesis and fluorescence investigations



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ABSTRACT

Synthesis and spectroscopic investigations of a series of donor- π -acceptor systems containing pyridine as the electron withdrawing group and an amino derivative (dimethylamino, diphenylamino, carbazole and julolidine) as electron donating group, separated by a π -spacer are described. The effect of varying donors on absorption and emission properties was studied in different solvents. All the molecules investigated exhibit pronounced positive polarity dependent solvatochromic shifts of up to ~141 nm. Strong fluorescence quantum yields are also observed for dienes containing carbazole and diphenylamine donors. This behavior suggests the presence of highly polar emitting states as a result of π - π^* intramolecular charge-transfer (ICT). The observations were corroborated by a linear relation of the fluorescence maximum (ν_{max}) versus the solvent polarity function (Δf) from the Lippert–Mataga correlation. The emission lifetime shows a decay profile consistent with the formation of one species (**1** and **3**) and two species (**2** and **4**) in the excited state.

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1. Introduction

π -conjugated substrates bearing π -electron donor (D) and a π -electron acceptor substitutions exhibiting intramolecular charge transfer (ICT) have gained prominence for use as functional organic materials [1–6]. Among many known substrates, derivatives such as donor-acceptor substituted diphenylpolyenes have attracted attention as model compounds to understand the light induced conformational processes of biological substrates [7] and also as fluorescence probes [8]. Replacement of CH of the phenyl ring of diphenylpolyenes by nitrogen (N) leads to an isoelectronic species that is expected to have significant influence on the electronic properties due to the presence of (n, π^*) states [9]. Consequently, neutral styryl and butadienyl pyridine analogs have been synthesized and were investigated for their solution and/or solid state photochemical [10–12] and photophysical properties [13–15]. Examples of photochemical investigations include regioselective photodimerization [16,17], formation of pre-organized molecular ladderane like structures through hydrogen bonding interactions [18] and photoisomerization studies [10,12,14]. Apart from its role

towards photochemical transformations, the lone pair of electrons on the nitrogen atom of the pyridine contributes to a coordinate covalent bonding with Lewis acid sites of TiO_2 surface lending its utility as anchoring group for dye-sensitized solar cells applications [19–21]. Because of the facile protonation of pyridine moiety and its role in deactivating effect of the (n, π^*) state [22], these substrates have also been utilized as potential fluorescence probes for biological applications [23–28] and also for non-linear optical (NLO) applications [29,30]. In contrast to research investigations on unsubstituted pyridylbutadiene derivatives, the emission properties of the electron donor or acceptor substituted heterocyclic (pyridine) derivatives of butadienes are scarce. Here in, we report synthesis and solvatochromic properties of novel amino [dimethylamino, diphenylamino, carbazole and julolidine] substituted 4-pyridylbutadiene derivatives (Fig. 1). Through this study, we also intend to examine influence of extended π -conjugation on the steady state and time resolved emission properties of the substrates. The results suggest remarkable fluorescence properties characterized by intramolecular charge transfer (ICT).

2. Experimental

The reagents required for the synthesis of pyridyl substituted derivatives were obtained from Sigma–Aldrich, Alfa Aesar, Acros

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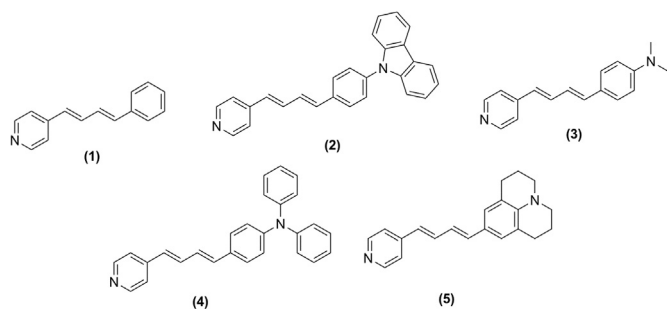


Fig. 1. Structures of synthesized 4-pyridyl-4-phenylbutadiene derivatives.

and S.D. Fine. The solvents utilized for the synthesis and spectral studies were dried using reported procedures. ^1H and ^{13}C NMR spectra were carried out using 500 MHz Bruker Avance spectrometer in CDCl_3 with tetramethylsilane as an internal standard. Accurate mass analysis was performed using Waters-Synapt G2S (ESI-QToF) mass spectrometer. Absorption spectra were recorded on Analytik Jena, Specord 210 model UV–vis spectrophotometer. Steady state fluorescence studies were performed utilizing Horiba Jobin-Yvon fluorolog-3 spectrofluorimeter and relative fluorescence quantum yields were measured using quinine sulfate (0.545 in 0.5 N H_2SO_4) as a standard [31]. The concentrations used for fluorescence experiments are typically in the order of 10^{-5} M. The excitation wavelengths were set at the absorption maxima (λ_a) of the compounds while recording their emission spectra. Fluorescence life-times were determined by Edinburgh Life Spec II instrument at excitation wavelengths of 360 nm for (2), 405 nm for (3–5). The percent error associated with the lifetime studies is 0.1–0.3%.

2.1. X-ray crystallographic details

Crystallographic data for the compound (4) was collected on Xcalibur, Gemini with EOS detector diffractometer. The reflection data was integrated and reduced using CrysAlisPro and Superflip [32] and the structure was refined using SHELXS97 [33]. ORTEP diagrams of the compound generated using ORTEP-3. The single crystals of (4) were grown in acetone solvent system. The crystallographic data reveal that the compound (4) crystallized into a triclinic crystal system with space group P-1 with $Z = 2$ and shows a *trans*-configuration. Crystallographic data and the ORTEP diagram are given in the supporting information [Tables C1–C3 and Fig. C1].

2.2. Synthesis of (1), (3), (4) and (5)

The synthetic scheme for the preparation of dienes (1), (3–5) is given in Scheme 1c. In a typical procedure [15], a mixture of diphenyl (4-picolyl)phosphane oxide [34] (1 equiv), NaH (2.5 equiv), 18-crown-6 (0.5 equiv) was stirred in 40 mL of dry THF at 0 °C. After 30 min of stirring, 4-substituted cinnamaldehyde (1 equiv) in dry THF was added drop wise and allowed to stir for 10 h at room temperature. The reaction mixture was then filtered over celite and the desired product was purified by column chromatography using neutral silica gel using 30% ethyl acetate/petroleum ether.

2.2.1. *N,N*-dimethyl-4-((1*E*,3*E*)-4-(pyridin-4-yl)buta-1,3-dienyl)aniline (3)

Brown solid, ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.50 (d, 2H), δ 7.36–7.35 (d, 2H), δ 7.15–7.09 (dd, 1H, $J = 15.5$ Hz), δ 6.80–6.68 (m, 4H), δ 6.47–6.44 (d, 1H, $J = 15.5$ Hz), δ 2.99 (s, 6H); ^{13}C NMR (CDCl_3 ,

125 MHz, ppm) δ 150.56, 149.89, 136.54, 134.68, 128.03, 126.95, 123.93, 120.42, 112.29, 40.34. HRMS $[\text{M}+1]^+$ 251.1550.

2.2.2. *N,N*-diphenyl-4-((1*E*,3*E*)-4-(pyridin-4-yl)buta-1,3-dienyl)aniline (4)

Yellow solid, ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.51–8.50 (d, 2H), δ 7.32–7.26 (m, 8H), δ 7.14–7.09 (m, 5H), δ 7.05–7.00 (m, 4H), δ 6.86–6.80 (m, 1H, $J = 15.5$ Hz), δ 6.73–6.70 (d, 1H, $J = 15.5$ Hz), δ 6.53–6.49 (d, 1H, $J = 15.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 149.96, δ 148.06, δ 147.36, δ 144.9, δ 135.56, δ 134.06, δ 130.58, δ 129.36, δ 128.58, δ 127.65, δ 126.39, δ 124.81, δ 123.39, δ 123.02, 120.54. HRMS [ESI] $[\text{M}+1]^+$ 375.1859.

2.2.3. 9-((1*E*,3*E*)-4-(pyridin-4-yl)buta-1,3-dienyl)-1,2,3,5,6,7-hexahydroxyrido[3,2,1-*ij*]quinoline (5)

Brown solid; ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.48–8.47 (d, 2H), 7.23–7.22 (2H, d), 7.12–7.07 (m, 1H, $J = 15.5$ Hz), 6.91 (s, 2H), 6.73–6.68 (m, 1H, $J = 15.5$ Hz), 6.62–6.59 (d, 1H, $J = 15$ Hz), 6.42–6.39 (d, 1H, $J = 15$ Hz), 3.19–3.17 (4H, t), 2.76–2.73 (4H, t), 1.97–1.95 (4H, t); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 151.7, 149.8, 145.4, 143.3, 136.9, 134.8, 126.2, 125.8, 124.0, 123.0, 121.2, 120.3, 49.9, 27.7, 21.8 HRMS $[\text{M}+1]^+$ 303.1868.

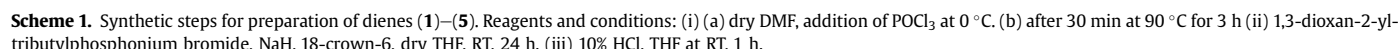
2.3. Synthesis of 9-((1*E*,3*E*)-4-(pyridin-4-yl)buta-1,3-dien-1-yl)phenyl)-9H-carbazole (2)

Derivative (2) was synthesized by a method [35] showed in Scheme 1d. A mixture of carbazole (60 mg, 0.350 mmol), 4-((1*E*,3*E*)-4-(4-bromophenyl)buta-1,3-dienyl)pyridine diene (13) (100 mg, 0.350 mmol), CuI (0.0350 mmol), 18-Crown-6 (0.012 mmol), K_2CO_3 (100 mg, 0.7 mmol) and 1 ml of 1,3-Dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU) was put into a round bottom flask, and then heated at 170 °C for 13 h under nitrogen atmosphere. After cooling to room temperature, the mixture was quenched with 1 N HCl, and the precipitate was washed with $\text{NH}_3\text{--H}_2\text{O}$ and water. The residue was extracted with ethyl acetate, dried over Na_2SO_4 and then concentrated under vacuum. The reaction mixture was purified on silica-gel column chromatography using 35% ethylacetate/hexane as eluent.

Characterization data: Orange solid ^1H NMR (CDCl_3 , 500 MHz, ppm) δ 8.57 (m, 2H), δ 8.15–8.14 (d, 2H), δ 7.69–7.67 (d, 2H), δ 7.57–7.56 (d, 2H), 7.46–7.40 (m, 4H), 7.31–7.29 (m, 4H), 7.21–7.16 (m, 1H, $J = 15.5$ Hz), 7.07–7.02 (m, 1H, $J = 15.5$ Hz), 6.89–6.85 (d, 1H, $J = 15.5$ Hz), 6.66–6.62 (d, 1H, $J = 15.5$ Hz); ^{13}C NMR (CDCl_3 , 125 MHz, ppm) δ 151.73, 150.21, 144.48, 140.69, 137.49, 135.83, 134.63, 133.34, 130.37, 128.93, 128.03, 127.21, 126.00, 123.51, 120.70, 120.36, 120.11, 109.79. HRMS $[\text{M}+1]^+$ 373.1699.

2.4. Computational details

Density functional theory (DFT) calculations have been performed using Gaussian 09 *ab initio* quantum chemical software package. DFT has been used for the ground-state properties and time-dependent DFT (TDDFT) for the estimation of ground to excited-state transitions. The geometry optimization of the molecules obtained using non-local functional B3LYP with 6-31G (d, p) basis set without any symmetry constraints. The minimized geometry was further confirmed by vibrational analysis, resulting in no imaginary frequencies and used as the input for further calculations to obtain the frontier molecular orbitals (FMOs) and single-point TDDFT studies (first 15 vertical singlet–singlet transitions) to obtain the UV–Vis spectra. The integral equation formalism polarizable continuum model (PCM) within the self-consistent reaction field (SCRF) theory, has been used for TDDFT calculations to describe the solvation of the dye in acetonitrile solvent. The



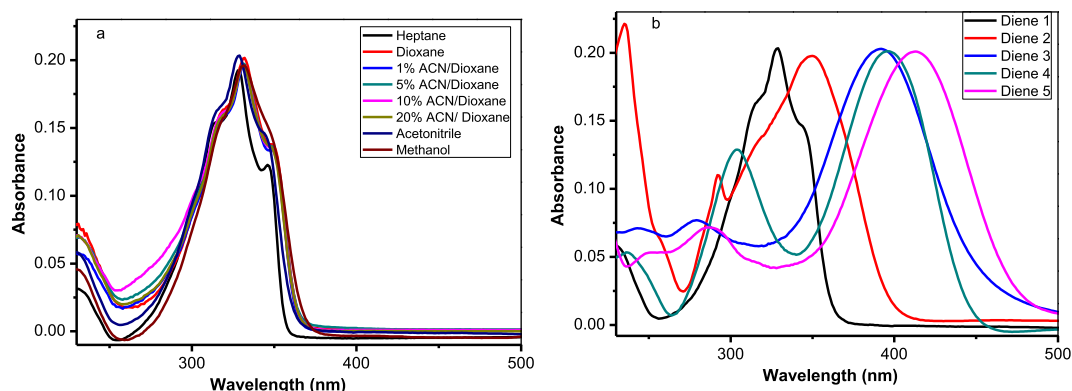
3. Results and discussion

Fig. 1 gives structural details of the dienes investigated. Diene **(1)** is a simple un-substituted 4-pyridyl-4-phenylbutadiene derivative. Diene **(2)** is substituted with carbazole while dienes **(3)**, **(4)** and **(5)** have dimethylamine, diphenylamine and julolidine substituents respectively. These amino derivatives function as electron donors while the heterocyclic pyridine ring behaves as the electron acceptor. **Table 1** summarizes the absorption and fluorescence data of dienes **(1–5)** in different solvents. The absorption spectrum of diene **(1)** in different solvents is shown in **Fig. 2a**. This unsubstituted diene absorbs (λ_a) at ~332 nm in acetonitrile. Upon introduction of electron donating moieties, significant absorption

changes are observed. The lowest shift (+18 nm) is obtained for diene (**2**) containing a carbazole group and a maximum shift (+81 nm) was observed for diene (**5**) containing julolidine [Fig. 2b]. Despite increase in the electron donating strength, only a small (+4 nm) wavelength shift was observed for diene (**4**) as compared to diene (**3**). This small increase is due to sharing of the lone pair of electrons on nitrogen between the adjacent phenyl rings and rest of the molecule. In case of diene (**2**), the carbazole ring system twists out of the plane with respect to the aryl group resulting in decreased electron donating strength. The absorption at ~300 nm in dienes (**2**) and (**4**) is attributed to the π - π^* transition of the triphenylamine or carbazole moiety. The other band located at about 360–390 nm with stronger intensity is due to the intramolecular charge transfer (ICT) absorption band [Fig. 2b and Fig. S2]. The alkyl substitution on nitrogen (**5**) increases the donating capacity through positive inductive effect (+I) effect resulting in larger absorption shifts. The possibility of planarization in the system is also another contributing factor [36]. Based on the observed absorbance data, the strength of electron donors can be

Table 1Absorption and emission data of diene (**1–5**) in various nonpolar to polar solvents.

Solvent	λ_a (nm)	λ_f (nm)	Stokes shift (cm^{-1})	Φ_f	λ_a (nm)	λ_f (nm)	Stokes shift (cm^{-1})	Φ_f
	(2)				(3)			
Heptane	360	392	2267	0.78	383	446	3678	0.023
Dioxane (D)	356	436	5154	0.55	392	488	4019	0.021
1% AcN/D	356	439	5310	0.47	393	495	5243	0.017
5% AcN/D	356	445	5618	0.50	393	504	5604	0.019
10% AcN/D	355	454	6063	0.50	392	508	5825	0.019
20% AcN/D	354	460	6409	0.45	394	522	6223	0.019
AcN	350	492	8246	0.32	392	540	6992	0.018
Methanol	353	496	8167	0.02	394	551	7232	0.016
	(4)				(5)			
Heptane	393	472	4259	0.40	403	442	2189	0.033
Dioxane (D)	395	481	4526	0.30	413	518	4998	0.031
1% AcN/D ^a	397	491	4822	0.16	—	—	—	0.031
5% AcN/D	397	498	5108	0.17	414	520	4924	0.032
10% AcN/D	396	504	5411	0.17	414	530	5387	0.033
20% AcN/D	397	513	5695	0.15	416	547	5757	0.035
AcN	396	534	6526	0.16	413	569	6639	0.034
Methanol	399	540	6544	0.02	419	583	6714	0.016

^a AcN is acetonitrile. Quinine sulfate (0.545 in 0.5 N H₂SO₄ is used as standard).**Fig. 2.** Normalized UV spectra of (a): (**1**) in varying solvent polarity; (b): (**1–5**) in acetonitrile (ACN is acetonitrile).

given as $\text{H} < \text{Carbazole} < \text{N, N-dimethyl} \leq \text{N, N-diphenyl} < \text{Julolidine}$.

The dienes show vibrational structure in non-polar heptane and a smooth structure less absorption spectrum in solvents of higher polarity. This is attributed to involvement of charge transfer and strong solute–solvent interactions. Solvent polarity variations lead to small absorption wavelength shifts (~ 4 – 16 nm) [Fig. 2b and Fig. S1 & S2]. Among the dienes, (**5**) shows a maximum shift of 16 nm from non-polar heptane to acetonitrile, and carbazole containing (**2**) shows an absorption shift of about 7 nm.

To understand the effect of the amino donating groups on electronic, optical and geometrical properties of the dienes (**1–5**), density functional theory (DFT) calculations were performed using Gaussian 09 *ab initio* quantum chemical software package. The optimized geometry with dihedral angles, molecular orbital amplitude plot of the highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) of the dienes (**1–5**) are shown in Fig. 3. The optimized geometries obtained from B3LYP/6-31g (d, p) level of theory shows that all the dienes except (**2** & **4**) are almost planar in nature. In diene (**2**), carbazole is twisted out of the plane of the diene system with the dihedral angle of 54.1° . Similarly in diene (**4**), a large torsion angle of $\sim 47^\circ$ observed between the phenyl rings present in the starburst triphenylamine (TPA) segment. The steric repulsion induced by the diphenylamine unit in TPA derivative twisted out the plane of the diene system to the dihedral angle of 37.1° . This out of plane twisting results in

lowered absorption maxima, contrary to expected absorption maxima based solely on electron donating strength. This is substantiated from TDDFT simulation studies. In all the molecules, the HOMOs are completely delocalized over the entire molecule, whereas the LUMOs are mainly populated over the unsaturated chain and the pyridine unit. This charge separation observed from the distribution of HOMO and LUMO indicates that the HOMO $\rightarrow$ LUMO transition bears a considerable intramolecular charge-transfer (ICT) character.

TDDFT calculations were used to examine the vertical excitation energy of the dienes using B3LYP functional. The absorption spectra show a small underestimation in gas phase (not shown) and used the same functional further in the framework of polarizable continuum model (PCM) with acetonitrile as solvent. The trend in these computed values is in reasonable agreement with the experimentally observed wavelength maximum. The plot of TDDFT simulated spectra of the dienes (**1–5**) is depicted in Fig. 4. The comparison of computed HOMO–LUMO energy difference, lowest excitation energies along with their oscillator strength, nature of transitions and the ground state dipole moment of all the dienes using the B3LYP level of theory with experimental observations were summarized in Table S1. The relative tendency in the absorption wavelength is interpreted by means of molecular orbitals composition which is essential to determine the extent of charge-separation. The HOMO to LUMO transition for all the dienes (**1–5**) are calculated to be 97%, 79%, 93%, 86% and 92% respectively.

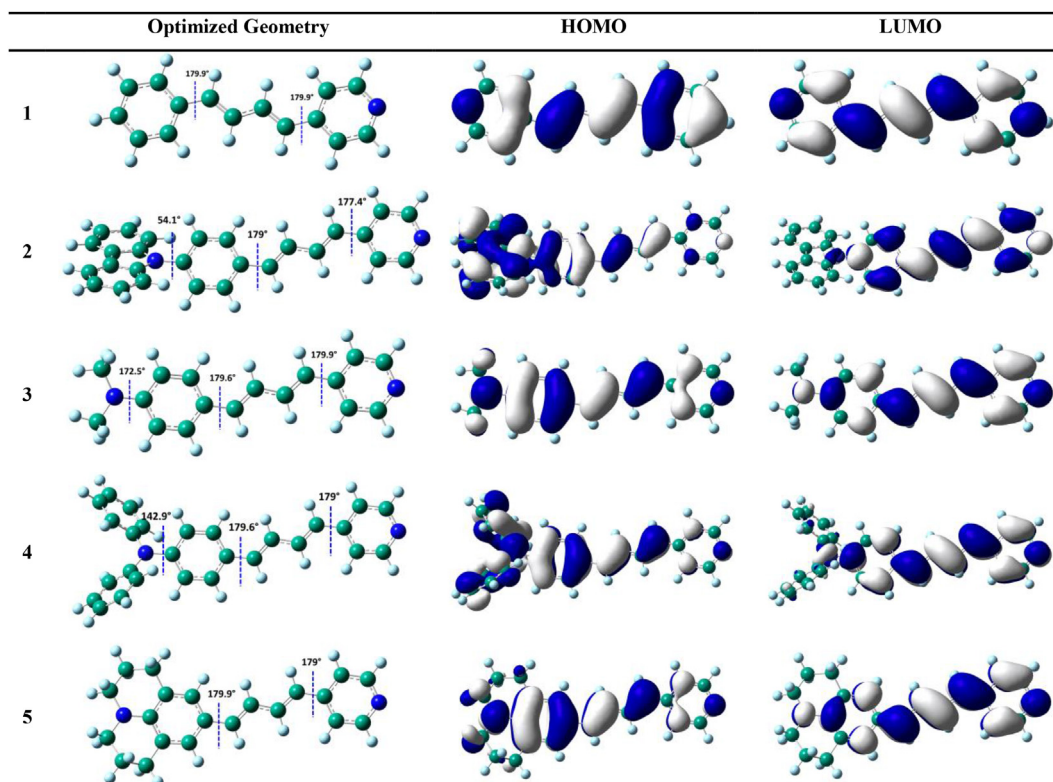


Fig. 3. Optimized geometries and their computed isodensity (0.02) surfaces of HOMO and LUMO of the dienes (1)–(5).

Dienes (2–5) show considerable ICT nature besides π – π^* transition, whereas in diene (1), π – π^* transition is more predominant [37,38]. It is worth noting that the HOMO to LUMO transition of dienes (2) and (4) containing carbazole and triphenylamine as electron donors are comparatively lower (Table S1). This may be attributed to the non-planar donor-acceptor interaction which leads to poor overlap of orbital interactions over the system.

3.2. Fluorescence properties in solution

Table 1 detail the absorption and fluorescence data of the investigated dienes. Diene (1) has very weak fluorescence and the spectrum is highly noisy (Fig. S3). The weak emission is due to fast deactivation of the molecules in the excited state through free rotation of the molecules as the excited state has less double bond

character compared to the ground state processes and also due to strong non-radiative losses through processes such as internal conversion [39,40]. In comparison, the amino derivatives (2–5) generally result in broad, structure-less emission band with strong solvatochromic emission shifts (λ_f) with the increase in solvent polarity. Among the dienes investigated, diene (5) containing the julolidine group has a maximum bathochromic shift (+141 nm) from heptane to acetonitrile while diene (4) bearing a diphenylamino group leads to a minimum (+68 nm) shift [Fig. 5]. The enhanced strength of electron donating group due to the presence of alkyl groups in julolidine result in huge solvatochromic emission shifts. Such a large solvatochromic shifts observed can be attributed to twisted intramolecular charge transfer (TICT) and this attribute was utilized as viscosity or polarity dependent fluorescence probes [41,42]. Diene (3), with dimethylamino groups also exhibit large solvent polarity dependent emission shifts. In comparison, a related derivative of (3) containing a phenyl ring in place of a pyridine ring shows an emission shift of 56 nm [43]. Despite twisting out of plane, carbazole containing diene (2) shows a bathochromic shift of ~100 nm. This strong bathochromic shift in dienes clearly shows that fluorescence originates as a consequence of pronounced increase in charge separation due to intramolecular charge transfer (ICT). This ICT state was also reflected through observance of large a Stokes shift for these dienes in polar solvents. Large Stokes shift indicates least overlap of absorption and emission and this characteristic enables their use as biological labels [44]. Among the dienes, (2) containing carbazole exhibits larger Stokes shift as compared to other dienes. Although more twisting was expected in carbazole substituted compound, it can experience large electron delocalization resulting in a greater ICT character [45]. The calculated quantum yields are also higher for carbazole containing (2) than other dienes. The quantum yields for diphenylamine containing (4) are also higher indicating the potential utility of these

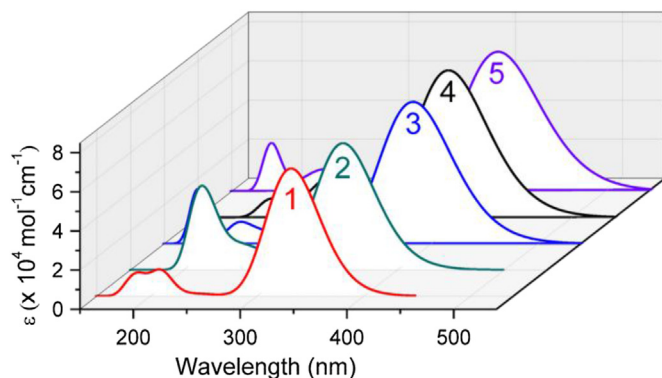


Fig. 4. Simulated absorption spectra obtained with TD-DFT/B3LYP/6-31G (d, p) level of theory.

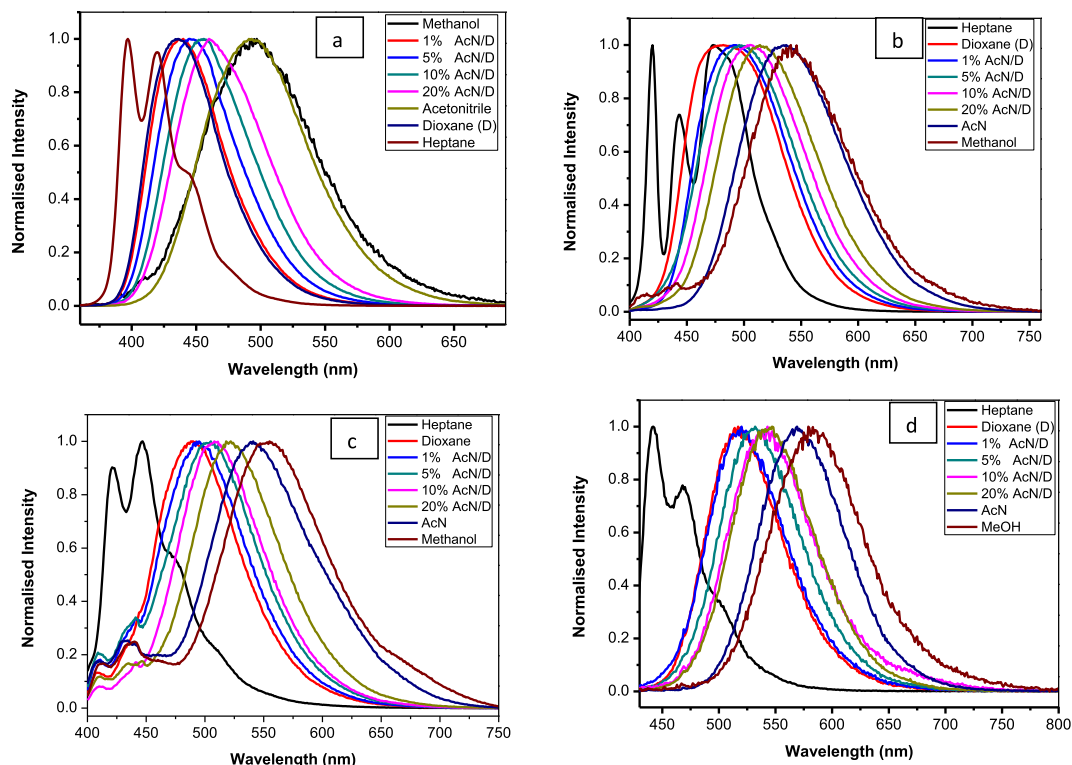


Fig. 5. Emission spectra of (a) **2**, (b) **4**, (c) **3** and (d) **5**.

chromophores for biological or optical applications. The dienes containing aliphatic amino substitutions (**3** and **5**) both show lower quantum yield of fluorescence. Despite the restriction caused by the aliphatic ring, diene (**5**) shows comparable quantum yields with diene (**3**). To further examine the solvatochromic shift, the excited state dipole moment (μ_e) of dienes (**2–5**) was calculated using Lippert–Mataga equation [46]. The dipole moment (μ_e) of the ICT excited states can be calculated from the slope (m_f) of the plot of the Stokes shift with Δf according to eq

$$\nu_{ss} = \left[2(\mu_e - \mu_g)^2 / hca^3 \right] \Delta f + \nu_{ss}^0$$

where, ν_{ss} is the Stokes shift, μ_g is the ground state dipole moment and were obtained using DFT calculations utilizing Gaussian Software, a is the solvent cavity (Onsager) radius. The solvent parameter Δf represents solvent polarity and polarizability and defined as

$$\Delta f = [(\epsilon - 1)/(2\epsilon + 1)] - [(n^2 - 1)/(2n^2 + 1)]$$

where ϵ and n are solvent dielectric constant and refractive index respectively. The Onsager radius (a) calculated by the formula

$$a = (3M/4N\pi d)^{1/3}$$

Table 2

Calculated Onsager radius, slope of the curve, ground and excited state dipole moments of dienes investigated.

Compound	$a(\text{\AA})$	m_f	$\mu_g(\text{D})$	$\mu_e(\text{D})$
2	5.28	10,924	1.8522	14.47 ± 0.014
3	4.63	7982	7.6166	16.47 ± 0.022
4	5.28	7346	5.0880	15.45 ± 0.005
5	4.93	6569	8.3659	17.18 ± 0.022

In this, (N) is Avogadro number, (M) is the molecular weight, and (d) is the density and taken as 1 g/cm^3 [47]. The estimated dipole moments (μ_e) are listed in Table 2 along with calculated values of a , m_f , μ_g , for dienes (**2–5**). The plots of $\Delta\nu$ ($\nu_A - \nu_F$) vs Δf are shown in Fig. S4. In all the cases, a linear correlation with a positive solvatochromism was observed indicating their solvent sensitive behavior due to presence of intramolecular charge transfer (ICT) emissive states.

The ICT state is also reflected by large change in excited state dipole moment. The ICT states of diene (**2–5**) have larger dipole moments in the excited state than in the ground state as a result of the charge separation between the donor and acceptors. The order of μ_e is (**5**) > (**3**) > (**4**) > (**2**). The observed excited state dipole moments confirm the earlier observations of greater charge transfer character for julolidine substituted diene (**5**). The competing processes of sharing of lone pair of electrons in (**2**) and (**4**) and the bulkier donating groups in the form of triphenylamine

Table 3

Fluorescence lifetime data in homogeneous solvents. Diene (**2**) was excited at 360 nm. Diene (**3**), (**4**) and (**5**) were excited at 405 nm (error percentage-0.1–0.3%).

Diene	Solvent	τ_1	τ_2	χ^2
(2)	Dioxane	1.32	—	1.03
	20% ACN/Dioxane	1.87	—	1.08
	Acetonitrile	2.52	—	1.04
(3)	Dioxane	0.11 (98.49%)	1.13 (1.51%)	0.86
	20% ACN/Dioxane	0.16 (90.89%)	0.54 (8.70%)	0.88
	Acetonitrile	0.18 (91.75%)	0.50 (7.87%)	0.88
(4)	Dioxane	1.24	—	0.92
	20% ACN/Dioxane	1.53	—	1.04
	Acetonitrile	1.82	—	0.90
(5)	Dioxane	0.25 (91.14%)	2.50 (8.86%)	0.97
	20% ACN/Dioxane	0.47 (97.03%)	2.53 (2.96%)	1.02
	Acetonitrile	0.57 (99.80%)	2.77 (0.20%)	0.90

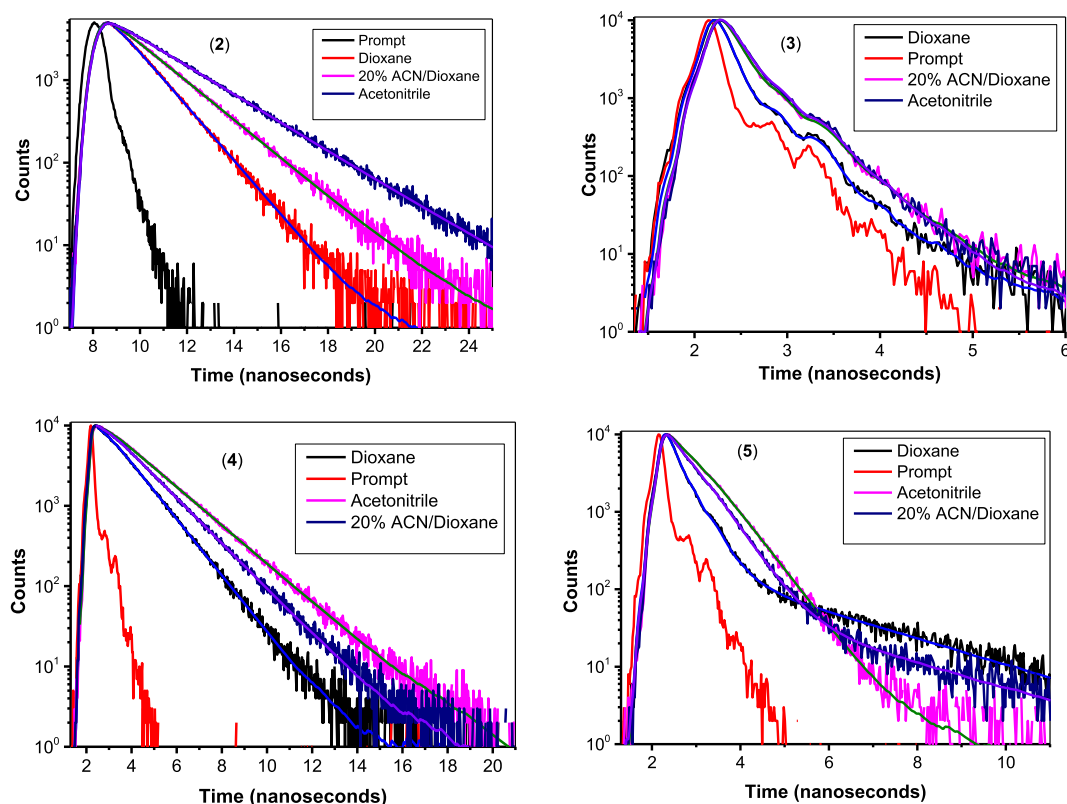


Fig. 6. Excited state decay profile of dyes (2–5) in different solvents. Excitation of 360 nm for (2) and (b) 405 nm for (3–5).

and carbazole lead to reduction in electron delocalization in excited state and therefore result in decreased μ_e values in comparison to (3) and (5). The presence of alkyl (methyl) groups on nitrogen facilitates the availability of electrons for electron charge transfer during the excited state resulting in increase in μ_e for diene (3) and (5).

Room temperature lifetimes of dyes in different solvents are shown in Table 3. Dienes (2) and (4) bearing carbazole and triphenylamine moieties show single exponential decay while dyes (3) and (5) show bi-exponential decay with major component having population greater than 90% with lifetime in the range of 0.11 ns–0.57 ns. The minor component (with a population less than 10%) has a lifetime in the range of 0.50 ns–2.77 ns. It is possible that both the dyes containing dimethylamino and julolidine have excited states that contribute to conformational changes due to their significant intramolecular charge transfer nature [Fig. 6]. Thus it can be said that the fluorescence majorly originates from a single excited state species in the case of (2) and (4) but originates from two excited states in the case of (3) and (5) due to conformational changes. Such biexponential decay is also reported in similarly substituted stilbene derivative [48].

4. Conclusions

In summary, we have designed and synthesized arylbutadienes containing different amino substituted derivatives as electron-donating groups and pyridine as an electron-accepting group. Their excited state properties are strongly solvent-dependent, while their absorption spectra show moderate changes in various solvents. The nature of electron donating group markedly influences the emission shifts with julolidine electron-donating substituent causing greater red-shift of the fluorescence

maximum, indicating efficient intramolecular charge transfer behavior. It can further be proposed from these studies that such strongly solvatochromic probes can be useful materials for optical and biological applications.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.dyepig.2015.08.018>.

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