

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/42253611>

Aromatic Fumaronitrile Core-Based Donor–Linker–Acceptor–Linker–Donor (D- π -A- π -D) Compounds: Synthesis and Photophysical Properties

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY A · MARCH 2010

Impact Factor: 2.69 · DOI: 10.1021/jp9115589 · Source: PubMed

CITATIONS

22

READS

23

3 AUTHORS:



Krishna Panthi

University of Texas at Austin

21 PUBLICATIONS 81 CITATIONS

[SEE PROFILE](#)



Ravi M Adhikari

Bowling Green State University

14 PUBLICATIONS 422 CITATIONS

[SEE PROFILE](#)



Thomas Kinstle

Bowling Green State University

25 PUBLICATIONS 185 CITATIONS

[SEE PROFILE](#)

Aromatic Fumaronitrile Core-Based Donor–Linker–Acceptor–Linker–Donor (**D- π -A- π -D) Compounds: Synthesis and Photophysical Properties**

Krishna Panthi,[†] Ravi M. Adhikari,[‡] and Thomas H. Kinstle*,[†]

Department of Chemistry, Center for Photochemical Sciences, Bowling Green State University, Bowling Green, Ohio 43403, and Angstrom Technologies, Inc., Florence, Kentucky 41042

Received: December 5, 2009; Revised Manuscript Received: February 18, 2010

A new class of aromatic fumaronitrile core-based compounds with different donors and linkers has been synthesized and well characterized. Compounds **1** and **2** have indole and 2-phenylindole groups as electron donors, respectively. Compounds **3** and **4** have a diphenylamino group as the electron donor, and compound **5** has a 3,6-di-*tert*-butylcarbazole group as an electron donor. These compounds absorb in the blue-to-green region and emit in the blue-to-red region depending on the electron donor, linker, and solvents. The quantum yields of fluorescence of these compounds in solution are measured and found to be moderate, but in solid states, they are high. These compounds display strong emission solvatochromism that is reflected by a large shift in their fluorescence emission maxima on changing the solvents. This change is accompanied by a successive decrease in fluorescence intensity. The fluorescence lifetimes of these compounds are measured in different solvent and found to vary from <1 to 7 ns. Optical switching of these compounds with solvents, concentration, and excitation energy have been studied. The correlation between the functional group and optical properties has been established to some extent. The ability of these compounds to function as colorimetric and luminescence pH sensors is demonstrated with color changes and luminescence switching upon the addition of trifluoroacetic acid. The potentiality of these compounds for application in optoelectronics has been optically assessed.

Introduction

Organic compounds with good photoluminescence responses are promising candidates for a variety of optoelectronic applications. Conjugated organic compounds exhibit a variety of interesting optical, electrical, and photoelectric properties in the solid state.¹ The advantages of organic compounds over inorganic ones are their cost and the ease of processing. Moreover, the use of functional groups has endowed the molecular materials with unique and interesting optoelectronic properties.^{2–4}

Many conjugated organic light emitting compounds are highly emissive in their dilute solutions but become weakly luminescent when fabricated into devices.⁵ In the solid state, the molecules aggregate to form less emissive species, such as excimers, leading to a reduction in their luminescence efficiency.⁶ The conjugated materials are practically utilized in the solid state commonly as thin films. Many groups have attempted to diminish aggregate formation through elaborate chemical, physical, and engineering approaches. Swager and coworkers found 3.5 times higher quantum yield of fluorescence (Φ_F) for poly(*p*-phenyleneethynylene) film than that for its solution.^{7,8}

Donor–acceptor compounds having an aromatic fumaronitrile core have attracted significant attention as candidates in electroluminescent (EL) devices because they emit efficiently in the solid state.^{9–11} It is assumed that the enhanced emission in the solid state is due to the intramolecular planarization or a specific aggregation (H- or J-aggregation) in such compounds. Such aggregation-enhanced emissive materials are promising as emitters in highly efficient OLEDs.^{8,12} Motivated by their likely

application for use in EL devices, we chose to synthesize and study the optical properties of electron donor–acceptor compounds containing an aromatic fumaronitrile core showing higher Φ_F in the solid state than in solution. Fumaronitrile core-based compounds have already attracted significant attention as candidates in EL devices.^{9,10}

We describe here the synthesis and characterization of a novel series of aromatic fumaronitrile core-based electron donor–acceptor compounds 2,3-bis(4-(1*H*-indol-1-yl)phenyl)fumaronitrile (**1**), 2,3-bis(4-(2-phenyl-1*H*-indol-1-yl)phenyl)fumaronitrile (**2**), 2,3-bis(4-(diphenylamino)phenyl)fumaronitrile (**3**), 2,3-bis(4-(2-(4-(diphenylamino)phenyl)ethynyl)phenyl)fumaronitrile (**4**), and 2,3-bis(4-(2-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)ethynyl) phenyl)fumaronitrile (**5**) (Figure 1). We chose the carbazolyl, indolyl, and diphenylaminyl donors with and without a π system extending phenylethyynyl moiety to compare the optical effect of phenylethyynyl on the same donor and acceptor. Not only do these compounds exhibit intense luminescence in solution and in solid state but they also show excellent stability. In the pursuit of stable and efficient organic compounds for optoelectronic application, it is important to establish some correlation between the fluorescence quantum yield and the π structure of fluorophores containing donor and acceptor.¹³ So, we also tried to find such a direct correlation between the functional group, π conjugation length, and donor/acceptor strength versus Φ_F .

Because diphenylfumaronitrile was used as the core, concentration-related fluorescence quenching in the solid state should be greatly reduced because of the interaction of anti-parallel dipoles.¹⁴ Carbazole derivatives show high emission quantum yields in the solid state, and the compounds can easily be modified at the 3, 6, and 9*H* positions to tune the optical properties.^{15,16} Likewise, the diphenylamino group shows high

* Corresponding author. E-mail: tkinstl@bgsu.edu.

[†] Bowling Green State University.

[‡] Angstrom Technologies, Inc.

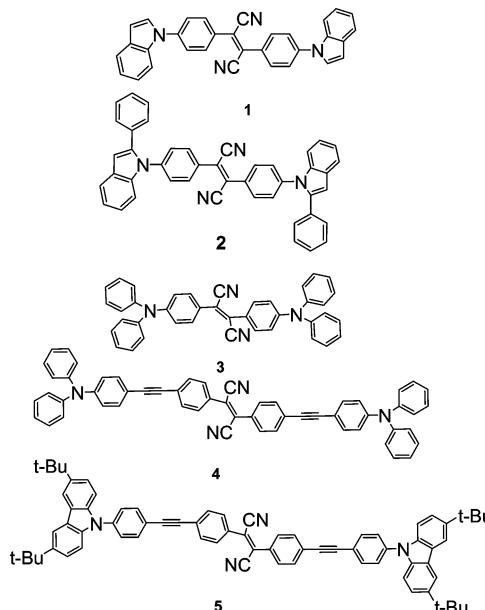


Figure 1. Structures of compounds **1–5**.

emission efficiency as a dopant in electroluminescence studies when attached to a cyano acceptor.¹⁷ Finally, indole-containing compounds have been used for the preparation of luminescent chelate compounds and can be used as effective red EL materials.¹⁸

Experimental Section

Materials. The synthesis of compounds **1–5** is described in the Supporting Information. Hexanes, toluene, dichloromethane (DCM), acetonitrile (ACN), and tetrahydrofuran (THF) are HPLC grade.

Measurements. Fluorescence quantum yields in solutions were measured following a general method using riboflavin (0.3 in ethanol) and anthracene (0.27 in ethanol) as the standard.^{19,20} Dilute solutions of these compounds in appropriate solvents were used for recording the fluorescence. Sample solutions of these compounds in quartz cuvettes were degassed for ~15 min. The degassed solutions had an absorbance of 0.06 to 0.09 at absorbance maxima. The fluorescence spectra of each of the sample solutions were recorded three to four times and an average value of integrated areas of fluorescence used for the calculation of Φ_F . The refractive indices of solvents at the sodium D line were used.

Values of Φ_F in the solid state were measured following a literature method.²¹ A DCM solution of sample was cast as a thin film on a spherical quartz plate and then allowed to dry. The plate was then inserted into an integrating sphere, and the required spectra were recorded. The samples were excited at their absorption maxima in DCM. It is well known that for compounds showing an overlap of the absorption and the emission spectra (a small Stokes shift), the use of an integrating sphere results in a substantial loss of emission because of absorption of the emitted light.

To measure the fluorescence lifetimes (τ_F), we put the samples in different solvents in quartz cuvettes. Fluorescence decay profiles of the argon-degassed samples were measured using a single photon-counting spectrofluorimeter. Decays were monitored at the corresponding emission maximum of the samples. In-built software allowed the fitting of the decay spectra ($\chi = 1$ to 1.5) and produced the fluorescence lifetimes.

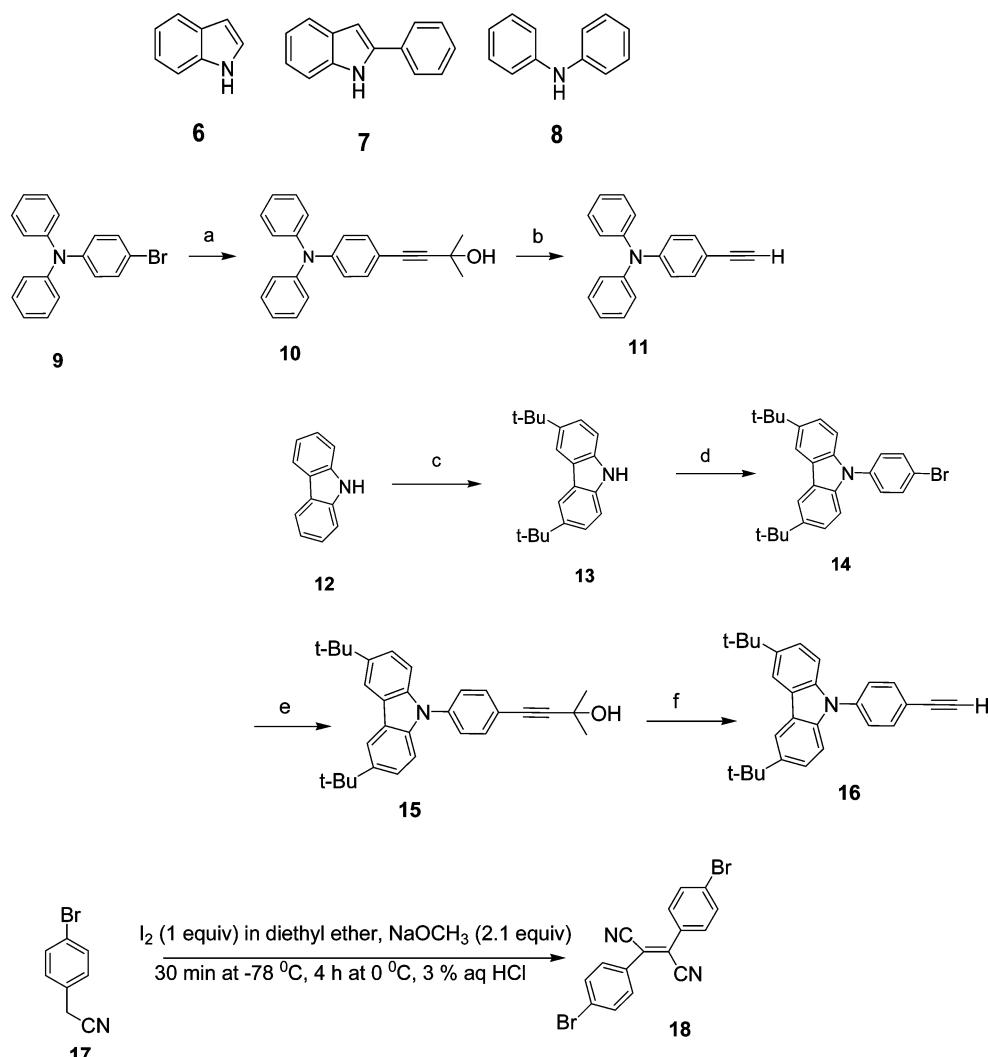
Results and Discussion

Compounds **6** (indole), **7** (2-phenylindole), and **8** (diphenylamine) were purchased from Sigma-Aldrich and used without purification. Compound **11** (*N*-(4-ethynylphenyl)-*N*-phenylbenzamine) was prepared from commercially available **9** (4-bromotriphenylamine) by Sonogashira coupling to 3-methyl butyn-3-ol, followed by reverse addition (Scheme 1). Similarly, compound **16** (3,6-ditert-butyl-9-(4-ethynyl-phenyl)-9*H*-carbazole) was synthesized from commercially available **12** (carbazole) in four steps involving alkylation, aromatic substitution, Sonogashira coupling, and deprotection (Scheme 1).¹⁵ Compound **18** (bis(4-bromophenyl)fumaronitrile) was synthesized from compound **17** (4-bromophenylacetonitrile) in one step (Scheme 1) following literature procedure.⁹ Compounds **6**, **7**, **8**, **11**, and **16** were then coupled to compound **18** under similar conditions to obtain compounds **1–5** (Scheme 2 and the Supporting Information).

All compounds **1–5** are solid and soluble in common organic solvents such as toluene, DCM, ACN, and THF. The visible color of the compounds **1–5** are yellow, deep orange, red, dark red, and orange, respectively. These materials are perfectly stable in the solid state and could be stored without the need for any special precautions.

Absorption and Emission Spectra in Solution. The optical properties of the synthesized D- π -A- π -D compounds were investigated by UV-vis absorption and photoluminescence (PL) spectroscopy using DCM solutions at room temperature. Representative examples of the absorption and emission spectra recorded in DCM are shown in Figures 2 and 3, respectively, and the data obtained are summarized in Table 1. The absorption maxima of these compounds range from 300 to 484 nm. The peak around 290–350 nm is due to absorption by carbazole or indole or biphenyl moiety. Similarly, peaks at 390–425 nm are absorption by the intramolecular charge transfer complex (ICT) formed by some compounds even in the ground state.²² The presence of a strong electron donating (ED) group, an electron withdrawing (EW) group, or both in **3** and **4** induces the formation of strong ICT. Compound **5** forms the twisted intramolecular charge transfer state (TICT) in the presence of polar solvents.^{23,24} So, a weak band in the region of 425 nm is due to the absorption by TICT for **5**. Interestingly, the absorption of compound **4** is blue-shifted from that of compound **3** even though the former has two π -extending phenylethyne moieties. This indicates that the ethynyl groups allow free rotation in the molecule to conformations in which electrons cannot be delocalized easily from the nitrogen atom of the donors to the acceptors vide infra.

When excited at their A_{\max} , dilute solutions of **1–5** in DCM showed violet to red emission (Figure 3). Despite the similar linker length and acceptor, the emission maxima vary from 360 to 614 nm. This indicates that the emission is mostly dependent on the linkers and donors of these compounds vide infra. Compound **1** has an indole moiety as ED and has the most red-shifted emission of all. It forms strong ICT upon excitation. So, in this compound, an excited ICT state is responsible for the emission in the red region with large Stokes shift. Compound **2** has a weaker phenyl-substituted indole as an ED group because nitrogen lone pair of electrons is delocalized by the phenyl group. Additionally, the presence of the bulky phenyl group causes planarity distortion of the phenylindole with the rest of the molecule, thereby lowering the conjugation. The formation of the ICT excited state is thus impeded. On keeping EA and linker constant, Φ_F in solution increases with the stronger ED (Table 2). But in the solid state, Φ_F follows a

SCHEME 1: Synthesis of Compounds 11, 16, and 18^a

^a Reagents and conditions (a) 2-Methyl-3-butyn-2-ol, CuI, Pd(PPh₃)₂Cl₂; (b) KOH; (c) t-BuCl, ZnCl₂; (d) 1,4-dibromobenzene, K₂CO₃, Cu, 18-crown-6; (e) 2-methyl-3-butyn-2-ol, CuI, Pd(PPh₃)₂Cl₂; (f) KOH.

SCHEME 2: Synthesis of Compounds 1–5

	Products	Yield
18 + Pd(OAc) ₂ , P(t-Bu) ₃ , Cs ₂ CO ₃ (4 equi.), reflux	6 → 1 7 → 2 8 → 3 11 → 4 16 → 5	84% 57% 76% 72% 60%

reverse order. A similar trend is observed in **3**, which has a stronger ED than **1** or **2**. In compounds **4** and **5**, which have same EA and linker, Φ_F is higher for the compound with weaker ED both in solution and in solid state. Red-shifted emission was expected for compounds **4** and **5** as compared with others because of the presence of the extra phenylacetylene moiety in the linker. However, we observed a blue-shifted emission for them. The increased length of linkers distorts the planar structure, and hence conjugation is impeded. Similar behavior of linkers has been reported in similar compounds.²⁵ Moreover, their strange emissive behavior could also be due to the different kind of hybridization of the bond. The triple bond is sp hybridized, which is of linear configuration and substituents can rotate freely in solution because of small energy barrier, thus leading to a more twisted structure for **4** and **5** than similar double-bonded compounds.²⁶

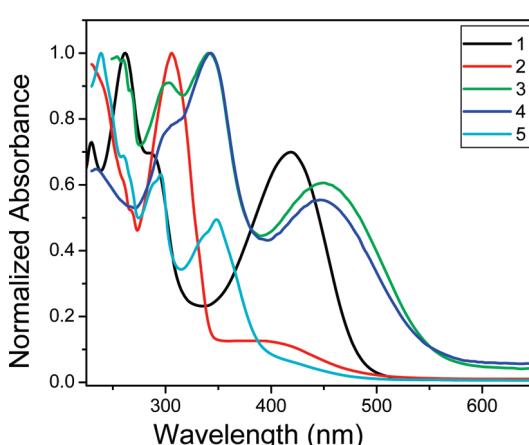


Figure 2. Normalized absorption spectra of **1–5** in DCM.

The magnitudes of the Stokes shifts indicate large (vibrational, electronic, geometric) differences between the excited state reached immediately after absorption and the excited state from which the emission starts. Charge-transfer processes should be fairly effective because of the presence of a π-donor and a π-acceptor group on these compounds.²⁷ This effect also leads to a very low degree of self-absorption of emitted light.

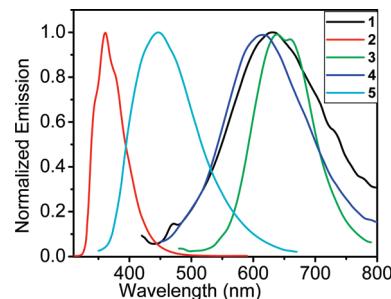


Figure 3. Normalized emission spectra of **1–5** in DCM. (Compounds were excited at the corresponding A_{\max} . Compounds **1–5** were excited at 418, 306, 450, 440, and 347 nm, respectively.)

Therefore, these compounds are predicted to perform well in organic light-emitting diodes and as laser dyes.

Solvatochromism: Optical Switching With Solvents. In an effort to gain further insight into the photophysical processes in these compounds, we investigated their absorption and emission behaviors in different solvents. The results of these investigations are summarized in Table 1. The absorption spectra are nearly independent of solvent polarity except for a slight insignificant shift that indicates a negligible intramolecular interaction between donor and acceptor groups in the ground state. In contrast, the emission spectra exhibit distinct solvent dependence. Broad structureless emission and larger Stokes shifts were observed for compounds **1–3** on increasing the solvent polarity along with a successive decrease in the fluorescence intensity. Compounds **4** and **5** showed the reverse behavior. This kind of behavior has been explained fully for various chromophores containing donor–acceptor units.¹⁴ In general, the absorption and emission maxima are gradually red-shifted when the compounds are dissolved in the nonpolar hexanes to polar ACN. Surprisingly, both absorption and emission are either the same or blue-shifted in ACN with respect to medium polar solvents like toluene or DCM for compounds **4** and **5** vide infra.

Compound **2** shows a much smaller solvatochromic effect for absorption and emission. (See the Supporting Information.)

TABLE 1: Absorption Maximum (A_{\max}), Emission Maximum (λ_{\max}), Molar Absorptivity (ϵ), Stokes Shifts, and Solid-State Quantum Yields of **1–5 Recorded in Four Different Solvents^a**

compound	solvent	absorption (A_{\max}) (nm)	molar ext. coefficient ϵ ($\text{dm}^3 \text{cm}^{-1} \text{mol}^{-1}$)	emission (λ_{\max}) (nm)	Stokes shifts (nm)	solid state Φ_F
1	hexanes	391	19 147	516	125	0.80
	toluene	414		550	136	
	DCM	418		631	213	
	ACN	400		552	152	
2	hexanes	304	38 933	351	47	0.49
	toluene	306		360	54	
	DCM	306		360	54	
	ACN	305		360	54	
3	hexanes	456	25 177	560	104	0.38
	toluene	479		603	122	
	DCM	450		637	177	
	ACN	480		700	220	
4	hexanes	440	47 178	566	126	0.55
	toluene	450		630	180	
	DCM	440		614	174	
	ACN	420		528	108	
5	hexanes	346	16 496	477	131	0.64
	toluene	346		513	177	
	DCM	347		446	99	
	ACN	345		446	101	

^a Excitation is at A_{\max} for each compound in corresponding solutions. Solid-state Φ_F values were measured by using an integrating sphere (errors within 15% range).

TABLE 2: Photophysical Data of π -Conjugated Compounds **1–5 in Different Solvents^a**

compd	solvents	Φ_F	τ_F (ns)	K_F (s^{-1})	K_{nr} (s^{-1})	A_{π} (\AA)
1	hexanes	0.15	0.88	1.70×10^8	9.65×10^8	-1.73
	toluene	0.43	6.25	6.88×10^7	9.12×10^7	-0.28
	DCM	0.1	1.34	7.46×10^7	6.71×10^8	-2.20
	ACN	0.02	3.51	5.69×10^6	4.99×10^8	-2.43
2	hexanes	0.12	1.63	7.36×10^7	5.39×10^8	-1.99
	toluene	0.10	0.01	1.0×10^{10}	9.10×10^{10}	-2.20
	DCM	0.01	1.01	9.90×10^6	9.80×10^8	-4.59
	ACN	<0.01	1.42	7.042×10^6	6.97×10^8	-4.74
3	hexanes	0.16	1.00	1.6×10^8	8.4×10^8	-1.65
	toluene	0.10	1.42	7.04×10^{10}	7.0×10^{11}	-2.29
	DCM	0.01	0.35	2.85×10^7	2.82×10^9	-4.59
	ACN	<0.01	0.07	1.42×10^8	8.00×10^{10}	-6.33
4	hexanes	0.49	2.24	2.18×10^8	2.28×10^8	-0.20
	toluene	0.80	3.20	2.50×10^8	6.12×10^7	1.40
	DCM	0.74	7.65	9.64×10^7	3.36×10^7	1.05
	ACN	0.01	2.09	4.78×10^8	4.74×10^8	-4.59
5	hexanes	0.43	2.33	1.84×10^8	2.45×10^8	-0.28
	toluene	0.77	3.42	2.25×10^8	6.7×10^7	1.21
	DCM	0.12	3.40	3.5×10^7	2.5×10^8	-1.96
	ACN	0.08	3.42	2.33×10^7	2.68×10^8	-2.44

^a Compounds were excited at the corresponding A_{\max} representing the $\pi-\pi^*$ transition for τ_F and Φ_F . The τ_F and Φ_F were measured from argon-saturated solutions, and decay was monitored at the corresponding λ_{\max} . The Φ_F values for **1**, **3**, and **4** are relative to that of riboflavin (0.30 in ethanol). The Φ_F values for **2** and **5** are relative to that of anthracene (0.27 in ethanol).

Also, the Stokes shift in all solvents for this compound is much smaller (50 nm) in comparison with other compounds for the reason described above. The compounds **1** and **3** show positive solvatochromism. The cases of compounds **4** and **5** are different because a systematic solvatochromic effect is not observed among solvents like in hexanes, toluene, and DCM (Figures 5 and 6 and the Supporting Information). Compound **4** shows positive solvatochromic effect from hexanes to toluene and negative solvatochromism from toluene to ACN (Figures 5 and 6). In toluene a red-shifted emission is observed, which is probably due to the stabilization of excited state by aromatic electrons of toluene. The excitation spectra obtained by monitoring the emission at the emission maximum of **4** (Supporting

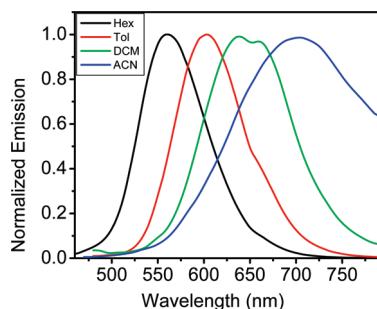


Figure 4. Normalized absorption and emission spectra of **3** in hexanes, toluene, DCM, and ACN. (Emission spectra are recorded at the respective A_{\max} of the samples. They are excited in hexanes at 456 nm, toluene at 479 nm, DCM at 450 nm, and ACN at 480 nm).

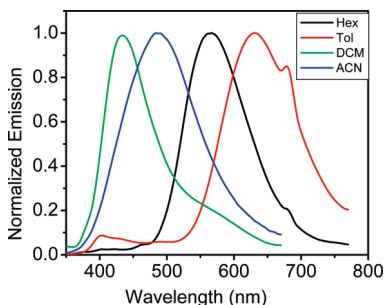


Figure 5. Emission spectra of **4** in hexanes, toluene, DCM, and ACN excited at 340 nm.

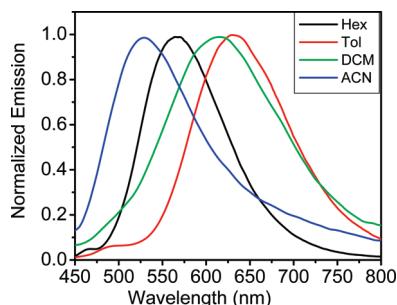


Figure 6. Emission spectra of **4** in hexanes, toluene, DCM, and ACN excited at 440 nm.

Information) shows that the emission is due to radiative deactivation of both local excited (LE) and ICT excited state in nonpolar solvents (hexanes and toluene), but in polar solvents such as ACN and DCM, the emission occurs predominantly from the LE state. In its ground state, **4** forms ICT state in polar solvents. On excitation, a red-shifted emission is observed in nonpolar solvents, but in polar solvents, a blue shift emission, a property called negative solvatochromism, is observed.²⁸ This suggests that the dipole moment of **4** decreases on excitation, and thus the less polar ICT excited state becomes more stable in nonpolar solvents and less stable in polar solvents. The same holds true for **5**, where TICT forms instead of ICT (Supporting Information). The nonplanar alignment of the carbazolyl moiety with 9H-substituted phenyl group is responsible for the formation of TICT.²⁹ Therefore, this abnormal solvatochromic behavior of compounds **4** and **5** is probably due to their different donors and to the formation of TICT or ICT in their singlet states.^{23,24}

Compound **4** shows interesting emission properties. When a DCM solution is excited at 340 nm, emission in the blue region was observed, and on exciting the same solution at 440 nm, we observed emission in the red region only (Figures 5 and 6). DCM is less polar than ACN, so upon excitation, very little

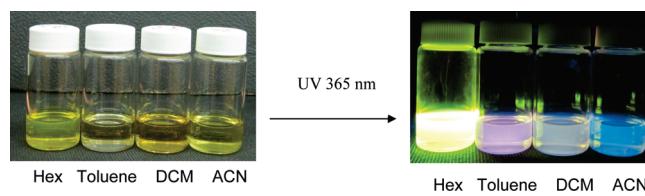


Figure 7. Solutions of compound **4** in different solvents (A) hexanes, (B) toluene, (C) DCM, and (D) ACN. The left side of the Figure is under day light, and the right side is under UV 365 nm.

formation of ICT excited state occurs. When exciting DCM solution of **4** at 340 nm, we observed emission mainly on the blue region with a shoulder around 575 nm. The emission in the blue region is due to the LE state, and that around 575 nm is from the ICT excited state. When exciting the same solution at 440 nm, we observed emission primarily in the red region, which is emission from the ICT state only. The same results were not observed in other solvents because only LE was formed in ACN and predominantly ICT was formed in toluene and hexanes. Changes in the emission color of **4** in different solvents on excitation at 365 nm is illustrated in Figure 7.

Significantly high Stokes shifts of 213 nm for **1**, 220 nm for **3**, and 180 nm for compound **4** are observed. The absorption and emission spectra of compound **3** show 104 nm Stokes shifts in hexanes, 122 nm in toluene, 177 nm in DCM, and 220 nm in ACN (Figure 4).

Correlation between Quantum Yield and Magnitude A_{π} of the π Conjugation Length. We tried to establish correlations among Φ_F , donor strength, and length of linker in these compounds. Because no simple correlations could be observed, a possible correlation between the Φ_F and the magnitude (A_{π}) of the π conjugation length in the excited singlet state has been discussed. We derive A_{π} from the radiative (rate constant: k_r) and radiationless process (rate constant: k_{nr}).¹³ The obtained k_r and k_{nr} values are shown in Table 2. On absorption of light, unshared electrons on the nitrogen atom of the donor group promote to the acceptor. Because the acceptor and donor are strong, the excited state is a charge transfer state with partial positive charge on the N atom of donor and partial negative charge on nitrile moiety. The k_r is the rate constant for the return process of an n -electron from the EA group promoted to the excited singlet (S_1) state to the ED in the ground (S_0) state of a D- π -A- π -D system molecule accompanying fluorescence emission.

Similarly, k_{nr} is the rate constant for the radiationless process due to internal conversion and intersystem crossing. The magnitude of conjugation length may be defined as the distance between dipoles arising from S_0 to S_1 transition (light absorption). Thus, k_{nr} is considered to be the rate constant of radiationless decay due to the electron transfer (ET) from the negative charge to the positive charge. As shown in Table 2, the k_r values increase and the k_{nr} values decrease with π conjugation length of the D- π -A- π -D system, suggesting that the k_r/k_{nr} value might be related to π extension in the S_1 state of the D- π -A- π -D molecule. The magnitude of conjugation length (A_{π}) is derived from k_r and k_{nr} . On plotting Φ_F against A_{π} (Figure 8), a line with a positive slope is obtained. From this graph, we can see that increasing the strength of the ED, the length of the linker, or both also increases the Φ_F .

Fluorescence Switching With Concentration: Concentration Quenching. A significant fluorescence quenching of compounds **1–5** has been observed in THF at higher concentrations (Supporting Information). For example, the fluorescence intensity almost triples when the concentration of compound **5**

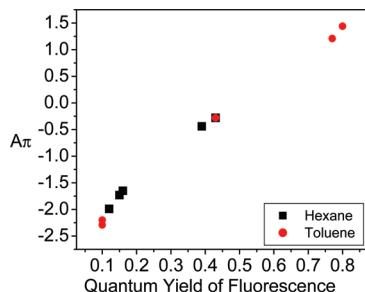


Figure 8. Plot of quantum yield versus π conjugation length in hexanes and toluene for compounds **1–5**.

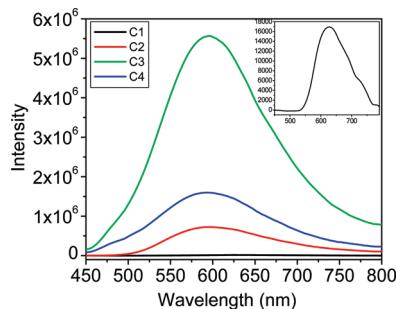


Figure 9. Emission spectra of **4** recorded in THF at different concentrations: (C1) 7.3×10^{-4} M, (C2) 7.3×10^{-5} M, (C3) 7.3×10^{-6} M, and (C4) 7.3×10^{-7} M. (Inset: the enlarged spectrum of **4** recorded at 7.3×10^{-4} M).

is increased from 4.5×10^{-7} to 4.5×10^{-6} M, but it decreases by almost the same amount when the concentration is increased to 4.5×10^{-5} M and is almost completely quenched at a concentration at 4.5×10^{-3} M. Although the fluorescence intensity is significantly decreased at a higher concentration, the λ_{max} remains unchanged. A similar type of behavior is shown by all other compounds (Supporting Information). Although no considerable quenching behavior of fluorescence was observed in compounds **4**, **3**, and **2**, in compound **1**, quenching was observed even at 3.1×10^{-5} M concentrations. However, in these cases, the λ_{max} values were found to be slightly blue-shifted. This might be due to the aggregation at higher concentration. In compound **5**, there is no shift on emission with concentration change, which is probably because the tertiary butyl groups prevent aggregation.

In Figure 9, the emission spectra of **4** in THF at different concentrations are plotted. At higher concentration, the emission appears mainly in the 500–600 nm region and on dilution, the emission appears mainly in the region of 400–500 nm with an increase in intensity. We did not observe such significant shift on emission with the other compounds, although there is concentration quenching in all of them. To investigate this interesting property of **4** further, we measured emission spectra in DCM and found a similar but more significant effect (Supporting Information).

Excitation Energy Dependence Fluorescence; Edge Excitation Red Shift (EERS). Contrary to Kasha's rule, fluorescence of **4** depends on the excitation energy. Compound **4** in DCM was excited with different energies (340, 400, and 440 nm) at the same concentration. The emission spectra obtained are plotted in Figure 10A,B,C. The switching of emission with excitation energy was observed. On excitation at 340 nm, emission was found mainly on the blue region with lower intensity in the red region. On excitation of same solution at 400 nm, a perfect white emission is observed, and on excitation of the same solution with 440 nm, we observed the emission

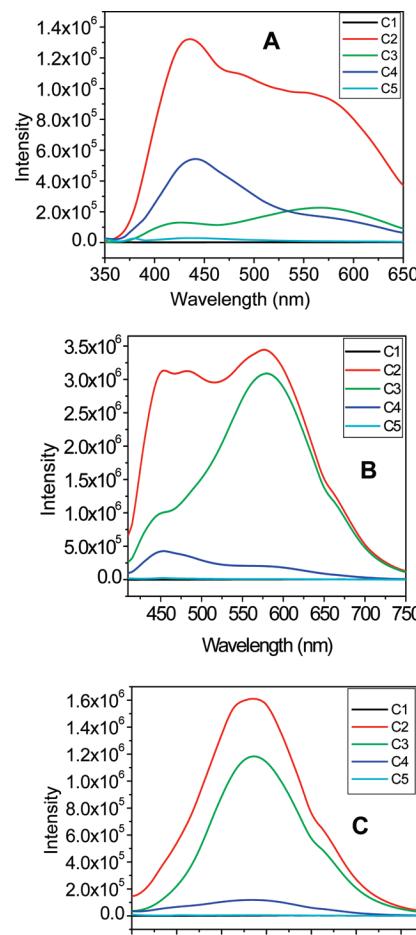


Figure 10. Emission spectra of compound **4** in DCM at different concentrations. (A) excitation wavelength 340 nm, (B) excitation wavelength = 400 nm, and (C) excitation wavelength 440 nm. C1 = 5.55×10^{-4} M, C2 = 2.22×10^{-4} M, C3 = 6.93×10^{-5} M, C4 = 2.22×10^{-5} M, and C5 = 2.22×10^{-6} M concentration.

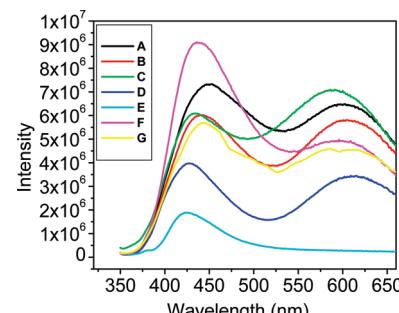


Figure 11. Emission spectra of DCM solutions of compound **4** in the presence of TFA and Et₃N at various pH. (A) DCM, (B) TFA (pH 4), (C) TFA (pH 3), (D) TFA (pH 2), (E) TFA (pH 1), (F) Et₃N (pH 9), and (G) Et₃N during neutralization of D (pH 6).

mainly in the red region. This effect has been referred to as EERS or red-edge excitation shift.³⁰ This phenomenon can be described by considering the emission contribution from additional excited species. In a case when the reorientation relaxation time is larger than the fluorescence time, the total fluorescence emission spectrum is a composite of fluorescence emission from differently solvated species governed by Franck–Condon excited-state distribution (F-CESD) that is a function of excitation energy.^{30–32} For a polar compound in polar solvent, the energy required to excite the solvated species is a



Figure 12. Change in color of DCM solutions of compound **4** in the presence of TFA and Et₃N at various pH. (A) DCM, (B) TFA (pH 4), (C) TFA (pH 3), (D) TFA (pH 2), (E) TFA (pH 1), (F) Et₃N (pH 9), (G) Et₃N during neutralization of D (pH 6), and (H) Et₃N during the neutralization of E (pH 5).

function of solvent orientation. If the excitation energy is smaller, then only limited configurations of the ground state may be excited. The excitation with particular energy will excite only the particular fraction of total fluorophore population, which is surrounded by solvent dipoles.

Fluorescence Switching With a Change in pH. The nitrogen atoms of donors are basic centers that can be protonated. Therefore, the effect of protonation on the optical properties of DCM solutions of **1–5** was also studied. DCM solutions of some compounds underwent a significant color change in the presence of trifluoroacetic acid (TFA). This color change was found to be reversible. Representative spectra for the change in optical properties with a change in pH for compound **4** are illustrated in Figure 11, and the color change under UV light at 365 nm is given in Figure 12.

There is not a remarkable change in absorption spectra on addition of TFA on DCM solution of **4**. However, the emission completely switches from the white region to the blue region upon addition of TFA. In DCM, the emission is a consequence of radiative deactivation from both excited ICT and LE state at this particular concentration. The ICT state is responsible for emission in the red region, and the LE state is responsible for emission in the blue region. When TFA is added, the ICT state becomes less prominent as H⁺ from TFA consumes the lone pair of electrons from N of the donor, forming N⁺, so no charge-separated ICT is possible. The protonated species emits in blue region. Again, on addition of triethyl amine (Et₃N), the proton is removed by it, ICT becomes more prominent, and emission by both the LE and ICT states occurs in the blue and orange-red region. This property of **4** could find the application as pH sensors. Similar but less significant effects have been observed for compounds **1** and **5**. Compounds **2** and **3** did not show a similar change in optical properties on the addition of the same amounts of TFA (Supporting Information).

Conclusions

A class of aromatic fumaronitrile core-based D- π -A- π -D compounds is synthesized and fully characterized, and their optical properties are studied. A direct correlation between the functional group, π conjugation length, and donor/acceptor strength versus Φ_F has been studied. Fluorescence switching with concentration, excitation energy, and solvent polarity is illustrated. Potential application of these compounds as a pH

sensor is optically assessed with a change in emission color with a change in pH. Their optical properties in solution and in the solid state indicate that these compounds could find application in optoelectronic device fabrication.

Acknowledgment. This present work has been partially supported by grant NSF-EXP 40000/10380080. We thank the donors of these funds. We thank Dr. Sujewa S. Palayangoda for suggestions concerning synthesis and Dr. Douglas C. Neckers and Puran De for instruments and assistance.

Supporting Information Available: Experimental details and ¹H and ¹³C NMR spectra of compounds **1–5**, **10**, and **11**, UV-visible spectra in different solvents, excitation spectra, emission spectra in THF at different concentrations, and absorption and emission spectra during the addition of TFA and Et₃N in DCM maintaining different pH of compounds **1–5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) Sheats, J. R.; Barbara, P. F. *Acc. Chem. Res.* **1999**, *32*, 191.
- (2) Wong, M. S.; Li, Z. H.; Tao, Y.; D'Iorio, M. *Chem. Mater.* **2003**, *15*, 1198.
- (3) Morin, J. F.; Drolet, N.; Tao, Y.; Leclerc, M. *Chem. Mater.* **2004**, *16*, 4619.
- (4) Leclerc, N.; Sanaur, S.; Galmiche, L.; Mathevet, F.; Attias, A. J.; Fave, J. L.; Roussel, J.; Hapiot, P.; Lemaitre, N.; Geffroy, B. *Chem. Mater.* **2005**, *17*, 502.
- (5) Friend, R. H.; Gymer, R. W.; Holmes, A. B.; Burroughes, J. H.; Marks, R. N.; Taliani, C.; Bradley, D. D. C.; Dos Santos, D. A.; Bredas, J. L.; Lögdlund, M.; Salaneck, W. R. *Nature* **1999**, *397*, 121.
- (6) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765.
- (7) Deans, R.; Kim, J.; Machacek, M. R.; Swager, T. M. *J. Am. Chem. Soc.* **2000**, *122*, 8565.
- (8) Chen, J.; Xu, B.; Ouyang, X.; Tang, B. Z.; Cao, Y. *J. Phys. Chem. A* **2004**, *108*, 7522.
- (9) Yeh, H.-C.; Yeh, S.-J.; Chen, C.-T. *Chem. Commun.* **2003**, 2632.
- (10) Chen, C.-T. *Chem. Mater.* **2004**, *16*, 4389.
- (11) Kim, D. U.; Paik, S. H.; Kim, S.-H.; Tsutsui, T. *Synth. Met.* **2001**, *123*, 43.
- (12) Chen, H. Y.; Lam, J. W. Y.; Luo, J. D.; Ho, Y. L.; Tang, B. Z.; Zhu, D. B.; Wong, M.; Kwok, H. S. *Appl. Phys. Lett.* **2002**, *81*, 574.
- (13) Yamaguchi, Y.; Matsubara, Y.; Ochi, T.; Wakamiya, T.; Yoshida, Z. *J. Am. Chem. Soc.* **2008**, *130*, 13867.
- (14) Palayangoda, S. S.; Cai, X.; Adhikari, R. M.; Neckers, D. C. *Org. Lett.* **2008**, *10*, 281.
- (15) Liu, Y.; Nishiura, M.; Wang, Y.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 5592.

- (16) Yeh, H.-C.; Wu, W.-C.; Wen, Y.-S.; Dai, D.-C.; Wang, J.-K.; Chen, C.-T. *J. Org. Chem.* **2004**, *69*, 6455.
- (17) Adachi, C.; Tokito, S.; Tsutsui, T.; Saito, S. *Jpn. J. Appl. Phys.* **1988**, *27*, 713.
- (18) Li, Q.; Zou, J.; Chen, J.; Liu, Z.; Qin, J.; Li, Z.; Cao, Y. *J. Phys. Chem. B* **2009**, *113*, 5816.
- (19) Scaiano, J. C. *Handbook of Organic Photochemistry*; CRC Press: Boca Raton, FL, 1989; Vol. I.
- (20) Melhuish, W. H. *J. Phys. Chem.* **1961**, *65*, 229.
- (21) de Mello, J. C.; Wittmann, H. F.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.
- (22) Fu, H.; Loo, B. H.; Xiao, D.; Xie, R.; Ji, X.; Yao, J.; Zhang, B.; Zhang, L. *Angew. Chem., Int. Ed.* **2002**, *41*, 962.
- (23) Yu, M.-X.; Chang, L.-C.; Lin, C.-H.; Duan, J.-P.; Wu, F.-I.; Chen, I.-C.; Cheng, C.-H. *Adv. Funct. Mater.* **2007**, *17*, 369.
- (24) Nikolaev, A. E.; Myszkiewicz, G.; Berden, G.; Meerts, W. L.; Pfanstiel, J. F.; Pratt, D. W. *J. Chem. Phys.* **2005**, *122*, 84309.
- (25) Adhikari, R. M.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2009**, *74*, 3341.
- (26) Shao, H.; Chen, X.; Wang, Z.; Lu, P. *J. Lumin.* **2007**, *127*, 349.
- (27) Achelle, S.; Nouira, I.; Pfaffinger, B.; Ramondenc, Y.; Ple, N.; Lopez, J. R. *J. Org. Chem.* **2009**, *74*, 3711.
- (28) Allen, D. W.; Li, X. *J. Chem. Soc., Perkin Trans. 2* **1997**, 1099.
- (29) Lakowicz, J. R. *Principles of Fluorescence Spectroscopy*; Springer: New York, 2006.
- (30) Itoh, K.-i.; Azumi, T. *J. Chem. Phys.* **1975**, *62*, 3431.
- (31) Fletcher, N. *J. Phys. Chem.* **1968**, *72*, 2742.
- (32) Khalil, O. S.; Seliskar, C. J.; McGlynn, S. P. *J. Chem. Phys.* **1973**, *58*, 1607.

JP9115589