

Synthesis and Characterization of Conjugated Pyridine-(*N*-diphenylamino) Acrylonitrile Derivatives: Photophysical Properties

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Received: December 21, 2011

Accepted: January 5, 2012

Published: April 1, 2012

doi:10.5539/jmsr.v1n2p181

URL: <http://dx.doi.org/10.5539/jmsr.v1n2p181>

The authors would like to acknowledge VIEP-BUAP for financial support and M. C. Vladimir Carranza for assistance with the EI mass spectrometry.

Abstract

We have synthesized four novel highly conjugated and fluorescent compounds, 2-(phenyl)-3-(4-diphenylaminophenyl) acrylonitrile (**I**), 2-(2'-pyridyl)-3-(4-diphenylamino-phenyl) acrylonitrile (**II**), 2-(3'-pyridyl)-3-(4-diphenylaminophenyl) acrylonitrile (**III**) and 2-(4'-pyridyl)-3-(4-diphenylaminophenyl) acrylonitrile (**IV**) by the Knoevenagel condensation. In solution, the UV-vis spectra showed two maxima for each compound, one at ~296-300 nm and the other at ~403-428 nm. The compounds showed fluorescence emission in CHCl₃ solution as well as in the state solid. The fluorescence quantum yield for the compounds in powder form showed values ranging from 0.07-0.11. Structures were confirmed with IR, MS, and NMR spectroscopy. Molar coefficient absorption, absorbance, fluorescence emission spectra and fluorescence quantum yield (Φ_f) were compared to evaluate the effects of the diphenylamino-substituents and the position of nitrogen on the electronic properties of phenylpyridylacrylonitriles compounds.

Keywords: Conjugated compounds, Cyano derivatives, Optical properties, Fluorescent compounds, Powder fluorescence quantum yield, *N*-diphenylphenyl derivatives

1. Introduction

Low molecular weight and oligomeric organic compounds with optical or electrical properties have been widely used as dyes in organic electronic devices, including organic light emitting diodes (OLEDs), solar cells, organic

semiconductor lasers, etc. (Gondek, *et al.*, 2008; Patra, *et al.*, 2002; Yu, *et al.*, 1995; Shaheen, *et al.*, 2001; Tessler, Denton & Friend, 1996; Samuel & Turnbull, 2007). Typically, these dyes have a donor-acceptor structure that controls their photophysical properties (Patra, *et al.*, 2002; Zhou, *et al.*, 2008; Adès, *et al.*, 2000). Aromatic amines are among the most important derivatives as materials for hole transport in nanodevices (Pai, Yanus & Stolka, 1984; Naito & Miura, 1993; Okutsu, *et al.*, 1997; Thelakkat, *et al.*, 1999; Yakushchenko, *et al.*, 1999; Strzelec, *et al.*, 2001; Jiang, *et al.*, 2002; Loy, Koene & Thompson, 2002; Xin, *et al.*, 2002; Chen, *et al.*, 2003; Satoh, *et al.*, 2003; Salbeck, 1996; Strohriegl & Grazulevicius, 2002), and have been used in a wide range of structures, either as separate layers (Salbeck, 1996; Friend, 1999) or covalently attached to light emitting layers (Loy, Koene & Thompson, 2002; Redecker, *et al.*, 1999; Miteva, *et al.*, 2001; Ego, *et al.*, 2002). In addition, aromatic amines have been tested as blue emitters in organic LEDs (Tong, *et al.*, 2004) and as components of electroluminescent bipolar devices (Justin Thomas, *et al.*, 2002), while arylamines have been used in applications such as antioxidants (Tong, *et al.*, 2001; Esteves, *et al.*, 2001). Triphenylamines, with their characteristic propeller starburst molecular structure, have been widely used in opto- and electroactive materials due to their good electro-donating and transporting capabilities (Ning & Tian, 2009; Chen, *et al.*, 2009; Zhang, *et al.*, 2009). On the other hand, cyano-substituted compounds, with high electron affinities, show good optical and electrical properties. Molecules with the electron-withdrawing cyano group on the central phenylene ring are strongly fluorescent (Pond, *et al.*, 2002). In particular, some cyano-substituted compounds have been reported to show unique enhanced emission rather than fluorescence quenching in the solid state (Wang, *et al.*, 2011).

Also, poly (phenylenevinylene) compounds (low molecular weight and polymers) are of great interest because they belong to the family of organic materials that possess strong π -electron conjugation; i.e., they extend electron delocalization. Particularly, the synthesis, structure and photophysical behavior of the *trans* isomers of 4-(*N*-phenylamino) stilbene have been reported by Yang *et al.* (2002). A comparison of their results with data for 4-aminostilbene and 4-*N,N*-dimethylaminostilbene indicated that introduction of *N*-phenyl substituents to 4-aminostilbenes led to a more planar ground-state geometry about the nitrogen atom, a red shift of the absorption and fluorescence spectra, and a less distorted structure with a larger charge-transfer character for the fluorescent excited state. Consequently, the *N*-phenyl derivatives showed low photoisomerization quantum yields and high fluorescence quantum yields at room temperature. These investigators described the *N*-phenyl substituted effect as an “amino conjugation effect.”

In addition, the high electron affinity of pyridine makes it an important electron-acceptor group. Dailey *et al.* described the poly(2,5-pyridinediyl) (PPY) moiety as an efficient electron transport layer in bilayer polymeric LEDs. The OLEDs with a PPY layer exhibited external quantum efficiency 60 times greater than that of similar devices without a PPY layer (Dailey, *et al.*, 1998). Epstein *et al.* described poly (*p*-pyridine)- and poly(*p*-pyridylvinylene)-based polymers as emissive layers in light emitting devices (Epstein, *et al.*, 1996).

Finally, the route of synthesis is an important factor to obtain the desired dye structures for a specific application. Some dyes with donor-acceptor structures have been formed in a Heck coupling reaction with palladium-catalysis (Patra, *et al.*, 2002), while others have been formed in the Knoevenagel condensation (Knoevenagel, 1896). Our group previously has synthesized different conjugated compounds with the Knoevenagel condensation, without any catalyst and under solvent-free conditions (Percino, *et al.*, 2007, 2008, 2006, 2010). This method was successfully used to synthesize α , β -diphenylacrylonitrile, α -(2-pyridyl)- β -(phenyl) acrylonitrile, α -(3-pyridyl)- β -(phenyl)-acrylonitrile, α -(phenyl- β -(2-pyridyl)acrylonitrile, 1,4-bis[1-(2-cyano-2-phenyl)vinyl] -benzene, 1,4-bis[1-(2-cyano-2'-pyridyl)vinyl]benzene and 1,4-bis[1-(2-cyano-3-pyridyl)-vinyl]benzene (Percino, *et al.*, 2010). A series of *E*-isomers of 3-(4-substituted phenyl)-2-arylacrylonitriles (aryl, phenyl or pyridyl) were also prepared. Compounds with chloro-, fluoro-, or dimethylamino substituted aryls and with cyano groups attached to the double bond of acrylonitrile have been synthesized (Percino, *et al.*, 2011). Recently, three novel acrylonitrile derivatives modified with the *N*-ethyl-3-carbazolecarboxaldehyde group to form a D- π -A structure have been reported (Pérez-Gutiérrez, 2011). These compounds were 2-(2'-pyridyl)-3-(*N*-ethyl-(3'-carbazolyl))acrylonitrile, (2-(3'-pyridyl)-3-(*N*-ethyl-(3'-carbazolyl))acrylonitrile, and 2-(4-pyridyl)-3-(*N*-ethyl-(3'-carbazolyl))-acrylonitrile. These three compounds showed UV-vis absorption wavelength maxima in solution at 380, 378, and 396 nm, respectively, whereas in the solid state their absorption maxima (λ_{max}) were observed at 398, 390, and 442 nm, respectively. The fluorescence emission maxima for these compounds were observed at 540, 540 and 604 nm, respectively.

The aim of the present study was to synthesize fluorescent compounds that exhibit a strong emission which could be correlated to the structural properties of the molecules. We have prepared a series of *N,N*-diphenylaminophenylpyridineacrylonitrile compounds that exhibited fluorescence in the solid state as well as in solution. We have attempted to relate the intensities and positions of the emission bands as well as their quantum

yields to the nature of the substituent on the structure, i. e., the -CN substituent on the vinylene moiety of the compound or the position of the N atom on the pyridine ring. However, we also considered that these interesting properties could be caused by the presence of the -N(Ph)₂ group which confers to the structures a high degree of conjugation. Each compound (Scheme 1) reported in the present work was characterized by IR, ¹H-NMR, MS, UV-Vis, fluorescence spectroscopy and fluorescence quantum yield (Φ_f).

2. Experimental Section

2.1 Materials and Instrumentation

Phenylacetonitrile, 2-pyridylacetonitrile, 3-pyridylacetonitrile, hydrochloride 4-pyridylacetonitrile and *p*-diphenylaminophenylcarboxaldehyde were acquired from Aldrich Chemical Co. and were purified before use. Melting points were measured with an SEV (0-300 °C) apparatus and were reported as uncorrected values. IR spectra of the products were recorded on a Vertex (model 70, Bruker Optics, Germany) 750 FT-IR spectrophotometer by attenuated total reflectance (ATR). ¹H NMR and ¹³C NMR spectra were obtained in CDCl₃ and DMSO-*d*₆ on a Varian 400 MHz NMR spectrometer (Varian NMR, Walnut Creek, CA). The electron ionization (EI) spectra were acquired on a Jeol MStation 700-D mass spectrometer (Jeol USA, Peabody, MA). The UV-vis and fluorescence spectra were acquired with a Spectrometer SD2000 (Ocean Optics, Dunedin, FL). For compounds in solution, absorption was measured at room temperature in CHCl₃. For compounds in solid state, absorption was measured using pellets prepared with KBr. A UV/Vis DT 1000 CE light source (Analytical Instrument Systems, Inc., Flemington, NJ) was used for measuring absorption. The molar absorption coefficient (ϵ) was calculated according to the Beer-Lambert law $A = \epsilon cl$ (Gordon & Ford, 1972). The excitation source for measuring the fluorescence and fluorescence quantum yield (Φ_f) was a laser diode at a wavelength of 405 nm. The Φ_f was measured on compounds in powder form with the experimental setup described by De Mello *et al.* (1997) and these values were compared with the quantum yield of Alq₃ as a reference.

2.2 Syntheses of Compounds I-IV

The synthesis of compounds **I** to **IV** was performed according to Scheme 1. Compounds **I** to **IV** were obtained by mixing 1:1:1 molar amounts of arylacetonitrile, *p*-(dimethylaminophenyl) aldehyde and piperidine. Piperidine acted as both catalyst and solvent. All reactions were reflux reactions, conducted in the absence of another solvent at 100 °C with reaction times of 24-36 h. At all times during the reaction, the mixtures appeared oily with a brown to red color. All mixtures were neutralized with a solution of HCl (2N) to precipitate the products as powders and afterwards, were washed with H₂O. The products were purified by recrystallization with a solvent mixture of methanol: hexane (3:1) for **I** and **III**, ethyl acetate:hexane (2:1) for **II** and hexane:dichloromethane (4:1) for **IV**. All compounds were characterized by IR, ¹H-NMR, EI mass spectrometry, UV, fluorescence spectroscopy, and fluorescence quantum yield (Φ_f).

3. Results and Discussion

The synthesis of compounds **I** to **IV** was performed according to Scheme 1, and following a similar procedure recently reported for dimethylaminophenylacrylonitrile derivatives [2-(phenyl)-3-(4-dimethylaminophenyl) acrylonitrile, 2-(2'-pyridyl)-3-(4-dimethylaminophenyl)acrylonitrile, 2-(3'-pyridyl)-3-(4-dimethylamino-phenyl) -acrylonitrile, and 2-(4'-pyridyl)-3-(4-dimethylaminophenyl)acrylonitrile] (Percino, *et al.*, 2011). The temperature was constant at 100 °C for all reactions. The reaction times for the syntheses varied from 24-36 h, depending on the phenyl- and *ortho*-, *meta*-, and *para*- positions of the pyridine (Table 1). The yields in the present syntheses were smaller than those recently reported (Percino, *et al.*, 2011), indicating that the aromatic aldehyde may play a more important role than the cyano methylene group (-CH₂CN). The compounds were only obtained in the presence the piperidine catalyst which could be explained by the low reactivity of the -COH group through the -N(Ph)₂ or -N(CH₃)₂ moieties, which are strong electron donating groups. Also regardless of the position of the N on the pyridine ring, we observed similar reactivity of the reagents and similar yields. A lower reactivity was observed for the 3 or *meta* position, as was expected.

3.1 FT-IR and NMR Characterization.

For newly synthesized compounds **I-IV**, signals for a conjugated double bond $\nu(-C=C-)$ of an alkene at ~1625 cm⁻¹ not were observed (Williams & Fleming, 1980) –as occurred in compounds that contain N(CH₃)₂ around of 1613-1610 cm⁻¹ (Percino, *et al.*, 2011)– and this behavior could be attributed the overlap of the signals arising from the $\nu(-C=C-)$ from the aromatic and pyridine rings. This evidence may indicate that the electrons in the compounds exhibit a higher extent of delocalization. The electrons from π bonds are delocalized or spread out over the whole system (acting as a group of interacting conjugated atoms) (Table 2). The bands at 2209, 2204, 2212 and 2209 cm⁻¹ were assigned to the -CN group and are an indication that even with the -C $\equiv$ N attached to

the alkene double bond, the presence of the $-N(Ph)_2$ in the *p*-position induced a strong conjugation. Also, the band around of 758 cm^{-1} for **I-IV** was assigned to a $\delta(C-H)$ vibration from a double bond in each compound.

The 1H -NMR data in CD_3Cl solution showed a general deshielding effect on the protons of the compounds (Table 2). Thus the proton H-3 for compounds **I-IV** appears at 7.297, 8.429, 7.524, and 7.809 ppm (7.54 ppm corresponds to the chemical shift of a proton in a double bond) (Xie, *et al.*, 2005). The same protons associated with the $-N(CH_3)_2$ substituent were reported at 7.41, 8.33, 7.43 and 7.01 ppm for the respective phenyl, *ortho*, *meta* and *para* locations of the nitrogen atom in pyridine, indicating a moderate deshielding effect on the protons due to the presence of $-N(CH_3)_2$ rather than $-N(Ph)_2$ as well as an effect related to the presence of $-CN$ group.

3.2 One Photon Absorption and Emission

The UV absorption spectra of compounds **I-IV** both in liquid $CHCl_3$ and in the solid state (Figure 1a and 1b, respectively) showed two major absorption bands: one at λ_{max} 296-301 nm, corresponding to the $n \rightarrow \pi^*$ transition for the electron transfer from the amine moieties to the acrylonitrile in the main 4-diphenylaminophenyl chromophores, and a second absorption band with λ_{max} at 416-427 nm. The longer wavelength bands may be assigned to $\pi-\pi^*$ transition of the conjugated $RRC=CR_2R_2$ segments (Gordon, 1972). This longer wavelength chromophore for the new compounds was red shifted, as compared to similar previously synthesized compounds that contained the $N(CH_3)_2$ group (λ_{max} at 381-406 nm) (Scheme 2 and Figure 2). The extended delocalization of the nitrogen pair onto the additional two phenyl groups from $-N(Ph)_2$ accounts for the red shift of the absorption band [49]. The molar absorptivity coefficient (ϵ) is an intrinsic property of a species and provides a useful point of comparison for different compounds. Compounds **I-IV** displayed values of ϵ that exceeded 10,000 (Figure 1c), and the extinction coefficients of the newly synthesized compounds were also higher those of previously synthesized analogues bearing the $-N(CH_3)_2$ group (Figure 2b). The short wavelength bands at ~ 300 nm also showed values of $\epsilon > 2 \times 10^4$ that exceeded the corresponding values of ϵ for the compounds with the $-N(CH_3)_2$. Furthermore, we detected a small bathochromic effect between isomers (**I=II** < **III=IV**) that can be attributed to the position of the nitrogen atom in the ring.

3.3 Emission Characterization

The normalized absorption (UV) and photoluminescence (PL) emission spectra of **I-IV** in chloroform solution are shown in Figure 3. Compounds **I-IV** were highly fluorescent both in solution and in the solid state. The photoluminescence spectra of the molecules in chloroform as well as in the solid state were characterized by strong emissions with maxima at 521-530 nm for the all compounds whereas in the solid state, the emission maxima appeared at 506 for **I**, 535 for **II** and **III**, and 542 nm for **IV**. In both solution and in the solid state, the wavelength of emission corresponded to green light. The emission band of compound **I** is blue-shifted with respect to that of **II-IV** (Figure 4). This effect could be due to the absence of the pyridine moiety in compound **I**. All compounds displayed considerable Stokes shifts, indicating a substantial geometrical difference between the ground and excited states. The fluorescence quantum yield values in the solids were of 0.07, 0.08, 0.11 and 0.09 for **I-IV**, respectively. We also compared the fluorescence emissions of compounds **I-IV** with the fluorescence of compounds of the recently reported $-N(CH_3)_2$ analogues which only exhibit PL in the solid state (Figure 5) (Percino, 2008). The dimethylamino derivatives showed PL emission maxima over a wider range of wavelengths, from 507-616 nm. These compounds displayed significant differences in their electronic spectra due to the presence of electron-donating functional groups.

The results for the compounds **I-IV** are interesting because recently several compounds have been reported that exhibit a strong fluorescence in either the liquid or solid states. For organic molecules, aggregation is a common phenomenon that occurs in solution of high concentrations. However, one deleterious side effect of aggregation is the problem of emission quenching due to strong electronic interactions, hydrogen bonding or $\pi-\pi$ stacking (Xie, *et al.*, 2005; Lamand & Tang, 2005; Kraft, Grimsdale & Holmes, 1998). Therefore, the compounds reported in the present paper are interesting emission properties similar to reported by Tang and coworkers. They recently observed a novel phenomenon that overcomes fluorescence quenching in aggregation, which they called aggregation-induced emission (AIE) (An, *et al.*, 2002; Lim, *et al.*, 2004). Molecules exhibiting emission behavior which depends on its aggregative state are of particular interest because the aggregation-dependent luminescence which can find applications in the fields of sensors or OLED.

4. Conclusions

N,N-Diphenylaminophenylpyridineacrylonitrile derivatives showed high fluorescence in the liquid as well as in the solid state. The compounds were prepared via the Knoevenagel procedure from the reaction of *N,N*-diphenylaminophenylbenzaldehyde and phenylacrylonitriles in the presence of piperidine as a catalyst. The intensities and positions of the emission bands in the newly synthesized compounds as well as their quantum yields

could be related to the nature of the substituents on the structure, i. e., the -CN substituent on the vinylene moiety of the compound and the position of the N atom on the pyridine ring, but the interesting properties could also be caused by the high degree of conjugation conferred to the compounds by the -N(Ph)₂ group. It is also interesting to note that compound **III** has an inherently higher fluorescence quantum yield in the solid state and that its fluorescence emission appears as a clear red shift. Given this, such systems may be regarded as potentially promising candidates for electroluminescent devices.

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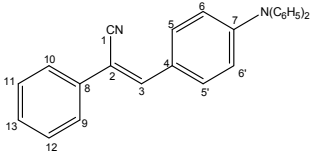
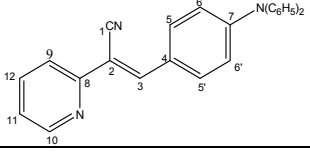
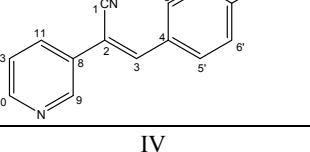
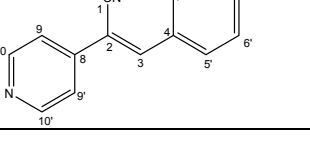
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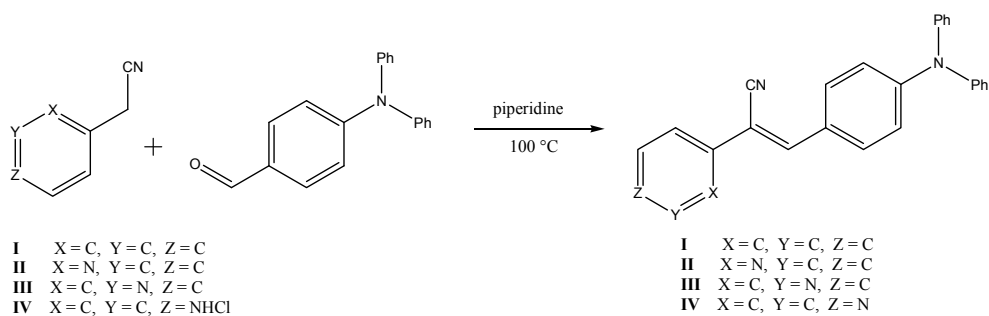
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Table 1. Conditions, yields and properties of the compounds shown in Scheme 1

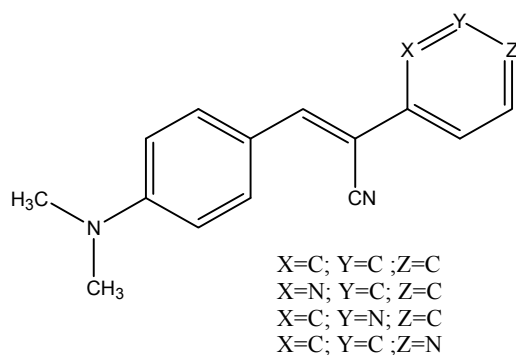
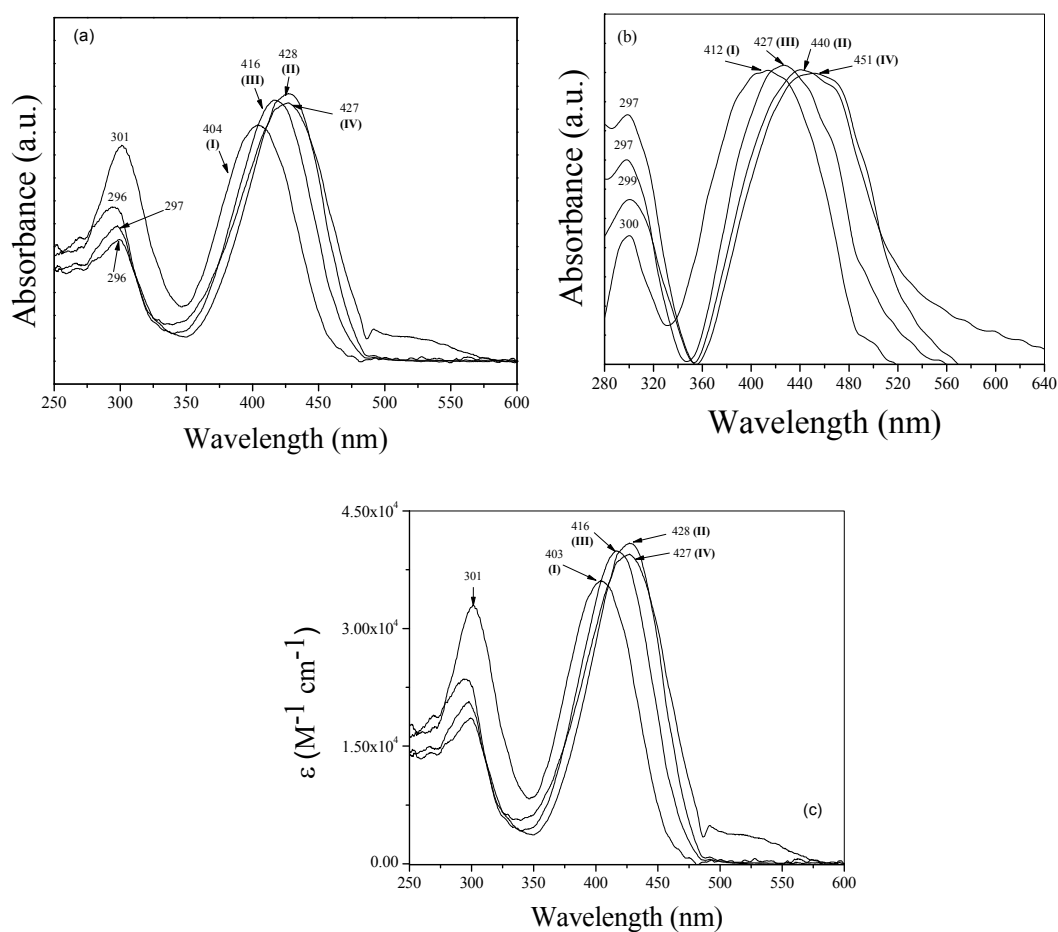
Compound	Temp. °C	Time h	Yield %	Appearance	Melting point °C	Solubility
I	100	36	42	Yellow powder	162-164	Toluene, CHCl ₃ , THF, EtOH, MeOH, Me ₂ CO, DMSO, ethyl acetate.
II	100	24	32	Yellow-orange powder	142-144	CHCl ₃ , THF, C ₆ H ₅ OH, Me ₂ CO, MeOH, DMSO
III	100	36	19	Yellow powder	108-110	CHCl ₃ , THF, Me ₂ CO, EtOH, MeOH, DMSO
IV	100	34	31	Orange powder	153-155	CHCl ₃ , THF, Me ₂ CO, acetone, EtOH, MeOH, DMSO

Table 2. Spectral characterization of the compounds I-IV in Scheme 1

Compound	Spectral characterization
	IR (KBr), $\tilde{\nu}$ /cm ⁻¹ : 3033(w), 2209(s, C≡N), 1586(broad, C=C Ar and C=C), 1492(s, vC-H double bond), 758(s, C-H, CR ₁ R ₂ =CR ₃ H). ¹ H NMR (400 MHz, CDCl ₃), δ (ppm): 7.784-7.762 (d, 1H, H _{5,5'}), 7.654-7.633 (d, 1H, H _{6,6'}), 7.348-7.327 (d, 1H, H _{6,6'}), 7.059-7.037 (d, 1H, H _{5,5'}), 7.441-6.924 (m, 15H, Ar). 7.297 (s, 1H, H ₃), EI, <i>m/z</i> (<i>I_r</i> /%): 372(100) (M), 371 (10) (M ⁺).
	IR (KBr), $\tilde{\nu}$ /cm ⁻¹ : 3034(w), 3003(w), 2204(s, C≡N), 1582(broad, C=C Ar and C=C), 1490(s, vC-H double bond), 758(m, CH, CR ₁ R ₂ =CR ₃ H). ¹ H NMR (400 MHz, CDCl ₃), δ (ppm): 8.620-8.609 (d, 1H, H ₁₀), 8.429 (s, 1H, H ₃), 7.905-7.883 (d, 2H, H _{5,5'}), 7.791-7.725 (m, 2H, Ar), 7.347-7.308 (m, 3H; H ₁₁ , Ar), 7.269-7.240 (m, 2H, Ar). 7.184-7.123 (m, 6H; H ₉ , ₁₂ , Ar), 7.047-7.025 (d, 2H, H _{6,6'}), EI, <i>m/z</i> (<i>I_r</i> /%): 373 (100), 372 (55) (M ⁺).
	IR (KBr), $\tilde{\nu}$ /cm ⁻¹ : 3035(w), 2212(s, C≡N), 1584(broad, C=C Ar and C=C), 1494(s, vC-H double bond), 761 (m, CH, CR ₁ R ₂ =CR ₃ H). ¹ H NMR (400 MHz, CDCl ₃), δ (ppm): 8.959 (s, 1H, H ₉), 8.597 (s, 1H, H ₁₀), 8.121-8.104 (d, 1H, H ₁₁), 7.524 (s, 1H, H ₃), 7.364-7.138 (m, 11H Ar), 7.824-7.802 (d, 2H, H _{5,5'}), 7.051-7.29 (d, 2H, H _{6,6'}), EI, <i>m/z</i> (<i>I_r</i> /%): 373 (100), 372 (30) (M ⁺).
	IR (KBr), $\tilde{\nu}$ /cm ⁻¹ : 3033(w), 2209(s, C≡N), 1581(broad, C=C Ar and C=C), 1493(s, vC-H double bond), 757(s, C-H, CR ₁ R ₂ =CR ₃ H). ¹ H NMR (400 MHz, CDCl ₃), δ (ppm): 8.662-8.649 (d, 2H _{10, 10'}), 7.927-7.896(m, 4H, H _{9,9'} , H _{5,5'}), 7.807 (s, 1H ₃) 7.401-7.266; 7.259-7.241; and 7.229-7.196 (m, 10H, C ₆ H ₅), 7.022-6.997 (m, 2H, H _{6,6'}). EI, <i>m/z</i> (<i>I_r</i> /%): 373 (100) (M ⁺), 372 (18).



Scheme 1. Synthesis of 2-(phenyl)-3-(4-diphenylaminophenyl)acrylonitrile (I), 2-(2'-pyridyl)-3-(4-diphenylaminophenyl)acrylonitrile (II), 2-(3'-pyridyl)-3-(4-diphenylamino-phenyl)acrylonitrile (III) and 2-(4'-pyridyl)-3-(4-diphenylaminophenyl)acrylonitrile (IV)

Scheme 2. *N,N*-Dimethylaminophenylacrylonitriles derivatives (from ref. 46)Figure 1. Absorbance spectra of compounds **I-IV** in (a) CHCl_3 and (b) solid state (KBr) as well as (c) the molar absorptivity values (ϵ) of the compounds

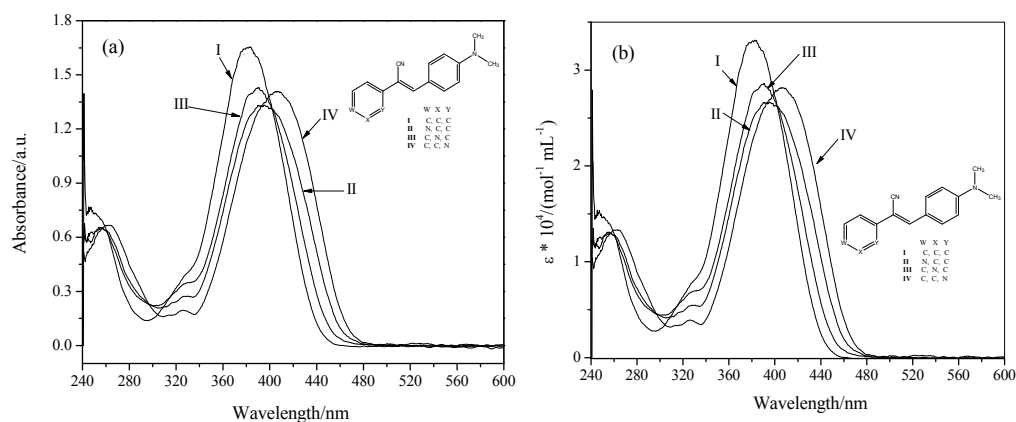


Figure 2. Absorbance (a) and molar absorptivity ϵ (b) of phenyl, *ortho*, *meta* and *para* compounds synthesized with the $-N(CH_3)_2$ substituent in $CHCl_3$ (from ref. 46)

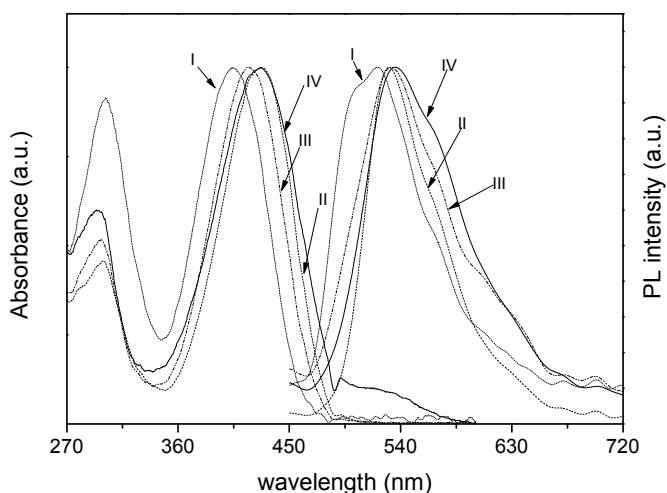


Figure 3. Absorbance and luminescence emission for the compounds I-IV in chloroform solution. I (....), II (- - -), III (- · - ·), and IV (—)

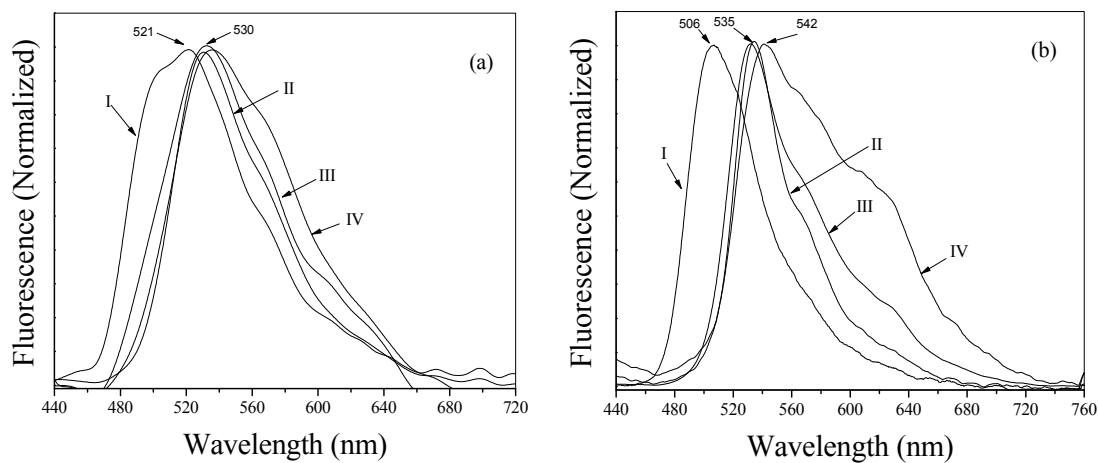


Figure 4. PL emissions of compounds I-IV in (a) CH_3Cl and (b) in solid state. Excitation wavelength for both conditions was 368 nm

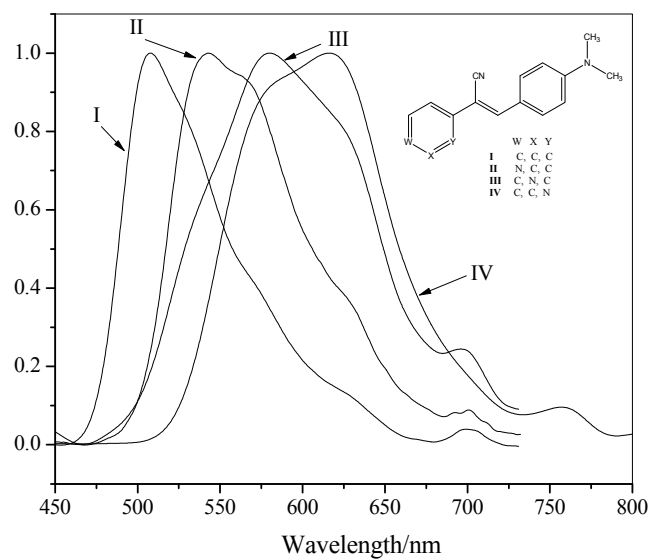


Figure 5. PL emission of previously reported compounds containing $-N(CH_3)_2$ substituents (from ref. 46 in solid state. Excitation wavelength in the studies was 368 nm