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Fluorescence of substituted pyrrolyl pyridines

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Abstract

The absorbance and fluorescence of 2-(1-pyrrolyl)-pyridine and three methylated derivatives have been studied in a variety of solvents. Absorbance spectra of the molecules were found to exhibit minor solvent dependence. The fluorescence spectra for all derivatives, however, show large red shifts in more polar solvents. Dual fluorescence has also been observed, consistent with locally excited and twisted intramolecular charge transfer (TICT) emission. Fluorescence intensity was also found to diminish in more polar solvents, consistent with a twisted excited state geometry for these molecules. The position and number of methyl substituents were found to affect the degree of charge-transfer emission. Quantum mechanical density functional calculations of ground state and vertical transition energies are presented to describe observed spectral behavior. Calculations include bulk solvation effects.

Keywords: Fluorescence; Intramolecular charge transfer; Solvent dependence

1. Introduction

Molecules that exhibit solvent-dependent fluorescence are of interest for a variety of uses, since the emission can be sensitive to solvent polarity, acidity, viscosity, and temperature [1–5]. A large number of linked donor–acceptor systems have been studied, with a number of possible mechanisms explored as causes for the anomalous fluorescence. Twisted intramolecular charge transfer (TICT) states have been used to describe the emission in several of these systems, in which conformational changes from the planar form in the excited state take place due to stabilization of the twisted form of the excited molecule in more polar solvents. Pyrrole containing systems such as cyano-phenyl pyrroles [5] have been found to exhibit TICT emission, as well as a number of amine-containing molecules. The dual fluorescence of *p*-dimethylaminopyridine and methylated derivatives [6] is also assigned to TICT emission, and effects of steric hindrance due to methyl groups were noted.

In this study, 2-(1-pyrrolyl)-pyridine and three methylated derivatives, 3-methyl-2-(1-pyrrolyl)-pyridine, 2,4-dimethyl-6-(1-pyrrolyl)-pyridine, and 5-methyl-2-(1-pyrrolyl)-pyridine were studied by UV-Vis and fluorescence spectroscopy in various solvents. The structures of the molecules are shown in Fig. 1. Unlike other fluorescent molecules that exhibit large stokes shifts in polar solvents, these bridged pyrrole–pyridine systems are also of interest because of their ability to form cyclometallated complexes with metals such as palladium and rhodium [7]. Since cyclometallated complexes with transition metals have recently gained a great deal of attention for use as emitters in phosphorescent organic light emitting diodes [8], an understanding of the excited state behavior of potential ligands is of importance for the design of efficient systems. The phosphorescence in similar complexes could be maximized through a better understanding of the excited state properties of the ligands, since the lowest excited state in some phosphorescent metal complexes can be considered primarily a ligand-centered state [9]. This study will address the effect of methyl

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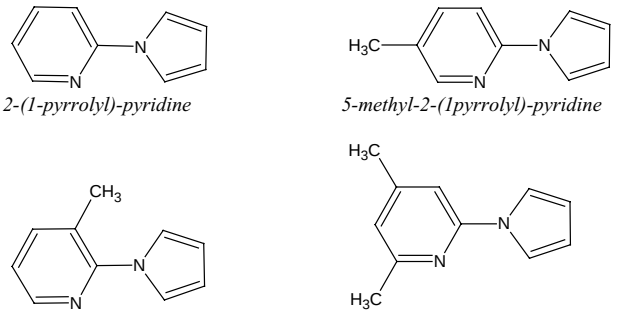

Fig. 1. Structures of molecules studied.

substitution on a fluorescent molecule with C, N binding capability.

2. Materials and methods

2.1. Materials

All molecules were synthesized following a literature method for the synthesis of 2-pyrrolylpyridines [7]. The substituted 2-aminopyridine starting materials (2-aminopyridine, 2-amino-3-picoline, 2-amino-4,6-dimethylpyridine, and 2-amino-5-methylpyridine) were purchased from Aldrich and were used without further purification. Each was reacted with dimethoxytetrahydrofuran in glacial acetic acid solvent in air atmosphere. The reaction mixture was extracted with ether and dried with $MgSO_4$ prior to removal of solvent. Purification of the compounds was done using column chromatography on silica gel with CH_2Cl_2 eluent. The 5-methyl derivative was also purified by sublimation using a tube furnace and vacuum pump. The compounds were checked for purity by thin-layer chromatography and/or NMR. Solvents were used as purchased without further purification.

2.2. Instruments and procedures

Absorbance spectra were obtained using a Unicam UV/4 spectrophotometer. All solutions used for fluorescence measurements were adjusted to provide 0.100 ± 0.005 absorbance at the wavelength used for fluorescence excitation (284 nm). More concentrated solutions were used for lifetime measurements. Fluorescence emission and excitation spectra were obtained using a QuantaMaster fluorescence system from PTI, Inc. Fluorescence emission spectra were corrected for phototube response. Lifetime measurements used a StobeMaster fluorescence lifetime system with air discharge gas. All molecules were stored refrigerated and in the dark to prevent degradation over time, and all molecules were freshly purified or checked for purity before spectroscopic measurements. Nuclear magnetic resonance spectra were obtained in deuterated chloroform using a Bruker 400 MHz spectrometer.

2.3. Computation

The ground-state potential energy surface of 2-(1-pyrrolyl)-pyridine was explored with respect to rotation about the central C–N bond. Geometries of the non-planar rotational minimum, planar rotational transition state and perpendicular rotational transition state were determined using the B3LYP hybrid density functional [10,11] coupled with the 6-31G* basis set [12]. Analytic harmonic frequencies were determined in order to confirm the minima and transition states and to provide enthalpic and entropic corrections at 298 K. Vertical excitation energies were determined for the first six singlet excited states of each ground-state geometry via time-dependent density functional theory [13] (TD-DFT), also at the B3LYP/6-31G* level. For both ground and excited-state calculations, bulk solvation effects were accounted for using the integral equation formalism polarizable continuum model [14] (IEF-PCM). All calculations were performed using Gaussian03 for Macintosh OSX [15].

3. Results and discussion

3.1. Absorbance

3.1.1. 2-(1-Pyrrolyl)-pyridine

The room-temperature absorption spectra of substituted pyrrolyl pyridines obtained in a wide variety of solvents exhibit only slight shifts with solvent. Representative spectra are shown in Fig. 2. The spectrum for 2-(1-pyrrolyl)-pyridine shows two main peaks, a weaker long wavelength peak at 284 nm and a stronger band at 256 nm (in hexane), though a shoulder on the higher energy peak is evidence of another transition. No significant tailing is observed on the long wavelength region. A shoulder in nonpolar solvents, however, is evidence for another transition energy on the low energy side. The major long-wavelength peak exhibits only very slight shifts, even in polar solvents. According to molecular modeling (vide infra), this transition is due to a locally excited transition involving net transfer of electron density from the pyrrole to the pyridyl acceptor.

Spectra of the methyl-substituted derivatives display similar absorption spectra, though the existence of an additional peak in the high-energy region becomes more apparent. A plot of absorbance for the three methylated derivatives in cyclohexane is shown in Fig. 2.

The spectra for all methylated derivatives also show very slight solvent dependence, with the long wavelength peak tending to exhibit slight blue shifts in more polar solvents. The spectra do not appear to change with concentration. The spectra in very nonpolar solvents show a bit of structure on the lowest energy peak.

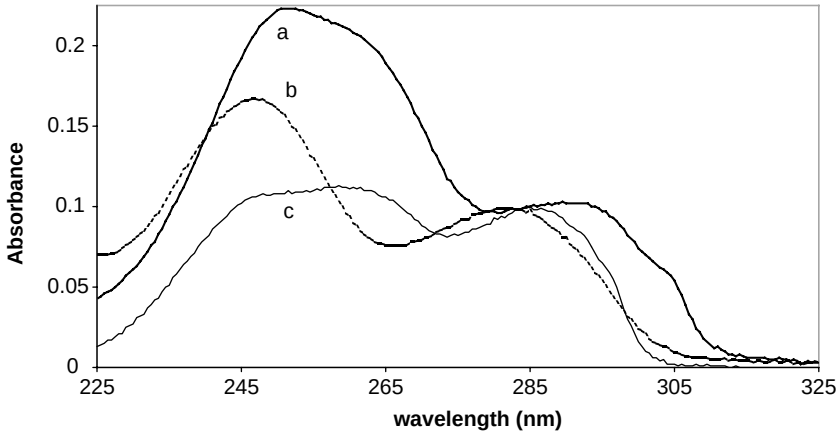

Fig. 2. UV-Vis absorption spectra in cyclohexane of: (a) 2-(1-pyrrolyl)-pyridine (b) 3-methyl-2-(pyrrol-1-yl)-pyridine; (c) 2,4-dimethyl-6-(1-pyrrolyl)-pyridine.

4. Fluorescence

4.1. 2-(1-Pyrrolyl)-pyridine

Fluorescence spectra were obtained for each of the four molecules in several solvents of varying polarities. The fluorescence spectra of 2-(1-pyrrolyl)-pyridine in various solvents are shown in Fig. 3, and peak positions are listed in Table 1. The spectra show a large Stokes shift in more polar solvents, accompanied by a dramatic decrease in intensity and an increase in the width (FWHM) of the peak. The slight bump in the spectra is due to scattering. The molecule exhibits a large solvatochromic shift of fluorescence, indicating a high degree of charge-transfer for the emitting state. The fluorescence spectra obtained at different concentrations are also the same, so emission is unlikely to be due to complexation. The excitation spectra show features corresponding to those in the absorbance spectra, demonstrating that the emissions are not due to impurities. Also, fluorescence measurements of deoxygenated solution demonstrated the expected minor intensity difference, proving that the long wavelength emissions are not due to phosphorescence.

A closer examination of the spectra suggests that the molecule exhibits dual fluorescence. The first peak, due to a locally excited state, shows only modest solvent shift. In solvents of medium polarity, a second peak emerges. This peak becomes dominant in high polarity solvents. This second peak also shows a large solvent dependence, consistent with emission from a twisted intramolecular charge transfer (TICT) state.

The emission maxima and relative intensity are shown in Table 1. The red-shifting with solvent is consistent with the

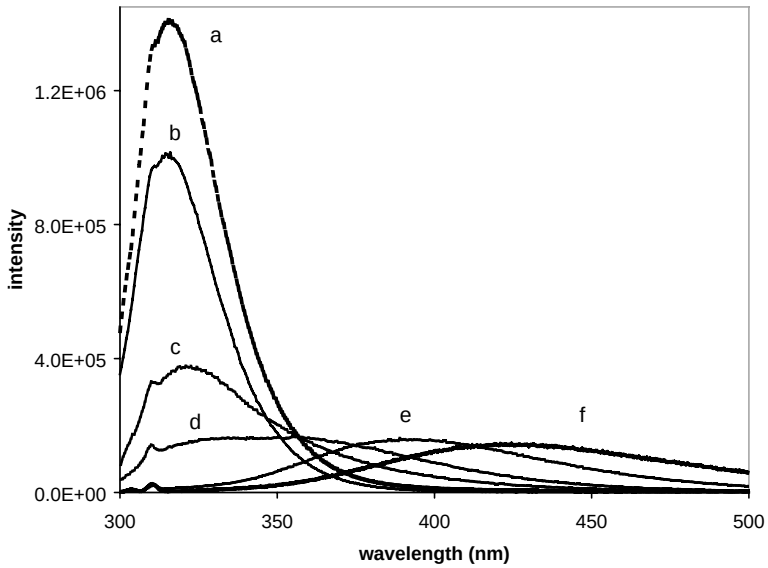

Fig. 3. Fluorescence spectra of 2-(1-pyrrolyl)-pyridine in various solvents with excitation at 284 nm: (a) cyclohexane; (b) hexane; (c) dichloromethane; (d) butyl ether; (e) chlorobutane; (f) acetonitrile.

Table 1
Fluorescence peak maxima for molecules of the study in various solvents

Solvent	2-(1-Pyrrolyl)-pyridine		3-Methyl-2-(1-pyrrolyl)-pyridine		5-Methyl-2-(1-pyrrolyl)-pyridine		2,4-Dimethyl-6-(1-pyrrolyl)-pyridine	
	Absorbance peak (nm)	Fluorescence maximum (nm)	Absorbance peak (nm)	Fluorescence maximum (nm)	Absorbance peak (nm)	Fluorescence maximum (nm)	Absorbance peak (nm)	Fluorescence maximum (nm)
Hexane	284	312	282.5	319.5	291	321	–	–
Cyclohexane	286	312.5	283	320	292	320.5	287	311.5
Butyl ether	284.5	317	282	328.5	291	322	286	312
Ether	284.5	321	280.5	336	291	323.5	285	312
Butyl chloride	284	327.5	281	358	289	325	285	–
THF	283.5	382.5	280	376.5	288	386	285.5	313
Dichloromethane	283	391.5	280	392	289	392	285	315.5
Acetonitrile	282	421	277.5	417	288	421	284	378
Ethyl acetate	283	388.5	280	386	–	–	285.5	–
DMSO	–	–	–	–	292	425.5	287	388

charge-transfer nature of the fluorescence. The peak position readings are affected by the overlapping of the two emission peaks in solvents of low polarity. The increase in the contribution of the TICT emission is consistent with a lowering of the energy of the twisted state relative to that of the planar excited state [16]. The decrease in intensity in more polar solvents is dramatic, as seen in Fig. 3.

The fluorescence is not due to the protonated species, since no fluorescence was observed in protonic solvents water or alcohol. The fluorescence quenching in these solvents is not due to dielectric constant, since acetonitrile has a larger dielectric constant than ethanol. The quenching in protonic solvents is not unexpected, since fluorescence quenching is also observed in 2-(2′-pyridyl indoles) [17] and in *n*-pyrrole-containing molecules in alcohols [5]. In our system, the effect may be due to interaction of the pyridyl nitrogen with the protons of the solvent. Absorbance spectra at various pH values show a decrease in the peak at 284 nm and a new peak at longer wavelength. An isosbestic point is observed at 289 nm, consistent with two species (protonated and unprotonated) giving rise to the observed spectrum. Molecular modeling calculations (MOPAC) predict that protonation at the pyridyl nitrogen will result in spectra similar to that which is observed. Protonation at the pyrrolyl nitrogen is ruled out because this would require sp^3 geometry at the site and the loss of resonance stabilization energy from delocalization through the extended pi system.

Overall, the spectra are consistent with emission from two closely lying excited states, with TICT emission dominating in all but the least polar solvents.

4.1.1. 3-Methyl-2-(pyrrol-1-yl)-pyridine

Representative spectra of the 3-methyl derivative are shown in Fig. 4. As can be seen from the figure, the spectral

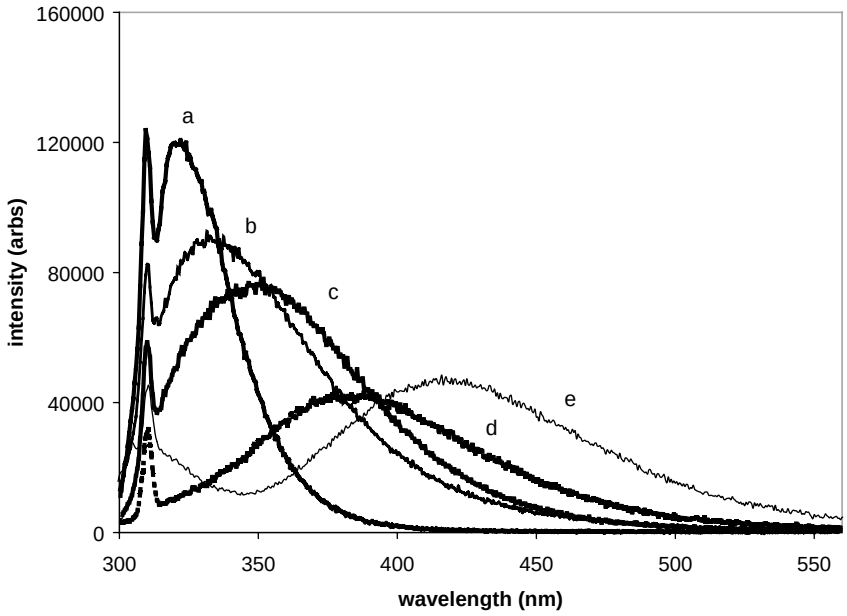

Fig. 4. Fluorescence spectra of 3-methyl-2-(1-pyrrolyl)-pyridine in various solvents with excitation at 284 nm: (a) cyclohexane; (b) ether; (c) chlorobutane; (d) ethyl acetate; (e) acetonitrile.

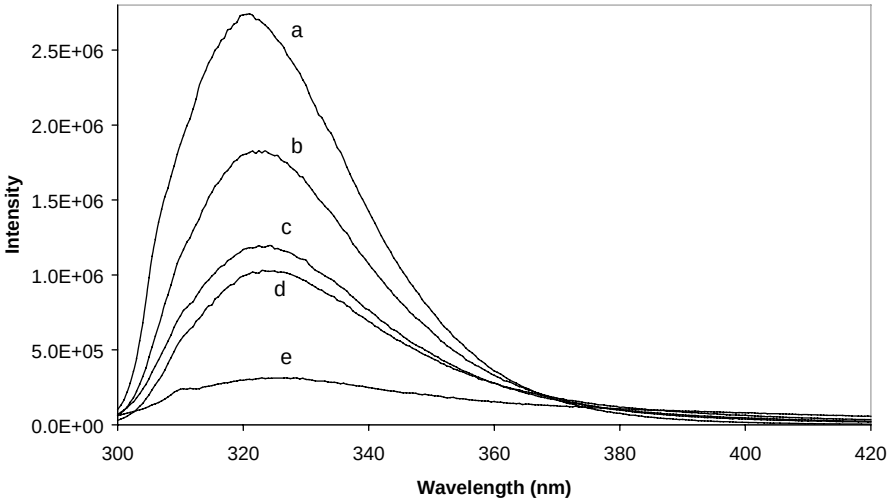

Fig. 5. Fluorescence spectra of 5-methyl-2-(1-pyrrolyl)-pyridine in solvents of low to medium polarity: (a) cyclohexane; (b) butyl ether; (c) ether; (d) butyl chloride; (e) tetrahydrofuran.

shifts are similar to those observed for the unmethylated derivative (peak positions are listed in Table 1). However, the emission intensity of the 3-methyl derivative in non-polar solvents is much lower. The sharp feature at high energy is due to scattering. The decrease in fluorescence intensity is consistent with the fact that the molecule is necessarily twisted in the ground state due to the steric interaction of the methyl group with the hydrogen atom on the pyrrole ring. This leads to loss of overlap between the two ring systems. The TICT emission appears dominant in the spectra, and it is theorized that the twisted conformation allows the TICT excited state to be reached faster upon excitation. This kinetic effect has been proposed for similar systems such as methyl substituted phenyl pyrroles [18].

4.2. 5-Methyl 2-(1-pyrrolyl)-pyridine

Unlike the molecules above, the 5-methyl derivative does not show as large a shift in emission wavelength for solvents of low to medium polarity. This is evidence that the locally excited state is more favorable compared to the TICT state, due to the donating effect of the methyl groups, which make the pyridine a poorer acceptor. The intensity of the emission is quite strong, especially in nonpolar solvents, consistent with a greater contribution from the planar excited state. Intensity decreases as solvent polarity increases (Fig. 5). This behavior is consistent with increased stabilization of and contribution from the CT state for emission in these solvents. In polar solvents, dual emission is clearly observed, with the red-shifted TICT peak becoming dominant (Fig. 6).

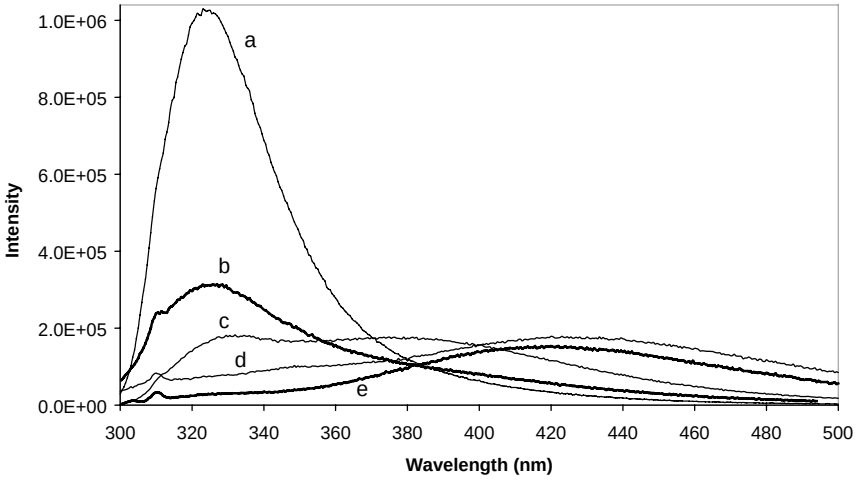

Fig. 6. Fluorescence spectra of 5-methyl-2-(1-pyrrolyl)-pyridine in higher-polarity solvents: (a) butyl chloride; (b) tetrahydrofuran; (c) dichloromethane; (d) dimethyl sulfoxide; (e) acetonitrile.

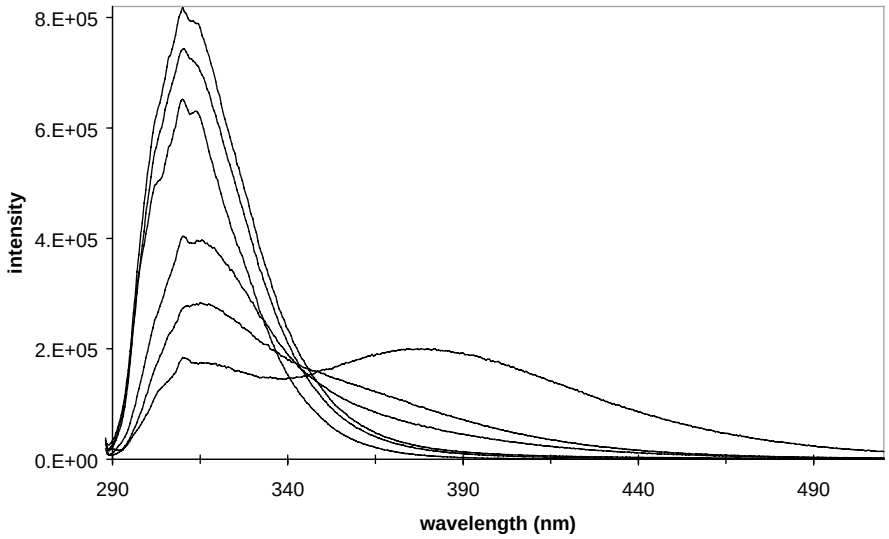

Fig. 7. Fluorescence spectra of 2,4-dimethyl-6-(1-pyrrolyl)-pyridine in various solvents with excitation at 284 nm. From top to bottom at 315 nm: butyl ether, ether, cyclohexane, tetrahydrofuran, dichloromethane, acetonitrile.

The stabilization of the large dipole moment in very polar solvents results in the TICT state becoming the lowest state for solvents of high polarity.

Since the lowest energy UV transition for these molecules is from a pyrrole donor to the pyridyl acceptor, methyl substitution at the acceptor (the pyridine ring) should result in decreased charge transfer, due to the donating properties of the methyl group. As expected, methyl substitution at the 5-position does result in stabilization of the planar form in the excited state, evidenced by decreased tendency of TICT emission.

4.2.1. 2,4-Dimethyl-6-(1-pyrrolyl)-pyridine

Representative spectra of the 2,4-dimethyl derivative are shown in Fig. 7. As in the 5-methyl derivative, minimal spectral shift occurs in solvents of low polarity. The electron-donating effect is even more pronounced for the 2,4-dimethyl derivative, which does not exhibit TICT emission in the medium polarity solvent tetrahydrofuran. Two peaks are clearly visible in highly polar solvents DMSO and acetonitrile. The excitation spectra confirm that the two peaks are due to the same species. The position of the CT band is not as red shifted as for the other molecules, suggesting a slight decrease in the CT nature of the excited state.

In summary, all of the molecules display fluorescence consistent with TICT behavior, with the charge transfer nature of the emission becoming more dominant in more polar solvents. The effect of the methyl substitution is to change the solvent dependence and to provide competition between emission from planar and twisted configurations. The fluorescence peak maxima do not have a linear dependence with bulk solvent parameters such as Δf, perhaps indicative of specific solvent–molecule interactions.

4.3. Lifetimes

Fluorescence lifetimes for 5-methyl-2-(1-pyrrolyl)-pyridine were obtained in solvents of varying polarity. Due to poor spectral overlap between the molecular absorption and the lamp profile, intensities are weak, especially for spectra in polar solvents. Excitation was into the long-wavelength region of the absorption spectrum. The observed fluorescence lifetime increases substantially in more polar solvents, going from a value of ∼1 ns in the nonpolar solvent hexane (short wavelength emission) to ∼7 ns in DMSO (charge transfer emission). The increase in lifetime with increasing solvent polarity is consistent with results found for *p*-cyanophenyl pyrrole [18], and with the decreased quantum efficiency of emission in polar solvents.

4.4. Computation

4.4.1. Ground-state rotational potential energy surface

Density functional calculations at the B3LYP/6-31G* level reveal that the minimum energy structure of 2-(1-pyrrolyl)-pyridine is non-planar in both cyclohexane and acetonitrile (see Table 2). The dihedral angle between the two ring systems in the minimum energy geometry is found to be 5.4° in cyclohexane and 11.3° in acetonitrile. This is a significantly smaller angle than is found in related 1-phenylpyrrole, where the dihedral is found to be 41.1° [19]. This difference presumably arises due to reduced steric interactions in the pyridyl system. With one less ipso hydrogen compared to phenyl, the pyridyl ring is able to assume a more planar arrangement with the pyrrole ring. It is significant to note the solvent dependence of the dihedral in the ground-state minimum, with the polar solvent favoring a more highly twisted ground state.

Table 2
Summary of the rotational potential energy surfaces of 2-(1-pyrrolyl)-pyridine in cyclohexane and acetonitrile

	Twist angle (°)	Total energy[a] (hartrees)	Relative energy[b] (kcal/mol)
In cyclohexane			
Minimum	5.4	−457.14672	0.0
Planar TS	0.0	−457.14424	1.6
Perpendicular TS	90.2	−457.13555	7.0
In acetonitrile			
Minimum	11.3	−457.14472	1.3
Planar TS	0.0	−457.14302	2.3
Perpendicular TS	90.4	−457.13568	6.9

[a] Total electronic energy including all thermal, entropic and solvation corrections.
[b] Energy relative to the ground-state minimum in cyclohexane.

The total and relative energies are tabulated in Table 2. The rotational potential energy surfaces in cyclohexane and acetonitrile are quite similar. Being a relatively non-polar molecule, the ground state of 2-(1-pyrrolyl)-pyridine is slightly more stable in cyclohexane than in acetonitrile. However, the barrier for rotation is reduced in the more polar solvent, from 7 kcal/mol in cyclohexane to 5.6 kcal/mol in acetonitrile. In fact, the perpendicular transition states in either solvent are isoenergetic, suggesting that increased charge separation in the twisted geometry is stabilized in acetonitrile. In either case, rapid rotation about the central C–N bond is predicted at room temperature.

4.4.2. Vertical excitation energies

Vertical excitation energies were computed using time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G* level, and are tabulated in Table 3. From the ground state geometry, the computed transitions show excellent agreement with the experimental UV spectra. Four significant features are computed within the window of the experimental spectra, and each matches well with a feature observed in the experiment.

Of particular interest is the nature of each transition. For a transition to be a charge-transfer transition, there must be significant rearrangement of the electron density. Examination of the molecular orbitals computed at the B3LYP/6-31G* level (Fig. 8) shows that the lowest energy transition in both cyclohexane and acetonitrile involves exclusively the HOMO-LUMO transition and is characterized by transfer of electron density from the pyrrole to the pyridine. All other transitions are comprised at least in part by local transitions, and the transition near 245 nm, which is the most prominent both computationally and experimentally, is exclusively a local excitation, mainly from HOMO-1 to LUMO+1. Thus, the lowest-lying excited state is suggested to be a charge-transfer state. It is noted that the lowest energy transition corresponds to the long wavelength shoulder observed in the experimental absorption spectrum in non-polar solvents. This weak feature is not observed in more polar solvents, consistent with the calculated blue shift that causes it to be obscured by the more intense higher energy peaks.

Table 3
Computed vertical transitions (nm)

Vertical transition	Cyclohexane (computed)	Acetonitrile (computed)
S1	290.56 (0.004)	284.59 (0.004)
S2	273.61 (0.035)	267.78 (0.086)
S3	267.30 (0.144)	263.03 (0.113)
S4	247.75 (0.496)	244.08 (0.438)

Computed oscillator strengths are given in parenthesis.

Upon closer inspection, the TD-DFT calculations firmly support the assignment of the S1 state as a twisted intramolecular charge transfer state. Table 4 gives the energies of S1, computed as vertical transitions from S0. It is immediately clear that the perpendicular geometry of S1 is more stable than the near-planar geometry in either solvent. Thus, not only does excitation to S1 involve a significant charge transfer, the excitation is likely to result in a near 90° twist about the central C–N bond. It may then be concluded that calculations at the B3LYP/6-31G* level firmly support the characterization of 2-(1-pyrrolyl)-pyridine as a TICT molecule. The calculations at this level of theory do not account well for the relative change in local versus TICT emission with change in solvent. It must be remembered, however, that the excited state energies have been calculated vertically from the ground state geometries, with no attempt to optimize the geometries of the excited states.

Of further interest is the fact that the S1 state is stabilized in acetonitrile relative to cyclohexane, in contrast to the behavior of the ground state. This is consistent with the observed red shift in the experimental fluorescence spectrum. While the computed shift is much too small, the direction of the shift is qualitatively correct. A more detailed computational study of the excited states of 2-(1-pyrrolyl)-pyridine is underway which will allow a more detailed analysis of fluorescence behavior of this molecule.

Table 4
Total and relative energies of the near-planar and perpendicular geometries on the vertical S1 surface

	Total energy[a] (hatrees)	Relative energy[b] (kcal/mol)
In cyclohexane		
Near-planar	−456.99241	96.8
Perpendicular	−456.99588	87.7
In acetonitrile		
Near-planar	−456.99605	94.6
Perpendicular	−456.99802	86.3

[a] Total electronic energy including all thermal, entropic and solvation corrections.
[b] Energy relative to the ground-state minimum in cyclohexane (see Table 2).

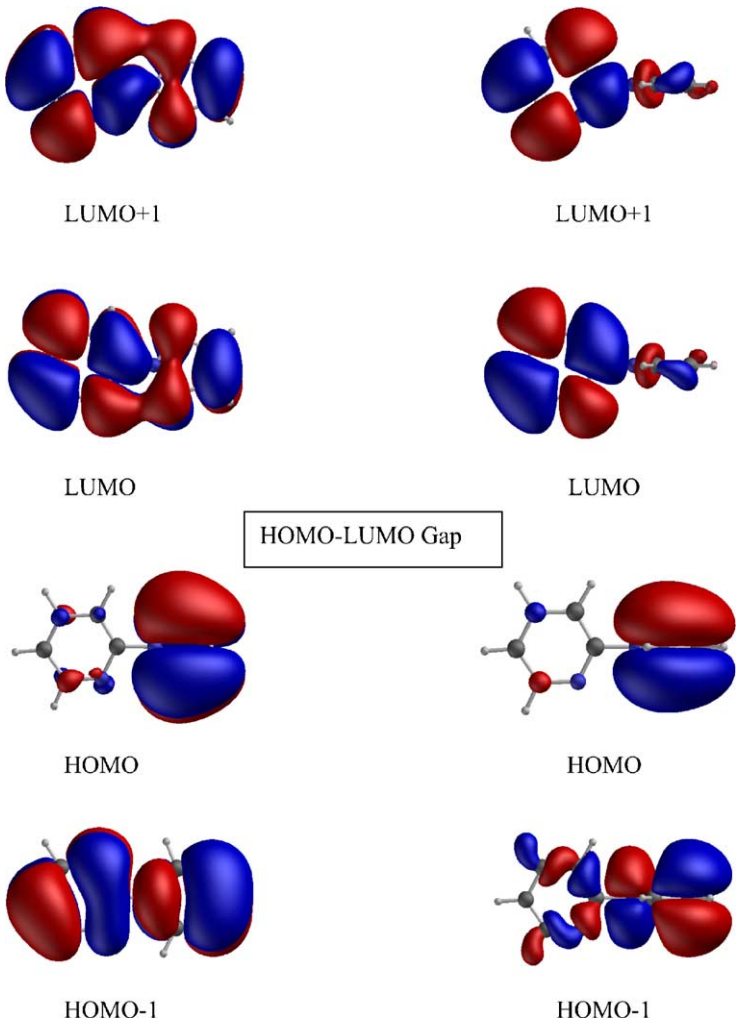

Fig. 8. Molecular orbitals computed at the B3LYP/6-31G* level for the minimum and perpendicular structures. The relative ordering is independent of solvent effects.

5. Conclusions

Substituted pyrrolyl–pyridines were found to exhibit solvent dependent emission and dual fluorescence, consistent with twisted intramolecular charge transfer emission. The fluorescence peak maxima for all compounds shift to the red with increasing solvent polarity. The effect of the methyl groups in the 5- and 2,4-positions on the pyridine ring was to decrease TICT emission relative to that from the planar excited state. Methyl substitution at the 3-position however, resulted in increased contribution from CT emission even in non-polar solvents due to the twisted geometry imposed by steric effects.

This series of pyrrolyl–pyridines is able to form cyclometallated complexes with transition metals. An understanding of the relationship between LE and TICT states will aid in design of better phosphorescent complexes. Further study is planned to synthesize and characterize the photophysics of similar metal complexes.

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