Matrix Dependence of Light Emission from TCNQ Adducts

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Abstract

The reactions of primary and secondary amines with 7,7,8,8, tetracyanodiquinodimethane (TCNQ) lead to mono- and di-substituted adducts. Fluorescence emission has been observed for several of these compounds. The luminescence property of the TCNQ adducts, 7-(2,6, dimethyl-morpholino)-7-(4-methyl piperidino)-8,8-dicyanoquinodimethane (MORPIP) and 7,7-(*N*- (3-aminopropyl) cyclohexyamino)-8,8-

dicyanoquinodimethane (AMINO) were investigated in a variety of environments. These included alcohol solutions and crystals at room temperature and glass forming solvents and polymer films as a function of temperature. The fluorescence quantum yields and Stokes' shifts were found to be very sensitive to the matrix. Crystal structure data shows that the molecules are non-planar in the ground state. The matrix effect is discussed in terms of the conformational change during photo-excitation and the constraint imposed on this by the matrix.

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1. Introduction

Since the first synthesis[1] and study of the basic chemistry[2] of TCNQ in 1962, the chemistry of adducts of TCNQ has been extensively explored.[3,4,5] Recently this class of compounds has attracted interest because of their non-linear optical properties. While much of this work has focussed on single crystals and the large molecular hyperpolarisibity (β) of these compounds [6,7,8,9] they have also been shown, both experimentally and theoretically, to possess large ground state dipole moments (μ).[10,11] The product $\mu\beta$ is, therefore, very large. $\mu\beta$ is a useful molecular figure of merit characterising the second order non-linearity of poled polymer films containing the chromophores.[12] Thus, there is continuing interest in these TCNQ adducts as components of electro-optical polymers. In contrast, the fluorescent emission of non-linear optical chromophores has attracted little attention. Generally it has been regarded as a problem since fluorescence excited by either harmonics or two-photon absorption can affect measurements of non-linear optical coefficients, even when the fluorescence from the chromophores is weak. However, we have discovered that certain of our TCNQ adducts show intense, matrix dependent fluorescence. [11,13]

Interest in organic light emitting chromophores has expanded rapidly since the discovery of efficient electro-luminescence (EL), its use in light emitting devices[14,15,16] and its potential for electrically pumped solid state lasers.[17,18] The measurement of photo-luminescence has been used extensively to characterise fluorescent chromophores and identify potential materials for use in EL devices. Measurements of radiative lifetimes and fluorescence quantum yields of fluorophores are routinely performed in solution.[19] Fluorescence in solution is affected by solvent polarity, the solvatochromism observed for polar molecules can be very large.[20] Fluorescence is also affected by solvent viscosity.[21] Alcohols provide a solvent system where both polarity and viscosity can be varied. The polarity of the solvent can be changed for normal alcohols by extending the molecular length.[22,23] The viscosity of the solvent can be controlled by changing the number of hydroxyl groups, this leads to the enhancement of the hydrogen bonding network in the medium and increased viscosity, e.g. as in diethylene glycol and glycerol.[24,25] A study of fluorescent life times and quantum yields was undertaken for two of our chromophores (MORPIP and AMINO) dissolved in a series of normal alcohols, diethylene glycol and glycerol to evaluate the influence of the viscosity and polarity of the medium on their luminescence properties.

The fluorescence was first observed visually from a MORPIP sample placed adjacent to an ultra-violet lamp used for exciting fluorescence on TLC plates. A bright yellow emission was observed from crystalline material deposited inside a test tube above a weakly fluorescing acetonitrile solution. This observation indicated that the environment of the chromophore had a large effect on the emission. Studies were therefore undertaken of the two adducts as crystalline powders and incorporated into solid, amorphous matrices. These included glass-forming solvents at low temperature and polymers. The latter were studied as the incorporation of fluorophores into polymer matrices has been used in the fabrication of electro-luminescent devices. The quantum efficiency of the fluorescence was found to depend on both matrix and temperature. Details of the study of the fluorescence of these TCNQ adducts in solution and solid matrices are presented here and complement our earlier brief communication.[13]

2. Experimental

7,7,8,8-Tetracyanoquinodimethane (TCNQ) of 98% purity was obtained from Lancaster Ltd. 2,6 Dimethyl morpholine, 4-methyl piperidine and *N*- (3-aminopropyl) cyclohexylamine of 97% purity were obtained from Aldrich Ltd. All solvents used were HPLC grade. These chemicals were used without further purification.

2.1 Synthesis

2.1.1 7-(2,6-dimethylmorpholino)-7-(4-methylpiperidine)-8,8-dicyanoquinomethane (MORPIP)

7-(2,6-dimethylmorpholino)-7-(4-methylpiperidine)-8,8-dicyanoquinomethane (MORPIP) was prepared in a two-stage reaction. 2,6-dimethyl morpholine (0.527ml, 4.8mmol was added to a solution of TCNQ (1g, 4.8mmol) in 100ml tetrahydrofuran (THF) heated at 50°C. The mixture was stirred at 50°C for 3 hours, cooled to room temperature and then stirred overnight. The solvent was removed under vacuum. The residue was re-crystallised in acetonitrile twice and dried under vacuum. 0.52g of 7-(2,6, dimethylmorpholino)-7,8,8-tricyanoquinodimethane, yield 36%, was obtained. 4-methyl piperidine (0.2ml, 2mmol) was added to a solution of 7-(2,6, dimethylmorpholino)-7,8,8-tricyanoquinodimethane (0.4g, 1.36mmol) in THF (30ml) heated at 50°C and stirred for 30 min at 50°C. The product was observed to precipitate. The solution was cooled to room temperature and stirred for one hour. The yellow precipitate was collected by filtration and dried under vacuum. Re-crystallisation of the solid was carried out with acetonitrile. Yellow crystals of MORPIP were obtained (0.24g, 46%). Analytical data: λ_{max} 417nm in acetonitrile. Microanalysis, calculated for

$C_{22}H_{28}N_4O$: % C 72.5, H 7.74, N 15.37, found: % C 72.13, H 7.70, N 15.18. Mass spectrum: 364(M^+) (100%, molecular ion). Decomposition temperature 260°C. The molecular structure was confirmed by X-ray crystallography[5], detailed accounts of X-ray crystallographic data for TCNQ adducts will be presented elsewhere[26].

2.1.2 7,7-(*N*- (3-aminopropyl) cyclohexyamino)-8,8- dicyanoquinodimethane (AMINO)

7,7-(*N*- (3-aminopropyl) cyclohexyamino)-8,8- dicyanoquinodimethane (AMINO) was prepared by adding *N*(3-aminopropyl) cyclohexylamine (0.5ml, 2.8mmol) to TCNQ (0.5g, 2.4mmol) in acetonitrile (30ml) heated to 50°C. The mixture was stirred at 50°C for three hours and cooled to room temperature. The product precipitated and was collected by filtration. The precipitate was recrystallised from acetone and dried under vacuum. A brown powder (0.23g, yield 31.1%) was obtained. Analytical data: NMR:(*d*-DMSO), δ 7.1ppm, doublet, benzene protons (2H); δ 6.8ppm, doublet, benzene protons (2H); δ 3.6ppm, quintet, amine proton (lH); δ 3.45ppm, triplet; -(CH_2)- next to NH (2H); δ 3.35ppm, triplet, -(CH_2)- next to N (2H); δ 1.95ppm, triplet; cyclohexane proton next to N (lH); δ 1.7 and 1.0ppm, cyclohexane and -(CH_2)- protons (12 H). IR: 2179, 2132cm^{-1} (nitrile stretching). λ_{max}: 368nm in acetonitrile. Microanalysis: Calcd for

$C_{19}H_{22}N_4$:% C 74.48, H 7.24, N 18.28. Found:% C 74.46, H 7.35, N 18.28. Mass spectrum: 306(M+) (100%, molecular ion). Decomposition temperature: 220°C.

The NMR spectrum was recorded in *d*-DMSO, a polar solvent. Therefore, the aromatic protons sense different electronic environments due to the charge separation between the donor and acceptors groups. These protons are observed as doublets at δ 7.1 and 6.8ppm. This splitting is observed in other TCNQ adducts.[10]

2.2. Physical Characterisation

Room temperature emission and photo-excitation spectra were recorded with a Perkin Elmer Luminescence Spectrometer, LS 50B, and absorption spectra were recorded with a Perkin Elmer Lambda 19 spectrophotometer. MORPIP solutions were prepared in methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, ethylene glycol, and glycerol without degassing. After filtration (0.5μm filters) solutions were diluted to give an optical density 0.055 ± 0.01 at 375nm. A reference solution of quinine sulphate dihydrate in 0.5M sulphuric acid with the same optical density was also prepared. The quantum yield of quinine sulphate dihydrate is 51% and relatively temperature independent.[27] The quantum yields of the MORPIP solutions were calculated by comparing the integrated emission intensity of the quinine sulphate dihydrate solution to that of samples. All of the emission spectra were measured with the same slit widths.

Thin films of poly(methylmethacrylate) (PMMA) and bis-phenol-A poly(carbonate) (PC) were prepared as described in the following example. MORPIP (11mg) and PMMA pellets (1.218g) were dissolved in 3ml of tetramethyl urea (TMU). The mixture was stirred for several days to ensure complete dissolution. Glass substrates were cleaned with acetone and a mixture of acetone and isopropanol. For films prepared by spin coating the PMMA solution was dropped on to the substrate and the spin coater was switched on. A spin rate of spinner 2000rpm for ten to fifteen seconds gave optically clear PMMA films. Dip coated films were prepared by the slow withdrawal of the clean substrate from the solution. The films were kept in an oven at 80°C for three to five days under vacuum to ensure complete removal of solvent prior to spectral measurements.

The photoluminescence quantum yield (PLQY) of polymer thin films prepared as described above, and polycrystalline samples deposited on to Spectrosil substrates was determined at room temperature using an integrating sphere (Labshere) to collect the light emitted in all directions.[28] The excitation was provided by the 442 nm line of a CW HeCd laser (Kimmon) and the excitation intensity was about 0.5 mW on an area of 2mm^2. Optical densities of the samples at the excitation wavelength were at least.

Low temperature emission and photo-excitation spectra were recorded with an ISA Fluoromax fluorimeter. Low temperature absorption spectra were recorded with a Perkin Elmer Lambda 15 spectrophotometer. MORPIP solutions were prepared in glass forming solvents, either 1-propanol or 2-methyl tetrahydrofuran (2MTHF). Typically the optical density of these solutions at the absorption maximum was below 0.5. The sample was placed inside an Oxford Instruments cryostat in a special low temperature cuvette. The absorption, emission and photo-excitation spectra were first recorded at room temperature. The cryostat was then cooled with liquid nitrogen and the temperature of the sample was varied with an Oxford Instrument temperature controller. Absorption, emission and photo-excitation spectra were obtained in the range from room temperature to 80K. Data were obtained for polymer thin film samples mounted in the same cryostat.

Fluorescence lifetimes were measured using the time-correlated single photon counting technique.[29] Samples were excited with a cavity dumped DCM dye laser (Coherent 7210 cavity dumper and 700 Series dye laser) that was synchronously pumped with the second harmonic of a mode locked Nd:YAG laser (Coherent Antares 76-s). The resulting 3.8MHz pulse train could be tuned over the range 610-680nm. The detection system comprised a 0.22m subtractive dispersion double monochromator (Spex 1680), a microchannel plate (Hamamatsu R3809U), a 1GHz amplifier and timing discriminator (EG&G Ortec 9327), a time-to-amplitude converter (Tennelec TC864) and a multichannel pulse to height analyser (Tennelec PCA II). Excitation and detection wavelengths were selected from the steady state data. Solutions in glass forming solvents and polymer films were prepared and mounted in the cryostat as described above. Fluorescence lifetimes were recorded at room temperature, 200K, 125K and 80K.

3. Results

Fluorescence emission has been observed from many of the TCNQ adducts we have synthesised. The emission is more intense for the asymmetrically substituted adducts than for the symmetrically substituted compounds we have studied. We have, therefore, concentrated our studies on two asymmetrically substituted adducts one with two distinct substituents (MORPIP) and one with an asymmetrically substituted fused ring (AMINO). The structure of these compounds is, in general, intermediate between the two limiting forms, the neutral state with quinoid structure and the fully charge separated zwitterionic state with benzenoid structure, [5, 10, 26, 30] which are shown in Figure 1. The actual structure will be determined by the reaction field acting on the molecule, [10, 31] which will depend on the environment, e.g. on solvent polarity. X-ray crystallographic data show that the electron donor moieties (amino groups) and the π-conjugation unit (the benzene ring) are not coplanar. [6, 9, 26, 30] The twist angle between the molecular components is approximately 45°. In addition the observed and calculated ground state dipole moments are large.[6, 10, 11, 13, 32] Thus, these molecules are expected to show sizeable solvatochromism and be affected by the constraints placed on changes in molecular conformation by rigid matrices.

The combined effect of the solvatochromic shift of the ground and excited electronic energy levels gives rise to a solvent dependent Stokes' shift. There is an extensive literature on the modelling of solvent-solute interactions.[33] However, a simple approach leading to the Lippert equation, is often adequate.[19, 34, 35, 36, 37, 38] In terms of the dielectric constant (ε) and refractive index (n) of the medium the absorption and emission energies, relative to the gas phase values, are given by

$$v_{\mathrm{max}}^{\mathrm{abs}} = v_0^{abs} - \frac{2\mu_g(\mu_e - \mu_g)}{hca^3}\left[\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right)\right] \tag{1}$$

$$v_{\mathrm{max}}^{\mathrm{em}} = v_0^{em} - \frac{2\mu_e(\mu_e - \mu_g)}{hca^3}\left[\left(\frac{\varepsilon - 1}{2\varepsilon + 2}\right) - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right)\right] \tag{2}$$

The Stokes' shift is then given by the difference

$$\Delta v = v_{\mathrm{max}}^{\mathrm{abs}} - v_{\mathrm{max}}^{\mathrm{ems}} = \frac{2(\mu_e - \mu_g)^2}{hca^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right) + \text{constant} \tag{3}$$

Where $\left(((\varepsilon - 1)/(2\varepsilon + 1)) - ((n^2 - 1)/(2n^2 + 1))\right)$ is the polarity parameter (Δf), which is often referred to as the solvent density parameter, μ_e and μ_g are the excited and ground state dipole moments and a is the radius of the spherical Onsager cavity surrounding the solute molecule. Equation 3 is often referred to as the Lippert equation. Alternative forms using different polarity parameters are also used; both forms are modified if the effect of solvent molecule reorientation is included.[34, 39] All have been used to describe the behaviour of chromophores in polar solvents with some degree of success. This reflects the fact that the polarity parameters are somewhat similar to one another. We choose to use the Lippert formalism to provide a consistent analysis of the experimental data. Deviations from the Lippert equation can result from specific solvent interactions,[19, 40] and relaxation of the approximations involved in its derivation.[41, 42] Experimental data is presented below for the different media used as hosts for the chromophores.

3.1 Absorption and emission of alcohol solutions

The intensity of the room temperature emission from alcoholic solutions of MORPIP and AMINO show a strong solvent dependence. This is illustrated in Figure 2, which shows the raw data for the emission of MORPIP solutions. Both emission and absorption spectra for MORPIP and AMINO are broad and featureless, scaled emission spectra and examples of absorption spectra are shown in Figure 3. Comparison of absorption and fluorescence excitation spectra shows that they are identical within experimental error. The variation in the energy of the absorption maximum for MORPIP and AMINO dissolved in normal alcohols, methanol to hexanol, are plotted using Equation 1 in Figure 4. Similar results are obtained for a wider range of solvents, i.e. THF, dichloromethane (DCM), acetone, dimethyl formamide (DMF) and acetonitrile. This trend is not maintained for chloroform, a somewhat less polar solvent. The hypsochromic shift for the more polar solvents is a result of the stabilisation of the benzenoid "zwitterionic" structure. In low polarity solvents the molecules will be close to the intermediate, equal bond length structure.

Although all the emission profiles are similar the Stokes' shift and quantum yields for MORPIP and AMINO vary considerably, as shown in Table 1. The dependence of the Stokes' shifts on Δf for the normal alcohol solutions is plotted in Figure 4 together with the absorption data. For MORPIP the slopes of the best-fit lines to both sets of data are the same within the fitting error, while for AMINO the slopes are similar. These results indicate that the change of the dipole moments between the excited and the ground states must be approximately constant for these solutions and, from Equations 1 and 3, that the excited state dipole must be small. The emission spectra in Figures 2 and 3 bear out this conclusion as they display little dependence on solvent. This is shown quantitatively in Figure 5, where the emission data is plotted according to Equation 2. This shows a negligible dependence of the position of the emission spectra maxima on solvent polarity for MORPIP and a weak dependence for AMINO.

Evidence for specific solvent interactions is shown in Figure 6(a), where the Stokes' shifts for MORPIP and AMINO in diethylene glycol and glycerol do not fit the trend observed for the normal alcohols. Although diethylene glycol ($\Delta f = 0.266$) and glycerol ($\Delta f = 0.265$) have almost the same polarity as butanol ($\Delta f = 0.264$) they have larger Stokes' shifts. These solvents have two and three-dimensional hydrogen bonding networks and high viscosity, 30.2nP for diethylene glycol and 934nP for glycerol. Thus, because of the large difference in viscosity Δf is not an appropriate parameter to model the solvent interaction. However, $E_T(30)$ solvent polarity scale does provide a good fit for the Stokes' shifts for all the solutions considered here, Figure 6(b). This is because the $E_T(30)$ scale is not model based but is an experimentally determined microscopic polarity parameter, which takes into account the solvent-solute interaction.[20]

Similarly we observe that the fluorescence quantum yields in normal alcohols are linearly dependent on Δf, but the values for diethylene glycol and glycerol do not follow this fit, as shown in Figure 7(a). The fluorescence quantum yields of the glycerol solutions are more than ten times larger than that of the normal alcohol solutions. In this instance the use of the $E_T(30)$ scale did not give a better fit to the data, Figure 7(b). This suggests an additional effect for solutions in viscous solvents. Previous studies indicate that this is due to the constraint placed on changes in molecular conformation during excitation by the hydrogen-bonding networks.[24, 25]

3.2 Glass forming solvents

Solvents that form low temperature glasses have been extensively employed as matrices for fluorophores.[43, 44] If the increase in fluorescence quantum yield in viscous solvents is due to the constraining effect of the hydrogen bonding network a similar effect can be anticipated in glassy matrices. Suitable glass forming solvents are 1-propanol, [24, 45] 2MTHF [46] and a 2:2:5 mixture of ether, ethanol and isopentane (EPA).[47] The use of 1-propanol glasses allows a direct comparison to be made with the room temperature solution data. Spectra were recorded for MORPIP in 1-propanol, 2MTHF and EPA glasses and for AMINO in an EPA glass. A summary of data obtained for MORPIP and AMINO at 294K and 80K in these solvents is given in Table 2.

The absorption and emission spectra of MORPIP in 1-propanol as a function of temperature are shown in Figure 8. The absorption spectra became sharper at low temperature but with no indication of any vibronic structure, the small feature just below 26,000cm^{-1} is an instrumental artefact. Thus, inhomogeneous broadening[48] dominates even at 80K. There is an increase in optical density, which is commensurate with the observed narrowing of the absorption band. The shift of the absorption maximum to higher energy is commensurate with the increased density and polarity parameter (Δf) at low temperatures. Cooling produces a larger shift in the position of the emission maximum than that of the absorption maximum, c.f. Figure 8. The nett effect is that the Stokes' shift decreases from ca. 4,400cm^{-1} at room temperature to ca. 2,900cm^{-1} at 80K. The increase in density and Δf at low temperature would be expected to give a larger Stokes' shift, c.f. Equation 1. Thus, the constraint placed on molecular conformation by the glassy matrix has a significant effect on the emission process. Precise determinations were not made of the fluorescence quantum efficiencies below room temperature. However, a dramatic increase in emission intensity was observed in the glassy phase, which is formed at ca.200K, c.f. Figure 7(b). The integrated emission intensity rises sharply below 250K becoming approximately constant below 200K, Figure 10. The quantum yield is estimated to be 13% at 80K compared with room temperature value of 0.4%. Non-radiative decay is cut off at low temperature[44] so the increase of emission intensities is influenced both by this and by changes in the interaction of the MORPIP with the host medium.

In contrast the data for MORPIP in 2MTHF, Table 2, show that the maximum of the absorption and emission spectra shifts by smaller, similar, amounts between 294K and 80K. Consequently, there is a small increase in Stokes' shift between 294K and 80K. If this shift is attributed solely to the solvatochromic shift, which results from the density change of the medium, then on the basis of the trend line in Figure 4(b) Δf must increase by ca. 0.02 between 294K and 80K. While data is available for the dielectric constant (ε) over the range 296K to 208K comparable data is not available for the refractive index (n); however, on the basis of data for similar solvents Δf should increase by ca. 0.03 over this temperature range. Thus, the observed change in Stokes' shift is somewhat smaller than expected if it is due solely to solvatochromism. Emission spectra of MORPIP in 2MTHF at various temperatures are shown in Figure 9. The increase in emission intensity (i.e. quantum yield) at low temperatures is similar to that for the 1-propanol glass, c.f. Figure 10.

For MORPIP in EPA the shifts in the maximum in absorption and emission between 294 and 80K are similar and there is a small decrease in the Stokes' shift, c.f. Table 2. Over the same temperature range there is a distinct difference between the shifts with temperature for the maximum in absorption and emission of AMINO in EPA although the values are the smallest measured, c.f. Table 2. This results in a significant increase in Stokes' shift for AMINO in comparison to a decrease for MORPIP.

3.3 Crystalline powders

Fluorescent emission from a TCNQ adduct was first observed visually for microcrystalline powder formed above an acetonitrile solution in a test tube. The fluorescence quantum yields were determined for thin layers of micro-crystals spread on a non-fluorescent silica substrate in the integrating sphere apparatus. Values obtained for the PLQY lie in the range 2 to 10%. We attribute this variation to the difficulty in obtaining rapidly precipitated powders with consistent crystallite size and quality.

3.4 Polymer matrices

Films of PMMA and PC containing MORPIP and AMINO were prepared by spin and dip coating. PMMA films containing MORPIP were obtained from solutions in DMF, tri-methyl urea (TMU) and DCM and films containing AMINO were obtained from DMF and TMU solutions. PC films containing MORPIP were obtained from DCM solutions. These films were used to determine fluorescence quantum yields at room temperature, in the integrating sphere apparatus, and study the temperature dependence of the absorption and emission spectra from room temperature down to 80K. Absorption and emission spectra for films containing MORPIP prepared from DMF and TMU solutions at room temperature, 200 and 80K are shown in Figure 11. Initial visual observations suggested that the fluorescence intensity was dependent on the solvent used to produce the PMMA films. However, this was not confirmed by quantitative measurements, which are the same within experimental error. Room temperature and low temperature data are listed in Tables 3 and 4, respectively. Quantitative data was not obtained for the AMINO samples but qualitatively the emission observed was comparable to that from the MORPIP in PC sample.

At 80K the intensities of emission for MORPIP in the PMMA films prepared from TMU and DMF solutions was about 2 and 3 larger than that at 294K, c.f. Figure 11. This is in contrast with the much larger increase, ca thirty to one hundred times, of the emission intensity between room and low temperature in glass forming solvents. This reflects the modest changes in density in the polymer films and the large change from a fluid to a glassy matrix in the glass forming solvents.

3.5 Fluorescence lifetime

The fluorescence lifetime of MORPIP in 1-propanol was determined at 294 and 80K by the time resolved single photon counting technique. The sample was excited at 340nm and the emission was detected at 520nm at 294K and 450nm at 80K close to the emission maximum at these temperatures, c.f. Table 2. The fluorescence decays observed are shown in Figure 12. The decay time at room temperature was too short to measure the temporal profile of the observed emission being essentially identical with that of the excitation pulse. The 80K signal was fitted with a single exponential decay with a lifetime of 2.5 ± 0.2 nanoseconds. The quality of fit was good with a small, random residue and a quality of fit parameter of 1.1, value of 1.0 corresponding to a perfect fit.[29]

4. Discussion

In principle equations 1 to 3 can be used to estimate the μ_g and μ_e for MORPIP and AMINO. However, the values obtained depend crucially on the factor a^3, where a is the radius of the Onsager cavity enclosing the molecule in solution. The model of a spherical cavity is widely applied although it is clear that for elongated molecules a more complex model with an ellipsoidal cavity should be used.[10, 49] While this approach is strictly correct the additional complication is not justified given that the analysis will not yield precise values. The crystal structure of MORPIP gives a volume per molecule of ca. 530 Å^3.[11, 13] If this is taken as the volume of the Onsager cavity then $a \approx 4$Å. The slopes of the plots of absorption and emission maxima and the Stokes shift for MORPIP, Figures 4 and 5, are 19700 ± 3300 cm^{-1} (R = 0.948), 160 ± 1700 cm^{-1} (R = -0.049) and 18100 ± 2800 cm^{-1} (R = 0.956), respectively. Using this data the values found are $\mu_g = 12 \pm 5$ D and $\mu_e = -0.1 \pm 1$ D, respectively. Crystal structure data is not available for AMINO. However, although AMINO has only one bulky substituent the molecular volume will be similar to that of MORPIP so that $a \approx 4Å$ is a reasonable approximation. The slopes of the plots of absorption and emission maxima and the Stokes shift for AMINO, Figures 4 and 5, are 32400 ± 2700 cm^{-1} (R = 0.984), 3500 ± 800 cm^{-1} (R = 0.913) and 25100 ± 1200 cm^{-1} (R = 0.995), respectively.. In this case μ_g = 16 ± 3 D and μ_e = 2 ± 1 D. The value obtained for μ_g from the spectral data is similar to that of 15D found both theoretically and experimentally, in chloroform, DCM and acetone, for MORPIP.[11, 13] This agreement is reasonable given the approximations involved, the ellipsoidal shape of the molecules and the large value of μ_g.

Use of different analyses does not yield significantly better results. The method of Koutek[50] has been shown by Ravi et al[51] and Kumar et al[52] to give reasonable results for μ_e for molecules with modest μ_g, i.e. 3-7D. Fitting data for MORPIP and AMINO leads to values for μ_g and μ_e of ca. 5 and 1D, respectively. The former is much smaller than the value of 15D determined for MORPIP and the latter does not reflect the difference in solvent dependence of the fluorescence, Figure 5, between AMINO and MORPIP.

The fluorescence quantum yields of MORPIP and AMINO dissolved in normal alcohols fall in the range 0.1 to 1% (Table 1). The values are larger, up to 20%, in the viscous solvents diethylene glycol and glycerol. The values for AMINO are about twice those found for MORPIP in the same solvent. When the Stokes' shifts are plotted as a function of polarity parameter (Δf) the results for the viscous solvents depart from the trend for the other alcohols, Figure 6(a). Although this discrepancy is removed when the parameter $E_T(30)$ is used rather than Δf , Figure 6(b), the quantum yield data for the viscous solvents remain anomalous, Figure 7, showing a strong effect of solvent viscosity on fluorescence intensity. The fluorescence properties of chromophores, which undergo large conformational changes on photo-excitation, are strongly influenced by solvent viscosity. Tetra-phenyl ethylene (TPE) has been extensively studied. [25, 53, 54] The lifetime of TPE increases from 6ps in low viscosity solvents to 60ps in ethylene glycol and 600ps in glycerol.[25] This has been attributed to the viscous media hindering the rotation of the phenylene moieties thereby limiting non-radiative decay of the excited state, which is induced by the torsion motion of the phenylenes. A decrease in non-radiative decay will lead to an increase in fluorescence quantum yield as observed for MORPIP and AMINO.

There is other experimental evidence that there are significant conformational changes between ground and excited state in the TCNQ adducts. As noted earlier X-ray crystallographic data show that the electron donor moieties (amino groups) and the π-conjugation unit (the benzene ring) in the TCNQ adducts are not coplanar.[6, 9, 26, 30] In MORPIP and related compounds the twist angle between the molecular components in the molecular ground state is approximately 45°. Despite this both theory and experiment show that the ground state dipole moments of these molecules are large.[6, 10, 11, 13, 55] As noted above for MORPIP μ_g is found to be approximately constant at ca. 15 Debye in chloroform, DCM and acetone solutions. This is in accord with the result that for alcohol solutions the change in dipole moment on excitation is constant and $\mu_e \cong 0$, i.e. μ_g is approximately constant. This behaviour is somewhat different from that of adducts made with tertiary amines, which are rigid planar molecules. The dipole moments of these molecules increase as the polarity of the solvent is increased.[10, 56] Thus, we deduce that the molecular geometry of MORPIP does not remain fixed as the molecular environment, e.g. solvent polarity, is changed. The small value of μ_e is, therefore, likely to be a consequence of a change in the torsion angle between the component parts of the molecule.

MOPAC96-AMI calculations give a larger value for μ_e for a planar geometry (~10D) than for a 90º twist (~6D).[7] However, these values are significantly larger than we find experimentally. Recently these calculations have been performed for a series of adducts with twist angles between ~40º to ~75º and give values for μ_e in the range 9 to 13D, all much larger than our result. However, theoretical modelling using *ab initio* methods shows that the dipole moment increases as the twist angle increases and that the excited state has a more planar geometry. Hence, we believe that in low viscosity solvents these molecules undergo significant changes in conformation on photo-excitation. Restriction of the change in molecular conformation by viscous solvents leads to enhanced fluorescence, i.e. the relaxed excited state has a low fluorescence quantum yield, while that of the hindered excited state is much higher.

This hypothesis is also capable of explaining the trends observed with solid matrices. The molecular packing in a crystal lattice will leave limited free volume for molecular deformation on photo-excitation. Hence, a larger fluorescence quantum efficiency is to be expected for crystals than for solutions, as visually observed.

We note that the steric hindrance for AMINO, due to the bulky cyclo-hexyl group attached to the cyclic substituent will be much greater than for MORPIP, see Figure 1.

Molecular modelling shows that a twist angle of 45° between the molecular sub-units is possible for AMINO, with some slight deformation of the molecular framework. However, a large reduction in twist angle on excitation is not possible. This suggests a smaller change in molecular conformation as a function of solvent polarity and on excitation for AMINO than for MORPIP. It also offers an explanation for the non-zero value of μ_e for AMINO and the higher fluorescence intensity for AMINO in all the solvents used. As the viscosity of diethylene glycol and glycerol derive from hydrogen-bonding network they will interact strongly with AMINO and produce significant effects on the fluorescence despite the increased inflexibility of this molecule.

The effects that are observed for polymer matrices and glass forming solvents can be explained in the same general terms. The differences in spectra and fluorescence quantum yield in the polymer matrices reflect both the polarity and density of the media. PC has a higher polarity then PMMA and a distinct spectral shift is observed. The differences in quantum efficiency reflect differences in the free volume available in the different polymers. Although fluorescence intensity for MORPIP in glass forming solvents was not determined as precisely as that of the room temperature solutions and films a dramatic increase from an initially small value was observed on cooling to 80K.

The increase in fluorescence for polymer films over the same temperature range was much smaller. This reflects the change from a fluid to a solid environment as the glass forms. Initially the adduct is free to relax with minimal constraint giving a low fluorescence quantum efficiency. This increases as the solvent viscosity increases constraining the changes in molecular conformation on excitation and becomes constant as the glass solidifies into a phase with low thermal expansion, c.f. Figure 10. By comparison the polymers films undergo some contraction and reduction in free volume on cooling but the change in the molecular environment is much less pronounced than for the glass forming solvents.

The fluorescence lifetime measurements provide further evidence that rapid non-radiative decay occurs when the adducts are dissolved in low viscosity solvents while viscous and solid matrices constrain molecular relaxation and open up a radiative decay channel. The decay of the fluorescence of MORPIP in propanol at room temperature, shown in Figure 12(a), is identical with the laser excitation pulse. Thus, the excited molecules decay on a time scale either comparable to or shorter than the instrumental resolution, i.e. $\leq$30psec. However, at 80K the decay is well characterised by a single exponential with a time constant of 2.5nsec, Figure 12(b). Some increase in fluorescence and lifetime is to be expected at low temperatures due to the reduction in thermally induced non-radiative decay. However, the large changes observed are indicative of a significant change in the character of the emission process, from a predominantly non-radiative process in solution at room temperature to a predominantly radiative process in the glass at low temperature.

Similar data has been obtained for other adducts with different substituents so we believe that the behaviour reported here for MORPIP and AMINO is representative of this class of compounds. The molecules have large μ_g and a molecular conformation in which the plane of the substituents is twisted with respect to the conjugated ring and CN moieties. When the molecules are free to relax the excited state has a much smaller μ_e and the molecular geometry is less twisted and may in some instances be close to planar, e.g. MORPIP. At room temperature the decay from this state is predominantly non-radiative. In environments where the molecular relaxation is inhibited decay can occur by a radiative process. In situations where the constraint imposed by the environment is strong the radiative pathway is strongly favoured. This behaviour may be viewed as an inverse of that where the ground state is planar and the excited state is twisted with greater charge transfer in the excited state, i.e. TICT.

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Figure Captions

Figure 1 Molecular structures of (a) MORPIP, shown in the extreme quinoid and benzenoid forms, and (b) AMINO, shown in the quinoid form.

Figure 2 Unscaled emission spectra of MORPIP in alcoholic solvents. From least to most intense spectra the solvents are methanol, ethanol, propanol, butanol, pentanol, hexanol, diethylene glycol and glycerol.

Figure 3 Absorption (to the right) and emission spectra (to the left) for (a) MORPIP and (b) AMINO in solution in methanol (squares), propanol (circles), hexanol (triangles), pentanol (star), diethylene glycol (inverted triangles), and glycerol (diamonds). The fluorescence spectra have been multiplied in (a) by factors of 15, 7, 4, 4 and 1 and in (b) by factors of 20, 10, 6, 5 and 1 for methanol, propanol, hexanol, diethylene glycol and glycerol solutions respectively. The emission was excited at the peak of the photo-excitation spectrum/ at 375 nm.

Figure 4 The energy of the absorption maximum (triangles) and Stokes' shift (diamonds) plotted according to Equations 1 and 3 for (a) MORPIP and (b) AMINO dissolved in normal alcohols (methanol to hexanol).

Figure 5 Observed shifts in emission maxima, with excitation at the peak of the photo-excitation spectrum/ at 375 nm, for alcohol solutions of MORPIP (squares) and AMINO (circles) plotted according to Equation 2.

Figure 6 Stokes' shift for alcohol solutions of MORPIP (squares) and AMINO (circles) plotted versus (a) Δf and (b) $E_T(30)$.

Figure 7 Fluorescence quantum yield for alcohol solutions of MORPIP (squares) and AMINO (circles) plotted versus (a) Δf and (b) $E_T(30)$. The trend lines are shown for the normal alcohols; MORPIP, full line: AMINO, dash line.

Figure 8 (a) Absorption and (b) emission spectra of MORPIP in 1-propanol at 294 (triangles), 200 (squares), 150 (circles) and 80K (diamonds).

Figure 9	Emission spectra of MORPIP in 2-methyl THF at 294 (triangles), 200 (squares), 150 (circles) and 80K (diamonds).
Figure 10	Integrated emission intensity of MORPIP in 1-propanol (squares) and 2-methyl THF (circles) as a function of temperature.
Figure 11	Spectra of the MORPIP doped PMMA films (a) absorption (right) and emission (left) for films cast from DMF solution at 294 (triangles), 200 (circles) and 80K (diamonds), (b) excitation (right) and emission (left) for films cast from TMU solution at 294 (triangles), 200 (circles) and 80K (diamonds).
Figure 12	Fluorescence decay of the emission of MORPIP dissolved in 1-propanol at (a) 294 and (b) 80K.

Table 1. Stokes' shifts and quantum yields for alcohol solutions of MORPIP and AMINO at room temperature.

Solvent	MORPIP		AMINO		Δf	Viscosity (nP) [c]
	Stokes' shift (cm^{-1}) [a]	Quantum yield (%)[b]	Stokes' shift (cm^{-1}) [a]	Quantum yield (%)[b]		
Methanol	5160	0.1	7380	0.22	0.309	0.544
Ethanol	4620	0.1	6770	-	0.290	1.07
1-Propanol	4240	0.4	6500	0.53	0.275	1.95
1-Butanol	4150	0.5	6160	-	0.264	2.54
1-Pentanol	3970	0.7	6010	1.3	0.254	3.62
1-hexanol	4010	1.0	5670	-	0.243	4.58
Diethylene Glycol	5040	1.4	7990	2.32	0.266	30.2
Glycerol	5400	11.8	6630	21.8	0.265	934

a: accuracy ± 100cm^{-1}, b: accuracy ca. ± 10% of value, c: the values of viscosity were taken from CRC solvent handbook.

Table 2 Observed changes in spectra of MORPIP and AMINO in glass forming solvents at room and low temperature.

	Solvent (K)	Absorption Maximum (cm^{-1}) [a]	Emission Maximum (cm^{-1}) [b]	Absorption Shift (cm^{-1}) [c] 294 to 80 K	Emission Shift (cm^{-1}) [d] 294 to 80 K	Stokes' Shift (cm^{-1}) [e]
MORPIP	Propanol (294)	23600	19200			4400
	(80)	24900	22000	1300	3000	2900
	2MTHF (294)	21400	18300			3100
	(80)	22700	19200	1300	900	3500
	EPA (294)	22500	19530			3000
	(80)	25100	22570	2600	2990	2600
AMINO	EPA (294)	27030	24070			2960
	(80)	28520	24420	1200	350	3830

a: accuracy ± 50 cm^{-1}, b: accuracy ± 100 cm^{-1}, c: accuracy ± 100 cm^{-1},

d: accuracy ± 100 cm^{-1}, e: accuracy ± 70 cm^{-1}

Table 3 Room temperature absorption and emission data for polymer films containing MORPIP and AMINO obtained from different solvents.

Adduct	Polymer	Casting solvent	Absorption maximum (cm^{-1})^{a}	Emission maximum (cm^{-1})^{a}	Stokes' shift (cm^{-1})^{b}	Quantum Yield (%)^{c}
MORPIP	PMMA	DMF	22620	19100	3520	21
		TMU	22570	19250	3320	21
		DCM	22420	18760	3660	19
	PC	DCM	21930	18330	3600	7 ± 2
AMINO	PMMA	DMF	26950	21210	5740	^{d}
		TMU	26980	21340	5640	^{d}

a: accuracy ± 50 cm^{-1}, b: accuracy ± 100 cm^{-1}, c: accurate to ± 5% of value unless noted, ^{d} see text.

Table 4 Low temperature absorption and emission data for polymer films containing MORPIP obtained from DMF and TMU solutions.

Casting solvent	Temperature (K)	Absorption maximum (cm^{-1})[a]	Emission maximum (cm^{-1})[a]	Stokes' shift (cm^{-1})[b]
DMF	294	22400	18200	4200
	200	22400	18500	3900
	80	22700	18700	4000
TMU	294	22400	18900	3500
	200	22400	1900	3400
	80	22600	19200	3500

a: accuracy ± 100 cm^{-1}, b: accuracy ± 200 cm^{-1}.

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