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Matrix dependence of blue light emission from a novel NH_2-functionalized dicyanoquinodimethane derivative

Marek Szablewski,[1]* David Bloor,[1] Yasuyuki Kagawa,[1†] Ravi Mosurkal,[1‡] Jacqueline M. Cole,[2¶] Stewart J. Clark,[1] Graham H. Cross[1] and Lars-Olof Pålsson[1]

[1]Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK
[2]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

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ABSTRACT: The reactions of primary and secondary amines with (cyclohexa-2,5-diene-1,4-diylidene)-dimalononitrile (TCNQ) lead to mono- and disubstituted dicyanoquinodimethane derivatives and fluorescence emission has been observed for several of these compounds. We report the luminescence properties, synthesis and crystal structure of the novel dicyanoquinodimethane derivative 2-{4-[amino-(2,6-dimethyl-morpholin-4-yl)-methylene]-cyclohexa-2,5-dienylidene}-malononitrile (Ammor), a unique example of an asymmetric dicyanoquinodimethane derivative in which one of the nitrile groups has been replaced with an NH_2 moiety, which provides a reactive centre for potential further substitution or tethering to larger molecules or polymers. The luminescence properties of the title compound were investigated in a variety of environments, including alcohol solutions at room temperature and a glass-forming solvent at low temperature. The fluorescence quantum yields and Stokes' shifts of the blue emission were found to be very sensitive to the matrix. The crystal structure of the subject compound was determined, revealing that the molecules are non-planar in the ground state. The environmentally sensitive emission is discussed in terms of the conformational change during photoexcitation and the constraint imposed on this by the matrix. This behaviour is also compared with that of other related amino-functionalized dicyanoquinodimethane derivatives. Copyright © 2006 John Wiley & Sons, Ltd.

KEYWORDS: TCNQ; matrix-dependent fluorescence

INTRODUCTION

The chemistry of adducts of TCNQ (cyclohexa-2,5-diene-1,4-diylidene)-dimalononitrile) has been the focus of research[1–3] ever since TCNQ was first synthesized[4] and its basic chemistry studied[5–12] between 1962 and 1964. Substitution of one or two nitrile groups by a range of primary, secondary and tertiary amines is well documented,[7,13] leading to the recent synthesis of a range of mono and bisubstituted dicyanoquinodimethane derivatives.[14–17] In contrast, substitution of one of the nitrile groups of TCNQ with an NH_2 moiety has been reported only twice. The bis amino derivative 2-(4-diaminomethylene-cyclohexa-2,5-dienylidene)-malononitrile (**1**, Fig. 1), was prepared by the direct action of ammonia on a THF solution of TCNQ,[7] whereas the preparation of 2-[4-(amino-pyrrolidin-1-yl-methylene)-cyclohexa-2,5-dienylidene]-malononitrile (**2**, Fig. 1) was carried out by the action of ammonia in THF on 2-[4-(cyano-pyrrolidin-1-yl-methylene)-cyclohexa-2,5-dienylidene]-malononitrile.[18] The availability of a 'free' NH_2 has implications on the luminescence properties of the molecule as well as providing a reactive centre on the chromophore that could act as a tethering site to larger macromolecules or polymers.

In this paper we describe a novel procedure for the synthesis of a dicyanoquinodimethane derivative in which two of the TCNQ nitrile groups have been substituted, one with a 2,6-dimethylmorpholino moiety and one with an NH_2 group. The compound 2-{4-[amino-(2,6-dimethyl-morpholin-4-yl)-methylene]-cyclohexa-2,5-dienylidene}-malononitrile ('Ammor') (**5**, Fig. 1) was synthesized by the unexpected reaction of 1,3-bis(3,3,3-trifluoropropyl) tetramethyl disilazane on 2-{4-[cyano-(2,6-dimethyl-morpholin-4-yl)-methylene]-cyclohexa-2,5-dienylidene}-malononitrile, in contrast to the two previous examples of such compounds in which the presence of the free amino group in the product was achieved by the direct action of ammonia.

These derivatives have recently attracted renewed interest because of their non-linear optical properties. Most of these investigations have concentrated on the properties of single crystals.[14,15,19–22] These compounds

**Correspondence to:* M. Szablewski, Department of Physics, University of Durham, South Road, Durham DH1 3LE, UK.
E-mail: marek.szablewski@dur.ac.uk
†Present address: Corning International K.K., 35 Kowa Bldg, 3rd Floor, 14-1-4 Akasaka1-chome, Minatoku, Tokyo 107-0052, Japan.
‡Present address: Center for Advanced Materials, University of Massachusetts, 1 University Ave, Lowell, MA 01854, USA.
¶Office mailing address: St. Catherine's College, Cambridge, CB2 1RL, UK.

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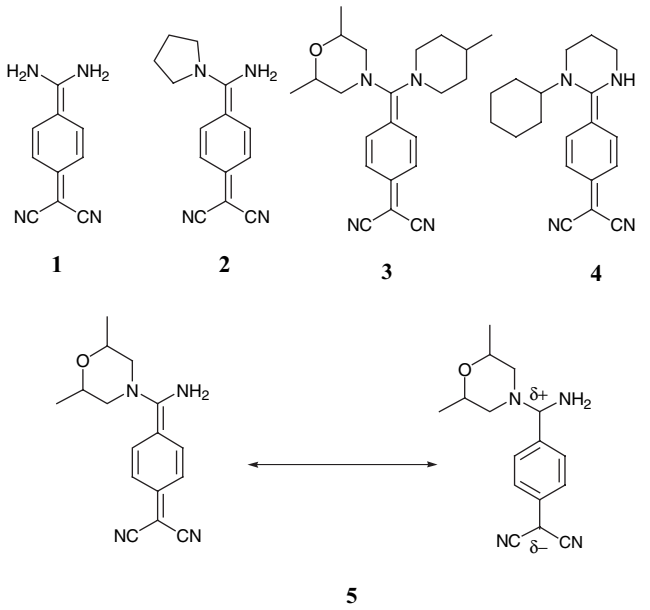

Figure 1. Molecular structures of dicyanoquinodimethane derivatives: (**1**) 2-(4-diaminomethylene-cyclohexa-2,5-dienylidene)-malononitrile, (**2**) 2-[4-(amino-pyrrolidin-1-yl-methylene)-cyclohexa-2,5-dienylidene]-malononitrile, (**3**) 2-{4-[(2,6-dimethyl-morpholin-4-yl)-(4-methyl-piperidin-1-yl)-methylene]-cyclohexa-2,5-dienylidene}- malononitrile ('Morpip'), (**4**) 2-[4-(1-cyclohexyl-tetrahydro-pyrimidin-2-ylidene)-cyclohexa-2,5-dienylidene]-malononitrile ('Amino') and (**5**) 2-{4-[amino-(2,6-dimethyl-morpholin-4-yl)-methylene]-cyclohexa-2,5-dienylidene}-malononitrile ('Ammor'); the limiting neutral and zwitterionic structures of Ammor are shown

have structures that are intermediate between the limiting forms, the charge-separated (zwitterionic) form with a benzenoid structure and the neutral form with a quinoid structure, as shown in Fig. 1. In a given environment the structure is determined by the reaction field acting on the molecule,[23] e.g. in solution it is dependent on solvent polarity. Crystal structures show that the molecules are not planar. Typically the twist angle between the planes of the electron donor moieties and the π-conjugation unit is ca. 45°. In addition, the observed and calculated ground-state dipole moments are large.[24–26] Thus, these molecules are expected to show sizeable solvatochromism and this has been used to estimate the molecular hyperpolarizibity (β).[25] The product $\mu\beta$, which is a useful figure of merit for characterizing the second-order nonlinearity of poled polymer films containing the chromophores,[27] is found to be large. Thus, there is interest in the development of these dicyanoquinodimethane derivatives as the active components of electro-optical polymers.

In addition to the interesting non-linear optical properties we have discovered that certain dicyanoquinodimethane derivatives, e.g. 'Morpip' (**3**) and 'Amino' (**5**) (Fig. 1), show intense fluorescence in specific environments or under certain conditions.[24] This topic has also attracted interest following the discovery of efficient electroluminescence from organic light-emitting chromophores and its use in light-emitting devices.[28–30] Electroluminescence has also been observed for one of our adducts.[31] Photoluminescence is simpler to observe than electroluminescence and has been used extensively to characterize materials with potential for use in electroluminescence devices. The parameters of interest are the radiative lifetimes and fluorescence quantum yields, both quantities that are determined in solution [32] as well as in the solid state (films). Fluorescence spectra are affected by solvent polarity and the solvatochromism, which can be large for polar molecules,[33] providing information about the dipole moment of the excited state.[24] Fluorescence is also affected by solvent viscosity.[34] Alcohols provide a solvent system where both polarity and viscosity can be varied. A study of fluorescent lifetimes and quantum yields was undertaken for Ammor in solution in normal alcohols, diethylene glycol and glycerol.

The polarity of the solvent can be changed for normal alcohols by extending the molecular length.[35,36] The viscosity of the solvent can be controlled by changing the number of hydroxyl groups, which leads to enhancement of the hydrogen-bonding network in the medium and increased viscosity, e.g. as in diethylene glycol and glycerol.[37,38] Further studies of the interactions of these dyes in liquid-crystal hosts and on the fluorescence of such systems have been reported elsewhere.[39,40]

EXPERIMENTAL

Materials

(Cyclohexa-2,5-diene-1,4-diylidene)-dimalononitrile (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. 1,3-Bis(3,3,3-trifluoropropyl) tetramethyl disilazane was obtained from Fluorochem Ltd. All solvents used were HPLC grade. These chemicals were used without further purification.

Synthesis

2-{4-[Amino-(2,6-dimethyl-morpholin-4-yl)-methylene]-cyclohexa-2,5-dienylidene}-malononitrile (Ammor) (5, Fig. 1). To 2-{4-[cyano-(2,6-dimethyl-morpholin-4-yl)-methylene]-cyclohexa-2,5-dienylidene}-malononitrile[14] (0.39 g, 1.33 mmol) in THF (30 ml) heated at 50 °C was added 1,3-bis(3,3,3-trifluoropropyl) tetramethyl disilazane (0.47 ml, 1.2 equiv.), which was then stirred for 4 h at 50 °C. A brown precipitate was observed. The solution was cooled to room temperature and stirred overnight. The precipitate was collected by filtration and dried under vacuum. Recrystallization of the solid was carried out in hot methanol. A light green/yellow powder was obtained (0.20 g, 54%).

^{1}H NMR (d_6DMSO): d 9.1 ppm, 8.7 ppm, singlets—N—H_2 (2H), d 7.2 ppm, 6.8 ppm, doublet- bisubstituted

quinoidal ring protons (4H); d 1.1 ppm, broad singlet—CH_3 (6H); d 3.0 ppm and d 3.7 ppm, broad multiplets (6H), morpholine ring protons. IR: 3350 cm^{-1}, 3161 cm^{-1} (aliphatic primary amine), 2171 cm^{-1}, 2126 cm^{-1}(CN), 1595 cm^{-1} (N—H bending vibration), 1326 cm^{-1} (C—N stretching of the primary amine). MS: 281.03 ($M^+ - 1$) (50% base) EI^+. Decomposition temp 260 °C. λ_{max} (acetonitrile) 394 nm.

Fluorescence and absorption spectra

Absorption spectra were recorded with a Perkin-Elmer Lambda 19 spectrophotometer. Fluorescence and photoexcitation spectra were recorded at room temperature using a Jobin Yvon Horiba Fluoromax 3 spectrometer.

Ammor solutions were prepared in methanol, ethanol, 1-propanol, 1-butanol, 1-pentanol, 1-hexanol, ethylene glycol and glycerol without degassing. Solutions were filtered (0.5 μm filters) and diluted to give an optical density of 0.055 ± 0.01 at 375 nm. The fluorescence quantum yield was measured according to the comparative method.[41] Quinine sulphate dihydrate in 0.5 M sulphuric acid with the same optical density was used as a reference solution. The quantum yield for quinine sulphate dihydrate is relatively temperature independent and has a value of 51%.[42] The quantum yields of the Ammor solutions were determined from a comparison of the integrated emission intensity of the samples with that of the quinine sulphate dihydrate solution. Constant slit widths were used for all the measurements.

Fluorescence spectra were recorded at low temperature with an ISA Fluoromax fluorimeter. Ammor solutions were prepared in 1-propanol, a glass-forming solvent. The optical density at the absorption maximum of these solutions was kept below 0.5. Samples were placed in a special low-temperature cuvette inside an Oxford Instruments cryostat. Emission spectra were recorded over the range from room temperature to 80 K; the sample temperature was stabilized using an Oxford Instruments temperature controller.

The time-correlated single photon counting technique was used to determine fluorescence lifetimes.[43] The excitation source was a cavity dumped DCM dye laser (Coherent 7210 cavity dumper and 700 Series dye laser) synchronously pumped by the second harmonic of a mode-locked Nd:YAG laser (Coherent Antares 76-s). This provides a 3.8 MHz pulse train that could be tuned between 610 and 680 nm. Sample emission was detected using a 0.22 m double monochromator (Spex 1680), a microchannel plate (Hamamatsu R3809U), a 1 GHz 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). 1-Propanol solutions were prepared and mounted in the cryostat as described above. Fluorescence lifetimes were recorded at room temperature and 80 K.

X-ray diffraction

Single-crystal x-ray diffraction was used to determine the crystal structure of Ammor. Single crystals were grown by slow evaporation of Ammor from methanol and thence mounted onto an Enraf Nonius CCD diffractometer, using the oil-drop method. Graphite monochromated Mo Kα radiation (0.71073 Å) was employed for the experiment, at a sample temperature of 180(2) K, using an Oxford Cryosystems Cryostream. Data were collected covering a hemisphere of reciprocal space, affording 99% of all unique data, out to the 2θ value of 40 °. Cell parameters were refined by applying the HKLScalepack software package[43] to data from all regions of reciprocal space at the point of data reduction, which employed HKLDenzo and Scalepack programs.[44] An empirical absorption correction was applied to the resulting data.[45] There was no evidence for any crystal decay during the experiment. The structure was solved by direct methods using SHELXS-97[46] and subsequent difference Fourier synthesis and then refined by full-matrix least-squares methods on F^2 using SHELXL-97.[46] Atomic scattering factors were taken from *International Tables for Crystallography, Volume C, Mathematical, Physical and Chemical Tables*.[47] Positional and anisotropic displacement parameters were refined for all non-hydrogen atoms. Positional parameters for hydrogen atoms were modelled according to their expected geometry and their isotropic displacement parameters were modelled using the riding formalism $U_{iso}(H) = 1.2\,U_{iso}(C)$, except for the methyl hydrogen atoms where $U_{iso}(H) = 1.5U_{iso}(C)$. All crystal, data collection and refinement parameters are available from the Cambridge Crystallographic Data Centre, deposition number CCDC 283409.

Calculations

The calculations have been carried out within the *ab initio* density functional formalism using the CASTEP code.[48] We use the generalized gradient approximation[49] for the exchange and correlation interaction, which gives improved accuracy on molecular properties over the local spin density approximation[50] Ultrasoft *ab initio* pseudo potentials[51] were used to describe the ion-valence electron interactions. The valence electronic wave functions have been expanded in a plane-wave basis set using an energy cut-off of 380 eV, which converges the total energy of the unit cell to better than 2 meV $atom^{-1}$. We used a preconditioned conjugate gradient method[52] to minimize the total energy and also conjugate gradients to relax the ionic positions under the influence of the Hellmann–Feynman forces. The electronic charge density of the relaxed structure is used to calculate the dipole moment. For excited-state calculations a similar method is used except that a constrained conjugate gradient minimization is used to retain an electron in the first excited state.

RESULTS AND DISCUSSION

X-ray crystallography

The crystal structure of Ammor is shown in Fig. 2. The dicyanoquinodimethane component that is common to all dicyanoquinodimethane derivatives (i.e. all atoms shown to the left of N3 in Fig. 2) is very similar to Morpip (**3**, Fig. 1), as judged by the similar nitrile bond geometries and the results of a bond-length alternation (BLA) analysis of Ammor and Morpip, which follows the calculation methodology of Ref. 15.

$$D^{S}_{TCNQ} = \sum_{i=l}^{N_b} |b^{s}_{i} - b^{TCNQ}_{i}|/N_b$$

$$\chi_s = [(D^{ZWIT}_{TCNQ} - D^{s}_{TCNQ})/D^{ZWIT}_{TCNQ}] \times 100$$

where D^{S}_{TCNQ} represents the deviation of structure S from that of TCNQ (comprising a purely quinoidal electronic configuration) ($D^{AMMOR}_{TCNQ} = 0.037625$; $D^{MORPIP}_{TCNQ} = 0.03525$), D^{ZWIT}_{TCNQ} represents the deviation of the canonical zwitterion electronic configuration, artificially constructed from known C···C single and double bond lengths, b^{s}_{i} is the length of each of the $N_b = 8$ non-hydrogen bonds that lie in the benzenoid ring or immediately vicinal to it and χ_s is the resultant percentage of quinoidal:aromatic (zwitterionic) character that the benzenoid ring possesses.

The resulting values of χ_s for Ammor and Morpip are 29(2)% and 33(2)%, respectively, i.e. their benzenoid rings show identical levels of quinoidal:aromatic character, within experimental error. Complementary solvatochromatism measurements corroborate these findings, the same trends but with just a slight change in slope being observed for Ammor and Morpip: see Fig. 6a (square) herein (Ammor) and fig. 4a in Ref. 23 (Morpip).

The substituents adjoining C10 via N3 and N4 form a plane in Ammor that lies 66.5(5)° to the mean plane comprising the aforementioned common TCNQ-based motif. This compares with an analogous twist angle of 44(1)° in Morpip. The larger displacement of this plane in Ammor when compared with Morpip may be due to the less sterically hindered environment around the small free amine group in Ammor rather than the large piperidine functionality in Morpip. The 1,4-*N*,*O*-3,5-dimethyl-substituted ring exhibits bond lengths that are entirely expected for a saturated ring and forms a chair-shaped configuration; the C10—N3 and C10—N4 bonds show no anomalies and are identical within experimental error.

Ammor crystallizes in the monoclinic space group, $P2_1/c$, with a packing arrangement depicted by Fig. 3. Each molecule lies antiparallel to its neighbour in undulating layers held together by hydrogen bonds. In particular, the hydrogen bonds, N3—H3B···O1 (H···O = 2.149 Å; NHO = 169.8°; symmetry code: x,0.5 − y,−0.5 + z) and N3—H3A···N2 (H···N = 2.151 Å; NHN = 177.3°; symmetry code: x − 1,y,z) are moderately strong interactions, whereas weak hydrogen bonds of the type C—H···X may also be present: C11—H11A···N1 (H···N = 2.501 Å, CHN = 144.9°; symmetry code: 1 − x,y − 0.5,1.5 − z), C5—H5A···N1 (H···N = 2.567 Å, CHN = 135.2°; symmetry code: 1 − x,−y,2−z) and C11—H11B···N2 (H···N = 2.519 Å, CHN = 148.7°; symmetry code: x − 1,y,z).

Morpip, which crystallizes in the orthorhombic space group $P2_12_12_1$, shows no evidence of possessing any hydrogen bonding in its packing configuration that comprises molecules stacked directly on top of each other along the *a*-axis direction, the arrangement of molecules in each alternate layer being anti-parallel to the adjacent one (see Fig. 4).

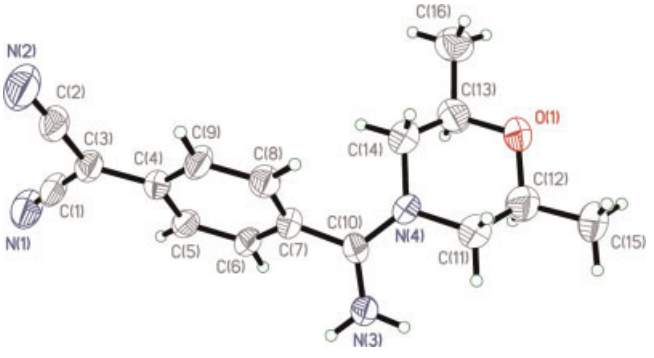

Figure 2. The crystal structure of Ammor showing anisotropic displacement parameters on all non-hydrogen atoms at the 50% probability level

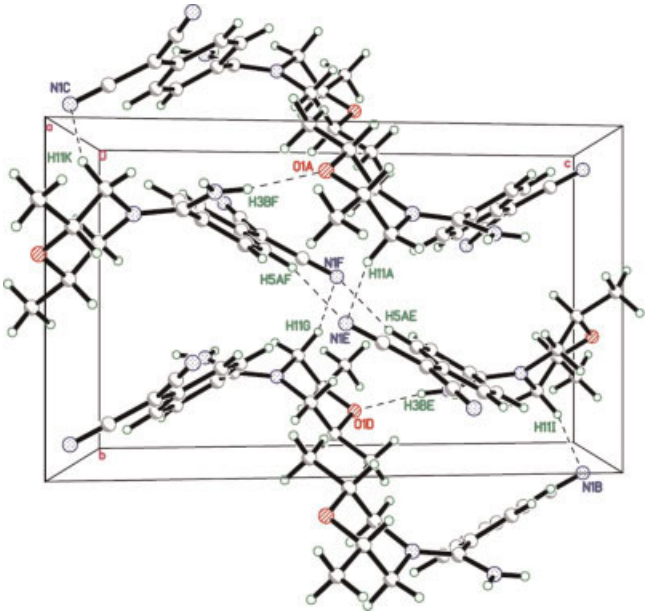

Figure 3. Molecular packing arrangement of Ammor as viewed down the *a*-axis. Hydrogen bonds involving N2 are not visible here because they occur principally along the *a*-axis

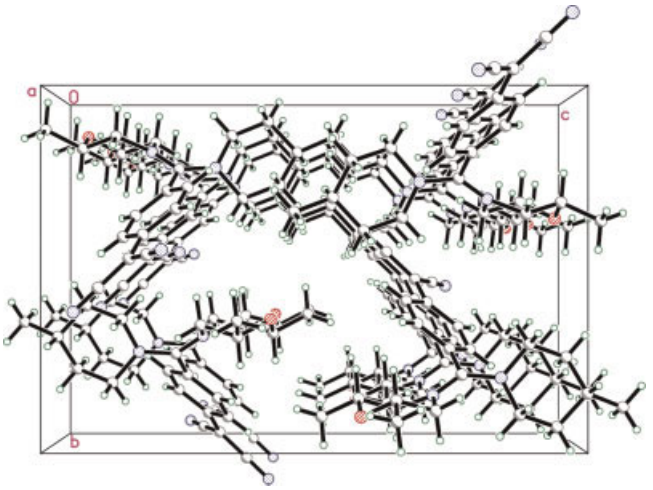

Figure 4. Molecular packing arrangement of Morpip as viewed down the *a*-axis (from data with CCDC deposition number 139387)

Fluorescence spectra

The absorption and emission spectra of Ammor in solution are broad and featureless, with an emission intensity that is strongly solvent dependent (see Fig. 5). The Stokes shift and fluorescence quantum yields for Ammor are listed in Table 1. These results are similar to those we have obtained for the fluorescence emission of other dicyanoquinodimethane derivatives. In particular the intensity of emission of Ammor is comparable with that of Morpip and Amino.[24]

The solvatochromic shift of the ground and excited electronic states results in a solvent-dependent Stokes shift. The literature describing the modelling of solvent–solute interactions is extensive.[53] The Lippert formalism

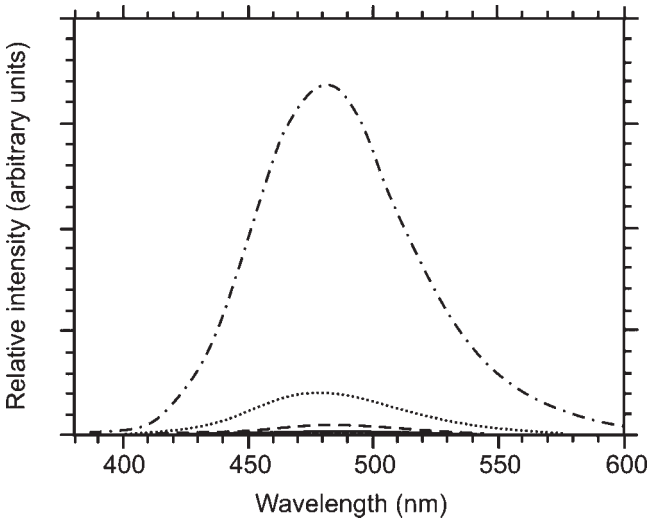

Figure 5. Emission spectra of Ammor dissolved in normal alcohols and glycerol. Plots are from top to bottom: glycerol, pentanol, propanol and methanol

Table 1. Absorption maxima, Stokes shifts and fluorescence quantum yields of Ammor solutions

Solvent	Absorption maximum (cm^{-1})	Stokes shift (cm^{-1})	Quantum yield (%)
Methanol	26600[a]	5810[b]	0.16[c]
Ethanol	25970	5230	—
1-Propanol	25840	5050	0.4
1-Butanol	25510	4680	—
1-Pentanol	25380	4660	1.4
1-Hexanol	25190	4440	—
Diethylene glycol	26320	5570	1.5
Glycerol	26810	6060	12.4

[a] Error $\pm 50\,cm^{-1}$.
[b] Error $\pm 100\,cm^{-1}$.
[c] Error is 10% of the value.

provides a simple model for the analysis of experimental data.[54–58] The energy of absorption and emission, relative to the gas phase values, is given by

$$\nu_{\max}^{\text{abs}} = \nu_0^{abs} - \frac{2\mu_g(\mu_e - \mu_g)}{hca^3}\left[\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right)\right] \quad (1)$$

$$\nu_{\max}^{\text{em}} = \nu_0^{em} - \frac{2\mu_g(\mu_e - \mu_g)}{hca^3}\left[\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) - \frac{1}{2}\left(\frac{n^2 - 1}{2n^2 + 1}\right)\right] \quad (2)$$

where ε is the dielectric constant and n is the refractive index of the solvent, μ_e and μ_g are the dipole moments of the excited and ground state and a is the radius of the spherical Onsager cavity surrounding the solute molecule. The Stokes shift is just the difference in these energies, hence:

$$\Delta\nu = \nu_{\max}^{\text{abs}} - \nu_{\max}^{\text{ems}} = \frac{2(\mu_e - \mu_g)^2}{hca^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right] + \text{constant} \quad (3)$$

where the quantity in square brackets is termed the polarity parameter (Δf). A variety of different parameters have been used to describe solvent interaction and incorporate effects such as solvent molecule reorientation with varying degrees of success.[59] The Lippert formalism provides a reasonable interpretation of the experimental data for Morpip and Amino[24] in a series of normal alcohols, however when the degree of hydrogen bonding is greatly increased (i.e. in glycerol, without a corresponding large increase in molecular weight) a large deviation from the Lippert formalism is observed, hence deviations from the Lippert formalism can be used to

measure the extent of special interactions such as hydrogen bonds. Following this example we plot the data for Ammor in solution in the normal alcohols according to Eqns (1)–(3) in Fig. 6.

A problem in the use of eqns (1)–(3) to estimate μ_g and μ_e is that the results obtained depend crucially on the radius of the Onsager cavity (a) enclosing the solute molecule. In addition, for molecules like Ammor the spherical cavity should be replaced by an ellipsoidal cavity.[17,60] This additional complication is not justified here because the analysis does not yield exact values for μ_g and μ_e. A reasonable estimate[17,24] for a can be deduced from the crystal structure (Using unit cell volume = 1518.9 Å^3, $Z = 4$), which gives a volume per molecule of ca. 380 Å^3 and $a \approx 4.0$ Å. The plots of absorption and emission maxima and the Stokes shift (Fig. 6) yield slopes of $23370 \pm 3650\,\text{cm}^{-1}$ ($R = 0.954$), $630 \pm 900\,\text{cm}^{-1}$ ($R = 0.329$) and $20330 \pm 1980\,\text{cm}^{-1}$ ($R = 0.982$), respectively. Using these data the values found are $\mu_g = 11 \pm 4$ D (calc. 13.03 D) and $\mu_e = 0.3 \pm 1$ D (calc. 0.35D). These results are similar to those for Morpip with a large μ_g and $\mu_e \sim$ zero. This has been attributed to a large conformational change between ground and excited states.[24]

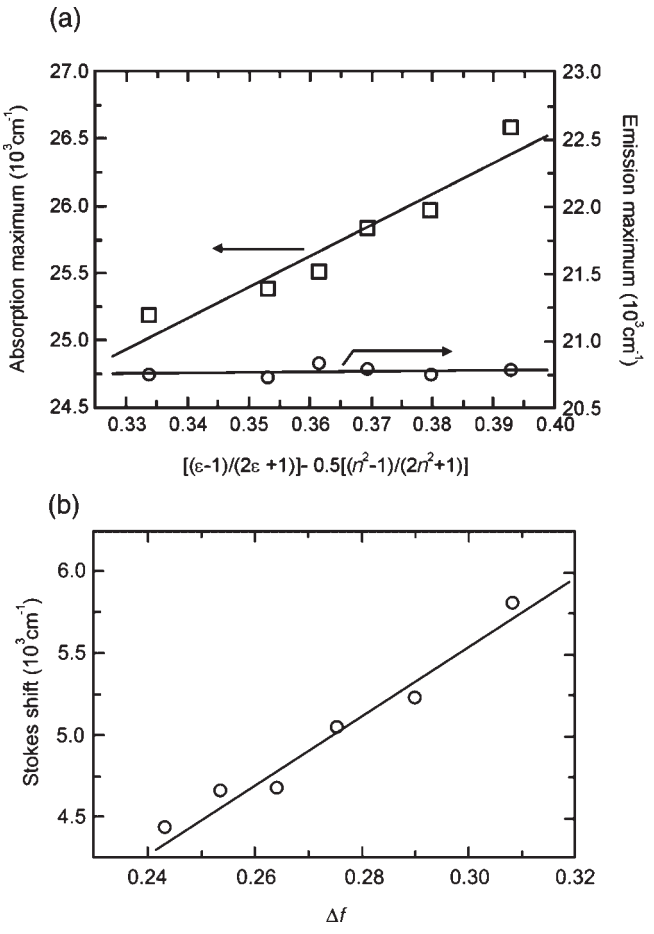

Figure 6. Plots of absorption and fluorescence maxima (a) and Stokes shift (b) for Ammor dissolved in normal alcohols versus Δf

The occurrence of a large conformational change on photoexcitation means that viscous (i.e. solvents such as glycerol giving rise to many hydrogen bonding interactions) solvents have a large influence on the emission. Thus, the Stokes shifts observed for diethylene glycol and glycerol solutions are much larger than predicted by the Lippert formalism (i.e. the largest deviations from the Lippert formalism). Use of the empirical parameters $E_T(30)$ and E_T^N, which incorporate the effects of hydrogen bonding, present in these viscous solvents, provides a good fit to all the data (Fig. 7(a)). However, the variation in the fluorescence quantum yields is not described well by either Δf or $E_T(30)$ (Fig. 7(b)). This indicates that the conformational change possible in low viscosity solvents is inhibited in high viscosity solvents. Increased fluorescence is also observed in solid media, such as polymers and low-temperature glasses. Again the results observed are similar to those of Morpip.[24] (Table 2 compares

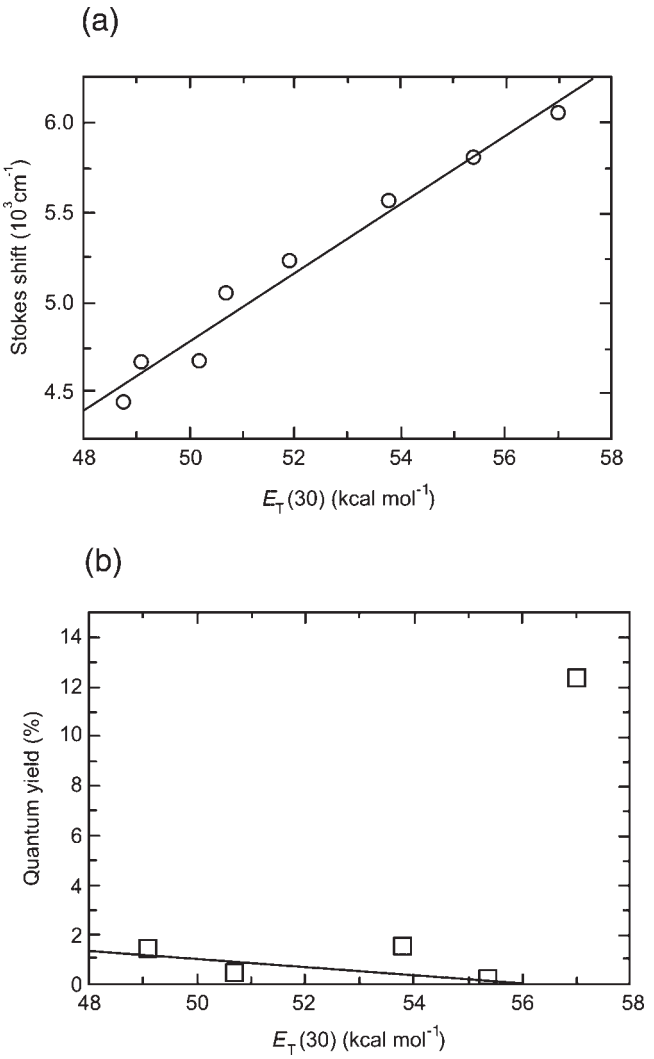

Figure 7. Plots of Stokes shift (a) and fluorescence quantum yields (b) for Ammor dissolved in normal alcohols, diethylene glycol and glycerol versus $E_T(30)$. The trend line for the normal alcohols is plotted in (b) and the outlying data point is the glycerol result

Table 2. Comparison of spectroscopic data for Morpip and Ammor in a range of solvents

Dye	Medium	$\Delta\nu$ (cm^{-1})	$PLQY_e$ [%]
Amino	Methanol	7380	0.22
	Ethanol	6770	—
	Propan-1-ol	6500	0.53
	Butan-1-ol	6160	—
	Pentan-1-ol	6010	1.3
	Hexan-1-ol	5670	—
	Diethylene glycol	7985[a]	2.3[a]
	Glycerol	6630[a]	21.8[a]
Ammor	Methanol	5810	0.16
	Ethanol	5230	—
	Propan-1-ol	5050	0.4
	Butan-1-ol	4680	—
	Pentan-1-ol	4660	1.4
	Hexan-1-ol	4440	—
	Diethylene glycol	5570	1.5
	Glycerol	5900	12.4
Morpip	Methanol	5160	0.1
	Ethanol	4620	0.1
	Propan-1-ol	4240	0.4
	Butan-1-ol	4150	0.5
	Pentan-1-ol	3970	0.7
	Hexan-1-ol	4010	1.0
	Diethylene glycol	5040[a]	1.4[a]
	Glycerol	5400[a]	11.8[a]

[a] Data taken from Ref 24.

Stokes shifts and fluorescence quantum yields obtained for both Morpip and Ammor). This indicates that the relaxed excited state decays predominantly by a non-radiative mechanism whereas the hindered state decays radiatively. This conclusion is supported by the measurements of fluorescence lifetime in 1-propanol (see Fig. 8).

At room temperature the fluorescence decay is indistinguishable from the excitation pulse, whereas at 80 K a good fit is obtained to a single exponential decay with a lifetime of 2.3 ± 0.2 ns. A pronounced increase in fluorescence intensity is observed in the low-temperature glassy phase relative to the room-temperature solution.

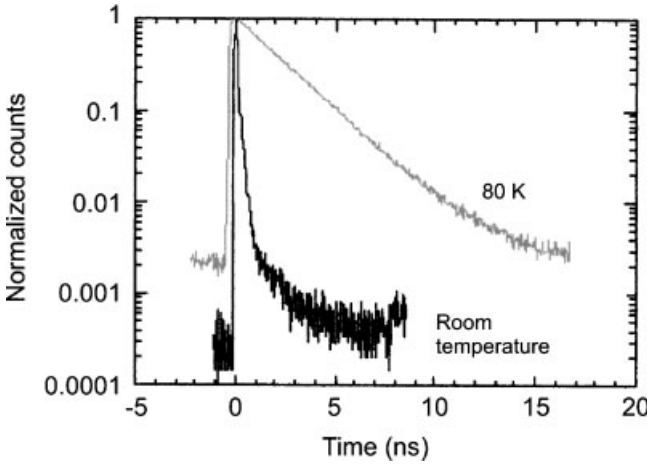

Figure 8. Fluorescence decay of Ammor: (a) in 1-propanol solution at room temperature; (b) in the glassy phase at 80 K

Thus, there is a clear transition from a fast non-radiative decay to a slower radiative decay.

CONCLUSION

Ammor, the asymmetrically amino-substituted dicyanoquinodimethane derivative, has been successfully synthesized and characterized. In line with related compounds[24] Ammor displays an environmentally sensitive fluorescence emission. Theoretical calculations and experimental data indicate that the ground-state dipole moment is significantly larger than the excited-state dipole moment. This observation has been attributed to a large conformational change between ground and excited states. The occurrence of a large conformational change on photoexcitation means that viscous solvents and solid media, in which the chromophore is dissolved, have a large influence on the emission. Fluorescence lifetime measurements at low temperatures show an increase in the intensity of the blue emission giving rise to a single exponential decay with a nanosecond lifetime, whereas at room temperature the fluorescence decay is indistinguishable from the excitation pulse, thus indicating a transition from a fast non-radiative decay to a slower radiative decay with decrease in temperature.

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