The Effect of High Pressure on the Twisted Intramolecular Charge Transfer of 2-(4-Dimethylaminonaphthalen-1-ylmethylene) Malononitrile

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The effect of pressure up to 65 kbar has been measured on the steady-state and time-dependent fluorescence of 2-(4-dimethylaminonaphthalen-1-ylmethylene)malononitrile (DMANMN) in four polymer matrixes [poly(methyl methacrylate), poly(acrylic acid), poly(vinyl chloride) and cellulose acetate]. The fluorescence intensity increases with pressure by a factor of 24−34 in different polymers. The formation of a twisted intramolecular charge transfer state is effectively retarded by pressure above 40 kbar. The abnormal photophysics of DMANMN in poly(acrylic acid) is the result of protonation of the dimethylamino group.

Introduction

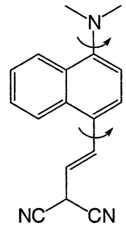
Since the observation of dual fluorescence for 4-(dimethylamino) benzonitrile (DMABN), its emission mechanism has been extensively investigated.[1−8] Several mechanisms have been proposed to explain the appearance of low-energy fluorescence, such as twisted intramolecular charge transfer (TICT),[1−3] planar intramolecular charge transfer (PICT),[4,5] rehybridization by intramolecular charge transfer (RICT),[6,7] and wagged intramolecular charge transfer (WICT).[8] Among them, TICT is the most accepted explanation for the dual fluorescence phenomenon.

The TICT mechanism has been verified by some experimental tests.[9−11] Kwok et al.[9] have recorded the Raman spectrum of the CT excited state of DMABN. They conclude that the observed C−N and C≡N stretching frequencies are reasonably explained by the TICT model. Techert et al.[10] have recorded a powder diffraction pattern after ultraviolet photoexcitation. After analyzing the data by adjusting the torsional and wagging angles of the dimethylamino group as fitting parameters, they have concluded that the dimethylamino plane is twisted to about 10° from the benzene plane in the excited state in the solid state. Recently, Dobkowski et al.[11] have reported that at −90 °C the dual fluorescence of a desymmetrized analogue, 2-(*N*-methyl-*N*-isopropylamino)-5-cyanopyridine in methanol is accompanied by syn−anti isomerization around the C−N bond, which offers direct evidence for the TICT model.

According to the TICT mechanism, upon excitation, the planar molecule initially forms an intramolecular charge transfer (ICT) state, and then the donor part undergoes twisting, until the donor orbital is perpendicular to the acceptor orbital. This results in a complete electron transfer. High-energy fluorescence is associated with the local excited state (LE), while low-energy fluorescence is from the TICT state.

Later, it was realized that many TICT states are nonfluorescent and are responsible for the rapid quenching of fluorescence from the LE state.[12−16] *p*-*N*,*N*-dimethylaminobenzylidenemalononitrile (DMABMN) is such an example: only LE fluorescence is observed. The effect of high pressure on the photophysical properties of DMABMN in several polymer matrices has been extensively studied in this laboratory.[17−19] The most striking photophysical property of DMABMN is that its fluorescence quantum yield is very sensitive to local polarity and viscosity of the surroundings. To investigate the effect of aromatic groups on the rotation of single bonds in such molecules, we have synthesized a new flexible molecule, 2-(4-dimethylaminonaphthalen-1-ylmethylene) malononitrile (DMANMN) (see Scheme 1). Except for a red-shift of the absorption and fluorescence maxima with respect to DMABMN, the photophysical behaviors of the two compounds are quite similar in many polymeric solvents. The naphththalenyl group does not show an apparent effect on the rotation of single bonds. To our surprise, DMANMN in PAA displays a unique two-band fluorescence, while DMABMN in PAA or DMANMN in other polymers does not exhibit the high-energy band. In this paper, we report the pressure effect on the photophysics of DMABMN in PAA and three other polymers with different polarity.

SCHEME 1. Structure of DMANMN



Experimental Section

4-(Dimethylamino)-1-naphthaldehyde and malononitrile were purchased from Aldrich. 2-(4-Dimethylaminonaphthalen-1-ylmethylene)malononitrile (DMANMN) was synthesized by reflux of 4-(dimethylamino)-1-naphthaldehyde and malononitrile in methanol with a drop of pyridine/acetic acid as a catalyst. The product was purified by repeated recrystallization in methanol until the elemental analysis was satisfactory (Anal. Calcd for $C_{17}H_{15}N_3$: C 78.13%, H 5.79%, N 18.08%; found: C 77.98%, H 5.68%, N 18.13%).

Four polymers were used as the host material. Poly(methyl methacrylate) (PMMA, medium molecular weight), poly(acrylic

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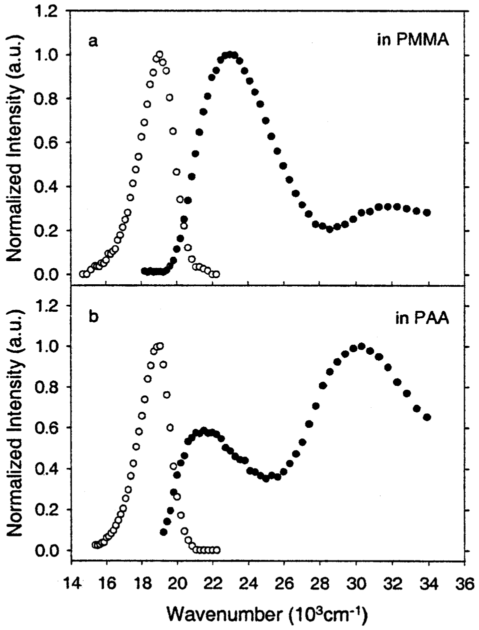


Figure 1. Absorption (●) and fluorescence spectra (○) of DMANMN in PMMA (a) and PAA (b).

acid) (PAA, MW = 250 000, T_g = 106 °C), poly(vinyl chloride) (PVCl, high molecular weight, $M_n \approx$ 99 000), and cellulose acetate (CAC, acetyl content 39.8%) were all obtained from Aldrich, and used without further purification, because they did not emit when irradiated at the excitation wavelength (441 nm).

The samples were prepared by dissolving DMANMN and one polymer in a photometric grade solvent (PAA in methanol, PMMA in chloroform, PVCl and CAC in THF) and then pouring the transparent solution into a glass dish. After the solvent evaporated at room temperature, the blend film was dried for several days in a vacuum oven. The concentration of DMANMN was 0.05 wt % in all cases.

The operation of the high-pressure diamond anvil cell (DAC) has been described in detail elsewhere.[20−22] For steady-state measurements, the emission spectra were obtained via excitation with the 441.6 nm line of a HeCd laser. The absorption apparatus utilized light from a Xenon lamp, which was transmitted to and from the surface of the diamonds by optical fibers. For the time-dependent decay, the samples were excited by 100 fs pulses from an 80 MHz mode-locked Ti:sapphire laser after frequency doubling to 420 nm with a BBO crystal. The detection system involved a Spex 0.27 m monochromator, a Tennelec 863 time-to-amplitude converter, an Ortec 582 discriminator, and a Hamamatsu R1564 photomultiplier.

In all cases, the results represented the average of at least two loads. The scatter among the results from different loads was never over ±10%. Upon release of pressure, the spectra were highly reversible.

Results and Discussion

1. Atmospheric Pressure. Typical absorption and emission spectra for DMANMN in two polymers at 1 atm are shown in Figure 1. The data for CAC, PVCl, PMMA, and PAA are summarized in Table 1. The emission spectra exhibit only one band in each polymer, and the shapes are also similar. The absorption spectra have multiple bands and are noticeably different. In PMMA, PVCl, and CAC, the low-energy peak (charge transfer peak) is dominant. In PMMA, the optical density of high-energy band is only 30% of maximum absorption. However in PAA, the high-energy absorption becomes dominant, and the maximum absorption ratio (high-energy peak/low-energy peak) is about 1.7.

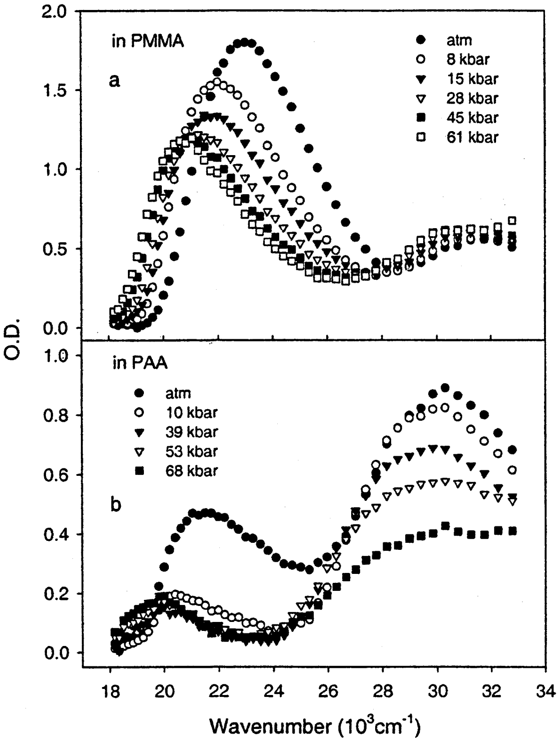


Figure 2. Effect of pressure on absorption spectra of DMANMN in PMMA (a) and PAA (b).

TABLE 1. Fluorescence and Absorption Data of DMANMN at 1 atm

matrix	$I(0)/I_{PMMA}(0)$	ν_f (0) (10^{3}cm^{-1})	ν_a(0) (10^{3}cm^{-1})
CAC	1.04	19.00	22.64
PVCl	0.76	18.76	22.06
PMMA	1.00	19.00	22.96
PAA	2.40	18.95	21.40

The absorption and fluorescence spectra of intramolecular charge-transfer compounds are sensitive to the polarity of the solvent, but a polarity effect cannot explain the anomalous absorption in PAA. PAA (poly(acrylic acid)) is a polymeric acid. Besides acting as a solvent, PAA might interact with the base group, dimethylamino($-N(CH_3)_2$), leading to protonation of the dimethylamino group, and the protonation prohibits the intramolecular charge-transfer reaction. As shown in the absorption spectra, both protonated molecules and unreacted molecules (neutral molecules) exist in PAA. The shape of the fluorescence spectrum and the fluorescence position of DMANMN in PAA are close to those in the other three polymers, which implies that the fluorescence is still from the neutral molecules. Perhaps the cation molecules cannot be excited by the 441.6 nm laser line at atmospheric pressure. The unusual behavior of DMANMN in PAA will be discussed further in the following sections.

2. Pressure Dependence. The pressure dependence of the absorption spectra of DMANMN in PMMA, PVCl, and in CAC are similar (Figure 2a). The situation in PAA is quite different (Figure 2b). The fluorescence spectra of DMANMN in PMMA, PVCl, and in CAC are similar. Only one fluorescence peak is observed at all pressures (typical spectra in CAC is shown in Figure 3a). However, the spectra in PAA are quite different (Figure 3b). Figure 4 presents the normalized pressure dependence ($I(p)/I(0)$) of the fluorescence intensity in all four media. The curves were obtained by averaging data from 3 to 4 loads. For DMANMN in PMMA and PVCl, $I(p)/I(0)$ increases by

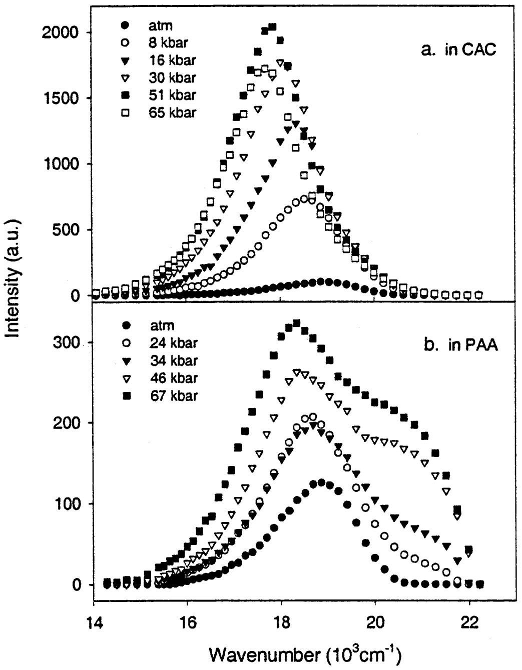


Figure 3. Effect of pressure on fluorescence spectra of DMANMN in CAC (a) and PAA (b).

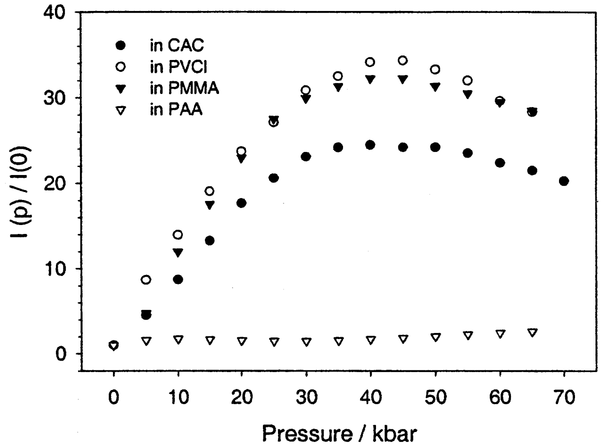


Figure 4. Effect of pressure on the normalized fluorescence of DMANMN in four polymers.

TABLE 2. Fluorescence Data of DMANMN at $p_{\max}$

matrix	$p_{\max}$ (kbar)	$I(p_{\max})/I(0)$	ν_f ($p_{\max}$) (10^3 cm^{-1})
CAC	40	24.5	17.94
PVCl	43	34.4	17.80
PMMA	42	32.4	18.01

more than a factor of ~30. However, in PAA, the ratio increases by less than 4.

For each polymer except PAA, we can determine the pressure, $p_{\max}$, at which $I(p)/I(0)$ is a maximum, the normalized fluorescence at $p_{\max}$, and the wavenumber of the fluorescence peak (Table 2).

The effect of pressure on the Stokes shift of DMANMN in four polymers is presented in Figure 5. The Stokes shift in PAA is much lower than in the other three polymers, both at 1 atm and higher pressures.

In general, the above results indicate that the fluorescence properties of DMANMN in PAA differ from the three other polymers. In particular, in PAA, a new high-energy emission band appears above 24 kbar (see Figure 3b). As mentioned in the preceding section, we attribute the new emission to the cation form of DMANMN (see Scheme 2). As seen in Figures 2b and 3b, there exists a strong overlap between the absorption and cation fluorescence. The reabsorption effect may be one of the reasons that at the lower pressure range (0−24 kbar), the cation fluorescence is invisible. At elevated pressure, the emission peaks red-shift much faster than the absorption bands. Thus, the overlap decreases with the increase of pressure. Another reason is that the emission of the cation molecule increases rapidly with pressure. The cation molecule is still a weak intramolecular charge-transfer compound; pressure is taking the same role of suppressing the free motor effect.

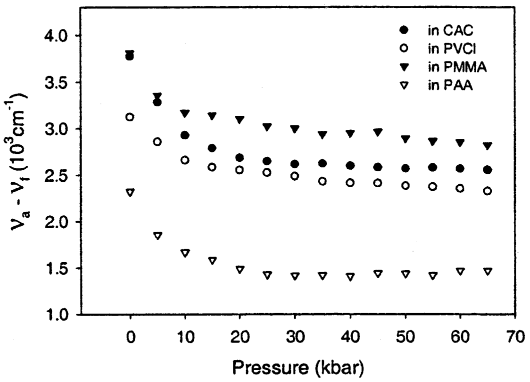


Figure 5. Effect of pressure on the Stokes shift of DMANMN in four polymers.

3. Time Decay. To further characterize the excited states of DMANMN, we also measured the fluorescence decay time in four polymers at different pressures (Table 3). The results show that at low pressures, all of the fluorescent decays are multiexponential. This implies that a local excited state (LE) is involved in a reversible reaction. However, at pressures above 25 kbar, the fluorescence decay becomes a single exponential; the charge-transfer state (TICT) is blocked by pressure. To quantitatively analyze the decay behavior of DMANMN, we use a model shown in Scheme 3 to describe the process.

From Scheme 3, the decay function of the relative fluorescence intensity is given by:

$$\frac{I(t)}{I(0)} = A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t) \tag{1}$$

where

$$A_1 = \frac{k_{\rm LE} + k_{\rm T} - k_2}{k_1 - k_2} \tag{1a}$$

$$A_2 = \frac{k_1 - k_{\rm LE} - k_{\rm T}}{k_1 - k_2} \tag{1b}$$

$$k_{1,2} = \frac{1}{2}\{(k_{\rm LE} + k_{\rm T} + k_{-\rm T} + k_{\rm TICT}) \pm [(k_{-\rm T} + k_{\rm TICT} - k_{\rm LE} - k_{\rm T})^2 + 4k_{\rm T}k_{-\rm T}]^{1/2}\} \tag{1c}$$

$$k_{\rm LE} = k_{\rm LE}^{\rm r} + k_{\rm LE}^{\rm nr}; \quad k_{\rm TICT} = k_{\rm TICT}^{\rm nr}$$

From eqs 1a, 1b, and 1c we obtain:

$$k_{\rm LE} + k_{\rm T} = A_1 k_1 + A_2 k_2 \tag{2}$$

$$k_{\rm TICT} + k_{-\rm T} = A_2 k_1 + A_1 k_2 \tag{3}$$

$$k_{\rm T} k_{-\rm T} = A_1 A_2 (k_1 - k_2)^2 \tag{4}$$

A_1, k_1, and k_2 can be obtained by fitting the fluorescence decay curves with eq 1. Fitting results for $k_{\rm LE} + k_{\rm T}$ and $k_{\rm T}k_{-\rm T}$ are

SCHEME 2. Protonation of DMANMN

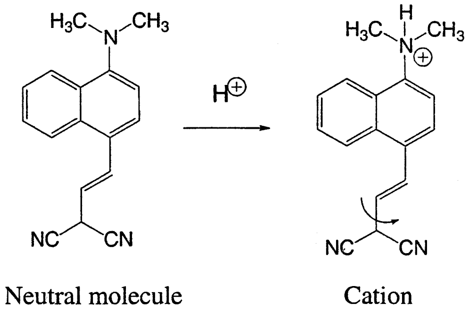
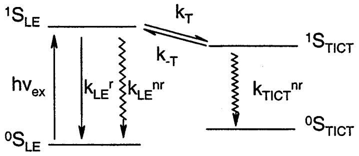


TABLE 3. Exponential Fitting Results and the Calculated $k_{LE} + k_T$ and k_Tk_{-T} Data

matrix	pressure kbar	measured position nm	exponential fitting results				$k_{LE} + k_T$ $10^9 s^{-1}$	k_Tk_{-T} $10^{18} s^{-2}$
			A_1	τ_1/ns	A_2	τ_2/ns		
PAA	atm	527	0.46	2.2	0.54	0.35		
	10	533	0.77	3.9	0.23	0.96		
	20	537	0.90	4.5	0.10	0.33		
		470	0.61	5.2	0.39	1.5		
	39	540	1.00	5.6	-	-		
		470	0.79	5.0	0.21	1.1		
	62	548	1.00	5.9	-	-		
		470	0.79	4.9	0.21	1.2		
CAC	atm	530	0.35	0.66	0.65	0.11	6.4	13.1
	11	540	0.61	3.2	0.39	0.57	0.87	0.49
	22	545	0.69	4.4	0.31	1.75	0.33	0.03
	41	560	1.00	4.6	-	-	0.22	0
	61	564	1.00	5.1	-	-	0.20	0
PMMA	atm	525	0.32	0.68	0.68	0.1	7.3	15.8
	10	540	0.65	3.2	0.35	0.61	0.78	0.40
	20	545	0.71	4.4	0.29	1.6	0.34	0.03
	38	558	1.00	4.5	-	-	0.22	0
	64	560	1.00	4.9	-	-	0.20	0
PVCl	atm	530	0.35	0.65	0.65	0.11	6.4	13.0
	8	540	0.56	2.8	0.44	0.52	1.0	0.61
	17	545	0.71	3.9	0.29	1.5	0.38	0.03
	39	555	1.00	4.5	-	-	0.22	0
	64	565	1.00	4.9	-	-	0.20	0

SCHEME 3. Model for the Processes Involved in the Excited State of DMANMN



presented in Table 3. k_Tk_{-T}, which is associated with the equilibrium of LE and TICT excited states, decreases with pressure, and becomes zero at ~40 kbar. This implies that TICT does not take place above 40 kbar. Meanwhile, $k_{LE} + k_T$ values drop rapidly with pressure below 30 kbar, then reach a value corresponding to the rate of decay of the LE state to the ground state (k_{LE}). This is consistent with the steady-state results.

Conclusions

We find that pressure greatly enhances the fluorescence intensity of DMANMN in CAC, PMMA, and PVAc. This is explained as the suppression of twist in the excited state by increasing pressure. When the pressure is over 40 kbar, the population of TICT states is completely suppressed. Lifetime measurements and the calculated rate constants $k_{LE} + k_T$ and k_Tk_{-T} support this interpretation. The anomalous photophysical behavior of DMANMN in PAA is the result of protonation of the dimethylamino moiety. Absorption spectra show that the protonation takes place in the ground state.

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