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The First Intramolecular Charge Transfer Transition Based on 2-Ureido-4[1*H*]-pyrimidinone Binding Module

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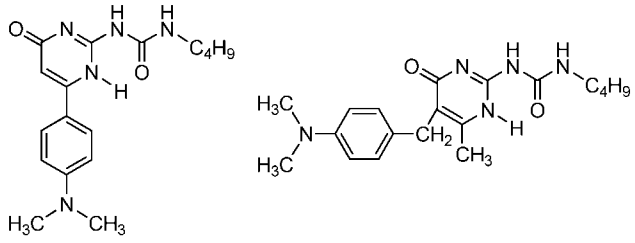
The first intramolecular charge transfer transition based on 2-ureido- 4[1*H*]-pyrimidinone binding module was reported.

Keywords intramolecular charge transfer, 2-ureido-4[1*H*]-pyrimidinone binding module, stockes shift, $E_T(30)$.

Due to the strength, directionality, and specificity, arrays of multiple hydrogen bonds are useful building blocks for the reliable assembly of complex structures.[1] Since 1998, self-complementary quadruply hydrogen-bonded homodimers have received increasing attention.[2] Particularly the 2-ureido-4[1*H*]-pyrimidinone AADD binding module developed by Meijer *etc*. has shown extensive applications in assembling supramolecular oligomers and polymers.[3] However, there are relatively few examples[4] given on their spectroscopic properties, especially on their native photophysical characteristics. Here we reported for the first time that the intramolecular charge transfer state was involved in this attractive 2-ureido-4[1*H*]-pyrimidinone binding module, which significantly depended on the substitutents of pyrimidinone. Unlike pyrimidinone **2** with the *N*,*N*-dimethylaminophenyl connected via a methylene at 5-position (Chart 1), compound **1** with 6-substituted *N*,*N*-dimethylaminophenyl group exhibited a red-shift of the lowest absorption band and broad as well as featureless fluorescence in dilute solution at room temperature. Steady-state and time-resolved fluorescence measurements in various polar solvents revealed that the lowest excited state of compound **1** was derived from the intramolecular charge transfer (ICT) state.

Compound **1** was synthesized by treatment of ethyl acetate in THF with 2 equiv. of LDA in −78 ℃ for 5 min before addition of acyl chloride, as shown in Scheme 1. The reaction mixture was stirred for 15 min to give the *β*-keto esters, which reacted with gunidinium carbonate in refluxing absolute ethanol and then with butylisocyanate in refluxing pyridine to afford compound **1**[5] in good yield. Compound **2** was prepared by condensation of 4-(dimethylamino)benzaldehyde and ethyl acetoacetate. After hydrogenation, the intermediate reacted with gunidinium carbonate and butylisocyanate respectively, following the same procedures as described in the syntheses of compound **1**. ^{1}H NMR spectra revealed that compound **1** and **2** existed as assemblies **1.1** and **2.2** in $CDCl_3$. The large downfield shift for N-H protons provided direct evidence for the involvement of strong hydrogen bonding. Their AADD hydrogen-bonding motif was determined by 2D-NOESY spectra. No other binding modes were observed. Dilution of the solutions of the compounds in $CDCl_3$ to 1×10^{-5} mol•dm^{-3} did not lead to observable dissociation, giving a lowest estimation of binding constant of 1×10^7 dm^3•mol, which was in good agreement with the value for a similar compound.[3]



1 **2**

Chart 1 The structures of compounds **1** and **2**.

The absorption spectra of compound **1** and **2** were taken in dichloromethane and presented in Figure 1a. Both compounds exhibited intense vibronic-structured absorption bands at $\lambda < 300$ nm with extinction coefficients on the order of 10^4 dm^3•mol^{-1}•cm^{-1}. Moderately intense low-energy absorption band in the region of 300—380 nm was observed for compound **1**, while the same feature was absent for compound **2**. The absorption spectral properties were found to follow Beer's

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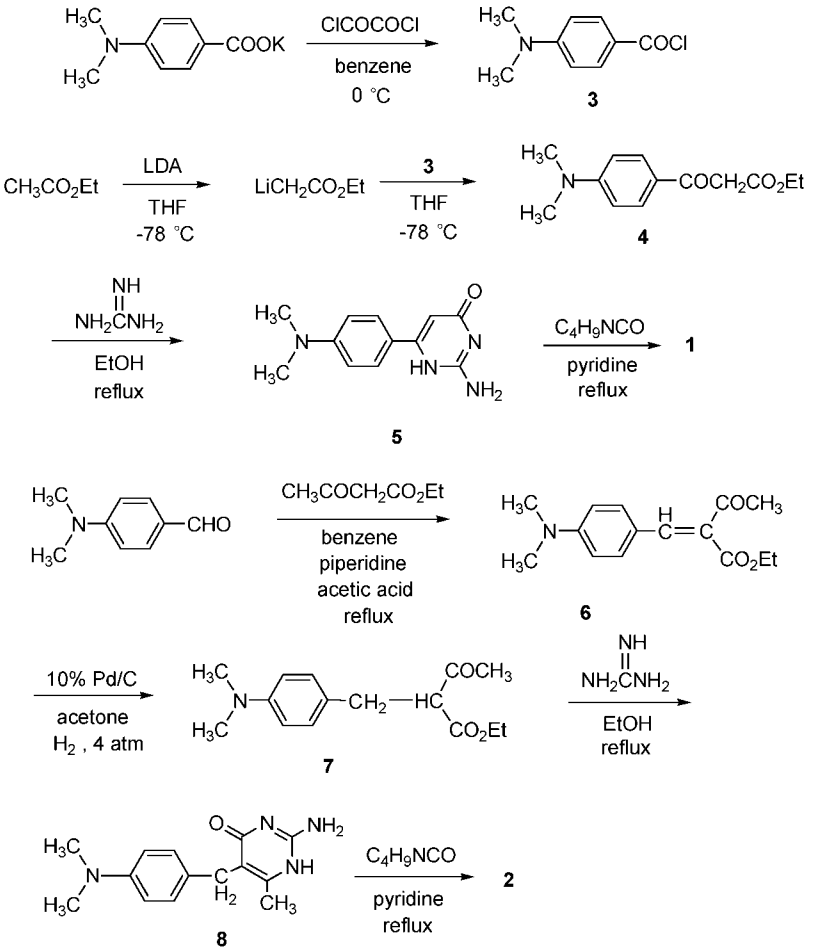
Scheme 1 The synthesis of compounds **1** and **2**



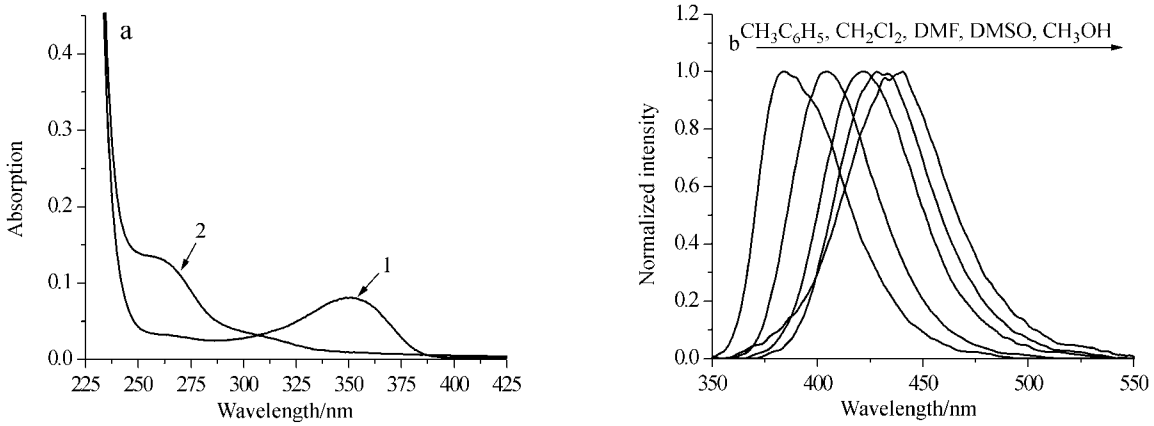


Figure 1 (a) The absorption spectra of compounds **1** and **2** in CH_2Cl_2. (b) The normalized fluorescence spectra of **1** in various solvents.

Law at concentrations below 1×10^{-4} mol•dm^{-3}, suggesting no any significant complex aggregation occurred.

In contrast to the nonemissive compound **2**, compound **1** displayed broad and featureless fluorescence with high quantum yield (0.87) in dilute solution at room temperature, which was found to be substantially red-shifted spanning over 100 nm along the polarity of solvents (Figure 1b). For example, **1** exhibited the fluorescence with the maximum wavelength at 385 nm in toluene and 440 nm in methanol respectively when excited at 350 nm. An excimeric emission was not preferred because the fluorescence maximum was independent of the concentration of **1** ranged from 10^{-7}—10^{-5} mol•dm^{-3}. The fluorescence independent of excitation wavelength mirrored the excitation spectrum, which was identical with that of the absorption spectrum.

Such spectral changes upon introducing the *N*,*N*-dimethylaminophenyl moiety into 2-ureido-4[1*H*]-

pyrimidinone binding module at 6-substituted position prompted an investigation into the nature of the excited state. To exclude the interference of AADD hydrogen bonding, polar solvents were adopted to carry out the solvatochromic measurements. The photophysical parameters of compound **1** are listed in Table 1. It was noted that both the absorption and fluorescence wavelength were red-shifted with increasing solvent polarity.

The Stockes shift $\Delta\nu$ calculated from the maxima of the absorption and fluorescence wavelength correlated well with the empirical parameters of solvent polarity $E_T(30)$.[6] The linear dependency of $\Delta\nu$ vs $E_T(30)$ shown in Figure 2 suggested that the excited-state be charge transfer characteristic in nature.[7,8] Most important was that the substituent *N*,*N*-dimethyl aminophenylmoiety influences the delocalization of excitation energy of the pyrimidinone binding module of compound **1**, where a planar and highly emissive ICT excited state was employed.

The response of lifetime was also susceptible to the changes in solvent polarity. With increasing the polarity of the solvents, the fluorescence lifetime of compound **1** increased initially as expected, and then decreased suddenly in higher polar solvents. This observation may be rationalized by the fact that additional nonradiative decay of the twisted intramolecular charge transfer state (TICT) mechanism was involved, which was in line with the Rettig's observations from dimethylamino benzoic acid ethyl ester.[9]

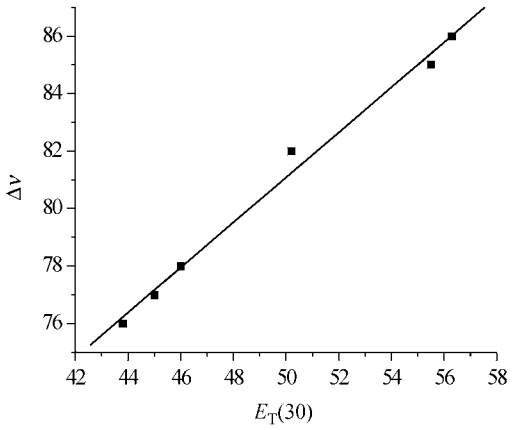


Figure 2 Plot of the Stockes shift $\Delta\nu$ of **1** vs $E_T(30)$ in various polar solvents.

In summary, we observed that the lowest excited-state of 6-*N*,*N*-dimethylaminophenyl substituted 2-ureido-4[1*H*]-pyrimidinone binding module **1** was charge transfer characteristic. The substituent and solvent effects noted here were interpreted in terms of intramolcular charge transfer state. An important nonradiative decay path leading to a TICT might be involved in highly polar solvents.

Table 1 The photophysical properties of compound **1** in various solvents

Solvent	1,2-Ethanediol	MeOH	Butanol	DMSO	DMF	CH_2Cl_2	$CH_3C_6H_5$
$E_T(30)$	56.3	55.5	50.2	45.0	43.8	41.1	33.7
λ_{em}/nm	448	440	430	428	424	404	385
λ_{ab}/nm	362	355	352	351	348	350	339
$\Delta\nu$/nm	86	85	78	77	76	54	46
τ/ns	1.2	1.3	2.0	1.9	2.0	1.6	1.2

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5 Compound **1**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 13.95 (s, 1H), 12.25 (s, 1H), 10.44 (s, 1H), 7.72 (d, J=6.9 Hz, 2H), 6.93 (d, J=8.9 Hz, 2H), 6.42 (s, 1H), 3.47—3.45 (m, 2H), 3.21 (s, 6H), 1.79—1.77 (m, 2H), 1.59—1.55 (m, 2H), 1.11 (t, J=7.3 Hz, 3H). Anal. calcd for $C_{17}H_{23}N_5O_2$: C 61.99, H 7.04, N 21.26; found C 61.87, H 6.98, N 21.17. Compound **2**: ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 12.86 (s, 1H), 11.92 (s, 1H), 10.19 (s, 1H), 7.14 (d, J=8.4 Hz, 2H), 6.67 (d, J=6.4 Hz, 2H), 3.71 (s, 2H), 3.22—3.27 (m, 2H), 2.90 (s, 6H), 2.23 (s, 3H), 1.54—1.62 (m, 2H), 1.36—1.42 (m, 2H), 0.93 (t, J=7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 400 MHz) δ: 172.6, 156.9, 153.3, 149.3, 143.9, 129.1, 128.2, 118.1, 113.1, 41.0, 39.8, 31.4, 29.7, 20.3, 17.5, 13.9. Anal. calcd for $C_{19}H_{27}N_5O_2$: C 63.84, H 7.61, N 19.59; found C 63.77, H 7.64, N 19.63.

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