

Communications

Synthesis of 2,3-Dicyanopyrazine Dimers Linked with Cyclobutane Ring by [2+2]Photocycloaddition

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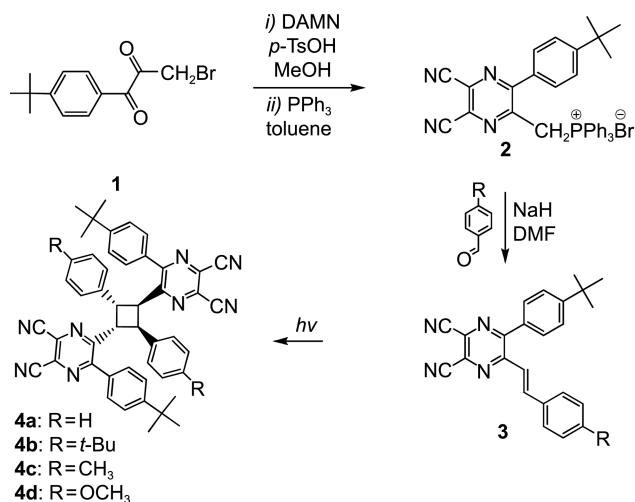
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The photochemical [2+2] cycloaddition reactions have been the subject of extensive investigations and have played an important role in the development of mechanistic organic photochemistry.¹⁻⁴ Stilbene has been extensively studied as it has an absorption band in the near UV region and only on the photochemical reactive site, which yields simple reaction products.⁵ Our efforts have focused on the development of new fluorescence materials based on the 2,3-dicyanopyrazine system, because the resulting compound has advantages in thermal and chemical stability. Thus, new 2,3-dicyanopyrazine system materials were synthesized and subjected to a photocycloaddition reaction with different electron affinities. Specifically, 2,3-dicyanopyrazine with the introduction of a *t*-butylphenyl unit was studied and tested to verify the improvement in structural stability and solubility.

The synthetic route is summarized in Scheme 1. Compound **1** was synthesized by bromination of methyl group of 1-(4-*tert*-butylphenyl)propan-1-one, described in recent literature,⁶ however we followed the preparing method from our previously described method.⁷ The α -diketone **1** was reacted with diaminomaleonitrile (DAMN) to afford the pyrazine based heterocycle, which was treated with 1.5 equiv. of

triphenylphosphine in toluene to afford a [(3-(4-*tert*-butylphenyl)-5,6-dicyanopyrazin-2-yl)methyl]triphenylphosphonium bromide **2** with 70% yield. The Wittig salt **2** with one equivalent of aryl aldehyde in the presence of 1.2 equivalent of NaH results in the styryl compound **3**. The variety of alkyl groups from the aryl aldehyde was announced in Table 1. The new compounds were characterized by FT-IR and ¹H-NMR spectroscopy. The medium intensity band at the 2227-2237 cm⁻¹ region was due to stretching of the CN groups. The strong intensity band at the 1604-1621 cm⁻¹ region was due to stretching of the C=C groups. The ¹H-NMR spectra of the 2,3-dicyanopyrazine compounds showed doublet



Scheme 1. Synthetic route for 2,3-dicyanopyrazines.

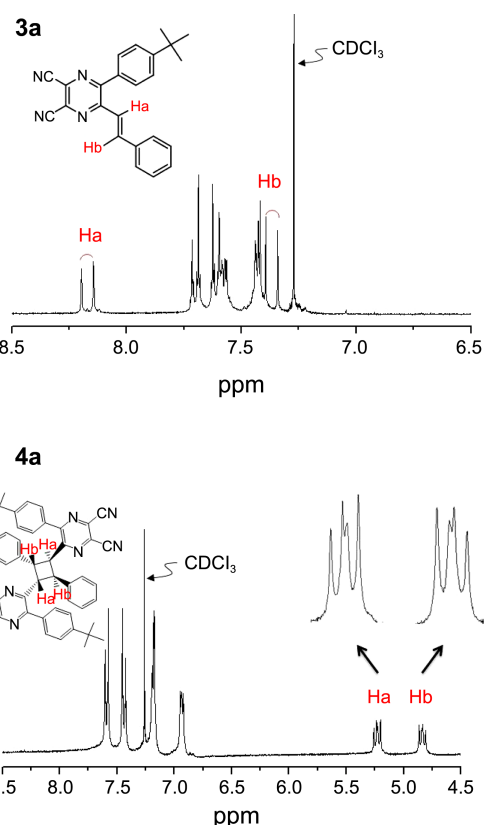


Figure 1. ¹H-NMR spectra of **3a** and **4a**.

Table 1. Optical and electrochemical properties of **3** and **4**

	R	$^a\lambda_{\text{abs}}/\lambda_{\text{em}}$ (nm)	LUMO (eV)	HOMO (eV)
3a	H	358/425	-3.54	-6.32
3b	<i>t</i> -Bu	386/454	-3.45	-6.2
3c	CH ₃	389/459	-3.45	-6.29
3d	OCH ₃	408/502	-3.21	-5.81
4a	H	318/388	-2.83	-6.07
4b	<i>t</i> -Bu	343/414	-2.78	-6.0
4c	CH ₃	348/420	-2.74	-6.04
4d	OCH ₃	365/458	-2.58	-5.68

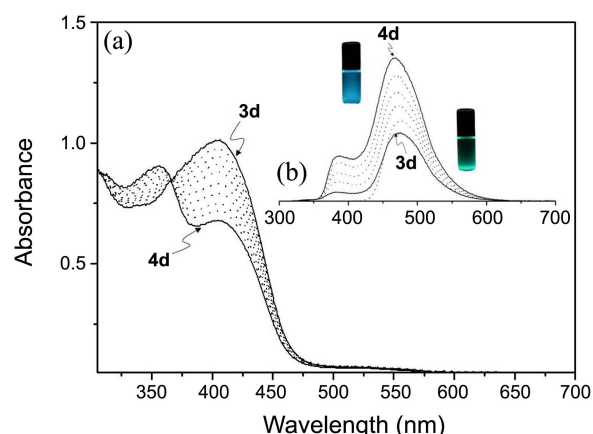
^ain CHCl₃

peaks at 8.1-8.2 ppm, indicating the presence of the typical *E*-configuration ($J = 15.6$ Hz) of the proton in the olefinic moiety.

The photocycloaddition reaction was performed in a benzene solution of **3** with irradiation of 365 nm light emitted from the high-pressure mercury lamp (450 W of strength at 365 nm) at room temperature. Figure 1 shows ¹H-NMR spectra of **3a** and **4a**, and shows two sets of doublets for two paired protons on the cyclobutane ring were observed at 5.2 and 4.8 ppm ($J_1 = 10.2$ Hz, $J_2 = 7.2$ Hz). The overlapped area of both doublet peaks shows a similar intensity with the rest other peaks. The cyclobutane ring would be necessarily received a steric hindrance between aromatic substituents, and we can assume the conformation during the cycloaddition reaction may be progressed to the more stable form. Two conformation models, which were knowable from the coupling tendency with adjacent protons, were introduced in Figure S1 (see the supplementary materials), and it was concluded that the NMR spectrum mainly suggested from the head-to-tail structure in the case of **4a**.⁸

Optical and electrochemical properties were announced in Table 1. Compounds **3** show absorption (λ_{abs}) and emission (λ_{em}) maxima at 358-408 nm and 425-502 nm, respectively. The electron-donating character of the substituents in compounds **3** and **4** strongly reflected their absorption spectra in producing bathochromic shifts depending on their electron-donating ability. While the cyclobutane ring of dimers induced a discrete π -conjugation with aryl substituents to show a hypsochromic shift of absorption and emission spectra, the fluorescence intensity was increased and specific lowest unoccupied molecular orbital (LUMO) levels were formed compare to monomers as shown in Figure 2.

The calculated HOMO and LUMO energy levels obtained from the oxidation potentials and the estimated bandgap (E_g) and levels from the UV edge in the electronic absorption

**Figure 2.** Absorption (a: 1.063×10^{-5} mol L⁻¹) and emission (b: 1.063×10^{-7} mol L⁻¹) spectra of **3d** and **4d** in CHCl₃.

spectra are also listed in Table 1. As the oxidation potentials decreased with increasing electron-donating ability, the HOMO level was estimated in more positive positions and narrow band gaps were simultaneously exhibited in the optical results.

Compounds **4** shows emission in solid state and has different solubility in common organic solvents compare to monomers **3**. Thus, we will apply it to negative photoresists and the further research progress including stereochemical study will be reported elsewhere.

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