Journal of Atomic and
Molecular Sciences

ISSN 2075-1303

Global Science Press

The solvent effects on the energy gap between the nπ* state and ππ* state and fluorescence of benzoyleneurea

Received Oct.8, 2018,
Accepted Nov.24, 2018,

DOI: 10.4208/jams.100818.112418a

http://www.global-sci.org/jams/

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Abstract. Benzoyleneurea (BenzU), a fluorescent nucleobase analog, exhibits strong solvent dependent fluorescence intensity. With the increasing of the concentration of polar and protic solvents, BenzU exhibits enhanced fluorescence. To understand the photophysical properties of BenzU, the energy gaps (*ΔE*) between dark nπ* state and bright ππ* state of BenzU are calculated in several solvents. The solvent dielectric constant and hydrogen bond between BenzU and protic solvent both have effects on *ΔE*. And the fluorescence quantum yields of BenzU are linear response to *ΔE*. Furthermore, we find that the more hydrogen bonds are formed between BenzU and protic solvent, the higher *ΔE* and fluorescence intensity are obtained.

Keywords: Fluorescence quantum yields; Hydrogen bonds; Solvent effects;

Introduction

The photo-initiated processes in modified nucleobases are discussed intensively in the past decades.[1-3] People are concerned about how modifying the structure affects the behavior of the excited state of bases molecules.[4-5] A more practical motivation is being able to obtain fluorescence emissive nucleobase analogs. Fluorescence is a sensitive and versatile technique for studying nucleic acid dynamics which is preferred over other techniques.[6] The nature nucleobases have very small fluorescence quantum yields associated with ultrashort excited state lifetimes.[7-9] Replacing the nature nucleobases with fluorescent nucleobase analogs can be used as fluorescent probes to study the interaction of nucleic acids with other biomolecules. Some of the fluorescent nucleobase analogs were used to explore environmental features of DNA/RNA. [10-11]

The fluorescence quantum yields of fluorophores are frequently affected by environmental solvents. [12] The factors that affect fluorescence emission spectra include solvent viscosity, [13-14] polarity, [15-17] and specific solvent and fluorophore interaction17-20. The specific effects can due to hydrogen bonding, charge-transfer interactions, etc.17-19 It was reported that hydrogen bonding enhanced the fluorescence emission and induced larger Stokes shift. [17, 21]

It is well known that Nucleobases, uracil and thymine, have two lowest singlet excited state, dark nπ* state and bright ππ* state. [8, 22-26] It was found that water (or hydrogen bonding) and substituents have effects on nπ* state and ππ* state of DNA/RNA bases.[4-5,26-32] However, there are seldom reports focusing on solvent effects on the excited state dynamics of fluorescent nucleobases analogs.

Herein, we report the photophysic properties of benzoyleneurea (hereafter BenzU, **Figure 1**) in several solvents and solvent mixtures. BenzU is a uracil derivative. It provides 4 π-electrons to uracil forming a large delocalization. The fluorescence quantum yields of BenzU are sensitive to the solvent polarity and hydrogen bond. BenzU may be a good candidate as an environmental probe. In order to elucidate the excited state dynamics of BenzU, the energy gaps between nπ* state and ππ* state of BenzU were calculated using time-dependent density functional theory (TD-DFT) methods.

Experimental section

Absorption spectra were obtained using a PerkinElmer Lambda 35 double-beam spectrometer. The fluorescence spectra were recorded on a Horiba Jobin Yvon FluoroMax-4P spectrofluorometer. The fluorescence lifetime were probed by using time-correlated single photon counting (TCSPC) method. A 295 nm NanoLED (1.4 ns FWHM) was used as pulse laser source. The fluorescence lifetime were recorded at 365 nm fluorescence emission.

The benzoyleneurea (BenzU) was purchased from Tokyo Chemical Industry (Shanghai). It was used without further purification. The concentrations of BenzU in solvents were about to 10^{-6} M. All the solvents used here were analytic degree and were purchased from J&K Chemical or Sinopharm chemical Reagent.

Computational section

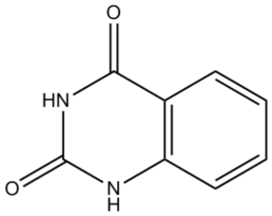

Figure 1: Molecular structure of benzoyleneurea.

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Density functional theory (DFT) and time-dependent DFT Calculations were performed using Gaussian 09 programs. [33] The equilibrium geometries of the ground state were optimized using DFT method. The calculations considered the solvent effects to be performed in the presence of a solvent by placing the solute in a cavity within the solvent reaction field (SCRF). The polarizable continuum model (PCM) using the integral equation formalism variant is used in SCRF. The B3LYP functional and the 6-311+G (d,p) basis set were used for all calculations. The vertical excited energies with linear-response (LR) were calculated at optimized geometries using TD-DFT method. TD-DFT was also used to optimize the equilibrium geometries of the nπ* state and ππ* state. After the geometry optimization, the frequency analysis was performed.

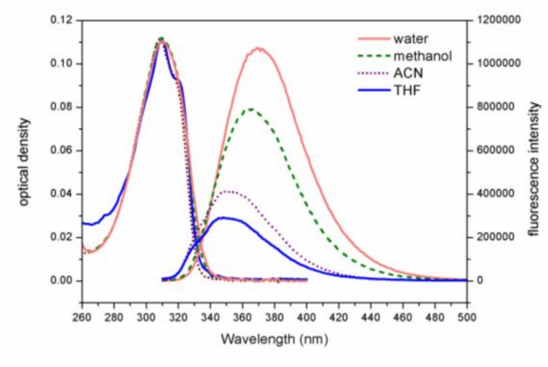

Figure 2: The absorption and fluorescence spectra of BenzUspectra of BenzU in 5 solvents.

The potential energy profiles of excited states of BenzU in gas phase were checked with CC2 type calculations for better discussion. [34] These CC2 calculations were carried with the TURBOMOLE program suite, [35] making use of the resolution-of-the-identity (RI) approximation for the evaluation of the electron-repulsion integrals. The cc-pVTZ basis set has been employed in RI-CC2 calculations.

Results and Discussion

The absorption spectra of BenzU in 5 solvents are shown in **Figure 2**. It shows BenzU has vibrational structure in non-protic solvents, acetonitrile (MeCN), tetrahydrofuran (THF) and 1,4-dioxane (DOX). While in protic solvents, water and

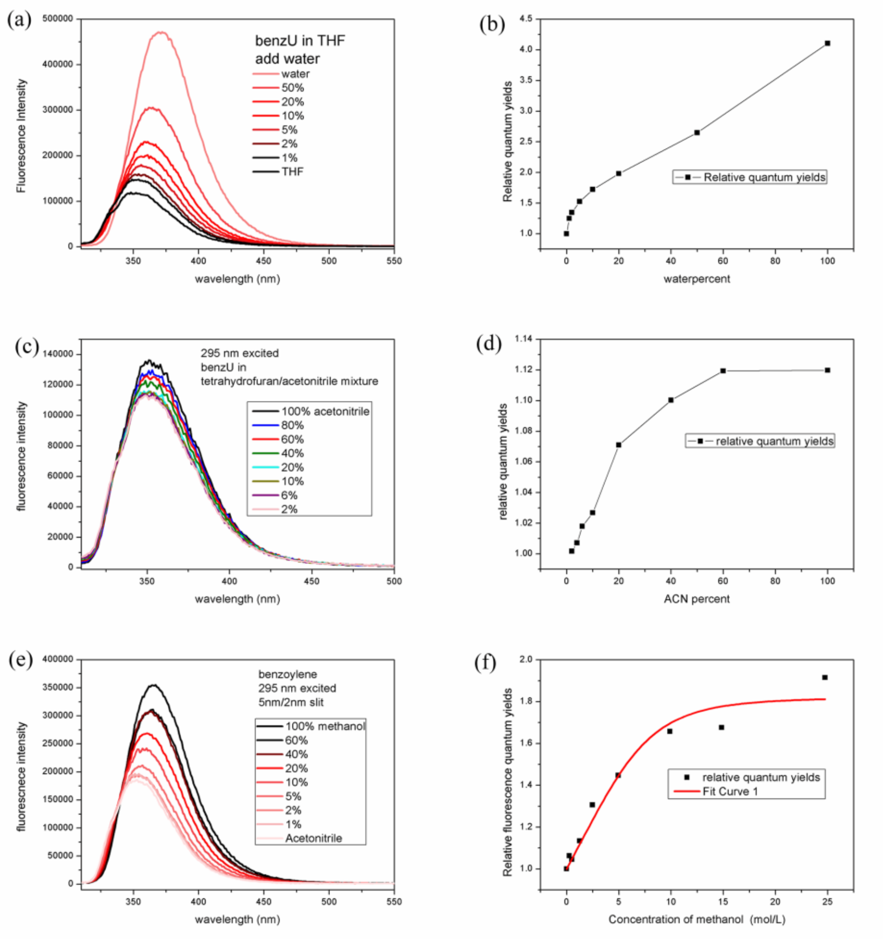

Figure 3: (a) Fluorescence of BenzU in THF/water mixture, (b) The fluorescence quantum yields of BenzU in THF/water mixture with increase of water concentration, (c) Fluorescence of BenzUin THF/MeCN mixture, (d)The fluorescence quantum yields of BenzUin THF/MeCN mixture with increase of water concentration, (e) Fluorescence of BenzUin MeCN/methanol mixture, (f)The fluorescence quantum yields of BenzUin MeCN/methanol mixture with increase of methanol concentration,the solid red line wasfitted line using eq.3.The fluorescence quantum yields of BenzU at percent zero were set to 1 in (c), (e) and (f).