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Fluorescent turn-on detection and assay of water based on 4-(2-dimethylaminoethyloxy)-*N*-octadecyl-1,8-naphthalimide with aggregation-induced emission enhancement

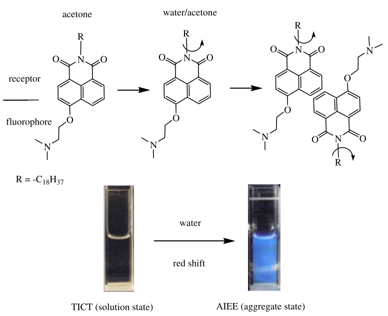
Yang Sun [a,*,1], Xuhua Liang [b], Song Wei [b], Jun Fan [b], Xiaohui Yang [a,*,1]

[a] *Department of Chemistry & Chemical Engineering, Xi'an University of Arts and Science, Xi'an, Shaanxi 710069, China*
[b] *School of Chemical Engineering, Northwest University, No. 229 Taibai North Road, Xi'an, Shaanxi 710069, China*

HIGHLIGHTS

- ▶ 4-(2-Dimethylaminoethyloxy)-*N*-octadecyl-1,8-naphthalimide (DON) was synthesized.
- ▶ The effect of solvents on spectral characteristic of DON was investigated.
- ▶ Semi-empirical molecular orbital calculations by ADF were studied.
- ▶ A fluorometric method of detecting for water content was developed.

GRAPHICAL ABSTRACT



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ABSTRACT

The photophysical properties of 4-(2-dimethylaminoethyloxy)-*N*-octadecyl-1,8-naphthalimide (DON) consisting of donor and acceptor units were investigated in different solutions. Changing from a non-polar to a polar solvent increased the solvent interaction and both the excitation and emission spectra were shifted to longer wavelength and intensity decreased through taking advantage of twisted intramolecular charge transfer (TICT). Density functional theory (DFT) calculations and spectral analyses revealed that such fluorophores were capable of sensing protons by intramolecular charge transfer (ICT). Empirical and quantum mechanical calculations showed that the electron donating effect of the dimethylamino group decreased the change in dipole moment on excitation which resulted in a fluorescence quantum yield remarkably enhanced as the solvent polarity increased. In alkaline media the fluorescence of DON was quenched owing to photoinduced electron transfer being disabled in acidic media. The pK_a of the 1,8-naphthailimide dye was 6.70, which defines the dye as a highly efficient "*off–on*" switch. DON exhibited a typical aggregation-induced emission enhancement (AIEE) behavior that it is virtually nonemissive in organic solvent but highly luminescent in water, as a result of the restriction of free intramolecular rotation of a C–N bond and the non-planar configuration in the aggregate state. The hydrophobicity of octadecyl group provided DON with a fluorescent response to water based on AIEE and the water-dependent spectral characteristics of DON, and the AIEE of DON caused by the effect of water and formation of *J*-aggregation states. In the range of 0–79.8% (v/v), the fluorescence intensity of DON in acetone solution increased as a linear function of the water content. The optimum detection limits were of 0.011%, 0.0021%, and 0.0033% of water in acetone, ethanol, and acetonitrile, respectively. Satisfactory reproducibility, reversibility and a short response time were realized.

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* Corresponding authors. Tel.: +86 29 88566558.
E-mail addresses: 66160692@qq.com (Y. Sun), yangxh1127@yahoo.com.cn (X. Yang).

[1] Yang Sun and Xiaohui Yang are co-first author.

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Introduction

The detection and quantification of small amounts of water are of great significance in several fields of chemistry and industry. Many analytical approaches and techniques have been established for the determination of water in a wide variety of organic solvents, such as Karl Fischer titration method [1], chromatographic methods [2], electrochemical methods based on impedance [3], resistance [4], capacitance [5], conductivity [6], and amperometry [7] as well as spectroscopic techniques [8].

Among the various systems available for water detection, fluorescence methods for water sensing, such as lifetime, intensity and wavelength ratiometric sensing have been widely studied owing to their high sensitivity and reasonable selectivity. Recently, the use of multi-informational dye systems, which are more convenient in terms of required instrumentation and skill, have been shown to be successful for measuring the water content in organic solvents. Ooyama et al. [9–11] described a series of fluorescence sensors for detection of water in organic solvents based on photo-induced electron transfer (PET) of anthracene and phenylaminonaphtho[1,2-*d*]oxazol-2-yl-type. Zhang and Niu et al. [12–14] reported on the synthesis of fluorescence probes and indicators for determining water content in dioxane, acetonitrile and ethanol based on the 1,8-naphthalimide. Chang and coworkers recently prepared several fluorescence water probes based on fluorescein derivative [15], merocyanine dyes [16], 8-hydroxyquinoline derivative [17] and a phenol-indole dye [18]. However, in almost all cases, the fluorescence intensity of probes are decreased upon the increase of water content, which could be attributed to both a specific interaction between water and fluorophore as well as an increase in the polarity of the solvent mixture. Therefore, the exact determination of water content in organic solvents is difficult using such fluorescent dyes, as the fluorescence intensity is strongly affected by the polarity of the solution.

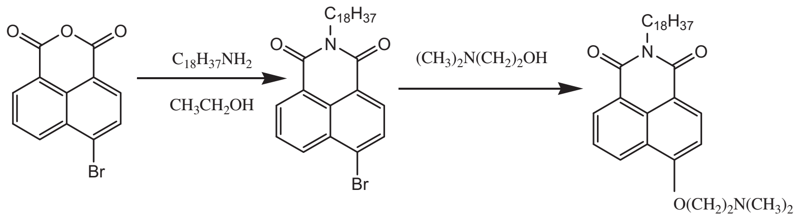
However, in almost all cases, organic dye molecules tend to aggregate when dispersed in aqueous media. The aggregation usually quenches fluorescence, which limits the effective ranges of the probes. Thus, development of simple and stable fluorescence bioprobes without aggregation-caused quenching (ACQ) would be very rewarding work. Recently, a phenomenon, namely aggregation-induced emission (AIE) or "aggregation-induced enhanced emission" (AIEE), which is exactly opposite to the ACQ, discovered by Tang et al. [19–23].

In this work, the intramolecular charge transfer (ICT) upon excitation of the naphthalimide ring was enhanced by the introduction of an amino moiety with electron deficient property to naphthalimide. A derivative of naphthalimide, 4-(2-dimethylaminoethyloxy)-*N*-octadecyl-1,8-naphthalimide (DON), was reported and used as a fluorescence probe due to its favorable sensitivity to solvent polarity. With increasing of water content, the fluorescence intensity of DON was dramatically enhanced and the spectra exhibited a red shift. The fluorescence probe results in acetone, ethanol, and acetonitrile solutions of different water content were displayed. On the basis of this, the fluorescent turn-on detection and assay of water based on DON with AIEE was developed. The successful fabrication of the proposed probe presented satisfactory linear range and low detection limits and was a useful example of the use of naphthalimide derivatives for fluorescence probes to detect water.

Experimental

Reagents

Octadecylamine, *N*,*N*-dimethylethanolamine, 4-bromo-1,8-naphthalic anhydride were purchased from Aldrich. All organic solvents were of analytical-reagent grade and used as dried to eliminate any water residue before the experiment. The 4-(2-dimethylaminoethyloxy)-*N*-octadecyl-1,8-naphthalimide (DON) was prepared according to the reported procedures, and its structure was characterized by chemical and spectroscopic methods (^{1}H NMR, IR) and compared with the data reported in the literature [24], and the synthetic route was shown in Scheme 1. The stock solution of DON was prepared in the dry solvent (1.0×10^{-5} mol/L). The sample solutions with different water contents in the pure organic solvents were freshly prepared prior to the measurement according to the following procedures. A certain bulk of double-distilled water was added in a 10 mL volumetric flask by micropi-



Scheme 1. Synthesis of 4-(2-dimethylaminoethyloxy)-*N*-octadecyl-1,8-naphthalimide (DON).

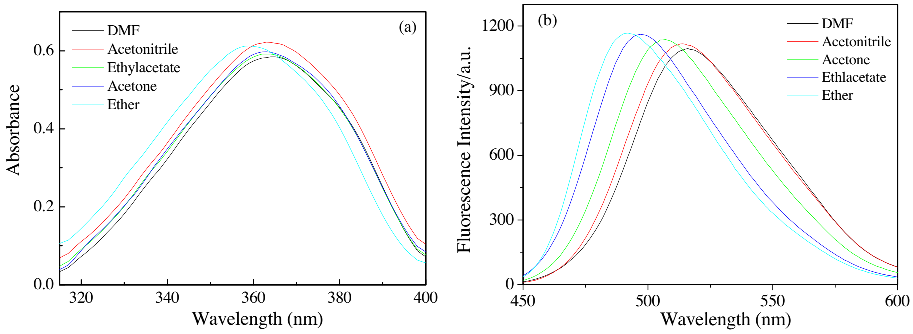


Fig. 1. Absorption (a) and fluorescence spectra (b) of DON (1.0×10^{-6} mol/L) in different solvents.