



## Full Length Article

## Excited-state proton transfer of 4-hydroxyl-1, 8-naphthalimide derivatives: A combined experimental and theoretical investigation



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## ABSTRACT

The photophysical properties of N-butyl-4-hydroxyl-1, 8-naphthalimide (BOH) and N-(morpholinoethyl)-4-hydroxy-1, 8-naphthalimide (MOH) in various solvents are presented and the density functional theory (DFT)/time-dependent density functional theory (TDDFT) methods at the B3LYP/TZVP theoretical level are adopted to investigate the UV-visible absorption and emission data. An efficient intermolecular excited-state proton transfer (ESPT) reaction occurs for both compounds in DMSO, methanol and water. In aqueous solution, both BOH and MOH can be used as ratiometric pH probes and perform as strong photoacids with  $pK_a^* = -2.2, -2.4$ , respectively. Most interestingly, in the steady-state fluorescence spectra of BOH and MOH in concentrated HCl, an unexpected blue-shifted band is observed and assumed to originate from the contact ion pair (CIP) formed by hydronium ion and the anionic form of the photoacid resulted from ESPT. Theoretical calculations are used to simulate the CIP in the case of BOH, which afford reasonable results compared with the experimental data.

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## 1. Introduction

Upon photoexcitation, aromatic alcohols (ROH) such as naphthols, hydroxyquinolines, and hydroxypyrene may increase the acidity dramatically. Research on this photoinduced deprotonation is first described by Förster in 1949 [1] and still attracting intensive attention in the field of biology and physical chemistry [2–11]. The Eigen–Weller model for proton transfer is used to depict this process, where the initial short-range proton transfer forms a contact ion pair (CIP) as a reaction intermediate followed by diffusion controlled separation of the ions [12,13].

Recently, Brouwer and coworkers synthesized and characterized some hydroxy-substituted 1, 8-naphthalimide derived “super” photoacids, where the hydroxyl group is located at the 3 or 6 position of the naphthalimide ring [6,14]. However, for 4-hydroxyl-1, 8-naphthalimide derivatives, which are extensively used for designing turn-on or ratiometric fluorescent indicators for bioimaging [15–29], the photophysical properties and the excited-state proton transfer (ESPT) reactions are rarely studied [30].

In this contribution, the steady-state absorption and emission spectra of two 4-hydroxyl-1, 8-naphthalimide derivatives (BOH and MOH, Scheme 1) in organic solvents and water with various pH values are recorded. The density functional theory (DFT)/time-dependent density functional theory (TDDFT) methods at B3LYP/TZVP theoretical level are adopted to investigate the UV-visible

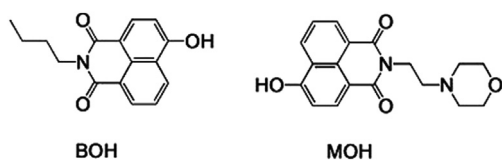
absorption and emission data. In the study of the ESPT of 5-cyano-2-naphthol in sub- and supercritical water, Kobayashi et al. [31] found that the band of their excited neutral ( $ROH^*$ ) and anionic ( $RO^{-*}$ ) species were replaced by a single band of unknown  $X^*$  in the steady-state fluorescence spectra; they assigned the fluorescence of their unknown chemical species as CIP; however, their attempts of using theoretical calculations to gain a stable structure as the direct evidence for the existence of the CIP failed. In this paper, we present the observation of an unexpected blue-shifted single band in the fluorescence spectra of BOH and MOH in concentrated HCl, which is distinct from the fluorescence of the neutral or anionic species and is assumed to emit from the CIP resulted from the ESPT reaction. Meanwhile, the DFT/TDDFT methods were used to gain more insight into the CIP formed by  $BO^{-*}$  and hydrated proton. The calculated absorption and fluorescence peaks were used to test the proposed CIP models by comparing with our experimental data. The structural changes of the hydrogen-bonded complexes from the ground-state ( $S_0$ ) to the first excited-state ( $S_1$ ) and the potential curves of the ESPT reaction along the hydrogen-bond coordinate are also discussed.

## 2. Experimental section

## 2.1. Instruments and materials

Steady-state UV-visible absorption spectra were measured on a Lambda 35 UV-visible Spectrophotometer (Perkin-Elmer) with

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Scheme 1. Chemical structures of BOH and MOH.

matched 10-mm quartz cuvettes. Fluorescence spectra were obtained from Fluoromax-4 Spectrofluorometer (Horiba-Jobin Yvon, monochromator calibrated). Except for the samples in  $\text{H}_2\text{SO}_4$  aqueous solutions ( $17 \pm 1^\circ\text{C}$ ), all the other experiments were performed at room temperature ( $26 \pm 1^\circ\text{C}$ ).

Acetonitrile, toluene, dimethylsulfoxide (DMSO), dichloromethane (DCM) and methanol were purchased from reputable suppliers and used as received (HPLC grade). Ultrapure water (resistivity  $18.2 \text{ M}\Omega \text{ cm}$ ) from a Millipore water purification system was used throughout. All the solvents were checked for fluorescent impurities prior to use. Other chemicals were of analytical grade without further purification. Phosphate buffer (50 mM) with various pH values were prepared by mixing the aqueous solutions of monosodium phosphate (50 mM), sodium hydrogen phosphate (50 mM) or phosphoric acid (50 mM), measured with an Ohaus pH meter STARTER2100. Phosphate buffer saline (PBS) was aqueous solution of phosphate (10 mM), NaCl (8.0 g/L) and KCl (0.2 g/L), pH 7.3. Spectra in phosphate or HCl aqueous solutions were collected from samples of BOH and MOH diluted from their DMSO stock solutions.

The 4-hydroxy-1,8-naphthalimide derivatives (BOH and MOH) were synthesized following procedures described in the literatures [17,22]. NMR and mass spectra were recorded to characterize the compounds. For BOH:  $^1\text{H}$  NMR (500 MHz,  $\text{d}^6$ -DMSO)  $\delta$  (ppm): 11.84 (s, 1H), 8.50 (dd,  $J=8.5$  Hz, 1H), 8.43 (dd,  $J=7.0$  Hz, 1H), 8.33 (d,  $J=8.0$  Hz, 1H), 7.73 (t,  $J=7.8$  Hz, 1H), 7.14 (d,  $J=8.0$  Hz, 1H), 4.01 (t,  $J=7.5$  Hz, 2H), 1.63–1.57 (m, 2H), 1.39–1.32 (m, 2H), 0.94 (t,  $J=7.5$  Hz, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{d}^6$ -DMSO)  $\delta$  (ppm): 13.63, 19.76, 29.69, 39.02, 109.85, 112.56, 121.71, 122.29, 125.41, 128.73, 129.07, 130.95, 133.37, 160.13, 162.89, 163.56. MS (API-ES):  $m/z$ , Calcd. for  $\text{C}_{16}\text{H}_{15}\text{NO}_3$ : 269.11, found:  $[\text{M}-\text{H}]^-$  268.16. For MOH:  $^1\text{H}$  NMR (400 MHz,  $\text{d}^6$ -DMSO)  $\delta$  (ppm): 8.53 (dd, 1H,  $J=8.2$  Hz), 8.46 (dd, 1H,  $J=7.2$  Hz), 8.35 (d,  $J=8.4$  Hz, 1H), 7.77–7.73 (m, 1H), 7.13 (d, 1H,  $J=8.0$  Hz), 4.17 (t, 2H,  $J=7.0$  Hz), 3.55 (t, 4H,  $J=4.6$  Hz), 2.60–2.50 (m, 6H).  $^{13}\text{C}$  NMR ( $\text{d}^6$ -DMSO, 100 MHz)  $\delta$  (ppm): 164.20, 163.47, 161.26, 134.13, 131.61, 129.77, 129.48, 125.96, 123.02, 122.21, 112.65, 110.57, 66.58, 56.12, 53.82, 36.91. HRMS (ESI) Calcd. for  $\text{C}_{18}\text{H}_{19}\text{N}_2\text{O}_4$   $[\text{MH}^+]$  327.1345, found 327.1358.

## 2.2. Theoretical calculation details

DFT and TDDFT methods were used to do theoretical simulations in this work with Gaussian09 programs [32]. The Becke's three-parameter hybrid exchange functional with a Lee–Yang–Parr gradient-corrected correlation (B3LYP) [33] was used as a method of choice. The triple- $\zeta$  valence quality with one set of polarization functions (TZVP) basis sets [34] were used in all the calculations. Environmental effects (here, water or acetonitrile, as in the experiment) were accounted for using the IEFPCM solvation model. The vertical excitation and emission energies are based on the optimized geometries with no constraints to all the atoms, bonds, angles or dihedral angles during the optimizations. Vibrational frequencies are analyzed to confirm the validity of the stationary points.

## 3. Results and discussion

### 3.1. Spectra in organic solvents

Emission spectra of BOH and MOH in several organic solvents are presented in Fig. 1. There is only one fluorescence band emitted by  $\text{ROH}^*$  in DCM, toluene or acetonitrile, while in DMSO or methanol, two fluorescence bands which are assigned to  $\text{ROH}^*$  and  $\text{RO}^-$  are monitored. In DMSO or methanol, the absorption spectra indicate that both  $\text{RO}^-$  and  $\text{ROH}$  exist in the ground-state (Figs. S1, S2). In the presence of HCl (12 mM) in DMSO or methanol, the compounds predominately exist as the neutral forms in the ground state; however, there are still two emission bands in the spectra of those solutions (Fig. S3). Thus, it is evident that BOH and MOH undergo ESPT reactions efficiently in DMSO or methanol, but not in DCM, toluene or acetonitrile.

The absorption and fluorescence spectral properties of the two compounds in the above solvents, including the absorption and fluorescence maxima ( $\lambda_a$ ,  $\lambda_f$ ), the fluorescence quantum yield ( $\Phi_f$ ) values, are summarized in Table 1. The absorption maxima for samples in DMSO and methanol, where both the neutral and anionic forms exist, are determined by spectral decomposition with a sum of two gaussians. As for the emission data, we noted that Brouwer and coworkers reported the requirement of three rather than two gaussians to fit the fluorescence spectrum of EG-dHONI in DMSO [6]; in our case, a sum of three gaussians was required to fit the curves for samples in DMSO and methanol (Fig. S4), since two gaussians were not adequate to model the spectra (Fig. S5).

In contrast to BOH, the  $\Phi_f$  values of MOH in aprotic solvents such as toluene, DCM or acetonitrile are substantially small. To investigate this effect of substitution, theoretical calculations were carried out by using the Gaussian 09 program with acetonitrile as

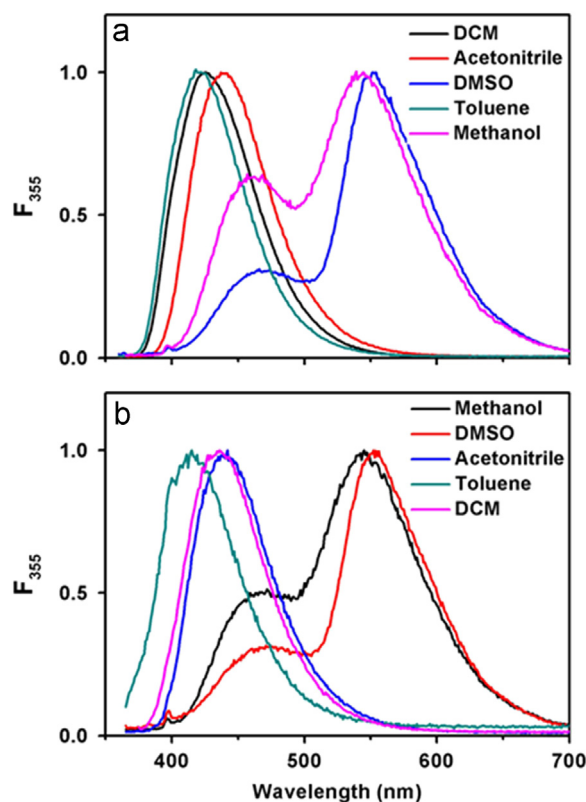


Fig. 1. Normalized fluorescence spectra of (a) BOH and (b) MOH in organic solvents (the excitation wavelength,  $\lambda_{\text{ex}}=355$  nm). The concentrations of these solutions are  $10^{-6}$ – $10^{-5}$  M.

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