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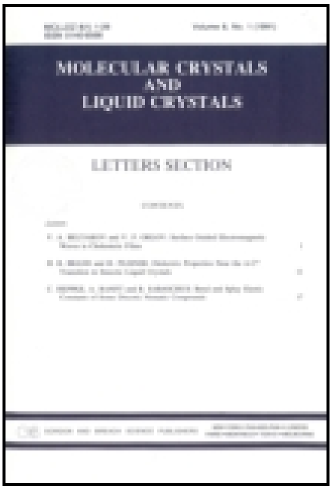

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Arylmaleimide Based Fluorescence On-Off Modulated by Ac_2O/HCl

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In this contribution, a dye (HBM) with naphthalene and bisindolylmaleimide incorporated together was synthesized and characterized by NMR and mass spectroscopic techniques. Weak emission of HBM was ignited by addition of Ac_2O with the emission centered at 580nm. Moreover, the ignited emission can also be quenched by addition of HCl. A toggle-switchable "off-on" model can be established based on the reversible process. The underlying mechanism was proposed as esterification/hydrolysis reaction. Calculation of frontier molecular orbitals uncovers the reason for reversible ignition/quench fluorescence emission of HBM further.

Keywords Bisindolylmaleimide; "off-on"; fluorescence emission; frontier molecular orbitals

Introduction

Small organic molecules have been act as an attractive area in device fabrication, sensor configuration, signal switches, molecular logic, machines etc [1–5]. Out of various types of small molecular devices with variety of fascination behavior, utilizing fluorescence signal to translate molecular recognition event is the most convenient method.

Bisindoylmaleimide (**BIM**), the core structural framework, is present as the subunit of biologically active metabolites isolated from Streptomycetes, including staurosporine and rebeccamycin. Most aryl or arylamine substituted 3,4-diarylmaleimide show strong luminescence in solution and in solid [6–13]. The research focus on photonic applications was emerged in recent decades, which has been demonstrated by the application of **BIM** derivatives as electroluminescent materials [9, 14]. Maleimide is an electron-deficient heterocyclic ring. Introducing another electron sensitive group to the imide unit is a convenient

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way to modulate the electron distribution over the molecular system. Based on the chemical modification of **BIM**, photo-physical properties, such as the emission wavelength, quantum yield, Stokes's shift, and solid emission, could be obtained according to the requirement of the designed fluorescent molecules. With electron withdrawing or electron donor arylamine attached, effect charge transfer and consequent electro properties have been demonstrated by documents.

In this contribution, hydroxyl naphthalene was introduced to arylamine substituted **BIM**. Our intention was to impose influence on the sensitive group and understand the corresponding properties through detailed study and structural analysis. Achieving the controlled fluorescence is of significant in the biological application for **BIM** derivatives, which has been well documented [15, 16].

Experimental

General Procedures and Materials

The solvents used in the reaction were carefully dried according to the standard procedure and stored over 4Å molecular sieve. All the reagent-grade chemicals were purchased from Sigma-Aldrich CO. LLC. (South Korea) and used without further purification. Melting points were determined on a Mel-Temp® IA9200 digital melting point apparatus in a glass capillary and were uncorrected. All synthesized compounds were routinely characterized by TLC and ^{1}H NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

^{1}H and ^{13}C NMR Spectroscopy

^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AM-400 spectrometer operating at frequencies of 400 MHz for proton 100 MHz for carbon in DMSO-d_6. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0$) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet) as well as *b* (broad). Coupling constants (J) are given in Hertz.

Mass and High Resolution Mass Spectra (HRMS)

The mass spectra measured on a LC-MS (Waters UPLC-TQD) mass spectrometer. High resolution mass spectra (HRMS) were measured on a Brucker microOTOF II Focus instrument.

UV-Vis and Emission Spectra

The absorption spectra were measured with a PERSEE TU-1900 and an Agilent 8453 spectrophotometer. Emission spectra were measured with Shimadzu RF-5301PC fluorescence spectrophotometer. The solvents used in photochemical measurement were spectroscopic grade and were purified by distillation. The stock solution of compounds (2×10^{-3} M) was prepared in THF, and a fixed amount of these concentrated solutions were added to each experimental solution. All the experiments were done repeatedly, and reproducible results were obtained. Prior to the spectroscopic measurements, solutions were deoxygenated by bubbling nitrogen through them.

Theoretical Calculations

For the theoretical study of excited state photo-physics of the compound, the *DMol*^{3} program packaged in *Material Studio* (Accelrys Software Inc., US) was used [17, 18]. The ground state geometries and the frontier molecular orbital of the compound were calculated using the density function theory (DFT) with the B3LYP hybrid functional and the double numerical plus *d*-functions (DND) atomic orbital basis set.

Synthesis

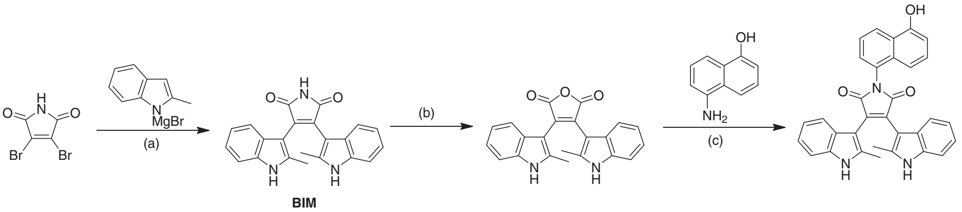
The synthesis of substituted **BIM**, *N*-(5-hydroxynaphthalen)-bis-3,4-(2-methylindol-3-yl)maleimide (**HBM**), was outlined in Scheme 1. **BIM** was obtained by the coupling between dibromomaleimide and 2-methylindole protected by Grignard reagent. The subsequent hydrolysis of **BIM** in aqueous KOH yielded bis-2-methylindolylmaleic acid anhydride [12, 13, 19]. Imidization of bis-2-methyindolemaleic anhydride with 5-aminonaphthalen-1-ol yielded the target compound.

Bisindoylmaleimide

A solution of ethylmagnesium bromide in ethyl ether (7 ml) was prepared from magnesium turnings (0.52 g, 19.5 mmol) and bromoethane (1.5 ml, 19.5 mmol). Under nitrogen atmosphere, the ethylmagnesium bromide solution was added to a solution of 2-methylindole (2.6 g, 19.5 mmol) in 35 ml toluene. After heating to 60°C for 1h, a solution of dibromomaleimide (1.0 g, 3.9 mmol) in THF (7 ml) was added. The mixture was heated to reflux for 24h, then cooled to room temperature and diluted with EtOAc (100 ml). The organic layer was washed with aq. 1N HCl (50 ml), water (50 ml) and brine (50 ml) in succession, and was dehydrated over anhydrous $MgSO_4$. The residue after evaporation of the solvent was purified by chromatography with EtOAc/hexane (2:1) afforded 1.2 g (86%). Melting point: 184–186°C.

^{1}H NMR(400 MHz, DMSO–d_6): δ (ppm) 11.29 (1H, *s*), 10.94 (1H, *s*), 10.87 (1H, *s*), 7.21 (2H, *d*, $J = 8.0$ Hz), 6.99 (2H, *d*, $J = 8.0$ Hz), 6.94 (2H, *t*, $J = 8.0$ Hz), 6.73 (2H, *t*, $J = 8.0$ Hz), 1.95 (6H, *s*); ^{13}C NMR(100 MHz, DMSO–d_6): δ (ppm): 172.3, 135.3, 135.2, 134.8, 131.8, 126.8, 126.5, 120.7, 119.9, 119.2, 119.0, 118.7, 118.3, 110.5, 12.9; MS(EI, 70 eV) m/z 355 (M^+); HRMS calcd for $C_{22}H_{17}N_2O_3$ 355.1321, found 355.1319.

Bis-2-methyindolemaleic anhydride. Bisindoylmaleimide (1.0 g, 2.9 mmol) was suspended in 10% aqueous potassium hydroxide (200 ml). The mixture was heated to reflux for 3h.



Scheme 1. Synthetic route and conditions: (a) toluene/Et_2O/THF (5:1:1), refl. 24h; (b) 10% aq. KOH, refl. 40min; (c) 2N HCl; (d) THF/Ca_2CO_3, refl. 48h.

Then it was cooled to room temperature and acidified with 2N HCl. A large amount of red precipitate formed. The collected precipitate was washed with water. The filtration was extracted with ethyl acetate (30 mL × 3) and dried over anhydrous $MgSO_4$. After the solvent evaporated, the residue and the collected precipitate was combined and purified by silica gel column chromatography with ethyl acetate/petroleum ether (2:1) as the eluent, affording red sold (1.0 g, yield 100%).

^{1}H NMR (400 MHz, DMSO–d_6): δ (ppm): 11.50 (2H, s), 7.27 (2H, *d*, $J = 8.0$ Hz), 7.07 (2H, *d*, $J = 7.6$ Hz), 7.01 (2H, *t*, $J = 7.6$ Hz), 6.80 (2H, *t*, $J = 7.6$ Hz), 2.02 (6H, *s*); ^{13}C NMR (100 MHz, DMSO–d_6): δ (ppm): 166.4, 139.3, 139.2, 136.0, 135.8, 132.5, 126.6, 121.7, 120.1, 119.9, 111.4, 103.1, 13.5; MS(EI, 70 eV) m/z 356 (M^+); HRMS calcd for $C_{22}H_{16}N_2O_3$ 356.1161, found 356.1164.

N-(5-hydroxynaphthalen)-bis-3,4-(2-methylindol-3-yl)maleimide (HBM). Bis-2-methylindolylmaleic acid anhydride (50 mg, 0.14 mmol), 5-aminonaphthalen-1-ol (24 mg, 0.15 mmol) dissolved in 25 mL THF. Potassium carbonate (15 mg) was added to the above solution and heated to reflux for about 48 h. The reaction process was monitored by TLC. The reaction was quenched until the bis-2-methylindolylmaleic acid anhydride was disappeared on TLC. After cooling to room temperature, the reaction mixture was poured to water (25 mL) and the organic phase was separated. Aqueous was extracted with ethyl acetate (25 mL × 3). The collected organic phase was dried over $MgSO_4$. After separation of $MgSO_4$, the organic solvent was evaporated in vacuum. Crude product was purified by silica gel column chromatography with ethyl acetate/petroleum ether (2:3) as the eluent, affording dark red solid (40 mg, yield 57%).

^{1}H NMR(400 MHz, DMSO–d_6): δ (ppm): 11.38 (2H, s), 10.38 (1H, s), 8.30–8.28 (*d*, $J = 8.0$ Hz, 1H), 7.68 (1H, s), 7.61–7.58 (1H, m), 7.43 (1H, s), 7.26–7.24 (*d*, $J = 8.0$ Hz, 3H), 7.12–7.11 (*d*, $J = 7.6$ Hz, 2H), 7.00–6.95 (3H, m), 6.80–6.76 (2H, *d*, $J = 7.2$ Hz), 2.07 (6H, s); 171.0, 154.1, 136.0, 132.4, 131.6, 129.5, 128.2, 125.9, 124.6, 121.4, 119.9, 119.7, 111.2, 108.9, 103.7, 13.6; MS (EI, 70 eV) m/z 497 (M^+); HRMS calcd for $C_{32}H_{23}N_3O_3$ 497.1739, found 497.1754.

N-(5-acetatenaphthalen)-bis-3,4-(2-methylindol-3-yl)maleimide (HBM-E). **HBM** (20 mg, 0.04 mmol), acetic anhydride (10.2 mg, 0.1 mmol) dissolved in THF 5 mL. The mixture was heated to reflux for about 6 h, which was monitored by TLC. After cooled to room temperature, the solvent was evaporated in vacuum. The residue was loaded on silica gel column and eluted with ethyl acetate/petroleum ether (3:2), affording red powder (8 mg, yield 37%).

^{1}H NMR(400 MHz, DMSO-d_6): δ (ppm): 11.35 (2H, s), 8.02 (*d*, $J = 8.0$ Hz, 1H), 7.93 (*d*, $J = 8.0$ Hz, 2H), 7.74–7.72 (*m*, 3H), 7.58–7.52 (*m*, 2H), 7.35 (*t*, $J = 8$ Hz, 2H), 7.13 (*d*, $J = 8$ Hz, 2H), 6.79–6.76 (*m*, 2H), 2.31 (*s*, 3H), 2.09 (*s*, 6H); ^{13}C NMR (100 MHz, DMSO–d_6): δ (ppm): 170.6, 169.6, 153.2, 136.1, 133.2, 131.9, 130.7, 128.2, 127.7, 127.3, 127.0, 126.5, 123.8, 122.8, 121.3, 119.8, 119.3, 111.1, 110.5, 103.8, 21.3, 13.5; MS (EI, 70 eV) m/z 539 (M^+); HRMS calcd for $C_{34}H_{25}N_3O_4$ 539.1845, found 539.1847.

Result and Discussion

Figure 1 shows the absorption spectra of conjugate **HBM** in THF. A broad absorption band ranged from 400 to 500 nm, which can be assigned to the π–π^* transitions from the S_0 to S_1 and S_2 states. Another intense absorption band locates at 280 nm. The intense located at 280 nm corresponds to the naphthalene moiety introduced. The naphthalene moiety is

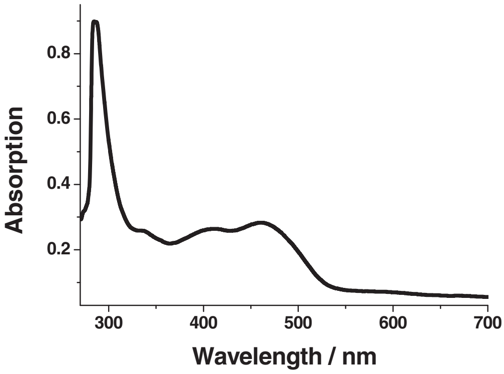


Figure 1. Absorption spectra of **HBM** (2.0×10^{-5} M) in THF.

twist out of the plane of imide ring and leads to the naphthalene and **BIM** acting as two independent chromophores connected through a single covalent bond. The ratio of molar extinction coefficients $\varepsilon_{280\text{nm}}$ (280 nm) and $\varepsilon_{\mathbf{BM}}$ (460 nm) were estimated to be ca. 4.5×10^4 and 1.4×10^4 L·mol^{-1}·cm^{-1}. The longest maximum absorption (460 nm) is the characteristic absorption band of **BIM**. Only 12 nm red shift was observed with respect to that of **BIM** [12]. This indicates very weak electronic coupling between the two integrated chromophores, bisindolylmalimide and naphthalene. Similar contour were observed for **HBM** in nonpolar solvents such as toluene and dioxane and in polar solvents such as chloroform and ethanol. There was no color fading observed by long time placement in solvents (DMF, DMSO, EtOH) and solid, demonstrating the stability of **HBM**.

HBM shows very weak emission in THF (Figure 2). It is different from other **BIM** derivatives with strong emission intensity in solution or in solid. Generally, naphthalene, a strong blue emitter, was incorporated with a longer wavelength emitter and the energy transfer from will be efficient from shorter wavelength emitter to the longer one. However, this event was blocked in **HBM** molecular system. It is interesting that the emission of **HBM** can be turned on by the addition acetic acid. Upon addition of acetic anhydride, the emission intensity increased gradually with the emission peak around 580 nm. The fluorescence emission can be quenched by the addition of HCl. It is reversible by repeated

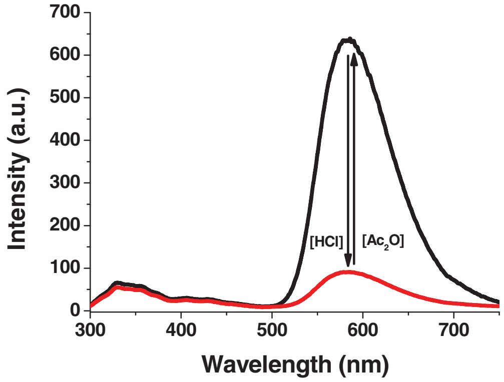
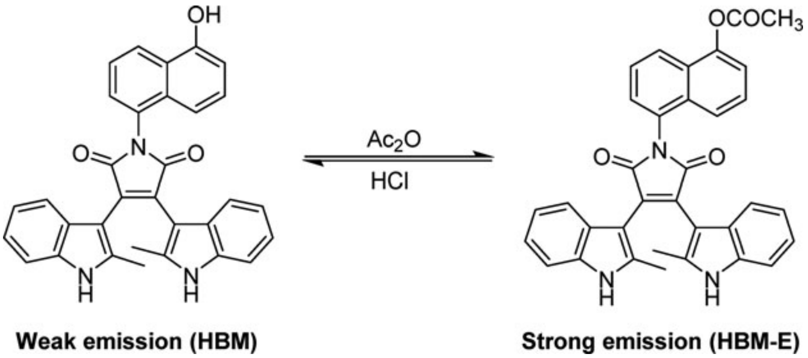


Figure 2. Fluorescence emission spectra upon the addition of Ac_2O and HCl.



Scheme 2. Proposed mechanism by addition of Ac_2O/HCl.

addition of Ac_2O/HCl, as depicted in Figure 2. The underlying mechanism was given in Figure 4, and **HBM** was esterified yielding an ester (**HBM-E**). **HBM** was esterified by the addition of acetic anhydride and the fluorescence was also activated. Upon addition of HCl, the ester group was hydrolyzed to hydroxyl again and the intramolecular transfer from naphthalene to bisindolylmaleimide was blocked and quenched the fluorescence emission. A fluorescence "off-on" model can established based on the **HBM** molecular systems. It is obvious that once the hydroxyl was esterified, the emission of bisindolylmaleimide and the energy transfer from naphthalene to bisindolylmaleimide was actuated. Before the addition of Ac_2O, the emission of **HBM** was weak and the quantum yield was estimated to be lower than 0.01 with the excited wavelength at 280 and 460 nm both. After the addition of Ac_2O, the hydroxyl transformed to ester group and the emission of **BIM** was recovered (Scheme 2). Both 280 nm and 460 nm excitation of **HBM** can excite the 580 nm emission. The Stokes shift was estimated to be 100 nm with 460 nm excitation. And because of the introduction of naphthalene, a strong deep blue emitter, the pseudo-Stokes shift was calculated to be 300 nm. The quantum yields (Φ_{280} and Φ_{460}) were estimated to be 0.28 and 0.32, respectively.

To better comprehend the geometrical, electronic, and optical properties of **HBM**, we undertook a comprehensive computational investigation using Material Studio. To reduce the run times in the first instance, the ground-state energy-minimized structures were calculated using DFT and LDA/DN basis set [17, 18]. Further refinement and optimization on structures were undertaken using DND/B3LYP basis set.

The size and signs of frontier molecules orbitals are illustrated in Figure 3. Distinctive contributions of each atomic orbital are discernible in the HOMO and LUMO diagrams. The striking feature of the electron density distribution is in HOMOs of **HBM** and **HBM-E**. There is obvious difference in HOMO between **HBM** and **HBM-E**. For **HBM**, the electron density is well distributed on bisindolylmalimide unit. Small part of electron density spread to naphthalene unit. In contrast, the distribution of HOMO in HBM-E spread over bisindolylmalimide with being neglected electron density distribution on naphthalene unit. It is obvious that the electron density distribution on the naphthalene unit more or less depends on the electronic properties. The strong electron donor ability leads to part of electron density distribution on naphthalene unit. Once the hydroxyl was esterified, the electron donor ability of oxygen atom substituted on naphthalene unit was weaken significantly and consequently results the HOMO distribution away from naphthalene unit, which make it more like the **BIM** itself. There appears to be a regular trend in the LUMOs

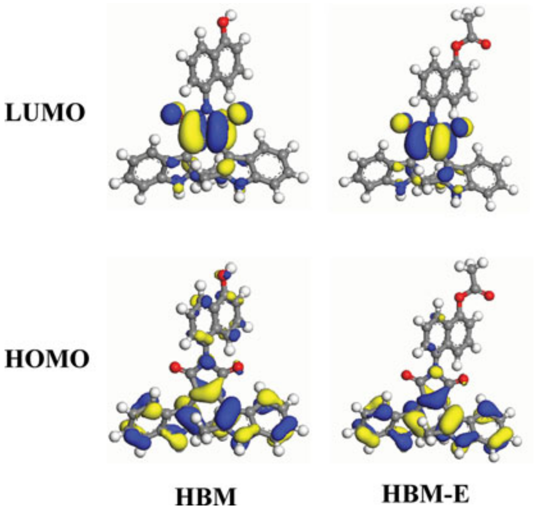


Figure 3. Representative HOMO and LUMO diagrams of **HBM** and **HBM-E** obtained from Dmol^3 calculations.

for **HBM** and **HBM-E**, where the electron-deficient maleimide rings always contribute to the LUMOs mainly and the fused pyrrole ring of indole partly contribute to the LUMOs. It is clearly indicated that effective charge transfer states in donor-acceptor molecular systems were formed in **HBM**, and lead to the fluorescent quenching. Without effective charge transfer states in donor-acceptor molecule systems, strong emissions was ignited for **HBM-E**. In addition, the rotation of naphthalene unit around the C-N single bond accounts for the non-radiative transition of **HBM** in the excited state. In **HBM-E**, esterified hydroxyl lowered the electron density of naphthalene, and thus led to the suppressed non-radiative transition in some degree. Therefore, the emission of **HBM-E** was recovered. Modification of the electron push-pull system in bisindolylmaleimide backbone is an effective method in designing fluorescent bisindolylmaleimide derivatives.

Conclusions

In summary, a new *N*-(5-hydroxynaphthalen)-bis-3,4-bis(2-methylindol-3-yl)maleimide dye (**HBM**) was synthesized and fully characterized. In the molecular system, naphthalene was connected with bisindolylmaleimide through covalent single bond, which lead to a highly twisted molecular configuration.

Due to the incorporated of the deep blue emitter, naphthalene, the absorption around 280nm was increased. The weak emission of **HBM** in THF can be activated by addition of Ac_2O with the emission peak 580 nm. The ignited emission can also be quenched by HCl addition. And an "off-on" switch model was established based on this reversible process. Computational results of frontier orbitals suggest that an efficient charge transfer of **HBM** quenched the fluorescence emission. Esterified hydroxyl weakens the electron compatibility to naphthalene and results the HOMO distribution similar to **BIM**, consequently recovering the fluorescence emission. These results are important clue for design functionalized **BIM** derivatives. Our efforts towards the application of **BIM** derivatives as fluorescent probe and biological purpose are currently underway.

Acknowledgments

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