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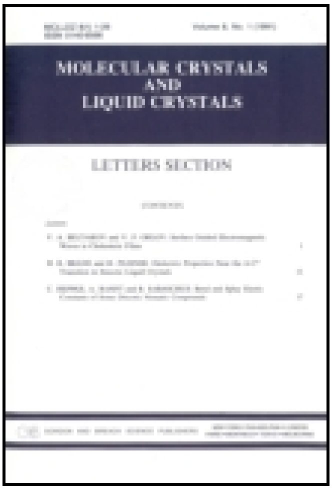

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Fluorescence Quench of Arylmaleimide with a Substituted Anthracene

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In this contribution, a bindolylmaleimide dye (ABM) with anthracene substituted through a covalent single bond was synthesized and characterized by NMR and mass spectroscopic techniques. Emission of ABM was investigated in various solvents. The emission intensity of ABM is weak in dioxane and toluene, and negligible in other solvents. Frontier molecular orbitals calculation for ABM was carried out based on Dmol^3 *package suit. Intramolecular charger transfer and free rotation of anthracene contributed to the non-radiative relaxation.*

Keywords Bisindolylmaleimide; emission; frontier molecular orbitals; non-radiative relaxation

Introduction

Research focused on small organic molecules has been attracted significant attention of scientists and emphasis was put on the application of emission device, fluorescent sensor, logic gate, and molecular machine [1–4]. Among various methods in signal transformation, utilizing the signal of fluorescence emission is the best choice for translating molecular recognition event.

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 [5–12]. Due to the steric hindrance between two indole rings, the configuration of **BIM** was twisted our of the imide plane, which also benefit to the formation of amorphous. Maleimide is an electron-deficient heterocyclic ring. Two indole

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rings act as electron-donor unit in **BIM** molecular system. The build-in donor-acceptor system leads to the typical emission of **BIM** (560 nm). The research focused on photonic applications was emerged only in recent decades, which demonstrates the excellent advantages as electroluminescent materials [8, 13]. Introducing electron donor or acceptor units provides the convenient way of modulating the electronic properties of **BIM** [12]. From the point of design and synthesis, it is convenient through imidization of bisindolymaleic acid anhydride to yielding the modified molecular system. And further fictionalization could be developed at the substitutes further, and alternating the electronic properties of **BIM**. Based on the purposeful modification of **BIM**, photo-physical properties, such as the emission wavelength, quantum yield, Stokes's shifts, and solid emission, could be available and developed for practical applications. With electron withdrawing or electron donor arylamine attached to **BIM**, excellent performance has been demonstrated by documents.

In this contribution, anthracene, a violet emitter, was introduced to imide ring of **BIM**. Detailed investigation of its optical properties benefits to deep understanding the inherent character of **BIM**.

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. 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 NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

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

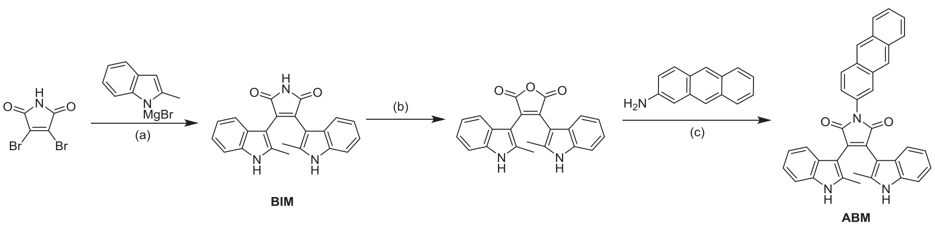
^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AM-400 spectrometer operating at frequencies of 400 MHz for proton 100 MHz for carbon in DMSO-d_6. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0$) as internal standard and expressed in 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. The emission spectra were measured with a 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



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

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 [14, 15]. 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**, 1-(anthracen-2-yl)-3,4-bis(2-methylindol)maleimide (**ABM**), 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. Imidization of bis-2-methyindolemaleic anhydride with 5-aminonaphthalen-1-ol yielded the target compound **ABM.**

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(100MHz, 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. 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 (100MHz, 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.

1-(Anthracen-2-yl)-3,4-bis(2-methylindol)maleimide (ABM)

Bis-2-methylindolylmaleic acid anhydride (50 mg, 0.14 mmol), 2-amineanthracene (29 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 27 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 eluant, affording dark red solid (18 mg, yield 24%). Melting point: 333–334°C.

^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm): 11.40 (2H, s), 8.68–8.65 (2H, *d*, $J = 8.8$ Hz), 8.26–8.21 (2H, *m*), 8.13 –8.11 (2H, *m*), 7.72–7.70 (1H, *d*, $J = 8.8$ Hz), 7.56–7.53 (2H, *m*), 7.26–7.24 (2H, *d*, $J = 8$ Hz), 7.19 (2H, *s*), 7.00–6.96 (2H, *d*, $J = 7.6$ Hz), 6.81–6.77 (2H, *m*), 2.06 ppm (6H, *s*); ^{13}C NMR (100MHz, DMSO-d_6): δ (ppm): 170.4, 136.0, 131.9, 131.9, 131.2, 130.2, 130.2, 129.1, 128.6, 128.5, 126.7, 126.5, 126.4, 126.4, 125.5, 125.3, 121.4, 120.1, 119.7, 111.1, 103.7, 13.6; MS(EI, 70 eV) m/z 531 (M^+); HRMS calcd for $C_{36}H_{25}N_3O_2$ 531.1947, found 531.1950.

Result and Discussion

Figure 1 shows the absorption spectra of **ABM** and the corresponding model chromophore of anthracene and **BIM** in THF. A major absorption band was observed for **ABM** in the visible region centered at 475 nm with a shoulder centered at 410 nm, which can be assigned to the π–π^* transitions from the S_0 to S_1 and S_2 states, respectively. It can be found clearly that the typical absorption of anthracene 340, 358, and 378nm. The three typical absorption peaks was also observed in that of **ABM**. The absorption peaks observed in **ABM**, including 344, 363, 382 nm, exhibits superimposed effect, which is also the sum of the absorption spectra of anthracene and **BIM**. It is indicates that **ABM** behaves as two separately conjugated chromophores connected through a single covalent bond. Only a slight red shift (4 nm) in the band corresponding to the anthracene moiety was observed. In contrast, the red shift in the band of corresponding to **BIM** was estimated to be 10 nm. It indicates that there is a very weak electronic coupling between the two

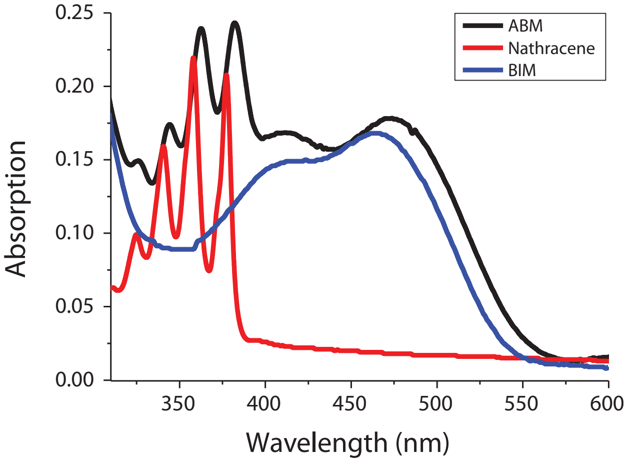


Figure 1. Absorption spectra of **ABM** (1.0×10^{-5} M) in THF.

integrated chromophores. Similar contour were observed for **ABM** in nonpolar solvents such as toluene and dioxane and in polar solvents such as chloroform, ethanol, and DMF. Detailed absorption/emission peaks, absorption coefficients, and Stokes shifts in various solvents are collected in Table 1.

The emission intensity is largely different in various solvents (Table 1). Figure 2 shows the emission spectra of **ABM** in several different polarity solvents. In dioxane, the emission peak was observed at 571 nm and it is almost identical to the emission peak of **BIM** (569 nm) [11]. The emission in toluene is weaker than that in dioxane with the emission peak around 567 nm. In chloroform, the emission peak is similar to that in toluene except the broadened contour. It is almost negligible for the emission in other solvents, such as DMF, ethanol, chloroform. Apart from the solvents mentioned here, other solvents were also applied in the emission measurement of **ABM** and negligible emission intensity

Table 1. Optical data of **ABM** (1.0×10^{-5} M) in various solvents

	UV-Vis		Fluorescence		
Solvent	λ_{abs} (nm)	$\log\varepsilon_{max}$	λ_{em} (nm)	Φ_F	Stokes shift (nm)
Toluene	363/383/468	3.82/3.83/3.60	567	0.03	184
Dichloromethane	362/382/469	3.88/3.88/3.71	—	—	—
Chloroform	363/382/471	3.56/3.54/2.93	—	—	—
THF	363/382/475	3.63/3.65/3.47	566	0.01	184
Dioxane	362/381/460	3.77/3.77/3.52	571	0.08	190
Ethanol	360/380/488	3.70/3.68/3.56	—	—	—
Acetonitrile	360/380/458	3.81/3.81/3.63	—	—	—
DMF	360/380/470	3.37/3.38/3.50	—	—	—
DMSO	364/384/480	3.82/3.79/3.57	—	—	—

Note: The fluorescence quantum yield of each compound was determined with reference to quinine bisulfate in 0.05 M H_2SO_4 aqueous solution ($\Phi_F = 0.51$). Emissions are corrected.

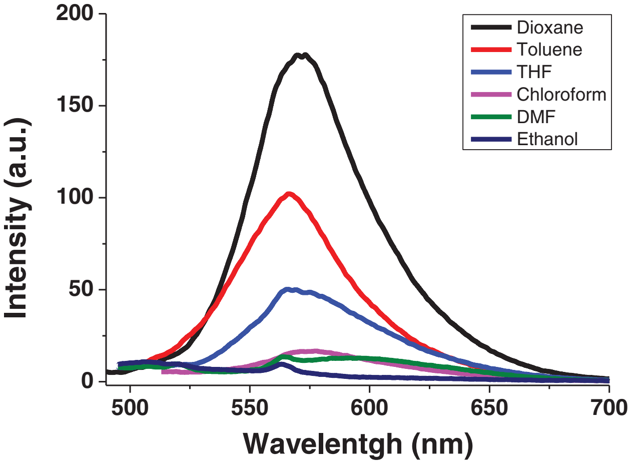


Figure 2. Fluorescence emission spectra of **ABM** in various solvents.

was observed. The quantum yields of **ABM** in dioxane and toluene were estimated to be 0.08 and 0.03, respectively. The quantum yields were lower than 0.01 in other solvents. All in all, the emission behavior is different from the documented **BIM** derivatives with strong emission around 570 nm. It is interesting that only a few number of **BIM** derivatives exhibit very weak emission according to the published references. It is not difficult to understand that the anthracene unit should be twist out of the plane of imide plane due to the steric hindrance. Generally, an energy transfer cassette will be constructed with this violet emitter incorporated to **BIM** [12, 16]. A through-bond energy transfer from anthracene to **BIM** will occur and strong emission of **BIM** was observed with excitation wavelength of anthracene. However, the rule malfunctioned in **ABM**. What happened to **ABM**?

To better comprehend the geometrical, electronic, and optical properties of **ABM**, 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 [14, 15]. Further refinement and optimization on structures were undertaken using DND/B3LYP basis set.

The calculated electron density distributions in the frontier molecular orbitals (FMOs) of **ABM** are shown in Fig. 3. The transitions HOMO→LUMO are possible with the oscillator strength (f) calculated to be 0.075. Careful analysis of the FMOs shows that, for the anthracene is twisted with imide plane, the electron density located on imide moiety without the LUMO spread over to anthracene. The LUMO distribution on imide ring exhibits the electron withdrawing character, which is in agreement with previously published calculations on similar **BIM** derivatives [12]. The HOMO spread over anthracene primarily with a little electron density located at the indole and imide moieties. Generally, such localization results the increase in the energy difference between HOMO and LUMO levels due to the intramolecular repulsion. However, the HOMO/LUMO energy gap of **ABM** is calculated to be 1.46 eV and lower than that of **BIM** (1.65 eV). It indicates that the introduction of anthracene unit weaken the framework in some degree. The electron density distribution located separately on the donor anthracene (in HOMO) and the acceptor imide moieties (in LUMO) accounts for the possibility of radiative photoinduced electron transfer followed by nonradiative relaxation. Plainly, the modest distortion of the imide backbone is benefit to the deactivation of the **BIM** S_1 state. The greater the molecular framework

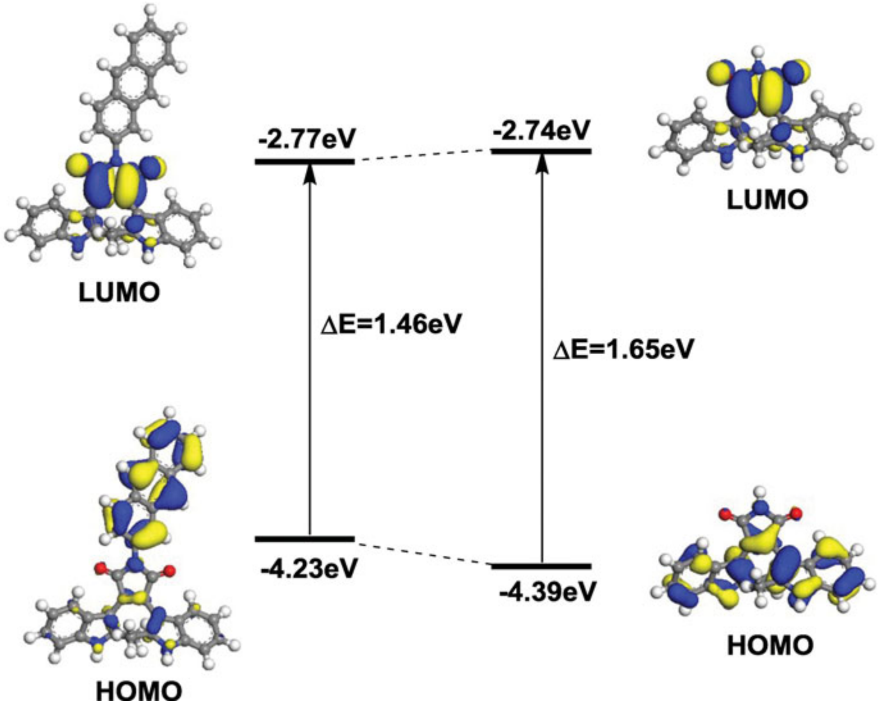


Figure 3. Representative HOMO and LUMO diagrams of **ABM** and **BIM** obtained from *Dmol*^{3} calculations.

distorted, the more efficient the non-radiative of the molecule is. For **ABM** molecular system, the substituted anthracene is relatively unhindered, thus lower the quantum yield of fluorescence. Free rotation of the anthracene in the compounds is very likely, even for excited states. It would appear that a steric effect is controlling the non-radiative relaxation.

Conclusions

In summary, a new 1-(anthracen-2-yl)-3,4-bis(2-methylindol)maleimide dye (**ABM**) was synthesized and fully characterized. In the molecular system, anthracene was connected with bisindolylmaleimide through covalent single bond. The absorption spectra of **ABM** shows the superimpose effect of anthracene and bisindilylmaleimide. Emission investigation shows the weak emission character in various different polarity solvents. The incorporation of violet emitter does not configure a molecular with strong emission.

Computational results of frontier orbitals suggest that an efficient charge transfer occurred in **ABM**. The emission quench of **ABM** can be attributed to the non-radiative relaxation. The free rotation of the anthracene may deactivate the **BIM** S_1 state. This provides the important clues for designing the required emission materials. Chemical modification is important in controlling the emission character of **BIM** derivatives. Our efforts towards the design and synthesis of **BIM** derivatives are currently underway in our lab.

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