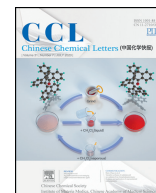




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Communication

Free radical oxidation reaction for selectively solvatochromic sensors with dynamic sensing ability



Fengjuan Shen, Tao Wang, Xudong Yu*, Yajuan Li

College of Science, Hebei University of Science and Technology, Shijiazhuang 050080, China

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ABSTRACT

A novel BODIPY (boradiazaindacene) dye denoted as BODIPY-DT containing terpyridine unit has been designed and characterized. The dye is found to be selective and visual solvatochromic sensor toward DMF among test organic solvents. The sensing process displays time-controllable, dynamic signal outputs in the emission colors including red, purple, yellow and even white emission colors. It is presented that selective free radical oxidation reaction happens during the recognition process.

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Selective and visualized sensing toward organic solvents is gaining increasing attentions in the last decade due to the importance of organic solvents in environment, industry and chemistry [1–5]. Although there have been tremendous works about the fluorescent dyes that have solvatochromic properties in organic solvents, visual discrimination of solvents with similar structure or polarity is still a big challenge. To this end, small organic molecules, supramolecular and polymeric films, metal-organic frameworks (MOFs), silicon elastomeric and MoS₂ monolayers have been widely developed as selective solvatochromic sensors [6–10]. Recently, we have also demonstrated that gel is a good platform for selective solvent recognition and efficient solvent separation *via* gel formation approach [11,12]. However, it is still difficult to program selective solvent sensors to demonstrate time-controllable, dynamic signal outputs.

Fluorescent approach for analyst sensing has been well-established in the past decades. As a result, a number of fluorescent chemosensors have been designed [13–19]. Among a set of organic dyes, BODIPY derivatives (borondipyrrromethene or 4,4-difluoro-4-bora-3a,4a-diazasindacene) have been paid increasing attention due to its superior optical properties in intense absorption profile, tunable and long wave emission from yellow to near infrared emission, as well as high fluorescence quantum yields [20–24]. BODIPY dyes have been widely developed to construct chemosensors toward external stimuli such as amino acid, phosgene, fructose, nitric oxide anions and metal ions. Additionally, some

BODIPY derivatives have been shown to possess solvatochromic properties [25–29]. However, it is still a challenge to fabricate BODIPY-based sensors that is able to discriminate solvents with similar structures and polarities.

Recently, we also showed that terpyridine derivatives with specific photophysical properties display extensive application in functional gels and sensors [12,30,31]. Herein, a novel photoactive BODIPY derivative BODIPY-DT with terpyridine motif as blue emission group and BODIPY-acetylene as red emission group was designed and characterized, which could generate singlet oxygen efficiently in specific solvent of DMF in sunlight at room temperature (Scheme 1). The compound BODIPY-DT in DMF could further be oxidized by singlet oxygen *via* radical reaction and the oxidation process displayed dynamic emission colors. We attempted to demonstrate a novel means of selective and dynamic solvent sensing toward DMF based on the free radical oxidation reaction at room temperature, and such sensing process was accompanied with dynamic emission color changes *via* time-controlled energy transfer from resulted terpyridine species to BODIPY species. This method for specific sensing toward DMF is visual, dynamic, and simple without expensive equipment.

Dye BODIPY-DT (Scheme 1a) was synthesized by coupled reactions of iodized substituted BODIPY derivative and terpyridine acetylene (synthesis of BODIPY-DT is deposited in Supporting information). Fluorescence spectra of fresh BODIPY-DT in different organic solvents were shown in Fig. S1 (Supporting information). It was observed that BODIPY-DT solutions displayed intense and broad peaks around 620 nm and weak peaks at about 403 nm, which were ascribed to BODIPY-acetylene and DT segments respectively. Under UV light (365 nm), the fresh and fuchsia

* Corresponding author.

E-mail address: chemyxid@163.com (X. Yu).



Scheme 1. (a) The chemical structure of BODIPY derivative (BODIPY-DT). (b) The emission colors of BODIPY-DT (10^{-5} mol/L) in different organic solvents after staying at room temperature in sunlight for 5 h. From left to right: DMF, DMSO, THF, acetone, *p*-dimethylbenzene, CH_2Cl_2 , methylbenzene, CHCl_3 , methoxyethanol, acetonitrile, $\text{CH}_3\text{COOC}_2\text{H}_5$.

BODIPY-DT solutions expressed red emission color (Fig. S2 in Supporting information). However, we observed that the diluted solution of fresh BODIPY-DT (10^{-5} mol/L) in DMF undergone visual and spontaneous color changes from pink to colorless completely after staying for more than 5 h in sunlight (Fig. S3a in Supporting information). Meanwhile, the emission color also displayed significant changes from red to yellow-green (Scheme 1b). Such changes were further investigated by fluorescent spectra. As seen from Fig. 1 and Fig. S2a, the intensity value of emission peak at 620 nm of dye BODIPY-DT in DMF decreased remarkably, and a novel peak at 520 nm appeared. Whereas, weaker fluorescent responses of BODIPY-DT were observed for other organic solvents. It was noted that the BODIPY-DT in acetonitrile had no color because of the poor solubility. However, the red emission could be observed in the presence of a very small amount of BODIPY-DT. These results confirmed that BODIPY was very selective in visual detecting DMF among test organic solvents.

As analogues of DMF, BODIPY-DT (10^{-5} mol/L) in the solvents of DMAc (*N,N*-dimethylacetamide) and DEF (*N,N*-diethylformamide) were also studied after irradiation by UV light for 5 h (Fig. S4 in Supporting information). It was found that the emission color changed from red to pink red in DMAc, and emission color changed from violet to white was observed for BODIPY-DT in DEF. This revealed that the different emission color changes endow visual recognition of DMF analogues, and the changes were relevant to the amide structure of solvent molecules.

Furthermore, we also checked the emission color changes of BODIPY-DT in mixed solvents of DMF and other solvents triggered by UV light for over 5 h. In the mixed solvents of DMF and THF (*v:v* = 1:1), or DMF with other organic solvent such as acetone, 1,4-dimethyl

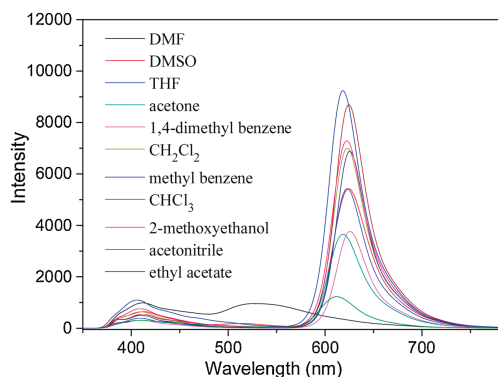


Fig. 1. The fluorescent spectra of BODIPY-DT solutions (10^{-5} mol/L) after staying for 24 h at room temperature in sunlight.

benzene, CH_2Cl_2 , methyl benzene, CHCl_3 , 2-methoxy ethanol, acetonitrile, and ethyl acetate, there were no obvious color or emission color changes. In the solvent mixtures of DMF/DMAc, or DMF/DEF, color fading and emission color changes could also be clearly observed (Fig. S5a in Supporting information). In particular, in the solvent of DMF/DMSO mixture, the emission color changes from red to darkseagreen (Fig. S5b in Supporting information). While, such color change is not found in pure DMSO, and the reason will be discussed in the following part.

Interestingly, the sensing process of BODIPY-DT toward DMF exhibited dynamic fluorescent emission color changes. As seen from Fig. 2b, after staying for 30 min in sunlight, the emission color changed to pink, then to white (after 1.5 h). Finally, stable yellow-green emission color was observed. The emission color change process was also examined by fluorescent spectra excited at 289 nm. From 0–24 h, the fluorescent intensities of emission peaks at 620 nm decreased regularly and significantly. Simultaneously, an increase at 520 nm in intensity was observed, which indicated the generation of novel terpyridine species (Fig. 3a). Notably, the changes also happened during the fluorescence test process in which xenon lamp is used. The CIE (International Commission on Illumination) chromaticity for these intermediates could be seen in Fig. 3b and Table S1 (Supporting information), the CIE chromaticity coordinates of BODIPY-DT blue-shifted obviously along with time. The changes were also examined by UV–vis experiments. As seen in Fig. S6 (Supporting information), the absorption peaks of BODIPY-DT centered at 579 and 409 nm disappeared with time aging from UV–vis experiments, indicating the destruction of BODIPY-DT structure. The results suggested that the color changes were highly related with light, and BODIPY-DT was able to selective recognize DMF among test organic solvents with visualized color or emission color changes.

The mechanism for the dynamic color changes in molecular level had been first studied. Previous study showed the BODIPY dyes as photosensitizers usually promoted the generation of singlet oxygen with the intersystem crossing (ISC) process [32–36]. We assumed that the interaction process might be related with the oxidation process, in which singlet oxygen was photosensitized by BODIPY-DT. DPBF (diphenylisobenzofuran) was generally regarded as the highly efficient trapping agent for $^1\text{O}_2$, and herein was used to demonstrate the formation of singlet oxygen. As seen from Fig. 4a, when the solution mixture of BODIPY-DT (10^{-5} mol/L) and DPBF (5×10^{-5} mol/L) was exposed to UV light (from 0 min to 90 min), the significant decrease in the absorption of DPBF (with maximum absorption peak centered at 413 nm) was monitored. Conversely, there was little spectral change for BODIPY-DT, indicating DPBF was first oxidized by $^1\text{O}_2$; from 90 min to 280 min (Fig. S7 in Supporting information), the absorption peak of BODIPY-DT centered was further decreased, suggesting the oxidation reaction of BODIPY-DT by $^1\text{O}_2$. As expected, the oxidation process was also accompanied with obvious emission color changes (Fig. S8 in

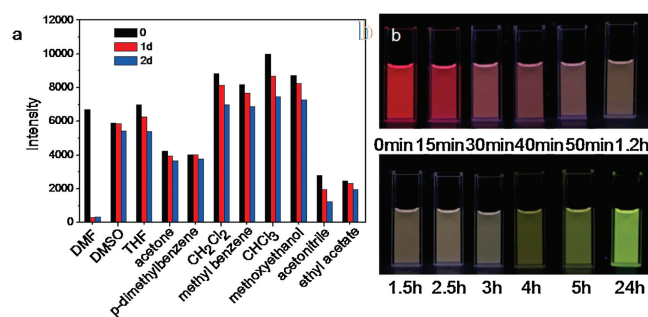


Fig. 2. (a) Changes in fluorescence intensity of BODIPY-DT (10^{-5} mol/L), λ_{ex} = 289 nm, λ_{em} = 620 nm) in different organic solvents at room temperature in sunlight over 24 h. (b) The emission colors evolution of BODIPY-DT (10^{-5} mol/L) in DMF in dark at different time at room temperature in sunlight.

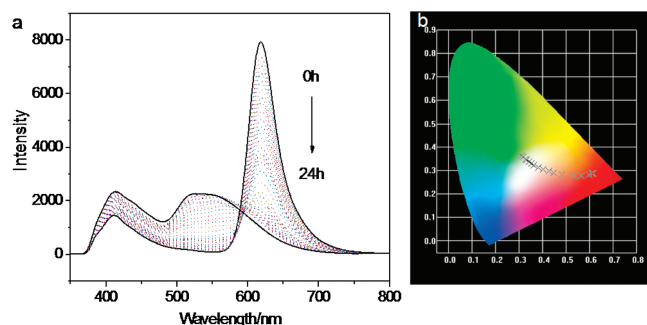


Fig. 3. (a) The fluorescent spectrum changes of BODIPY-DT (10^{-5} mol/L) in DMF from 0 to 24 h at room temperature in sunlight. (b) The CIE 1931 chromaticity diagram for intermediates of BODIPY-DT at different times.

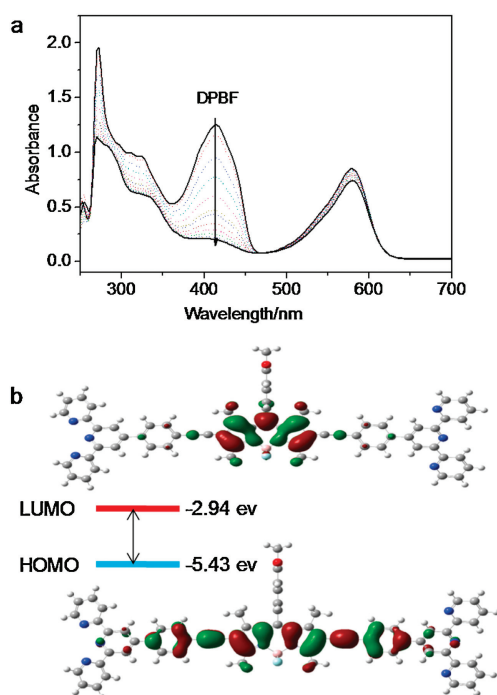


Fig. 4. (a) The singlet oxygen ($^1\text{O}_2$) photosensitizing measurement of compounds BODIPY-DT under UV light. (b) HOMO and LUMO molecular orbitals for BODIPY-DT calculated at B3LYP/6–31 G level.

Supporting information). As oxidation interaction, the products of BODIPY-DT had been checked by MS. The resulted compounds gave intense peaks with m/z values of 764.7, 525.5, 562.3, which corresponded to the compounds $(6+\text{Na})^+$, $(7+\text{Na})^+$ and $(8+\text{Na})^+$ of BODIPY-DT oxidized derivatives (Fig. S9 in Supporting information). Moreover, the peaks positioned at 338.0 and 354.1 were assigned to the terpyridine species **9** and **10** containing $-\text{CHO}$ and $-\text{COOH}$ units respectively. The above results confirmed that acetylene motif was oxidized to aldehyde and acid motifs, and the pyrrole units were destroyed. ^1H NMR data for the resulting mixtures also displayed the peaks of $-\text{CHO}$ and $-\text{COOH}$ which appear around 10.4 and 12.1 respectively (Fig. S10 in Supporting information).

In addition, the conformation of BODIPY-DT was further optimized using density functional theory methods at the level of B3LYP/6–31 G prior to population analysis of the frontier molecular orbitals (FMOs) (Fig. 4b). The result reveals that the electronic density of BODIPY-DT in the HOMO with energy level of -2.94 eV is mainly located on the alkynyl and pyrrole groups, which tends to lose electron in the presence of $^1\text{O}_2$. Therefore, the oxidation reaction

could be summarized as following (Fig. 5a): Upon photoexcitation, the BODIPY-DT with singlet excited state is first populated (S_0-S_1), and then reach to triple excited state (T_1), resulting in the generation of singlet oxygen $^1\text{O}_2$ followed by oxidation of BODIPY-DT with destruction of alkynyl and pyrrole motifs. It should be noted that the resulted terpyridine derivative is very stable even in UV light irradiation. From the above results, it presented that the dynamic emission color changes were ascribed to the efficient energy transfer from terpyridine derivatives to BODIPY species, which was controlled by time-resolving chemical reaction.

The second problem was that why this reaction was only clearly observed in DMF and its analogues rather than other test solvents, leading to selective recognition toward DMF. On considering the structure of the solvent molecules and the previous reports [36], we envisioned that the base of DMF as electron donor might played a vital role for accelerating the generation of singlet oxygen just at room temperature in sunlight, and BODIPY-DT containing electron deficient groups including BF_2 and terpyridine units behaved as electron acceptor; whereas, other organic solvents did not have the alkalinity as that as DMF. To further demonstrate the importance of base in accelerating the generation of singlet oxygen, Et_3N was introduced into the BODIPY-DT solution in order to study the base effect on the oxidation reaction. Simultaneously, other conditions including heat and UV irradiation were also compared. As seen from Fig. 5b and Fig. S11 (Supporting information), in the presence of Et_3N (10 equiv. of BODIPY-DT), the fluorescence intensity decreased most quickly in sunlight than that of other conditions, and significant color or emission color changes could be easily observed within 1 min by naked eye. It could be also observed that other factors such as heat, UV irradiation were also favorable for the reaction. Such results indicated that the photo-oxygenation and oxidation interaction were strongly promoted by base medium. Additionally, Foote *et al.* reported that DMF was able to react with singlet oxygen to form peroxide that also could oxidize BODIPY-DT [37,38]. This might be also important for the reaction that happens just at room temperature in sunlight in DMF.

As discussed above, singlet oxygen $^1\text{O}_2$ and base medium were both important for such radical interaction. To further prove this conclusion, the $^1\text{O}_2$ photosensitizing of BODIPY-DT in THF/ Et_3N or 1,4-dimethyl benzene/ Et_3N solvent mixture triggered by UV light was also studied. As seen from Fig. S12 (Supporting information), after irradiation for 90 min, there was no significant changes in UV-vis spectra of DPBF solution, indicating that singlet oxygen $^1\text{O}_2$ is not generated. Meanwhile, no drastic color or emission color changes were observed in the solvent mixtures. Similar phenomena were also found in the solvent mixtures of Et_3N with other organic solvents including THF, acetone, 1,4-dimethyl benzene, CH_2Cl_2 , methyl benzene, CHCl_3 , 2-methoxy ethanol, acetonitrile, and ethyl acetate.

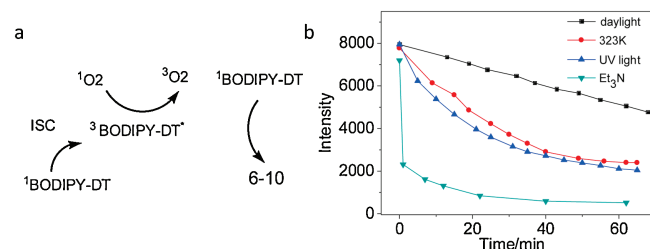


Fig. 5. (a) The possible reaction mechanism of BODIPY oxidized by $^1\text{O}_2$. (b) The fluorescence spectral changes of DMF solution of BODIPY-DT ($\lambda_{\text{ex}}=289$ nm, $\lambda_{\text{em}}=620$ nm) under different conditions: in daylight at room temperature; heat insulation at 50°C ; UV light; DMF solution containing Et_3N (10 equiv.) in sunlight at room temperature.

On the other hand, when BODIPY-DT in the mixed solvent of DMSO/Et₃N was triggered by light (365 nm) for 2 h, the color faded quickly and the emission color changed from red to darkseagreen. The generation of ¹O₂ was further certified by singlet oxygen photosensitizing measurement as seen from Fig. S13 (Supporting information). Therefore, the radical reaction could just happen both in DMSO/DMF and DMSO/Et₃N mixture, which made DMSO as another special solvent in the second-step sensing visually and selectively. However, to date, the role of DMSO in radical generation process is not clear and the relevant reports are very rare.

In conclusion, a novel BODIPY based fluorescent sensor for selective, dynamic and visual sensing of DMF is developed for the first time. This work described above presents a novel solvatochromic sensor strategy based on chemical interactions for the first time. By taking advantage of energy transfer of resulting fluorophores produced in the reaction process, we are able to prepare solvatochromic sensors that can achieve the demanding task of visualized discrimination of solvents. Finally, the sensing process displays time-controllable, dynamic signal outputs in the emission colors. Especially, white emission color is also achieved, which is also meaningful for preparing full-color emission systems with dynamic characteristics. We believe that the novel strategy developed in this study would have wide application in the fields of solvatochromic sensors and light harvesting systems.

Declaration of competing interest

The authors declare that there are no conflicts of interest.

Acknowledgments

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:<https://doi.org/10.1016/j.ccllet.2019.12.025>.

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