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A new 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN) derivative with tetrathiafulvalene unit: modulation of the dual fluorescence of DMABN by redox reaction of tetrathiafulvalene unit

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Abstract

A new derivative of 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN) (compound **1**) with TTF unit is reported. Compound **1** exhibits dual fluorescence, and moreover the dual fluorescence behavior can be modulated by reversible oxidation and reduction of TTF unit of **1** either chemically or electrochemically. Accordingly, a new molecular fluorescence switch is realized by coupling the features of TTF and DMABN.

Keywords: DMABN; TICT; Tetrathiafulvalene; Fluorescence switch

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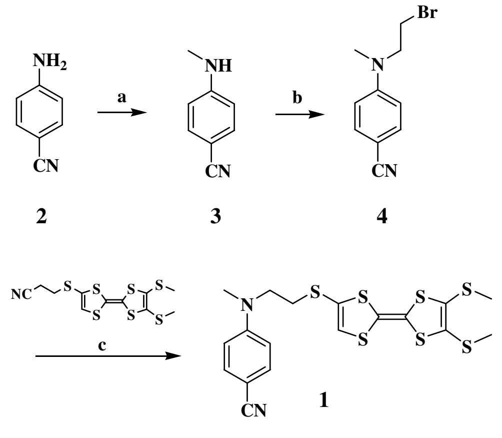
It is known that 4-(*N*,*N*-dimethylamino)benzonitrile (DMABN) and its derivatives, as a class of organic donor–acceptor compounds, exhibit dual fluorescence, one related to the local excited state ('B' band), and the other ascribed to the twisted intramolecular charge-transfer (TICT) state ('A' band).[1,2] Since the first observation by Lippert et al.,[1] a number of DMABN and its ana-logues have been investigated regarding the TICT mechanism.[3–11] These studies clearly show that the dual fluorescence behavior is influenced by the substituents incorporated into DMABN. By making use of the feature of DMABN, several ion-sensors based on DMABN as a dual-fluorescent fluorophore have been described in recent years.[12–16] We have just recently reported DMABN derivatives with boronic acid/boronate groups as ratiometric fluorescence sensors for saccharides and fluoride ion.[17,18]

Herein, we will report a new derivative of DMABN with one tetrathiafulvalene (TTF) unit (**1**, Scheme 1) with a view



Scheme 1. Synthetic procedure for compound **1**: (a) MeI, reflux, 45%; (b) 3 M H_2SO_4, bromoacetaldehyde diethyl acetal; $NaBH_4$, 18%; (c) $CsOH{\cdot}H_2O$, 4-(2-cyanoethylthio)-4′,5′-(dimethylthio)-tetrathiafulvalene, 75%.

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to building a new molecular fluorescence switch by coupling the features of DMABN and TTF. The design rationale is described as follows: a neutral species of TTF can be reversibly transformed into the corresponding species with positive charges, radical cation ($TTF^{\cdot+}$), and dication (TTF^{2+}), by either chemical or electrochemical oxidation at easily accessible potential.[19–24] As a result, the electron donating ability of TTF can be tuned by reversible redox reactions. Moreover, TTF and $TTF^{\cdot+}/TTF^{2+}$ show different absorption spectra.[25–28] Therefore, it is expected that (1) oxidation of TTF unit may have an influence on the ground/excited state conformation of DMABN unit of 1; (2) oxidation of TTF unit may alter the intramolecular energy/electron transfer process within compound **1**; accordingly, it may be possible to reversibly modulate the dual fluorescence behavior of DMABN unit of compound **1**.

The target compound **1** was synthesized through three steps starting from 4-aminobenzonitrile (**2**, Scheme 1). Compound **3** was yielded after reaction of compound **2** with MeI. After reaction with 3-bromo-1,1-diethoxypropane, followed by treatment with $NaBH_4$, compound **3** was converted to compound **4** in 18% yield, which was further reacted with 4-(2-cyanoethylthio)-4′,5′-(dimethylthio)-tetrathiafulvalene in the presence of $CsOH{\cdot}H_2O$ leading to compound **1** in 75% yield.[29] The synthetic details are provided in Supplementary data.

Figures 1 and 2 show the absorption and fluorescence spectra of **1** and those after the addition of different amounts of Fe^{3+}. The absorption spectrum of **1** is almost the superposition of those of DMABN and TTF units, indicating that there is no detectable interaction between DMABN and TTF units. As expected, compound **1** exhibits dual fluorescence, showing two fluorescence bands centered at 350 nm and 432 nm, which can be ascribed to the corresponding B band (from the local excited state) and A band (from the TICT state), respectively. The intensity ratio of the two fluorescence bands at 350 nm for B band and 432 nm for A band (I_B/I_A) was measured to be 0.74.

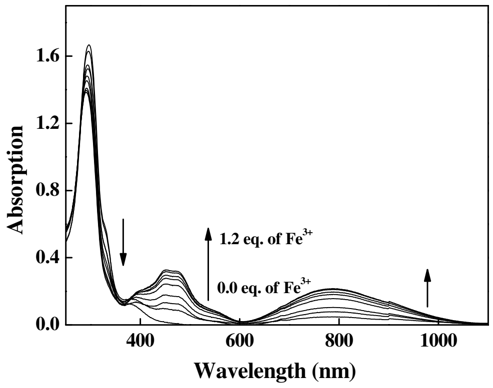

Fig. 1. Absorption spectrum of compound **1** (5.0×10^{-5} M in CH_2Cl_2) and those in the presence of different amounts of $Fe(ClO_4)_3$.

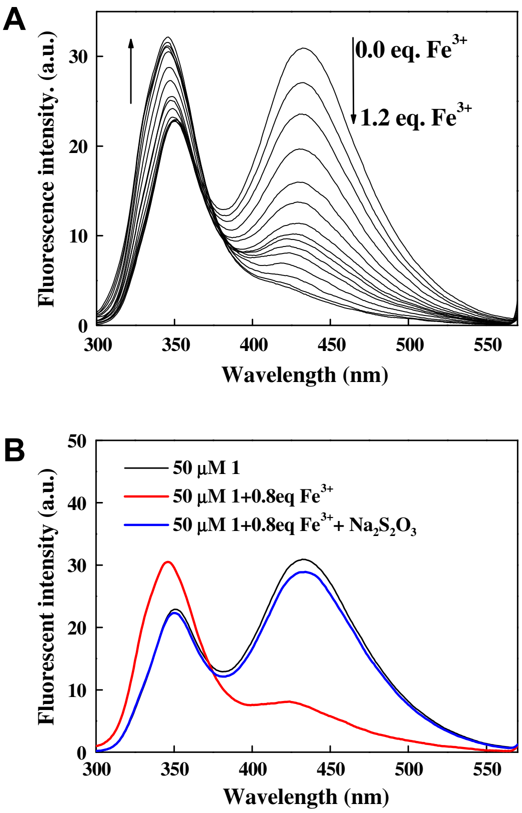

Fig. 2. (A) The fluorescence spectrum of compound **1** (5.0×10^{-5} M in CH_2Cl_2) and those in the presence of different amounts of $Fe(ClO_4)_3$. (B) The reversible variation of the fluorescence spectrum of compound **1** (5.0×10^{-5} M in CH_2Cl_2) after oxidation by Fe^{3+} and further reduction by $Na_2S_2O_3$.

It is known that TTF and its analogues can be oxidized stoichiometrically by Fe^{3+}. New absorption bands around 460 nm and 800 nm emerge gradually after the addition of Fe^{3+} to the solution of **1** as shown in Figure 1, where the absorption spectra of **1** in the presence of different amounts of Fe^{3+} are displayed. The appearance of absorption bands around 460 nm and 800 nm indicates the formation of the radical cation of TTF unit according to previous reports.[25–28] Simultaneously, variation of the fluorescence spectrum of **1** is detected after the addition of Fe^{3+}; the fluorescence intensity of B band at about 300–400 nm increases slightly while that of A band in the range of 400–500 nm decreases gradually (see Fig. 2A). For instance, after reaction with 1.0 equiv of Fe^{3+} the fluorescence intensity of **1** at 350 nm within B band increases by 37%, and that at 432 nm within A band decreases by 88% compared to the corresponding initial intensities of **1** before the addition of Fe^{3+}.[30] Accordingly, the intensity ratio of the two fluorescence bands at 350 nm for B band and 432 nm for A band ($I_B/I_A = 8.3$) increases by 11 times compared to that before oxidation by Fe^{3+}. As anticipated, the radical cation of TTF unit of **1** can be transformed into the neutral unit by treatment with excess sodium thiosulfate ($Na_2S_2O_3$); consequently, both absorption and fluorescence spectra of **1** after oxidation by Fe^{3+} can be restored by further reaction with $Na_2S_2O_3$ (see Fig. 2B). Therefore, modulation of the dual fluorescence behavior of **1** can be realized by reversible chemical oxidation and reduction of TTF unit of **1**.

It is also possible to modulate the dual fluorescence behavior of **1** by reversible electrochemical oxidation and reduction of TTF unit of **1**. Oxidation of the solution of **1** containing *n*-Bu_4NPF_6 (28 mM), which was performed by applying an oxidation potential of 0.80 V (vs Ag wire) to the solution, also led to the increase for B band and the decrease for A band of **1** as shown in Figure 3A. This is similar to the fluorescence spectral variation observed for **1** after chemical oxidation as discussed above. Such fluorescence spectral change is obviously due to the transformation of the neutral TTF unit into the corresponding cation radical, since the oxidation potential (0.8 V vs Ag wire) employed for the electrochemical experiment is higher than that of the first oxidation potential of TTF unit of **1** [$E^1_{1/2}$(ox) (vs Ag/AgCl) = 0.57 V].[31] But, the fluorescence intensity variation after electrochemical oxidation was small compared to that observed after chemical oxidation (see Fig. 2). This was likely due to the fact that electrochemical oxidation was carried out for a short period and thus not all molecules of **1** in the solution were oxidized. After the application of a reduction potential of 0.1 V (vs Ag wire) to the electrochemically oxidized solution for 3.0 min, the fluorescence spectrum of **1** was restored (see Fig. 3B). This is simply due to the reduction of the radical cation of TTF unit into the neutral TTF unit.

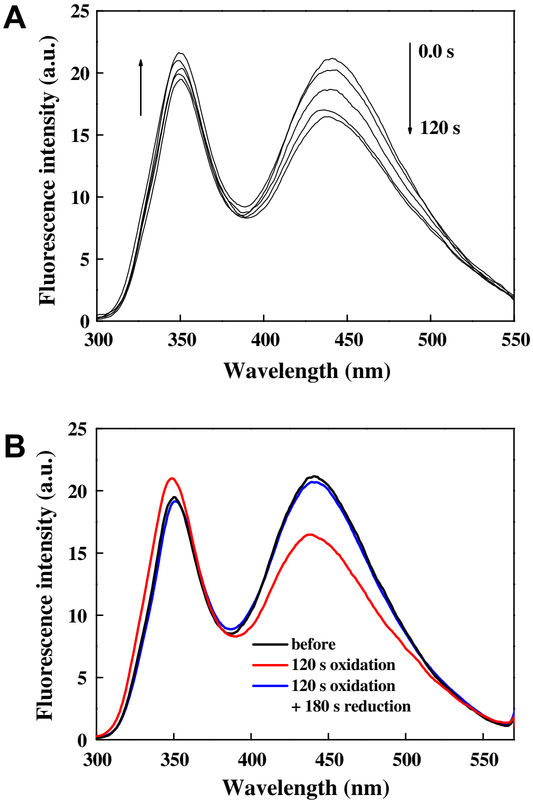

Fig. 3. (A) Fluorescence spectra of the solution of compound **1** (5.0×10^{-5} M in CH_2Cl_2) containing *n*-Bu_4NPF_6 (28 mM) after applying an oxidation of 0.8 V (vs Ag wire) for different periods; (B) fluorescence spectrum of the solution of compound **1** (5.0×10^{-5} M in CH_2Cl_2) containing *n*-Bu_4NPF_6 (28 mM) and those after applying an oxidation of 0.8 V (vs Ag wire) for 120 s and further by applying reduction potential of 0.1 V (vs Ag wire) for 180 s.

The above results clearly show that the dual fluorescence behavior of **1** can be modulated by reversible oxidation and reduction of TTF unit of **1**. A quasi-reversible redox wave at 1.41 V was detected for **1**, which should be due to the oxidation of DMABN unit. But, no redox wave at low potential was observed. Therefore, both electron accepting and donating abilities of DMABN unit are rather weak. Accordingly, the corresponding photoinduced electron transfer between TTF and DMABN units within **1** may not occur. However, the intramolecular energy transfer process may be responsible for this dual fluorescence modulation. As discussed above, the DMABN unit of **1** exhibits two emission bands, B band in the range of 300–400 nm and A band in the range of 400–500 nm. As displayed in Figure 1, the neutral TTF unit shows strong absorption around 350 nm, while the corresponding radical cation absorbs in the range of 400–550 nm besides in the range of 600–1000 nm. Therefore, the B band of the fluorescence spectrum of **1** with a neutral TTF unit would be quenched to some extent due to the intramolecular energy transfer since there is a spectral overlap between the fluorescence B band and the absorption spectrum of TTF unit. On the other hand, the A band of the fluorescence spectrum of **1** after oxidation (with TTF$^{\cdot+}$ unit) would decrease because there is a spectral overlap between the fluorescence A band and the absorption spectrum of the radical cation of TTF unit and thus intramolecular energy transfer would take place. An influence of oxidation of TTF unit on the ground/excited state conformation of DMABN unit of **1** may also contribute to the dual fluorescence variation observed for **1** after chemical/electrochemical oxidation of TTF unit.

In summary, a new derivative of 4-(*N*,*N*-dimethylamino)-benzonitrile (DMABN) (compound **1**) with TTF unit was designed and synthesized with a view to building a new molecular fluorescence switch by coupling the features of TTF and DMABN. Compound **1** exhibits dual fluorescence, and moreover the dual fluorescence behavior can be modulated by reversible oxidation and reduction of TTF unit of **1** either chemically or electrochemically.

Acknowledgments

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Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2007.12.087.

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29. Characterization data of compound **1**: mp = 137–138 °C; $R_f = 0.24$ (CH_2Cl_2:petroleum = 1:1); ^1H NMR ($CDCl_3$): δ 2.40 (s, 6H), 2.85 (t, 2H, $J = 7.0$ Hz), 3.03 (s, 3H), 3.63 (t, 2H, $J = 7.1$ Hz), 6.38 (s, 1H), 6.65 (d, 2H, $J = 8.3$ Hz), 7.46 (d, 2H, $J = 8.2$ Hz). ^{13}C NMR ($CDCl_3$): δ 19.3, 32.0, 38.7, 52.1, 98.4, 111.7, 113.3, 120.4, 123.3, 126.0, 127.7, 127.8, 133.8, 151.0. EI MS: m/z 486 (M^+); HRMS (EI): Anal. Calcd for ($C_{18}H_{18}N_2S_7{}^+$): 485.9515; found: 485.9520.
30. When more than 2 equiv of Fe^{3+} were added, typical absorption bands for the dication of TTF unit were observed. The fluorescence intensities of both A band and B band decreased slightly.
31. Two reversible oxidation waves with $E^1_{1/2}$(ox) (vs Ag/AgCl) = 0.57 V and $E^2_{1/2}$(ox) (vs Ag/AgCl) = 0.93 V were detected for compound **1**.