

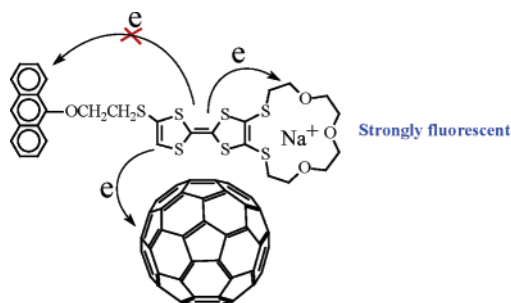
A New Tetrathiafulvalene–Anthracene Dyad Fusion with the Crown Ether Group: Fluorescence Modulation with Na⁺ and C₆₀, Mimicking the Performance of an “AND” Logic Gate

Guanxin Zhang, Deqing Zhang,* Yucheng Zhou, and Daoben Zhu*

Center for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

dqzhang@iccas.ac.cn

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In this Note, we describe a new TTF–anthracene dyad fusion with the crown ether unit. It is interesting to find that the fluorescence of this new dyad can be modulated with Na⁺ and C₆₀, and its fluorescence intensity can be largely enhanced only in the presence of both Na⁺ and C₆₀. Such fluorescence modulation behavior mimics the performance of a two-input “AND” logic gate.

Tetrathiafulvalene (TTF) and its derivatives were originally studied for the development of electrically conducting materials.¹ The unique feature of TTF and its derivatives is that they are strong electron donors and that they can be reversibly oxidized and reduced.² For this reason, D–A molecules and supra-molecules containing TTF units have been investigated for studies of molecular level devices such as molecular switches, molecular shuttles, and even molecular logic circuits.³ Cation and anion sensors based on TTF derivatives have also been reported.⁴ For example, recognition motifs incorporating the TTF unit into the macrocycles containing a crown ether have been well documented and such molecules show electrochemical recognition of various metal cations.^{4a–d} In their cases, in the presence of metal ions the oxidation potentials of the TTF unit

in such macrocycles are anodically shifted, implying that the electron donating abilities of the TTF unit are reduced. We have recently reported a redox fluorescence switch based on the TTF–anthracene dyad,⁵ which can react with ¹O₂ to afford strong chemluminescence and as a result such a TTF–anthracene dyad was found to be a selective probe for ¹O₂.⁶ Moreover, the photoinduced electron transfer process within the TTF–anthracene dyad can be modulated by assembly on the surfaces of gold nanoparticles.⁷ After incorporation of receptor units, these TTF–anthracene dyads are capable of sensing sugars and anions.⁸

It is well-known that C₆₀ is an electron acceptor. It has been reported that both intramolecular and intermolecular photo-induced electron transfer can occur efficiently between C₆₀ and TTF derivatives.⁹ Thus, it is possible to tune the intramolecular photoinduced electron-transfer process between TTF and an electron acceptor units by addition of C₆₀ to the solution. In this Note, we want to report a new tetrathiafulvalene dyad fusion with the crown ether group (dyad **1**, Scheme 1). It is anticipated that the fluorescence of dyad **1** will be enhanced after addition of metal ions. But, the results show that the fluorescence only increases slightly in the presence of Na⁺. In addition, the fluorescence of dyad **1** can also be slightly enhanced by addition of C₆₀. However, in the presence of both Na⁺ and C₆₀ the fluorescence of dyad **1** can be largely enhanced. If C₆₀ and Na⁺

(3) See for examples: (a) Pease, A. R.; Jeppesen, J. O.; Stoddart, J. F.; Luo, Y.; Collier, C. P.; Heath, J. R. *Acc. Chem. Res.* **2001**, *34*, 433 and further references therein. (b) Farren, C.; Christensen, C. A.; FitzGerald, S.; Bryce, M. R.; Beeby, A. *J. Org. Chem.* **2002**, *67*, 9130. (c) Loosli, C.; Jia, C.; Liu, S.-X.; Haas, M.; Dias, M.; Levillain, E.; Neels, A.; Labat, G.; Hauser, A.; Decurtins, S. *J. Org. Chem.* **2005**, *70*, 4988. (d) Li, H.; Jeppesen, J. O.; Levillain, E.; Becher, J. *Chem. Commun.* **2003**, 846. (e) Asakawa, M.; Ashton, P. R.; Balzani, V.; Credi, A.; Mattersteig, G.; Matthews, O. A.; Montalti, M.; Spencher, N.; Stoddart, J. F.; Venturi, M. *Chem. Eur. J.* **1997**, *3*, 1992. (f) Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1216. (g) Tseng, H.; Vignon, S.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2003**, *42*, 1491. (h) Jeppesen, J.; Vignon, S.; Stoddart, J. *Chem. Eur. J.* **2003**, *9*, 4611. (i) Liu, Y.; Flood, A. H.; Stoddart, J. F. *J. Am. Chem. Soc.* **2004**, *126*, 9150. (j) Steurman, D.; Tseng, H.; Peters, A.; Flood, A.; Jeppesen, J.; Nielsen, K.; Stoddart, J.; Heath, J. *Angew. Chem., Int. Ed.* **2004**, *43*, 6486. (k) Huang, T.; Tseng, H.; Sha, L.; Lu, W.; Brough, B.; Flood, A. H.; Yu, B.; Celestre, P. C.; Chang, J.; Stoddart, J. F.; Ho, C. *Nano Lett.* **2004**, *4*, 2065. (l) Jang, S. S.; Jang, Y. H.; Kim, Y.; Goddard, W. A.; Flood, A. H.; Laursen, B. W.; Tseng, H.-R.; Stoddart, J. F.; Jeppesen, J. O.; Choi, J. W.; Steurman, D. W.; DeLonno, E.; Heath, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 1563.

(4) (a) Hansen, T. K.; Jørgensen, T.; Stein, P. C.; Becher, J. *J. Org. Chem.* **1992**, *57*, 6403. (b) Trippé, G.; Levillain, E.; Le Derf, F.; Gorgues, A.; Sallé, M.; Jeppesen, J. O.; Nielsen, K.; Becher, J. *Org. Lett.* **2002**, *4*, 2461. (c) Le Derf, F.; Mazari, M.; Mercier, N.; Levillain, E.; Trippé, G.; Riou, A.; Richomme, P.; Becher, J.; Garin, J.; Orduna, J.; Gallego-Planas, N.; Gorgues, A.; Sallé, M. *Chem. Eur. J.* **2001**, *7*, 447. (d) Lyskawa, J.; Le Derf, F.; Levillain, E.; Mazari, M.; Sallé, M.; Dubois, L.; Viel, P.; Bureau, C.; Palacin, S. *J. Am. Chem. Soc.* **2004**, *126*, 12194. (e) Heuzé, K.; Mézière, C.; Fourmigué, M.; Batail, P.; Coulon, C.; Canadell, E.; Auban-Senzier, P.; Jérôme, D. *Chem. Mater.* **2000**, *12*, 1898. (f) Nielsen, K. A.; Jeppesen, J. O.; Levillain, E.; Becher, J. *Angew. Chem., Int. Ed.* **2003**, *42*, 187.

(5) Zhang, G.; Zhang, D.; Guo, X.; Zhu, D. *Org. Lett.* **2004**, *6*, 1209.

(6) (a) Zhang, G.; Li, X.; Ma, H.; Zhang, D.; Li, J.; Zhu, D. *Chem. Commun.* **2004**, 18, 2072. (b) Li, X.; Zhang, G.; Ma, H.; Zhang, D.; Zhu, D. *J. Am. Chem. Soc.* **2004**, *126*, 11543.

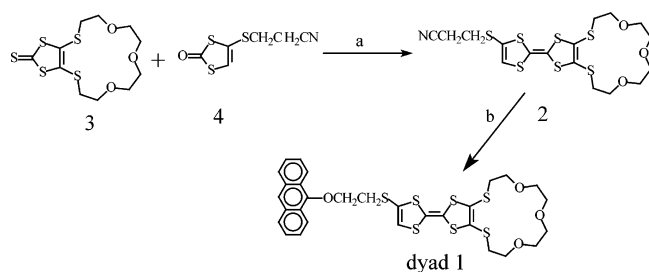
(7) Zhang, G.; Zhang, D.; Zhao, Z.; Zhang, J.; Zhu, D. *Chem. Eur. J.* **2006**, *12*, 1067.

(8) (a) Wang, Z.; Zhang, D.; Zhu, D. *J. Org. Chem.* **2005**, *70*, 5729. (b) Lu, H.; Xu, W.; Zhang, D.; Zhu, D. *Chem. Commun.* **2005**, 4777. (c) Lu, H.; Xu, W.; Zhang, D.; Chen, C.; Zhu, D. *Org. Lett.* **2005**, *7*, 4629.

(9) (a) Guldi, D. M.; Prato, M. *Acc. Chem. Res.* **2000**, *33*, 695 and further references therein. (b) Alam, M.; Watanabe, A.; Ito, O. *J. Photochem. Photobiol., A* **1997**, *104*, 59.

(1) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo, M. H. *Organic Superconductors (Including Fullerenes)*; Prentice Hall: Englewood Cliffs, NJ, 1992.

(2) (a) Nielsen, M. B.; Lomholt, C.; Becher, J. *Chem. Soc. Rev.* **2000**, *29*, 153. (b) Bryce, M. R. *J. Mater. Chem.* **2000**, *10*, 589. (c) Bryce, M. R. *Adv. Mater.* **1999**, *11*, 11. (d) Segura, J.; Martín, N. *Angew. Chem., Int. Ed.* **2001**, *40*, 1372. (e) Rovira, C. *Chem. Rev.* **2004**, *104*, 5289 and further references therein.

SCHEME 1. The Synthetic Approach to Dyad 1^a

^a Reagents and conditions: (a) Δ , $\text{P}(\text{OCH}(\text{CH}_3)_2)_3$, 38%. (b) $\text{CsOH}/\text{CH}_3\text{OH}$, 9-(2-bromoethoxy)anthracene, THF, rt, 85%.

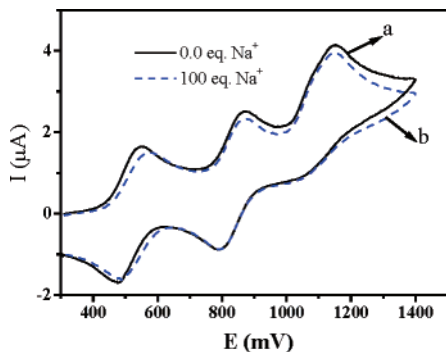


FIGURE 1. Cyclic voltammograms of dyad **1** (0.1 mM) in the absence and presence of 100 equiv of Na^+ in CH_2Cl_2 (scanning rate 50 mV/s); platinum wires as working and counter electrodes, Ag/AgCl as reference electrode, $n\text{-Bu}_4\text{NPF}_6$ (0.05 M) as the supporting electrolyte.

are regarded as two input signals, and the fluorescence of dyad **1** as the output signal, such fluorescence modulation of dyad **1** mimics the performance of an “AND” logic gate.

Synthesis of dyad **1** started from compound **3** and compound **4** (Scheme 1), which were prepared according to the previously reported procedure.¹⁰ Coupling of **3** and **4** in the presence of tri(isopropyl)phosphite led to compound **2** in 38% yield. Deprotection of 2-cyanoethyl groups of **2** with the aid of CsOH and sequentially reaction with 9-(2-bromoethoxy)anthracene afforded dyad **1** in 85% yield after purification with column chromatography.

As reported previously for other TTF–anthracene dyads,^{5,8a} three oxidation waves were detected for **1**; the first two reversible ones ($E_{1/2} = 0.52$ and 0.83 V) corresponded to the oxidation of the TTF unit into the radical cation and dication, respectively, and the third one ($E^{\text{ox}} = 1.15$ V) was ascribed to the irreversible oxidation of anthracene unit. Upon addition of Na^+ , the first oxidation peak was anodically shifted. For example, when 100 equiv of Na^+ was added to a 2 mL solution of dyad **1** (0.1 mM), the first oxidation potential was changed from 0.55 to 0.58 V (Figure 1). This result is similar to those of TTF derivatives with crown ether units.⁴ But no further oxidation potential change was observed if more than 100 equiv of Na^+ were added. Other metal ions such as Li^+ , K^+ , and Zn^{2+} could not cause the shift of the oxidation potentials of dyad **1**. This is likely owing to the size of the crown ether unit of dyad **1**.

(10) (a) Jia, C.; Zhang, D.; Xu, W.; Zhu, D. *Org. Lett.* **2001**, *3*, 1941. (b) Jia, C.-Y.; Zhang, D.-Q.; Guo, X.-F.; Wan, S.-H.; Xu, W.; Zhu, D.-B. *Synthesis* **2002**, *15*, 2177.

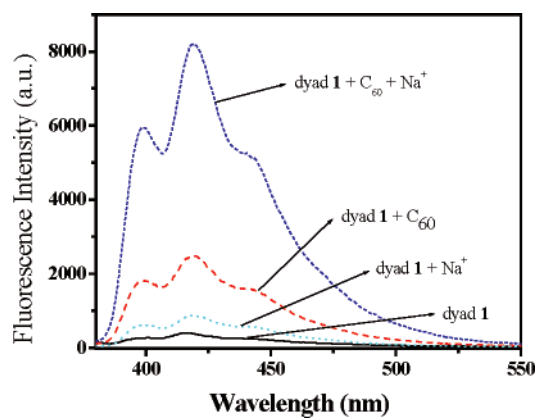


FIGURE 2. Fluorescent spectra of dyad **1** (5 mL, 10 μM in CH_2Cl_2) in the presence of 2 equiv of C_{60} (4.2 mM in PhCl), 100 equiv of Na^+ (77.6 mM in CH_3OH), and 2 equiv of C_{60} + 100 equiv of Na^+ ; the excitation wavelength is 370 nm.

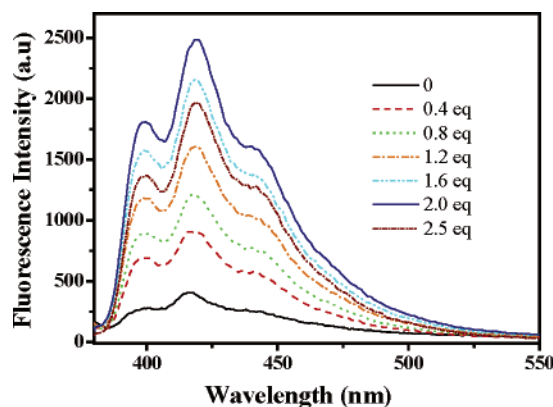


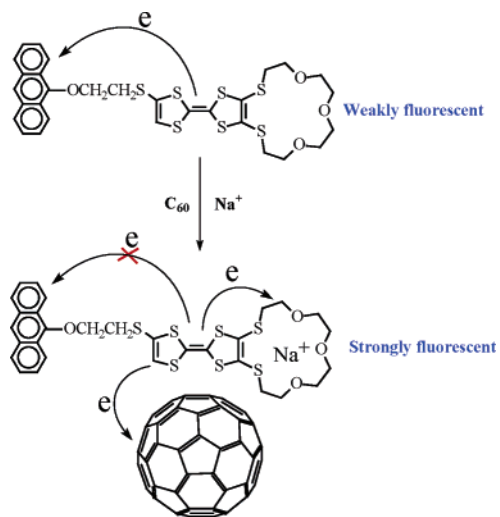
FIGURE 3. Fluorescent spectra of dyad **1** (5 mL, 10 μM in CH_2Cl_2) in the presence of different amounts of C_{60} (4.2 mM in PhCl); the excitation wavelength is 370 nm.

As expected, dyad **1** shows weak fluorescence with a rather low fluorescence quantum yield of 0.011, due to the photoinduced electron transfer between TTF and anthracene units.¹¹ Upon addition of Na^+ , the fluorescence of dyad **1** started to increase. This can be understood by considering the oxidation potential shift, i.e., the reduction of the electron donating ability of dyad **1** in the presence of Na^+ as discussed above. But the fluorescence intensity of dyad **1** was only slightly enhanced as shown in Figure 2. The corresponding fluorescence quantum yield increases to 0.013 after addition of 100 equiv of Na^+ . However, further fluorescence enhancement was not observed after addition of more than 100 equiv of Na^+ .

With regard to addition of C_{60} to the solution of dyad **1**, it also led to fluorescence enhancement as displayed in Figure 3. This is likely due to the fact the intermolecular photoinduced electron transfer between C_{60} and TTF would impair the corresponding intramolecular photoinduced electron transfer

(11) The fluorescence quantum yields were determined by using 9,10-diphenylanthracene in CH_2Cl_2 as a reference. The free energy (ΔG_{PET}) for the photoinduced electron transfer from the TTF unit to the anthracene unit (in CH_2Cl_2) was calculated with the Rehm–Weller equation: $\Delta G_{\text{PET}} = -\lambda(\text{ex.}) - E(\text{red.}) + E(\text{ox.}) - e^2/\epsilon r = -0.82$ eV, with $E(\text{ox.}) = 0.55$ eV (for the TTF unit), $E(\text{red.}) = -1.89$ eV (for the anthracene unit), $\lambda(\text{ex.}) = 370$ nm (excitation wavelength), and $e^2/\epsilon r = -0.1$ eV; see: (a) Rehm, D.; Weller, A. *Isr. J. Chem.*, **1970**, *8*, 259. (b) Grabowski, Z. R.; Dobkowski, J. *Pure Appl. Chem.* **1983**, *55*, 245.

SCHEME 2. The Possible Mechanism for the Observed Fluorescence Enhancement under the Combined Actions of Na^+ and C_{60}



between TTF and anthracene units, thus leading to fluorescence enhancement. The corresponding fluorescence quantum yield increased from 0.011 for the pure solution of dyad **1** to 0.019 after addition of 2.0 equiv of C_{60} . But if more than 2.0 equiv of C_{60} were added to the solution of dyad **1**, the fluorescence intensity of the solution started to decrease. This is likely due to the competition of energy transfer from the excited anthracene unit to the C_{60} since there is spectral overlap between the fluorescence spectrum of anthracene and the absorption spectrum of C_{60} .

Interestingly, when both C_{60} and Na^+ were added to the solution of dyad **1**, the fluorescence intensity of the solution was largely enhanced as shown in Figure 2. The fluorescence quantum yield of the solution of dyad **1** containing 100 equiv of Na^+ and 2.0 equiv of C_{60} was measured to be 0.050, nearly five times higher than that of the pure solution of dyad **1**. It should be noted that the addition sequence of C_{60} and Na^+ did not affect the final fluorescence spectrum. Therefore, it can be concluded that the fluorescence of dyad **1** can be largely enhanced only by the combined actions of C_{60} and Na^+ (see Scheme 2). Accordingly, if C_{60} and Na^+ are viewed as two input signals I_1 and I_2 , respectively, and the fluorescence of dyad **1** as the output signal (O_1), the manner of the fluorescence variation of dyad **1** in the presence of $\text{C}_{60}/\text{Na}^+$ mimics the performance of an “AND” logic gate.¹²

In summary, a new TTF–anthracene dyad fusion with crown ether was synthesized and characterized. Due to the action of Na^+ with the crown ether unit, the fluorescence intensity of this new dyad was enhanced in the presence of Na^+ . On the other hand, the increase of the fluorescence intensity of this new dyad was found upon addition of C_{60} , owing to the intermolecular photoinduced electron transfer between C_{60} and the TTF unit. But in either case the fluorescence intensity of this new dyad was only slightly enhanced. It was interesting to

note that the fluorescence intensity of this new dyad was largely enhanced in the presence of both Na^+ and C_{60} . Such a fluorescence modulation manner observed for this new dyad mimics the function of a two-input “AND” logic gate. Incorporation of more recognition units into TTF derivatives and establishment of new logic gates will be addressed in our further studies.

Experimental Section

Synthesis of Compound 2. A solution of **3** (0.36 g, 1.02 mmol) and **4** (0.22 g, 1.1 mmol) in tri(isopropyl)phosphite (10 mL) under N_2 was stirred and warmed to 120 °C, and maintained at this temperature for 5 h; during this time the reaction mixture turned dark red. After cooling, the tri(isopropyl)phosphite was removed in a vacuum to afford viscous red oil. After separation by column chromatography, compound **2** was obtained as a yellow oil in 38% yield (0.2 g): ^1H NMR (300 MHz, CDCl_3) δ 2.74 (t, 2H), 3.01 (m, 6H), 3.72 (m, 12H), 6.60 (s, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 18.6, 30.6, 35.8, 70.0, 70.7, 71.6, 110.0, 114.0, 117.5, 123.9, 126.2, 128.3. HRMS: Anal. Calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3\text{S}_7$ 510.9566, found 510.9574.

Synthesis of Dyad 1. To a solution of compound **2** (0.26 g, 0.51 mmol) in anhydrous degassed THF (20 mL) was added a solution of $\text{CsOH}\cdot\text{H}_2\text{O}$ (0.95 g, 0.56 mmol) in anhydrous degassed methanol (2 mL) over a period of 5 min. The mixture was stirred for an additional 30 min during which a solution of 9-(2-bromoethoxy)-anthracene (0.18 g, 0.61 mmol) in anhydrous degassed THF (20 mL) was added. The solution was stirred overnight. After separation by column chromatography compound **1** was obtained as a yellow solid in 85% yield (0.3 g): mp 110–112 °C; ^1H NMR (300 MHz, CDCl_3) δ 2.99 (t, 4H), 3.38 (t, 2H), 3.72 (m, 12H), 4.42 (t, 2H), 6.51 (s, 1H), 7.49 (m, 4H), 7.97 (d, 2H), 8.25 (s, 1H), 8.34 (d, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 35.8, 36.0, 70.0, 70.7, 71.6, 73.5, 114.9, 122.2, 122.7, 123.4, 124.6, 125.5, 125.6, 126.4, 128.3, 128.4, 128.6, 132.3, 150.23. MS (MALDI-TOF) 677.9. Anal. Calcd for $\text{C}_{30}\text{H}_{30}\text{O}_4\text{S}_7$: C, 53.07; H, 4.45; S, 33.05. Found: C, 52.60; H, 4.46; S, 32.58.

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Supporting Information Available: Purification of solvents and starting materials; fluorescence and cyclic voltammetric measurements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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(12) The first single molecular AND Logic Gate was reported by: de Silva, A. P.; Gunaratne, H. Q. N.; McCoy, C. P. *Nature* **1993**, *364*, 42. For recent reviews and results, see: (a) de Silva, A. P.; McClenaghan, N. D. *Chem. Eur. J.* **2004**, *10*, 574. (b) Raymo, F. M. *Adv. Mater.* **2002**, *14*, 401. (c) Steinitz, D.; Remacle, F.; Levine, R. D. *ChemPhysChem* **2002**, *3*, 43. (d) Balzani, V.; Venturi, M.; Credi, A. *ChemPhysChem* **2003**, *4*, 49. (e) Balzani, V.; Credi, A.; Venturi, M. *Chem. Eur. J.* **2002**, *8*, 5534. (f) Uchiyama, S.; McClean, G. D.; Iwai, K.; de Silva, A. P. *J. Am. Chem. Soc.* **2005**, *127*, 8920. (g) Qu, D.; Wang, Q.; Tian, H. *Angew. Chem., Int. Ed.* **2005**, *44*, 5296. (h) Wang, H.; Zhang, D.; Guo, X.; Zhu, L.; Shuai, Z.; Zhu, D. *Chem. Commun.* **2004**, 670. (i) Andréasson, J.; Terazono, Y.; Albinsson, B.; Moore, T. A.; Moore, A. L.; Gust, D. *Angew. Chem., Int. Ed.* **2005**, *44*, 7591.