ORGANIC LETTERS

2007
Vol. 9, No. 4
547−550

Dual-Fluorescent Donor–Acceptor Dyad with Tercarbazole Donor and Switchable Imide Acceptor: Promising Structure for an Integrated Logic Gate

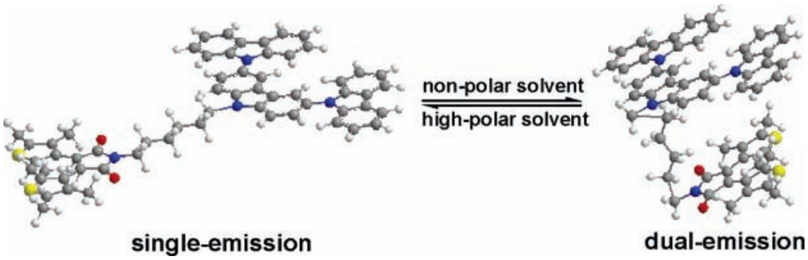
Zujin Zhao, Yajun Xing, Zixing Wang, and Ping Lu*

Chemistry Department, Zhejiang University, ZJ 310027, P. R. China

pinglu@zju.edu.cn

Received October 23, 2006

ABSTRACT



A dual-fluorescent donor-acceptor (D–A) dyad with tercarbazole (donor) and 2,3-dithienylmaleimide (acceptor) was synthesized and characterized. The emission intensity of long wavelength could be regulated by either bistable structures of the dyad or the polarities of solvents. By mimicking the function of an integrated logic gate, a 2-input AND logic operation is established.

Design and synthesis of molecule with optoelectronic property for molecular-scale information processing have become an active research area.[1] Molecular devices which function as wires,[2] switches,[3] logic gates,[4] and so on, have been reported. Mimicking the functions of logic gates used in modern computing is of particular interest.[4,5] Photochromic compounds are promising candidates due to their reversible structural interconversion in response to external optical, chemical, and thermal stimulation.[3a] And each isomer of the photochromic compound can represent ‘0’ or ‘1’ of a digital code.[6] Among these compounds, diarylethenes with heterocyclic rings have attracted more attention for their excellent thermal stability and resistance to fatigue and potential use in photonic device applications such as erasable memory media and optical switching.[3b] Moreover, development of complex systems with several reversible functions in a single molecule is a significant progress of molecular switches.[7] Meanwhile, many of molecular-scale logic gates have been constructed with D−A systems.[2b,c,8,9] If the fluorescence intensity of the fluorophore (donor) can be regulated by the controlled stimulation of acceptor in response to external

---

(1) Ratner, M. A.; Jortner, J. *Molecular Electronics*; Blackwell Scientific: Oxford, 1997; pp 5−72.

(2) (a) Davis, W. B.; Svec, W. A.; Ratner, M. A. Wasielewski, M. R. *Nature* **1998**, *396*, 60. (b) Schlicke, B.; Belser, P.; de Cola, L.; Sabbioni, E.; Balzani, V. *J. Am. Chem. Soc.* **1999**, *121*, 4207.

(3) (a) Feringa, B. L. *Molecular Switches*; Wiley-VCH Express: New York, 2001; pp 37−62. (b) Irie, M. *Chem. Rev.* **2000**, *100*, 1685.

(4) (a) Ghosh, P.; Bharadwaj, P. K.; Mandal, S.; Ghosh. S. *J. Am. Chem. Soc.* **1996**, *118*, 1553. (b) de Silva, A. P.; Dixon, I. M.; Gunaratne, H. Q. N.; Gunnlaugsson, T.; Maxwell, P. R. S.; Rice, T. E. *J. Am. Chem. Soc.* **1999**, *121*, 1393. (c) Remacle, F.; Speiser, S.; Levine, R. D. *J. Phys. Chem. B* **2001**, *105*, 5589.

(5) Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391.

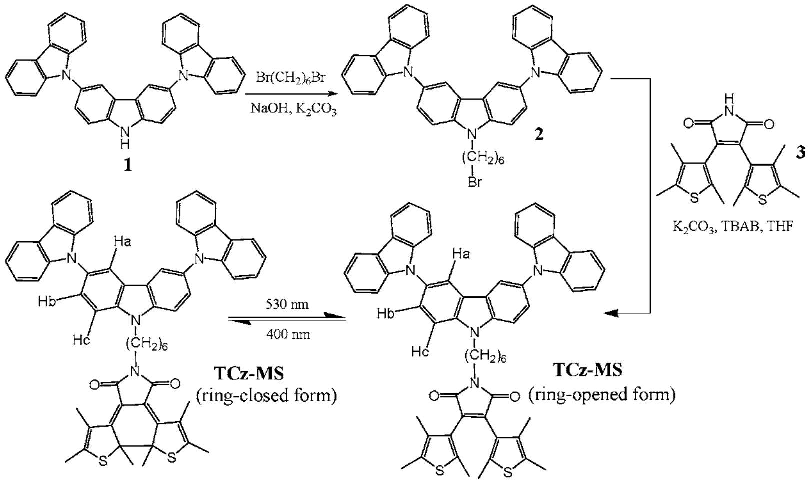
(6) (a) Liu, Z.; Yasseri, A. A.; Lindsey, J. S.; Bocian, D. F. *Science* **2003**, *302*, 1543. (b) Malval, J. P. Gosse, I.; Morand, J. P.; Lapouyade, R. *J. Am. Chem. Soc.* **2002**, *124*, 904. (c) Myles, A. J.; Wigglesworth, T. J.; Branda, N. R. *Adv. Mater.* **2003**, *15*, 745.

(7) (a) Xiao, S.; Yi, T.; Li, F.; Huang, C. *Tetrahedron Lett.* **2005**, *46*, 9009. (b) Choi, H.; Ku, B. S.; Keum, S. R.; Kang, S. O.; Ko, J. *Tetrahedron* **2005**, *127*, 8922. (c) Wang, S.; Li, X. C.; Chen, B. Z.; Luo, Q. F.; Tian, H. *Macromol. Chem. Phys.* **2004**, *205*, 1497.

(8) (a) Smit, K. J.; Warman, J. M. *J. Luminesence* **1988**, *42*, 149. (b) McClenaghan, N. D.; Passalacqua, R.; Loiseau, F.; Campagna, S.; Verheyde, B.; Hameurlaine, A.; Dehaen, W. *J. Am. Chem. Soc.* **2003**, *125*, 5356.

10.1021/ol062605r CCC: $37.00

Scheme 1



signals, the corresponding molecular logic gate can be designed.[9b,10]

Carbazole or tercarbazole are widely investigated as donors due to their potential value for solar energy storage and efficient luminescence.[8,11] At the same time, the hexatriene backbone has been extensively studied due to its potential use in photonic device applications.[3a,12] In our previous work, a D−A molecule with flexibly bonded tercarbazole (donor) and phathalimide (acceptor) was reported as a solvent polarity sensor.[13] In this paper, a D−A dyad with covalently bonded tercarbazole (donor) and 2,3-dithienylmaleimide (acceptor), with switchable property, was synthesized and characterized. By spectral investigation, dual fluorescence was also clearly observed in nonpolar or low-polar solvents. The emission intensity was well controlled by alternating external light or solvent polarity, which implied that this D−A dyad might be used as signal communication in a single molecular level.

Synthetic route to the D−A dyad (**TCz-MS**) is illustrated in Scheme 1. Tercarbazole (**1**)[13] and photochromic 2,3-dithienylmaleimide (**3**)[14] were prepared according to the reference method. Treatment of **1** with an excess amount of 1,6-dibromohexane and NaOH afforded **2**, which subsequently reacted with **3** under alkali condition to yield **TCz-MS**.

Concerning switchable 2,3-dithienylmaleimide (**3**), absorption wavelengths for the ring-closed and ring-opened structures were determined at 400 and 530 nm, respectively. This reversible optical property could also be seen for tercarbazole attached switchable 2,3-dithienylmaleimide (**TCz-MS)**. When a freshly prepared and degassed cyclohexane solution of **TCz-MS** was irradiated at 400 nm for a certain period, the yellow solution turned to red. When this red solution was irradiated at 530 nm for a period, the color of solution returned back to yellow. In terms of absorption spectra of **TCz-MS** in cyclohexane solution, the peak at 373 nm became higher and a new characteristic peak at 512 nm appeared as irradiation continued for about 30 min because of the ring-closing reaction of 2,3-dithienylmaleimide (Figure 1). While the ring-closed form of **TCz-MS** was irradiated at 530 nm for a while, a reversed phenomenon was observed and the structure turned to ring-opened form.

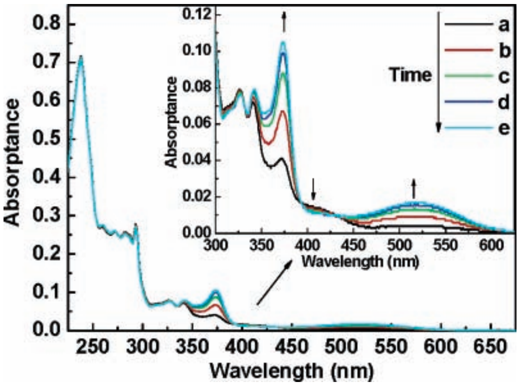


Figure 1. Absorption spectra of **TCz-MS** with a gradual irritation at 400 nm: ring-opened acceptor (a), ring-closed acceptor (e) (1×10^{-5} M, cyclohexane, 25 °C).

In ring-opened state, dual fluorescence emissions[15] were observed for **TCz-MS** in nonpolar or low-polar solvents, such as cyclohexane (Figure 2). The short-wavelength emission of **TCz-MS** was at 385 nm, which came from local excited emission of tercarbazole. The long-wavelength

---

[9] (a) Bahr, J. L.; Kodis, G.; de la Garza, L.; Lin, S.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **2001**, *123*, 7124. (b) Brown, G. J.; de Silva, A. P.; Pagliari, S. *Chem. Commun.* **2002**, 2461.

[10] Norsten, T. B.; Branda, N. R. *J. Am. Chem. Soc.* **2001**, *123*, 1784.

[11] (a) van Dijk, S. I.; Groen, C. P.; Hartl, F.; Brouwer, A. M.; Verhoeven, J. W. *J. Am. Chem. Soc.* **1996**, *118*, 8425. (b) Grabowski, Z. R.; Rotkiewicz, K. *Chem. Rev.* **2003**, *103*, 3899.

[12] Irie, M. *Chem. Rev.* **2000**, *100*, 1685.

[13] Xing, Y.; Lin, H.; Wang, F.; Lu, P. *Sens Actuator, B* **2006**, *114*, 28.

[14] Irie, M.; Mohri, M. *J. Org. Chem.* **1988**, *53*, 803.

[15] Lippert, E.; Lüder, W.; Moll, F.; Nägele, H.; Boos, H.; Prigge, H.; Seibold-Blankenstein, I. *Angew. Chem.* **1961**, *73*, 695.

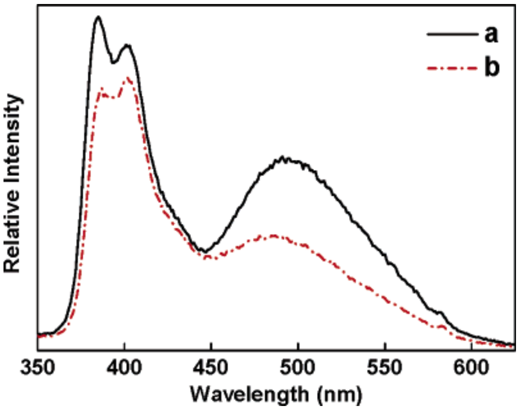


Figure 2. Emission spectra of **TCz-MS** in, for example, ring-opened state (a) and ring-closed state (b) (excited at 300 nm, 1 × 10^{-6} M, cyclohexane, 25 °C).

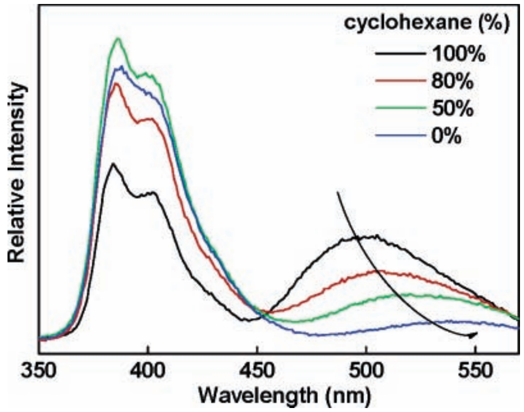


Figure 3. Emission spectra of **TCz-MS** in cyclohexane/ethyl acetate with different volume fractions (excited at 300 nm, 1 × 10^{-6} M, 25 °C).

emission of **TCz-MS** was at 495 nm, which might arise from the complexed exciplexes ($^{+}$D||A^{-}) emission.[13,16] The time-resolved fluorescence measurements detected biexponential decay with shorter and longer lifetimes in **TCz-MS**, which resembled our previous results[13] (see the Support Information). The quenching, as well as the red shift, of the long-wavelength emission was observed for **TCz-MS** as the solvent polarity increased (Figure 3). Meanwhile, this quenching was also observed at higher temperatures (Figure 4) due to the unstability of $^{+}$D||A^{-} at higher temperatures. VT-^{1}H NMR (Figure 5) further proved the existence of $^{+}$D||A^{-}. Chemical shifts of H$_a$, H$_b$, and H$_c$ (indicated in Scheme 1), assigned for central carbazole, gradually moved to higher field as temperature changed from 65 to 25 °C, which resulted from the shielding effect of $^{+}$D||A^{-}.

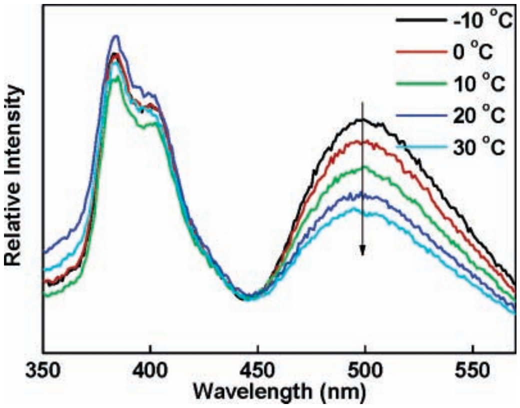


Figure 4. Emission spectra of **TCz-MS** at different temperatures (excited at 300 nm, 1 × 10^{-6} M, hexane).

In ring-closed state, intensities of the dual emission, especially for the long-wavelength emission, decreased (Figure 2). The decreasing emission at long-wavelength was well associated with the increasing absorption at 500 nm. According to Irie's hypothesis, this fluorescence quenching might be due to the overlap of emission band with absorption band at 500 nm, which resulted in nonradiative fluorescence resonance energy transfer (FRET) in photoexcited singlet state of donor and acceptor.[16] After the solution was irradiated at 530 nm for a moment, fluorescence intensity could be restored to its ring-opened value. As a net result, emission intensity of **TCz-MS** at 500 nm could be regulated by interconversion. Moreover, alternation of relative fluorescence intensity could be repeated consecutively. Figure 6 shows several switching cycles based on the reversible pericyclic reaction.

Due to the dependence of the fluorescence intensity of this D−A dyad on the external simulations, ultraviolet light (300 nm for excitation of tercarbazole), UV−vis light (400 nm for ring closing reaction/530 nm for ring opening reaction), and polarity of solvent (cyclohexane/etheyl acetate), it is possible to mimic the function of an integrated

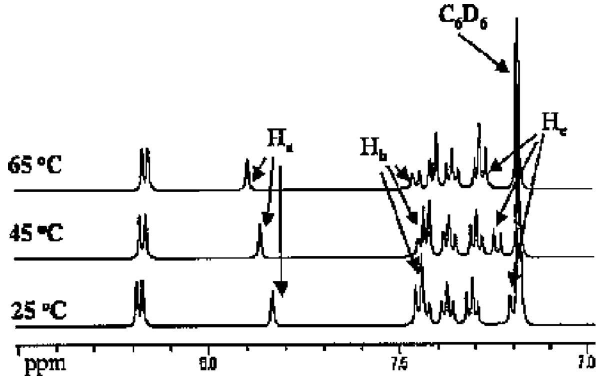


Figure 5. VT-^{1}H NMR of **TCz-MS** in C$_6$D$_6$.

---

(16) Choi, L.-S.; Collins, G. E. *Chem. Commun.* **1998**, 893.

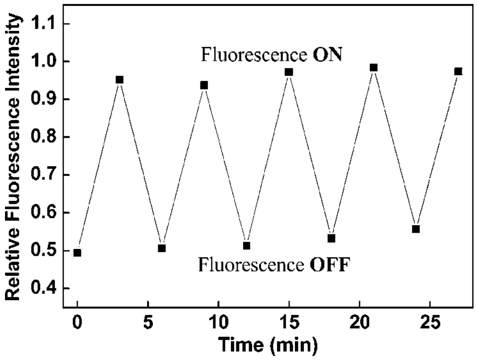


Figure 6. Reversible modulation of the fluorescence intensity at 500 nm for **TCz-MS** with alternate irradiation at 400 and 530 nm (excited at 300 nm, 1 × 10^{-6} M, cyclohexane, 25 °C).

2-input AND logic gate[9b,14,17] which requires that two inputs are both applied as digital 1 to the appropriate points of the gate in order to elicit an output of digital 1 (Figure 7a). The emission performance of **TCz-MS** is used as the example for mimicking the logic gate. Excitation at 300 nm is the power supply. Two input signals are input$_1$ (400 or 530 nm) and input$_2$ (high- or low-polar solvent). Output signal is the long-wavelength emission of the exciplex. The input$_1$ signal is *off* when radiation at 400 nm is used. The input$_2$ signal is *off* when high-polar solvent is used. The output signal is *off* when emission intensity at 500 nm is smaller than 0.7 (I_r < 0.7), while it is *on* when emission intensity is larger than 0.7 (I_r > 0.7). The physical electronic symbol of 2-input AND logic gate and the truth table are given in Figure 7b.

(a)

input$_1$	input$_2$	output
0	0	0
1	0	0
0	1	0
1	1	1

(b)

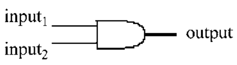


Figure 7. (a) Truth table; (b) physical electronic symbol of 2-input **AND** logic gate.

In conclusion, a D−A dyad with dual fluorescence was synthesized and characterized. The emission intensity of long wavelength could be regulated by either bistable molecular structures or the polarity of solvent. By mimicking the function of an integrated logic gate, a 2-input AND logic operation is established.

Acknowledgment. Ping Lu thanks the National Nature Science Foundation (20374045) and the Nature Science Foundation of Zhejiang Province (R404109).

Supporting Information Available: Experimental and characterization of **TCz-MS** and time-resolved fluorescence results for **TCz-MS** in cyclohexane. This material is available free of charge via the Internet at http://pubs.acs.org.

OL062605R

---

(17) (a) Guo, X.; Zhang, D.; Zhou, Y.; Zhu, D. *J. Org. Chem.* **2003**, *68*, 5681. (b) Gunnlaugsson, T.; M-Donail, D. A.; Parker, D. *Chem. Commun.* **2002**, 2461.