DOI: 10.1002/asia.200600037

Pyrene-Based Dual-Mode Fluorescence Switches and Logic Gates That Function in Solution and Film

Weidong Zhou, Yongjun Li, Yuliang Li,* Huibiao Liu, Shu Wang, Cuihong Li, Mingjian Yuan, Xiaofeng Liu, and Daoben Zhu*[a]

Abstract: A dual-mode fluorescence switch controlled by external inputs such as protons and metal ions is described, and each state corresponds to a specific fluorescent emission peak. Based on the reversible changes of the fluorescence emission of the switch responding to different external stimuli, the corresponding integrated logic gates and communication networks have been constructed in solid film or in solution.

Keywords: fluorescence · logic gates · molecular switch · pyrene

Introduction

Molecular switches that are controllable, reversible, and readable at a molecular level are of great interest because of their potential applications in the creation of nanometer-scale molecular devices,[1] especially in the field of logic operations.[2] A large number of molecular switches have so far been designed based on systems whose emission properties can be modulated by external inputs, such as pH,[3] temperature,[4] light,[5] redox potential,[6] and metal ions.[7] Among these, dual-mode fluorescence switches with two alternative *on* states, attracted much attention recently.[8] Pyrene exhibits its unique excimer behavior and therefore has been widely utilized in the design of fluorescent sensors, by introducing two pyrene subunits close to each other.[9] However, little has been reported on the exploitation of this property of pyrene for the design of molecular switches and the corresponding logic gate, especially in solid films. We have presented one logic circuit based on reversible regulation of pyrene excimer fluorescence by light and metal ions in the presence of spiropyran.[10a]

Herein, we report a particularly simple hingelike molecular switch that undergoes a reversible conformational transformation in response to external stimuli such as protons and metal ions; each state corresponds to a specific fluorescence emission peak. In the free state, it forms a stable intramolecular excimer owing to strong π–π interactions between the two pyrene planes, corresponding to one of the *on* states of the switch. When acid or metal ions are added, the two pyrene planes are separated from each other and open the hinge; the switch exhibits monomer emission and switches to the other *on* state. As shown in Figure 1, the molecular switch 2,6-di(pyrenylethylaminomethyl)pyridine (PPP) exhibits distinct conformations and fluorescence under different inputs. Remarkably, in the form of a film on a quartz slide, the acid-induced fluorescence switch acts reversibly as an *on–off* switch, in contrast to the *on–on* switch in solution. On the basis of the reversible changes in the fluorescence emission of the switch in response to different external stimuli, the corresponding integrated logic gates and communication networks were constructed in a solid film or in solution.

Results and Discussion

In the free state, the excimer emission is dominant over that of the monomer. As shown in Figure 2, the monomer/excimer emission ratio of PPP is not strongly affected by the polarity of the solvents, with the exception of dimethyl sulfoxide, in which the excimer emission is quenched completely owing to strong solvation. This indicates that PPP is always present in the folded conformation, regardless of the polarity of the solvents. In this way, molecular switches based on PPP can be utilized to a much wider extent than previous models,[9,10] which only work in limited solvents.

[a] W. Zhou, Prof. Y. Li, Y. Li, H. Liu, S. Wang, C. Li, M. Yuan, X. Liu, D. Zhu
Key Laboratory of Organic Solids, Center for Molecular Sciences
Institute of Chemistry, Chinese Academy of Sciences
Beijing 100080 (China)
Fax: (+86) 10-82616576
E-mail: ylli@iccas.ac.cn
zhudb@iccas.ac.cn

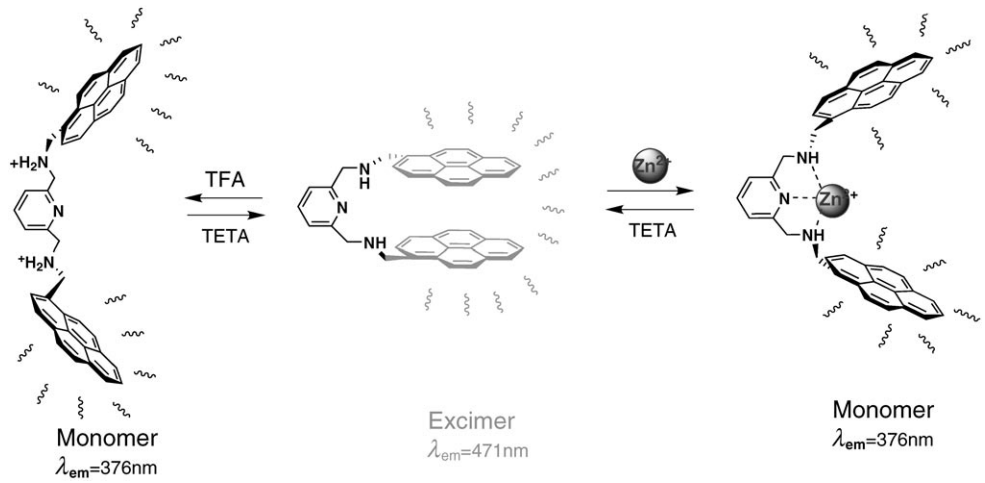


Figure 1. The proposed models for the molecule switch PPP under different input conditions. TFA = trifluoroacetic acid; TETA = triethylenetetramine.

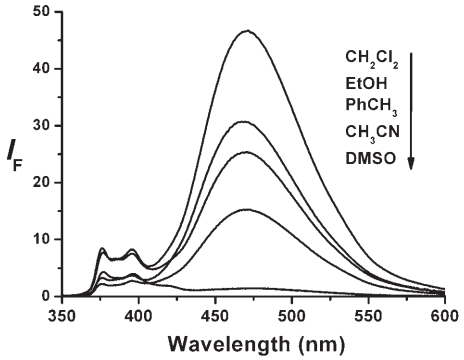


Figure 2. The fluorescence emission spectra of PPP in different solvents (5 μM, λ_{ex} = 344 nm).

As shown in Figure 3a, the fluorescence intensity of the monomer emission at 376 nm increases gradually at the expense of the excimer emission at 471 nm upon the addition of TFA, thus indicating the decomposition of the excimer and the alternating conformation of the molecular system. This can be attributed to two reasons: First, the nitrogen atom of the pyridine group, the TFA anion, and the two hydrogen atoms of one of the amine cations form strong hydrogen bonds, which may change the conformation of the bonds linked to the two pyrene units. Furthermore, the hydrogen bonding may cause the TFA skeleton to attach to the tether receptor and result in strong steric hindrance between the two pyrene planes to destroy the π–π stacking interactions. Upon the addition of more TFA, the other amine group will also be protonated successively and form $PPPH_2^{2+}$, leading to strong intramolecular electrostatic repulsion between the two amine cations and decomposition of the excimer. Similar to the results of Stoddart and coworkers,[11] analysis of the ^{1}H NMR spectra did not reveal any protonation of the nitrogen atom of the pyridine group by TFA. As expected, the emission intensity of the excimer still decreased with the gradual increase of TFA beyond 1.0 equivalent relative to PPP, and did not decrease very much after the addition of 3 equivalents of TFA (Figure 3a). However, when TETA or Et_3N is added to the $PPPH_2^{2+}$ system, the amine cations are deprotonated and lead to the disappearance of the electrostatic repulsion and the recovery of the excimer at the expense of monomer emission. Furthermore, the quantum yields of PPP and PPH_2^{2+} are similar (1.2:1) to each other, revealing the comparative fluo-

Abstract in Chinese:

本文设计合成了一个基于芘的可逆的双荧光开关，它是通过酸碱或金属锌离子调控分子的构象实现的。固态下，此开关在酸碱蒸汽的调控下表现为可逆的单荧光开关。同时，本文还设计了相应于此开关的逻辑门。

Editorial Board Member

Daoben Zhu *was born in Shanghai, China (1942). He completed his PhD at the East China Univ. of Science and Technology (1968). He is Prof. and Director of the Organic Solids Laboratory of the Institute of Chemistry, Chinese Academy of Sciences. He became an academician of the Chinese Academy of Sciences in 1997. His research interests include molecular materials and devices. He has contributed much to the development and promotion of research institutions and academic societies in China and is currently Vice-President of the Chinese Chemical Society and of the Chinese Materials Society.*

"Chemistry—An Asian Journal *covers the progress of chemistry in Asia, which is receiving ever greater attention in the world. I sincerely hope this new journal will have a bright future."*

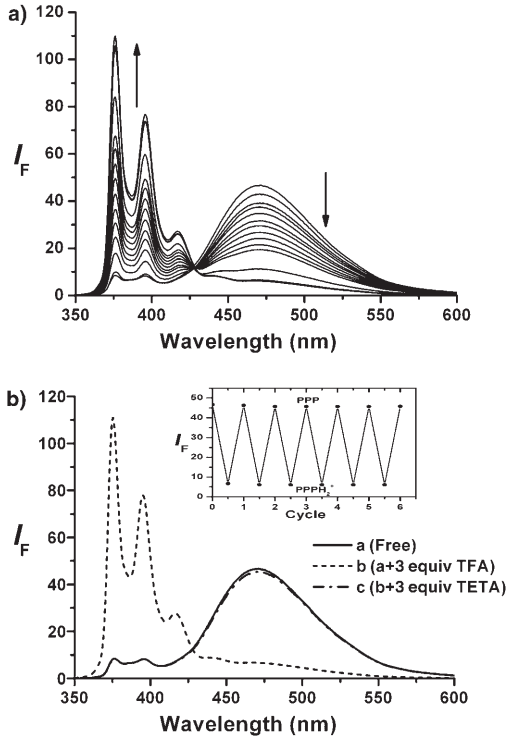


Figure 3. a) Fluorescence titration spectra of PPP (5.0 μM) with TFA (blank, 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9, 1.0, 3.0, 5.0, 10.0 equiv) in CH_2Cl_2 ($\lambda_{ex}=344$ nm). b) Fluorescence spectra of PPP upon the alternating additions of TFA and TETA in CH_2Cl_2 (5 μM, $\lambda_{ex}=344$ nm). The inset shows fluorescence intensity (at 471 nm) changes after alternating additions of TFA (half integers) and TETA (integers) over six complete cycles.

rescence response intensity of this molecular switch upon the variation of the external inputs, which exhibits an advantage over traditional fluorescence switches in which one response is much stronger than the other.[8] This process can be repeated rapidly (<10 s) many times without degradation through alternate addition of TFA and TETA, which is visually perceived through a sharp fluorescence change from 471 to 376 nm (Figure 3b).

To investigate the change in the molecular conformation in the absence of the effect of the hydrogen bonds from the acid anion, $PPPH{\cdot}PF_6$ and $PPPH_2{\cdot}2PF_6$ were synthesized (Scheme 1). Protonation of PPP with an equal and an excess amount of TFA and subsequent anion exchange generated $PPPH{\cdot}PF_6$ and $PPPH_2{\cdot}2PF_6$, respectively. This way, the steric hindrance resulting from the TFA anion skeleton disappears, and electrostatic repulsions become the dominant effect for the change in the conformation of the $PPPH_2^{2+}$ system. As shown in Figure 4, the fluorescence emission of $PPPH{\cdot}PF_6$ did not exhibit any differences to that of PPP which indicates that the single intramolecular hydrogen bond without the effect from TFA does not alternate the folded conformation. This is in accordance with the ^{1}H NMR spectra (Figure 5) in which the signals of the pyrene unit in $PPPH{\cdot}PF_6$ did not show any apparent downfield shift with respect to those in PPP. In contrast, $PPPH_2{\cdot}2PF_6$ showed strong monomer emission and weak excimer emission, which can be ascribed to a large electrostatic repulsion between two protonated amines exclusively. Therefore, if only two amine moieties were protonated completely, the tether would be unfolded, regardless of the hydrogen bond from the acid anions. As illustrated in Figure 5, the signals for the hydrogen atoms of the aromatic pyrene units generally shift

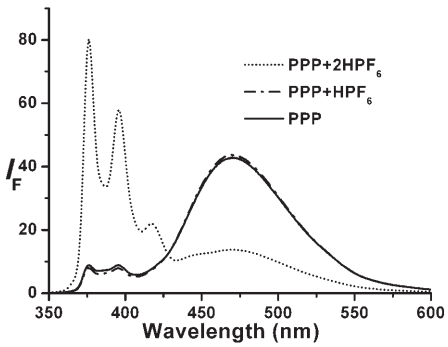
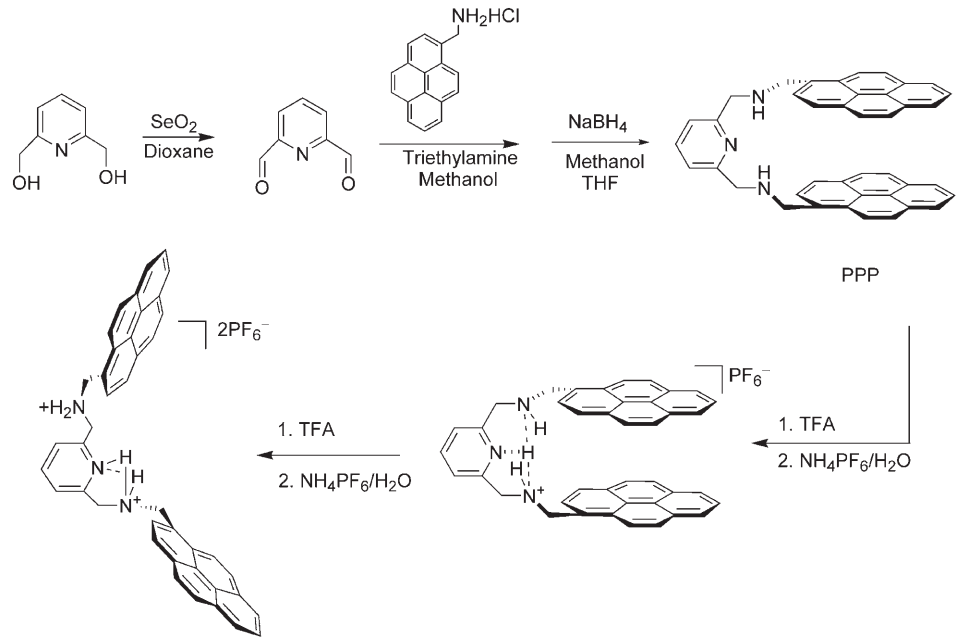


Figure 4. Fluorescence intensity of PPP, $PPPH{\cdot}PF_6$, and $PPPH_2{\cdot}2PF_6$ in CH_2Cl_2 (5 μM, $\lambda_{ex}=344$ nm).



Scheme 1. Synthesis of PPP, $PPPH{\cdot}PF_6$, and $PPPH_2{\cdot}2PF_6$.

CHEMISTRY
AN ASIAN JOURNAL

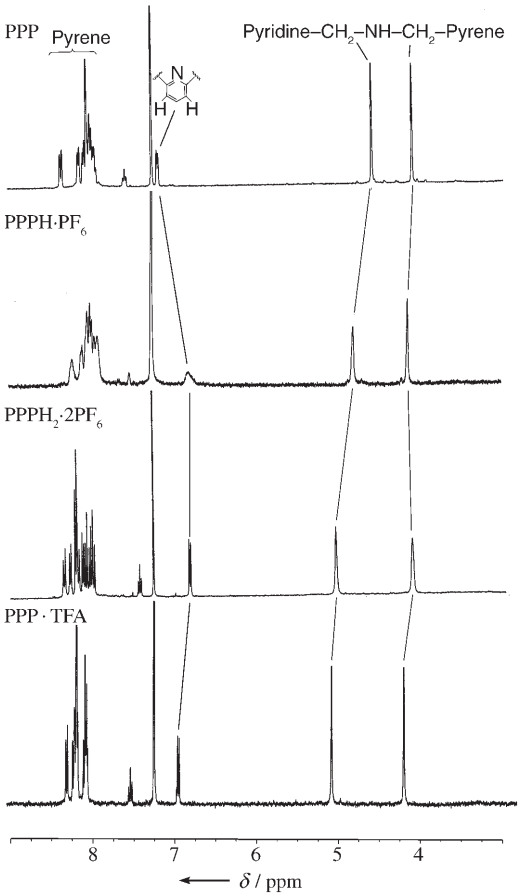


Figure 5. Partial ^{1}H NMR spectra (400 MHz, CD_3Cl) of PPP and of its protonated compounds PPPH·PF_6, $PPPH_2$·2 PF_6, and $PPPH_2$·2 CF_3COO.

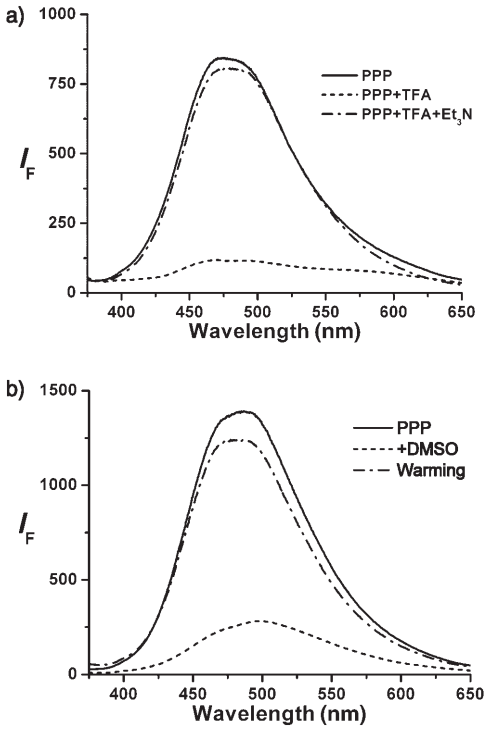


Figure 6. The fluorescence spectra of the quartz slides coated with PPP film upon exposure to different vapors: a) blank, TFA, TFA + Et_3N; b) blank, DMSO, warming under reduced pressure.

to lower magnetic fields upon protonation from PPP to $PPPH_2^{2+}$; this phenomenon is a result of the disappearance of the magnetic shielding effect from the aromatic rings, which face each other to a greater extent in PPP.[12]

To see if the same principles could be demonstrated to work in environments that are more relevant to materials applications, we prepared thin transparent films of PPP on quartz slides by evaporation of solutions of PPP in dichloromethane. A broad peak at around 480 nm was detected when slides coated with the PPP film were illuminated with UV light (353 nm) which suggests that PPP adopts the folded conformation and exhibits excimer emission in the solid state. However, exposure of the PPP-coated slide to TFA vapor (a test tube with a solution of TFA was placed in the vicinity of the film) resulted in a nearly complete quenching of the fluorescence of the film (Figure 6a) which indicates that $PPPH_2^{2+}$ loses its fluorescence in the solid state, possibly owing to the strong inter- and intramolecular repulsion interactions. As expected, when the resulting quartz slide was subsequently exposed to Et_3N vapor ($PPPH_2^{2+}$ converted into PPP), the excimer emission recovered its original strong intensity. The behavior of PPP implies that this acid–base-induced fluorescence *on–off* switch in the solid film can act as a reversible fluorescence probe to detect acid vapor in the atmosphere. Furthermore, no fluorescence was detected when slides coated with PPP were exposed to DMSO vapor (by gently warming an open beaker of the solvent in the vicinity of the film for 5 min) (Figure 6b), as had been observed in solution. Moreover, this system is also reversible: warming the slide to 70 °C at 0.1 Torr for 15 min to drive off absorbed solvent resulted in recovery of the fluorescence emission.[13] An exciting extension of the fluorescence switch studies has been the development of molecular equivalents of logic gates and implementation of these gates in molecular arithmetic.[14] As anticipated, a distinct pattern of quenching resulting from a thin film of PPP upon exposure to DMSO vapor and then TFA vapor was observed (Figure 7a). In this way, the response of PPP to the different combinations of two stimuli (protons and DMSO) composes a "NOR" logic gate (G1; Table 1). Furthermore, this logic gate can be operated with full reversibility as a film, because both the DMSO and the TFA stimuli can be removed by warming under reduced pressure and by exposure to Et_3N vapor, respectively.

Table 1. Truth table for the logic gate G1.[a] < W = 1

Input 1 (TFA)	Input 2 (DMSO)	Output (Fluorescence)
0	0	1
0	1	0
1	0	0
1	1	0

[a] 0 = *off*, 1 = *on*.

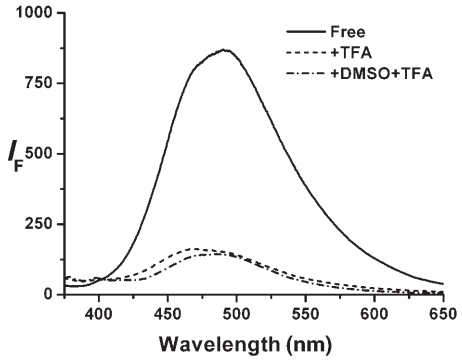


Figure 7. The fluorescence spectra of the PPP-coated quartz slides upon exposure to different vapors (blank, TFA, DMSO + TFA).

Taking account of the chelate effect of the pyridine–dimethylamine unit, we investigated the binding properties of PPP towards different metals with respect to fluorescence changes.[9,10,14] Among the metal ions tested, Zn^{2+} and Cd^{2+} caused significant extinction of excimer emission and a corresponding increase in monomer emission, in contrast to all other metal ions. Notably, at concentrations of Zn^{II} greater than 1.4 equivalents relative to PPP, the pyrene excimer emission showed little deviation of I_{471}/I_{376} which might be closely related to the formation of a 1:1 complex with the metal ion. Furthermore, the folded conformation and the resulting excimer emission were recovered by the addition of TETA (3 equiv) to the PPP–Zn^{2+} complex (Figure 8). Consequently, PPP can act as another molecular switch through a complexation/dissociation cycle with Zn^{2+} ions.

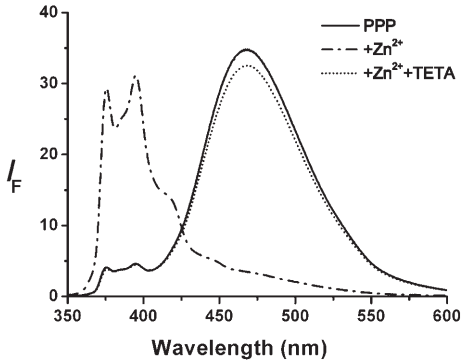


Figure 8. The fluorescence spectra of PPP (5 μM) under different conditions (blank, Zn^{2+}, Zn^{2+} + TETA) in EtOH, excitation length is 344 nm.

From a logic viewpoint,[14,15] it can be argued that the PPP system exhibits logic operation (G2) if the three inputs are defined as chemical species (H^+, Zn^{2+}, and TETA) and the outputs are defined as fluorescence emissions at 376 nm and 471 nm (Figure 9 and Table 2). Indeed, two output signals cannot be *on* simultaneously; they correspond to two distinct states of the molecular switch that cannot coexist in solution. In this logic operation, the molecular switch reads a string of three binary inputs and writes a specific combination of two binary outputs. For example, when the three stimuli are all *off*, the input string is 000. Under these conditions, the molecular switch is in state PPP, which only exhibits excimer emission at 471 nm. As a result, the two output signals 01 and 02 are *off* and *on*, respectively, and the output string is 01. All the possible combinations of input data and the corresponding output strings are illustrated in Table 2. As shown in the combinational logic circuit (Figure 10), the three inputs are elaborated through a series of AND, NOT, NOR, and OR operations to produce the two outputs 01 and 02.

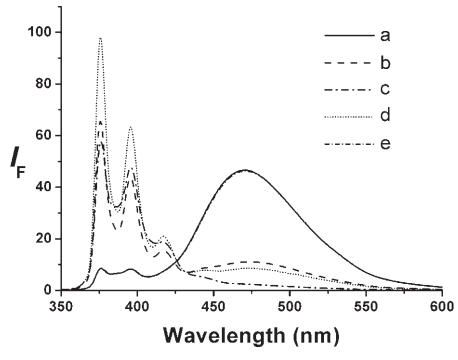


Figure 9. Fluorescence emission spectra for PPP (5 μM) in CH_2Cl_2/CH_3CN (5:1, *v*/*v*) under different input conditions (a: blank; b: TFA; c: Zn^{2+}; d: TFA + Zn^{2+}; e: TFA + Zn^{2+} + TETA). Excitation wavelength: 344 nm.

Table 2. Truth table for the logic gate G2.

Input data			Output data	
*I*1 (TFA)	*I*2 (Zn^{2+})	*I*3 (TETA)	*O*1 (λ_{em}=376 nm)	*O*2 (λ_{em}=471 nm)
0	0	0	0	1
0	0	1	0	1
0	1	0	1	0
1	0	0	1	0
0	1	1	0	1
1	0	1	0	1
1	1	0	1	0
1	1	1	0	1

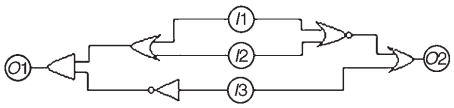


Figure 10. The logic circuit equivalent to the molecular switch transduces the inputs into the outputs through AND, NOT, OR, and NOR operations.

Conclusions

We have presented a simple molecular switch with dual fluorescence responses driven by acid or metal ions owing to the alternation of the excimer/monomer emissions of the pyrene units, which can work reversibly without any degradation in solution. Furthermore, two *on–off* switches were constructed in a solid film by using exposure to chemical vapor as a stimulus. Significantly, this series of switches can be exploited as reversible one-output and two-output logic

gates in solid film and in solution, respectively, owing to the unique response to chemical inputs.

Experimental Section

The chemical reagents were purchased from Acros or Aldrich Corporation and utilized as received, unless indicated otherwise. All solvents were purified by standard procedures. UV/Vis spectra were taken on a Hitachi U-3010 spectrometer, and fluorescence spectra were measured on a Hitachi F-4500 spectrofluorometer. ^{1}H NMR spectra were obtained on a Bruker Avance DPS-400 spectrometer. EI-MS mass spectra were recorded on a Bruker Biflex EI-MS.

2,6-Pyridinedicarbaldehyde: A mixture of 2,6-pyridinedimethanol (139 mg, 1 mmol) and SeO_2 (1.1 g, 10 mmol) in dioxane (20 mL) was heated at reflux for 4 h in the dark. The resulting mixture was filtered, and the filtrate was concentrated in vacuo. The residue was purified by silica-gel column chromatography (eluent: CH_2Cl_2) to provide pure 2,6-pyridinedicarbaldehyde (60 mg, 0.44 mmol, 45%) as a colorless solid. M.p.: 125 °C; ^{1}H NMR ($CDCl_3$, 298 K): δ = 8.08 (t, J = 7.7 Hz, 1H), 8.18 (d, J = 7.7 Hz, 2H), 10.17 ppm (s, 2H); EIMS: m/z: 135; elemental analysis: calcd for $C_7H_5NO_2$ (%): C 62.22, H 3.73, N 10.37; found: C 62.31, H 3.77, N 10.31.

PPP: A solution of 2,6-pyridinedicarbaldehyde (40 mg, 0.30 mmol) in methanol (10 mL) was added dropwise over 30 min to a solution of 1-pyrenylmethylamine hydrochloride (160 mg, 0.6 mmol) and triethylamine (60 mg, 0.6 mmol) in methanol (20 mL). The reaction mixture was stirred at room temperature for 4 h, after which time the Schiff base precipitate was isolated by filtration and immediately dissolved in THF/MeOH (8:1 v/v; 100 mL), followed by the addition of $NaBH_4$ (100 mg, 2.7 mmol).The reaction was quenched by the addition of H_2O (2 mL) after 2 h, and the mixture was concentrated in vacuo. The residue was dissolved in CH_2Cl_2 (100 mL), washed three times with distilled water, and dried with anhydrous Na_2SO_4. The residue was purified by silica-gel column chromatography (eluent: MeOH/CH_2Cl_2 1:9) to provide pure PPP (117 mg, 0.21 mmol, 70%) as a colorless solid. M.p.: 72 °C; ^{1}H NMR ($CDCl_3$, 298 K); δ = 4.08 (s, 4H), 4.68 (s, 4H), 7.09 (d, J = 7.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 1H), 7.93–8.19 (m, 16H), 8.37 ppm (d, J = 9.2 Hz, 2H); EIMS: m/z: 565; elemental analysis: calcd for $C_{41}H_{31}N_3$ (%): C 87.05, H 5.52, N 7.43; found: C 87.0, H 5.61, N 7.40.

PPPH·PF_6 and $PPPH_2$·2PF_6: PPP (40 mg, 0.07 mmol) was dissolved in Me_2CO and TFA (5.3 μL, 0.07 mmol) in Me_2CO was added to the solution. After evaporation of the solvent, the residual pale yellow solid was dissolved in H_2O/acetone (1:3), and a saturated aqueous solution of NH_4PF_6 was added. The acetone was then removed, and the aqueous solution was extracted with CH_2Cl_2 several times. The organic extracts were dried with anhydrous Na_2SO_4, and the solvent was evaporated to dryness to yield the monoprotonated product PPPH·PF_6 as a white powder (41 mg, 86%). M.p.: 105 °C; ^{1}H NMR ($CDCl_3$, 298 K): δ = 4.12 (s, 4H), 4.8 (s, 4H), 6.83 (s, 2H), 7.53 (s, 1H), 7.93–8.10 (m, 16H), 8.23 ppm (s, 2H); ESIMS: m/z: 566 $[M-PF_6]^+$; elemental analysis: calcd for $C_{41}H_{32}N_3PF_6$ (%): C 69.19, H 4.53, N 5.9; found: C 68.97, H 4.31, N 5.53. $PPPH_2$·2PF_6 was prepared by using a similar procedure as described for the preparation of PPPH·PF_6, but with excess TFA. M.p.: 123 °C; ^{1}H NMR ($CDCl_3$, 298 K): δ = 4.12 (s, 4H), 5.05 (s, 4H), 6.83 (d, J = 7.7 Hz, 2H), 7.46 (t, J = 7.8 Hz, 1H), 8.00–8.21 (m, 14H), 8.27 (d, J = 7.8 Hz, 2H), 8.34 ppm (d, J = 9.26 Hz, 2H); ESIMS: m/z: 567 $[M-2PF_6]^{2+}$; elemental analysis: calcd for $C_{41}H_{33}N_3P_2F_{12}$ (%): C 57.42, H 3.88, N 4.90; found: C 57.31, H 3.96, N 4.78.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (20531060, 10474101, 20418001, 20571078, and 20421101) and the Major State Basic Research Development Program (2006CB300402).

[1] a) A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher, T. E. Rice, *Chem. Rev.* **1997**, *97*, 1515–1566; b) L. Fabbrizzi, M. Licchelli, P. Pallavicini, *Acc. Chem. Res.* **1999**, *32*, 846–853; c) B. L. Feringa, *Molecular Switches*, Wiley-VCH, Weinheim, **2001**; d) V. Balzani, A. Credi, F. M. Raymo, J. F. Stoddart, *Angew. Chem.* **2000**, *112*, 3484–3530; *Angew. Chem. Int. Ed.* **2000**, *39*, 3348–3391.

[2] a) Special Issue on Photochromism: Memories and Switches: *Chem. Rev.* **2000**, *100*, 1683–1890; b) V. Balzani, A. Credi, S. J. Langford, F. M. Raymo, J. F. Stoddart, M. Venturi, *J. Am. Chem. Soc.* **2000**; *122*, 3542–3543; c) A. P. de Silva, I. M. Dixon, H. Q. N. Gunaratne, T. Gunnlaugsson, P. R. S. Maxwell, T. E. Rice, *J. Am. Chem. Soc.* **1999**, *121*, 1393–1394; d) A. P. de Silva, N. D. McClenaghan, *J. Am. Chem. Soc.* **2000**, *122*, 3965–3966.

[3] a) J. F. Callan, A. P. de Silva, N. D. McClenaghan, *Chem. Commun.* **2004**, 2048–2049; b) A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *Chem. Commun.* **1996**, 2399–2400; c) Y.-D. Cao, Q.-Y. Zheng, C.-F. Chen, Z.-T. Huang, *Tetrahedron Lett.* **2003**, *44*, 4751–4755.

[4] S. Uchiyama, N. Kawai, A. P. de Silva, K. Iwai, *J. Am. Chem. Soc.* **2004**, *126*, 3032–3033.

[5] a) L. Gobbi, P. Seiler, F. Diederich, *Angew. Chem.* **1999**, *111*, 737–740; *Angew. Chem. Int. Ed.* **1999**, *38*, 674–678; b) A. Beyeler, P. Belser, L. De Cola, *Angew. Chem.* **1997**, *109*, 2878–2881; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2779–2781.

[6] a) L. Fabbrizzi, M. Licchelli, S. Mascheroni, A. Poggi, D. Sacchi, M. Zema, *Inorg. Chem.* **2002**, *41*, 6129–6136; b) G. De Santis, L. Fabbrizzi, M. Licchelli, N. Sardone, A. H. Velders, *Chem. Eur. J.* **1996**, *2*, 1243–1250; c) G. Zhang, D. Zhang, X. Guo, D. Zhu, *Org. Lett.* **2004**, *6*, 1209–1212.

[7] a) A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *J. Am. Chem. Soc.* **1997**, *119*, 7891–7892; b) S. A. de Silva, B. Amorelli, D. C. Isidor, K. C. Loo, K. E. Crooker, Y. E. Pena, *Chem. Commun.* **2002**, 1360–1361.

[8] a) M. T. Albelda, M. A. Bernardo, P. Díaz, E. García-España, J. Seixas de Melo, F. Pina, C. Soriano, S. V. Luis, *Chem. Commun.* **2001**, 1520–1521; b) D.-H. Qu, Q.-C. Wang, J. Ren, H. Tian, *Org. Lett.* **2004**, *6*, 2085–2088; c) A. Bencini, A. Bianchi, C. Lodeiro, A. Masotti, A. J. Parola, F. Pina, J. Seixas de Melo, B. Valtancoli, *Chem. Commun.* **2000**, 1639–1640; d) Y. Shiraishi, Y. Tokitoh, G. Nishimura, T. Hirai, *Org. Lett.* **2005**, *7*; 2611–2614.

[9] a) I. Aoki, H. Kawabata, K. Nakashima, S. Shinkai, *J. Chem. Soc. Chem. Commun.* **1991**, 1771; b) S.-Y. Moon, N. J. Youn, S. M. Park, S.-K. Chang, *J. Org. Chem.* **2005**, *70*, 2394–2397; c) J. Y. Lee, S. K. Kim, J. H. Jung, J. S. Kim, *J. Org. Chem.* **2005**, *70*, 1463–1466; d) S. K. Kim, S. H. Lee, J. Y. Lee, J. Y. Lee, R. A. Bartsch, J. S. Kim, *J. Am. Chem. Soc.* **2004**, *126*, 16499–16506; e) S. Nishizawa, Y. Kato, N. Teramae, *J. Am. Chem. Soc.* **1999**, *121*, 9463–9464.

[10] a) X. Guo, D. Zhang, T. Wang, D. Zhu, *Chem. Commun.* **2003**, 914; b) T. Jin, K. Ichikawa, T. Koyama, *J. Chem. Soc. Chem. Commun.* **1992**, 499; c) R.-H. Yang, W.-H. Chan, A. W. M. Lee, P.-F. Xia, H.-K. Zhang, K. A. Li, *J. Am. Chem. Soc.* **2003**, *125*, 2884–2885.

[11] a) K. C.-F. Leung, F. Arico, S. J. Cantrill, J. F. Stoddart, *J. Am. Chem. Soc.* **2005**, *127*, 5808–5810; b) F. Arico, T. Chang, S. J. Cantrill, S. I. Khan, J. F. Stoddart, *Chem. Eur. J.* **2005**, *11*, 4655–4666; c) P. T. Glink, A. I. Oliva, J. F. Stoddart, A. J. P. White, D. J. Williams, *Angew. Chem.* **2001**, *113*, 1922–1927; *Angew. Chem. Int. Ed.* **2001**, *40*, 1870–1875.

[12] a) Y. Suzuki, T. Morozumi, H. Nakamura, M. Shimomura, T. Hayashita, R. A. Bartsh, *J. Phys. Chem. B* **1998**, *102*, 7910–7917; b) B. Bodenant, F. Fages, M.-H. Delville, *J. Am. Chem. Soc.* **1998**, *120*,

7511–7519; c) P. Reynders, W. Kuehnle, K. A. Zachariasse, *J. Am. Chem. Soc.* **1990**, *112*, 3929–3939.
[13] D. A. Leigh, M. Á. F. Morales, E. M. Pérez, J. K. Y. Wong, C. G. Saiz, A. M. Z. Slawin, J. Adrian, *Angew. Chem.* **2005**, *117*, 3122–3127; *Angew. Chem. Int. Ed.* **2005**, *44*, 3062–3067.
[14] A. P. de Silva, N. D. McClenaghan, *J. Am. Chem. Soc.* **2000**, *122*, 3965–3966.
[15] a) A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *Nature* **1993**, *364*, 42; b) S. Iwata, K. Tanaka, *J. Chem. Soc. Chem. Commun.* **1995**, 1491; c) A. P. de Silva, H. Q. N. Gunaratne, C. P. McCoy, *J. Am. Chem. Soc.* **1997**, *119*, 7891; d) T. Gunnlaugsson, D. A. MacDonail, D. Parker, *J. Am. Chem. Soc.* **2001**, *123*, 12866; e) A. Credi, V. Balzani, S. J. Langford, J. F. Stoddart, *J. Am. Chem. Soc.* **1997**, *119*, 2679.

Received: February 24, 2006

