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Synthesis and thermal modulation of the fluorescence of a pyrene-arylmaleimide dyad and its Diels–Alder adduct

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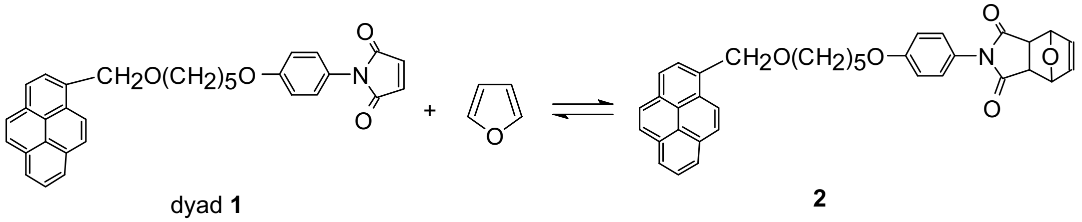
Abstract—The fluorescence of a pyrene-arylmaleimide dyad and its Diels–Alder adduct can be thermally modulated through reversible Diels–Alder reaction of arylmaleimide unit with furan. Moreover, the fluorescence intensities of the Diels–Alder adduct of dyad **1** with furan vary linearly with the temperatures of the corresponding solutions, demonstrating that these molecules are interesting compounds for studies of fluorescent molecular thermometers.

Temperature is an important property of environment, thus monitoring temperature is essential in many fields. However, in some cases, like in micro-sized domains or harsh environments, a conventional thermometer is impractical.[1] In this respect, the development of fluorescent molecular thermometers is highly desirable[2a,b] and has the edge over physical thermal probes of temperature for fluid systems and systems under electromagnetic irradiation in that flow patterns and field lines are not disturbed by the presence of these molecular probes.[2c–f] Several fluorescent molecular thermometers have been described. They are based on exciplexe,[3] excimers,[4] cyclodextrin complexes of phosphors and intramolecular charge-transfer fluorophores,[5] twisted TICT fluorophores,[1a] polymers showing temperature-induced phase transition,[6] spin crossover complexes,[7] vibrational energy changes in the excited state,[8] quasi-reversible photodissociation,[9] and lanthanide complexes.[10] Herein, we report the synthesis and thermal modulation of the pyrene-1,4-disubstituted arylmaleimide dyad **1** (abbrev. as arylmaleimide, Scheme 1) and its Diels–Alder (D–A) adduct **2**. The results indicate that these molecules are interesting compounds for studies of fluorescent molecular thermometers.

The design rationale is based on the tuning of the photoinduced electron transfer (PET) process within dyad **1** through the reversible D–A reaction between arylmaleimide unit and furan. In general, maleimide is both a good electron acceptor and a reactive dienophile. For instance, maleimide can react with furan leading to the corresponding D–A adduct, and at elevated temperature the *retro* D–A reaction occurs (Scheme 2).[11]



dyad **1**

2

Scheme 1.

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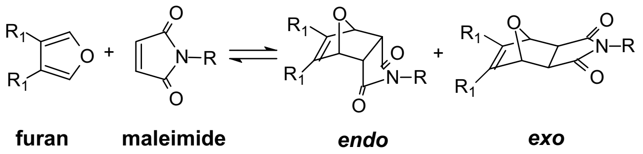
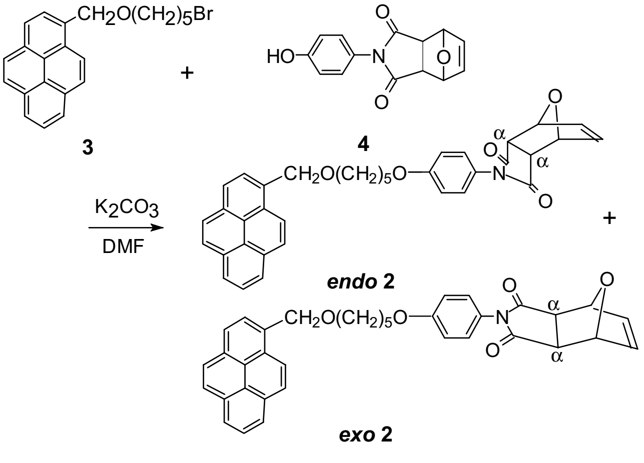


Scheme 2.

Compared with arylmaleimide itself, its D–A adduct with furan shows weak electron accepting ability.[12] Thus, it is possible to tune the electron accepting ability of arylmaleimide through the reversible D–A reaction with furan. Accordingly, in a dyad formed by linking arylmaleimide to a fluorescent donor unit such as pyrene, it would be possible to tune the intramolecular PET process within this dyad, which in turn modulates the fluorescence of pyrene unit. On one hand, it can be expected that dyad **1** is weakly fluorescent owing to the intramolecular PET process, and the fluorescence of its D–A adduct **2** with furan (Scheme 1) would be enhanced, due to the fact that the electron acceptor unit in the D–A adduct **2** becomes weaker and thus the corresponding PET process would be prohibited. The D–A adduct **2** can be converted to dyad **1** by heating. Therefore, a thermal induced fluorescence switch can be realized based on dyad **1** through reversible D–A reaction with furan. It is worthwhile to mention that Li and coworkers[13] have reported very recently the reversible fluorescence and aggregation behavior of multi-maleimides bearing electron-donating chromophores. On the other hand, the reaction rates of both the D–A reaction of arylmaleimide with furan and the corresponding *retro* D–A reaction should be dependent on the temperature of the solution. As a result, the fluorescence intensity of the solution would become dependent on the temperature of the solution. Thus, dyad **1** and its D–A adduct **2** might be interesting compounds for studies of fluorescent molecular thermometers.

The synthesis of the D–A adduct **2** is shown in Scheme 3. Reaction of **3**, which was prepared by the reaction of 1-pyrenemethanol pyrene and 1,5-dibromopentane with the usual procedure, and **4**[14] in the presence of anhydrous K_2CO_3 led to the mixture of *endo* and *exo* isomers of **2**.[15] The separation of *exo* and *endo* **2** was achieved with column chromatography. Structural assignment of the *endo* and *exo* isomers was made based on the ^1H NMR spectra (see Supplementary data) according to the previous results:[16] the one with the chemical shift of α-H at 3.67 ppm was *endo* **2** and that with the chemical shift of α-H at 2.98 ppm was *exo* **2**. The *retro* D–A reaction of the *endo* and *exo* isomers of **2** led to dyad **1**.[17] The *retro* D–A reaction of the *endo* isomer occurred when the solution was heated to 60 °C in benzene. The *endo* **2** was completely transferred to dyad **1** when the solution was kept at 60 °C for 3 h. But, the corresponding *retro* D–A reaction of *exo* **2** could not take place until the solution was heated to 100 °C in toluene.



Scheme 3.

As expected, dyad **1** showed rather weak fluorescence (Fig. 1) with low quantum yield[18] at 20 °C ($\Phi_F = 0.022$ in DMF) due to the intramolecular PET reaction between the excited pyrene unit and arylmaleimide unit. On the contrary, both *endo* and *exo* **2** were strongly fluorescent. The quantum yields of *endo* and *exo* **2** were determined to be 0.148 and 0.159, respectively, at 20 °C in DMF. The strong fluorescence of *endo* and *exo* **2** was due to the fact that the D–A adduct of arylmaleimide and furan showed weak electron accepting ability compared with arylmaleimide and as a result, the PET process would be prohibited. These results indicated that the fluorescence of dyad **1** can be reversibly modulated in the presence of furan through the reversible D–A reaction, and accordingly a thermally induced fluorescence switch can be established based on dyad **1**.

The fluorescence spectra of dyad **1** in the presence of furan or furfuryl alcohol were measured in the temperature range of 25–60 °C. The fluorescence intensity of the solution was enhanced by increasing the temperature (see Supplementary data). Such fluorescence enhancement was obviously due to the transformation of dyad **1** to **2**. But, on the basis of ^1H NMR data (see Supplementary), the molar ratio of dyad **1** that was transformed to *endo* and *exo* **2** was rather small.

The fluorescence spectra of *endo* **2** were measured at different temperatures in DMF (Fig. 2A). Before each measurement the solution of *endo* **2** was kept for

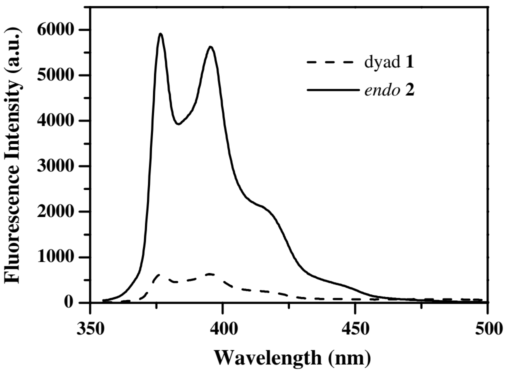


Figure 1. Fluorescence spectra (λ_{ex} = 340 nm) of dyad **1** (1.0×10^{-5} M) and *endo* **2** (1.0×10^{-5} M) in DMF.

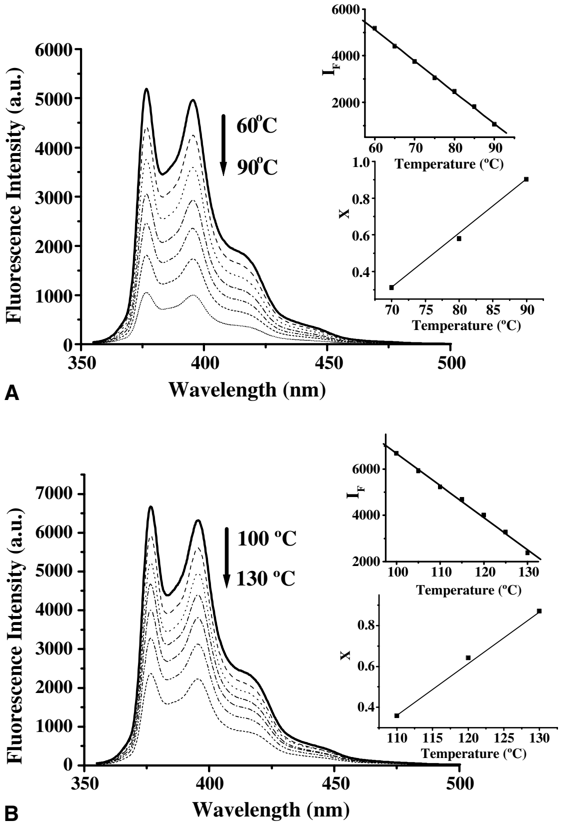


Figure 2. (A) Fluorescence spectra ($\lambda_{ex} = 340$ nm) of the DMF solution of *endo* **2** (1.0×10^{-5} M) recorded over the temperature range 60–90 °C; Inset shows the I_F at 394 nm versus temperature profile, and the profile for the relative amount (in molar, *x*) of *endo* **2** that was transformed to dyad **1** versus the temperature; (B) fluorescence spectra ($\lambda_{ex} = 340$ nm) of the DMF solution of *exo* **2** (1.0×10^{-5} M) recorded over the temperature range 100–130 °C; Inset shows the I_F at 394 nm versus temperature profile, and the profile for the relative amount (in molar, *x*) of *exo* **2** that was transformed to dyad **1** versus the temperature.

10 min at the temperature.[19] As shown in Figure 2A, the fluorescence intensity of the solution started to decrease when it was heated to 60 °C, and further decrease was observed at temperature higher than 60 °C. Such fluorescence reduction was due to the transformation of the *endo* isomer of **2** into dyad **1** through the *retro* D–A reaction. But, the decrease of fluorescence intensity stopped when the temperature reached 90 °C. This was probably due to the fact that the major fraction (~90%) of *endo* **2** in the solution was transformed to dyad **1** after the solution was heated at 90 °C for 10 min. The profile of the fluorescence intensity of the solution, measured either at 394 or 376 nm, versus temperature gave good linear relationship (see the inset of Fig. 2A).

^{1}H NMR spectra of the solution of *endo* **2** were recorded after it was heated at 70, 80, and 90 °C, respectively, for 10 min (see Supplementary data). Based on these ^{1}H NMR data, the relative amount (in molar) of *endo* **2** that was transformed to dyad **1** was estimated at each temperature,[20] and it increased linearly with the temperature as illustrated in the inset of Figure 2A. The ^{1}H NMR data also indicated that the amount (in molar) of dyad **1** formed in the solution increased linearly with the temperature. As mentioned above, *endo* **2** showed strong fluorescence while dyad **1** displayed weak fluorescence. Thus, it was understandable that the fluorescence intensity of the solution of *endo* **2** decreased linearly with the temperature. The results of ^{1}H NMR and fluorescence spectra were consistent.

Similarly, the fluorescence spectra of *exo* **2** were also measured after the solution was heated. As mentioned above, the *retro* D–A reaction of the *exo* isomer of **2** occurred at elevated temperature. As shown in Figure 2B, the fluorescence intensity of the *exo* isomer of **2** did not decrease until the temperature reached 100 °C. Further fluorescence reduction was observed by increasing the temperature of the solution, but the fluorescence intensity reached the minimum after the solution was heated at 130 °C for 10 min. As for the *endo* isomer of **2**, there was a good linear plot of the fluorescence intensity at 394 or 376 nm versus the temperature of the solution as shown in the inset of Figure 2B. Similarly, the relative amount of *exo* **2** (in molar) that was converted into dyad **1** increased linearly with the temperature (see inset of Fig. 2B).[20]

As control experiments, the fluorescence spectra of 1-pyrenemethanol were measured in the mixed solvent of THF/furan and DMF under the same conditions employed for dyad **1** and the *endo* and *exo* isomers of **2**. The results indicated that variation of the fluorescence spectra of 1-pyrenemethanol under these conditions was rather minor (see Supplementary data). Thus, it could be ruled out that the change of the fluorescence intensity of dyad **1** and *endo* and *exo* **2** was due to the physical thermal effect.

In summary, the pyrene-arylmaleimide dyad **1** and its D–A adduct **2** were synthesized and characterized. Dyad **1** was weakly fluorescent, while its D–A adduct, *endo* and *exo* **2** showed strong fluorescence. This was because arylmaleimide and its D–A adduct showed different electron accepting abilities, and as a result the PET processes within dyad **1** and *endo* and *exo* isomers of **2** could be tuned through such D–A reaction. Accordingly, a thermally induced fluorescence switch can be established based on dyad **1**. The fluorescence spectra of dyad **1** containing furan (and furfuryl alcohol) and those of *endo* and *exo* **2** were measured after being heated at different temperatures. For the solutions of *endo* and *exo* **2**, the fluorescence intensities show good linear relations with the temperatures of the corresponding solutions in the ranges of 60–90 and 100–130 °C, respectively. These unique properties indicate that *endo* and *exo* **2** are interesting compounds for studies of fluorescent molecular thermometers. Further investigations including structural optimization (e.g., spacer and chromophore unit) and dynamics of the corresponding D–A reaction are underway.

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Supplementary data

Synthesis and characterization of dyad **1**, the *endo* and *exo* **2** and the reference compounds **5** and **6**; the fluorescence spectra of dyad **1** in DMF/furfuryl alcohol; the profiles for the relative fluorescence intensity versus the reaction time for *endo* and *exo* **2**; the plots of relative intensity (I/I_0) versus temperature for the solutions of dyad **1**, *endo* and *exo* **2** and 1-pyrenemethanol in different temperature range; ^{1}H NMR spectra of dyad **1**, *endo* and *exo* **2** after being heated; the differential pulse voltammogram of compound **5** in DMF. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2005.04.135.

References and notes

1. (a) Chapman, C. F.; Liu, Y.; Sonek, G. J.; Tromberg, B. *J. Photochem. Photobiol.* **1995**, *62*, 416; (b) Schrum, K. F.; Williams, A. M.; Haerther, S. A.; Ben-Amotz, D. *Anal. Chem.* **1994**, *66*, 2788.
2. (a) Chandrasekharan, N.; Kelly, L. A. In *Reviews in Fluorescence 2004*; Geddes, C. D., Lakowitz, J. R., Eds.; Kluwer Academic: New York, 2004; pp 21–40; (b) Baker, G. A.; Baker, S. N.; McCleskey, T. M. *Chem. Commun.* **2003**, 2932; (c) Goss, L. P.; Smith, A. A.; Post, M. E. *Rev. Sci. Instrum.* **1989**, *60*, 3702; (d) Kolodner, P.; Katzir, A.; Hartsough, N. *Appl. Phys. Lett.* **1983**, *42*, 749; (e) Kolodner, P.; Tyson, J. A. *Appl. Phys. Lett.* **1982**, *40*, 782; (f) Kolodner, P.; Tyson, J. A. *Appl. Phys. Lett.* **1983**, *42*, 117.
3. Chandrasekharan, N.; Kelly, L. A. *J. Am. Chem. Soc.* **2001**, *123*, 9898.
4. Lou, J.; Hatton, T. A.; Laibinis, P. E. *Anal. Chem.* **1997**, *69*, 1262.
5. (a) Brewster, R. E.; Kidd, M. J.; Schuh, M. D. *Chem. Commun.* **2001**, 1134; (b) Figueroa, I. D.; El Baraka, M.; Quiñones, E.; Rosario, O.; Deumié, M. *Anal. Chem.* **1998**, *70*, 3974.
6. (a) Uchiyama, S.; Matsumura, Y.; de Silva, A. P.; Iwai, K. *Anal. Chem.* **2003**, *75*, 5926; (b) Uchiyama, S.; Matsumura, Y.; de Silva, A. P.; Iwai, K. *Anal. Chem.* **2004**, *76*, 1793.
7. Engeser, M.; Fabbrizzi, L.; Licchelli, M.; Sacchi, D. *Chem. Commun.* **1999**, 1191.
8. Schrum, K. F.; Williams, A. M.; Haerther, S. A.; Ben-Amotz, D. *Anal. Chem.* **1994**, *66*, 2788.
9. de Silva, A. P.; Gunaratne, H. Q. N.; Jayasekera, K. R.; O'Callaghan, S.; Sandanayake, K. R. A. S. *Chem. Lett.* **1995**, 123.
10. Sabbatini, N.; Guardigli, M.; Bolletta, F.; Manet, I.; Ziessel, R. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1501.
11. Reversible D–A reactions have been utilized for the studies of macromolecular architectures, thermally cleavable/reassembling dendrons and dendrimers, and NLO functional materials: (a) Chen, X.; Dam, M.; Ono, K.; Mal, A.; Shen, H.; Nutt, S. R.; Sheran, K.; Wudl, F. *Science* **2002**, *295*, 1698; (b) Haller, M.; Luo, J.; Li, H.; Kim, T.-D.; Liao, Y.; Robinson, B. H.; Dalton, L. R.; Jen, A. K.-Y. *Macromolecules* **2004**, *37*, 688; (c) Luo, J.; Haller, M.; Li, H.; Kim, T.-D.; Jen, A. K.-Y. *Adv. Mater.* **2003**, *15*, 1635; (d) Gheneim, R.; Perez-Berumen, C.; Gandini, A. *Macromolecules* **2002**, *35*, 7246; (e) McElhanon, J. R.; Wheeler, D. R. *Org. Lett.* **2001**, *3*, 2681; (f) Gousse, C.; Gandini, A.; Hodge, P. *Macromolecules* **1998**, *31*, 314; (g) Laita, H.; Boufi, S.; Gandini, A. *Eur. Polym. J.* **1997**, *33*, 1203.
12. Reduction potential of 4-methoxyarylmaleimide (**5**, see Supplementary data) was measured with the differential pulse voltammetry to be −1.03 V in DMF (potential are reported by reference to SCE), no reduction wave was not detected for the D–A adduct of **5** with furan (compound **6**, see Supporting data) under identical conditions.
13. Zhang, X.; Li, Z.-C.; Li, K.-B.; Du, F.-S.; Li, F.-M. *J. Am. Chem. Soc.* **2004**, *126*, 12200.
14. Compound 4 was prepared according to the literatures: (a) Park, J. O.; Jang, S. H. *J. Polym. Sci., Part A: Polym. Chem.* **1992**, *30*, 723; (b) Liu, Y.; Ling, Y.-Z. *Chin. J. Pharm.* **1991**, *22*, 8. Based on the ^{1}H NMR spectrum, the *endo* and *exo* isomers of **4** exist in 1:1 ratio, and the sample was not separated and used for reaction.
15. Characterization data of *endo* and *exo* **2** are provided in Supporting data.
16. Zhan, Z.; Chen, R. *Synth. Commun.* **2000**, *30*, 3527.
17. Characterization data of dyad **1** are provided in Supporting data.
18. The quantum yields presented in this letter were calculated by reference to 9,10-diphenylanthracene; the excitation wavelength is 370 nm.
19. For each fluorescence measurement, a 2 ml solution of *endo* **2** in DMF was prepared and carefully sealed. The solution was kept in a constant temperature trough for 10 min (the temperature was controlled with a thermocouple). After that, the fluorescence spectrum of *endo* **2** was measured using a Hitachi-4500 spectrometer in a quartz cell. The fluorescence spectra of *exo* **2** were measured similarly.
20. The yields of dyad **1** after heating *endo* **2** at 70, 80, and 90 °C for 10 min were estimated to be 0.31, 0.58, and 0.90, respectively, based on the ^{1}H NMR data; the yields of dyad **1** after heating *exo* **2** at 110, 120, and 130 °C for 10 min are 0.36, 0.64, and 0.88, respectively, again based on ^{1}H NMR data.