

# A novel pyrenophane bearing tetraazathiapentalene skeleton

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A novel pyrenophane incorporating macrocyclic tetraazathiapentalene is synthesised and characterised. The absorption and fluorescence spectra in  $\text{CH}_2\text{Cl}_2$  clearly showed  $\pi$ - $\pi$  interaction between two pyrene rings including pyrene excimer emission.

**Keywords:** pyrenophane, excimer, tetraazathiapentalene

Recently, much attention has been focused on the fluorescence behaviour of a variety of supramolecules from the viewpoints of molecular recognition and molecular devices.<sup>1</sup> Pyrene and its derivatives can be utilised not only as fluorescent probes,<sup>2,3</sup> but as host and guest molecules.<sup>4</sup> However, little is known about the excimer formation of pyrenes bearing a hypervalent tetraazathiapentalene skeleton, although recently Inouye et al. have reported flexible pyrenophanes.<sup>4b,5</sup> We now report a synthesis of a macrocyclic tetraazathiapentalene derivative **1** as a new type of rigid and fluorescent supramolecule showing  $\pi$ - $\pi$  interaction between two pyrene rings in the ground and excited states.<sup>6</sup>

The target molecule **1** was prepared as follows: Tetraazathiapentalene framework (**4a–b**) was prepared from a cyclic thiourea using an excess of methyl isothiocyanate according to the method reported previously.<sup>7,8</sup> Then, treatment of **4a** with 1,6-dimethyl pyrene diisothiocyanate in benzene afforded **1** in a 16% isolated yield (Scheme 1). The reference compounds **2** and **3** were also prepared from **4b** by a similar method. The structures of **1–3** were determined by their spectral properties and elemental analyses. The IR and  $^1\text{H}$  NMR spectra of **1** showed the absence of characteristic absorption of an isothiocyanate group and a methyl signal. The broadening of the UV-vis spectrum of **1** might be due to the strong  $\pi$ - $\pi$  stacking interaction in the ground state, as shown in Fig. 1. The fluorescence spectrum of **1** showed an intramolecular excimer emission of pyrene at 460 nm accompanying a monomer emission of pyrene at 408 nm (Fig. 2).<sup>9</sup> The blue shifted emission maximum of the excimer, compared to that of the intermolecular pyrene excimer at 500 nm, can be reasonably explained by the short distance between two pyrene rings and the rigidity of **1**.<sup>3,4</sup> The molecular model of **1** supported the above observation, although the X-ray structure of **1** was not obtained yet.

The relative fluorescence intensity of **2** was quite low, compared to that of **3**, and the fluorescence of **3** did not show any intramolecular excimer emission (Fig. 3).

The fluorescence of pyrene in dichloromethane was efficiently quenched by **4b** in an intermolecular manner through probably photoinduced electron transfer (PET) process.<sup>10</sup> These results clearly show that the conformation between the pyrene ring and the tetraazathiapentalene ring is important for the intramolecular fluorescence quenching via PET process and the formation of excimer emission. In fact, the PM3 calculations<sup>11</sup> of **2** and **3** exhibit large dihedral angles between the pyrene and the tetraazathiapentalene rings, and the two pyrene rings of **3** were hardly able to overlap each other (Fig. 4). On the other hand, the PM3 calculation of **1** showed the sandwich type structure, where the two pyrene rings were almost overlapped.

In conclusion, we have synthesised and characterised a new type of macrocyclic pyrenophane **1**. The shorter fluorescence

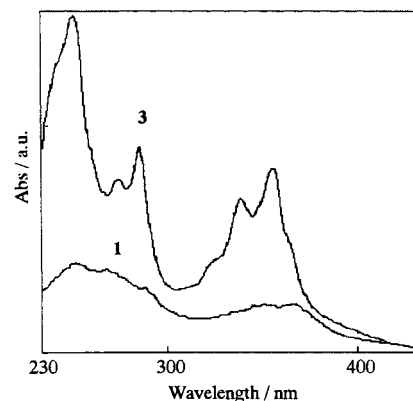


Fig. 1 UV-vis spectra of **1** and **3**. [**1**]=[**3**]= $10^{-5}$  M in  $\text{CH}_2\text{Cl}_2$ .

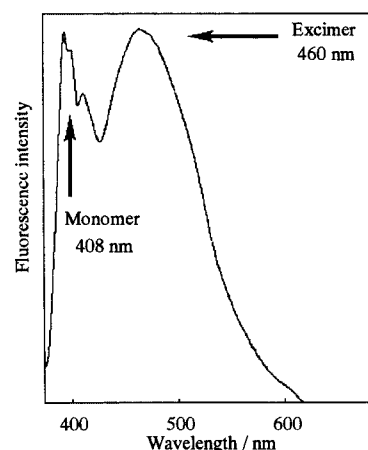


Fig. 2 Fluorescence spectrum of **1**. [**1**]= $10^{-5}$  M in  $\text{CH}_2\text{Cl}_2$  excited at 340 nm.

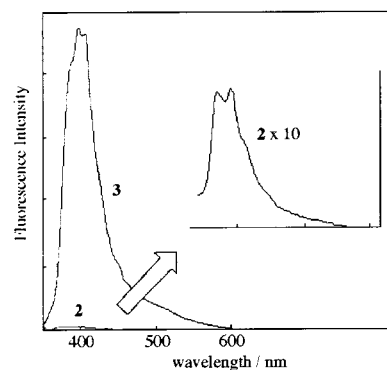
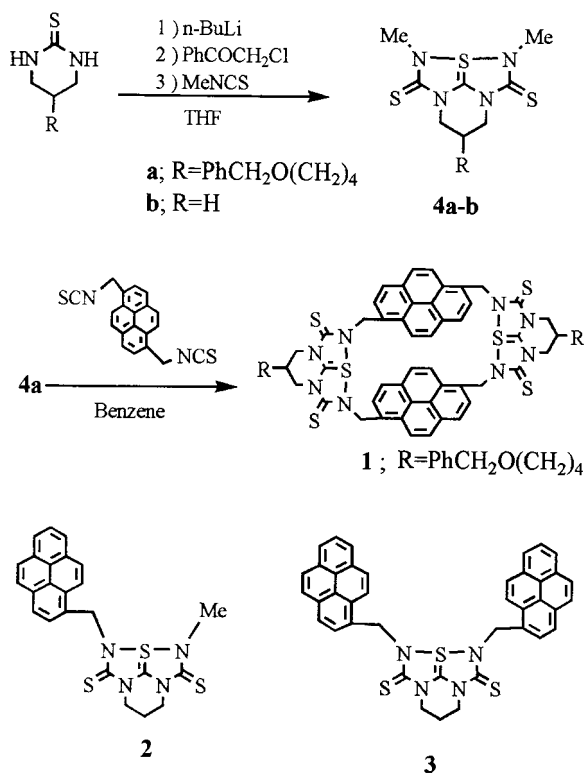


Fig. 3 Fluorescence spectra of **2** and **3**. [**2**]=[**3**]= $10^{-5}$  M in  $\text{CH}_2\text{Cl}_2$  excited at 340 nm.

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Scheme 1

maximum of excimer for **1** is due to the short distance between two pyrene rings, compared to those of the inter- and intra-molecular flexible excimers.<sup>3,4</sup> The absence of excimer emission of **3** was explained by the rigid conformation of **3** due to the steric hindrance. The tetraazathiapentalene derivatives having more flexible pyrene units are now under investigation.

### Experimental

<sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Varian Mercury 300 (300 and 75 MHz) spectrometer for solutions in CDCl<sub>3</sub>. IR spectra were obtained on a JASCO FT/IR-230 spectrometer and fluorescence spectra on a JASCO FP-770 spectrofluorometer. UV/VIS spectra were performed on a JASCO V-530 spectrophotometer.

Pyrenophane **1** and pyrenyl-substituted tetraazathiapentalenes **2** and **3** were prepared by the procedure reported previously.<sup>7</sup>

**Pyrenophane (1):** m.p. 230–232 °C (decomp.); λ<sub>max</sub> (log ε in CH<sub>2</sub>Cl<sub>2</sub>) = 357 (7.76) nm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 1.27 (m, 4H), 1.54–1.72 (m, 8H), 2.20 (m, 2H), 3.50 (m, 4H+4H), 3.64 (br, 4H), 4.51 (s, 4H), 5.34 (br, 4H), 5.78 (br, 4H), 7.29 (m, 10H), 8.00–8.25 (m, 16H); IR (KBr) 2926, 2849, 1577, 1523, 1458, 1239, 1110, 842, and 667 cm<sup>-1</sup>; Anal. Calcd for C<sub>70</sub>H<sub>64</sub>N<sub>8</sub>O<sub>2</sub>S<sub>6</sub>: C, 67.71; H, 9.02; N, 5.20. Found: C, 67.41; H, 8.83; N, 4.89.

**Compound (2):** m.p. 153–154 °C; λ<sub>max</sub> (log ε in CH<sub>2</sub>Cl<sub>2</sub>) = 347 (6.50), 330 (6.42), 316 (6.25), 273 (6.67), and 2.66 (6.78) nm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.34 (m, 2H), 3.22 (s, 3H), 4.33 (m, 1H), 4.39 (t, 2H, J=5.9 Hz), 4.47 (t, 1H, J=5.9 Hz), 5.67 (s, 2H), 8.04 (m, 4H), 8.15 (m, 3H), 8.33 (d, 1H, J=9.4 Hz); IR(KBr) 2917, 1577, 1534, 1490, 1236, 1115, 842, and 675 cm<sup>-1</sup>; Anal. Calcd for C<sub>24</sub>H<sub>20</sub>N<sub>4</sub>S<sub>3</sub>: C, 68.18; H, 4.42; N, 10.84. Found: C, 67.89; H, 4.48; N, 10.81.

**Compound (3):** m.p. 143–145 °C; λ<sub>max</sub> (log ε in CH<sub>2</sub>Cl<sub>2</sub>) = 347 (6.80), 331 (6.73), 278 (6.85), and 268 (6.78) nm; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 2.01 (m, 2H), 3.28 (t, 1H, J=5.5 Hz), 4.14 (t, 1H, J=7.0 Hz), 4.70 (m, 2H), 5.53 (d, 4H, J=4.7 Hz), 7.49 (m, 9H), 8.05 (m, 5H), 8.18 (m, 4H); IR (KBr) 2926, 2849, 1542, 1490, 1420, 1273, 1100, 844, and 667 cm<sup>-1</sup>; Anal. Calcd for C<sub>40</sub>H<sub>28</sub>N<sub>4</sub>S<sub>3</sub>: C, 72.70; H, 4.27; N, 8.48. Found: C, 72.44; H, 4.40; N, 8.19.

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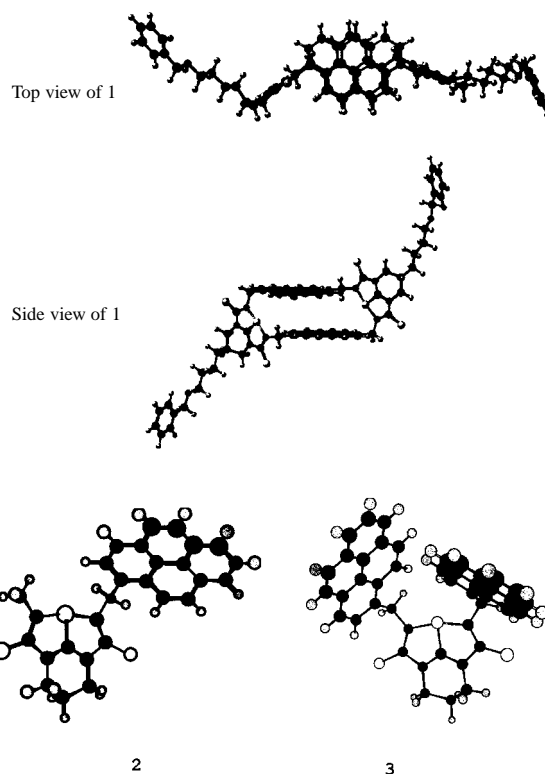


Fig. 4 Structures of 1–3 by PM3 calculations.

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### References

- 1 A.P. De Silva, H.Q.N. Gunaratne and C.P. McCoy, *Nature*, 1993, **364**, 42; A.P. De Silva, H.Q.N. Gunaratne, T. Gunnlaugsson, A.J.M. Huxley, C.P. McCoy, J.T. Rademacher and T.E. Rice, *Chem. Rev.*, 1997, **97**, 1515; M. Enomoto and T. Aida, *J. Synth. Org. Chem., Jpn.*, 1999, **57**, 924; L. Fabbri, M. Licchekki and P. Pallavicini, *Acc. Chem. Res.*, 1999, **32**, 846; M. Irie and K. Matsuda, *J. Am. Chem. Soc.*, 2000, **122**, 7195; S. Nishizawa, Y.-Y. Cui, M. Minagawa, K. Morita, Y. Kato, S. Taniguchi, R. Kato and N. Teramae, *J. Chem. Soc. Perkin Trans. 2*, 2002, 866; T. Gunnlaugsson, A.P. Davis, G.M. Hussey, J. Tierney and M. Glynn, *Org. Bioorg. Chem.* 2004, **2**, 1856.
- 2 H. Mihara, Y. Tanaka, T. Fujimoto and N. Nishino, *J. Chem. Soc., Perkin. Trans. 2*, 1995, 1915; D.Y. Sasaki and B.E. Padilla, *J. Chem. Soc., Chem. Commun.*, 1998, 1581; H. Imahori, Y. Nishimura, H. Norieda, H. Karita, I. Yamazaki, Y. Sakata and S. Fukuzumi, *J. Chem. Soc., Chem. Commun.*, 2000, 661.
- 3 F.C. DeSchryver, P. Collart, J. Vandendriessche, R. Goedeweeck, A. Swinnen and M. Von. Der Auweraer, *Acc Chem. Res.*, 1987, **20**, 159; D. Declercq, P. Delbeke, F.C. DeSchryver, L. Van Meervelt and R.D. Miller, *J. Am. Chem. Soc.*, 1993, **115**, 5702; K.A. Zachariasse and W. Kühnle, *Zh. Phys. Chem.*, 1976, **101**, 267; K.A. Zachariasse, G. Duveneck and W. Kühnle, *Chem. Phys. Lett.*, 1985, **113**, 337.
- 4 (a) I. Aoki, T. Harada, T. Sakaki, Y. Kawahara and S. Shinkai, *J. Chem. Soc., Chem. Commun.*, 1992, 1341; (b) M. Inouye, K. Fujimoto, M. Frusyo and H. Nakazumi, *J. Am. Chem. Soc.*, 1999, **121**, 1452; (c) T. Aoyagi, H. Ikeda and A. Ueno, *Bull. Chem. Soc. Jpn.*, 2001, **74**, 157.
- 5 T. Umemoto, S. Satani, Y. Sakat, and S. Misumi, *Tetrahedron Lett.*, 1975, 3159; R.H. Mitchell, R.J. Corruthers and J.C.M. Zwiinkels, *Tetrahedron Lett.*, 1976, 2585; H.A. Staab and R.G.H. Kirrstetter, *Liebigs, Ann. Chem.*, 1979, 886; A. Bilyk, M.M. Harding, P. Turner and T.W. Hanbly, *J. Chem. Soc., Dalton. Trans.*, 1994, 2783.

- 6 N. Matsumura, M. Tomura, O. Mori, M. Ukawa and S. Yoneda, *Heterocycles*, 1987, **26**, 3097; N. Matsumura, R. Hirase and H. Inoue, *Tetrahedron Lett.*, 1994, **35**, 899.
- 7 N. Matsumura, T. Konishi, H. Hayashi, M. Yasui, F. Iwasaki, and K. Mizuno, *Heterocycles*, 2000, **53**, 1239; N. Matsumura, T. Konishi, H. Hayashi, M. Yasui, F. Iwasaki and K. Mizuno, *J. Heterocyclic Chem.*, 2002, **39**, 189.
- 8 N. Matsumura, M. Tomura, O. Mori, Y. Tsuchiya, S. Yoneda and K. Toriumi, *Bull. Chem. Soc. Jpn*, 1988, **61**, 2419.
- 9 Fluorescence lifetimes of **1**, **2**, and **3** in CH<sub>2</sub>Cl<sub>2</sub> were obtained by single photon counting method (HORIBA NAES-550). **1**; 20 and 6 ns, **2**; 19 ns, **3**; 31 ns.
- 10 Recently, we have reported the PET reaction of tetraazathiapentalene with trialkylamines; H. Hayashi, N. Matsumura and K. Mizuno, *Chem. Lett.*, 2002, 510.
- 11 MOPAC version 97; CS MOPAC., Tokyo and CAChe 3.2 for windows, Fujitsu, co., Tokyo.