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Unique Hydrogen Bonds between 9-Anthracenyl Hydrogen and Anions

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Received April 29, 2004

Abstract: Unique hydrogen bonds of the 9-H of anthracene moieties in hosts **1** and **2** with fluoride and pyrophosphate ions were observed on the basis of the ^{1}H NMR experiments. Furthermore, hosts **1** and **2** act as a colorimetric sensor and a fluorescent chemosensor for the recognition of fluoride ion, respectively.

The recognition and sensing of anions has become the focus of considerable attention[1] because of the important roles played by anions in biological, industrial, and environmental processes. Of particular interest in this regard are “colorimetric anion sensors” and “fluorescent chemosensors for anions”. Recent efforts to investigate anion binding by naked eye detection[2] and through fluorescent changes[3] may provide important results.

We report herein on new colorimetric sensor and fluorescent sensors for fluoride and pyrophosphate ions in which two *p*-nitrophenylurea groups or two phenylurea groups are immobilized on the 1,8-position of anthracene. A new colorimetric sensor displays a unique color change upon the addition of fluoride ions. Furthermore, unique hydrogen bonds between the 9-H of anthracene with fluoride and pyrophosphate ions are described on the basis of the ^{1}H NMR experiments.

Our synthesis began with 1,8-dinitroanthraquinone. Modifying the published procedures,[4] 1,8-diaminoanthraquinone was obtained in a 73% yield. 1,8-Diaminoanthracene was also synthesized following the published procedure.[5] Treating this diaminoanthracene or 1-aminoanthracene with *p*-nitrophenyl isocyanate in CH_2Cl_2 afforded **1** or **3** in 75% or 82% yield, respectively. Application of similar procedures to phenylisocyanate gave **2** and **4** in 80% and 85% yield, respectively (Figure 1).

Because of the low solubility of hosts **1**−**4**, the NMR data was obtained in DMSO-d_6. Upon the addition of anions, downfield shifts of the N−H protons were clearly observed.

For example, upon addition of 4 equiv of chloride ions, dramatic downfield shifts of the amide N−H peaks were observed for hosts **1** ($\Delta\delta = 1.71$ ppm), **2** ($\Delta\delta = 1.05$ ppm), **3** ($\Delta\delta = 1.86$ ppm), and **4** ($\Delta\delta = 0.85$ ppm).

Recently, Lee et al. reported[6] a strapped calix[4]pyrrole in which not only four pyrrole hydrogens but also an aromatic hydrogen in a strap form hydrogen bonds with fluoride and chloride ion. These unique hydrogen bonds between aromatic hydrogens and anions were confirmed by the large downfield shifts of the aromatic hydrogens ($\Delta\delta = 0.41$ for F^-, 0.96 for Cl^-).[6a] Other examples of receptors in which aromatic hydrogens participate in hydrogen bonding with anions have also been reported.[7]

A partial ^{1}H NMR spectrum is shown in Figure 2, and each peak was assigned based on the 2D COSY spectrum. When tetrabutylammonium chloride was added to the solution of **2**, large downfield shifts of the amide N−H bonds as well as 9-H of the anthracene moiety were

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(1) For recent reviews for anion receptors, see; (a) Martínez-Máñez, R.; Sancenón, F. *Chem. Rev.* **2003**, *103*, 4419. (b) McCleskey, S. C.; Metzger, A.; Simmons, C. S.; Anslyn, E. V. *Tetrahedron* **2002**, *58*, 621. (c) Beer, P. D.; Gale, P. A. *Angew. Chem., Int. Ed.* **2001**, *40*, 486. Wiskur, S. L.; Ait-Haddou, H.; Lavigne, J. J.; Anslyn, E. V *Acc. Chem. Res.* **2001**, *34*, 963. (d) Snowden, T. S.; Anslyn, E. V. *Chem. Biol.* **1999**, *3*, 740. (e) Antonisse, M. M. G.; Reinhoudt, D. N. *Chem. Commun.* **1998**, 143. (f) Schmidtchen, F. P.; Berger, M. *Chem. Rev.* **1997**, *97*, 1609. (g) Rudkevich, D. M.; Brzozka, Z.; Palys, M.; Visser, H. C.; Verboom, W.; Reinhoudt, D. N. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 467.

(2) (a) Lee, D. H.; Im, J. H.; Son, S. U.; Chung, Y. K.; Hong, J.-I. *J. Am. Chem. Soc.* **2003**, *125*, 7752. (b) Ho, H. A.; Leclerc, M. *J. Am. Chem. Soc.* **2003**, *125*, 4412. (c) Han, M. S.; Kim, D. H. *Angew. Chem., Int. Ed.* **2002**, *41*, 3809. (d) Zhong, Z.; Anslyn, E. V *J. Am. Chem. Soc.* **2002**, *124*, 9014. (e) McCleskey, S. C.; Metzger, A.; Simmons, C. S.; Anslyn, E. V. *Tetrahedron* **2002**, *58*, 621. (f) Piotr, P.; Janusz, J. *Chem. Commun.* **2002**, 2450. (g) Sancenón, F.; Descalzo, A. B.; Martínez-Máñez, R.; Miranda, M. A.; Soto, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 2640. (h) Yamaguchi, S.; Akiyama, S.; Tamao, K. *J. Am. Chem. Soc.* **2001**, *123*, 11372. (i) Lee, D. H.; Lee, K. H.; Hong, J.-I. *Org. Lett.* **2001**, *3*, 5. (j) Lee, D. H.; Lee, H. Y.; Lee, K. H.; Hong, J.-I. *Chem. Commun.* **2001**, 1188. (k) Miyaji, H.; Sessler, J. *Angew. Chem., Int. Ed.* **2001**, *40*, 154. (l) Kim, J.; Mcquade, T.; McHugh, S. K.; Swager, T. M. *Angew. Chem., Int. Ed.* **2000**, *39*, 3868. (m) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3666. (n) Black, C. B.; Andrioletti, B.; Try, A. C.; Ruiperez, C.; Sessler, J. L. *J. Am. Chem. Soc.* **1999**, *121*, 10438. (o) Lavigne, J. J.; Anslyn, E. V. *Angew. Chem., Int. Ed.* **1999**, *38*, 3666.

(3) (a) Yoon, J.; Kim, S. K.; Singh, N. J.; Lee, J. W.; Yang, Y. J.; Chellappan, K.; Kim, K. S. *J. Org. Chem.* **2004**, *69*, 581. (b) Lee, J. Y.; Cho, E. J.; Mukamel, S.; Nam, K. C. *Org. Chem.* **2004**, *69*, 943. (c) Cho, E. J.; Moon, J. W.; Ko, S. W.; Lee, J. Y.; Kim, S. K.; Yoon, J.; Nam, K. C. *J. Am. Chem. Soc.* **2003**, *125*, 12376. (d) Ojida, A.; Inoue, M.; Mito-oka, Y.; Hamachi, I. *J. Am. Chem. Soc.* **2003**, *125*, 10184. (e) Kim, S. K.; Singh, N. J.; Kim, S. J.; Kim, H. G.; Kim, J. K.; Lee, J. W.; Kim, K. S.; Yoon, J. *Org. Lett.* **2003**, *5*, 2083. (f) Ojida, A.; Mito-oka, Y.; Inoue, M. Hamachi, I. *J. Am. Chem. Soc.* **2002**, *124*, 6256. (g) Kim, S. K.; Yoon, J. *Chem. Commun.* **2002**, 770. (h) Gunnlaugsson, T.; Davis, A. P.; O’Brien, J. E.; Glynn, M. *Org. Lett.* **2002**, *4*, 2449 and references therein. (i) Ojida, A.; Park, S.-k.; Mito-oka, Y.; Hamachi, I. *Tetrahedron Lett.* **2002**, *43*, 6193. (j) Wu, F.-Y.; Li, Z.; Wen, Z.-C.; Zhou, N.; Zhao, Y.-F.; Jiang, Y,-B. *Org. Lett.* **2002**, *4*, 3203. (k) Causey, C. P.; Allen, W. E. *J. Org. Chem.* **2002**, *67*, 5963. (l) Gunnlaugsson, T.; Davis, A. P.; Glynn, M. *Chem. Commun.* **2001**, 2556. (m) Nishizawa, S.; Kaneda, H.; Uchida, T.; Teramae, N. *J. Chem. Soc., Perkin Trans. 2* **1998**, 2325. (n) Fabbrizzi, L.; Faravelli, H.; Francese, G.; Licchelli, M.; Perotti, A.; Taglietti, A. *Chem. Commun.* **1998**, 971. (o) Cooper, C. R.; Spencer, N.; James, T. D. *Chem. Commun.* **1998**, 1365. (p) Vance, D. H.; Czarnik, A. W. *J. Am. Chem. Soc.* **1994**, *116*, 9397.

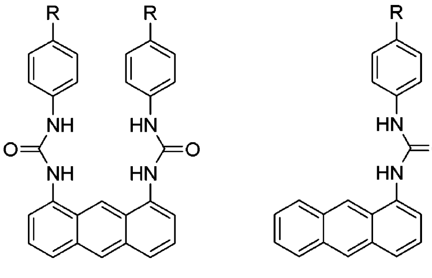
(4) Bu, X.; Deady, L. W.; Finlay, G. J.; Baguley, B. C.; Denny, W. A. *J. Med. Chem.* **2001**, *44*, 2004.

(5) Gosztola, D.; Wang, B.; Wasielewski, M. R. *J. Photochem. Photobiol. A: Chem.* **1996**, *102*, 71.

(6) (a) Yoon, D.-W.; Hwang, H.; Lee, C.-H. *Angew. Chem., Int. Ed.* **2002**, *41*, 1757. (b) Lee, C.-H.; Na, H.-K.; Yoon, D.-W.; Won, D.-H.; Cho, W.-S.; Lynch, V. M.; Shevchuk, S. V.; Sessler, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 7301.

(7) (a) Tomàs, S.; Prohens, R.; Vega, M.; Rotger, M. C.; Deyà, P. M.; Ballester, P.; Costa, A. *J. Org. Chem.* **1996**, *61*, 9394. (b) Jeong, K.-S.; Cho, Y. L. *Tetrahedron Lett.* **1997**, *38*, 3279.

10.1021/jo049281+ CCC: $27.50



1; R = NO_2
2; R = H

3; R = NO_2
4; R = H

FIGURE 1. Structures of compounds **1**−**4**.

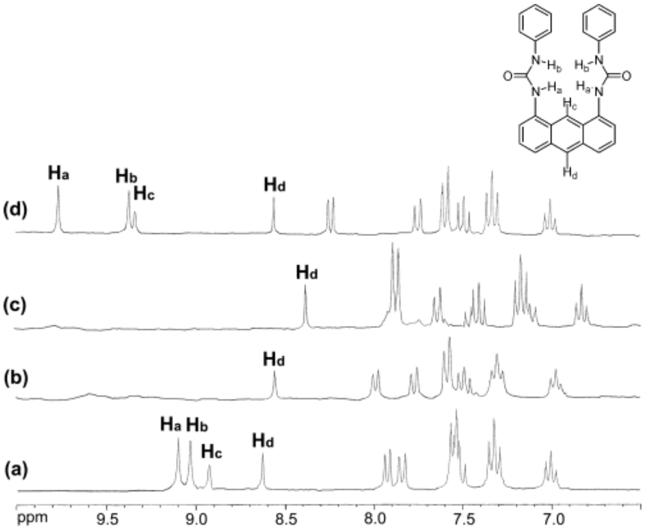


FIGURE 2. Partial ^1H NMR (250 MHz) of **2** (1 mM) in DMSO-d_6 at 25 °C: (a) compound **2** only; (b) **2** + 1 equiv of tetrabutylammonium fluoride; (c) **2** + 7 equiv of tris(tetrabutylammonium) hydrogenpyrophosphate; (d) **2** + 10 equiv of tetrabutylammonium chloride.

observed (Figure 2). On the other hand, when tris(tetrabutylammonium)hydrogen pyrophosphate or tetrabutylammonium fluoride were added to the solution of **2** in DMSO-d_6, four amide N−H signals as well as 9-H in the anthracene moiety, displayed severe broadness. We also observed a similar result with host **1**. However, hosts **3** and **4** only displayed this broadness of the amide N−H peaks and large downfield shifts of the 9-H of anthracene moiety when fluoride or pyrophosphate ions were added (Figure 3). Along with the large downfield shifts of the 9-H peaks of **1** and **2** obtained with Cl^-, these observations concerning the ^1H NMR spectra obtained with fluoride and pyrophosphate led us to the conclusion that the 9-H of anthracene moiety formed a strong hydrogen bond with the anions in DMSO. Hosts **1** and **2** have extremely rigid binding sites for anions and the 9-H of anthracene moiety can participate in anion recognition more efficiently than that in hosts **3** and **4**.

Temperature-dependent ^1H NMR studies in DMF-d_7 are displayed in Figure 4. At −5 °C, the amide peaks as well as 9-H of anthracene moiety concomitantly began to appear in the partial ^1H NMR spectrum of host **2** in the presence of 7 equiv of pyrophosphate. Similar results were observed in the presence of F^- (see the Supporting Information).

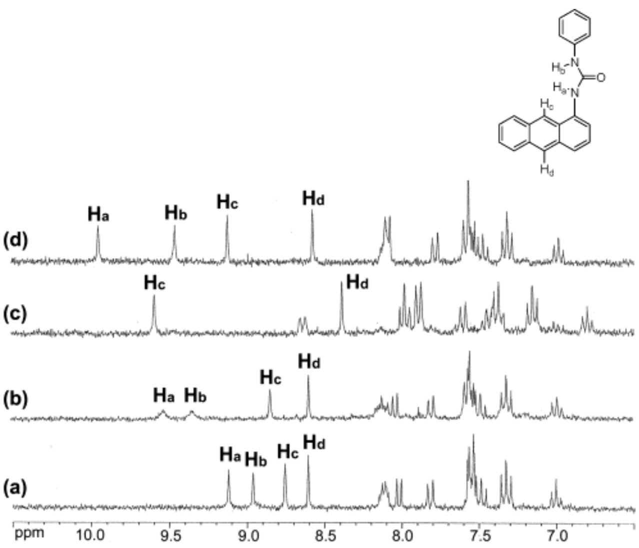


FIGURE 3. Partial ^1H NMR (250 MHz) of **4** (1 mM) in DMSO-d_6 at 25 °C: (a) compound **4** only; (b) **4** + 1 equiv of tetrabutylammonium fluoride; (c) **4** + 7 equiv of tris(tetrabutylammonium) hydrogenpyrophosphate; (d) **4** + 10 equiv of tetrabutylammonium chloride.

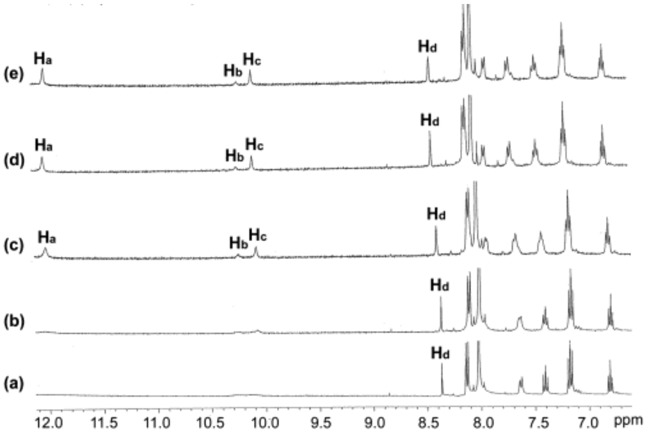


FIGURE 4. Partial ^1H NMR (400 MHz) of **2** (6 mM) in DMF-d_7 upon addition of tris(tetrabutylammonium) hydrogenpyrophosphate (7 equiv): (a) 25 °C, (b) 10 °C, (c) −5 °C, (d) −15 °C, (e) −30 °C.

The changes in color were studied in DMSO by the addition of 300 equiv of the corresponding anions (F^-, $H_2PO_4^-$, Cl^-, Br^-, I^-, HSO_4^-, acetate, and pyrophosphate, each added as their tetrabutylammonuim salts) to solutions of host **1** (0.01 mM). There was a unique color change from pale yellow to red when fluoride or pyrophosphate ions were added. Figure 5 illustrates the UV absorption spectra of these experiments. Host **1** displays unique new peaks (λ_{max} = 485 nm) with a red-shift of 129 nm upon the addition of fluoride or pyrophosphate ions. It is worth mentioning that host **1** can easily differentiate pyrophosphate from $H_2PO_4^-$ by naked eye detection.

The unique color changes with F^- and pyrophosphate can be rationalized by three combined factors explained previously by other reports. The excited state in a complex can be more stabilized by anion binding, resulting in a bathochromic shift in the absorption maxima as well as a color change.[2a,i,j,8] The selective color changes for F^- and pyrophosphate can be rationalized on the basis

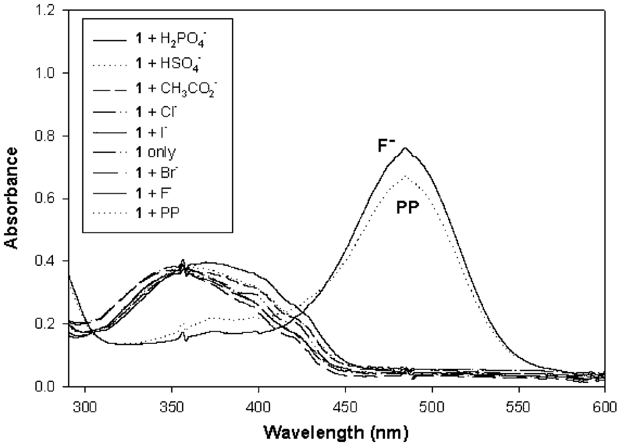


FIGURE 5. UV absorption changes of **1** (0.01 mM) upon addition of the tetrabuthylammonium salt of $H_2PO_4^-$, HSO_4^-, $CH_3CO_2^-$, Cl^-, I^-, Br^-, PP, and F^- (300 equiv) in DMSO.

of the guest basicity and the partial negative charge at the 9-position of anthracene moiety which can be generated by a strong interaction between anion and 9-H of anthracene. Recently, a naphthalene derivative bearing two urea groups at the 1,8-position was reported to show a unique absorption and fluorescent peak with fluoride ion.[3b,c] In these reports, calculations suggested that the increased anionic character of urea nitrogen due to the strongly charged hydrogen bonding between fluoride and amide protons of the urea can be the reason for this observation.

For hosts **2** and **4**, a fluorescence method made it possible to readily follow their binding with anions. Upon the addition of the tetrabutylammonium salts of anions in DMSO, fluorescent quenching effects were observed (see the Supporting Information). For example, from the fluorescent titration experiments, the association constants were calculated as being 108 000 (host **2** with F^-), 9700 (host **2** with Br^-), 6000 (host **2** with pyrophosphate), 4000 (host **4** with F^-), and 2600 (host **4** with pyrophosphate) M^{-1}, respectively (errors < 10%).[9] There was not any significant fluorescent change upon the addition of up to 500 equiv of Br^- to the solution of **4**. The selectivity for fluoride is around 100 times than that for bromide. Furthermore, two urea groups in host **2** generate a better binding site for anions than just one urea group in host **4**, showing higher values (~250 times) in its association constants. Furthermore, these fluorescent data were productively compared with UV data.

In conclusion, unique hydrogen bonds of the 9-H of anthracene moieties in hosts **1** and **2** with fluoride and pyrophosphate ions were observed in a first time based on the ^1H NMR experiments. Furthermore, hosts **1** and **2** act as a colorimetric sensor and a fluorescent chemosensor for the recognition of fluoride ion, respectively. The anthracene moieties in hosts **1** and **2** act not only as a fluorescent or colorimetric source but also as templates for introducing the binding selectivity.

Experimental Section

1,8-Bis(4-nitrophenylurea)anthracene (1). 1,8-Diaminoanthracene was prepared obtained from 1,8-diaminoanthraquinone[1] following the published procedure.[2] A solution of 1,8-diaminoanthracene (100 mg, 0.48 mmol) and 4-nitrophenyl isocyanate (328 mg, 2.00 mmol) in dry CH_2Cl_2 (25 mL) was refluxed for 2 h. As soon as 4-nitrophenyl isocyanate was added, a white precipitate was formed. After cooling to room temperature, the solid was filtered and washed with $CHCl_3$. Analytically pure **1** was obtained in 75% yield (193 mg): mp 300 °C dec; ^1H NMR (DMSO-d_6) δ 9.77 (s, 2H, NH), 9.16 (s, 2H, NH), 8.88 (s, 1H), 8.68 (s, 1H), 8.19 (d, 4H, $J = 9.2$ Hz), 7.93 (d, 2H, $J = 8.6$ Hz), 7.84 (d, 2H, $J = 8.3$ Hz), 7.74 (d, 4H, $J = 9.2$ Hz), 7.55 (t, 2H, $J = 8.3$ Hz); ^{13}C NMR (DMSO-d_6) δ 154.3, 152.8, 146.4, 141.1, 133.6, 131.8, 127.4, 125.7, 125.3, 124.3, 117.5, 115.3, 114.7; HRMS (FAB) m/z 537.1523 $(M + H)^+$, calcd for $C_{28}H_{21}N_6O_6$ 537.1523.

1,8-Bis(phenylurea)anthracene (2). Application of procedure A to 100 mg of 1,8-diaminoanthracene (0.48 mmol) and 238 mg of phenyl isocyanate (2.00 mmol) in dry CH_2Cl_2 (25 mL) gave 202 mg of **2** (82% yield): mp 305 °C dec; ^1H NMR (DMSO-d_6) δ 9.11 (s, 2H, NH), 9.04 (s, 2H, NH), 8.92 (s, 1H), 8.63 (s, 1H), 7.92 (d, 2H, $J = 6.9$ Hz), 7.84 (d, 2H, $J = 6.9$ Hz), 7.54 (m, 6H), 7.32 (t, 4H, $J = 7.5$ Hz), 7.01 (t, 2H, $J = 7.3$ Hz); ^{13}C NMR (DMSO-d_6) δ 153.1, 141.1, 134.2, 131.8, 128.9, 127.3, 125.8, 125.3, 123.1, 121.9, 118.2, 117.0, 114.0; HRMS (FAB) m/z 469.1610 $(M + Na)^+$, calcd for $C_{28}H_{22}N_4O_2Na$ 469.1640.

1-(4-Nitrophenylurea)anthracene (3). Application of procedure A to 100 mg of 1-aminoanthracene (0.52 mmol) and 344 mg of 4-nitrophenyl isocyanate (2.1 mmol) in dry CH_2Cl_2 (25 mL) gave 149 mg of **3** (80% yield): mp 275−278 °C; ^1H NMR (DMSO-d_6) δ 9.83 (s, 2H, NH), 9.18 (s, 2H, NH), 8.75 (s, 1H), 8.63 (s, 1H), 8.24 (d, 2H, $J = 9.2$ Hz), 8.14 (m, 2H), 7.98 (d, 1H, $J = 7.0$ Hz), 7.89 (d, 1H, $J = 7.0$ Hz), 7.79 (d, 2H, $J = 9.2$ Hz), 7.55 (m, 3H); ^{13}C NMR (DMSO-d_6) δ 152.6, 146.5, 141.1, 133.4, 131.88, 131.2, 131.0, 128.3, 127.9, 126.9, 126.2, 126.1, 125.6, 125.4, 125.3, 124.2, 120.1, 117.6, 117.2; HRMS (FAB) m/z 358.1196 $(M + H)^+$, calcd for $C_{21}H_{16}N_3O_3$ 358.1192.

1-(Phenylurea)anthracene (4). Application of procedure A to 100 mg of 1-aminoanthracene (0.52 mmol) and 250 mg of phenyl isocyanate (2.1 mmol) in dry CH_2Cl_2 (25 mL) gave 138 mg of **4** (85% yield): mp 282−285 °C; ^1H NMR (DMSO-d_6) δ 9.12 (s, 2H, NH), 8.96 (s, 2H, NH), 8.76 (s, 1H), 8.61 (s, 1H), 8.13 (m, 2H), 8.02 (d, 1H, $J = 7.4$ Hz), 7.82 (d, 1H, $J = 7.4$ Hz), 7.52 (m, 5H), 7.33 (t, 2H, $J = 7.4$ Hz), 7.01 (d, 1H, $J = 7.3$ Hz); ^{13}C NMR (DMSO-d_6) δ 152.6, 139.8, 134.1, 131.9, 131.1, 130.8, 128.9, 128.3, 127.9, 127.2, 126.7, 125.9, 125.6, 125.2, 123.1, 122.7, 121.9, 120.4, 119.8, 118.2, 118.0, 115.8; HRMS (FAB) m/z 312.1251, calcd for $C_{21}H_{16}N_2O$ 312.1263.

Acknowledgment. This work was fully supported by a Grant (No. 2002-042-C00045) from the Korea Research Foundation.

Supporting Information Available: The Experimental Section, NMR spectra, and fluorescent spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) Nishizawa, S.; Kato, R.; Hayashita, T.; Teramae, N. *Anal. Sci.* **1998**, *14*, 595.

(9) (a) Conners, K. A. *Binding Constants*; Wiley: New York, 1987. (b) Association constants were obtained using the computer program ENZFITTER, available from Elsevier-BIOSOFT, 68 Hills Road, Cambridge CB2 1LA, U.K..