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Tweezers-like aromatic molecules and their luminescent properties depending on the structures

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ABSTRACT

Di(hydroxyphenyl)pyrimidine with two anthryl substituents **1a** was synthesized and characterized by X-ray crystallography and NMR spectroscopy. The molecule prefers 'U'-shaped conformation supported by intramolecular O–H···N hydrogen bonds in the solid state and in solution. The CHCl₃-solvated compound binds two CHCl₃ molecules between the two parallel anthryl planes. Hexylation of the OH groups of **1a** produces **1c** whose diarylpyrimidine core contains these aromatic planes with O···H–C interaction and helical alignment. Compound **1c** shows strong emission from the anthryl groups (410 nm, ϕ = 0.39), while luminescence is not observed for **1a** partly due to quenching via PET (photo-induced electron transfer) process.

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Compounds having polyaromatic partial structure, such as anthryl and pyrenyl groups in their molecules have potentially photoluminescent properties, but they sometimes show no emission due to quenching via energy transfer or electron transfer.^{1–3} Conformation of the molecules influences the quenching process and their photoluminescent efficiency. The aromatic molecules with flexible skeleton are used as the molecular tweezers which are capable of binding the guest molecules, such as TCNO (tetracyanoquinodimethane), TCNE (tetracyanoethylene) and trinitrofluorenone, by their two arms.^{4,5} Functionalization of silica surface by the compounds and selective separation of aromatic hydrocarbon molecules were also reported.⁶ Luminescent properties of the tweezers-like molecules are often used as probes for change in the intermolecular interactions between the arms of molecular tweezers and the guest molecules.^{7,8} In this study, we synthesized the new aromatic compounds having two anthryl groups which change relative positions of the two aromatic arms like a pair of tweezers depending on the substituents. Luminescence properties depending on the molecular structures are also mentioned.

Our design of the molecules is shown in Figure 1. Di(hydroxyphenyl)pyrimidine units of compound **1a** should form a π -conjugated plane owing to the O–H…N hydrogen bonds. Rotation of C–C bonds between the pyrimidine and aryl groups would change the conformation of the molecule and spacial relation between the two anthryl groups. Scheme 1 summarizes synthesis of **1a**, **1b** and **1c**. Their model compounds 9-(4-hydroxyphenyl)anthracene (**2a**) and 9-(4-methoxyphenyl)anthracene (**2b**) (Fig. 1) were also prepared. The Pd-complex-catalyzed coupling reaction of 4,6-diiodo-

* Corresponding author. E-mail address: kosakada@res.titech.ac.jp (K. Osakada). 2-methylpyrimidine and 5-bromo-2-methoxyphenyl boronic acid in dioxane/water yields 4,6-di(bromoaryl)-2-methylpyrimidine in 44% yield. Subsequent Suzuki–Miyaura coupling reaction of the product with 9-anthrylboronic acid forms **1b** in 71% yield. Demethylation of **1b** by BBr₃ in CH₂Cl₂ yields **1a** (68%). Hexylation of **1a**, giving **1c**, was achieved by using 1-iodohexane and K₂CO₃ (65% yield).

Figure 2 shows structures of $1a(CHCl_3)_2$ and 1c determined by X-ray crystallography. The molecule 1a adopted 'U'-shape conformation having two parallel anthracene units.⁹ Position of the OH hydrogen atom, H1, of 1a was determined from Fourier synthesis. Short contact between H1 and N1 keeps planarity of the rings **A** and **B**. Two anthryl planes are situated at parallel positions with distance of 8.0 Å. Two CHCl₃ molecules exist between them and keep the conformation by C–H··· π interaction with the anthryl groups. Close contact of the CHCl₃ hydrogen, H18, and the centroid of the **C** ring of **1a** and almost liner C25–H18···centroid of **C** angle are consistent with the C–H··· π attractive interaction.¹⁰ These CHCl₃ molecules in the crystals of **1a** were confirmed by elemental



 $R^1 = H (1a), Me (1b), n-hex (1c)$ $R^2 = H (2a), Me (2b)$

Figure 1. Structure of 1a-1c and 2a-2b.





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Scheme 1. Synthesis of 1a-1c.

analyses as well as the thermogravimetric analysis (TGA) showing weight loss in two stages at 140 °C (11%) and at 180 °C (12%). Further significant weight loss was not observed below 400 °C, which suggests thermal stability of **1a**.

IR spectrum of **1a** in KBr disk shows a broad v(OH) peak at 2710 cm⁻¹ shifted by the O-H…N hydrogen bond. ¹H NMR signals of **1a** and **1c** in Figure 3 were assigned by the ¹H-¹H and ¹³C-¹H COSY spectra. ¹H NMR signal at $\delta_{\rm H}$ 14.0 ($H_{\rm k}$) is assigned to that having O-H…N hydrogen bond in the di(hydroxyaryl)triazine group. The position is at lower magnetic field position than that reported for 2,4-di(2'-hydroxyaryl)-1,3,5-triazine by Kramer and co-workers ($\delta_{\rm H}$ 13.2).¹¹ The pyrimidine hydrogen and a C₆H₃ hydrogen, $H_{\rm b}$ and $H_{\rm c}$ of **1a** ($\delta_{\rm H}$ 7.85, 7.73), were observed at higher magnetic field positions than H_b and H_c of **1c** ($\delta_{\rm H}$ 7.49, 8.04), which are ascribed to the shielding effect on H_b by the C₆H₃ rings and the hydrogen bond between H_c and N atom in **1c**, respectively. These results suggest that **1a** and **1c** adopt the conformation shown in Scheme 1 not only in the solid state but also in the CDCl₃ solution.

Figure 4 shows the absorption and emission spectra of **1a** and **1c** as well as their model compounds, **2a** and **2b** (Figure 1), whose data were summarized in Table 1. Compounds **1a**, **1c**, **2a**, and **2b**, show typical absorption band of the anthryl group at similar positions (λ_{max} = 368 nm) in CHCl₃. The absorption band of **1a** is trailed up to ca. 440 nm, and the compound shows yellow color in its CHCl₃ solution, while CHCl₃ solution of **1c** is colorless. The



Figure 2. Molecular structure of (A) **1a** (CHCl₃)₂ and (B) **1c**. ORTEP drawings are shown in 50% probability. A part of hydrogen atoms were omitted for simplicity.



Figure 3. ¹H NMR spectra of (A) 1a and (B) 1c in CDCl₃ (400 MHz, rt).

molecular absorption coefficient ε of **1a** and **1c** (24500 and 25700 M⁻¹ cm⁻¹) are larger than the double of those of **2a** and **2b** (9700 and 9100 M⁻¹ cm⁻¹).

Excitation of a CHCl₃ solution of **1c** at 368 nm, corresponding to π - π^* transition of the anthryl group, causes emission at 410 nm (φ = 0.39). Photoluminescence of **1a** under same conditions is almost negligible (φ <0.01). In order to obtain further insights on different optical properties of **1a** and **1c**, luminescent properties of **2a** and **2b** were investigated. Compound **2a** with OH groups in the phenyl group bonded to anthryl group shows luminescence (φ = 0.31) similar to **2b** with OMe group (φ = 0.33), although emission from **1a** having pyrimidine core is quenched efficiently. Addition of excess pyridine to the solution ([**2a**] = 1.0×10^{-3} mM, [pyridine] = 1.0×10^{2} mM) causes decrease of the intensity to φ = 0.05.

Efficient quenching of luminescence of **2a** in the presence of pyridine is ascribed to intramolecular photo-induced electron transfer (PET) between the excited state of anthryl group and electron rich phenoxy group formed by partial deprotonation with pyridine.^{12,13} Much weaker emission intensity of **1a** than that of **1c** can be also explained by significant quenching of the luminescence of **1a**. The stable canonical form **1a**' has the phenoxy groups formed



Figure 4. (A) Absorption $(1.0 \times 10^{-2} \text{ mM})$ and (B) emission $(1.0 \times 10^{-3} \text{ mM})$ spectra of (a) **1a**, (b) **1c**, (c) **2a**, (d) **2b**, and (e) **2a** $(1.0 \times 10^{-3} \text{ mM})$ + pyridine $(1.0 \times 10^2 \text{ mM})$ (CHCl₃, 20 °C).

Table 1 Absorption and emission data of **1a**, **1c**, **2a**, **2b**, and anthracene

Compound	Absorption ^a λ _{max} /nm	$\varepsilon/M^{-1} cm^{-1}$	Emission ^b λ _{max} /nm	φ^{c}
1a 1c 2a 2a + py ^e 2b Anthracene	368 368 368 368 368 368 359	24500 25700 9700 14600 9100 7200	- 410, 428 412, 429 412, 428 414, 428 405	<0.01 0.39 0.31 (0.35 ^d) 0.05 0.33 (0.36 ^d) (0.09 ^d)

[Compound] = 1.0×10^{-2} mM, CHCl₃, 20 °C.

[Compound] = 1.0×10^{-3} mM, CHCl₃, 20 °C, $\lambda_{ex} = \lambda_{max}$ (absorption).

с Quantum yield. Standard sample: quinine $(1.0 \times 10^{-3} \text{ mM})$ in H₂SO₄(aq), $\varphi_{\text{std}} = 0.546.$

[Compound] = 2.0×10^{-3} mM.

 $[pyridine]/[2a] = 1.0 \times 10^5.$



Scheme 2. Canonical forms of 1a.

by strong O-H-N hydrogen bonds with the neighboring pyrimidine group (Scheme 2).

In summary, we obtained new aromatic compounds 1a and 1c. The intramolecular hydrogen bonds of di(hydroxyphenyl)pyrimidine group in **1a** maintain the 'U'-shape conformation in the solid as well as in the solution, while 1c adopts quite different conformation due to C-H-O interaction. These molecules with similar chemical structures but different conformation and optical properties can be employed as the fundamental motif of the compounds which show switching behavior. Further studies on the compounds and the derivation are now in progress.¹⁴

Acknowledgments

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Supplementary data

Supplementary data (experimental procedures and spectral data for new compounds associated with this article can be found, in the online version. CCDC nos. 822408 and 822409 contain the supplementary crystallographic data for **1a**(CHCl3)2 and **1c**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/ data_request/cif) associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2011.05.080.

References and notes

- 1. (a) Hawker, C. J.; Wooley, K. L. Science 2005, 309, 1200; (b) Berresheim, A. J.; Müller, M.; Müllen, K. Chem. Rev. 1999, 99, 1747; (c) Grimsdale, A. C.; Müllen, K. Angew. Chem., Int. Ed. 2005, 44, 5592; (d) De Schryver, F. C.; Vosch, T.; Cotlet, M.; Van der Auweraer, M.; Müllen, K.; Hofkens, J. Acc. Chem. Res. 2005, 38, 514; (e) Yamamoto, T. Macromol. Rapid Commun. 2002, 23, 583.
- 2. (a) Brédas, J. L.; Silbey, R.; Boudreaux, D. S.; Chance, R. R. J. Am. Chem. Soc. 1983, 105, 6555; (b) Setayesh, S.; Grimsdale, A. C.; Weil, T.; Enkelmann, V.; Müllen, K.; Meghdadi, F.; List, E. J. W.; Leising, G. J. Am. Chem. Soc. 2001, 123, 946; (c) Yamamoto, T.; Hayashi, Y.; Yamamoto, A. Bull. Chem. Soc. Jpn. 1978, 51, 2091.
- Suzaki, Y.; Chihara, E.; Takagi, A.; Osakada, K. Dalton Trans. 2009, 9881.
- (a) Chen, C.-W.; Whitlock, H. W., Jr. J. Am. Chem. Soc. 1978, 100, 4921; (b) Zimmerman, S. C.; VanZyl, C. M. J. Am. Chem. Soc. 1987, 109, 7894; (c) Zimmerman, S. C.; Wu, W. J. Am. Chem. Soc. 1989, 111, 8054; (d) Zimmerman, S. C. Top. Curr. Chem. 1993, 165, 71.
- (a) Klärner, F.-G.; Kahlert, B. Acc. Chem. Res. 2003, 36, 919; (b) Harmata, M. Acc. Chem. Res. 2004, 37, 862.
- (a) Zimmerman, S. C.; Saionz, K. W.; Zeng, Z. Proc. Natl. Acad. Sci. U.S.A. 1993, 90, 1190; (b) Zimmerman, S. C.; Saionz, K. W. J. Am. Chem. Soc. 1995, 117, 1175.
- Recent examples of molecular tweezers (a) Chen, G.; Bouzan, S.; Zhao, Y. Tetrahedron Lett. 2010, 51, 6552; (b) Legouin, B.; Gayral, M.; Uriac, P.; Cupif, J.-F.; Levoin, N.; Toupet, L.; van de Weghe, P. Eur. J. Org. Chem. 2010, 5503; (c) Legouin, B.; Gayral, M.; Uriac, P.; Tomasi, S.; van de Weghe, P. Tetrahedron: Asymmetry 2010, 21, 1307; (d) Hisamatsu, Y.; Aihara, H. Chem. Commun. 2010, 46, 4902; (e) Leblond, J.; Gao, H.; Petitjean, A.; Leroux, J.-C. J. Am. Chem. Soc. 2010, 132, 8544; (f) Ulrich, S.; Petitjean, A.; Lehn, J.-M. Eur. J. Inorg. Chem. 2010, 1913; (g) Pérez, E. M.; Martín, N. Pure Appl. Chem. **2010**, 82, 523; (h) Wallentin, C.-J.; Wixe, T.; Wendt, O. F.; Bergquist, K.-E.; Wärnmark, K. Chem. Eur. J. 2010, 16, 3994; (i) Tatar, A.; Čejka, J.; Král, V.; Dolenský, B. Org. Lett. 2010, 12, 1872; (j) Skibiński, M.; Gómez, R.; Lork, E.; Azov, V. A. Tetrahedron 2009, 65, 10348; (k) Marquis, R.; Kulikiewicz, K.; Lebedkin, S.; Kappes, M. M.; Mioskowski, C.; Meunier, S.; Wagner, A. Chem. Eur. J. 2009, 15, 11187; (I) Lee, C.-H.; Yoon, H.; Jang, W.-D. Chem. Eur. J. 2009, 15, 9972; (m) Nishiuchi, T.; Kuwatani, Y.; Nishinaga, T.; Iyoda, M. *Chem. Eur. J.* **2009**, *15*, 6838.
- 8 Hunter, C. A.; Lawson, K. R.; Perkins, J.; Urch, C. J. J. Chem. Soc., Perkin Trans. 2 2001. 651.
- A molecule of **1a** in the single crystal, obtained from a CHCl₃ solution, has crystallographic C2. The crystallographically independent unit observed by X-ray crystallography is composed of half of **1a** and one molecule of CHCl₃.
- 10. Suezawa, H.; Yoshida, T.; Umezawa, Y.; Tsuboyama, S.; Nishio, M. Eur. J. Inorg. Chem 2002 3148
- Stueber, G. J.; Kieninger, M.; Schettler, H.; Busch, W.; Goeller, B.; Franke, J.; 11. Kramer, H. E. A.; Hoier, H.; Henkel, S.; Fischer, P.; Port, H.; Hirsch, T.; Rytz, G.; Birbaum, J.-L. J. Phys. Chem. 1995, 99, 10097.
- 12. de Silva, A. P.; Fox, D. B.; Huxley, A. J. M.; Moody, T. S. Coord. Chem. Rev. 2000, 205 41
- Iwasa, J.; Ono, K.; Fujita, M.; Akita, M.; Yoshizawa, M. Chem. Commun. 2009, 13. 5746.
- 14. Preliminary studies were conducted on the host-guest complexation of 1a with the guest molecules. The ¹H NMR measurement of a mixture of **1a** and π acceptors, such as TCNQ, TCNE and PFB (pentafluorobenzene), in CDCl₃, DMSO d_6 and benzene- d_6 ([1a] = [Guest molecule] = 1.0 mM, rt and 50 °C, 24 h), however, did not show shift of the signals caused by the complexation. We are exploring the conditions suited for the formation of the host-guest complexes.