Solid state structures and photophysical properties of (trimethylsilyl)methyl-substituted anthracenes and pyrenes†

Masaki Shimizu,* Hironori Tatsumi, Kenji Mochida and Tamejiro Hiyama

Received (in Cambridge, UK) 31st October 2007, Accepted 7th February 2008
First published as an Advance Article on the web 27th February 2008
DOI: 10.1039/b716770a

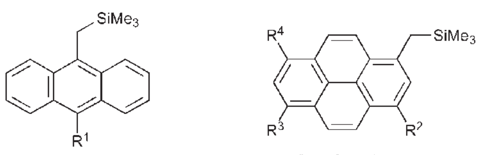
(Trimethylsilyl)methyl groups incorporated at 9- and 9,10-positions of anthracenes and at 1,3,6,8-positions of pyrenes were found to orient perpendicular to the aromatic frameworks in their crystals and induce red-shift of UV absorption and fluorescence spectra and enhancement of fluorescence quantum yields as compared with the parent hydrocarbons.

Most extensively studied recently are π-conjugated molecules as advanced materials for applications in the field of organic electronics such as light-emitting diodes, field-effect transistors, and solar cells.[1] Since such functional π-conjugated compounds are used as solid thin films for the practical applications, molecular design that control not only electronic but also solid-state structures of the materials is of great significance.[2] Incorporation of organosilyl moieties such as disilanyl and triorganosilyl groups into an arene is one of effective ways for tuning electronic structure of the parent π-system since such the silicon introduction into arenes perturbs the parent conjugated system *via* σ–π (σ*–π*) conjugation.[3] Therefore, it is of great importance to find silicon substituents that adapt an ideal geometry for σ–π (σ*–π*) conjugation in solid states. We recently prepared tris(trimethylsilyl)silyl (TTMSS)-substituted anthracenes and disclosed that a Si–Si σ-bond of the TTMSS group was perpendicular to the anthracene plane in the crystal.[4] The TTMSS introduction was effective for lowering the LUMO, leading to bathochromic shifts of UV and fluorescence spectra, while the anthracene ring was bent due to the bulkiness of TTMSS group. Considering that planarity of a conjugated system is one of factors that govern the electronic and optical properties, it is of particular interest to explore silyl substituents that not only alter electronic structure of a π-conjugated system but also orient in solid state so as to maximize σ–π (σ*–π*) conjugation without causing distortion of the π-planar framework. To this end, we turned our attention to (trimethylsilyl)methyl (TMSM) group since a benzylic carbon–silicon bond could participate in π-conjugated system[5] and X-ray studies of TMSM-substituted benzene[6] and pyridinium cation[7] disclosed that the CH_2–$SiMe_3$ bonds positioned orthogonal to the benzene and positively charged pyridine planes, respectively. We report herein structures and photophysical properties of TMSM-substituted anthracenes **1** and pyrenes **2** (Fig. 1).[8]

Anthracenes **1** and pyrenes **2** were prepared in 21–95% yields by Kumada–Tamao coupling reactions of the corresponding bromides and commercially available Me_3SiCH_2MgCl (ESI†).

Single crystals of **1a**,‡ **1b**,§ and **2c**¶ were obtained by recrystallization from hexane, ethanol and hexane/*i*-PrOH (3 : 1), respectively. The molecular structures of those disclosed by X-ray diffraction study are shown in Fig. 2. The Si(1)–C(15) bond of **1** was found to direct perpendicular to the anthracene plane as expected. Both **1b** and **2c** crystallized in monoclinic space group $P2_1/c$ with the center of symmetry at centroid of the anthracene and pyrene framework, respectively. The Si(1)–C(8) bond of **1b**, and the Si(1)–C(9) and Si(2)–C(13) bonds of **2c** were positioned almost orthogonal to and upside of the aromatic planes and the remaining Si–C(benzylic) bonds in **1b** and **2c** were oriented in their downside. In all cases, the aromatic planes were flat, indicating that the substitution of TMSM groups did not induce any distortion of the aromatic planes in contrast to the TTMSS group. The geometry of silicon atoms was significantly deformed from a normal tetrahedral shape. The bond angles of Si–C(benzylic)–C(aromatic) ranged from 114.56(9)° to 117.77(11)°, which was much larger than the standard value (109.5°) of an sp^3-hybridized silicon atom.

Ultraviolet and fluorescence spectra of **1** and **2** measured in cyclohexane at room temperature are shown in Fig. 3–6 and the data are summarized in Table 1, together with those of 9-methyl- and 9,10-dimethylanthracenes **1a′** and **1b′**, and 1-methyl, 1,6-dimethyl and 1,3,6,8-tetramethylpyrenes **2a′–2c′** for comparison. Absorption spectra of **1** and **2** (Fig. 3 and 4) showed almost similar vibrational structures, respectively, while the presence of $SiMe_3$ groups at benzylic positions induced a bathochromic shift of the spectra compared with those of the corresponding **1′** and **2′**. Fluorescence spectra of **1** and **2** (Fig. 5 and 6) also displayed vibrational structures and red-shifted by the silicon substitution. As the number of TMSM groups increased, both absorption and fluorescence spectra of **1** and **2** exhibited a bathochromic shift. Conservation of the vibrational structures



1a (R^1 = H)
1b (R^1 = CH_2SiMe_3)

2a (R^2 = R^3 = R^4 = H)
2b (R^2 = R^4 = H, R^3 = CH_2SiMe_3)
2c (R^2 = R^3 = R^4 = CH_2SiMe_3)

Fig. 1 TMSM-substituted anthracenes **1** and pyrenes **2**.

Department of Material Chemistry, Graduate School of Engineering, Kyoto University, Kyoto University Katsura, Nishikyo-ku, Kyoto 615-8510, Japan. E-mail: shimizu@npc05.kuic.kyoto-u.ac.jp; Fax: +81 75 383 2445; Tel: +81 75 383 2444

† Electronic supplementary information (ESI) available: Experimental procedures and characterization. CCDC 662226–662228. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b716770a

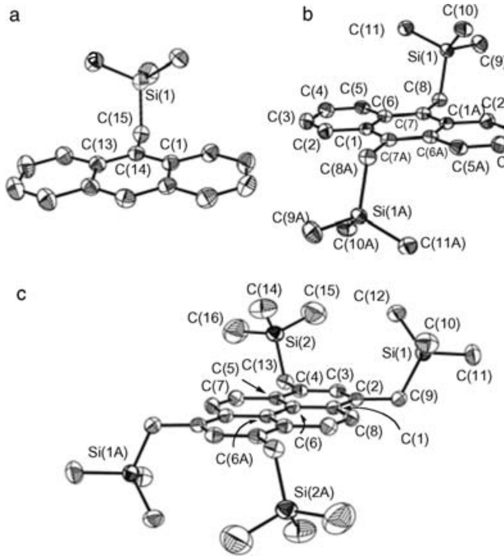


Fig. 2 ORTEP drawings of **1a** (a), **1b** (b), and **2c** (c) with ellipsoids shown at 30% probability. Hydrogen atoms have been omitted for clarity. The atoms numbering with an A letter in **1b** and **2c** are at equivalent positions ($1 - x, -y, 1 - z$) and ($2 - x, 1 - y, 1 - z$), respectively.

sharply contrasts with the observation that fluorescence spectra of TTMSS-substituted anthracenes were broadened and completely structureless,[4] which may reflect the difference in flatness of the aromatic framework. Fluorescence quantum yields of **1** and **2** were higher than those of **1a′**, TTMSS-substituted anthracenes,[4] and **2′**, respectively. Hence, these results indicated that the introduction of TMSM groups was more effective for extension of conjugation length than that of TTMSS groups.

Solid films of **1** and **2** prepared by spin-coating from their CH_2Cl_2 solution also exhibited blue or green emission upon UV irradiation at 355 nm (Fig. 7 and 8). Emission maxima of **1a** and **1b** were almost the same in the solid state. Thus, in comparison to the spectra measured in cyclohexane (Fig. 5), a bathochromic shift of **1b** resulting from changing its state from solution to thin film was smaller than that of **1a**. The spectrum of **2a** also displayed only broadened structure, while **2b** and **2c** exhibited dual emission consisting of a monomer-like one with structured spectrum in violet to blue emitting region, and excimer or exciplex-like one with a broadened and red-shifted band. These observations may suggest that di- and tetra-substitution of TMSM groups into an arene can diminish excimer or exciplex formation in solid state and lead to enhancing efficiency of solid-state fluorescent emission.

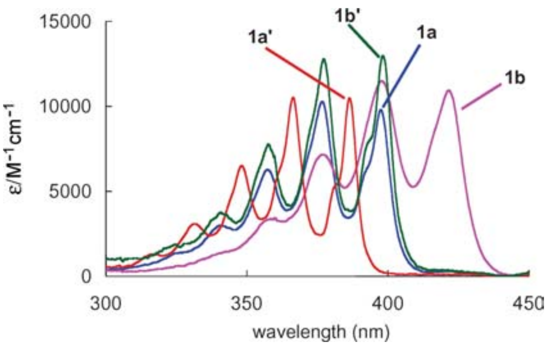


Fig. 3 UV spectra of **1** and **1′** (1×10^{-5} M in cyclohexane).

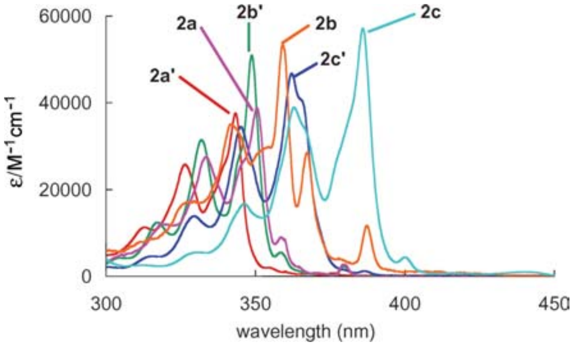


Fig. 4 UV spectra of **2** and **2′** (1×10^{-5} M in cyclohexane).

Molecular orbital calculations of methyl or H_3SiCH_2-substituted anthracenes and pyrenes were carried out by DFT method at B3LYP/6-31G*//B3LYP/6-31G* level. The energies of HOMOs and LUMOs are summarized in Chart S1 (ESI†). When silyl groups were substituted at benzylic positions of methylated anthracenes and pyrenes, LUMO levels were considerably lowered with slight decrease of HOMO levels in all cases. Accordingly, the HOMO–LUMO gaps narrowed by the silicon substitution, in consistent to the red shift of absorption maxima. Meanwhile, the HOMO–LUMO gaps became narrower in proportion to the number of incorporated silylmethyl groups, which resulted from slight lowering of LUMO levels and large elevation of HOMO levels. The enhancement of HOMO level is ascribed to the σ–π conjugation between a σ-orbital of Si–C(benzylic) bond and p-orbitals of the aromatic rings.

In summary, we have demonstrated that introduction of TMSM groups into anthracene and pyrene leads to the extension of the conjugated systems, and Si–C(benzylic) bonds of the TMSM groups adapts an ideal conformation for

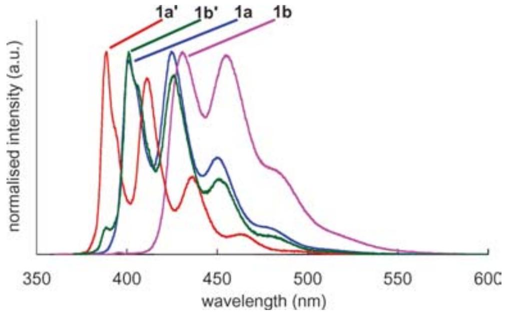


Fig. 5 Fluorescence spectra of **1** and **1′** (1×10^{-6} M in cyclohexane, excitation wavelength 355 nm).

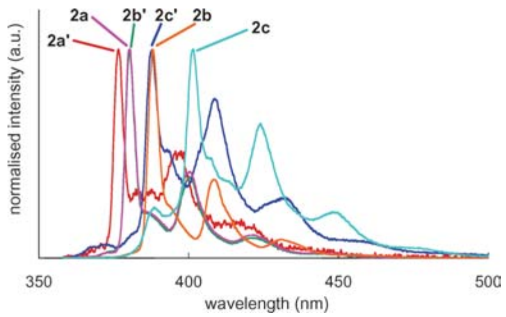


Fig. 6 Fluorescence spectra of **2** and **2′** (1×10^{-6} M in cyclohexane, excitation wavelength 355 nm).

Table 1 Photophysical properties of anthracenes **1** and pyrenes **2**

1 or **2**	λ_{abs}/nm (ε/M^{-1} cm^{-1})^a	λ_{em}/nm^{bc}	$\Phi_f{}^d$
1a	398 (9590)	402	0.72
1a′	386 (10 480)	388	0.32
1b	422 (10 900)	432	0.66
1b′	398 (12 930)	401	0.72
2a	351 (39 260)	381	0.48
2a′	343 (37 520)	377	0.07
2b	359 (53 360)	388	0.65
2b′	349 (50 900)	380	0.17
2c	386 (57 050)	402	0.49
2c′	362 (46 700)	388	0.11

[a] Absorption maximum measured in cyclohexane (1×10^{-5} M). [b] Emission maximum of the strongest fluorescence measured in cyclohexane (1×10^{-6} M). [c] Irradiated with an UV light (λ = 355 nm). [d] Calculated with anthracene as a reference (Φ_f = 0.32).

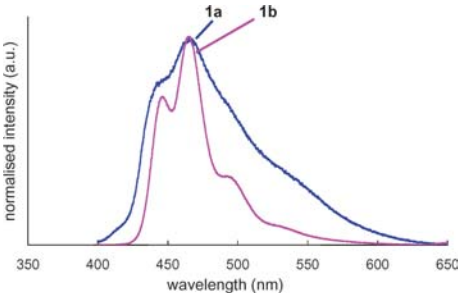


Fig. 7 Fluorescence spectra of **1** in the solid state (excitation wavelength 355 nm).

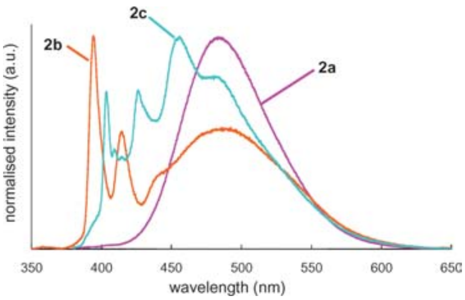


Fig. 8 Fluorescence spectra of **2** in the solid state (excitation wavelength 355 nm).

efficient σ–π conjugation in the solid states. Further studies on preparation of TMSM-substituted functional π-conjugated compounds and their applications to strongly emissive solid materials are in progress in our laboratory.

Notes and references

‡ Crystallographic data for **1a**: $C_{18}H_{20}Si$, M = 264.43, orthorhombic, space group *Pbca*, a = 17.266(4) Å, b = 7.1904(17) Å, c = 25.133(6) Å, V = 3120.2(13) Å^3, Z = 8, D_{calc} = 1.126 Mg m^{-3}, T = 300 K, reflections collected: 17 759, independent reflections: 3411 (R_{int} = 0.0272), Final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0496, w$R2$ = 0.1288, R indices (all data): $R1$ = 0.0669, w$R2$ = 0.1415. CCDC 662226.

§ Crystallographic data for **1b**: $C_{22}H_{30}Si_2$, M = 350.64, monoclinic, space group $P2_1/c$, a = 12.4707(9) Å, b = 6.2382(5) Å, c = 14.2962(11) Å, β = 111.4620(10)°, V = 1035.05(14) Å^3, Z = 2, D_{calc} = 1.125 Mg m^{-3}, T = 300 K, reflections collected: 5986, independent reflections: 2232 (R_{int} = 0.0186), Final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0370, w$R2$ = 0.1007, R indices (all data): $R1$ = 0.0406, w$R2$ = 0.1042. CCDC 662227.

¶ Crystallographic data for **2c**: $C_{32}H_{50}Si_4$, M = 547.08, monoclinic, space group $P2_1/c$, a = 13.524(3) Å, b = 10.663(3) Å, c = 12.834(3) Å, β = 109.495(4)°, V = 1744.7(8) Å^3, Z = 2, D_{calc} = 1.041 Mg m^{-3}, T = 300 K, reflections collected: 9289, independent reflections: 3243 (R_{int} = 0.0196), Final R indices [$I > 2\sigma(I)$]: $R1$ = 0.0552, w$R2$ = 0.1695, R indices (all data): $R1$ = 0.0614, w$R2$ = 0.1771. CCDC 662228.

1 (*a*) *Electronic Materials: The Oligomer Approach*, eds. K. Müllen and G. Wegner, Wiley-VCH, Weinheim, 1998; (*b*) *Handbook of Oligo- and Polythiophenes*, ed. D. Fichou, Wiley-VCH, Weinheim, 1999; (*c*) *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001; (*d*) *Molecular Devices and Machines*, eds. V. Balzani, M. Venturi and A. Credi, Wiley-VCH, Weinheim, 2003; (*e*) *Functional Organic Materials*, eds. T. J. J. Müller and U. H. F. Bunz, Wiley-VCH, Weinheim, 2007; (*f*) U. Scherf and K. Mullen, *Synthesis*, 1992, 23–38; (*g*) A. Kraft, A. C. Grimsdale and A. B. Holmes, *Angew. Chem., Int. Ed.*, 1998, **37**, 402–428; (*h*) U. Mitschke and P. Bäuerle, *J. Mater. Chem.*, 2000, **10**, 1471–1507; (*i*) M. Bendikov, F. Wudl and D. F. Perepichka, *Chem. Rev.*, 2004, **104**, 4891–4945; (*j*) J. E. Anthony, *Chem. Rev.*, 2006, **106**, 5028–5048; (*k*) J. E. Anthony, *Chem. Rev.*, 2007, **107**, 923–1386 (Thematic issue-Organic electronics and optoelectronics).

2 (*a*) J. Cornil, D. Beljonne, J.-P. Calbert and J.-L. Bredas, *Adv. Mater.*, 2001, **13**, 1053–1067; (*b*) F. J. M. Hoeben, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491–1546.

3 (*a*) C. G. Pitt, *J. Organomet. Chem.*, 1973, **61**, 49–70; (*b*) H. Sakurai, *J. Organomet. Chem.*, 1980, **200**, 261–286; (*c*) R. West, *J. Organomet. Chem.*, 1986, **300**, 327–346; (*d*) H. Sakurai, *Pure Appl. Chem.*, 1987, **59**, 1637–1646; (*e*) H. Bock, *Angew. Chem., Int. Ed. Engl.*, 1989, **28**, 1627–1650; (*f*) J. Dubac, A. Laporterie and G. Manuel, *Chem. Rev.*, 1990, **90**, 215–263; (*g*) E. Colomer, R. J. P. Corriu and M. Lheureux, *Chem. Rev.*, 1990, **90**, 265–282; (*h*) H. Shizuka and H. Hiratsuka, *Res. Chem. Intermed.*, 1992, **18**, 131–182; (*i*) H. Bock and B. Solouki, *Chem. Rev.*, 1995, **95**, 1161–1190; (*j*) R. West, in *Comprehensive Organometallic Chemistry II*, eds. E. W. Abel, F. G. A. Stone and G. Wilkinson, Pergamon, Oxford, 1995, vol. 2, pp. 77–110; (*k*) S. Yamaguchi and K. Tamao, *Bull. Chem. Soc. Jpn.*, 1996, **69**, 2327–2334; (*l*) S. Kyushin, M. Ikarugi, M. Goto, H. Hiratsuka and H. Matsumoto, *Organometallics*, 1996, **15**, 1067–1070; (*m*) J. Ohshita and A. Kunai, *Acta Polym.*, 1998, **49**, 379–403; (*n*) S. Yamaguchi and K. Tamao, *J. Chem. Soc., Dalton Trans.*, 1998, 3693–3702; (*o*) M. Hissler, P. W. Dyer and R. Réau, *Coord. Chem. Rev.*, 2003, **244**, 1–44; (*p*) D. D. H. Yang, N. C. C. Yang, I. M. Steele, H. Li, Y. Z. Ma and G. R. Fleming, *J. Am. Chem. Soc.*, 2003, **125**, 5107–5110.

4 M. Shimizu, K. Oda, T. Bando and T. Hiyama, *Chem. Lett.*, 2006, **35**, 1022–1023.

5 (*a*) H. Sakurai, M. Ochiai and M. Kira, *Chem. Lett.*, 1972, 87–88; (*b*) J. B. Lambert and R. A. Singer, *J. Am. Chem. Soc.*, 1992, **114**, 10246–10248; (*c*) M. Shimizu, K. Watanabe, H. Nakagawa, T. Becker, S. Sugimoto and T. Hiyama, *Chem. Lett.*, 2001, 1090–1091; (*d*) H. Maeda, K. I. Nishimura, K. Mizuno, M. Yamaji, J. Oshima and S. Tobita, *J. Org. Chem.*, 2005, **70**, 9693–9701; (*e*) M. Shimizu, T. Kawaguchi, K. Oda and T. Hiyama, *Chem. Lett.*, 2007, **36**, 412–413.

6 S. W. Carr, M. Motevalli, D. L. Ou and A. C. Sullivan, *J. Mater. Chem.*, 1997, **7**, 865–872.

7 (*a*) A. Happer, J. N. G, B. Pool and J. White, *J. Organomet. Chem.*, 2002, **659**, 10–14; (*b*) K. Hassall, S. Lobachevsky and J. M. White, *J. Org. Chem.*, 2005, **70**, 1993–1997.

8 Preparation of **1a** and **1b**, and their oxidation to the radical cations were studied: (*a*) W. Kaim and H. Bock, *Chem. Ber.*, 1978, **111**, 3585–3595; (*b*) W. Kitching, H. A. Olszowy, I. Schott, W. Adcock and D. P. Cox, *J. Organomet. Chem.*, 1986, **310**, 269–284; (*c*) S. R. Sirimanne, Z. Li, D. R. Vander Veer and L. M. Tolbert, *J. Am. Chem. Soc.*, 1991, **113**, 1766–1769. Meanwhile, no structural analysis and photophysical properties of **1** were reported except for fluorescence quantum yields and decay lifetimes of **1a** in methylcyclohexane, acetonitrile, methanol, 2-methylpropanol and tetrahydrofuran; (*d*) J.-P. Desvergne, R. Bonneau, G. Dörr and H. Bouas-Laurent, *Photochem. Photobiol. Sci.*, 2003, **2**, 289–296.