Photochemical &
Photobiological
Sciences

Effects of Substituents in Silyl Groups on the Absorption, Fluorescence and Structural Properties of 1,3,6,8-Tetrasilylpyrenes

SCHOLARONE™
Manuscripts

Photochemical & Photobiological Sciences

Paper

Effects of Substituents in Silyl Groups on the Absorption, Fluorescence and Structural Properties of 1,3,6,8-Tetrasilylpyrenes

Hajime Maeda,*[a] Tsubasa Suzuki[a] and Masahito Segi[a]

1,3,6,8-Tetrasilylpyrenes and related germyl and stannyl derivatives were synthesized, and their absorption and fluorescence spectroscopic and structural properties were elucidated. The results show that the UV-vis absorption maxima of these substances in CH_2Cl_2 solutions shift to longer wavelengths as the size of the alkyl groups and numbers of phenyl groups on silicon increase. Fluorescence quantum yields of tetrasilylpyrenes in cyclohexane are larger than that of pyrene, and a pentamethyldisilyl derivative has an emission efficiency of 0.79. Except in the case of the $SiMe_2H$ derivative, excimer emission was not observed in concentrated solutions of these substances. The $SiMe_2H$ and $SiMe_3$ derivatives were shown to form CT complexes with tetracyanoethylene in CH_2Cl_2 solutions. The calculated energy barriers for rotation of the silyl groups about the Si-C bond increases as the steric bulk of the silyl group increases. ^{29}Si NMR chemical shifts were found to depend on the sizes of the alkyl groups and numbers of phenyl groups. Data arising from theoretical calculations suggest that the silyl groups act as electron-donating groups, and the donating ability of the groups decreases in the order $SiR_3 > GeR_3 > SnR_3$.

Introduction

The effects of introducing silyl and silylethynyl groups on arenes have been extensively studied and much attention has been given to the unique properties of silyl-substituted aromatic compounds.[1–14] Pyrene is a common fluorophore because it has advantageous features including photochemical inertness, a high fluorescence quantum yield and displaying both monomer and excimer emission. These properties have been used in the elucidation of structures of macromolecules.[15–18] Because the introduction of silyl-substituents on pyrene often enhances its fluorescence intensity, silylpyrenes have been utilized as fluorescent probes for elucidation of the geometries of oligonucleotides,[19–21] oligoDNAs[22–28] and steroids.[29] Highly emissive silyl-substituted pyrenes have not only been used as fluorescent probes, but they also have been employed in the development of fluorescent materials for organic light emitting diodes (OLEDs),[30] circularly polarized luminescence (CPL) materials[31] and fluorescent nanoparticles.[32] In addition, dipyrenylsilanes,[33,34] silyl-tethered pyrenophanes,[35,36] pyrene-substituted oligosilanes,[37–44] polysilanes,[45,46] siloxanes,[47,48] dendrimers[49] and other π-conjugated molecules[50–52] have been explored and $\sigma^{(*)}$-$\pi^{(*)}$,[53,54] d-π^{*},[55] and intramolecular

charge transfer (ICT)[45,56] interactions in the ground and excited states of silylpyrene derivatives have been discussed.

In earlier efforts, we investigated the effects of introducing silyl and silylethynyl groups on the properties of naphthalene,[57–60] phenanthrene,[57] anthracene,[57] perylene,[61] stilbene[62] and pyrene.[57,63–68] In a study of silylpyrene derivatives, we showed that the fluorescence quantum yield (Φ_f) of pyrene (0.32)[69] is increased by introduction of Me_3Si groups. For example the Φ_f of 1,3,6,8-tetrakis(trimethylsilyl)pyrene is 0.56.[57] In the study described below, we explored the effects of substituents in silyl groups on absorption and fluorescence properties, as well as the silicon substituents on the molecular structures of 1,3,6,8-tetrasilylpyrenes and related compounds.

Results and discussion

Tetrasilylpyrenes containing different silicon substituents in their silyl groups and related germanium and tin compounds 2-13 were synthesized by using the routes shown in Scheme 1. The pathways began with reaction of pyrene (1) with 4.6 equiv of Br_2 to form 1,3,6,8-tetrabromopyrene (14) in 96% yield.[70] Lithiation of 14 with t-BuLi followed by addition of excesses of the corresponding chlorosilanes, chlorogermanes, and chlorostannanes generated the respective tetrasilylpyrenes (2-9), tetragermylpyrenes (10,11) and tetrastannylpyrenes (12,13). The isolated yields from 14 are shown in Table 1.

[a.] Division of Material Chemistry, Graduate School of Natural Science and Technology Kanazawa University, Kakuma-machi, Kanazawa, Ishikawa 920-1192, Japan. Fax: +81-76-234-4800; Tel: +81-76-264-6290; E-mail: maeda-h@se.kanazawa-u.ac.jp
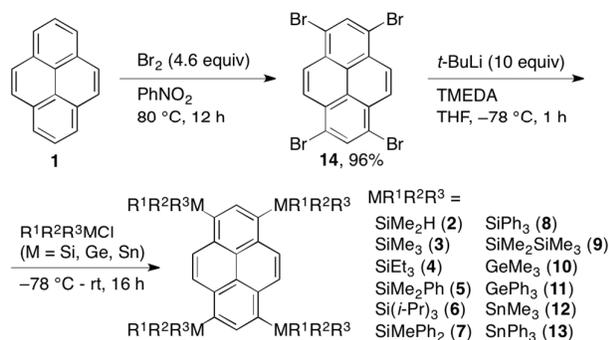
Scheme 1. Synthesis of 1,3,6,8-tetrasilylpyrenes and related compounds.
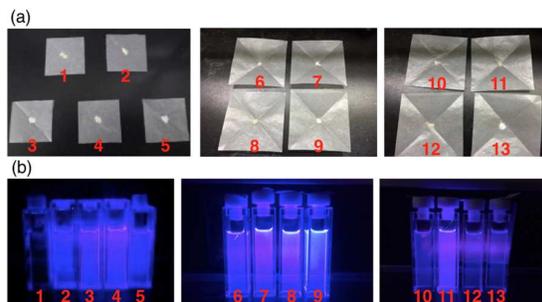
Figure 1. Colors of (a) solids and (b) luminescence in aerated CH_2Cl_2 solutions (1.0×10^{-5} M, λ_{ex} = 254 nm) of **1-13**.

The synthesized compounds **2-13** are colorless solids (Figure 1(a)) and display bluish purple fluorescence in CH_2Cl_2 solutions when irradiated with UV (254 nm) light. Especially interesting is the observation that the intensities of fluorescence of **2-9**, which can be seen using naked eyes, are larger than that of **1** (Figure 1(b)).

UV-vis absorption spectra of pyrene (**1**) and its derivatives **2-13** were obtained using 1.0×10^{-5} M CH_2Cl_2 solutions (Figure 2,

Table 1). Inspection of the data shows that the absorption maxima of **2-13** are shifted to longer wavelengths and their molar absorption coefficients (ε) are larger than those of **1**. A comparison of the data for the silyl derivatives demonstrates that the absorption maxima shift to longer wavelengths as the size of the alkyl group increases (SiMe₃ (**3**) < SiEt₃ (**4**) < Si(i-Pr)₃ (**6**)) and with increasing numbers of phenyl groups on silicon (SiMe₃ (**3**) < SiMe₂Ph (**5**) < SiPh₂Me (**7**) < SiPh₃ (**8**)). Changes in
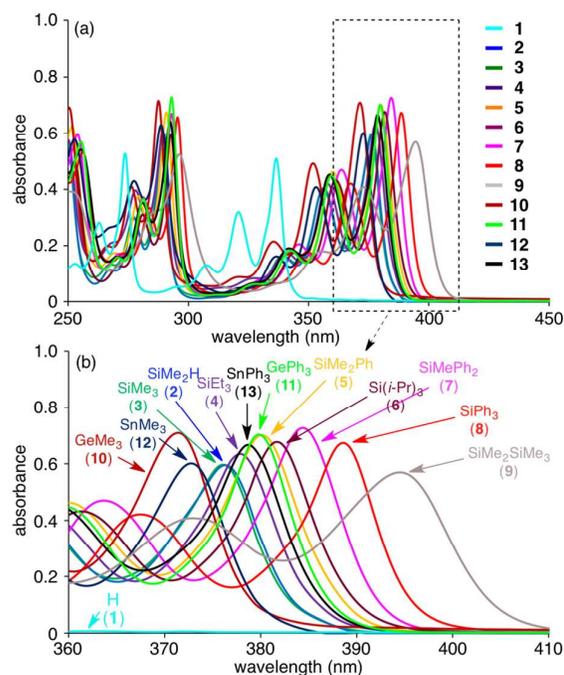
Figure 2. UV-vis absorption spectra of **1-13**, 1.0×10^{-5} M in aerated CH_2Cl_2. Spectra (b) is an expansion of the dotted area of spectra (a).

Table 1. Yields, photophysical properties, and calculated data for pyrene derivatives.

Compound	$MR^1R^2R^3$	Yield (%)[a]	Absorption		Fluorescence			Calculation[g]			
			λ_{abs}[b] (nm)	$\log \varepsilon$[c]	λ_{em}[d] (monomer) (nm)	Φ_f[e]	λ_{em}[f] (excimer) (nm)	HOMO (eV)	LUMO (eV)	Energy gap (eV)	Charge density on $MR^1R^2R^3$[h]
1	H	–	337	4.69	370	0.32[i]	472	−5.459	−1.532	3.928	–
2	SiMe₂H	12	376	4.77	388	0.49	502	−5.409	−1.780	3.629	0.430
3	SiMe₃	28	376	4.78	386	0.56[j]	–[k]	−5.326	−1.709	3.617	0.422
4	SiEt₃	41	378	4.80	388	0.65	–[k]	−5.335	−1.746	3.589	0.494
5	SiMe₂Ph	17	380	4.85	389	0.63	–[k]	−5.370	−1.760	3.610	0.463
6	Si(i-Pr)₃	15	382	4.83	390	0.55	–[k]	−5.289	−1.725	3.564	0.503
7	SiMePh₂	16	384	4.86	392	0.70	–[k]	−5.407	−1.808	3.599	0.475
8	SiPh₃	3	389	4.83	395	0.62	–[k]	−5.372	−1.779	3.594	0.476
9	SiMe₂SiMe₃	20	394	4.76	404	0.79	–[k]	−5.245	−1.698	3.547	0.450
10	GeMe₃	38	371	4.85	379	0.20	–[k]	−5.314	−1.654	3.660	0.423
11	GePh₃	5	380	4.85	387	0.33	–[k]	−5.415	−1.913	3.502	0.418
12	SnMe₃	60	373	4.78	381	0.03	–[k]	−5.251	−1.713	3.538	0.400
13	SnPh₃	31	379	4.82	386	0.03	–[k]	−5.376	−1.713	3.663	0.401

[a] Isolated yield from tetrabromopyrene (**14**). [b] Absorption maximum appeared at longest wavelength, 1.0×10^{-5} M in aerated CH_2Cl_2. [c] Logarism of molar absorption coefficient, 1.0×10^{-5} M in aerated CH_2Cl_2. [d] Fluorescence maximum of monomer appeared at shortest wavelength, 1.0×10^{-5} M in aerated CH_2Cl_2. Excitation wavelength (λ_{ex}) is λ_{abs} in this Table. [e] Fluorescence quantum yield, degassed by using the freeze-pump-thaw method, 1.0×10^{-5} M (**2-12**) or 1.0×10^{-6} M (**13**) in cyclohexane. [f] Fluorescence maximum of excimer, saturated solution in aerated CH_2Cl_2. Excitation wavelength (λ_{ex}) is λ_{abs} in this Table. [g] Calculated by using B3LYP/3-21G. [h] Mulliken charge. [i] Data from ref 69. [j] Data from ref 57. [k] Not observed.

the absorption maxima suggest that HOMO energies increase with the increasing electron-donating abilities of the alkyl groups and with phenyl group promoted extension of π-conjugation. Disilane **9** exhibits the largest bathochromic shift into the visible light region owing to the presence of $\sigma^{(*)}$(Si-Si)-$\pi^{(*)}$(pyrene) conjugation.[71–74] The absorption maxima of the germyl and stannyl analogues appear at shorter wavelengths compared with those of the corresponding silyl compounds (GeMe$_3$ (**10**) < SnMe$_3$ (**12**) < SiMe$_3$ (**3**); SnPh$_3$ (**13**) < GePh$_3$ (**11**) < SiPh$_3$ (**8**)). This phenomena suggest that $\sigma^{(*)}$(Si-C)-$\pi^{(*)}$(pyrene) interactions more effectively extend π-conjugation of pyrene than those in the germyl and stannyl analogues.[53,54]

Inspection of fluorescence spectra of **1-13**, obtained using aerated 1.0×10^{-5} M CH$_2$Cl$_2$ solutions (Figure 3), shows that maxima shift to longer wavelengths in the same order as do shifts in the corresponding absorption maxima. Stokes shifts in the spectra of **2-13** are 6-12 nm, indicating that only small structural changes occur upon excitation. The fluorescence intensities of the silyl derivatives **2-9** are larger than that of **1**. Inspection of the fluorescence quantum yield (Φ_f) data, determined using degassed 1.0×10^{-5} M cyclohexane solutions, shows that emission efficiencies of silyl derivatives **2-9** (0.49-0.79) are larger than that of **1** (0.32) and that disilane **7** has the largest Φ_f (0.79). Moreover, the Φ_f of germyl derivatives **10** (0.20) and **11** (0.33) are smaller than those of the analogous silyl derivatives, and the emission efficiencies of
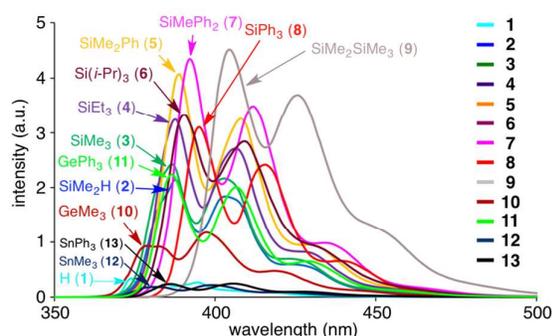
Figure 3. Fluorescence spectra of **1-13**, 1.0×10^{-5} M in aerated CH$_2$Cl$_2$. Excitation wavelengths (λ_{ex}) are λ_{abs} in Table 1.
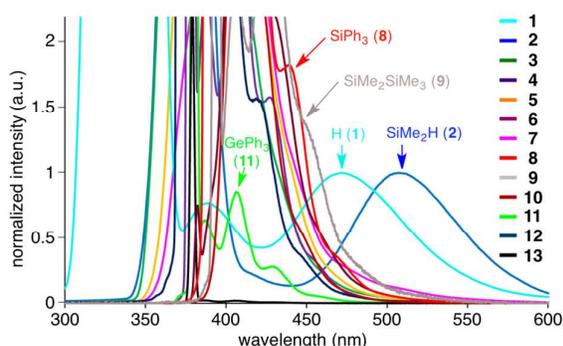
Figure 4. Fluorescence spectra of **1-13**, saturated concentration in aerated CH$_2$Cl$_2$. Excitation wavelengths (λ_{ex}) are λ_{abs} in Table 1.
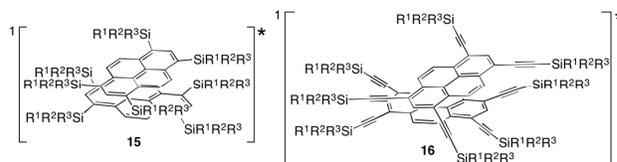
Figure 5. Possible structures of excimers.

the stannyl derivatives **12** (0.03) and **13** (0.03) are even lower. These results indicate that heavy atom effects in **12** and **13** enhance the rates of intersystem crossing from excited singlet state to excited triplet state.[75,76]

Pyrene (**1**) in highly concentrated solutions is known to fluoresce from excited dimer (excimer) at a longer wavelength than that of the monomer.[77–79] Accordingly, fluorescence spectra of **1-13** at saturated concentrations in aerated CH$_2$Cl$_2$ solutions were recorded (Figure 4). Most of these compounds do not display excimer emission, the single exception being the SiMe$_2$H substituted derivative **2** whose excimer emission maxima is 502 nm, which is 30 nm longer wavelength than that of **1** (472 nm).

There are some suggested structures of pyrene excimers, such as parallel or orthogonal, partial or full overlapped structures.[77–79] Although we do not have any evidence for the structures of excimers, we would like to suggest the structure like **15** as shown in Figure 5. Our recent study demonstrated that most of 1,3,6,8-tetrakis(silylethynyl)pyrenes emit fluorescence from excimer **16** in fluorescence measurement of their concentrated solutions.[68] However, this study clarified that observation of excimer fluorescence of tetrasilylpyrenes is very limited to only SiMe$_2$H derivative. The difference is explained as that steric bulk of silyl groups directly attached on pyrene prevents close approach of two molecules, with keeping parallel π-π interaction of two pyrene core, whereas steric bulk of silyl groups on **16** does not work so seriously to form excimers. This non-observation of excimer emission from tetrasilylpyrenes is a surprising result because even pyrene-core dendrimers are known to emit excimer fluorescence.[49,80]

Because pyrene (**1**) is an electron-rich aromatic hydrocarbon, it forms ground state charge-transfer (CT) complexes with electron deficient substances such as tetracyanoethylene (TCNE).[81,82] In this study, we investigated the ability of the tetrasilylpyrenes to form CT complexes with TCNE. The UV-vis-nir absorption spectra of individual 1.0×10^{-2} M CH$_2$Cl$_2$ solutions of **1**, **2**, **3**, **6** and TCNE do not contain absorption bands above 500 nm (Figure 6(a)). However, individual CH$_2$Cl$_2$ solutions of **1**, **2**, and **3** containing added TCNE display absorption bands ascribable to CT complexes (Figure 6(b)). In contrast, a CT related absorption band is not present in the spectrum of a CH$_2$Cl$_2$ solution of **6** containing TCNE. Moreover, the absorption maxima associated with the CT complexes of **1**, **2**, and **3** with TCNE shift to longer wavelengths in the order of pyrene (**1**, 719 nm) < SiMe$_2$H (**2**, 770 nm) < SiMe$_3$ (**3**, 814 nm). In addition, the spectra of solutions of TCNE and **1** and **3** contain second CT bands (**1** (495 nm) and **3** (531 nm)).[81] The colors of solutions containing **1**, **2**, and **3** along with TCNE are black, reddish brown, and pale purple, respectively (Figure 7).

These colors also indicate the formation of CT complexes. However, a CH_2Cl_2 solution of **6** remains colorless even after addition of TCNE. The wavelengths of absorption maxima, which reflect the stabilities of the CT complexes, correlate with electron-donating ability of pyrene derivatives and steric hindrance involved in formation of CT complexes. The experimental results outlined above show that the HOMO energies of the pyrene derivatives become higher in the order of **1** < **2** < **3**. This finding is consistent with the electropositive nature of silicon and the electron-donating character of silyl substituents. The inability of **6** to form a CT complex with TCNE is attributed to steric hindrance caused by the triisopropylsilyl groups.

With the aim of gaining information about the structural consequences of introducing silyl groups on the pyrene core, molecular orbital calculations were carried out by using the
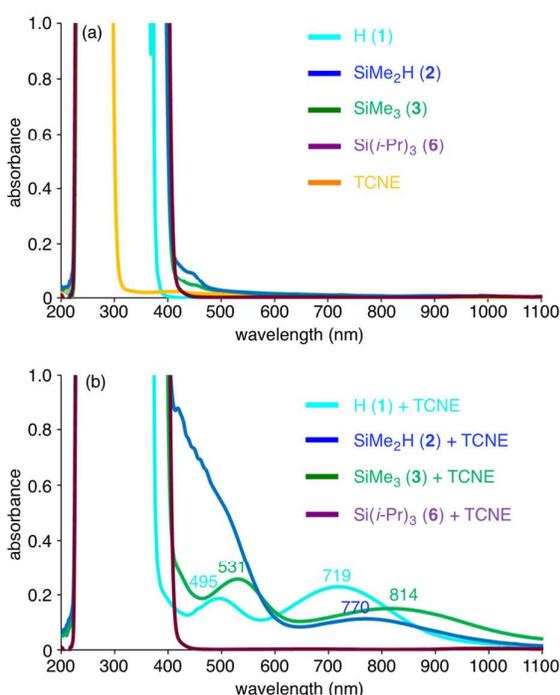
Figure 6. (a) UV-vis-nir absorption spectra of pyrene (**1**) and its derivatives (**2**, **3**, and **6**), 1.0×10^{-2} M in aerated CH_2Cl_2 solutions. (b) UV-vis-nir absorption spectra of mixed solutions of pyrene (**1**) and its derivatives (**2**, **3**, and **6**) with TCNE, 1.0×10^{-2} M each in aerated CH_2Cl_2 solutions.
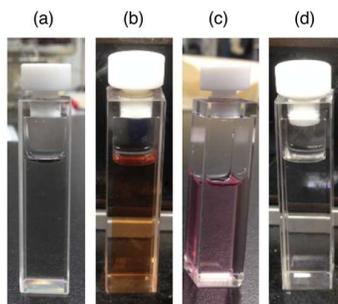
Figure 7. Colors of charge-transfer complexes of (a) **1** + TCNE, (b) **2** + TCNE, (c) **3** + TCNE, and (d) **6** + TCNE, 1.0×10^{-2} M each in aerated CH_2Cl_2 solutions.
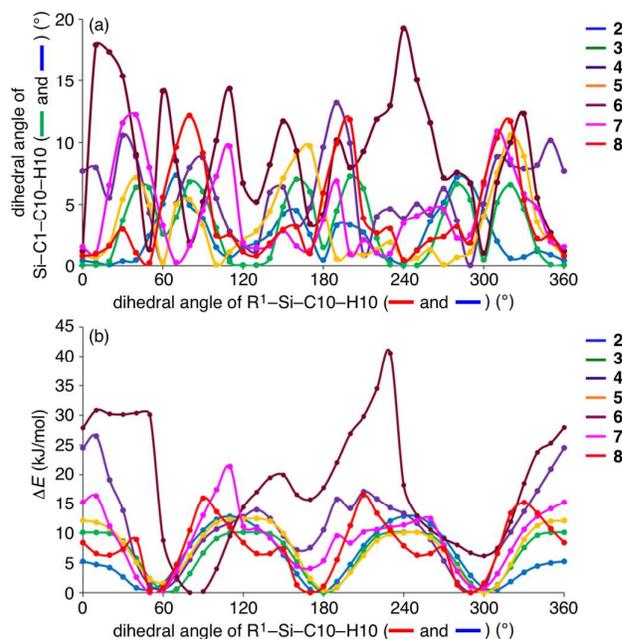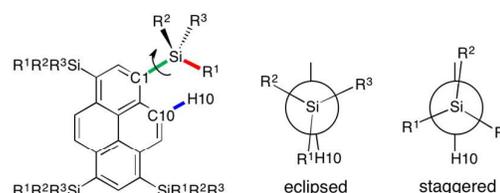
Figure 8. (a) Plots of Si–C1–C10–H10 dihedral angle vs R^1–Si–C10–H10 dihedral angle and (b) ΔE vs R^1–Si–C10–H10 dihedral angle, calculated on pyrene derivatives **2-8** using the B3LYP/3-21G basis set.

B3LYP/3-21G basis set. For this purpose, conformers arising from rotation in ten degree increments about the C1(pyrene)–Si bond (green bond in Figure 8) in each of the silyl substituted pyrenes **2-8** were subjected to geometry optimization. In Figure 8 are given plots of the dihedral angle about the Si–C1–C10–H10 bond (green and blue bonds in Figure 8) vs dihedral angle about the R^1–Si–C10–H10 bond (red and blue bonds) in the optimized structures, and of the relative energy differences (ΔE) vs the R^1–Si–C10–H10 dihedral angle in conformers arising from rotating the silyl substituent ($SiR^1R^2R^3$) by 360 degree. The maximum dihedral angles and ΔEs are listed in Table 2. Analysis of the results in Figure 8(a) demonstrates that the maximum Si–C1–C10–H10 dihedral angles increase with increasing steric bulk of the silyl substituent in each substituted pyrene. The case of $Si(i\text{-}Pr)_3$ derivative **6** is special in that a dihedral angle of 19.3 degrees is reached in the eclipsed conformer, and that this angle does not decrease to 0 degree even in the staggered conformer. In addition, inspection of the plots given in Figure 8(b) shows that conformers having the silyl groups staggered have lower energies than those in which they are eclipsed. Moreover the results show that the energy differences between high and low energy conformers depends on the size of silyl groups, especially for the $Si(i\text{-}Pr)_3$ derivative **6** which has the largest rotational barrier of 40.6 kJ/mol.

^{29}Si NMR spectroscopy was employed to explore the nature of silicon atoms in the silyl-substituted pyrenes (Table 3). The Si resonances are observed to shift up field as the number of phenyl groups increases (SiMe$_3$ (**3**) < SiMe$_2$Ph (**5**) < SiMePh$_2$ (**7**) < SiPh$_3$ (**8**)), and to shift downfield as the size of the alkyl groups increase (SiMe$_3$ (**3**) > SiEt$_3$ (**4**) > Si(*i*-Pr)$_3$ (**6**)). These results show that the electronegative (phenyl) and electropositive (alkyl) groups promote respective shielding and deshielding effects.[83,84]

HOMO and LUMO distributions and energies were calculated for the pyrene derivatives using the B3LYP/3-21G basis set (Table 1). The results show that the HOMO-LUMO energy gap decreases with increasing size of the alkyl groups and the number of phenyl groups. The existence of positive charge densities on the MR^{1}R^{2}R^3 groups indicates that silyl, germyl, and stannyl groups act as electron donors and that the electron donating ability decreases in the order of SiR$_3$ > GeR$_3$ > SnR$_3$. In contrast to results arising from calculations with the tetra-*tert*-butyl derivative **17**, when four SiMe$_3$ groups are bonded to the pyrene core, the HOMO and LUMO energies become lower and the gap between these molecular orbitals decreases (Figure 9). These phenomena are caused by control of the extension of conjugation by the nature of the silyl groups including (i) positive inductive (+I) effect caused by the electropositive character (low electronegativity) of silicon,[85,86] (ii) α effect promoted by σ*–π interactions,[87–89] and (iii) σ*–π* interaction that decreases LUMO energies.[54] The HOMO-

LUMO energy gaps are further decreased in Si(*i*-Pr)$_3$ (**6**) and SiPh$_3$ (**8**) derivatives because of the increase in the HOMO

Table 2. Maximum dihedral angles of silyl groups with peri-hydrogens and rotational barriers of silyl groups [a]

Compound	SiR^{1}R^{2}R^3	Dihedral angle[b] (°)	ΔE[c] (kJ/mol)
2	SiMe$_2$H	7.4	12.9
3	SiMe$_3$	7.3	10.2
4	SiEt$_3$	13.2	26.5
5	SiMe$_2$Ph	10.6	12.5
6	Si(*i*-Pr)$_3$	19.3	40.6
7	SiMePh$_2$	12.2	21.4
8	SiPh$_3$	12.2	16.5

[a] Calculated by B3LYP/3-21G. [b] Maximum dihedral angle for Si–C1–C10–H10 bond (green and blue bonds) while silyl group rotates 360° (Figure 8(a)). [c] Rotational barrier while silyl group rotates 360° (Figure 8(b)).

Table 3. ^{29}Si NMR chemical shifts[a]

Compound	SiR^{1}R^{2}R^3	δ (ppm)
2	SiMe$_2$H	−18.6 (^{1}J(Si-H) = 176.6 Hz)
3	SiMe$_3$	−6.6
4	SiEt$_3$	−4.2
5	SiMe$_2$Ph	−6.6
6	Si(*i*-Pr)$_3$	5.4
7	SiMePh$_2$	−9.3
8	SiPh$_3$	−13.5
9	SiMe$_2$SiMe$_3$	−21.2, −18.0

[a] 100 MHz in CDCl$_3$. SiMe$_4$ was used as an internal standard.
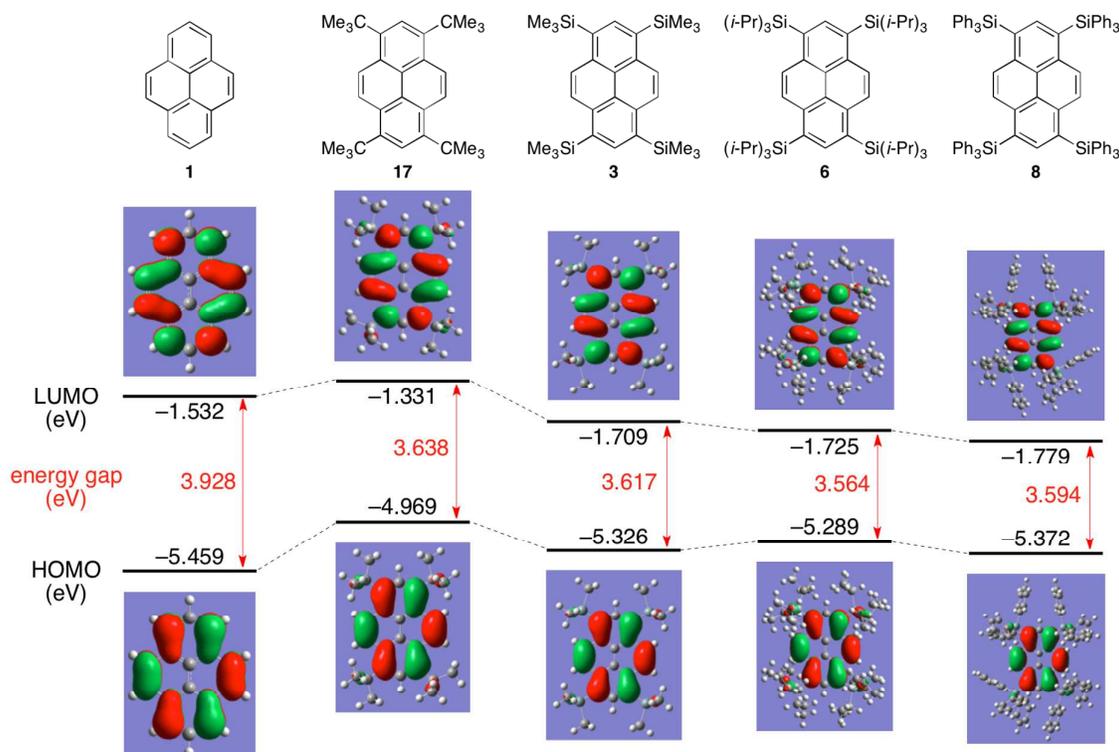
Figure 9. Molecular orbital distributions and energies of HOMO and LUMO levels calculated by using the B3LYP/3-21G basis set.

energy promoted by the electron donating character of the Si(*i*-Pr)$_3$ group, and extension of conjugation caused by the phenyl groups on silicon, respectively. The loss of planarity and large rotational barrier are found in calculation, however, it is concluded that they do not have large influence on the photophysical properties of pyrene.

Conclusions

In the above study, we synthesized 1,3,6,8-tetrasilylpyrenes **2-9**, and related germyl and stannyl substituted pyrene derivatives **10-13**. The UV-vis absorption spectra of these substances in 1.0×10^{-5} M CH$_2$Cl$_2$ solutions have absorption maxima that shift to longer wavelengths with increasing size of the alkyl groups and the number of phenyl groups on silicon. The fluorescence maxima of the pyrene derivatives display Stokes shifts of 6-12 nm and shift to longer wavelengths with increasing size of the silicon substituents and numbers of phenyl groups in the same manner as do the corresponding absorption maxima. Fluorescence quantum yields (Φ_f) of the silyl derivatives in degassed cyclohexane solutions are larger than that of pyrene, and the Φ_fs of the corresponding germyl and stannyl derivatives are lower than those of the silyl substituted pyrenes as a consequence of heavy atom effects on singlet to triplet intersystem crossing rates. The results of fluorescence studies show that these substances at saturated concentrations in CH$_2$Cl$_2$ do not exhibit excimer emission with the exception of **2**. Silyl substituted pyrenes **2** and **3** form colored CT complexes with TCNE in CH$_2$Cl$_2$ solutions. The results of theoretical calculations show that the barrier for rotation about Si-C bonds by 360 degree increases with increasing bulkiness of the silyl groups. The barrier for this process in the Si(*i*-Pr)$_3$ derivative **6** is estimated to be 40.6 kJ/mol and the planarity of pyrene core is partially lost. ^{29}Si NMR resonances in the spectra of the tetrasilylpyrenes shift upfield with increasing number of phenyl groups and downfield with increasing size of the alkyl groups. The calculated positive charge densities indicate that the silyl substituents act as electron-donating groups with decreasing donating abilities in the order of SiR$_3$ > GeR$_3$ > SnR$_3$. The combined results of this effort show that 1,3,6,8-tetrasilylpyrenes will be useful fluorescent materials because they have high fluorescence quantum yields and energy wasting excimer formation can be minimized by using bulky silicon substituents.

Experimental

Materials and equipment

THF was distilled from CaH$_2$ and then from Na. CH$_2$Cl$_2$ and cyclohexane were distilled from CaH$_2$. Other chemicals were used as purchased. Melting points were determined on a Gallenkamp MFB-595 melting point apparatus. ^{1}H and ^{13}C NMR spectra were recorded using a JEOL JMN LA-400 (400 MHz and 100 MHz, respectively) or a JEOL ECA-500 (500 MHz and 125 MHz, respectively) spectrometer with Me$_4$Si as an internal standard. ^{29}Si NMR spectra were recorded using a JEOL ECA-500 (100 MHz) spectrometer with Me$_4$Si as an internal standard. IR spectra were determined by using a Shimadzu FTIR-8300 spectrometer. UV-vis spectra were recorded using a Hitachi U-2900 spectrophotometer. Fluorescence spectra were recorded using a Hitachi F-2500 or a Jasco FP-8000 spectrophotometer. Low- and high-resolution mass spectra were recorded on a JEOL JMS-700 and JMS-SM102A instruments, respectively. HPLC separations were performed using recycling preparative HPLC instruments, Japan Analytical Industry Co. Ltd., LC-908 JAIGEL-H (GPC) column. Column chromatography was conducted by using Kanto-Chemical Co. Ltd., silica gel 60 N (spherical, neutral, 0.04-0.05 mm). Thin-layer chromatography was performed using Merck Kiesel gel 60 F$_{254}$ plate, and spots were detected by using UV light and phosphomolybdic acid ethanol solution with heating. Theoretical calculations using the B3LYP/3-21G basis set were performed by with the Gaussian 09 software package.

Preparation of 1,3,6,8-tetrabromopyrene (14)

To a stirred nitrobenzene (300 mL) solution of pyrene (**1**, 4.045 g, 20 mmol) was slowly added Br$_2$ (4.7 mL, 92 mmol). The resulting solution was stirred at 80 °C for 12 h and 1 M NaOH aq (150 mL) was added. The formed solid was washed with CHCl$_3$ to give 1,3,6,8-tetrabromopyrene (**14**, pale green solid, 10.065 g, 96% yield). Lit.[70] This substance was used without purification for further reactions.

Preparation of 1,3,6,8-tetrakis(dimethylsilyl)pyrene (2)

To a stirred THF (90 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.522 g, 1 mmol) and TMEDA (1.17 g, 10 mmol) was added dropwise *tert*-BuLi (1.6 M in pentane, 6.2 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Me$_2$HSiCl (1.09 g, 10 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H$_2$O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na$_2$SO$_4$, and concentrated in vacuo. Silica gel column chromatography (hexane) of the residue followed by HPLC (GPC) gave 1,3,6,8-tetrakis(dimethylsilyl)pyrene (**2**, 0.051 g, 12% yield). Colorless solid; mp 182 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.62 (d, J = 3.7 Hz, 24H), 5.08 (sept, J = 3.7 Hz, 4H), 8.41 (s, 2H), 8.43 (s, 4H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ −2.80, 124.28, 127.78, 132.26, 136.51, 138.70 ppm; ^{29}Si NMR (100 MHz, CDCl$_3$): δ −18.6 (^1J(Si-H) = 176.6 Hz) ppm; IR (KBr): 737, 1015, 2874 cm^{-1}; MS (EI): m/z (relative intensity, %) 375 (50), 434 (100, M$^+$); HRMS (EI): calcd for C$_{24}$H$_{34}$Si$_4$, 434.1738; found, 434.1745.

Preparation of 1,3,6,8-tetrakis(trimethylsilyl)pyrene (3)

To a stirred THF (100 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.518 g, 1 mmol) and TMEDA (1.17 g, 10 mmol) was added dropwise *tert*-BuLi (1.6 M in pentane, 6.2 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred

ARTICLE

for 1 h at −78 °C. Me₃SiCl (1.10 g, 10 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H₂O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na₂SO₄, and concentrated in vacuo. The solid was washed with hexane to give 1,3,6,8-tetrakis(trimethylsilyl)pyrene (**3**, 0.137 g, 28% yield). Lit.[57]

Preparation of 1,3,6,8-tetrakis(triethylsilyl)pyrene (4)

To a stirred THF (75 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.517 g, 1 mmol) and TMEDA (1.11 g, 10 mmol) was added dropwise *tert*-BuLi (1.6 M in pentane, 6.2 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Et₃SiCl (1.53 g, 10 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H₂O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography (hexane) of the residue followed by HPLC (GPC) gave 1,3,6,8-tetrakis(triethylsilyl)pyrene (**4**, 0.272 g, 41% yield). Pale yellow solid; mp 272 °C (dec); ^{1}H NMR (400 MHz, CDCl₃): δ 1.03 (t, J = 7.1 Hz, 36H), 1.15 (q, J = 8.1 Hz, 24H), 8.32 (s, 2H), 8.33 (s, 4H) ppm; ^{13}C NMR (400 MHz, CDCl₃): δ 1.02, 5.00, 7.80, 125.00, 127.55, 131.03, 136.66, 140.28 ppm; ^{29}Si NMR (100MHz, CDCl₃): δ −4.2 ppm; IR (KBr): 1250, 2137, 2955 cm^{-1}; MS (EI): m/z (relative intensity, %) 658 (100, M⁺); HRMS (EI): calcd for $C_{40}H_{66}Si_4$, 658.4242; found, 658.4239.

Preparation of 1,3,6,8-tetrakis(dimethylphenylsilyl)pyrene (5)

To a stirred THF (90 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 1.039 g, 2 mmol) and TMEDA (2.10 g, 20 mmol) was added dropwise *tert*-BuLi (1.6 M in pentane, 12.4 mL, 20 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Me₂PhSiCl (3.33 g, 20 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H₂O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography (CHCl₃:hexane = 1:1) of the residue followed by recrystallization from hexane:CH₂Cl₂ = 1:1 gave 1,3,6,8-tetrakis(dimethylphenylsilyl)pyrene (**5**, 0.254 g, 17% yield). Colorless solid; mp 230 °C; ^{1}H NMR (400 MHz, CDCl₃): δ 0.73 (s, 24H), 7.28-7.37 (m, 12H), 7.52-7.54 (m, 8H), 8.11 (s, 4H), 8.35 (s, 2H) ppm; ^{13}C NMR (400 MHz, CDCl₃): δ −0.52, 124.76, 127.86, 128.44, 129.03, 131.99, 134.25, 136.70, 138.97, 140.61 ppm; ^{29}Si NMR (100 MHz, CDCl₃): δ −6.6 ppm; IR (KBr): 698, 833, 1250 cm^{-1}; MS (EI): m/z (relative intensity, %) 660 (25), 738 (100, M⁺); HRMS (EI): calcd for $C_{48}H_{50}Si_4$, 738.2990; found, 738.2989.

Preparation of 1,3,6,8-tetrakis(triisopropylsilyl)pyrene (6)

To a stirred THF (50 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.777 g, 1.5 mmol) and TMEDA (1.80 g, 15 mmol) was added dropwise *tert*-BuLi (1.61 M in pentane, 9.32 mL, 15 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. *i*-Pr₃SiCl (12.84 g, 15 mmol) was slowly added at −78

°C, and the solution was stirred at rt for 16 h. H₂O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography (hexane) of the residue followed by recrystallization from CHCl₃ gave 1,3,6,8-tetrakis(triisopropylsilyl)pyrene (**6**, 0.185 g, 15% yield). Colorless solid; mp 302 °C (dec); ^{1}H NMR (400 MHz, CDCl₃): δ 1.20 (d, J = 7.6 Hz, 72H), 1.80 (sept, J = 7.4 Hz, 12H), 8.29 (s, 4H), 8.47 (s, 4H) ppm; ^{13}C NMR (400 MHz, CDCl₃): δ 13.27, 19.23, 125.43, 128.37, 129.95, 137.09, 141.86 ppm; ^{29}Si NMR (100 MHz, CDCl₃): δ 5.4 ppm; IR (KBr): 706, 883, 2866, 2947 cm^{-1}; MS (EI): m/z (relative intensity, %) = 59 (100), 207 (8), 827 (8, M⁺); HRMS (EI): calcd for $C_{52}H_{90}Si_4$, 827.6198; found, 827.6205.

Preparation of 1,3,6,8-tetrakis(methyldiphenylsilyl)pyrene (7)

To a stirred THF (80 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.520 g, 1 mmol) and TMEDA (1.16 g, 10 mmol) was added dropwise *tert*-BuLi (1.6 M in pentane, 6.2 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. MePh₂SiCl (2.30 g, 10 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H₂O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography (CHCl₃:hexane = 1:9) of the residue followed by HPLC (GPC) gave 1,3,6,8-tetrakis(methyldiphenylsilyl)pyrene (**7**, 0.156 g, 16% yield). Colorless solid; mp 265 °C; ^{1}H NMR (400 MHz, CDCl₃): δ 0.84 (s, 12H), 7.24 (t, J = 7.3 Hz, 16H), 7.33 (t, J = 7.4 Hz, 8H), 7.45 (d, J = 6.6 Hz, 16H), 8.01 (s, 4H), 8.12 (s, 2H) ppm; ^{13}C NMR (400 MHz, CDCl₃): δ −1.56, 124.64, 127.85, 129.07, 129.27, 130.56, 135.24, 136.53, 137.20, 143.31 ppm; ^{29}Si NMR (100 MHz, CDCl₃): δ −9.3 ppm; IR (KBr): 829, 1427, 3047 cm^{-1}; MS (EI): m/z (relative intensity, %) 197 (100), 987 (4, M⁺); HRMS (EI): calcd for $C_{68}H_{58}Si_4$, 987.3694; found, 987.3681.

Preparation of 1,3,6,8-tetrakis(triphenylsilyl)pyrene (8)

To a stirred THF (90 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.520 g, 1 mmol) and TMEDA (1.25 g, 10 mmol) was added dropwise *tert*-BuLi (1.6 M in pentane, 6.2 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Ph₃SiCl (4.66 g, 15 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H₂O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na₂SO₄, and concentrated in vacuo. Silica gel column chromatography (CHCl₃:hexane = 1:2) of the residue followed by HPLC (GPC) gave 1,3,6,8-tetrakis(triphenylsilyl)pyrene (**8**, 0.038 g, 3% yield). Colorless solid; mp 215 °C (dec); ^{1}H NMR (400 MHz, CDCl₃): δ 7.16 (t, J = 7.6 Hz, 24H), 7.29 (t, J = 7.4 Hz, 12H), 7.40 (d, J = 6.6 Hz, 24H), 7.87 (s, 4H), 8.16 (s, 2H) ppm; ^{13}C NMR (400 MHz, CDCl₃): δ 124.41, 127.75, 129.32, 129.96, 134.62, 136.24, 137.73, 145.18 ppm; ^{29}Si NMR (100 MHz, CDCl₃): δ −13.5 ppm; IR (KBr): 698,

1107, 3067 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 259 (100), 1235 (2, M$^+$); HRMS (EI): calcd for C$_{88}$H$_{66}$Si$_4$, 1235.4320; found, 1235.4333.

Preparation of 1,3,6,8-tetrakis(pentamethyldisilyl)pyrene (9)

To a stirred THF (80 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.518 g, 1 mmol) and TMEDA (1.32 g, 10 mmol) was added dropwise *tert*-BuLi (1.77 M in pentane, 5.65 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Me$_3$SiMe$_2$SiCl (1.55 mL, 8 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H$_2$O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na$_2$SO$_4$, and concentrated in vacuo. The solid was washed with hexane and acetone to give 1,3,6,8-tetrakis(pentamethyldisilyl)pyrene (**9**, 0.146 g, 20% yield). Colorless solid; mp 232 °C; ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.11 (s, 36H), 0.65 (s, 24H), 8.22 (s, 4H), 8.26 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ −1.90, −1.54, 124.68, 127.81, 134.06, 136.10, 138.37 ppm; ^{29}Si NMR (100 MHz, CDCl$_3$): δ −21.2, −18.0 ppm; IR (KBr): 795, 826, 1246, 2947 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 415 (72), 503 (56), 722 (100, M$^+$); HRMS (EI): calcd for C$_{36}$H$_{66}$Si$_8$, 772.3319; found, 722.3328.

Preparation of 1,3,6,8-tetrakis(trimethylgermyl)pyrene (10)

To a stirred THF (80 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.518 g, 1 mmol) and TMEDA (1.25 g, 10 mmol) was added dropwise *tert*-BuLi (1.77 M in pentane, 5.65 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Me$_3$GeCl (1.0 g, 6.53 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H$_2$O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na$_2$SO$_4$, and concentrated in vacuo. The solid was washed with hexane to give 1,3,6,8-tetrakis(trimethylgermyl)pyrene (**10**, 0.255 g, 38% yield). Colorless solid; mp 340 °C (dec); ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.70 (s, 36H), 8.22 (s, 4H), 8.28 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 0.18, 125.50, 127.70, 135.32, 136.19, 137.07 ppm; IR (KBr): 822, 1238, 2970 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 320 (28), 655 (93), 670 (100, M$^+$); HRMS (EI): calcd for C$_{28}$H$_{42}$Ge$_4$, 670.0152; found, 670.0137.

Preparation of 1,3,6,8-tetrakis(triphenylgermyl)pyrene (11)

To a stirred THF (60 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.210 g, 0.40 mmol) and TMEDA (0.52 g, 4 mmol) was added dropwise *tert*-BuLi (1.61 M in pentane, 2.48 mL, 4 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Ph$_3$GeCl (1.17 g, 3.45 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H$_2$O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na$_2$SO$_4$, and concentrated in vacuo. The residue was treated with acetone, CHCl$_3$, and hexane to give solid. The solid was washed with CHCl$_3$ to give 1,3,6,8-tetrakis(triphenylgermyl)pyrene (**11**, 0.026 g, 5% yield).

Colorless solid; mp 234 °C (dec); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.18 (t, *J* = 7.4 Hz, 24H), 7.29 (t, *J* = 7.6 Hz, 12H), 7.39 (d, *J* = 6.8 Hz, 24H), 7.90 (s, 4H), 8.18 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 125.00, 128.13, 128.88, 129.69, 132.15, 135.25, 136.59, 136.78, 142.40 ppm; IR (KBr): 698, 1431, 3067 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 154 (100), 288 (27).

Preparation of 1,3,6,8-tetrakis(trimethylstannyl)pyrene (12)

To a stirred THF (70 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.520 g, 1 mmol) and TMEDA (1.21 g, 10 mmol) was added dropwise *tert*-BuLi (1.77 M in pentane, 5.65 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Me$_3$SnCl (1.91 g, 10 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H$_2$O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na$_2$SO$_4$, and concentrated in vacuo. The solid was washed with hexane. Recrystallization from acetone-hexane gave 1,3,6,8-tetrakis(trimethylstannyl)pyrene (**12**, 0.508 g, 60% yield). Colorless solid; mp 229 °C (dec); ^{1}H NMR (400 MHz, CDCl$_3$): δ 0.55 (s, 36H), 8.02 (s, 4H), 8.30 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ −8.06, 125.72, 129.74, 137.17, 139.12, 141.27 ppm; IR (KBr): 768, 1531, 2978 cm^{-1}; MS (EI): *m/z* (relative intensity, %) 165 (88), 675 (62), 839 (100), 854 (87, M$^+$); HRMS (EI): calcd for C$_{28}$H$_{42}$Sn$_4$, 853.9363; found, 853.9315.

Preparation of 1,3,6,8-tetrakis(triphenylstannyl)pyrene (13)

To a stirred THF (70 mL) solution of 1,3,6,8-tetrabromopyrene (**14**, 0.520 g, 1 mmol) and TMEDA (1.18 g, 10 mmol) was added dropwise *tert*-BuLi (1.77 M in pentane, 5.65 mL, 10 mmol) over 15 min at −78 °C. The solution was stirred for 1 h at −78 °C. Ph$_3$SnCl (2.31 g, 6 mmol) was slowly added at −78 °C, and the solution was stirred at rt for 16 h. H$_2$O (100 mL) was then added and the mixture was extracted with EtOAc (100 mL × 3). The combined organic layers were washed with brine (100 mL × 3) dried over Na$_2$SO$_4$, and concentrated in vacuo. The solid was washed with THF. Silica gel column chromatography (CHCl$_3$) gave solid which was then washed with acetone to give 1,3,6,8-tetrakis(triphenylstannyl)pyrene (**13**, 0.489 g, 31% yield). Colorless solid; mp 305 °C (dec); ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.17 (t, *J* = 7.2 Hz, 24H), 7.29 (t, *J* = 7.2 Hz, 12H), 7.40 (d, *J* = 6.8 Hz, 24H), 7.87 (s, 4H), 8.16 (s, 2H) ppm; ^{13}C NMR (100 MHz, CDCl$_3$): δ 128.59, 137.21 ppm; IR (KBr): 698, 1427, 3063 cm^{-1}; MS (EI): *m/z* (relative intensity, %) = 119 (75).

Fluorescence quantum yields

Cyclohexane solutions of **2-12** (1.0 × 10^{-5} M), **13** (1.0 × 10^{-6} M, because of low solubility) and **3** (1.0 × 10^{-6} M) were degassed by using freeze-pump-thaw cycles. Fluorescence spectra were recorded at 298 K using a 1 cm path length cell. Fluorescence quantum yields (Φ_f) of **2** and **4-13** were determined by using **3** as a standard with a known Φ_f of 0.56 in cyclohexane.[57] The Φ_fs were calculated employing the equation

$$\Phi_f(spl) = \Phi_f(std) \times [I(spl)/I(std)] \times [A(std)/A(spl)]$$

ARTICLE

where Φ_f(spl) and Φ_f(std) are the fluorescence quantum yields of the sample and standard, respectively, I(spl) and A(spl) are integrated fluorescence intensities obtained from spectra in which the horizontal axis is converted from wavelength to wavenumber, and the absorbance at excitation wavelength (λ_{ex}). I(std) and A(std) are those of the standard. Excitation wavelengths (λ_{ex}) and concentrations of solutions of sample and standard were identical in each determination. λ_{ex}s used for each determination were 335 (**2**, **4**, **5**, **7**, **8**), 350 (**9-13**), and 378 (**6**) nm.

Acknowledgements

References

1   M. G. Steinmetz, Organosilane Photochemistry, *Chem. Rev.*, 1995, **95**, 1527–1588.
2   S. Kyushin, M. Ikarugi, M. Goto, H. Hiratsuka and H. Matsumoto, Synthesis and Electronic Properties of 9,10-Disilylanthracenes, *Organometallics*, 1996, **15**, 1067–1070.
3   S. Yamaguchi, S. Akiyama and K. Tamao, Synthesis, Structures, Photophysical Properties, and Dynamic Stereochemistry of Tri-9-anthrylsilane Derivatives, *Organometallics*, 1998, **17**, 4347–4352.
4   T. Karatsu, T. Shibata, A. Nishigaki, K. Fukui and A. Kitamura, π–π and σ–π Interactions in α,ω-Dinaphthyl and -Dianthryl Oligosilanes in Solution, *Chem. Lett.*, 2001, **30**, 994–995.
5   S. Kyushin, N. Takemasa, H. Matsumoto, H. Horiuchi and H. Hiratsuka, 2,3,6,7,10,11-Hexakis(dimethylsilyl)triphenylene, *Chem. Lett.*, 2003, **32**, 1048–1049.
6   T. Karatsu, T. Shibata, A. Nishigaki, A. Kitamura, Y. Hatanaka, Y. Nishimura, S. Sato and I. Yamazaki, π–π and σ–π Interactions in α,ω-Di-(9-anthryl) and Di-(1-naphthyl) Oligosilanes Studied by Time-Resolved Fluorescence in Solution, *J. Phys. Chem. B*, 2003, **107**, 12184–12191.
7   T. Karatsu, M. Terasawa, S. Yagai, A. Kitamura, T. Nakamura, Y. Nishimura and I. Yamazaki, Time-resolved fluorescence of α-(9-anthryl)-ω-(1-naphthyl)-oligosilanes: intramolecular electronic energy and charge transfer through π–π and σ–π interactions, *J. Organomet. Chem.*, 2004, **689**, 1029–1035.
8   T. Karatsu, R. Hazuku, D. Nishioka, S. Yagai, N. Kobayashi and A. Kitamura, Photoluminescence and Electroluminescence of 9,10-Bis(silylethynyl)anthracene, *J. Photopolym. Sci. Tech.*, 2005, **18**, 65–68.
9   S. Kyushin, Y. Ishikita, H. Matsumoto, H. Horiuchi and H. Hiratsuka, Yellow-green Fluorescence of 5,11- and 5,12-Bis(diisopropylsilyl)naphthacenes, *Chem. Lett.*, 2006, **35**, 64–65.

10 S. Kyushin, T. Matsuura and H. Matsumoto, 2,3,4,5-Tetrakis(dimethylsilyl)thiophene: The First 2,3,4,5-Tetrasilylthiophene, *Organometallics*, 2006, **25**, 2761–2765.
11 T. Karatsu, R. Hazuku, M. Asuke, A. Nishigaki, S. Yagai, Y. Suzuri, H. Kita and A. Kitamura, Blue electroluminescence of silyl substituted anthracene derivatives, *Org. Electron.*, 2007, **8**, 357–366.
12 K. Asai, G. Konishi, Y. Nakajima, S. Kawauchi, F. Ozawa and K. Mizuno, Enhanced absorption and fluorescence efficiency of silylethynyl-functionalized oligothiophenes and thieno[3,2–b]thiophene, *J. Organomet. Chem.*, 2011, **696**, 1266–1271.
13 Y. Hakoda, M. Aoyagi, K. Irisawa, S. Kato, Y. Nakamura and M. Yamaji, Photochemical synthesis and photophysical features of ethynylphenanthrenes studied by emission and transient absorption measurements, *Photochem. Photobiol. Sci.*, 2016, **15**, 1586–1593.
14 F. Xu, T. Nishida, K. Shinohara, L. Peng, M. Takezaki, T. Kamada, H. Akashi, H. Nakamura, K. Sugiyama, K. Ohta, A. Orita and J. Otera, Trimethylsilyl Group Assisted Stimuli Response: Self-Assembly of 1,3,6,8-Tetrakis((trimethylsilyl)ethynyl)pyrene, *Organometallics*, 2017, **36**, 556–563.
15 A. P. de Silva, H. Q. N. Gunaratne, T. Gunnlaugsson, A. J. M. Huxley, C. P. McCoy, J. T. Rademacher and T. E. Rice, Signaling Recognition Events with Fluorescent Sensors and Switches, *Chem. Rev.*, 1997, **97**, 1515–1566.
16 S. Karuppannan and J.-C. Chambron, Supramolecular Chemical Sensors Based on Pyrene Monomer–Excimer Dual Luminescence, *Chem. Asian J.*, 2011, **6**, 964–984.
17 E. Manandhar and K. J. Wallace, Host–guest chemistry of pyrene-based molecular receptors, *Inorg. Chim. Acta*, 2012, **381**, 15–43.
18 J. J. Bryant and U. H. F. Bunz, Click To Bind: Metal Sensors, *Chem. Asian J.*, 2013, **8**, 1354–1367.
19 T. Moriguchi, M. Hattori, T. Sekiguchi, M. Ichimura, T. Kato and K. Shinozuka, Synthesis and Properties of Oligonucleotides Containing Silylated Pyrene Derivatives, *Nucleic Acids Symposium Series*, 2008, **52**, 255–256.
20 T. Moriguchi, M. Ichimura, M. Kato, K. Suzuki, Y. Takahashi and K. Shinozuka, Development of the excimer probe responsible for DNA target bearing the silylated pyrenes at base moiety, *Bioorg. Med. Chem. Lett.*, 2014, **24**, 4372–4375.
21 T. Moriguchi, D. Moki, T. Sekiguchi, T. Kato and K. Shinozuka, Synthesis and Properties of Novel Fluorescently Labeled Oligonucleotides Possessing Silylated Pyrene at the 5'-Terminus, *Chem. Lett.*, 2015, **44**, 44–46.
22 K. Shinozuka, T. Sekiguchi, Y. Ebara and T. Moriguchi, Synthesis, Duplex-forming Ability and Fluorescent Property of OligoDNA Bearing Silylated Fluorophore, *Nucleic Acids Symposium Series*, 2007, **51**, 7–8.
23 T. Sekiguchi, Y. Ebara, T. Moriguchi and K. Shinozuka, Novel sequence-responding fluorescent oligoDNA probe bearing a silylated pyrene molecule, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 6883–6886.
24 M. Mogi, Md. G. Uddin, M. Ichimura, T. Moriguchi and K. Shinozuka, Modified OligoDNA Having Two Consecutive Silylated-pyrene Moieties in Minor Groove Exhibiting an Excimer Fluorescent Siganl upon Binding to Fully Complementary DNA Strand, *Chem. Lett.*, 2010, **39**, 1254–1255.
25 Md. G. Uddin, T. Moriguchi, M. Ichimura and K. Shinozuka, Synthesis and Properties of Molecular Beacon DNA Probe Bearing Novel Silylated Pyrene Derivative, *Key Eng. Mater.*, 2012, **497**, 47–50.
26 Md. G. Uddin and A. T. M. Z. Azam, A Novel Oligo-DNA Probe Carrying Non-nucleosidic Silylated Pyrene Derivatives: Synthesis and Excimer Forming Ability, *Am. J. Biochem. Mol. Biol.*, 2013, **3**, 175–181.

27 T. Moriguchi, S. Hida, F. Yoneda and K. Shinozuka, Synthesis and Spectroscopic Properties of a Novel Bifunctional Pyrene Derivative and its Incorporation into OligoDNA, *Aust. J. Chem.*, 2014, **68**, 256–259.

28 J. A. Chowdhury, T. Moriguchi and K. Shinozuka, Pseudo-Dumbbell-Type Molecular Beacon Probes Bearing Modified Deoxyuridine Derivatives and a Silylated Pyrene as a Fluorophore, *Bull. Chem. Soc. Jpn.*, 2015, **88**, 496–502.

29 T. Moriguchi, M. Hosaka, A. Yoshinari, A. Ozaki, T. Takeuchi and K. Shinozuka, Cholesterol Analogs Labeled with Novel Silylated Fluorescent Compounds, *Chem. Lett.*, 2009, **38**, 966–967.

30 M. J. Sung, H. Chubachi, R. Sato, M.-K. Shin, S.-K. Kwon, Y.-J. Pu and Y.-H. Kim, Dimethylsilyl-linked anthracene-pyrene dimers and their efficient triplet-triplet annihilation in organic light emitting diodes, *J. Mater. Chem. C*, 2017, **5**, 1090–1094.

31 S. Koga, S. Ueki, M. Shimada, R. Ishii, Y. Kurihara, Y. Yamanoi, J. Yuasa, T. Kawai, T. Uchida, M. Iwamura, K. Nozaki and H. Nishihara, Access to Chiral Silicon Centers for Application to Circularly Polarized Luminescence Materials, *J. Org. Chem.*, 2017, **82**, 6108–6117.

32 M. Taki, S. Azeyanagi, K. Hayashi and S. Yamaguchi, Color-tunable fluorescent nanoparticles encapsulating trialkylsilyl-substituted pyrene liquids, *J. Mater. Chem. C*, 2017, **5**, 2142–2148.

33 S. Kondo, Y. Bie and M. Yamamura, Ratiometric Fluorescence Detection of Anions by Silanediol-based Receptors Bearing Anthryl and Pyrenyl Groups, *Org. Lett.*, 2013, **15**, 520–523.

34 S. Kondo, Y. Taguchi and Y. Bie, Solvent dependent intramolecular excimer emission of di(1-pyrenyl)silane and di(1-pyrenyl)methane derivatives, *RSC Adv.*, 2015, **5**, 5846–5849.

35 Y. Yamauchi and M. Fujita, Self-assembled cage as an *endo*-template for cyclophane synthesis, *Chem. Commun.*, 2010, **46**, 5897–5899.

36 K. Imai, S. Hatano, A. Kimoto, J. Abe, Y. Tamai and N. Nemoto, Optical and electronic properties of siloxane-bridged cyclic dimers with naphthylene or pyrenylene moieties, *Tetrahedron*, 2010, **66**, 8012–8017.

37 D. Declercq, F.C. De Schryver and R.D. Miller, Fluorescence behaviour of pyrene substituted tri- and hexa-silanes, *Chem. Phys. Lett.*, 1991, **186**, 467–473.

38 D. Declercq, P. Delbeke, F. C. De Schryver, L. Van Meervelt and R. D. Miller, Ground- and Excited-State Interaction in Di-1-pyrenyl-Substituted Oligosilanes, *J. Am. Chem. Soc.*, 1993, **115**, 5702–5708.

39 F. C. De Schryver, D. Declercq, S. Depaemelaere, E. Hermans, A. Onkelinx, J. W. Verhoeven and J. Gelan, Photophysics of linked donor–acceptor systems: through-space and through-bond interactions, *J. Photochem. Photobiol. A*, 1994, **82**, 171–179.

40 J. Gelan, P. Adriaensens, D. Vanderzande, D. Declercq, E. Hermans and F. C. De Schryver, Full ^{1}H and ^{13}C NMR Chemical Shift Assignment of 1-Pyrenyl Substituted Oligosilanes as a Tool To Differentiate between Intramolecular "Through Space" and "Through Bond" Ground State Interactions, *J. Am. Chem. Soc.*, 1994, **116**, 7877–7884.

41 L. Gherghel, M. Baumgarten, D. Declerq and F. C. De Schryver, The radical anions of silyl-substituted pyrenes and silyl-bridged dipyrenes, *Chem. Phys. Lett.*, 1995, **232**, 567–570.

42 E. Hermans, F. C. De Schryver, G. B. Dutt, J. van Stam, S. De Feyter, N. Boens and R. D. Miller, Global compartmental analysis of the fluorescence decay surface of intramolecular chain mediated and through space excited-state complex formation of a silane linked donor-acceptor system, *New J. Chem.*, 1996, **20**, 829–838.

43 C. A. van Walree, V. E. M. Kaats-Richters, L. W. Jenneskens, R. M. Williams and I. H. M. van Stokkum, Intramolecular excimer and exciplex emission of 1,4-dipyrenyl substituted cyclohexasilane, *Chem. Phys. Lett.*, 2002, **355**, 65–70.

44 V. E. M. Kaats-Richters, T. J. Cleij, L. W. Jenneskens, M. Lutz, A. L. Spek and C. A. van Walree, Synthesis and Structure of *cis*-1,4-Di(1-pyrenyl)decamethylcyclohexasilane, *Organometallics*, 2003, **22**, 2249–2258.

45 H. Wang, Z. Zhu, B. Zhang, Y. Cao and C. Tung, Twisted intramolecular charge transfer in polydimethylsilylene bearing pyrenyl groups, *Chin. Chem. Lett.*, 1991, **2**, 135–138.

46 H. Wang, Z.-Y. Zhu, B.-W. Zhang, Y. Cao and C.-H. Tung, Photophysical behaviour of polydimethylsilylene-bearing pyrenyl groups, *J. Photochem. Photobiol. A*, 1992, **63**, 33–44.

47 B. M. Moore, S. M. Ramirez, G. R. Yandek, T. S. Haddad and J. M. Mabry, Asymmetric aryl polyhedral oligomeric silsesquioxanes (ArPOSS) with enhanced solubility, *J. Organomet. Chem.*, 2011, **696**, 2676–2680.

48 G. R. Yandek, B. M. Moore, S. M. Ramirez and J. M. Mabry, Effects of Peripheral Architecture on the Properties of Aryl Polyhedral Oligomeric Silsesquioxanes, *J. Phys. Chem. C*, 2012, **116**, 16755–16765.

49 A. G. Vitukhnovsky, M. I. Sluch, V. G. Krasovskii and A. M. Muzafarov, Study of polyallylcarbosilane dendrimer structure by pyrenyl excimer formation, *Synth. Met.*, 1997, **91**, 375–377.

50 T. Lee, I. Jung, K. H. Song, C. Baik, S. Kim, D. Kim, S. O. Kang and J. Ko, Highly Efficient Hydrosilylation of Diyne and Triyne π-Electron Bridges: Its Application to Fluorescent Dyes and Silylene-Spaced Vinylarene Compounds, *Organometallics*, 2004, **23**, 4184–4191.

51 K. Imai, T. Sasaki, J. Abe and N. Nemoto, Synthesis and properties of poly(tetramethyl-1,6-silpyrenylenesiloxane) derivative with phenyl groups on pyrenylene moiety, *Polym. Bull.*, 2012, **68**, 1589–1601.

52 Y. Niko, S. Sasaki, S. Kawauchi, K. Tokumaru and G. Konishi, Design of Weak-Donor Alkyl-Functionalized Push–Pull Pyrene Dyes Exhibiting Enhanced Fluorescence Quantum Yields and Unique On/Off Switching Properties, *Chem. Asian J.*, 2014, **9**, 1797–1807.

53 D.-D. H. Yang, N. C. Yang, I. M. Steele, H. Li, Y.-Z. Ma and G. R. Fleming, Photochemistry of Dianthrylsilanes: A Study of σ,π^*-Interaction, *J. Am. Chem. Soc.*, 2003, **125**, 5107–5110.

54 Y. Niko, S. Kawauchi, S. Otsu, K. Tokumaru and G. Konishi, Fluorescence Enhancement of Pyrene Chromophores Induced by Alkyl Groups through $\sigma-\pi$ Conjugation: Systematic Synthesis of Primary, Secondary, and Tertiary Alkylated Pyrenes at the 1, 3, 6, and 8 Positions and Their Photophysical Properties, *J. Org. Chem.*, 2013, **78**, 3196–3207.

55 H. Shizuka, Y. Sato, Y. Ueki, M. Ishikawa and M. Kumada, The $2p\pi^*-3d\pi$ Interaction in Aromatic Silanes. Fluorescence from the $^1(2p\pi, 3d\pi)$ Intramolecular Charge-transfer State, *J. Chem. Soc. Faraday Trans. 1*, 1984, **80**, 341–357.

56 M. Kobayashi, N. Hayakawa, T. Matsuo, B. Li, T. Fukunaga, D. Hashizume, H. Fueno, K. Tanaka and K. Tamao, (*Z*)-1,2-Di(1-pyrenyl)disilene: Synthesis, Structure, and Intramolecular Charge-Transfer Emission, *J. Am. Chem. Soc.*, 2016, **138**, 758–761.

57 H. Maeda, H. Ishida, Y. Inoue, A. Merpuge, T. Maeda and K. Mizuno, UV absorption and fluorescence properties of fused aromatic hydrocarbons having terimethylsilyl, trimethylgermyl, and trimethylstannyl groups, *Res. Chem. Intermed.*, 2009, **35**, 939–948.

58 H. Maeda, T. Maeda and K. Mizuno, Absorption and Fluorescence Spectroscopic Properties of 1- and 1,4-Silyl-Substituted Naphthalene Derivatives, *Molecules*, 2012, **17**, 5108–5125.

59 M. Yamaji, H. Maeda, K. Minamida, T. Maeda, K. Asai, G.-I. Konishi and K. Mizuno, Emission and transient absorption measurements of substitution effects of C–C triple bonds on relaxation processes of the fluorescent state of naphthalenes, *Res. Chem. Intermed.*, 2013, **39**, 321–345.

60 H. Maeda, T. Fujii, K. Minamida and K. Mizuno, Fluorescence properties of 1-(silylethynyl)naphthalenes and 1,4-bis(silylethynyl)naphthalenes in solutions, thin films and solid states, *J. Photochem. Photobiol. A*, 2017, **342**, 153–160.

61 M. Yamaji, H. Maeda, Y. Nanai and K. Mizuno, Substitution effects of C–C triple bonds on the fluorescent properties of perylenes studied by emission and transient absorption measurements, *Chem. Phys. Lett.*, 2012, **536**, 72–76.

62 H. Maeda, K. Nishimura, K. Mizuno, M. Yamaji, J. Oshima and S. Tobita, Synthesis and Photochemical Properties of Stilbenophanes Tethered by Silyl Chains. Contraol of ($2\pi +$ 2π) Photocycloaddition, Cis-Trans Photoisomerization, and Photocyclization, *J. Org. Chem.*, 2005, **70**, 9693–9701.

63 H. Maeda, Y. Inoue, H. Ishida and K. Mizuno, UV Absorption and Fluorescence Properties of Pyrene Derivatives Having Trimethylsilyl, Trimethylgermyl, and Trimethylstannyl Groups, *Chem. Lett.*, 2001, **30**, 1224–1225.

64 H. Maeda, T. Maeda, K. Mizuno, K. Fujimoto, H. Shimizu and M. Inouye, Alkynylpyrenes as Improved Pyrene-Based Biomolecular Probes with the Advantages of High Fluorescence Quantum Yields and Long Absorption/Emission Wavelengths, *Chem. Eur. J.*, 2006, **12**, 824–831.

65 A. M. Ara, T. Iimori, T. Nakabayashi, H. Maeda, K. Mizuno and N. Ohta, Electric Field Effects on Absorption and Fluorescence Spectra of Trimethylsilyl- and Trimethylsilylethynyl-Substituted Compounds of Pyrene in a PMMA Film, *J. Phys. Chem. B*, 2007, **111**, 10687–10696.

66 T. Tamai, M. Watanabe, H. Maeda and K. Mizuno, Fluorescent Polymer Particles Incorporating Pyrene Derivatives, *J. Polym. Sci. A*, 2008, **46**, 1470–1475.

67 M. Yamaji, H. Maeda, Y. Nanai and K. Mizuno, Substitution Effects of C–C Triple Bonds on Deactivation Processes from the Fluorescent State of Pyrene Studied by Emission and Transient Absorption Measurements, *ISRN Phys. Chem.*, **2012**, 103817.

68 H. Maeda, T. Shoji and M. Segi, Effects of substituents on silicon atoms upon absorption and fluorescence properties of 1,3,6,8-tetrakis(silylethynyl)pyrenes, *Tetrahedron Lett.*, 2017, **58**, 4372–4376.

69 *Handbook of Fluorescence Spectra of Aromatic Molecules, Second Edition*, ed. I. B. Berlman, Academic Press, New York and London, 1971.

70 K. Ogino, S. Iwashima, H. Inokuchi and Y. Harada, Photoelectric Emission and Electrical Conductivity of the Cesium Complex with Pyrene Derivatives, *Bull. Chem. Soc. Jpn.*, 1965, **38**, 473–477.

71 C. G. Pitt and H. Bock, $\sigma-\pi$ Mixing in Phenylpentamethyldisilane, *J. Chem. Soc. Chem. Commun.*, **1972**, 28–29.

72 H. Sakurai, Spectra and some reactions of organopolysilanes, *J. Organomet. Chem.*, 1980, **200**, 261–286.

73 R. Gleiter, W. Schäfer and H. Sakurai, Evidence for a Strong σ/π Interaction in 3,4,7,8-Tetrasilacycloocta-1,5-diyne and

74 3,4,7,9,11,12-Hexasilacyclododeca-1,5,9-triyne, *J. Am. Chem. Soc.*, 1985, **107**, 3046–3050.

74 H. Sakurai, Structure and reaction controlled by strong sigma/pi interactions, *Pure Appl. Chem.*, 1987, **59**, 1637–1646.

75 I. B. Berlman, Empirical Study of Heavy-Atom Collisional Quenching of the Fluorescence State of Aromatic Compounds in Solution, *J. Phys. Chem.*, 1973, **77**, 562–567.

76 J. M. G. Martinho, Heavy-Atom Quenching of Monomer and Excimer Pyrene Fluorescence, *J. Phys. Chem.*, 1989, **93**, 6687–6692.

77 Th. Förster, Excimers, *Angew. Chem. Int. Ed.*, 1969, **8**, 333–343.

78 F. C. De Schryver, P. Collart, J. Vandendriessche, R. Goedeweeck, A. M. Swinnen and M. van der Auweraer, Intramolecular Excimer Formation in Bichromophoric Molecules Linked by a Short Flexible Chain, *Acc. Chem. Res.*, 1987, **20**, 159–166.

79 F. M. Winnik, Photophysics of Preassociated Pyrenes in Aqueous Polymer Solutions and in Other Organized Media, *Chem. Rev.*, 1993, **93**, 587–614.

80 M. Ogawa, A. Momotake and T. Arai, Water-soluble poly(aryl ether) dendrimers as a potential fluorescent detergent to form micelles at very low CMC, *Tetrahedron Lett.*, 2004, **45**, 8515–8518.

81 H. Kuroda, I. Ikemoto and H. Akamatu, The Crystal Structure of the Pyrene-Tetracyanoethylene Complex, *Bull. Chem. Soc. Jpn.*, 1966, **39**, 547–551.

82 A. S. Tiwary and A. K. Mukherjee, Performance of the M06 family of functionals in prediction of the charge transfer transition energies of the naphthalene-TCNE and pyrene-TCNE molecular complexes, *Chem. Phys. Lett.*, 2014, **610–611**, 19–22.

83 E. A. Williams, NMR spectroscopy of organosilicon compounds, in *The Chemistry of Organic Silicon Compounds*, ed. S. Patai and Z. Rappoport, John Wiley & Sons Ltd, New York, 1989, pp. 511–554.

84 C. R. Ernst, L. Spialter, G. R. Buell and D. L. Wilhite, Silicon-29 Nuclear Magnetic Resonance. Chemical Shift Substituent Effects, *J. Am. Chem. Soc.*, 1974, **96**, 5375–5381.

85 H. Bock, Fundamentals of Silicon Chemistry: Molecular States of Silicon-Containing Compounds, *Angew. Chem. Int. Ed. Engl.*, 1989, **28**, 1627–1650.

86 J. S. Panek, Silicon Stabilization, in *Comprehensive Organic Synthesis Vol. 1*, ed. B. M. Trost and I. Fleming, Pergamon Press, Oxford, 1991, pp 579–627.

87 H. Alt, E. R. Franke and H. Bock, Birch Reductions of Trimethylsilyl Substituted Aromatic Compounds Controlled by (Si<–C$_\pi$) interactions, *Angew. Chem. Int. Ed.*, 1969, **8**, 525–525.

88 J. C. Giordan, Negaive Ions: Effect of α- vs. β-Silyl Substitution on the Negative Ion States of π Systems, *J. Am. Chem. Soc.*, 1983, **105**, 6544–6546.

89 W. Setaka, C. Kabuto and M. Kira, An ESR Study of a Tetrasilaspirobiindane Anion Radical. Stereoelectronic Electron-Accepting Effects of Trialkylsilyl Groups, *Chem. Lett.*, 1999, **28**, 317–318.

For Graphical Abstract

Effects of Substituents in Silyl Groups on the Absorption, Fluorescence and Structural Properties of 1,3,6,8-Tetrasilylpyrenes
Hajime Maeda,* Tsubasa Suzuki and Masahito Segi

In this effort, we prepared and characterized photophysical properties of 1,3,6,8-tetrasilylpyrenes, focussing on the effects of substituents on silicon atoms.