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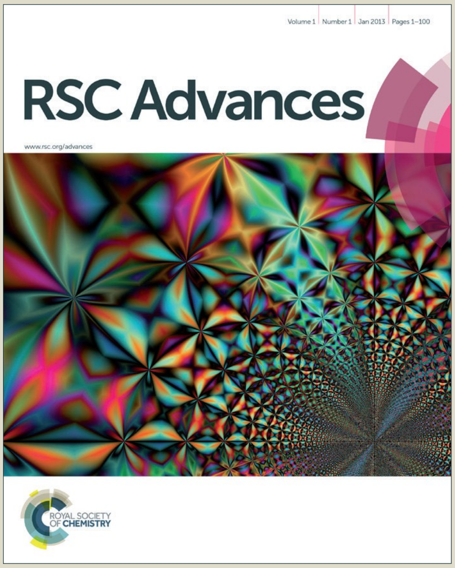

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Solvent Dependent Intramolecular Excimer Emission of Di(1-pyrenyl)silane and Di(1-pyrenyl)methane Derivatives †

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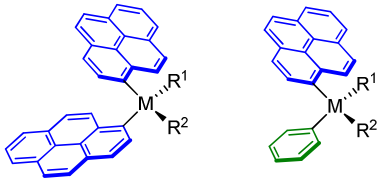
Di(1-pyrenyl)silane and di(1-pyrenyl)methane derivatives showed unprecedented intramolecular excimer emission in polar organic solvents such as DMSO and the ratio of excimer/monomer emissions strongly depends on the dielectric constants of the solvents.

Pyrene is a useful fluorophore due to the characteristic properties such as relatively long lifetime, sensitive solvatochromism on monomer emissions.[1-3] In general, pyrene molecules in excited and ground states intermolecularly stack to form so-called a sandwich excimer resulting in structureless broad emission at around 470 nm.

During the course of our study on silanol-based anion receptors,[4,5] we have reported that a silanediol bearing two 1-pyrenyl groups showed favorable ratiometric fluorescence changes upon the addition of oxoanions such as acetate and dihydrogen phosphate, in which monomeric emission was diminished concomitant with enhancement of emission at longer wavelength (excimer-like emission). Moreover, we have found that the weak excimer-like emission was observed in polar organic solvent such as acetonitrile even in the absence of these guest anions.

The photophysical properties of α,ω-di(1-pyrenyl)alkanes[6] and α,ω-di(1-pyrenyl)oligosilanes[7,8] have been widely studied. For instance, 1,3-di(1-pyrenyl)propane have been applied to a viscosity sensor by the formation of an intramolecular excimer resulting in the change of excimer/monomer emission ratio.[9,10] Surprisingly, the photophysical properties of di(1-pyrenyl)methane and di(1-pyrenyl)silane derivatives have scarcely been disclosed even though these structures are simple. In this paper, we demonstrate that these di(1-pyrenyl)silane and methane derivatives (Scheme 1) show novel intramolecular excimer emission, which depends on the dielectric constants of solvents.



1a: M = Si, $R^1 = R^2 = OH$
1b: M = Si, $R^1 = R^2 = OSiMe_3$
1c: M = Si, $R^1 = R^2 = Me$
3a: M = C, $R^1 = OH$, $R^2 = H$
3b: M = C, $R^1 = R^2 = H$

2: M = Si, $R^1 = R^2 = Me$
4: M = C, $R^1 = OH$, $R^2 = H$

Scheme 1 Diarylsilane and diarylmethane derivatives.

Di(1-pyrenyl)silanediol **1a** was prepared according to the previously reported procedure.[5] Reaction of **1a** with chlorotrimethylsilane in the presence of pyridine in THF gave di(1-pyrenyl)bis(trimethylsiloxy)silane **1b** in 83% yield. After lithiation of 1-bromopyrene by BuLi in THF, the produced 1-pyrenyllithium was reacted with 0.5 equiv of tetrachlorosilane, followed by the produced dichlorodi(1-pyrenyl)silane was quenched with excess MeMgI in ether to give **1c** in 23% yield. Dimethylphenyl(1-pyrenyl)silane **2** was prepared from 1-pyrenyllithium with trichlorophenylsilane, followed by the addition of MeMgI in 41% yield.

The UV-vis spectra of **1a**, **1b** and **1c** in various organic solvents were found to show typical pyrenyl spectra as shown in Fig. S15. Small shifts but similar spectral shapes of **1a**–**c** on the solvents were found. These results imply small electronic perturbation of these compounds and no interaction between two pyrenyl groups in a ground state in these solvents.

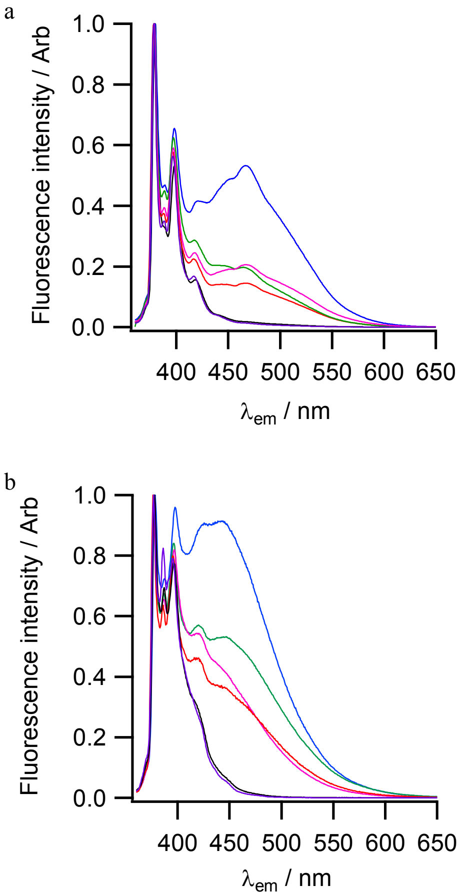


Fig. 1. Normalized fluorescence spectra of **1a** (a) and **3a** (b) in DMSO (—), ethylene glycol (—), DMF (—), MeCN (—), $CHCl_3$ (—) and cyclohexane (—). λ_{ex} = 348 nm at 298 K.

The fluorescence spectra of **1a** excited at 348 nm in apolar solvents such as $CHCl_3$ and cyclohexane showed typical structured monomer emission of the pyrenyl group at 370–420 nm as depicted in Fig. 1a. Interestingly, in more polar solvents such as DMSO, ethylene glycol, DMF and MeCN, broad and structureless emissions of **1a** at around 470 nm were clearly observed. The intensity of the emission at 470 nm was significantly dependent on the solvent. Similar but slightly smaller changes were observed for **1b** and **1c**, in which silanol hydroxy groups of **1a** were substituted to trimethylsiloxy and methyl groups, respectively (Fig. S17), clearly indicating that hydrogen bondings of the silanol groups and/or oxygen atom neighboring to silicon atom are not necessary for the emission at 470 nm. It should be noted that dimethylphenyl(1-pyrenyl)silane **2**, in which one pyrenyl group of **1c** was substituted to phenyl group, showed only monomer emission of the pyrenyl group in all solvents (Fig. S17). In addition, the fluorescence intensity ratio at 470 and 378 nm (I_{470}/I_{378}) of **1c** in DMSO, MeCN, and $CHCl_3$ was constant in the range of concentration between 3.5×10^{-7} and 3.7×10^{-5} mol dm^{-3} as shown in Fig. S18. These results clearly rejected an intermolecular excimer formation of excited and ground state molecules, and strongly suggested that the fluorescence emission at 470 nm is attributed to the intramolecular interaction of two pyrenyl groups of **1a**–**c**.

Surprisingly, carbon analog, di(1-pyrenyl)methanol **3a**[11] showed the largest spectral changes in polar solvents (Fig. 1b). The fluorescence intensity at 447 nm was comparable to the intensity of the monomer emission at 377 nm in DMSO. Again, di(1-pyrenyl)methane **3b**[11] showed weaker but still significant emission at around 450 nm in DMSO and other polar organic solvents than **3a** (Fig. S17). These results revealed that the central silicon atom of **1** is not necessary, and p_π–d_π–p_π hyperconjugation on the pyrenyl–Si–pyrenyl is not a main factor for the intramolecular excimer emission in polar solvents. Shorter C–C bonds of **3** than Si–C bonds of **1** may be effective for overlapping of two pyrenyl groups in the excited state. Phenyl(1-pyrenyl)methanol **4**[12] showed only monomer emissions in all solvents tested (Fig. S17), implying two pyrenyl groups are fundamental components for the excimer emissions as discussed above. The quantum yields of **1c** and **3a** in $CHCl_3$, MeCN and DMSO were measured and summarized in Table 1. The quantum yields were 0.044–0.109 in all solvents except for **3a** in DMSO (Φ_F = 0.324).

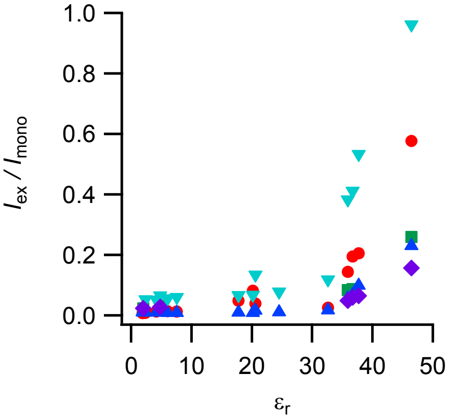


Fig. 2. Effect of dielectric constant (ε_r) of solvents on the ratios of excimer-like and monomer emissions (I_{470}/I_{378} for **1a**–**c** and I_{447}/I_{377} for **3a** and **3b**). λ_{ex} = 348 nm. ●: **1a**, ■: **1b**, ▲: **1c**, ▼: **3a** and ◆: **3b**.

The ratios of fluorescence intensities at 470 and 378 nm for **1a** and **1c** in sixteen solvents, and for **1b** in five solvents were plotted against various solvent parameters,[13] namely, dielectric constant (ε_r), solvent viscosity, acceptor number (*AN*), donor number (DN^N), Dimroth-Reichardt parameter (E_T^N) and solvent orientation polarizability factor (Δf) as shown in Figs. 2, S18 and S19. In these plots, dielectric constant was found to be the most suitable parameter for the correlation with I_{470}/I_{378}. In low polarity solvent (ε_r<30), I_{470}/I_{378} values of **1a-c** were smaller than 0.05, however, I_{470}/I_{378} increased as the ε_r of the solvent is increasing over 30. The same trends were also observed for **3a** and **3b** (Fig. S20). These results suggests that the excimer of **1** and **3** may be stable in these polar solvents (ε_r>30). The excimer/monomer intensity ratios of **1** and **3** were in the order of **1a**>**1b**>**1c** and **3a**>**3b**, which may due to the hydrogen bonding of the substituents on the central atom with the solvent molecules surrounding the probes.

The excitation spectra of **1c** monitored at 379 and 470 nm were completely overlapped to the UV-vis spectra of **1c** in $CHCl_3$, MeCN and DMSO, respectively (Fig. S21), suggesting that both fluorescence emissions were originated from the identical excitation process from the ground to the excited states in these solvents.

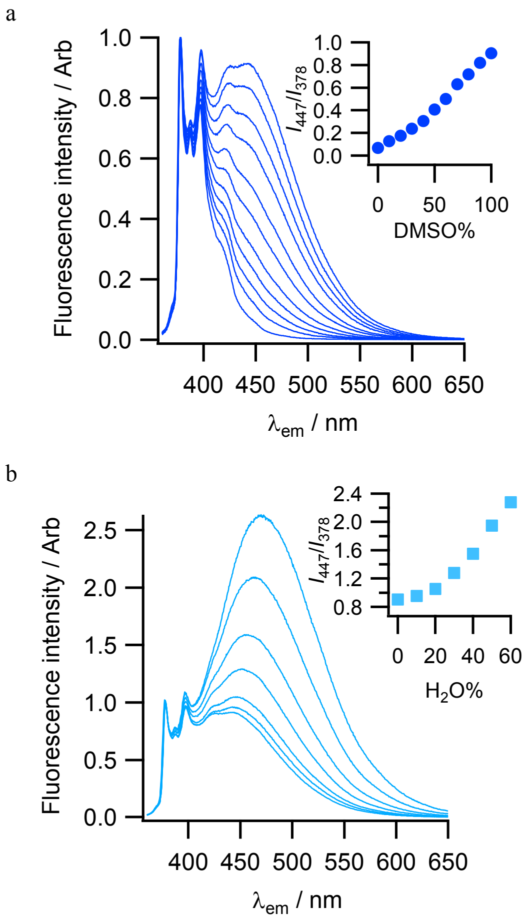


Fig. 3. Effect of DMSO–$CHCl_3$ (a) and water–DMSO (b) on fluorescence spectra of **3a**. [**3a**] = 2.0×10^{-6} mol dm^{-3}, λ_{ex} = 348 nm at 298 K.

In the next step, fluorescence spectra of **3a** in mixed solvents were studied for environment sensors. I_{447}/I_{378} of **3a** were sequentially increased with increasing the content of DMSO (ε_r = 46.45) in $CHCl_3$ (ε_r = 4.81) mixed solvent (Fig. 3a). Fig. 4 shows the picture of the fluorescence emission of **3a** in DMSO–$CHCl_3$ and light blue emission was clearly observed in increasing amount of DMSO. It should be noted that I_{447}/I_{378} of **3a** were also dramatically increased with increasing amount of water (ε_r = 78.30) in DMSO up to 60% (*v*/*v*) as shown in Fig. 3b. Above 60% of water in DMSO, **3a** was precipitated to prevent the fluorescence measurement. These changes support that fluorescence at 447 nm of **3a** was also dependent on bulk nature of solvent such as dielectric constants and was not result from the specific interaction between **3a** and solvent molecules. Probe **1c** also showed similar results as shown in Figs. S22 and S23. Probes **1** and **3** can be used for an environmental sensor in biological samples due to the fluorescence changes in this region.

Fig. 4. The fluorescence emission of **3a** in 0, 20, 40, 60, 80, and 100% DMSO (*v*/*v*) in $CHCl_3$ excited around 365 nm (from left). [**3a**] = 1.25×10^{-5} mol dm^{-3}.

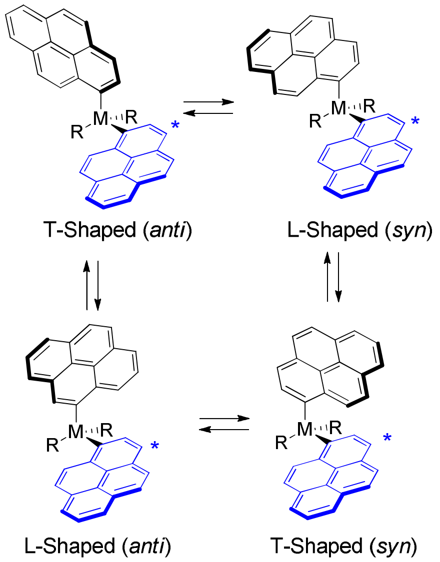
Table 1 Quantum yields of **1c** and **3a** in organic solvents

Solvent	Φ_F [a]	
	1c	**3a**
$CHCl_3$	0.109	0.074
MeCN	0.044	0.076
DMSO	0.074	0.324

[a] The quantum yields determined were all relative to that of quinine sulfate in 0.5 mol dm^{-3} sulfuric acid (Φ_F = 0.546).

Karatsu et al. reported that dimethyldi(1-naphthyl)silane and di(1-anthryl)dimethylsilane showed only monomer emissions in cyclohexane and MeCN.[7] Fluorescence spectra of dimethyldi(1-naphthyl)silane in DMSO, MeCN and $CHCl_3$ showed monomer emissions and no excimer emission could be detected even in DMSO (Fig. S24), suggesting larger π–surfaces are necessary for this excimer emissions of diarylsilane and diarylmethane derivatives. Fluorescence intensity and excimer/monomer ratio of **3a** in DMSO were not altered under aerobic and anaerobic (argon saturated) conditions (Fig. S25). Boo and co-workers reported excimer emissions of bis(9-fluorenyl)methane[14] and di(9-fluorenyl)dimethylsilane[15], respectively. These compounds can form slightly bent sandwich excimers like 1,3-diarylpropane since the carbon atoms at 9-position of two fluorenyl groups are sp^3 carbons.

Di(1-pyrenyl)methane and silane derivatives cannot form a typically observed sandwich excimer due to the connection of two pyrenyl groups by a single atom (Si or C), then two pyrenyl groups adopt only perpendicular conformation. The mechanism of the excimer emissions of the probes has not been fully understood at present. The wavelengths of excimer emissions in polar organic solvents of **1** and **3** were independent on solvent polarity rejecting intramolecular charge transfer (ICT) mechanism. Excited-state intramolecular proton transfer (ESIPT) and twisted intramolecular charge transfer (TICT) mechanisms are also inconceivable.[16] In the ground and excited states, probes **1** and **3** can form four conformers as depicted in Scheme 2. Monomer emission arises from T-shaped (*anti*) or L-shaped (*anti*) conformers, which have smaller dipole moments. These structures are stable in less polar solvents. In polar solvents, excimer emission may be from more polar conformers in the excited state such as L-shaped (*syn*) or T-shaped (*syn*) conformers as observed for stable dimer (55° dimer)[17,18] or T-shaped excimer[19,20] of anthracene, respectively, by partially overlapping of the large π-surfaces of the pyrenyl groups.



Scheme 2 Plausible conformers of di(1-pyrenyl)silane and methane derivatives.

In conclusion, we have shown novel intramolecular excimer emissions of di(1-pyrenyl)methane and di(1-pyrenyl)silane derivatives. The emissions strongly depend on the dielectric constant of the solvents. It should be mentioned that silanol and alcoholic hydroxy groups of **1c** and **3a** could be easily decorated with functional groups via siloxane, ether or ester linkages to yield versatile functional materials showing fluorescence response to the dielectric constants around the di(1-pyrenyl)methane and di(1-pyrenyl)silane moieties for biological and environmental applications. Mechanism of the emissions in polar solvents in detail including theoretical calculations of the excited state will be studied in due course. Moreover, preparation and photophysical properties of other symmetrical and asymmetrical biarylsilane and methane derivatives will also be studied.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Detailed experimental and analytical data as well as additional figures. See DOI: 10.1039/c000000x/

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