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Solubility of novel silicon phthalocyanines substituted with polyfluoroalkyloxy groups at axial sites

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Abstract

A range of novel phthalocyanine structures containing polyfluoroalkyloxy groups at the axial sites have been successfully synthesised. They were tested for solubility in a number of solvents. The polyfluoroalkyloxy groups were found to impart higher solubility than the corresponding polyfluoroalkanoyloxy and alkoxy derivatives. The highest solubility was found in ether.

Keywords: Phthalocyanines; Polyfluoroalkoxy group; Solubility; Self-quenching; Fluorescence; Naphthalocyanine

1. Introduction

Phthalocyanines (Pcs) are important compounds due to not only their blue hue but also their electronic properties. They have been proposed and used as advanced materials such as ink, toner, sensitizers, catalysts, charge generation material in OPC, and recording materials in CD-R. Introduction of bulky substituent(s) at the axial sites of Pcs has been shown to reduce the intermolecular π–π interactions to increase the solubility [1]. The more bulky the substituent(s), the more soluble in the phthalocyanine derivatives. Though the size of a fluorine atom is similar to that of a hydrogen atom, perfluoroalkyl groups are more bulky than the corresponding alkyl groups [2]. Silicon Pcs substituted with polyfluoro- and perfluoroalkanoyloxy groups have been reported to show improved solubility [3]. Since, generally, less polar materials can show higher solubility, the ether derivatives might be expected to be more soluble than the ester derivatives. No paper or patents concerning the solubility of axially polyfluoroalkyloxy-substituted Pcs have been reported so far. We report herein the UV–vis absorption and fluorescence spectra and solubility of silicon Pcs and napthalocyanine (Nc) substituted with polyfluoroalkyloxy groups at the axial sites.

2. Results and discussion

2.1. Synthesis

Silicon Pcs **1a–e** and Nc **2c** substituted with polyfluoroalkyloxy groups were synthesized by the reaction of dichloro(phthalocyaninato)silicon and dichloro(naphthalocyaninato)silicon with alcohols

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in the presence of sodium hydride, respectively. Silicon Pcs substituted with alkoxy **1b′** and **1d′** and perfluorobutanoyloxy groups **3** were also prepared as reference compounds. Their structures are shown in Fig. 1.

2.2. UV–vis absorption and fluorescence spectra

The UV–vis absorption spectra of **1c** and **2c** are shown in Fig. 2. Characteristic absorption bands of the Pc and Nc systems were observed at 672 and 784 nm, respectively. The emission maxima (λ_{em}) of **1c** and **2c** were observed at 685 and 803 nm, respectively. The fluorescence of **1c** was much more intense than that of **2c**.

The UV–vis absorption spectral data from the other derivatives are indicated in Table 1. The absorption maximun (λ_{max}) and λ_{em} of ether derivative **1a** was slightly more hypsochromic compared with the ester derivative **3**, respectively (runs 1 and 9 in Table 1). No remarkable difference in the λ_{max} and λ_{em} values between the fluorine-containing derivatives **1b** and **1d** and fluorine-free derivatives **1b′** and **1d′** was observed (runs 2, 4, 6 and 7). The λ_{max} and λ_{em} values for ether derivatives **1a**–**e** were observed around 672 and 685 nm, respectively (runs 1–5), indicating that the nature of the polyfluoroalkyloxy group did not affect the λ_{max} and λ_{em}. No remarkable difference in the relative fluorescence intensity (RFI) among the ether derivatives **1a**–**e**, **1b′**, and **1d′** was observed (runs 1–7).

The dendrimer having Rhodamine B in the core has been reported to improve self-quenching of fluorescence [4]. The relationship between the concentration of Pc and fluorescence intensities is shown in Fig. 3. The fluorescence intensity of all compounds increased up to the concentration of 1.8×10^{-6} mol dm^{-3}, and then decreased with increasing concentration. This result suggests that these substituents at the axial sites are not bulky enough to surround the chromophore.

2.3. Solubility

The solubilities of **1**–**3** in hexane, ether, and methyl perfluorobutyl ether are also indicated in Table 1. The Pcs and Nc were more soluble in the

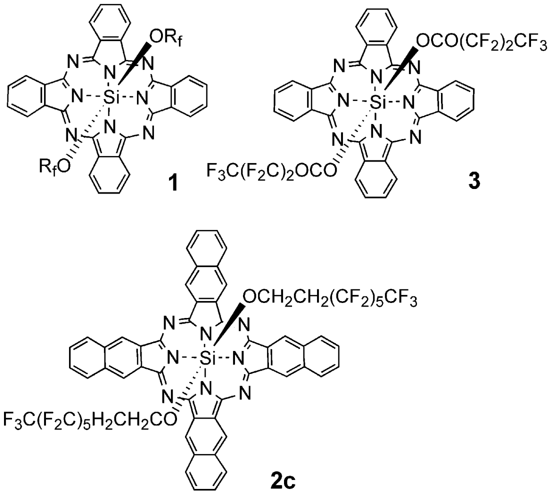

Fig. 1. Phthalocyanines (**1** and **3**) and naphthalocyanine (**2c**).

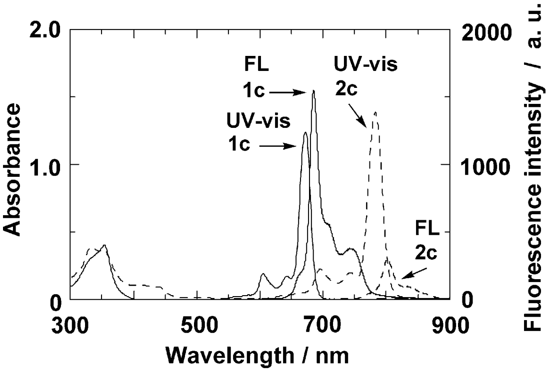

Fig. 2. UV–vis absorption and fluorescence spectra of **1c** and **2c**.

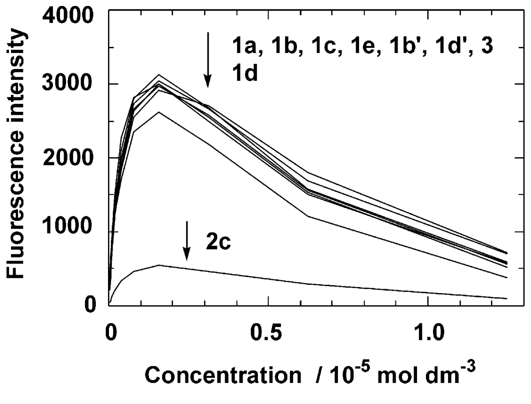

Fig. 3. Self-quenching of Pcs and Nc in dichloromethane.

Table 1
Physical properties of silicon Pcs and Nc

Run	Compd	R_f	λ_{max} (ϵ)[a]	λ_{em}[a]	RFI[b]	Solubility[c]/$\times 10^{-5}$ mol dm^{-3}		
			mn	nm		Hexane	Ether	Methyl nonfluorobutyl ether
1	**1a**	$CF_3(CF_2)_2CH_2$	674 (271,000)	690	97	2.27	81.6	<0.05
2	**1b**	$CF_3(CF_2)_3CH_2CH_2$	672 (258,000)	685	99	2.76	198	0.10
3	**1c**	$CF_3(CF_2)_5CH_2CH_2$	672 (242,000)	685	100[d]	3.79	387	2.75
4	**1d**	$CF_3(CF_2)_9CH_2CH_2$	672 (270,000)	686	93	2.42	254	0.60
5	**1e**	$(CF_3)_2CF(CF_2)_6CH_2CH_2$	672 (269,000)	685	104	3.20	297	1.87
6	**1b**′	$CH_3(CH_2)_5$	671 (238,000)	683	100	2.08	69.4	<0.05
7	**1d**′	$CH_3(CH_2)_{11}$	672 (259,000)	685	101	1.98	65.3	<0.05
8	**2c**	–	784 (267,000)	803	18	2.82	243	2.24
9	**3**	–	691 (293,000)	705	91	0.49	11.4	<0.05

[a] Measured in dichloromethane at the concentration of 5×10^{-6} mol dm^{-3}.

[b] Relative fluorescence intensity measured in dichloromethane at the concentration of 1.5×10^{-6} mol dm^{-3}.

[c] Measured at 25 °C.

[d] A reference value for RFI.

following order of solvent: ether > hexane > methyl perfluorobutyl ether > perfluorohexane. Fluorine-containing substrates have been reported to be soluble in fluorous solvents such as perfluorohexane and perfluoromethylcyclohexane [5]. Unfortunately, these fluorine-containing Pcs and Nc were not soluble in perfluorohexane at all, due to the low fluorine content [<48% (**1d**)] in the molecule. The ether derivative **1a** was more soluble than the ester derivative 3 (runs 1 and 9 in Table 1). The solubilities of polyfluoroalkyloxy derivatives **1b** and **1d** were larger than those of fluorine-free derivatives **1b**′ and **1d**′, respectively (runs 2, 4, 6, and 7). The octyl derivative **1c** was the most soluble among the butyl **1a**, hexyl **1b**, octyl **1c**, and dodecyl **1d** derivatives, indicating that the introduction of long polyfluoroalkyloxy group does not always increase the solubility (runs 1–4), probably due to the oil repelling nature of the fluoro moiety. A similar result has been reported for the solubility of perfluoroalkyl-substituted azo dyes [6]. Terminally branched derivative **1e** was more soluble than the non-branched derivative **1d** (runs 4 and 5). Pc derivative **1c** was more soluble than the Nc derivative **2c** (runs 3 and 8).

Thus, the polyfluoroalkyloxy groups did not completely encapsulate the chromophore. However, the polyfluoroalkyloxy group probably reduces the intermolecular interactions between the Pc rings to increase the solubility.

3. Experimental

3.1. Instruments

Melting points were measured with a Yanagimoto MP-52 micro-melting-point apparatus. NMR spectra were taken on a Varian Inova 400 spectrometer. UV–vis absorption and fluorescence spectra were recorded on Hitachi U-3500 and F-4500 spectrometers, respectively.

3.2. Materials

Dichloro(phthalocyaninato)silicon and dichloro-(naphthalocyaninato)silicon were purchased from Sigma-Aldrich Co., Ltd. Polyfluoroalkanols were purchased from Daikin Chemical Co., Ltd. Reference compounds **1b**′ [7], **1d**′ [7], and **3** [8] were synthesized as described in literature.

3.3. Synthesis of Pcs *1a–e* and Nc *2c*

To dry toluene (2 ml) were added dichloro (phthalocyaninato)silicon or dichloro(naphthalocyaninato)silicon (0.33 mol), sodium hydride (2.3 mmol), and polyfluoroalcohol (1.32 mmol). The mixture was refluxed (**1a**: 12 h, **1b**: 6 h, **1c**: 9 h, **1d**: 12 h, **1e**: 48 h, **2c**: 12 h) under a nitrogen atmosphere. After the reaction was complete, the mixture was poured into brine. The product was extracted with toluene (3 × 50 ml) and dried over anhydrous sodium sulfate. The product was purified by column chromatography (SiO_2, CH_2Cl_2) and recrystallised from toluene. The physical and spectral data are shown below.

3.3.1. *Bis(1H,1H-heptafluorobutoxy)phthalocyaninosilicon (**1a**)*

Yield 58%; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ −1.57 to −1.48 (m, 4H), 8.40–8.42 (m, 8H), and 9.68–9.70 (m, 8H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −52.04 (t, J = 8.8 Hz, 4F), −46.11 to −45. 97 (m, 4F), and −4.67 (t, J = 8.8 Hz, 6F).

3.3.2. *Bis(1H,1H,2H,2H-nonafluorohexyloxy)-phthalocyaninosilicon (**1b**)*

Yield 51%; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ −1.78 (t, J = 6.6 Hz, 4H), −0.98 to −0.86 (m, 4H), 8.35–8.38 (m, 8H), and 9.64–9.67 (m, 8H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −49.27 to −49.16 (m, 4F), −48.34 to −48.24 (m, 4F), −38.20 to −38.03 (m, 4F), and −3.94 to −3.87 (m, 6F).

3.3.3. *Bis(1H,1H,2H,2H-tridecafluorooctyloxy)-phthalocyaninosilicon (**1c**)*

Yield 88%; mp 233–234 °C; ^{1}H NMR ($CDCl_3$) δ −1.78 (t, J = 6.6 Hz, 4H), −0.98 to −0.86 (m, 4H), 8.35–8.38 (m, 8H), and 9.64–9.67 (m, 8H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −49.30 to −49.13 (m, 4F), −47.87 to −47.71 (m, 4F), −46.28 to −46.13 (m, 4F), −45.64 to 45.47 (m, 4F), −38.29 to −38.10 (m, 4F), and −3.67 (t, J = 9.9 Hz, 6F).

3.3.4. *Bis(1H,1H,2H,2H-uneicosafluorododecyloxy)-phthalocyaninosilicon (**1d**)*

Yield 15%; mp 227–229 °C; ^{1}H NMR ($CDCl_3$) δ −1.78 (t, J = 6.6 Hz, 4H), −0.98 to −0.86 (m, 4H), 8.35–8.38 (m, 8H), and 9.64–9.67 (m, 8H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −48.42 to −48.29 (m, 4F), −47.34 to −47.20 (m, 4F), −45.09 to −44.62 (m, 12F), −44.41 to −44.07 (m, 12F), −37.83 to −37.56 (m, 4F), and −3.02 to −2.92 (m, 6F).

3.3.5. *Bis[1H,1H,2H,2H-9-(trifluoromethyl)-nonadecafluorodecaoxy]phthalocyaninosilicon (**1e**)*

Yield 21%; mp 213–214 °C; ^{1}H NMR ($CDCl_3$) δ −1.78 (t, J = 6.6 Hz, 4H), −0.98 to −0.86 (m, 4H), 8.35–8.38 (m, 8H), and 9.64–9.67 (m, 8H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −47.36 to −47.10 (m, 4F), −44.72 to −44.65 (m, 4F), −44.41 to −44.15 (m, 4F), −43.44 to −43.16 (m, 4F), −37.78 to −37.55 (m, 4F), −37.50 to −37.15 (m, 4F), and −6.00 to −5.88 (m, 14F).

3.3.6. *Bis(1H,1H,2H,2H-tridecafluorooctyloxy)-naphthalocyaninosilicon (**2c**)*

Yield 7%; mp >300 °C; ^{1}H NMR ($CDCl_3$) δ −0.93 (t, J = 6.3 Hz, 4H), −0.51 to −0.43 (m, 4H), 7.92–7.94 (m, 8H), 8.65–8.67 (m, 8H), and 10.09 (s, 8H); ^{19}F NMR ($CDCl_3$, ext. CF_3COOH) δ −48.99 to −48.96 (m, 6F), −46.55 to −46.68 (m, 12F), and −3.59 to −3.57 (m, 8F).

3.4. *Solubility measurement*

A saturated solution of the substrate was prepared at 25 °C. The solution was filtered and diluted to measure the UV–vis absorption spectrum. The solubility was calculated on the basis of the known molar absorption coefficient in the solvent at the absorption maximum.

4. Conclusions

Phthalocyanines substituted with polyfluoroalkyloxy groups at the axial sites are found to give greater solubility than their polyfluoroalkanoyloxy and alkoxy derivatives. The highest solubility was found in ether.

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