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Synthesis and Photophysical Properties of Silica-Gel-Supported Photofunctional (Phthalocyaninato)silicon Complexes

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The photophysical properties and surface structures of silica-gel-supported photofunctional (phthalocyaninato)silicon complexes (SiPc-SiO_2) were investigated in terms of their electronic absorption, fluorescence, singlet-oxygen luminescence, and nitrogen adsorption/desorption isotherms. The nitrogen/desorption isotherms indicate that the planes of SiPcs Aanchored by axial ligands are parallel to the silica gel surface. In the proposed structure the tetradentate Pc ligands are considered to coordinate with the silica gel particles, since central elements of SiPcs, such as Si–O–Si–OH, are similar to constituents of silica gel. It was shown that the addition of an organic solvent (chloroform, cyclohexane, etc.), whose refractive index is comparable to that of the silica gels, increases the transparency of the silica gels. This method of adding the solvent allows to quantitatively analyze the photophysical properties and is useful for investigating other modified silicas. The intensities of fluorescence and singlet-oxygen luminescence decrease with an increase in the amount of SiPcs due to interactions between the SiPcs in aggregates. By changing the amount of SiPcs, solid materials were prepared based on Pc complexes with both monomeric photophysical properties and a high ability for singlet-oxygen generation. The electronic absorption spectra of SiPc-SiO_2 indicate that a wide optical window is maintained between the Soret and Q absorption bands, even for high concentrations of SiPcs ([SiPc] $\approx 10^{-2}$ M). This results in deep-green solids, which is unlike the blue color of the crystals or concentrated solutions ($>10^{-5}$ M) of $SiPc(OH)_2$.
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Introduction

Phthalocyanine (Pc) derivatives have attracted considerable attention from the viewpoint of their various applications.[1–4] Pcs tend to form aggregates because of their large π-conjugated systems that provide their strong π–π interactions. The π–π interactions in the solid state, i.e. crystals and thin layers, induce useful conductivity, which is applicable to semiconductors or photoconductors,[5] but they also have disadvantages in terms of reducing the monomeric photophysical properties, i.e. the sharp Q absorption band, intense fluorescence, and ability for singlet-oxygen ($^1\Delta_g$) generation.[6] Although recent quantum chemical calculations allow us to calculate the monomeric Q absorption band, it is very difficult to predict a broadened Q band for solid Pcs.[5b] This originates from the strong π–π interactions including exciton and charge-transfer interactions. Singlet oxygen ($^1\Delta_g$) produced by the energy transfer from Pcs in the excited triplet (T_1) state to triplet molecular oxygen ($^3\Sigma_g$) has been shown to be useful for photodynamic cancer therapy, photooxidation of toxic molecules, and photoproduction of important intermediates for other chemicals.[7,8] Since solid photocatalysts based on red-light active Pcs have several advantages, i.e. the wider variation of reaction media, selective excitation of Pcs, and easy removal by filtration,[8g] it is important to realize that solid materials based on Pc complexes have a high ability for singlet-oxygen generation. Therefore, solid-material-supported (silica, zeolite, or polymer) Pcs have been investigated.[8] In order to prepare solid Pcs with efficient monomeric photophysical and photochemical properties, it is important to compare the spectroscopic data from the solids and solutions. However, the reflection spectra of the solid materials cannot be directly compared with the transmittance spectra in solution because of a difference in units and the absence of a solvent. In addition, the scattering of light prevents the quantitative analysis of the luminescence.

Recently, we have prepared (phthalocyaninato)silicon (SiPc) supported on silica gels (SiPc-SiO_2) by employing the high dehydration reactivity of OH axial ligands (Scheme 1).[9] In this study, the addition of chloroform, which increases the transparency of silica gels, allows us to measure both the transmittance spectra and the lumines-

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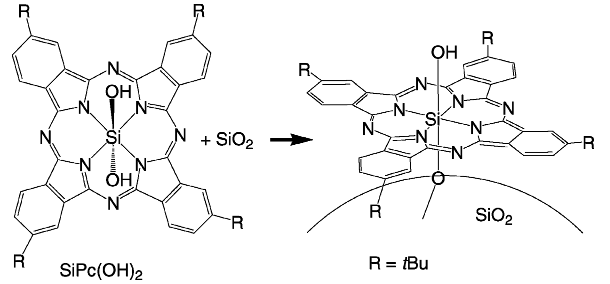
cence without scattering the light. This has revealed that SiPc-SiO_2 is a promising material and has a sharp Q band, intense fluorescence, and the ability for singlet-oxygen ($^1\Delta_g$) generation. In the present study, we have investigated the photophysical properties of SiPc-SiO_2, i.e. electronic absorption, fluorescence, and singlet-oxygen luminescence, by systematically changing the amount of SiPcs. In particular, we have investigated several organic solvents and shown that the addition of a solvent [chloroform ($CHCl_3$), cyclohexane (CHX), etc.], whose refractive index is comparable to that of silica gels, increases the transparency of the silica gels;[10] further, employing an integral sphere accessory is useful for the quantitative analysis of the transmittance spectra. This method of adding the solvent allows us to directly compare the spectroscopic data, and thus, we have succeeded in preparing a solid material based on Pc complexes having both monomeric photophysical properties and a high ability for singlet-oxygen generation. In addition, the surface structures are investigated by nitrogen adsorption/desorption isotherms, which suggest that the SiPc planes anchored by axial ligands are parallel to the silica gel surface.



Scheme 1. Molecular structure of $SiPc(OH)_2$ and the proposed surface structure of SiPc-SiO_2.

Results and Discussion

Synthesis and Reaction Mechanism

Several SiPc-SiO_2 materials were prepared as follows. A toluene solution (15 mL) containing $SiPc(OH)_2$ and silica gel was stirred overnight and then refluxed for 8–72 h. For the synthesis of SiPc-SiO_2 **1**, **10**, **30**, and **100**, 0.5, 5, 15, and 50 mg of $SiPc(OH)_2$ were added to the toluene solution, respectively. By washing with CH_2Cl_2/MeOH (3:1, v/v) a negligibly small amount of $SiPc(OH)_2$ (<3%) was removed. In addition, the SiPcs did not separate from the SiO_2, even upon addition of a 1 M NaOH solution and extraction with $CHCl_3$.

In these reactions, the color of the silica gels was different before and after refluxing in the toluene solution. For example, a blue toluene solution containing 5×10^{-5} M $SiPc(OH)_2$ was admixed with silica gel when preparing SiPc-SiO_2 **10**. This blue color originates from the broad bands at around 600–800 nm (Figure 1A), which results from the exciton or charge-transfer interaction between SiPcs in aggregates.[5,6,11] After the addition of silica gel and stirring of the toluene solution overnight, a colorless supernatant fluid and a blue precipitate of silica gel were obtained. Upon refluxing of the toluene solution, the color of the SiO_2 changed from blue to green. This green color of SiPc-SiO_2 **10** appears to be that of monomeric $SiPc(OH)_2$, whose concentration was <10 μM. In order to investigate this color change, the diffuse reflectance spectra of the blue and green silica gels were measured (Figure 1).[12] The reflectance spectrum of the blue silica gels exhibits both the sharp band and the broad band at around 600–800 nm, which are similar to those found in the electronic absorption spectrum of the toluene solution containing 5×10^{-5} M $SiPc(OH)_2$. This indicates that aggregates of $SiPc(OH)_2$ are adsorbed

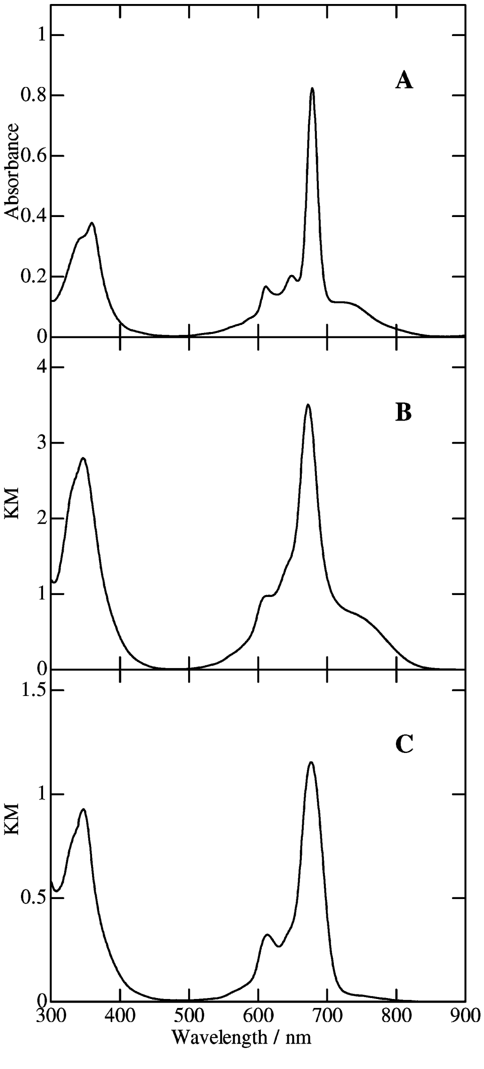


Figure 1. Electronic absorption spectrum of a blue toluene solution containing 5×10^{-5} M $SiPc(OH)_2$ (A) and diffuse reflectance spectra of silica gels before and after refluxing in the toluene solution (B and C). After the addition of silica gel and stirring of the blue toluene solution overnight, a blue precipitate of silica gel was obtained (B). C shows the diffuse reflectance spectrum of SiPc-SiO_2 **10**. The KM values were controlled by mixing with normal SiO_2.

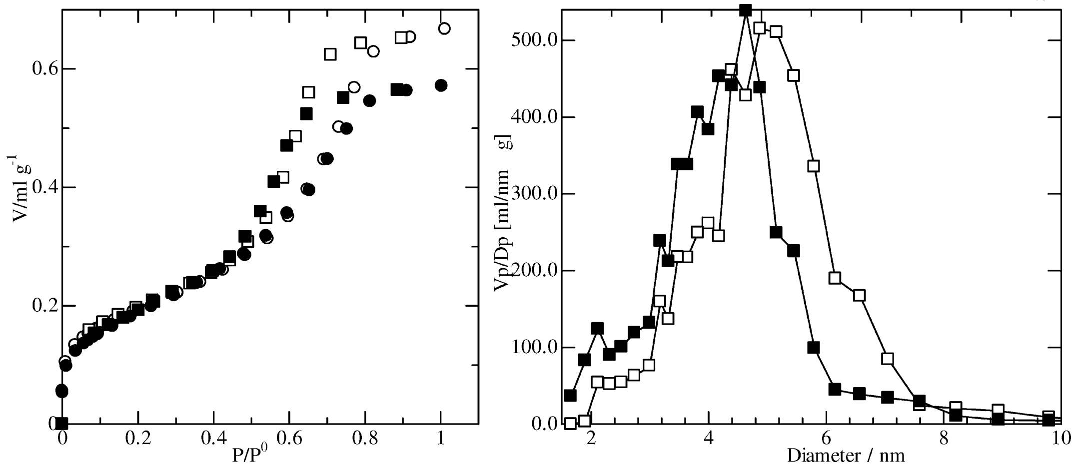


Figure 2. Nitrogen adsorption/desorption isotherms (left: ■□: desorption; ●○: adsorption) and pore-size distributions (right; obtained from the desorption isotherm) for SiPc-SiO_2 **100** (■●) and normal SiO_2 (□○).

onto silica gels as is. On the other hand, the reflectance spectrum of the green silica gels exhibits only the sharp Q absorption band without the broad band due to aggregates. Therefore, the reflux of the toluene solution disperses the aggregates, and the resultant monomeric SiPcs are adsorbed onto SiO_2.[13–15]

The nitrogen adsorption/desorption isotherms at 77 K were measured for SiPc-SiO_2 **100** and normal SiO_2, as shown in Figure 2.[16] The pore volume of SiPc-SiO_2 **100** (571 mL/g) is significantly smaller than that of normal SiO_2 (667 mL/g). The narrow pore-size distribution of SiO_2 evaluated by the Dollimore–Heal method for the desorption isotherms exhibits a mean pore diameter of 4.8 nm (Figure 2). After the reaction with SiPcs the mean pore diameter decreases (4.2 nm). Since the nitrogen adsorption/desorption isotherms are similar between untreated SiO_2 and SiO_2 refluxed in toluene, these decreases in the pore volume and diameter must be caused by the SiPcs remaining in the pores. In contrast to these decreases, the Brunauer–Emmett–Teller (BET) surface area of SiPc-SiO_2 **100** (442 m^2/g) is comparable to that of normal SiO_2 (450 m^2/g).

Electronic Absorption, Fluorescence, and Singlet-Oxygen Luminescence

The diffuse transmittance spectra of SiPc-SiO_2 **1**, **10**, and **100** in $CHCl_3$ and diffuse reflectance spectra of SiPc-SiO_2 **1**, **100**, and $SiPc(OH)_2$ powder are shown in Figure 3. In the case of SiPc-SiO_2 **1**, the Q band peak in the diffuse transmittance spectrum is redshifted as compared to the diffuse reflectance spectrum from which the solvation energies are directly evaluated as 360 and 290 cm^{-1} for $CHCl_3$ and CHX, respectively.[17] The bandwidth of the Q band of SiPc-SiO_2 **1** [full width at half-maximum (FWHM) in $CHCl_3$: 580 cm^{-1}] is broader than that of $SiPc(OH)_2$ (380 cm^{-1}). This is consistent with the previous studies, where π–π* transitions of aromatic organic molecules broaden because of the silanols in silica gels.[10] The bandwidth of the Q band in $CHCl_3$ increases in the order SiPc-SiO_2 **1** (580 cm^{-1}) < **10** (680 cm^{-1}) < **30** (860 cm^{-1}) < **100** (1300 cm^{-1}). While the electronic absorption spectra of

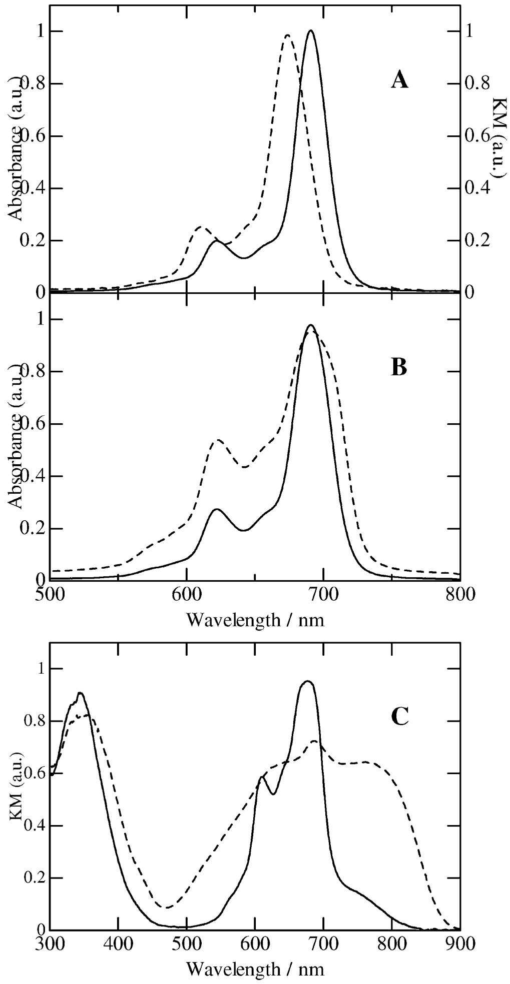


Figure 3. Diffuse transmittance spectra of SiPc-SiO_2 **1** (A, solid line), **10** (B, solid line), and **100** (B, broken line) in $CHCl_3$, and diffuse reflectance spectra of SiPc-SiO_2 **1** (A, broken line), **100** (C, solid line), and $SiPc(OH)_2$ powder (C, broken line). The absorbance and KM values were controlled by mixing with normal SiO_2.

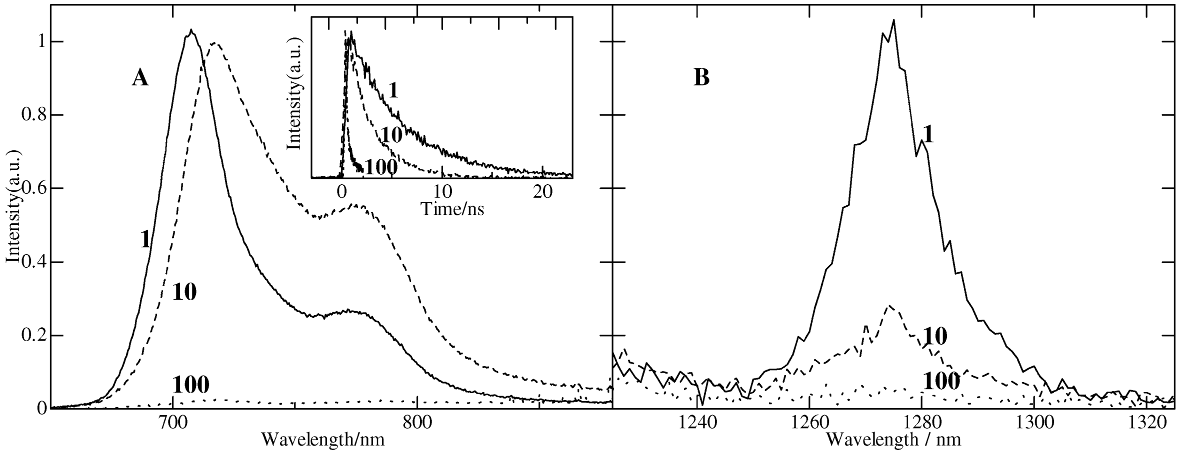


Figure 4. Fluorescence (A) and singlet-oxygen luminescence (B) spectra of SiPc-SiO_2 **1** (solid line), **10** (broken line), and **100** (dotted line) in $CHCl_3$. The inset shows the fluorescence decays of SiPc-SiO_2 **1** (solid line), **10** (broken line), and **100** (dotted line) in $CHCl_3$.

SiPc-SiO_2 **1** and **10** are attributable to the monomeric SiPc, the Q absorption band of SiPc-SiO_2 **100** is obviously broadened. In the magnetic circular dichroism (MCD) spectrum of SiPc-SiO_2 **100**, the Faraday A term from the μ-oxo dimer of the SiPcs could not be observed. Therefore, the broadness originates from the formation of the aggregates since the intermolecular interactions between SiPcs, such as exciton or charge-transfer interactions, change the Q band energy. It is noted that in contrast to the broad Q band of the $SiPc(OH)_2$ powder (FWHM = 6000 cm^{-1}), a wide optical window between 400 and 600 nm is maintained for all SiPc-SiO_2, even at very high concentrations ([SiPc] ≈ 10^{-2} M for SiPc-SiO_2 **100**).

Figure 4 shows the fluorescence spectra of SiPc-SiO_2 **1**, **10**, and **100** in $CHCl_3$. When the fluorescence spectra were measured without dilution by SiO_2, the fluorescence intensity decreased in the order **1** ≈ **10** > **30** >> **100**. This fluorescence quenching is quantitatively analyzed by the fluorescence lifetime, which decreases in the order **1** (τ = 5.5 ns) > **10** (2.9 ns) > **30** (1.1 ns) > **100** (0.18 ns). It is worth noting that the fluorescence lifetime (τ = 5.5 ns) of SiPc-SiO_2 **1** in $CHCl_3$ is the same as that (τ = 5.5 ns) of $SiPc(OH)_2$ in $CHCl_3$. In other words, we have succeeded in preparing solid materials based on Pcs with monomeric photophysical properties. This also indicates that the $S_1 \rightarrow S_0$ internal conversion and $S_1 \rightarrow T_1$ intersystem crossing are independent of the SiO_2 surface (here, S_1, T_1, and S_0 denote the lowest excited singlet, lowest excited triplet, and singlet ground states, respectively). Therefore, the fluorescence quenching mechanism correlates with the aggregation behavior. Here, exciton–exciton annihilation is not the dominant dynamics since the fluorescence decays were independent of the power of the excitation light.

Singlet oxygen ($^1\Delta_g$), which is produced by the energy transfer from SiPcs in the T_1 state to the triplet molecular oxygen ($^3\Sigma_g$), was investigated from the viewpoint of its photocatalytic properties. Similar to the fluorescence results, singlet-oxygen ($^1\Delta_g$) luminescence decreases in the order SiPc-SiO_2 **1** > **10** > **30** >> **100**.

Surface Structures

The nitrogen adsorption/desorption isotherms indicate that the pore volume and pore size decrease due to the reaction with SiPcs since they remain in the pores. The volume of a SiPc molecule was evaluated to be 1.6 nm^3 based on the number of mols used in the reaction and the decrease in the pore volume. In order to quantitatively discuss these points, the optimum structure of $SiPc(OH)_2$ was calculated using the PM3 Hamiltonian, as shown in Figure 5. The optimum structure (1.6 nm^3 ≈ 1.6 nm × 1.6 nm × 0.6 nm) is consistent with the volume evaluated by the nitrogen adsorption/desorption measurements, which indicates that SiPcs remain in the pores. The mean value of the diameter evaluated from the pore size distributions decreases after the reaction with SiPcs, and the decrease was evaluated as ca. 0.6 nm. This change is consistent with the thickness of the optimum structure (0.6 nm), which suggests that the plane of SiPc is parallel to the SiO_2 surface. This surface structure can explain the small change in the BET surface area between SiPc-SiO_2 and normal SiO_2. In addition, by washing with CH_2Cl_2/MeOH (3:1, v/v), a negligibly small amount of $SiPc(OH)_2$ (<3%) was eluted, while (tetra-*tert*-butylphthalocyaninato)zinc without the OH axial ligands was almost completely eluted. Because of the high dehy-

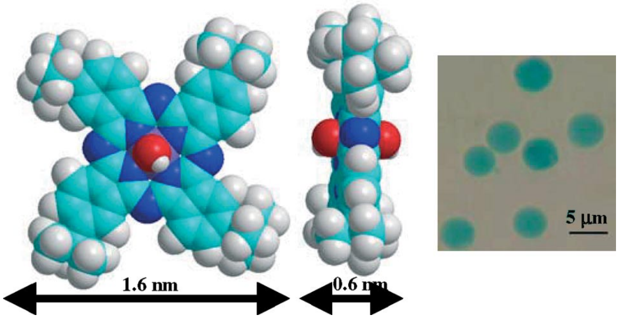


Figure 5. Optimized molecular structures of $SiPc(OH)_2$ (left) and optical microscopic photograph of SiPc-SiO_2 **100** (right).

dration reactivity of the OH axial ligands of SiPc(OH)$_2$,[18,19] SiPcs are considered to be anchored on the silica gel surface. This is supported by the spectroscopic analyses, where the Q absorption band of SiPc-SiO$_2$ **1** (FWHM = 580 cm^{-1}) with a perfectly monomeric fluorescence lifetime is broader than that of SiPc(OH)$_2$ (FWHM = 380 cm^{-1}) due to the interaction with silanols on the SiO$_2$ surface.[10] It is noted that since central elements of SiPcs, such as Si–O–Si–OH, are similar to constituents of SiO$_2$ in the proposed structure, the tetradentate Pc ligands are considered to coordinate with the silica gel particles.[20,21] This overcomes the difficulty of inserting the constituents of particles into the hole of a tetradentate ligand.

Photophysical Properties

The addition of a solvent, CHCl$_3$ or CHX, which increases the transparency and decreases the scattering of light, allows us to quantitatively analyze the photophysical properties. This occurs because the refractive index of the solvent is comparable to that of SiO$_2$. From these quantitative analyses it is shown that the photophysical properties strongly depend on the amount of SiPcs supported. For example, the fluorescence lifetime decreases in the order **1** (τ = 5.5 ns) > **10** (τ = 2.9 ns) > **30** (τ = 1.1 ns) > **100** (τ = 0.18 ns). From the evaluated surface areas of SiO$_2$, the planes of the SiPcs (2.7 nm^2) occupy 0.25, 2.5, 7.5, and 25% of the SiO$_2$ surface area in the case of SiPc-SiO$_2$ **1**, **10**, **30**, and **100**, respectively. The density of silanols on the SiO$_2$ surface is 5/nm^2, which is sufficient for the aggregation of Pcs (2.7 nm^2).[22] Therefore, this quenching may originate from the increases in the Franck–Condon factor because of the exciton or charge-transfer interactions in the aggregated SiPcs, which is consistent with the results of previous studies.[6,11] In particular, the most intense singlet-oxygen ($^1\Delta_g$) luminescence of SiPc-SiO$_2$ **1** is three times that of SiPc-SiO$_2$ **10**, while the electronic absorption spectrum of SiPc-SiO$_2$ **10** is generally attributable to the monomeric SiPc. These results suggest that performing analyses only on the electronic absorption spectra is insufficient, and it is necessary to investigate the excited-state dynamics for preparing photocatalysts based on Pcs. Therefore, SiPc-SiO$_2$ **1** exhibits the highest ability for singlet-oxygen generation.[23]

It is worth nothing that the green color of SiPc-SiO$_2$ **100** ([SiPc] ≈ 10^{-2} M) is similar to that of monomeric SiPc(OH)$_2$ (<10^{-5} M), while SiPc(OH)$_2$ exhibits a blue color in the solid state or concentrated solutions (>10^{-5} M) as a result of the strong π–π interactions. This originates from the wide optical window between 400 and 600 nm. The strong π–π interactions resulting in the very broad Q band generally make it difficult to estimate the color of the Pc pigment. Since the green color of our solid SiPc-SiO$_2$ is similar to that of monomeric SiPc(OH)$_2$, this study demonstrates that color pigments can be prepared as expected.

Conclusions

In this study we have investigated the photophysical properties and surface structures of SiPc-SiO$_2$. The nitrogen adsorption/desorption isotherms indicate that the plane of SiPc is parallel to the SiO$_2$ surface. In the proposed structure the tetradentate Pc ligands are considered to coordinate with the silica gel particles since central elements of SiPcs, such as Si–O–Si–OH, are similar to constituents of SiO$_2$. This is in contrast to the difficulty of inserting particles into the hole of a tetradentate ligand and hence overcomes this problem.

The addition of a solvent whose refractive index is comparable to that of SiO$_2$ allows us to quantitatively analyze the photophysical properties because of the increase in the transparency of the silica gels. By using this solvent effect, we have succeeded in preparing solid materials based on Pc complexes with both monomeric photophysical properties and a high ability for singlet oxygen generation. Therefore, this method of adding the solvent will be applicable for investigating other solid materials. In addition, it is worth noting that the green color of SiPc-SiO$_2$ **100** ([SiPc] ≈ 10^{-2} M) is similar to that of monomeric SiPc(OH)$_2$ (<10^{-5} M), while SiPc(OH)$_2$ in the solid state or concentrated solutions (>10^{-5} M) exhibits a blue color due to the strong π–π interactions. The wide optical window that is present even at high concentrations will be useful for optical limiting.[24] From the viewpoint of the modification of silica surfaces, our study provides novel, simple techniques. For example, SiPc-SiO$_2$ materials are promising as a stationary phase for high-performance liquid chromatography for the separation of π-electron-rich polyaromatic hydrocarbons,[25] since it is easy to modify silica gels by SiPcs. In addition, self-assembled monolayers of SiPcs on silica will leave more free space in the pores,[26] since the planes of SiPcs are parallel to the silica surfaces.

Experimental Section

SiPc(OH)$_2$ was synthesized according to previously reported methods.[18] The SiPc-SiO$_2$ materials were prepared as follows. A toluene solution (15 mL) containing SiPc(OH)$_2$ and SiO$_2$ (100 mg, Wakosil 5SIL, Wako Pure Chemical Industries) was stirred overnight and then refluxed for 8–72 h.[9,18,19] Here, 0.056, 0.56, 1.68, and 5.6 mg (= 7 μmol) of SiPc(OH)$_2$ were included in the toluene solution (15 mL) for the synthesis of SiPc-SiO$_2$ **1**, SiPc-SiO$_2$ **10**, SiPc-SiO$_2$ **30**, and SiPc-SiO$_2$ **100**, respectively. After filtration and washing with CH$_2$Cl$_2$/MeOH (3:1, v/v), a negligibly small amount of SiPc(OH)$_2$ (<3%) was removed, and SiPc-SiO$_2$ was isolated.

The diffuse reflectance and transmittance spectra of solid samples were both measured with a JASCO U570 spectrophotometer by employing an integral sphere accessory. The diffuse reflectance spectra were obtained in the %R mode without regular reflection and were converted using the Kubelka–Munk function. The diffuse transmittance spectra were measured in the absorbance mode with regular reflection. We observed an increase in the transparency of silica gels upon the addition of several organic solvents (CHX, cyclohexanol, CHCl$_3$, and dichloromethane). This occurs because the refractive index of SiO$_2$ is comparable to that of the solvents. Therefore, CHCl$_3$ or CHX (Nacalai Tesque Inc.) was employed as a solvent.[10] By using normal SiO$_2$ with CHCl$_3$ or CHX as a reference, the effect of the grafted SiPcs upon the transmittance light can be selectively monitored, which yields the exact absorption spectrum of the SiPcs. The scattered light originating from silica gels was also considered by employing the integral sphere accessory, which provides a stable baseline. The magnitude of absorbance or %R was controlled by diluting SiPc-SiO_2 with normal SiO_2.

The fluorescence and singlet-oxygen ($^1\Delta_g$) luminescence spectra were measured with a monochromator (JASCO CT-25CP) and a photomultiplier (Hamamatsu Photonics R5509-42) cooled to 193 K.[27] The bandwidth of the fluorescence spectra was 3 nm. The fluorescence lifetimes were measured with a picosecond light pulser (Hamamatsu Photonics PLP-02/041; 408 nm; 59 ps FWHM) and a streak-scope (Hamamatsu Photonics, C4334-02).[27] The fluorescence and singlet-oxygen luminescence were measured by adding $CHCl_3$ or CHX as a solvent in order to decrease the scattering of light. Samples without dilution by normal SiO_2 were irradiated by an He-Ne laser and a dye laser (Sirah CSTR-LG532-TRI-T) pumped with an Nd:YAG laser (Spectra Physics INDI 40; 532 nm; 7 ns FWHM) for the fluorescence and singlet-oxygen ($^1\Delta_g$) luminescence measurements, respectively. MCD measurements were performed with a JASCO J-720 spectrodichrometer equipped with a JASCO permanent magnet (0.47 T).[28] Nitrogen adsorption/desorption experiments were performed with an Autosorb-1 (Yuasa Ionics) at 77 K.

Supporting Information (see also the footnote on the first page of this article): Pore-size distributions obtained from the adsorption isotherm.

Acknowledgments

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[12] In order to prevent the elution of $SiPc(OH)_2$, blue silica gels were not rinsed.

[13] The diffuse reflectance spectrum of SiPc-SiO_2 **1** did not change, even upon heating (at 453 K) under vacuum.

[14] When preparing SiPc-SiO_2 **1**, a green toluene solution containing 5×10^{-6} M $SiPc(OH)_2$ was used. In this case, the diffuse reflectance spectra did not change before and after refluxing.

[15] $SiPc(OH)_2$ was eluted from silica gels treated with CH_2Cl_2/MeOH.

[16] The isotherms of our samples were characterized as type IV, and thus the pore sizes evaluated by the nitrogen adsorption/desorption processes were different. From the adsorption isotherms the mean pore diameters were evaluated as 4.8 and 4.2 nm for normal SiO_2 and SiPc-SiO_2 **100**, respectively (Supporting Information).

[17] In the diffuse reflectance spectra the Soret band is more intense, which may originate from the conversion method using the Kubelka–Munk function.

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[21] The optical microscopic photograph indicates that SiPc-SiO_2 particles disperse (Figure 5).

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