

Exciplex Emission in the POSS Possessing Two Kinds of Luminophores

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Abstract: Here we report the synthesis and luminescent properties of the modified polyhedral oligomeric silsesquioxane (POSS) that possesses two types of luminophores, cyanobenzene and *N,N*-diethylaniline for inducing significant emission not only from each dye but also from molecular interactions on the POSS core. From the optical measurements in the diluted solution, we observed both locally-excited emission and excimer emission originating from intramolecular interactions assisted by POSS. Moreover, highly-efficient exciplex emission was observed from the thin film, indicating that the interaction between luminophores easily occurs in the solid state by accumulating two kinds of molecules in the single POSS molecule. Finally, we also found that the modified POSS showed a unique acid responsiveness which can be caused by protonation at two types of amino moieties. In this manuscript, it is shown that POSS is able to play various roles at the same time: recruiting excited molecules to form exciplexes, suppressing concentration quenching in the solid state, and imparting stimulus responsiveness to exciplexes.

Introduction

Polyhedral oligomeric silsesquioxane (POSS) has a rigid cubic structure based on Si–O bonds and various functional groups can be introduced at the eight vertices.^{1–13} Therefore, it is possible to impart inorganic properties of the POSS core to organic compounds. There is growing interests in this material as an organic–inorganic hybrid material. For example, it has been reported that thermal stability of polymers was able to be improved by introducing POSS into the polymer side-chain.^{14–16} In addition, POSS-core dendrimers can encapsulate hydrophobic substances into a hydrophobic space around the POSS core in aqueous media and have been utilized for reaction fields^{17–22} or biomaterials such as biomedical probes and drug delivery systems.^{23,24} Recently, based on high thermal stability, three-dimensional structure and sparse space around POSS, various applications have been achieved to obtain functional luminescent materials such for thermally stable emission,^{25–28} organic light-emitting diodes,^{29,30} accelerating chemiluminescence reactions,³¹ and fluorescent sensors^{32–41} by accumulating luminophores in POSS. Moreover, stimuli-responsive materials have been constructed by regulating intra/intermolecular interactions connected to the POSS core.^{42,43}

We have previously synthesized POSS having eight pyrenes, which are well known to exhibit excimer emission, and reported that the POSS showed efficient intramolecular excimer emission.⁴⁴ Excimer emission is a luminescence from a complex formed by the same luminophores.^{45–47} If we can induce the exciplex emission, which is the luminescence from an

excited complex formed by charge transfer between different types of luminophores, it is possible to tune luminescence color and stimulus-responsive properties. Exciplex emission has also attracted attention for using in fluorescent sensors^{48–53} and organic light-emitting diodes^{55–58} by utilizing its unique luminescent properties. Compared to excimer, the selection of the pair of luminophores is crucial to observe efficient emission from the exciplex. It was reported that exciplex emission from the octasilicate-core dendrimer with 16 terminal units composed of alternative carbazole and 1,8-naphthalimide groups in diluted chloroform solution.⁵⁹ However, it is still challenging to develop versatile design to observe exciplex emission in the fluid system.

Herein, we show that POSS is a scaffold for accumulating different types of excited molecules and subsequently inducing intramolecular interactions between them followed by exciplex emission. Cyanobenzene and *N,N*-diethylaniline were chosen as luminophores because they have been known to form an exciplex pair.^{60,61} Since the linker length should affect the intramolecular interaction, we used the same length of the linker which showed highly efficient intramolecular interaction.⁴⁴ From the optical measurements, exciplex emission was observed even in the diluted solutions, indicating that POSS is able to support to recruit intramolecular interactions between the excited molecular units. Moreover, the POSS exhibited efficient exciplex emission in the solid states. These results mean that the POSS is a useful scaffold for enhancing side-chain interactions between two kinds of luminophores.

Results and Discussion

As shown in Scheme 1, POSS derivatives (**DPOSS**, **CPOSS**) having *N,N*-diethylaniline or cyanobenzene as luminophores were prepared through reductive amination with each unit.^{62,63} Since the reductive amination may lead to tertiary reactions when the reaction is carried out in a single step, the aldehydes were removed once after imination before the reduction. From the results of ¹H and ²⁹Si NMR spectra of the POSS derivatives, it was confirmed that octa-substituted molecule was obtained. **DCPOSS** having both cyanobenzene and *N,N*-diethylaniline units was synthesized through the same method as **DPOSS** and **CPOSS**. **DCPOSS62**, **DCPOSS53**, and **DCPOSS44** (the number represents the introduction ratio of the *N,N*-diethylaniline unit) were successfully synthesized by changing the feed ratio of the aldehydes. The feed ratios of each aldehyde and the modification ratios of each **DCPOSS**, and the yields are listed in Table 1. The modification ratios were calculated from the ratios of the integrated ¹H NMR peaks of hydrogens which were bonded to the aromatic ring detected in Figure 1 (cyanobenzene: 7.56 ppm and *N,N*-diethylaniline: 6.61 ppm). It is noted that each **DCPOSS** was obtained as mixtures and the modification ratio was estimated as average values. The presence of many POSS derivatives was confirmed by mass spectroscopy (MS) data.

Scheme 1. Syntheses of DPOSS, CPOSS, and DCPOSS

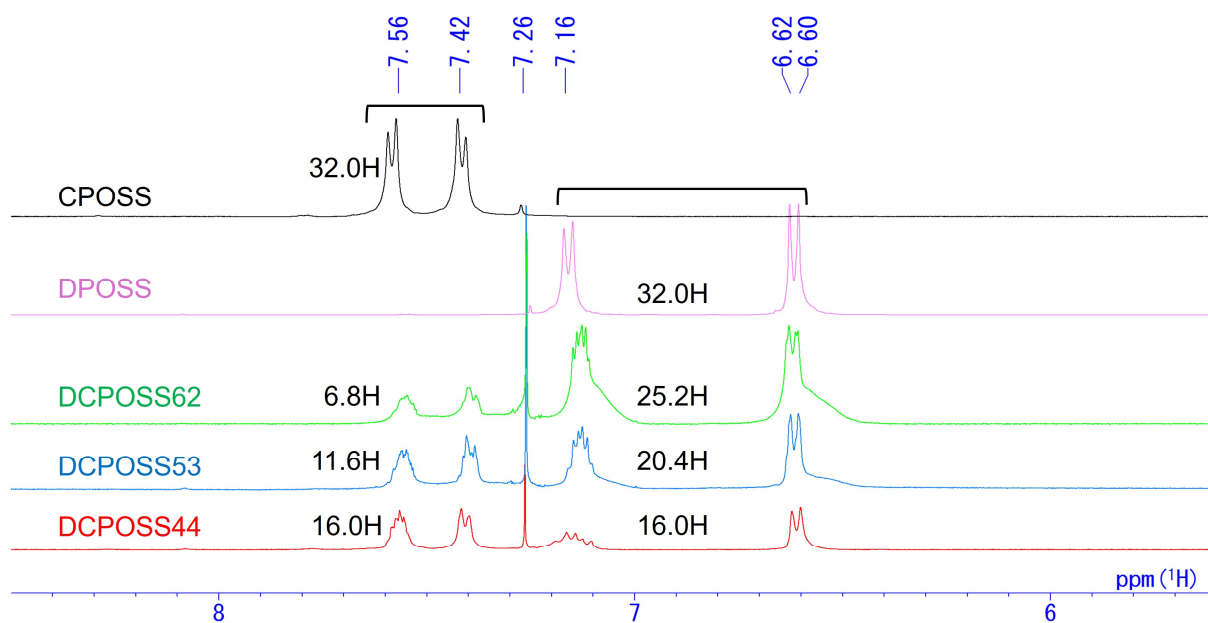
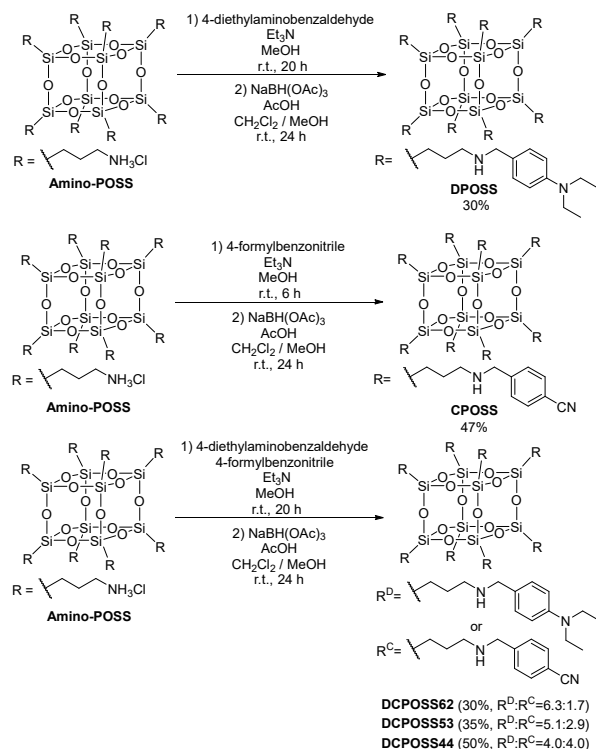


Figure 1. ^1H NMR spectra in aromatic regions of **CPOSS** (black), **DPOSS** (pink), **DCPOSS62** (green), **DCPOSS53** (blue), and **DCPOSS44** (red) in CDCl_3 (400 MHz). The integral value of each signal is shown in the figure.

Table 1. Feed ratios, $R^D : R^C$, and yields of three **DCPOSS** derivatives

Entry	Feed ratio (D:C)	$R^D : R^C$	Yield (%)	Sample
1	8:2	6.3:1.7	30	DCPOSS62
2	7:3	5.1:2.9	35	DCPOSS53
3	6:4	4.0:4.0	50	DCPOSS44

UV–vis absorption, photoluminescence (PL), and fluorescence lifetime measurements of **DPOSS**, **CPOSS**, and three **DCPOSS** were performed in cyclohexane under diluted condition (Figure 2 and Table 2). Cyclohexane was chosen as a solvent because it is generally known that the PL intensity of the exciplex emission increases with the less polarity of the solvent.⁶⁴ To prevent the formation of the aggregates in the less polar solvent, the mixed solution (cyclohexane/ CHCl_3 , 99/1, v/v) was prepared from the chloroform solution of the POSS derivatives. In addition, to discuss the effect of the interaction only in the single molecule, the UV–vis absorption and PL spectra were measured at 1.0×10^{-6} M. Accordingly, aggregates were hardly formed during the measurements because there was little increase in the absorbance due to scattering in the long wavelength region (Figure 2a). As shown in Figure 2b, broad peaks at around 340 and 430 nm were observed from the three **DCPOSS** solutions. The similar peak at around 340 nm was observed in the spectrum of **DPOSS**, indicating that the luminescence was derived from the *N,N*-diethylaniline units. On the other hand, the peak at around 430 nm was found to be relatively long-lived from the results of fluorescence lifetime measurements (Table 2). It is generally known that the exciplex emission is observed as a long-lived broad

peak at long wavelengths compared to the monomer emission. Therefore, it is strongly suggested that the emission at around 430 nm should be derived from the formation of exciplex between *N,N*-diethylaniline and cyanobenzene. Considering the dilute condition of 1.0×10^{-6} M, it is suggested that the exciplex emission should be induced through the intramolecular interaction between the side-chains of POSS. Furthermore, comparing three **DCPOSS** derivatives with variable modification ratios, emission intensity and efficiency from the exciplex were maximal in **DCPOSS44**, where the number of cyanobenzene and *N,N*-diethylaniline should be almost equivalent. The broad peak of the **CPOSS** in Figure 2b could be inferred due to the excimer emission of cyanobenzene.

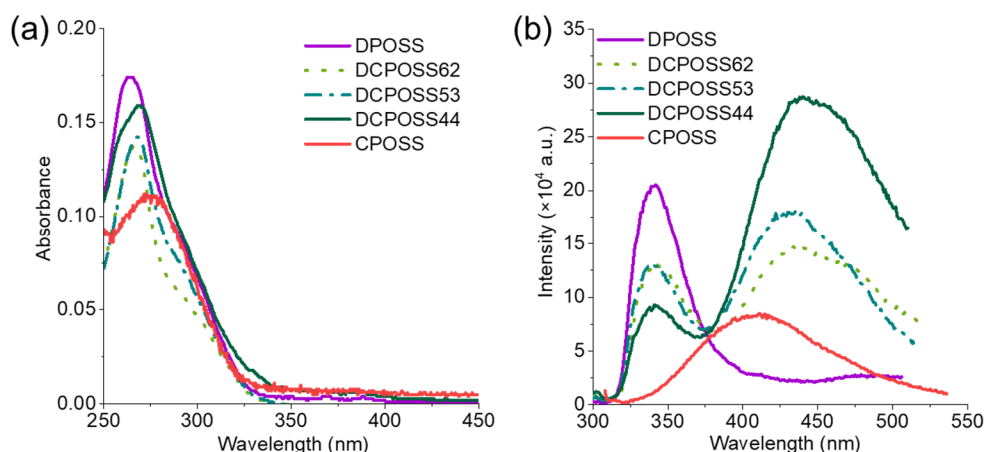


Figure 2. (a) UV-vis absorption and (b) PL spectra of **DPOSS**, **DCPOSS62**, **DCPOSS53**, **DCPOSS44**, and **CPOSS** in cyclohexane/ CHCl_3 (1.0×10^{-6} M, 99/1, v/v) excited at wavelengths of absorption maxima. The solution concentration was calculated based on the molecular weight each POSS derivative.

Table 2. Wavelengths of absorption, emission, and fluorescence lifetimes of **DPOSS**, **DCPOSS62**, **DCPOSS53**, **DCPOSS44**, and **CPOSS**^a

Compounds	DPOSS	DCPOSS62	DCPOSS53	DCPOSS44	CPOSS
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$\lambda_{\text{abs,max}}$ (nm)	266	267	267	268	272
$\lambda_{\text{em,max}}$ (nm)	339	342/431	338/428	341/440	411
Φ_{PL}^b / %	1.4	3.1	3.3	4.2	1.7
τ (ns)	2.23	3.82/12.29	3.44/14.33	2.25/29.7	1.96

^aIn cyclohexane/CHCl₃ (1.0×10⁻⁶ M, 99/1, v/v) excited at wavelengths of absorption maxima.

^bRelative fluorescence quantum yields based on the absolute fluorescence quantum yield of **DCPOSS62**.

In order to investigate the solvent dependency of photophysical properties, UV–vis absorption and PL spectra of **DCPOSS44** were measured in various solvents (Figures 3a and 3b, and Table 3). It was observed that, as increasing the polarity of the solvent, the intensity of the broad emission peak decreased and the maximum emission wavelength shifted to the longer wavelength region. It is generally known that the intensity of exciplex emission is stronger at the less polar solvents and bathochromic shift of the maximum emission wavelength as increasing solvent polarity.⁶⁴ These facts support the speculation that the broad peak could be derived from the exciplex emission. The maximum emission wavelength from the *N,N*-diethylaniline unit at around 340 nm showed dependency on the solvent polarity, suggesting that emission should have a charge-transfer character.

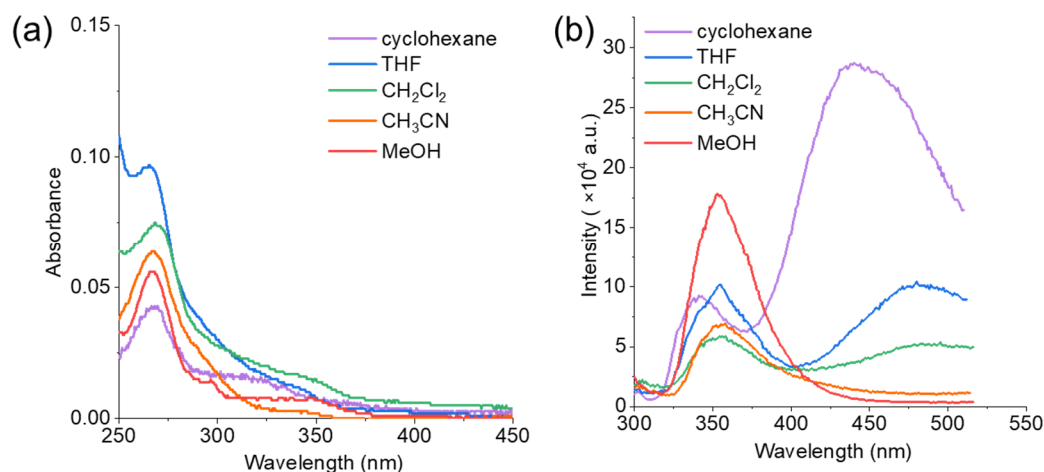


Figure 3. (a) UV–vis absorption and (b) PL spectra of **DCPOSS44** in various solvents containing 1 v/v% of CHCl_3 (1.0×10^{-6} M) excited at wavelengths of absorption maxima.

Table 3. Wavelengths of absorption, emission maxima, and emission intensity of **DCPOSS44** in various solvents containing 1 v/v% of CHCl_3 (1.0×10^{-6} M)

Solvents	cyclohexane	THF	CH_2Cl_2	CH_3CN	MeOH
$\lambda_{\text{abs,max}}$ (nm)	268	266	268	267	268
$\lambda_{\text{em,max}}$ (nm)	341/440	354/474	354/473	355/ND	355/ND
Intensity ($\times 10^4$ a.u.) (Exciplex)	28.7	10.0	5.00	ND	ND

To evaluate the optical properties of **DCPOSS44** in the solid-state, thin films were prepared using a spin-coating method. For comparison, mixed films of **DPOSS** and **CPOSS**, which cannot exhibit exciplex emission within the single molecule, were also prepared in the same manner. Figure 4 shows the UV–vis absorption and PL spectra of **DCPOSS44** and **DPOSS/CPOSS** mixture films with a D/C ratio of 1/1. In the PL spectra of the both compounds, only one peak derived from exciplex emission at around 460 nm was observed (Figures 4a and 4b). The optical measurements of these films were performed after annealing the films at 80 °C for 2 h. The **DCPOSS44** film was able to maintain the exciplex emission, whereas monomer emission was observed from the mixed film (Figures 4c and 4d). These results represent that the monomer emission was significantly induced by molecular rearrangement after annealing in the two-components mixed film. In other words, the intramolecularly mixed **DCPOSS** can exhibit higher efficient exciplex emission than the intermolecularly mixed **DPOSS/CPOSS** films. The intramolecularly mixed POSS was highly compatible with each other and did not

cause phase separation, and therefore the situation was favorable for the formation of stable exciplexes. These results indicate that POSS is a useful scaffold for enhancing interaction between two kinds of molecules not only in solution but also in solid.

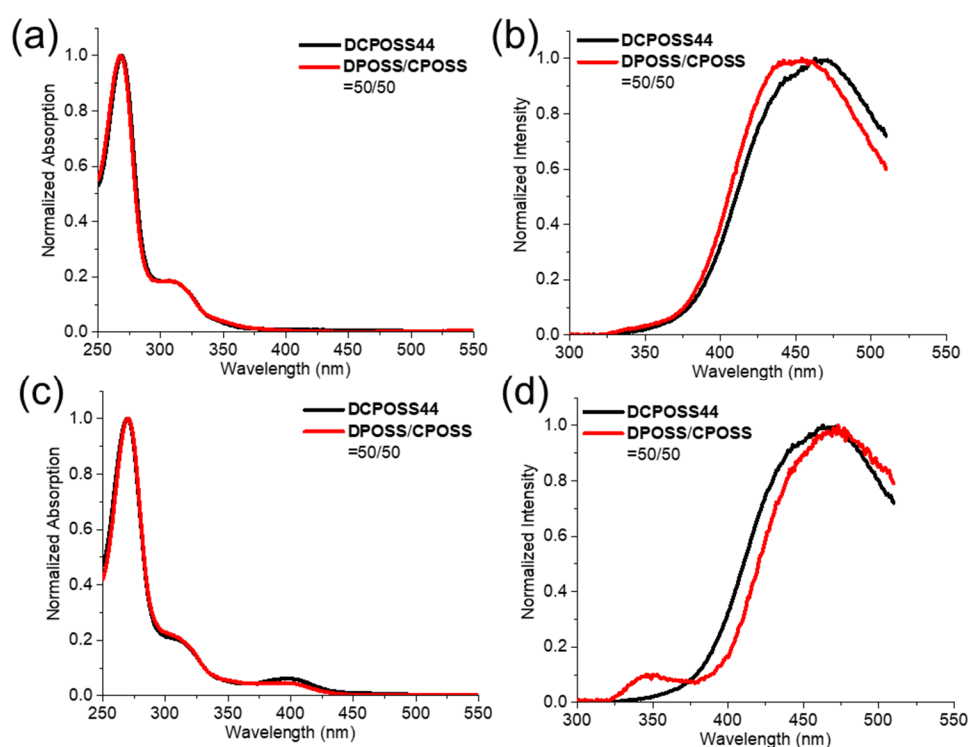


Figure 4. UV-vis absorption and PL spectra of **DCPOSS44** and **DPOSS/CPOSS** mixture films before (a,b) and after (c,d) annealing excited at wavelengths of absorption maxima.

Finally, we attempted to apply this system for demonstrating a fluorescence sensor by regulating the degree of intramolecular exciplex formation. **DCPOSS44** has two types of amines in the linkers and the *N,N*-diethylaniline moieties, and therefore it is expected that the optical properties of **DCPOSS44** are variable in response to acid in multiple steps. The optical properties of **DCPOSS44** were measured with various concentrations of trifluoroacetic acid (TFA) in cyclohexane solutions of **DCPOSS44** at 1.0×10^{-6} M using TFA (Figure 5). By adding

TFA with below 5 equivalents toward POSS, intensity of monomer emission hardly changed as the concentration of TFA increased, meanwhile the exciplex emission intensity decreased. Subsequently, as more than 5 equivalents of TFA were added, the intensity of both emission bands decreased. The reason for this acid-responsiveness is attributable to the presence of two different amines in POSS. Since the pK_a of the conjugated acid of anilines is generally 6 to 7 and that of the conjugated acid of the secondary amine is 10 to 11, it is assumed that the POSS is preferentially protonated by the secondary amine, which is the linker between the luminophores and POSS. The protonation of the secondary amines causes electrostatic repulsion between the side-chains because of the positive charge of the secondary ammonium ion. This may have made it difficult for the formation of exciplex emission. Furthermore, when the amount of TFA exceeds 5 equivalents, the tertiary amine on the *N,N*-diethylaniline should be protonated. Since the monomer emission of *N,N*-diethylaniline is originating from intramolecular charge transfer, the monomer emission should be quenched by the protonation of the tertiary amines. Thus, the expression of intramolecular exciplex emission on POSS should provide the multi-step detection properties for acidic molecules.

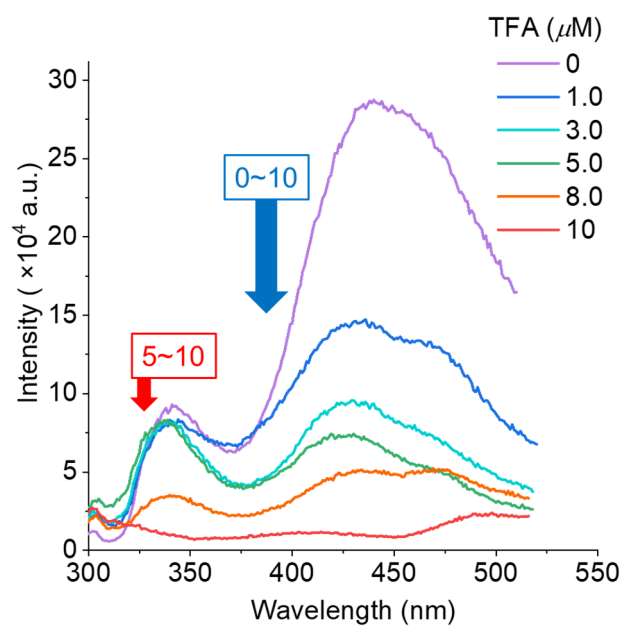


Figure 5. PL spectra of **DCPOSS44** with various concentrations of TFA in cyclohexane/CHCl₃ (1.0×10^{-6} M, 99/1, v/v) excited at wavelengths of absorption maxima.

Conclusion

POSSs having two kinds of luminophores which can form exciplex were successfully synthesized through reductive amination. The results of optical measurements under dilute solution conditions showed that exciplex emission originating from the intramolecular interaction between cyanobenzene and *N,N*-diethylaniline. **DCPOSS44** also exhibited highly efficient exciplex emission in the thin film state. Furthermore, **DCPOSS44** performed a unique acid-responsive property because of the presence of two different amines. These results indicate that POSS is a versatile scaffold not only for accumulating and stabilizing excited molecules followed by a radiation process but also for inducing solid-state emission via the photochemical process inside the POSS molecule although POSS itself doesn't have luminescent properties.

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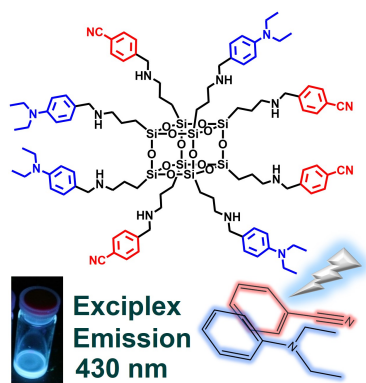
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We successfully monitored sufficient exciplex emission from a small exciplex pair, cyanobenzene and *N,N*-diethylaniline, even in diluted solution by accumulating them in the single polyhedral oligomeric silsesquioxane (POSS) molecule. We also found that the dye-modified POSS showed a unique acid responsiveness which can be caused by protonation at two types of amino moieties, an amino linker and *N,N*-diethylaniline.