ORGANOMETALLICS

Siloxy-Substituted Cyclopentadiene Showing Aggregation-Enhanced Emission: An Application of Cycloaddition of Isolable Dialkylsilylene

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Supporting Information

ABSTRACT: Cycloaddition of an isolable dialkylsilylene converted nonemissive 2,3,4,5-tetraphenylcyclopentadienone to an emissive siloxycyclopentadiene, which shows aggregation-enhanced emission behavior with a light blue fluorescence ($\lambda_{\rm em} = 474$ nm, $\Phi_{\rm F} = 0.11$) in the solid state rather than in solution.



A lthough molecular luminescence is generally quenched in the condensed phase, some polyarylated compounds such as cyclopentadiene, silacyclopentadienes (siloles), fulvenes, and butadienes show unusual strong emission in the solid state rather than in solution. This unique emission behavior has been rationalized by suppression of the undesired nonradiative quenching process involving rotation of peripheral aryl rings and $\pi-\pi$ stacking of the central aromatic core in the solid state and is called "aggregation-enhanced emission (AEE)" or "aggregation-induced emission (AIE)".^{1,2} In recent years, AEE-active molecules have received much attention because of their advantage for emissive functional materials.

The AEE-active molecules are often synthesized by transition metal catalyzed reactions. However, because the residual transition metals occasionally cause trouble in their usage as materials,³ non-transition metal routes for the synthesis are increasingly demanded. In this aspect, cycloaddition of silylenes (silicon version of carbenes) may have an advantage for the synthesis of the AEE active molecules, because dialkylsilylene 1 (R_2^HSi ;, Chart 1)⁴ is now available as an isolable but reactive





Scheme 1. Plausible Reaction Mechanism



compound toward aromatic ketones and other substrates without transition metal catalysts. In addition, the bulky dialkylsilyl group may serve as a good isolator between aromatic cores of the silylene-incorporated AEE molecules.⁵⁻⁷ Recently, dihydrocyclopenta[a]indene 2, which shows AEE behavior, has been synthesized by palladium-catalyzed trimerization of diphenylacetylene.^{2g} The skeletal structure of 2 is quite similar to 3, synthesized by Belzner and co-workers using the reaction of a base-stabilized transient diarylsilylene [Ar₂Si:, Ar = 2-(dimethylaminomethyl)phenyl] with 2,3,4,5-tetraphenylcyclopentadienone (tetracyclone), while its luminescence behavior has not been reported.^{6c} These studies prompted us to investigate the reaction of dialkylsilylene 1 with tetracyclone.⁸ The reaction gives the desired cycloadduct 4 in a high yield, while siloxyfulvene 5 (a 2:1 adduct of 1 with tetracyclone) is obtained as a sole byproduct depending on the conditions. Compound 4 shows remarkable AEE in the solid state.

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Figure 1. Molecular structure of 4. Thermal ellipsoids are drawn at the 30% probability level. Selected bond lengths (Å): Si1-O1 = 1.6976(17), Si1-C7 = 1.878(3), O1-C1 = 1.359(3), C1-C2 = 1.473(3), C1-C5 = 1.352(4), C2-C3 = 1.355(4), C3-C4 = 1.520(4), C4-C5 = 1.516(3), C5-C6 = 1.454(3), C6-C7 = 1.419(4), C6-C11 = 1.399(4), C7-C8 = 1.400(3), C8-C9 = 1.390(4), C9-C10 = 1.382(4), C10-C11 = 1.387(4).



Figure 2. Packing diagram of 4 along the *b*-axis. Tetraphenylcyclopentadiene units are shown in red.

When 1 was added to a toluene solution of one equivalent of tetracyclone, the color of the solution turned from purple of tatracyclone to dark red. After usual workup, fluorescent, pale yellow solid of 4 was isolated in 81% yield with a trace amount of unprecedented 1:2 adduct 5, having siloxypentafulvene and 7-silanorbornene moieties, as a red-brown solid. The yield of 5 increased to 46% by the reaction of two equivalents of 1 with tetracyclone in hexane.⁹

A plausible formation mechanism of **4** and **5** is displayed in Scheme 1. Formation of **4** and **5** suggests the existence of π extended fulvene 7 as a relatively long-lived intermediate. Thus, ring closure of carbonyl silaylide **6** formed by complexation of **1** with tetracyclone would afford π -extended fulvene 7.¹⁰ Thermal rearomatization of 7 via hydrogen shift would provide **4**,



Figure 3. Emission spectra of 4 in THF–water mixed solvents (colored solid lines) and normalized emission spectrum in the solid state (dotted black line). These spectra were obtained by excitation at each $\lambda_{\rm max}$ in solution and 350 nm in the solid state.

similarly to the reaction of Belzner's silylene with tetracyclone, 5c while the [1+4] cycloaddition of 7, having a reactive cyclohexadiene moiety, with another silylene 1 would give 5.¹¹

The molecular structure of 4 was unequivocally determined by X-ray structural analysis, as shown in Figure 1. A cyclopentadiene moiety with a saturated C4 atom exists in 4 with C1-C5 and C2-C3 lengths of 1.352(4) and 1.355(4) Å and C1-C2, C3-C4, and C4-C5 lengths of 1.473(3), 1.520(4), and 1.516(3) Å, respectively. The cyclopentadiene ring and the silvlated benzene ring are almost coplanar, with an interplane angle of 0.84°, indicating effective conjugation between the cyclopentadiene and the phenyl ring. As shown in Figure 2, 4 forms a lamellar structure consisting of a bulky 2,2,5,5-tetrakis(trimethylsilyl)-1-silacyclopentane moiety $(R_{2}^{H}Si:)$ and π -systems (given in red) in the solid state. Each phenylcyclopentadiene core of 4 is well segregated by the peripheral phenyl rings. Although the shortest intermolecular C…C distance was 3.298 Å in the crystal (Figure S7, in the Supporting Information), no significant $\pi - \pi$ stacking exists. The R^H₂SiO unit works as an effective isolator of the aromatic core.

The UV-vis absorption spectrum of 4 in THF (Figure S1, Supporting Information) showed an absorption band at 374 nm ($\varepsilon = 1.56 \times 10^4$) assignable to the $\pi \to \pi^*$ (HOMO \to LUMO) transition.¹² With increasing the water content, absorption tailing due to light scattering indicating the aggregation of 4 was observed, but the transition band was not significantly shifted. As expected, compound 4 shows typical aggregation-enhanced emission behavior, as shown in Figure 3. The very weak fluorescence of 4 in THF solution is observed at 474 nm with a quantum yield ($\Phi_{\rm F}$) of 0.25% when the $\pi \rightarrow \pi^*$ (HOMO \rightarrow LUMO) transition band of 4 at 374 nm is excited. Emission intensity of 4 in a THF-water (1:9) mixed solvent, however, is enhanced by 21 times compared to that in THF solution (Figure S2, in the Supporting Information). A fine powder of 4 on a glass plate displays much more intense light blue fluorescence at 476 nm with a $\Phi_{
m F}$ of 11%, which is 40 times enhanced compared to that in the THF solution. Notably, the emission band shapes of 4 in various solvents and in the solid state are similar to each other, which is consistent with the well π -segregated packing structure

of 4, as shown in Figure 2.¹³ The emission behavior of 4 can be explained by the reported AEE mechanism; nonradiative decay owing to rotation of phenyl rings and $\pi - \pi$ stacking would be suppressed in the solid state by the peripheral phenyl rings and the bulky silylene moiety.^{1,2}

The emission properties $(\lambda_{max} \text{ and } \Phi_F)$ of 4 are similar to those of dihydrocyclopenta[*a*]indene 2 $(\lambda_{max} = 458 \text{ nm}, \Phi_F)$ (in 1:9 THF–water mixed solvent) = 11.7%).^{2g} Although the emission band of 4 was red-shifted by 20 nm compared to that of 2, probably due to the electronic effect of the siloxy group R^H_2SiO connected to the π -core, the bulky R^H_2SiO unit does not affect the AEE nature of tetraphenylcyclopentadiene significantly, as expected by the crystal structure.

In summary, we have demonstrated that cycloaddition of silylene 1 with tetracyclone giving a siloxycyclopentadiene is a promising synthetic route of AEE molecules without transition metal catalysts. Further investigation is in progress.

ASSOCIATED CONTENT

S Supporting Information

Synthetic details and physical data of 4 and 5; theoretical studies of model compounds for assignment of the UV–vis absorption bands. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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(9) Molecular structure and packing diagram of **5** determined by Xray structural analysis are shown in Figures S8 and S9 in the Supporting Information. Similarly to **4**, the lamellar structure was observed for the crystal of **5**. Compound **5** shows a weak absorption at 447 nm ($\varepsilon = 769$) (HOMO \rightarrow LUMO transition) and an intense band assignable to the HOMO-1 \rightarrow LUMO transition at 398 nm in hexane solution. Although some dibenzofulvenes showed AEE behavior,^{2e} compound **5** does not show detectable fluorescence both in solution and in the solid state, probably due to its small molar extinction coefficient.

(10) In our previous report, the silicon atom of the dimethylsilylenecyclopentadienone complex, a cyclopentadienone silaylide, was found to be positively charged by computational studies, suggesting electrophilic addition of the silicon to an intramolecular aromatic ring would be reasonable. For details, see ref 8a.

(11) Intermediate 7 was not observed during the reaction. The details of the isomerization of 7 to 4 via formally [1,7] hydrogen shift remains open.

(12) Assignment of UV-vis absorption bands are based on the TD-DFT calculations of the model compounds described in the Supporting Information.

(13) The emission spectrum of powdery 4 has two less-resolved maxima, which may be attributed to emission from a different phase such as crystalline and amorphous phases and/or Davydov splitting.