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Synthesis and Photophysical Properties of Two Strongly Fluorescent Bis(diquinaldinatoalumino)-9-silafluorenes

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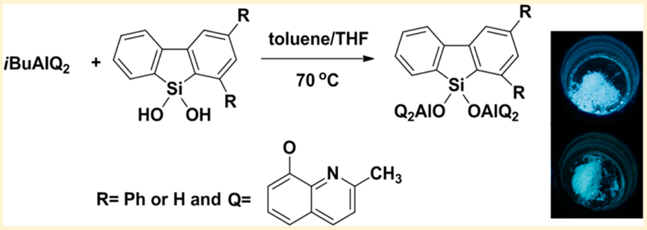
Supporting Information

ABSTRACT: Two novel highly fluorescent blue light emitting compounds were synthesized: 9,9-bis(diquinaldinatoalumino)-1,3-diphenyl-9-silafluorene (**4**) and 9,9-bis(diquinaldinatoalumino)-9-silafluorene (**7**). Combining silafluorene and quinaldinate aluminum moieties resulted in molecules with high quantum yield efficiency both in solution (31–34%) and in the solid state (79–92%). **4** showed intense electroluminescence, 4090 cd/m^2 at 15 V, and the mechanochromism of **7** was revealed.



Silafluorenes are π-conjugated organosilicon compounds with remarkable optical and electronic properties. Due to their special electronic structure they can be applied in electron transporters and emitters for fabrication of organic light emitting diodes (OLEDs) and photovoltaic cells.[1,2] Several kinds of silafluorene derivatives have been synthesized in order to obtain blue-emitting compounds, oligomers, or polymers.[3−5] Some silafluorene complexes have also been reported,[6] but the combination of another fluorescent moiety with silafluorenes in one molecule seems to be novel. Here we provide the synthesis and optical characterization of two blue light emitting silafluorene derivatives attached to diquinaldinato aluminum groups.

Tris(8-hydroxyquinolinato)aluminum (Alq$_3$) is a favored material for fabrication of electroluminescent devices as an electron transporter and emitter.[7] It is stable and emits green light with good quantum efficiency in the solid state. Alq$_3$ can be transformed into blue- or white-emitting compounds by doping or introducing different substituents.[8,9] Tris(2-methyl-8-oxyquinolinato)aluminum (AlQ$_3$) showed a significant blue shift in the emission spectrum (λ_{max} 479 nm) and increased emission intensity.[10,11] AlQ$_3$ is not stable in air; thus, (μ-oxo)bis(bis(2-methyl-8-quinolinolato)aluminum(III)) (Q$_2$Al(μ-O)AlQ$_2$) was also investigated and found to be very similar to AlQ$_3$ in its optical properties; it shows the same blue shift due to methyl substitution.[12,13]

For high-performance OLED applications a large solid-state quantum yield is very beneficial. Our objective was to provide compounds that show high fluorescence quantum yield without the need for doping, which would simplify the final fabrication process of electronic devices. This objective was approached by combining two blue-emitting moieties, diquinaldinatoaluminum and silafluorene. Compound **1**, isobutylaluminodiquinaldinate (*i*BuAlQ$_2$), can be synthesized according to a known method;[14] 9,9-dichloro-1,3-diphenyl-9-silafluorene (**2**)[4] and 9,9-dichloro-9-silafluorene (**5**)[3] are known as well. The starting materials 9,9-dihydroxy-1,3-diphenyl-9-silafluorene (**3**) and 9,9-dihydroxy-9-silafluorene (**6**) were prepared by hydrolysis of **2** and **5**, respectively, similarly to some silole derivatives[15] (see the Supporting Information). 9,9-Bis(diquinaldinatoalumino)-1,3-diphenyl-9-silafluorene (**4**) and 9,9-bis(diquinaldinatoalumino)-9-silafluorene (**7**) were formed in the reactions of *i*BuAlQ$_2$ (**1**) with **3** and **6**, as depicted in parts a and b of Scheme 1.

Silafluorene complexes **4** and **7** were identified by ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, X-ray crystallography analysis, and mass spectra. Crystal structures of **4** and **7** are presented in Figures 1 and 2, respectively. We found two stereoisomers of **7**, which are shown in Figure 2, but we could not separate them; thus, all results in this paper refer to the isomer mixture.

Q$_2$Al(μ-O)AlQ$_2$ exhibits an absorption band at 365 nm and a fluorescence emission at 485 nm, while Alq$_3$ has its characteristic absorption band at 395 nm and fluorescence emission at 517 nm. Methyl substitution caused a significant blue shift in both the absorption and emission spectra.

1,3,9,9-Tetraphenyl-9-silafluorene has an absorption band at 330 nm and an emission maximum at 368 nm; the quantum yield efficiency in CH$_2$Cl$_2$ solution is 17% while it is 42% in solid state.[4] The absorbance of its unsubstituted analogue 9,9-diphenyl-9-silafluorene ranges around 310 nm, and the emission is at 348 nm with 10% quantum yield efficiency in CH$_2$Cl$_2$ solution and 16% in the solid state.[4] It was revealed that phenyl substitution at positions 1 and 3 on the silafluorene

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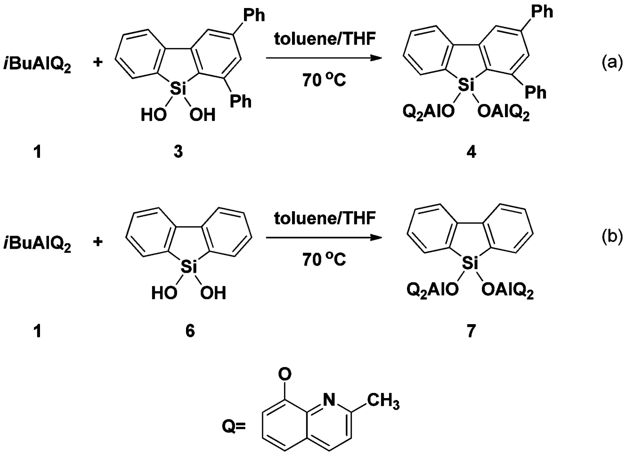
Scheme 1. Synthetic Route for the Synthesis of 9,9-Bis(diquinaldinatoalumino)-1,3-diphenyl-9-silafluorene (4) and 9,9-Bis(diquinaldinatoalumino)-9-silafluorene (7)



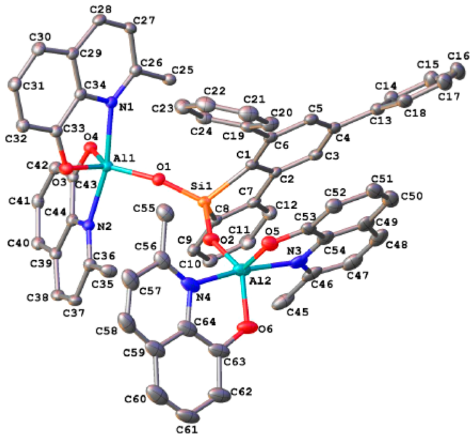


Figure 1. Single-crystal structure of **4** determined by X-ray diffraction (XRD). The displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted for clarity.

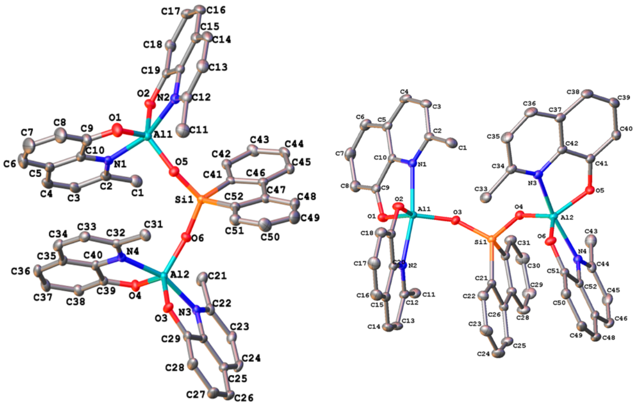


Figure 2. Single-crystal structures of the two stereoisomers of **7** determined by X-ray diffraction (XRD). The displacement ellipsoids are drawn at the 50% probability level. All H atoms have been omitted for clarity.

ring causes a significant red shift in both absorption and emission spectra, and also the fluorescence quantum yield efficiency was improved.[4]

For compounds **4** and **7** the absorbance at about 250−260 nm is the most intense. This range belongs to the absorption of the phenyl rings. The second most significant peaks range around 350−360 nm, and they could be used for excitation. In comparison to Alq_3 or to $Q_2Al(\mu\text{-}O)AlQ_2$ their absorbance is blue-shifted (see the Supporting Information), but in comparison to the analogous silafluorene molecules, a significant red shift occurred.

The fluorescence emission of **4** and **7** is also blue-shifted in comparison to Alq_3 and $Q_2Al(\mu\text{-}O)AlQ_2$ (Figure 3) and red-shifted in comparison to the analogous silafluorenes.

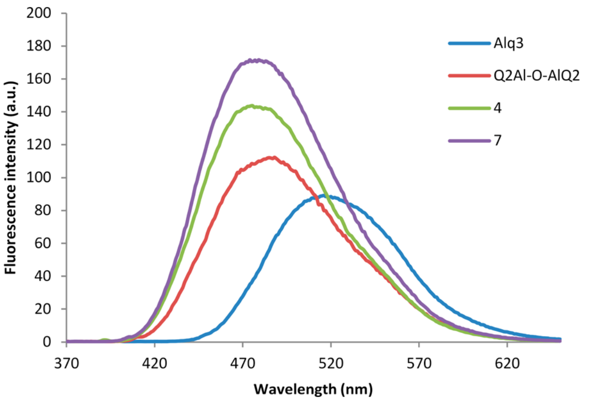


Figure 3. Fluorescence spectra of **4** and **7** compared to those of Alq_3 and $Q_2Al(\mu\text{-}O)AlQ_2$ (10 ppm solutions in THF).

Single peaks on all spectra indicate that in the combined molecules, **4** and **7**, new chromophores were created. They do not have distinguishable absorption or emission, but the silafluorene and the aluminoquinaldinate moieties interact and enhance each other's emission. According to the excitation spectra (see the Supporting Information) the aluminoquinaldinate fragment is dominant in the emission in solution, but in the solid state this dominance might disappear, as is indicated by the exceptionally high quantum yield efficiencies and the blue shift of the fluorescence maxima.

When **4** and **7** are compared to previously reported silole−aluminoquinaldinate compounds,[15] the major differences appear in solution. While the silole complexes are barely emissive in organic solvents, **4** and **7** are good fluorescing compounds. On the other hand, **4** and **7** do not show aggregation-induced emission (AIE) in water−THF solution like siloles, but they do not show aggregation-caused quenching (ACQ), either.

Fluorescence quantum yield efficiency (Φ_F) was investigated in THF with quinine sulfate in 0.1 N sulfuric acid (H_2SO_4) as the standard.[16] Both compounds **4** and **7** exhibit high Φ_F values in solution, and they are even more enhanced in the solid state (see Table 1). When the silafluorene and the aluminoquinaldinate moieties are blended, enhanced fluorescence efficiency can be observed also in solution. The outstanding solid-state fluorescence quantum yield efficiency can be attributed to the structure of these complexes: none of these compounds are planar, and therefore they do not have $\pi-\pi$ stacking interactions in solid state, which usually causes ACQ.[17] **4** displays an extremely high quantum yield of 92%, in comparison to 35% for Alq_3 and 24% for $Q_2Al(\mu\text{-}O)AlQ_2$. This even more enhanced Φ_F in comparison to that for **7** can be explained by the restricted intramolecular rotation (RIR) of the phenyl groups. On comparison of **4** and **7**, phenyl

Table 1. Photophysical Properties of Silole Complexes **4** and **7** in Comparison to Those of Alq_3 and $Q_2Al(\mu\text{-}O)AlQ_2$[a]

compd	λ_{ab} (nm)	λ_{em} (nm)	Φ_F(soln)	λ_{em}(solid) (nm)	Φ_F(solid)
4	250; 350[b]	476	0.34	470	0.92
7	260; 360[b]	476	0.31	461	0.79
$Q_2Al(\mu\text{-}O)AlQ_2$	250; 312; 365[b]	485	0.24	485	0.24
Alq_3	260; 395[b]	517	0.11	512	0.35
quinine sulfate	347[b]	445	0.54		

[a] Abbreviations: λ_{ab} = absorption maximum in THF solution, λ_{em} = emission maximum in THF solution, Φ_F(soln) = fluorescence quantum yield in THF solution determined using quinine sulfate in 0.1 N H_2SO_4 as a standard, λ_{em}(solid) = emission maximum in the solid state, Φ_F(solid) = fluorescent quantum yield of solid powder determined by a calibrated integrating sphere. Excitation wavelength: 325 nm. [b] Excitation wavelength in solution.

substitution has a positive effect on Φ_F while it does not influence the emission range and induces a blue shift of the maximum only in the solid state (Figures 4 and 5).

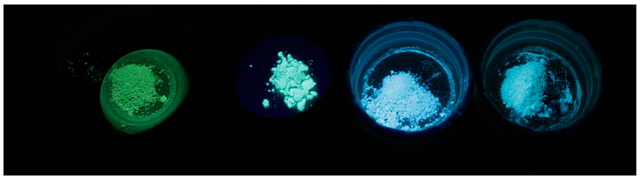


Figure 4. Fluorescing microcrystals (from left to right): Alq_3, $Q_2Al(\mu\text{-}O)AlQ_2$, **4**, **7**.

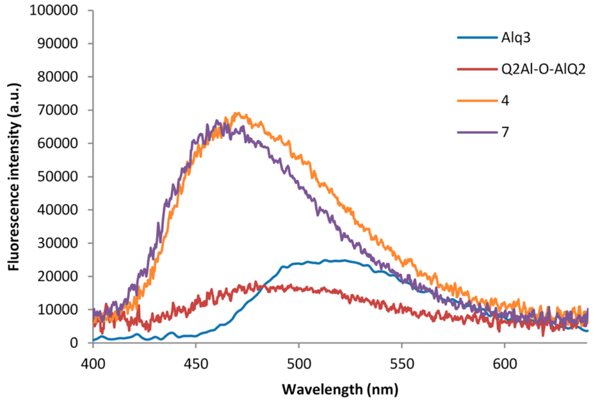


Figure 5. Fluorescence spectra of **4** and **7** compared to Alq_3 and $Q_2Al(\mu\text{-}O)AlQ_2$ in the solid state.

In the preparation of samples for the solid-state fluorescence measurements, the mechanochromism of **7** was observed and investigated further. Crystalline **7** had its emission maximum at 461 nm; after grinding it became slightly greenish with λ_{max} 481 nm. When the powder was treated with acetone vapor, the emission reverted to the original blue color (Figures 6 and 7). The color change might occur due to very small changes in the crystal lattice, as the powder X-ray diffraction (XRD) data of **7** before and after grinding do not show significant differences (see the Supporting Information).

Finally a light-emitting device with the structure ITO/NPB/**4**/TPBi/LiF/Al was fabricated. At 15 V this device emitted greenish blue light at 512 nm with a maximum luminance of 4090 cd/m^2 (for Alq_3: 520 nm and 19500 cd/m^2). Its onset voltage was 4.8 V, the peak external quantum efficiency 1.07%, and the current efficiency 2.92 cd/A at 39.2 mA/cm^2 current density (for Alq_3: 3.0 V, 1.6%, 5.13 cd/A at 8.74 mA/cm^2) (see the Supporting Information.) Though these characteristic values are less advantageous than those of Alq_3, with device optimization OLEDs made of these novel compounds can be improved. Due to the exceptionally high solid-state fluorescence results other applications will be the subject of further investigations as well.

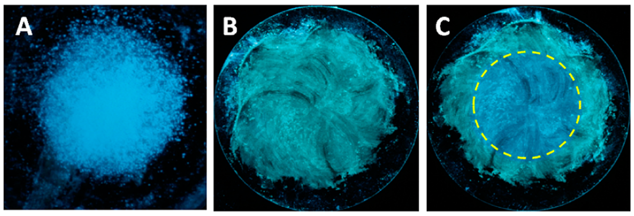


Figure 6. Mechanochromism of **7**. Solid-state emission before (A) and after grinding (B) and then after fuming by acetone vapor (C). The photographs were taken under 365 nm UV irradiation.

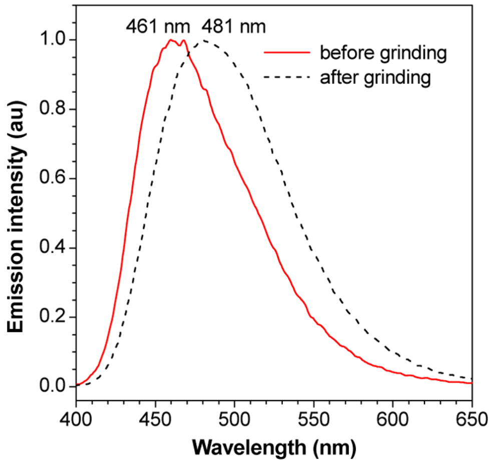


Figure 7. Photoluminescence spectra of a solid powder of **7** before and after grinding. Excitation wavelength: 341 nm.

In summary, we have prepared two new highly fluorescent diquinaldinatoalumino−silafluorene complexes. The combination of strong emitters and electron transporters, silafluorenes and aluminoquinaldinate, in one molecule has led to an intense blue emission with a 2.6-fold increase of fluorescence efficiency in the solid state in comparison to the standard Alq_3. Mechanochromic behavior of **7** was also revealed. An organic light-emitting device with the structure ITO/NPB/**4**/TPBi/LiF/Al was fabricated, which emits greenish blue light at 512 nm with luminance of 4090 cd/m^2 at 15 V. Thus, these silafluorene−aluminoquinaldinate compounds appear to be suitable candidates for use in organic electronics.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text, figures, tables, and CIF files giving detailed experimental procedures and characterization data for the products and crystallographic data for **4** and **7**. This material is available free of charge via the Internet at http://pubs.acs.org. The crystal structures are available free of charge from the Cambridge Crystallographic Data Center; the CCDC codes are CCDC-

942623 for compound **4** and CCDC-942624 and CCDC-966617 for compound **7**.

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Notes

The authors declare no competing financial interest.

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