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Facile Synthesis of Functional Alkoxysilane Precursor with Short Linkers toward Organosilica Hybrids with a High Density of Chromophores

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Tetraphenylpyrene (TPPy)-bridged alkoxysilane precursors with short linkers were synthesized by development of a facile synthetic route, and sol–gel polymerized to transparent organosilica films which showed higher absoption coefficient than the conventional route due to dense accumulation of TPPy units in the films.

Organosilica hybrids, synthesized by sol–gel polymerization of organic-bridged alkoxysilane precursors ($R[Si(OR')_3]_n$, $n > 2$, R: functional organic group, R′: Me, Et), are a new class of functional organic–inorganic hybrid materials in which organic groups are covalently and homogeneously embedded in the robust silica networks.[1,2] Recently, these materials have received considerable attention in various areas such as optical materials,[3] photocatalyst,[4] and electronic devices due to their organic functionalities and high stability.[5] For the development of these applications, efficient light absorption and/or strong intermolecular interaction are essential factors. Consequently, the high density accumulation of organic chromophores in the organosilica hybrids has become a currently interesting work in this field.

The density of chromophores in organosilica hybrids should strongly depend on the molecular architecture of the alkoxysilane precursor. Thus, precursors with chromophores directly attached with silyl groups, which are typically prepared by halogen–lithium and –magnesium exchange reactions[2a] or rhodium-catalyzed silylation of aryl halides,[6] are the most desirable for dense accumulation. However, the synthesis of desired functional alkoxysilane precursor is generally difficult, because the high reactivity of trialkoxysilyl groups is likely to cause side reactions such as polymerization and decomposition during these silylation reactions and purification. Furthermore, conventional routes are often limited in terms of difficulties in the preparation of halogenated substrate and functional tolerance in their reaction conditions. In addition, the Si–C bonds of this type of precursors sometimes cleave during the acidic or basic sol–gel polymerization.[7] Meanwhile, coupling reaction of silane coupling agents with hydroxy- or amino-substituted substrate has been widely used for the synthesis of functional organosilane precursors due to easiness in the preparation of substrates and mild reaction conditions.[8] We recently reported the synthesis of 1,3,6,8-tetraphenylpyrene (TPPy)-bridged alkoxysilane precursor **1-U3** by coupling of tetrahydroxy-substituted TPPy with triethoxy(isocyanatopropyl)silane and its conversion to the transparent periodic mesostructured organosilica film with efficient blue fluorescence emissions (Figure 1).[9] However, the long linkers in **1-U3** were also found to limit light absorption efficiency of the hybrid films. It is required to establish silylation routes other than direct silylation for dense accumulation of the organic-bridging groups (e.g., TPPy in **1-U3**). There have been few reports, however, on successful synthesis of high functional organosilane precursors with short linker.[10]

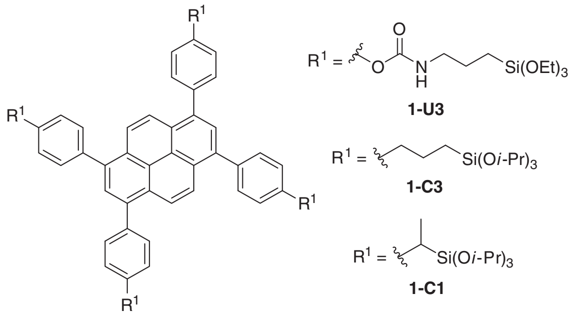


Figure 1. TPPy-bridged alkoxysilane precursors **1-U3**, **1-C3**, and **1-C1**.

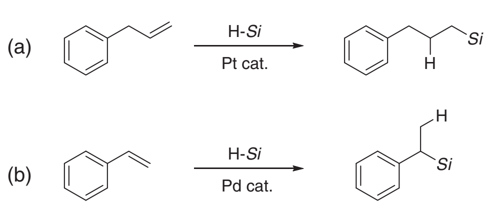
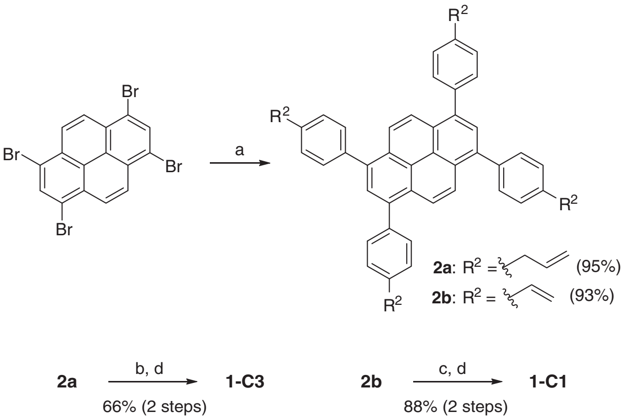


Figure 2. Regioselective hydrosilylation of olefinic aromatics catalyzed by platinum- or palladium-catalyst.

Herein, we report facile synthetic routes of aromatic-bridged alkoxysilanes with short linkers, their sol–gel conversions to organosilica films, and optical properties of the films.

We synthesized novel TPPy-bridged alkoxysilane precursors with short linkers, **1-C3** and **1-C1** (Figure 1). To develop the synthetic route of these precursors, we employed two main reactions, regioselective hydrosilylation and the Suzuki–Miyaura coupling. It is well-known that the platinum-catalyzed hydrosilylation of allyl-substituted compound gives the γ-silylated (linear) product (Figure 2a).[11] On the other hand, palladium-catalyzed hydrosilylation of vinyl-substituted compound furnishes the α-silylated (branched) product (Figure 2b).[12] Therefore, organosilane precursors with short linkers could be prepared from olefinic aromatics by regioselective hydrosilylation.[13]

The efficient synthetic route of olefinic aromatics has been limited to the allylation of unstable lithiated species.[10a] Although this method has been applied to the synthesis of various olefinic aromatics, the reaction requires moisture-free and cryogenic conditions and often results in low yields or undesired product.



Scheme 1. Synthetic routes to newly designed TPPy-bridged alkoxysilane precursors; **1-C3** and **1-C1**. Reagents and conditions: (a) $[Pd(PPh_3)_4]$, K_2CO_3 (aq), 4-allylphenylboronic acid, 1,4-dioxane, 90 °C for **2a**, $[Pd(PPh_3)_4]$, K_3PO_4 (aq), 4-vinylphenylboronic acid, 1,4-dioxane, 80 °C for **2b**; (b) $H_2[PtCl_6]\cdot 6H_2O$, $HSiCl_3$, benzene, 40 °C; (c) $[PdCl(\pi\text{-}C_3H_5)]_2$, *rac*-H-MOP, $HSiCl_3$, benzene, 40 °C; (d) *i*-PrOH, pyridine, CH_2Cl_2, 0 °C–rt.

To overcome these limitations and difficulties, we employed a useful approach, the Suzuki–Miyaura coupling of aryl halide with olefin-substituted phenylboronic acid as shown in Scheme 1.[14]

The olefinic TPPy derivatives **2a** and **2b** were synthesized by the palladium-catalyzed Suzuki–Miyaura coupling of 1,3,6,8-tetrabromopyrene with 4-allylphenylboronic acid or 4-vinylphenylboronic acid, respectively (Scheme 1). Each reaction successfully proceeded in the presence of $[Pd(PPh_3)_4]$ (12 mol %) as catalyst and gave the desired product **2a** and **2b** in 95% and 93% yield, respectively. Fortunately, undesired side reactions such as isomerization and polymerization of olefinic moiety were not observed. The obtained **2a** and **2b** were then regioselectively hydrosilylated with trichlorosilane in the presence of platinum or palladium catalyst, respectively. The use of $H_2[PtCl_6]\cdot 6H_2O$ (Speier's catalyst)[11] was found to be effective for **2a**. The hydrosilylation proceeded regioselectively at γ-position of four allyl groups and gave the TPPy-bridged trichlorosilane in almost quantitative yield. The 4-fold hydrosilylation of **2b** was carried out in the presence of $[PdCl(\pi\text{-}C_3H_5)]_2$/*rac*-H-MOP.[12] As expected, the reaction regioselectively proceeded at α-positions of four vinyl groups and furnished the desired TPPy-bridged trichlorosilane quantitatively. However, the obtained chlorosilanes were too moisture-sensitive to handle as a precursor for the organosilica hybrids. Thus, these trichlorosilyl groups were transformed into relatively stable triisopropoxysilyl groups by quenching with 2-propanol in the presence of pyridine as a base, which afforded desired TPPy-bridged alkoxysilane precursors with short linkers **1-C3** and **1-C1** in 66% and 88% yield, respectively (Figures S1–S4).[15,18]

From TPPy-bridged organosilanes **1-U3**, **1-C3**, and **1-C1**, organosilica hybrid films could be obtained by sol–gel polymerization in the presence of hydrochloric acid and water in propylene glycol propyl ether. Transparent yellow films without cracks and inclusions were successfully obtained from all the precursors (Figure S5[18]). The use of the high boiling point solvent facilitates the formation of uniform thickness of film due to the suppression of heterogeneous shrinkage during solvent evaporation.[16] The thicknesses of **1-U3-F**, **1-C3-F**, and **1-C1-F** were 1450 ± 50, 455 ± 30, and 235 ± 30 nm, respectively. The change in the thickness can be attributed to the difference in the viscosity of the sol solutions.

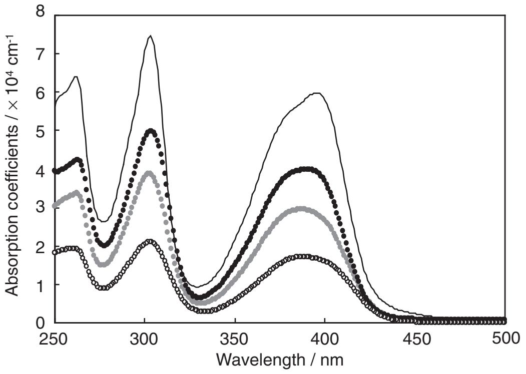


Figure 3. Dependence of the absorption coefficients for **1-U3-F** (white circles), **1-C3-F** (gray circles), **1-C1-F** (black circles), and **TPPy-F** (solid line) on the wavelength. The absorption coefficients were obtained by normalizing the absorbance of the films at every wavelength according to the film thicknesses.

We evaluated the optical properties of TPPy-bridged alkoxysilane precursors and derived organosilica films to elucidate the effects of the linker length on accumulation state of TPPy moieties in these silica hybrids. The novel TPPy precursors **1-C3** and **1-C1** showed primary similar absorption and fluorescence properties compared with those of conventional precursor **1-U3** and their parent TPPy molecule (Figure S6[18]). This suggests that the present linkers hardly influenced the electronic ground and excited state of these precursors in diluted condition. In contrast, optical properties of derived organosilica films were quite different from one another. Figure 3 shows the wavelength dependence of the absorption coefficients (absorbance normalized by the film thickness) for organosilica and TPPy molecular films (**TPPy-F**). The absorption coefficient was significantly increased in the order of **1-U3-F** ($17000\,cm^{-1}$) < **1-C3-F** ($29400\,cm^{-1}$) < **1-C1-F** ($39900\,cm^{-1}$) < **TPPy-F** ($59800\,cm^{-1}$). It is quite reasonable to observe the difference in absorption coefficients because the ratios of TPPy moiety to whole molecules are completely different in their precursors. The maximum wavelengths of absorption spectra (λ_{max}) slightly red-shifted with respected to that for corresponding precursor solutions due to intermolecular interaction between TPPy moieties at the ground state. However, the observed red shift in the films is very small and shift values do not depend on the linker length. This may be attributed to the bulky structure of TPPy which inhibits dense packing of TPPy moiety in organosilica hybrids.

Figure 4 shows fluorescence emission spectra for the organosilica and TPPy molecular films. The organosilica film **1-U3-F** showed broad emission bands at 450 and 470 nm which are assignable to monomer-like and excimer emissions, respectively.[9] The existence of the strong monomer-like band and the relatively small red shift of the excimer band suggest relatively weak intermolecular interaction between the TPPy moieties in the excited state due to the long linker length in **1-U3**. In

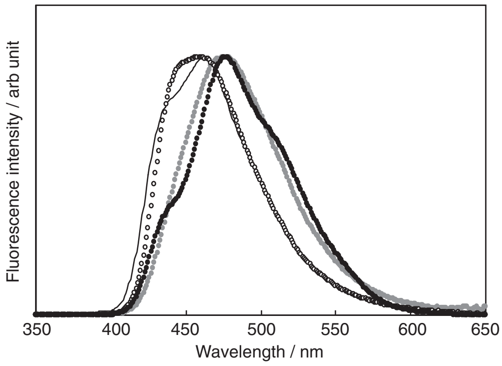


Figure 4. Fluorescence emission spectra of **1-U3-F** (white circles), **1-C3-F** (gray circles), **1-C1-F** (black circles), and **TPPy-F** (solid line). The excitation wavelength was 380 nm for all samples.

contrast, organosilica films **1-C3-F** and **1-C1-F** mainly showed the excimer emission band at 478 nm, which is red-shifted from that of **1-U3-F**, together with a weak monomer-like emission at 440 nm. In addition, **1-C1-F** showed a shoulder possibly due to the emission from TPPy dimer at 510 nm.[17] These results strongly suggest that the shortening of the linker effectively enhanced intermolecular interaction between the TPPy moieties in the excited state. On the other hand, **TPPy-F** showed a fluorescence spectrum similar to that of **1-U3-F** despite the densest packing of the TPPy moieties possibly due to their different molecular arrangement from those of the organosilica films in which the TPPy moieties are fixed in the silica network.

In conclusion, we demonstrated the facile synthetic route of functional organic-bridged alkoxysilane with short linker by regioselective hydrosilylation. Novel TPPy-bridged alkoxysilane precursors with short linker were successfully synthesized using the present procedure with aim to increase the absorption coefficient of TPPy-bridged organosilica film. A significant improvement of the absorption coefficient of the film was observed by shortening of linker length due to the high density of TPPy moieties in the film.

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18 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.