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Synthesis and properties of chromophore-functionalized monovinylsilsesquioxane derivatives†

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A facile and efficient Pd-based Suzuki–Miyaura coupling reaction leading to mixed chromophores with styryl fragments, enabling their further application, is presented. We also disclose their use in the formation of monofunctionalized silsesquioxanes with a chromophore group covalently bound to a T_8 core that have been prepared *via* a cross-metathesis reaction. These new materials were studied in terms of their photophysical and also thermal properties.

Introduction

Polyhedral oligomeric silsesquioxane (SQ) derivatives have attracted extensive attention from the research community as nanometric building units/precursors of hybrid materials.[1] The particularly distinguished features of SQ compounds are the rigid Si–O–Si core, bulky structures, high thermal stability, and low dielectric constant. Because of their easily tunable physicochemical properties, SQs meet the requirements of many branches of science.[2–10] Interestingly, the use of silsesquioxanes as scaffolds for chromophores or SQ introduction into photoactive polymers/oligomers may affect their photoluminescent (PL) and/or electroluminescent (EL) properties. This is mainly due to the separation of their highly π-conjugated moieties and suppression of self-quenching or, in contrast to this, silsesquioxanes may be engaged in the electron delocalization and enhance the emissive properties of resulting frameworks.[11–19] The resulting SQ-based systems offer other advantages, *i.a.* enhanced thermal resistance, *i.e.* high glass-transition temperatures (T_g) and also stabilized color at higher temperatures, low polydispersity, solubility, and high purity.

The crucial aspect of this investigation is to find the best method to anchor the respective chromophore of a specific nature, taking into consideration its emission wavelength, luminance, and quantum efficiency.[11] The methodology applied is also in line with the reaction paths and synthetic possibilities used to obtain certain precursors of chromophore fragments that are to be anchored onto the rigid Si–O–Si core. This also imposes the requirements for the reactive groups on SQ reagents; the Si–HC=CH_2, Si–C≡CH, and Si–H groups are of chief interest here and the reactions that are used for their respective functionalization: cross-metathesis, Heck, silylative and thiol–ene coupling, Sonogashira or Friedel–Crafts reactions, and hydrosilylation are all of fundamental significance.[11,20–22]

Several groups have extensively examined the combination of SQs with organic luminescent dyes; however, these examples are mostly based on octafunctional silsesquioxane derivatives. In the predominant number of papers, the reactions leading to the desired SQ-based systems (of molecular and macromolecular architecture) exhibiting photoluminescent properties are based on cross-metathesis, Heck coupling and hydrosilylation.[11,23–37] The number of reports on the formation of monosubstituted SQs with chromophores and their photophysical properties is especially limited.[12,38–42]

Our group is experienced in the synthesis of SQs functionalized with arene moieties *via* silylative coupling and cross-metathesis reactions. These processes proceed *via* different mechanisms but as a final result (*E*)-isomers of 1-silyl-2-arylethylene substituents on SQ cores may be obtained stereoselectively.[43–47] Additionally, we have also reported on the synthesis of simple styrylarylenes based on carbazole,[48] ferrocene[49] and other arenes[50] using new Pd complex systems.

Prompted by the hitherto obtained results, we decided to design styrylarenes of high potential for interesting photophysical properties for target applications, *i.e.* anchoring them on the inorganic Si–O–Si core of SQs. The targeted synthetic procedure for the respective styrylarenes was to be based on the

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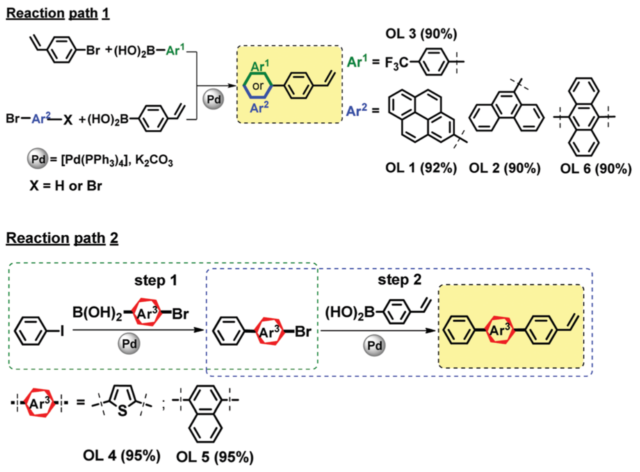
selective Suzuki–Miyaura reaction which involves the palladium-catalyzed coupling of aryl halides with organic boron compounds.[16,17] Our goal was to use the simplest Pd-based catalyst and elaborate mild reaction conditions in order to obtain mixed chromophore systems with high yields. Subsequently, these compounds were the reagents for the selective and efficient cross-metathesis reaction with monovinylsubstituted SQ. The obtained chromophore-anchored silsesquioxanes were evaluated in terms of their photophysical properties and quantum efficiencies in comparison with their bare chromophore derivatives. Additionally, we also verified the thermal stability for selected samples (TGA).

Results and discussion

Synthesis of chromophores by Suzuki–Miyaura coupling

One of the goals of the investigation was to synthesize styrylarene derivatives containing mixed chromophore systems *via* a selective Suzuki–Miyaura reaction.[51] Depending on the structure of the final styrylarenes, two synthetic pathways were proposed. The first was based on the one-step reaction between bromostyrene or bromoarene (Ar^2) and the respective areneboronic acid (Ar^1) or 4-vinylphanylboronic acid (Scheme 1 – reaction path 1). The second proposal was a two-step reaction path based on the coupling of iodophenyl with bromo-areneboronic acid (Ar^3) and then with 4-vinylphenylboronic acid (see Scheme 1 – reaction path 2).

This procedure led to mixed chromophore systems containing different arenes in their structure. The literature describes systems based on aromatic components such as trifluorophenylstyrene,[52] pyrene,[53] thiophene,[54] naphthalene[55] or phenanthrene derivatives.[56] However, reports on these kinds of styrylarene derivatives and their properties and use in functionalization of SQs are scarce. The advantage of the proposed methodology lies in its simplicity, *i.e.* a well-defined and commonly known palladium complex [$Pd(PPh_3)_4$] and K_2CO_3 as a base. The reactions were carried out in a homogeneous system using a two-phase water–organic system (K_2CO_3 in water/toluene and ethanol) and standard Schlenk techniques (inert gas atmosphere – Ar). We also used a small excess of boronic acids because of the risk of their contamination (commercial sources). For the two-step reaction path 2 we noticed incomplete conversion of substrates probably caused by the precipitation of intermediates (bromoarene Ar^3), which led to unwanted products. We decided to use the addition of THF to the reaction mixture to maintain the system's homogeneity during the reactions and this allowed for full conversions of reagents observed by GCMS analysis and TLC. The high synthetic potential of this protocol may be shown in its reproducibility as well as in high yields of the obtained styrylarenes, up to 95%.

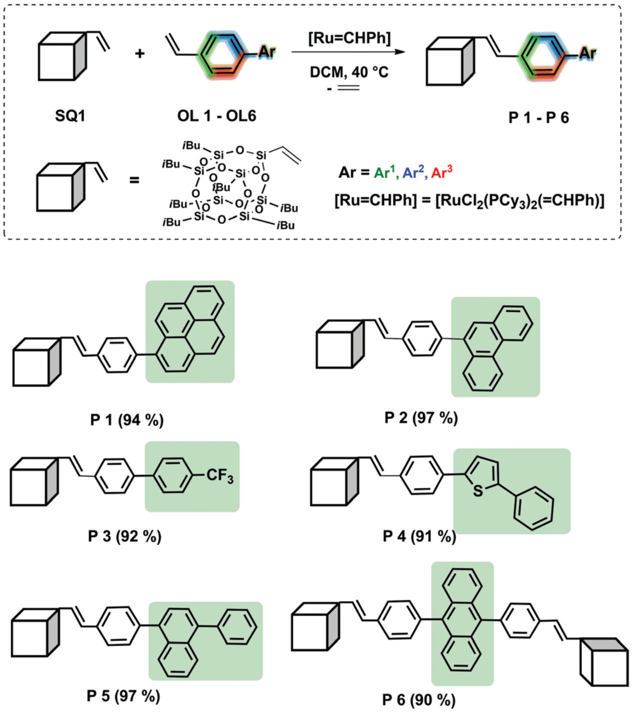


Scheme 1 General scheme of the synthesis of mixed styrylarenes obtained *via* a selective Suzuki–Miyaura coupling reaction.

Synthesis of functionalized silsesquioxanes

Having obtained these promising chromophores, we decided to anchor them onto the silsesquioxane T_8 core and obtain commercially unavailable derivatives. Based on our previous work, we treated equimolar amounts of monovinylsubstituted SQs (**SQ1**) and the corresponding unsaturated compounds (**OL 1–OL 5**) with the first generation Grubbs catalyst (1 mol%). In the case of **OL 6**, which contains two terminal vinyl groups, we used two equivalents of **SQ1** in the presence of 2 mol% of the Grubbs catalyst. The reaction mixtures were heated at 40 °C for 24 h. For all tested chromophores, nearly quantitative yields and exclusive formation of *E* products were obtained (Scheme 2).

All newly obtained products were characterized through spectroscopic and spectrometry methods (see the ESI†). These materials are air-stable and soluble in many commonly used solvents (*i.e.* dichloromethane, tetrahydrofuran, toluene, benzene,



Scheme 2 Cross-metathesis of **SQ** with chromophores **OL 1–OL 6** mediated by the 1st Grubbs catalyst. Reaction conditions: DCM, 40 °C, [Ru] = 1 mol%, argon. Isolated yields.

and chloroform), which makes them easy to purify by column chromatography.

Photophysical properties

Photophysical measurements were performed to examine how the presence of the silsesquioxane moiety changes the photophysical and luminescent properties of the polycyclic aromatic hydrocarbons to which it was attached. The results obtained for the silsesquioxane containing chromophores were analyzed and compared to the respective arenes themselves in dichloromethane. Absorption and emission parameters such as the absorption maxima ($\lambda_{\mathrm{Abs,max}}$), molar absorption coefficients (ε), fluorescence maxima ($\lambda_{\mathrm{f,max}}$), fluorescence lifetimes (τ_{S}) and fluorescence quantum yields (Φ_{f}) of the investigated compounds: **P 1**–**P 6** and reference compounds: **OL 1**–**OL 6** were determined (Table 1). The respective absorption and emission spectra of **P 1**–**P 6** and **OL 1**–**OL 6** are collected in Fig. 1.

Differences in photophysical properties between the chromophores and their functionalized silsesquioxane products were observed for the pairs of compounds **P 1** and **OL 1**, **P 3** and **OL 3**, **P 4** and **OL 4** and **P 5** and **OL 5**. In general, red-shifts in the emission spectra of the silsesquioxane containing arenes compared to the emission spectra of their respective chromophores are the general trend in these systems.

This observation is in line with many examples known from the literature, in which the presence of silicon causes a red shift in emission.[11,57,58] For the SQs functionalized with one chromophore group this effect may be decreased in comparison to the octafunctionalized SQs. Interestingly, for **P 2** and **P 6** there are no changes in the $\lambda_{\mathrm{f,max}}$ emission spectra and insignificant variations of the fluorescence lifetime and quantum yield may be noted. In the case of **P 3** and **P 4**, 4–9 nm red-shifts in the emission spectra may be reported along with no changes in the fluorescence lifetime. However, a meaningful decrease of the fluorescence quantum yield, *i.e.* 7.6 fold, for **P 3** should be noted when compared to the respective chromophore **OL 3**. For **P 1** and **P 5**, we observed not only considerable red-shifts in the emission spectra (up to 9 nm) but also a slight increase in the fluorescence quantum yield. The emission spectra of **OL 1** in dichloromethane had a vibrational structure with the two maxima at 387 nm and 407 nm, whereas the emission spectrum of **P 1** in this solvent was broad and shifted 8 nm toward longer wavelengths (see Fig. 2 and Table 1). Interestingly, for **P 1**, a three fold decrease in the fluorescence lifetime was noted in comparison to **OL 1**. For this pair of compounds, the photophysical measurements were performed in *n*-hexane as well as dichloromethane (Fig. 2).

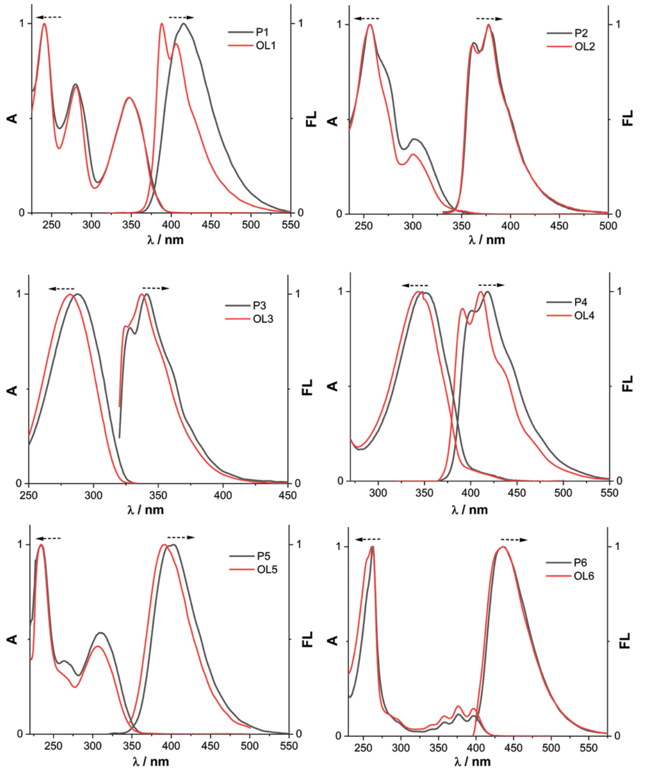


Fig. 1 Normalized absorption and emission spectra of compounds **P 1**–**P 6** and **OL 1**–**OL 6** in DCM.

Table 1 Absorption and emission properties of compounds in DCM at RT

Entry	Compound	$\lambda_{\mathrm{Abs,max}}$ [nm]	$\varepsilon_{\max}$ [$\mathrm{M^{-1}\,cm^{-1}}$]	$\lambda_{\mathrm{f,max}}$ [nm]	$\tau_{\mathrm{S}}{}^{a}$ [ns]	Φ_{f}
1	**P 1**	242	52 400	415	3.1^{b}	0.89^{c}
		279	35 100			
		346	30 000			
2	**OL 1**	242	48 900	387, 407	9.6^{b}	0.74^{c}
		281	32 000			
		347	29 100			
3	**P 2**	256	55 700	363, 378	15.0^{b}	0.29^{b}
		304	22 100			
4	**OL 2**	256	48 700	361, 378	15.8^{b}	0.21^{b}
		301	15 500			
5	**P 3**	288	31 900	328, 341	$<0.5^{b}$	0.13^{b}
6	**OL 3**	282	25 600	324, 338	$<0.5^{b}$	$\sim1.0^{c}$
7	**P 4**	348	34 650	400, 419	0.6^{d}	0.38^{e}
8	**OL 4**	344	22 800	391, 410	0.6^{d}	0.36^{d}
9	**P 5**	234	45 800	401	1.4^{b}	0.86^{b}
		267	17 400			
		312	24 400			
10	**OL 5**	234	43 800	392	1.4^{b}	0.76^{b}
		307	20 100			
11	**P 6**	262	141 900	435	3.0^{d}	0.75^{c}
		358	10 400			
		376	16 600			
		397	15 400			
12	**OL 6**	262	99 000	435	3.6^{d}	0.78^{c}
		357	10 000			
		377	14 900			
		397	13 800			

[a] Determined from single exponential decay fits of fluorescence kinetic traces. [b] $\lambda_{\mathrm{exc}} = 300$ nm. [c] $\lambda_{\mathrm{exc}} = 310$ nm. [d] $\lambda_{\mathrm{exc}} = 255$ nm. [e] $\lambda_{\mathrm{exc}} = 360$ nm.

The emission appeared to be sensitive to different solvent polarity. There were 16 nm and 5 nm solvatochromic shifts for compounds **P 1** and **OL 1**, respectively. The phenomenon of solvent polarity dependent emission spectrum shifts is known for stilbene substituted derivatives of T_8 and $T_{10/12}$ studied *i.e.* by Laine *et al.*[15,16,37] The changes in solvent polarity were proved to affect the possible aggregation of chromophore moieties. It was additionally noted that the number of chromophore substituents at Si–O–Si and the symmetry of the resulting silsesquioxane

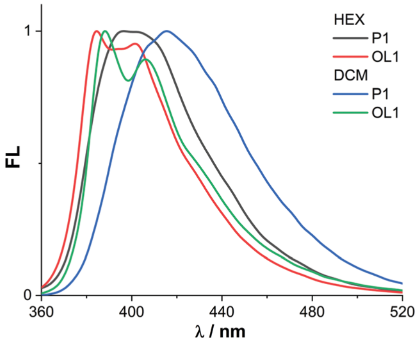


Fig. 2 Fluorescence spectra of compounds: **P 1** and **OL 1** in *n*-hexane (HEX) and in dichloromethane (DCM).

Table 2 Thermal properties of selected olefins (**OL 1** and **OL 5**) and SQ-containing products (**P 1** and **P 5**) (measured in N_2)

Entry	Compound	$T_{5\%}$ [°C]	T_{max} [°C]	Residue at 1000 °C [%]
1	**P 1**	303.6	449.9	8.8
2	**OL 1**	253.0	415.5	23.3
3	**P 5**	348.7	445.8	12.8
4	**OL 5**	280.6	417.7	13.5

systems also influence the magnitude of the $\lambda_{f,max}$ red-shifts.[16,24] This may account for the rather small red-shift values obtained for SQs with one chromophore moiety at their core. However, the obtained results are in accordance with the limited reports on the fluorescence properties of monofunctionalized SQs bearing one chromophore group anchored to the Si–O–Si core *via* a styryl fragment.[40,41]

Thermal properties

The thermal stability of selected olefins (**OL 1** and **OL 5**) and SQ-based products (**P 1** and **P 5**) which exhibited the most significant red-shifted emission was investigated with thermogravimetric analysis in a nitrogen atmosphere. The results are summarized in Table 2 and presented in Fig. 3.

The analysis of the obtained results revealed that the incorporation of the specific silsesquioxane core into the multiaromatic units (**OL 1** and **OL 5**) strongly influences the thermal properties of the resulting products, namely, the $T_{5\%}$ and T_{max} values significantly increased when compared to the unmodified chromophores. The initial decomposition temperatures $T_{5\%}$ for **P 1** and **P 5** are higher than 300 °C and amount to 303.6 and 348.7 °C respectively.

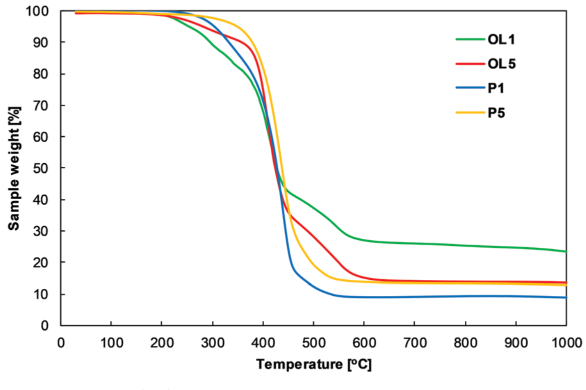


Fig. 3 TGA curves (N_2) obtained for selected compounds: **P 1** and **P 5** and **OL 1** and **OL 5** respectively.

The observation that compounds containing incorporated silsesquioxanes revealed higher thermal stability is in accordance with other scientific reports.[11,56–58] This is strictly related to the high stability of the SQ core, because of the high dissociation energy of the Si–O bond, which is much higher than for typical organic units containing C–C and C–H bonds.[59,60]

Conclusions

Herein, we presented a highly effective and advantageous synthetic protocol due to its simplicity, based on tetrakis(triphenylphosphine)palladium(0) Suzuki–Miyaura coupling for chromophores with one (**OL 1–OL 5**) or two styryl moieties (**OL 6**). The styryl fragment enabled their further application for selective cross-metathesis functionalization of monovinylsubstituted cubic T_8 silsesquioxane, to yield respective compounds: **P 1–P 6**. All of the obtained compounds were fully characterized by ^1H, ^{13}C, and ^{29}Si NMR spectra, and MALDI-TOF-MS analysis to confirm their structures. They were also verified in terms of their absorption and emission properties. The respective fluorescence spectra revealed the general tendency of red-shifted emission observed for organosilicon and silsesquioxane-functionalized arenes. Furthermore, the emission spectra dependence on the polarity of the applied solvent was revealed. Interestingly, in the case of **P 1** and **P 5** not only were the red-shifts in emission noted but also a noticeable increase of fluorescence quantum yields in comparison with the respective chromophores, which may be unusual for only monofunctionalized SQs bearing one chromophore group attached to a Si–O–Si core. These findings encourage further investigations on the possible dependence of this phenomenon on the number of chromophore groups at the SQ core as well as their type. An additional direction of study would be the verification of the thermal resistance of **P 1** and **P 5** in comparison to their bare chromophore derivatives (**OL 1** and **OL 5**). As expected for SQ modified arenes, the $T_{5\%}$ and T_{max} values were raised fundamentally, which is in accordance with extensive literature on this issue. Consequently, and as reported earlier, this is another report on SQ-based hybrid materials that confirms the interesting photo- and thermal properties of these systems. Again, they are promising organic–inorganic derivatives to be applied in the production of efficient emissive devices.

Conflicts of interest

There are no conflicts of interest to declare.

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