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Ordering Minimalist Bridged Polysilsesquioxane Films under Visible LED Light Irradiation

Lingli Ni,^{*†} Mei Wu,[†] Feng Chen,[†] Irena Deroche,[§] Abraham Chemtob,[§]

[†] Key Laboratory for Palygorskite Science and Applied Technology of Jiangsu Province, College of
Chemical Engineering, Huaiyin Institute of Technology, 223003 Huaian, People's Republic of
China

[§] Institute of Material Science of Mulhouse, CNRS, UMR 7361, University of Haute-Alsace, 15 rue
Jean Starcky 68057 Mulhouse Cedex, France

***Corresponding author:**

Dr. Lingli Ni; E-mail: nilingli520@126.com; Tel: +86 517 8355 9056; Fax: +86 517 8355 9056

15 **Abstract:**

16 A visible light-mediated sol-gel process can promote the ordering of hexylene, octylene and
17 decylene-bridged polysilsesquioxane with very simple organosilane building blocks having only a short
18 alkylene bridging group: $(\text{CH}_3\text{O})_3\text{SiC}_n\text{H}_{2n}\text{Si}(\text{OCH}_3)_3$ ($n = 6, 8, 10$). Photocondensation and self-assembly of
19 films are promoted through exposure to a light-emitting diode (405 nm). The solvent-free synthesis involves
20 very low light intensity (0.1 mW/cm^2) and a minimum amount of photoacid generator (0.5 wt%) acting as
21 photocatalyst. X-ray diffraction and scanning electron microscopy prove the high level of organization, while
22 real-time Fourier transform infrared spectroscopy shows conformational ordering of alkylene chains
23 throughout irradiation. Molecular modeling reveals a multilayer structure based of the stacking of a single
24 polysiloxane chain, with organic groups attached to adjacent Si atoms showing up and down orientation.

25 **Keywords:** bridged polysilsesquioxane, sol-gel photopolymerization, self-assembly, lamellar structure

26

27

1. Introduction

Self-directed organosilane assembly via sol-gel process is an attractive route to synthesize highly ordered polysilsesquioxanes (SQs) (1-5). In contrast to most sol-gel materials, these organosilica hybrids have the unique feature of being mesoscopically organized without the need for additional surfactant, which enables a single step synthesis and brings added value for many different applications including photonics (6) and smart devices (7). Central to self-organization is the development of strong enough secondary interactions (i.e. van der Waals, π - π stacking and H-bonding) between the specific organic moieties of the organosilane precursors to overcome the disorder forces induced by random silanol condensation reactions (8-15). To achieve this, particular precursor architectures are necessary as well as a high level of control of sol-gel process since any change of temperature, solvent, catalyst or concentration may encourage or limit the self-assembly mechanism. Only a handful of precursors have so far resulted in SQs possessing long range organization. The typical organosilane architecture comprises two specific structural features: mono- or bis-silylated terminal groups together with an organic moiety able to develop hydrophobic interactions (long enough alkyl or alkylene chains) or/and hydrogen bonds (ureido, amide groups), π - π stacking etc. (1, 16, 17).

Recently, our group introduced a different photochemical route to synthesize highly ordered SQs (18-21). In this approach, an organosilane-based film is irradiated in bulk in the presence of Brønsted superacids generated in situ by the UV-decomposition of a photoacid generator (PAG) based on diaryliodonium ($\text{Ph}_2\text{I}^+\text{X}^-$) or triarylsulfonium ($\text{Ph}_3\text{S}^+\text{X}^-$) salts. Compared to conventional sol-gel process, photopolymerization offers several conventional advantages such as storable, ready-to-use, solvent-free formulation with no pot-life issue since the photocatalyst (photoacid) is released on demand. Additionally, two aspects are particularly meaningful and appropriate to self-assembly: the facile control of condensation rates (via irradiance) and water concentration within the film (via relative humidity: RH). The former can

50 prevent early gelation that would kinetically trap the system in a transient non-ordered state, while the latter
51 can enhance the hydrophilic/hydrophobic contrast, and drive ultimately nanophase segregation. This offers a
52 unique level of kinetic and thermodynamic control to mediate self-assembly. Both passive (alkyl/alkylene)
53 (19-21) and active (ester, carboxylic acid functionalized) (18) lamellar hybrids have already been achieved
54 via photoacid-catalyzed sol-gel process.

55 At this stage, other important questions arise concerning the development of self-directed organosilane
56 sol-gel photopolymerization: firstly, can we make the process less demanding in terms of precursor's
57 structure? In other, words, the challenge is to promote SQ ordering with the simplest building blocks possible,
58 e.g. bridged precursors containing only short alkylene group such as hexylene, octylene and decylene. An
59 objective like this has proven to be unattainable under conventional sol-gel process (22, 23). Secondly, how
60 can processing conditions be improved in terms of eco-efficiency? Clearly, the best solution today is to rely
61 on energy-saving and safer visible light-emitting diodes (LEDs) instead of Hg arc lamps. These two
62 important issues have been addressed in details in the present report.

63 **(i). Ordering minimalist precursors.** Since interchain cohesion via van der Waals interactions
64 increases with increasing length of the hydrophobic group, there is often a direct relationship between the
65 level of ordering of the alkylene bridged SQ and the organic chain length. The concept of sufficient
66 hydrophobic chain length for self-assembly is not unique to organosilane, but also controls surfactant
67 micellization or liquid crystal formation. For example, below 10 carbons, salts of straight-chain fatty acids
68 ($C_nH_{2n+1}COO^- M^+$) are too soluble to have surface activity in water (24). Consequently, achieving long-range
69 organization with hydrocarbon-based hydrophobic group shorter than C_{10} has never been described in the
70 literature (23). Zhao and al. reported in 2006 hexylene- and octylene-Bridged SQ using either surfactant
71 templating or high dilution conditions resulting in dimer structure (T^1 siloxane species only) and not a

cross-linked siloxane structure (25). As shown in Scheme 1, the present study focuses on the comparative self-assembly and condensation of three bridged precursor films: $(\text{CH}_3\text{O})_3\text{SiC}_n\text{H}_{2n}\text{Si}(\text{OCH}_3)_3$ ($n = 6, 8, 10$) denoted as BC_nTMS .

(ii). Improving photoprocess eco-efficiency. Medium-pressure mercury arc lamp is the workhorse in radiation curing, and the main energy source used in all studies dealing with sol-gel photopolymerization. However, such lamp is energy intensive, involves toxic heavy metal, requires cooling system and operates under high voltages. In this work, we used a visible LED irradiation at 405 nm in the presence of an adequate visible light non-ionic PAG [(5-propylsulfonyloxyimino-5H-thiophen-2-ylidene)-2-methylphenyl-acetonitrile], releasing *n*-propane sulfonic acid catalyst. Ozone-free and mercury-free visible LED control offers significant advantages over mercury arc lamp, including lower cost, high monochromaticity, safer emission wavelength, smaller heat generation, longer life time (26-29). To the best of our knowledge, it is the first use of LED for the synthesis of highly organized lamellar SQ.

Scheme 1. Visible LED-activated sol-gel polymerization process of alkylene-bridged trimethoxysilane precursors BC_nTMS [$(\text{CH}_3\text{O})_3\text{SiC}_n\text{H}_{2n}\text{Si}(\text{OCH}_3)_3$, $n = 6$ (a), 8 (b), 10 (c)].

2. Experimental section

2.1 Chemicals

1,6-Bis(trimethoxysilyl)hexane (95 %) and 1,8-bis(trimethoxysilyl)octane (95 %) were supplied by Gelest. Trimethoxysilane and 1,9-decadiene were purchased from Aladdin and TCI chemicals (Shanghai),

92 respectively. Nonionic photoacid generator Irgacure PAG103 [(5-propylsulfonyl-
93 oxyimino-5H-thiophen-2-ylidene)-2-methylphenyl-acetonitrile] was provided by BASF. All of the chemicals
94 were used as received.

95 **2.2 Synthesis of 1,10-Bis(trimethoxysilyl)decane**

96 1,10-Bis(trimethoxysilyl)decane was prepared according to the previous literature procedure (30).
97 Typically, 6.9 g of 1,9-decadiene (0.05 mol), 12.3g of trimethoxysilane (0.1 mol) and 0.35 ml of
98 chloroplatinic acid in isopropanol (2.73×10^{-3} M) were mixed together by magnetic stirring, then the mixture
99 were heated to 100 °C and refluxed for 6 hours under nitrogen atmosphere. After distillation of the reaction
100 mixture under vacuum, 6.7 g (35 % yield) of 1,10-Bis(trimethoxysilyl)decane was collected. ^1H NMR (400
101 MHz, CDCl_3): δ (ppm) 0.58 (t, 4 H), 1.17–1.6 (m, 34 H), 3.7 (q, 12 H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm)
102 10.3, 18.3, 22.7, 29.2, 29.5, 33.2, 58.2.

103 **2.3 Synthesis of hybrid films derived from alkylene-bridged trimethoxysilane precursors**

104 In a typical procedure, photoacid generator (PAG103, 0.5 % wt) was dissolved in a BC_nTMS precursor
105 to form a photolatent solution in the absence of light ($\lambda < 500$ nm). The λ_{max} absorption of this PAG is located
106 at 405 nm (31), which overlaps quite well with the LED emission spectrum spanning 385-420 nm (Figure S1,
107 ESI). Then the resultant formulation was deposited on a silicon wafer by spin coating (1000 rpm, 20 s) to
108 produce a liquid film (~ 3 μm). Irradiation was provided at room temperature by a LED lamp (Shenzhen
109 xianghe, 20 W) at an incident light intensity of 0.1 mW/cm^2 . The samples were irradiated during 30 min to
110 yield solid SQ films (~ 4 μm). The relative humidity (RH) during irradiation was controlled by using a
111 saturated NaCl solution in a customized environmental cell. The resulting samples were characterized by a
112 range of techniques: FTIR, X-ray diffractions (XRD), scanning electron microscopy (SEM), ^{29}Si solid state
113 NMR.

114 2.4 Characterization

115 Infrared spectra were recorded by a Nicolet-5700 Fourier transform infrared spectrophotometer. The
116 resolution of the infrared spectra was 2 cm^{-1} . X-ray diffraction patterns (XRD) were obtained on a Bruker
117 D8-Discover diffractometer with fixed slits using Cu/K α radiation ($\lambda = 1.5418\text{ \AA}$) and θ - 2θ mounting. Before
118 analysis, films on silicon wafers were directly deposited on a plastic sample holder. Data were collected
119 between 1 and $30^\circ 2\theta$ degrees (XRD) with a scanning step of 0.01° s^{-1} . Birefringent properties of the hybrid
120 films were investigated by the polarized optical microscope (POM) of Leica DMLP. Morphologies of the
121 samples were characterized by scanning electron microscopy (SEM, Hitachi S3000N microscope working at
122 25kV). The samples being non-conductive, they have been metalized with gold (15 nm thickness). The
123 transmission electron microscopy (TEM) observations were performed with a FEI TECNAI G² TF20
124 microscope operating at 200 kV. The samples for TEM measurements were prepared by dropping their water
125 suspensions onto the surface of copper observation grids. The ^{29}Si cross polarization magic angle spinning
126 (CP-MAS) solid state NMR spectra was performed on a Bruker Avance III 400 spectrometer with a Bruker
127 double channel 7 mm probe. In this case, zirconium rotors were employed at 79.48 MHz using a recycling
128 delay of 5 s, a spinning frequency of 4 kHz and a contact time of 4 ms. ^{29}Si chemical shift is relative to
129 tetramethylsilane. The condensation degree of the siloxane network was calculated according to the equation
130 of $CD(\%) = \sum_n n \frac{T^n}{f}$, where n is the siloxane bonds attached to the central silicon functionality ($f = 3$ here).

131 The geometry optimization of the ordered SQ structures was obtained through the energy minimization
132 of the microscopic structural models prepared from scratch, using Forcite, the molecular mechanics module
133 implemented within the Molecular Studio package. The calculations were based on the Dreiding force field,
134 suited for a hybrid SiO_2 - organic system, using default database parameters and the conjugate gradient
135 minimization algorithm with following convergence criteria: $5.0 \times 10^{-5}\text{ kcal/mol}$, $0.002\text{ kcal/(mol}\cdot\text{\AA)}$, and

136 5.0×10^{-5} Å, for energy, forces and displacement respectively.

137

138 3. Results and discussion

139 3.1 Efficiency of visible LED activated sol-gel photopolymerization

140 The three $\text{BC}_n\text{TMS/PAG}$ films ($n = 6, 8, 10$) were subjected to LED irradiation (385-420 nm, 0.1
141 mW/cm^2) during 30 min, leading to solid hybrid coating. Efficiency of the photoinduced sol-gel
142 polymerization was first assessed by FTIR spectroscopy. Figure 1 shows the FTIR spectrum of the
143 nanocomposite films derived from BC_6TMS (BC_6SQ) as well as that of the precursor (spectra of the other
144 nanocomposite films derived from BC_8TMS and BC_{10}TMS are provided in Figure S2 of ESI). The sharp and
145 strong CH_3 symmetric stretch assigned to methoxysilyl group (Si-O-CH_3) at 2840 cm^{-1} almost vanished after
146 UV exposure, suggesting a high hydrolysis degree ($> 97\%$). Meanwhile, a broad band arose in the spectral
147 region spanning $3000\text{--}3700\text{ cm}^{-1}$ attributed to O-H stretching vibrations of the newly created silanols (Si-OH).
148 In accordance with hydrolysis reactions, a strong band at 930 cm^{-1} appeared due to the Si-O stretching
149 vibration of silanols. The presence of asymmetric stretching bands of siloxane bonds (Si-O-Si) at 1100, 1070
150 and 790 cm^{-1} proved finally the formation of SQ network. Similar observations were also observed for the
151 other two precursors of BC_8TMS and BC_{10}TMS .

152

153 **Figure 1.** FTIR spectra of BC_6TMS film before and after the sol-gel photopolymerization in the presence of
154 PAG.

The ^{29}Si CP-MAS NMR spectra of the three synthesized BC_nSQ hybrid films are displayed in Figure 2.

The three signals corresponding to T^1 [-49 ppm, $\text{C-Si(OR)}_2(\text{O-Si})$], T^2 [-58 ppm, $\text{C-Si(OR)}(\text{O-Si})_2$] and T^3 [-68 ppm, C-Si(O-Si)_3] siloxane species were observed in all instances. Deconvolution and integration of these signals showed a moderate degree of condensation of 65, 67 and 70% for BC_6SQ , BC_8SQ and BC_{10}SQ films (32). It is noteworthy to mention that much less condensed SQ structures ($\approx 35\%$) were obtained in studies involving a conventional sol-gel process of the same precursors (25, 33). In addition, the present films were obtained at very low irradiance (0.1 mW/cm^2) with a lamp providing no thermal input which could contribute to condensation.

Figure 2. ^{29}Si solid state CP-MAS NMR spectra of the visible LED cured BC_nSQ hybrid films derived from BC_nTMS precursors.

3.2 Photoinduced ordering of alkylene bridged polySQ films

Figure 3 displays the X-ray diffraction patterns of the visible LED-cured alkylene bridged SQ films derived from the three BC_nTMS precursors. Remarkably, the film derived from hexylene precursor (trace **a**) yields a lamellar structure with (001) and (003) reflections, indicating a basal spacing value of approximately $12.3 \text{ \AA}$. Upon increasing the alkylene chain length to C_8 (octylene, trace **b**) and C_{10} (decanene, trace **c**), the level of organization of the resulted hybrid films increases as demonstrated by the increased number and intensity of their reflection peaks. Because of the photoacid catalyzed hydrolysis, alkylene-silanol species

173 (HOSiC_nH_{2n}Si-OH, n=6, 8 or 10) with amphiphilic structures has been generated. Increasing the length of the
 174 bridging group has the effect of enhancing the intermolecular or intramolecular London dispersion forces
 175 between alkylene chains, and emphasizing the hydrophilic-hydrophobic contrast between the two moieties of
 176 the surfactant. Those two aspects result in greater enthalpic association forces, leading to a higher
 177 organization with longer alkylene chains. Additionally, we note that the basal spacing value of BC₈SQ and
 178 BC₁₀SQ also increased to 14.2 Å and 16.2 Å respectively. One should also emphasize the difference with
 179 periodically ordered mesoporous hybrids extensively investigated in the literature (2, 34) because in the
 180 present case the supramolecular assembly process results from the organosilica species themselves and no
 181 longer from a self-directing agent. Consequently, our SQ structure exhibit a long-range order arising from
 182 organized organic units and not from mesopores.

183
 184 **Figure 3.** XRD patterns of the visible LED cured BC_nSQ hybrid films derived from BC_nTMS precursors
 185 [(CH₃O)₃C_nH_{2n}(OCH₃)₃, n = 6 (a), 8 (b), 10 (c)].

186 Further investigation of hybrid film nanostructure was performed by a set of microscopy techniques.
 187 SEM observations revealed that all of these three products had lamellar morphology (Figure 4, left column).
 188 As displayed in Figure 4 of right column, the POM images of BC₆SQ (a) and BC₈SQ (b) showed a regular
 189 and well-defined shape indicative of their crystalline nature. They both had quite homogeneous worm-like
 190 birefringent domains, suggesting a microscopic anisotropic organization. Clearly, more results about

191 molecular orientational and conformational behavior in these anisotropic hybrid materials could be extracted
 192 from polarized FTIR. Nevertheless, only BC₁₀SQ, revealed unambiguously a strip-shaped structures by TEM
 193 as shown in Figure 5. Short bridging groups impose low interlamellar distance, that makes the observation
 194 difficult with a conventional (non high resolution) TEM.

195 **Figure 4.** SEM and POM micrographs of the visible light cured BC_nSQ hybrid films: (a) BC₆SQ, (b) BC₈SQ,
 196 (c) BC₁₀SQ.
 197

198 In addition, alkylene chain conformation has been investigated by FTIR characterization. C-H
 199 stretching region between 3000 to 2800 cm⁻¹ holds valuable information as regards hydrocarbon chain
 200 environment and conformation (35-37). For instance, antisymmetric (*d*) and symmetric (*d*⁺) stretching
 201 vibration of methylene group (-CH₂-) arose respectively at 2920 cm⁻¹ and 2850 cm⁻¹ in crystalline
 202 polyethylene; while in solution, they shift at 2926 cm⁻¹ and 2854 cm⁻¹ due to a greater incidence of *gauche*
 203 defects. Figure 6 displays the evolution of the C-H stretching region during the photopolymerization of the
 204 three BC_nTMS precursors. Prior to irradiation, broad *d* and *d*⁺ absorption bands were found at 2926 cm⁻¹ and
 205 2854 cm⁻¹ (2858 cm⁻¹ of BC₆TMS, trace **a**) respectively, suggestive of conformationally disordered alkyl
 206 chains (*gauche*). After visible light polymerization, the positions of the methylene stretching modes of all the

three BC_nPS films had significantly shifted to lower wavenumbers. $\nu(d^-)$ and $\nu(d^+)$ were thus observed at 2922 cm⁻¹ and 2851 cm⁻¹ (2856 cm⁻¹ of BC₆SQ, trace **a**) respectively, indicating a high proportion of *trans* conformation of alkylene bridged chains (35). Further, the narrow full width at half maximum (fwhm) values of d^- and d^+ for BC₆SQ (trace **a**, 20 and 15 cm⁻¹), BC₈SQ (trace **b**, 17 and 15 cm⁻¹) and BC₁₀SQ (trace **c**, 17 and 14 cm⁻¹) were consistent with values observed for highly crystalline poly(*n*-octadecyl silsesquioxane) (15 and 11 cm⁻¹) (32). These FTIR data provided another evidence for ordered alkylene bridged polysilsesquioxane films.

Figure 5. TEM image of the visible light cured BC₁₀SQ hybrid film.

Figure 6. Comparison between the FT-IR spectra of the visible light cured BC_nPS (—) and BC_nTMS precursor (---) at C-H stretching region [*n* = 6 (**a**), 8 (**b**), 10 (**c**)].

3.3 Molecular modeling of the ordered polysilsesquioxane structure

Although an extensive computational effort has been made to study of organosilane self-assembled monolayers (SAMs) (38) as regards to chain thickness, packing and tilt angle, very few molecular simulation studies have focused on ordered SQs. Molecular modeling techniques based on Molecular Mechanics (MM) and/or Density Functional Theory (DFT) could be of utility for elucidating the ordering process and the final structure of the self-assembled organosilica. Recently, Jiang et al. used the quantum chemical modeling in order to clarify the microscopic structure of the investigated organosilane (11). Bantignies et al. combined the FTIR and XRD to the DFT based molecular modeling in order to depict the organic fragments long range structuring (39), and Dieudonné applied molecular mechanics to prepare a microscopic model of the synthesized organo-bridged SQ (40). Finally, molecular DFT was successfully applied to study the Si-C bond cleavage of organosilane precursors during polycondensation to organosilica hybrids (41) and the geometries and energies of several organosilicate molecules in the gas phase (42).

Figure 7. Modeling of bridged silsesquioxane lamellar mesostructure formed by the self-assembly and condensation of $(\text{CH}_3\text{O})_3\text{SiC}_{10}\text{H}_{20}\text{Si}(\text{OCH}_3)_3$ precursors: (a) the two-dimensional network formed by -Si-O-Si- condensed linear and parallel chains with the bridging alkylenes with the interlayer distance of 16.4 Å. (b) The three-dimensional structure created by stacking the two dimensional layers. (c) The simulated XRD patterns for such a prepared model.

237 In the present study, we used molecular modeling to achieve a realistic microscopic model of the
238 bridged SQ lamellar structures, possibly matching the aforementioned experimental data. The starting
239 structural model for geometry optimization was based upon lamellar d-spacing value (XRD data), *trans*
240 alkylene chains conformation (FTIR data), and a majority of T² siloxane species (NMR data). When building
241 the theoretical model of the nanolayer, two head-to-head and the head-to-tail packings were found to be
242 possible. While a head-to-head arrangement yields a double -(Si-O-Si)_n- polysiloxane central chain, with
243 alkyl chains of adjacent Si atoms pointing towards the same direction (not represented here), a head-to-tail
244 assembly leads to a single -(Si-O-Si)_n- backbone, with alkyl chains attached to adjacent Si atoms showing up
245 and down orientation. Due to the steric hindrance imposed by the alkylene chains, the first model was ruled
246 out and only the second “head-to-tail packed” model was considered for further geometry optimization as
247 represented in Figure 7. For sake of simplicity, this theoretical model comprises T² siloxane species,
248 consequently each silicon atom carries one terminal OH group. Under this conditions of condensation, the
249 bis-silylated molecular precursors condensed into a two-dimensional network of linear and parallel
250 -(Si-O-Si)_n- chains (Figure 7a). Stacking these 2D structures in the direction perpendicular the plane resulted
251 in a 3D lamellar structure (Figure 7b). In our model the predominating interaction between two layers
252 corresponds to strong hydrogen bonds formed between dangling hydroxyl groups. Moreover, the existence of
253 experimentally evidenced more condensed T³ species (20-35%) suggests the formation of orthogonal
254 siloxane links between these planes. Presumably, a too high condensation degree can induce constraints,
255 which may alter the level of ordering. Interestingly, the theoretical interlayer distances obtained from the
256 geometry optimization were in a good agreement with the experimental ones (12.5 Å, 14.4 Å and 16.4 Å from
257 simulation versus 12.3 Å, 14.2 Å and 16.2 Å from experimental measurements). The optimized molecular
258 models of the SQ layers have revealed systems of closely packed chains in extended all-trans conformations.

259 The typical distances separating hydrogen atoms of two neighboring alkyl chains were comprised between
260 2.6 – 2.9 Å.

261 **3.4 Self-assembly mechanism**

262 As sol-gel photopolymerization proceeds in bulk and not excess in water or polar solvents as described
263 for most examples of the literature, self-assembly is no longer entropy-driven but becomes enthalpy-driven,
264 which can be advantageous as regards self-assembly. The enthalpic cohesive forces (negative ΔH) depend
265 non only from van der Waals forces between alkyl chains but also the solvophobic forces that emanates from
266 the less favorable interactions between surfactant alkyl chains and water molecules (provided by the
267 atmosphere) compared to the more favorable water-water interactions. The magnitude of the solvophobic
268 forces can be thus related to the interfacial tension (water/hydrocarbon = 45 mJ m⁻²) and poorly on alkyl
269 chain length. The fact that water has not been added does not mean that it does not play a significant role.
270 Thin film conditions and high relative humidity ensures the presence of water-saturated film. As a result, in a
271 light induced self-assembly, the active role in the assembling process lies preferentially in the medium (water
272 molecules) rather than in the alkyl length. The cohesive forces are not negligible but add as additional
273 attractive forces in the present system. This combination of forces could account for the ability of C₆ or C₈
274 alkylenesilanes to self-assemble.

275

276 **4. Conclusion**

277 An environmentally friendly visible LED-mediated pathway to highly ordered lamellar alkylene bridged
278 SQ films (n = 6-10) has been demonstrated. A combination of FTIR and solid state ²⁹Si NMR analyses
279 suggested that the *n*-propanesulfonic photoacid produced at 405 nm (0.1 mW/cm²) and ambient temperature
280 was efficient enough to catalyze the hydrolysis and polycondensation reactions, yielding well-condensed a

281 siloxane network. Very low exittance and visible light irradiation open perspective for the use of
282 sunlight-induced polymerization, which could be of interest for coating deposition and outdoor
283 self-photopolymerization. Precise control of the sol-gel process (slow condensation, absence of organic
284 solvents) takes maximum advantage of the noncovalent interactions between conjugated alkylene moieties,
285 as well as solvophilic interactions. The most important achievement is that ordering was possible with the
286 minimalist building block BC₆TMS. We believe the use of our sustainable approach can be useful to access
287 novel ordered SQs structures with a much broader range of organosilanes, normally poorly conducive to
288 self-assemble by conventional sol-gel process. The replacement or chemical modification of the alkyl group
289 by functional groups opens avenue for more technology advanced applications.

290

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294

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