

# Preparation and optical properties of hybrid sol-gel systems containing doubly anchored oligoarylenevinylenes

Robert J. P. Corriu,\* Peter Hessemann and Gérard F. Lanneau

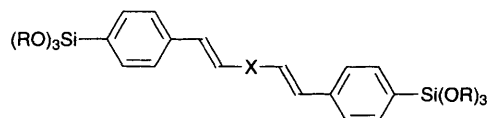
Unité Mixte CNRS/RP/USTL No. 44, Département de Chimie Organique Fine, Université de Montpellier II, Sciences et Techniques du Languedoc, 34095 Montpellier Cedex 5, France

The sol-gel transformation of bis-trialkoxysilyl-substituted oligoarylenevinylenes allows the covalent connection of photoluminescent segments into silsesquioxane xerogels.

Because of their high optical purity, excellent dielectric properties and transparency over the whole visible range, silica sol-gel materials are very suitable materials for optical and electrooptical applications.<sup>1</sup> A variety of dyes and luminescent materials have been embedded in silica frameworks.<sup>2,3</sup> The connection of the organic moiety with the inorganic network lowers mobility of the organic segment in the gel and thermal relaxation processes in sol-gel systems with oriented organic segments can be reduced.<sup>4</sup>

Hybrid organic-inorganic solids of general formula  $(RO)_3Si-Y-Si(OR)_3$  have been investigated in recent years.<sup>5-8</sup> They provide a possibility for the nonreversible and covalent inclusion of chromophores into silica frameworks.

Oligo- and poly-1,4-phenylenevinylenes (OPV/PPV) exhibit very promising properties in the field of light-emitting diodes or nonlinear optics<sup>9</sup> and their encapsulation in silica matrices improves the electrooptical properties.<sup>10</sup> We focused on the covalent introduction of OPV segments in silica sol-gel systems. Here, we report the synthesis of the bis-trialkoxysilylated arylenevinylenes **1-5** with different central moieties X and their subsequent transformation into silica gels.



compound	X	R
1	1,4-phenylene	Me
2	9,10-anthrylene	Me
3	4,4'-biphenylene	Me
4	2,7-fluorylene	Me
5	4,4'-stilbylene	Et

The precursors were prepared by Pd-catalysed cross-coupling reactions of halogenoarenes with styrene derivatives (Heck reaction).<sup>11,12</sup> The reactions were carried out in acetonitrile or triethylamine in the presence of  $Pd(O_2CMe)_2$  and  $P(C_6H_4MeO)_3$ . The products were purified by recrystallisation from hexane-toluene and were obtained in 50-62% yield.

The oligomers are accessible by two procedures, either by the reaction of a divinyl-substituted central unit with 4-bromophenyltrimethoxysilane (method A) or by the coupling reaction of a trialkoxysilylated styrene derivative with a dibromo-substituted arene (method B). Because of their tendency towards radical polymerisation, method A is only possible for the coupling reaction with 1,4-divinylbenzene ( $X = 1,4-C_6H_4$ ). As many dibrominated compounds are commercially available, method B is a more universal approach for the synthesis of the trialkoxysilylated conjugated precursors.

In contrast to the unsubstituted compounds, which are highly crystalline solids of low solubility,<sup>13</sup>  $Si(OR)_3$  substitution

results in increased processability. The silylated precursors are soluble in organic solvents such as toluene, THF or acetone and exhibit strongly decreased melting points [mp: 176 (**1**), 202 (**2**), 210 (**3**), 140 (**4**), 211 °C (**5**)].

The sol-gel technique allows the introduction of the chromophores in the gel in variable amounts up to 72 mass% for gel **9**.

Following standard conditions, the gels were prepared in THF solution with a minimum of 3 equiv. of water and in the presence of 1 mol% of  $NH_4F$  as catalyst.<sup>8</sup> By cocondensation of the precursor **1** in the presence of various amounts of tetramethoxysilane, gels with different concentrations of the covalently incorporated fluorophore are accessible (Table 1). Transparent gels formed within several hours at room temperature. After curing for 5 d at room temperature, the gels were powdered and washed with THF, acetone and methanol and finally were dried *in vacuo* at 100 °C.

The molecular structure of silicon atoms can be detected by  $^{29}Si$  CPMAS NMR spectroscopy. This method allows the distinction between silicon atoms attached to three or four oxygen atoms and gives qualitative information about their degree of condensation ( $T^m$  and  $Q^n$  resonances). Characterisation of gels **6** and **9** by  $^{29}Si$  CPMAS NMR spectroscopy showed the signals of  $T^1$ -,  $T^2$ - and  $T^3$ -bridged silicon nuclei, corresponding to differently condensed substructures  $RSi(O_2Si)_x(OR)_{3-x}$  ( $x = 1-3$ ). The predominant environment of the silicon atoms in the gels corresponds to a  $T^2$   $RSi(OR)(OSi)_2$  coordination as for other silsesquioxanes.<sup>5-8</sup> The complete absence of Q resonances in the spectra of gels **6** and **9** confirms that no Si-C cleavage occurred during the polycondensation procedure. The  $^{29}Si$  CPMAS NMR spectra of gels **7** and **8** show the additional Q resonances of silicon attached to four oxygen atoms due to hydrolysis of  $Si(OMe)_4$ . Neither the DSC thermograms nor TEM examination of all the gels revealed any signs of crystallinity.

The optical properties of chromophores afforded information about conformational structure and environment in silica frameworks.<sup>3</sup> We have recently described the organisation of organic segments in gel systems.<sup>14,15</sup> Here, we use photoluminescence (PL) spectroscopy as a versatile method for probing the conformation and environment of the chromophores in the sol-gel network.

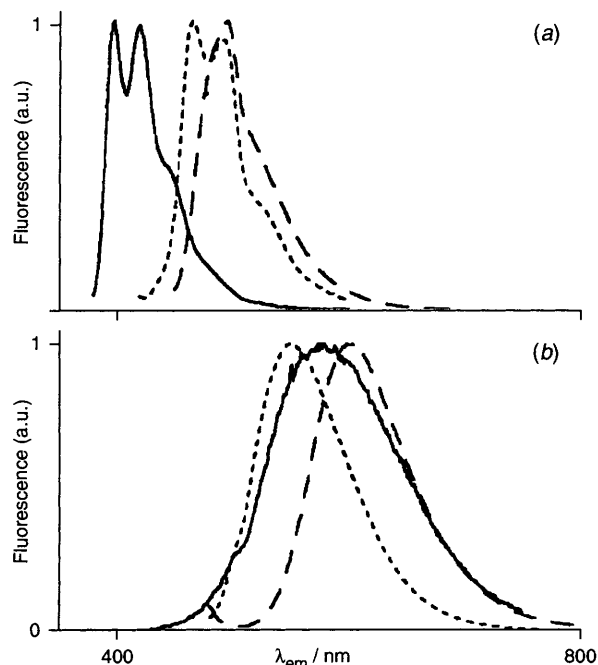
The wavelengths and shapes of the UV-VIS and fluorescence spectra of the precursors are in agreement with those for the unsubstituted oligomers.<sup>12</sup> The  $Si(OMe)_3$  substitution results in

Table 1 Mass ratios of the starting materials in the preparation of gels 6-9

Gel	Precursor (mass%)	$Si(OMe)_4$ (mass%)
6	1 (100)	—
7	1 (40)	60
8	1 (10)	90
9	2 (100)	—

a slight red shift in the UV–VIS and fluorescence spectra of ca. 8–10 nm.

In agreement with other oligophenylenevinyls, the PL spectrum of **1** shows a red shift in the solid state compared with that in solution. Such a variation can be explained in terms of a decreased  $\pi$ – $\pi^*$  transition energy due to higher planarity in the solid state.<sup>16</sup> The PL spectra of the gels<sup>6–8</sup> show maxima at 495–496 nm, similar to the values of the precursor in the solid state. However, the high-energy emission of the precursor at 466 nm is totally absent [Fig. 1(a)]. By comparison of the fluorescence spectra of the precursors with those of the gels, we



**Fig. 1** (a) PL spectra of the precursor **1** in THF (—) and in KBr (---) and of the corresponding gel **6** (· · · · ·), (b) PL spectra of the precursor **2** in THF (—) and in KBr (---) and of the corresponding gel **9** (· · · · ·)

**Table 2** Spectroscopic data of the bis-trialkoxysilylated 1,4-arylenevinyls **1–5** and the gels **6–9**

Compound	$\lambda_{\text{abs}}^a/\text{nm}$ (log $\epsilon$ )	$\lambda_{\text{em}}/\text{nm}$	
		Solid <sup>b</sup> ( $\lambda_{\text{ex}}^c/\text{nm}$ )	Solution <sup>a</sup> ( $\lambda_{\text{ex}}/\text{nm}$ )
<b>1</b>	362 (4.81)	466/494 (409)	399/421 (362)
<b>2</b>	411 (4.28)	552 (468)	585 (420)
<b>3</b>	353 (4.86)	453/471 (420)	405/238 (353)
<b>4</b>	374 (4.85)	485 (423)	412/435 (362)
<b>5</b>	387 (4.87)	495 (439)	431/459 (397)
<b>6</b>	—	496 (440)	—
<b>7</b>	—	496 (440)	—
<b>8</b>	—	495 (439)	—
<b>9</b>	—	600 (468)	—

<sup>a</sup> In THF. <sup>b</sup> As KBr pellet. <sup>c</sup> Excitation wavelengths in emission spectroscopy of solids and gels were determined from the maximum values in their excitation spectra.

can conclude a planar conformation of the covalently incorporated distyrylbenzene units in the gels.

Distyrylanthracene derivatives have been shown to be nonplanar systems<sup>17,18</sup> and they exhibit different behaviour in PL spectroscopy (Table 2). Maxima in the emission spectra of the unsubstituted distyrylanthracene show a blue shift in the solid state in comparison with the solution [ $\lambda_{\text{em}}$  (solution) 500 nm,  $\lambda_{\text{em}}$  (solid) 575 nm]. The blue shift in the emission maximum of the silylated precursor **2** [Fig. 1(b)] in the solid state is weaker (552 vs. 585 nm in solution). Unexpectedly, the emission maximum of gel **9** was found at 600 nm. A possible interpretation for this variation might be a more planar conformation in the gel, which decreases the  $\pi$ – $\pi^*$  transition energies and results in an enhanced conjugation of the  $\pi$ -electronic system.

#### Footnotes

† 4-Styryl-trimethoxysilane and 4-styryl-triethoxysilane were obtained by the coupling reaction of 4-styrylmagnesium chloride<sup>19</sup> with chlorotrimethoxysilane<sup>8</sup> or tetraethoxysilane in THF, and subsequent distillation.

‡ All new compounds gave satisfactory spectroscopic and analytical data, e.g. bis-1,4-(4-trimethoxysilylstyryl)benzene **1a**: <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  3.65 (18 H, s), 7.16 (4 H, dd,  $J$  16.8 Hz), 7.53 (4 H, s), 7.61 (8 H, 2d,  $J$  8.2 Hz); <sup>13</sup>C NMR (CDCl<sub>3</sub>)  $\delta$  51.23, 126.44, 127.39, 128.84, 129.02, 129.69, 135.60, 137.12, 139.38; <sup>29</sup>Si NMR (CDCl<sub>3</sub>)  $\delta$  –54.38; UV–VIS (CHCl<sub>3</sub>);  $\lambda_{\text{max}}/\text{nm}$  (log  $\epsilon/\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ ) 362 (4.81); Anal. Calc. for C<sub>28</sub>H<sub>34</sub>O<sub>6</sub>Si<sub>2</sub>: C, 64.30; H, 6.55; Si, 10.74. Found: C, 64.24; H, 6.50; Si, 10.65%.

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