

Photoluminescence of Titanosilsesquioxanes in Solution and Its Relevance for the Understanding of the Emission of Titanosilicates**

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Titanium-containing (alumino)silicates are important industrial catalysts for aromatic hydroxylation and alkene epoxidation reactions.^[1–8] It is widely accepted that the catalytic sites are four-coordinate titanium atoms that are bipodally or tripodally bound to the framework of the (alumino)silicate. The improvement of the efficiency and activity of these materials is a continuous task, which would be facilitated by a deeper understanding of the active site structure and the characteristics of the corresponding transition states. For this reason, the development of more powerful, routine characterization techniques that specifically enable the minor proportion of the active titanium atoms to be monitored is required. The resulting structural information and novel experimental techniques should allow the design, preparation, and characterization of titanium-containing solids having the optimum activity and selectivity as heterogeneous catalysts.

A significant contribution in this area have been the recent reports showing that photoluminescence can be applied in titano(alumino)silicates, particularly Ti/MCM-41 and TS-1 to the determination of titanium atom distribution among different populations that have distinctive coordination spheres.^[8–11] Depending on the sample preparation and post-synthetic treatments, two different weakly emitting titanium atoms were reported ($\lambda_{\text{em}} = 430, 490 \text{ nm}$), that were assigned to tripodally bound titanol groups and to tetrapodally bound titanium atoms, respectively.

These initial reports have been more recently challenged by the observation that as-synthesized and silylated samples of mesoporous titanosilicates obtained by direct incorporation of titanium during the hydrothermal crystallization of the solid exhibits a remarkably more intense photoluminescence and have emission maxima at much shorter wavelengths ($\lambda_{\text{em}} = 390 \text{ nm}$).^[12] The intensity of the emission drops dramatically and λ_{em} shifts to longer wavelengths upon calcination and template decomposition of the original, as-synthesized Ti/MCM-41.

A fruitful strategy to understand the architecture and the catalytic activity of the active titanium sites in titanosilicates has been to synthesize simple model molecules, wherein the titanium atoms have precise coordination spheres to emulate those thought to exist in titanosilicates.^[13–16] In recent papers, several groups have used homogeneous soluble titanosilsesquioxanes as model compounds.^[17] They have proposed, based on the results obtained by extended X-ray absorption fine structure (EXAFS) spectroscopy, X-ray absorption near-edge structure (XANES) measurements, and molecular dynamics calculations, that the most active sites of Ti/MCM-41 are four-coordinate titanium atoms tripodally anchored to the silicate framework.^[17]

Owing to the controversy surrounding the assignment of emission maxima, we have studied the photoluminescence of a series of titanosilsesquioxanes in solution. In principle they can serve as soluble model molecules to facilitate assignment of the photoluminescence observed in Ti/MCM-41 samples to specific coordination environments, thereby providing firm evidence to support or challenge previously reported assignments. In addition, photoluminescence measurements in solution have allowed us to obtain, for the first time, a whole set of quantum yields and quenching rate constants that cannot be measured for opaque solids. This quantitative measurement of photo-physical parameters associated with titanium atoms is important in order to achieve a full understanding the photoluminescence of titanosilicates.

The structure and characteristics of the series of titanosilsesquioxanes under scrutiny are contained in Table 1. A full account of the synthesis and characterization of these compounds has been previously reported by one of us.^[15, 16] The set has been selected to encompass a range of possible titanium coordination forms that are thought to be present in solid titanosilicates. With the exception of **4**, the titanosilsesquioxanes contains a single four-coordinate Ti atom. In this series, Ti atoms can be bonded to the polycyclic silsesquioxane skeleton by three bonds ("tripodal", as in **1–3**) or it can be connected to the cyclic framework by only two bonds ("bipodal", as in **5**). In the case of tripodal Ti, the fourth coordination site is saturated either by a trimethylsilyloxy group (as in $[\text{Ti}(\text{OSi})_4]$) or by a simple alkoxy group. Compound **4** purposely contains a certain amount of the titanosilsesquioxane dimer that should allow one to address the influence of pentacoordinate, bridged " $\text{Ti}-(\mu\text{-OR})_2\text{-Ti}$ " atoms on the photoluminescence. A comparison between **3** and **4** should additionally allow one to assess the sensitivity of this technique in determining the distribution of Ti atoms among different families of sites.

All the titanosilsesquioxanes studied are highly soluble in dichloromethane and cyclohexane. Studying the photolumines-

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Table 1. Structure and relevant structural parameters of the series of titanosilsesquioxanes studied in this work.

Com- pound	Structure ^[a]	Ti coordination
1		tripodal
2		tripodal
3		tripodal
4		as 3 + penta-coordinate Ti dimer
5		bipodal

[a] R = cyclo-C₆H₁₁.

cence of these compounds in different solvents permits one to obtain a set of absolute photoluminescence quantum yields and quenching rate constants, and also to determine the influence of polarity on the emission intensity and photoluminescence spectra. As far as we know, none of these data have ever been reported for titanosilsesquioxanes. These important photophysical parameters cannot be measured for opaque solids, such as titanosilicate powders, since the number of photons actually adsorbed from the incident radiation cannot be accurately determined.

The absorption spectrum of titanosilsesquioxanes in dichloromethane shows an intense band at $\lambda_{\text{max}} \approx 215$ nm, with a tail up to 300 nm. The broadness of this absorption band suggests that the 0,0-transition is at a longer wavelength than λ_{max} (see below). In cyclohexane, the absorption band shows a bathochromic shift ($\lambda_{\text{max}} \approx 225$ nm) but the onset of the absorption band also starts at 300 nm. These values for λ_{max} are typical for isolated titanium atoms and the relatively minor but significant shift in λ_{max} reflects the influence of solvent polarity on the electronic transition. The corresponding extinction coefficients are presented in Table 2. Even though sample 4 contains some dimeric "Ti-(μ -OR)₂-Ti" units, they are not apparent in its transmission UV spectrum.

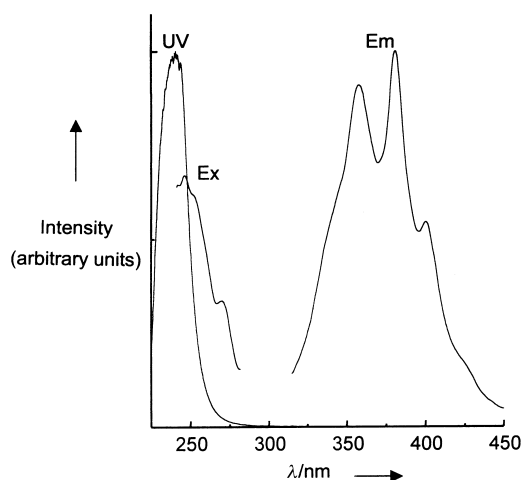
Table 2. Molar extinction coefficients ϵ , quantum yields ϕ , and luminescence lifetimes τ obtained for titanosilsesquioxanes 1–5 in solution.

Com- pound	Dichloromethane			Cyclohexane			
	ϵ [M ⁻¹ cm ⁻¹]	ϕ (N ₂) $\times 10^4$	τ (N ₂) ^[a,b] [ns]	ϵ [M ⁻¹ cm ⁻¹]	ϕ (N ₂) $\times 10^2$	τ (N ₂) [ns]	τ (O ₂) ^[a] [ns]
1	3595	4.8	3.5	34460	2.9	34.4	16.38
2	5170	6.0	2.8	10750	3.0	30.4	16.8
3	6130	10.0	6.2	9880	2.8	30.1	17.7
4	6470	7.9	4.2(72) 1.2(28)	9540	2.4	42.6(65) 3.5(35)	15(78) 3.3(22)
5	7915	5.3		7540	1.3	35	13.6

[a] From the best fit to first-order decays. Compound 4 has two monoexponential lifetimes, whose relative contributions are indicated within brackets.

[b] Lifetimes under oxygen are too short to be measured with our apparatus.

Upon UV excitation, all titanosilsesquioxanes 1–5 emit and the emission spectra are independent on the excitation wavelength over the range 220–280 nm. This is expected for pure compounds which have a single fluorophore. Figure 1 shows the absorption, emission, and excitation spectra of 1 in dichloromethane. The emission spectra of the rest of the series upon 250 nm excitation are compiled in Figure 2. From the crossing point of the absorption and emission spectra and assuming that both spectra involve the same electronic states, the 0,0-

**Figure 1.** UV/Vis absorption (UV), emission (Ex; $\lambda_{\text{exc}} = 250$ nm), and excitation (Ex; $\lambda_{\text{em}} = 360$ nm) spectra of 1 in CH₂Cl₂ recorded at room temperature after a nitrogen purge.

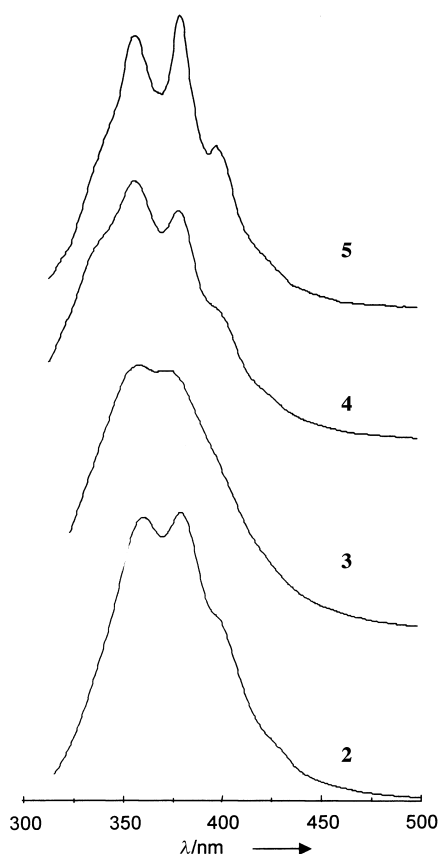


Figure 2. Emission ($\lambda_{\text{ex}} = 250 \text{ nm}$) spectra of 2–5 in CH_2Cl_2 recorded at room temperature after a nitrogen purge.

transition could be experimentally measured, to provide a value of about 306 nm.

Interestingly, the emission spectra of compounds 1–4 at room temperature all exhibit vibrational fine structure. The vibration energy was very similar in all these samples ($E_{\text{vib}} \sim 1300 \text{ cm}^{-1}$). These values correspond to the wavenumbers of the Ti–O bond observed in Raman or IR spectroscopy. Thus, this vibrational structure can be taken as an evidence to show that Ti atoms participate in the emitting moiety that is observed by photoluminescence spectroscopy. As an example, Figure 3 presents the Raman spectra of titanosilsesquioxanes 1–5 in dichloromethane, in which the position of the Ti–O vibration observed in the emission spectra has been indicated.

The most significant feature of the emission spectra of 1–5 with respect to some earlier reports concerning the photoluminescence of solid titanosilicate samples is the wavelength of the maximum emission intensity. As can be seen in Figures 1 and 2, the whole series 1–5 emit in the range between 350 and 390 nm, well below the $\lambda_{\text{em}} = 490 \text{ nm}$ reported earlier for four-coordinate, tetrapodally bound titanium atoms^[8–11] and coincident with that previously reported by us for silylated Ti/MCM-41 samples.^[13] Thus, the present spectra lend strong support to our assignment of the 390 nm emission to four-coordinate titanium present in titanosilicates. Furthermore, no significant variations in the wavelength of the emission maxima are observed for titanosilsesquioxanes having tripodal or bipodal titanium atoms

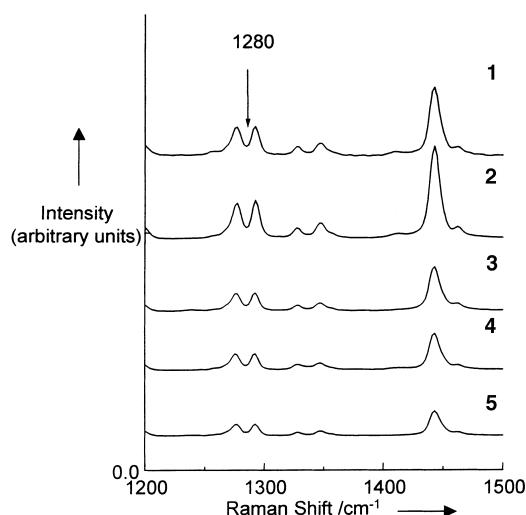


Figure 3. FT-Raman spectra of 1–5 in CH_2Cl_2 . The vibration corresponding to the fine structure observed in Figures 1 and 2 is indicated with an arrow.

or “Ti-(μ -OR)₂-Ti” dimers. Given the fact that emissions for solid samples are characterized by much broader emission bands as compared to solution spectra, it can be concluded that it is not possible to distinguish between tripodal and bipodal titanium atoms in titanosilicates exclusively on the photoluminescence spectra. However, it still remains to be seen whether titanol groups emit in a different region. Since titanosilsesquioxanes having a $\equiv\text{Ti-OH}$ group are not stable compounds, it is not possible to address this point using titanosilsesquioxanes as model compounds and this question remains open. The possibility that the titanol groups emit at a different wavelength would reconcile our photoluminescence spectra with those reported by other groups.

It has been stated that titanosilicates exhibit an intense photoluminescence but no quantum yields have been reported. In this study, we have measured absolute emission quantum yields at room temperature in dichloromethane and cyclohexane, that clearly prove that Ti–O groups are, in reality, very weakly photoluminescent fluorophores. The values of quantum yields after nitrogen purging are included in Table 2. No large variation in the emission quantum yield values was found for the five titanosilsesquioxanes, both for the data measured under nitrogen or oxygen. Oxygen reduces the emission quantum yield by a factor of about two in every case but does not totally quench the photoluminescence. We also noted that the presence of oxygen results in the disappearance the vibrational fine structure of the emission and a blue shift of λ_{em} . In cyclohexane, the emission quantum yields for all the titanosilsesquioxane are similar and are about two orders of magnitude higher than the values measured in dichloromethane. This can be rationalized on the basis that dichloromethane is somehow quenching the emission of Ti–O groups. Related precedents, that report dichloromethane can interact with weakly emitting azo compounds through an aborted hydrogen transfer mechanism to decrease the photoluminescence intensity, can be found in the literature.^[18] By applying the Stern–Volmer

equation^[19] and given that the lifetime of fluorescence lifetime in the absence of quencher is 3.5 ns (see below), the quenching rate constant of the photoluminescence by oxygen in dichloromethane can be calculated. The value obtained ($2.4 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$) indicates that the quenching is predominantly a diffusion-controlled process.

Analysis of the photoluminescence kinetics is a powerful tool to gain information about site distribution and relative population as well as the influence of the environment on the emitting fluorophores. However, in spite the importance of time-resolved studies in emission spectroscopy, there is a paucity of emission lifetime measurements in titanosilicates. We measured emission time profile for the series of titanosilsesquioxanes, both in dichloromethane and in cyclohexane (Table 2). In the absence of oxygen, all the emission decays occur on the nanosecond timescale and one order of magnitude longer in cyclohexane than in dichloromethane. This observation is in agreement with our previous measurements of much higher emission quantum yields in cyclohexane than in dichloromethane, which suggests a special photoluminescence quenching mechanism in dichloromethane.^[18] All the kinetic results, except that for **4**, can be fitted to single exponential decays, to indicate that there is only a single family of light-emitting titanium atoms. The corresponding lifetimes can be, then, obtained from the best fit to the experimental decay. A list of the values are summarized in Table 2. As expected, oxygen purging not only reduces the emission intensity but shortens the lifetime of the emission. A selection of representative emission decays under different conditions together with the corresponding fit from which lifetimes have been obtained are shown in Figure 4.

In the case of **4**, in which a mixture of monomeric and dimeric titanosilsesquioxane exists, a single first-order decay does not fit. An adequate fit is obtained by considering two superimposed monoexponential decays. Taking into account that the lifetime of the pure titanosilsesquioxane monomer **3** (see Table 2), it seems reasonable to conclude that the short and long components of **4** correspond to the decay of the dimer and monomer, respectively. The relative contribution of the shorter lifetime component to the total emission is around 30% (see Table 2), which is in reasonable agreement with the amount of dimer

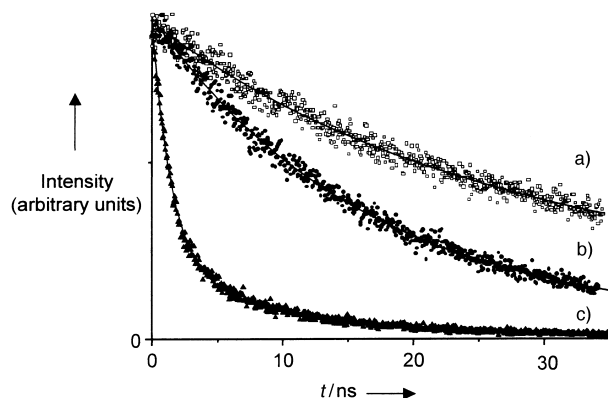


Figure 4. Photoluminescence decays of **1** ($\lambda_{\text{ex}} = 250 \text{ nm}$) monitored at 375 nm in cyclohexane under nitrogen (a) or oxygen (b), or in dichloromethane under nitrogen (c).

present in **4**. It is worth noting that while photoluminescence spectrum do not report the presence of two types of titanium atoms in **4** (monomer plus dimer), the kinetic analysis of the emission decay is much more informative in this respect. Precedents which use the fit of the emission decay to determine the relative population of different families of a fluorophore abound in the literature.

The photoluminescence time profile of the titanosilicates has been studied.^[12] Thus, it is of interest to compare the decay of titanosilicates with that measured here for titanosilsesquioxane in solution since this can give a good indication of how valid soluble titanosilsesquioxanes are as model compounds for solid titanosilicates. Figure 5 provides a comparison of the emission

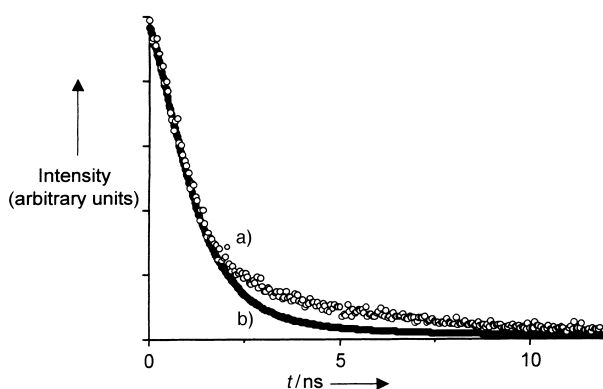


Figure 5. Comparison of the photoluminescence decay of **1** in dichloromethane under nitrogen (a) with that of silylated Ti-MCM-41 (b).

decay of silylated Ti-MCM-41 with that of titanosilsesquioxane **1** in dichloromethane. The similarity between these two decays is remarkable and experimentally supports the validity of using titanosilsesquioxane to investigate the photophysical properties of solid titanosilicates.

From the results presented on the photoluminescence of titanosilsesquioxanes in solution, it can be concluded that Ti–O is, in general, a weakly emitting group. The emission quantum yields are, however, strongly influenced by the experimental conditions of the measurements and particularly by the nature of the solvent. The wavelength recorded for the emission maxima is well below 400 nm and is apparently rather insensitive to the solvent and to the bipodal, tripodal, or dimeric structure of the titanosilsesquioxane. This observation lends strong support to our previous assignment of an emission at $\lambda = 390 \text{ nm}$ observed for titanosilicates as characteristic of four-coordinate titanium atoms lacking bonded OH groups.

Experimental Section

Compounds **1**–**5** correspond to the same samples as those prepared and characterized in refs. [15, 16]. The solvents used were of spectrophotometric grade and used as received. Except for oxygen-purged measurements, titanosilsesquioxanes were handled under a nitrogen atmosphere in a glove box and weighed amounts of them transferred to Suprasil quartz tubes. In most of the experiments, the tubes sealed under vacuum (10^{-4} Torr) or, alternatively, capped with

septa for quenching experiments. In the latter case, the photoluminescence measurements were measured shortly after preparation. UV/Vis spectra of compounds **1–5** in solution (10^{-3} – 10^{-4} M) were collected on Cary 5-G Varian spectrophotometer. Emission and excitation spectra were recorded in a Edinburgh FS-900 spectrophotometer. Quantum yields were obtained using a solution of naphthalene in cyclohexane as reference, whose optical density matched that of the samples at the excitation wavelength. For oxygen quenching, the solutions were purged with an oxygen stream for at least 10 min before photoluminescence measurements. Lifetimes were measured with a FL-900 single-photon counting photometer using a nanosecond hydrogen flash lamp.

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Physical Consequences of a Mechanically Interlocked Architecture: Benzylic Amide Catenane NH Stretching Vibrations as Sensitive Probes for Weakly Hydrogen-Bonding Environments**

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One of the issues still to be fully explored in the interlocking of molecular-level components to form catenanes and rotaxanes is the nature of the physical and chemical effects that can be induced or influenced through such architectures.^[1] The weak intercomponent forces generally used to promote the assembly of such structures, combined with the restricted degrees of freedom imposed on the components by interlocking, provide a situation unlike either supramolecular systems (in which the weakly bound components are normally exchangeable between assemblies) or conventional molecular architectures (where the rules of covalent bonding tend to impose rigorous requirements on every bond distance and angle). The benzylic isophthalamide macrocycle **1** is remarkable in that it can be studied under all three situations (Scheme 1); as a simple macrocycle, a supramolecular complex with (and sensor for) CO₂^[2] or as an interlocked dimer in the form of the [2]catenane **2**.^[3] Differences,

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