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Studies of organic–inorganic solids possessing sensitive oligoarylene–vinylene chromophore-terminated phosphonates

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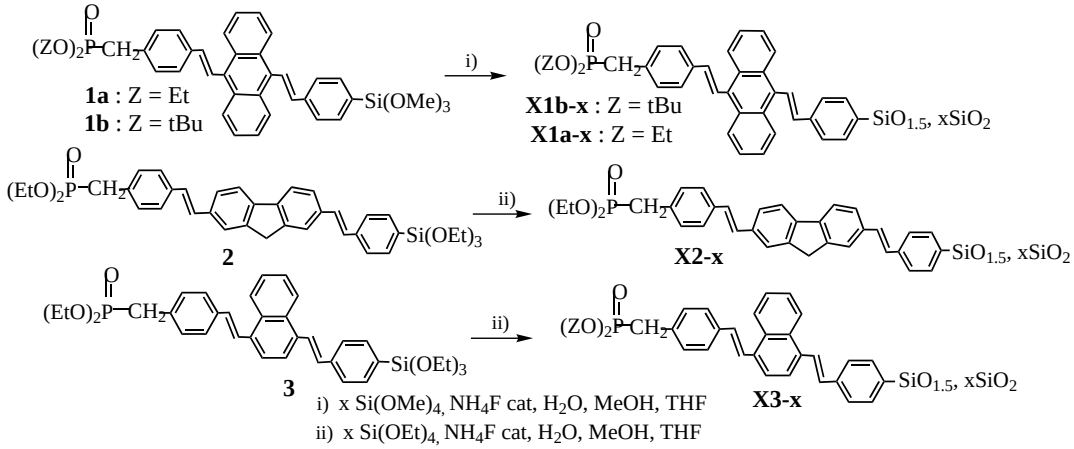
Abstract—The syntheses of xerogels possessing a phosphonate group covalently linked to a silica matrix through a fluorescent carbon backbone are described. BET and fluorescent analyses showed different behaviors for closely related structures. Hydrolysis of Et and *t*-Bu phosphonates in the presence of sensitive π-conjugated anthryl chromophore is described.

The synthesis of organically modified silicas is an important developing field, due to the mild conditions of the sol–gel processing which is compatible with sensitive molecular precursors and biological molecules.[1] The preparation of silica based materials possessing covalently bonded phosphonate group functionality has been recently described.[2] These materials would have a wide range of applications in areas such as extraction and separation devices and catalysis. We have recently reported the synthesis[3] and gelation[2d–e] of fluorescent phenylene–vinylene derivatives possessing trimethoxysilane and diethylphosphonate functionalities,[2d] and their luminescent behaviors were a function of the organic part content inside the solid. Aggregation of the chromophores at high content of the organic part were observed. We present here the gelation of fluorenyl, anthracenyl and naphthyl phenylene–vinylene derivatives to get further information about the orientation of the chromophores inside the solid, particularly at high content. Hydrolysis of the phosphonate ester group[2e] of the anthryl derivative is reported.

Precursors **1** and **2** have been synthesized and their fluorescent behavior analyzed in solution.[3] The



Scheme 1. Gelation of compounds **1**–**3**.

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alkoxysilane moiety was reacted by using the NH_4F-catalyzed sol–gel method[2d] (Scheme 1). The gels were analyzed by EDX, IR, ^{29}Si, ^{13}C, ^{31}P solid-state NMR and the spectroscopic data were similar to those observed for phenylene–vinylene compounds.

The same gelation procedure was applied for methoxy and ethoxy silyl derivatives. No differences were detected by spectroscopic techniques. The gels were well condensed[2d] (**Q1** and **T1** signals were not observed, **T3**, **Q3** **Q4** were the major signals by cpmas ^{29}Si NMR). The organic part was not damaged (no cleavage of the Si–C bond). BET experiments showed that the specific surfaces areas for **X2**, **X3** were high even at high proportion of the organic part inside the solid (Table 1). Mesoporous solids were obtained for $x=15$–100. Xerogels **X2-15**, **100**; **X3-15**, **100** presented a narrow distribution of mesopores (30–43 Å). The microporous distribution was not significant (<20%). **X3-50** presented a mesoporous character as well, but the distribution of mesopores was larger (50–65 Å). The specific surface was the highest observed and the isotherm hysteresis did not close, which suggests that some pores have an ink bottle shape with small pore openings that do not facilitate N_2 desorption. The texture of solids **X2**, **X3** was thus fairly different from that observed for π-conjugated phenylene–vinylene compounds.[2d] By contrast, solids **X1** derived from anthracene presented a texture similar to that observed for biphenylene–vinylene compounds. Many parameters are involved in the sol–gel procedure and the formation of solids is controlled by kinetic factors. The leaving group on Si, (EtO versus MeO), the organic part and the temperature could best explain the differences of texture observed.[4] The presence of the chromophore in xerogels **X1**, **X2**, **X3** was characterized by fluorescence studies. Fluorescence did not depend on the excitation wavelength, it was highly dependent on the proportion of chromophores inside the solid. The behavior of **X3** (naphthyl group) (Fig. 1) was similar to that of phenylene–vinylene compounds. Aggregates were observed at high content ($x=0$, 5) of the organic part inside the solid with a $\lambda m_{em}=520$ nm, but no excimers were detected. By increasing the proportion of silica, λm_{em} was progressively shifted to the blue. The gradual decrease of the chromophore proportion gives rise to a distribution of aggregate geometries with an important effect on λm_{em}. The monomer emission appeared at low content of the organic part, with a blue shift of λm_{em} up to 470 nm. By contrast the fluorenyl derivative (Fig. 2) presented an excimer formation for $x=0$–10, with a broad red-shift band at 600 nm. Thus, the inorganic

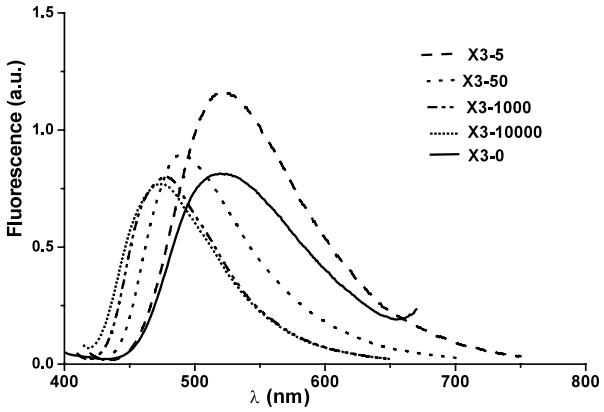

Figure 1. Fluorescence of xerogels **X3-x**.

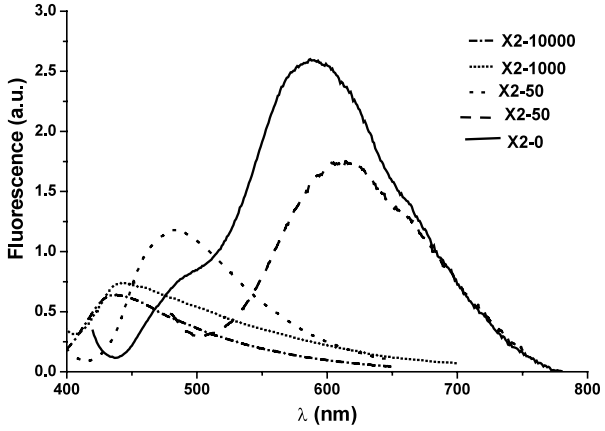

Figure 2. Fluorescence of xerogels **X2-x**.

matrix was favorable for a face-to-face sandwich orientation required for formation of excimers with compound **2**. This orientation should be present in the ground state, as compound **2** presented no excimers in solution. By increasing x to 15, excimers abruptly disappeared and λm_{em} was shifted to the blue at 490 nm. At low proportion of the organic part in the solid, fluorescence of the monomer was observed with λm_{em} at 450 nm. Xerogels **X1-0-100** presented the same fluorescence curve as compound **1** in solution. The large band at 600 nm was characteristic of the excimer emission. In contrast to **X2**, the excimer band did not disappear but was progressively shifted to the blue by increasing x ($\lambda m_{em}=580$ nm for $x=100$) (Fig. 3).

The monomer emission at 500 nm was observed for $x>1000$. We observed no differences of behavior between chromophore **1a** and **1b**, which showed that Et

Table 1. BET of Xerogels **X2**–**X3**

Xerogel	Isotherm	Porous diameter (Å)	Microporous contribution (% volume)	Specific surface area ($m^2\ g^{-1}$)
X2-15	IV	30	None	148
X2-100	I and IV	37	19	419
X3-15	I and IV	40	18	513
X3-50	IV	50–65	None	957
X3-100	IV	43	9	460

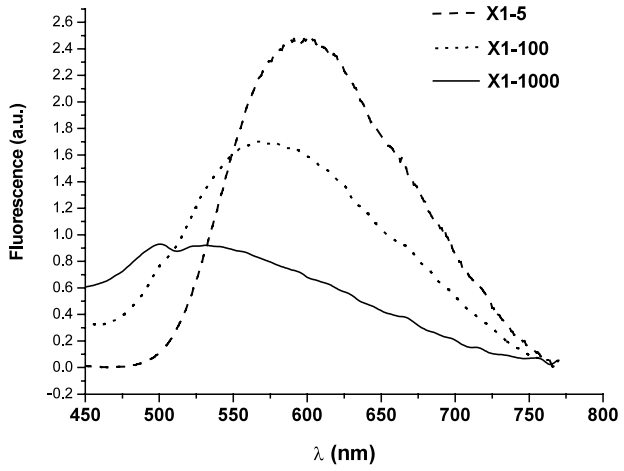

Figure 3. Fluorescence of xerogels **X1-x**.

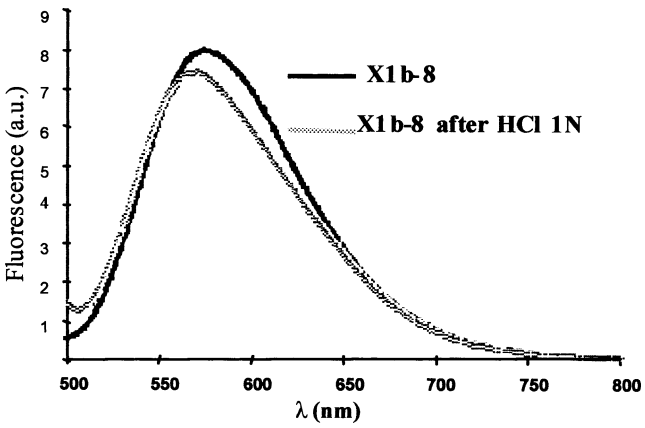

Figure 4. Fluorescence of xerogels **X1b-8** and **X1b-8** after HCl 1N.

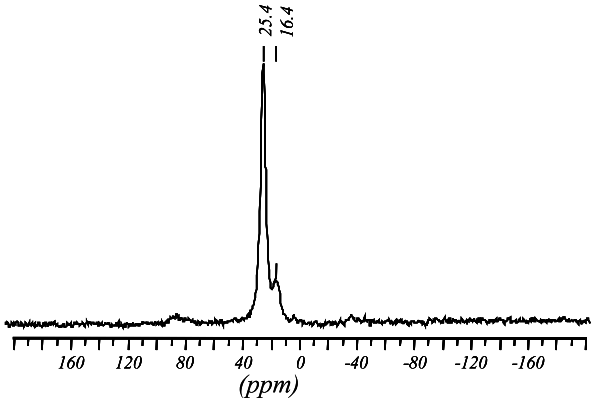

Figure 5. ^{31}P hpdec mass NMR of **X1b** after treatment by HCl 1N.

or *t*-Butyl phosphonate group has no influence on the anthrylene–vinylene–phenylene fluorescence emission. The texture of solids **X1**, **X2**, **X3** results from the synergy between the organic backbone and the inorganic matrix, chromophore–matrix interactions are thus fairly different from one chromophore to another which led to various luminescent behaviors and diverse porosity distributions, even if the structure of the precursors is close. We were then interested in the cleavage of the phosphonate ester groups of xerogels **X1**. We have shown previously that TMSBr at 50°C was efficient in the cleavage of ethyl phosphonates and was compatible with a π-conjugated vinylene–phenylene backbone structure. However, with xerogels **X1a**, we encountered difficulties to properly cleave the ethyl phosphonate groups by this method. After addition of TMSBr, the orange–red material turned black immediately, free phosphonic acid was detected with other species by hpdecmas ^{31}P NMR, and we lost the fluorescence signal of the chromophore. The π-conjugated vinylene anthrylene chromophore seems to be sensitive to treatment by TMSBr. As an alternative, we turned to the *tert*-butyl phosphonate ester **X1b** which has been shown to be cleaved in very mild conditions. Xerogel **X1b** was treated by HCl 1N at 50°C. We were pleased to find that the excimer fluorescent emission was not lost (Fig. 4).

^{31}P hpdec mass NMR showed a major signal at 25.4 ppm which corresponds to the free phosphonic group. A minor part of phosphonic groups was bonded to silica (signal at 16.4 ppm). Thus, the *t*-butylphosphonate is the protective group of choice for the synthesis of phosphonic acids possessing a sensitive carbon backbone (Fig. 5).

In conclusion, we have shown that precursors with closely related structures could have fairly different behaviors after gelification, as analyzed by BET and fluorescence. The presence of excimer was detected for **X1** and **X2**, which shows that a silica matrix could favor the geometry required for excimer formation. The efficiency of the *t*-butyl protecting group was demonstrated with sensitive molecules. Applications of phosphonic acids supported silicas are in progress and will be reported in due course.

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