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LETTERS

Efficient syntheses of new phosphonate terminated trialcoxysilane derived oligoarylenevinylene fluorophores

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Abstract

The syntheses of new molecules derived from oligoarylenevinylene, possessing two assembling functionalities (trialcoxysilane and phosphonate) are described. Two successive Heck reactions were carried out to afford the highly functionalized compounds **3a–g** in average overall yields. The optical properties of **3a–g** were then studied.

The organic molecules possessing a trialcoxysilane group and a second assembling functionality (Scheme 1) have been widely studied for applications in a variety of different fields.[1]

$$(RO)_3Si—ALK—X$$

X : NH_2, NR_1R_2, SH, S-SR_3, PPh_2, PEt_2... R : Me, Et ALK : carbon chain

Scheme 1.

Amine-terminated trialcoxysilanes (X=NH_2, NEt_2) were used extensively for surface modifications[1a] which led to efficient supported catalysts,[1b] self-assembly metal colloid monolayers,[1c,d] or enzymatically modified lipid monolayers.[1e] Phosphine-terminated trialcoxysilanes (X=PPh_2, PEt_2) were commonly used in order to bind metal complexes to support materials.[1f–h] Sulfur-terminated trialcoxysilanes (X=SH, S-SR) were covalently bonded to silica for modification of polymer properties (silica charged rubbers)[1a] or to metal oxide electrodes for studies of new redox behaviours.[1h] However phosphonate-terminated trialcoxysilanes have been much less described, which is surprising due to the interesting properties of phosphonates.[2] One application has been recently reported which deals with a ^{29}Si and ^{31}P NMR study of the cogelification of diethylphosphatoethyltriethoxysilane (R=Et, Alk=CH_2-CH_2, X=PO_3Et_2) with tetraethoxysilane.[3] Furthermore, the backbone of the molecules in Scheme 1 is usually simple, essentially constituted of aliphatic carbon chains. Backbones containing stilbenoid compounds and related oligophenylenevinylene structures have never been described, to the best of our knowledge.

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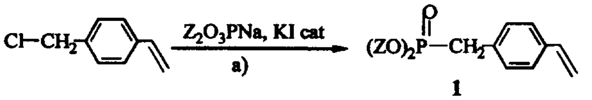
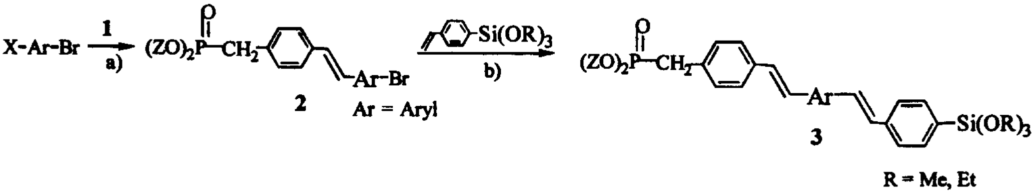
Due to their unique optical, optoelectronic and charge conducting properties, such molecules derived from stilbenoids[8] would find use in a variety of materials science applications. In connection with our work on hybrid organic–inorganic nanostructured solids[4a] and luminescent materials,[4b] we describe here the syntheses of new phosphonate-terminated trialcoxysilanes possessing an oligoarylenevinylene backbone.

As many iodo-bromo or dibromo-substituted arenes are easily accessible or commercially available, we considered using a double Heck cross-coupling reaction procedure. Indeed, the mild conditions of the Heck reaction are particularly suitable for the preparation of our oligoarylenevinylene derivatives. We first prepared ethyl 4-phosphonatomethylstyrene (Z=Et) by nucleophilic displacement of 4-chloromethylstyrene with sodium diethyl phosphite at rt in 90% yield (Scheme 2). This substitution gave a higher yield than the Arbuzov reaction[5] which required higher temperatures and longer reaction times in the case of benzylic chlorides. Interestingly, the substitution of 4-chloromethylstyrene with sodium ditertbutylphosphite (Z=*t*-Bu), which has not been described to our knowledge, was achieved in 70% yield at 50°C. These styrenes were then reacted in the first Heck reaction (Scheme 3) with different halogeno-paradisubstituted arenes (Table 1). The phosphine-free conditions we used for iodo-bromo substituted arenes (compounds **3a–c**, Table 1) were described by Heck[6a] and were selective for iodine, which afforded the monosubstituted intermediates **2** in good yields. However, in the case of dibromo-substituted arenes (compounds **3d–g**), we used standard conditions[6b] which gave the intermediates **2** in an average yield due to the low solubility of high molecular weight arenes and to the presence of the corresponding diphosphonates as side-products.



Scheme 2. (a) Z=Et: THF, rt. Z=*t*Bu: THF, 50°C



Scheme 3. (a) X=I: Pd(OAc)$_2$, Et$_3$N, MeCN, X=Br: Pd(OAc)$_2$, TOP, Et$_3$N, PhMe, DMF. (b) Pd(OAc)$_2$, TOP, Et$_3$N, PhMe, DMF

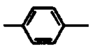
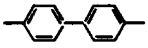
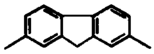
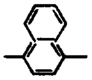
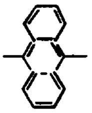
Intermediates **2** were then submitted to the second Heck reaction with 4-trialcoxysilylstyrene[7] (Scheme 3). As the alcoxysilane group improved the solubility of **3**, the reaction proceeded in good yield even for high molecular weight arenes (compounds **3d–g**). The products **3** were highly sensitive towards hydrolysis; thus, ammonium salts and catalyst were removed by filtration of the crude product over dry silanized silica, which afforded **3** in good purities and in average overall yields from the dihalogenated arenes (Table 1).

The two assembling functions were characterized by ^{31}P and ^{29}Si NMR spectroscopies and the chemical shifts were in agreement with the literature.

The optical properties of the compounds **3** were then studied. The excitation and photoluminescence (PL) spectra of the products **3a–c**, **3d–e**, **3f–g** are shown in Figs. 1–3, respectively.

The excitation spectra coincide with the absorption spectra, indicating that they are dominated by the wavelength-dependent absorption probability. The excitation and emission spectra for the compounds **3a–e** are nearly symmetric, in agreement with the Franck–Condon's principle and the Stokes' shift, for rigid molecules. Both excitation and emission spectra shift to the red in going from the phenylene or

Table 1

Compounds	Ar	Z	X	R	Overall Yield	λ ex (nm)	λ em (nm)	δ^{29}Si (ppm)	δ^{31}P (ppm)
3a		Et	I	Me	63 %	361	422	-54.4	27.7
3b		t-Bu	I	Me	60 %	357	422	-54.3	19.1
3c		Et	I	Me	65 %	357	426	-54.8	27.5
3d		Et	Br	Et	48 %	376	433	-57.2	27.6
3e		Et	Br	Et	54 %	393	446	-57.2	27.5
3f		Et	Br	Me	35 %	437	583	-54.3	27.4
3g		t-Bu	Br	Me	45 %	437	598	-54.3	19.1

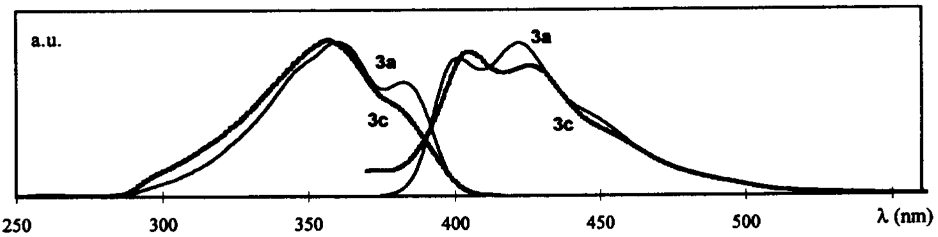


Figure 1. Excitation and emission spectra of the compounds 3a, 3c, recorded in THF at 10^{-5} M

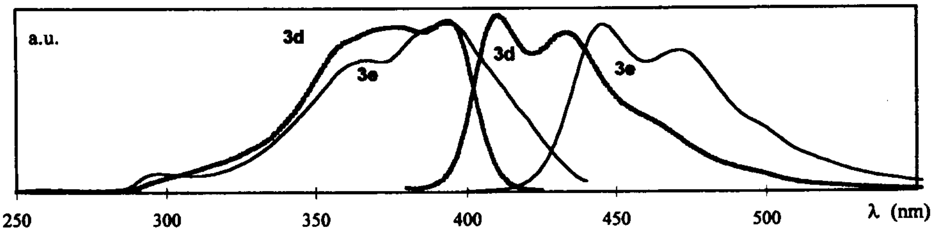


Figure 2. Excitation and emission spectra of the compounds 3d–e, recorded in THF at 1.07×10^{-6} M and 0.87×10^{-6} M, respectively

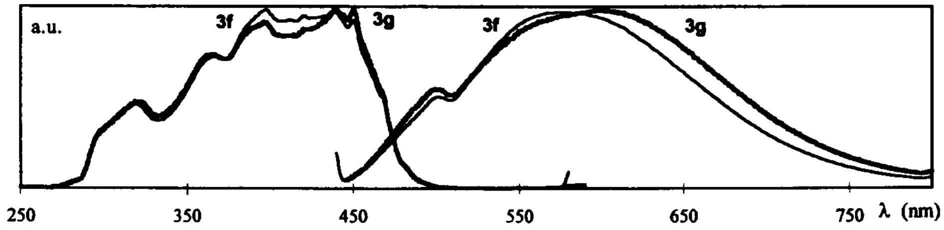


Figure 3. Excitation and emission spectra of the compounds 3f–g, recorded in THF at 8.53×10^{-5} M and 8.64×10^{-5} M, respectively

biphenylene derivatives **3a–c** to the compounds **3d–e** derived from fluorene, naphthalene. This shift is consistent with a decrease in transition energy as electronic delocalization is extended. Maximum emission wavelengths ranged from 400 to 470 nm and were similar to those observed for trimethoxysilyl[4b] disubstituted oligophenylenearylene or phosphonic acid[9] disubstituted oligophenylenevinylene derivatives. Changing the terminal group does not affect the fluorescence properties of the chromophore, thus the curves **3b** (not shown) are superimposed on **3a**.

The behaviour of anthracene derivatives **3f–g** (Fig. 3) was different from that of the compounds **3a–e**, certainly because of excimer formation (PL maxima were shifted to 600 nm). Additional experiments are in progress to analyze this behaviour and the behaviour of **3a–e** at higher concentrations.

Photoluminescence is a very sensitive method, particularly suitable for the detection of organic molecules in a solid matrix.[4b] It could bring information about the conformation of molecules,[10] in the solid as well[4b] as in solution. Thus, PL could be a useful tool for analyses of chromophore environment and interactions on solid surfaces. The exploitation of our derivatives for modifications of surface oxides is in progress and will be reported in due course.

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