ELSEVIER

Journal of Organometallic Chemistry 627 (2001) 239–248

Journal of Organo metallic Chemistry

www.elsevier.nl/locate/jorganchem

Functional chiral hybrid silica gels prepared from (*R*)- or (*S*)-binaphthol derivatives

Anne Brethon, Peter Hesemann, Luc Réjaud, Joël J.E. Moreau *, Michel Wong Chi Man

Laboratoire de Chimie Organométallique, Hétérochimie Moléculaire et Macromoléculaire, UMR CNRS 5076, Ecole Nationale Supérieure de Chimie de Montpellier, 8 rue de l'Ecole Normale 34296 Montpellier Cedex 05, France

Received 19 December 2000; accepted 28 February 2001

Abstract

We describe the synthesis of new functional bis-trialkoxysilylated binaphthol derivatives **I**–**V** containing protected OH groups and cyano-, pyridyl- and carbamate-functionalities starting from optically pure (*R*)- or (*S*)-2,2′-dihydroxy-1,1′-binaphthyl (BINOL) and their subsequent transformation to hybrid silica gels via the sol–gel process. (*R*)-**I** was obtained by protection of hydroxyl groups of (*R*)-6,6′-dibromo-BINOL with MEM-chloride, halogen metal exchange with *n*-butyllithium and coupling of the metalated (*R*)-BINOL species with chlorotrimethoxysilane. The synthesis of (*R*)-**II,** (*R*)-**III**, (*R*)-**IV** and (*R*)/(*S*)-**V** was realized through silylation of 6,6′-dibromo-BINOL derivatives under Heck-reaction conditions using vinyl-triethoxysilane and palladium acetate/tri-*o*-tolyl phosphine.

The sol–gel hydrolysis and polycondensation of the precursors (*R*)-**I**-(*R*)-**V** led to hybrid organosilicate gels (*R*)-**A**–(*R*)-**E** incorporating C_2-symmetric chiral binaphthyl moieties. The attached functional groups are preserved after sol–gel transformation. Deprotection of the MEM–BINOL unit of (*R*)-**I** was performed following two pathways: in the first case, treatment of the gels (*R*)-**A** with a ten-fold excess of zinc bromide, and secondly by hydrolysis polycondensation of (*R*)-**I** in the presence of nickel or palladium salts. The solids, consisting of a chiral hybrid network, were characterized by solid state NMR, FTIR, TEM and nitrogen sorption analysis. These materials may open new perspectives for applications in heterogeneous catalysis and molecular recognition.

Keywords: Hybrid silica gels; 2,2′-Dihydroxy-1,1′-binaphthyl

---

1. Introduction

Sol–gel derived hybrid materials [1–3] have a great potential in combining organic and inorganic fragments at the molecular level. For example, the preparation of heterogeneous catalysts by use of this approach proved to be of interest [4]. As part of our interest in selective heterogeneous catalysis [5], we prepared hybrid containing chiral organic units. Rather than embedding chiral molecules in a silica matrix [6] we synthesized chiral hybrid networks by introduction of chiral organic substructures via sol–gel hydrolysis of a functionalized chiral precursor [7]. This approach recently led to an interesting hybrid solid with chiral helical morphology [8].

The immobilization of chiral diamine–rhodium complexes in hybrid silica-based materials upon sol–gel condensation of silylated chiral diaminocyclohexane derivatives was achieved [7c]. Interestingly, these materials compared favorably to related homogeneous catalyst in asymmetric catalysis. A significant increase of the enantioselectivity was observed in the hydrogen-transfer reduction of prochiral ketones using the hybrid catalyst. It was attributed to a matrix effect of the chiral support since the whole network consisted in the assembly of chiral units. However, these materials were solids with low porosity. The latter may be attributed to the presence of flexible alkyl chains in the hybrid solids. The generation of porosity in hybrid materials was shown to be dependent not only on the reaction

---

* Corresponding author. Tel.: +33-467-147211; fax: +33-467-147212.

E-mail address: jmoreau@cit.enscm.fr (J.J.E. Moreau).

0022-328X/01/$ - see front matter

PII: S0022-328X(01)00758-6

conditions but also on the rigidity of the silylated precursor molecule [2,3,9]. We therefore studied the use of rigid chiral structures. Chiral hybrid materials with high porosity and surface area are of particular interest in the fields of molecular recognition, chromatography and heterogeneous catalysis.

Here, we report the convenient synthesis of several functional precursors derived from 2,2′-dihydroxy-1,1′-binaphthyl (BINOL) and the preparation of the corresponding hybrid solids by the sol–gel process. We chose the BINOL substructure as the chiral source because it is a rigid molecule with C_2 symmetry accessible in gram scale quantity [10]. Chiral BINOL and its derivatives give high degrees of asymmetric induction in various homogeneous enantioselective catalyzed reactions and are also widely used sources of chirality in enantioselective host–guest chemistry [11]. The synthesis of BINOL derivatives of diphosphonic acids was recently described [12], however, the preparation of hybrid organic-inorganic phosphonates from these precursors was not reported.

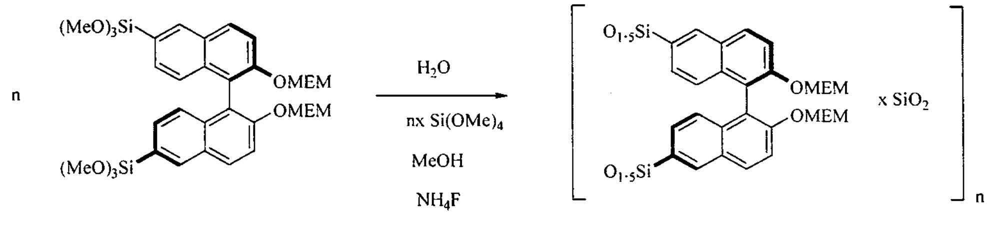
2. Results and discussion

2.1. Synthesis of the molecular precursors

The silylated precursor molecules **I**–**V** were synthesized in multistep reactions shown in Scheme 1.

In order to synthesize a rigid structure where the functional silicon atom are directly attached to the aromatic ring, we first prepared the (*R*)-(+)-2,2′-bis-(methoxyethoxymethyl)-6,6′-bis(trimethoxy-silyl)binaphthyl (*R*)-**I**.

R-(+)-BINOL was brominated in dichloromethane at − 78°C leading to the corresponding *R*-(−)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl [13]. The hydroxyl groups were then protected upon reaction with sodium hydride followed by the addition of methoxyethoxymethyl chloride (MEM-Cl) in THF [14]. The treatment of the formed 6,6′-dibromo-2,2′-di-MEM-1,1′-binaphthyl with two molar equivalents of *n*-BuLi then allowed metallation by lithium-bromide exchange at the 6,6′ positions [15]. It was followed by reaction of a three-fold excess of $ClSi(OMe)_3$ at − 78°C which afforded (*R*)-**I** in quantitative yield.



(1)

(R)-I

(R)-A: x = 0

(R)-A.5: x = 5

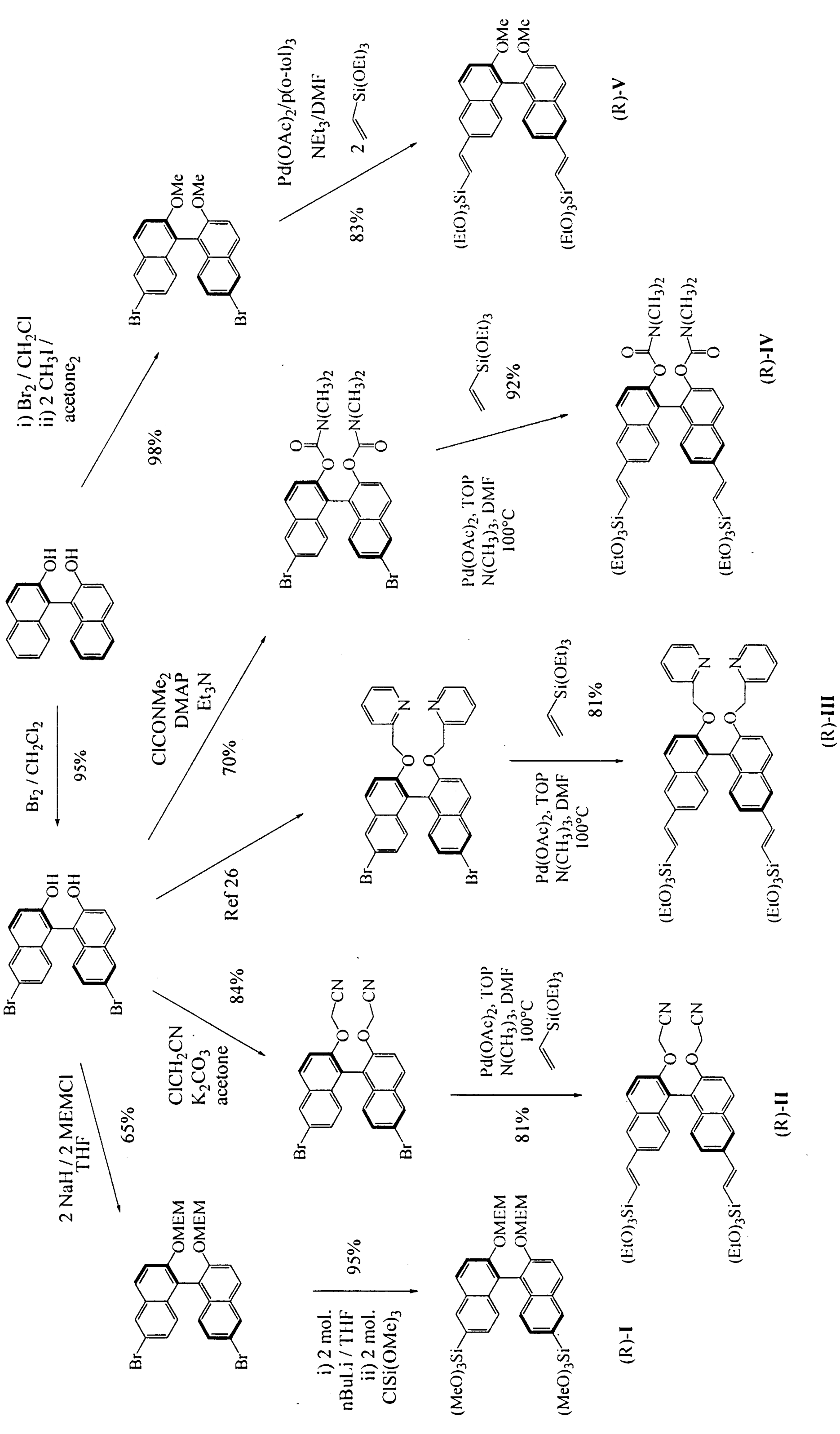
We also studied the introduction of a short rigid spacer between the functional silicon atom and the aromatic ring. As shown in Scheme 1, the 6,6′dibromo-BINOL was treated with chloro-acetonitrile to give a good yield of the corresponding cyanoether. The introduction of a functional silicon atom to the 6,6′ positions was achieved by a palladium-catalyzed Heck coupling reaction with vinyltriethoxysilane [16]. The reaction occurred easily in dimethylformamide at 95°C and led to (*R*)-**II** in good yields using 0.5 mol% of catalyst. This approach was extended to other (*R*)-BINOL derivatives. The molecular precursors (*R*)-**III** and (*R*)-**IV** were prepared under similar conditions starting from (*R*)-6,6′-dibromo-BINOL, which was first reacted with 2-picolylchloride [17] or dimethylcarbamylchloride [18]. These intermediates were silylated by Heck coupling with vinyltriethoxysilane to give the functional chiral molecules (*R*)-**III** and (*R*)-**IV,** respectively. Also the BINOL-derived precursor (*R*)-**V** was prepared in a similar way by methylation of (*R*)-BINOL [19], subsequent bromination and Heck coupling as above. The enantiomeric precursor (*S*)-**V** was prepared starting from (*S*)-BINOL. In all cases, the overall yield of the three-step synthesis was of 60–80%. The coupling reactions occurred with high selectivities since no side product was observed by NMR spectroscopy. While the starting material were crystalline solids, the trialkoxysilylated precursors are viscous liquids which turns into glassy solids at − 30°C and are highly soluble in ethanol, THF and chlorinated solvents.

2.2. Preparation of hybrid gels

2.2.1. Gels from (R)-I

The preparation of hybrid gels with (*R*)-**I** was performed in methanol using NH_4F as fluoride catalyst [20] with or without added tetramethoxysilane (TMOS) (Eq. (1)).

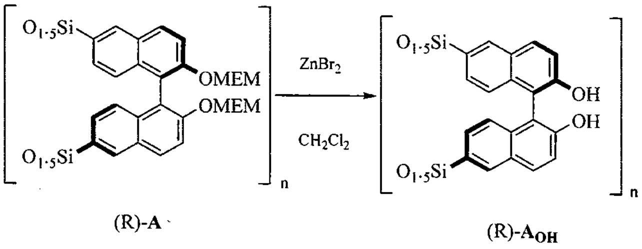
In the case of the gel (*R*)-**A** prepared without added TMOS, gelation occurred within 1 min whereas in the presence of 5 mole equivalents of TMOS, the gel (*R*)-**A.5** formed after 42 h. The materials were analyzed by



Scheme 1. Synthesis of silylated (*R*)-BINOL derivatives **I**–**V**.

solid state NMR using cross polarization-magic angle spinning (CP-MAS) technique [21] which allows the recording of high-resolution solid-state NMR spectra. The ^{13}C CP-MAS-NMR spectra of (*R*)-**A.5** (Fig. 1a) shows the presence of the organic moieties in the solid with chemical shifts at 120, 124, 130, 134, 152 (binaphthyl unit), 51 (residual methoxy group), 59, 69, 72 and 97 (MEM group) ppm. Similar observations have been made with the gel (*R*)-**A**. The environment of the silicon atoms can be detected by solid state ^{29}Si CP-MAS-NMR spectroscopy. This method allows the distinction between the silicon atoms bonded to three or four oxygen atoms and gives qualitative information about the degree of condensation (T^m and Q^n resonances, $m = 0$–3, $n = 0$–4). The ^{29}Si-NMR, in the case of (*R*)-**A**, exhibits a broad signal centered at -61.9 ppm (T [$RSiO_3$] units) indicating that no Si–C bond cleavage had occurred during the hydrolysis–condensation process (Fig. 1c). Gel (*R*)-**A.5** presents two sets of resonances: the first one, similarly to gel (*R*)-**A**, corresponds to the T units (centered at -66.8 ppm) and the second one (centered at -101.8 and -110.8 ppm) represents the Q^3 and Q^4 (SiO_4) substructures arising from the hydrolysis–condensation of TMOS (Fig. 1d). The surface properties of the two gels (*R*)-**A** and (*R*)-**A.5** were analyzed by nitrogen sorption experiments according to BET [22]. Despite the presence of a rigid aromatic bridging unit in the hybrid network, a poorly porous material was obtained. The materials had a low porosity and BET surface areas were 9 and 2.8 $m^2\,g^{-1}$, respectively.

We also studied the preparation of gels containing free aromatic OH subtituents. The attempted removal of the MEM group was made using zinc bromide [23] as reactant. Two pathways were actually considered to obtain solid materials with the free BINOL unit. Efforts to obtain the deprotection of the precursor (*R*)-**I** failed and resulted for every trial in the formation of an insoluble white powder. It probably arises from a condensation reaction of the liberated phenoxy group with methoxy substituent at silicon, leading to oligomerization of precursor (*R*)-**I**. We therefore attempted the deprotection of gel (*R*)-**A** in a solid–liquid reaction. It was successful after 4 days, upon treatment with $ZnBr_2$ at r.t., as a suspension in dichloromethane and led to gel (*R*)-$\mathbf{A_{OH}}$ (Eq. (2)).



(2)

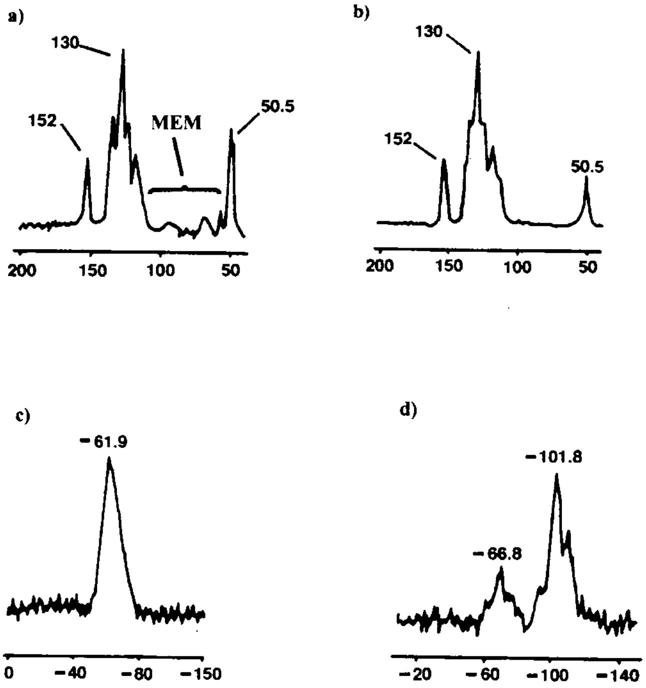
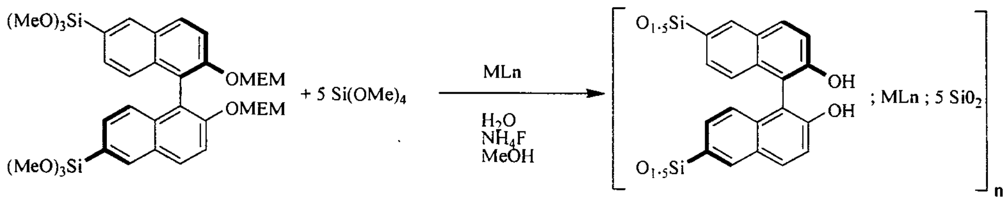


Fig. 1. Solid state CP-MAS-NMR spectra: (a) ^{13}C CP-MAS-NMR spectrum of Xerogel (*R*)-**A.5**; (b) ^{13}C CP-MAS-NMR spectrum of Xerogel (*R*)-A_{OH}; (c) ^{29}Si CP-MAS-NMR spectrum of Xerogel (*R*)-**A**; and (d) ^{29}Si CP-MAS-NMR spectrum of Xerogel (*R*)-**A.5**.

The analysis of the solid indicated a Si–C ratio of 1:11. The complete cleavage of the MEM group was monitored by ^{13}C solid state NMR (Fig. 1b) in which the signals at 58, 69, 72 and 97 (MEM group) ppm had disappeared. Only residual MeO groups are visible with a resonance line at 50 ppm. The ^{29}Si solid state NMR exhibits a unique broad signal centered at -68.3 ppm corresponding to T^3 [$RSi(OSi)_3$] unit. It indicates an enhanced condensation at silicon during the zinc bromide treatment of gel (*R*)-**A** and is consistent with the decrease of the residual methoxy group observed in the ^{13}C solid state NMR. The BET analysis of the obtained material showed a higher surface area (28 $m^2\,g^{-1}$) than the corresponding starting material (2.8 $m^2\,g^{-1}$).

Whereas a large excess of $ZnBr_2$ was necessary to cleave the MEM protecting group, we found that addition of catalytic amounts of transition metals salts (Ni, Pd) during sol–gel hydrolysis–condensation lead to solid formation together with removal of the MEM. The gels were prepared by hydrolysis–polycondensation of (*R*)-**I** with 5 mol% of metal salt in MeOH and in the presence of NH_4F as catalyst (Eq. (3)). Gelation occurred within 1 day. The wet gels were dried and the solids characterized. The gels recovered after the washing and drying were white whereas the filtrates showed coloration indicative of the presence of the corresponding metallic species in solution. This indicates that the metal was not retained in the solids. Elemental analysis gave metal–silicon ratios of 0.3–0.9‰ for the gels



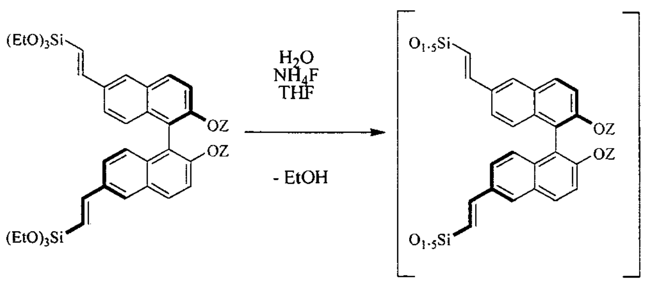
(3)

X: MLn = Ni(OAc)$_2$
Y: MLn = Pd(OAc)$_2$

containing Pd and Ni (expected value 0.7%). The very low amount of remaining metal confirmed the removal of the metal salts upon washing. Moreover, the ^{13}C CP-MAS solid state NMR of the gels exhibited the aromatic signals of the BINOL units but do not show signals of the MEM-group. It indicates that cleavage of the protecting group had occurred owing to the Lewis acid character, the metal salts probably catalyzed the removal of the MEM protecting group during the hydrolysis–condensation process.

2.2.2. Gels from (R)-II, (R)-III, (R)-IV and (R)-V

The hydrolysis–condensation of (*R*)-**II**–**V** using a stoichiometric amount of H_2O in the presence of NH_4F (1 mol%) led to the organic–inorganic hybrid material (*R*)-**B**–**E** (Eq. (4)).



(R)- **II**, Z = CH_2CN
(R)- **III**, Z = $CH_2C_5H_4N$
(R)- **IV**, Z = $CONMe_2$
(R)- **V**, Z = OMe

(R)- **B**, Z = CH_2CN
(R)- **C**, Z = $CH_2C_5H_4N$
(R)- **D**, Z = $CONMe_2$
(R)- **E**, Z = OMe

(4)

The preservation of the functional groups after the sol–gel process was confirmed by elemental analysis, solid state NMR and FTIR spectroscopy. The solid state ^{13}C CP-MAS-NMR spectra of (*R*)-**B**, (*R*)-**C**, (*R*)-**D** and (*R*)-**E** indicates the presence of aromatic and vinylic carbons (156, 149 ppm, broad signal in the range from 140 to 110 ppm). In the spectra of (*R*)-**B** and (*R*)-**C**, resonance lines of methylene groups are masked by the signals of residual ethoxy groups, whereas the spectrum of (*R*)-**D** shows a signal at 35 ppm attributed to the dimethylcarbamate groups. The ^{13}C-NMR spectrum of (*R*)-**E** also indicates the presence of aromatic and vinylic carbon and of methoxy groups (58 ppm). Two signals of low intensity at 18 and 56 ppm indicate the presence of residual ethoxysilyl groups in the solid.

The characterization by ^{29}Si CP-MAS-NMR spectroscopy showed only the signals of the T^2 [RSi(OR)(OSi)$_2$] and T^3 [RSi(OSi)$_3$]-bridged silicon nuclei, no T^1 unit being detected. The predominant environment for silicon atoms found in gel (*R*)-**B**–**E** corresponds to a T^3 [RSi(OSi)$_3$]-coordination. The complete absence of Q [SiO_4] resonances confirms that no Si–C cleavage occurred during the hydrolysis–condensation step.

Nitrogen sorption experiments with (*R*)-**B**, (*R*)-**C**, (*R*)-**D** and (*R*)-**E** indicate the formation of low porous materials with BET surface areas in the range of 0.3–6.9 $m^2\,g^{-1}$.

2.2.3. Optical properties of (R)-V and of gel (R)-E

Hybrid sol–gel incorporating organic fluorophores are of interest for the elaboration of electroluminescent devices [24]. Interestingly solutions of (*R*)-**II**–**V** showed intense blue fluorescence due to the extended π-electronic system [25]. We therefore studied the optical properties of the precursor molecule (*R*)-**V** and the corresponding gel (*R*)-**E**. In general, the absorption and emission spectra of hybrid materials incorporating covalently bound fluorescent dyes are significantly broadened and shifted toward longer wavelengths in comparison with the molecular dyes in solution [24,26]. UV–vis and fluorescence spectra of the precursor (*R*)-**V** and the gel (*R*)-**E** differ in the same way. Compared to the precursor (*R*)-**V**, the absorption spectra of the hybrid material (*R*)-**E** shows a shift of about 80 nm from 272/308 nm (precursor (*R*)-**V**) to a much broader absorption with a maximum at 356 nm (Fig. 2a). The photoluminescence of (*R*)-**E** also shows a bathochromic shift from 367/384 (**V**) to 439 nm, but is only slightly broadened (Fig. 2b). These effects can be attributed to interactions between the chromophores and the formation of dye aggregates within the hybrid amorphous material [24].

The silylated precursor molecules (*R*)-**II**, (*R*)-**III** and (*R*)-**IV** as well as the hybrid gels (*R*)-**B**, (*R*)-**C** and (*R*)-**D** show comparable luminescence properties. We are currently investigating the emission properties of related chiral polymeric structures.

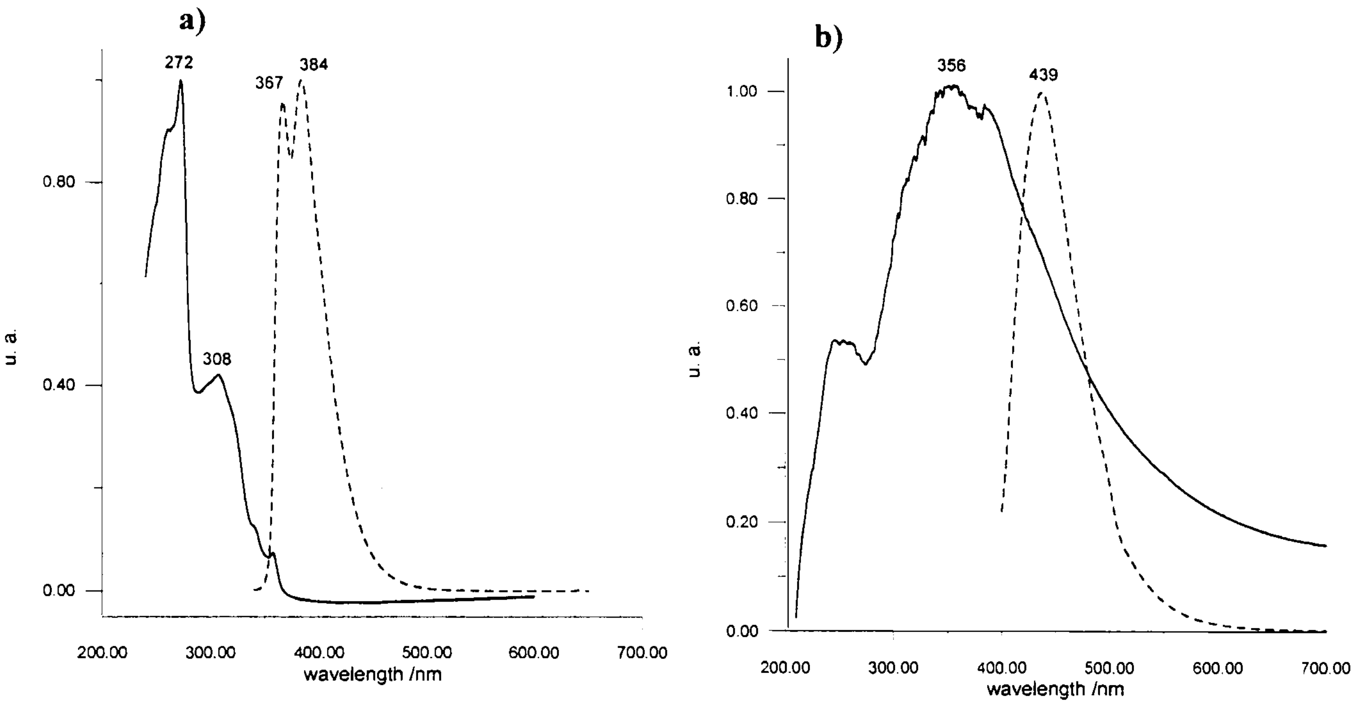


Fig. 2. UV–Vis (—) and fluorescence (- - -) spectra of precursor (*R*)-**II** (THF) (a) and of gel (*R*)-**B** (KBr pellet) (b).

3. Conclusions

In conclusion, we have synthesized five new chiral bis-trialkoxysilylated BINOL derivatives. Two different silylation reactions were employed: (1) coupling of a chlorosilane with a lithiated BINOL intermediate [(*R*)-**I**] and (2) Heck coupling reaction of brominated BINOL derivatives with vinyltriethoxysilane [(*R*)-**II**]–[(*R*)-**V**]. The Heck coupling reaction was found to be quite general as it tolerates many functional groups and offers a simple access to a variety of silylated BINOL precursors. The molecular precursors (*R*)-**I** to (*R*)-**V** were hydrolyzed by the sol–gel process to give the corresponding hybrid gels (*R*)-**A** to (*R*)-**E** incorporating functional chiral BINOL entities. We think that these chiral hybrid gels open new perspectives in the development of solid supports for heterogeneous asymmetric catalysis and molecular recognition. Furthermore, several precursors and hybrid gels show interesting optical properties which makes them potential candidates for the development of enantioselective fluorescent chemosensors [27]. We are currently investigating the emission properties of related chiral polymeric structures. All the prepared materials are of low porous solids. The synthesis of enantioselective supports for catalysis and separation techniques requires some further studies on the control of the porosity of the material and of the secondary structure of the hybrid network. The synthesis of a chiral three-dimensional network with controlled pore structure is under investigation.

4. Experimental

All reactions were performed under nitrogen or argon atmosphere using Schlenk tube techniques. ^{1}H-, ^{13}C- and ^{29}Si-NMR spectra in solution were recorded on Bruker AC-200 and AC-250 spectrometers. Deuterated chloroform was used as NMR solvent and chemical shifts are reported as δ-values in parts per million relative to tetramethylsilane. *J*-values are in Hz. Solid state ^{13}C and ^{29}Si CP-MAS-NMR spectra were recorded on a Bruker FT AM 200 and 400 apparatus. IR-spectra were determined with a Perkin–Elmer SPECTRUM 1000 FTIR spectrometer. Melting points were determined with an Electrothermal IA9000 SERIES apparatus. Mass spectra were measured on a JEOL MS-DX 300 mass spectrometer. Optical rotations were measured on a Perkin–Elmer polarimeter 241. Elemental analyses were carried out by the 'Service Central de Micro-Analyse du CNRS' at Vernaison (France). BET measurements were performed with a Micromeritics Gemini 2360. For SEM and TEM analyses LEICA *S* 360 type Cambridge and TEM 1200EX2 apparatus, respectively, were used. All solvents and reagents were obtained from commercial sources and used without purification, unless otherwise noted. In experiments requiring dry solvents, THF, toluene and diethyl ether were distilled from sodium-benzophenone, DMF was distilled from CaH_2, dichloromethane was distilled from P_2O_5 and alcohols were distilled from Mg.

The preparation of (*R*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl [13], (*R*)-2,2′-dimethoxy-1,1′-binaphthyl [19] and (*R*)-6,6′-dibromo-2,2′-di(2-picolyloxy)-1,1′-binaphthyl [17] were carried out as described in the literature. (*R*)-6,6′dibromo-2,2′-dimethoxy-1,1′-binaphthyl was prepared according to a reported method for the bromination of 2,2′-diethoxy-1,1′-binaphthyl [25].

*4.1. (R)-6,6′-Bis(trimethoxysilyl)-2,2′-di(methoxyethoxymethyloxy)-1,1′-binaphthyl [(R)-**I**]*

4.1.1. (R)-6,6′-Dibromo-2,2′-di(methoxyethoxy-methyloxy)-1,1′-binaphthyl

A solution of 6.7 g (15 mmol) of (*R*)-6,6′-dibromo-2,2′-dihydroxy-1,1′-binaphthyl in THF (60 ml) was added dropwise under nitrogen to a suspension of 1.3 g (52.5 mmol) of NaH (97%) in THF (20 ml) cooled to − 10°C, and placed in a three-neck flask equipped with a magnetic stirrer, a condenser and two addition funnels. Then, 4.5 g (34.5 mmol) of 2-methoxyethoxymethyl chloride was added dropwise. The reaction mixture was stirred during 3 h at − 10°C and 12 h at r.t. (r.t.). At this time, 60 ml of water was introduced. The phases were separated. The aqueous phase was extracted three times with CH_2Cl_2. The combined organic phases were dried ($MgSO_4$) and evaporation of the solvent under reduced pressure yielded a crude product which was recrystallized in ether to give white crystals of (*R*)-6,6′-dibromo-2,2′-di(methoxyethoxy-methyloxy)-1,1′-binaphthyl (6 g, 65%): m.p. 120.5–121°C. $[\alpha]_D^{25}$ + 18.5 (*c* 0.4, THF); ^{1}H-NMR ($CDCl_3$): $\delta = 3.29$ (s, 6H), 3.34–3.46 (m, 8H), 5.06 (d, $J = 7$ Hz, 2H), 5.19 (d, $J = 7$ Hz, 2H), 6.95 (d, $J = 9$ Hz, 2H), 7.27 (dd, $J = 9$ and 2 Hz, 2H), 7.63 (d, $J = 9$ Hz, 2H), 7.86 (d, $J = 9$ Hz, 2H), 8.03 (d, $J = 2$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): $\delta = 153.5$, 133.3, 130.9, 129.9, 129.7, 128.7, 127.2, 120.6, 118.2, 118.0, 94.1, 71.3, 67.6, 58.9 ppm; *m*/*e* MS FAB + /NBA 620 (M^+, 17.4), 89 ($CH_3OCH_2CH_2OCH_2^+$, 100). Anal. Found: C, 54.16; H, 4.87; Br, 25.85. Calc.for $C_{28}H_{28}O_6Br_2$: C, 54.21; H, 4.55; Br, 25.76%.

*4.1.2. (R)-6,6′-Bis(trimethoxysilyl)-2,2′-di(methoxyethoxymethyloxy)-1,1′-binaphthyl (R)-**I***

In a schlenk tube under inert atmosphere, 11.6 g (18.7 mmol) of (*R*)-6,6′-dibromo-2,2′-di(methoxyethoxymethyloxy)-1,1′-binaphthyl are solubilized in THF (95 ml). To this solution cooled to − 80°C, was added dropwise 16.1 ml of BuLi (2.5 M in hexane). The mixture was stirred at this temperature for 1 h and then added dropwise to a solution cooled to − 80°C of 11.7 g (74.8 mmol) of degassed chlorotrimethoxysilane in THF (60 ml). The reaction mixture was stirred for 30 min at − 80°C and then 2 h at r.t. After removal of the solvent under vacuo, the residue was extracted with toluene and filtered under nitrogen atmosphere. Evaporation of the solvent under reduced pressure yielded an orange viscous product which was dried under vacuum for 12 h. Attempts to purify the product by distillation, by crystallization and by chromatographic methods all failed and resulted in decomposition of the compound (13 g, 99%): ^{1}H-NMR ($CDCl_3$): $\delta = 3.27$ (s, 6H), 3.36–3.45 (m, 8H), 3.64 (s, 18H), 5.06 (d, $J = 7$ Hz, 2H), 5.18 (d, $J = 7$ Hz, 2H), 7.11 (d, $J = 9$ Hz, 2H), 7.40 (dd, $J = 9$ and 2 Hz, 2H), 7.63 (d, $J = 9$ Hz, 2H), 7.99 (d, $J = 9$ Hz, 2H), 8.22 (d, $J = 2$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): $\delta = 154.0$, 136.7, 135.5, 131.0, 130.5, 129.8, 126.7, 124.9, 121.6, 117.6, 94.5, 71.7, 67.8, 59.2, 51.3 ppm; ^{29}Si-NMR ($CDCl_3$): $\delta = -53.9$(s). Anal. Found: C, 57.56; H, 6.85; Si, 8.30. Calc. for $C_{34}H_{46}O_{12}Si_2$: C, 58.10; H, 6.60; Si, 7.99%.

*4.2. (R)-2,2′-Dicyanomethoxy-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl [(R)-**II**]*

4.2.1. (R)-6,6′-Dibromo-2,2′-dicyanomethoxy-1,1′-binaphthyl

A solution of 4.60 g (10.4 mmol) (*R*)-6,6′-dibromo-2,2′dihydroxy-1,1′-binaphthyl in 150 ml acetone was placed under argon at r.t. Potassium carbonate (5.73 g, 41.5 mmol) and chloroacetonitrile (2.6 ml, 3.1 g, 41 mmol) were added with stirring and the mixture was heated at reflux for 18 h. After cooling to r.t., water (100 ml) was added and the suspension was stirred at r.t. for 2 h. The volatiles were evaporated. The suspension was extracted with EtOAc. After drying over $MgSO_4$, the organic solvent was evaporated and the crude product was purified by column chromatography (silica gel, hexane–AcOEt 1:1) to give 4.54 g (84%) of the desired product: m.p. 188–191°C; ^{1}H-NMR ($CDCl_3$): $\delta = 4.68$ (s, 4H), 6.97 (d, $J = 9.1$ Hz, 2H), 7.38 (dd, $J = 2.0$, 9.0 Hz, 2H), 7.51 (d, $J = 9.2$ Hz, 2H), 8.00 (d, $J = 9.2$ Hz, 2H), 8.10 (d, $J = 1.9$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): $\delta = 54.7$, 115.1, 115.6, 119.2, 120.3, 127.0, 129.9, 130.4, 130.8, 131.4, 132.1, 152.0 ppm; FTIR (ν_{max}, cm^{-1}, KBr): 2927, 1584, 1495, 1276, 1217, 1073, 911, 812; *m*/*z* [FAB (+)] (%) 522 (14, M + 1); $[\alpha]_D^{25}$ − 46.3° (*c* 1.006, CH_2Cl_2). Anal. Found: C, 54.98; H, 3.00; N, 5.39. Calc. for $C_{24}H_{14}N_2O_2Br_2$: C, 55.20; H, 2.70; N, 5.36%.

*4.2.2. (R)-2,2′-Dicyanomethoxy-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl (R)-**II***

(*R*)-6,6′-Dibromo-2,2′-dicyanomethoxy-1,1′-binaphthyl (4.18 g, 8 mmol), palladium acetate (3.6 mg, 0.016 mmol) and $P(o\text{-}C_6H_4CH_3)_3$ (30.0 mg, 0.1 mmol) were placed in a two-necked flask under argon. Freshly distilled DMF (50 ml), Et_3N (6.7 ml, 49 mmol) and triethoxyvinylsilane (4.3 ml, 20.0 mmol) were added. The resulting solution was heated to 100°C. After 44 h at 100°C, the reaction mixture was allowed to cool to r.t. and filtered. The solvents were evaporated from the orange solution under gentle heating giving orange foam, which was extracted with diethyl ether. After filtration, solvents were again removed under reduced pressure. The resulting orange oil turned into a glassy solid at −30°C. Yield: 4.85 g (6.5 mmol, 81%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.26$ (t, $J = 6.8$ Hz, 18H), 3.87 (q, $J = 7.0$ Hz, 12H), 4.66 (s, 4H), 6.20 (d, $J = 19.3$ Hz, 2H), 7.08 (d, $J = 8.8$ Hz, 2H), 7.34 (d, $J = 19.$ 2 Hz, 2H), 7.46–7.52 (m, 4H), 7.90 (bs, 2H), 8.05 (d, $J = 8.9$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): $\delta = 18.3$, 54.8, 58.7, 115.2, 115.3, 118.5, 120.6, 124.8, 125.6, 127.7, 130.4, 131.0, 133.9, 134.5, 148.5, 152.3 ppm; FTIR (ν_{max}, cm^{-1}, KBr): 2975, 2887, 1673, 1574, 1479, 1276, 1208, 1166, 1074, 958, 807; m/z [FAB (+)] (%) 740 (19, M + 1), 79 (100); $[\alpha]_D^{25}$ −160.7° (c 1.005, CH_2Cl_2); UV–vis (λ_{max}, nm, $CHCl_3$) (log ε) = 270 (4.84). Anal. Found: C, 65.15; H, 6.25; N, 4.15. Calc. for $C_{40}H_{48}N_2O_8Si_2$: C, 64.84; H, 6.53, N, 3.78.

*4.3. (R)-2,2′-Di(2-picolyloxy)-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl [(R)-**III**]*

(R)-2,2′-Di(2-picolyloxy)-6,6′-di[(2-triethoxysilyl)-ethenyl]-1,1′binaphthyl [(R)-**III**] was synthesized following a similar procedure as described for the precursor (R)-**II** starting from (R)-6,6′-dibromo-2,2′-di(2-picolyloxy)-1,1′-binaphthyl (1.00 g, 1.6 mmol), palladium acetate (8.0 mg, 0.09 mmol) and P(o-$C_6H_4CH_3$)$_3$ (60 mg, 0.2 mmol), DMF (20 ml), Et_3N (2.0 ml, 14 mmol) and triethoxyvinylsilane (1.0 ml, 4.7 mmol). Yield: 1.10 g (1.3 mmol, 81%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.27$ (t, $J = 7.1$ Hz, 18H), 3.90 (q, $J = 7.0$ Hz, 12H), 5.21(s, 4H) 6.18 (d, $J = 19.2$ Hz, 2H), 6.73 (d, $J = 7.9$ Hz, 2H), 7.00–7.50 (m, 12H), 7.89 (bs, 2H), 7.97 (d, $J = 9.0$ Hz, 2H), 8.44 (dm, 2H); ^{13}C-NMR ($CDCl_3$): $\delta = 18.3$, 58.6, 71.4, 115.3, 117.1, 120.0, 120.7, 122.2, 123.9, 125.7, 127.8, 129.3, 130.1, 133.6, 134.3, 136.5, 148.7, 149.0, 154.2, 157.5 ppm; FTIR (ν_{max}, cm^{-1}, KBr): 2973, 2884, 1272, 1167, 1073, 961, 830, 807; m/z [FAB (+)] (%) 845 (25, M + 1), 93 (100, CH_2–C_5H_4N); $[\alpha]_D^{25}$ −80.1° (c 2.172, CH_2Cl_2); UV–vis (λ_{max}, nm, $CHCl_3$) (log ε) = 271 (4.95). Anal. Found: C, 68.13; H, 6.59; N, 3.47.Calc. for $C_{48}H_{56}N_2O_8Si_2$: C, 68.22; H, 6.68, N, 3.31%.

*4.4. (R)-2,2′-Bis-(dimethylcarbamoyloxy)-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl [(R)-**IV**]*

4.4.1. (R)-6,6′-Dibromo-2,2′-bis-(dimethylcarbamoyloxy)-1,1′-binaphthyl

(R)-6,6′-Dibromo-2,2′-dihydroxy-1,1′-binaphthyl (1.00 g/2.25 mmol) was dissolved in 10 ml of CH_2Cl_2. To the homogeneous solution were added 61 mg (0.5 mmol) of 4-dimethylaminopyridine (DMAP), 0.7 ml (5 mmol) of Et_3N and finally 1.0 ml (11 mmol) of dimethylcarbamylchloride. After stirring at r.t. for 2 h, the reaction mixture was heated under reflux during 4 h. After cooling to r.t., the solvents were pumped off. The crude product was dissolved in CH_2Cl_2. After aqueous work-up, and evaporation of the solvent, the product was purified by column chromatography (silica gel, CH_2Cl_2) to give 920 mg (70%) of the desired product. ^{1}H-NMR ($CDCl_3$): $\delta = 2.28$ (s, 6H), 2.69 (s, 6H), 7.09 (d, $J = 9.1$ Hz, 2H), 7.35 (dd, $J = 1.9$, 9.0 Hz, 2H), 7.58 (d, $J = 8.9$ Hz, 2H), 7.87 (d, $J = 9.0$ Hz, 2H) 8.10 (bs, 2H); ^{13}C-NMR ($CDCl_3$): $\delta = 35.7$, 36.4, 119.5, 123.4, 123.8, 127.7, 127.9, 128.2, 129.9, 131.8, 132.2, 147.8, 153.8 ppm; FTIR (ν_{max}, cm^{-1}, KBr): 2929, 1728, 1586, 1489, 1390, 1229, 1162; m/z [FAB (+)] (%) 587 (15, M + 1), 72 (100); $[\alpha]_D^{25}$ +3.5° (c 1.032, CH_2Cl_2).

*4.4.2. (R)-2,2′-Bis-(dimethylcarbamoyloxy)-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl (R)-**IV***

(R)-2,2′-Bis-(dimethylcarbamoyloxy)-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl (R)-**IV** was synthesized following a similar procedure as described for the precursor (R)-**II** starting from 586.3 mg (1 mmol) of (R)-6,6′-dibromo-2,2′-bis-(dimethylcarbamoyloxy)-1,1′-binaphthyl, 2.2 mg (0.01 mmol) of palladium acetate, 18 mg (0.06 mmol) of P(o-$C_6H_4CH_3$)$_3$, 0.83 ml (6 mmol) of Et_3N, 0.57 g (3 mmol) of vinyltriethoxysilane and 5 ml of DMF. The desired product was obtained as a yellow oil. Yield: 0.70 g (92%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.27$ (t, $J = 7.0$ Hz, 18H), 2.25 (s, 6H), 2.68 (s, 6H), 3.89 (q, $J = 7.0$ Hz, 12H), 6.23 (d, $J = 19.2$ Hz, 2H,), 7.23 (d, $J = 9.0$ Hz, 2H), 7.35 (d, $J = 19.3$ Hz, 2H), 7.50(dd, $J = 1.5$, 8.9 Hz, 2H), 7.58 (d, $J = 8.9$ Hz, 2H), 7.90 (bs, 2H), 7.96 (d, $J = 9.0$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): $\delta = 18.3$, 35.7, 36.4, 58.7, 118.2, 123.0, 123.6, 123.9, 126.3, 127.5, 129.4, 131.2, 133.5, 134.6, 147.9, 148.8, 154.0 ppm; FTIR (ν_{max}, cm^{-1}, KBr): 2974, 2926, 2886, 1732, 1389, 1229, 1165, 1077, 960, 831, 806, 779; m/z [FAB (+)] (%) 805 (10, M + 1), 72 (100, OC–N(CH_3)$_2$); $[\alpha]_D^{25}$ −116.7° (c 0.979, CH_2Cl_2); (λ_{max}, nm) (log ε) 266 (4.89). Anal. Found: C, 62.58; H, 6.98; N, 3.68. Calc. for $C_{42}H_{56}N_2O_{10}Si_2$: C, 62.66; H, 7.01, N, 3.48%.

*4.5. (R)-2,2′-Dimethoxy-6,6′-di[(2-triethoxysilyl)-ethenyl]-1,1′binaphthyl [(R)-**V**]*

(R)-2,2′-Dimethoxy-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl [(R)-**V**] was synthesized following a similar procedure as described for the precursor (R)-**II** starting from (R)-6,6′dibromo-2,2′-dimethoxy-1,1′-binaphthyl (4.72 g, 10 mmol), palladium acetate (5.0 mg, 0.022 mmol), P(o-$C_6H_4CH_3$)$_3$ (40.8 mg, 0.134 mmol), DMF (50 ml), Et_3N (8.4 ml, 60 mmol) and triethoxyvinylsilane (4.8 ml, 22.7 mmol). The desired product was obtained as a yellow oil. Yield: 5.86 g (8.5 mmol, 85%). ^{1}H-NMR ($CDCl_3$): $\delta = 1.27$ (t, $J = 7.0$

Hz, 18H), 3.77 (s, 6H), 3.89 (q, $J = 7.0$ Hz, 12H,), 6.16 (d, $J = 19.4$ Hz, 2H), 7.07 (d, $J = 8.8$ Hz, 2H), 7.36 (d, $J = 19.4$ Hz, 2H), 7.41–7.47 (m, 4H), 7.87 (bs, 2H), 7.97 (d, $J = 9.0$ Hz, 2H); ^{13}C-NMR ($CDCl_3$): $\delta = 18.1$, 56.4, 58.4, 114.1, 116.4, 119.2, 123.5, 125.3, 127.8, 128.8, 129.8, 132.7, 134.0, 149.0, 155.3; ^{29}Si-NMR ($CDCl_3$):$\delta = -55.9$ (s); FTIR (ν_{max}, cm^{-1}, KBr): 2973, 2884, 1582, 1481, 1268, 1167, 1075, 958, 830, 807, 776; m/z [FAB (+)] (%) 691 (35, M+1), 79 (100); $[\alpha]_D^{25}$ $-138.1°$ (c 1.005, CH_2Cl_2); UV–vis (λ_{max}, nm, $CHCl_3$) = 267 (4.85). Anal. Found: C, 66.24; H, 6.95. Calc. for $C_{38}H_{50}O_8Si_2$: C, 66.05; H, 7.29%.

4.5.1. *(S)-2,2′-Dimethoxy-6,6′-di[(2-triethoxysilyl)-ethenyl]-1,1′binaphthyl (S)-**V***

By the same synthetic procedure, (*S*)-(+)-2,2′-dimethoxy-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl was obtained starting with (*S*)-2,2′dihydroxy-1,1′-binaphthyl. All intermediates show the same physical and spectroscopical properties as the (*R*)-enantiomers with the exception of their optical rotation: (*S*)-(+)-2,2′-dimethoxy-6,6′-di[(2-triethoxysilyl)ethenyl]-1,1′binaphthyl: $[\alpha]_D^{25}$ $+137.5°$ (c 1.013, CH_2Cl_2). Hydrolysis and polycondensation of (*R*)-**I**.

To a solution of 2 g (2.87 mmol) of (*R*)-**I** in 3 ml of methanol were added 3 mg of NH_4F and 157 µl of water. After 1 min of reaction, an opaque gel was formed. Then, the gel obtained was allowed to stand for 48 h. After this time, the solid was powdered, washed with ether and dried under vacuum for 24 h yielding 1 g of a beige powder (60% yield based on $C_{28}H_{28}0_9Si_2$). FTIR (ν_{max}, cm^{-1}, KBr): 3434 ($\nu_{Si–OH}$), 2923 ($\nu_{C–H}$), 1090 ($\nu_{Si–O–Si}$) cm^{-1}; ^{13}C CP-MAS-NMR: $\delta = 152.5$, 134.4, 129.9, 123.5, 120.0, 96.6, 72.0, 68.8, 58.7, 50.5 ppm; ^{29}Si CP-MAS-NMR: δ centered at -61.9 ppm; N_2 BET surface area 9 m^2 g^{-1}.

4.5.2. *Hydrolysis and polycondensation of (R)-**I** with five equivalents of TMOS*

To 2.9 g (4.13 mmol) of (*R*)-**I** and 3.14 g (20.65 mmol) of TMOS in 29 ml of MeOH were added 0.966 ml of water and 29 µl of NH_4F 1 M. The homogeneous solution was allowed to stand at 25°C. An opaque gel was formed within 42 h. After an ageing of one week, the solid was powdered, washed with ether and then dried in vacuum at r.t. yielding 3.1 g of a beige powder (87% yield based on $C_{28}H_{28}0_{19}Si_7$). FTIR (ν_{max}, cm^{-1}, KBr): 3444 ($\nu_{Si–OH}$), 2923 ($\nu_{C–H}$), 1068 ($\nu_{Si–O–Si}$) cm^{-1}; ^{13}C CP-MAS-NMR: $\delta =$ 153.1, 144.7, 134.9, 129.0, 124.6, 118.0, 95.7, 69.7, 57.8, 50.5 ppm; ^{29}Si CP-MAS-NMR: $\delta = -66.8$, -101.8, -110.8; N_2 BET surface area 2.8 m^2 g^{-1}. Anal. Found: C, 32.68; H, 2.87; Si, 3.9.

4.6. *Procedure for cleavage of the O–MEM bond in the silica gels formed with (R)-**I***

5.65 g (25 mmol) of zinc dibromide dried under vacuum for 16 h at 110°C were introduced under nitrogen atmosphere in a Schlenk tube containing 1.3 g (2.3 mmol) of the gel (*R*)-**A.5**. After addition of 30 ml of CH_2Cl_2, the heterogeneous reaction mixture was stirred at r.t. for 4 days. After centrifugation and removal of CH_2Cl_2, the solid was washed with a soxhlet apparatus in ethanol for 24 h. Then, the deprotected material was dried under vacuum for 24 h to yield 0.78 g of solid (87%). ^{13}C CP-MAS-NMR: $\delta = 153.8$, 135.3, 128.8, 113.8 ppm; ^{29}Si CP-MAS-NMR: δ centered at -68.3 ppm; N_2 BET surface area 28 m^2 g^{-1}. Anal. Found: C, 56.00; H, 4.26; Si, 11.1.

4.7. *General procedure for hydrolysis and polycondensation of (R)-**I** with five equivalents of TMOS and 5 mol% of metal salts*

1.21 g (1.73 mmol) of (*R*)-**I** and 5 mol% of nickel acetate or palladium acetate were dissolved in 2 ml of MeOH. The mixture was stirred for 30 min. A solution of 1.31 g (8.64 mmol) of TMS with 12 µl of NH_4F 1 M, 405 µl of water and 2 ml of methanol was then added. Gelation occurred in 18 h for nickel and palladium salts. After ageing for 3 days, the gels were powdered, washed with diethylether and then dried in vacuum at r.t. Anal. Found: Cogel/ Pd: C, 37.7; H, 3.6; Si, 24.75, Pd, 0.03. Cogel/ Ni: C, 37.1; H, 4.14; Si, 30.55, Ni, 0.06. ^{13}C CP-MAS-NMR (similar for both gels) $\delta = 153.2$, 135.1, 128.6, 124.4, 118.2, 50.4 ppm. ^{29}Si CP-MAS-NMR (similar for both gels) $\delta = -69.2$, -76.4, -101.2; N_2 BET surface area, 9 m^2 g^{-1} for cogel Pd, 10 m^2 g^{-1} for cogel Ni.

4.8. *General procedure for the preparation of gels (R)-**B**, **C**, **D**, **E***

The preparation of (*R*)-**E** is given as our example: 4.90 g (7.1 mmol) of (*R*)-**V** were dissolved in 4 ml of THF. A solution of 0.014 mmol NH_4F (1 M) and 0.268 ml of water in 3.1 ml of THF was added with stirring. Gelification of the mixture occurred after 4 h. The mixture was allowed to stand for further 4 days. After this time, the solid was powdered, washed with acetone, extracted by THF for 24 h in a soxhlet apparatus and finally dried under vacuum at 111°C for 12 h to give 4.22 g of (*R*)-**E** as a yellow powder. Anal. Found: $C_{25.9}H_{22.8}0_{6.24}Si_2$: C, 63.49; H, 4.68; Si, 11.45. Calc. for complete condensation $C_{26}H_{20}0_5Si_2$: C, 66.65; H, 4.30; Si, 11.98. ^{29}Si CP-MAS-NMR: δ center at -80.5 ppm; ^{13}C CP-MAS-NMR $\delta = 156$, 149, 140–110, 58; N_2 BET surface area 6.7 m^2 g^{-1}.

The gels (*R*)-**B**, (*R*)-**C** and (*R*)-**D** were prepared in a similar way. The exact quantities of the used reagents and yield are listed below:

Xerogel	Precursor/ mg (mmol)	H_2O (μl)	NH_4F (1 M) (μl)	Yield (mg)	BET surface area ($m^2\,g^{-1}$)
(*R*)-**B**	(*R*)-**II**/730 (0.98)	51	2	586	0.3
(*R*)-**C**	(*R*)-**III**/480 (0.56)	22	11	337	6.9
(*R*)-**D**	(*R*)-**IV**/720 (0.95)	36	19	453	4.3

Spectroscopic and analytical data of the gels:

(*R*)-**B**: FTIR (ν_{max}, cm^{-1}, KBr): 3449, 2973, 2220, 1573, 1277, 1214, 1066; ^{13}C CP-MAS-NMR: $\delta = 152.5$, 149.0, 134.0, 130.3, 125.8, 120.1, 58.8, 17.8 ppm.

(*R*)-**C**: FTIR (ν_{max}, cm^{-1}, KBr): 3441, 1596, 1276, 1102; ^{13}C CP-MAS-NMR: 154.3, 147.2, 133.4, 128.8, 121.6 ppm.

(*R*)-**D**: FTIR (ν_{max}, cm^{-1}, KBr): 3435, 2927, 1729, 1391, 1229, 1165, 1073; ^{13}C CP-MAS-NMR: $\delta = 153.7$, 148.3, 133.8, 131.1, 124.0, 58.9, 35.4, 17.7 ppm; ^{29}Si CP-MAS-NMR: δ center at -68.8 ppm.

References

[1] (a) C. Sanchez, F. Ribot, New J. Chem. 18 (1994) 989. (b) R.M. Laine, C. Sanchez, C.J. Brinker, E. Giannelis (Eds.), Organic/Inorganic Hybrid Materials, MRS Symposium, vol. 519, 1998. (c) L. Klein, M. DeGuire, F. Lorraine, J. Mark (Eds.), Organic/Inorganic Hybrid Materials II, MRS Symposium, vol. 576, 1999. (d) R.M. Laine, C. Sanchez, C.J. Brinker (Eds.), Organic/Inorganic Hybrid Materials III, MRS Symposium, vol. 628, 2000.

[2] (a) K.J. Shea, D.A. Loy, O.W. Webster, J. Am. Chem. Soc. 114 (1992) 6700. (b) D.A. Loy, K.J. Shea, Chem. Rev. 95 (1995) 1431 (and references therein).

[3] (a) R.J.P. Corriu, J.J.E. Moreau, P. Thépot, M. Wong Chi Man, Chem. Mater. 4 (1992) 1217; Chem. Mater. 8 (1996) 100. (b) R.J.P. Corriu, D. Leclercq, Angew. Chem. Int. Ed. Engl. 35 (1996) 1420 (and references therein).

[4] (a) U. Schubert, New J. Chem. 18 (1994) 1049. (b) U. Schubert, N. Hüsing, A. Lorenz, Chem. Mater. 7 (1995) 2012.

[5] J.J.E. Moreau, M. Wong Chi Man, Coord. Chem. Rev. 178–180 (1998) 1073.

[6] (a) Y. Shvo, Y. Becker, M. Gal, Chem. Commun. (1994) 2719. (b) D. Shabat, F. Grynszpan, S. Saphier, A. Turniansky, D. Avnir, E. Keinan, Chem. Mater. 9 (1997) 2258. (c) F. Gelman, D. Avnir, H. Schumann, J. Mol. Catal. A Chem. 146 (1999) 123.

[7] (a) A. Adima, J.J.E. Moreau, M. Wong Chi Man, J. Mater. Chem. 7 (1997) 2331. (b) P. Hesemann, J.J.E. Moreau, Tetrahedron: Asymmetry 11 (2000) 2183. (c) A. Adima, J.J.E. Moreau, M. Wong Chi Man, Chirality 12 (2000) 411.

[8] J.J.E. Moreau, L. Vellutini, M. Wong Chi Man, C. Bied, J. Am. Chem. Soc. 123 (2001) 1509.

[9] R.J.P. Corriu, Angew. Chem. Int. Ed. Engl. 39 (2000) 1376 (and references therein).

[10] J.K. Whitesell, Chem. Rev. 89 (1989) 1581.

[11] A.P. Marchand, H.-S. Chong, B. Ganguly, Tetrahedron: Asymmetry 10 (1999) 4695 (and references therein).

[12] P.A. Jaffrès, N. Bar, D. Villemin, J. Chem. Soc. Perkin Trans. 1 (1998) 2083.

[13] G.D.Y. Sogah, D.J. Cram, J. Am. Chem. Soc. 101 (1979) 3035.

[14] B.J. Brisdon, R. England, K. Reza, M. Sainsbury, Tetrahedron 49 (1993) 1103.

[15] Y. Nakamura, S. Takeuchi, Y. Ohgo, D.P. Curran, Tetrahedron Lett. 41 (2000) 57. (b) Y. Nakamura, S. Takeuchi, Y. Ohgo, D.P. Curran, Tetrahedron 56 (2000) 351.

[16] (a) R.F. Heck, Org. React. 27 (1982) 345. (b) H. Yamashita, B.L. Roan, M. Tanaka, Chem. Lett. 12 (1990) 2175. (c) D. Brondani, PhD thesis, Université de Montpellier II, France, 1995.

[17] Q.-S. Hu, W.-S. Huang, D. Vitharana, X.-F. Zheng, L. Pu, J. Am. Chem. Soc. 119 (1997) 12454.

[18] M.R. Dennis, S. Woodward, J. Chem. Soc. Perkin Trans. 1 (1998) 1081.

[19] D.S. Lingenfelter, R.C. Helgeson, D.J. Cram, J. Org. Chem. 46 (1981) 393.

[20] R.J.P. Corriu, D. Leclercq, A. Vioux, M. Pauthe, J. Phalippou, in: J.D. Mackenzie, D.R. Ulrich (Eds.), Ultrastructure Processing of Advanced Materials, Wiley, New York, 1988.

[21] M. Mehring, High Resolution-NMR Spectroscopy in Solids, Springer, Berlin, 1976.

[22] S. Brunauer, P.H. Emmett, E. Teller, J. Am. Chem. Soc. 60 (1938) 309.

[23] E.J. Corey, J.-L. Givas, P. Ulrich, Tetrahedron Lett. 11 (1976) 809.

[24] M. Schneider, J. Hagen, D. Haarer, K. Müllen, Adv. Mater. 12 (2000) 351 (and references therein).

[25] H.J. Deussen, E. Hendrickx, C. Boutton, D. Krog, K. Clays, K. Bechgaard, A. Persoons, T. Bjornholm, J. Am. Chem. Soc. 118 (1996) 6841.

[26] R.J.P. Corriu, P. Hesemann, G.F. Lanneau, Chem. Commun. (1996) 1845.

[27] D. Wang, T.-J. Liu, W.-C. Zhang, W.T. Slaven IV, C.-J. Li, Chem. Commun. (1998) 1747.