

Silica Hybrid Containing (*R*)-2, 2'-Binaphtho-20-crown-6 Moieties via the Sol-Gel Process

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(*R*)-6,6'-Bis(triethoxysilylethen-2-yl)-2,2'-binaphtho-20-crown-6 (precursor, *R*-2) derived from (*R*)-2,2'-BINOL derivative was synthesized by Pd-catalyzed Heck reaction of (*R*)-6,6'-dibromo-2,2'-binaphtho-20-crown-6 (*R*-1) intermediate with vinyltriethoxysilane. The hydrolysis and polycondensation of the precursor gave rise to the corresponding xerogel. Both precursor and xerogel were analysed by NMR, FT-IR, UV, CD spectra, fluorescent spectroscopy, polarimetry and elemental analysis. The precursor and xerogel can emit strong blue fluorescence and are expected to have the potential application in the separation of chiral molecules as fluorescent sensor. The precursor exhibits strong Cotton effect in its circular dichroism (CD) spectrum indicating that it is a highly rigid structure.

Keywords (*R*)-2,2'-BINOL, organic silicon, sol-gel, Heck reaction

Introduction

The sol-gel process constitutes one of the most important route for the preparation of inorganic amorphous solids.^{1,2} The mild reaction conditions of the sol-gel approach allow a deliberate tailoring of hybrid organic-inorganic materials by hydrolysis and polycondensation of molecular precursors functionalized by hydrolysable triethoxysilane groups.³ Such silica hybrid materials consisting of covalently linked organic and inorganic components are well defined at the molecular level. They have received considerable attention in different research areas, as they combine both the properties of the organic moieties (optical, electrical and electrochemical) and the inorganic framework (porosity and hydrophilicity).^{4,5} The preparation of a molecularly defined hybrid network bearing alternating chiral centers and siloxane units was achieved by sol-gel hydrolysis of suitable precursors containing one non-hydrolyzable silicon-carbon bond. The hybrid materials can lead to the properties of electro-optical sensors, asymmetric catalysis, enantioselective and molecular recognition by controlling the chiral organic substructure and inorganic framework at the well-defined molecular level.^{2,6,7} BINOL-derived chiral crown ethers have been recognized as efficient selectors for the separation of chiral

amines or α -aminoacides in chiral HPLC, useful chiral ligands in asymmetric catalysis and highly selective chiral luminescent sensors.⁸⁻¹²

The immobilization of chiral crown ethers in silica matrices may allow the facile access to reusable heterogeneous catalysts or sensors. The design and characterization of novel sol-gel systems are of great economical and ecological interest and may allow the development of new industrial processes. The current interest of our work in hybrid silica-based materials is to use sol-gel process for the preparation of new functional materials by design: organic-inorganic hybrids are solids with tunable properties, which may allow to tailor catalytic or separation properties. The aim of our research is the elaboration of functional materials based on chiral building blocks for asymmetric catalysis and molecular recognition. In our study precursor, *i. e.*, (*R*)-6,6'-bis(triethoxysilylethen-2-yl)-2,2'-binaphtho-20-crown-6 (*R*-2), derived from BINOL derivative was synthesized by Pd-catalyzed Heck reaction of (*R*)-6,6'-dibromo-2,2'-binaphtho-20-crown-6 (*R*-1) intermediate with vinyltriethoxysilane. The hydrolysis and polycondensation of the precursor gave rise to the corresponding organic-inorganic hybrid xerogel by sol-gel transformation of precursor (*R*)-6,6'-bis(triethoxysilylethen-2-yl)-2,2'-binaphtho-20-crown-6 (*R*-2).

Experimental

Instruments and reagents

All reactions were performed under nitrogen or argon atmosphere using Schlenk tube techniques. ¹H NMR, ¹³C NMR and ²⁹Si NMR spectra in solution were recorded on a Bruker AC-200 and a AC-250 spectrometers. Deuterated chloroform was used as NMR solvent, chemical shifts were reported as δ values relative to tetramethylsilane, and *J* values are in Hz. Xerogel ²⁹Si NMR was recorded on a Bruker WP 250 FT AM 300 apparatus. IR spectra were determined with a Perkin-Elmer SPECTRUM 1000 FT-IR spectrometer. Optical rotations were measured on a Perkin-

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Elmer polarimeter 241. Fluorescent spectra were determined on a Model 8100 spectrometer. Circular dichroism (CD) spectra were carried on a JASCO J-810 spectropolarimeter. Elemental analyses were carried out by the "Service Central de Micro-Analyse du CNRS" at Vernaison (France). (*R*)-1, 1'-Di-2-naphthol (BINOL) was purchased from Aldrich and directly used without purification. In experiments requiring dry solvents, THF and diethyl ether were distilled from sodium-benzophenone, DMF was distilled from CaH₂, and CH₂Cl₂ was distilled from P₂O₅.

Preparation of precursor

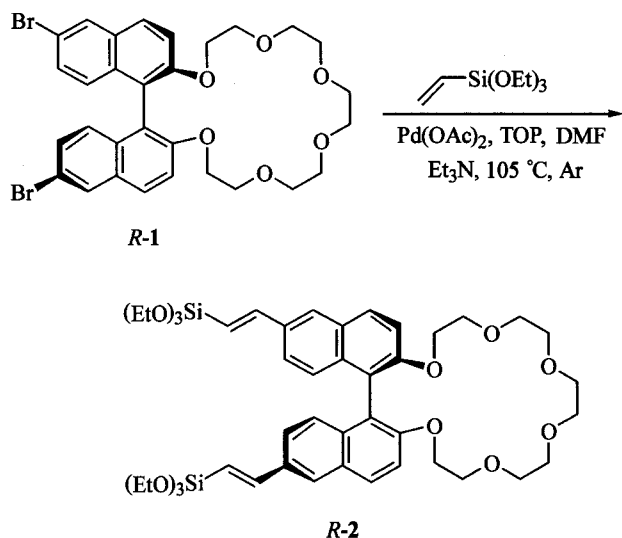
Pentaethyleneglycolditosylate [Ts (OCH₂CH₂)₅OTs] and *R*-1 were synthesized according to literature.^{8,13}

[Ts (OCH₂CH₂)₅OTs] ¹H NMR (CDCl₃) δ: 2.43 (s, 6H), 3.56 (s, 8H), 3.58 (s, 4H), 3.66 (t, *J* = 4.6 Hz, 4H), 4.14 (t, *J* = 5.0 Hz, 4H), 7.32 (d, *J* = 7.8 Hz, 4H), 7.77 (d, *J* = 8.2 Hz, 4H); ¹³C NMR (CDCl₃) δ: 21.65, 68.66, 69.28, 70.49, 70.58, 70.73, 127.97, 129.85, 132.52, 144.91.

R-1 $[\alpha]_D^{25} + 22.6$ (c 0.34, CH₂Cl₂); ¹H NMR (CDCl₃) δ: 3.39 (t, *J* = 4.0 Hz, 4H), 3.43–3.67 (m, 8H), 3.97–4.07 (m, 4H), 4.14–4.25 (m, 4H), 6.96 (d, *J* = 9.0 Hz, 2H), 7.25 (dd, *J* = 9.0, 2.5 Hz, 2H), 7.47 (d, *J* = 9.0 Hz, 2H), 7.82 (d, *J* = 9.2 Hz, 2H), 7.99 (d, *J* = 1.9 Hz, 2H); ¹³C NMR (CDCl₃) δ: 69.75, 69.79, 70.49, 70.65, 70.87, 116.89, 117.51, 120.01, 127.11, 128.56, 129.65, 129.82, 130.41, 132.47, 154.77; IR (KBr) ν: 2869.6, 1584.6, 1493.5, 1326.2, 1269.8, 1069.8, 876.0, 809.1 cm⁻¹; HRMS *m/z* (%): 646 (M⁺ - 1, 16), 39 (100).

Synthesis of *R*-2 was shown in Scheme 1.

Scheme 1 Synthesis of *R*-2



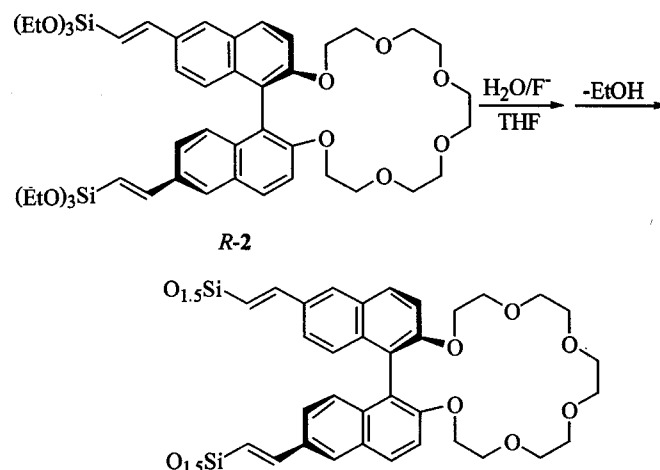
R-1 (647 mg, 1 mmol), 0.4% Pd(OAc)₂ (1.1 mg), 2.4% P(OC₆H₄CH₃)₃ (TOP) (7.3 mg) and 5

equivalents of Et₃N (0.85 mL) were dissolved in 15 mL of freshly distilled DMF, followed by the addition of vinyltriethoxysilane (0.45 mL, 2.0 mmol) via a syringe. After stirring and heating at 105 °C overnight under Ar and at 115 °C for 2 h, the mixture was cooled down to room temperature. After filtration of the resulting triethylammonium salt and catalyst, the solvent was removed under reduced pressure with an oil heating bath at 100 °C. 20 mL of ether was added to the viscous residue under Ar to precipitate out a large amount white triethylammonium salt. After filtration, the solution was evaporated under reduced pressure under Ar. The yellow viscous product *R*-2 was dried *in vacuo* overnight under 80 °C oil bath. The final yield is 95% (821 mg). The precursor shows a moderate to good solubility in ethanol, ether, THF, CH₂Cl₂ and CHCl₃. $[\alpha]_D^{25} - 104.7$ (c 0.75, CH₂Cl₂); ¹H NMR (CDCl₃) δ: 1.27 (t, *J* = 7.0 Hz, 18H), 3.39–3.65 (m, 12H), 3.80 (q, *J* = 8.0 Hz, 12H), 3.90–4.06 (m, 4H), 4.15–4.25 (m, 4H), 6.16 (d, *J* = 19.2 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 10.0 Hz, 2H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.85 (s, 2H), 7.93 (d, *J* = 8.8 Hz, 2H); ¹³C NMR (CDCl₃) δ: 18.29, 58.59, 69.75, 70.61, 70.67, 70.87, 116.17, 116.80, 120.36, 123.65, 125.71, 127.72, 129.23, 129.76, 133.04, 134.72, 149.17, 155.05; ²⁹Si NMR δ: -55.77; IR (KBr) ν: 2973.1, 1583.8, 1479.5, 1274.8, 1075.7, 958.1, 807.5 cm⁻¹. Anal. calcd for C₄₆H₆₄O₁₂Si₂: C 63.95, H 7.52; found C 63.86, H 7.46.

Preparation of xerogel

The hydrolysis/polycondensation of the precursors was shown in Scheme 2. The preparation of hybrid gel was performed in THF using NH₄F as fluoride catalyst. *R*-2 (865 mg, 1 mmol) was dissolved in 2 mL of THF, and then 54 μL of H₂O and 13 μL of saturated NH₄F solution were dropped into the above solution, respectively. The solution

Scheme 2 Sol-gel process of xerogel



was vigorously stirred at room temperature until sol formation. The sol was allowed to stand for one week and gave rise to yellow solid xerogel. The xerogel was scattered to get a powder, which was washed with THF and ether for several times. The xerogel was dried overnight *in vacuo*. The final product was obtained in 85% yield (464 mg). ^{29}Si NMR (solid) δ : -69.3, -71.6, -76.9; IR (KBr) ν : 2851.7, 1578.2, 1474.2, 1271.4, 1088.7, 800.0 cm^{-1} . Anal. calcd for $\text{C}_{34}\text{H}_{34}\text{O}_9\text{Si}_2$: C 61.90, H 5.61; found C 63.55, H 5.33.

Results and discussion

UV spectrum of precursor *R-2* was determined in THF solution, strongest absorption was observed at 272 nm ($\epsilon_{272} = 8.23 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), and the largest absorption λ_{max} appeared at 307 nm ($\epsilon_{307} = 3.79 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). By comparing the UV absorption wavelengths of the precursor *R-2* with *R-1*, in which the strongest peak observed is 238 nm ($\epsilon_{238} = 1.41 \times 10^5 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and the largest λ_{max} appears at 283 nm ($\epsilon_{283} = 1.22 \times 10^4 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$). It was concluded that there is a larger red-shift in the electronic absorption of the precursor due to the effective π conjugated segment of naphthyl group with vinyltriethoxysilane. The precursor and xerogel can emit very strong blue light under ultraviolet light (366 nm), but *R-1* can not show visible fluorescence, fluorescent wavelengths of *R-1* appear at 369 and 381 nm in ultraviolet region (Fig. 1). The precursor *R-2* and xerogel show strong blue fluorescence due to the extended π -electronic system.¹⁴ The fluorescent wavelengths $\lambda_{\text{max}}^{\text{F}}$ of precursor *R-2* in THF solution are 387 and 401 nm, but in the KBr solid state, the emitting wavelength of xerogel appears at 435 nm (Fig. 1). It can be attributed to the interaction between the chromophores and formation of fluorescent dye aggregates within the hybrid amorphous xerogel.^{3,15}

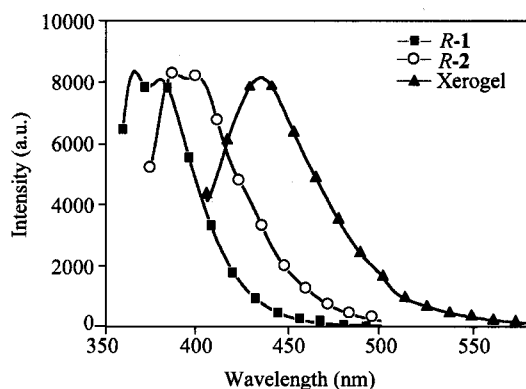


Fig. 1 Fluorescent spectra of *R-1* (THF solution, $\lambda_{\text{ex}} = 366$ nm), *R-2* (THF solution, $\lambda_{\text{ex}} = 334$ nm) and xerogel (solid, KBr disc, $\lambda_{\text{ex}} = 394$ nm).

The optical rotation ($[\alpha]_{\text{D}}^{25} - 104.7$, CH_2Cl_2) of the precursor *R-2* is much larger than *R-1* ($[\alpha]_{\text{D}}^{25} + 22.6$, CH_2Cl_2). The precursor *R-2* exhibits stronger CD signals with positive and negative Cotton effect in its circular dichroism spectrum (Fig. 2). The molecular ellipticity of precursor *R-2* is: $[\theta]_{\lambda} = +1.28 \times 10^5$ (254 nm), -1.83×10^5 (272 nm) and $+1.22 \times 10^4$ (317 nm); and the molecular ellipticity of *R-1* is: $[\theta]_{\lambda} = -1.49 \times 10^5$ (245 nm) and $+8.59 \times 10^3$ (287 nm). The largest molecular ellipticity of *R-1* with Cotton effect was observed at 287 nm (Fig. 2), but *R-1* molecular ellipticity $[\theta]_{\lambda}$ of Cotton effect is weaker, the long wavelength CD effect of the precursor *R-2* is regarded as the more extended conjugated structure.¹⁶

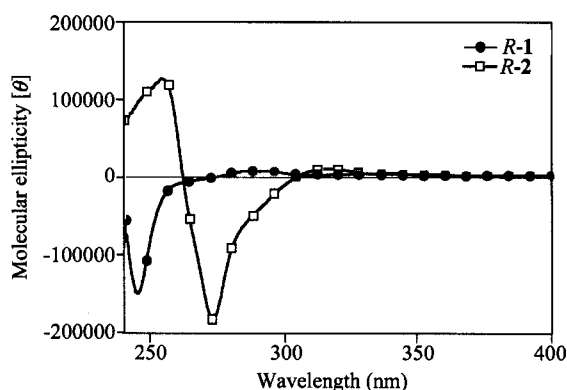


Fig. 2 CD spectra of *R-1* and *R-2*.

Conclusion

Heck reaction was found to offer a simple access to the silylated (*R*)-BINOL precursor. The precursor was hydrolyzed by the sol-gel process to give the corresponding hybrid xerogel under the very mild condition. Both precursor and xerogel incorporating the functional chiral BINOL moieties open new perspectives in the development of solid supports for heterogeneous asymmetric catalyst and chiral molecular recognition. Furthermore, xerogel material shows interesting optical property, which is expected to have the potential application in the development of enantioselective fluorescent chemosensor for the separation of chiral molecules. The further investigation on the design of the novel organic-inorganic hybrids with tunable properties at the well-defined molecular level is being pursued.

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