Ideal Exciton Spectra in Single- and Double-Screw-Sense Helical Polysilanes

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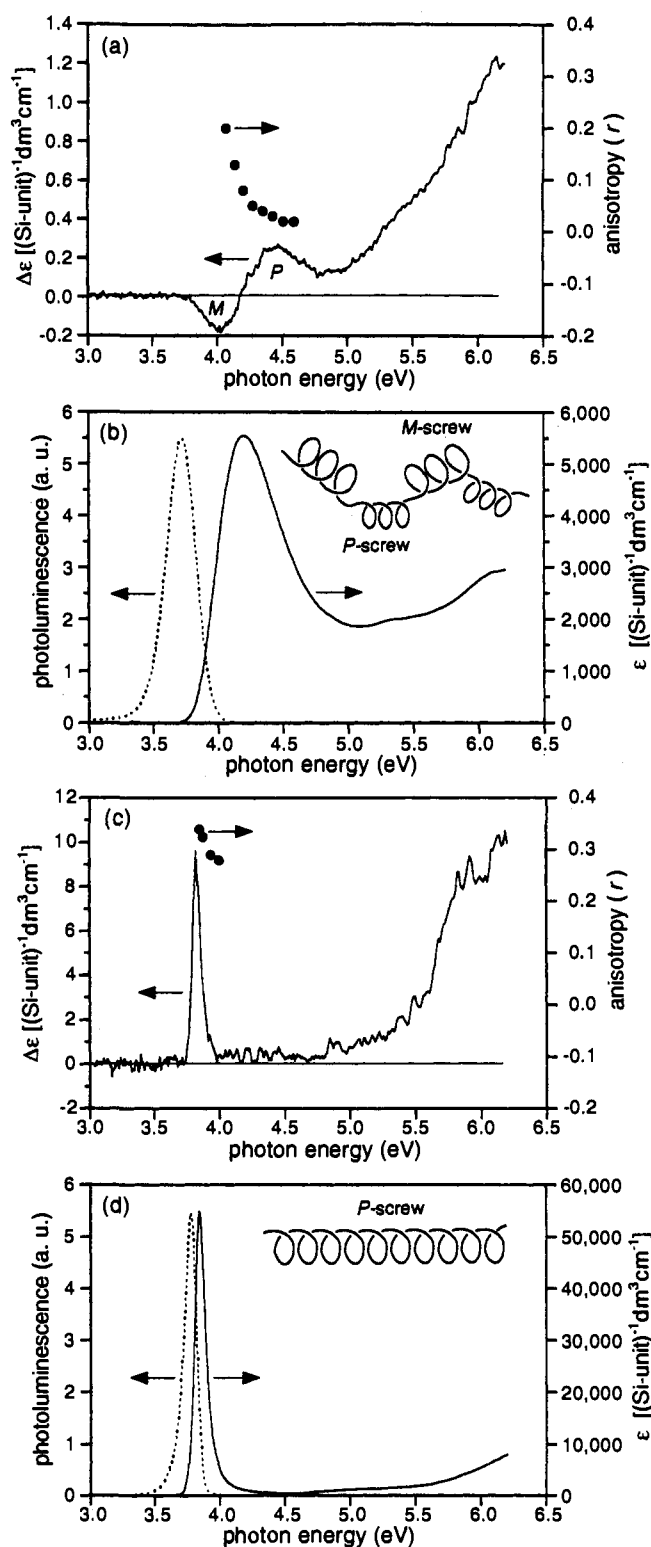
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Helicity and its optical activity have long been discussed in macromolecular stereochemistry,[1–5] but the relationship between the helix and its intrinsic photophysical properties is still unclear. This is because most optically active organic polymers lack the absorbing band exhibiting the emitting band, due to a rigid main chain in solution. Chainlike polysilane, especially, exhibits excitonic UV absorption and photoluminescence (PL) due to its Si σ conjugating backbone.[6,7] To directly clarify the inherent optical spectra associated with its helical structure, we obtained two types of optically active polysilanes: a nonsegmented, single-screw-sense, extended rigid-rod helix and a segmented, double-screw-sense, broken-rod helix. Here we find the ideal one-dimensional exciton spectral characteristics of the nonsegmented helical conformation in solution at room temperature: (i) it exhibits extremely intense, narrow UV absorption, (ii) its CD spectral profile fits completely within the UV spectrum, and (iii) the PL spectral profile is a mirror image of either the UV or the CD spectrum.

Chainlike organopolysilane has an optical band gap of 3.0–4.5 eV assigned to the lowest $Si\sigma$–$Si\sigma^*$ transition parallel to a chain axis.[8,9,10] Its UV and PL spectra are highly sensitive to changes in degree of Si σ conjugation, which is influenced by helical conformation, defects, and segmentation.[7,11,12] Although most polysilanes in solution exhibit very broad UV and narrow PL spectra and show marked excitation energy dependence on PL anisotropy,[12] these features have been satisfactorily explained by a simplified "segment model": a polysilane chain is a collection of relatively short segments consisting of 10–20 Si atoms with different photoexcitation energies.[6,12] This model predicts that, if polysilane has nonsegmented, one-screw-sense helicity, the PL spectrum should be a mirror image of either the UV or the CD spectrum, resulting in a single photoexcitation state. Furthermore, in this case, the PL anisotropy value approaches the theoretical limit of 0.4 expected from the random distribution of rigid-rod absorbing and emitting chromophores in rigid media. From a comparison of CD, UV, and PL spectra in two types of optically active polysilanes (Chart 1),[13] we identified the exact nature of a one-dimensional exciton associated with their helical structures.
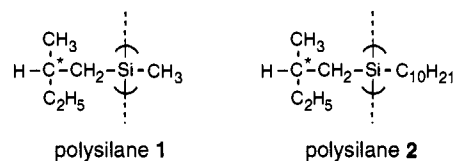
Figures 1a and 1b show the CD, UV, and PL spectra depicting the excitation energy dependence of the PL anisotropy of poly-[methyl((S)-2-methylbutyl)silane] (**1**) in isooctane at 20 °C. Polysilane **1** exhibits both the positive Cotton band at 4.5 eV and the negative Cotton band at 4.0 eV, which are associated with

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Figure 1. Characteristics of optically active polysilane **1** and **2** in isooctane at 20 °C.[13] (a) CD spectrum and *r* of polysilane **1**, (b) UV and PL spectra and *P*- and *M*-screw-sense diastereomeric helix model of polysilane **1**, (c) CD spectrum and *r* of polysilane **2**, and (d) UV and PL spectra and *P*-screw-sense helix model of polysilane **2**. *P* and *M* denote the helicity of the silicon skeleton.

the broad UV absorption at 4.2 eV and the narrow PL band at 3.7 eV, respectively. The optical band gap of polysilane has been demonstrated theoretically to increase as the helical tortion angle decreases.[9,14] If we establish that the full width at half maximum (fwhm) of the PL band is almost identical to that of the negative Cotton band, we can establish from these spectra a structural

Chart 1. Chemical Structures of Two Types of Optically Active Polysilanes

polysilane **1**   polysilane **2**

model in which a polysilane chain is composed of both a *P*-screw-sense, tight helical segment with a 4.5-eV optical band gap and an *M*-screw-sense, loose helical segment with a 4.0-eV gap. The marked excitation energy dependence on PL anisotropy indicates that the two segments are broken at their junction, as illustrated in Figure 1b. This model can be further confirmed by the following photolysis experiment[15] and preliminary molecular mechanics (MM2) calculations based on standard parameters with an Si–Si bond length of 2.332 Å and an Si–Si–Si bond angle of 111.3°.

When polysilane **1** in isooctane is decomposed at the negative Cotton band for several hours, the band almost disappears and the positive Cotton band profile almost matches the remaining blue-shifted UV band. Since the value of P_w decreases from 440 to 9, the segment length responsible for the positive Cotton band is estimated to be 9. While polysilane **1** is irradiated at the positive Cotton band, both the bisigned CD and UV bands are bleached, producing a very low molecular weight species. The MM2 calculations for this octamer suggest that both *P*- and *M*-screw-sense diastereomeric helices can coexist along the same chain with a high barrier height of 40–60 kcal/mol: two steric energy minima are obtained at torsion angles of 170° and –160° in an isotactic configuration and similarly yielded at 170° and –150° in a syndiotactic configuration.

When the methyl substituent in polysilane **1** was replaced with an *n*-decyl one, there was a serendipitous change in the optical spectra. Figures 1c and 1d display the UV, CD, and PL spectra and excitation energy dependence of the PL anisotropy of poly-[*n*-decyl((*S*)-2-methylbutyl)silane] (**2**) in isooctane at 20 °C. Several spectroscopic features of polysilane **2** differ significantly from those of polysilane **1**. First, its CD spectral profile at 3.9 eV exactly matches the corresponding 3.9-eV UV absorption:

(13) Fujiki, M. *Jpn. Kokai Tokkyo Koho* JP 05 202528, 1993. These polymers were prepared by Na-mediated condensation of the corresponding dichlorosilane bearing a (*S*)-2-methylbutyl substituent in hot toluene in the presence of 15-crown-5 (2 mol %). The typical yields of these polymers were 7–20%. For polysilane **1**, the weight-average degree of polymerization (P_w) is evaluated to be 440, and the number-average degree of polymerization (P_n) is 140 from GPC analysis based on polystyrene standards. Polysilane **2** has a bimodal molecular weight distribution such that $P_w = 5700$, $P_n = 3700$ (25%) and $P_w = 500$, $P_n = 240$ (75%).

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the PL spectral profile is an identical mirror image of either the UV or the CD spectrum. Second, PL anisotropy depends only slightly on the photoexcitation energy ranging from 0.28 to 0.34 around the 3.9-eV UV band but almost reaches the theoretical value of a rigid-rod chromophore. Finally, compared with the UV spectra of polysilane **1**, its absorptivity, $\epsilon = 55\,000$ [(Si unit)$^{-1}$·dm^3·cm^{-1}], is 10 times greater and its fwhm value, 0.10 eV, diminished by one-sixth. The MM2 calculations for this octamer with either an isotactic or a syndiotactic configuration suggest that the most favorable conformer is strongly fixed to only a *P*-screw-sense with a torsion angle of 170°. This fixing effect is primarily due to the rigid silicon skeleton and its adjacent carbon atoms, locked by the chiral and *n*-decyl chains. Indeed, we observed the broad ^{29}Si NMR signal located at –22.5 ppm due to the main chain (60 MHz, toluene-d_8 at 80 °C)[16] and ^{13}C NMR signals due to the side chains (75 MHz, chloroform-d_1 at 40 °C), typically $\nu_{1/2} \sim 90$ Hz for both. There was no marked temperature dependence of the UV and CD spectra observed between –10 °C and 60 °C. The conformational structure of **2** is now assumed to be a 7$_3$ helix or its nearly equal loose helix, since its UV absorption energy is close to that of poly(di-*n*-butylsilane), taking on a 7$_3$ helical form in a solid,[11] and Kuhn's dissymmetry factor ($g = \Delta\epsilon/\epsilon$), 1.8 × 10^{-4}, is very weak. We conclude that the novel exciton spectra of polysilane **2** is the first direct spectroscopic evidence of a nonsegmented, *P*-screw-sense, extended rigid-rod helical polysilane that is stable even in solution at room temperature,[17] as illustrated in Figure 1d.

Up to now, there has been a wide gap between macromolecular and low molecular stereochemistry,[3] but the emergence of nonsegmented, single-screw-sense helical polysilane narrows this gap and highlights further functions. In the examples, it serves as an ultrafine-wire-size model in quantum-wire semiconductor research,[18,19] since it gives ultimately intense, narrow UV absorption, which closely fits the UV spectrum simulated for a one-dimensional exciton in an idealized polysilane.[7] This polysilane is also promising as enantiorecognitive chiral support for chromatographic applications[20] because of its hydrophobic property and the high thermal stability of the helix.

(16) This chemical shift of helical, *chiral* polysilane **2** is very close to that of optically inactive poly(di-*n*-hexylsilane) with *trans*-planar, *achiral* conformation in the solid state.[11] The unexpected downfield chemical shift of polysilane **2** is now assumed to originate from elongation of the Si–Si bond length due to sterically-hindered, β-branched alkyl moieties.

(17) A similar *P*-helical structure can also be gained in other optically active polysilane homologues: poly(bis((*S*)-2-methylbutyl)silane) and poly-(alkyl((*S*)-2-methylbutyl)silane), where the alkyl is ethyl, *n*-propyl, *n*-butyl, *n*-pentyl, isobutyl, *n*-hexyl, *n*-heptyl, *n*-octyl, *n*-nonyl, *n*-dodecyl, or β-phenetyl group. Details will be submitted elsewhere.

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