

Molecular Electronics

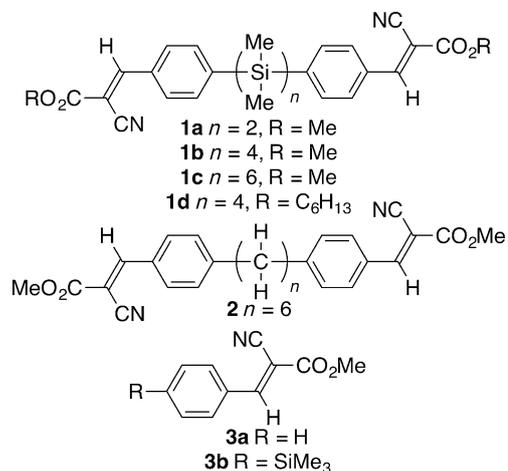
Photoinduced Charge Separation in Molecular Silicon

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Abstract: Interest in molecular silicon semiconductors arises from the properties shared with bulk silicon like earth abundance and the unique architectures accessible from a structure distinctly different than rigid π -conjugated organic semiconductors. We report ultrafast spectroscopic evidence for direct, photoinduced charge separation in molecular silicon semiconductors that supports the viability of molecular silicon as donor materials in optoelectronic devices. The materials in this study are σ - π hybrids, in which electron-deficient aromatic acceptors flank a σ -conjugated silicon chain. Transient absorption and femtosecond-stimulated Raman spectroscopy (FSRS) techniques revealed signatures consistent with direct, optical charge transfer from the silane chain to the acceptor; these signatures were only observed by probing excited-state structure. Our findings suggest new opportunities for controlling charge separation in molecular electronics.

The attractive features of flexible electronic devices motivate interest in the structure–function relationships underlying high-performance molecular semiconductors. Although the tetrahedral semiconductor silicon dominates the electronics industry, most molecular semiconductors are based on π -conjugated organic cores.^[1] Yet molecular silicon presents significant attractive opportunities for materials: similar to the bulk semiconductor, it is earth abundant, and the unique tetrahedral and flexible structure of an oligosilane chain lends itself to new and distinct architectures in molecular electronics. Inspired to explore the structural diversity of molecular silicon semiconductors, we recently described the synthesis and electronic characterization of a new class of hybrid organo-silicon materials **1 a–c** (Scheme 1).^[2] Record-setting mobilities for a device with an oligosilanyl active layer (up to $0.06 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) were observed and attributed in part to a crystal-packing structure inaccessible to all-organic analogs.

Silicon is not only the dominant semiconductor for electronics, but also for solar cells, raising questions about molecular silicon's photophysical properties and potential for optoelectronic device applications.^[3,4] An attractive potential of Si-



Scheme 1. Structures of materials used in this study.

based molecular hybrids in particular is the prospect for optically manipulating charge separation between electron-rich Si and covalently bound electron-deficient acceptors. Herein, we show explicitly that the photoresponses of the organosilanes **1 a–c** involve a direct σ -to- π electron transfer from silicon to an organic acceptor and that the degree of charge transfer depends on the silane chain length. We also demonstrate that the silanes' photophysical properties are similar in the solution and solid state. Insights from our work support the viability of molecular forms of silicon as photoresponsive materials in optoelectronic devices and offer prescriptions for manipulating charge separation in hybrid materials.

An arresting feature of **1 a–c** is their yellow color in solution and in the film state.^[2] In contrast, permethylated oligosilanes^[5] and carbon-based analogues **2** and **3 a**^[2] are colorless, implicating the silicon chain as an essential contributor to the photophysical properties of the hybrid materials. We hypothesize an intramolecular charge transfer from silicon to the electron-deficient cyanovinyl-substituted arene, an idea supported by solution-phase studies that suggested intermolecular charge transfer from permethylated oligosilanes to the powerful oxidant tetracyanoethylene (TCNE).^[6] Incomplete mechanistic understanding of this Si-to-acceptor charge transfer has limited the development of molecular silicon electronic materials. To this end, we have conducted a definitive spectroscopic study of charge separation in the covalently linked hybrid materials **1 a–c**.

Steady-state spectroscopic characterization (IR and electronic) of **1 a–c** showed that charge separation does not occur in the ground state. Figure 1 presents FTIR spectra of **1 a** and **b** in

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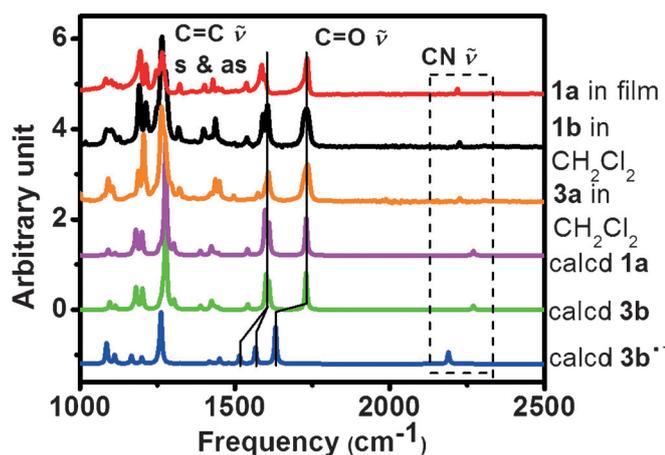


Figure 1. FTIR spectra of **1a** in a film and **1b** and **3a** in dichloromethane. Calculated IR spectra of **1a**, neutral **3b**, and reduced **3b⁻** are plotted for comparison. Spectra are scaled according to the C=O feature intensity.

film and solution, respectively. Key-vibrational frequencies exhibit no appreciable dependence with morphology and comparison with the IR spectrum of **3a** in solution shows that these features arise predominantly from the cyanovinyl moiety. Ground state IR spectra of **1a** and **3b** were calculated at the DFT^[7a]/CAM-B3LYP/6-31+G* level^[7b] with the Gaussian 09 package,^[7c] calculated spectra exhibit remarkable agreement with experiment after scaling by 0.950 and broadening by 4 cm⁻¹.

In contrast, the calculated spectrum of the reduced acceptor **3b⁻** predicted that the excess electron induces a significant bathochromic shift of the C=C, C=O, and C≡N stretches and strongly perturbs the vibrational structure between 1500 and 1700 cm⁻¹. Our calculations showed that the C=C bond in particular lengthens from 1.35 to 1.42 Å upon reduction, reflecting reduced bond order and correspondingly lower vibrational frequency. Thus, the experimental IR spectra agree closely with the calculated spectrum of the neutral (rather than reduced) acceptor. Additional evidence against ground-state charge transfer comes from the observed position of the C≡N stretch (ca. 2220 cm⁻¹), which matches that of prototypical cyanovinyl acceptors, such as tetracyanoquinodimethane (TCNQ):^[8] the nitrile frequency in neutral TCNQ and the charge-transfer salt TTF-TCNQ were observed at 2222 and 2201 cm⁻¹, respectively.^[9]

The electronic absorption spectroscopy of **1a–c** further supports that any charge separation must occur in the excited rather than ground state. Figure 2 illustrates that the UV/Vis absorbance spectrum of **1b** is dominated by a broad and intense transition around 350 nm (Figure 2, solid lines), giving rise to its characteristic yellow color. DFT^[7a] and TF-DFT^[7d] calculations indicate that the low-energy side of this feature is associated with a HOMO-LUMO transition, with the HOMO localized predominantly on the electron-rich silanyl core and the LUMO on the cyanovinyl end groups. Transitions localized on only the cyanovinyl moiety are predicted to fall at higher energies.^[2] The position of maximum absorbance varies only weakly with solvent polarity. In contrast, significant batho-

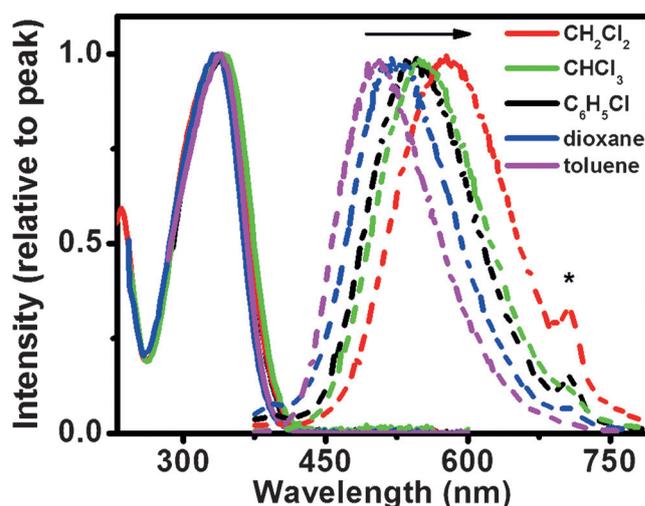


Figure 2. UV/Vis absorption (solid lines) and dispersed fluorescence (dash lines) of **1b** in various solvents. Second-order scatter from the fluorescence excitation ($\lambda = 360$ nm) is marked with an asterisk. The emission peak red-shifts with increasing solvent polarity (noted by the black arrow).

chromism of the dispersed fluorescence with increasing dielectric strength was observed, which is characteristic of excited-state charge transfer in donor-acceptor systems (Figure 2, dash lines).^[6,8]

Ultrafast spectroscopic methods are best suited for characterizing an excited-state charge-transfer mechanism. Figure 3 presents the ultrafast transient absorption spectrum of **1b** dissolved in dichloromethane 1 ps after excitation at 360 nm (plotted in red). The two primary features of the transient spectrum include a positive feature peaked near 450 nm and a weaker negative feature centered at 640 nm. The former appeared instantaneously (within the 200 fs time resolution of the experiment) and corresponds with absorption from the photoprepared excited state. The negative feature appeared in

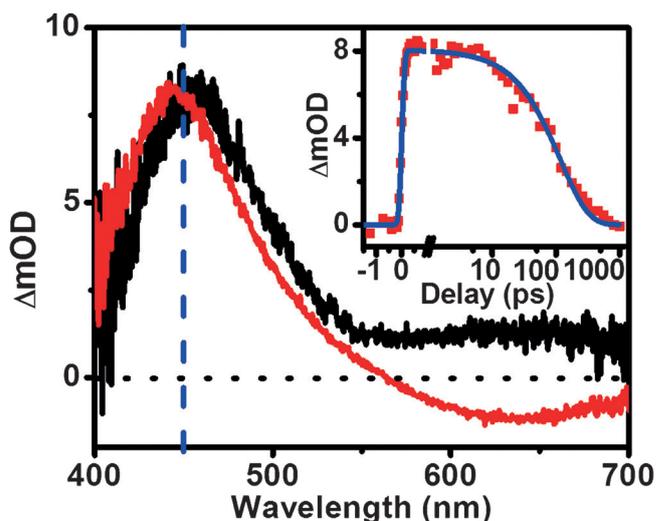


Figure 3. TA spectra of **1b** in dichloromethane solution (red) and **1d** cast as a film (black) probed 1 ps after excitation at 360 nm. The TA spectrum of the **1d** film is scaled by a factor of four for comparison with solution data. Inset: Transient decay of excited **1b** in solution as probed at 450 nm.

the same wavelength range as the steady-state fluorescence, and therefore corresponded with stimulated emission (SE) from the excited state. Both features were observed to decay within hundreds of picoseconds; the 450 nm transient exhibits a lifetime of 119 ps, as was determined with a single-exponential fit (inset of Figure 3).

Greater structural insight was obtained by applying a vibrationally sensitive probe of the excited state.^[10] Herein, we have used femtosecond stimulated Raman spectroscopy (FSRS) to interrogate the properties of photoexcited **1 a–c**. FSRS uses the combination of a narrowband (ca. 20 cm^{-1}) Raman excitation and ultrafast (< 100 fs) broadband probe to stimulate Raman transitions of multiple vibrational modes coherently.^[11] In our measurements, resonantly enhanced excited-state FSRS spectra were obtained by using a Raman-excitation wavelength of 480 nm. The photoselectivity on resonance enables us to characterize charge-separated character of the electronic state that underlies the transient absorbance peaked at 450 nm.^[12]

The excited-state FSRS (ER) spectra of **1 a–c** and the ground-state FSRS (GR) spectrum of **1 c** are plotted in Figure 4. The ground-state spectrum exhibited a feature discernible from noise near 1600 cm^{-1} ; the weak intensity of this spectrum can be attributed to a lack of resonant enhancement with the ground-state transition in the near UV. In contrast, the Raman spectra of the excited oligomers exhibited a series of intense resonantly enhanced features between 1000 and 1650 cm^{-1} . Time-resolved measurements showed that all of these features decay simultaneously on a timescale commensurate with the decay of (Figure 3) the transient electronic absorption spectrum and therefore can be assigned to vibrations of the corresponding photoprepared electronic state.

The Raman features apparent in Figure 4 arise largely from cyanovinyl vibrational modes. We calculated Raman spectra of the neutral and reduced forms of **3 b** in their optimized ground-state geometries with the same computational level

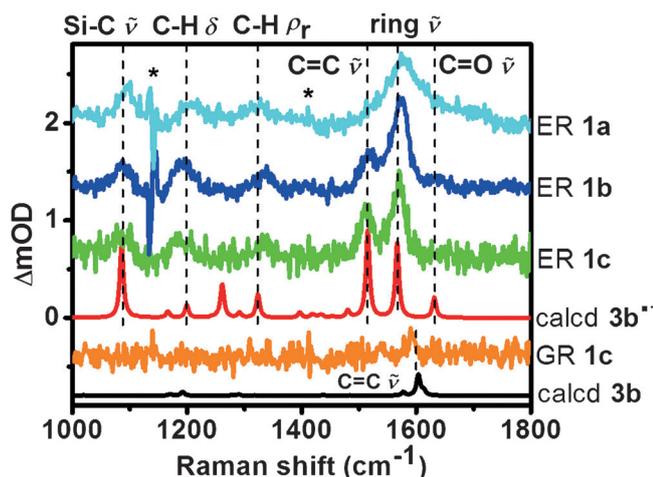


Figure 4. Excited-state Raman (ER) of **1 a–c** and ground-state Raman (GR) of **1 c** in dichloromethane with $\lambda = 360$ nm actinic and 480 nm Raman excitations. The time delay between actinic and Raman pulses is 10 ps. Calculated Raman spectra of neutral and reduced forms of **3 b** are also plotted for comparison. Residual solvent signals at 1139 and 1415 cm^{-1} are marked with asterisks.

and package used to compute their IR spectra for Figure 1. Calculated Raman spectra for the neutral and reduced model structures are plotted with the data in Figure 4.

Although our calculated Raman spectra did not account for resonance enhancement, comparisons between experiment and calculations showed reasonable agreement. The most intense excited-state features observed correspond with C=C stretching (1516 cm^{-1}) and ring stretching (1568 cm^{-1}) in the reduced cyanovinyl arene moiety. A weaker C=O stretching band appeared at 1630 cm^{-1} , whereas three features in the region between 1000 and 1400 cm^{-1} arise from vibrational modes associated with the arene ring of the negatively charged acceptor (Si–C stretch, C–H bend, and C–H rock). The ground-state feature at 1592 cm^{-1} is consistent with the C=C stretching mode predicted for the neutral cyanovinyl. We note that because the C=C and C=O stretches are both IR and Raman active the predicted vibrational spectra of **3 b** and **b[–]** are consistent. Thus, Figures 1 and 4 in combination illustrate that charge separation occurred in the excited, but not ground states of these compounds.

Figure 4 also reveals a correlation between the C=C stretching frequency and silane chain length: For **1 b** and **c**, the C=C and ring stretching modes are separated by 54 and 60 cm^{-1} , respectively, with partial overlap of these features in the spectrum of the former. For compound **1 a**, the C=C and ring stretching modes merge entirely. This correlation implies that the degree of photoinduced charge transfer is related to the electron-donating strength of the silane chain,^[4,13] a general property of charge transfer complexes.^[8]

To establish the relevance of the optical charge-transfer mechanism in the solid state, we explored the photoresponse of **1 d** drop-cast as a film on a glass slide. We have previously shown that replacement of the methyl ester with an *n*-hexyl ester resulted in a more continuous film morphology without perturbing solution phase electronic properties.^[2] Figure 3 compares the TA spectra of **1 d** in film (black line) with **1 b** in dichloromethane (red line), both probed 1 ps after 360 nm excitation. Both excited samples exhibited the absorption band near 450 nm attributed to the reduced cyanovinyl arene moiety based on the results of our resonant FSRS measurements. This similarity reveals that charge transfer within the oligosilane compounds can be induced by photoillumination in the solid state as well. The most significant difference between the two TA spectra is the lack of stimulated emission from the film, which may reflect intermolecular charge separation; further characterization of photoinduced electron transfer and transport in the solid-state is underway.

In conclusion, we have characterized the photophysics of a series of σ - π hybrid materials by using a combination of steady-state and transient spectroscopies. These compounds undergo Franck–Condon (optical) intramolecular electron transfer from the silane to cyanovinyl moieties upon excitation. This is illustrated most clearly with excited-state FSRS spectra that showed reduction of the cyanovinyl arene moiety in the photoprepared excited state. Additionally, the frequency of the C=C stretch mode is correlated with the length of the central silane chain and is related to the degree of charge transfer.

Similar transient spectroscopy of these compounds in the solution and film states indicates that photoinduced intramolecular charge transfer also occurs in the solid state. Notably, our work is distinguished from the body of research in which silicon chains bridge aromatic donors and acceptors,^[14] because the silane chain itself is the electron donor in our materials. Thus, σ - π hybrids, such as compounds **1a-c**, present interesting new possibilities for controlled, light-driven manipulation of charge in molecular silicon-material architectures.

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Keywords: charge transfer · molecular electronics · optoelectronics · organosilanes · Raman spectroscopy

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