Communication

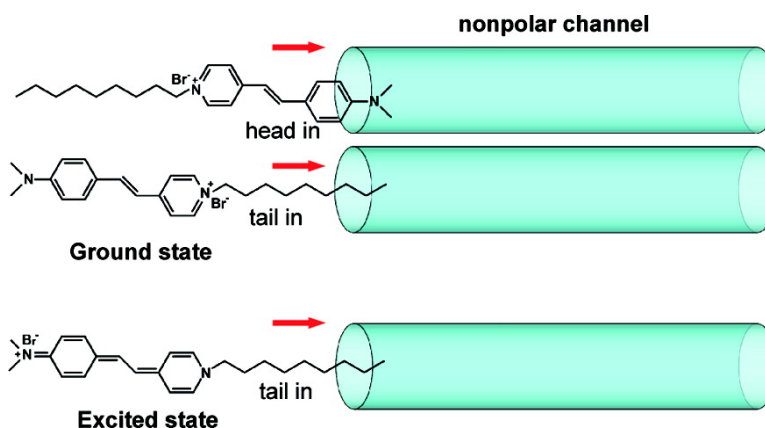# Aligned Inclusion of Dipolar Dyes into Zeolite Channels by Inclusion in the Excited State

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Aligned Inclusion of Dipolar Dyes into Zeolite Channels by Inclusion in the Excited State

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The ability to organize dipolar molecules in uniform orientations has been a big challenge since they have a strong tendency to self-assemble centrosymmetrically, leading to cancellation of individual dipole moments. Some successes have been made during their organization into thin films on substrates.[1-3] The three most widely investigated methodologies were the formation of Langmuir–Blodget films,[1] self-assembled monolayers,[2] and the electrically polled polymer films imbedded with dipolar molecules.[3] However, because of their lack of mechanical, thermal, and chemical strengths, the produced thin films are not practically applicable.

Orientation-controlled inclusion of dipolar molecules into zeolites has been examined as a novel approach.[4,5] Thus, Stucky and co-workers reported that AlPO$_4$-5 (an aluminophosphate zeolite having straight channels) powders included with *para*-nitroaniline or the analogous compounds generate second harmonics (SH) with the intensities far exceeding that of quartz powders.[4] Marlow and co-workers revealed that the SH-generating activities arose as a result of the spontaneous inclusion of the dipolar compounds into the channels of AlPO$_4$-5 with the nitro group first arising from the intrinsically higher affinity of the AlPO$_4$-5 channels to nitro than amino group.[5] However, the resulting inclusion materials do not bear practical applicability due to their powder states and to the molecules' relatively low second-order hyperpolarizability (β) constants ($\sim 35 \times 10^{-30}$ esu).

As a means to turn the above novel findings into a novel methodology for production of practically useful second-order nonlinear optical materials, we chose higher-β dipolar dyes and have developed methods of orientation-controlled inclusion into zeolite channels. For this, hemicyanine (HC, $\beta \geq 770 \times 10^{-30}$ esu) dyes with the kinetic diameter of ~ 5.79 Å (Supporting Information, SI-1) and silicalite-1 films whose straight channels (aperture size = 5.4×5.6 Å) were oriented vertically (b-orientation) with respect to the glass supports were chosen.[6] The degrees of uniform orientation (DUOs) of the included dyes were evaluated by measuring $d_{33}/d_{33}(\text{max})$, where d_{33} and $d_{33}(\text{max})$ are a tensor component of the quadratic nonlinear susceptibility of a HC-including silicalite-1 film and its theoretical maximum under the condition that all the included HC dyes are uniformly oriented, respectively (SI-2).

Knowing that silicalite-1 channels are hydrophobic, as a strategy, HC dyes with long alkyl chains on the pyridinium (HC-*n*, $n \geq 18$, where n = number of carbon chains, see Scheme 1A) were prepared, and they were subsequently included into the hydrophobic channels with the hope to include alkyl groups first due to the hydrophobic–hydrophobic interaction between the attached long alkyl groups and the silicalite-1 channels.[6a] Indeed, HC-*n* dyes with $n \geq 18$ were included into silicalite-1 channels with high DUOs (>0.67). However, shorter-chain HCs such as HC-9 showed a very poor DUO (0.08).[6a] This suggested that the hydrophilic center is localized at the pyridinium part and both the 1,4-(dimethylamino)-

Scheme 1 *a*
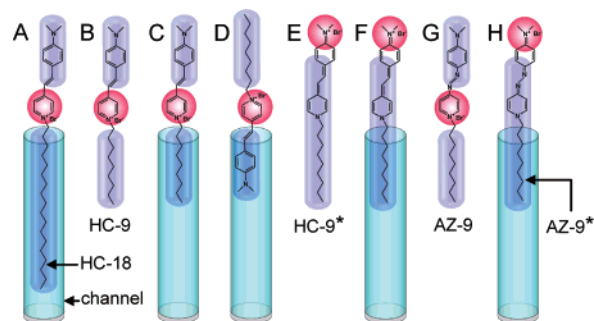
a The illustration shows the initial step of HC-18 inclusion into a hydrophobic silicalite-1 channel with the hydrophobic alkyl chain first (A), presence of two hydrophobic parts on both sides and one hydrophilic part at the center in HC-9 (B), the inclusion of HC-9 into a channel with the alkyl (C) and dimethylamine (D) part first, localization of a hydrophilic part at the terminal in HC-9* (E), inclusion of HC-9* into a channel with the alkyl part first (F), presence of two hydrophobic parts on both sides and one hydrophilic part at the center in AZ-9 (G), and inclusion of AZ-9* into a channel with the alkyl part first (H).

phenylenevinyl and *n*-nonyl groups are almost equally hydrophobic (Scheme 1B), thereby allowing the molecule to enter the channels with either the alkyl (Scheme 1C) or the dimethylamino part (Scheme 1D) first with almost no preference.

In the case of HC, theoretical studies have shown that, in the excited state, a substantial amount of positive charge density develops at the dimethylamine terminal while almost all of the positive charge density disappears from the pyridinium ring (Scheme 1E).[7] This leads to the shift of the hydrophilic part from the center to the very end of the molecule. We therefore hypothesized that a larger fraction of photoexcited HC-9 (HC-9*) molecules would enter the channels with the alkyl part first (Scheme 1F), as if it became a longer chain HC. However, despite the fact that numerous types of molecules have been included into zeolites ever since zeolites were discovered,[8] no case has ever been reported regarding the inclusion of photoexcited molecules. We now report that DUO of HC-9 increases by 3.4 times when the dye molecules were photoexcited during its inclusion into the channels.

Glass plates coated with b-oriented silicalite-1 films (thickness = ~ 400 nm) on both sides (SL/G) and HC-9 were prepared as described elsewhere.[6a] A rectangular, double-walled stainless steel chamber with the internal dimension of $20 \times 10 \times 35$ mm^3 was prepared. The chamber had four confronting quartz widows, a water inlet, and an outlet (SI-3). A Teflon support ($20 \times 10 \times 3$ mm^3) having a groove with the size of $10 \times 1 \times 1$ mm^3 was placed at the bottom of the container so that the direction of the groove become parallel with the direction of beam passage.

A methanol solution of HC-9 (30 mL, 0.1 mM) was introduced into the chamber and the solution was cooled to 5 °C by passing cold water through the jacket. A line-polarized laser beam (cw,
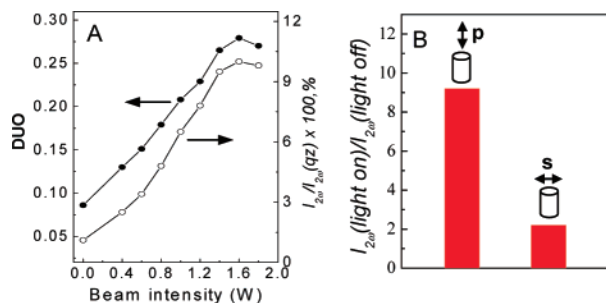
Figure 1. Plots of the DUO and $[I_{2\omega}/I_{2\omega}(qz) \times 100]$ (in %) with respect to the laser beam intensity (A) and the effect of the beam polarization direction (p or s) on the $I_{2\omega}$(light on) to $I_{2\omega}$(light off) ratio (B).

488 nm, beam size = 3 mm) from an Ar$^+$-ion laser (Spectra Physics, 2017-AR-5) was passed through the quartz windows. Since the molar extinction coefficient of HC-9 at 488 nm was 42 570 M^{-1} cm^{-1}, irradiation of HC-9 molecules with the laser beam ensured photoexcitation of the molecules. A SL/G plate (10 × 25 × 1 mm^3) was quickly inserted into the groove of the Teflon support. This allowed the formation of 3-mm wide beam envelopes on both silicalite-1 films along the SL/G plate (SI-3).

The beam intensity was varied from 0.0 to 2.0 W. The polarization was either parallel (p-polarization) or perpendicular (s-polarization) to the direction of the channels. After 6 h, the SL/G was quickly removed from the solution, washed with fresh methanol, and dried by blowing dry N$_2$ over the plate. The number of molecules that enter each channel (N_C) in methanol at 5 °C remained constant ($\sim$13) regardless of the power of laser beam from 0.0 (dark) to 2.0 W (SI-4).

Interestingly, relative $I_{2\omega}$ (at 70° of the Maker fringe, see SI-5) with respect to that of 3-mm thick Y-cut quartz (a reference)[6] $[I_{2\omega}/I_{2\omega}(qz) \times 100$, in %] almost linearly increased from 1.5 to 10% with increasing the laser power from 0.0 to 1.6 W and then slightly decreased upon further increasing the power to 2.0 W (Figure 1A).[9] This means that DUO increased almost linearly from 0.08 to 0.27 with increasing the laser power from 0.0 to 1.6 W, which corresponds to a $\sim$3.4-fold increase (Figure 1A). Calculation shows that 1.25 molecules out of 6 molecules which enter each channel with the dimethylamine side part first in the dark changed orientation to the alkyl side upon irradiation at 1.6 W, a 21% increase (SI-6). Comparison with the DUOs of HC-12 (0.2) and HC-15 (0.38) in the dark suggests that HC-9* behaves like HC-13, which is an interesting observation.

An independent measurement revealed that, at 1.6 W, the input irradiance starts exceeding the total absorption by the dyes in the solution along the beam passage (by $\sim$0.01%). On the basis of the above, and because photoexcitation and relaxation generally take place in two very different time scales of $\sim$10^{-15} and $\sim$10^{-9} s, respectively, and the molar extinction coefficient of HC-9 is very high at 488 nm (vide supra), it is reasonable to expect that a majority of HC-9 molecules that are oriented in the polarization direction would exist in the excited-state at 1.6 W.

The ratio of $I_{2\omega}$ with light on with respect to that with light off $[I_{2\omega}$(light on)/$I_{2\omega}$(light off)] was 9.2 and 2.0 for p- and s-polarization direction, respectively (Figure 1B). This indicates that those molecules that are oriented parallel to the channel direction in the vicinity of the silicalite-1 film mostly enter the channels in the excited state (Scheme 1F).

We also synthesized azo-bridged HC-9 analogue (AZ-9, Scheme 1G) and tested the applicability of the light-induced DUO increase (SI-7). The measured N_C of AZ-9 in methanol at 5 °C after 24 h

(8.1, regardless of irradiation at 1.6 W) was still smaller than that of HC-9 ($\sim$13), indicating that the inclusion rate of AZ-9 was slower than that of HC-9. The absorption maximum appeared at 553.5 nm (λ_{max}) and the molar extinction coefficient in methanol was 57 974 cm^{-1} M^{-1} (SI-8). The measured relative $I_{2\omega}$(light on) with p-polarized light at 1.6 W (λ = 514.5 nm) and $I_{2\omega}$(light off) were 9.7 and 0.87%, respectively (SI-9). Accordingly, $I_{2\omega}$(light on)/$I_{2\omega}$-(light off) was 11, indicating that photoexcited AZ-9 (AZ-9*) preferentially enters channels with a higher preference to the alkyl side (Scheme 1H).

We have thus clearly demonstrated a novel method to organize (dipolar) molecules in uniform orientations. Although DUOs achieved in this report are not satisfactory, this report opens new areas of research on the achievement of higher DUOs by photo-excitation and the study of its effect on the dynamics and kinetics of molecular diffusion at the solution−zeolite interfaces. Most of all, this report demonstrates that molecules can be incorporated into zeolite pores in the excited states. We believe that this methodology can be developed into a method of freezing molecules in the excited states by confining the excited molecules in zeolite nanopores for those molecules whose kinetic diameters decrease in the excited states.

Supporting Information Available: Experimental details, raw experimental data, and definitions. This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) The decrease of $I_{2\omega}$ (and hence d_{33}) at a higher laser power (2.0 W) is ascribed to a large increase in local temperature.

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