Optical property control of dye molecules using CHA and AFI nanoporous crystals

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The optical properties of disperse red 1 (DR1) dye molecules can be changed by controlling the molecular configurations using AlPO4-5 (AFI) and SAPO-47 (CHA) single crystals. Polarized and temperature dependent absorption spectra show that DR1 molecules exist as cis configuration in the cages of CHA crystals. The absorption band for cis-configuration is centered at 432 nm, which does not depend on polarization angle and temperature. However, DR1 molecules are well aligned in the channels of AFI crystal with trans configuration. Its absorption band is centered at 520 nm, which shows strongly anisotropic polarizability and shifts to long wavelength with increasing temperature. It can be used as polarizer and temperature sensor. The second harmonic generation (SHG) and photoluminescence (PL) investigations show that the DR1 trans isomers in AFI matrix have potential applications in nonlinear optics.

OCIS codes: 160.1190, 160.4236, 220.4241, 300.1030.

doi: 10.3788/COL201210.S11601.

Dye molecules have strong absorption bands in the visible region and are widely used in dye lasers, solar cells, and optoelectronic devices[1−3], etc. The molecular physical property is determined by the arrangement of the alternating single-double bonds (conjugated bonds) in a dye molecule. Azobenzene and many of its derivatives, such as disperse red 1 (DR1) molecules, have reversible transformations named trans and cis configurations[4,5]. Trans isomers and cis isomers often have different optical properties, which arise from the differences in the overall dipole moment. Controlling the configurations of dye molecules has many important applications for nano-photonics, nano-electronics, medicine, and bioinformatics, etc. There are different techniques to assemble molecules on substrates, including scanning tunneling microscopy techniques[6], self-assembled mechanism[7], atomic force microscope based dip-pen nanolithography[8], etc. However, it is difficult to control cis and trans dye molecules separately, since the energy difference between trans and cis configurations is small. Dye molecules can transform from the more stable trans configuration to the less stable cis configuration upon irradiation with ultraviolet (UV) or visible light.

In this letter, we present a template approach to obtain the cis and trans isomers of DR1 molecules separately. The templates are AlPO4-5 (AFI) and SAPO-47 (CHA) single crystals. DR1 molecules have been introduced into the nanoporous matrix of the AFI and CHA single crystals using physical diffusion method (DR1@AFI, DR1@CHA). Polarized and temperature dependent absorption spectra show that DR1 molecules in the CHA matrix exist as cis configuration. The absorption peak for cis-configuration is centered at 432 nm, which does not depend on polarization angle and temperature. However, DR1 molecules are well aligned in the AFI matrix with trans configuration. Its absorption peak is centered

at 520 nm, which shows strongly anisotropic polarizability and shifts to long wavelength with increasing temperature. It can be used as polarizer and temperature sensor. The second harmonic generation (SHG) and polarized photoluminescence (PL) investigations show that the trans DR1 molecules in AFI matrix have potential applications in nonlinear optics.

CHA and AFI single crystals were both synthesized using hydrothermal method. As-synthesized crystals were characterized by X-ray powder diffraction (XRD) using a Philips PW1830 diffractometer at room temperature. The crystal size and morphology were investigated by scanning electron microscopy (SEM) (JEOL, Model: JSM-6049LA).

Figure 1 shows the morphologies of the CHA and AFI single crystals, respectively. The typical AFI crystal size can reach 500 μm in length and 100 μm in diameter. The cubic CHA crystals have the average dimension of 100 μm, and the crystal quality is good. The inset shows their related framework structures. Their structure consists of alternating tetrahedra of aluminum and phosphorus linked by oxygen.

Figure 2 shows the XRD patterns of CHA and AFI single crystals. The diffraction pattern has been scanned over the angular range from 5° to 50° (2θ). The spectrum reveals a high crystallinity, as shown by the sharp peak profiles in Fig. 2. The peaks at 9.5°, 13°, 16°, 18°, 21°, 23°, 25°, 30.5°, and 31° are characteristics of CHA crystals which possess well-defined cages with the size of 0.65×1.1 nm[9], and the peaks at 7.5°, 13°, 15°, 20°, 21°, 22.5°, 26°, 29°, 30.5°, and 35° are characteristics of AFI crystals that have open one dimensional channels with inner diameter of 0.73 nm[10].

DR1 molecules (Aldrich Chemical Co., 95%, powder) were incorporated into the matrix of CHA and AFI single crystals by the vapor-phase diffusion method. Both
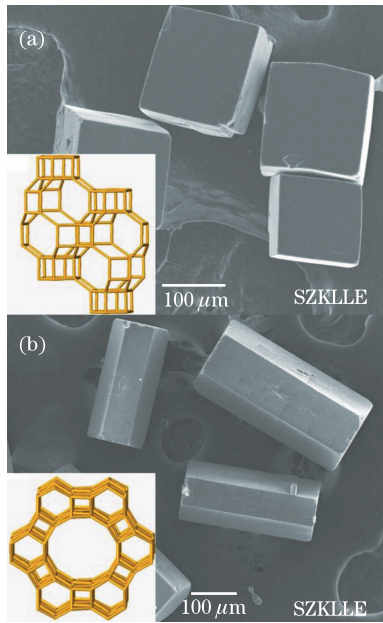
Fig. 1. SEM images of synthesized (a) CHA and (b) AFI single crystals. The inset shows their related framework structures.
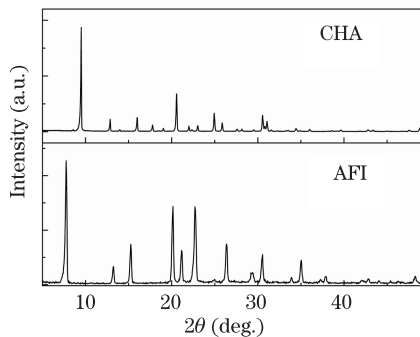

Fig. 2. XRD patterns of CHA and AFI crystals.

CHA and AFI crystals were firstly calcined at 580 °C in O_2 atmosphere for about 48 h to remove the organic templates in the matrix. The calcined crystals were then sealed together with DR1 molecules in a Pyrex tube at a vacuum of 10^{-1} Pa. With rising temperature, DR1 was introduced to the matrix by physical adsorption. The DR1 loaded crystals (DR1@AFI, DR1@CHA) are magenta, and DR1@AFI behaves as a good polarizer.

As shown in Fig. 3, DR1 molecules have two transformations named trans and cis configurations. When it absorbs photons, DR1 molecule can isomerize from the ground state (trans-configuration) to the meta-stable excited state (cis-configuration) with a large change in the molecular dipole moment.

In order to characterize the optical properties of DR1@AFI and DR1@CHA, we measured the polarized and temperature dependent absorption spectra of the samples. Before the measurements, we mounted the sample in a small hole drilled on a ceramic plate with epoxy resin and polished the sample to a thickness as thin as about 30 μm. The prepared sample was mounted on a high precision XYZ stage. The collimated light beam from a 75-W tungsten-halogen lamp was focused to the sample by a long working distance reflecting objective. A linear polarizer was placed before the sample. The incident light spot was around 50 μm as monitored by an optical microscope. The transmitted light was collected by another reflecting objective and then coupled into an optical fiber. The depolarized signal by the multimode fiber was then dispersed by a 0.5-m triple grating monochromator and detected by a photomultiplier tube (PMT). A standard mercury lamp was used to calibrate the wavelength of the monochromator and a quartz-tungsten-halogen irradiation source was used for calibrating the detection sensitivities of the systems at different wavelengths. In order to investigate the thermal properties of the DR1 molecules, we measured the absorption spectra under different temperatures using closed cycle cryostat (CS-204AI 4K Closed Cycle Cryostat). The measuring range is 5-290 K.

Due to the confinements of the channels or cages of the templates, the DR1@AFI and DR1@CHA single crystals show different optical properties. Figure 4 shows the polarized absorption spectra for DR1@AFI and DR1@CHA single crystals, respectively. In the experiment, the polarization angle was tuned from 0° (the light polarized parallel to the crystal channel direction, E//c) to 90° (the light polarized perpendicular to the crystal channel direction, E⊥c), as shown in the inset of the figure.

At θ=0°, the absorption spectrum of DR1@AFI (marked by open circles) can be decomposed into two bands by Lorentzian lines with peak wavelengths at 520 and 430 nm. The 520-nm band dominates the spectrum, and its intensity amplitude becomes negligible at $\theta = 90°$ (E⊥c). In contrast, the 430-nm band is less polarization dependent. The very different polarization behavior of the two bands indicates that they might originate from two different structures of DR1 molecules.

Using a simple "free-electron" quantum mechanical model[11], we can estimate the lowest absorption energy for DR1 molecules with trans configuration

$$\Delta E = \left(\frac{h^2}{8mL^2}\right)(n_2^2 - n_1^2) = \left(\frac{h^2}{8mL^2}\right)(N+1) = \frac{hc}{\lambda},$$
(1)

where m is the mass of the electron, h is Planck's constant, L is the length of the atom chain with conjugated bonds in DR1 molecules, N is the π-electrons in the chain. Each carbon atom in the chain can provide one π-electron, and each nitrogen atom can provide two.
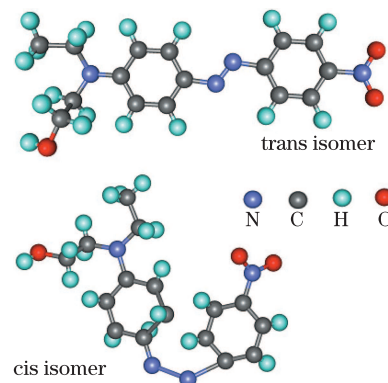

Fig. 3. Trans and cis configurations of DR1 molecule.

Approximately, the conjugated bonds chain length is

$$L = \alpha[(P-1)l_{CC} + l_{NN} + 4l_{CN}], \qquad (2)$$

where P is the number of carbon atoms in the chain, α is the expansion coefficient (empirical) due to the influence of π electrons in the phenyl rings connected to the N atoms. As a first-order approximation, we use C—C length of benzene (0.140 nm) for l_{CC}, C—N length of pyridine (0.134 nm) for l_{CN}, and N-N length of Nitrogen (0.125 nm) for l_{NN}. If $\alpha=1$ (which means no expansion in the carbon chain of the DR1 molecule), we get the longest absorption wavelength of 521 nm. Thus, we assign the 520-nm absorption band to the absorption by trans configured DR1 molecules in AFI channels. The measured band has a small blue shift compared with calculated result, which might be due to the framework confinement. As can be seen in Fig. 4, the little shoulder centered at around 430 nm in the absorption band of DR1@AFI shows no obvious polarization. It might be due to the absorption of cis-like DR1 molecules formed in some mesochannels (partial destruction of the interchannel walls in some places in the AFI crystals).

In comparison with DR1@AFI crystals, the absorption spectra of DR1@CHA do not show obvious anisotropic polarizability. The absorption band is centered at around 432 nm. The DR1 molecules are scrunched in the CHA cages since the cage size is only 0.65×1.1 (nm) which is small to contain the DR1 molecules with trans configuration. Due to the strong interactions between framework and dye molecules, the absorption band shifts obviously to short wavelength.

According to the configurations of trans isomer and cis isomer, the thermal response of DR1@AFI and DR1@CHA should also be different. Figure 5 shows the temperature dependent absorption spectra of DR1@AFI and DR1@CHA. The incident light is polarized parallel to the crystal channel direction (E//c). In the left column of Fig. 5, the absorption band centered at 520 nm for DR1@AFI shifts to long wavelength with increasing temperature. The shift is about 15 nm for trans configuration. It can be explained by the bond expansion in DR1 molecules when the temperature increases. In Eq. (2), the bond expansion leads to the increase of chain
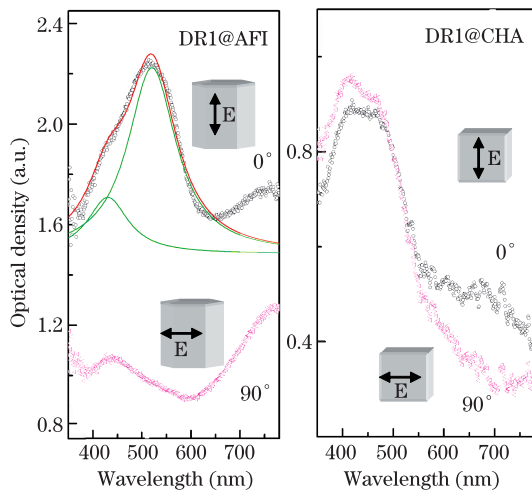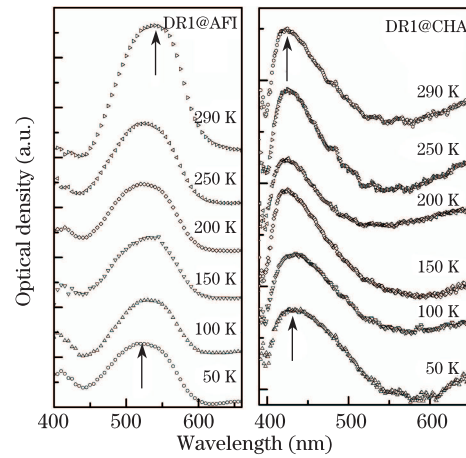

Fig. 5. Temperature dependent absorption spectra of DR1@AFI and DR1@CHA samples.

length L, thus leads to the red shift of absorption peak. However, the absorption band for cis configuration in the right column does not show obvious shift with increasing temperature. Since the molecule is scrunched in the CHA cages, thermal expansion can lengthen the bonds, thus can make the atoms at the molecular ends closer. And the atom interactions should be stronger, which leads to the blue shift of the absorption band. Due to the compensation of thermal expansion and atoms interactions, the absorption band of cis isomer does not show obvious temperature response.

Since the DR1@AFI crystals show obvious anisotropic absorption spectra and have strong temperature response, they can be used as polarization-selective devices or temperature sensor.

The polarization of the absorption spectra of the DR1@AFI complex indicates that the dipole moments of the included dye molecules are oriented preferentially along the crystal channel axis. Since the enclosed species of DR1 dye molecules have an elongated shape and exhibit a transition dipole moment along their elongation axis, the dipoles end up oriented parallel to the AFI c-axis as well. It will show particular emission properties. Thus we measured polarized PL spectra and studies the SHG properties of DR1@AFI crystals.

Polarized PL spectra were measured using an Ar laser (488 nm) as excitation source for a single DR1@AFI crystal. The laser power is 20 mW. The excitation laser was focused on a spot of about 20-μm diameter by a long working distance UV microscope objective, which was monitored by an optical microscope. A notch filter at 488 nm was used to cut off the laser light. A linear polarizer was placed in the collection path before the signals entered into a multimode fiber. The depolarized signal was then dispersed by a 0.5-m monochromator (the entrance and exit silt width was 0.2 mm) and collected by a PMT detector. The primary SHG investigation was carried out using a 1 064-nm (Nd:YAG) laser as incident light beam. It was focused onto the sample by an objective. The laser focus spot was 50 μm in diameter, the pulse duration is 10 ns and the laser power density was about 0.1 MW/cm^2. A vision system was used to view the crystal and image it onto a monitor. The output signal from the sample was dispersed by a quartz prism, and

Fig. 4. Polarized absorption spectra for DR1@AFI and DR1@CHA single crystals.

then the signal was collected into the monochromator by a quartz lens, and recorded by a CCD detector. A long wavelength cutoff filter was used before the entrance slit in order to cutoff the 1 064-nm signal.

Figure 6 shows the polarized PL spectra for a single DR1@AFI crystal. The polarization angle was tuned from $0°(E//c)$ to $90°(E\perp c)$. The PL spectra were corrected by the system sensitivity in the whole measurement wavelength region. The PL from the sample is strongly polarized parallel to the channel direction. The integrated intensity of the axis-parallel component is about 4 times larger than that of the axis-perpendicular component. There are two bands in the PL spectra centered at 530 (marked by C1) and 560 nm (marked by C2) in the $\theta=0°$ polarization, as shown in the inset of Fig. 6. And the PL spectrum for $\theta=90°$ is also fitted by two Lorentzian lines (C1 is the same for both $\theta=0°$ and $\theta=90°$ polarization). The intensity of C2 band decreases monotonically with increase of the polarization angle, which corresponds to the DR1 trans isomers. And C1 band is less polarization dependent, which might due to the emission from cis-like DR1 molecules formed in the mesochannels.

Figure 7 shows the investigation of SHG of DR1@AFI single crystal. The incident laser wavelength is 1 064 nm, and the measured wavelength of the collected laser beam is 532 nm. The inset shows that strong green light can be observed. The laser frequency is doubled after it passes
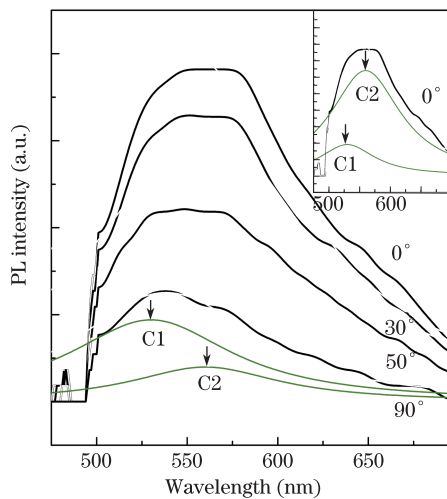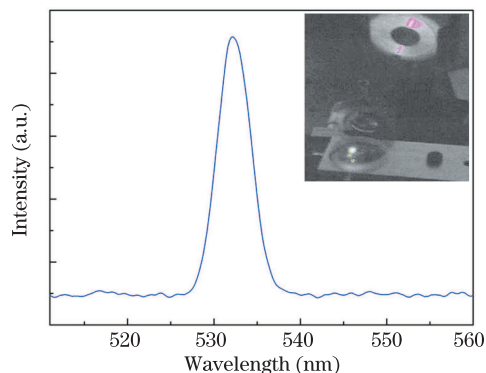
through the DR1@AFI crystal. In the experiment, we have replaced the DR1@AFI sample with empty AFI single crystal. There is no SHG effect, which indicates that the observed nonlinear effect comes from the DR1 molecule contained in the AFI matrix. To account for this nonlinearity, we use the relationship between molecular dipole moment D and external electric field E, $D=D_0+aE+bE^2+cE^3+\cdots$. Here D_0 is the permanent dipole moment of the molecule, a is the linear polarizability, b is the first hyperpolarizability, and c is the second hyperpolarizability. If the molecule possesses an inversion center, all terms of even order in the electric field disappear. Thus only noncentrosymmetric molecules will have second-order nonlinear optical properties (NLO). DR1 is a push-pull chromophore with very interesting NLO properties. According to previous investigations, the first hyperpolarizability of trans-DR1 is 5 times larger than that of cis-DR1[4]. Since the dominant structure of DR1 molecules in AFI channels is trans-configuration, DR1@AFI sample shows obvious SHG effect.

In conclusion, the optical properties of DR1 dye molecules can be changed by controlling the molecular configurations using CHA and AFI single crystals. Polarized and temperature dependent absorption spectra show that DR1 molecules in the CHA matrix have cis configuration. The absorption peak for cis-configuration is at 432 nm, which does not depend on polarization angle and temperature. However, DR1 molecules are well aligned in the AFI matrix with trans configuration. Its absorption peak is at 520 nm, which shows strongly anisotropic polarizability and shifts to long wavelength with increasing temperature. It can be used as polarizer and temperature sensor. The SHG and PL investigations show that the trans DR1 isomers in AFI matrix have potential applications in nonlinear optics.

Fig. 6. Polarized emission spectra for a single DR1@AFI crystal.

Fig. 7. SHG effect of DR1@AFI sample.

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