

Supporting information for :

## **Mapping of the organization of p-nitroaniline in SAPO-5 by second-harmonic generation microscopy**

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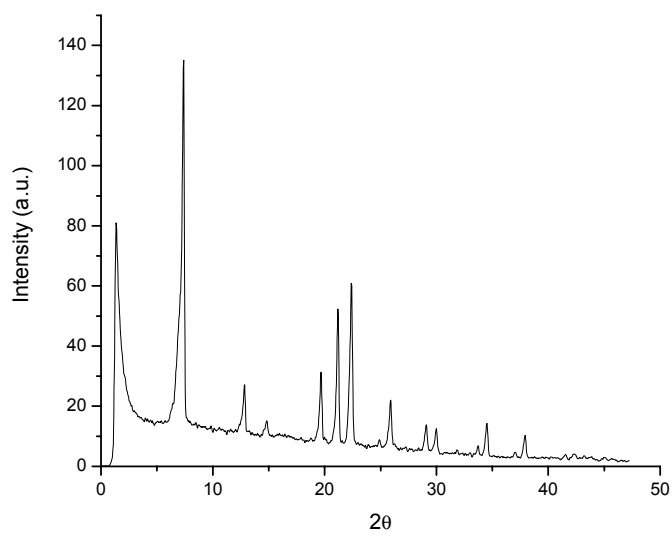
## S1: Experimental section

SAPO-5 was prepared under continuous stirring from H<sub>3</sub>PO<sub>4</sub> (85 wt %), tripropylamine ( $\geq 98\%$ ), aluminium isopropoxide ( $\geq 98\%$ ) and bi-distilled water via a modification of the procedure described by Fan et al. (Phys. Chem. Chem. Phys., 2001, 3, 3240). First, Al-isopropoxide was hydrolyzed in water under continuous stirring at 40°C. Dilute H<sub>3</sub>PO<sub>4</sub> was added to the slurry. Subsequently, the mixture was aged for 15 min under gentle stirring. Then, the template tripropylamine (TPA) was introduced dropwise after which the gel was aged for another 30 min. A single portion of Ludox-AS40 was further added to the synthesis gel. The molar composition of the final gel was 1 Al<sub>2</sub>O<sub>3</sub> : 0.99 P<sub>2</sub>O<sub>5</sub> : 0.6 Pr<sub>3</sub>N : 400 H<sub>2</sub>O : 0.01 SiO<sub>2</sub>. After stirring for another 30 min, the gel was loaded into a Teflon lined stainless steel autoclave. The hydrothermal treatment was carried out dynamically at 190°C for 15h. After crystallization, all autoclaves were quenched under cold water flow, the crystals were centrifuged, washed thoroughly with bi-distilled water and dried at 60°C for 24h.

The SAPO crystals were calcined under an O<sub>2</sub> flow. After slowly heating the crystals (at 1°C/minute), the sample was left at 600°C for 15h. Thereafter the crystals were characterized by Scanning Electron Microscopy (SEM, Philips XL 30 FEG ) and a powder X-ray diffractogram was measured on a STOE StadiP operating in high-throughput mode using CuK $\alpha$  radiation with a wavelength of 1.541 Å. The PNA molecules were introduced into the SAPO-5 crystals via a gas-phase loading process by contacting the evacuated SAPO-5 crystals with saturated PNA vapour at 150°C for 24h. The amount of adsorbed PNA was determined by thermogravimetric analysis (TA instruments, TGA Q500) under O<sub>2</sub>-atmosphere and with a heating rate of 10°C/minute until 1000°C. The infrared spectrum of dry, PNA-loaded SAPO-5 crystals in KBr pellets was recorded on a Fourier Transform Infrared spectrometer (Bruker, IFS 66v/S).

The microscopy images were taken with an inverted wide-field microscope (Olympus, IX-71) coupled to a femtosecond Ti-sapphire laser. Images were recorded in transmission geometry with an EM-CCD camera (Hamamatsu, C9100-13). By using appropriate filters, the set-up can be used to record both two-photon fluorescence images and SHG images. With a polarizer and a half-wave plate in the incident laser beam, we were able to record polarization patterns for each position on the image.

S2: X-ray diffractogram of SAPO-5 after calcination



### S3: Theory

SHG, a second-order nonlinear optical effect, can be described by its nonlinear polarization  $P(2\omega)$ , given by

$$P(2\omega) = \chi^{(2)} E(\omega) E(\omega)$$

with  $E$  the electric field of the fundamental light at frequency  $\omega$  and  $\chi^{(2)}$  the second-order susceptibility that quantifies the nonlinear optical response.  $\chi^{(2)}$  is a third-rank tensor with 27 components. The number of nonvanishing susceptibility components however, depends upon the symmetry of the medium under investigation. Furthermore, also the particular experimental configuration will limit the number of components that can be addressed. For an experimental situation where the fundamental light is incident under normal incidence and if we assume that the crystal is in the  $xy$ -plane (Figure S1), we can write the nonlinear polarization in the most general case as :

$$\begin{aligned} P &= \chi_{xxx}^{(2)} E_x E_x + \chi_{xyy}^{(2)} xyy E_y E_y + 2\chi_{xyx}^{(2)} E_y E_x + \chi_{yxx}^{(2)} E_x E_x + \chi_{yyy}^{(2)} E_y E_y + 2\chi_{yyx}^{(2)} E_y E_x \\ &= \chi_{xxx}^{(2)} E_0^2 \cos^2 \alpha + \chi_{xyy}^{(2)} E_0^2 \sin^2 \alpha + 2\chi_{xyx}^{(2)} E_0^2 \cos \alpha \sin \alpha + \chi_{yxx}^{(2)} E_0^2 \cos^2 \alpha + \chi_{yyy}^{(2)} E_0^2 \sin^2 \alpha + 2\chi_{yyx}^{(2)} E_0^2 \cos \alpha \sin \alpha \end{aligned}$$

With the angle  $\alpha$  the polarization angle (Figure S1). Note that in the used experimental configuration, there is no  $z$ -component of the polarization because the polarization does not radiate in the direction of propagation. Also, the electric field of the incident light has no  $z$ -component. This equation can be further simplified if we make additional assumptions concerning the symmetry of the crystal. If we choose the laboratory coordinate system such that the  $x$ -axis coincides with the long crystal axis  $c$ , a mirror plane in the  $xz$ -plane is expected for the PNA-loaded SAPO-5 crystal. This is in agreement with earlier SHG-studies of PNA-loaded AIPO-5 crystals. Moreover, the measured data in these study are in agreement with such a mirror plane. In case of such a mirror plane, all susceptibility components with an uneven number of  $y$ -indices will vanish, and the polarization simplifies to

$$P = \chi_{xxx}^{(2)} E_0^2 \cos^2 \alpha + \chi_{xyy}^{(2)} E_0^2 \sin^2 \alpha + 2\chi_{yyx}^{(2)} E_0^2 \cos \alpha \sin \alpha$$

The second-harmonic intensity is proportional to the square of the polarization. Hence the second-harmonic intensity is given by

$$\begin{aligned} I(2\omega) &\propto \left| \chi_{xxx}^{(2)} E_0^2 \cos^2 \alpha + \chi_{xyy}^{(2)} E_0^2 \sin^2 \alpha + 2\chi_{yyx}^{(2)} E_0^2 \cos \alpha \sin \alpha \right|^2 \\ &\propto \left| \chi_{xxx}^{(2)} \cos^2 \alpha + \chi_{xyy}^{(2)} \sin^2 \alpha + 2\chi_{yyx}^{(2)} \cos \alpha \sin \alpha \right|^2 I(\omega)^2 \end{aligned}$$

If we now define the ratio  $X/Y$  as the ratio of intensities for measurements with an input polarization of  $\alpha = 0^\circ$  and  $90^\circ$ , we obtain :

$$\frac{X}{Y} = \frac{\left| \chi_{xxx}^{(2)} \right|^2}{\left| \chi_{xyy}^{(2)} \right|^2}$$

This ratio is sensitive to changes in orientation of PNA, since both susceptibility components are function of the tilt angle and the hyperpolarizability  $\beta$  of PNA. If we assume that PNA has only one hyperpolarizability component  $\beta_{z'z'z'}$  along the long molecular axis  $z'$ , the  $xyy$

component will vanish if PNA is oriented along the  $x$ -direction, and the ratio  $X/Y$  goes to infinity. The second-harmonic intensity can then be described by

$$I(2\omega) \propto \left(\chi_{xxx}^{(2)}\right)^2 (\cos \alpha)^4 I(\omega)^2$$

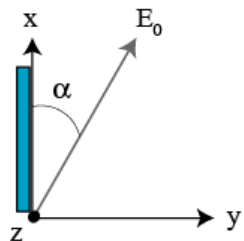


Fig. S1 : Orientation of the coordinate system used in our calculations. The blue rectangle represents the SAPO crystal,  $E_0$  is the fundamental electric field amplitude and  $\alpha$  the polarization angle.

Under the reasonable assumption that PNA has only one hyperpolarizability component, the relation between the nonlinear susceptibility and the hyperpolarizability is given by

$$\begin{aligned}\chi_{xxx}^{(2)} &= Nf \beta_{z'z'z'} \langle \cos^3 \theta \rangle \\ \chi_{xyy}^{(2)} = \chi_{yyx}^{(2)} = \chi_{yxy}^{(2)} &= Nf \beta_{z'z'z'} \langle \cos \theta \sin^2 \theta \rangle\end{aligned}$$

With  $\theta$  the tilt angle, defined as the angle between the long molecular axis of PNA and the long crystal axis  $c$ . It is indeed clear that the ratio of these two equations is a measure for the average tilt angle  $\theta$ , hence so is  $X/Y$ .