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Electronic Supplementary Information

Inclusion Induced Second Harmonic Generation in Low Dimensional Supramolecular Crystals

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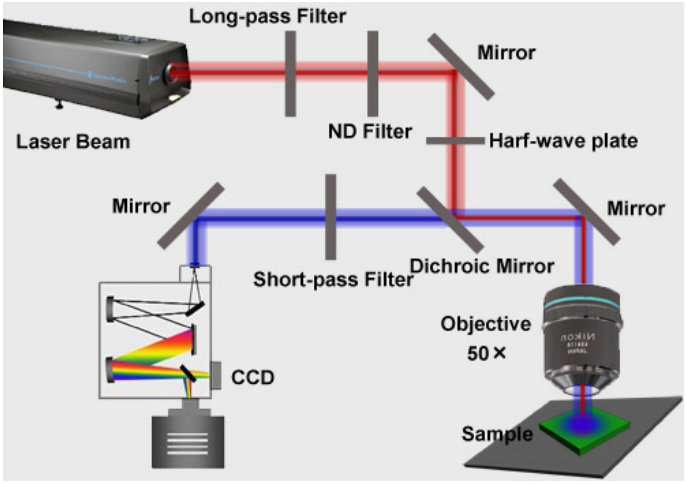

Fig. S1 Schematic demonstration of the experimental setup for the SHG measurements. The SHG measurements were carried out in a back-scattering geometry using an inverted microscope (Nikon, Ti-U). A 830 nm pulsed Ti:sapphire laser (Spitfire, Spectra-Physics) with a repetition rate of 80 MHz and duration of 100 *fs* was focused to a beam spot size of 2 μm to excite single LDSCs using an objective lens (Nikon CFLU Plan, 50×, N.A. = 0.8). The laser polarization was controlled by a half-wave plate. The intensity of the fundamental beam was varied by rotating a round variable neutral density filter and was monitored by a power meter. The fundamental beam passing through the sample was rejected by an appropriate filter, and the generated bright SHG signal was recorded with a CCD (ProEm, Princeton Instruments) after dispersed by a monochromator (SP-2358, Acton).

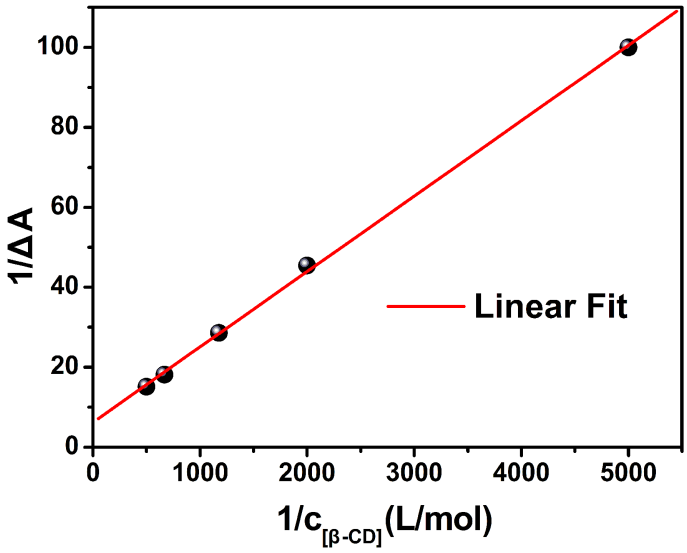

Fig. S2 The β-CD concentration dependence of the change in the absorbance of the PNA aqueous solution. ΔA is the change in the absorbance of the PNA with the addition of β-CD, $c_{[\beta\text{-}CD]}$ is the concentration of the β-CD. The plot of $1/\Delta A$ versus $1/c_{[\beta\text{-}CD]}$ shows excellent linear fit, indicating that the molecular ratio of PNA to β-CD in the complex is 1:1.

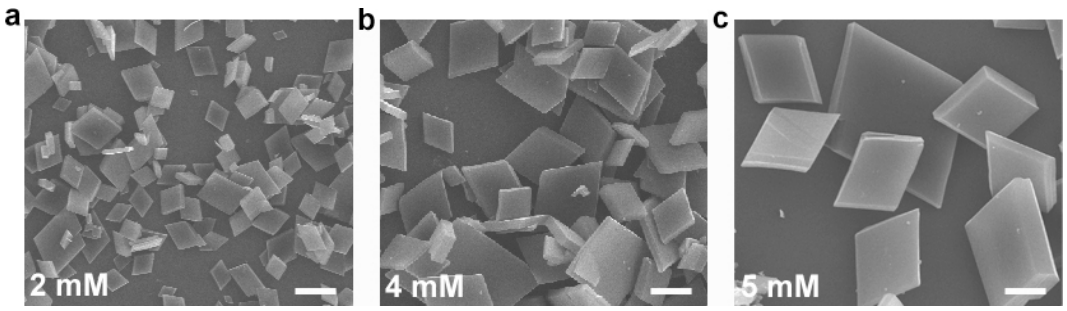

Fig. S3 SEM images of the W-LDSCs obtained with different PNA@β-CD concentrations. (a) 2 mM, (b) 4 mM, and (c) 5 mM. All scale bars are 10 μm. With the increase of the concentration of the solution from 2 to 5 mM, the edge length of the W-LDSCs grows from 6 to 15 μm.

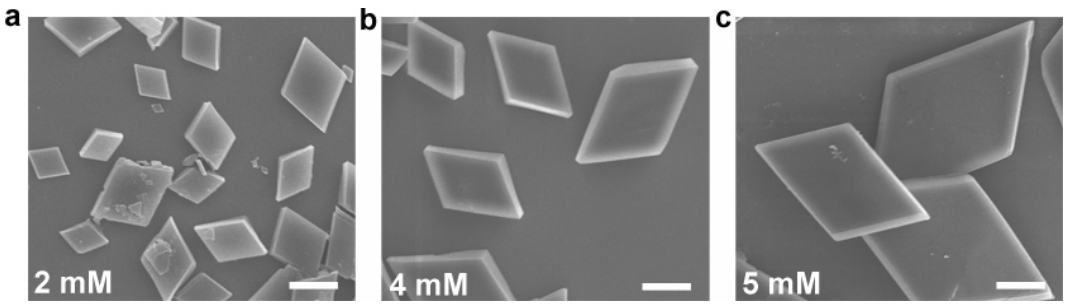

Fig. S4 SEM images of the E-LDSCs obtained with different PNA@β-CD concentrations. (a) 2 mM, (b) 4 mM, and (c) 5 mM. All scale bars are 20 μm. With the increase of the concentration of the solution from 2 to 5 mM, the edge length of the E-LDSCs grows from 20 to 50 μm.

Theory

Second harmonic generation can be described by its nonlinear polarization $P_i(2\omega)$ at frequency 2ω, given by:

$$P_i^{(2)} = \sum_{j,k} \chi_{ijk}^{(2)} E_j E_k$$

with $\chi^{(2)}_{ijk}$ a component of the second-order susceptibility tensor and $E_{j,k}$ the electric field component of the fundamental light. The number of nonvanishing susceptibility components $\chi^{(2)}_{ijk}$ depends on the symmetry of the medium and the experimental configuration. For our experimental situation where the fundamental light is normally incident to the XY-plane of a single LDSC (Fig. 3d), some nonvanishing components are addressed: $\chi^{(2)}_{YYY}$, $\chi^{(2)}_{YXX}$, $\chi^{(2)}_{XYX}$, $\chi^{(2)}_{XXY}$. (see T. Verbiest, K. Clays and V. Rodriguez, Second-order nonlinear optical characterization techniques, an introduction, (CRC Press: Boca Raton, 2009.)) Here, we assume that PNA has only 1 dominant hyperpolarisability component β_{YYY}, because other susceptibility components are at least 5 to 10 smaller than the *YYY* components (see S. J. Lalama and A. F. Garito, *Phys. Rev. A*, 1979, **20**, 1179.). All these components can be written as a function of the molecular hyperpolarisability of PNA, given by

$$\chi_{YYY}^{(2)} = Nf\,\beta_{YYY}\cos^3\varphi$$

$$\chi_{YXX}^{(2)} = \chi_{XYX}^{(2)} = \chi_{XXY}^{(2)} = Nf\,\beta_{YYY}\cos\varphi\,\sin^2\varphi$$

with N the number density of molecules and f a local field factor, φ the angle between long molecular axis of PNA and specific crystallographic direction of the LDSCs.

If the polarization dependence of the SH emission is included, we obtain:

$$I(2\omega) \propto \left|\chi_{YYY}^{(2)} E^2 \sin^2\theta + \chi_{YXX}^{(2)} E^2 \cos^2\theta\right|^2 + \left|\chi_{XYX}^{(2)} E^2 \sin\theta\cos\theta + \chi_{XXY}^{(2)} E^2 \sin\theta\cos\theta\right|^2$$

with θ the rotation angle of the electric field E of the fundamental light. If PNA is oriented in straight dipole chains along specific crystallographic direction of crystals, the functional form of the polarization dependence should be a two-lobe pattern:

$$I(2\omega) \propto a\,\cos^4\theta$$

Based on our experimental results (Fig. 3e and f), the SH intensities of the single LDSC follows a two-

lobe polarization pattern, which indicates that PNA molecule is oriented in straight dipole chains along specific crystallographic direction of the low dimensional supramolecular crystals. The difference in the stacking forms of inclusion supramolecules in the two kinds of LDSCs produces distinct PNA molecular orientations, which leads to different angular polarization dependence of the SHG signals.