

Supporting information

Optical Cavity Enhancement of Visible Light-Driven Photochemical Reaction in the Crystalline State

Ikuto Sasaki,^{a,b} Kiyonori Takahashi,^a Farsai Taemaitree,^{a,b} Takayoshi Nakamura,^a James A. Hutchison,^c Hiroshi Uji-i^{a,b,d} and Kenji Hirai^{a,b*}

^a *Research Institute for Electronic Science (RIES) and Division of Information Science and Technology, Graduate School of Information Science and Technology, Hokkaido University, N20W10, Sapporo, Hokkaido 001-0020, Japan.*

^b *Graduate School of Information Science and Technology, Hokkaido University, Sapporo, Hokkaido, Japan.*

^c *School of Chemistry and ARC Centre of Excellence in Exciton Science, The University of Melbourne, Masson Road, Parkville, Victoria 3052, Australia*

^d *Department of Chemistry, Division of Molecular Imaging and Photonics, KU Leuven, Celestijnenlaan 200F, Leuven B-3001, Belgium.*

E-mail: hirai@es.hokudai.ac.jp

Experimental Details

X-ray crystallography

2,4-dimethoxy- β -nitrostyrene (DN) was dissolved in toluene. The solution was slowly evaporated to form single crystals. X-ray data collection was conducted at 94K on Rigaku XtaLab Synergy diffractometer with a single microfocus Mo-K α X-ray radiation source ($\lambda = 0.7105 \text{ \AA}$), equipped with a hybrid pixel (HyPix) array detector (HyPix-6000HE). The crystal structural analysis was performed using Olex2. The structures were solved by using direct method (SHELXT) and refined by using full-matrix least-squares techniques on F^2 using SHELXL-2018. All non-hydrogen atoms were refined anisotropically.

Fabrication of film containing DN crystals

An aqueous solution of polyvinyl alcohol (PVA; 5mg/mL, 500 μ L) was dropcasted on a quartz glass substrate and spin-coated at 3500rpm for 10 seconds. Polystyrene (PS; 11mg) and DN (12.5mg) were dissolved in toluene (500 μ L). The solution of PS and DN was dropcasted on PVA layer and spin-coated at 4500rpm for 10 seconds. On top of the PS layer containing DN crystals, an aqueous solution of PVA (5 mg/mL, 500 μ L) was dropcasted and spin-coated at 3500 rpm for 10 seconds.

Fabrication of Optical Cavities containing 2,4-dimethoxy- β -nitrostyrene crystals

10 layers, consisting of SiO₂ and Ta₂O₅, were sequentially deposited on a quartz substrate by sputtering (Taishou Optical, Co., Ltd.), serving as a Distributed Bragg Reflection (DBR) mirror. The DBR mirror reflects light only within the 350 nm to 400 nm range (Figure S4). An aqueous solution of PVA (5 mg/mL, 500 μ L) was dropcasted onto the DBR mirror and spin-coated at 3500 rpm for 10 seconds. PS (5.5 mg) and DN (6.25 mg) were dissolved in toluene (500 μ L). The solution of PS and DN was dropcasted onto the PVA layer and spin-coated at 4500 rpm for 10 seconds. On top of the PS layer containing DN crystals, an aqueous solution of PVA (5 mg/mL, 500 μ L) was dropcasted and spin-coated at 3500 rpm for 10 seconds. Finally, 40 nm of Ag was sputtered onto the PVA layer.

Raman spectroscopy

To assess the progression of photocyclization, Raman spectroscopy was conducted at an excitation wavelength of 785 nm using a Raman microscope (Renishaw, inVia). In addition to the Raman signals of carbon-carbon double bonds (around $\sim 1600 \text{ cm}^{-1}$), signals corresponding to hydroxyl stretching vibrations appeared around $3200\sim 3300 \text{ cm}^{-1}$, which are attributed to the PVA layer. Since the photocyclization does not affect the hydroxyl groups, the relative intensity of carbon-

carbon double bonds against hydroxyl stretching vibrations was estimated to determine the reaction rate.

Photoirradiation

The photoirradiation of the samples was conducted using a Xe lamp (LAX-C100, Asahi Spectra) equipped with specific bandpass filters. The bandpass filters with wavelengths of HB0365 (345~385 nm) and HQBP410-VIS ϕ 25 (405~415 nm) were employed (Asahi Spectra). The irradiance was estimated to be 7.55×10^{-2} W/cm² and 1.86×10^{-2} W/cm², respectively.

UV-vis spectroscopy

UV-vis absorption and transmission spectra were obtained by using V-750 (JASCO Corporation).

Transfer Matrix Simulations

The transmittance (T), reflectance (R) and absorption ($A = 1-T-R$) within the optical cavity and non-cavity structures were simulated using in-house code in Matlab. The sample conditions were set as follows: the distributed Bragg reflector (DBR) consists of 10 alternating layers of SiO₂ and Ta₂O₅, with the thicknesses of each layer specified as follows: 10. SiO₂ - 105 nm, 9. Ta₂O₅ - 70 nm, 8. SiO₂ - 50 nm, 7. Ta₂O₅ - 35 nm, 6. SiO₂ - 60 nm, 5. Ta₂O₅ - 45 nm, 4. SiO₂ - 50 nm, 3. Ta₂O₅ - 145 nm, 2. SiO₂ - 60 nm, 1. Ta₂O₅ - 35 nm. The substrate is SiO₂. The refractive indices of SiO₂ and Ta₂O₅ were 1.5 and 2.1, respectively. Additionally, the polymer layers and Ag mirror had the following thicknesses: polystyrene (PS, 56 nm for resonant cavity, 100 nm for non-resonant cavity), polyvinylalcohol buffer layers (70 nm each), and Ag (40 nm for cavity, 0 nm for non-cavity). The absorbance intensity of the PS film containing 2,4-dimethoxy- β -nitrostyrene (DN) crystals was obtained through experiments, as shown in Figure S1. The imaginary part of the refractive index of the DN layer was integrated to estimated absorption rate in resonant cavity versus non-cavity structures.

Crystal Structure

Table S1. Crystallographic data of 2,4-dimethoxy- β -nitrostyrene

	CCDC #2339682
Chemical Formula	C ₁₀ H ₁₁ NO ₄
Formula Weight	209.201 gmol ⁻¹
Crystal System	Monoclinic
Space Group	P2 ₁ /c (#14)
Temperature / K	94 K
<i>a</i> / Å	3.85270(10)
<i>b</i> / Å	15.8701(5)
<i>c</i> / Å	15.9967(6)
β / °	94.588(3)
<i>V</i> / Å ³	974.95(5)
<i>Z</i>	4
GOF on <i>F</i> ²	1.036
<i>R</i> ₁ [<i>I</i> > 2σ(<i>I</i>)] ^a	0.0425
<i>R</i> _w [<i>I</i> > 2σ(<i>I</i>)] ^b	0.1076

$$^a R_1 = \sum ||F_o| - |F_c|| / |F_o|. \quad ^b R_w = [(\sum w(|F_o|^2 - |F_c|^2)^2) / \sum w(F_o^2)^2]^{1/2}.$$

Absorbance of DN Crystals

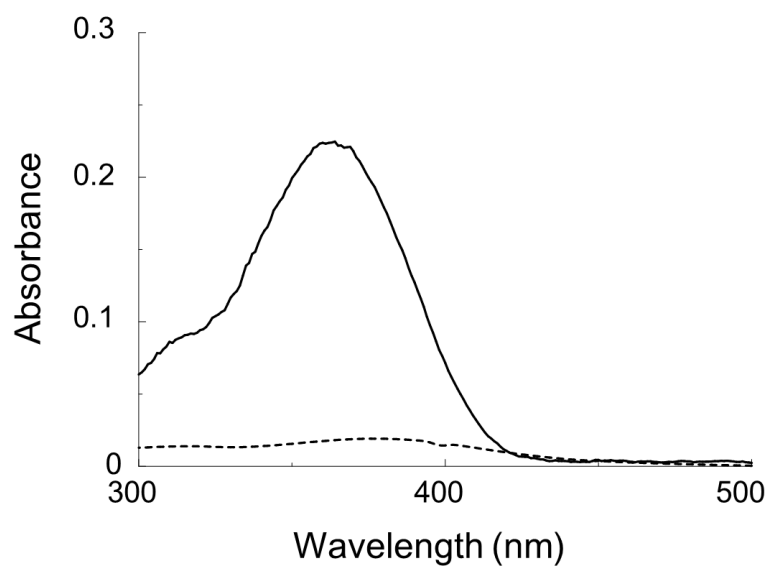


Figure S1. Absorbance of bare PS film containing DN crystals before UV irradiation (solid) and after UV irradiation (dotted line).

Raman Spectra of PS Films Containing DN Crystals

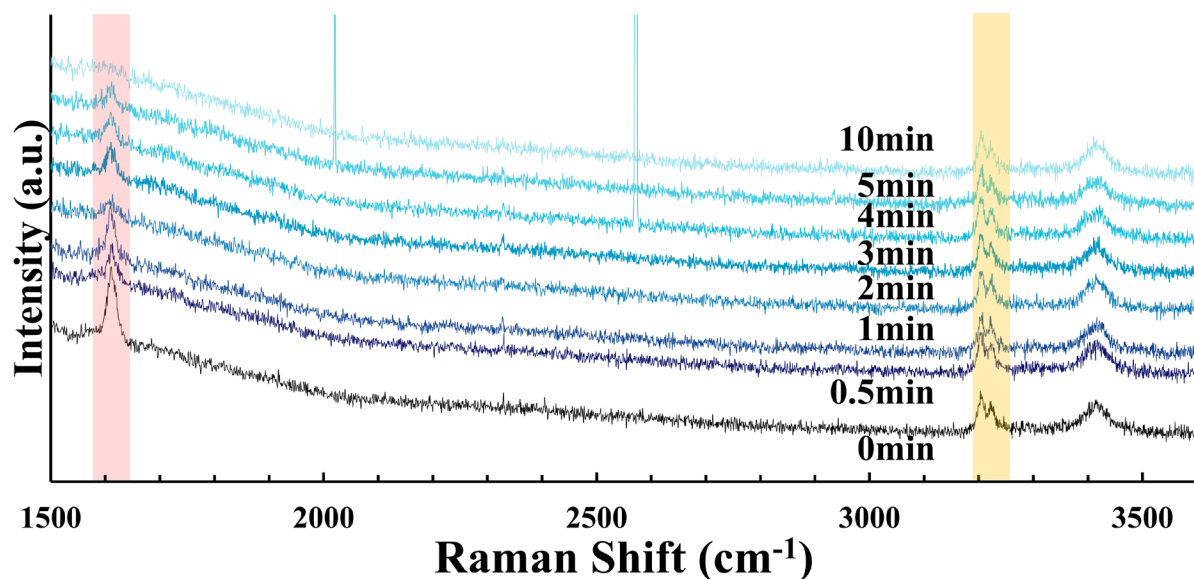


Figure S2. Raman spectra of PS films containing DN crystals before and after UV irradiation. The exposure time of UV light was varied from 0 to 10 minutes. The red and yellow shadows indicate Raman signals from carbon-carbon double bonds and hydroxyl groups. While the intensity of hydroxyl group does not change upon UV irradiation, the intensity of carbon-carbon double bond decreased.

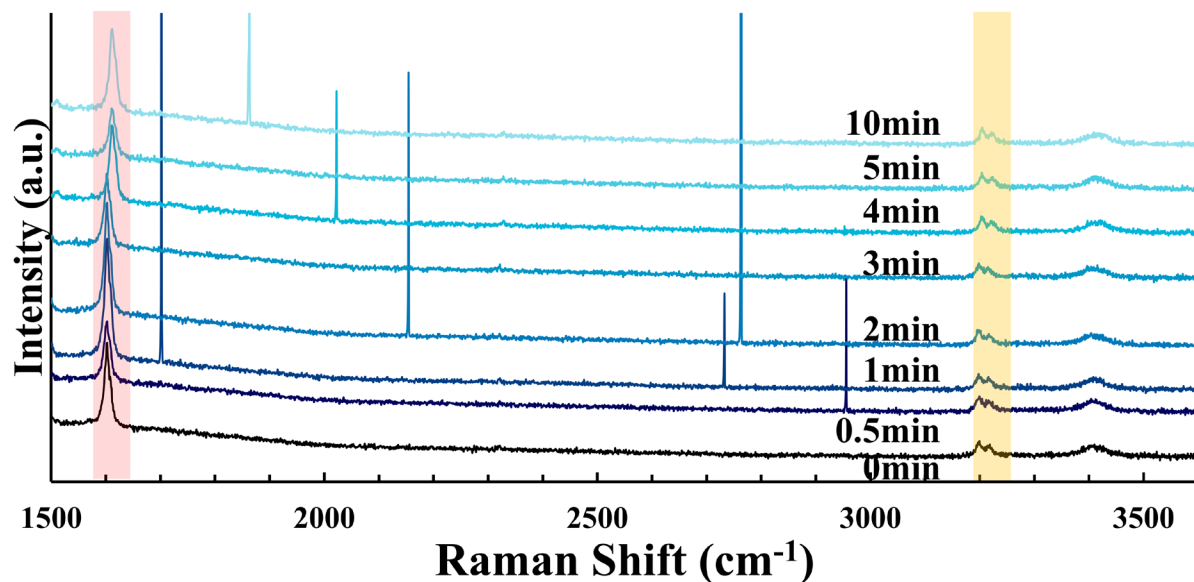


Figure S3. Raman spectra PS films containing DN crystals before and after visible light irradiation. The exposure time of visible light was varied from 0 to 10 minutes. The red and yellow shadows indicate Raman signals from carbon-carbon double bonds and hydroxyl groups. While the intensity of hydroxyl group does not change upon visible light irradiation, the intensity of carbon-carbon double bond decreased.

Light Irradiation (450nm~) on DN under Strong Coupling

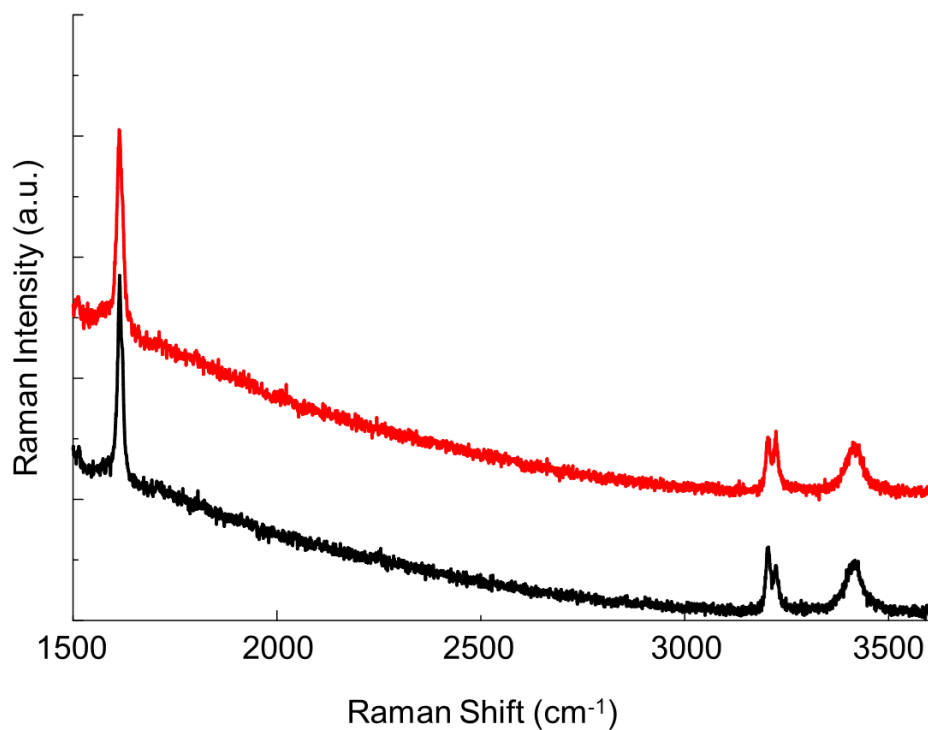


Figure S4. Raman spectra of DN in an FP cavity before light irradiation (black) and after 10 minutes of light irradiation with wavelengths above 450 nm (short-wavelength cut filter LVX450, 450 nm~).

Transmission Spectrum of DBR Mirror

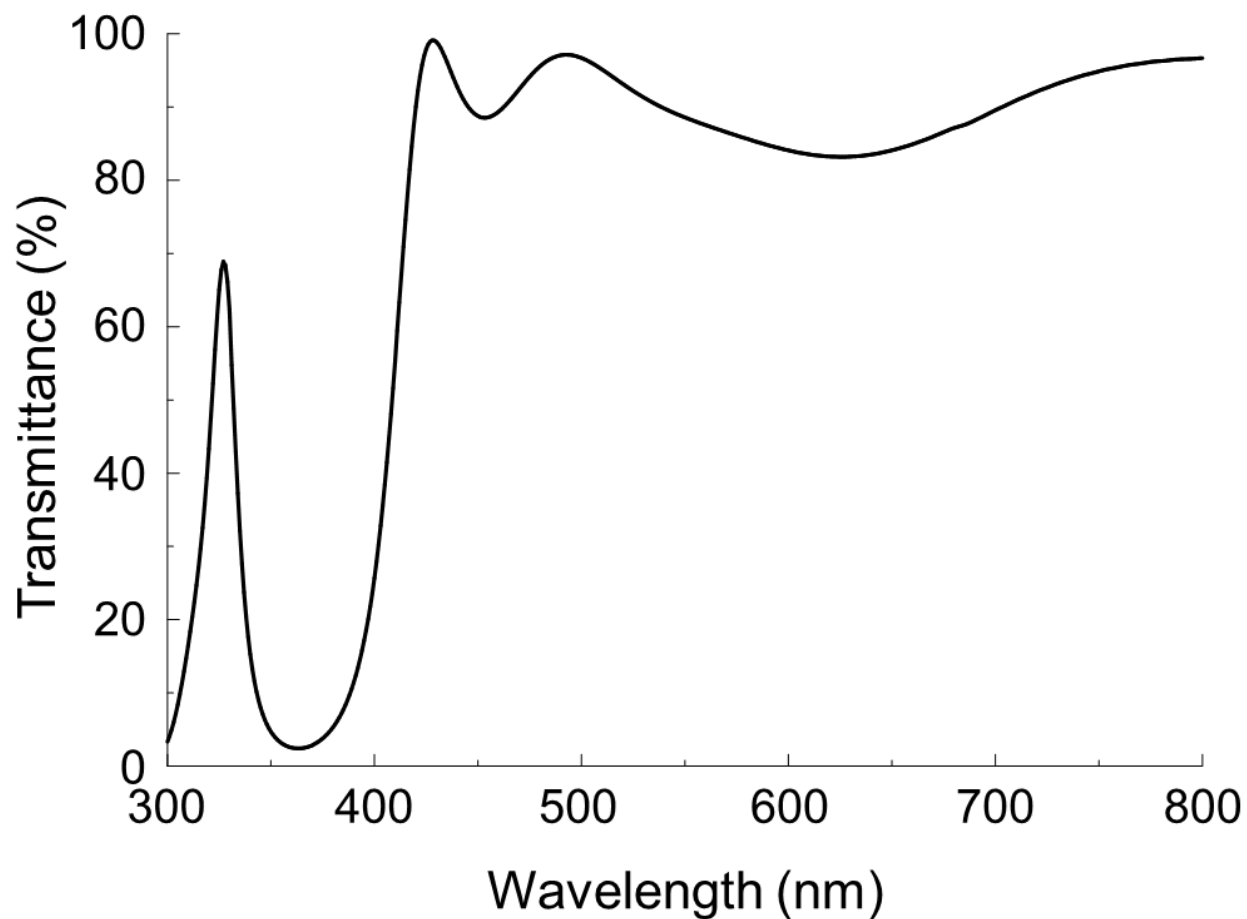


Figure S5. Transmission spectrum of DBR mirror. The DBR mirror act as the reflective mirror around 375 nm which corresponds to the absorbance of DN crystals. However, the DBR mirror allows the irradiation of visible light and 785 nm laser of Raman spectroscopy.

Fitting Coupled Oscillator Model

The polariton dispersion in Figure 2 is calculated by using the coupled harmonic oscillator model. The equation describes the 2×2 matrix CHO Hamiltonian:

$$\begin{pmatrix} E_{cavity}(\theta) & \Omega \\ \Omega & E_{Exciton} \end{pmatrix} \begin{pmatrix} \alpha \\ \beta \end{pmatrix} = E \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$$

where θ represents the incidence angle; $E_{cavity}(\theta)$ is the cavity photon energy as a function of θ , $E_{Exciton}$ is the exciton energy of DN at 3.306 eV (375 nm) and Ω is the coupling strength. The magnitudes α^2 and β^2 correspond to the photonic and the excitonic fraction, respectively.

The cavity photon dispersion is given by:

$$E_{cavity}(\theta) = \sqrt{\left(E_{cavity}^2 \times \left(1 - \frac{\sin^2 \theta}{n^2} \right)^{-1} \right)}$$

where E_{cavity} represents the cavity modes energy at $\theta = 0^\circ$, n is the refractive index. The theoretical fitting dispersion of the uncoupled cavity modes is shown in Figure 2b (dotted line). Diagonalization of this Hamiltonian yields the eigenvalues, $E_{\pm}(\theta)$, which represents the upper and lower polariton (UP and LP) in-plane dispersions,

$$E_{\pm}(\theta) = \frac{E_{exciton} + E_{cavity}(\theta)}{2} \pm \frac{1}{2} \sqrt{(E_{Exciton} - E_{cavity})^2 + 4\hbar^2 \Omega^2}$$

Normalized Conversion

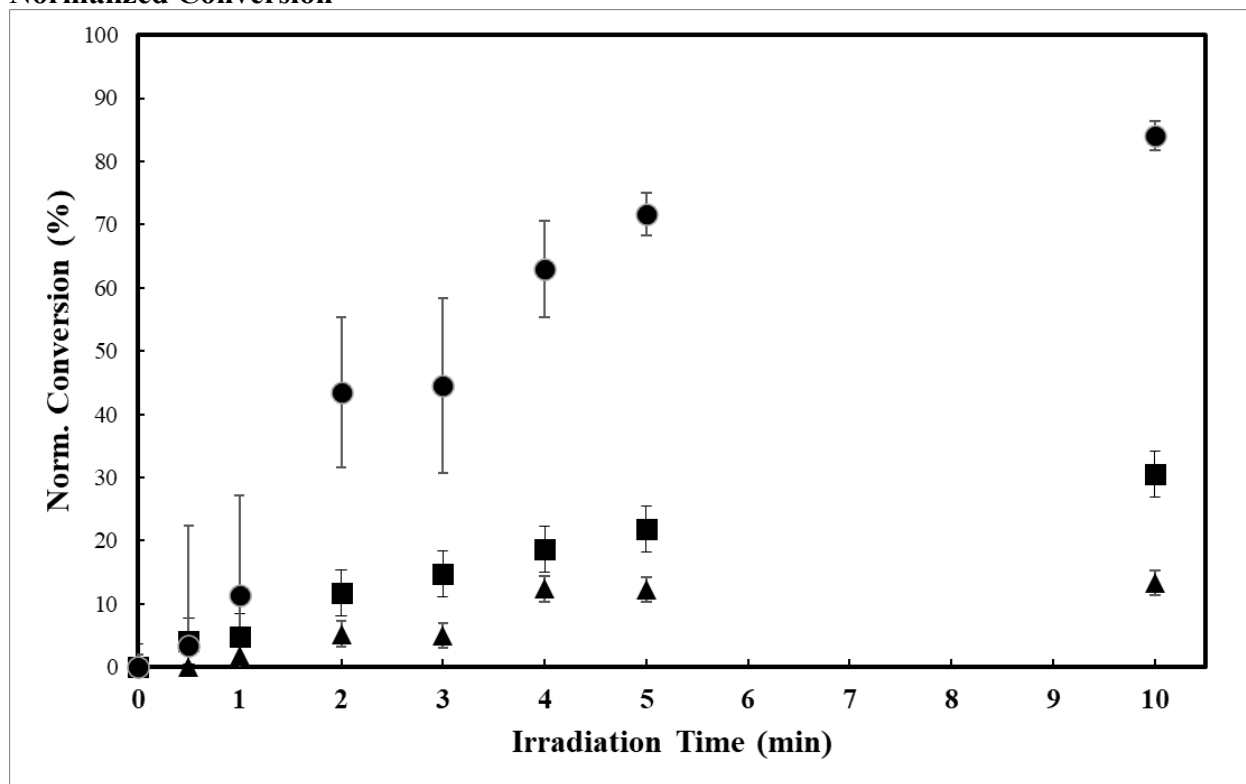


Figure S6. The conversion normalized by irradiance ($7.6 \times 10^{-2} \text{ W/cm}^2$): UV light irradiation without strong coupling (orange squares), visible light irradiation without strong coupling (black triangles), and visible light irradiation under strong coupling (purple circles).

Transmittance Spectra of DN Crystals in Detuned Cavities

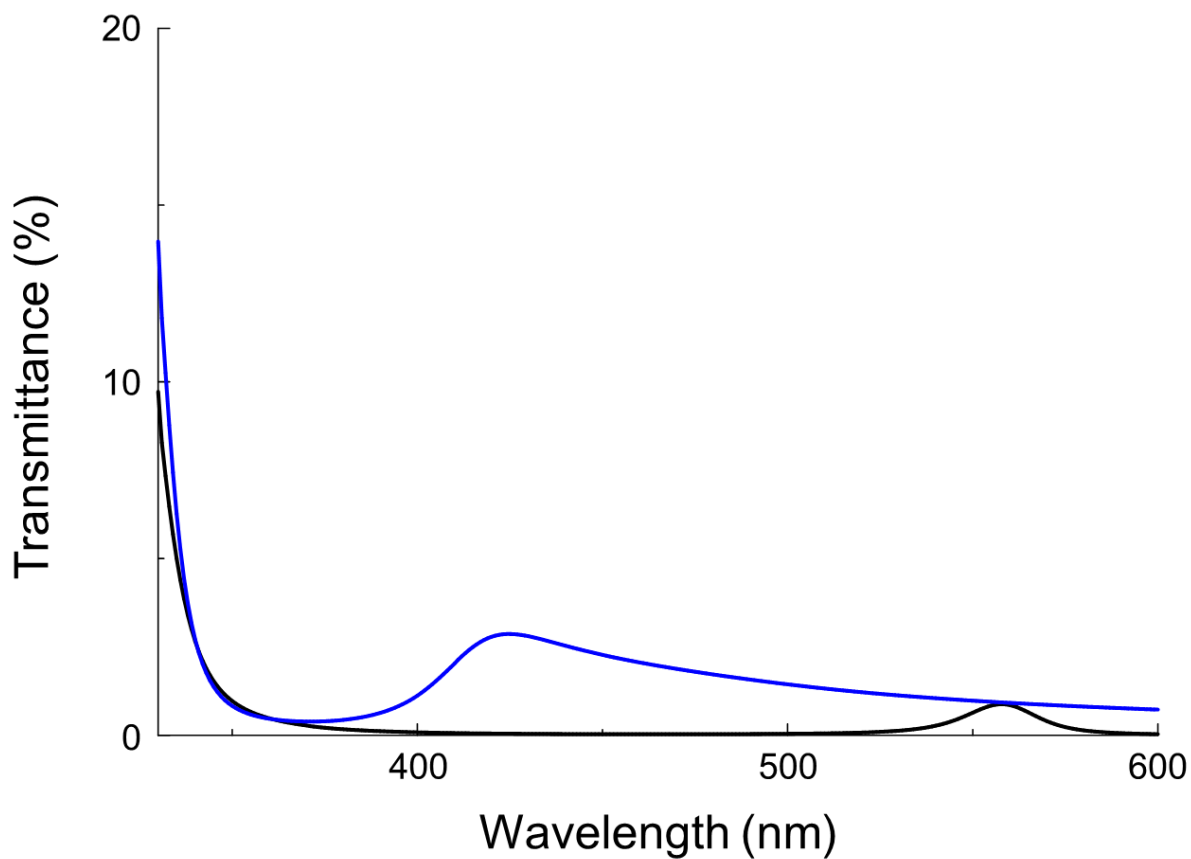


Figure S7. Transmittance spectra of cavities with the mirror separation detuned from the exciton of DN (365nm). The cavity with both Ag mirrors exhibits the cavity mode at 558 nm (black). As the DBR mirror does not reflect light around 558 nm, the cavity mode was not observed in this wavelength region (blue). In essence, the detuned cavity with Ag and DBR mirrors functions similarly to a half-mirror cavity.

Raman Spectra of DN Crystals in Detuned Cavities

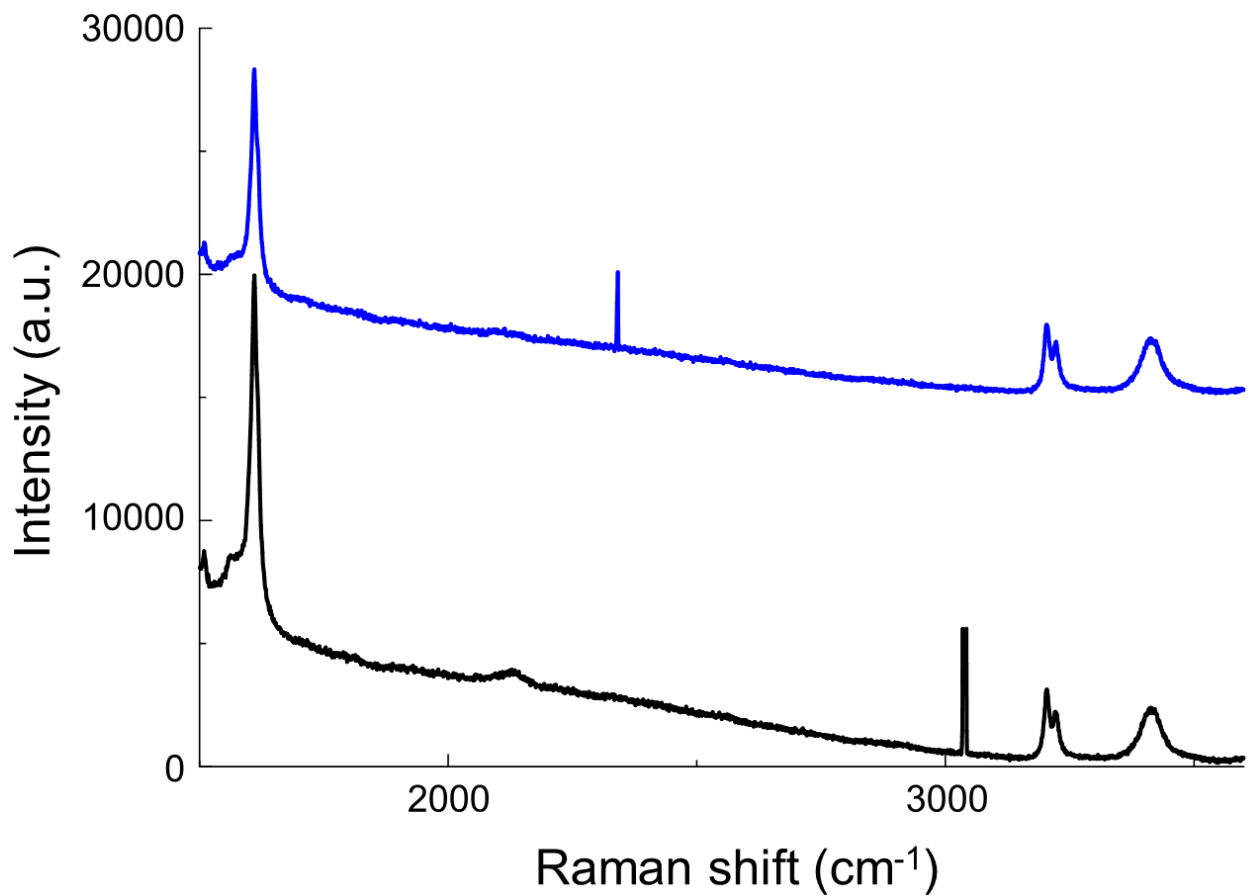


Figure S8. Raman spectra of DN in detuned cavities: 0 min (black) and 10 min (blue) irradiation on cavities.

Estimation of Reaction Kinetics

The reaction kinetics of photocyclization of DN can be assumed to be the secondary reaction. The chemical kinetic equation can be written as the Eq. S1. $[A]$ is the concentration of DN. k is the reaction kinetics. t is the time.

$$-\frac{d[A]}{dt} = k[A]^2 \text{ (Eq. S1)}$$

Eq. S1 can be deformed as follows.

$$-\frac{d[A]}{[A]^2} = k dt \text{ (Eq. S2)}$$

$$-\int_0^t \frac{d[A]}{[A]^2} = k \int_0^t dt \text{ (Eq. S3)}$$

Eq. S3 can be deformed as follows. $[A]_0$ and $[A]_t$ are the concentration of DN at the initial state and at a certain time.

$$\frac{1}{[A]_t} - \frac{1}{[A]_0} = kt \text{ (Eq. S4)}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0} \text{ (Eq. S5)}$$

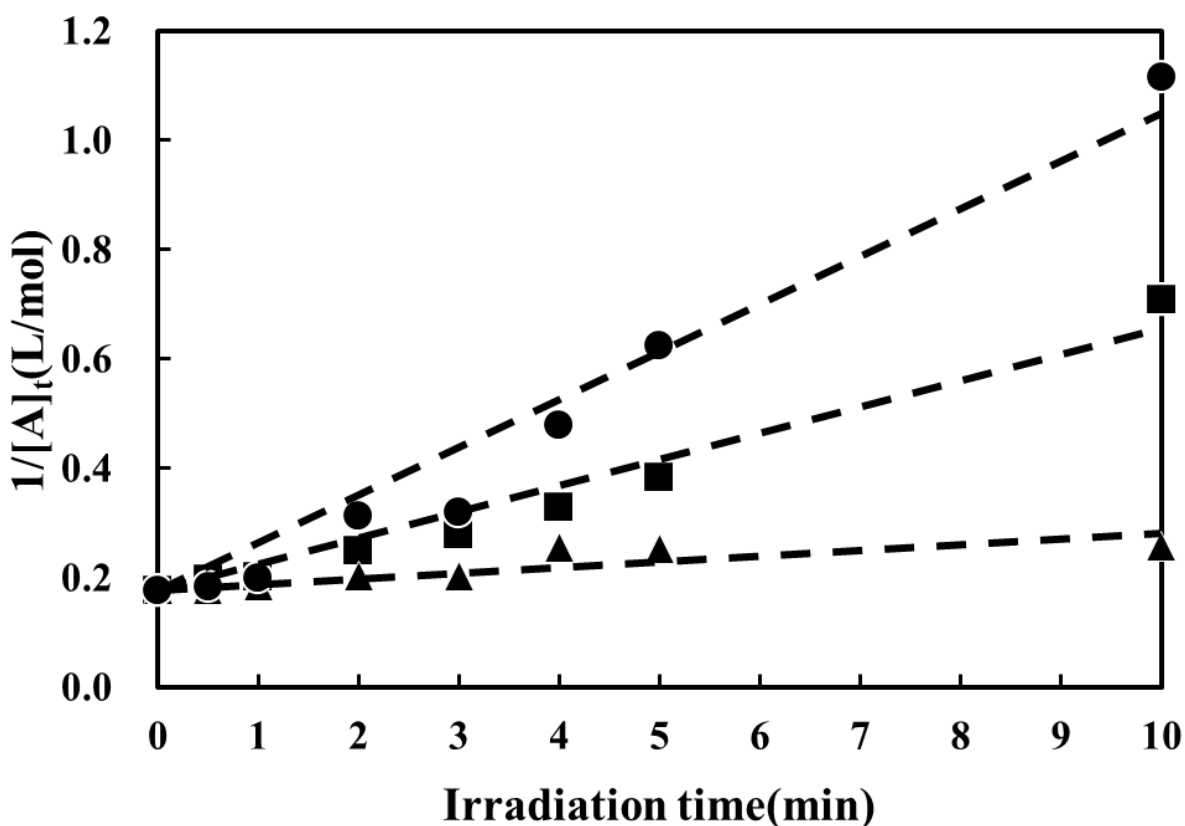


Figure S9. Plot of $1/[A]_t$ against time: UV light irradiation without strong coupling (orange squares), visible light irradiation without strong coupling (black triangles). The slope indicates k . The k values for UV light irradiation without strong coupling (orange squares), visible light irradiation without strong coupling (black triangles) are estimated to be 1.1×10^{-2} , 4.8×10^{-2} and 8.7×10^{-2} (s^{-1}) respectively.

The photocyclization rate of DN under visible light irradiation under strong coupling remains slower than that of direct UV irradiation on bare DN crystals. Nevertheless, the ability to drive the photocyclization under milder conditions (visible light irradiation) at an appreciable rate via strong light-matter interactions, should lead to less side-product formation, and much greater ability to drive the reaction with sustainable solar energy.

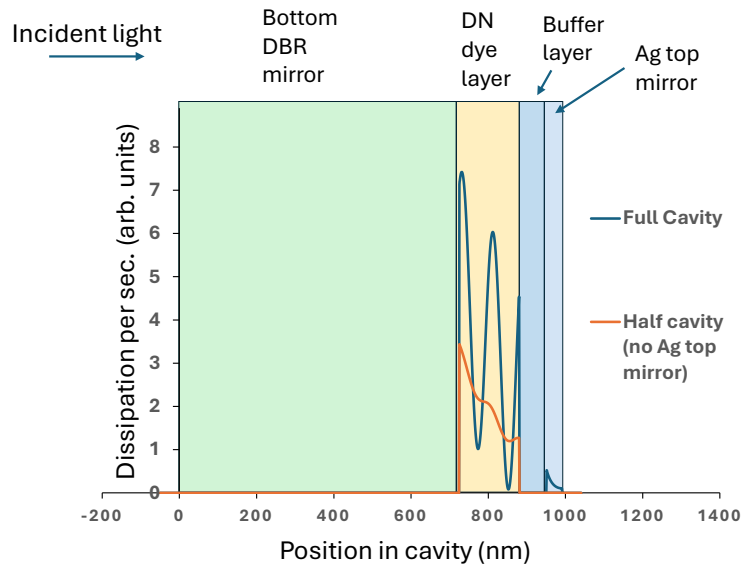


Figure S10. Relative photon dissipation rate (absorption rate) in the cavity and non-cavity structure (‘half-cavity’ without silver top mirror) as a function of position in the cavity, summed over the wavelengths 405-415 nm that are irradiated experimentally, as calculated by Transfer Matrix Method. This absorption correlates with the field strength and imaginary dielectric constant across the structure. The summed absorption across the DN layer is predicted to be higher for the cavity sample by 1.74 times, due to the better confinement of the optical field by the reflective silver top mirror. The different shaded areas indicate the position of the bottom distributed Bragg reflector (DBR) mirror, the DN crystal dye layer, a dielectric buffer layer (PVA), and the silver top mirror (only present for the cavity sample, absorption is also present in this layer). Irradiation is from the DBR mirror side.