Supporting Information for

Colossal Absorption of Molecules inside Single Terahertz Nano Antennas

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1. Derivation of quantum mechanical absorption cross section

The general definition of cross section originates from $\frac{dS}{dz} = -\sigma NS$ where dS is the Poynting vector absorbed between the points z and $z+dz$ along the path of a beam, N is the number of absorbing molecules per unit volume, and σ is the molecular absorption cross section. Following the Fermi's golden rule, one molecule absorbs $\frac{2\pi}{\hbar}\mu^2 E^2 \rho(\hbar\omega_0)\hbar\omega_0$ (Joule per second) where μ is the electric dipole moment of a molecule, $\rho(\hbar\omega_0)$ is the density of states, ω_0 and E are the resonant angular frequency and the electric field of the incident light, respectively. We define a volume Adz (A: surface area, dz: differential thickness), inside which molecular absorption is occurring. By energy conservation,

$$
\begin{aligned}
&[S(z) - S(z+dz)]A = (NAdz) \times \frac{2\pi}{\hbar}\mu^2 E^2 \rho(\hbar\omega_0)\hbar\omega_0 \\
&\Rightarrow \frac{dS}{dz} = -N \times \frac{2\pi}{\hbar}\mu^2 E^2 \rho(\hbar\omega_0)\hbar\omega_0 \equiv -\sigma NS \\
&\Rightarrow \sigma = \frac{2\pi}{\hbar}\mu^2 E^2 \rho(\hbar\omega_0)\frac{\hbar\omega_0}{S} = \frac{2\pi}{\hbar}\mu^2 \rho(\hbar\omega_0)\hbar\omega_0 \frac{E^2}{S}
\end{aligned}
$$

Therefore σ is in general sensitive to the electromagnetic environment of E^2/S.

2. Terahertz time-domain measurement and estimation of field enhancements

We measure the transmission spectra of single nano slot antennas in the wavelength range from 0.3 THz to 2.0 THz using conventional terahertz time-domain spectroscopy[1]. We use a femtosecond Ti:Sapphire laser oscillator with an 80 MHz repetition rate. The p-polarized terahertz pulses with polarization perpendicular to the long axis of the rectangle are normally incident on the sample. Figure S1 presents a schematic of our experimental setup.

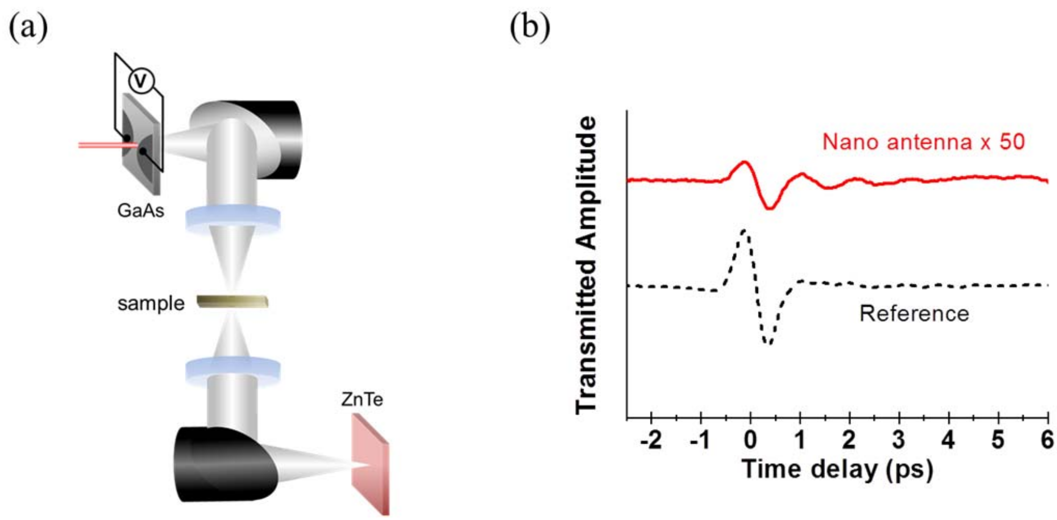

Figure S1. (a) Terahertz time-domain spectroscopy using electro-optic sampling measures far-field transmitted amplitudes at a ZnTe detector. Using terahertz lens (Tsurupica lens), we tightly focus terahertz wave with the spot size of about 1 mm. (b) Electro-optic sampling signal in time domain, through the 50 nm-wide slot antenna (top, red solid line), and the 1 mm × 1 mm aperture-only reference signal (bottom, black dashed line).

To estimate field enhancements using our setup[1], we first measured the transmitted electric field E^{A}_{far} at the detector through the substrate-only, with a 1.0 mm × 1.0 mm reference aperture on top in contact (Fig. S1(b), black dashed line). We then measure the electric field for the nano slot sample, denoted E^{S}_{far} (Fig. S1(b), red solid line). The normalized amplitude t is defined by the ratio between the two measured amplitudes: $t = \left| E^{S}_{far} / E^{A}_{far} \right|$. Following the Kirchhoff approximation and integral formalism, we obtain $E^{A}_{far} = \left(e^{ikR} / i\lambda R \right) \int E_{inc} dA_{aperture} = \left(e^{ikR} / i\lambda R \right) E_{inc} A_{aperture}$ where $A_{aperture}$ is the aperture area and R is the distance from the aperture to the detector. Likewise, using Kirchhoff integral formalism, $E^{S}_{far} = \left(e^{ikR} / i\lambda R \right) \int E^{slot}_{near} dA_{slot} = \left(e^{ikR} / i\lambda R \right) \left\langle E^{slot}_{near} \right\rangle A_{slot}$ where A_{slot} is the area of the nano slot and $\left\langle E^{slot}_{near} \right\rangle$ is the *unknown*, averaged field at the slot. Dividing the two equations, we obtain the desired near-field enhancement factor $\left\langle E^{slot}_{near} \right\rangle / E_{inc} = t / \beta$ with the coverage ratio $\beta = A_{slot} / A_{aperture}$.

3. Analytical calculation based on modal expansion with slot antenna array

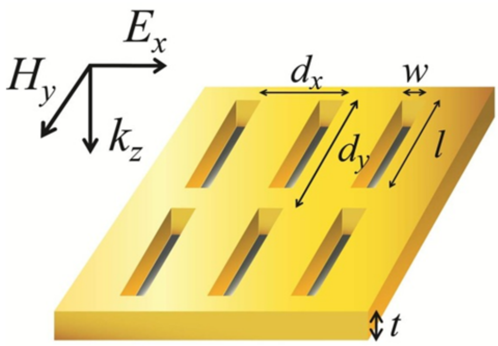

Figure S2. Schematic of an infinite array of slot antennas with a width *w*, a length *l*, a thickness *t*, a horizontal period d_x, and a vertical period d_y in a thin perfect electric conductor (PEC) film.

We perform an analytical calculation based on modal expansion assuming perfect electric conductor (PEC) and infinite array of slot antennas, as shown in Fig. S1. In an earlier work[2], with the single mode approximation counting only the half-wavelength mode for each slot, we obtain, for the normalized electric field amplitudes and energy flux (Poynting vector) at the output aperture,

$$E_x = \frac{8}{\pi k_0}\frac{\beta}{D}, \quad S_z = \frac{32}{\pi^2 |D|^2}\left|\frac{\beta}{k_0}\right|^2 \mathrm{Re}(W_3),$$

where $\beta^2 = \varepsilon_2 k_0^2 - \left(\frac{\pi}{l}\right)^2$, $D = -i\sin(\beta h)\left(\frac{\beta^2}{k_0{}^2} + W_1 W_3\right) + \cos(\beta h)\frac{\beta}{k_0}(W_1 + W_3)$, where ε_2 is the dielectric constant inside the slot, h is the metal film thickness, W_1 and W_3 are the coupling strengths of electromagnetic waves to the internal mode at the air-aperture and the aperture-substrate interfaces, respectively (for more details, see reference 1 of SI). In a thin metal film, within the conditions $\beta h << 1; d_x, d_y >> l$, the normalized electric field amplitudes and energy flux at the resonance wavelength λ_{res} , satisfying $h\frac{2\pi}{\lambda_{res}}\left(\varepsilon_2 - \left(\frac{\lambda_{res}}{2l}\right)^2\right) = \mathrm{Im}(W_1 + W_3)\Big|_{\lambda=\lambda_{res}}$, have the forms (n_1, n_3 :refractive indices of air and the substrate, respectively):

$$E_x \approx \frac{8}{\pi k_0}\frac{k_0}{\mathrm{Re}(W_1 + W_3)} = \frac{3l}{w}\frac{n_{eff}^2}{n_1^{\;3} + n_3^{\;3}},$$
$$S_z \approx \frac{32}{\pi^2}\frac{\mathrm{Re}(W_3)}{|W_1 + W_3|^2} = \frac{12}{\pi}\frac{l}{w}\frac{n_3^{\;3} n_{eff}^2}{\left(n_1^{\;3} + n_3^{\;3}\right)^2},$$

where $n_{eff} = \lambda_{res}/2l$ is the effective refractive index of our structure. Note that the cross section enhancement factor $\Sigma = \frac{E^2}{Z_0 S}$ is proportional to $1/w$.

4. Molecular absorption enhancements inside slot antenna array in a PEC film estimated by the analytical model

Using the analytical model above, we obtain the Poynting vector (S_z) enhancement spectrum of a slot antenna array with l = 90 μm, w = 50 nm, h = 50 nm, d_x = 90 μm, and d_y = 100 μm, as shown in Fig. S2a (black solid line). Both the peak position of this spectrum and the enhancement are in good agreement with experiments without RDX (Fig. 1d of the main text).

Fig. S2b shows the dielectric constants of RDX molecules, assuming a homogeneous Drude-Lorentz model, estimated from the measured absorption of the RDX film on the bare substrate (Fig. 1b). With the estimated dielectric constants inside the slot, we observe a dramatic decrease of the S_z enhancement at the resonance, as shown in Fig.

S2a (red dashed line), and estimate the molecular absorption enhancement of about 4×10^{6}, which is in agreement with the experimental values within a factor of two.

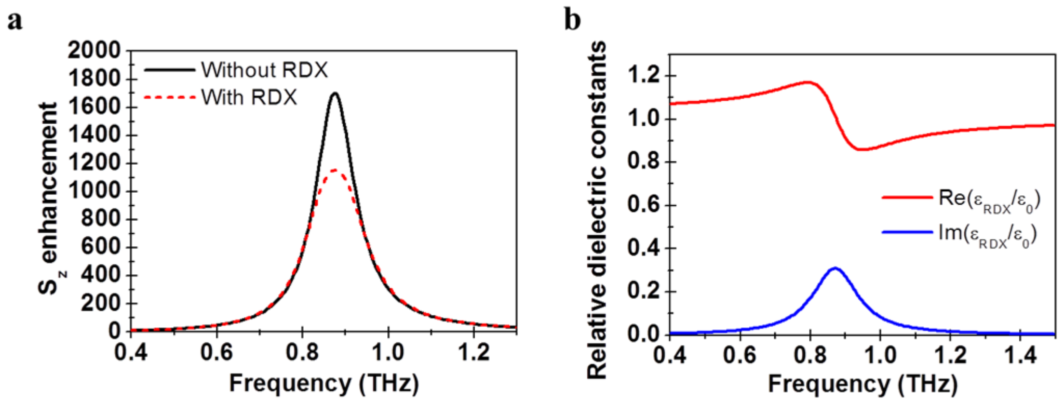

Figure S3. a, Poynting vector (S_z) enhancements without and with RDX are obtained by the analytical model based on the modal expansion assuming PEC. **b,** Dielectric constants of RDX molecules are estimated by the Drude-Lorentz model based on the bulk RDX experimental results.

5. Molecular absorption enhancements inside slot antenna array in a real metal film estimated by the FDTD simulations

For a better understanding of molecular absorption enhancement of THz nano slot antenna within a *real metal* film, three-dimensional Finite Difference Time Domain (FDTD) analysis was carried out[3]. To implement the response of real metal in the FDTD analysis within the frequency range of interest, the Drude model was adopted for the calculation of the dielectric parameters of the metal (gold)[4]: $\varepsilon(\omega)=\varepsilon_\infty-\dfrac{\omega_p{}^2}{\omega(\omega+i\gamma)}$, where ε_∞=1, ω_p=1.37×10^4 (THz), γ=40.7 (THz). We design our nano slot antenna array structure with RDX molecules inside, top, and bottom (Fig. S3a) to better illustrate the essential physics without the loss of generality. We used the Drude-Lorentz estimation, already shown in Fig. S2b, to the dielectric constant of RDX molecule layers in the simulated structure.

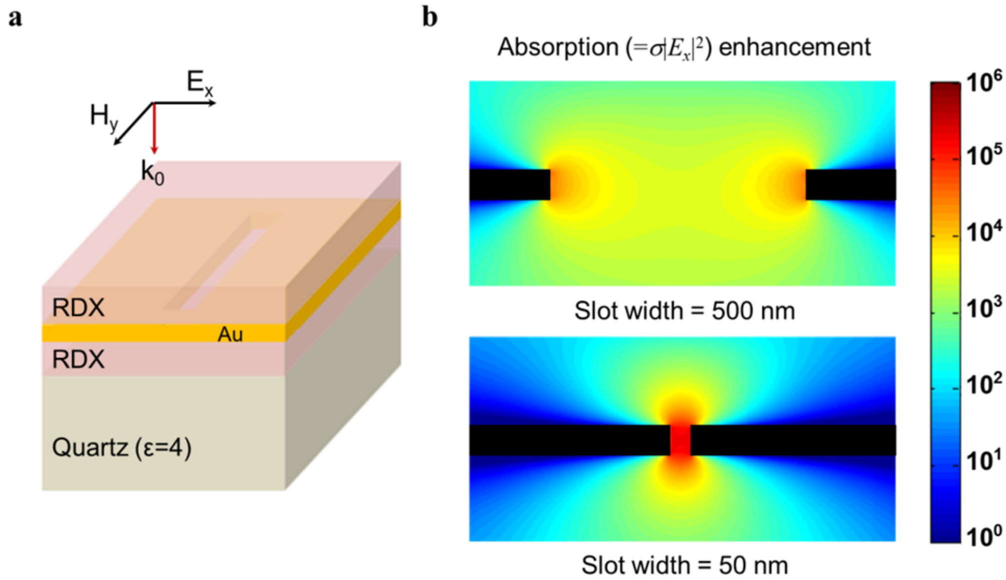

Figure S4. a, Schematic diagram of our nano slot antenna structure surrounded by RDX molecules inside, top (thickness of 200 nm), and bottom (thickness of 200 nm) for FDTD simulations. **b**, Absorption patterns of $\sigma|E_x|^2$, where σ is the conductivity of RDX molecules, are simulated by FDTD analysis with the slot widths of 500 nm and 50 nm, respectively.

Fig. S3b shows the absorption patterns of $\sigma|E_x|^2$, where $\sigma = \omega \mathrm{Im}(\varepsilon_{RDX})$ is now an effective conductivity of RDX molecules at resonance, obtained from the full scale numerical analysis at the resonance of 0.87 THz, zoomed in for an area of 800 nm by 400 nm with 500 nm- and 50 nm-width slot antenna samples (Au thickness of 50 nm). For the sake of clarity, the small loss inside metal is masked out in the plot. The absorption enhancement inside the 500 nm-width slot is approximately 2500 relative to the unperturbed incident field. When we narrow the slot width to 50 nm, as shown in Fig. S3b (bottom), the absorption enhancement is much stronger, close to 10^6 at its maximum. This is also in good qualitative agreement with the absorption enhancements estimated by PEC calculations and THz experiments.

It is noted that the absorption enhancement decreases dramatically away from the slot: from 10^6 (inside the slot) to 10^0 (at 200 nm away from the slot). Even though the coverage ratio of the slot is of the order of 10^{-6}, total absorption of molecules outside the slot can be ignored because the direct transmission is only 0.0025 %.

References

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