

Supplementary Information

Plasmonic polymer nanoantenna arrays for electrically tunable and electrode-free metasurfaces

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Materials and methods

Fabrication of Si master templates

Si master templates were prepared using e-beam lithography. Briefly, a 2 μm thermal oxide layer was grown on a fresh 4" Si wafer of 500 μm thickness (N-type, Si-Mat) using an oxidation furnace (Centrotherm, 1050 °C, 780 minutes). A 20 nm thick chromium layer was deposited using e-beam evaporation (AVAC HVC600), followed by sputtering of 24 nm thick SiO₂ (FHR MS-150 Sputter) was carried out to obtain a hard mask for RIE of nanostructures. Next, ARP 6200.13 resist (diluted in Anisole, 1:1 ratio, Allresist GmbH) was spin-coated at 3000 rpm for 60 s and baked at 180°C for 5 min. Electron beam lithography (EBL, JEOL JBX-9300FS) was carried out and the features obtained were etched using RIE (50 sccm NF₃, 25 W RF-power, 8 mbar pressure), to get nanostructures of desired depths. Finally, the sputtered SiO₂ was removed with a CF₄ etch

(Plasmatherm RIE, 40 sccm CF₄, 100 W RF-power, 100 mT pressure) and the chromium layer was removed using a chromium etchant (SunChem AB, Sweden). The substrate was then cleaned using piranha solution (con. H₂SO₄ and H₂O₂ at 2:1 ratio, 120 °C) for 10 minutes, rinsed with deionized water, and dried using a nitrogen gun.

Fabrication of PEDOT:Sulf films

Double-side polished (DSP) Si wafer substrates (3.0×2.5 cm²) were precleaned. Oxidant solution for polymerization of 3,4-ethylenedioxythiophene (EDOT, Sigma-Aldrich) monomer was prepared by mixing 0.03 g of iron(III) trifluoromethane sulfonate (Fe(OTf)₃, Alfa Aesar), 0.2 g of the triblock copolymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (Sigma-Aldrich) and 0.8 g of 99.5 % ethanol. Oxidant films were deposited by spin coating at 1500 rpm for 30 s on the substrates and annealed at 70 °C for 30 s on a hotplate. The samples were transferred into a heated vacuum chamber at 30 °C and placed next to EDOT droplets cast on a glass substrate. After 40 min of polymerization at a pressure of 70 mbar, the samples were taken out, rinsed with ethanol multiple times to remove the by-products and unreacted residues, and blown with nitrogen. To replace the OTf counterions in the resulting PEDOT:OTf with sulfate counterions (HSO₄⁻), the samples were soaked in 1M H₂SO₄ for 10 min at room temperature and rinsed with deionized water, followed by baking on the hotplate at 50 °C for 10 min. Samples were then soaked in acetone for 10 min and blown with nitrogen to remove the residual photoresist.

Fabrication of PEDOT:Sulf nanostructures

Before each replication process, hydrophobic treatment of the original template or mold was performed by exposing the surface to vapors of 0.03 M trichloro(1H,1H,2H,2H-

perfluorooctyl)silane (FOTS, Sigma-Aldrich) dissolved in hexane for 1 h, followed by annealing at 120 °C for 20 min. The first mold was prepared on glass substrates. For better adhesion, the glass substrates were covered with glass primer (Changsung Sheet) by spin coating at 3000 rpm for 40 s, followed by baking at 135 °C for 10-20 min. 1-2 drops of a polyurethane acrylate (PUA) resin (311RM, Changsung Sheet) were deposited on a Si master template and covered with a glass substrate. After UV curing and removing the excessive resin, the glass substrate with nanopatterned resin was detached from the Si master, which constitutes the first mold. The second and third molds were prepared by repeating the same replication process multiple times. Only the last molds for photoresist patterning were fabricated using more flexible PUA resin (ERM, Changsung Sheet) and polydimethylsiloxane (PDMS) substrates. Photoresist (AZ5214E, MicroChemicals, diluted with propylene glycol monomethyl ether acetate by 1:5 volume ratio) was cast on the last mold, and then directly sandwiched between the mold and the PEDOT:Sulf film. After drying at 50 °C for 30 min and subsequently cooling down to room temperature, the detachment of the mold left the photoresist nanopatterns on the PEDOT:Sulf film. Reactive oxygen plasma etching (12 sccm, 50 W) was applied using the photoresist nanopatterns as a mask. To confirm complete etching of the exposed part of the PEDOT:Sulf films not covered with photoresist, multiple times of etching for a short time (~15 s) was applied and the extinction spectra were measured between each etching process.

Fabrication of electrically tunable devices

PEDOT:Sulf films with nanostructures were prepared as partially covering DSP Si wafer substrates. 40 nm thick Au electrodes with 2 nm thick Cr adhesion layers were deposited using e-beam evaporation; one electrode was placed on top of the PEDOT:Sulf and the other was on the

empty area of the substrate. The ion gel layer was prepared in a similar way to the previous work [1]. It starts with preparing a solution of poly[(vinylidene fluoride)-co-hexafluoropropylene] (PVDF-HFP, $M_n = 130000$, Sigma-Aldrich) in acetone at a 1:6 weight ratio. The solution was stirred overnight at 50 °C to completely dissolve PVDF-HFP in acetone. The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM⁺][TFSI⁻], Sigma-Aldrich) was then added into the PVDF-HFP:acetone solution at 4:7 ratio, and the final solution was stirred on a hotplate at 50 °C for 30 min. The ion gel solution was spin-coated at 500 rpm for 60 s to complete the devices. The spin-coated ion gel was dried at 60 °C for 1 h.

Optical and electrical measurements

All extinction spectrum measurements were performed using Fourier transform infrared (FT-IR) microscopy (HYPERION II, Bruker) in a spectral range from 800 cm^{-1} to 2500 cm^{-1} (from 2.5 μm to 12.5 μm). A linear polarizer was used to control the polarization of the incident light. The knife edge aperture limits the detected signal to a square area with a side length of approximately 100 μm in the sample. This enables the measurements of the signal only from the (inverted) nanostructure arrays. Transmission ($T = I_t/I_0$) was measured to determine the extinction ($E = 1 - T$), where I_t and I_0 are the transmitted light intensity with a test sample and a reference sample, respectively. All electrical measurements were conducted using a source meter (2450, Keithley).

Finite-Difference Time-Domain (FDTD) Simulations

FDTD Solution (Lumerical) was used to determine the simulated spectra. The complex permittivity of PEDOT:Sulf determined by ellipsometry in the previous work was imported for the simulations [2]. The simulation consists of an optically thick Si substrate (Si (Silicon) – Palik)

and a PEDOT:Sulf nanostructure array on top. A plane-wave polarized in the x -axis with a wavelength range of 1-12 μm was used as an incoming source from the substrate side. The mesh size was set to 5 nm for all three axes. Anti-symmetric, symmetric, and perfectly matched layers (PML) boundary conditions were respectively used for the x -, y -, and z -axis to establish the periodic nanostructure array in the xy -plane. A transmission (T) monitor was installed on the opposite side of the incoming light source to calculate the extinction ($E = 1 - T$), mimicking the experiments.

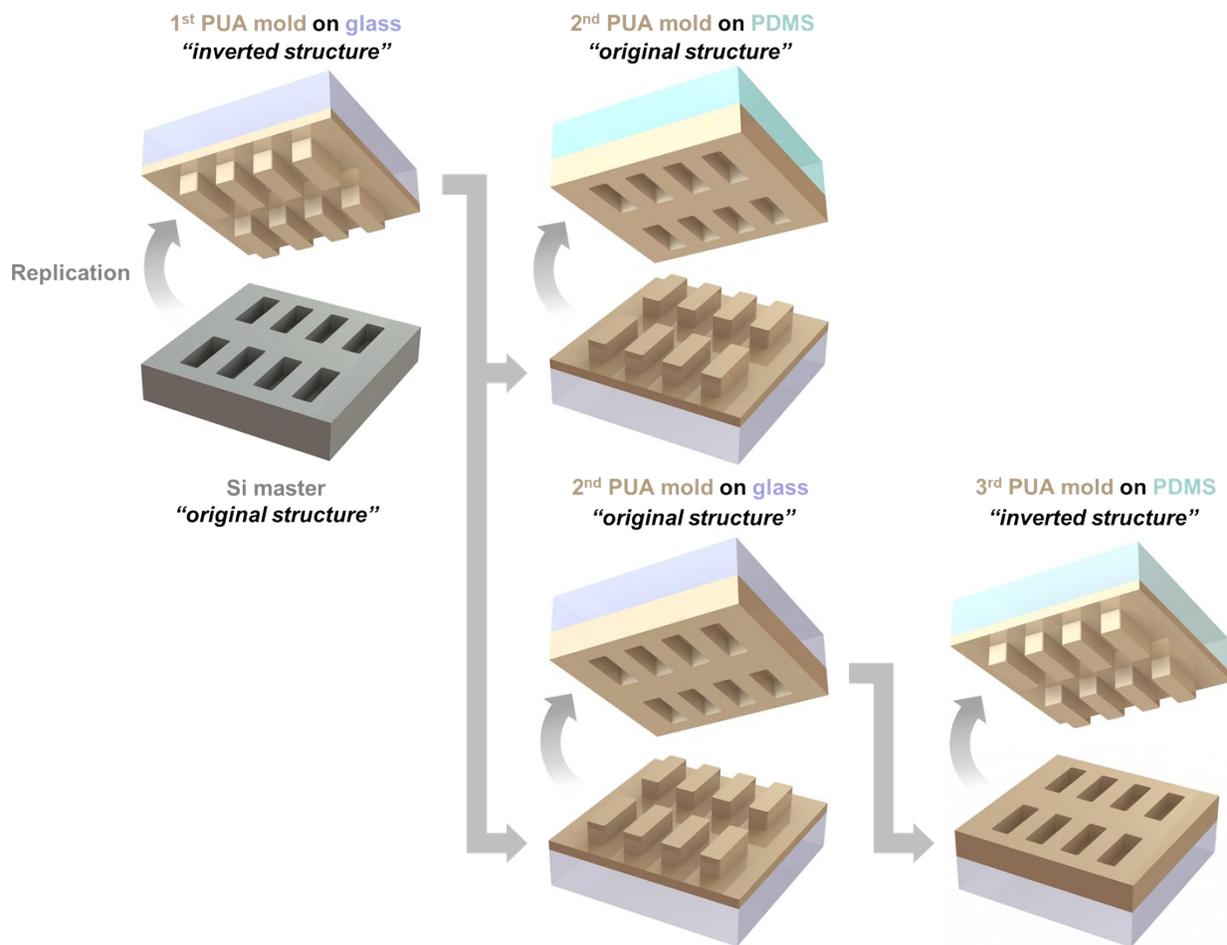


Figure S1. Fabrication scheme of various PUA molds from the silicon master structure. Even (odd) number of times replications result in the PUA mold with an original (inverted) structure.

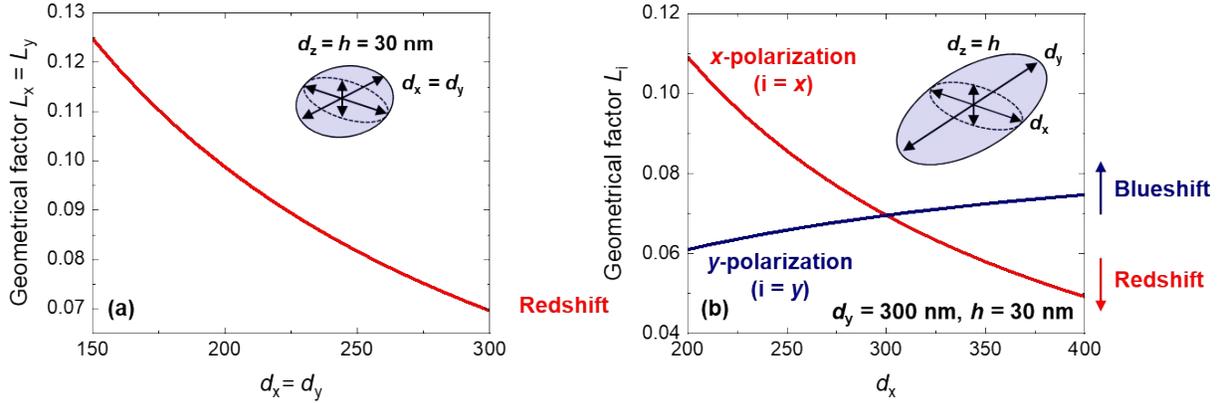


Figure S2. Geometrical factor L_i as a function of d_x of (a) nanodisks and (b) nanorods when approximated as spheroids and ellipsoids, respectively.

The extinction cross section can be calculated using dipolar polarizability as follows.

$$\sigma(\lambda) = k \operatorname{Im}[\alpha_i(\lambda)]$$

Here, $\alpha_i(\lambda)$ is the polarizability of an ellipsoid with three characteristic dimensions, d_x , d_y , and d_z , along the principal axes ($i = x, y, z$) [3].

$$\alpha_i(\lambda) = \frac{\pi d_x d_y d_z}{2} \frac{\varepsilon(\lambda) - \varepsilon_m}{3\varepsilon_m + 3L_i(\varepsilon(\lambda) - \varepsilon_m)},$$

where $\varepsilon(\lambda)$ is the complex permittivity of the ellipsoid material, ε_m is the permittivity of the surrounding medium, and L_i is a geometrical factor given as below:

$$L_i = \frac{d_x d_y d_z}{16} \int_0^\infty \frac{dq}{(q + d_i^2/4)f(q)}, \quad f(q) = \sqrt{(q + d_x^2/4)(q + d_y^2/4)(q + d_z^2/4)}.$$

The plasmon resonance condition is satisfied when the real part of the denominator of α_i becomes zero, i.e. $L_i = \varepsilon_m / (-\operatorname{Re}[\varepsilon(\lambda)] + \varepsilon_m)$. Therefore, the resonance for the ellipsoid with smaller (larger) L_i occurs when the magnitude of the negative permittivity becomes larger (smaller) at the longer (shorter) wavelength, which indicates a redshift (blueshift) of the plasmon resonance. Figure S2a

explains the redshift with increasing diameter $d = d_x = d_y$ when nanodisks are approximated as spheroids. Figure S2b explains the redshift (blueshift) with increasing d_x for x -(y -)polarization shown in Figs. 2k-2n, by approximating nanorods as ellipsoids.

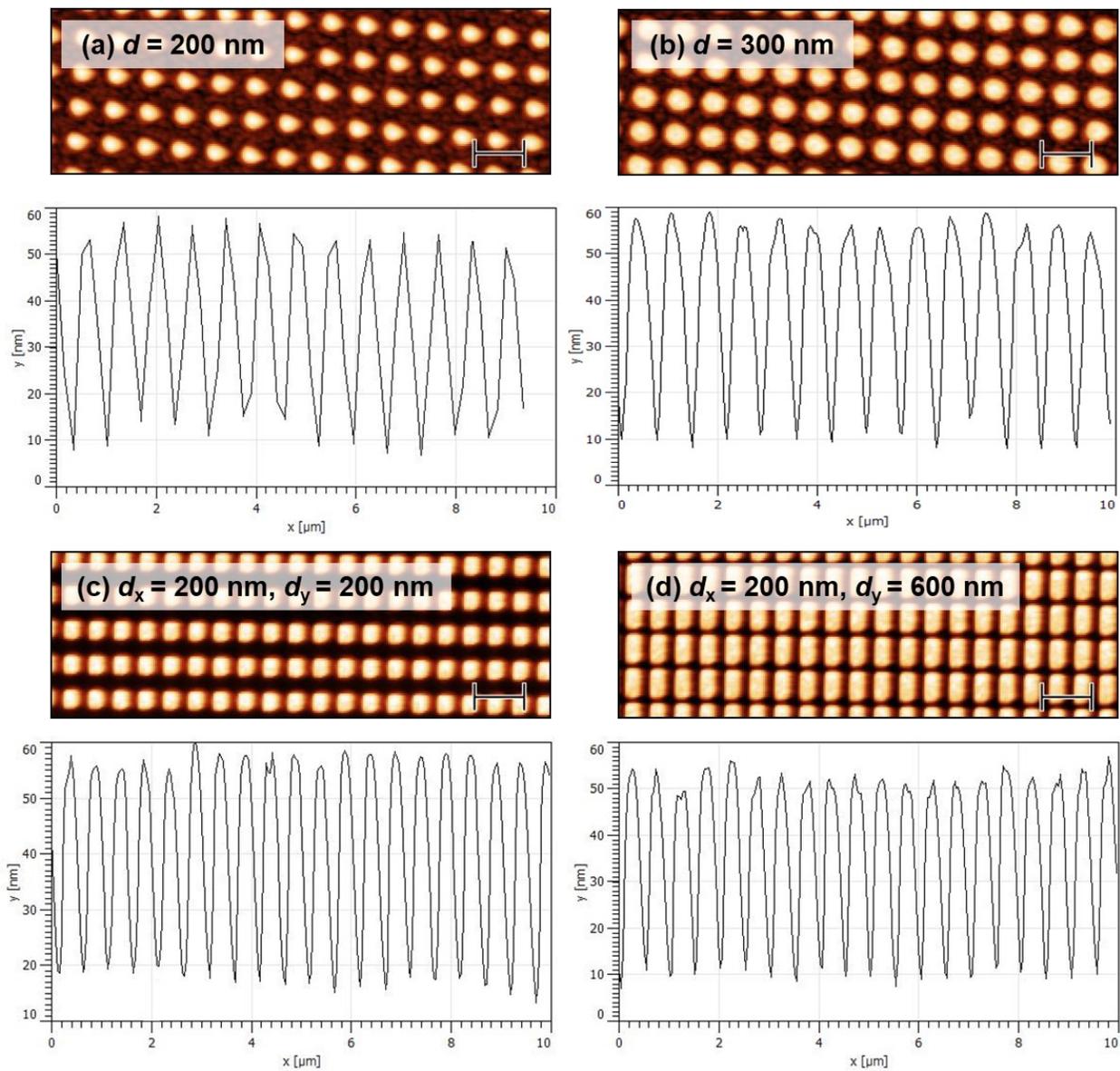


Figure S3. (a, b) Atomic force microscopy images of resulting PEDOT:Sulf nanodisk arrays with different diameters. (c, d) Same for nanorod arrays with different d_x and d_y . The scale bars are all 1 μm . The height of the entire nanostructures, 35-45 nm, indicates 5-15 nm thick photoresist leftover on top of 30 nm thick PEDOT:Sulf nanostructures.

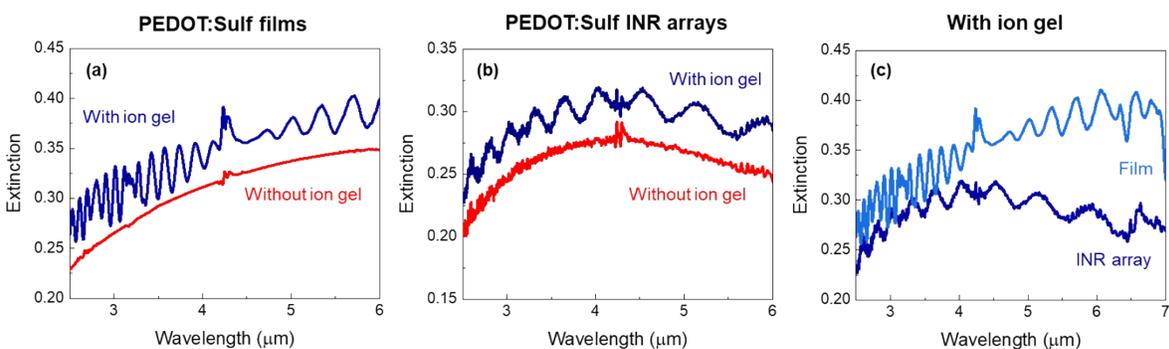


Figure S4. Extinction spectra before and after ion gel deposition (a) for PEDOT:Sulf films and (b) for PEDOT:Sulf INR arrays. (c) The same spectra with ion gel plotted in the same scale for a direct comparison.

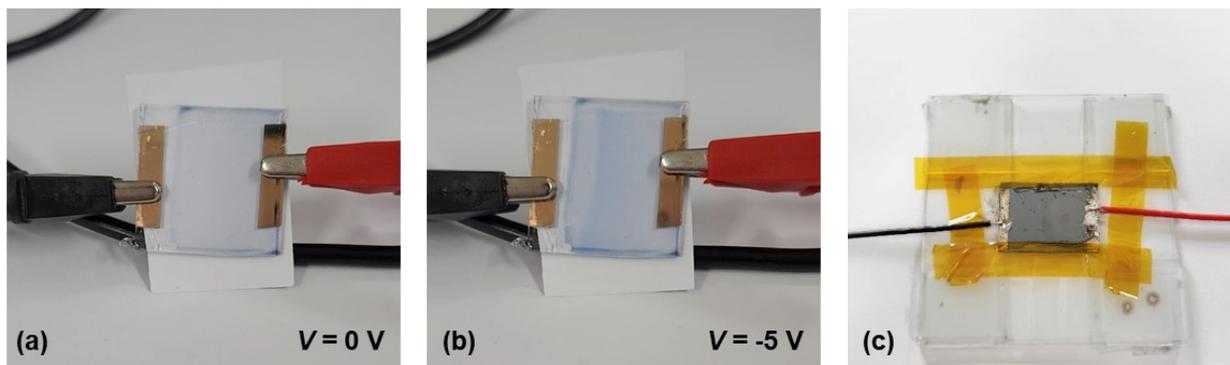


Figure S5. Photos of devices with in-plane configuration for the applied voltages of (a) 0 V (i.e. oxidized state) and (b) -5 V (i.e. reduced state). Glass substrates were used to see the color change by bare eyes. (c) A photo of the same device built on a Si substrate for the FTIR measurements.

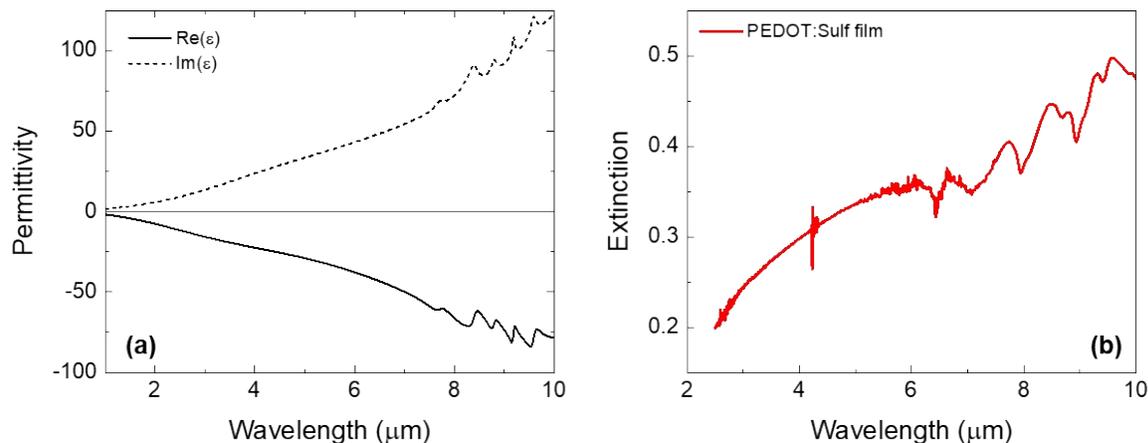


Figure S6. (a) Complex permittivity values for PEDOT:Sulf obtained using ellipsometry measurements in our previous study [2]. (b) Extinction spectrum for PEDOT:Sulf film. Both clearly show that PEDOT:Sulf can behave like a metal up to 6 μm with no molecular vibration modes therein.

References

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