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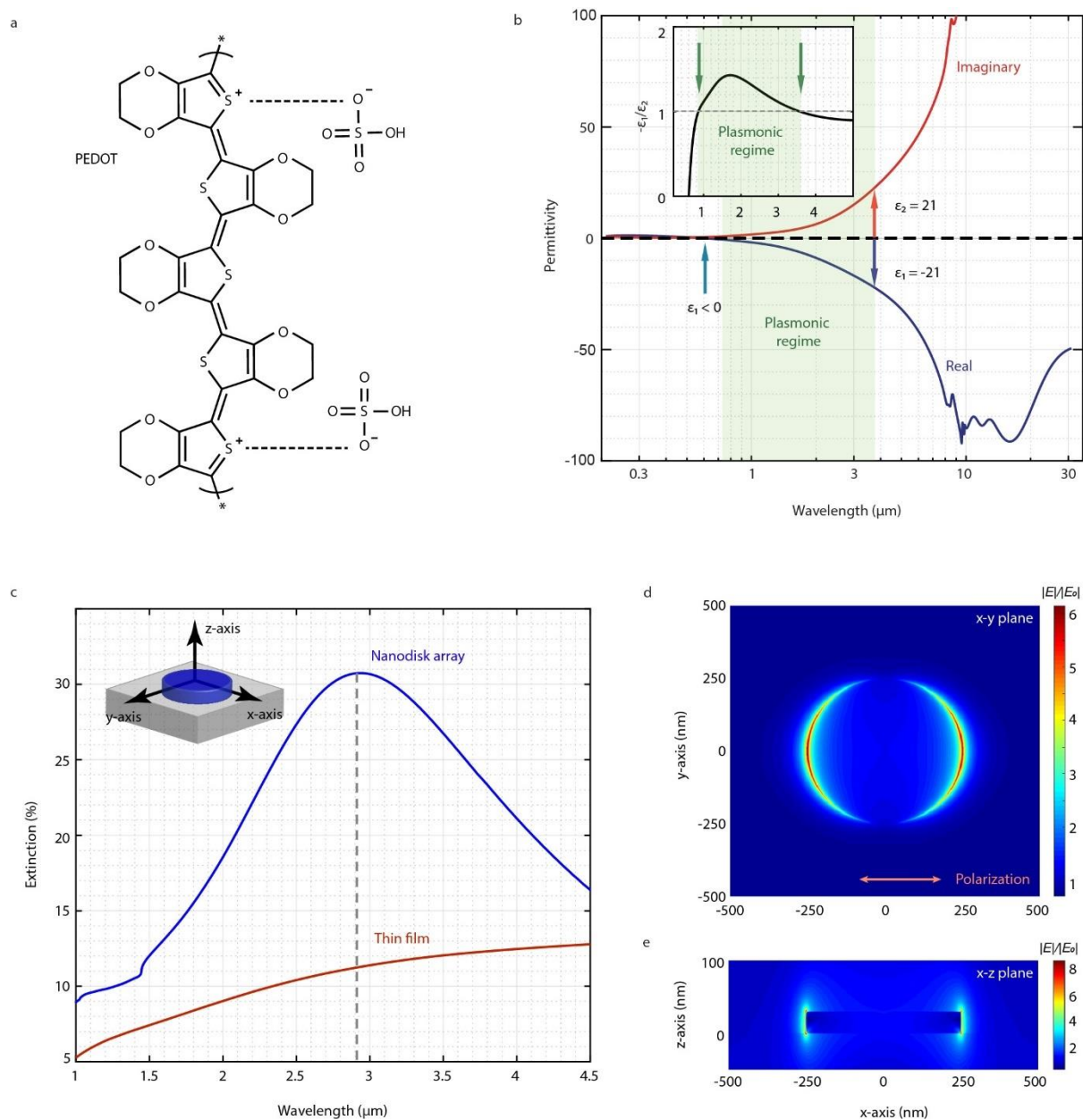
Conductive Polymer Nanoantennas for Dynamic Organic Plasmonics

Shangzhi Chen¹, Evan S. H. Kang¹, Mina Shiran Chaharsoughi¹, Vallery Stanishev², Philipp Kühne², Hengda Sun¹, Chuanfei Wang¹, Mats Fahlman¹, Simone Fabiano¹, Vanya Darakchieva² and Magnus P. Jonsson^{1*}

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Being able to dynamically shape light at the nanoscale is one of the ultimate goals in nanooptics¹. Resonant light-matter interaction can be achieved using conventional plasmonics based on metal nanostructures, but their tunability is highly limited due to fixed permittivity². Materials with switchable states and methods for dynamic control of light-matter interaction at the nanoscale are therefore desired. Here we show that nanodisks of a conductive polymer can support localised surface plasmon resonances in the near-infrared and function as dynamic nanooptical antennas, with their resonance behaviour tuneable by chemical redox reactions. These plasmons originate from the mobile polaronic charge carriers of a poly[3,4-ethylenedioxythiophene:sulfate (PEDOT:Sulf) polymer network. We demonstrate complete and reversible switching of the optical response of the nanoantennas by chemical tuning of their redox state, which modulates the material permittivity between plasmonic and dielectric regimes via non-volatile changes in the mobile charge carrier density. Further research may study different conductive polymers and nanostructures and explore their use in various applications, such as dynamic metaoptics and reflective displays.

We prepared thin conductive polymer films of poly[3,4-ethylenedioxythiophene:sulfate] (PEDOT:Sulf, see Fig. 1a), which can provide high electrical conductivity and metallic character^{3,4}. Using vapour phase polymerization and sulfuric acid treatment (see Methods), we obtained films with electrical conductivity exceeding 5000 S/cm (see Supplementary Table. 1). Their complex and anisotropic permittivity was determined by ultrawide spectral range ellipsometry, employing an anisotropic Drude-Lorentz model as described previously (see Supplementary Table. 2)⁵. Fig. 1b shows the resulting in-plane permittivity of a thin PEDOT:Sulf film with thickness of 32 nm (Supplementary Fig. 1 presents the raw data). The shaded area highlights a spectral region (0.8 to 3.6 μm) in which the film has negative real permittivity and lower magnitude imaginary permittivity, which we define as plasmonic regime. This optically metallic and plasmonic character is related to the high conductivity within the thin film due to high concentration ($2.6 \times 10^{21} \text{ cm}^{-3}$, determined by ellipsometry, see Supplementary Table. 1 and Supplementary Information for details) of mobile positive polaronic charge carriers. We also note that the mobility is highly anisotropic^{5,6} and the out-of-plane real permittivity (Supplementary Fig. 2a) is primarily positive throughout the measured range, making the conductive polymer thin film a natural hyperbolic material⁷ (Supplementary Fig. 3).

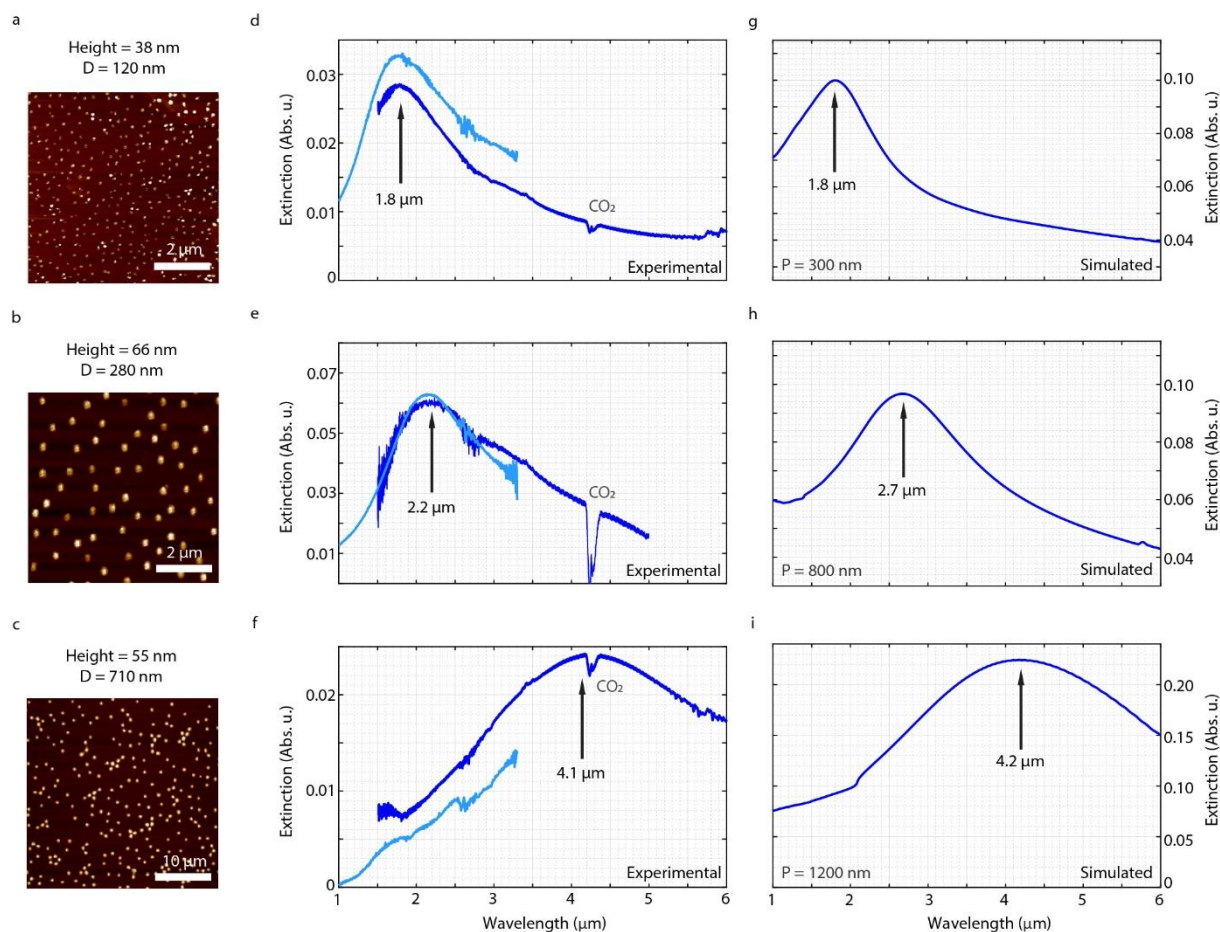


43
 44 **Fig. 1 | Material properties and calculated plasmonic resonances for PEDOT:Sulf in its high-conductivity**
 45 **oxidised state.** **a**, Chemical structure of PEDOT:Sulf. **b**, In-plane permittivity dispersion of PEDOT:Sulf in its
 46 oxidised state (blue curve: real part; red curve: imaginary part). The shaded spectral range between 0.8 to 3.6
 47 μm is defined as plasmonic regime where the real permittivity is below zero and its magnitude is larger than the
 48 imaginary component [inset: Negative ratio of the real and imaginary permittivity ($-\varepsilon_1/\varepsilon_2$)]. **c**, Simulated
 49 extinction spectrum for a PEDOT:Sulf nanodisk array (blue curve), with disk thickness of 30 nm, diameter of 500
 50 nm, and array period of 1000 nm. The small extinction kink at about 1.4 μm disappears when examining single
 51 nanodisks instead of arrays (Fig. S4) and is attributed to lattice scattering of the array (see Fig. S5a). The red curve
 52 shows the extinction for a non-structured thin PEDOT:Sulf film scaled to the same material coverage as the disks
 53 (scaled by $\pi/16$). Inset: a schematic illustration of a PEDOT:Sulf nanodisk on a glass substrate with x-, y-, and z-
 54 axes indicated. **d**, **e**, Calculated nearfield profiles at the wavelength of the extinction maximum (2.9 μm) for one
 55 of the PEDOT:Sulf nanodisks of the array in **c** (mesh size: $1\times 1\times 1\text{ nm}^3$ around the nanodisk): **d**, x-y in-plane
 56 direction 2 nm above the nanodisk; **e**, x-z cross-section through the center of the nanodisk. The colour scale bars
 57 show the electric field strength relative to the incident light ($|E|/|E_0|$).

58 The measured optical properties of the thin PEDOT:Sulf film imply that nanostructures of
 59 the material should be able to sustain plasmonic resonances. Indeed, the calculated optical

60 extinction (see Methods for details) for a PEDOT:Sulf nanodisk array (thickness of 30 nm,
61 nanodisk diameter of 500 nm and array period of 1000 nm) shows a clear resonance peak at
62 around 2.9 μm (Fig. 1c), which is absent for the non-structured thin film. Examining the optical
63 nearfield profile at resonance (2.9 μm) for one of the nanodisks reveals that the extinction
64 peak originates from a dipolar mode (Fig. 1d and e), with enhanced fields on the opposite
65 edges of the nanodisk in the polarization direction of the incident light. The optical nearfield
66 patterns slightly above (Fig. 1d) and through the nanodisk (Fig. 1e) both resemble that of
67 traditional gold nanodisk antennas (comparison in Supplementary Fig. 4). Varying the array
68 period for fixed nanodisk dimensions did not significantly shift the resonance wavelength
69 (Supplementary Fig. 5b), confirming that the extinction peak originates from localized
70 nanooptical modes rather than grating effects. In fact, also single nanodisks (Supplementary
71 Fig. 6a) show the same nanooptical behaviour, with almost identical resonance positions as
72 the periodic arrays (Supplementary Fig. 6b), and without the small grating-induced kink at
73 shorter wavelengths as present for the periodic arrays (see Supplementary Fig. 5). To verify
74 the plasmonic character of the resonance, we also evaluated the optical response for
75 nanodisks made from an artificial material with permittivity originating only from the
76 polaronic charge carriers (“Transport function”, see Supplementary Fig. 7b and
77 Supplementary Information section B7 for details). Those nanodisks exhibit an extinction
78 resonance peak with even higher intensity and smaller width compared with the response of
79 the original nanodisks (see Supplementary Fig. 7b). We thereby conclude that the nanooptical
80 resonance originates primarily from the mobile charge carriers in the conducting polymer and
81 that it is plasmonic in character (see more detailed discussion in Supplementary Information
82 section B8).

83 To experimentally verify excitation of plasmons in conductive polymer nanostructures, we
84 fabricated short-range ordered arrays of PEDOT:Sulf nanodisks on sapphire substrates, using
85 a modified version of colloidal lithography⁸ (see Methods and Supplementary Fig. 8 for details).
86 The protocol could provide large areas of nanodisks of desired diameters, visualized by atomic
87 force microscopy (AFM) for nanodisk diameters of 120 nm, 280 nm, and 710 nm in Fig. 2a, b,
88 and c, respectively (more AFM images and line sections of single nanodisks are provided in
89 Supplementary Fig. 9). The nanodisks all originate from 30 nm thick PEDOT:Sulf films, while
90 the final thickness of the disks varied somewhat due to residual PMMA [poly(methyl
91 methacrylate)] remaining on top of the disks after fabrication (Supplementary Fig. 10).
92 Importantly, the fabricated polymer nanodisk samples exhibit clear extinction peaks (Fig. 2d,
93 e, and f), verifying the simulated nanooptical behaviour. As expected for plasmonic
94 nanoantennas, the resonance positions increase with disk diameter. The experimental results
95 largely match the simulated predictions (Fig. 2g, h, and i) in terms of spectral shapes, peak
96 widths and resonance wavelengths. Small differences in peak positions are attributed to
97 geometrical differences and imperfections of the fabricated nanodisks. The experimental
98 peaks also show somewhat larger broadening, as expected for measured ensembles
99 compared with simulated arrays composed of identical nanostructures⁹.



100
 101 **Fig. 2 | Extinction spectra of PEDOT:Sulf nanodisk antennas.** Three different sizes of short-range ordered
 102 nanodisk arrays were made on sapphire substrates: **a**, AFM image of 120 nm diameter nanodisks; **b**, AFM image
 103 of 280 nm diameter nanodisks; **c**, AFM image of 710 nm diameter nanodisks. The diameter and height
 104 measurements are in **Supplementary Fig. 9**. **d**, **e**, and **f**, Experimental measured extinction spectra of 120 nm,
 105 280 nm, and 710 nm diameter nanodisks. UV-Vis-NIR measurements are plotted in light blue and FTIR
 106 measurements are in dark blue. **g**, **h**, and **i**, Simulated extinction spectra of 120 nm, 280 nm, and 710 nm diameter
 107 nanodisk arrays. In the simulation, the PEDOT:Sulf thickness was 30 nm and the excessive thickness (8 nm, 36
 108 nm, and 25 nm respectively) comes from remaining unremoved PMMA layer. The features between 2.7 μm and
 109 3.3 μm (with multiple closely-packed sharp peaks) and at 4.3 μm in the experimental spectra (**d**, **e**, and **f**)
 110 are due to absorption by water vapour and carbon dioxide¹⁰, respectively, and therefore absent in the simulated spectra.

111 The results above indicate that the resonance position of the polymer nanodisk antennas
 112 can be tuned by geometry. Fig. 3a presents the simulated extinction for 30 nm thick single
 113 PEDOT:Sulf nanodisks of varying diameter on a substrate with refractive index of 1.6.
 114 Normalized extinction versus diameter is presented in Fig. 3c as colour maps. It is clear that
 115 the resonance position redshifts with increasing diameter, enabling tuning in a large spectral
 116 range from around 2 μm to around 4 μm for disks with sizes ranging from 200 nm and 700 nm
 117 in diameter. The spectral tunability can likely be extended further by other geometries. While
 118 the nanodisk resonances redshift with increasing disk diameter, they instead blueshift with
 119 increasing thickness, as presented in Fig. 3d and 3f for nanodisks with fixed diameter of
 120 500 nm (normalized extinction spectra corresponding to Fig. 3a and 3d are shown in
 121 Supplementary Fig. 11). Both these geometrical dependencies match expectations based on
 122 plasmonic nanodisk resonances¹¹⁻¹³.

123 To enable analytical calculation of the optical response, we approximate the nanodisks as
 124 oblate spheroids with diameter D and thickness t , which in the quasi-static limit $D \ll \lambda$ gives
 125 the dipolar polarizability α as²

$$\alpha(\lambda) = V \frac{\varepsilon(\lambda) - \varepsilon_s}{\varepsilon_s + L[\varepsilon(\lambda) - \varepsilon_s]} \quad (1)$$

126 where V is the volume of the spheroid and ε_s is the permittivity of the surrounding medium.
 127 We use the in-plane permittivity of PEDOT:Sulf as $\varepsilon(\lambda)$ and set $\varepsilon_s = 1.69$ as the effective
 128 surrounding permittivity for disks in air on a substrate with refractive index 1.6 (see Methods).
 129 L is a geometrical factor that equals 1/3 for a sphere ($D = t$) and decreases for increasing
 130 nanodisk ratio ($D > t$, see Supplementary Fig. 12). To fulfil the resonance condition of
 131 maximum polarizability when L decreases, the magnitude of the negative permittivity needs
 132 to increase. Because the permittivity of the conductive polymer increases in magnitude with
 133 wavelength (see Fig. 1b), the resonance position therefore redshifts with increasing aspect
 134 ratio (D/t). This illustrates why the resonance of the PEDOT:Sulf nanoantennas redshifts with
 135 increasing disk diameter and blueshifts with increasing disk thickness. Larger disks require
 136 corrections for finite wavelength effects, which gives the corrected polarizability as^{14,15}

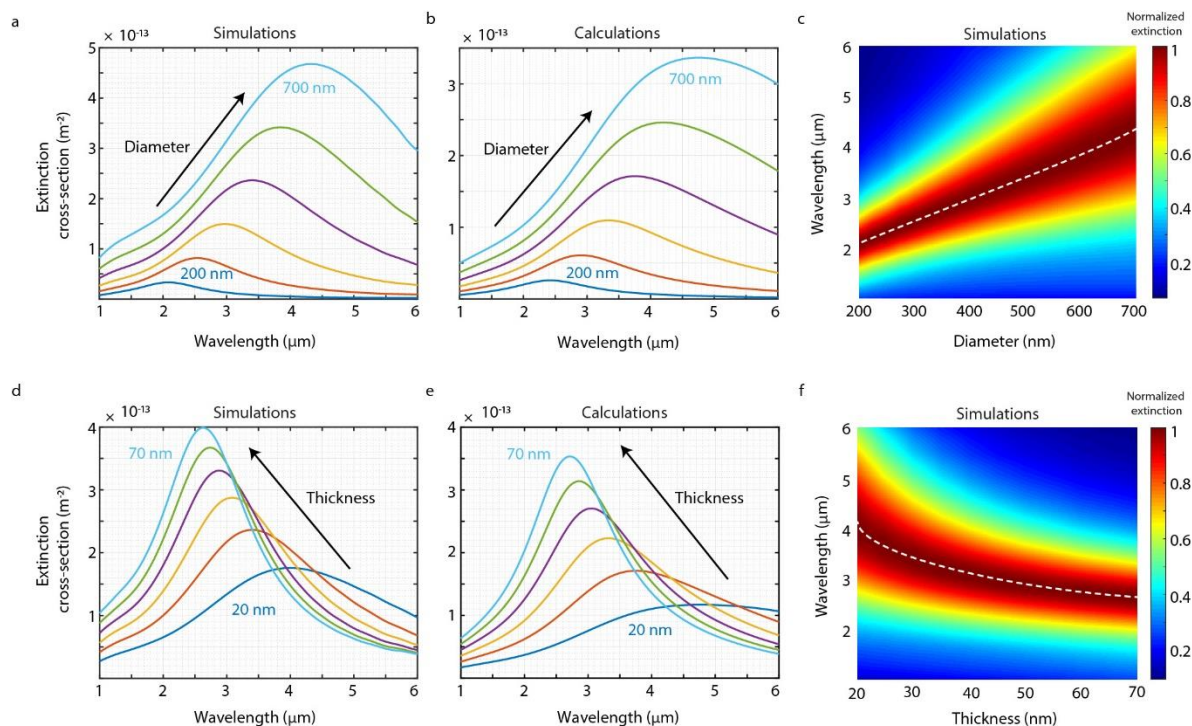
$$\alpha'(\lambda) = \alpha(\lambda) \left[1 - \frac{k^2}{2\pi D} \alpha(\lambda) - i \frac{k^3}{6\pi} \alpha(\lambda) \right] \quad (2)$$

137 where k is the wave number of the incident light. The extinction cross-section $\sigma(\lambda)$ can now
 138 be calculated *via*²

$$\sigma(\lambda) = k \text{Im}[\alpha'(\lambda)] \quad (3)$$

139

140 Fig. 3b and 3e show the final calculated extinction cross sections of single PEDOT:Sulf
 141 oblate spheroids, with sizes corresponding to the simulated nanodisks in Fig. 3a and 3d,
 142 respectively. The calculated results based on the dipolar polarizability match the results from
 143 the full simulations quite well, both in terms of extinction magnitude and its increase with
 144 aspect ratio, and in terms of peak positions and their redshift with increasing nanodisk aspect
 145 ratio. The results thereby further corroborate that the observed extinction peaks of the
 146 PEDOT:Sulf nanodisks originate from dipolar plasmonic excitations. However, while the
 147 presented organic plasmonic systems provide optical behaviour similar to conventional
 148 plasmonic systems, they are different in that the plasmons are based on collective oscillations
 149 of mobile polaronic charge carriers, including bipolarons formed by coupling of positive charge
 150 pairs and local chain distortions¹⁶.



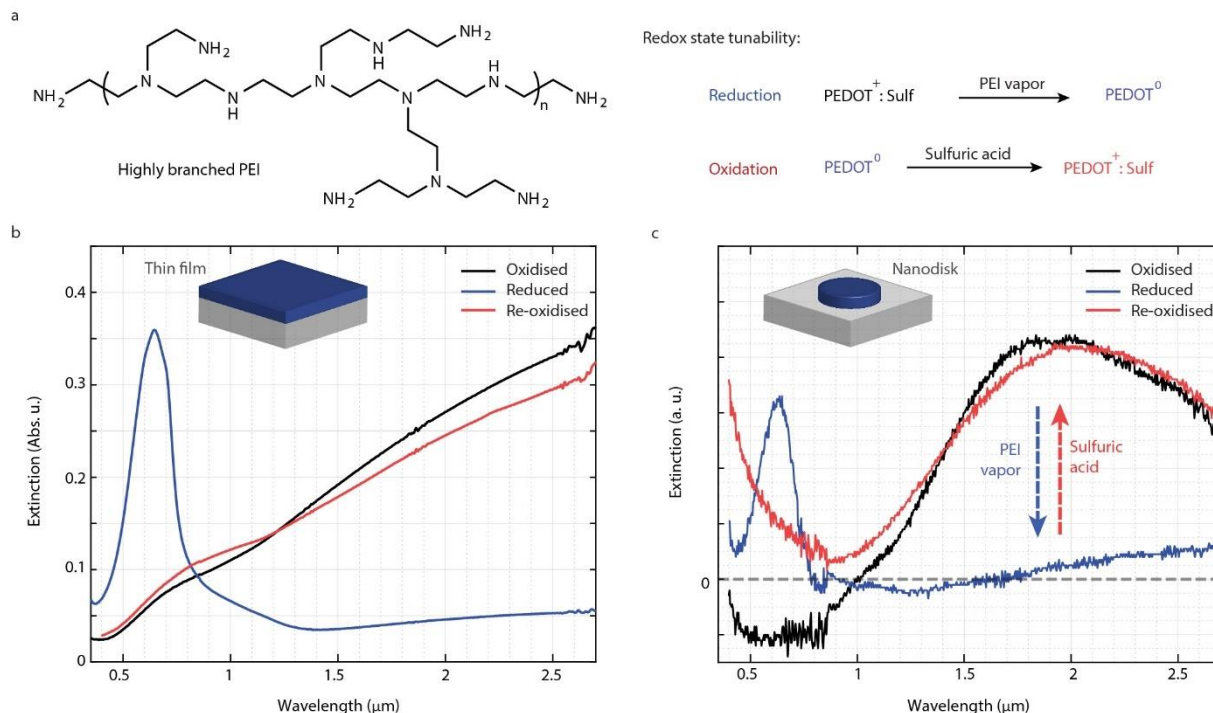
151
 152 **Fig. 3 | Geometry dependence of single PEDOT:Sulf nanodisk localized plasmons.** **a**, Simulated extinction cross-
 153 section of 30 nm thick single nanodisks of different diameters (diameter step size = 100 nm, substrate refractive
 154 index = 1.6). **b**, Analytically calculated extinction cross-section for oblate spheroids corresponding to the nanodisk
 155 sizes in **a**. **c**, Colour map of simulated normalized extinction versus diameter for single 30 nm thick nanodisks. **d**,
 156 Simulated extinction cross-section of 500 nm in diameter single nanodisks with different thickness (thickness
 157 step size = 10 nm, substrate refractive index = 1.6). **e**, Analytically calculated extinction cross section for oblate
 158 spheroids corresponding to the nanodisk sizes in **d**. **c**, Colour map of simulated normalized extinction versus
 159 diameter for single 30 nm thick nanodisks. **f**, Colour map of simulated normalized extinction versus
 160 thickness for single 500 nm in diameter nanodisks. The white dashed lines in **c** and **f** indicate the resonance peak position and
 161 its shift with changes in diameter and thickness, respectively. The colour scale bars in **c** and **f** present the
 162 normalized extinction. See **Supplementary Fig. 11** for normalized extinction spectra corresponding to **a** and **d**.

163 Finally, we demonstrate that the conductive polymer nanoantennas can be switched on
 164 and off. Among various approaches to tune nanophotonic systems, recent research has
 165 explored tuning by modulating the free charge carriers in plasmonic systems, including
 166 electrical gating¹⁷ and photo-carrier excitation¹⁸. While this approach is rather limited for
 167 traditional plasmonic materials, conductive polymers hold great promise since their polaronic
 168 charge carrier concentration can be modulated by several orders of magnitude *via* their redox
 169 state¹⁹. Here, we control the redox state chemically, by exposing PEDOT:Sulf to the vapour of
 170 a highly branched poly(ethylenimine) (PEI, see chemical structure in left panel of Fig. 4a). PEI
 171 contains volatile amines, such as ethyleneimine dimers and trimers, that are known to
 172 effectively reduce PEDOT as well as other semiconducting materials²⁰. Optical extinction
 173 spectroscopy of a (non-structured) thin PEDOT:Sulf films visualizes the process *via* almost
 174 complete reduction of the free charge carrier absorption in the IR and the emergence of a
 175 neutral state peak at around 600 nm (see Fig. 4b)²⁰. For the reduced polymer, PEI reduces the
 176 polaronic charge carrier concentration in PEDOT by donating electrons to it, and complexing
 177 the Sulf counterions (see Supplementary Fig. 13b). This results in a material with largely
 178 reduced electrical conductivity (schematic mechanism in Fig. 4a right panel)²⁰. The process is
 179 reversible and we can recover the original optical properties of the PEDOT film *via* acid

180 treatment of the reduced film (see Methods). This process re-oxidises the material, for which
181 the neutral state disappears and the absorption returns to that of the initial pristine film (Fig.
182 4b). Knowing that the optical material properties of PEDOT:Sulf can be reversibly modulated,
183 we utilize this feature to actively tune our polymer nanodisk metasurfaces. The black curve in
184 Fig. 4c shows the extinction spectra of a sample with PEDOT:Sulf nanodisks in their oxidised
185 pristine state, with plasmonic resonance peak at around 1900 nm. This peak completely
186 disappears upon PEI vapour treatment, for which the material in the nanodisks is no longer
187 plasmonic, due to drastic reduction of the polaronic charge carrier concentration. Indeed, the
188 neutral state material absorption emerges at 600 nm for the PEI treated metasurfaces.
189 Importantly, the optical properties are not volatile, but stable over time and we observe only
190 minimal extinction changes of the sample after one week (see Supplementary Fig. 14). By re-
191 oxidising the sample with sulfuric acid, the plasmonic resonance peak recovers to its initial
192 state, with both similar intensity and width as for the original plasmonic metasurface (Fig. 4c).
193 This process was also verified by X-ray photoelectron spectroscopy (XPS), which shows
194 successful removal of PEI residues from the re-oxidised PEDOT:Sulf films (see Supplementary
195 Fig. 13). We also note that the increase in extinction below 800 nm for the re-oxidised sample
196 (Fig. 4c) is likely due to different probe areas combined with some polystyrene beads
197 remaining after fabrication (similar effects were observed for samples before and after bead
198 removal, Supplementary Fig. 15). Indeed, other samples did not show such increase in
199 extinction for lower wavelengths after re-oxidisation (see Supplementary Fig. 16). We also
200 note that some samples showed an initial decrease in peak intensity after the first on-off redox
201 cycle (Supplementary Fig. 16), which may be due to some more loosely bound nanodisks being
202 removed during the switching process. Differences in exact oxidation state before and after
203 switching may also play a role. Importantly, the spectra rapidly stabilized after the initial cycles
204 and the nanodisks could be repeatedly switched on and off for multiple cycles (here tested for
205 in total 6 cycles).

206 We have demonstrated that nanodisks made of highly conductive polymers can function
207 as optical nanoantennas to form active plasmonic metasurfaces. While previous research
208 investigated hybrid systems based on the combination of metallic nanostructures and
209 conductive polymers^{21,22}, the polymer itself here acts as the plasmonic material, without
210 presence of any inorganic metals. Our research thereby expands the palette of materials for
211 plasmonics beyond conventional metals and other recently explored materials, such as
212 transparent conductive oxides²³, polycyclic aromatic hydrocarbons²⁴, and graphene²⁵. The
213 plasmonic behaviour of these nanoantennas is dynamically tuneable via the redox state of the
214 conductive polymer, where future work may also explore electrochemical modulation or
215 other means of dynamic control²⁶. Besides improving the fundamental understanding of the
216 intriguing physics of these nanoantenna systems, future work may explore their use in a
217 multitude of areas, ranging from dynamic metaoptics and metatronics to plasmon-enhanced
218 electrochemistry and reflective displays. To that end, the possibility to modify conductive
219 polymers by side chain engineering²⁷ makes them versatile and may enable applications that
220 are not feasible with conventional materials. These applications may also benefit from
221 additional features of conductive polymers, including low cost, flexibility, bio-compatibility,
222 and processability in solution¹⁹. The future also holds promise for conductive polymers with

223 yet further improved plasmonic properties, for example, based on strategies to improve
 224 electrical conductivity and lower defect density, such as by effective chain alignment²⁸ or
 225 sequential doping²⁹. We hope that our study of redox-tunable conductive polymer
 226 plasmonics will inspire research in this interdisciplinary field of manipulating light-matter
 227 interactions at the nanoscale.



228 **Fig. 4 | Redox state tunability of PEDOT:Sulf nanodisk antennas.** **a**, Chemical structure of highly branched PEI
 229 (left panel) and redox state tunability mechanism for the PEDOT-based material (right panel). The plus sign (+)
 230 indicates that PEDOT is in its oxidised state, whereas 0 denotes PEDOT is in its reduced state. **b**, Measured
 231 extinction for thin PEDOT:Sulf film on glass at different redox states. **c**, Measured extinction for PEDOT:Sulf
 232 nanodisks on glass (thickness of 43 nm and nanodisk diameter of 140 nm) at different redox states.
 233

234

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297

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303 Author contributions

304 M.P.J. conceived and supervised the project. S.C., V.S., P.K., and V.D. performed ellipsometry
305 measurements and data analysis. S.C. and M.S.C. fabricated the nanostructures. S.C., M.P.J.
306 and E.S.H.K. performed numerical simulations. H.S. and S.C. performed PEI vapour
307 treatments supervised by S.F. C. W. and M. F. performed XPS measurements and analysis.
308 S.C. performed all the other characterizations. S.C. and M.P.J. organized the data and wrote
309 the manuscript. All authors reviewed and commented on the manuscript.

310 Competing interests

311 The authors declare no conflicts of interest.

312 Data availability

313 The data that support the plots within this paper and other findings of this study are available
314 from the corresponding author upon reasonable request.

315 Additional information

316 Supplementary information is available in the online version of the paper. Reprints and
317 permission information is available online at www.nature.com/reprints. Correspondence and
318 requests for materials should be addressed to M.P.J.

319 Figure captions

320 **Fig. 1 | Material properties and calculated plasmonic resonances for PEDOT:Sulf in its high-conductivity**
321 **oxidised state. a**, Chemical structure of PEDOT:Sulf. **b**, In-plane permittivity dispersion of PEDOT:Sulf in its
322 oxidised state (blue curve: real part; red curve: imaginary part). The shaded spectral range between 0.8 to 3.6
323 μm is defined as plasmonic regime where the real permittivity is below zero and its magnitude is larger than the
324 imaginary component [inset: Negative ratio of the real and imaginary permittivity ($-\varepsilon_1/\varepsilon_2$)]. **c**, Simulated
325 extinction spectrum for a PEDOT:Sulf nanodisk array (blue curve), with disk thickness of 30 nm, diameter of 500
326 nm, and array period of 1000 nm. The small extinction kink at about 1.4 μm disappears when examining single
327 nanodisks instead of arrays (Fig. S4) and is attributed to lattice scattering of the array (see Fig. S5a). The red curve
328 shows the extinction for a non-structured thin PEDOT:Sulf film scaled to the same material coverage as the disks
329 (scaled by $\pi/16$). Inset: a schematic illustration of a PEDOT:Sulf nanodisk on a glass substrate with x-, y-, and z-
330 axes indicated. **d, e**, Calculated nearfield profiles at the wavelength of the extinction maximum (2.9 μm) for one
331 of the PEDOT:Sulf nanodisks of the array in **c** (mesh size: $1\times 1\times 1\text{ nm}^3$ around the nanodisk): **d**, x-y in-plane
332 direction 2 nm above the nanodisk; **e**, x-z cross-section through the center of the nanodisk. The colour scale bars
333 show the electric field strength relative to the incident light ($|E|/|E_0|$).

334 **Fig. 2 | Extinction spectra of PEDOT:Sulf nanodisk antennas.** Three different sizes of short-range ordered
335 nanodisk arrays were made on sapphire substrates: **a**, AFM image of 120 nm diameter nanodisks; **b**, AFM image
336 of 280 nm diameter nanodisks; **c**, AFM image of 710 nm diameter nanodisks. The diameter and height
337 measurements are in **Supplementary Fig. 9**. **d, e**, and **f**, Experimental measured extinction spectra of 120 nm,
338 280 nm, and 710 nm diameter nanodisks. UV-Vis-NIR measurements are plotted in light blue and FTIR

339 measurements are in dark blue. **g, h, and i**, Simulated extinction spectra of 120 nm, 280 nm, and 710 nm diameter
340 nanodisk arrays. In the simulation, the PEDOT:Sulf thickness was 30 nm and the excessive thickness (8 nm, 36
341 nm, and 25 nm respectively) comes from remaining unremoved PMMA layer. The features between 2.7 μm and
342 3.3 μm (with multiple closely-packed sharp peaks) and at 4.3 μm in the experimental spectra (d, e, and f) are due
343 to absorption by water vapour and carbon dioxide¹⁰, respectively, and therefore absent in the simulated spectra.

344 **Fig. 3 | Geometry dependence of single PEDOT:Sulf nanodisk localized plasmons.** **a**, Simulated extinction cross-
345 section of 30 nm thick single nanodisks of different diameters (diameter step size = 100 nm, substrate refractive
346 index = 1.6). **b**, Analytically calculated extinction cross-section for oblate spheroids corresponding to the nanodisk
347 sizes in **a**. **c**, Colour map of simulated normalized extinction versus diameter for single 30 nm thick nanodisks. **d**,
348 Simulated extinction cross-section of 500 nm in diameter single nanodisks with different thickness (thickness
349 step size = 10 nm, substrate refractive index = 1.6). **e**, Analytically calculated extinction cross section for oblate
350 spheroids corresponding to the nanodisk sizes in **d**. **c**, Colour map of simulated normalized extinction versus
351 diameter for single 30 nm thick nanodisks. **f**, Colour map of simulated normalized extinction versus thickness for
352 single 500 nm in diameter nanodisks. The white dashed lines in **c** and **f** indicate the resonance peak position and
353 its shift with changes in diameter and thickness, respectively. The colour scale bars in **c** and **f** present the
354 normalized extinction. See **Supplementary Fig. 11** for normalized extinction spectra corresponding to **a** and **d**.

355 **Fig. 4 | Redox state tunability of PEDOT:Sulf nanodisk antennas.** **a**, Chemical structure of highly branched PEI
356 (left panel) and redox state tunability mechanism for the PEDOT-based material (right panel). The plus sign (+)
357 indicates that PEDOT is in its oxidised state, whereas 0 denotes PEDOT is in its reduced state. **b**, Measured
358 extinction for thin PEDOT:Sulf film on glass at different redox states. **c**, Measured extinction for PEDOT:Sulf
359 nanodisks on glass (thickness of 43 nm and nanodisk diameter of 140 nm) at different redox states.

360 **Methods**

361 **Thin film deposition.** PEDOT:trifluoromethanesulfonate (PEDOT:OTf) thin films were prepared first as
362 precursors of PEDOT:Sulf films. PEDOT:OTf thin films were deposited *via* vapour phase polymerization
363 (VPP) as reported in the literature.^{5,30} The oxidant solution for EDOT polymerization was prepared by
364 mixing 0.03 g of iron (III) trifluoromethanesulfonate (Fe[OTf]₃, from Alfa Aesar), 0.2 g of tri-block co-
365 polymer poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) (PEG-PPG-PEG
366 or P-123, average $M_n \sim 5,800$, from Sigma-Aldrich) and 0.8 g of 99.5% ethanol (from Solveco). Oxidant
367 films were deposited by spin-coating at 1500 rpm for 30 s onto pre-cleaned sapphire or glass substrates
368 (sonicated in cleaning detergent, de-ionized water, acetone, and isopropanol each for 10 min
369 respectively and treated with oxygen-plasma at 200 W for 5 min before use). After 30 s baking on a
370 hotplate at 70 °C, the samples were transferred into a heated vacuum desiccator [Vacuo-temp, from
371 SELECTA]. EDOT ($142.18 \text{ g mol}^{-1}$, from Sigma-Aldrich) droplets were drop-casted onto a glass substrate
372 on a hot plate at 30 °C in the desiccator to ensure its evaporation. After 30 min of polymerization at a
373 pressure of 70 mBar, the samples were taken out from the desiccator and washed with ethanol
374 multiple times to remove byproducts and unreacted residues, followed by air-drying with nitrogen. To
375 further enhance the electrical properties of the samples, we used an acid treatment by soaking the
376 samples in 1 M sulfuric acid (H₂SO₄) for 10 min at room temperature followed by washing in DI water
377 for 10 seconds and heating at 100 °C for another 10 min³⁰. Upon acid treatment, the OTf counterions
378 in the PEDOT:OTf films were replaced by sulfate counterions (HSO₄⁻), as clear from the removal of
379 fluorine signals in X-ray photoelectron spectroscopy results (XPS, see Supplementary Fig. 14a).

380 **Nanoantenna fabrication.** The detailed process flow for nanodisk array fabrication is shown in
381 Supplementary Fig. 8, which is a modified version of colloidal lithography.⁸ Briefly, a 4 wt% PMMA
382 [poly(methyl methacrylate)], $M_w \sim 996,000$, from Sigma-Aldrich) solution in anisole (from Sigma Aldrich)
383 was spin-coated onto the as-prepared PEDOT:Sulf thin films. Soft baking at 140 °C for 10 min was then
384 applied. The samples were treated with reactive oxygen plasma (50 W, 250 mTorr) for 5 s to increase
385 the hydrophilicity of the surface. In order to functionalize the PMMA surface to be positively charged,
386 2 wt% poly(diallyldimethylammonium chloride) (PDDA, 522376 from Sigma-Aldrich) in DI water was
387 dropped on the samples. After 1 min, the samples were rinsed with deionized water for 40 s and dried
388 with nitrogen stream. Negatively charged polystyrene nanoparticles (PS beads with different
389 diameters, 0.2-0.3 wt% in deionized water, from Microparticles GmbH) were then dropped on the
390 samples. After 10-30 min, the samples coated with PS beads were rinsed with DI water and dried with
391 nitrogen stream resulting in a sparse monolayer of PS beads on the PMMA/PEDOT:Sulf thin films. A
392 heat treatment at 100 °C for 2 min were applied to the samples to improve the adhesion of PS beads
393 on the samples. Reactive oxygen plasma etching (250 mTorr, 50 W) for 3-5 min were applied to the
394 samples, using the PS beads monolayer as mask. Depending on the size of PS beads and thickness of
395 PMMA and PEDOT:Sulf thin films, the time interval of etching can be varied to ensure a complete
396 removal of PMMA and PEDOT:Sulf parts that are not covered by the mask. The samples were then
397 placed into an acetone bath and soaked for 10-30 min followed by a mild sonication for 3 min and
398 nitrogen stream drying to remove PMMA and PS beads and finally the PEDOT:Sulf nanodisks were
399 obtained. In this study, three different diameters of PS beads were used: 239 nm (PS-ST-0.25,
400 Microparticles GmbH), 497 nm (PS-ST-0.50, Microparticles GmbH), and 1046 nm (PS-ST-1.0,
401 Microparticles GmbH).

402 **Vapour treatment of thin films and nanoantennas.** The vapour treatment was conducted inside a N₂-
403 filled glovebox by exposing the samples to the vapour of ethyleneimine dimers and trimers by heating
404 a vial containing highly branched poly(ethylene imine) liquid (PEI, $M_w \sim 800$, from Sigma-Aldrich) at
405 120 °C for 5 min.²⁰ After the vapour treatment, the samples were annealed at 120 °C for another 5 min.

406 To re-oxidise the samples, they were put into 1 M sulfuric acid bath for 10 min followed by a drying
407 process of 10 min at 100 °C on a hot plate.

408 **Ellipsometry.** PEDOT:Sulf thin film samples were measured at normal ambient conditions at room
409 temperature. The films were deposited on 2-inch single side polished *c*-plane sapphire wafers (from
410 Semiconductor Wafer Inc.). Ellipsometric data for PEDOT:Sulf thin films were collected using three
411 different ellipsometers covering a wide spectral range from 0.0028 eV to 5.9 eV. UV-Vis-NIR
412 measurements were performed on a J. A. Woollam Co. RC2[®] spectroscopic ellipsometer for five
413 incident angles (40°, 50°, 60°, 70°, and 80°) and spectral range from 0.73 eV (1690 nm) to 5.90 eV (210
414 nm). Infrared measurements were performed on a J. A. Woollam Co. IR-VASE[®] spectroscopic
415 ellipsometer for two incident angles (50° and 70°) and spectral range from 28.0 meV (230 cm⁻¹) to 1.0
416 eV (7813 cm⁻¹). THz measurements were performed on the THz ellipsometer at the Terahertz Materials
417 Analysis Center (THEMAC) at Linköping University.³¹ Three incident angles (40°, 50°, and 60°) were
418 used for THz measurements, in the spectral range between 2.8 meV (0.67 THz) and 4.0 meV (0.97 THz).
419 The typical ellipsometer measures the complex reflectance ratio ρ at different frequencies, as obtained
420 from $\rho = r_p/r_s = \tan(\Psi)e^{i\Delta}$, where r_p and r_s are the complex Fresnel reflection coefficients for p- and s-
421 polarized light; Ψ shows the amplitude ratio change of the two polarizations; and Δ indicates the phase
422 difference between them.³² WVASE[®] (J. A. Woollam Co.) software was used for data analysis and an
423 anisotropic Drude-Lorentz model was employed for model fitting and optical parameter extraction for
424 the PEDOT:Sulf thin films.⁵ Details for data analysis were described in Supplementary Information.

425 **Electrical, chemical and structural characterization.** Sheet resistance, R_s , of the thin film was measured
426 using a 4-point probe set-up using a Signatone Pro4 S-302 resistivity stand and a Keithley 2400. Film
427 thickness t was determined by a surface profiler (Dektak 3st, Veeco). The thickness of the PEDOT:Sulf
428 films varied in the range from 30 to 40 nm. The electrical conductivity can then be calculated by $\sigma =$
429 $1/(R_s t)$. Atomic force microscopy (AFM) was employed for surface morphology characterization, in
430 tapping mode using a Veeco Dimension 3100. The morphological images were analysed using
431 Nanoscope Analysis software (Bruker). X-ray Photoemission experiments were carried out using a
432 Scienta ESCA 200 spectrometer under ultrahigh vacuum conditions at a base pressure of 1×10^{-10} mbar.
433 The XPS measurements have been done with a monochromatic Al K α X-ray source, providing photons
434 with energy of 1,486.6 eV. The XPS spectra are normalized to the C1s peak.

435 **Optical characterization.** The extinction spectra in the Vis-NIR range (400 nm to 3300 nm) were
436 measured using a UV-Vis-NIR spectrometer (Lambda 900, Perkin Elmer Instruments). The extinction
437 spectra include transmission losses due to both absorption and scattering. Fourier-transform infrared
438 spectroscopy (FTIR) measurements were performed in the spectral range from 1333 nm (7500 cm⁻¹)
439 to 5000 nm (2000 cm⁻¹) or 6667 nm (1500 cm⁻¹) using an Equinox 55 spectrometer (Bruker). FTIR
440 spectra were acquired in absorbance mode using a resolution 4 cm⁻¹ and 100 scans. Samples deposited
441 on 20×20×0.5 mm double-side polished sapphire substrates (from Semiconductor Wafer Inc.) were
442 made for FTIR and UV-Vis-NIR measurements.

443 **Optical numerical simulations.** Numerical simulations (electric nearfield intensity and farfield spectra)
444 of the electromagnetic response of PEDOT:Sulf nanoantennas were performed *via* the finite-difference
445 time-domain (FDTD) method using the commercial software Lumerical FDTD Solutions
446 (<http://www.lumerical.com/fdtd.php>). The optical parameters for the PEDOT:Sulf thin film were taken
447 as the anisotropic complex permittivity obtained from the ellipsometry measurements. For periodic
448 nanodisk arrays and thin films, the spectra and nearfield profiles were recorded *via* field and power
449 monitors. Periodic PEDOT:Sulf nanodisk arrays (or thin film) were placed on top of glass or sapphire
450 substrates. The structures were illuminated by a planewave light source at normal incidence. Anti-
451 symmetrical and symmetric boundaries were used for the *x*-axis (parallel to polarization) and *y*-axis

452 (normal to polarization) and perfectly matched layer (PML) were used for the z-axis (parallel to light
453 incident direction). For single nanodisks, spectra were obtained using a total field/scattered field and
454 by extracting the extinction cross-section of isolated PEDOT:Sulf nanodisks on a sapphire substrate.
455 Geometry parameters are indicated in each graph (diameter, thickness, and array period) and the
456 mesh size was typically $3 \times 3 \times 3 \text{ nm}^3$, or $2 \times 2 \times 2 \text{ nm}^3$ for the smaller size disks. The optical parameters
457 for gold³³, glass³⁴ and PMMA^{35,36} were taken from literature while the permittivities of sapphire
458 substrate and PEDOT:Sulf were determined by ellipsometry. In the analytical calculations, the effective
459 permittivity of the surroundings was calculated based on an average refractive index of air and
460 sapphire ($\epsilon_s = [(n_{\text{air}} + n_{\text{sapphire}})/2]^2$). The refractive index of sapphire is 1.75 at about $1 \mu\text{m}$ and 1.6 at
461 about $5 \mu\text{m}$ and for simplicity we fix $n_{\text{sapphire}}=1.6$ which gives $\epsilon_s=1.69$.

462

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