Organic near-infrared epsilon-near-zero materials with large optical nonlinearity

Author Information

Qili Hu¹, Xinlan Yu¹, Hongqi Liu¹, Jiahuan Qiu², Sen Liang¹, Guanan Chen¹, Miao Du², Hui Ye¹,†

¹State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou, P. R. China
²MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, P. R. China

† Corresponding author: huiye@zju.edu.cn

Keywords: Epsilon-near-zero, organic optical nonlinearity, hot electron,

Abstract

Epsilon-near-zero (ENZ) materials have shown great potential for nonlinear optical applications, such as photon generation, all-optical switch, and time refraction because of the ultrafast hot electrons and hot-electron-induced nonlinearity enhancement. Recently, n-type inorganic ENZ materials, especially transparent conductive oxides (TCOs), with femtosecond hot-electron responses (<500fs) and huge optical nonlinearity enhancement (>2000 times) have been reported detailedly. Here, modified poly(3,4-ethylenedioxythiophene) (PEDOT) p-type organic films exhibit vanishing real permittivity near 1550nm, namely in the conventional band (C band) for optical communications. We find that PEDOT films have a 100 times larger nonlinear response than indium tin oxide (ITO), a kind of classic inorganic ENZ material, in the non-ENZ region and a similar but less hot-carrier induced enhancement of optical nonlinearity. Furthermore, hot holes in modified PEDOT (p-type) films exhibit a longer relaxation time and a lower enhancement multiple of electron temperature than hot electrons in n-type inorganic ENZ materials. Our findings firstly offer new promising tunable organic ENZ
materials with ENZ wavelengths in optical communication bands and reveal unique properties of organic ENZ materials as distinct from inorganic ENZ materials, which provide more possibility for on-chip nanophotonic devices, nonlinear optics, and plasmonics.

**Introduction**

Organic optical nonlinear materials are attractive candidates for all-optical signal processing, frequency conversion, and other nonlinearity-related applications because of their more superior optical nonlinearity and phase-matching possibilities than their inorganic counterparts. For example, silicon-organic hybrid waveguides containing π-conjugated organic molecules have shown modulation speeds exceeding $100 \text{ Gb} \cdot \text{s}^{-1}$ while the typical modulation speed of purely silicon modulators based on free carrier injection is $40 \text{ Gb} \cdot \text{s}^{-1}$; organic single crystals deliver a 24 times higher THz electric field and ~3 times broader bandwidth, compared to the inorganic standard 1.0 mm thick ZnTe crystals.

Recently, epsilon-near-zero (ENZ) materials represented by transparent conductive oxides (TCOs) have attracted unprecedented attention due to their much-enhanced nonlinearity in the ENZ wavelength region and ultrafast hot electrons. Indium tin oxide (ITO), as one example, has shown ~2000-fold enhancement of the nonlinear refractive index $n_2$ and nonlinear absorption coefficient $\alpha_2$ at the ENZ wavelength than those out of the ENZ region because the energy of heated electrons in the conduction band redistribute under the irradiation of laser pulse, resulting in the ultrafast elevated temperature of electrons inside materials. This phenomenon is known as hot-electron-induced optical nonlinearity enhancement. However, there is still a lack of organic ENZ materials with large optical nonlinearity and research about the behavior of hot electrons in p-type ENZ materials.

Here, a kind of p-type π-conjugated polymer widely used in solar cells, Poly(3,4-ethylenedioxythiophene) (PEDOT), was used to form the film with regularly arranged PEDOT molecules by self-assembly. The preferred-oriented PEDOT films have facilitated carrier mobility and carrier concentration and acquired a resultant ENZ wavelength in the conventional band (C band) for optical communications. Consequently, the ENZ wavelength of the PEDOT film blue shift from 5267nm to 1555nm. The nonlinear refractive index $n_2$ and nonlinear
The absorption coefficient $\alpha_2$ of modified PEDOT films measured via the Z-scan method are two orders of magnitude higher than those of ITO films at the non-ENZ wavelengths. Meanwhile, the ENZ enhancement multiple for optical nonlinear responses of PEDOT (22-fold) within the ENZ wavelength region is relatively lower than those of ITO (2200-fold) due to the larger imaginary permittivity of PEDOT compared to that of ITO at ENZ wavelengths. The underlying reason is that the temperature of hot carriers was elevated only two times for PEDOT but ten times for ITO in the two-temperature model. As a result, the maximum hot-electron-induced nonlinear optical response of PEDOT and ITO has similar values, roughly $n_2 = 0.1 \text{ cm}^2/\text{GW}$ and $\alpha_2 = -5000 \text{ cm}/\text{GW}$. We also find hot holes in p-type PEDOT films exhibit a longer relaxation time $\tau_{\text{PEDOT}} = 1.81 \text{ ps}$ compared to hot electrons in n-type ITO films $\tau_{\text{ITO}} = 0.65 \text{ ps}$ through pump-probe techniques, which is consistent with simulations in the two-temperature model.

**Results and discussion**

As given in Methods, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT: PSS) solution (Clevios PH1000) is processed by ethylene glycol to remove the excess PSS component. Then PEDOT dropped on the glass substrate (Fig. 1(a)) starts to form a nanofibril-based network via self-assembly when heated at 160°C because of the drying dynamics at coffee rings. Finally, we obtain the PEDOT film with a preferred orientation and a crystalline degree better than the pristine PEDOT: PSS film prepared by spin-coating (Fig. 1(c)).

Fig. 1(b) represents the root-mean-square (RMS) of the surface roughness of the modified PEDOT is 8.04nm. For the pristine PEDOT: PSS film, XRD patterns have two characteristic peaks: $2\theta = 17.7^\circ (d = 5.0\text{Å}), 25.78^\circ (d_{010} = 3.5\text{Å})$, where the lattice spacing is calculated using Bragg’s law. The two high angle reflections at $2\theta = 17.7^\circ$ and $25.78^\circ$ are indexed to the amorphous halo of PSS component, and the PEDOT thiophene ring $\pi-\pi$ stacking distance $d_{010}$, respectively. Through the self-assembly of PEDOT with the reduced PSS component, two new distinct characteristic peaks ($2\theta = 6.96^\circ (d_{100} = 12.69\text{Å}), 12.32^\circ (d_{200} = 7.178\text{Å})$) arise in XRD patterns of modified PEDOT (Fig. 1(c)). These two peaks at $6.96^\circ$ and $12.32^\circ$ are assigned to the first and second reflection of the alternate inter-lamella stacking.
distance. Compared to the weak peaks ($d_{100}$ and $d_{200}$) of PEDOT: PSS reported in literatures\textsuperscript{18,20} (that is hard to recognize in our XRD results of the pristine PEDOT: PSS), the $d_{100}$ and $d_{200}$ peaks of modified PEDOT film represents shifts to higher angles (shorter inter-lamella distance) like those of acid-treated PEDOT: PSS film\textsuperscript{18,20}. It proves that reducing PSS components can decrease the inter-lamella charge hopping distance to enhance the electrical conductivity\textsuperscript{18,20}. Meanwhile, the higher intensity and sharpness of the $d_{100}$ and $d_{200}$ peak suggest a change in the PEDOT structure from a coil to a more linear crystalline configuration, which means that self-assembly caused by coffee-ring effects during dry annealing helps improve the crystalline degree of modified PEDOT film. Consequently, the modified PEDOT films exhibit a carrier mobility of $5.8 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$, ~250 times larger than that of the pristine PEDOT: PSS, and a carrier concentration $n$ of $1.037 \times 10^{21} \text{cm}^{-3}$, ~10 times larger than that of the pristine PEDOT: PSS (Table. 1). According to the Drude model, the increase of the carrier concentration $n$ will result in the blueshift of the plasmon frequency $\omega_p$.

$$\omega_p = \frac{ne^2}{\varepsilon_0 m^*} \propto \sqrt{n}$$

where $e$, $\varepsilon_0$, and $m^*$ represent, electron charge, vacuum permittivity, and effective mass of free carriers, respectively. Thus, the modified PEDOT film with 10 times larger carrier concentration $n$ will show ~3.3 times larger plasmon frequency $\omega_p$. Although we use the Drude-Lorentz model instead of the pure Drude model to acquire the permittivity of PEDOT\textsuperscript{21}, the ENZ frequency $\omega_{ENZ}$ also keeps roughly proportional to the square root of the carrier concentration $n$. As predicted above, the permittivity obtained by ellipsometry (Table. 1) shows that the modified PEDOT film has an ENZ wavelength $\lambda_{ENZ} = 1555\text{nm}$ (Fig. 1(d)) while the pristine PEDOT: PSS film has an ENZ wavelength $\lambda_{ENZ} = 5267\text{nm}$ (Fig. S4).

To investigate ENZ-induced enhancement of optical nonlinearity in organic ENZ materials, we characterized the nonlinear optical properties of our sample using the Z-scan technique. A schematic diagram of the experimental setup is shown in Fig. 2(a). A pump pulse with a repetition rate of 1kHz and a pulse duration of 150fs from an optical parametric generator were
used. Both closed- and open-aperture measurements were performed for wavelengths of 1300nm, 1550nm, 1800nm under the illumination of the p-polarized spatially filtered Gaussian beam. Note that 1300nm and 1800nm are out of the ENZ region while 1550nm is inside the ENZ region. To explore the hot-electron-induced angle effect of the nonlinear optical response inside the ENZ region\(^3\), we perform the Z-scan measurement for the ENZ wavelength under angles of 0°, 20°, 30°, 40°. 

**Fig. 2(b)** and **2(c)** show, respectively, representative closed-aperture and open-aperture signals from the modified PEDOT films on the glass substrate at \(\lambda = 1550\text{nm}\). The asymmetry in the closed-aperture signal increases with increasing angle of incidence due to the large change in the absorption.

According to formulas in Methods, we extracted the nonlinear refractive index \(n_2\) and nonlinear absorption coefficient \(\alpha_2\) from closed- and open-aperture signals. **Fig. 3(a)** and **3(b)** represent nonlinear optical response and the enhancement factor, defined relative to the values far from the ENZ spectral region (at \(\lambda = 1300\text{nm}\)) at normal incidence, as functions of the angle of incidence \(\theta\) when the wavelength of incidence is 1550nm (inside the ENZ wavelength region). The enhancement tends to increase with \(\theta\) for the whole measurement range (0° < \(\theta\) < 40°). **Fig. 3(c)** and **3(d)** illustrates that the nonlinear responses (\(n_2 = 4.7 \times 10^{-1} \text{ m}^2/\text{W} \) and \(\alpha_2 = -2.0 \times 10^{-9} \text{ m}/\text{W}\)) of the modified PEDOT are respectively \(\sim 100\) times higher than those of ITO (\(n_2 = 5 \times 10^{-18} \text{ m}^2/\text{W} \) and \(\alpha_2 = -3 \times 10^{-11} \text{ m}/\text{W}\)) in the non-ENZ region. The maximum enhancement factors for PEDOT, measured at \(\theta = 40°\), are 22.80 and 21.78 for \(n_2\) and \(\alpha_2\), and the corresponding values (\(n_2 = 1.062 \times 10^{-1} \text{ m}^2/\text{W} \) and \(\alpha_2 = -4.33 \times 10^{-8} \text{ m}/\text{W}\)) are roughly equal to the maximum values of ITO (\(n_2 = 1.1 \times 10^{-14} \text{ m}^2/\text{W} \) and \(\alpha_2 = -7 \times 10^{-8} \text{ m}/\text{W}\)). The observed nonlinearity dependent on the angle of incidence is mainly attributed to a modification of the energy distribution of conduction-band electrons as a consequence of the laser-induced electron heating, which is also known as hot electron. As different from ITO, PEDOT displays lower enhancement factors of optical nonlinear responses. The big difference between 22-fold and 2200-fold is attributed to the larger optical losses, which is the larger imaginary part of permittivity at ENZ wavelengths.
To further explain the enhancement mechanism, a two-temperature model is used to describe the optical nonlinearity enhancement mechanism. This model has been successfully applied to explain the ultrafast nonlinear response of metals and semiconductor ENZ materials irradiated by femtosecond pulses\textsuperscript{3,22-25}.

According to coupled differential equations provided in Methods, the nonlinearity enhancement is constricted by the elevated transient electron temperature $T_e$ after the arrival of the laser pulse and the relaxation time is limited by the electron-phonon coupling strength $g_{ep}$. The peak values of free-electron temperature $T_e$ are plotted in Fig. 4(b) as functions of the wavelength and the angle of incidence. The temperature profile exhibits the main features presented in our experimental results, namely an enhancement of the nonlinear response at ENZ wavelengths that keeps increasing with the angle of incidence in the range of $0^\circ < \theta < 40^\circ$. The increase of peak values of $T_e$ originates from increased energy absorbed by free carriers, which is caused by the increased absorptivity $A$ of samples. According to the Fresnel equation for TM-polarized light, the wavelength-dependent permittivity and the angle of incidence jointly contribute to the 22-fold enhanced $n_2$ and $\alpha_2$ at ENZ wavelength and $\theta = 40^\circ$. In Fig. 3(c) and 3(d), the $n_2$ and $\alpha_2$ enhancement factor for ITO are respectively 2200 and 2300 while the $n_2$ and $\alpha_2$ at ENZ wavelength for PEDOT only get a 22-fold enhancement compared to values out of the ENZ region, namely 1300nm. The lower enhancement multiple of $T_e$ resulting in the less enhanced nonlinearity of modified PEDOT films can be attributed to the less pronounced change of the complex refractive index $N$ which leads to the more inapparent change of the wavelength-and angle-dependent absorptivity $A$. Specifically, because $N@1300nm = 1.06 + 0.20i$ and $N@1550nm = 0.59 + 0.58i$ for PEDOT but $N@950nm = 1.25 + 0.06i$ and $N@1240nm = 0.42 + 0.41i$ for ITO, the discrepancy between the absorptivity of PEDOT for 1300nm, $\theta = 0^\circ$ and for 1550nm, $\theta = 40^\circ$ are less than that of ITO. Thus, the enhancement multiple of $T_e$ are 2 for PEDOT (Fig. 4(b)) but 10 for ITO (Fig. S5), which shows consistency with the map of absorptance of PEDOT and ITO (Fig. S7). Another theoretical perspective is the confined electrical field intensity inside the modified PEDOT film as functions of the wavelength and the angle of incidence (Fig. S2).
To verify the correctness of the two-temperature model for PEDOT, the degenerate pump-probe system is set up via 1030nm pulsed laser with the pulse width of 370fs and the repetition frequency of 100kHz, and the spectra of the probe beam is recorded as a function of the delay between the pump and the probe. Due to our pump wavelength ($\lambda_{pump} = 1030\text{nm}$) longer than the bandgap of PEDOT ($\lambda_{gap} = 500\text{nm}$), the electron in the conductive band undergoes an intraband transition and then get redistributed in picosecond timescale. Upon illuminating the sample with a TM pump pulse of $8.2\text{GW/cm}^2$ and $13\text{GW/cm}^2$, the measured transient absorption $\Delta A$ in Fig. 4(c) illustrates the time evolution of hot electrons of PEDOT with an exponential decay time $\tau$ of 1.81ps, and $\tau$ is defined as the time difference between the two time points at which the response value of hot electrons is $1/e$ of its peak value.

Since PEDOT is a p-type semiconductor, this kind of hot electrons in p-type semiconductors is also known as “hot holes”, which has different behaviors from hot electrons in n-type semiconductors. The pump-induced elevation of electronic temperature will give rise to a temperature-dependent Fermi level, causing the variation of the effective plasma frequency and the resultant change in the complex permittivity (details in Method). Thus, the transient absorptance $\Delta A$ can be fitted by the two-temperature model. Measured transient signals slightly mismatch with the simulated behaviors of hot electrons in the two-temperature model for the negative delay time. A possible reason is the pulse width of this laser gets a little broaden compared to the calibration value but this will not have a big influence on the decay time span for the “slow” optical nonlinearity caused by hot holes instead of hot electrons. Fig. 4(c) demonstrates the pump-intensity-dependent transient absorptance $\Delta A$ caused by hot holes in PEDOT. The nonlinear refractive index can be acquired via $n_2 = \Delta n/I_0$, and the calculated result $n_2 = 6.89 \pm 0.23 \times 10^{-16}\text{m}^2/\text{W}$ shows a consistency with our Z-scan results far away from the ENZ region.

As rare p-type semiconductors, the effective mass $m^*$ of PEDOT ($m^* = 5.8m_0$) is two orders of magnitude larger than that of common n-type inorganic semiconductors such as ITO ($m^* = 0.22m_0$), leading to much smaller electron-phonon coupling coefficient $g_{ep}$ and a resultant longer decay time $\tau$ of hot electrons. As shown in Fig. 4(d), hot holes in p-type organic ENZ materials represent longer relaxation time on account of the larger effective mass of carriers.
than hot electrons in n-type inorganic ENZ materials ($\tau_{\text{PEDOT}} = 1.81\,\text{ps}$ and $\tau_{\text{ITO}} = 0.65\,\text{ps}$). Note that although our pump wavelength is not located in the ENZ region of PEDOT, the two-temperature model (Fig. S8) indicates the relaxation time in the ENZ region is much longer than that outside of the ENZ region. In other words, hot holes within the ENZ region of PEDOT will still demonstrate a longer relaxation time than hot electrons within the ENZ region of ITO.

**Conclusion**

In summary, modified PEDOT films with an improved crystalline degree could have an ENZ wavelength at 1555nm, which is in the range of conventional band (C band) for optical communications. The modified PEDOT film exhibits optical nonlinear responses ($n_2$ and $\alpha_2$) 100 times larger than those of ITO at non-ENZ wavelengths and roughly equal to that of ITO at ENZ wavelengths, but the large optical loss limits the hot-carriers-induced optical nonlinearity enhancement. The hot holes in PEDOT demonstrate a longer relaxation time and less elevated free-electron temperature, causing the lower enhancement factor of nonlinear optical response at ENZ wavelengths than ITO. Our results not only give different time evolutionary behaviors of p-type ENZ materials (hot holes) compared to n-type ENZ materials (hot electrons) but also provide a resultantly different behavior of ENZ-induced nonlinearity enhancement between organic ENZ materials and inorganic ENZ materials. Our findings offer a strongly promising candidate of organic optical nonlinear materials for on-chip optical devices, flexible and reconfigurable metasurfaces, such as modulators, high harmonic generator, and ultrafast all-optical switch.

In the future, many other methods, such as acid treatment\textsuperscript{26}, blade coating\textsuperscript{27}, and oxidative chemical vapor deposition (oCVD)\textsuperscript{19}, to prepare highly-conductive PEDOT films can be further researched in order to tune the ENZ wavelength more widely, lessen optical losses, get a higher enhanced nonlinearity and different hot carriers behavior. Our previous reports\textsuperscript{21} and this work show that PEDOT films with boosted electrical conductivity can have an ENZ wavelength from 600nm to 1550nm, which covers all bands (B, O, E, S, C, L, U band) in optical communications and a part of the visible region hard to reach for ITO. Thus, PEDOT films with large optical nonlinearity, ease of processing, and ease of great tuning optical properties\textsuperscript{28,29} could be an
outstanding candidate for applications in nonlinear nanophotonics, nanophotonics, and plasmonics.

**Methods**

**Preparation of PEDOT films**

The PEDOT: PSS solution (Clevios PH1000) was dropped in ethylene glycol solution, left standing for 1 hour, and the upper layer solution was taken with a micro sampler. Drop the PEDOT: PSS solution on 15*15mm glass substrates. Dry annealing was performed at 160°C for 15 min.

**Materials characterization.**

The electrical properties of drop-cast PEDOT films were retrieved from Hall measurements (LakeShore 7604) completing with van der Pauw configuration. Atomic force microscopy (AFM, VEECO MultiMode) was used to characterize the surface morphology and surface roughness of films. Complex permittivity is extracted from the reflectance spectrum by fitting the data with the Drude-Lorentz dispersion model via ellipsometers (J. A. Woollam Co. M2000). The stylus profiler (Bruker DEKTAK-XT) was adopted to measure the real thicknesses of samples.

**Z-scan**

Open-aperture transmissivity

\[ T_{OA} = \frac{\ln[1 + q_0(z)]}{q_0(z)} \]

Closed-aperture transmissivity

\[ T_{CA} = 1 + \frac{4(z^2/z_0^2)\Delta\phi}{(z^2/z_0^2 + 9)(z^2/z_0^2 + 1)} \]

Where \( q_0 \) is the beam parameter along z-axis, \( z_0 \) is the Rayleigh length, \( \Delta\phi \) is the phase change of optical wavefronts.

\[ n_2 = \frac{T_{pv}}{0.405(1 - S)^{0.25}k_{eff}I_0} \left( \frac{m^2}{W} \right) \]

\[ \alpha_2 = \frac{q_0}{I_0k_{eff}} \left( \frac{m}{W} \right) \]
Where $T_{pv}$ is the difference between the peak and the valley in the closed-aperture transmissivity, $S$ is the linear transmissivity of aperture, $k$ is the wave vector, $L_{eff}$ is the effective thickness, $I_0$ is the peak intensity.

**Two-temperature model**

The laser-pulse-heated hot electrons at a non-thermal energy distribution act as a delayed source of heating. The dynamics of the conduction band electrons can be described by the coupled differential equations:

$$C_e \frac{dT_e}{dt} = -g_{ep}(T_e - T_l) + \frac{N}{2\tau_{ee}}$$

$$C_l \frac{dT_l}{dt} = g_{ep}(T_e - T_l) + \frac{N}{2\tau_{ep}}$$

$$\frac{dN}{dt} = -\frac{N}{2\tau_{ee}} - \frac{N}{2\tau_{ep}} + P$$

Where $C_e$ is the heat capacity of electrons (lattice), $T_e$ is the free-electron (lattice) temperature, $g_{ep}$ is the electron-phonon coupling coefficient, $\tau_{ee}$ is the electron-electron (electron-phonon) relaxation time, $N$ is the non-thermal energy density stored in the excited electrons. Here we ignore the influence of the lattice temperature to Cl and find a constant lattice heat capacity $C_l = 2.6 \times 10^6 J/m^3 K^{-1}$. Other parameters involved are estimated by following equations:

$$g_{ep} = \frac{0.562 n_e k_B^2 \Theta_D^2 v_F}{L_f T_l E_F}$$

$$\tau_{ep} = 2 C_e g_{ep}$$

$$\tau_{ee} = \gamma - \tau_{ep}$$

$$C_e = \frac{3\pi^2 n_e k_B T_e}{\sqrt{36T_F^2 + 4\pi^3 T_F^2}}$$

$$P(t) = AI_0 \alpha \exp\left(-2 \left(\frac{t}{\tau_p}\right)^2\right) \propto A^2$$

Where $n_e$ is the carrier density, $k_B$ is the Boltzmann’s constant, $\Theta_D$ is the debye temperature, $L_f$ is the electron mean free path, $E_F$, $v_F$, $T_F$ are the Fermi energy, Fermi velocity ($v_F = \sqrt{2m_eE_F}$), Fermi temperature ($T_F = \frac{E_F}{k_B}$) respectively, $\gamma$ is the Drude damping rate, $A$ is the absorptivity ($A = 1 - T - R$), $P$ is the absorbed power density, $I_0$ is the power intensity incident on the sample surface, $\tau_p$ is the laser pulse duration.
The electronic-temperature-dependent fermi level $\mu(T_e)$ is related to the fermi energy $E_f$ by:

$$\mu(T_e) \approx E_f \left[ 1 - \frac{\pi^2}{12} \left( \frac{T_e}{T_f} \right)^2 \right]$$

$A$ can be expressed via p-polarized Fresnel equations:

$$R = \tan^2\left( \frac{\theta_1 - \theta_2}{\theta_1 + \theta_2} \right)$$

$$T = \frac{n_2 \cos \theta_2}{n_1 \cos \theta_1} \frac{4 \sin^2 \theta_2 \cos^2 \theta_1}{\sin^2(\theta_1 + \theta_2) \cos^2(\theta_1 - \theta_2)}$$

$$A = 1 - T - R$$

Where $R$, $T$ and $A$ are reflectance, transmittance, absorptivity respectively, $\theta_1$ and $\theta_2$ are the angle of incidence and emergence respectively. The relation between between $\theta_1$ and $\theta_2$ obey the Snell’s Law $n_1 \sin \theta_1 = n_2 \sin \theta_2$.

**Drude-sommerfeld model**

The temperature-dependent Fermi level could be related with the change of carrier density $n$ via:

$$E_f = \frac{\hbar^2}{(2\pi)^2 \cdot (2m_e)} (3\pi^2 n)^{\frac{2}{3}}$$

Then the effective plasma frequency and permittivity could be determined by:

$$\omega_p = \sqrt{\frac{n \epsilon_e^2}{\epsilon_0 m_e}}$$

$$\epsilon = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\gamma \omega}$$

Equation for reflectivity of TM-polarized light in the case of a single film will provide the pump-induced change of refractive index and time evolution of the reflectivity.

$$\Gamma = \frac{\rho_1 + \rho_2 e^{2i\delta_1}}{1 + \rho_1 \rho_2 e^{2i\delta_1}}$$

$$\rho_1 = \frac{1 - n}{1 + n}$$

$$\rho_2 = \frac{n - n_{glass}}{n + n_{glass}}$$

$$\delta_1 = \frac{2\pi n l}{\lambda_0}$$

$$R = |\Gamma|^2$$
Data Availability

The data that support this study are available from the corresponding author upon request

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**Acknowledgements**

This work was supported by the State Key Laboratory of Modern Optical Instruments, Zhejiang University, *the National Natural Science Foundation of China (NNSFC; No. 91950205)*, and *National Key Scientific and Technological Infrastructure for Translational Medicine, Shanghai (No. TMSK-2020-125)*.

**Author contribution**

Q. H proposed the idea, and performed z-scan measurement; X. Y used Hall measurement, ellipsometer, and atomic force microscope; X. Y and J. Q prepared the sample; S. L helped perform the laser-related experiments; G. C provided experience about inorganic materials; M. D and H. Y are responsible for all these parts; Q. H wrote this manuscript; H. Y revised this manuscript.

**Competing interests**

The authors declare no competing interests.

**Table 1 Parameters of modified and pristine PEDOT films**

| Thickness (nm) | $\sigma$ ($S \cdot cm^{-1}$) | $R_s$ ($\Omega$) | $\mu$ ($cm^2 \cdot V^{-1} \cdot s^{-1}$) | $n$ ($10^{20} \ cm^{-3}$) | $\lambda_{ENZ}$ (nm) |
|----------------|-------------------------------|------------------|----------------------------------------|--------------------------|---------------------|
|                | PRISTINE PEDOT: PSS | MODIFIED PEDOT (this work) |
|----------------|---------------------|---------------------------|
|                |                     |                           |
|                | 85                  | 589                       |
|                | 0.381               | 961                       |
|                | 3.082 × 10^5        | 33.04                     |
|                | 0.0238              | 5.8                       |
|                | 1.003               | 10.37                     |
|                | 5267                | 1555                      |

$\sigma$, conductivity; $R_s$, square resistance; $\mu$, mobility; $n$, carrier concentration; $\lambda_{ENZ}$, ENZ wavelength;

Table 2: Angle- and wavelength-dependent nonlinear refractive index $n_2$ and nonlinear absorption coefficient $\alpha_2$ and corresponding enhancement factors.

| $\lambda$(nm) | $\theta$ (°) | $n_2$ $(10^{-2} cm^2 \cdot GW^{-1})$ | $\alpha_2/(10^3 cm \cdot GW^{-1})$ | $n_2$ enhancement factor | $\alpha_2$ enhancement factor |
|---------------|-------------|-------------------------------------|----------------------------------|-------------------------|-----------------------------|
| 1300          | 0           | 0.47                                | -0.20                            | 1                       | 1                           |
| 1800          | 0           | 0.53                                | -0.38                            | 1.14                    | 1.91                        |
| 1550          | 0           | 2.23                                | -0.94                            | 4.79                    | 4.75                        |
| 1550          | 20          | 4.90                                | -2.49                            | 10.52                   | 12.52                       |
| 1550          | 30          | 7.21                                | -3.14                            | 15.48                   | 15.81                       |
| 1550          | 40          | 10.62                               | -4.33                            | 22.80                   | 21.78                       |

$\lambda$, wavelength; $\theta$, angle of incidence; $n_2$, nonlinear refractive index; $\alpha_2$, nonlinear absorption coefficient; enhancement factor is defined as the ratio between the corresponding value and the value at $\lambda = 1300 nm, \theta = 0^\circ$. 
Fig. 1 (a) Sample structure. Modified PEDOT films are prepared on glass substrate by drop-casting and dry annealing. (b) Atomic force microscope (AFM) 3D height images of modified PEDOT films with a scanning area of $5 \times 5 \mu m$. (c) X-ray diffraction (XRD) patterns of modified PEDOT (red line) and pristine PEDOT: PSS (black line). (d) Real (Red) and imaginary (Blue) permittivity of PEDOT acquired by ellipsometer. ENZ wavelength of PEDOT is located at 1550nm and imaginary permittivity at the ENZ wavelength is $\varepsilon'' = 0.75$. 
Fig. 2 (a) Experimental setup. The Z-scan measurement were performed using 150fs with repetition rate of 1kHz from an optical parametric generator. A spatially filtered p-polarized Gaussian beam is focused onto the sample with the angle of incidence $\theta$ by a lens L1. (b) Closed- and (c) open-aperture Z-scan signals at $\lambda = 1550\,\text{nm}$ and $\theta = 0^\circ$ (square), $20^\circ$ (circle), $30^\circ$ (upward triangle), $40^\circ$ (downward triangle) for the modified PEDOT film with an ENZ wavelength of 1555nm. The solid lines represent theoretical fits to the experimental data.
Fig. 3 The values (square) and corresponding enhancement (triangle) compared with values at 1300nm at normal incidence for (a) $n_2$ and (b) $\alpha_2$ at $\lambda = 1550\text{nm}$ are plotted as functions of the angle of incidence $\theta$. (c) (d) Comparison between the nonlinearity enhancement factor caused by ENZ effect of modified PEDOT and ITO. The enhancement factor is defined as the ratio between $n_2$ and $\alpha_2$ under current situations and $n_2$ and $\alpha_2$ out of ENZ regions. Detailed value is given in Table. 2 and Table. S1.
Fig. 4 Numerical modeling of the hot-electron dynamics of PEDOT and pump-probe results. (a) Transient response of the free-electron temperature $T_e$ and lattice temperature $T_l$. The decay time $\tau$ is defined as the difference between the time at which $T_e$ decreases to the $1/e^2$ of the peak temperature. (b) Map of the peak temperature of $T_e$ in the PEDOT film calculated as a function of $\theta$ and $\lambda$. Both calculations assume a normally incident laser with an intensity of 20 $GW/cm^2$. (c) Measured transient absorption $\Delta A$ of PEDOT via pump-probe techniques under pump pulse intensities of 8.2$GW/cm^2$ (blue line) and 13$GW/cm^2$ (green line). Pump-probe configuration: 1030nm Nd laser with repetition frequency of 100kHz and pulse width of 370fs. (d) Comparison of the normalized transient response of PEDOT (blue line and dots) and ITO (black dashed line). $\tau_{PEDOT} = 1.81\text{ps}$ and $\tau_{ITO} = 0.65\text{ps}$. 
Supporting information

Author Information

Qili Hu¹, Xinlan Yu¹, Hongqi Liu¹, Jiahuan Qiu², Sen Liang¹, Guanan Chen¹, Chengcan Han¹, Miao Du², Hui Ye¹,†

1 State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou, P. R. China
2 MOE Key Laboratory of Macromolecular Synthesis and Functionalization, Department of Polymer Science and Engineering, Zhejiang University, Hangzhou, P. R. China

Fig. S1 Open-aperture signals for wavelength of 1800nm (a) and 1300nm (b). Closed-aperture signals for wavelength of 1800nm (c) and 1300nm (d).
Table. S1 Nonlinear refractive index $n_2$ and nonlinear absorption coefficient $\alpha_2$ of various ENZ films.

| Materials     | $n_2$ ($10^{-2} cm^2GW^{-1}$) | $\alpha_2$ ($10^{3} cm^3GW^{-1}$) | Comments                  |
|---------------|-------------------------------|-----------------------------------|---------------------------|
| Au(20, 21)    | 0.12                          | 0.122                             | z-scan; @600nm; $\theta = 0^\circ$ |
| TiN(22)       | -1.3                          | -0.68                             | z-scan; @780nm; $\theta = 0^\circ$ |
| ITO(9)        | 0.005                         | -0.003                            | z-scan; @970nm; $\theta = 0^\circ$ |
| ITO(9)        | 0.215                         | -0.159                            | z-scan; @1240nm; $\theta = 0^\circ$ |
| ITO(9)        | 11                            | -7                                | z-scan; @1240nm; $\theta = 60^\circ$ |
| AZO(23)       | 0.035                         | -0.025                            | XPM; @1310nm               |
| HTJSq(24)     | 3.5                           | -2.539                            | z-scan; @565nm; $\theta = 45^\circ$ |
| TDBC(24)      | 17                            | -3.404                            | z-scan; @500nm; $\theta = 45^\circ$ |
| PEDOT: PSS(25)| ~                             | -1.606                            | z-scan; @800nm; $\theta = 0^\circ$ |
| PEDOT (this work) | 0.47                      | -0.2                              | z-scan; @1300nm; $\theta = 0^\circ$ |
| PEDOT (this work) | 2.23                      | -0.94                             | z-scan; @1550nm; $\theta = 0^\circ$ |
| PEDOT (this work) | 10.62                     | -4.33                             | z-scan; @1550nm; $\theta = 40^\circ$ |

Au, gold; TiN, titanium nitride; ITO, indium tin oxide; AZO, aluminum-doped zinc oxide; HTJSq, [2,4-bis[8-hydroxy-1,1,7,7-tetramethyljulolidin-9-yl] squaraine]; TDBC, sodium [5,6-dichloro-2-[5,6-dichloro-1-ethyl-3-(4-sulphobutyl)-benzimidazol-2-ylidene]-propenyl]-1-ethyl-3-(4-sulphobutyl)-benzimidazolum hydroxide]; PEDOT: PSS, poly(3,4-ethylenedioxythiophene) polystyrene sulfonate.

XPM, cross phase modulation; $\theta$, angle of incidence; @ represents the incident wavelength.
Fig. S2 Electrical field enhancement at the air-PEDOT interface for obliquely incident TM polarized light is plotted as a function of the angle of incidence $\theta$ and wavelength.

Fig. S3 AFM 2D height image
Fig. S4 Permittivity of spin-coated PEDOT film

Fig. S5 Two-temperature model for ITO, copied from M. Zahirul Alam et al.¹

Fig. S6 Main electronic transition in PEDOT, copied from Jesper Edberg et al.²
Fig. S7 Absorptance vs wavelength and angle of incidence $\theta$.

Fig. S8 Numerically simulated decay time as functions of wavelength and the angle of incidence $\theta$.

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