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Quest for organic plasmonics

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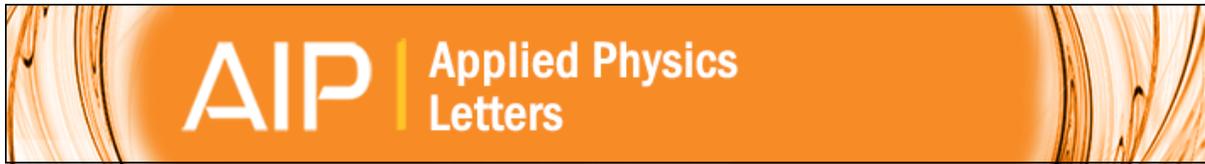
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Quest for organic plasmonics

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Many photonic metamaterials and plasmonic devices, in spite of their unparalleled responses to light waves and nearly fantastic applications, suffer from absorption loss in constituent metallic components. Unfortunately, none of the known techniques aimed to conquer the absorption loss has led to a revolutionary technological breakthrough, prompting a continuing quest for efficient solutions to the loss problem. In this letter, we study optical properties of non-metallic organic plasmonic and epsilon-near-zero materials and demonstrate propagation of a surface plasmon polariton at the interface between solid organic dye and air. © 2013 AIP Publishing LLC.

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Localized surface plasmons (resonant oscillations of free electrons in metallic nanoparticles) and surface plasmon polaritons (surface electromagnetic wave propagating along interface between metals and dielectrics) play an increasing role in a vast variety of applications, including, but not limited to sensing,¹ information technology,² biomedical testing,³ and treatment.⁴ They often determine unparalleled optical properties of metamaterials (engineered composite materials with rationally designed geometry, composition, and arrangement of subwavelength building blocks), whose applications range from sub-diffraction imaging^{5–9} and nano-scale lithography¹⁰ to quantum optics¹¹ and heat management.¹² The use of metallic inclusions in metamaterials allows one to span a broad range of effective dielectric permittivities of composite media, ranging from record-high positive to negative values. Of particular interest are the ranges (i) $1 > \epsilon' > 0$ essential for transformation optics and realization of an optical cloak,^{13,14} (ii) $\epsilon' \approx 0$ desired for nanocircuitry applications,¹⁵ and (iii) $\epsilon' < 0$ used in a variety of plasmonic systems and devices.¹⁶ (In this work, ϵ' and ϵ'' designate real and imaginary parts of complex relative permittivity, $\epsilon = \epsilon' + i\epsilon''$.) However, unfortunately, metallic nanoinclusions are sources of strong absorption loss. This hinders many dream applications of metamaterials and plasmonics and motivates scientists and engineers to search for efficient solutions to the loss problem.

As it has been predicted theoretically^{17–21} and demonstrated experimentally,^{22–29} loss in metamaterials and plasmonic systems can be conquered by optical gain in an adjacent dielectric. However, achieving high critical value of optical gain ($\geq 1000 \text{ cm}^{-1}$) is a challenging technological task calling for alternative technical solutions.

Among passive loss reduction techniques are (i) perfection of metallic film quality,^{30–34} (ii) use of difficult-to-handle alkali metals,^{35,36} (iii) alloying and doping noble metals,^{36,37} and (iv) modification of metallic surface with organic molecules.³⁸ Unfortunately, despite of numerous incremental improvements, none of these methods has led to a bold technological breakthrough.

Doped semiconductors present an interesting alternative to metals as potential plasmonic materials. However, at low doping level the plasma frequency is too low, limiting plasmonic behavior to the mid-infrared range,³⁹ and at high doping levels (e.g., in transparent conducting oxides) material disorder results in relatively high optical losses.^{36,40,41} Nevertheless, transparent conducting oxides have been claimed to be superior to metals in several metamaterial and plasmonic applications in the near-infrared spectral range.³⁶ Another emerging range of plasmonic materials, nitrides of titanium and zirconium, have negative dielectric permittivity in the visible and infrared parts of the spectrum; however, their losses are higher than those in noble metals.⁴²

The question arises whether metal-free metamaterials and plasmonic systems, which do not suffer from excessive damping loss, can be realized in the visible range? With no doubts, inexpensive materials with such advanced properties can impact whole technological fields of nanoplasmonics and metamaterials.

In this work, we show that purely organic materials with negative, near-zero, and smaller than unity dielectric permittivities ϵ' can be easily fabricated and demonstrate propagation of a surface plasmon polariton at the material/air interface.

Our approach can be explained in simple terms of the Lorentz and Clausius-Mossotti models, describing responses of condensed molecular and atomic systems to electromagnetic waves.⁴³ At a number of simplifying assumptions, which are well satisfied in the majority of dielectric solids and liquids, both quantum⁴⁴ and classical⁴³ approaches result in the same expressions for real and imaginary components of relative permittivity ϵ in the vicinity of an absorption resonance,

$$\begin{aligned} \epsilon' &= \epsilon_b + \frac{f \left(\frac{\epsilon_b + 2}{3} \right)^2 \left(\frac{Nq^2}{\epsilon_0 m} \right) \frac{(\bar{\omega} - \omega)}{2\bar{\omega}}}{(\bar{\omega} - \omega)^2 + \left(\frac{\Delta\omega}{2} \right)^2} \\ &= \epsilon_b + \frac{\epsilon''_{\max} \Delta\omega \frac{(\bar{\omega} - \omega)}{2}}{(\bar{\omega} - \omega)^2 + \left(\frac{\Delta\omega}{2} \right)^2}, \end{aligned} \quad (1)$$

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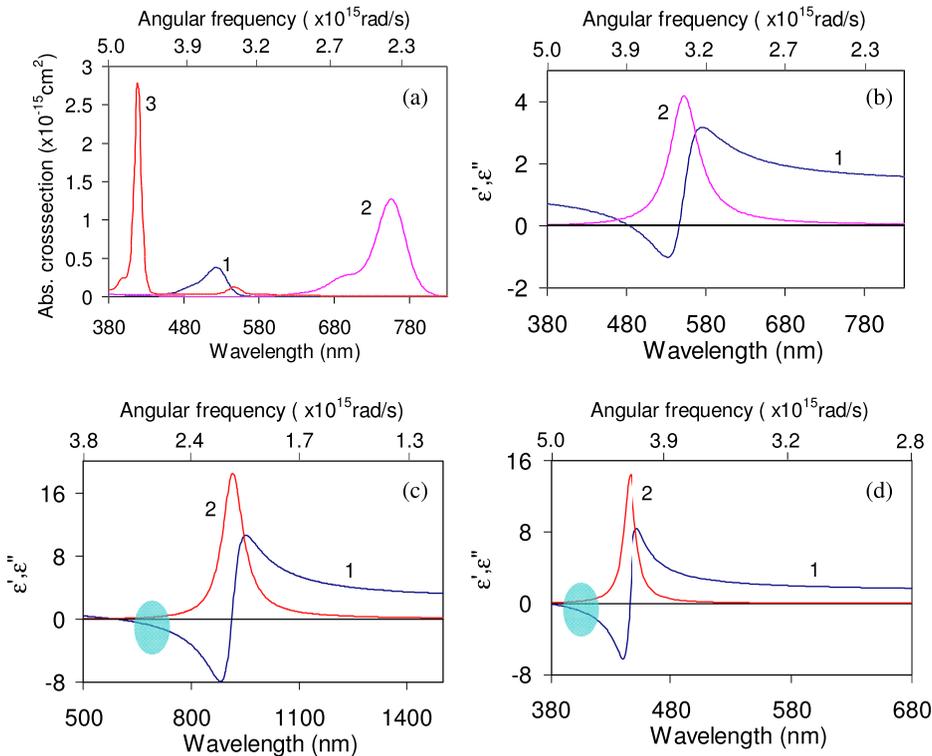


FIG. 1. (a) Absorption cross section spectra of R6G (1), HITC (2), and ZnTPP (3), measured in diluted dichloromethane solutions. (b)–(d) Spectra of real ϵ' and imaginary ϵ'' parts of dielectric permittivities calculated for solid compounds of R6G (b), HITC (c), and ZnTPP (d) molecules in the Lorentz model approximation (Eqs. (1)–(3)). The ranges of negative ϵ' and small ϵ'' are marked with ellipses.

$$\epsilon'' = \frac{f \left(\frac{\epsilon_b + 2}{3} \right)^2 \left(\frac{Nq^2}{\epsilon_0 m} \right) \left(\frac{\Delta\omega}{4\bar{\omega}} \right)}{(\bar{\omega} - \omega)^2 + \left(\frac{\Delta\omega}{2} \right)^2}. \quad (2)$$

Here ϵ_b is the “bulk” relative permittivity (which can be due distant high-frequency resonances of the same absorbing molecules or a host medium), f is the transition’s oscillator strength, N is the number density of dye molecules, q and m are the electron charge and the electron mass, respectively, ϵ_0 is the vacuum permittivity, $\Delta\omega$ is the transition’s bandwidth, $\bar{\omega}^2 = \omega_0^2 - \frac{Nq^2}{3\epsilon_0 m}$, ω_0 is the resonance frequency of isolated absorbing molecules in vacuum, and ϵ''_{max} is the maximal imaginary part of relative permittivity at $\omega = \bar{\omega}$.⁴⁵

In the vicinity of the resonance, the spectrum of $\epsilon'(\omega)$ has a characteristic wave-like behavior, with the amplitude of the perturbation proportional to the maximal value of $\epsilon''(\omega)$ (Eqs. (1) and (2)). Correspondingly, if the absorption line is strong enough, $\epsilon''_{max} \gg 1$, real part of relative permittivity ϵ' can become negative, Figs. 1(b)–1(d). Since $\epsilon''(\omega)$ decays faster than $(\epsilon'(\omega) - \epsilon_b)$, as frequency ω is tuned off the resonance, there can exist a frequency range at which ϵ' is negative and ϵ'' is insignificantly small, Figs. 1(c) and 1(d). (Even easier to achieve is a low-loss epsilon-near-zero regime.)

A similar phenomenon, commonly referred to as Reststrahlen effect in solids,⁴⁶ is known in many materials with strong phonon lines. Thus, broadly used in the metamaterial design SiC has strong negative dielectric permittivity band in the mid-infrared part of the spectrum.⁴⁷

Organic materials in our studies were thin films of three commercially available dyes with strong absorption bands, Rhodamine 6G chloride (R6G), hexamethylindotrycarbocyanine iodide (HITC), and zinc tetraphenylporphyrin (ZnTPP)

prepared without use of any polymeric host matrix. The dyes were dissolved in dichloromethane (DCM), dropped onto a glass substrate and dried to solid state in air. The thickness of the films, ranging from 40 to 160 nm, was measured using Dektak-6M profilometer.

By measuring transmission spectra of diluted dyes solutions with known concentrations of dye molecules, we have obtained the spectra of corresponding absorption cross sections σ_{abs} , Fig. 1(a). One can show that the combination of parameters $f q^2 / \epsilon_0 m$ entering Eqs. (1) and (2) can be evaluated, if the experimental values of the peak absorption cross section σ_{max}^{abs} and the absorption bandwidth $\Delta\omega_s$ are known in a diluted dye solution with known index of refraction $\sqrt{\epsilon_{bs}}$,

$$\frac{f q^2}{\epsilon_0 m} = \sigma_{max}^{abs} c \Delta\omega_s \sqrt{\epsilon_{bs}} \left(\frac{3}{\epsilon_{bs} + 2} \right)^2, \quad (3)$$

where c is the speed of light.

By combining Eq. (3) with Eqs. (1) and (2), one can calculate the spectra of real and imaginary parts of relative permittivity ϵ of a solid dye medium, if the molecular number density N , the absorption bandwidths $\Delta\omega$ and $\Delta\omega_s$, and the bulk permittivity ϵ_b are known. Such spectra calculated for solid R6G, HITC, and ZnTPP dye films are depicted in Figs. 1(b)–1(d). In this calculation, the molecular number densities N were evaluated based on molar weights MW known from the literature and volume densities ρ measured in compressed (at 1500 psi) pellets of dye powders; the absorption bandwidth in solid $\Delta\omega$ was assumed to be equal to the known absorption bandwidth in solution $\Delta\omega_s$; and ϵ_b was assumed to be equal to unity.⁴⁸ One can see that all three dye compounds show a promise of having negative real values of ϵ' , possibly even at relatively small ϵ'' .

One should note that the model above can be used only to estimate the order of magnitude of the effect, since an

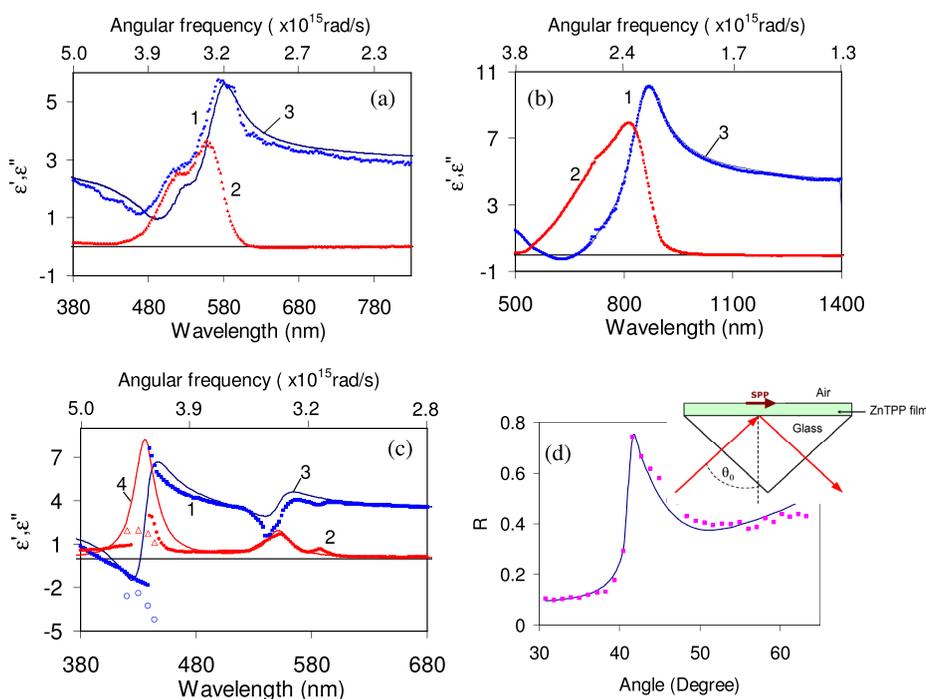


FIG. 2. (a–c) Real (ϵ' , trace 1) and imaginary (ϵ'' , trace 2) parts of the dielectric permittivity in R6G (a), HITC (b), and ZnTPP (c) retrieved from the experimental transmittance $T(\lambda)$ and reflectance $R(\lambda)$ spectra.⁴⁷ In Figures (a) and (b): trace 3—spectrum of ϵ' calculated through the Kramers-Kronig relations from the spectrum of ϵ'' (trace 2). In Figure (c): traces 3 and 4 are the fits to the spectra 1 and 2 with the model accounting for two Lorentzian bands (ϵ' —trace 3, and ϵ'' —trace 4); circles and triangles are, respectively, ϵ' and ϵ'' measured in the SPP experiments for four different wavelengths 420, 430, 438, and 444 nm. (d) SPP angular reflectance profile measured in ZnTPP film in the Kretschmann geometry (characters—experiment, solid line—fitting with the standard model of Ref. 16). Inset: Kretschmann attenuated total reflection setup.

increase of the absorption bandwidth, expected in condensed molecular systems, can reduce the amplitude of the wave-like perturbation in the spectrum of $\epsilon'(\omega)$, making negative values of ϵ' less negative or even positive. On the other hand, the effect of an increased bulk permittivity ϵ_b , also expected in solid molecular compounds, can lead to more negative or less negative values of ϵ' , depending on the other system parameters.

The reflectance $R(\lambda)$ and transmittance $T(\lambda)$ spectra of the dye films were taken in a spectrophotometer Lambda 900 equipped with an integrating sphere. The spectra of real ϵ' and imaginary ϵ'' parts of the dielectric constant were recalculated point by point from the spectra of R and T using the known formulas¹⁶ and the inverse-problem-solving routine described in Ref. 49. (Note that the *assumption-less* retrieval method used⁴⁹ did not depend on any model, e.g., Lorentz or Drude, that related to each other values of permittivities at different wavelengths.)

The extracted spectra $\epsilon'(\lambda)$ and $\epsilon''(\lambda)$ in the three dye films studied (Figs. 2(a)–2(c)) are reasonably close to the estimates based on the experimentally measured absorption cross sections in the diluted solutions (Figs. 1(b)–1(d)). Two dyes, HITC and ZnTPP, have negative values of ϵ' and one of them, ZnTPP, has negative ϵ' at reasonably small value of ϵ'' . As expected, the absorption bands in solid dye compounds are broadened in comparison to those in liquid solutions (the latter effect is particularly prominent in HITC, compare Figs. 1(c) and 2(b)) and the values of bulk permittivity ($\epsilon_b \sim 2.5$) significantly exceed unity.

Note that in R6G and HITC, real and imaginary parts of dielectric permittivity match each other fairly well via the Kramers-Kronig relations (Figs. 2(a) and 2(b)), confirming the validity of our experimental method.⁴⁹ The match was not as good in ZnTPP. When the extracted spectrum of ϵ' was fitted with the Kramers-Kronig abiding model accounting for two Lorentzian lines (at 430 nm and 560 nm), a substantial disagreement between the model and the experiment

was found in the spectrum of ϵ'' at $\lambda \approx 430$ nm, Fig. 2(c). Possible reasons for the mismatch include (i) presence of a strong absorption band outside of the spectral range studied, (ii) strong anisotropy of the ZnTPP film, which is typical to organic crystals, and (iii) difficult to control and monitor nonuniformity of the dye film and orientations of constituent nanocrystallines. The detailed study of this phenomenon is beyond the scope of this paper.

The substantially strong negative dielectric permittivity demonstrated in ZnTPP, suggests that this dye compound can function as a plasmonic material. The experimental demonstration of a surface plasmon polariton propagating at the ZnTPP/air interface has been conducted in the attenuated total reflection (ATR) setup in the Kretschmann geometry,¹⁶ see inset of Fig. 2(d). Following a standard routine,¹⁶ the reflection R of incident p polarized laser light was measured as a function of the incidence angle θ . The experiment was repeated at several wavelengths ranging from 420 to 444 nm. The angular reflectance profiles $R(\theta)$ (Fig. 2(d)) were fitted with the known theoretical model,¹⁶ in which real and imaginary parts of dielectric permittivity were used as fitting parameters. A good agreement between the theory and the experiment (see, e.g., Fig. 2(d)) was achieved at the values ϵ' and ϵ'' , which were reasonably close to those derived from the transmittance and reflectance measurements in Fig. 2(c).

To summarize, we have shown that negative real values of dielectric permittivities ϵ' can be achieved in purely organic solid-state materials. The propagation of a surface plasmon polariton at the organic material/air interface has been demonstrated in the Kretschmann geometry, paving the way to organic plasmonics and metamaterials. Although the imaginary part of dielectric permittivity was rather high in the surface plasmon polaritons (SPPs) wavelength range (e.g., $\epsilon'' = 1.9$ at $\lambda = 420$ nm in ZnTPP), it was significantly smaller in the epsilon-near-zero range, with the smallest absolute value of dielectric permittivity $|\epsilon|_{\min}$ equal to 0.63 at $\lambda = 396$ nm. The latter quantity is much smaller than that in gold ($|\epsilon|_{\min} = 3.34$

at $\lambda = 207$ nm (Ref. 50)) and a little bit larger than those in silver ($|\epsilon|_{\min} = 0.53$ at $\lambda = 326$ nm (Ref. 50)), indium tin oxide (ITO) ($|\epsilon|_{\min} = 0.29$ at $\lambda = 1200$ nm (Ref. 40)), and aluminum doped zinc oxide ($|\epsilon|_{\min} = 0.51$ at $\lambda = 1830$ nm⁴²). Optical losses in the spectral ranges corresponding to $\epsilon' < 1$ can be further reduced in compounds with stronger absorption lines, see Eqs. (1) and (2). On the other side of the resonance, the same materials can have substantially large values of dielectric permittivities ($\epsilon' \geq 10$) and strong dispersion, which can be of interest to a variety of photonic applications, including waveguiding and pulse-shaping.

When this work was completed, the authors became aware of Refs. 51 and 52 in which negative values of ϵ' have been reported in the vicinity of strong absorption lines, and SPPs (referred to as exciton surface polaritons⁵¹) have been propagated in the Otto configuration¹⁶ in the tetracyanoquinodimethane (TCNQ),⁵¹ and poly-2,4-hexadiene-1,6-diol bis(*p*-toluene sulfonate) (PTS)⁵² organic single crystals. The disadvantage of those materials, besides elaborate crystal growth, was very high loss ($\epsilon'' > 12$) in the spectral range of negative ϵ' . In another potentially very interesting organic plasmonic material, γ -cyclopropyl-bis(1,3,3-trimethylindole-9-*yl*) pentamethinium fluoroborate (CTIP), the dispersion was of Drude type rather than of Lorentzian type.⁵²

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