Linear and nonlinear optical responses of a dye anchored to gold nanoparticles dispersed in liquid and polymeric matrixes

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Abstract: The compound $[4-CH_3C_6H_4-SS-CH_2CH_2-N(CH_3)C_6H_4C(C_6H_4N(CH_3)_2)-4)_2]Cl (1a)$ consists of the triarylmethyl chromophore of crystal violet appended to an organic disulfide, to entail direct attachment of this dye to gold surfaces. Addition of 1a to colloidal dispersions of the metal produced a stable dispersion in methanol-water mixtures. Transmission electron microscopy of Freeze-Fracture sections shadowed with carbon and platinum confirmed that the dispersion remains unaggregated. Local-field effects and coupling to the surface plasmon of gold magnified the interaction of the chromophore with optical fields. A large oscillator strength in the visible spectrum (*f* ca. 35) and a first hyperpolarizability (β ca. 10⁻²⁶ esu, hyper-Rayleigh scattering) were observed as the colloid adsorbed dye molecules. A Hill-type analysis indicated that the adsorption process is cooperative. This combination of organic chromophore and nanoparticle was adapted for incorporation into PMMA-based composite films whose electrooptic coefficient ($r_{113} = 2.20 \text{ pm V}^{-1}$) is larger than the sum of the individual contributions of dye and metallic particles.

Key words: chromophores, colloids, gold, local-field effects, nonlinear optical materials.

Résumé : Le composé [4-CH₃C₆H₄-SS-CH₂CH₂-N(CH₃)C₆H₄C(C₆H₄N(CH₃)₂)-4)₂]Cl (**1a**) comprend le chromophore triarylméthyle du cristal violet fixé sur un disulfure organique qui permet d'attacher directement ce colorant sur des surfaces d'or. L'addition du composé **1a** à des dispersions colloïdales du métal conduit à la formation d'une dispersion stable dans des mélanges méthanol–eau. La microscopie électronique de transmission de sections Freeze-Fracture ombragées par du carbone et du platine permet de confirmer que la dispersion dans un état qui n'est pas agrégé. Les effets de champs locaux et le couplage de l'or à la surface plasmonique amplifient l'interaction du chromophore avec les champs optiques. Avec l'absorption de molécules de colorant par le colloïde, on a observé une grande force oscillatoire dans le spectre visible (*f* d'environ 35) ainsi qu'une première hyperpolarisabilité (β environ 10⁻²⁶ esu, diffusion hyper-Rayleigh). Cette combinaison de chromophore organique et de nanoparticule est adaptée à une incorporation dans des films composites à base de PMMA dont le coefficient électrooptique ($r_{113} = 2,20$ ppm V⁻¹) est supérieur à la somme des contributions individuelles du colorant et des particules métalliques.

Mots clés : chromophores, colloïdes, or, effets de champs locaux, matériaux optiques non linéaires.

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Introduction

It is predicted that a third of current electronic technologies for data transmission and processing will eventually be replaced by their faster photonic counterparts. The development of practical electrooptic and photorefractive applications depends on the availability of materials with large nonlinear optical (NLO) responses. Crystals of LiNbO₃, KH₂PO₄, and BaB₂O₄ are used to change the wavelength of

laser light through parametric processes. Such materials are expensive and cumbersome to tailor into the waveguide configurations that are compatible with optical fibre systems. Because of their processability, polymers and glasses with NLO properties are a convenient alternative to inorganic crystals. Conjugated polymers such as polydiacetylenes have inherent third-order NLO activity but most systems consist of a transparent host-matrix uniformly doped with a NLOactive species. Two kinds of such NLO dopants can be dis-

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tinguished: organic chromophores and nanoparticles of semiconductors or metals.

Second- (1, 2) and third-order NLO activity (3) can be induced with organic dyes. The nonlinear response of the composite is in principle proportional to the amount of chromophore present. However, large loadings have an unfavourable effect on mechanical properties, may decrease transparency, and lead to attenuation by dipolar coupling as the inter-chromophore distance decreases. It is therefore desirable to prepare chromophores with the largest hyperpolarizabilities possible. Systematic research during the past two decades has identified features such as a high degree of bond alternation that give organic molecules large hyperpolarizabilities (4). Furthermore, the NLO response of organic species can be augmented up to an order of magnitude when they are organized in orientationally correlated assemblies (5) and chiral supramolecular architectures (6). A remarkable achievement in this field was the preparation of a chromophore that conferred a polymer a high electrooptic coefficient of about 20 pm V⁻¹. This, in turn, led to the fabrication of a 0.1 THz electrooptic modulator operating with a drive voltage of less than 1.0 V (7).

A completely different class of NLO dopants includes small particles of gold, silver, or metal chalcogenides. Because of their inherent symmetry, dispersions of such particles have been considered only as third-order NLO materials (8, 9). A two-wave-mixing device capable of operating as an all-optical switch or gate has been demonstrated (10). The recent discovery of second-order NLO activity for liquid colloidal dispersions of gold (11, 12) opened the possibility of their use in electrooptic devices.

The optical response of metallic colloids arises from the ease with which electromagnetic fields excite electrons at the surface of the particles. Photo-excitation induces charge density oscillations, in particular a collective movement of electrons. This surface plasmon is partially responsible for the intense absorptions at 500-550 and 400 nm, which are characteristic of wine-red gold and yellow-brown silver hydrosols, respectively. It is well known that electronic excitation leads to an electric field redistribution near the metal surface, especially an enhancement in small step sites or protrusions (13, 14) as well as in tiny particles and their aggregates (15, 16). Molecules in the vicinity of such surfaces experience an intense electric field and an increase in their cross-sections for optical interactions. This antenna effect is thought to play an important role in surface enhanced Raman spectroscopy (17). Numerous theoretical calculations have predicted large enhancement factors for luminescence and light absorption of molecules on the surface of small metallic particles (18-20), with further enhancement of absorptivity for systems in which molecular electronic transitions and the plasmon resonance overlap.

Previous studies of the enhancement of linear optical responses in dye-metal composites have been carried out, depositing dyes on metal island films through sublimation, solvent evaporation, spin coating, or adsorption from liquid solutions (21–26). Those systems indeed exhibited stronger linear optical responses as compared to metal-free controls. Alternatively, dyes have been combined with colloidal dispersions and activated quartz slides have been dipped in the mixtures (27). On such heterogeneous surfaces it is not possible to unambiguously distinguish true local field enhancement from changes of composition due to preferential adsorption of dye on the metal. Thus quantitative conclusions must be drawn cautiously.

We are specifically interested in theoretical predictions of local field enhancements of the nonlinear response of chromophores (28–30). Experimentally, it has been reported that dispersions of gold clusters in polydiacetylenes induce an enhancement of the third-order susceptibility ($\chi^{(3)}$) by two orders of magnitude in comparison to the polymer alone (31, 32). In addition, strong hyper-Rayleigh scattering (HRS) has been observed for silver colloids in the presence of *para*-nitroaniline (33). Important factors such as particle aggregation, the actual distance of the chromophore to the surface, coupling of electronic excitations, and the particle shape have not been carefully considered.

In this report, we present the synthesis of an NLO active chromophore modified with a disulphide group **1a** (See below) to anchor the molecule to the surface of colloidal gold particles. We observed increases of the linear and nonlinear optical responses as the molecules are adsorbed onto the metal surface and produce stable dispersions of dye-coated metal colloids. We also prepared polymer films doped with these dye–gold particles and observed an enhanced electrooptic coefficient.



Experimental

Materials and methods

The manipulation of moisture sensitive materials was carried out under an atmosphere of dry nitrogen using Schlenk and dry box techniques. Organic solvents used for synthesis were purified by distillation over the appropriate drying agent. Most chemicals were obtained from Aldrich and used as received. The disulfide substituted aniline $4-CH_3C_6H_4$ -SS- CH_2CH_2 -N(CH₃)-C₆H₅ (**2**) was prepared stepwise; treating N-methyl aniline with ethylene sulfide to obtain C₆H₅N(CH₃)-CH₂CH₂-SH and reacting the corresponding lithium salt with $4-CH_3C_6H_4$ -SCI. HPLC grade methanol and Milli-QTM water were used for the preparation of **Fig. 1.** Mach-Zender Interferometric system for the measurement of electrooptic coefficients. P, polarizing beamsplitter; B, beamsplitter; C, chopper; S, test sample; R, reference sample; G, glass slide; L, microscope objective; D, silicon photodiode detector; H, pinhole; LA, lock-in amplifier; EA, electronic amplifier.



colloids. Soda-lime glass slides 1 mm-thick with a 200 Å layer of indium-tin oxide (ITO) were obtained from Delta Technologies and cleaned with acetone and aqueous NaOH.

Instrumentation

All NMR spectra were acquired in a Varian XL200 instrument. IR spectra were recorded in a Brucker IFS-48 FT spectrometer. Raman spectra were collected on a home-built instrument described elsewhere (34); the 514.5 nm line of an Ar⁺ laser was used to excite scattering with less than 30 mW of power to minimize sample degradation. Mass spectra were obtained on a KratosMS25RFA spectrometer, FAB was performed with a Xe source (7 kV, 0.4 mA) and an NBA matrix. A diode-array HP-8452A spectrophotometer was adapted with optical-fiber bundles to measure UV-Vis spectra in a custom-built thermostated cell holder with magnetic stirring. Transmission electron microscopy studies were conducted on a Jeol JEM2000FX instrument operating at 80.0 kV. Freeze fracture samples were prepared in a Reichert-Jung KF80 Universal Cryofixation Unit and shadowed in a BALZERS BAF300 Freeze-Etch Unit

Hyper-Rayleigh scattering measurements were performed with a custom-built instrument. A Q-switched Continuum Surelite II Nd:YAG laser provided the fundamental wavelength of 1064 nm in 5 ns pulses with a 10-Hz repetition rate. The laser output, 300–400 mJ per pulse, was reduced to approximately 2 mJ and controlled with the combination of a half-wave retarder, a polarizing cube, and a visible filter as attenuator. This pump beam was focussed onto the sample and the second harmonic signal collected on a photomultiplier with the appropriate sets of lenses. A broad-band infrared filter and an interferential filter were used to prevent all wavelengths but 532 nm from reaching the detector connected to an oscilloscope.

Thin film samples were prepared with a Headway photoresist spin-coater; their thickness was measured using a Dektak 3030ST surface profilometer. Transparent gold electrodes were produced in an Edwards Auto 306 metal-atom evaporator.

The second-order NLO properties of film samples were determined by measuring the Electrooptic coefficient r₁₁₃ in a custom-built set up. The experimental apparatus is shown in Fig. 1. The central element is a Mach-Zehnder interferometer operating with a randomly polarized He-Ne laser (632.8 nm, 8 mW) as the optical source. The input beam was polarized using a 50/50 polarizing beam-splitter and separated into the sample and reference arms using a second beam-splitter. For background measurements, the beam was modulated with a chopper operating 1000 Hz. The test and reference samples had identical structure, which improved the fringe visibility of the interferometer by balancing the light intensity of the arms. The reference arm also contained a glass slide that was rotated by a precision step motor with a controller interfaced to a microcomputer. This slide provided a variable path-length difference (and therefore a phase shift) between the two arms of the interferometer. The beams were recombined and a microscope objective $(20 \times)$ was used to expand the output light beam onto a silicon photodiode detector. The fringe visibility was improved further with the help of a pinhole ($d = 400 \ \mu m$). The detector was connected to a lock-in amplifier, which also provided an internal reference ($\Omega = 1000$ Hz) and oscillation for measurements of the modulated sample. The applied voltage $(V_{\rm rms})$ was controlled further using an electronic amplifier. Oscillations due to air drafts were minimized by enclosing the optical set-up in a plastic encasing and vibrations were damped using an optical table with pneumatic isolation.

Synthesis of 1a

By adaptation of a technique for the preparation of crystal violet, thionyl chloride (0.55 mL, 6.9 mmol) was carefully added to Micheler's ketone (1.84 g, 6.9 mmol) in 20 mL of toluene at 100°C. After 10 min a brown glassy phase separated from the solvent. Compound **2** (2.61 g, 9.0 mmol) was added with the help of 5 mL of toluene. The mixture was

cooled after 40 min and 1 mL of triethyl amine was added slowly with vigorous stirring. After 16 h the solvent was decanted and the residue was reprecipitated from ethanoltoluene, washed with warm hexane, and dried under vacuum. The crude product was purified by chromatography with a toluene-ethanol gradient of increasing polarity on a cellulose column. The product was obtained as a dark-purple microcrystalline solid with metallic lustre. Yield 11% (0.43 g, 0.7 mmol). UV–Vis (MeOH, MeOH 20%): λ_{max} (ϵ), 558 (94 000, 70 500), 590 nm (10 400, 68 400 mol⁻¹ dm³ cm⁻¹). FT-IR (KBr) (cm⁻¹): 422, 524, 562, 665, 722, 743, 758, 800, 828, 913, 942, 1063, 1133, 1173, 1227, 1295, 1335, 1363, 1445, 1478, 1522, 1583 (v). Resonance Raman (MeOH 20%, 2.9 × 10⁻⁵ M, 514 nm) (cm⁻¹): 1618, 1586, 1538, 1381, 1306, 1180, 920, 809, 434. ¹H NMR (200 MHz, CDCl₃) δ: 7.6–6.5 (m, 16H), 4.0–3.5 (m, 19), 2.4–2.1 (broad, 3H). FAB-MS (NBA) m/z (%): 540 ([M⁺], 20), 416 $([M^+ - HSC_4H_4CH_3], 10).$

Preparation of colloids

Gold dispersions stable in aqueous methanol were prepared by reduction of HAuCl₄ in glassware that had been carefully cleaned with aqua regia and rinsed with Milli-QTM water. All solutions were prepared in methanol 20% (w/v) and filtered through a 0.2 μ m PTFE membrane immediately before mixing. In a typical preparation NaBH₄ (6.6 mg, 0.17 mmol) was dissolved in 10 mL and added dropwise to HAuCl₄·3H₂O (11.0 mg, 2.8 × 10⁻² mmol) in 40 g of solvent mixture with vigorous stirring. After 1 h, 10 mL of a 0.4% (w/v) solution of H₂O₂ were added slowly to remove any excess of NaBH₄. The next day the sol was diluted to complete 100 mL. Colloids prepared this way were stable for weeks. Each batch was characterized by UV–Vis spectroscopy and TEM.

For adsorption studies, the UV–Vis spectra and (or) hyper-Rayleigh scattering intensity were measured as the gold sol was titrated in a cuvette with small additions of a dilute solution of **1a** under vigorous stirring with delay period of 10 s after each addition for equilibration.

Transmission electron microscopy

Colloid samples for routine particle-size measurements were prepared by solvent evaporation on carbon-coated copper grids (300 mesh). To examine the morphology of a colloid, a drop of the liquid sample was frozen at -142° C (liquid propane). The sample was then cut and etched at -102° C under high vacuum, and a replica was made by shadowing with platinum and carbon (200 V, 100 mA each). The replica was deposited on a plain-copper grid (300 mesh) with distilled water.

Preparation of dye-colloid dispersions in polymer films

A conductive strip was patterned on an ITO slide by acid etching. Films of about 10 μ m thickness were cast from a solution of PMMA in *iso*-propanol/toluene (39% w/v) that also contained dodecylamine-coated gold particles (0.22% metal/polymer by weight) (35) and (or) **1a** (0.05 molar ratio to gold). The films were allowed to age in order to remove residual solvents and a thin layer of gold was deposited to serve as a transparent electrode.

Results and discussion

We designed an experiment in which colloidal metallic particles were to be mixed with a NLO dye in solution while their linear (absorbance) and nonlinear (second harmonic scattering) optical responses could be monitored. Guided by published theoretical predictions, we focussed on those factors that would maximize local field effects, namely minimal separation between the chromophore and metal surface and overlap of electronic excitations of dye and metal particle.

The chromophore of crystal violet (**1b**), the tris(*para*dialkylaminophenyl)methyl cation, was chosen for this study, since it displays (*a*) extensive overlap of its visible absorption ($\lambda_{max} = 590$ nm) with the plasma resonance of colloidal gold, (*b*) a large octupolar hyperpolarizability (36), and (*c*) an emission in hyper-Rayleigh scattering that is well separated from multi-photon fluorescence when irradiated at 1064 nm (37).

In recent years, there has been considerable development of self-assembly processes at interfaces. A number of protocols for efficient adsorption of molecules on gold surfaces have been successfully extended to the derivatisation of gold nanocrystals, especially with organosulfur compounds: thiols, disulfides, and sulfides (38–40). We decided to use a disulfide group to directly anchor the chromophore to the surface of gold colloidal particles, using a short chain to maximize interaction with the particle.

It is known that metal colloids in water adsorb many organic molecules, including dyes. However, in some cases it is uncertain whether the molecules are truly in contact with the surface of the particle or sit on top of other adsorbates. The anionic 4,5-benzoindotricarbocyanine builds a multilayered structure onto gold hydrosols stabilized with poly(vinyl alcohol). This is accompanied by a bathocromic shift from 778 to 895 nm but no enhancement of absorbance (41). Silver colloids with adsorbed malachite green (**1c**) require inorganic salts as stabilizing agents. The ions may be a mayor component of the surface structure, since the number and intensity of bands in the visible and Raman spectra are strongly influenced by the salts (42, 43).

Synthesis and properties of 1a

Common methods for the preparation of triarylmethyl dyes involve oxidation steps that are incompatible with some sulfur functional groups. Coupling of the disulfidecontaining aniline 2 with Micheler's ketone, activated with thionyl chloride, avoided harsh conditions, but the overall yield was low and repeated chromatographic elutions were necessary to remove impurities. The product was identified by the peak of its cation in the FAB mass spectrum. The ¹H NMR spectrum displayed a complex broadened pattern due to dynamic exchange of the conformers defined by different orientations of the disulfide bond. Variable temperature studies confirmed the fluxional nature of the structure but failed to simplify completely the spectrum up to 90°C in DMSOd₆. The same phenomenon was observed in the disulfide substituted aniline 2. The purity of the product was assessed by chromatography and UV-Vis spectroscopy. Figure 2 compares its spectrum to that of a commercial sample of crystal violet (95%+ pure). In pure methanol their spectra are virtually identical, with maxima at 590 nm and shoulders



at 558 nm due to the formation of aggregates. On the basis of the calculated molar absorptivities 1a was considered pure and used without further treatment. Different from 1b, 1a is sparingly soluble in water and solubilization is facilitated by addition of alcohol. In methanol 20% (w/v) the total absorptivity is smaller and the aggregate's band is well resolved. For all adsorption studies, the equilibrium of self-association was neglected, since the two maxima followed the Beer-Lambert law within the range of concentrations employed.

Adsorption of 1a onto gold colloids

Gold colloids prepared in methanol 20% were titrated with 1a while their visible absorption spectra were monitored. The result of a typical titration is shown in Fig. 3. Upon addition of the dye an intense band appears at long wavelengths; its position depends on the diameter of the particles ($\lambda_{\text{max}} = 740 \text{ nm}$ for $d = 13 \pm 5 \text{ nm}$ and 676 nm for d = 6 ± 2 nm). The absorbance kept increasing after each addition until a certain amount of dye, characteristic for each size of colloid, was reached. As well, the height of this peak depended linearly on the total concentration of gold for a single size of particle. This behaviour suggests that the new band is due to the dye molecules adsorbed on the surface of the colloidal particles and that the surface is eventually saturated. In the case of 13 nm particles and based on the amount of dye adsorbed by the colloid, the oscillator strength (f) was estimated to be close to 35 for this band.

However, the changes observed in the visible spectrum also resemble those due to particle aggregation; thus appropriate control experiments were performed. We noted that addition of NaCl, *p*-tolyldisulfide, and even **1b** as flocculating agents to the 13 ± 5 nm colloid each produced a distinctive maximum always at 704 nm, as shown in Fig. 4. More important, those aggregated colloids were extremely unstable and precipitated within seconds; colloids treated with **1a** did not require any stabilizer and were stable for days provided that all glassware was scrupulously clean, all solutions were filtered to exclude nucleation points, and evaporation was prevented. As the visible spectra alone are not evidence against aggregation, the morphology of colloids treated with **1a** was examined by transmission electron mi-

Fig. 3. UV–Vis spectra in MeOH 20% (w/v): (*a*) **1a** 19.3 × 10^{-6} mol dm⁻³; (*b*) gold colloid ($d = 6 \pm 2$ nm, C_{Au} = 2.1 × 10^{-4} mol dm⁻³, v₀ = 3.045 mL); (*c*) to (*l*) evolution after addition of **1a** (1.2 × 10^{-4} mol dm⁻³) in 0.025 mL increments. Inset: dependence on the absorbance at 680 nm on the concentration of added **1a**.



Fig. 4. Visible spectra of control experiments in MeOH 20% (w/v): (*a*) gold colloid, $d = 13 \pm 5 \text{ nm}$, $\lambda_{\text{max}} = 526 \text{ nm}$, $C_{\text{Au}} = 2.8 \text{ mol } \text{dm}^{-3}$, $v_0 = 3.0 \text{ mL}$. (*b*) a + 0.25 mL saturated NaCl, t = 10 s, $\lambda_{\text{max}} = 704 \text{ nm}$; (*c*) flocculated b at t = 500 s; (*d*) a + 0.15 mL (4-CH₃C₆H₄S)₂ 2.0 × 10⁻⁴ mol dm⁻³, t = 30 s, $\lambda_{\text{max}} = 704 \text{ nm}$; (*e*) a + 0.10 mL **1b** 2.1 × 10⁻⁴ mol dm⁻³, t = 30 s, $\lambda_{\text{max}} = 706 \text{ nm}$. (*f*) a + 0.25 mL **1a** 2.9 × 10⁻⁴ mol dm⁻³, t = 30 min, $\lambda_{\text{max}} = 740 \text{ nm}$.



croscopy. Freeze-fracture sections of the same samples used for absorbance measurements were shadowed with carbon and platinum. The micrograph in Fig. 5 displays wellseparated metal nanoparticles following a radial distribution of mass with a coefficient practically equal to 2.0; thus the particles are evenly spread in two dimensions. This is in striking contrast with the well-known properties of flocculated metal colloids, whose aggregation proceeds through a mechanism of collisions between clusters and results in highly branched structures with radial distribution coefficients of about 1.75. Because of the non-integer value of this "Hausdorf dimension", such aggregates are usually considered to be "fractal" (44). On the basis of the stability of the **1a**–gold dispersions and the radial distributions in the



electron micrographs we concluded that colloidal particles treated with **1a** remain in dispersion.

After ruling out aggregation as the cause of the changes in the visible spectra, the absorbance data were used to examine in detail the process of dye adsorption onto the colloid. The inset of Fig. 3 shows the dependence of absorbance, at the maximum of the new band, on the concentration of added dye; it resembles a Langmuir isotherm. However, the corresponding Scatchard plots (45) were highly nonlinear. Figure 6 shows the linear fit that is obtained with eq. [1], which is Hill's model for cooperative adsorption. P is the fraction of occupied binding sites, C_{1a} the concentration of dye added to the dispersion, K the equilibrium constant, and $n_{\rm H}$ the Hill coefficient. For several samples of different particle size the correlation coefficients were about 0.99, and $n_{\rm H}$ values larger than 1.0 (see Table 1). This is consistent with the cooperative character of the process. Similar behaviour is known for the assembly of rotaxanes on functionalised gold nanocrystals (46). Analysis of Hill plots obtained by colorimetric titration of three separate batches of colloid afforded consistent values for the adsorption equilibrium constant, which was temperature insensitive within the experimental error between 15 and 55°C.

[1]
$$\ln\left(\frac{P}{1-P}\right) = n_{\rm H} \ln C_{1a} + n_{\rm H} \ln K$$

Raman spectroscopy was used to investigate the orientation of the chromophore with respect to the metallic surface. In solution, the spectrum of the dye was acquired under resonance conditions. Only those modes involving the chromophore were preferentially enhanced for scattering, thus the spectrum of **1a** was virtually identical to that of **1b** (47, 48) without any vibrations from the pendant disulfide branch. Upon adsorption on the gold colloid, a surface-enhanced spectrum with a larger signal-to-noise ratio was obtained, but it did not reveal any new features. Similar spectra were expected because resonance is the dominant effect in surface enhanced Raman spectroscopy of tryphenylmethane dyes (49). A perpendicular orientation of the chromophore with respect to the surface would entail a reduction of symmetry, but none of the anticipated band splittings were observed. **Fig. 6.** Hill plot for the colorimetric titration of gold colloid ($d = 6 \pm 2$ nm, C_{Au} = 2.1 × 10⁻⁴ mol dm⁻³) with **1a** from absorbance measurements at 680 nm.



Table 1. Hill analyses for the adsorption of **1a** on colloidal gold at room temperature.

Particle size (nm)	Method	n_H	ln K
6 ± 2	Absorbance, 680 nm	2.0 ± 0.1	15.9 ± 0.1
13 ± 5	Absorbance, 800 nm	1.3 ± 0.5	14 ± 0.1
7 ± 2	Absorbance, 800 nm	2.6 ± 0.1	14 ± 1
7 ± 2	HRS, 532 nm	2.8 ± 0.3	13 ± 2

Therefore a parallel orientation is suggested. This arrangement of the chromophore on the surface provides the minimum distance possible to the metal surface, which is ideal for the enhancement of nonlinear optical properties.

HRS measurements

To evaluate its nonlinear optical response, one of the colloids used in the absorbance study $(d = 7 \pm 2 \text{ nm})$ was excited with the fundamental wavelength of 1064 nm and the scattered light was measured at the frequency of the second harmonic 532 nm. In this technique, the intensity of the signal $(S_{2\omega})$ depends on the square of the pump power (I_0) as modeled by eq. [2] (50). This includes a correction for absorbance (Abs); the constant G is characteristic of the experimental set-up and was evaluated with a standard of paranitroaniline in methanol. The term B^2 contains the sum of the orientational average of β^2 of each component multiplied by its number density N. The initial colloidal dispersions of gold in MeOH 20% produced second harmonic light on their own. Based on the accepted values of hyperpolarizabilities for water and methanol, we found $\beta_{Au} = (2.1 \pm 0.5) \times$ 10^{-27} esu per gold atom, in agreement with a previous report (11, 12).

[2]
$$S_{2\omega} = GB^2 I_0^2 10^{-\text{Abs}}, \quad B^2 = \sum N_i \langle B_i^2 \rangle$$

Addition of **1a** to the colloid produced unusually strong HRS signals, which deviated from the linear dependence on the square of the pump intensity. As seen in Fig. 7, this was especially true for the samples with larger amounts of dye and may be due to the activation of nonlinear processes of higher order such as three-photon fluorescence and third

Fig. 7. Dependence of the HRS intensity, S_{20} , on the fundamental intensity, 1064 nm, of a gold colloid ($d = 7 \pm 2$ nm, $C_{Au} = 2.0 \times 10^{-4}$ mol dm⁻³) upon addition of increasing amounts of **1a**. Inset: Magnification of the response at low pump intensity.



harmonic generation. The magnitude of B^2 was extracted from the initial slopes and used to construct a Hill plot that was consistent with the one obtained from absorbance measurements (Table 1). After subtraction of the contribution from gold and evaluation of the amount of 1a that saturates the surface of the particles, a value of β ca. $10^{-26}\mbox{ esu was es-}$ timated for the chromophore. This is at least one order of magnitude larger than the reported values for the parent dye, 1b. Since the dye-coated particles absorb strongly at the wavelength of the second harmonic, the apparent increase of hyperpolarizability could be due to resonant enhancement. This interpretation should be approached cautiously. The direct electronic interaction between metal and chromophore cannot be ruled out at this point; the new band in the visible absorption spectrum may arise from a dye-gold charge transfer, in which case the coated metallic particle should be regarded as a new "molecular" entity with its own oscillator strength and hyperpolarizability. Furthermore, the optical properties that were observed are the collective response of a set of colloidal particles with a variety of sizes and shapes; it is known that contributions from only a few "hot particles" may dominate local field effects (51). Measurements under aggregation conditions were not possible because of the instability of such samples.

Electrooptic coefficients of polymer films

To take advantage of the intense NLO activity of the gold–1a combination, the dispersion must be incorporated into a suitable matrix. The dye 1a is very soluble in polar organic solvents, whereas gold colloids are not. Long-chain alkyl amines readily adsorb on gold nanoparticles and render them dispersible in toluene. Such amine coatings are only kinetically stable and can be readily replaced by stronger adsorbates with sulfur functional groups, including 1a. Concentrated PMMA solutions in toluene–isopropanol mixtures were used to prepare thin films on glass slides. Samples were prepared with and without dodecylamine-coated colloids and (or) 1a in appropriate proportions. The films were placed between transparent electrodes of ITO and gold

Fig. 8. Electrooptic-experiment interferometer fringe profiles for the measurement of films containing (*a*) gold–amine dispersions, (*b*) 1a, (*c*) gold–1a dispersion.



and were subject to a transversal modulated voltage. This caused a variation of refractive index due to the nonlinear susceptibilities of the material (Pockel's effect). With a Mach-Zender interferometer the phase retardation of a laser beam propagating parallel to the electric field was measured. Measurements were carried out with a variable phase on the reference arm of the interferometer to determine the amplitude of intensity at the modulating frequency. The electrooptic coefficient r_{113} was defined by eq. [3] (52), where λ is the wavelength of the probe laser beam, *n* the refractive index of the material, $V_{\rm rms}$ the root-mean-square modulating potential, I_{Ω} and I_0 the intensity out of the interferometer modulated and unmodulated, respectively.

$$[3] r_{113} = \frac{\lambda}{\pi n^3 V_{\rm rms}} \frac{I_{\Omega}}{2\sqrt{2I_0}}$$

The fringe profiles from which the EO coefficients were extracted are displayed in Fig. 8. The combined gold-1a sample had an EO coefficient ($r_{113} = 2.20 \text{ pm V}^{-1}$) larger than those of the films containing only $1a (0.80 \text{ pm V}^{-1})$ or amine-coated gold particles (0.36 pm V⁻¹) in the same concentrations. The observed coefficient is even larger than the sum of the individual contributions. Current efforts are directed towards maximizing the activity of such composites. Despite the intense harmonic light scattered by dye-coated colloids in liquid dispersion, the observed nonlinear processes are inherently incoherent because of the random distribution of particles. The activity of the polymeric films may be a consequence of anisotropy induced by spincasting. It can be conceived that more efficient composites will be accessible by tailoring the morphology of the metal dispersion into two- or three-dimensional arrays (53-57).

Conclusions

We have derivatized a triarylmethyl dye by appending a short hydrocarbon arm with a disulfide group to anchor the chromophore to the surface of nanoscopic gold particles. The colloids treated with this dye were stable. Adsorption of the derivatized molecule proceeded by a cooperative process that was followed by monitoring the linear and nonlinear optical responses. TEM demonstrated that aggregation is not a factor in these observations. Similarly, an enhanced electrooptic coefficient was observed for polymer films that contained both the dye and gold particles. The observed enhancement of optical properties offers opportunities to implement methodologies for chemical analysis and sensors. There is considerable interest in composites containing metal nanoparticles for chemical analysis (58), sensing (59), and nanoscale electronics (60). Local field enhancement of the NLO response of a chromophore will be advantageous for the construction of devices with combined functionality. For example, metallic particles can be grafted on waveguides for an evanescent wave to probe spectroscopically species and chemical processes at the surface (34).

Supplemental material available

Hill plot obtained from HRS measurements.⁴

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References

- T.J. Marks and M.A. Ratner. Angew. Chem., Int. Ed. Engl. 34, 155 (1995).
- S.R. Marder, B. Kippelen, A.K.Y. Jen, and N. Peyghammbarian. Nature (London), 388, 845 (1997).
- R.R. Tykwinski, U. Gubler, R.E. Martin, F. Diederich, C. Bosshard, and P. Guenter. J. Phys. Chem. B, 102, 4451 (1998).
- 4. T. Verbiest, S. Houbrechts, M. Kauranen, K. Clays, and A. Persoons. J. Mater. Chem. 7, 2175 (1997).
- E. Kelderman, G.J.T. Heesink, L. Derhaeg, T. Verbiest, P.T.A. Klaase, W. Verboom, J.F.J. Engbersen, N.F. Van Hulst, and K. Clays. Adv. Mater. (Weinheim, Fed. Repub. Ger.). 5, 925 (1993).
- M. Albota, D. Beljonne, J.-L. Bredas, J.E. Ehrlich, J.-Y. Fu, A.A. Heikal, S.E. Hess, T. Kogej, M.D. Levin, S.R. Marder, D. Mccord-Maughon, J.W. Perry, H. Rockel, M. Rumi, G. Subramaniam, W.W. Webb, X.-L. Wu, and C. Xu. Science (Washington, D.C.), 281, 1653 (1998).
- Y. Shi, C. Zhang, H. Zhang, J.H. Bechtel, L.R. Dalton, B.H. Robinson, and W.H. Steier. Science (London), 288, 119 (2000).
- 8. L.L. Beecroft and C.K. Ober. Chem. Mater. 9, 1302 (1997).
- N.N. Lepeshkin, W. Kim, V.P. Safonov, J.G. Zhu, R.L. Armstrong, C.W. White, R.A. Zuhr, and V.M. Shalaev. J. Nonlinear Opt. Phys. Mater. 8, 191 (1999).
- E. Giorgetti, G. Margheri, L. Palchetti, S. Sottini, and M. Mennig. Appl. Phys. B: Lasers Opt. B67, 587 (1998).
- F.W. Vance, B.I. Lemon, and J.T. Hupp. J. Phys. Chem. B, 102, 10091 (1998).
- P. Galletto, P.F. Brevet, H.H. Girault, R. Antoine, and M. Broyer. Chem. Commun. (Cambridge), 581 (1999).
- Y. Suchorski, W.A. Schmidt, and J.H. Block. Appl. Surf. Sci. 76–77, 101 (1994).

- 14. Y. Suchorski, W.A. Schmidt, J.H. Block, and H.J. Kreuzer. Vacuum, 45, 259 (1994).
- V.M. Shalaev, V.A. Markel, E.Y. Poliakov, R.L. Armstrong, V.P. Safonov, and A.K. Sarychev. J. Nonlinear Opt. Phys. Mater. 7, 131 (1998).
- V.M. Shalaev, V.P. Safonov, E.Y. Poliakov, V.A. Markel, and A.K. Sarychev. ACS Symp. Ser. 679, 88 (1997).
- A. Campion and P. Kambhampati. Chem. Soc. Rev. 27, 241 (1998).
- 18. M. Kerker. J. Colloid Interface Sci. 105, 297 (1985).
- 19. C.F. Eagen. Appl. Opt. 20, 3035 (1981).
- 20. H.G. Craighead and A.M. Glass. Opt. Lett. 6, 248 (1981).
- A.M. Glass, A. Wokaun, J.P. Heritage, J.G. Bergman, P.F. Liao, and D.H. Olson. Phys. Rev. B, Cond. Matter, 24, 4906 (1981).
- 22. S. Garoff, D.A. Weitz, T.J. Gramila, and C.D. Hanson. Opt. Lett. 6, 245 (1981).
- 23. D.A. Weitz and S. Garoff. Proc. Int. Conf. Lasers, 55 (1982).
- O. Stenzel, S. Wilbrandt, A. Stendal, U. Beckers, K. Voigtsberger, and C. Von Borczyskowski. J. Phys. D: Appl. Phys. 28, 2154 (1995).
- O. Stenzel, A. Stendal, K. Voigtsberger, and C. Von Borczyskowski. Sol. Energy Mater. Sol. Cells, 37, 337 (1995).
- M. Ihara, K. Tanaka, K. Sakaki, I. Honma, and K. Yamada. J. Phys. Chem. B, **101**, 5153 (1997).
- N. Kometani, M. Tsubonishi, T. Fujita, K. Asami, and Y. Yonezawa, Langmuir. 17, 578 (2001).
- A.E. Neeves and M.H. Birnboim. J. Opt. Soc. Am. B: Opt. Phys. 6, 787 (1989).
- 29. A.E. Neeves and M.H. Birnboim. Opt. Lett. 13, 1087 (1988).
- 30. P. Ye and Y.R. Shen. Phys. Rev. B: Condens. Matter. 28, 4288 (1983).
- A.W. Olsen and Z.H. Kafafi. Mater. Res. Soc. Symp. Proc. 206, 175 (1991).
- 32. A.W. Olsen and Z.H. Kafafi. J. Am. Chem. Soc. 113, 7758 (1991).
- K. Clays, E. Hendrickx, M. Triest, and A. Persoons. J. Mol. Liq. 67, 133 (1995).
- 34. J. Baldwin, N. Schuehler, I. S. Butler, and M. P. Andrews. Langmuir. 12, 6389 (1996).
- 35. D.V. Leff, L. Brandt, and J.R. Heath. Langmuir. **12**, 4723 (1996).
- J. Zyss, V. Thai Chau, C. Dhenaut, and I. Ledoux. Chem. Phys. 177, 281 (1993).
- 37. T.W. Chui and K.Y. Wong. J. Chem. Phys. 109, 1391 (1998).
- M. Brust, M. Walker, D. Bethell, D.J. Schiffrin, and R. Whyman. J. Chem. Soc., Chem. Commun. 801 (1994).
- L.A. Porter, Jr., D. Ji, S.L. Westcott, M. Graupe, R.S. Czernuszewicz, N.J. Halas, and T.R. Lee. Langmuir. 14, 7378 (1998).
- X.-M. Li, M.R. De Jong, K. Inoue, S. Shinkai, J. Huskens, and D.N. Reinhoudt. J. Mater. Chem. 11, 1919 (2001).
- 41. P.C. Lee, and D. Meisel, J. Phys. Chem. 86, 3391 (1982).
- 42. U. Nickel, P. Halbig, H. Gliemann, and S. Schneider. Ber. Bunsen-Ges. **101**, 41 (1997).
- 43. E.J. Liang, X.L. Ye, and W. Kiefer. J. Phys. Chem. A, 101, 7330 (1997).
- 44. D.A. Weitz, M.Y. Lin, and C.J. Sandroff. Surf. Sci. 158, 147 (1985).
- 45. A.J. Gibb. *In* Medicinal Chemistry. *Edited by* C.R. Ganellin and S.M. Roberts. Academic Press, London. 1994. pp. 37–60.
- D. Fitzmaurice, S.N. Rao, J.A. Preece, J.F. Stoddart, S. Wenger, and N. Zaccheroni. Angew. Chem., Int. Ed. 38, 1147 (1999).

⁴ Supplementary data may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0S2, Canada (http://www.nrc.ca/cisti/irm/unpub_e.shtml for information on ordering electronically).

- 47. S. Schneider, G. Brehm, and P. Freunscht. Phys. Status Solidi B, **189**, 37 (1995).
- I. Persaud and W.E.L. Grossman. J. Raman Spectrosc. 24, 107 (1993).
- 49. A. Kudelski and J. Bukowska. Chem. Phys. Lett. 253, 246 (1996).
- 50. E. Hendrickx, K. Clays, and A. Persoons. Acc. Chem. Res. **31**, 675 (1998).
- S. Nie and S.R. Emory, Science (Washington, D.C.). 275, 1102 (1997).
- K.D. Singer, M.G. Kuzyk, W.R. Holland, J.E. Sohn, S.J. Lalama, R.B. Comizzoli, H.E. Katz, and M.L. Schilling. Appl. Phys. Lett. 53, 1800 (1988).
- 53. C.J. Kiely, J. Fink, M. Brust, D. Bethell, and D.J. Schiffrin. Nature (London), **396**, 444 (1998).

- 54. J. Fink, C.J. Kiely, D. Bethell, and D.J. Schiffrin. Chem. Mater. **10**, 922 (1998).
- G. Schmid, S. Peschel, and T. Sawitowski. Z. Anorg. Allg. Chem. 623, 719 (1997).
- 56. H. Fan, Y. Zhou, and G.P. Lopez, Adv. Mater. (Weinheim, Ger.), 9, 728 (1997).
- 57. R. Blonder and L. Sheeney. Chem. Commun. (Cambridge), 1393 (1998).
- 58. C.R. Martin and D.T. Mitchell. Anal. Chem. 70, 322A (1998).
- 59. S. Bharathi. Anal. Commun. 35, 29 (1998).
- R.P. Andres, J.D. Bielefeld, J.I. Henderson, D.B. Janes, V.R. Kolagunta, C.P. Kubiak, W.J. Mahoney, and R.G. Osifchin. Science (Washington, D.C.), 273, 1690 (1996).