Modified triphenylmethane dye for the efficient nonlinear generation of light in nanostructured materials

Xavier Vidal[a)]
*ICFO-Institut de Ciencies Fotoniques, Mediterranian Technology Park, 08860 Castelldefels, Spain
and Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Colom 11,
08222 Terrassa, Spain*

Jose Raul Herance, Jordi Marquet, and Jose Luis Bourdelande
*Departament Química, Universitat Autónoma de Barcelona, Unitat Química Orgànica,
08193 Bellaterra, (Barcelona), Spain*

Jordi Martorell
*ICFO-Institut de Ciencies Fotoniques, Mediterranian Technology Park, 08860 Castelldefels, Spain
and Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, Colom 11,
08222 Terrassa, Spain*

Many nonlinear photonic materials exhibit large extinction coefficients as a result of the active molecule absorption band. The authors show that it is possible to redshift the absorption resonance of such material without a significant alteration of the nonlinear response. A drastic reduction in the absorption coefficient at the wavelength of interest is obtained by adding a triple bond unit to these active molecules. In such case, the nonlinear optical response of a photonic material would be much better than the one obtained with the original molecule or by following the conventional procedure of adding a double bond unit instead. © *2007 American Institute of Physics.*
[DOI: 10.1063/1.2773934]

In recent years, considerable progress has been made in the fabrication of photonic crystals to be able to better control light while at the same time reduce scattering losses inherent from such type of structures.[1–3] On the other hand, it has been proven that these structures have the potential to host an efficient second order nonlinear interaction[4,5] which was very recently made visible to the naked eye.[6] Making nonlinear processes efficient in such structured materials may open applications for nonlinear optics in areas where the more traditional bulk inorganic single crystals cannot be used.[7] Unfortunately, the macroscopic nonlinear response is still considerably lower than in the inorganic bulk birefringent crystals. In many cases, the β coefficient is only different from zero in the neighborhood of the interfaces that separate the two dielectric materials that form the photonic crystal. In addition, the large absorption cross section of the organic molecules used as the nonlinear source prevents a quadratic growth of the conversion versus crystal length even when phase matching is achieved.

It is a well known fact that organic molecules adsorbed on the surface at the interface separating two different centrosymmetric materials enhance the second order nonlinear response of the noncentrosymmetric surface. In general, these molecules exhibit a considerable efficiency only when the generated light at the double frequency is resonant with one of the molecule absorption bands. This is not a problem when only one single interface is present, but the specific surface area of photonic structures is quite large and the second harmonic light would be reabsorbed in the consecutive interfaces and a significant reduction of the efficiency of the nonlinear process would occur.[6] Then, strategies to enhance such surface nonlinearity are needed to increase the effi-

ciency to a point where such materials could be implemented in useful devices.

In the present letter, we have chosen malachite green (MG), a derivative of the triphenylmethane, as the nonlinear molecule, shown in Fig. 1(a), which exhibits a rather significant conversion to second harmonic (SH) when adsorbed on the surface of polystyrene spheres,[8–10] that may also self-organize in a photonic crystal lattice.[4] In that case, we will see below that when a triple bond (tH) is inserted between the carbocation and the aromatic group without the parasubstitution, as shown in Fig. 1(b), the absorption coefficient at the wavelength of interest diminishes drastically.[11] On the contrary, a double bond (dH) inclusion at the same location [cf. Fig. 1(c)] results in a very small change in absorption. We will show below that such unconventional approach of adding a tH rather than a dH does not lead to a significantly lower β coefficient for the overall molecule. tH and dH MG homologs were synthesized according to bibliography.[12–14]

In nonlinear photonic crystals, the organic molecules are either physically adsorbed at the interface that separates the two materials that form the photonic structure[4] or chemically linked to some specific surface functional groups.[6] In both cases, the tensor elements of the sphere surface second order nonlinear susceptibility $\chi^{(2)}$ different from zero are $\chi^{(2)}_{33}$, $\chi^{(2)}_{31} = \chi^{(2)}_{32}$, and $\chi^{(2)}_{15} = \chi^{(2)}_{24}$. In a flat interface, the nonzero ele-
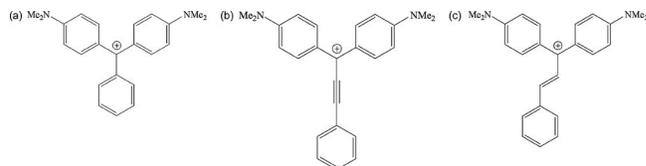

FIG. 1. Chemical structure of (a) malachite green, (b) the derivative of the triphenylmethane with a triple bond (tH), and (c) with a double bond (dH).
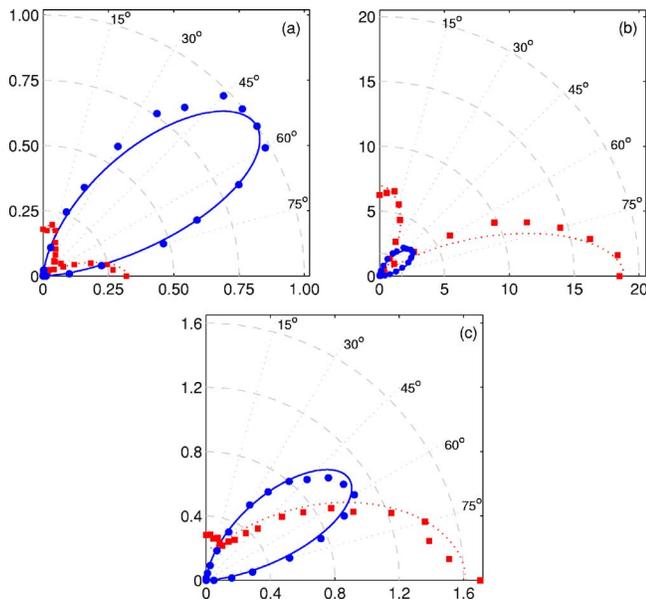

[a)]Electronic mail: xavier.vidal@icfo.es

FIG. 2. (Color online) Polar coordinate representation of the linear polarized SH intensity (ρ axis) as a function of the fundamental linear polarization (θ axis) from (a) the bare prism interface, (b) the MG monolayer, and (c) the tH monolayer. TE (solid circles: experiment and solid line: theory) and TM (solid squares: experiment and dotted line: theory) SH intensities. Both theoretical and experimental values were normalized to the maximum generation obtained from the bare prism interface.

FIG. 3. (Color online) Absorption spectrum of the MG (dotted line), the dH homolog (dashed line), and the tH homolog (solid line). The ε_{532} indicates the molar absorption at 532 nm for each chromophore.

ments are the same, which is a result of the $C_{\infty v}$ symmetry of the interface. One should expect some differences in the ratios of the several nonvanishing coefficients when comparing results from two different kinds of interfaces. However, the overall nonlinear response does not change significantly. We have performed a systematic study of the polarization dependence of the SH generation to determine the transversal magnetic (TM) polarization and transversal electric (TE) polarization SH field intensities as a function of the linear polarization of the fundamental field from the tH homolog and from MG. As mentioned in Refs. [15–19], the surface SH signal depends on the polarization and angle of the incident field. Surface SH measurements were performed using 6 ns laser pulses from a Nd:YAG laser. Monolayers were prepared as in Ref. [20] and second harmonic generation (SHG) measured from the back surface of a 60° prism, as described in Ref. [15]. There are two significant contributions to the surface nonlinear polarization source: the contribution from the bare interface $\chi_{int}^{(2)}$ and the one from the chromophore molecular layer $\chi_{ML}^{(2)}$.[21,22] We measured the TE and TM SH fields as a function of the polarization of the fundamental incident field in three different cases: When no substance was adsorbed on the prism surface, when MG was adsorbed on the back prism surface, and when the tH homolog was adsorbed on the back prism surface. These measurements are shown in Figs. 2(a)–2(c), respectively. It is possible to adjust exact analytical expressions we derived for the TE SH and TM SH intensities to the experimental measurements, as shown in Figs. 2(a)–2(c).

We observed that overall, the nonlinearity of the tH is lower than the one from MG, but this reduction is seen not to be proportionally equivalent for all polarization combinations. In fact, we observed that for some adequate combination of the polarization of the fields, the tH homolog may even have a larger efficiency than MG. For instance, TM SH
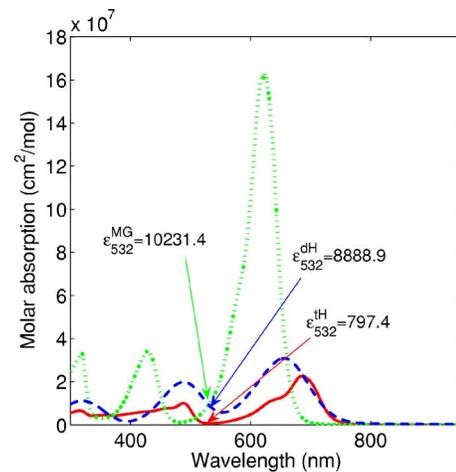
generation with the polarization of the incident field at 45° is more efficient for the tH than the MG, as we may see it by directly comparing Figs. 2(b) and 2(c). Such comparison seems to indicate that the change in nonlinearity is due to not only obviously a molecular structural change but also a change in conformation and a change in the orientation of the molecule with respect to the surface normal. Although from Fig. 2 alone it would not be possible to quantify the cause of the reduction, we may assert that the reduction due to a structural change is limited. Such limited reduction was unexpected given the low charge delocalization character of the single-triple conjugate bonds.[23,24]

We have also measured the SHG efficiency when dH is added instead of the tH. In accordance to Refs. [23] and [24], one should expect a better efficiency for the dH homolog. For a fix polarization, TE for the incident fundamental and TM for the SH generated, we determined the efficiency of monolayers of both MG homologs with respect to the efficiency of a monolayer of MG. Such measurements were done by depositing the layer on a microscope slide glass substrate. We obtained an efficiency of 32% with respect to MG for the dH and 12% for the tH. For such polarization combination, the efficiency conversion to SH from the bare glass substrate was below 1%.

Despite the smaller efficiency, the tH exhibits a key advantage for an efficient SHG in structured materials with a large specific surface area. The tH homolog acquires a more planar geometry with respect to the original MG.[11] This results in a significant redshift of the absorption band, as shown in Fig. 3. Moreover, at the wavelength of interest, ε_{532} is more than one order of magnitude lower for the tH with respect to MG. For the dH homolog, the ε_{532} coefficient remains similar to the one of MG (cf. Fig. 3). An absorption cross section one order of magnitude lower combined with a limited reduction on the nonlinear coefficients would lead to an efficiency that may be several orders of magnitude larger when a large number of surface layers are considered. We estimated what would be the efficiency as a function of the thickness of a given nonlinear photonic crystal of nanospheres, shown in Fig. 4, in each one of the three cases. In other words, when either the MG, tH, or dH would be adsorbed on the surface of the dielectric spheres that would form the photonic crystal. Note that the photonic crystal
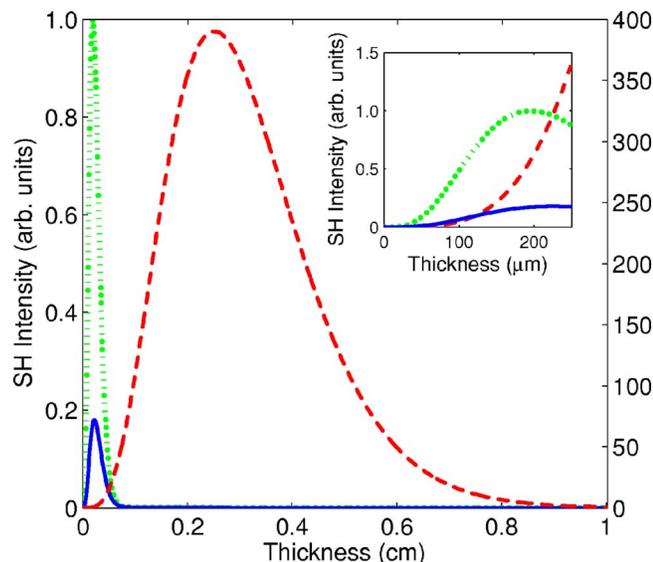
FIG. 4. (Color online) Predicted total SH intensity as a function of the size of the crystal when the molecule is MG (dotted line, left *y* axis), or dH (solid line, left *y* axis), or tH (dashed line, right *y* axis) for a TE fundamental incident at 45°. Normalization is to the maximum intensity of the MG. In the inset is a zoom of the first 224 μm.

structure provides a perfect phase matching mechanism.[4,6] We observe that since the absorption is similar for the MG and the dH homolog, the behavior of the efficiency is also similar, obtaining a lower conversion for the dH as a result of the lower nonlinear coefficients. On the other hand, although the nonlinear coefficient for the tH is the lowest, with a photonic crystal of 2.5 mm, we would obtain an efficiency that is over 400 times larger than the best conversion one would get with a MG photonic crystal. As seen in Fig. 4, the tH homolog would become more efficient already when a photonic crystal larger than 224 μm would be used. We performed some preliminary nonlinear measurements on powder samples[25] of MG and the tH homolog, and we observe that the scattered reflected signal for the tH case is 400% of the MG case. Such measurements indicate that when several molecular layers of material are used for SHG, the absorption plays a role that becomes more relevant than the nonlinearity itself. The procedure outlined could be applied to other types of organic nonlinear devices where a quasiphase matching mechanism is used.[26]

To conclude, we proposed a mechanism to chemically fine-tune the optical nonlinear response of organic molecules used in nonlinear photonic crystals. We have synthesized a nonlinear chromophore by the insertion of a triple bond in the backbone structure of MG. Such chemical tuning of the nonlinear properties of the molecule is a relevant tool when the wavelength of emission is fixed to a specific value. The addition of such triple bond results in a lower absorption at the wavelength of interest due to a large redshift of the peak of maximum absorption and an overall reduction of the ab-

sorption as well. At the same time, the nonlinear susceptibility does not change significantly. We estimated that in a nonlinear photonic crystal of just 2.5 mm, the tH homolog would perform over 400 times better than MG. For instance, one would be able to increase the efficiency reported in Ref. 6 by three orders of magnitude.

[1]Agustín Mihi, Manuel Ocaña, and Hernán Miguez, Adv. Mater. (Weinheim, Ger.) **18**, 2244 (2006).
[2]Chongjun Jin, Martin A. McLachlan, David W. McComb, Richard M. De la Rue, and Nigel P. Johnson, Nano Lett. **5**, 2646 (2005).
[3]Yu Liu, Xiang-Yang Liu, and Janaky Narayanan, J. Phys. Chem. C. **111**, 995 (2007).
[4]Jordi Martorell, Ramon Vilaseca, and Ramon Corbalan, Appl. Phys. Lett. **70**, 702 (1997).
[5]I. V. Soboleva, E. M. Murchikova, A. A. Fedyanin, and O. A. Aktsipetrov, Appl. Phys. Lett. **87**, 241110 (2005).
[6]Marc Maymó, Jordi Martorell, Albert Molinos-Gómez, and Francisco López-Calahorra, Opt. Express **14**, 2864 (2006).
[7]J. R. Herance, E. Peris, J. Vidal, J. L. Bourdelande, J. Marquet, and H. Garcia, Chem. Mater. **17**, 4097 (2005).
[8]N. Yang, W. E. Angerer, and A. G. Yodh, Phys. Rev. Lett. **87**, 103902 (2001).
[9]Elsa Y. C. Yan, Yan Liu, and K. B. Eisenthal, J. Phys. Chem. B **105**, 8531 (2001).
[10]Heather M. Eckenrode, Shih-Hui Jen, Jun Han, An-Gong Yeh, and Hai-Lung Dai, J. Phys. Chem. B **109**, 4646 (2005).
[11]Shuzo Akiyama, Shin'ichi Nakatsuji, Kenichiro Nakashima, Mituaki Watanabe, and Hiroyuki Nakazumi, J. Chem. Soc., Perkin Trans. 1 **12**, 3155 (1988).
[12]S. Nakatsuji, N. Okamoto, K. Nakashima, and S. Akiyama, Chem. Lett. **1986**, 329.
[13]S. G. R. Guinot, J. D. Hepworth, and M. Wainwright, Dyes Pigm. **47**, 129 (2000).
[14]S. E. Clayton, S. G. R. Guinot, J. D. Hepworth, and M. Wainwright, J. Chem. Soc., Perkin Trans. 2 **2**, 263 (2000).
[15]Tanya Kikteva, Dmitry Star, and Gary W. Leach, J. Phys. Chem. B **104**, 2860 (2000).
[16]B. Dick, A. Gierulski, G. Marowsky, and G. A. Reider, Appl. Phys. B: Photophys. Laser Chem. **38**, 107 (1985).
[17]G. Marowsky, A. Gierulski, R. Steinhoff, D. Dorsch, R. Eidenschnik, and B. Rieger, J. Opt. Soc. Am. B **4**, 956 (1987).
[18]Th. Rasing, G. Berkovic, Y. R. Shen, S. G. Grubb, and M. W. Kim, Chem. Phys. Lett. **130**, 1 (1986).
[19]Stefano Cattaneo and Martii Kauranen, Opt. Lett. **28**, 1445 (2003).
[20]A. S. Garoff, R. B. Stephens, C. D. Hanson, and G. K. Sorenson, Opt. Commun. **41**, 257 (1982).
[21]G. Berkovic, Y. R. Shen, G. Marowsky, and R. Steinhoff, J. Opt. Soc. Am. B **6**, 205 (1989).
[22]Stefano Cattaneo and Martii Kauranen, Phys. Rev. B **72**, 033412 (2005).
[23]David R. Kanis, Mark A. Ratner, and Tobin J. Marks, Chem. Rev. (Washington, D.C.) **94**, 195 (1994).
[24]M. Barzoukas, A. Fort, G. Klein, A. Boeglin, C. Serbutoviez, L. Oswald, and J. F. Nicoud, Chem. Phys. **153**, 457 (1991).
[25]S. K. Kurtz and T. T. Perry, J. Appl. Phys. **39**, 3798 (1968).
[26]G. Khanarian, M. A. Mortazavi, and A. J. East, Appl. Phys. Lett. **63**, 1462 (1993).