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# A High-Optical Quality Supramolecular Assembly for Third-Order Integrated Nonlinear Optics\*\*

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We describe the fabrication and characterization of an organic supramolecular assembly for integrated nonlinear optics that shows high-optical quality and an off-resonant third-order optical susceptibility three orders of magnitude higher than that of fused silica. The assembly, in the form of a thin film, is created by vapor deposition of a compact organic molecule with a large specific third-order polarizability. Atomic force microscopy (AFM) and scanning electron microscopy (SEM) confirm that the vapor deposited films are homogenous with surface height variations of less than 5 nm over distances of 0.5  $\mu\text{m}$  in films with a thickness of 1  $\mu\text{m}$ . The material is transparent for wavelengths above 700 nm, and it has a refractive index of  $1.8 \pm 0.1$  and a nonlinear index of  $(1.7 \pm 0.8) \times 10^{-13} \text{ cm}^2 \text{ W}^{-1}$  at a wavelength of 1.5  $\mu\text{m}$ .

All optical data processing and all optical switching require a material that has a large third-order susceptibility, a high-optical quality, and that is compatible with integrated nonlinear optics. It should be possible to easily process such a material into a thin film that supports waveguiding, and/or into a “nonlinear optical coating” that can be combined with passive waveguides into a hybrid system.

The recent development<sup>[1–3]</sup> of small organic molecules that combine a high off-resonant third-order polarizability with a small size (high specific third-order polarizability, defined as third-order polarizability per molecular mass<sup>[1]</sup>) motivated us to study how such molecules can be combined into a dense, randomly orientated amorphous supramolecular assembly for third-order integrated nonlinear optics. For such an assembly, the third-order susceptibility is related to the third-order polarizability in a similar way as when the molecules are dissolved into a solution,

$$\chi_{1111}^{(3)}(-\omega, -\omega, \omega, \omega) = f^4 \gamma_{\text{rot}} N \quad (1)$$

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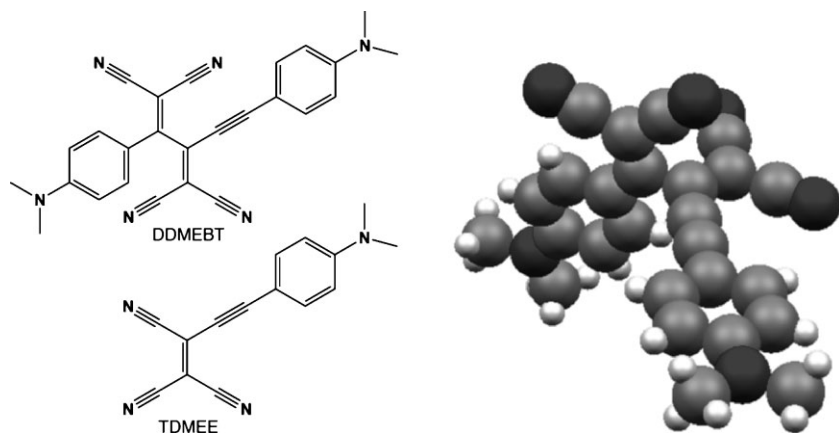
where  $f$  is a local field factor that in the Lorentz approximation is  $f = (n^2 + 2)/3$ , with  $n$  the refractive index of the assembly,  $N$  the number density of the molecules, and  $\gamma_{\text{rot}}$  the rotational average of the third-order polarizability of the molecule. Many of the molecules studied in refs. [1–3] have an off-resonant specific third-order polarizability of the order of  $2 \times 10^{-23} \text{ m}^5 \text{ V}^{-1} \text{ Kg}^{-1}$  at a wavelength of 1.5  $\mu\text{m}$ . Using this value, a refractive index of 1.8, and assuming a density of the supramolecular assembly similar to that of water one immediately arrives at a third-order susceptibility  $\chi_{1111}^{(3)} \simeq 2 \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$ , which is three orders of magnitude larger than the third-order susceptibility of fused silica.<sup>[4]</sup>

In this article, we demonstrate the creation of a high-quality molecular assembly with a high third-order optical nonlinearity using organic molecular beam deposition.

Vapor deposition of amorphous films is a technique that is compatible with many kinds of substrates, and presents several advantages when compared, e.g., to solution-based techniques. It operates in a clean high vacuum, enables precise and in situ control of film thickness, growth rate, substrate temperature, and is also compatible with numerous other vapor-phase fabrication techniques that involve masking and dry etching. Many of the compact molecules demonstrated in refs. [1–3] can be sublimated without decomposition, but only for a few do the intermolecular interactions allow the assembly of an amorphous phase without the formation of microcrystals or grains that would lead to light scattering and impact the optical properties.

The best homogeneity and linear optical properties for the vapor deposited organic film were obtained with the molecule 2-[4-(dimethylamino)phenyl]-3-[(4(dimethylamino)phenyl)ethynyl]buta-1,3-diene-1,1,4,4-tetracarbonitrile (DDMEBT). This molecule has been described (as molecule **2**) in ref. [2] and (as molecule **11**) in ref. [5]. Its solid-state form melts at a temperature of 191–193 °C, and the molecule has a decomposition temperature of 451 °C.<sup>[5]</sup> The details of the molecular synthesis protocol and chemical structure can be found in ref. [5]. The longest wavelength absorption peak for DDMEBT is centered around 527 nm. The third-order polarizability, measured in degenerate four-wave mixing (DFWM) with 20 ps long pulses at 1.5  $\mu\text{m}$ , is real with a value of  $\gamma_{\text{rot}} = 12 \pm 2 \times 10^{-48} \text{ m}^5 \text{ V}^{-2}$ , which is large both with respect to the size of the molecule and to the fundamental limit.<sup>[1,6–9]</sup>

As seen in Figure 1, DDMEBT has a non-planar structure,<sup>[2,5]</sup> in contrast to the structure of a donor-substituted



**Figure 1.** The molecule we used for the supramolecular assembly discussed in this work (DDMEBT) compared to another molecule we considered (TDMEE). A 3D spatial view of DDMEBT is shown on the right.

cianoethynylethene molecule such as TDMEE (1,1,2-tricyano-2-[(4-dimethylaminophenyl)ethynyl]ethene).<sup>[1,10]</sup> DDMEBT contains almost the complete TDMEE molecule as a sub-unit. It is thus 70% larger than TDMEE but it has a similar third-order polarizability.<sup>[1,2]</sup> This makes its specific third-order polarizability smaller than that of TDMEE ( $1.7 \times 10^{-23} \text{ m}^5 \text{ V}^{-1} \text{ kg}^{-1}$  vs.  $2.9 \times 10^{-23} \text{ m}^5 \text{ V}^{-1} \text{ kg}^{-1}$ , respectively), but its larger non-planar structure is the key to reducing intermolecular interactions and producing a high-optical quality homogenous film. In contrast, we have found that TDMEE thin films have a large surface roughness and contain micrometer-sized grains that cause light scattering.

DDMEBT thin films were fabricated by heating a powder of molecules to 130 °C in a crucible inside a vacuum of  $8 \times 10^{-7}$  Torr. The sublimating molecules then formed a molecular beam incident on a glass substrate kept at a temperature of 28 °C and positioned 20 cm above the crucible, with a deposition rate of approximately  $1 \text{ nm min}^{-1}$ . We performed several depositions that resulted in thin films of varying thicknesses between 140 and 950 nm.

To the naked eye, the DDMEBT organic thin films appear silvery dark, shiny, and reflective. The transmission spectra taken at normal incidence for three films with different thicknesses are shown in Figure 2. The films have a wide transparency range starting at wavelengths above 700 nm, with a modulation in the transmission at longer wavelengths that is a result of multiple reflections inside the film. The existence of such a clear transmission modulation with wavelength is a first direct indication of the flatness of the films and of small absorption and scattering losses.

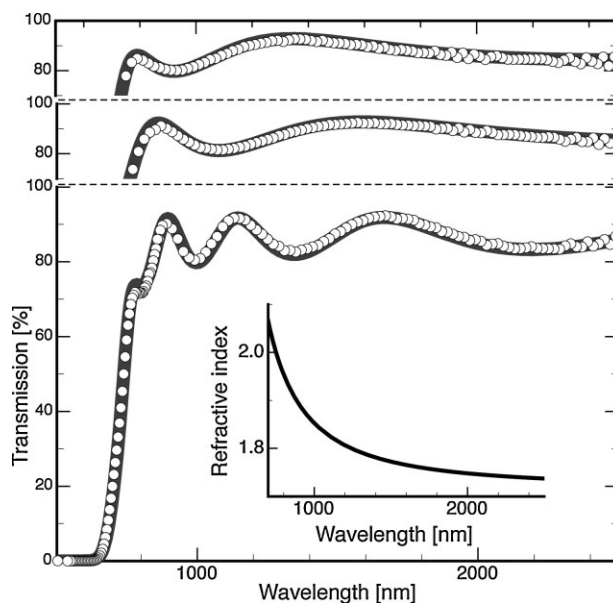
The thin film transmission can be modeled by taking into account the coherent multiple reflections inside the organic film, the main absorption peak of the molecular assembly, and the refractive index of the material and its dispersion. We performed a simultaneous least squares fit of the predictions of the model to the experimentally determined transmission spectra of films with three different thicknesses. The thicknesses of the films were measured independently by

AFM. The model fitted the experiment very well without any adjustable parameter other than those determining the refractive index dispersion, for which we used a simple one-oscillator Sellmeier-type model. The refractive index dispersion we obtained is shown in the inset of Figure 2. The linear refractive index of the DDMEBT organic thin film is  $1.8 \pm 0.1$  at  $1.5 \mu\text{m}$ .

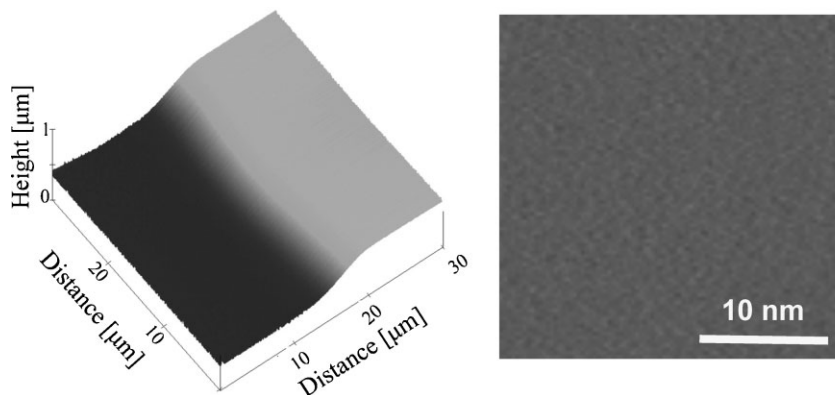
The fact that both the absolute value of the transmission and the position and contrast of the peaks and valleys in the infrared spectral range could be perfectly fitted for three films and independently determined thicknesses is already a quite good indication of the high-optical quality of the films. They clearly have a constant thickness over an area of several millimeters in diameters with any

variations in thickness within that area much smaller than the wavelength of the light inside the material, i.e., smaller than a few tens of nanometers.

The good optical quality and homogeneity of the thin films was further confirmed by the SEM and AFM measurements shown in Figures 3 and 4. The AFM measurements were done in tapping mode and multiple line scans could be taken over the same area without the sample being affected. AFM line scans on a  $500 \text{ nm} \times 500 \text{ nm}$  area, shown in Figure 4, reveal surface height variations below 5 nm for the 950 nm thick film. SEM measurements were performed using a HITACHI 4300 scanning electron microscope featuring a variable-pressure



**Figure 2.** Transmission spectra of three DDMEBT films with thicknesses (beginning from top) of 380, 450, and 950 nm, respectively. The data are represented by white circles and are shifted vertically for clarity. The thick solid curves are the results of a simultaneous least squares fit with the refractive index dispersion shown in the inset.



**Figure 3.** AFM and SEM images of a 380 nm thick DDMEBT film. Left: AFM image showing the transition from the region where the molecular beam was blocked by a shutter to the exposed region where the thin film was deposited. Right: SEM image of a  $25 \times 25 \text{ nm}^2$  area of the same film. The film appears to be featureless down to the nanometer scale.

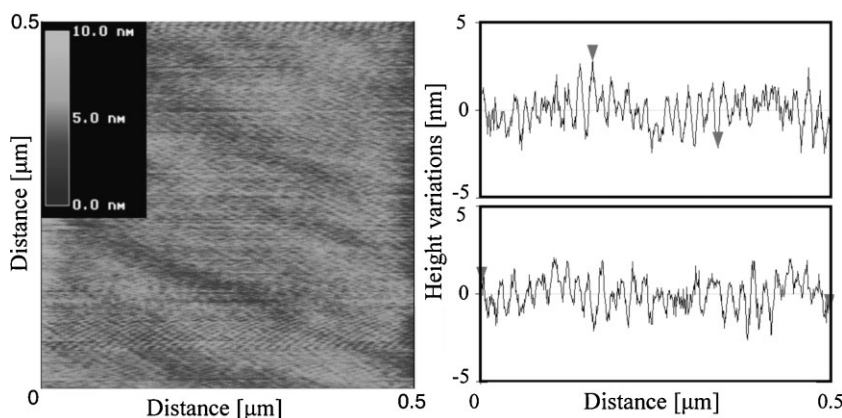
mode of operation and an environmental secondary electron detector (ESED). This enabled us to use accelerating voltages up to 8 kV without the need of a metallic coating to eliminate charging effects. SEM images, as exemplified by the one shown in Figure 3, do not show any features down to a size of 2 nm. Single molecular nanoclusters or grains, if present, must be smaller than this.

The third-order nonlinear optical susceptibility of the DDMEBT films was determined by DFWM at  $1.5 \mu\text{m}$ . We used a Clark-MXR laser (CPA-2001) pumping a traveling wave optical parametric amplifier system (TOPAS) from Light Conversion. We first determined the third-order susceptibility of our glass substrates (Erie Electroverre M-5227 glass with refractive index of 1.5126 at  $0.644 \mu\text{m}$ ) by comparing its DFWM signal to a fused-silica sample, using  $\chi_{1111}^{(3)} = 1.9 \times 10^{-22} \text{ m}^2 \text{ V}^{-2}$  for fused silica at  $1.5 \mu\text{m}$ . Then, the DFWM signal from the glass substrate alone was compared to that of the glass substrate with films of different thicknesses deposited on it. The laser pulses were 1 ps long, with a peak intensity of  $2 \text{ GW cm}^{-2}$ , and a repetition rate of 1 kHz. We

found a third-order susceptibility of the DDMEBT supramolecular assembly of  $\chi_{1111}^{(3)} = 2 \pm 1 \times 10^{-19} \text{ m}^2 \text{ V}^{-2}$  at the off-resonant wavelength of  $1.5 \mu\text{m}$ . This value is  $\sim 10^3$  times larger than that of fused silica and corresponds to a nonlinear refractive index  $n_2 = 1.7 \pm 10^{-13} \text{ cm}^2 \text{ W}^{-1}$  when the intensity dependence of the refractive index  $n$  is defined as  $n(I) = n(0) + n_2 I$ . For a review of some other organic films and the corresponding nonlinearities that have been reported in the literature we refer to ref. [11]. The variability in characterization conditions and methods that have been used in the past does not allow a direct comparison to our results without a deeper discussion. Here, we limit ourselves to comparing our results with the organic material with the highest off-resonant third-order nonlinearity that has been reported to date. This material is the single-crystal of poly(2,4-hexadiyne-1,6-diol di-*p*-toluenesulfonate) (PTS). The nonlinear refractive index of PTS is  $2.2 \pm 0.3 \times 10^{-12} \text{ cm}^2 \text{ W}^{-1}$  at  $1.6 \mu\text{m}$ ,<sup>[12]</sup> a value that is  $\sim 10$  times higher than that of DDMEBT amorphous films. However, it is important to note that this high value of the nonlinearity in PTS is observed only for one particular polarization direction of the light corresponding to the alignment of the chromophores in the crystal. The same density of the same chromophores, but randomly oriented like the DDMEBT molecules in our film, would produce a five times smaller third-order susceptibility (but with  $\chi_{1111}^{(3)} = \chi_{2222}^{(3)} = \chi_{3333}^{(3)}$ ). Another important point is that fabrication of extended single-crystal thin films of PTS is quite difficult,<sup>[13,14]</sup> and the inherent anisotropy of the material is an important handicap when it comes to integration with existing photonic devices. In contrast, by vapor deposition of DDMEBT we can easily cover a wide area (many square centimeters) of any substrate with a high-quality nonlinear film that has a large isotropic third-order susceptibility.

The properties of the DDMEBT organic thin film that we developed make it very attractive for use in integrated nonlinear optical devices. This could take the form of stand-alone DDMEBT waveguides, as well as of a hybrid system where the organic material provides the nonlinearity while an appropriate passive material provides for waveguiding. The flexibility of vapor deposition makes the second possibility particularly attractive, and it is therefore the first one that we pursued.

We deposited a DDMEBT thin film on a specially prepared silicon-on insulator waveguide<sup>[15]</sup> to create a new hybrid device that combines the perfection of silicon nanofabrication with the high third-order susceptibility of DDMEBT.<sup>[16]</sup> A key point was the fact that we were able to homogeneously fill



**Figure 4.** Surface relief of a 950 nm thick DDMEBT film, taken by an atomic force microscope over an area of  $0.5 \times 0.5 \mu\text{m}^2$ . Corresponding line scans are shown on the right-hand side, to highlight that surface roughness is limited to height variations of less than 5 nm.

with vapor deposited DDMEBT a 160 nm wide and 220 nm tall trench between two silicon waveguides.<sup>[16]</sup> Such a system is designed in such a way that the optical mode propagates essentially inside the trench between the waveguides, that is, inside the organic material.<sup>[15]</sup> The hybrid waveguide based on DDMEBT showed a record-high off-resonant nonlinearity and it was used to demonstrate an ultrafast all-optical switch for time-division demultiplexing of 120 and 170.8 Gbit s<sup>-1</sup> data streams.<sup>[16,17]</sup>

While we have not yet studied the properties and propagation losses of stand-alone DDMEBT waveguides, it has already been observed that in the hybrid waveguide mentioned above no significant propagation losses could be attributed to either intrinsic absorption or scattering losses in the DDMEBT film.<sup>[17]</sup> From this we can estimate the propagation losses in the DDMEBT material to be less than ~1 dB cm<sup>-1</sup>. This is indicative of both the high quality and homogeneity of the organic film, as well as its small absorption at the operating wavelength of 1.5 μm.

The DDMEBT supramolecular assembly that we presented here may represent one of best organic materials that have been demonstrated for integrated nonlinear optics. To the best of our knowledge, no other materials have been reported to date where the same combination of high off-resonant third-order susceptibility, easy fabrication of extended homogeneous films, and high-optical quality is observed.

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- [1] J. C. May, J. H. Lim, I. Biaggio, N. N. P. Moonen, T. Michinobu, F. Diederich, *Opt. Lett.* **2005**, *30*, 3057.
- [2] T. Michinobu, J. C. May, J. H. Lim, C. Boudon, J.-P. Gisselbrecht, P. Seiler, M. Gross, I. Biaggio, F. Diederich, *Chem. Commun.* **2005**, *6*, 737.
- [3] J. C. May, I. Biaggio, F. Bures, F. Diederich, *Appl. Phys. Lett.* **2007**, *90*, 251106.
- [4] D. Milam, *Appl. Opt.* **1998**, *37*, 546.
- [5] T. Michinobu, C. Boudon, J.-P. Gisselbrecht, P. Seiler, B. Frank, N. N. P. Moonen, M. Gross, F. Diederich, *Chem. Eur. J.* **2006**, *12*, 1889.
- [6] M. G. Kuzyk, *Phys. Rev. Lett.* **2000**, *85*, 1218.
- [7] M. G. Kuzyk, *Phys. Rev. Lett.* **2003**, *90*, 039902.
- [8] M. G. Kuzyk, *Opt. Lett.* **2000**, *25*, 1183.
- [9] M. G. Kuzyk, *Opt. Lett.* **2003**, *28*, 135.
- [10] N. N. P. Moonen, R. Gist, C. Boudo, J.-P. Gisselbrecht, P. Seiler, T. Kawai, A. Kishioka, M. Gross, M. Irie, F. Diederich, *Org. Biomol. Chem.* **2003**, *1*, 2032.
- [11] J. M. Hales, J. W. Perry, in: *Introduction to Organic Electronic and Optoelectronic Materials and Devices*, (Eds: S.-S. Sun, L. Dalton), CRC, Orlando **2008**, pp. 521–579.
- [12] B. L. Lawrence, M. Cha, J. U. Kang, W. Toruellas, G. Stegeman, G. Baker, J. Meth, S. Etamad, *Electron. Lett.* **1994**, *30*, 447.
- [13] M. Thakur, D. M. Krol, *Appl. Phys. Lett.* **1990**, *56*, 1213.
- [14] M. Liu, L. Freidrich, G. I. Stegeman, *CLEO Tech. Digest* **1998**, 207.
- [15] C. Koos, L. Jecome, C. Poulton, J. Leuthold, W. Freude, *Opt. Express* **2007**, *15*, 5976.
- [16] C. Koos, P. Vorreau, P. Dumon, R. Baets, B. Esembeson, I. Biaggio, T. Michinobu, F. Diederich, W. Freude, J. Leuthold, *Technical Digest Optical Fiber Communication Conference (OFC 2008)*, San Diego(CA), USA, February 24–28, **2008**, Postdeadline Paper PDP25.
- [17] C. Koos, T. Vallaitis, P. Vorreau, P. Dumon, R. Baets, B. Esembeson, I. Biaggio, T. Michinobu, F. Diederich, W. Freude, J. Leuthold, *J. Lightwave Technol.* **2009**, submitted.