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Spontaneous *in situ* thermal growth of oriented acentric nanocrystals of [(*E*)-*N,N*-dimethylamino-*N'*-methylstilbazolium][*p*-toluenesulfonate] embedded in a PMMA film on ITO generating stable SHG

Daniele Marinotto,^{*,a} Elena Lucenti,^b Guido Scavia,^c Renato Ugo,^a Silvia Tavazzi,^d Giovanni Mattei^c and Elena Cariati^{*,a}

^aDipartimento di Chimica and Centro di Eccellenza CIMAINA dell'Università degli Studi di Milano, UdR dell'INSTM, via Golgi 19, 20133 Milano, Italy

^bIstituto di Scienze e Tecnologie Molecolari del CNR (ISTM-CNR), via Golgi 19, 20133 Milano, Italy and UdR di Milano dell'INSTM.

^cIstituto per lo Studio delle Macromolecole (ISMAL), CNR, Via Bassini 15, 20133 Milano, Italy.

^dDipartimento Scienza dei Materiali, Università di Milano Bicocca, Via Cozzi 53, I-20125 Milano, Italy

^eDipartimento di Fisica dell'Università di Padova, via Marzolo 8, I-35131 Padova, Italy

Introduction

Organic and hybrid inorganic–organic nanostructured acentric materials based on molecular chromophores characterized by a large quadratic hyperpolarizability (β) have been widely investigated in the last two decades for their potential application in various electro-optical devices such as optical waveguides or frequency modulators.¹ To be of interest for technological applications, these materials must possess not only a satisfactory and long lasting macroscopic second order susceptibility ($\chi^{(2)}$) but also a significant chemical and thermal stability. Large $\chi^{(2)}$ values of nanostructured oriented materials have been obtained starting from molecular second order nonlinear optical (NLO) chromophores as building blocks by engineering their nano-organization in a non-centrosymmetric way. Among the many different strategies employed,²⁻⁷ electric poling of composite polymeric films with embedded polar molecular second order NLO chromophores⁸ is an intensively investigated approach.⁹ In the poling process the initial random dispersion in the polymeric matrix of the polar second order NLO chromophores is broken to

generate asymmetry by aligning their dipole moments under a strong directional electric field. However, such process suffers the outcome of an easy decay of the second harmonic generation (SHG) due to orientational relaxation of the aligned NLO chromophores and, often, of scattering losses originated from the inhomogeneity of the composite film. Moreover, the poling process is usually applied to composite polymeric films containing neutral polar second order NLO chromophores since ionic chromophores may produce, under the effect of the directional strong electric field, an opposite diffusion of cations and anions towards the surface of the film.

However, very recently some of us discovered a direct procedure involving ionic second order NLO chromophores based on a successful two step (electric poling and thermal annealing) process which produces *in situ* oriented nanocrystals of highly NLO active ionic acentric materials homogeneously dispersed in a poly(methyl methacrylate) (PMMA) film deposited on a glass substrate.¹⁰⁻¹¹ In this two step process an electric poling pretreatment of a dispersion of the ionic chromophore (*[(E)-N,N*-dimethylamino-*N'*-methylstilbazolium][*p*-toluenesulfonate],¹⁰ hereafter DAST, or *[(E)-N,N*-dimethylamino-*N'*-methylstilbazolium][Cu₅I₆]¹¹) in a PMMA film is followed by solely controlled annealing at a temperature higher than the glass transition temperature (T_g) of PMMA. The oriented NLO active polar nanocrystals generated *in situ* are sufficiently small and homogeneously dispersed to guarantee a good optical quality of the film, but large enough to be characterized by an extremely low mobility in the PMMA matrix thus producing a long lasting SHG. In particular, nonlinear optical coefficients d_{33} up to 5.3 and 3.5 pm/V were measured for the DAST/PMMA¹⁰ and the *[(E)-N,N*-dimethylamino-*N'*-methylstilbazolium][Cu₅I₆]/PMMA film,¹¹ respectively.

In this work, in the attempt to extend this methodology to other transparent substrates with semiconducting properties, we have prepared and investigated the behaviour of composite DAST/PMMA films deposited on Indium Tin Oxide (ITO). By following the above described two step process a second order NLO coefficient d_{33} higher than the one obtained by the same film on a glass substrate was measured.¹⁰ Such increase cannot be explained simply on the basis of the very low second order nonlinear response of ITO itself (whose effective second order NLO susceptibility

is about 2.4×10^{-10} esu).^{12,13} The generation of a second harmonic response of a composite polymeric film of dispersed red one deposited on ITO substrates was reported, but not quantified, by Ghebremichael *et al.*,¹³ who suggested that, at room temperature and in the absence of a poling electric field, a polar orientation of the second order NLO molecular chromophore was induced in the composited polymeric film at the ITO-film interface. However, according to our knowledge, no further investigations have been performed to optimize and possibly elucidate the role of the ITO substrate in inducing such polar orientation. To better analyze this aspect, in this work we have performed solely careful annealing of a DAST/PMMA film deposited on ITO. The results of this investigation indicate that it is possible to generate spontaneously oriented dipolar acentric nanocrystals of DAST by annealing only, that is by a one step process. Such polar orientation of DAST nanocrystals appears to be localized very close to the ITO-film interface since it decreases moving towards the surface of the composite film. Moreover, we have evidenced that different thermal pretreatments of the ITO substrate before the deposition of the DAST/PMMA film induce different SHG responses

Experimental Section

General comments

Poly(methyl methacrylate) (PMMA, $\overline{M}_w \sim 15000$; T_g 86,5°C as determined by differential scanning calorimetry), DAST, chloroform and methanol, were purchased from Sigma Aldrich and used as received. ITO was purchased from Delta Technologies, Limited. Fluorine doped tin oxide (FTO) was purchased from Solaronix. Electronic absorption spectra of the films were measured by transmission on a JASCO Corp. UV-530 spectrophotometer. Grazing Incidence X-ray Diffraction (GIXRD) measurements were carried out with a Panalytical X'PERT Pro MRD source Cu ($\text{CuK}\alpha$). Thin polymeric films were prepared with a Cookson Electronic Company P-6708D spin-coater. The spinning parameters were set at the following values: RPM 1: 700; Ramp 1: 1 s, Time 1: 5 s; RPM 2: 2000; Ramp 2: 5 s, Time 2: 80 s. Thermal annealing was performed in a laboratory

drying oven model Venticell 111 from MMM Medcenter Einrichtungen GmbH.

Preparation of composite DAST/PMMA thin films

Thin composite DAST/PMMA films were prepared by spin-coating on a slide of ITO or FTO few drops of a solution prepared dissolving 15mg of DAST (4 wt% with respect to PMMA) and 377mg of PMMA (10 wt% with respect to the solution) in 3mL of CHCl₃/CH₃OH (2/1 v/v).

Films with 20 wt% PMMA were prepared by dissolving 755mg of PMMA and 10mg of DAST (1.3 wt% with respect to PMMA) in 3mL of CHCl₃/CH₃OH (2/1 v/v).

The thickness of the films was $1.8 \pm 0.11 \mu\text{m}$ and $4.7 \pm 0.28 \mu\text{m}$ for 10 wt% and 20% PMMA films respectively, measured with α -step stylus profilometer, while the absorbance of the electronic spectra of the two films is comparable.

Thermal ramp

Thermal pretreatments of ITO and FTO substrates were performed in an oven at temperatures up to 240°C, or in an heating mantle with sand bath at 370°C, producing substrates hereafter indicated as: non preheated **ITO-not annealed** and **FTO-not annealed**; **ITO-annealed 240** and **FTO-annealed 240** preheated at 240°C for 8h and 4h respectively; **ITO-annealed 370** preheated at 370°C for 24h. Thermal annealings of composite thin films of DAST/PMMA deposited on ITO or FTO were performed in an oven with the following rate: 1h at 50°C, 1h 70°C, 1h30min at 90°C, 3h 120°C, 2h30min at 130°C, 1h at 140°C, 1h at 150°C and 4h at 160°C.

SHG measurements

In situ SHG measurements were carried out with a Q-switched Nd:YAG (Quanta System HYL-101) laser operating at 1064nm. The apparatus for the poling experiment is described elsewhere.^{10,11}

The absolute d_{33} value of the second order NLO coefficient of the composite polymeric material

was obtained (with an experimental error equal to 20%) by following the standard Maker fringe technique.¹⁴⁻¹⁶ In order to determine the nonzero independent components of the susceptibility tensor for films with $C_{\infty v}$ symmetry, measurements were performed at different polarizations: $p \rightarrow p$, $s \rightarrow p$, and $45^\circ \rightarrow s$ (indicated hereafter as pp, sp and 45s, where p and s indicate the polarization of the beam in the plane parallel and orthogonal to the incident one respectively). SH signal was normalized with respect to that of a calibrated quartz crystal wafer (X-cut) 1mm thick with d_{11} equal to 0.46 pm/V.¹⁴⁻¹⁶

Results and Discussion

A composite PMMA film containing 4 wt% of DAST was obtained by spin coating from $\text{CHCl}_3/\text{CH}_3\text{OH}$ (2/1 v/v) solutions on **ITO-not annealed** substrate. The film was poled at 8.5 kV for about 250 minutes and then, after turning off the electric field, carefully annealed up to 140°C. A constant SHG response was observed which remained stable also when cooling the film down to room temperature (Figure 1). This behavior is very similar to what reported by some of us after an analogous poling¹⁷ and annealing treatment of a DAST/PMMA film deposited on a glass substrate.¹⁰

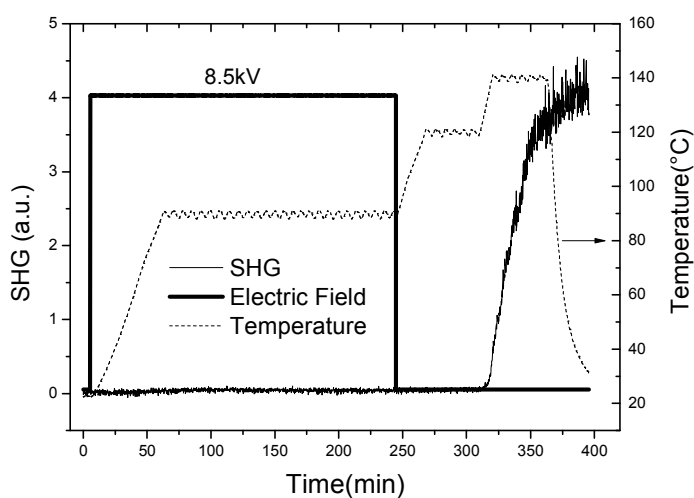


Figure 1. Poling and annealing of the composite DAST/PMMA film on **ITO-not annealed**

substrate.

The electronic absorption spectra of the DAST/PMMA film on **ITO-not annealed** after poling and annealing together with that of the pristine film are reported in Figure 2. The pristine film shows a single, large absorption band centered at 460 nm resembling that of DAST in solution.¹⁰ After poling and annealing the spectrum shows two bands: one broad centered at 490 nm and one red shifted and narrower at 550 nm. This spectrum closely resembles that of crystalline DAST in KBr and of DAST single crystals.¹⁸ The narrow absorption band at 550 nm has been reported as originated by the organization of the cationic component of the ionic chromophore into J aggregates and was reported as an evidence of the formation of crystalline nanoaggregates of DAST in the polymeric film.¹⁰

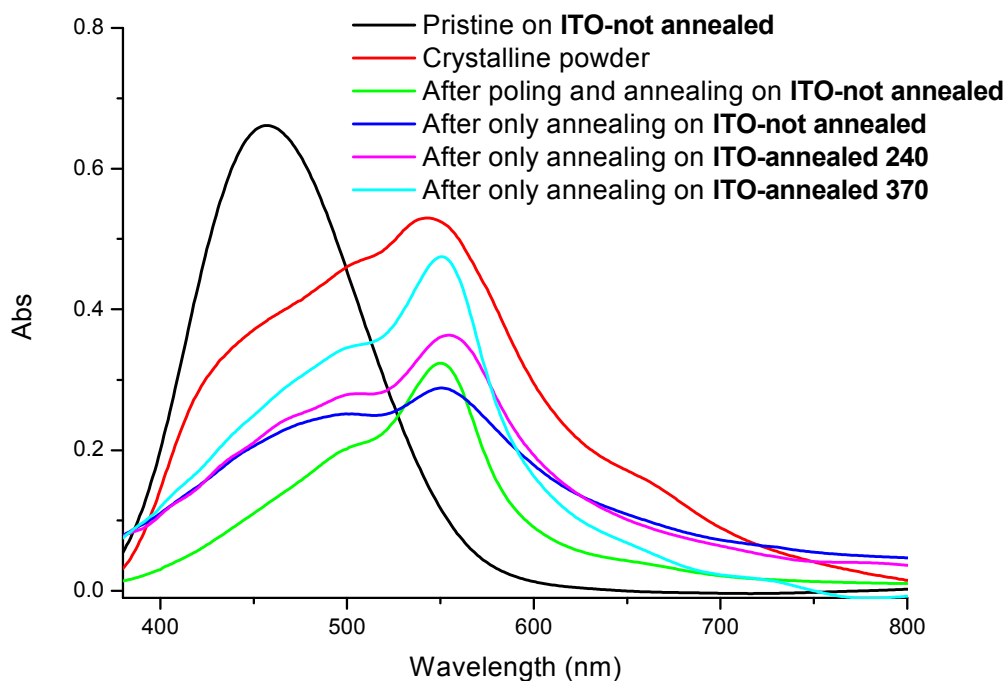


Figure 2. Electronic absorption spectra of composite DAST/PMMA films and of DAST powder in KBr.

By fitting the Maker fringes measurements (see SI Figure S1 as explicative of the methodology),¹⁹ we have calculated, for the poled and annealed DAST/PMMA film on **ITO-not annealed** substrate, a nonlinear optical coefficient, d_{33} , equal to 6.2 ± 1.24 pm/V, a value slightly higher than that measured for a DAST/PMMA film on a glass substrate undergoing the same treatment (5.3 ± 1.06 pm/V).¹⁰

In order to evaluate the possible contribution of the ITO itself to the overall SHG response of the final composite DAST/PMMA film, we have measured the intensity of pp, sp and 45s Maker fringes generated by **ITO-not annealed** itself. The pp component of the Maker fringes is much higher than the 45s one and the hardly discernible sp one (see Figure 3). Considering that the SH intensity of the oriented composite DAST/PMMA film on **ITO-not annealed** is always more than two or three orders of magnitude higher than that of **ITO-not annealed** itself, with confidence, we can neglect the ITO contribution to the SHG response of the DAST/PMMA film.

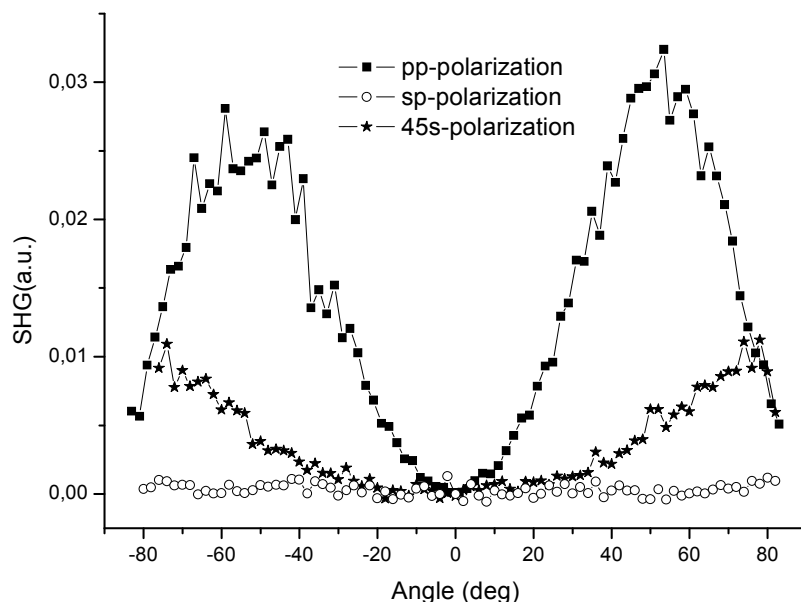


Figure 3. Maker fringes of **ITO-not annealed**.

The slightly higher d_{33} when the DAST/PMMA film is deposited on ITO could then be explained by admitting an additional spontaneous orientation of acentric polar DAST nanocrystals induced at the ITO-film interface, as suggested by Ghebremichael *et al.*¹³

Therefore, in order to verify this hypothesis, we have monitored the pp-Maker fringes of a pristine DAST/PMMA film deposited on **ITO-not annealed** but only thermally annealed (according to the ramp reported in the Experimental Section).

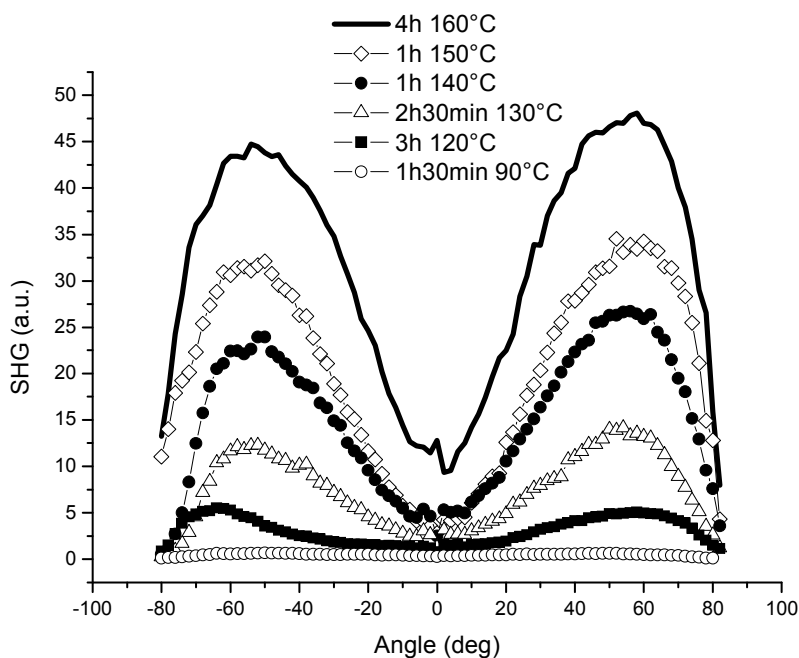


Figure 4. pp-Maker fringes of a DAST/PMMA film on **ITO-not annealed**.

The Maker fringes recorded after each thermal step show a SH intensity minimum at 0° angle of incidence (Figure 4), and a maximum at about 60° . This pattern indicates the presence of a polar order into the film, which, in analogy to our previous findings,¹⁰ could be considered of $C_{\infty v}$ symmetry with nanoaggregates (probably nanocrystals) of DAST, thermally originated and partially oriented perpendicularly to the thin film surface.¹⁶

Interestingly, the Maker fringes minimum and maximum intensity increases by increasing the temperature, reaching the highest and stable value after 4 hours at 160°C ; further heating at the

same or at higher temperatures led to film degradation. A careful control of the thermal ramp is a necessary condition, otherwise a very low dependence of the Maker fringes from the incident angle with a not null signal at 0° is observed. It is relevant also to mention that, by solely applying the same thermal ramp to a DAST/PMMA film deposited on a glass substrate, a disordered ensemble of crystalline grains of DAST in the PMMA matrix is obtained (see Figure 5 and 6).

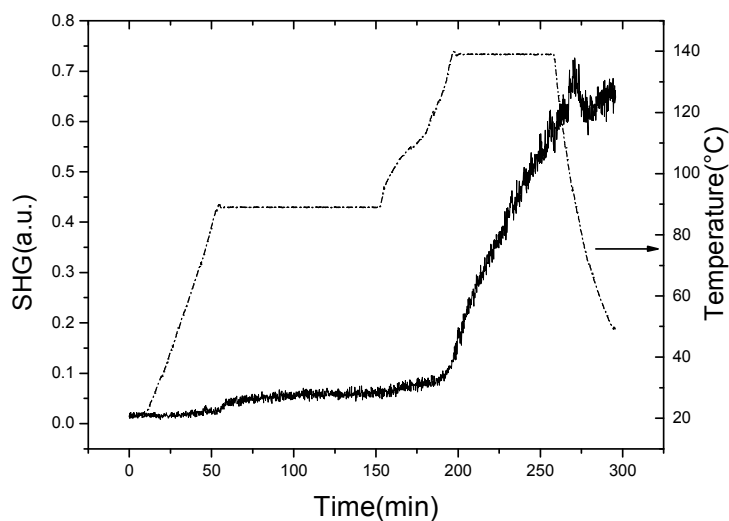


Figure 5. SHG of a heated composite DAST/PMMA film on a glass substrate: SH (continuous line) and temperature (dash dot).

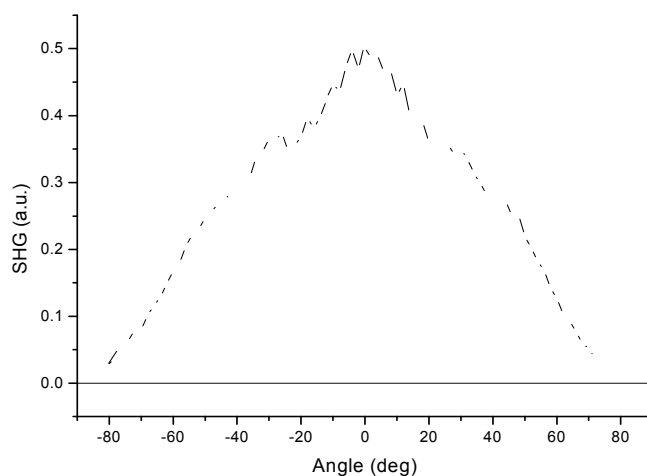


Figure 6. pp-Maker fringes of an annealed composite DAST/PMMA film on a glass substrate

Also the effect of different thermal pretreatments of the ITO substrate was found to be important in controlling the SHG response of DAST/PMMA film. PMMA films containing 4 wt% of DAST were prepared by spin coating from $\text{CHCl}_3/\text{CH}_3\text{OH}$ (2/1 v/v) solutions on ITO substrates preheated for 8 hours at 240°C and for 24 hours at 370°C .

The electronic absorption spectra of the composite DAST/PMMA films deposited on **ITO-annealed 240** and **ITO-annealed 370** after annealing only (using the same thermal ramp reported above) are shown in Figure 2. The spectra closely resemble the one obtained for the annealed only DAST/PMMA film on **ITO-not annealed**, even though an increase in the absorbance of the J aggregate band is observed on going from film deposited on **ITO-not annealed** to **ITO-annealed 370**.

By comparing the d_{33} calculated by the standard Maker fringe technique¹⁶ for the DAST/PMMA films on **ITO-not annealed**, **ITO-annealed 240** and **ITO-annealed 370** after annealing only (see Table 1), a clear SHG dependence on the thermal pretreatment of the ITO substrate was observed.

Table 1.

ITO	ITO-not annealed	ITO-annealed 240	ITO-annealed 370
d_{33} (pm/V)	3.18 ± 0.63	6.32 ± 1.26	7.05 ± 1.41

A film thickness of $1.85 \pm 0.11 \mu\text{m}$, $1.82 \pm 0.11 \mu\text{m}$ and $1.80 \pm 0.11 \mu\text{m}$, was measured on **ITO-not annealed**, **ITO-annealed 240** and **ITO-annealed 370** respectively

The d_{33} values of annealed only films on **ITO-annealed 240** and **ITO-annealed 370** are about twice that of film on **ITO-not annealed**.²⁰ Particularly relevant is the observation that the d_{33} value of the films on **ITO-annealed 240** and **ITO-annealed 370** are also higher than that previously obtained by applying the two step process of poling and annealing a composite DAST/PMMA film deposited on a glass substrate (about 5.3 pm/V) and approximately equal if not higher than the one obtained for the poled and annealed DAST/PMMA film on **ITO-not annealed** (6.2 pm/V). Heating treatments are known to induce extensive surface and bulk reconstruction in ITO films, generally by an increase in crystallinity of the In_2O_3 phase.²¹ Surface OH population deep changes were already reported to occur also during the calcination of $\text{In}(\text{OH})_3$ to In_2O_3 due to the release and transfer of protons.²² So it appears that, by increasing the temperature, the ITO surface increases its orientational power, which is probably of polar nature,²³ on the DAST/PMMA film thus producing higher values of the SH efficiency.

To test if the thermally oriented crystalline aggregates of DAST are concentrated close to the ITO substrate surface or rather into the bulk polymeric layer, we investigated the behaviour of the Maker fringes as a function of the thickness of DAST/PMMA film deposited on **ITO-annealed 370**. By increasing the film thickness, we worked with a solution containing 20 wt % of PMMA, while keeping constant the amount of the second order NLO chromophore in the film (as confirmed by UV visible absorption spectroscopy and profilometer measurements, see the Experimental), the SH intensity of the Maker fringes after annealing decreases considerably (see Figure 7 left) when compared with a thinner film (see see Figure 7 right). Moreover, an increase of the SH signal at 0°

is observed, suggesting a greater number of randomly distributed nanoaggregates produced by the annealing of the thicker film. Such trend is even more evident by observing that, for the 45s-Maker fringe component, the SH signal originated by the not oriented aggregates is predominant.

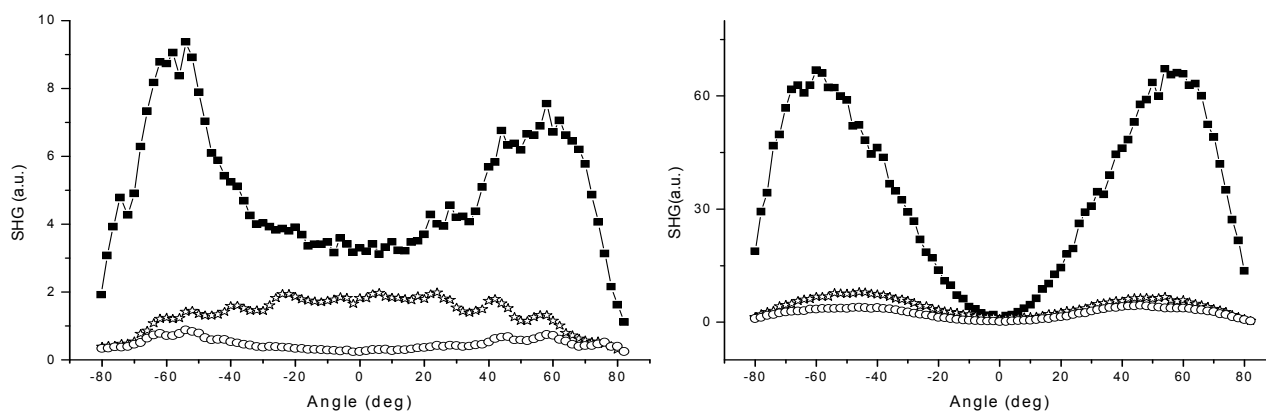


Figure 7. pp (square), sp (circle) and 45s (star) Maker fringes of the DAST/PMMA film on **ITO-annealed 370**. Left: 20 wt % of PMMA; right: 10 wt % of PMMA.

Composite DAST/PMMA films deposited on ITO and thermally annealed were investigated by X-ray diffraction (XRD) both in grazing incidence 2theta-scan mode (GIXRD) and in omega/2theta-scan mode and by Atomic Force Microscopy (AFM).

GIXRD measurements of DAST/PMMA films on **ITO-not annealed**, **ITO-annealed 240**, **ITO-annealed 370** indicate the absence of evident correlation of the DAST crystallinity with the different ITO texture (See SI Figure S2). The average crystallite size estimated from the DAST (004) peak at about 20° is for all the samples about 100 nm. DAST/PMMA on **ITO-not annealed** shows a slightly more pronounced texture on the (004) peak with respect to the other two samples on **ITO-annealed 240** and **ITO-annealed 370** (See SI Figure S6). The film on

ITO-annealed 370 has the largest texture of the ITO layer.

AFM morphologies investigation of the composite DAST/PMMA deposited on **ITO-not annealed** and **ITO-annealed 370** and only annealed are shown in Figure 8. Both films show an homogeneous distribution of DAST nanocrystals (diameter: 50-80nm for both) in the PMMA matrix, as observed for poled and annealed DAST/PMMA films deposited on a glass substrate,¹⁰ while no macroscopic differences are observed for the AFM images of **ITO-not annealed** and **ITO-annealed 370** themselves.

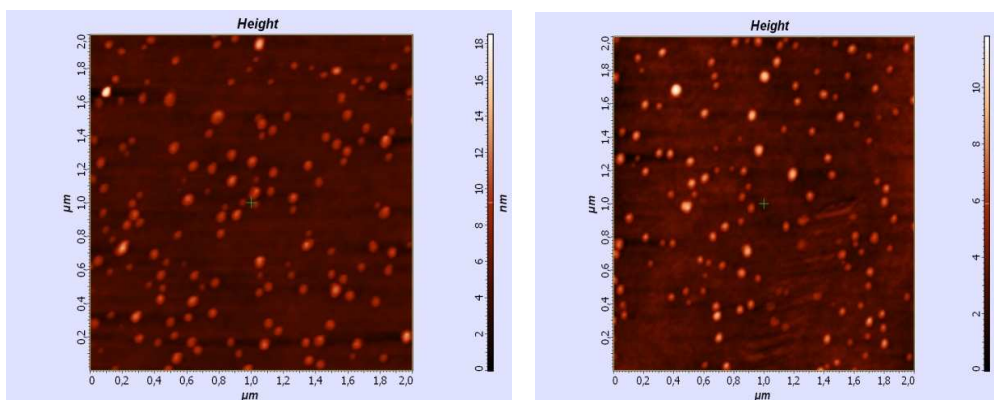


Figure 8. AFM images of the DAST/PMMA film deposited on **ITO-not annealed** (left) and **ITO-annealed 370** (right) after thermal annealing according to the thermal ramp described in the experimental.

To investigate if such spontaneous orientation of DAST nanocrystals by thermal annealing is induced also by other n-type semiconductors with high transmittance in the visible spectral range, we have performed similar measurements on DAST/PMMA films deposited on Fluorine doped Tin Oxide (FTO) substrates.

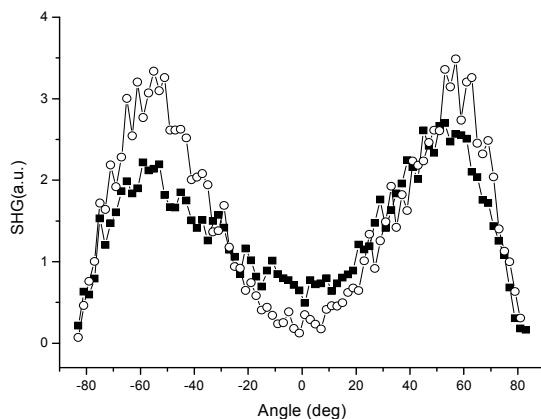


Figure 9. pp-Maker fringes for DAST/PMMA films on FTO: **FTO-not annealed** (square) and **FTO-annealed 240** (open circle).

In Figure 9 we report the pp-Maker fringes of two DAST/PMMA films on FTO generated after an annealing identical to that reported above for ITO substrates: one deposited on non preheated **FTO-not annealed** and the other on preheated (240 °C, 4h) **FTO-annealed 240**. The two films have thickness of $2.8 \pm 0.17 \mu\text{m}$ and $3.0 \pm 0.18 \mu\text{m}$ respectively measured by α -step stylus profilometer. In both cases it is evident the presence of an orienting mechanism very similar to that found using ITO as substrate, nevertheless the d_{33} values are smaller than the corresponding d_{33} measured on ITO (2.81 ± 0.56 and 3.26 ± 0.65 pm/V for the DAST/PMMA films deposited on **FTO-not annealed** and **FTO-annealed 240**, respectively). Even though further work should be done in order to optimize the procedure on this substrate, this result indicates the possible extension of our orienting methodology to other n-type semiconductors.

Conclusions

In this work we have extended to ITO substrates our two step poling/annealing procedure for the *in situ* production of oriented nanocrystals of DAST dispersed in a PMMA matrix. A nonlinear optical coefficient d_{33} higher than the one obtained on glass substrate was obtained.

This higher value is the result of a polar order induced on the dye-doped polymeric film at the ITO-film interface, indicating that the polarity of ITO surface is relevant in controlling the orientation process. By exploiting such induced polar order, we have demonstrated that oriented dipolar acentric nanocrystals of DAST can be grown *in situ* by solely and careful annealing, thus avoiding the detrimental effects often induced by the presence of a strong electric field. This leads not only to a spontaneous one step process of self orientation but also to a better second order NLO response from the DAST/PMMA film.

We have also shown how different thermal pretreatments of ITO itself can induce different SHG responses from the DAST/PMMA films. In particular, by preheating the ITO substrate at 370°C for 24 hours, a d_{33} value of 7.05 pm/V is obtained. This value is higher than that measured for the poled/annealed DAST/PMMA/glass system previously reported. In addition, preliminary results suggest that this methodology can be successfully applied to other transparent n-semiconductors.

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