PAPER

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,*[ab] Elena Lucenti,[b] Guido Scavia,[c] Renato Ugo,[a] Silvia Tavazzi,[d] Giovanni Mattei[e] and Elena Cariati*[ab]

A poly(methyl methacrylate) (PMMA) composite film containing 4 wt% of the strongly second order NLO active ionic material [(E)-N,N-dimethylamino-N′-methylstilbazolium][p-toluenesulfonate] (DAST) deposited on an ITO substrate shows by a two step process (electric poling followed by controlled thermal annealing) a nonlinear optical coefficient d_{33} higher than the one obtained on a glass substrate. 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 the ITO surface is relevant in controlling the orientation process. By exploiting such induced polar order, 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. In addition, different thermal pretreatments of ITO itself can induce different SHG responses from the DAST/PMMA films, the highest response being observed by preheating the ITO substrate at 370 °C for 24 hours.

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 chromophores[8] 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 a process suffers from 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

[a] *Dipartimento di Chimica and Centro di Eccellenza CIMAINA dell'Università degli Studi di Milano, UdR dell'INSTM, via Golgi 19, 20133 Milano, Italy. E-mail: daniele.marinotto@gmail.com; elena.cariati@unimi.it*

[b] *Istituto di Scienze e Tecnologie Molecolari del CNR (ISTM-CNR), UdR di Milano dell'INSTM, via Golgi 19, 20133 Milano, Italy*

[c] *Istituto per lo Studio delle Macromolecole (ISMAC), CNR, Via Bassini 15, 20133 Milano, Italy*

[d] *Dipartimento di Scienza dei Materiali, Università degli Studi di Milano Bicocca, Via Cozzi 53, I-20125 Milano, Italy*

[e] *Dipartimento di Fisica e Astronomia "Galileo Galilei" dell'Università degli Studi di Padova, via Marzolo 8, I-35131 Padova, Italy*

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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][Cu_5I_6][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^{-1} were measured for the DAST/PMMA[10] and [(E)-N,N-dimethylamino-N'-methylstilbazolium]-[Cu_5I_6]/PMMA films,[11] respectively.

In this work, in an 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 an increase cannot be explained simply on the basis of the very low second order nonlinear response of ITO itself (whose effective second order NLO susceptivity 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, $\overline{M_w} \sim 15\,000$; 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 (CuKα).

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 a few drops of a solution prepared dissolving 15 mg of DAST (4 wt% with respect to PMMA) and 377 mg of PMMA (10 wt% with respect to the solution) in 3 mL of $CHCl_3/CH_3OH$ (2/1 v/v).

Films with 20 wt% PMMA were prepared by dissolving 755 mg of PMMA and 10 mg of DAST (1.3 wt% with respect to PMMA) in 3 mL of $CHCl_3/CH_3OH$ (2/1 v/v).

The thickness of the films was 1.8 ± 0.11 μm and 4.7 ± 0.28 μm for 10 wt% and 20% PMMA films respectively, measured with an 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 a heating mantle with a sand bath at 370 °C, producing substrates thereafter indicated as: ITO-not annealed and FTO-not annealed (non-preheated); ITO-annealed 240 and FTO-annealed 240 (preheated at 240 °C for 8 h and 4 h respectively); ITO-annealed 370 (preheated at 370 °C for 24 h). Thermal annealing of composite thin films of DAST/PMMA deposited on ITO or FTO was performed in an oven with the following rates: 1 h at 50 °C, 1 h 70 °C, 1 h 30 min at 90 °C, 3 h 120 °C, 2 h 30 min at 130 °C, 1 h at 140 °C, 1 h at 150 °C and 4 h 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 1064 nm. 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 → p, s → p, and 45° → 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). The SH signal was normalized with respect to that of a calibrated quartz crystal wafer (X-cut) 1 mm thick with d_{11} equal to 0.46 pm V^{-1}.[14–16]

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Results and discussion

A composite PMMA film containing 4 wt% of DAST was obtained by spin coating from $CHCl_3$–CH_3OH (2/1 v/v) solutions on an 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 (Fig. 1). This behavior is very similar to what was reported by some of us after an analogous poling[17] and annealing treatment of a DAST/PMMA film deposited on a glass substrate.[10]

The electronic absorption spectra of the DAST/PMMA film on an ITO-not annealed substrate after poling and annealing together with that of the pristine film are reported in Fig. 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 to originate from the organization of the cationic component of the ionic chromophore into J aggregates and was reported as evidence for the formation of crystalline nanoaggregates of DAST in the polymeric film.[10]

By fitting the Maker fringes measurements (see ESI Fig. S1† for explanation of the methodology),[19] we have calculated, for the poled and annealed DAST/PMMA films on an ITO-not annealed substrate, a nonlinear optical coefficient, d_{33}, equal to 6.2 ± 1.24 pm V^{-1}, 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^{-1}).[10]

In order to evaluate the possible contribution of 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 Fig. 3). Considering that the SH
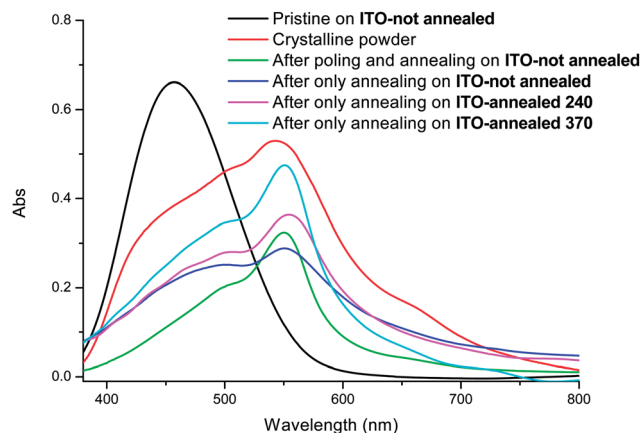
intensity of the oriented composite DAST/PMMA film on ITO-not annealed is always more than two or three orders of magnitude higher than that of ITO-not annealed itself, with confidence, we can neglect the ITO contribution to the SHG response of the DAST/PMMA film.

The slightly higher d_{33} value 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).

The Maker fringes recorded after each thermal step show a SH intensity minimum at 0° angle of incidence (Fig. 4), and a maximum at about 60°. This pattern indicates the presence of a polar order in 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
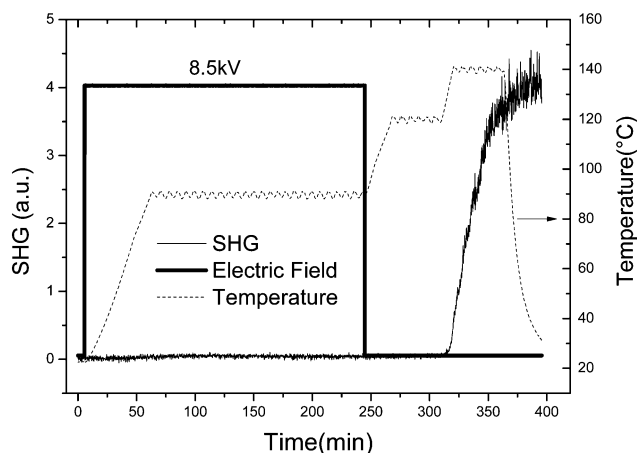

Fig. 2 Electronic absorption spectra of composite DAST/PMMA films and of DAST powder in KBr.

Fig. 1 Poling and annealing of the composite DAST/PMMA film on an ITO-not annealed substrate.
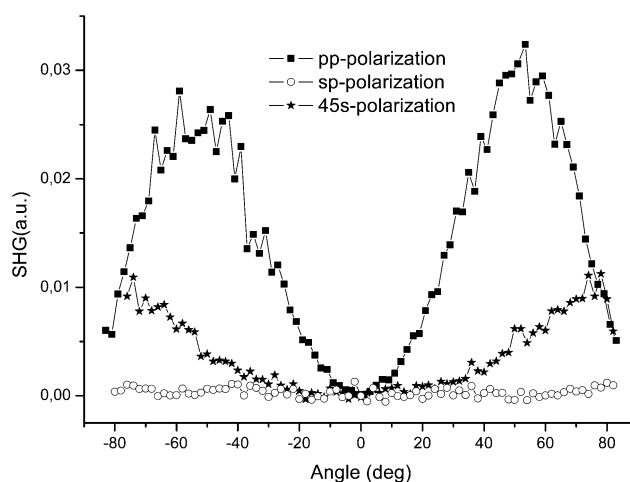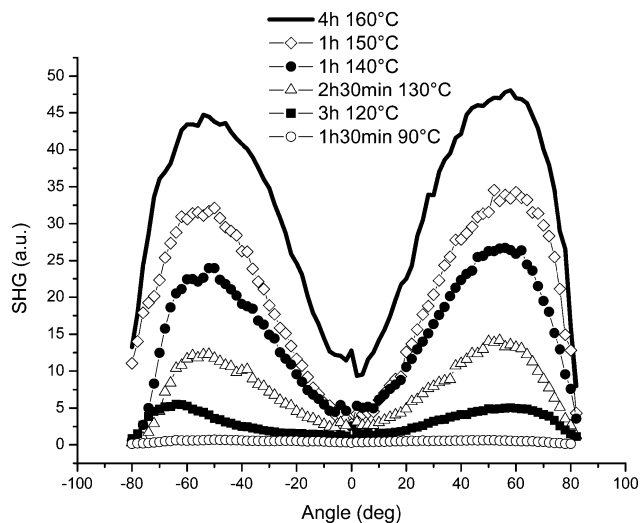

Fig. 3 Maker fringes of ITO-not annealed.

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

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

originated and partially oriented perpendicularly to the thin film surface.[16]

Interestingly, the Maker fringes' minimum and maximum intensities increase 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. 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 Fig. 5 and 6).

Also the effect of different thermal pretreatments of the ITO substrate was found to be important in controlling the SHG response of the DAST/PMMA film. PMMA films containing 4 wt% of DAST were prepared by spin coating from $CHCl_3$–CH_3OH (2/1 v/v) solutions on ITO substrates preheated for 8 hours at 240 °C and for 24 hours at 370 °C.
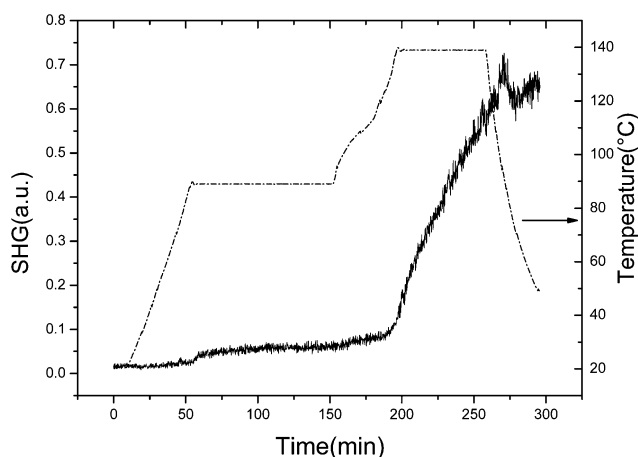
The electronic absorption spectra of the composite DAST/PMMA films deposited on ITO-annealed 240 and ITO-annealed 370 after annealing only (using the same thermal ramp reported above) are shown in Fig. 2. The spectra closely resemble the one obtained for the annealed only DAST/PMMA film on ITO-not annealed, even though an increase in the absorbance of the J aggregate band is observed on going from the film deposited on ITO-not annealed to ITO-annealed 370.

By comparing the d_{33} calculated by the standard Maker fringe technique[16] 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.

The d_{33} values of annealed only films on ITO-annealed 240 and ITO-annealed 370 are about twice that of the film on ITO-not annealed.[20] Particularly relevant is the observation that the d_{33} values 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^{-1}) 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^{-1}). 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 $In(OH)_3$ to In_2O_3 due to the release and

Fig. 5 SHG of a heated composite DAST/PMMA film on a glass substrate: SH (continuous line) and temperature (dashed dot).
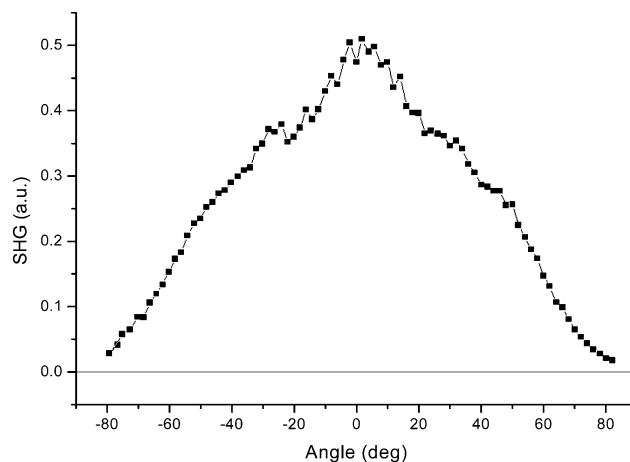
Table 1 Nonlinear optical coefficient d_{33} of DAST/PMMA film on different ITO substrates[a]

	ITO-not annealed	ITO-annealed 240	ITO-annealed 370
d_{33} (pm V^{-1})	3.18 ± 0.63	6.32 ± 1.26	7.05 ± 1.41

[a] A film of thickness of 1.85 ± 0.11 μm, 1.82 ± 0.11 μm and 1.80 ± 0.11 μm was measured on ITO-not annealed, ITO-annealed 240 and ITO-annealed 370 respectively.
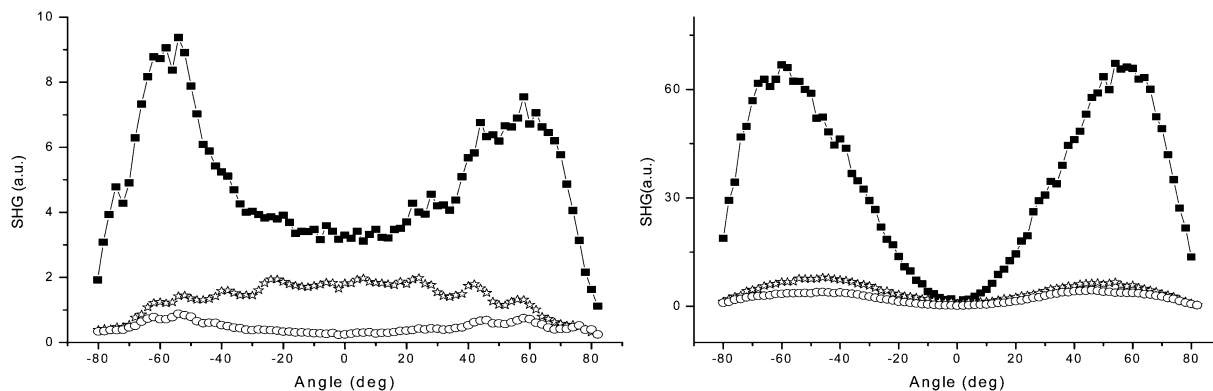
Fig. 7 pp (square), sp (circle) and 45s (star) Maker fringes of the DAST/PMMA film on ITO-annealed 370. Left: 20 wt% of PMMA; right: 10 wt% of PMMA.

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 the 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 section), the SH intensity of the Maker fringes after annealing decreases considerably (see Fig. 7 left) when compared with a thinner film (see Fig. 7 right). Moreover, an increase of the SH signal at 0° is observed, suggesting a greater number of randomly distributed nano-aggregates produced by the annealing of the thicker film. Such a trend is even more evident by observing that, for the 45s-Maker fringe component, the SH signal originated by the non-oriented aggregates is predominant.

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 DAST crystallinity with different ITO textures (see ESI Fig. S2†). The average crystallite size estimated from the DAST (004) peak at about 20° for all the samples is 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 ESI Fig. S6†). The film on ITO-annealed 370 has the largest texture of the ITO layer.

AFM morphologies of the composite DAST/PMMA deposited on ITO-not annealed and ITO-annealed 370 and after thermal treatment according to the ramp described in the Experimental section are shown in Fig. 8. Both films show a homogeneous distribution of DAST nanocrystals (diameter: 50–80 nm for both) in the PMMA matrix, as observed for poled and annealed DAST/PMMA films deposited on a glass substrate,[10] while no
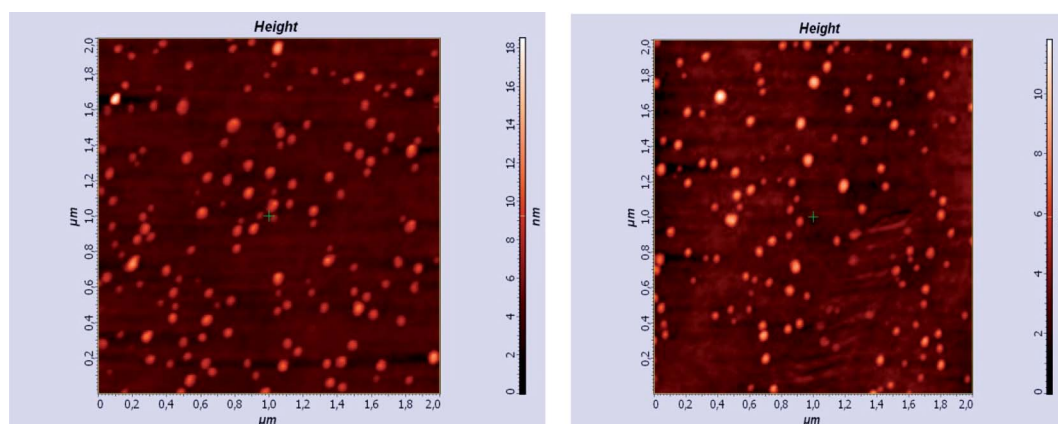

Fig. 8 AFM images of the DAST/PMMA film deposited on ITO-not annealed (left) and ITO-annealed 370 (right) after thermal treatment according to the thermal ramp described in the Experimental section.
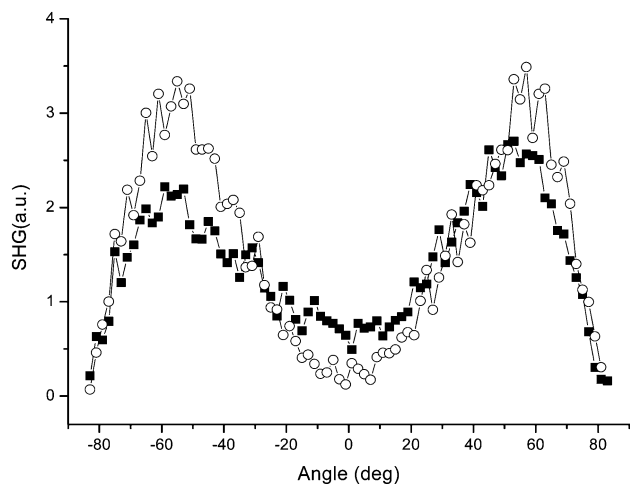
Fig. 9 pp-Maker fringes for DAST/PMMA films on FTO: FTO-not annealed (squares) and FTO-annealed 240 (open circles).

macroscopic differences are observed for the AFM images of ITO-not annealed and ITO-annealed 370 themselves.

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.

In Fig. 9 we report the pp-Maker fringes of two DAST/PMMA films on FTO generated after a thermal treatment identical to that reported above for ITO substrates: one deposited on non-preheated FTO-not annealed and the other on preheated (240 °C, 4 h) FTO-annealed 240. The two films have a thickness of $2.8 \pm 0.17 \, \mu m$ and $3.0 \pm 0.18 \, \mu m$ respectively measured using an α-step stylus profilometer. In both cases it is evident the presence of an orientation mechanism very similar to that found using ITO as a substrate, nevertheless the d_{33} values are smaller than the corresponding d_{33} values measured on ITO (2.81 ± 0.56 and $3.26 \pm 0.65 \, pm \, V^{-1}$ 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 orientation 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 a 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 the 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^{-1} 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.

Notes and references

1 (a) T. Kaino, B. Cai and K. Takayama, *Adv. Funct. Mater.*, 2002, **12**, 599; (b) W. Geis, R. Sinta, W. Mowers, S. J. Deneault, F. Marchant, K. E. Krohn, S. J. Spector, D. R. Calawa and T. M. Lyszczarz, *Appl. Phys. Lett.*, 2004, **84**, 3729; (c) L. Mutter, M. Koechlin, M. Jazbinsek and P. Günter, *Opt. Express*, 2007, **15**, 16828; (d) L. Mutter, M. Jazbinsek, C. Herzog and P. Günter, *Opt. Express*, 2008, **16**, 731.

2 (a) D. Q. Li, M. A. Ratner, T. J. Marks, C. H. Zhang, J. Yang and G. K. Wong, *J. Am. Chem. Soc.*, 1990, **112**, 7389; (b) H. E. Katz, G. Scheller, T. M. Putvinski, M. L. Schilling, W. L. Wilson and C. E. D. Chidsey, *Science*, 1991, **254**, 1485; (c) D. Q. Li, B. I. Swanson, J. M. Robinson and M. A. Hoffbauer, *J. Am. Chem. Soc.*, 1993, **115**, 6975; (d) H. E. Katz, W. L. Wilson and G. Scheller, *J. Am. Chem. Soc.*, 1994, **116**, 6636; (e) W. B. Lin, W. P. Lin, G. K. Wong and T. J. Marks, *J. Am. Chem. Soc.*, 1996, **118**, 8034; (f) S. K. Doughty, G. J. Simpson and K. L. Rowlen, *J. Am. Chem. Soc.*, 1998, **120**, 7997; (g) S. B. Bakiamoh and G. J. Blanchard, *Langmuir*, 2001, **17**, 3438; (h) M. E. Van der Boom, G. Evmenenko, P. Dutta and T. J. Marks, *Adv. Funct. Mater.*, 2001, **11**, 393; (i) A. Facchetti, A. Abbotto, L. Beverina, M. E. van der Boom, P. Dutta, G. Evmenenko, G. A. Pagani and T. J. Marks, *Chem. Mater.*, 2003, **15**, 1064; (j) A. Facchetti, L. Beverina, M. E. van der Boom, P. Dutta, G. Evmenenko, A. D. Shukla, C. E. Stem, G. A. Pagani and T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 2142; (k) H. Kang, G. Evmenenko, P. Dutta, K. Clays, K. Song and T. J. Marks, *J. Am. Chem. Soc.*, 2006, **128**, 6194; (l) E. H. Kang, T. Bu, P. Jin, J. Sun, Y. Yang and J. Shen, *Langmuir*, 2007, **23**, 7594; (m) T. Morotti, V. Calabrese, M. Cavazzini, D. Pedron, M. Cozzuol, A. Licciardello, N. Tuccitto and S. Quici, *Dalton Trans.*, 2008, 2974.

3 (a) G. J. Ashwell, E. J. C. Dawnay, A. P. Kuczynski, M. Szablewski, I. M. Sandy, M. R. Bryce, A. M. Grainger and M. Hasan, *J. Chem. Soc., Faraday Trans.*, 1990, **86**, 111; (b) Y. Q. Liu, Y. Xu, D. B. Zhu, T. Wada, H. Sasabe, X. S. Zhao and X. M. Xie, *J. Phys. Chem.*, 1995, **99**, 6957; (c) T. Verbiest, S. V. Elshocht, M. Kauranen, L. Hellemans, J. Snauwaert, C. Nuckolls, T. J. Katz and A. Persoons, *Science*, 1998, **282**, 913; (d) G. J. Ashwell, *J. Mater. Chem.*,

1999, **9**, 1991; (e) G. J. Ashwell, R. Hamilton, B. J. Wood, I. R. Gentle and D. J. Zhou, *J. Mater. Chem.*, 2001, **11**, 2966; (f) Y. Umemura, A. Yamagishi, R. Schoonheydt, A. Persoons and F. D. Schryver, *J. Am. Chem. Soc.*, 2002, **124**, 992; (g) Y. Wang, C. S. Wang, X. J. Wang, Y. Guo, B. Xie, Z. C. Cui, L. Y. Liu, L. Xu, D. M. Zhang and B. Yang, *Chem. Mater.*, 2005, **17**, 1265; (h) D. R. Talham, T. Yamamoto and M. W. Meisel, *J. Phys.: Condens. Matter*, 2008, **20**, 184006.

4 (a) P. G. Lacroix, A. V. Veret Lemarinier, R. Clément, K. Nakatani and J. A. Delaire, *J. Mater. Chem.*, 1993, **3**, 499; (b) P. G. Lacroix, R. Clément, K. Nakatani, J. A. Delaire, J. Zyss and I. Ledoux, *Science*, 1994, **263**, 658; (c) S. R. Marder, J. W. Perry and C. P. Yakymyshyn, *Chem. Mater.*, 1994, **6**, 1137; (d) T. Corradin, R. Clément, P. G. Lacroix and K. Nakatani, *Chem. Mater.*, 1996, **8**, 2153; (e) E. Cariati, R. Ugo, F. Cariati, D. Roberto, N. Masciocchi, S. Galli and A. Sironi, *Adv. Mater.*, 2001, **13**, 1665; (f) E. Cariati, R. Macchi, D. Roberto, R. Ugo, S. Galli, N. Casati, P. Macchi, A. Sironi, L. Bogani, A. Caneschi and D. Gatteschi, *J. Am. Chem. Soc.*, 2007, **129**, 9410; (g) E. Cariati, R. Macchi, D. Roberto, R. Ugo, S. Galli, N. Masciocchi and A. Sironi, *Chem. Mater.*, 2007, **19**, 3704; (h) E. Cariati, R. Macchi, E. Tordin, R. Ugo, L. Bogani, A. Caneschi, P. Macchi, N. Casati and A. Sironi, *Inorg. Chim. Acta*, 2008, **361**, 4004; (i) E. Cariati, R. Ugo, G. Santoro, E. Tordin, L. Sorace, A. Caneschi, A. Sironi, P. Macchi and N. Casati, *Inorg. Chem.*, 2010, **49**, 10894.

5 (a) P. W. Zhu, H. Kang, A. Facchetti, G. Evmenenko, P. Dutta and T. J. Marks, *J. Am. Chem. Soc.*, 2003, **125**, 11496; (b) A. Facchetti, E. Annoni, L. Beverina, M. Morone, P. Zhu, T. J. Marks and G. A. Pagani, *Nat. Mater.*, 2004, **3**, 910.

6 (a) R. D. Wampler, N. J. Begue and G. J. Simpson, *Cryst. Growth Des.*, 2008, **8**, 2589; (b) Y. Liu, X. Xu, F. Zheng and Y. Cui, *Angew. Chem., Int. Ed.*, 2008, **47**, 4538; (c) W. Bi, N. Louvain, N. Mercier, J. Luc, I. Rau, F. Kajzar and B. Sahraoui, *Adv. Mater.*, 2008, **20**, 1013; (d) A. Bossi, E. Licandro, S. Maiorana, C. Rigamonti, S. Righetto, G. R. Stephenson, M. Spassova, E. Botek and B. Champagne, *J. Phys. Chem. C*, 2008, **112**, 7900.

7 (a) S. D. Cox, T. E. Gier, G. D. Stucky and J. Bierlein, *J. Am. Chem. Soc.*, 1988, **110**, 2986; (b) S. D. Cox, T. E. Gier and G. D. Stucky, *Chem. Mater.*, 1990, **2**, 609; (c) F. Marlow, M. Wübbenhorst and J. Caro, *J. Phys. Chem.*, 1994, **98**, 12315; (d) O.-K. Kim, L.-S. Choi, H.-Y. Zhang, X.-H. He and Y.-H. Shih, *J. Am. Chem. Soc.*, 1996, **118**, 12220; (e) J. Hulliger, P. Rogin, A. Quintel, P. Rechsteiner, O. König and M. Wübbenhorst, *Adv. Mater.*, 1997, **9**, 677; (f) P. Reichsteiner, J. Hulliger and M. Flösheimer, *Chem. Mater.*, 2000, **12**, 3296; (g) H. S. Kim, S. M. Lee, K. Ha, C. Jung, Y. J. Lee, Y. S. Chun, D. Kim, B. K. Rhee and K. B. Yoon, *J. Am. Chem. Soc.*, 2004, **126**, 673; (h) K. Komorowska, S. Brasselet, G. Dutier, I. Ledoux, J. Zyss, L. Poulsen, M. Jazdzyk, H.-J. Egelhaaf, J. Gierschner and M. Hanack, *Chem. Phys.*, 2005, **318**, 12; (i) H. S. Kim,

K. W. Sohn, Y. Jeon, H. Min, D. Kim and K. B. Yoon, *Adv. Mater.*, 2007, **19**, 260.

8 D. M. Burland, R. D. Miller and C. A. Walsh, *Chem. Rev.*, 1994, **94**, 31.

9 (a) Y. Tu, Q. Zhang and H. Ågren, *J. Phys. Chem. B*, 2007, **111**, 3591; (b) L. R. Dalton, W. H. Steier, B. H. Robinson, C. Zhang, A. Ren, S. Garner, A. Chen, T. Londergan, L. Irwin, B. Carlson, L. Fifield, G. Phelan, C. Kincaid, J. Amend and A. Jen, *J. Mater. Chem.*, 1999, **9**, 1905.

10 R. Macchi, E. Cariati, D. Marinotto, D. Roberto, E. Tordin, R. Ugo, R. Bozio, M. Cozzuol, D. Pedron and G. Mattei, *J. Mater. Chem.*, 2010, **20**, 1885.

11 R. Macchi, E. Cariati, D. Marinotto, E. Tordin, R. Ugo, G. Santoro, M. C. Ubaldi, S. M. Pietralunga and G. Mattei, *J. Mater. Chem.*, 2011, **21**, 9778.

12 W. Wang, J. Xu, X. Liu, Y. Jiang, G. Wang and X. Lu, *Thin Solid Films*, 2000, **365**, 116.

13 F. Ghebremichael, C. Poga and M. G. Kuzyk, *Appl. Phys. Lett.*, 1995, **66**, 139.

14 P. D. Maker, R. W. Terhune, M. Nisenoff and C. M. Savage, *Phys. Rev. Lett.*, 1962, **8**, 21.

15 J. Jerphagnon and S. K. Kurtz, *Phys. Rev. B: Solid State*, 1970, **1**, 1739.

16 W. N. Herman and L. M. Hayden, *J. Opt. Soc. Am. B*, 1995, **12**, 416.

17 The local electric field acting on the NLO chromophores is usually determined as reported in R. H. Page, M. C. Jurich, B. Beck, A. Sen, R. J. Twieg, J. D. Swalen, G. C. Bjorklund and C. G. Wilson, *J. Opt. Soc. Am. B*, 1990, **7**, 1239. For various organic NLO chromophores embedded in a PMMA film, working under poling conditions similar to those applied in this paper, it falls in the range of 1.2–4.35 MV cm^{-1}. However, here this method cannot be applied since the absorption maximum shifts after poling due to the formation of J aggregates inside the PMMA matrix.

18 (a) F. Pan, M. S. Wong, C. Bosshard and P. Günter, *Adv. Mater.*, 1996, **8**, 592; (b) S. Follonier, M. Foerz, I. Biaggio, U. Meier, C. Bosshard and P. Günter, *J. Opt. Soc. Am. B*, 2002, **19**, 1990; (c) L. Mutter, M. Jazbinsek, M. Zgonik, U. Meier, C. Bosshard and P. Günter, *J. Appl. Phys.*, 2003, **94**, 1356.

19 Refractive indices for the determination of the non-linear optical coefficients d_{ij} were previously calculated by ellipsometry for the DAST/PMMA film on glass as reported in ref. 10.

20 It is important to stress that minor changes of the thermal ramp with respect to those reported in the Experimental section highly affect the SHG response.

21 T. P. Nguyen, P. Le Rendu, N. N. Dinh, M. Fourmigué and C. Mézière, *Synth. Met.*, 2003, **138**, 229.

22 J. J. Yang, C. Hongfei, W. N. Martens and R. L. Frost, *Appl. Spectrosc.*, 2011, **65**, 113.

23 (a) Z. Z. You and J. Y. Dong, *Appl. Surf. Sci.*, 2006, **253**, 2102; (b) J. S. Kim, R. H. Friend and F. Cacialli, *J. Appl. Phys.*, 1999, **86**, 2774.