

Thermal layer-by-layer preparation of oriented films of a Cu(I) ionic inorganic-organic hybrid material showing semiconducting and SHG properties

Daniele Marinotto,^{*,a,b} Silvia Giulia Danelli,^b Anna Giaretta,^b Elena Lucenti,^a Philipp Stadler,^{*,c} Elisa Tordin,^c Giovanni Mattei,^c Guido Scavia,^d Renato Ugo,^b and Elena Cariati^{*,b}

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

^bDipartimento di Chimica and Centro di Eccellenza CIMAINA dell'Università degli Studi di Milano, UdR dell'INSTM, 20133 Milano, Italy

^cInstitute for Organic Solar Cells (LIOS) and Institute of Physical Chemistry, Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria

^dDipartimento di Fisica e Astronomia "Galileo Galilei" dell'Università degli Studi di Padova, via Marzolo 8, 35131 Padova, Italy

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

Supporting Information Placeholder

ABSTRACT: Inorganic-organic hybrid materials have shown excellent optoelectronic device performances from single-layer solution-processed thin-films. Their electronic bands are coupled to the ionic interactions within the organic and the inorganic moieties. Exactly these features also allow a sequential deposition route so to implement thin films having inherently non-linear optical properties perpendicular to the substrate plane. Here, we demonstrate the sequential layer-by-layer path to prepare films of the inorganic-organic hybrid material [DAMS][Cu₅I₆] through a self-recognition process in the solid state between the first CuI layer and the successive [DAMS]I layer. A persistent non-linear optical behavior, typical of oriented films is consequently accessible on different substrates without electrical bias poling through the excellent self-recognition of dipoles aligned along the z-axis. In addition, semiconductive and preliminary photovoltaic properties of the film are observed. The work highlights all aspects of the solution-based films with potential to serve as versatile and robust optoelectronic active material.

Keywords: nonlinear optics, second harmonic generation, Maker fringes, thin film, hybrid optoelectronic material

The investigation of the properties and applications of new hybrid inorganic-organic materials is of current great interest. Synthetic perovskites, for example, are deeply studied materials due to their semiconducting properties¹ useful in innovative photovoltaic cell.²⁻⁴ Moreover, acentric layered hybrid materials, characterized by large SHG (Second Harmonic Generation) are under investigation in view of their application in various electro-optical devices⁵ such as optical waveguides or frequency modulators.⁶⁻⁷ One of the main technological drawback in the use of hybrid systems, often

of ionic character, is the difficulty in preparing stable thin films in standard working conditions.

In the last decade, we have investigated the origin of the significant second order NLO (non linear optical) properties of new hybrid ionic inorganic-organic materials.⁸⁻¹¹ However, when trying to develop potential application of our systems, we faced the problem of the preparation of stable and oriented films by the electric poling technique.¹²⁻¹³ The electric poling process is usually applied to composite polymeric films containing neutral polar second order NLO chromophores, since ionic species may produce an opposite diffusion of ions towards the surface of the film under the effect of the directional strong electric field. Though, recently, we discovered a direct procedure based on a successful two-step orientation process (electric poling followed by thermal annealing) which produces *in-situ* oriented dipolar nanocrystals of ionic organic ([DAMS][*p*-toluenesulfonate], hereafter DAST where DAMS is (E)-N,N-dimethylamino-N'-methylstilbazolium),¹⁴ or hybrid inorganic-organic ([DAMS][Cu₅I₆], hereafter **1**)¹⁵ homogeneously dispersed in a poly(methyl methacrylate) (PMMA) film. As a further improvement, we found a simpler processing in combination with a persistent orientation. In fact, oriented dipolar acentric nanocrystals of DAST embedded in PMMA were grown on Indium Tin Oxide (ITO) substrate by solely thermal annealing without electrical poling thanks to an induction effect due to the ITO surface polarity.¹⁶ However, when attempting to extend this annealing-only procedure to **1** we have faced the problem of the thermal degradation of **1**/PMMA thin films induced by the two days annealing ramp. Nevertheless, in a previous work¹⁰ we have reported that **1** and its Ag(I) analogue can be prepared by a solid state reaction between MI (M = Cu, Ag) and [DAMS]I, involving a first ball-milling mixing and a second thermal annealing step. According to this study we concluded that the formation of **1** and of its Ag analogue is the result of a selective solid state self-recognition process be-

tween a formal host ($M_5I_6^-$) - guest ($DAMS^+$) system. In this process, an intralayer guests ordering into J-aggregates takes place rather easily just upon ball-milling mixing, while a “macroscopic” asymmetric crystalline polarity is produced only at a later stage, by thermal induction. Starting from these observations, in this work we pursue a direct layer-by-layer deposition of **1** on ITO and glass substrates to produce by a one step, facile processing technique oriented thin films for SHG applications. We first spin-coat a CuI layer followed by a series of [DAMS]I layers, each one being thermally annealed at 160°C. Remarkably, the layered films display a persistent NLO response typical of oriented systems. In the same time, we evidence that **1** displays clear semiconducting behavior which stimulated a preliminary investigation of its thin film photovoltaic properties.

Experimental

CuI, [DAMS]I, KI and acetonitrile were purchased from Sigma Aldrich. CuI was recrystallized by dissolution in a saturated solution of KI in water and further precipitation with water. 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 ($CuK\alpha$) operating in grazing incidence and ω -2 θ -scan mode. AFM measurements were performed with a commercial AFM (NTMDT NTEGRA) operating in tapping mode with silicon cantilever typical resonant frequency 150 kHz. The photoconductivity has been measured by a lock-in technique (chopped light from monochromator and lock-in amplifier from Stanford Research Systems, Model SR830) using a thin-film layer on top of a lateral diode with 2.5 μ m distance at 1V bias (Keithley 2400 source meter). Photoelectron spectra in air (PESA) were recorded in air on a Riken Keiki AC-2 ultraviolet photoelectron spectrophotometer. ITO slides were purchased from Delta Technologies Limited and thermally pretreated in an heating mantle with sand bath at 370°C for 24h. No thermal treatment was performed on glass slides. ITO and glass slides were cleaned by washing with MilliQ water, acetone and dried with optical paper before use. The films were prepared by a Cookson Electronic Company P-6708D spin-coater. The spinning parameters were set at the following values: RPM 1: 800; Ramp 1:1 s, Time 1:5 s; RPM 2: 1500; Ramp 2: 5 s, Time 2: 40 s. Thermal treatments of the films after each DAMS-I deposition were performed in a laboratory drying oven model Venticell 111 from MMM Medcenter Einrichtungen GmbH. A thin layer of **1** was prepared by spin-coating on a slide of ITO, glass or Au-patterned Si/SiO_x wafer (for photoconductivity measurements) few drops of a filtered saturated solution prepared by dissolving 190 mg of CuI in 5 mL of CH₃CN. On this CuI layer the deposition of a layer of [DAMS]I was further performed by spin-coating few drops of a filtered saturated solution of [DAMS]I (37 mg in 10 mL of water), followed by thermal annealing for 1h at 160°C in an oven. We will refer to this latter procedure, that is [DAMS]I deposition and thermal annealing, as “cycle”. The thickness of the multilayer films was measured with α -step stylus profilometer Dektak XT and determined by averaging the values obtained at 2–3 different points on each sample. Film thicknesses ranging from 1.0 μ m to 1.4 μ m were measured for ITO substrates after 4 and 9 cycles, respectively. On glass, a thickness value of 0.96 μ m was measured after 4 cycles. SHG measurements were carried out with a Q-switched Nd:YAG (Quanta System HYL-101) laser operating at 1064 nm. In order to determine the nonzero independent components of the second order NLO coefficient d_{ij} tensor for films with $C_{\infty v}$ symmetry, we have followed the standard Maker fringes technique.^{17–19} SHG 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 sig-

nal 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.^{17,20–21} SH polarization measurements at a fixed angle of incidence ($\alpha = 0^\circ$) were performed by measuring the p-polarization SH signal while changing the polarization angle β (defined as the angle between the incident fundamental polarization direction and the incident plane) of the fundamental beam by rotating a 1/2 plate. β angles of 0° and 90° correspond to s- and p-polarization of the fundamental beam, respectively.

Results and Discussion

A CuI layer has been deposited by spin-coating from a CH₃CN saturated solution on an ITO slide preheated at 370°C for 24 hours (such thermal treatment being previously recognized as the one giving the best second order NLO response in the case of the thermal preparation of oriented DAST/PMMA composite films).¹⁶ The film electronic absorption spectrum displays a weak narrow feature at 403 nm (Figure 1) originating from the CuI absorption band-gap.^{22–23} A [DAMS]I layer has been subsequently deposited on the CuI by spin-coating from a water-saturated solution. The resulting film shows an electronic absorption spectrum (Figure 1) resembling the one reported for KBr pellets of crystalline [DAMS]I, with a broad charge transfer band centered at 503 nm (Figure 1).⁸ A successive thermal treatment at 160°C for 1h in air induces the self-organization of some [DAMS]⁺ chromophores into J-aggregates with formation of **1**, as expected to occur by the solid state self-recognition process identified by some of us.¹⁰ In agreement the electronic absorption spectrum of the film shows a strong narrow band at 580 nm, typical of the [DAMS]⁺ chromophores organized in J-aggregates, which resembles that of **1** in KBr pellet (Figure 1).¹⁵

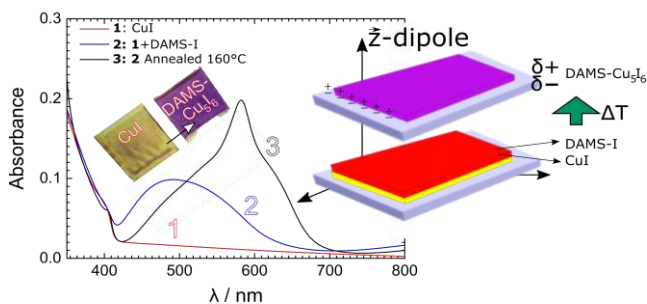


Figure 1. Electronic absorption spectra on ITO preheated at 370°C: first CuI layer (red), first [DAMS]I deposition on the CuI layer at room temperature (blue) and after 1h at 160°C (black).

Since a small shoulder at 403 nm attributable to unreacted CuI is still detectable in the electronic absorption spectrum of the film (Figure 1), a second layer of [DAMS]I has been spin-coated from a saturated water solution, exploiting the insolubility of the underneath CuI and **1** layers in water. After thermal treatment at 160°C, an increase of the absorption band at 580 nm is observed. The absorption intensity is further gradually increased by subsequent depositions of [DAMS]I layers and thermal annealings at 160°C. A linear correlation is found between the maximum absorption intensity of the band at 580 nm and the number of [DAMS]I layers up to the ninth deposition reaching finally a plateau (Figure 2).

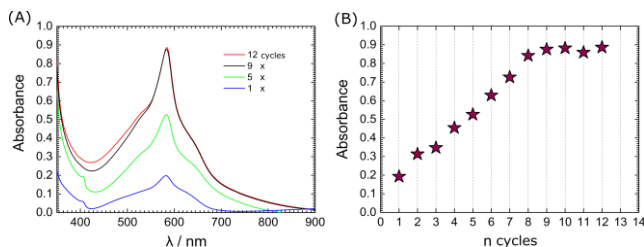


Figure 2. A) Electronic absorption spectra of films of **1** on ITO produced by deposition of a CuI layer followed by a series of [DAMS]I deposition/annealing cycles: 1 cycle (blue), 5 cycles (green), 9 cycles (black) and 12 cycles (red). B) Maximum absorption intensity at 580 nm vs. number of cycles.

In order to confirm the formation of a thin film of **1** by a series of cycles (each cycle including deposition of a [DAMS]I layer followed by thermal annealing at 160°C for 1h), a sample obtained after 5 cycles has been investigated by the X-ray diffraction technique (XRD) in grazing incidence 2 θ -scan mode (GIXRD) with a grazing angle of $\omega=0.5^\circ$. The indexed GIXRD profile can be assigned, in agreement with literature data, to the rhombohedral crystalline form of **1** with $a = b = 4.25 \text{ \AA}$ and $c = 38.2 \text{ \AA}$, whose (0 0 3n) reflections are evident (See SI, Figure S1).^{8,15} Using the Debye-Scherrer analysis, the crystalline domains of the thin film are estimated to be formed by nanocrystals of **1** with size about $D = 35 \text{ nm}$. The analysis of the XRD diffraction of the same sample but in ω -2 θ -scan mode indicates the same peak structure of the corresponding GIXRD measurement both in terms of the peak intensity and width, which is an indication that the size of the nanocrystals perpendicularly to the sample surface is comparable to that measured in grazing incidence, therefore suggesting a spherical shape of the nanocrystals (see SI Figure S1). This is confirmed by AFM morphologic investigations performed after 1 and 4 [DAMS]I deposition/annealing cycles. The sample after one cycle shows the presence of nanocrystal domains throughout the whole film reaching the substrate, while the film obtained after 4 cycles shows domains which display an elongated shape of micrometers length (see Figure 3).

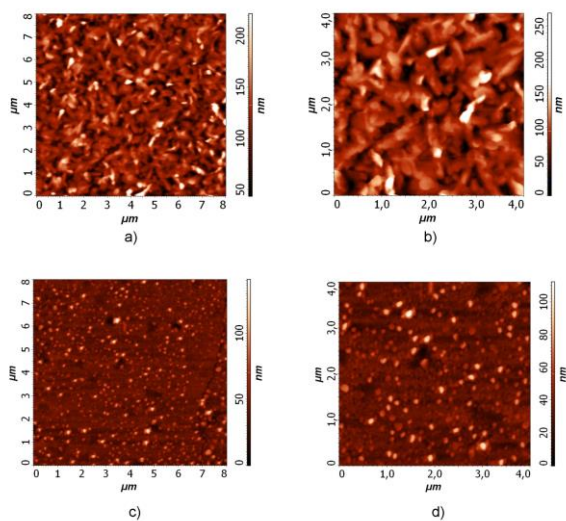


Figure 3. AFM images of films of **1** obtained after 1 (bottom) and 4 (top) [DAMS]I deposition/annealing cycles.

Based on the reports regarding layered hybrid inorganic-organic materials with semiconducting and photosensitizing properties (*i.e.* 2D perovskites)²⁴⁻²⁵ we also investigate the semiconducting behaviour of films of **1** by measuring its photoconductivity response on an ordinary Si/SiO_x wafer with lateral contacts. Thin films have been prepared on the SiO_x substrate by doctor blading a 50mg/ml solution of **1** in DMSO followed by heating at 150°C. An effective photocurrent spectrum has been obtained (see Figure 4-A) which allows an evaluation of the absorption edge at 1.7eV, consistent with the value (1.77 eV) of the excitation energy derived from the electronic absorption spectrum (see Figure 2-A). The valence band onset is at 5.25eV as obtained by photoelectron spectroscopy in air (see Figure 4-B). It appears thus that **1** behaves as a 2D layered semiconductor with a HOMO level at -5.25 eV and a LUMO level at -3.55 eV and a 1.7 eV band gap which is quite similar to that reported for various perovskites.³

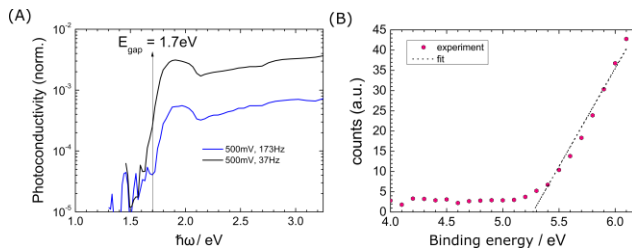


Figure 4. Electronic properties of **1**: (A) spectrally resolved photoconductivity; (B) Photoemission spectrum in air.

Evidence of the formation of oriented nanocrystals of **1** in the thin films prepared by the above described layer by layer deposition/annealing procedure, has been obtained by the measurement of their SHG response through the Maker fringes method.¹⁷ After each cycle the intensity of pp, sp and 45s Maker fringes has been determined. The pp component is always much higher than the hardly discernible 45s and sp ones. Moreover, the Maker fringes pattern shows a minimum at 0° angle of incidence and a maximum at about 60° (Figure 5-A) suggesting the presence of a polar order of C_{∞v} symmetry of the thermally originated nanocrystals of **1** partially oriented perpendicularly to the thin film surface.¹⁷

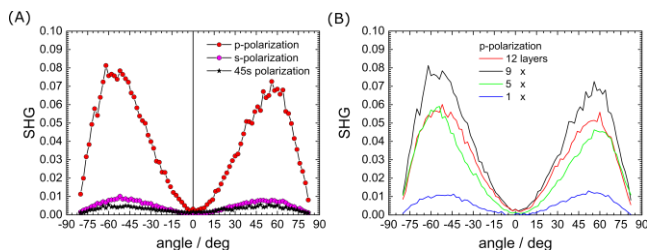


Figure 5. Maker fringes of neat films of **1** prepared by layer by layer depositions on ITO: A) pp (square), sp (circle) and 45s (star) components after 9 deposition/annealing cycles; B) pp component after various deposition/annealing cycles: 1 cycle (blue), 5 cycles (green), 9 cycles (black) and 12 cycles (red).

An increase of the SHG intensity with the number of cycles is observed by monitoring the pp component of the Maker fringes (see Figure 5-B). The maximum of the intensity is reached after nine cycles, in agreement with the increase of the absorbance in the electronic absorption spectrum (Figure 2-A). Further additions of [DAMS]I produced a slight decrease of the SHG intensity. This behavior is not related to a possible degradation of the film, as confirmed by the electronic absorption spectra (Figure 2-A), but

probably to both the growth of nanocrystals of **1** not oriented perpendicularly to the film surface and to scattering losses associated with the presence of polycrystalline domains with dimensions comparable to that of the wavelength of the laser (1.064 μm) (see AFM measurements in Figure 3). The former hypothesis is supported, for a film obtained after nine cycles, by SH polarization measurements at an angle of incidence (θ) of 0° with the SH signal at a fixed p-polarization as reported in Figure 6. It is known that for films with polar order of $C_{\infty v}$ symmetry, SH polarization measurements at θ equal to 0° give a null SH signal regardless the angle of polarization (β) of the fundamental beam.¹⁷ As evidenced in Figure 5, the non-zero SH value at $\beta=0$ and its dependence on β suggest the presence of some nanocrystals of **1** with orientation not perpendicular to the film surface.²⁰⁻²¹ We have evidence that the contribution of these not-oriented nanocrystals of **1** to the SH signal becomes more and more relevant with the number of cycles producing a decrease of the SHG signal, as expected for a decrease of the polar orientation of the nanocrystals of **1** by increasing the number of layers.

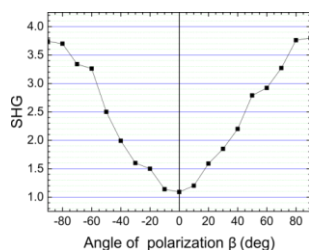


Figure 6. Measured SHG intensity vs. polarization angle at a fixed angle of incidence $\theta = 0^\circ$ for film on ITO obtained after nine [DAMS]I deposition/annealing cycles. β angles of 0° and 90° correspond to s- and p-polarization of the fundamental beam, respectively.

The second order NLO coefficient d_{33} of the film after 4 and 9 cycles, obtained *ex-situ* by the standard Maker fringe method, is 0.57 and 2.10 pm/V, respectively. These values are lower than those obtained from **1**/PMMA oriented films prepared on a glass substrate by the two-step poling/annealing procedure previously described by some of us.¹⁵ However, in this latter case **1** was dispersed and therefore diluted in a PMMA polymeric matrix, while in the present work it is obtained from pure oriented nanocrystals produced *in situ* so that the d_{33} value is probably affected by the strong self-absorption of **1**. Moreover, the persistent SHG signal obtained in the present study is reached in a one step process that doesn't require a poling treatment.

The CuI/[DAMS]I deposition/annealing procedure was also performed using glass as substrate. Electronic absorption spectra of the film prepared by deposition of five [DAMS]I layers on a CuI layer display a trend similar to that observed when ITO is used as substrate (see SI Figure S2-A). A linear increase of the absorption maximum at 580 nm (typical of **1**) with the number of cycles (see Figure S3) is observed up to a plateau which is reached at five cycles to be compared with the plateau at 9 cycles on ITO. The Maker fringe pattern confirms the presence of a polar order in the film with a $C_{\infty v}$ symmetry (see SI Figure S2-B), as observed when ITO is the substrate. The intensity of the pp Maker fringe component increases with the number of cycles up to the fourth, with a dramatic drop of the SHG response at the fifth cycle, in agreement with what observed for the electronic absorption spectra (Figure S2-A). Similarly to what observed on ITO substrates, this could be related mainly to the growth of nanocrystals of **1** not oriented perpendicularly to the film surface and to scattering losses. Moreover, the lower number of cycles after which a loss of polar orientation of nanocrystals of **1** takes place could be attributed to the different filmability induced by the surface of ITO and glass sub-

strates, as previously reported by some of us.¹⁶ The d_{33} of the oriented film of **1** on glass after 4 cycles was 0.88 pm/V, a value comparable to that obtained on ITO after the same number of cycles ($d_{33} = 0.57$ pm/V).

The sequential deposition process allows the generation of oriented thin films of **1**, a semiconductor with a bandgap of 1.7 eV. Therefore we preliminarily tested these films as photosensitizer in a photovoltaic system. We adapted the ITO substrate by covering its surface with a thin interlayer of ZnO and TiOx before depositing the series of CuI/[DAMS]I layers on top. The device was completed by a MoOx/Ag top electrode. Interestingly, a small photovoltaic effect in an open circuit voltage and a moderate photocurrent were observed (see Figure 7).

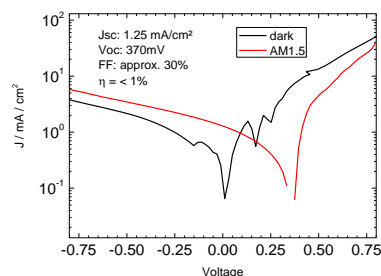


Figure 7. Preliminary photovoltaic evidence from the apparent J-V characteristics reproduced from as-grown sequential deposited CuI/[DAMS]I thin film on top of ITO/ZnO/TiOx substrate.

Conclusions

In this work neat thin films (about 1-1.5 μm) of oriented dipolar nanocrystals of **1** have been prepared by successive deposition/annealing cycles of layers of [DAMS]I over a CuI layer. After the first thermal annealing step at 160°C , oriented nanocrystals of **1** are formed, so that the successive [DAMS]I deposition/annealing cycles enlarge these nanocrystals promoting the manifestation of a “macroscopic” polarity. This goal is reached without electrical bias poling, ensuring a persistent NLO response. We show evidence that self-recognition in the solid state between CuI and the subsequent [DAMS]I layer established the desired order, similar to that of the layer-by-layer self-assembly of polar arrays of NLO chromophores.²⁶ In addition, the films are potentially interesting for optoelectronic applications, as their absorption and their ease of orientation yield a stable semiconducting system processed from solution from comparable inexpensive sources such as [DAMS]I and CuI, respectively. In conclusion, the straightforward step by step process of this technique opens new possibilities for the *in situ* preparation of thin films of inexpensive, not toxic, highly stable optoelectronic materials.

ASSOCIATED CONTENT

Supporting Information

GIXRD-data, AFM-data. This material is available free of charge via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

Corresponding Author

E-mail: daniele.marinotto@unimi.it; elena.cariati@unimi.it; philipp.stadler@jku.at

Notes

The authors declare no competing financial interests.

ACKNOWLEDGMENT

E.L. thanks Regione Lombardia for fundings (project “Tecnologie e materiali per l'utilizzo efficiente dell'energia solare” decreto 3667/2013).

REFERENCES

- (1) Mitzi, D. B. Hybrid Organic-Inorganic Electronics. In *Functional Hybrid Materials*; Wiley-VCH Verlag GmbH & Co. KGaA: 2004; pp. 347–386.
- (2) Grätzel M. The light and shade of perovskite solar cells. *Nat. Mater.* **2014**, *13*, 838–842.
- (3) Kazim, S.; Nazeeruddin, M. K.; Grätzel M.; Ahmad, S. Perovskite as Light Harvester: A Game Changer in Photovoltaics. *Angew. Chem. Int. Ed.* **2014**, *53*, 2812–2824.
- (4) Snaith H. J. Perovskites: The Emergence of a New Era for Low-Cost, High-Efficiency Solar Cells. *J. Phys. Chem. Lett.* **2013**, *4*, 3623–3630.
- (5) Lebeau, B.; Innocenzi, P. Hybrid materials for optics and photonics. *Chem. Soc. Rev.* **2011**, *40*, 886–906.
- (6) Kaino, T.; Cai, B.; Takayama, K. Fabrication of DAST Channel Optical Waveguides. *Adv. Funct. Mater.* **2002**, *12*, 599–603.
- (7) Mutter, L.; Jazbinšek, M.; Herzog, C.; Günter, P. Electro-Optic and Nonlinear Optical Properties of Ion Implanted Waveguides in Organic Crystals. *Opt. Express* **2008**, *16*, 731–739.
- (8) Cariati, E.; Ugo, R.; Cariati, F.; Roberto, D.; Masciocchi, N.; Galli, S.; Sironi, A. J-Aggregates Granting Giant Second-Order NLO Responses in Self-Assembled Hybrid Inorganic–Organic Materials. *Adv. Mater.* **2001**, *13*, 1665–1668.
- (9) Cariati, E.; Macchi, R.; Roberto, D.; Ugo, R.; Galli, S.; Casati, N.; Macchi, P.; Sironi, A.; Bogani, L.; Caneschi, A.; Gatteschi, D. Polyfunctional Inorganic–Organic Hybrid Materials: An Unusual Kind of NLO Active Layered Mixed Metal Oxalates with Tunable Magnetic Properties and Very Large Second Harmonic Generation. *J. Am. Chem. Soc.* **2007**, *129*, 9410–9420.
- (10) Cariati, E.; Macchi, R.; Roberto, D.; Ugo, R.; Galli, S.; Masciocchi, N.; Sironi, A. Sequential Self-Organization of Silver(I) Layered Materials with Strong SHG by J Aggregation and Intercalation of Organic Nonlinear Optical Chromophores through Mechanochemical Synthesis. *Chem. Mater.* **2007**, *19*, 3704–3711.
- (11) Cariati, E.; Ugo, R.; Santoro, G.; Tordin, E.; Sorace, L.; Caneschi, A.; Sironi, A.; Macchi, P.; Casati, N. Slow Relaxation of the Magnetization in Non-Linear Optical Active Layered Mixed Metal Oxalate Chains. *Inorg. Chem.* **2010**, *49*, 10894–10901.
- (12) Burland, D. M.; Miller, R. D.; Walsh, C. A. Second-Order Nonlinearity in Poled-Polymer Systems. *Chem. Rev.* **1994**, *94*, 31–75.
- (13) Tu, Y.; Zhang, Q.; Ågren, H. Electric Field Poled Polymeric Nonlinear Optical Systems: Molecular Dynamics Simulations of Poly(methyl Methacrylate) Doped with Disperse Red Chromophores. *J. Phys. Chem. B* **2007**, *111*, 3591–3598.
- (14) Macchi, R.; Cariati, E.; Marinotto, D.; Roberto, D.; Tordin, E.; Ugo, R.; Bozio, R.; Cozzuol, M.; Pedron, D.; Mattei, G. Stable SHG from in Situ Grown Oriented Nanocrystals of [(E)-N,N-Dimethylamino-N'-Methylstilbazolium][p-Toluenesulfonate] in a PMMA Film. *J. Mater. Chem.* **2010**, *20* (10), 1885–1890.
- (15) Macchi, R.; Cariati, E.; Marinotto, D.; Tordin, E.; Ugo, R.; Santoro, G.; Ubaldi, M. C.; Pietralunga, S. M.; Mattei, G. In Situ Growth in a PMMA Film of Oriented Nanocrystals of the Hybrid Inorganic–organic Acentric Material [(E)-N,N-Dimethylamino-N'-methylstilbazolium][Cu₂I₆]. *J. Mater. Chem.* **2011**, *21*, 9778–9783.
- (16) Marinotto, D.; Lucenti, E.; Scavia, G.; Ugo, R.; Tavazzi, S.; Mattei, G.; Cariati, E. 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. *J. Mater. Chem. C* **2014**, *2*, 8532–8538.
- (17) Herman, W. N.; Hayden, L. M. Maker Fringes Revisited: Second-Harmonic Generation from Birefringent or Absorbing Materials. *J. Opt. Soc. Am. B* **1995**, *12*, 416–427.
- (18) Maker, P. D.; Terhune, R. W.; Nisenoff, M.; Savage, C. M. Effects of Dispersion and Focusing on the Production of Optical Harmonics. *Phys. Rev. Lett.* **1962**, *8*, 21–22.
- (19) Jerphagnon, J.; Kurtz, S. K. Optical Nonlinear Susceptibilities: Accurate Relative Values for Quartz, Ammonium Dihydrogen Phosphate, and Potassium Dihydrogen Phosphate. *Phys. Rev. B* **1970**, *1*, 1739–1744.
- (20) Wang, W.; Xu, J.; Liu, X.; Jiang, Y.; Wang, G.; Lu, X. Second Harmonic Generation Investigation of Indium Tin Oxide Thin Films. *Thin Solid Films* **2000**, *365*, 116–118.
- (21) Tanaka, K.; Corbari, C.; Kazansky, P. G.; Sasai, J.; Hirao, K. Second-Harmonic Generation in CuCl Nanocrystal-Embedded Amorphous Indium Tin Oxide Thin Film. *Jpn. J. Appl. Phys.* **2003**, *42*, 6931–6932.
- (22) Tennakone, K.; Kumara, G. R. R. A.; Kottegoda, I. R. M.; Perera, V. P. S.; Aponso, G. M. L. P.; Wijayantha, K. G. U. Deposition of Thin Conducting Films of CuI on Glass. *Sol. Energy Mater. Sol. Cells* **1998**, *55*, 283–289.
- (23) Mohamed, S. A.; Gasiorowski, J.; Hingerl, K.; Zahn, D. R. T.; Scharber, M. C.; Obayya, S. S. A.; El-Mansy, M. K.; Sariciftci, N. S.; Egbe, D. A. M.; Stadler, P. CuI as Versatile Hole-Selective Contact for Organic Solar Cell Based on Anthracene-Containing PPE–PPV. *Sol. Energy Mater. Sol. Cells* **2015**, *143*, 369–374.
- (24) Smith, I. C.; Hoke, E. T.; Solis-Ibarra, D.; McGehee, M. D.; Karunadasa, H. I. A Layered Hybrid Perovskite Solar-Cell Absorber with Enhanced Moisture Stability. *Angew. Chem. Int. Ed.* **2014**, *53*, 11232–11235.
- (25) Cortecchia, D.; Arianita Dewi, H.; Yin, V.; Bruno, A.; Chen, S.; Baikie, T.; Boix, P. P.; Grätzel, M.; Mhaisalkar, S.; Soci, C.; Mathews, N. Lead-Free MA₂CuCl₃Br_{4-x} Hybrid Perovskites. *Inorg. Chem.* **2016**, *55*, 1044–1052.
- (26) Facchetti, A.; Annoni, E.; Beverina, L.; Morone, M.; Zhu, P.; Marks, T. J.; Pagani, G. A. Very Large Electro-Optic Responses in H-Bonded Heteroaromatic Films Grown by Physical Vapour Deposition. *Nat. Mater.* **2004**, *3*, 910–917.

SYNOPSIS

Thin films of oriented nanocrystals of highly, persistently NLO- and photo-active [DAMS][Cu₅I₆] (DAMS = (E)-N,N-dimethylamino-N'-methylstilbazolium), have been obtained by a one-step, facile deposition/thermal annealing of successive layers of [DAMS]I over a first CuI layer.

TOC

