Journal of Materials Chemistry

Cite this: J. Mater. Chem., 2011, 21, 15940

www.rsc.org/materials

PAPER

Synthesis, crystal structures, and solid state quadratic nonlinear optical properties of a series of stilbazolium cations combined with gold cyanide counter-ion[†]

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Received 12th May 2011, Accepted 8th July 2011 DOI: 10.1039/c1jm12105g

Three salts built up from (*E*)-4'-(dimethylamino)-stilbazolium (DMAS)H⁺, (*E*)-4'-(diethylamino)stilbazolium (DEAS)H⁺, (*E*)-4'-{2-(methoxymethyl) pyrrolidinyl}-stilbazolium (MPS)H⁺, and gold cyanide as a counter-ion, are reported. The crystal structures have been solved for (DEAS)H⁺ Au (CN)₂⁻ (*Cc* space group), and for (MPS)H⁺ Au(CN)₂⁻ (*P*1 space group). The semi-empirical (ZINDO) calculated static hyperpolarizability (β_0) of (MPS)H⁺ is equal to 147 × 10⁻³⁰ cm⁵ esu⁻¹, in solid state, which is 25% higher than that of the cation of the well known (*E*)-4'-(dimethylamino)methylstilbazolium tosylate (DAST). (MPS)H⁺ Au(CN)₂⁻ exhibits a unique crystal structure in which the cations are perfectly aligned. This combination of large hyperpolarizability and strict 1-dimensional character leads to a giant d_{zzz} quadratic susceptibility ($\chi^{(2)}$) tensor component estimated between ~4500 pm V⁻¹ (~11 × 10⁻⁶ esu) and 12 400 pm V⁻¹ (~30 × 10⁻⁶ esu) at 1.064 µm, by a confocal µ-SHG technique. The use of such material in ultra-thin devices is critically evaluated.

Introduction

Organic nonlinear optical (NLO) materials have long been recognized for their potential applications in telecommunications, all optical data processing and biological imaging.^{1,2} In molecular chromophores, the NLO response is ultimately related to the expression of the molecular polarizability, given by the following equation:³

$$\mu(E) = \mu_0 + \alpha E + \beta E^2 + \dots$$
 (1)

In this expression, μ_0 is the permanent dipole moment, α the linear polarizability and β the first hyperpolarizability (origin of the quadratic NLO behavior), *E* being the applied electric field

component of the light. The polarization (P) of a macroscopic material is again given by an expression analogous to (1), as follows:

$$P = \chi^{(1)}E + \chi^{(2)}E^2 + \dots$$
 (2)

 $\chi^{(2)}$ is the quadratic susceptibility, related to the underlying β and responsible for the bulk quadratic effects (*e.g.* second harmonic generation (SHG) and linear electro-optic behavior). An important point to note is that, for $\chi^{(2)}$ to be non zero, the crystal structure needs to lack centrosymmetry. Efficient NLO materials are therefore built up in two steps: (*i*) the design of highly polarizable species, containing strong donor and acceptor substituents connected by an extended π -conjugated bridge to ensure a large β value, and (*ii*) the engineering of the molecules into a non-centrosymmetric solid state environment.

Among many potential candidates, the salt (E)-4'-(dimethylamino)-*N*-methyl-stilbazolium tosylate (DAMS⁺ Ts⁻, Scheme 1), often called DAST, has become the most promising system, after the report of an exceptionally large SHG efficiency, up to 1000 times that of urea.⁴ This material then reached the step of commercial development in relation to its quadratic NLO effects (*e.g.* terahertz wave generation arising from nonlinear frequency mixing).⁵ These challenging capabilities have stimulated many synthetic programs for finding optimized NLO candidates based on the "push-pull" architecture of the benchmark DAST model, and have led to a research area which remains very active.⁶

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[†] Electronic supplementary information (ESI) available: Details about the experimental determination of d_{zzz} value. DFT coordinates for the 4 investigated chromophores. CCDC reference numbers 826266 and 826267. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1jm12105g



Scheme 1 Molecular structures of the 4 investigated chromophores

In the present contribution, we report on the synthesis, crystal structure, theoretical and experimental (second harmonic generation SHG measurement) NLO studies of new salts built up from the promising DAMS⁺ skeleton, combined with [Au $(CN)_2$ ⁻ anions. This anion was initially chosen for its capability to provide extended structures with iron(II), with the aim of making a material with additional magnetic properties.⁷ The NLO cations investigated in the present contribution are (E)-4'-(dimethylamino)-stilbazolium (DMAS)H⁺, (E)-4'-(diethylamino)-stilbazolium (DEAS)H+, and (E)-4'-{2-(methoxymethyl)pyrrolidinyl}-stilbazolium (MPS)H⁺ (Scheme 1), and lead to the three resulting $\{(DMAS)H^+ [Au(CN)_2]^-\}$ (1), $\{(DEAS)H^+ [Au(CN)_2]^-\}$ (2), and $\{(MPS)H^+ [Au(CN)_2]^-\}$ (3) materials. Among them, 3 is an intriguing NLO candidate, with a larger hyperpolarizability than DAST and a perfect alignment in solid state. Owing to these unique characteristics, additional NLO investigations were conducted by the non-traditional confocal μ -SHG technique to target the d_{zzz} component of the $\chi^{(2)}$ tensor. In the last section, this nearly 1-dimensional system is critically evaluated for potential applications as advanced materials in thin films devices.

Experimental section

Starting materials and equipment

K[Au(CN)₂] and all organic reagents and solvents were purchased from commercial sources and used as received. ¹H NMR spectroscopic measurements were done with an Avance DRX Bruker 300 MHz spectrometer.

Synthesis

4'-dimethyl- and 4'-diethylaminostilbazole (DMAS and DEAS). The synthesis was performed under argon atmosphere and all glass materials used were dried previously. 4-methylpyridine (1.78 mL, 20 mmol) and sodium hydride (0.5 g, 21 mmol) were mixed with 10 mL of distilled N,N'-dimethylformamide (DMF).

The mixture was heated at 60 °C for 2 h. Afterwards 4-(dimethylamino)benzaldehyde) or 4-(diethylamino)benzaldehyde) was added and the mixture was kept at this temperature for 7 h. The resulting solution was cooled to room temperature and poured into 150 mL of methanol. Bright yellow precipitates appeared immediately which was filtered and washed with a mixture of methanol/cool water (1:1) and dried under vacuum. Yield: 55% (DMAS), 62% (DEAS), ¹H NMR (CDCl₃) DMAS, δ (ppm): 8,49 (H1, 2H, d, J = 4.98 Hz), 7.44 (H2, 2H, d, J = 8.84 Hz), 7.30 (H3, 1H, d, J = 16.12 Hz), 6.80 (H4, 1H, d, J = 16.19 Hz), 7.38 (H5, 2H, d, J = 6.17 Hz), 6.71 (H6, 2H, d, J = 8.84 Hz), 3.02 (H7, 3H, s). ¹H NMR (CDCl₃) δ (ppm) (DEAS): 8.48 (H1, 2H, d, J = 6.13Hz), 7.42 (H2, 2H, d, J = 8.89 Hz), 7.35 (H5, 2H, d, J = 6.18 Hz), 7.27 (H3, 1H, d, J = 11.09 Hz), 6.77 (H4, 1H, d, J = 16.17 Hz), 6.67 (H6, 2H, d, J = 8.88 Hz), 3.40 (H7, 2H, q, J = 7.03 Hz), 1.20 (H8, 3H, t, J = 7.04 Hz).

4'-[2-(methoxymethyl)pyrrolidinyl]-stilbazole (MPS). А mixture of 4-picoline (3.2 mL, 5.5×10^{-2} mol) and NaH (1.32 g, 5.5×10^{-2} mol) in 10 mL of distilled DMF was heated for 2 h at 60 °C. Then, 4-[2-(methoxymethyl)pyrrolidinyl] benzaldehyde (7.2 g, 5.5×10^{-2} mol) diluted in 10 mL of DMF was added and the reaction mixture was heated for 7 more hours at 60 °C. After cooling, the resulting mixture was poured into 300 mL of water, which led to a red precipitate. The solid was filtered off, washed with water, and dried under vacuum. The crude product was then dissolved in hot heptane, filtered hot, evaporated to dryness, and finally purified by chromatography on SiO₂ (60A 70-200 mm) using heptane-AcOEt (7/3). Yield: 78% of MPS as a bright yellow solid. ¹H NMR (CDCl₃) d 8.488 (d, J = 5.8 Hz, 2H), 7.295 (d, J = 6.0 Hz, 2H), 7.405 (d,4 J = 8.8 Hz, 2H), 7.222 (d, J = 16.2 Hz, 1H), 6,764 (d, J = 16.2 Hz, 1H), 6.630 (d, J = 8.8 Hz, 2H), 3.918 (m, 1H), 3.42-3.53 (m, 2H), 3.373 (s, 3H), 3.199 (t, J = 8.9 Hz, 2H), 1.72–2.09 (m, 4H).

Synthesis and characterization of the stilbazolium salts. 1, 2, and 3 were formed accidentally investigating appropriate synthetic strategies to get iron(II) spin crossover coordination polymers susceptible of displaying ONL response. The pyridine nitrogen atom of DEAS and MPS ligands have strong tendency to protonate, affording the corresponding stilbazolium cation, which stabilizes via hydrogen bonding. The synthesis was performed by mixing under continuous stirring in an argon atmosphere a methanolic solution (10 mL) of Fe (BF₄)₂·6H₂O (0.148 mmol, 50 mg) and a solution of DMAS, DEAS or MPS ligands (0.30 mmol; 67.5, 75.7 and 88.3 mg, respectively) in dichloromethane (10 mL). To this mixture, a water solution (5 mL) of KAu(CN)₂ (0.30 mmol, 86.4 mg) was added drop-wise under stirring. The resulting solution was allowed to evaporate at room temperature using an argon stream. The same results have been obtained excluding the iron (II) salt. Red (1, 2) and pink (3) crystalline samples were formed in two weeks (yield ca. 60%). Appropriate single crystals were picked out from these samples. Anal. Calcd for C₁₇H₁₇AuN₄ (1): C, 43.05; H, 3.61; N, 11.81; Found. C, 42.68; H, 3.61; N, 11.63. Anal. Calcd for C₁₉H₂₁AuN₄ (2): C, 45.43; H, 4.21; N, 11.15; Found. C, 44.93; H, 4.12; N, 11.03. Anal. Calcd for C21H23AuN4O (3): C, 46.33; H, 4.26; N, 10.29; Found. C, 46.11; H, 4.19; N, 10.13.

X-ray data collection and structure determination

Single crystal X-ray diffraction. Diffraction data for 2, and 3 were collected with a Nonius Kappa-CCD single crystal diffractometer using Mo K α radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS-97 and refined by full-matrix least-squares on F^2 using SHELXL-97.⁸ All non-hydrogen atoms were refined anisotropically. The crystal-lographic data are summarized in Table 1.

Theoretical methods

The all-valence INDO (intermediate neglect of differential overlap) method,^{9,10} in connection with the sum over state (SOS) formalism was employed for the calculation of the electronic spectra and the molecular hyperpolarizabilities of the organic cations in the solid state.¹¹ Details for the computationally efficient INDO-SOS-based method for describing molecular optical nonlinearities have been reported elsewhere.¹² In the present

Table 1 Crystal data for 2, and 3^a

	2	3
Crystal Data		
Empirical formula	C10H21AuN4	C21H23AuN4O
Molecular weight	501.36	544.40
Crystal size/mm	$0.04 \times 0.06 \times 0.06$	$0.01 \times 0.02 \times 0.02$
Crystal system	Monoclinic	Triclinic
Space group	Cc	P1
a/Å	25.731(2)	6.615(1)
b/Å	8.0720(7)	7.6610(3)
c/Å	18.411(2)	10.2670(6)
$\alpha /^{\circ}$	90	83.806(2)
βl°	106.441(3)	83.545(2)
$\gamma /^{\circ}$	90	77.497(3)
V/Å ³	3667.6(5)	502.87(4)
Ζ	8	1
$ ho_{ m c}/{ m Mg}~{ m m}^{-3}$	1.816	1.798
Data Collection		
<i>T</i> /K	293	293
2θ range	$3.19 < 2\theta < 24.37$	$3.17 < 2\theta < 27.54$
Radiation (Mo Kα)/Å	0.71073	0.71073
<i>F</i> (000)	1928	264
Scan mode	$\theta - 2\theta$	$\theta - 2\theta$
No. of reflections		
Measured	5288	3270
Unique	3520	3104
Abs. coef. (μ)	8.029	7.331
Absorption corrections	Empirical	Empirical
T_{\min}	0.7463	0.8672
$T_{\rm max}$	0.8924	0.9303
Refinement		
Refined on	F^2	F^2
No. of variable	434	249
H-atom treatment	Mixed	Mixed
$R (\geq 2\sigma(I))$	0.0522	0.0360
wR	0.0911	0.0948
$\Delta \rho_{\rm max} (e {\rm \AA}^{-1})$	0.774	0.631
$\Delta \rho_{\min} (e \dot{A}^{-1})$	-0.771	-0.844
Flack parameter	0.07(4)	0.023(17)
GOF	1.046	1.017

^{*a*} R1 = $\Sigma ||Fo| - |Fc||/\Sigma|Fo|$; w*R* = [$\Sigma [w(Fo^2 - Fc^2)^2]/\Sigma [w(Fo^2)^2]$]^{*l*/2}. w = 1/ [$\sigma^2(Fo^2) + (m P)^2 + n P$] where P = ($Fo^2 + 2Fc^2$)/3; m = 0.0291 (**2**), and 0.0631 (**3**); n = 29.5342 (**2**), and 0.5090 (**3**).

approach, the mono-excited configuration interaction (MECI) approximation was employed to describe the excited states. The lowest 100 energy transitions were chosen to undergo CI mixing. All calculations were performed using the INDO/1 Hamiltonian incorporated in the commercially available software package ZINDO.13 Metrical parameters used for the calculations of (DEAS)H⁺ and (MPS)H⁺, were those obtained from the present crystal structure determination of 2 and 3, respectively. The proton linked to the pyridine moieties of the cation, which was not observed experimentally, was assumed to be located at 0.96 Å, according to the report of a N–H bond refined at 0.96(2) Å in a related dimethylamino-stilbazolium crystal structure.14 However, we have checked that a modification of this distance in the 0.91-1.01 A range affects only slightly the hyperpolarizability, with static β_0 values decreasing from 147.7 to 146.3×10^{-30} cm⁵ esu⁻¹. The calculation performed on DAMS⁺ for comparison was based on the structure of DAST, previously reported in the literature.15

Additionally, the properties in MeCN have been computed after full optimization of the molecular structures, using the Gaussian09 program package¹⁶ within the framework of the DFT at the B3LYP/6-31G** level,¹⁷ the polarizable continuum model (PCM) being used to account for solvent effect (acetoni-trile). The ZINDO spectra were calculated from the first 100 excited states.

NLO measurements

The nonlinear optical properties were evaluated in the solid state as the efficiency in second harmonic generation (SHG) expressed versus that of a reference (urea). The measurements were performed by the Kurtz-Perry powder technique,¹⁸ using a nanosecond Nd-YAG pulsed (10 Hz) laser operating at $\lambda = 1.064 \,\mu\text{m}$. Due to a residual absorption of stilbazole-based chromophores at the second harmonic ($\lambda = 532$ nm), the fundamental incident wavelength used for the experiments was that of the outgoing Stokes-shifted radiation ($\lambda = 1.907 \ \mu m$) generated by Raman effect in a hydrogen cell (1 m long, 50 atm.). The SHG signal was selected through a suitable interference filter, detected by a photomultiplier, and recorded on an ultrafast Tektronic TDS 620 B oscilloscope. Samples were powders obtained by grinding, and pressed between two glass plates. They were calibrated in the 50-80 µm range, by use of standard sieves. The thickness of the samples was 200 µm.

Owing to the strong 1-dimensional character of **3**, in solid state, the value of d_{zzz} (only non-vanishing tensor component of $\chi^{(2)}$) was determined. For this investigation, the technique of confocal μ -SHG was employed using a modified μ -Raman spectrometer (Horiba HR800) so that the backward waves are analyzed.¹⁹ This technique of high depth selectivity allows the investigation of the NLO response within a volume restricted to the vicinity of the surface (depth of focus), thus avoiding coherent effects and most of the absorption effect occurring in an experiment conducted by transmission.²⁰ In the present case, the thickness of the crystals of **3** were equal to *ca*. 2 μ m that minimizes absorption losses at the harmonic waves. Hence, no correction for absorption loss has been considered. The source was a 1064 nm diode pumped picosecond laser (EKSPLA PL2200: pulse duration 65 ps, repetition rate 2 kHz) focused at

the surface of the sample with a $50 \times$ NIR objective (numerical aperture—NA—equal to 0.42), and using an optimal pinhole of 100 μ m. The depth of focus was estimated to be *ca*. 3 μ m. The energy per pulse was always less than 100 nJ and adjusted by a power unit composed of a rotating half-wave plate followed by a Glan-Taylor prism. The incident power pulse was monitored by a fast InGaAs photodiode for quantitative power calibration purpose. A transparent polarized glass (formula: (1 - x)NaPO₃ + xNb_2O_5 , $x \approx 0.47$) where a NLO layer of *ca* 3 µm has been implemented at the anode during a poling process,²¹ and in which the *d* tensor components were previously determined $(d_{33} = 2.1)$ pm $V^{-1} = 5.0 \times 10^{-9}$ esu, $d_{31} = d_{33}/3$) was used as a reference for the calibration of the d value. Owing to the size of the crystal $(\sim 75 \times 50 \times 2 \,\mu\text{m}^3)$, no preferred orientation was possible except that, using a rotating stage, the crystal plate was oriented inplane so that the reflected µ-SHG signal was maximum. In addition, it was necessary to use a calibrated density filter to attenuate the excitation line (OD = 3 at 1064 nm) for 3 because of the huge efficiency of its response with regards to the reference sample. Finally, for both the reference and the crystal, polarized SHG intensities have been recorded as a function of the incident power so as to obtain a quadratic dependence of the harmonic NLO response. Assuming that the probed thickness is defined by the depth of focus (DOF) of the focused beam, the SHG intensity $(I_{2\omega})$ is related to the NLO susceptibility $d_{\rm eff}$ as follows:

$$(I_{2\omega}) \propto \text{DOF}^2 \times (d_{\text{eff}})^2 \times (I_{\omega})^2$$
 (3)

Results and discussions

Description of structures

Compound **2** crystallizes in the non-centrosymmetric monoclinic *Cc* space group. The asymmetric unit consists of two nonequivalent {(DEAS)H [Au(CN)₂]} entities, the molecular structures of which are shown in Fig. 1, with the atomic numbering scheme. The two π -conjugated skeletons of the cations defined by the fifteen N(4–5)C(4–16) and N(6–7)C(21–33) atoms are almost perfectly planar with largest deviations of 0.045 Å and 0.080 Å from mean planes observed at C(13) and C(33), respectively. The [Au(CN)₂]⁻ anions have quasi-linear structure with C–Au–C angles in the interval 174.7–177.7°. The [Au₁(CN)₂]⁻ and [Au₂(CN)₂]⁻ groups interact *via* strong hydrogen bonds through N2 and N4 with the N7 and N5 atoms of the pyridine groups of the corresponding (DEAS)H⁺, respectively. The N7...N2 distance is 2.85(3) Å (x + 1/2, y - 1/2, z + 1/22) while the N4…N5 distance is 2.74(3) Å (x - 1/2, -y + 1/2, -yz - 1/2). Furthermore, C···C intermolecular lateral contacts shorter than the sum of the van der Waals radii (3.7 A) indicate the presence of strong π - π interactions. The Au atoms are organized in pairs suggesting the occurrence of aurophilic interactions, however, the Au. Au distance is 3.6326(12) Å (x + 1/2, y - 1/2, z), and so higher than the sum of the van der Waals distance (3.4 Å). These intermolecular interactions define layers of 2 units which stack along c-a direction. The planarity of the two DEAS ligands indicates that the possibility for amine to pyridinium charge transfers, and hence for large molecular NLO response, will be nearly optimized in the cations. Nevertheless, the relative orientation of the two crystallographically independent units rotated each other by 175.8°, which shows that most of the contribution of one of the component is cancelled by that of the other one in the solid state. Therefore, it may be anticipated that crystals of 2 should exhibit an almost vanishing SHG efficiency.

Compound 3 crystallizes in the non-centrosymmetric triclinic P1 space group. The molecular structure is shown in Fig. 2, with the atomic numbering scheme. The π -conjugated skeleton defined by the fifteen N(1-2)C(1-13) atoms is roughly planar with a largest deviation of 0.152 Å from the mean plane observed at C(2), which suggests an efficient charge delocalization along the stilbazolium entity, and again a large molecular NLO response. The crystal packing is shown in Fig. 3. As in the precedent case, strong hydrogen bonding is established between the N1 atom of the pyridine moiety and the N3 atom of the quasi linear $[Au(CN)_2]^-$ anion $[N1\cdots N3$ distance = 2.74(2) Å (x + 2, y - 1, z); C-Au-C angle = 178.2(11)°]. What is immediately striking in the overall structure of this material is the fact that, due to the presence of a single molecule in the asymmetric unit in conjunction with the lack of symmetry of the P1 space group, all the chromophores are necessarily perfectly aligned in the solid. {(MPS)H [Au(CN)2]} should therefore be one of the very rare examples of nearly perfect 1-dimensional NLO crystal.

Although there is no significant interaction between (MPS)H⁺ entities in the crystal, the question of the origin of the overall and unique 1-dimensional chromophores alignment is naturally addressed in the crystals of **3**. In a previous paper, Nicoud *et al.* have discussed the solid state engineering in a series of 33 crystals built up from the 4'-donor substituted stilbazolium fragment



Fig. 1 ORTEP representation of the asymmetric unit of {(DEAS)H [Au(CN)₂]}. Thermal ellipsoids are represented at 50% probability. Red broken lines represent strong hydrogen bonds.



Fig. 2 ORTEP representation of the asymmetric unit of {(MPS)H [Au(CN)₂]}. Thermal ellipsoids are represented at 50% probability. Hydrogen bond interaction has been represented by a red broken line.

incorporated in zwitterionic building units.²² Their investigation points out how important intermolecular interactions (*e.g.* H-bond networks) are in the crystalline cohesion, and hence in the bulk NLO properties. In the case of **3**, the role of the Au $(CN)_2^-$ anion is anticipated to be a key parameter to account for the stabilization of the molecular alignment. To verify this idea, the main short contacts have been summarized in Table 2, and are shown in Fig. 4. Clearly two types of interactions are evidenced: (i) within a layer, where Au $(CN)_2^-$ plays a major role; and (ii) through a set of interlayer interactions where both (MPS) H⁺...[Au $(CN)_2$]⁻ and (MPS)H⁺...(MPS)H⁺ contacts take place. Finally, one half of the contacts reported in Table 2 involves the anion, which demonstrates its important role to account for the cohesion of the crystal of **3**.

The UV-visible electronic spectra for 1, 2, and 3 were recorded in

acetonitrile. Experimental and ZINDO computed absorption

maxima are listed in Table 3, while the experimental spectrum of

the relevant salt 3 is presented in Fig. 5. The geometries used for

the computations were both those obtained by DFT optimiza-

tions and those available from X-ray data. In any case, the

spectra are dominated by a single and intense band centred in the 450–500 nm domain ($\lambda_{max} = 477$ nm, $\varepsilon = 41$ 700 L mol⁻¹ cm⁻¹ for 3), with a tendency for red shift observed on changing the amine from dimethylamino, to pyrrolidinyl and finally diethylamino. This effect should slightly reinforce the β value of the stilbazo-lium based derivatives, with respect to the DAST reference materials (*vide infra*). Interestingly, these tendencies are observed at both experimental and theoretical level, making the use of the ZINDO computed electronic transitions relevant in the description of the NLO response of these salts in the next section.

NLO studies

The SHG efficiencies of the three $[Au(CN)_2]^-$ salts, recorded on calibrated powdered samples, are shown in Table 4. While **1** is SHG silent, probably in relation with a centrosymmetric crystal environment, **2** exhibits a residual efficiency, which is consistent with the pseudo-centrosymmetric packing of the (DEAS)H⁺ cations in the acentric *Cc* space group, as previously discussed. Compound **3**, in which the chromophores are all perfectly aligned exhibits a very large SHG efficiency up to 190 times that of urea. In order to analyse these results and the full capabilities of this 1-dimensional material, the present section is divided in



Fig. 3 Crystal packing of $\{(MPS)H [Au(CN)_2]\}$. Blue arrows have been added to the terminal atoms of the $[Au(CN)_2]^-$ group to highlight the relative orientation of the molecules.

Optical properties

Table 2 Short contact in the crystal structure of	e of 3	structure	the crystal	1	Short contact i	Table 2
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Intralayer contacts
N1····N3 (hydrogen bond) C14···C20' = 3.68(2) Å (x, y, z + 1) C18···C20' = 3.70(2) Å (x, y, z + 1)
Interlayer contacts
$\begin{array}{l} C1 \cdots C12' = 3.56(2) \stackrel{\text{A}}{\wedge} (x+1, y-1, z) \\ C2 \cdots C13' = 3.62(2) \stackrel{\text{A}}{\wedge} (x+1, y, z) \\ C5 \cdots C20' = 3.68(3) \stackrel{\text{A}}{\wedge} (x+1, y-1, z) \\ C5 \cdots C21' = 3.50(3) \stackrel{\text{A}}{\wedge} (x+1, y, z) \\ C6 \cdots C20' = 3.59(2) \stackrel{\text{A}}{\wedge} (x+1, y, z) \\ C9 \cdots C17' = 3.695(13) \stackrel{\text{A}}{\wedge} (x+1, y, z) \\ C10 \cdots C19' = 3.37(2) \stackrel{\text{A}}{\wedge} (x, y-1, z) \\ C11 \cdots C19' = 3.65(2) \stackrel{\text{A}}{\wedge} (x, y-1, z) \end{array}$

two parts to discuss the properties (*i*) at the molecular level, and (*ii*) at the solid state level.

(i) Molecular properties. The solid state NLO response of a molecular material (eqn (2)) is ultimately related to the hyperpolarizability (β) of discrete entities present in the crystal and exhibiting intramolecular charge transfers (eqn (1)). It is therefore important to use the solid state geometries for the computations. The calculated β values of (DEAS)H⁺, and (MPS) H⁺ are gathered in Table 5, and compared to that of DAMS⁺, the related chromophore of DAST, reference system regarded as one of the most efficient NLO materials reported to date.⁴ No crystal structure being available for 1, no solid state calculation was performed on (DMAS)H⁺. The values suggest that the present stilbazolium ions have a hyperpolarizability enhanced by about 25-30% versus that of the well known DAMS⁺ cation, with static hyperpolarizabilities (β_0 at zero laser frequency) equal to 144.0 \times 10^{-30} cm⁵ esu⁻¹ (average value of the $\beta_{\text{total}}^{\infty}$ hyperpolarizabilities reported in Table 5), 147.0×10^{-30} cm⁵ esu⁻¹, and 117.8×10^{-30} cm⁵ esu⁻¹, for (DEAS)H⁺, (MPS)H⁺, and DAMS⁺, respectively.

To analyse these differences more precisely, it has to be reminded that, within the sum over state (SOS) approach, β is related to all excited states of a molecule and can be partitioned into two components, so-called two-level ($\beta_{2\text{level}}$) and three-level ($\beta_{3\text{level}}$) terms.¹¹ In the present case, it clearly appears that $\beta_{2\text{level}}$ dominates the nonlinearity, $\beta_{3\text{level}}$ being reduced and directed in the opposite direction to that of β (Table 5). Therefore, it can readily be assumed that β is qualitatively described by the two-level term, which relates the NLO response to the optical transitions according to the following relation:²³

$$\beta_{2Level} = \sum_{i} \frac{3e^{2}\hbar f_{i}\Delta\mu_{i}}{2mE_{i}^{3}} \times \frac{E_{i}^{4}}{\left(E_{i}^{2} - (2\hbar\omega)^{2}\right)\left(E_{i}^{2} - (\hbar\omega)^{2}\right)}$$
(4)

In this equation, f_i , $\Delta \mu_i$, and E_i are the oscillator strength, the difference between ground and excited state dipole moment and the energy of the *i*th transition, respectively ($\hbar\omega$ being the energy of the incident laser beam). The main transitions with significant contributions to $\beta_{2\text{level}}$ are described in Table 6. If one considers that the data for $(DEAS)H^+$ are somewhat close to the average calculated for the two crystallographically independent molecules present in the crystal of 2, the overall behavior is very similar for any chromophores, with a single HOMO/LUMObased electronic transition, centered at 470–490 nm (intensity f =1.20–1.30) contributing around 95% to $\beta_{2\text{level}}$, which is usually the case in NLO chromophores having a strong "push-pull" character. This transition possesses a strong push-pull character with a large $\Delta \mu$ value between 17 and 18 Debye. The electronic charge transfers drawn in Fig. 6 for (MPS)H⁺ and DAMS⁺ clearly indicate that the origin of the NLO response is qualitatively the same in these systems, and are only slightly modulated by the different nature of the substituents.

Interestingly, the different values computed between the two chromophores present in 2 are of the same order of magnitude as those observed between DAMS⁺ and (MPS)H⁺. This encouraged us to check the intrinsic molecular properties by a study carried out on DFT optimized molecular structures as well. The data are gathered in Table 7, where the spectroscopic features are presented in relation to the concept of bond-length alternation (BLA).²⁴ A reduced BLA indicates a better charge delocalization through the π -conjugated bridge and therefore a possibility for enhanced NLO response. The data show a reduced BLA from 0.071 to 0.066 Å on going from DAMS⁺ (DAST) to (MPS)H⁺



Fig. 4 Short contacts in $\{(MPS)H [Au(CN)_2]\}$.

		ZINDO computed values					
	Experimental values	In MeCN (DFT geometry)	In solid state (X-ray geometry)				
1	470	473	n/a				
2	483	478	497 ^a				
3	477	477	494				
DAST	471	470	471				

 a Averaged value from the two independent (DEAS)H * present in the crystal cell.



Fig. 5 Optical spectra of (MPS)H⁺ [Au(CN)₂]⁻, in acetonitrile.

(3), which is indeed correlated to a better charge transfer, a red shift, and finally to enhanced NLO capabilities. Although the differences are modest, all data available lead to a set of structural (BLA), experimental (UV-visible spectra) and computed (solid state and DFT geometries) features which all suggest that the new 1-dimensional compound **3** exhibits better NLO capabilities than the promising DAST, at the molecular level.

(ii) Solid state property. The fact that a chromophore crystallizes in a non-centrosymmetric space group does not guarantee that the NLO response is optimized. In the case of 2, the examination of the crystal structures reveals that the asymmetric unit cell is built up from two molecules (*mol1* and *mol2* in Table 5), which are embedded in a nearly centro-symmetric environment. Indeed, the angle between the two calculated β is equal to 176.5°, thus cancelling most of the NLO effect with a modest resulting efficiency reduced to 0.5 time that of urea.

The situation encountered in compound **3** is much more appealing and can be compared to that of DAST, for which a record SHG efficiency of 1000 times that of urea has been

Table 4 Powdered SHG efficiencies at 1.907 μm for 1, 2, and 3

	SHG efficiencies ^a	Space groups		
Urea	1^b	$P42_{1}m$		
1	0	n/a		
2	0.5	Сс		
3	190	<i>P</i> 1		
a Paulia b Lise	l as a reference			

Table 5 ZINDO calculated hyperpolarizabilities (β in 10⁻³⁰ cm⁵ esu⁻¹) of (MPS)H⁺ and (DEAS)H⁺ at $\lambda = \infty$ (β_0) and 1.907 µm. The values for DAMS⁺ are provided as references

	λ/µm	$\beta_{ ext{total}}{}^{a}$	β_{2level}	β_{3level}	Angle between $\beta_{2\text{level}}$ and $\beta_{3\text{level}}$
(DEAS)H ⁺					
mol 1 ^b	8	152.4	248.3	96.1	177.8°
	1.907	241.2	361.8	120.6	_
mol 2^c	∞	135.6	209.8	74.7	174.8°
	1.907	206.0	297.4	92.0	_
(MPS)H ⁺	∞	147.0	231.8	85.1	176.0°
. ,	1.907	227.5	332.6	105.5	
DAMS ⁺	8	117.8	197.0	79.4	176.6°
	1.907	174.8	271.2	96.6	_

^{*a*} $\beta_{\text{total}} = \beta_{2\text{level}} + \beta_{3\text{level}}$. ^{*b*} Molecule 1 corresponds to that having a C=C central ethenyl bond length of 1.34 Å. ^{*c*} Molecule 2 corresponds to that having a C=C central ethenyl bond length of 1.35 Å.

reported.⁴ In solid state, the hyperpolarizability tensor (component β_{ijk} in the molecular framework) is related to the corresponding crystalline first-order nonlinearity tensor $\chi^{(2)}$ (component d_{IJK} in the crystalline framework).²⁵ Assuming a 1-dimensional character of the molecular tensor (which is totally justified in the present case), β has only one large coefficient along the charge transfer axis x of the molecule (namely β_{xxx}). The relations between β_{xxx} and d_{IJK} have been established for any space groups. For instance, in the case of the monoclinic *Cc* group (*e.g.* DAST), these expressions lead to the following relations:^{26,27}

$$d_{\rm ZXX} = N\beta_{\rm xxx}\cos\theta\sin^2\theta \tag{5}$$

$$d_{\text{ZZZ}} = N\beta_{\text{xxx}}\cos^3\theta \tag{6}$$

where the Lorentz local-field factors have been assumed to be equal to 1. All other components of the *d* tensor are negligible (θ is defined as the angle between β and the OY glide mirror of the crystal, N = Z/V is the number of molecule per unit volume). For DAST, Z = 4 and V = 2098.2 Å³, and $\theta = 20^{\circ}$,⁴ which, at the 1.907 µm wavelength, leads to:

$$d_{\rm ZXX} = 3.66 \times 10^{-8} \,\rm{cm}^2 \,\rm{esu}^{-1} \,(15.33 \,\rm{pm} \,\rm{V}^{-1}) \tag{7}$$

$$d_{ZZZ} = 27.65 \times 10^{-8} \,\mathrm{cm}^2 \,\mathrm{esu}^{-1} \,(115.8 \,\mathrm{pm} \,\mathrm{V}^{-1}) \tag{8}$$

In the case of **3** (*P*1 space group) and in the absence of any crystal symmetry, all the molecules are strictly aligned in the solid. Therefore, the *d* tensor is equal to its β molecular counterpart, scaled by N = 1/V (V = 502.9 Å³). This implies:

$$d_{ZZZ} = N \beta_{xxx} = 47.96 \times 10^{-8} \text{ cm}^2 \text{ esu}^{-1} (200.8 \text{ pm V}^{-1}) \quad (9)$$

Since the SHG intensity (P^{ω}) is proportional to the square of the *d* tensor, crystals of **3** are roughly expected to exhibit a potential SHG efficiency 3 times (200.8²/115.8²) higher than that of DAST.

At first, it seems therefore surprising that the Kurtz-Perry powder test indicates for **3** a SHG efficiency 5 times lower than that of DAST. However, two important parameters must be taken into account in order to express $I^{2\omega}$ in the powder test: (*i*)

Table 6	Energy (λ_{max}	_x in nm), (oscillator st	rength (ƒ), d	lipole mom	ent change	$(\Delta \mu \text{ in } \mathbf{D})$ b	etween grou	ind and ex	cited states,	contribution ((6) to $\beta_{2\text{level}}$, and
composi	tion of the do	ominant e	excited state	e involved i	n the NLC	response o	of (MPS)H ⁺	and (DEA	S)H⁺. Dat	a are provi	ded for DAMS	* as referen	nces

Compound	Transition	λ_{max}	f	$\Delta \mu$	state % ^a	Composition of CI expansion
(MPS)H ⁺	$1 \rightarrow 2$	494	1.30	17.0	90.5	$0.948\chi_{HOMO} \rightarrow $ LUMO
(DEAS)H mol 1	$1 \rightarrow 2$	507	1.02	20.9	88.1	$0.950\chi_{HOMO} \rightarrow $ LUMO
$mol \ 2$ DAMS ⁺	$\begin{array}{c} 1 \rightarrow 2 \\ 1 \rightarrow 2 \end{array}$	487 471	1.46 1.20	14.3 17.9	89.6 87.5	0.940χ _{HOMO} → LUMO 0.939χ _{HOMO} → LUMO
^{<i>a</i>} Contribution of	The transition to $\beta_{2 evel}$	calculated at $\lambda =$	= ∞.	1119	0,10	



Fig. 6 ZINDO-computed charge transfers in (MPS)H⁺ (top) compared to those of DAMS⁺ (bottom). The surface of the circles are proportional to the electron densities (white and black contributions indicate increases and decreases of electron densities, respectively).

 Table 7
 ZINDO computed data in relation with BLA (in Å) calculated on molecular structures optimized by DFT

			Bond-l	engths				
Chromophores	$\lambda_{max} \left(nm ight)$	f	a	b	с	$BLA = \frac{a+c}{2} - b$		
(DMAS)H ⁺ (DEAS)H ⁺ (MPS)H ⁺ DAMS ⁺	473 478 478 470	1.24 1.35 1.25 1.26	1.4352 1.4342 1.4346 1.4368	1.3677 1.3684 1.3682 1.3664	1.4368 1.4384 1.4360 1.4383	0.068 0.066 0.067 0.071		

the expression of the angular averaged d^2 tensor, and (*ii*) the efficiency–particle size relationship. Indeed, in powdered sample, $I^{2\omega}$ becomes proportional to the angular averaged d^2 value, the expression of which has previously been treated:^{18a,28}

$$\langle d^2 \rangle = (19/105) \sum_i (d_{iii})^2 + (13/105) \sum_{i \neq j} (d_{iii}) (d_{ijj}) + (44/105) \\ \times \sum_{i \neq j} (d_{iij})^2 + (13/105) \sum_{ijk} (d_{iij}) (d_{jkk}) + (5/7) (d_{ijk})^2$$

$$(10)$$

This expression clearly shows that a strictly 1-dimensional NLO crystal with a single non-zero d tensor component (*e.g.* 3) may have a more reduced powder efficiency than a multi-components material (*e.g.* DAST). More importantly, the efficiency is strongly dependent on the particle size.

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Like any highly efficient NLO material, DAST is phase matchable, which means that the SHG efficiency is roughly proportional to the particle size at least in the 0–100 μ m domain.^{18a} The giant efficiency of 1000 times that of urea reported by Marder was measured on non-calibrated samples,⁴ which suggests that tightly grinded ($\approx 10 \mu$ m) samples would likely lead to much reduced efficiencies.

By contrast, **3** is not phase matchable (because of its strong 1-dimensional character), which implies an inverse relation between efficiency and particle size, when the sizes are larger than the coherence length ($\geq 10-20 \mu m$).^{18a} We may therefore assume that experiments performed on much smaller ($\approx 10 \mu m$) crystals would provide efficiencies larger than the actual 190× urea value, recorded on a particle range of 50–80 µm. This point leads to the conclusion that **3** might be one of the most efficient NLO materials at the micron scale. To verify this possibility, the value of the d_{ZZZ} tensor component has been investigated, and determined by µ-SHG.

Fig. 7 shows the quadratic dependence of the polarized SHG signals ($I_{//}$ and I_{\perp}) obtained upon exciting a thin microcrystal of **3** (thickness around 2 µm) in which, to a large extent, the deleterious effect of light absorption may be neglected. The corresponding quadratic laws obeyed by $I_{//}$ and I_{\perp} can be easily deduced from a least-squares fitting procedure. We find $I_{//}$ (reference sample) = $45.5I_{\omega}^2$, $I_{//}(3) = 152.0 \times 10^6 I_{\omega}^2$ and $I_{\perp}(3) = 4.0 \times 10^6 I_{\omega}^2$.

A straight comparison between the polarized intensities I_{ll} of the reference and investigated sample (using eqn (3)) leads to d_{eff}



Fig. 7 Quadratic dependence of the polarized $(I_{l/l})$ SHG signal of the reference poled glass sample (squares) and of the crystal of 3 $(I_{l/l}: circles)$; I_{\perp} : full circles). Note the difference of intensity scales between the two materials.

 \thickapprox 3660 pm V^{-1} (~8.7 \times 10⁻⁶ esu) which is actually a huge dynamical (at 1064 nm) value as expected.

To estimate the quadratic susceptibility $d_{zzz} = N\beta_{xxx}^*$ of 3, where β_{xxx}^* is the molecular component β_{xxx} corrected from local field effects and N is the number density of molecules in the crystal. A more accurate interpretation requires the assumption that, due to its strong 1-dimensional character with a dominating β_{xxx} component, the dipolar molecule lies on a vertical mirror plane (pseudo-local symmetry) (Fig. 8). In this case, the x axis corresponds to the direction of light propagation and the incident polarization is along the z direction. Hence, I_{ll} is associated with the I_{ZZZ} term and I_{\perp} to the I_{YZZ} term in the (x, y, z)laboratory frame. The above mentioned assumption is supported by the fact that neither I_{ll} nor I_{\perp} signals could be detected when rotating at 90° the plate on top of which the sample was oriented in-plane to maximize its reflected µ-SHG signal. From this information, we can indeed deduce that the SHG tensor is now described by four components, namely d_{ZZZ} , d_{XZZ} , d_{ZXX} and d_{XXX} . Finally, we find that the dynamical value measured at 1.064 μ m $d_{zzz} = N\beta^*_{xxx}$ value ranges between ~4500 pm V⁻¹ (~10.8 \times 10 $^{-6}$ esu) and 12400 pm V^{-1} (~29.6 \times 10 $^{-6}$ esu). The static value extrapolated from the 2-level model (eqn (4)) is estimated between \sim 705 pm V⁻¹ (\sim 1.7 \times 10⁻⁶ esu) and 1940 pm V^{-1} (~4.6 × 10⁻⁶ esu). Details about the analytical calculations are provided in supplementary information.[†]

Critical evaluation of 1-dimensional devices with large hyperpolarizabilities

Recent years have witnessed the development of lasers with ultrashort (sub-pico) pulses of light (e.g. the Ti : sapphire laser) in which the radiation cannot be regarded as strictly monochromatic. These advanced technologies can reinforce the potential of nonlinear optics in the future photonics,²⁹ which should greatly benefit from the use of micron-thick materials, to avoid velocity dispersion during the traversal of the devices, the overall NLO efficiency being ensured by the possibility of giant values of the hyperpolarizabilities. The typical d_{zzz} range of standard NLO crystals present on the market place, such as LiNbO₃ and KTiOPO₄ (KTP), is around 20 pm V⁻¹ (\sim 4.8 × 10⁻⁸ esu) at 1.064 µm,³⁰ about three orders of magnitude below that of the present 3 material. This leads to the conclusion that a 1 mmthick lens could be replaced by a micron-thick crystal of 3, in which any velocity dispersion problem is avoided. The technique of microtomy, which is traditionally employed in biology, allows to cut single crystals embedded in polymer matrices at the



Fig. 8 Image of the crystal of **3** in the frame of the laboratory (left). The 1-dimensional molecule is located in the mirror plane (XZ) with an unknown azimuthal angle θ (right).

thickness of only few microns.³¹ This could provide an easy access to these intriguing materials, in which the absorbance, and related optical losses and chromophores damage, should be very limited even near resonance.

Conclusion

Three salts derived from the well known DAST NLO materials have been characterized. Among them, (MPS)H⁺ Au(CN)₂⁻ possesses the double intriguing feature of a very large molecular hyperpolarizability and a perfect 1-dimensional alignment in crystal state. This leads to a giant d_{zzz} tensor component (between 10.8×10^{-6} esu and 29.6×10^{-6} esu at 1.064 µm), a unique feature which would deserve more attention in micron-thick devices operating near resonance, where no absorption and velocity dispersion take place even with ultra-short (sub-pico) pulses of light.

Acknowledgements

We thank CALMIP (calcul intensif en Midi-Pyrénées, Toulouse, France) for computing facilities. V. R. thanks F. Adamietz for technical assistance and the Région Aquitaine for financial support in optical, laser, and computer equipment. This work has been supported by the University of Bordeaux 1 and the CNRS through the excellence chair of S.B. Financial support is acknowledged from the Spanish Ministerio de Ciencia e Innovación (MICINN) (CTQ2010-18414-FEDER).

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