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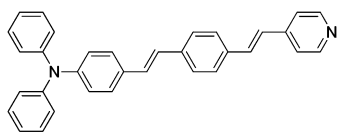
Solid state and solution fine tuning of the linear and nonlinear optical properties of (2-pyrene-1-yl-vinyl)pyridine by protonation–deprotonation reactions†

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The unexpected and acido-triggered reversible luminescence and non-linear optical properties of (2-pyrene-1-yl-vinyl)pyridine, a simple and highly transparent chromophore, are studied both in solution and in the solid state. Remarkably, for the first time the acidomodulation of the NLO response of a poled thin film is reported.

While the research on compounds with commutable emissive properties started some years ago, the possibility to trigger the NLO properties by an external stimulus has been evaluated more recently.¹ Of particular interest from both points of view are organic acidochromes which display substantial emissive and NLO variations due to their ability to alternate between two distinct chemical forms in response to the protonation–deprotonation process.²

In this regard, some of us have recently reported the solution acidochromic switch of the photoluminescence and of the second-order NLO properties of diphenyl-(4-{2-[4-(2-pyridin-4-yl-vinyl)-phenyl]-vinyl}-phenyl)-amine (DPVPA) upon exposure to HCl and ammonia vapours.³



DPVPA chemical structure

The alteration of the linear and nonlinear optical properties of the chromophore was induced by the modulation of its internal charge-transfer due to the external stimulus. In addition, this molecular target was chosen to demonstrate for the first time that electric-field-induced second harmonic (EFISH) generation

measurements can be used as a convenient alternative to the hyper Rayleigh scattering (HRS) technique to reveal a protonation–deprotonation NLO contrast. A similar interconversion process was also induced by exposure of powders or thin films of DPVPA dispersed in a polymethylmethacrylate (PMMA) matrix to acid–base vapours producing a reversible modification of the solid state emissive properties. On the other hand, no solid state NLO acidochromic switch was reported. The modulation of the second-order NLO properties of dispersed thin films is in fact a far more difficult task to be accomplished and remains a challenge requiring a reversible control of the noncentrosymmetric alignment of the NLO moieties. Solid state switching of second harmonic generation (SHG) has been previously demonstrated in poled polymers containing photochromic dyes,⁴ organic photochromic crystals,⁵ and Langmuir–Blodgett thin films of organometallic complexes.⁶ However, to the best of our knowledge no acidochromic SHG switch has been reported for thin films yet.

In this communication we report our results on the reversible acidochromic behaviour both in solution and in the solid state of (2-pyrene-1-yl-vinyl)pyridine, **1**, a simple and highly transparent chromophore characterized by unexpected and tunable second-order NLO properties. Pyrene and its derivatives have demonstrated to exhibit excellent chromophore features, thanks to their extended π -electron delocalized systems.⁷ In addition, the high rigidity of their polyaromatic systems should assure larger chemical and thermal stability with respect to the most commonly used chromophores, such as stilbenes and azobenzenes.⁸ For the same reason, pyrene-based chromophores should show further enhanced stability with respect to the recently investigated class of azaphenanthrene and azachrysene derivatives.⁹ Compound **1** was prepared in high yield and in one step only by Heck coupling (see Scheme 1) rather than following published procedures which require multiple steps.¹⁰

According to its reduced conjugation length, comparable to that of the classical stilbene system,¹¹ **1** is characterized by a high optical gap, with an absorption edge in CHCl₃ at 378 nm (Fig. 1). This absorption band is associated with an intramolecular charge transfer (ICT) transition emanating from pyrene towards the pyridine moiety

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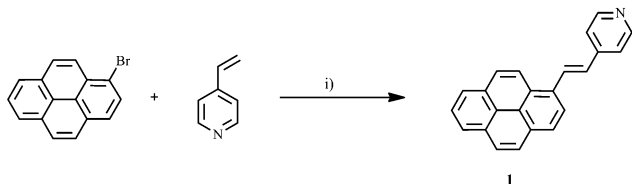
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Scheme 1 Synthesis of (2-pyrene-1-yl-vinyl)pyridine **1**. (i) Bis(tri-*t*-butylphosphine)-palladium(0)/toluene, 80 °C, 40 h, 90%.

(see the ESI† for a HOMO–LUMO plot together with the full set of theoretical results). The solution was prepared using CHCl_3 treated overnight with basic Al_2O_3 , otherwise an easy protonation of the pyridine fragment was observed (see the following). Upon exposure of the CHCl_3 solution of **1** to HCl vapours for few seconds, the absorption maximum is red shifted to 443 nm (due to charge transfer in the same direction as the neutral form) with a shoulder at 395 nm. The reverse transformation can be accomplished by treatment of the solution with NH_3 vapours. Interestingly, the protonation–deprotonation process is accompanied by a macroscopic variation in the emissive behaviour. In fact, **1** in CHCl_3 displays an intense emission centred at 450 nm (quantum yield, QY, equal to 65% using diphenylanthracene as the standard) which is shifted to 550 nm upon exposure to HCl (QY 19% using quinine sulfate in H_2SO_4 0.1 M as the standard) and restored after treatment with NH_3 vapours. The time required for the protonation–deprotonation process is related to the solution concentration: higher concentration solutions require longer time exposure to acid–base vapours. Fig. 1 shows the absorption and emission spectra recorded every 3 seconds before and after exposure to HCl vapours. Thanks to the higher sensitivity of photoluminescence spectroscopy, the complete transformation between protonated and deprotonated forms of **1** is safely assessed. In fact, while the transformation seems to be complete after 6 seconds by the absorption spectroscopy, it is necessary to wait for 3 more seconds, as evidenced by the emission spectra, for the process to be completely accomplished.

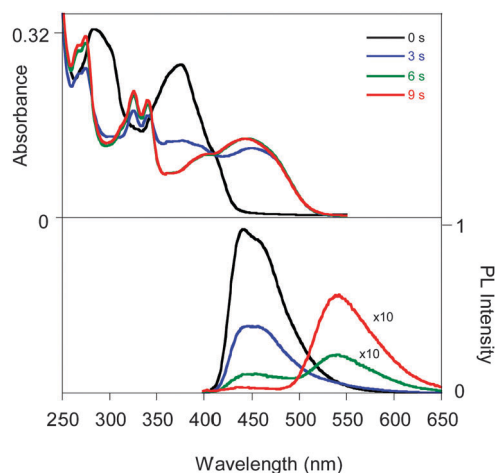


Fig. 1 Absorption (up) and emission (down) spectra of **1** in CHCl_3 solution at different times of exposure to HCl vapours.

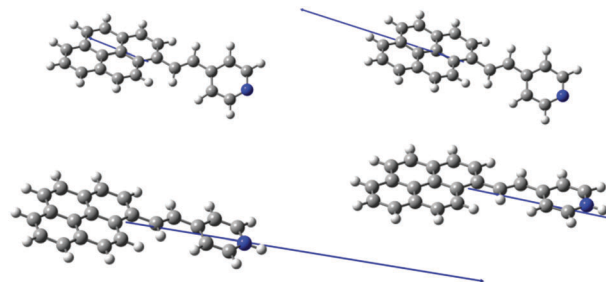


Fig. 2 Plots of the optimized PBE0/6-311++G(d,p) geometry of **1** in its neutral (above) and protonated (below) forms in CHCl_3 , along with their dipole moment of the ground state computed at the same level of theory (left) and of the excited state computed at the TD-PBE0/6-311++G(d,p) level (right). The center of mass is chosen as the origin of the dipole.

The measurement of $\mu\beta_\lambda$ of **1** was carried out in CHCl_3 (treated with basic Al_2O_3) solutions at 1907 nm non-resonant wavelength by the EFISH method. In spite of its relatively low dipole moment, μ (3.9 D, well reproduced by PBE0/6-311++G(d,p) calculations in chloroform, 4.4 D, and directed from pyridine to pyrene, see Fig. 2), **1** gives rise to unexpectedly large $\mu\beta_\lambda$ values (1500×10^{-48} esu at 10^{-4} M concentration), much higher than the most efficient push–pull 4,4'-disubstituted stilbenes.¹²

Such results can be interpreted in terms of the phenomenological Oudar two-level model,¹³ giving the CT contribution to the quadratic hyperpolarizability, $\beta_{\text{CT}} \propto (f\Delta\mu_{\text{eg}}/\Delta E_{\text{eg}}^2)$, wherein f is the oscillator strength, $\Delta\mu_{\text{eg}}$ is the difference between the dipole moment moduli of the excited and ground states, and ΔE_{eg} is the excitation energy. TD-PBE0/6-311++G(d,p) calculations in chloroform provide in fact a quite large oscillator strength for the lower energy transition, 1.27, and an increase of the excited state dipole moment with respect to the ground state ($\Delta\mu_{\text{eg}} = 7.1$ D), because the charge transfer involved in the excitation (see above) increases the negative charge localized on the pyridine moiety (see Fig. 2).

Upon exposure of the solution to HCl vapours until no presence of unreacted **1** is evident in the emission spectrum, an inversion of the sign of $\mu\beta_\lambda$ is observed (-950×10^{-48} esu). This result was unexpected on the basis of previous studies performed by some of us on several methylpyridinium salts of stilbazolic precursors. Alkylation of the pyridinic nitrogen provided invariably positive values of $\mu\beta_\lambda$, increasing with the enhancing electron-withdrawing character of the positively charged nitrogen atom.¹⁴ In the present case, the surprising change in the sign of $\mu\beta_\lambda$ of **1** upon protonation can be explained by a negative $\Delta\mu_{\text{eg}}$ value (-11.9 D from TD-PBE0/6-311++G(d,p) calculations in chloroform, which provide a reduced oscillator strength, 1.19, compared to **1**, in agreement with the observed spectra).¹⁵ In fact, the charge transfer associated with excitation of the protonated molecule is opposite to the direction of the large ground state dipole moment (20.8 D), which is oriented from pyrene to pyridine (see Fig. 2). The different behavior of the neutral and protonated species can be appreciated by looking at the trend of the respective electrostatic potential maps on going from the ground to the excited state (see Fig. S3, ESI†), showing an increased polarization for the former and the opposite for the latter. These results demonstrate not only the interesting properties of pyrene as an NLO chromophore, but also its

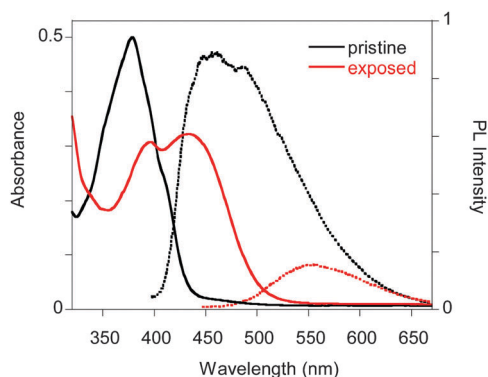


Fig. 3 Absorption and emission spectra of the 1/PMMA pristine film and after exposure to HCl vapours.

ambivalent donor–acceptor role. It is to be noted that a related phenomenon has been previously observed in some pyrrole-(π -bridge)-pyridine-based chromophores, which showed sign inversion of solvatochromism after alkylation of the pyridinic nitrogen.¹⁶

To study the solid state interconversion process, thin films of **1** dispersed in polymethylmethacrylate (PMMA) were prepared by spin coating few drops of a dichloromethane solution (1/PMMA = 2 wt%; PMMA = 10 wt% with respect to the solvent) on a glass substrate.¹⁷ By exposure of the 1/PMMA film to HCl vapours for 60 s, the initial absorption maximum is shifted from 378 nm (neutral form; $\epsilon = 4610 \text{ cm}^{-1}$) to lower energy with one absorption at 396 nm and a broad band at 434 nm ($\epsilon = 3915 \text{ cm}^{-1}$) and the emission maximum shifts from 446 nm (69% QY) to 546 nm (32% QY) (see Fig. 3). The reverse reaction is induced by exposure of the film to ammonia vapours for 30 s.

This interconversion can be exploited to produce a solid state second-order NLO acidochromic switch. Corona poling¹⁸ on the 1/PMMA pristine film was carried out at 9.7 kV while increasing the temperature at a rate of $1.8 \text{ }^\circ\text{C min}^{-1}$ up to $60 \text{ }^\circ\text{C}$. The temperature was maintained at $60 \text{ }^\circ\text{C}$ for 90 min and then gradually decreased to room temperature while monitoring the SHG response of the film (see Fig. S5, ESI[†]).¹⁹ A second-order NLO coefficient, d_{33} , value of the 1/PMMA poled film equal to $0.55(\pm 0.11) \text{ pm V}^{-1}$ was obtained.²⁰ The film was then stored in the dark for at least 72 h after poling, in order to ensure that the surface charges resulting from the deposition of ions on the film surface during the corona poling process²¹ were neutralized and a more stable SHG signal was reached (22 a.u.). The decay of the SHG signal after poling was determined by monitoring the film response for about 180 h (see Fig. S7, ESI[†]).

The SHG efficiency of the initial poled film and its switching performances in the presence of HCl/ammonia vapours were then monitored *ex situ* using a Maker fringe set-up²² at a fixed angle of 60° using a p–p polarization. After exposure to HCl vapours the SHG signal of the film increases up to 61 a.u., and then decreases to about 4 a.u. after treatment with ammonia vapours indicating a first acidswitch with a SHG drop of about 93.5% (see Fig. 4).²³ The observed decrease of the SHG signal during the switches is probably due to the partial irreversible loss of orientation through the acid–base treatment. Absorption spectra

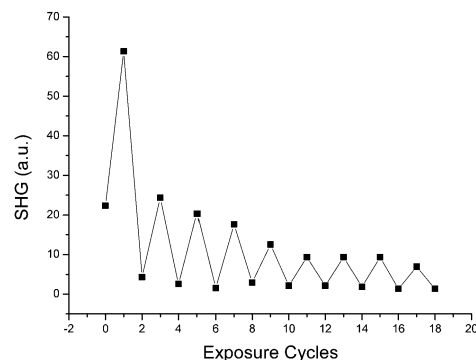


Fig. 4 Acidochromic SHG switch of the poled thin film.

recorded after each cycle confirm this behavior. In fact, the increase of the integrated area under absorption spectra (see Fig. S8, ESI[†]) indicates a loss of orientation of the chromophore during the switches and well correlates with the drop in the NLO response. This loss of the SHG signal has already been observed in other photochromic switches in the PMMA matrix.^{4,5,24} Besides, the integrity of the film after the repeated switches was also established by emission spectroscopy and by proving the invariance of the film thickness by profilometry (see Table S2, ESI[†]).

In this communication we report the large second-order NLO response of the highly transparent chromophore **1**. We also evidence the ambivalent donor–acceptor role of the pyrene unit resulting in an interesting acidochromic emissive and NLO switch both in solution and in the solid state. To our knowledge, this study represents the first demonstration of the acidomodulation of the NLO response of a thin film, opening a new avenue for preparation of convenient reversible-NLO switches.

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