**High piezoelectric output voltage from blue fluorescent *N,N*-dimethyl-4-nitroaniline nano crystals into poly-l-lactic acid electrospun fibers**

**Rosa Baptista, Bruna Silva, João Oliveira, Vahideh B. Isfahani, Bernardo Almeida, Mário R. Pereira, Nuno Cerca, Cidália Castro, Pedro V. Rodrigues, Ana Machado, Michael Belsley and Etelvina de Matos Gomes**

**Suplemmentary Information**

**SI 1.1** *Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (FTIR-ATR)*

The Fourier transformed infrared (FTIR) analysis of the electrospun fibres and NNDM4NA crystalline powder were recorded on a Jasco 4100 FTIR spectrometer in transmittance mode, in the range of 4500-600 *cm-1*, by averaging 32 scans and using a resolution of 8 cm-1. FTIR data were treated using software OriginPro 2017 SR2 (OriginLab Corporation, USA).

The incorporation of NNDM4NA in PPLA polymeric fibers was confirmed spectroscopically by the data collected, as indicated in Figure S1.

NNDM4NA exhibit the characteristics of conjugated double bonds with typical bands within the ranges 1660–1480 cm-1 which is in agreement with a high degree of push-pull (donor-acceptor) structural character.

NNDM4NA as a tertiary amine, has C-N stretching bands from 1250 *cm-1* to 1020 *cm-1*. In NNDM4NA spectrum, two bands appears at 1060 *cm-1* and 1095 *cm-1*, with weak to medium intensity, due to the lack of polarity of the C-N bond. These bands are overlapped with the PLLA more intense bands in NNDM4NA@PLLA spectrum.

For aromatic nitro compounds, the asymmetric and symmetric stretching vibration of NO2 group are assigned to an intense band in the region arround 1590 cm1-1600 *cm-1* and 1380-1390 *cm-1* which are due to the asymmetric and symmetric stretching vibration of the group [1-5]. The symmetric stretching vibration at 1304 *cm-1* fo NNDM4NA is shifted to 1315 *cm-1* inNNDM4NA@PLLA [6-7]. The bands in the region 1123 *cm-1* and 1177 *cm-1* are assigned to C-H and C-C bending vibrations. Weak bands at 1432 *cm-1* and 1462 *cm-1* in NNDM4NA are not present in NNDM4NA@PLLA, due to overlapping with the intense PLLA band at 1452 *cm-1*.

The band at 1502 *cm-1* in NNDM4NA, also associated with NO2 asymmetric stretching vibration, is shifted to 1529 *cm-1* in NNDM4NA@PLLA. The weak 1540 *cm-1* band in NNDM4NA is hidden by the polymer matrix in NNDM4NA@PLLA.

In NNDM4NA spectrum, the intense band at 1657 cm-1, which is mainly due to the in-plane bending modes of N(CH3)2, is absent in NNDM4NA@PLLA spectrum. The reason must be due to the fact that the nanocrystals are intercalated in the polymer chains and those groups are constrained inside the matrix.

Diagram

Description automatically generated

**Figure S1.** FTIR-ATR spectrum of PLLA (gray line), NNDM4NA powder (red line) and NNDM4NA@PLLA fiber array (blue line).

**SI 1.2.** *X-ray Diffraction*

Crystallinity and crystallographic orientation of *N,N*-Dimethyl-4-nitroaniline was studied by X-ray diffraction. The diffraction pattern using *θ*–2*θ* scans was recorded between 5º and 40º on a Philips PW-1710 X-Ray diffractometer with Cu-Kα radiation of wavelength 1.5406 *Å*. The lattice planes parallel to the substrate surface were determined from the reciprocal lattice vector of modulus (2/*λ*)sin*θ*, with *λ* the radiation wavelength and *θ* the Bragg angle. The X-ray diffraction pattern shows that NNDM4NA is crystallized inside the PLLA [8] polymer matrix with random orientation.



# Figure S2. NNDM4NA polymer fibers (a) and unit cell content with plane (020) in light purple (b). The measured X-ray pattern shows that there is crystallographic preferential orientation because the Bragg reflections (001) and (020) are for the fiber array, both more intense than (11-1) reflection, which is the most intense for randomly oriented.

# Using the Debye-Scherrer equation [9], the NNDM4NA crystallite size is given by [10]

(1)

In this equation the parameter K is a shape factor which we take to be 0.90, while λ is the X-ray wavelength. The full width half maximum of a (hkl) reflection is *β*hkl. This width was estimated using the Line Profile Analysis Software LIPRAS [10] to fit an asymmetric Pseudo Voight Profile toand  peaks. Both fit lead to a an average crystallite size of 38 nm. The relevant fit parameters are listed in Table S1, with the corresponding fits shown in Figure S3 a) and b).

Chart, histogram

Description automatically generated

**Figure S3**. Asymmetric Pseudo-Voigt fits ofandBragg reflections for NNDM4NA. The width of the reflections at half the maximum *β* and the calculated nanocrystals average size t are indicated.

**Table S1:** Crystallite size and fit parameter values for andBragg reflections

|  |  |  |  |
| --- | --- | --- | --- |
|  |  |  |  |
|  | 16.871º | 0.212º | 39.5 nm |
|  | 25.583º | 0.229º | 37.2 nm |

**SI 1.3.** *Confocal Laser Scanning Microscopy*

The autofluorescence of the fibers were observed with an Olympus™ FluoView FV1000 (Olympus, Tokyo, Japan) confocal scanning laser microscope, using a 40x objective, with several emission/detection settings: (i) excitation wavelength 405 nm, detection filters BA 430–470; BA 505-540; BA 480-495; (ii) excitation wavelength 458 nm, detection filters BA 505-605; BA 575-620; BA 535-565 or (iii) excitation wavelength 559 nm, detection filters BA 575-675; BA 655-755). Images were acquired with 800 x 800-pixel resolution. A 1 cm2 fiber mat with 600 μm thickness was observed on a glass slide. A scan over the sample was performed at room temperature.

**SI 1.4.** *Fluorescence lifetime decay*

The fluorescence lifetime was measured using a Single Photon Counting System, equipped with a NanoLed® as excitation light source (Horiba, Jovin-Yvon, IBH Ltd.) with peak emission at 370 nm and an impulse repetition rate of 1 MHz. The excitation wavelength was selected using a monochromator and the ﬂuorescence emission was selected using ﬁlters and detected by a photomultiplier (Hamamatsu R2949). Counting acquisition was made using a Becker&Hickl SPC-150 TCSPC board and data analysis was performed using the PicoQuant FluoFit software. A multi-exponential model was used to estimate the fluorescence lifetimes,

  (2)

 where  is the intensity as a function of time,  are the amplitudes and  are the decay lifetimes (ns). The goodness of ﬁt was assessed in terms residuals and autocorrelation function analysis. Each fluorescence fraction, , was determined using the equation,

(3)

Diagram

Description automatically generated

**Figure S4 and Table S2**. Fluoresce lifetime decay measured using a Single Photon Counting System, equipped with a NanoLed® as excitation light source (Horiba, Jovin-Yvon, IBH Ltd.) with peak emission at 370 nm and an impulse repetition rate of 1 MHz.

**References**

1. Kozich, V.; Werncke, W.; Dreyer, J.; Brzezinka, K. W.; Rini, M.; Kummrow, A.; Elsaesser, T. Vibrational excitation and energy redistribution after ultrafast internal conversion in 4-nitroaniline. *J. Chem. Phys.* **2002,** 117, 719-726.

2. Wang, W. C.; Shigeto, S. Infrared Electroabsorption Spectroscopy of N,N-Dimethyl-p-nitroaniline in Acetonitrile/C2Cl4: Solvation of the Solute and Self-Association of Acetonitrile. *J. Phys. Chem. A* **2011,** 115, 4448-4456.

3. Kimura, Y.; Hamamoto, T.; Terazima, M. Raman spectroscopic study on the solvation of N,N-Dimethyl-p-nitroaniline in room-temperature ionic liquids. *J. Phys. Chem. A* **2007,** 111, 7081-7089.

4. Szostak, M. M. A polarized infrared and Raman spectroscopic study of the electrooptic crystal m-nitroaniline. I—assignments of internal vibrations. *J. Raman Spectrosc.* **1979,** 8, 43-49.

5. Szostak, M. M. Vibronic couplings in vibrational spectra and nonlinear electrooptic properties of meta-nitroaniline crystal. *Chem. Phys.* **1988,** 121, 449-456.

6. Bhuvaneswari, G.; Prabavathi, N.; Guru, P. L. Crystal growth, experimental, and theoretical investigation of organic NLO material n,n-dimethyl-4-nitroaniline. *Int. J. Curr. Adv. Res.* **2018,** 7, 16442-16448.

7. Okwieka, U.; Szostak, M. M.; Misiaszek, T.; Turowska-Tyrk, I.; Natkaniec, I.; Pavlukojć, A. Spectroscopic, structural and theoretical studies of 2-methyl-4-nitroaniline (MNA) crystal. Electronic transitions in IR. *J. Raman Spectrosc.* **2008,** 39, 849-862.

8. Wasanasuk, K.; Tashiro, K.; Hanesaka, M.; Ohhara, T.; Kurihara, K.; Kuroki, R.; Tamada, T.; Ozeki, T.; Kanamoto, T. Crystal Structure Analysis of Poly(l-lactic Acid) α Form On the basis of the 2-Dimensional Wide-Angle Synchrotron X-ray and Neutron Diffraction Measurements. *Macromolecules* **2011,** 44, 6441-6452.

9. Hammond, C., *The Basics of Crystallography and Diffraction, Third Edition*. International Union of Crystallography Texts on Crystallography.

10. Esteves, G.; Ramos, K.; Fancher, C. M.; Jones, J. L. *LIPRAS: Line-Profile Analysis Software*, 2017.