

# Supporting Information

## **Outstanding Transparency/Nonlinearity Tradeoff In Strongly Nonlinear, UV Absorbing Zwitterionic Pyridinium-Tetrazolate. Synthesis, Electrochemical, Thermal and Single Crystal X-Ray Structural Characterization**

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- 1. Materials Synthesis, including crystal growing.**
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## 1. Materials Synthesis including crystal growing.

**General Procedures.**  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded using a Bruker AMX-500 spectrometer operating at 500 and 125.70 MHz, respectively. Coupling constants are presented in Hz. Absorption spectrometry was performed using a Jasco V570 spectrophotometer. Microwave enhanced reactions were performed in a CEM discover focused oven. All chemicals and solvents were purchased from Sigma-Aldrich Chemicals. Anhydrous DMF,  $\text{CH}_3\text{CN}$ , THF and 1,4-dioxane were used without further purification. Water and MeOH were HPLC grade solvents and were used without further purification. Piperidine and  $\text{CHCl}_3$  were dried over  $\text{MgSO}_4$  overnight and distilled immediately prior to their use.

Derivative 4-(1H-tetrazol-5-yl)pyridine (**2**) was prepared according to literature procedure.<sup>1</sup>

**1-methyl-4-(tetrazole-5-ate)pyridinium 1.** A suspension of derivative **2** (238 mg, 1.62 mmol) and anhydrous  $\text{K}_2\text{CO}_3$  (112 mg, 0.81 mmol) in MeOH (3 ml) was warmed at 40 °C and stirred till complete dissolution of the precipitate.  $\text{CH}_3\text{I}$  (312 mg, 2.20 mmol) was added to the colorless solution and the reaction mixture was heated under microwave irradiation at 130 °C for 90 min at a maximum irradiation power of 80 W. After the irradiation, the mixture was slowly cooled without removing the septum observing the slow precipitation of a light brown solid (flakes). After 4 h at room temperature, the brown precipitate was filtered under reduced pressure to give a light brown crystalline powder that was washed on the filter with 10 ml of MeOH (180 mg, 1.13 mmol, yield 70%). At this stage the product is already analytically pure and can be directly employed for optical characterization.

**Crystal growth.** The powder (100 mg) was suspended in 3 ml of fresh MeOH in a sealed tube. The suspension was heated under microwave irradiation at 130 °C for 3 min to give a colorless solution. The sealed tube was transferred in a bath of warm water (around 80°C) and the temperature was allowed to slowly equilibrate. After 10 h, the large off white crystals formed were removed with a spatula and submitted to X-ray characterization.  $^1\text{H}$  NMR ( $\text{D}_2\text{O}$ )  $\delta$  (ppm) 8.62 (2H, d,  $J = 6.66$ ), 8.20 (2H, d,  $J = 6.78$ ), 4.28 (3H, s). M.p. 238-239 °C. Anal. Calcd for  $\text{C}_7\text{H}_7\text{N}_5$ : C, 52.17 %; H, 4.38 %; N, 43.45 %. Found: C, 51.89 %; H, 4.53 %; N, 43.05 %.

**1-(2-ethylhexyl)-4-(tetrazole-5-ate)pyridinium 3.** A suspension of derivative **2** (500 mg, 3.40 mmol) and anhydrous  $K_2CO_3$  (235 mg, 1.70 mmol) in MeOH (4 ml) was warmed at 40 °C and stirred till complete dissolution of the precipitate. 2-ethylhexyl bromide (676 mg, 3.50 mmol) was added to the colorless solution and the reaction mixture was heated under microwave irradiation at 120 °C for 120 min at a maximum irradiation power of 80 W to give a brown suspension. The white precipitate, mainly KBr, was filtered and the resulting brown filtrate was evaporated to give a brownish oil. The oil was first washed with 10 ml of hexane and than sonicated in 10 ml of deionized water. The supernatant was discarded and the residue was taken up with iPrOH (20 ml). Slow evaporation at ambient temperature afforded the pure compound as off white crystals (176 mg, 0.68 mmol, 20 % yield).  $^1H$  NMR ( $CDCl_3$ )  $\delta$  8.41 (2H, d,  $J = 6.65$ ), 8.11 (2H, d,  $J = 6.72$ ), 4.45 (2H, t,  $J = 7.14$ ), 1.45-0.80 (15H, m). M.p. 205-206 °C. Anal. Calcd for  $C_{14}H_{21}N_5$ : C, 64.84 %; H, 8.16 %; N, 27.00 %. Calcd.  $C_{14}H_{21}N_5 \cdot 1/3 H_2O$ : C, 63.37; H, 8.23; N, 26.39. Found: C, 63.87 %; H, 7.95 %; N, 25.96 %.

## 2. Crystal Structure Determination Data for 1.

Cif file is attached to the present submission. The following paragraph reports relevant experimental information about the structure acquisition and relevant bond distances and angles.

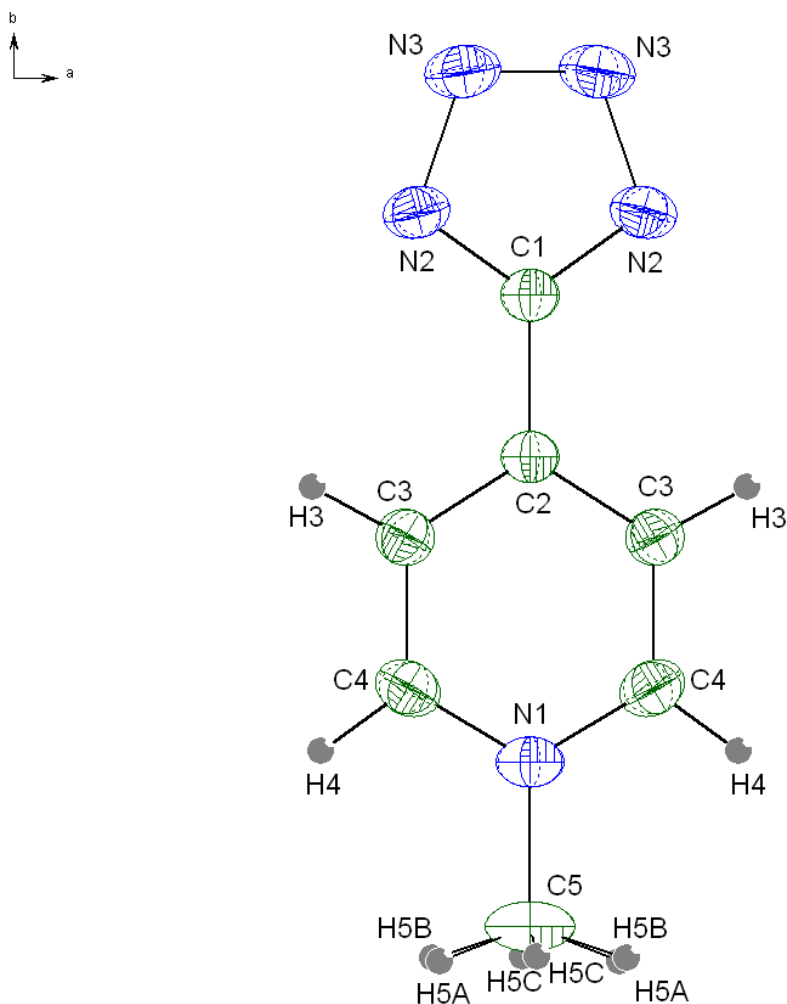


Figure S1. ORTEP plot of LB-ZW-01 at 298 K, with atom numbering scheme. Ellipsoids at 30% probability level

Sample description: Transparent light brown cristal. Dimensions: 0.25 x 0.15 x 0.15 mm.

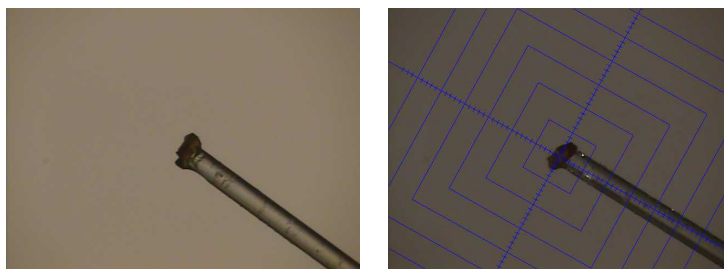


Figure S2. Picture of the single crystal of **1**.

Instrument: Bruker AXS Smart APEX

Source: normal focus sealed tube

Detector: CCD

Temperature: RT

Wavelength: Mo K $\alpha$  (0.71073 Å), graphite monochromator

Parameters: detector-sample distance: 50 mm,  $\omega$ -scan,  $2\theta = -30$  deg,  $-30$  deg  $<\omega < -210$  deg,  $\Delta\omega = 0.5$  deg,  $t / \text{frame} = 40$  s, 4 runs ( $\phi = 0, 90, 180, 270$  deg).

Measurement units: Å (estimated standard deviation, esd, under brackets)

_cell_length_a	10.5257(10)
_cell_length_b	10.8919(11)
_cell_length_c	7.0298(7)
_cell_angle_alpha	90.00
_cell_angle_beta	108.360(2)
_cell_angle_gamma	90.00
_cell_volume	764.91(13)
_cell_formula_units_Z	4
_cell_measurement_temperature	293(2)

**Space group : Monoclinic C2/c (No. 15)**

\_symmetry\_equiv\_pos\_as\_xyz

'x, y, z'

'-x, y, -z+1/2'

'x+1/2, y+1/2, z'

'-x+1/2, y+1/2, -z+1/2'

'-x, -y, -z'

'x, -y, z-1/2'

'-x+1/2, -y+1/2, -z'

'x+1/2, -y+1/2, z-1/2'

\_diffn\_reflms\_number 4877  
\_diffn\_reflms\_limit\_h\_min -13  
\_diffn\_reflms\_limit\_h\_max 13  
\_diffn\_reflms\_limit\_k\_min -14  
\_diffn\_reflms\_limit\_k\_max 14  
\_diffn\_reflms\_limit\_l\_min -9  
\_diffn\_reflms\_limit\_l\_max 9  
\_diffn\_reflms\_theta\_min 2.77  
\_diffn\_reflms\_theta\_max 27.51  
\_reflms\_number\_total 878  
\_reflms\_number\_gt 623  
\_reflms\_threshold\_expression >2sigma(I)

\_refine\_ls\_R\_factor\_all 0.0596  
\_refine\_ls\_R\_factor\_gt 0.0364  
\_refine\_ls\_wR\_factor\_ref 0.0950  
\_refine\_ls\_wR\_factor\_gt 0.0831  
\_refine\_ls\_goodness\_of\_fit\_ref 1.076

\_refine\_ls\_restrained\_S\_all 1.076  
\_refine\_ls\_shift/su\_max 0.012  
\_refine\_ls\_shift/su\_mean 0.001

**Fractionary coordinates (x,y,z) (esd under brackets):**

C1 C 0.5000 0.12982(16) 0.2500  
C2 C 0.5000 -0.00380(16) 0.2500  
C3 C 0.61306(14) -0.07005(13) 0.2516(2)  
C4 C 0.61061(15) -0.19554(14) 0.2507(2)  
C5 C 0.5000 -0.3921(2) 0.2500 0.0754(8)  
N1 N 0.5000 -0.25650(14) 0.2500 0.0531(5)  
N2 N 0.39713(12) 0.19817(11) 0.25869(18)  
N3 N 0.43879(13) 0.31422(11) 0.2553(2)  
H3 H 0.6960(16) -0.0286(12) 0.254(2)  
H4 H 0.6885(16) -0.2474(14) 0.250(2) 0.073(5)  
H5A H 0.582(4) -0.421(3) 0.206(8) 0.078(11)  
H5B H 0.411(4) -0.419(3) 0.141(7) 0.071(10)  
H5C H 0.507(6) -0.417(3) 0.388(6) 0.077(11)

**Geometry:**

**Selected bond distances:**

C1 N2 1.3312(14)  
C1 C2 1.455(2)  
C2 C3 1.3887(17)  
C3 C4 1.367(2)  
C3 H3 0.978(15)  
C4 N1 1.3390(17)

C4 H4 0.997(17)  
C5 N1 1.477(3)  
C5 H5A 1.05(4)  
C5 H5B 1.04(4)  
C5 H5C 0.98(4)  
N2 N3 1.3406(17)

### Selected bond angles

N2 C1 N2 111.99(16) . 2\_655  
N2 C1 C2 124.01(8)  
C3 C2 C3 117.39(18) 2\_655  
C3 C2 C1 121.30(9)  
C4 C3 C2 120.31(14)  
C4 C3 H3 118.5(8)  
C2 C3 H3 121.2(8)  
N1 C4 C3 120.73(14)  
N1 C4 H4 115.8(9)  
C3 C4 H4 123.5(9)  
N1 C5 H5A 107.4(19)  
N1 C5 H5B 106.0(18)  
H5A C5 H5B 109(2)  
N1 C5 H5C 106(2)  
H5A C5 H5C 113(2)  
H5B C5 H5C 115(2)  
C4 N1 C4 120.54(17) . 2\_655  
C4 N1 C5 119.73(9)  
C1 N2 N3 104.55(12)  
N3 N3 N2 109.46(7) 2\_655



### Selected torsion angles

N2 C1 C2 C3 -176.48(9)

N2 C1 C2 C3 3.52(9) 2\_655

C3 C2 C3 C4 0.28(10) 2\_655

C1 C2 C3 C4 -179.72(10)

C2 C3 C4 N1 -0.6(2)

C3 C4 N1 C4 0.29(10) ... 2\_655

C3 C4 N1 C5 -179.71(10)

N2 C1 N2 N3 -0.04(7) 2\_655

C2 C1 N2 N3 179.96(7)

C1 N2 N3 N3 0.10(18) ... 2\_655

### 3. TGA-DSC traces for Derivative 1

DSC-TGA traces were acquired on a Mettler-Toledo instrument under ambient atmosphere.

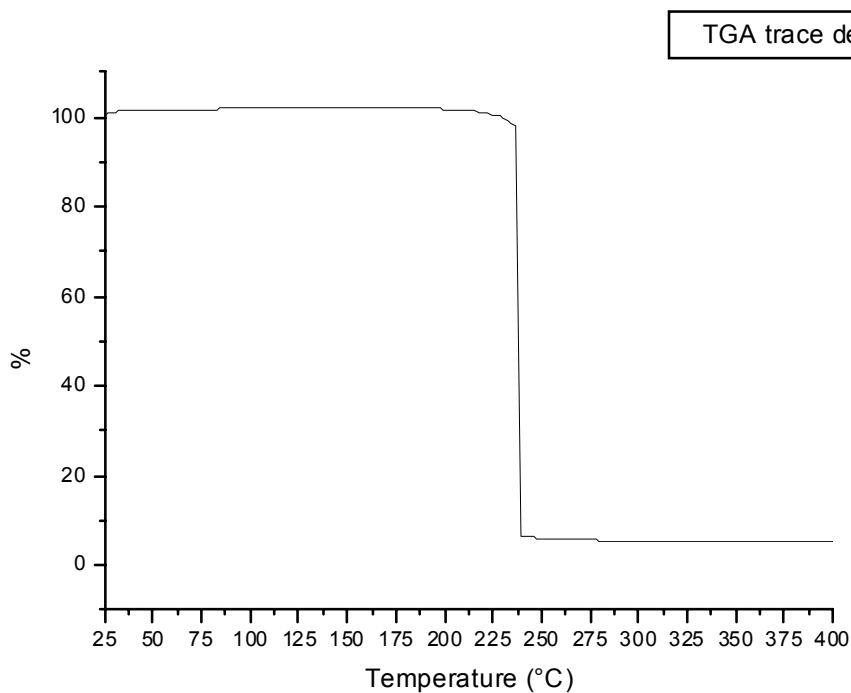


Figure S3. TGA trace for derivative 1.

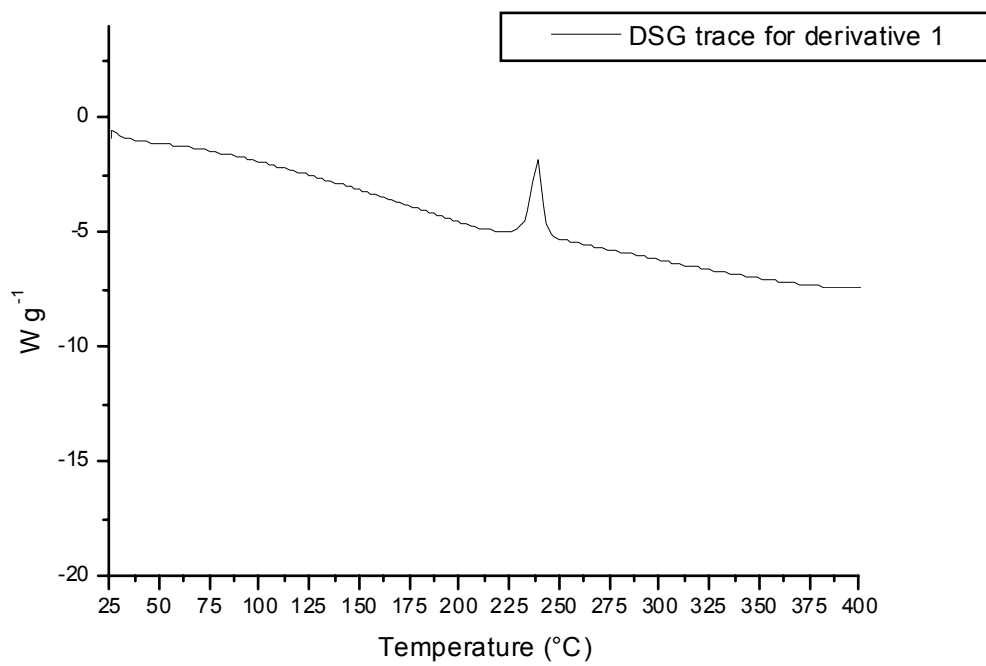


Figure S4. DSC trace for derivative 1.

#### 4. Electrochemical characterization of **1**.

For the electrochemical characterization derivative **1** was dissolved (concentration about  $10^{-4}$  M) in the supporting electrolyte that was a 0.1 M solution of tetrabutylammonium *p*-toluenesulfonate (Fluka, electrochemical grade,  $\geq 99.0\%$ ) in anhydrous acetonitrile (Aldrich, 99.8%). Cyclic Voltammeteries at scan rate of 100 mV/s were carried out using a PARSTA2273 potentiostat in a single chamber three electrodes electrochemical cell in a glove box filled with Argon ( $[O_2] \leq 1$  ppm). The working, counter and pseudo-reference electrodes were a Glassy Carbon (GC) disc, a Pt flag, and a Ag/AgCl wire, respectively. The GC disc was well polished with alumina 0.1  $\mu\text{m}$  suspension, sonicated for 15 min. in deionized water and washed with 2-propanol before using. The Ag/AgCl pseudo-reference electrode was calibrated before and after each measurement using a 1 mM ferrocene solution in the electrolyte, no more than 5 mV in difference was observed between two successive calibrations.

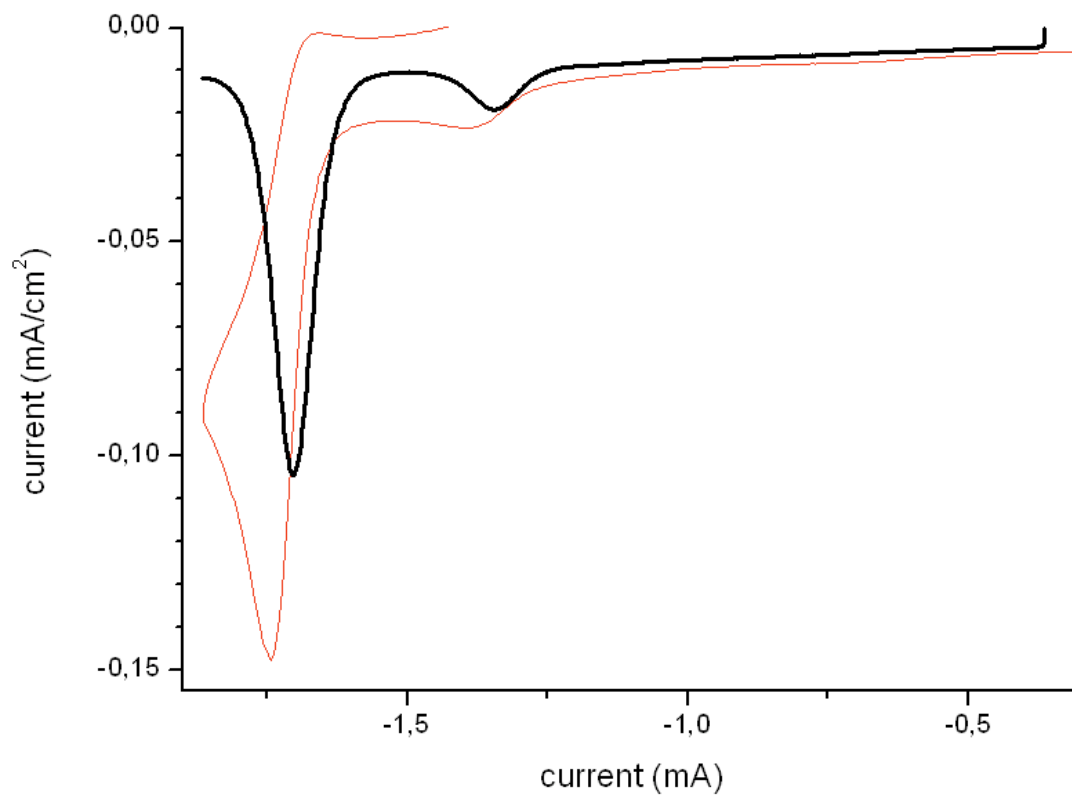


Figure S5. Cyclic Voltammetry (red curve) and Differential Pulse Voltammetry (black) curves for a 0.1 M solution of tetrabutylammonium *p*-toluenesulfonate in CH<sub>3</sub>CN of derivative **1**.

### 5. Details of the second order nonlinear optical characterization of **3**.

The second order nonlinear optical (NLO) properties of **3** were determined in liquid solution by the direct current electric-field-induced second harmonic (EFISH) generation method,<sup>2-4</sup> which can provide  $\gamma_{\text{EFISH}}$ , that is, the direct information on the molecular NLO properties, through eq 1:

$$\gamma_{\text{EFISH}} = \frac{\mu\beta}{5kT} + \gamma_0(-2\omega, \omega, \omega, 0) \quad (\text{eq.1})$$

where  $\frac{\mu\beta}{5kT}$  is the dipolar orientational contribution, being  $\beta_\lambda$  the projection along the dipole moment axis of the vectorial component  $\beta_{\text{VEC}}$  of the quadratic hyperpolarizability tensor,  $\mu$  is the static dipole moment,  $\omega$  is the fundamental wavelength of the incident photon, and  $\gamma_0(-2\omega; \omega, \omega, 0)$ , a third-order term at frequency  $\omega$  of the incident light, is the cubic electronic contribution to  $\gamma_{\text{EFISH}}$ . The values of  $\mu\beta_\lambda$  have been directly obtained from the EFISH measurements considering negligible the  $\gamma_0$  contribution to  $\gamma_{\text{EFISH}}$ . The EFISH measurements of sample **3** were carried out in DMF solutions at the same concentration ( $10^{-3}\text{M}$ ) working at a nonresonant incident wavelength of  $1.907 \mu\text{m}$ , using a Q-switched, mode-locked Nd<sup>3+</sup>:YAG laser, equipped with a Raman shifter. All experimental EFISH  $\beta_\lambda$  values are defined according to the "phenomenological" convention.<sup>5</sup>

## 6. References for the Supporting Information.

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<sup>1</sup> McManus, J. M.; Herbst, Robert M. Tetrazole analogs of pyridinecarboxylic acids. *Journal of Organic Chemistry* (1959), **24**, 1462-4.

<sup>2</sup> K. D. Singer and A. F. Garito, *J. Chem. Phys.*, 1981, **75**, 3572-3580.

<sup>3</sup> B. F. Levine and C. G. Bethea, *Appl. Phys. Lett.*, 1974, **24**, 445-447.

<sup>4</sup> I. Ledoux and J. Zyss, *Chem. Phys.*, 1982, **73**, 203-213.

<sup>5</sup> A. Willetts, J. E. Rice, D. M. Burland and D. P. Shelton, *J. Chem. Phys.*, 1992, **97**, 7590-7599.