



## The synthesis of chiral, cationic nonlinear optical dyes based on the 1,1'-binaphthalenyl unit

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### ABSTRACT

The *R* enantiomers of three, novel, 2D dipolar cations with 2,2'-bis(dimethylamino)-1,1'-binaphthalenyl electron donor groups connected to *N*-*R*-pyridinium acceptors were synthesised. The compounds displayed intense intramolecular charge-transfer bands in the visible region, the maximal energy of which decreased as *R* changed in the order Me > 2,4-dinitrophenyl > 2-pyrimidyl. Molecular quadratic nonlinear optical responses were determined for the chloride salts in methanol using femtosecond, hyper-Rayleigh scattering with 1300 and 800 nm lasers. The measured first hyperpolarizabilities  $\beta_{\text{HRS}}$  were in the range  $34\text{--}155 \times 10^{-30}$  esu and increased at both wavelengths, showing the expected inverse relationship with respect to the charge-transfer energies. Single crystal X-ray structures were determined for the precursor compounds (*R*)-6,6'-dibromo-2,2'-bis(dimethylamino)-1,1'-binaphthalenyl and (*R*)-2,2'-bis(dimethylamino)-1,1'-binaphthalenyl-6,6'-dicarbaldehyde, revealing an average dihedral angle between the naphthalenyl units of 73°. Making the assumption that this angle was similar to that found in the chromophores studies in solution allowed the determination of two independent tensor components,  $\beta_{\text{zzz}}$  and  $\beta_{\text{zxx}}$ . For these molecules the greatest proportion of the total first hyperpolarizability lay along the charge-transfer axis ( $\beta_{\text{zzz}}$ ), but the “off-diagonal”  $\beta_{\text{zxx}}$  values were still substantial ( $31\text{--}141 \times 10^{-30}$  esu) and larger when compared with those determined by hyper-Rayleigh scattering for other 2D dipoles in the literature.

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### 1. Introduction

There is continued interest in the synthesis and study of molecular nonlinear optical (NLO) materials, primarily inspired by various potential applications such as optical data processing and biological imaging [1]. Although most organic NLO compounds are charge neutral, salts are especially promising due to their often high stabilities and synthetic tailorability. By varying the counterion accompanying an active charged chromophore, it is possible to modify crystal packing arrangements to produce polar structures showing bulk quadratic NLO effects such as second harmonic generation (SHG) and electro-optic (EO) behaviour. Much attention has focused on stilbazolium species, especially (*E*)-4'-(dimethylamino)-*N*-methyl-4-stilbazolium tosylate (DAST) [2] and closely related compounds [3]. Because of their large EO coefficients, such materials are useful for terahertz (THz) wave generation via nonlinear frequency mixing, of relevance to a range of applications

including security scanning, biomedical analysis and space communications [4].

One approach to producing polar materials with some degree of control is to incorporate chirality into either the active chromophore or the accompanying ions if the compound is a salt. Resolved chiral species must inevitably crystallise noncentrosymmetrically, although it is noteworthy that this does not guarantee that the molecular dipoles will align favourably. This strategy has been adopted successfully with stilbazolium compounds by Andreu et al. who produced a chromophore bearing a 2-(methoxymethyl)pyrrolidinyl substituent which packs in the space group  $P2_1$  and gives a large powder SHG response of 80 times a urea standard (measured using a 1907 nm laser) [5]. The 1,1'-binaphthalenyl unit is a convenient chiral motif that has been incorporated into various neutral NLO compounds [6], including polymeric materials [6f–k] and also some charged organometallic species [7]. Very recently, Yan et al. reported a dicationic 1,1'-binaphthalenyl chromophore for use as a probe for imaging cell membranes via resonance-enhanced SHG [8], although the molecular-level NLO properties of this species were not described. Previous studies in our laboratory have shown that the static first hyperpolarizabilities  $\beta_0$  (the origin of quadratic NLO effects) of stilbazolium

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and related chromophores can be increased considerably by replacing the commonly used *N*-alkylpyridinium electron acceptors with *N*-aryl units [9]. This work has produced two new materials showing powder SHG activities similar to that of DAST (ca. 500 times urea at 1907 nm) [9a,c]. In addition, large single crystals of the compound (*E*)-4'-(dimethylamino)-*N*-phenyl-4-stilbazolium hexafluorophosphate (DAPSH) show a record non-resonant bulk NLO coefficient  $d_{111}$  of 290 pm V<sup>-1</sup> at 1907 nm [10]. In this report, we disclose preliminary investigations into the synthesis of 1,1'-binaphthalenyl derivatives containing *N*-arylpyridinium groups and their study by using the hyper-Rayleigh scattering (HRS) technique [11].

## 2. Experimental

### 2.1. Materials and procedures

The compound (*R*)-6,6'-dibromo-1,1'-binaphthalenyl-2,2'-diamine (**1**) was prepared according to a published procedure [8]. Tetrahydrofuran was dried over sodium and triethylamine was dried over CaH<sub>2</sub>, and both were freshly distilled before use. 4-Vinylpyridine was obtained commercially and fractionally distilled prior to use. All other reagents were obtained commercially and used as supplied. Products were dried overnight at room temperature in a vacuum desiccator (CaSO<sub>4</sub>) prior to characterisation.

### 2.2. General physical measurements

<sup>1</sup>H NMR spectra were recorded on an Inova 400 (compounds **2** and **3**) or a Bruker UltraShield 500 (all other compounds) spectrometer and all shifts are quoted with respect to TMS. The fine splitting of aryl ring AA'/BB' patterns is ignored and the signals are reported as simple doublets, with *J* values referring to the two most intense peaks. Elemental analyses were performed by the Micro-analytical Laboratory, University of Manchester. IR spectra were obtained as KBr discs with an ATI Mattson Genesis Series FTIR instrument, and mass spectra were measured using +electrospray on a Micromass Platform II spectrometer with acetonitrile as the solvent.

### 2.3. Synthesis

#### 2.3.1. (*R*)-6,6'-Dibromo-2,2'-bis(dimethylamino)-1,1'-binaphthalenyl, **2**

To 20% aqueous H<sub>2</sub>SO<sub>4</sub> (0.65 mL) and 40% aqueous formaldehyde (0.35 mL) in THF (1 mL) at 0 °C were added simultaneously a solution of **1** (150 mg, 0.339 mmol) in THF (8 mL) and NaBH<sub>4</sub> (188 mg, 4.97 mmol). Once the addition was complete, the solution was allowed to warm to room temperature and stirred for 70 min. It was then poured into 2% aqueous KOH (32 mL), and the organic layer was extracted with ethyl acetate and dried (MgSO<sub>4</sub>). The extracts were combined and concentrated under reduced pressure to afford a yellow-brown solid (170 mg). This material was purified by using column chromatography on silica gel with 99:1 *n*-hexane/ethyl acetate as the eluant. The first fraction was collected and evaporated to dryness under reduced pressure to afford a yellow powder. Yield 86 mg (51%).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 7.95 (d, 2H, *J* = 2.2 Hz, C<sub>10</sub>H<sub>5</sub>), 7.77 (d, 2H, *J* = 9.2 Hz, C<sub>10</sub>H<sub>5</sub>), 7.45 (d, 2H, *J* = 8.8 Hz, C<sub>10</sub>H<sub>5</sub>), 7.23 (dd, 2H, *J* = 9.1, 1.9 Hz, C<sub>10</sub>H<sub>5</sub>), 6.98 (d, 2H, *J* = 9.2 Hz, C<sub>10</sub>H<sub>5</sub>), 2.47 (s, 12H, Me). *m/z* = 499 ([C<sub>24</sub>H<sub>22</sub>Br<sup>79</sup>Br<sup>81</sup>N<sub>2</sub> + H]<sup>+</sup>), 497 ([C<sub>24</sub>H<sub>22</sub>Br<sup>79</sup>Br<sup>79</sup>N<sub>2</sub> + H]<sup>+</sup>), 501 ([C<sub>24</sub>H<sub>22</sub>Br<sup>81</sup>Br<sup>81</sup>N<sub>2</sub> + H]<sup>+</sup>). Anal. Calcd (%) for C<sub>24</sub>H<sub>22</sub>Br<sub>2</sub>N<sub>2</sub>: C, 57.85; H, 4.45; N, 5.62. Found: C, 57.78; H, 4.46; N, 5.47. Diffraction-quality crystals were grown by slow evaporation of a 99:1 *n*-hexane/ethyl acetate solution.

#### 2.3.2. (*R*)-2,2'-Bis(dimethylamino)-1,1'-binaphthalenyl-6,6'-dicarbaldehyde, **3**

To a solution of **2** (200 mg, 0.401 mmol) in dry THF (15 mL) under an argon atmosphere was added dropwise *n*-butyllithium (1.6 M in hexanes; 0.8 mL, 1.28 mmol) at -78 °C; the pale yellow solution turned deep red and then green-yellow and was stirred for 40 min at -78 °C. Dry DMF (0.3 mL, 3.87 mmol) was added dropwise at -78 °C and the reaction stirred for 10 min, then the solution was allowed to warm to room temperature and stirred for a further 3 h. The orange solution was poured into water (20 mL) and the organic layer extracted with ethyl acetate and dried (MgSO<sub>4</sub>). The extracts were combined and concentrated under reduced pressure to afford a yellow solid (150 mg). Purification was effected by using column chromatography on silica gel with 7:3 *n*-hexane/ethyl acetate as the eluant. The first fraction was collected and evaporated to dryness under reduced pressure to afford a yellow powder. Yield 90 mg (55%).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 10.07 (s, 2H, CHO), 8.29 (s, 2H, C<sub>10</sub>H<sub>5</sub>), 8.00 (d, 2H, *J* = 8.9 Hz, C<sub>10</sub>H<sub>5</sub>), 7.65 (d, 2H, *J* = 8.9 Hz, C<sub>10</sub>H<sub>5</sub>), 7.46 (d, 2H, *J* = 9.2 Hz, C<sub>10</sub>H<sub>5</sub>), 7.22 (d, 2H, *J* = 8.8 Hz, C<sub>10</sub>H<sub>5</sub>), 2.55 (s, 12H, Me). *m/z* = 419 ([M + Na]<sup>+</sup>).  $\nu$ (C=O) 1668 s cm<sup>-1</sup>. Anal. Calcd (%) for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>•0.7H<sub>2</sub>O: C, 76.33; H, 6.26; N, 6.85. Found: C, 76.32; H, 5.95; N, 6.67. Diffraction-quality crystals were grown by vapour diffusion of *n*-hexane into an ethyl acetate solution.

#### 2.3.3. (*R*)-6,6'-Bis-((*E*)-2-(pyridin-4-yl)vinyl)-2,2'-bis(dimethylamino)-1,1'-binaphthalenyl, **4**

Working in a glove box, **2** (120 mg, 0.241 mmol), Pd(OAc)<sub>2</sub> (72 mg, 0.321 mmol) and tri-*ortho*-tolylphosphine (146 mg, 0.480 mmol) were placed in a sealed pressure vessel. To this mixture was added triethylamine (5 mL) and 4-vinylpyridine (1.65 mL, 15.4 mmol) and the vessel was sealed tightly. The reaction was stirred at 110 °C for 16 h; initially the colour changed from pale yellow to bright orange, and the solution was then allowed to cool to room temperature. The Pd black formed was removed using a short column on silica gel with 1:1 dichloromethane/methanol as the eluant, and the solvents were evaporated to give a red oily solid. This material was further purified using column chromatography on silica gel with ethyl acetate as the eluant to give separation and then 1:1 ethyl acetate/methanol to bring off the product. The first major orange band was collected and evaporated to dryness under reduced pressure. Further purification was achieved by vapour diffusion of *n*-pentane into a chloroform solution, affording a yellow microcrystalline solid. Yield: 70 mg (50%).  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 8.56 (d, 4H, *J* = 6.0 Hz, C<sub>5</sub>H<sub>4</sub>N), 7.90–7.88 (4H, C<sub>10</sub>H<sub>5</sub>), 7.47–7.36 (6H, CH and C<sub>10</sub>H<sub>5</sub>), 7.37 (d, 4H, *J* = 6.0 Hz, C<sub>5</sub>H<sub>4</sub>N), 7.19 (d, 2H, *J* = 9.1 Hz, C<sub>10</sub>H<sub>5</sub>), 7.02 (d, 2H, *J* = 16.1 Hz, CH), 2.52 (s, 12H, Me). *m/z* = 548 ([M + H]<sup>+</sup>). Anal. Calcd (%) for C<sub>38</sub>H<sub>34</sub>N<sub>4</sub>•1/3CHCl<sub>3</sub>: C, 78.50; H, 5.90; N, 9.55. Found: C, 78.69; H, 6.13; N, 9.57. After heating for 24 h under vacuum: Anal. Calcd (%) for C<sub>38</sub>H<sub>34</sub>N<sub>4</sub>•1/5CHCl<sub>3</sub>: C, 80.41; H, 6.04; N, 9.82. Found: C, 80.74; H, 5.84; N, 9.71. After heating for a further 3 d under vacuum: Anal. Calcd (%) for C<sub>38</sub>H<sub>34</sub>N<sub>4</sub>•1/8CHCl<sub>3</sub>: C, 81.53; H, 6.12; N, 9.98. Found: C, 81.62; H, 5.63; N, 9.92.

#### 2.3.4. (*R*)-6,6'-Bis-((*E*)-2-(1-methylpyridin-4-yl)vinyl)-2,2'-bis(dimethylamino)-1,1'-binaphthalenyl iodide, [**5**]<sub>2</sub>

To a solution of **4**•1/8CHCl<sub>3</sub> (41 mg, 0.073 mmol) in acetone (12 mL) was added MeI (0.01 mL). The reaction was heated under reflux in the dark for 4 h, and a red precipitate began to form after 1 h. After cooling to room temperature, the solid was filtered off, washed with diethyl ether and dried. Yield: 52 mg (79%).  $\delta_{\text{H}}$  (CD<sub>3</sub>OD) 8.67 (d, 4H, *J* = 7.1 Hz, C<sub>5</sub>H<sub>4</sub>N), 8.15–8.13 (6H, C<sub>5</sub>H<sub>4</sub>N and C<sub>10</sub>H<sub>5</sub>), 8.07 (d, 2H, *J* = 16.1 Hz, CH), 8.01 (d, 2H, *J* = 8.8 Hz, C<sub>10</sub>H<sub>5</sub>), 7.64 (dd, 2H, *J* = 9.0, 2.0 Hz, C<sub>10</sub>H<sub>5</sub>), 7.57 (d, 2H, *J* = 9.1 Hz, C<sub>10</sub>H<sub>5</sub>), 7.41 (d, 2H, *J* = 15.9 Hz, CH), 7.17 (d, 2H, *J* = 8.8 Hz, C<sub>10</sub>H<sub>5</sub>), 4.30 (s, 6H, N<sup>+</sup>-Me), 2.56 (s, 12H, Me). *m/z* = 288 ([M - 2I]<sup>2+</sup>). Anal. Calcd

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