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SUPPORTING INFORMATION

Bent-core liquid crystals in the route to efficient organic nonlinear optical materials

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1. Experimental techniques.

NMR experiments were performed on Bruker ARX-300 MHz and a Bruker AV-400 MHz Avance spectrometer. Infrared spectra for all the compounds were obtained using of either a Mattson Genesis II FTIR or a Nicolet Avatar 360 (FTIR) spectrophotometer in the 400-4000 cm^{-1} spectral range. Microanalyses were performed with a Perkin-Elmer 2400 microanalyser. Mass spectrometry performed with a Microflex (MALDI-ToF). UV-Vis measurements were taken using an ATI Unicam UV4 spectrophotometer.

Mesomorphic properties were studied by optical microscopy using an Olympus BH2 microscope with crossed polarizers. The microscope was connected to a Linkam THMS 600 hot stage and an

Olympus DP-12 camera. Transition temperatures were determined by differential scanning calorimetry (DSC) using either a TA2910 differential calorimeter or a DSC Q20 or Q2000 calorimeter of TA Instruments. Each apparatus was calibrated with indium (156.6 °C, 28.44 J/g) and tin (232.1 °C, 60.5 J/g) using a scanning rate of 10 °C/min in most cases.

X-ray diagrams on non-oriented samples were carried out with a powder diffractometer equipped with a high-temperature attachment. Measurements were performed in Debye-Scherrer operation mode using Lindemann capillaries of diameter 0.6 mm. The materials were introduced in the isotropic phase into the capillaries. A linear position-sensitive detector, with an angular resolution better than 0.01º, was employed to detect the diffracted intensity in the 2θ interval 0º - 30º (θ is the diffraction angle). Monochromatic CuKα_1 radiation (λ=1.5406 Å) was used.

Homemade cells were designed for SHG measurements with in-plane electrodes for alignment purposes, using gaps between electrodes of about 100 μm. The measurements were performed with an experimental set-up described in detail elsewhere.[1] For the measurements at 1064 nm we used a Q-switched Nd-YAG laser with a pulse width of 6 ns and a frequency of 5 Hz. For the experiments at 1600 nm a Ti:Sapphire oscillator–regenerative amplifier laser system (Coherent) was used. A portion of the amplifier output drove an optical parametric amplifier (OPA) tunable in the 300-2600 nm range. In both cases a square-wave electric field (20 Hz, 7 V/μm) synchronized with the laser pulse was applied to polarize the material at the gap. The field strength was checked to be enough to saturate the SH signal.

The quadratic non linear response of compounds **A-E** in dichloromethane solution was accomplished by the electric field induced second harmonic (EFISH) technique. This experiment gives the scalar product $\mu\beta$ (β is the vector part of the first hyperpolarizability tensor and μ is the dipole moment). The excitation wavelength was 1907 nm to minimize absorption effects. This fundamental wavelength was obtained from a hydrogen Raman shifter pumped by the 1064 nm light from a Q-switched Nd:YAG laser (10 pps, 8 ns/pulse).

The vertically polarised fundamental beam was split in two (intensity ratio 10/1). The most intense was focused into the wedge shaped EFISH liquid cell. The other was directed to a NPP (N-(4-Nitrophenyl)-L-prolinol) powder sample whose second harmonic signal is used to correct for laser fluctuations. The voltage applied to the electrodes (2mm apart) across the liquid sample cell was 4.5 kV. The SH light from the sample and the NPP reference was detected with two photomultipliers (Hamamatsu R406), with suitable interference filters to remove the residual excitation light beyond the liquid cell and the NPP reference. From the intensity of the detected second harmonic light (Maker Fringes) $\mu\beta$ is determined. At least, two different concentrations (from $1x10^{-3}$ M to $5x10^{-3}$ M) of every compound have been measured several times. In the case of compound C the concentration had to be raised up to 10^{-2} M due to its low NLO response. Under the same experimental conditions $\mu\beta_0$ = $480x10^{-48}$ esu was obtained for azo dye DR1, being this value quite similar to the reported one by Dirk et al.[2]

2. Synthetic procedure.

The synthetic procedures for the bent-core compounds **A** and **B** are shown in **Scheme 1** and **Scheme 2** respectively. In case of intermediate compounds **5**[3] and **8**[4], the synthetic procedures were adapted from the methods described in literature. Commercial chemicals (reagent grade) were purchased from Aldrich Chemical Co., Fluka or Panreac and used without further purification. Solvents were purified and dried by standard techniques.

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[1] Pereda, N., Folcia, C.L., Etxebarria, J., Ortega, J., Ros, M. B. *Liq. Cryst.* **1998,** *24*, 451

[2] Dirk, C. W., Katz, H. E., Schilling, M. L., King, L. A., *Chem. Mater*. **1990**, *2*, 700-705

[3] Gimeno, N., Ros, M. B., Serrano, J. L., de la Fuente, M. R. *Angew. Chem.-Int. Edit.* **2004**, *43*, 5235.

[4] Shen, D., Pegenau, A., Diele, S., Wirth, I., Tschierske, C., *J. Am. Chem. Soc.* **2000**, *122*, 1593.

Work-up with azo-compounds were carried out under light filters and red light to prevent their photoisomerization in solution.

• ***4-aminobenzaldehyde (1)***

4-acetamidobenzaldehyde (7.0 g, 42.9 mmol) was dissolved in methanol (140 mL) and then sodium hydroxide (6.86 g, 171.6 mmol) dissolved in the minimum amount of water (ca. 50 mL) was added. The reaction mixture was refluxed during two hours, then it was cooled to room temperature and 100 mL of water were added to extract the product with dichloromethane (100 mL x 4). The organic layer was dried with saturated solution of NaCl and anhydrous sodium sulphate, the solvent evaporated and the yellow product obtained was purified by recrystallization from dichloromethane with hexane as precipitant. Yield: 64%. Mp: 80 ºC (79 ºC[5]).

^{1}H NMR (400 MHz, Acetone-d6), δ, ppm: 9.67 (s, 1H), 7.61 (d, *J* = 8.6 Hz, 2H), 6.75 (d, *J* = 8.6 Hz, 2H), 5.71 (s_{broad}, 2H).

IR (neat, KBr), cm^{-1}: 3463, 3426, 3345, 3325, 1667, 1625, 1584, 1557, 1518, 1158.

• ***4-[4-(piperazin-1-yl)phenylazo]benzaldehyde (2)***

Over a suspension of **1** (1.0 g, 8.25 mmol) in a mixture of HCl/H_2O (1:20) (55 mL) cooled in an ice-water bath, a solution of sodium nitrite (0.528 g, 7.43 mmol) in 5 mL of water was added dropwise. After 30 minutes phenylpiperazine (1.51 mL, 1.60 g, 9.91 mmol) was added at 0 ºC, the reaction mixture was stirred for three and a half hours at 0 ºC and at room temperature overnight. Then neutralization was carried out using sodium bicarbonate until a slightly basic pH. The obtained solid

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[5] CAS: 556-18-3. Data from Catalog of Chemical Suppliers Buyers Distributors and Custom Synthesis & Organic Synthesis & Bio-Synthesis Companies. http://www.chemcas.com/material/cas/archive/556-18-3.asp

was filtered off and washed with water, dried and washed with dichloromethane. Yield: 49%. Mp: decomposes at 200 ºC.

^{1}H NMR (300 MHz, DMSO-d6), δ, ppm: 10.09 (s, 1H), 8.08 (d, *J* = 8.5 Hz, 2H), 7.97 (d, *J* = 8.4 Hz, 2H), 7.89 (d, *J* = 9.0 Hz, 2H), 7.17 (d, *J* = 9.2 Hz, 2H), 3.64-3.58 (m, 4H), 3.24-3.18 (m, 4H).

IR (neat, KBr), cm^{-1}: 3451, 2924, 2824, 2614, 2486, 1686, 1597, 1510, 1451, 1239, 1204, 1134.

- ***4-[4-(4-n-tetradecylpiperazin-1-yl)phenylazo]benzaldehyde (3)***

A mixture of **2** (3.0 g, 10.2 mmol), and potassium carbonate (2.10 g, 15.3 mmol) in acetonitrile (50 mL) was stirred and heated under argon atmosphere at reflux temperature and 1-*n*-bromotetradecane (2.4 mL, 2.24 g, 10.71 mmol) was added dropwise. After 16 hours the reaction mixture was cooled to room temperature and poured over 150 mL of water. The product was extracted with mixture hexane-ethyl acetate (1:1) (3x70 mL) and the organic layer was dried with anhydrous sodium sulphate, the solvent evaporated and the solid purified by half-pressure chromatography on silica gel using dichloromethane as solvent and increasing polarity with ethanol to elute the product.

Yield: 54%. Mp: C 84 ºC Mesophase 1 125 ºC Mesophase 2 138 ºC Mesophase 3 to decompose at 160 ºC.

^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 10.07 (s, 1H), 8.03-7.87 (m, 6H), 6.97 (d, *J* = 9.2 Hz, 2H), 3.47-3.39 (m, 4H), 2.66-2.57 (m, 4H), 2.44-2.36 (m, 2H), 1.56-1.47 (m, 2H), 1.36-1.21 (m, 22H), 0.88 (t, *J* = 7.1 Hz, 3H).

IR (neat, KBr), cm^{-1}: 3090, 2922, 2849, 1708, 1603, 1508, 1448, 1239, 1163.

- ***2-cyano-3-{4-[4-(4-n-tetradecylpiperazin-1-yl)phenylazo]phenyl}acrylic acid (4)***

Piperidine (0.06 mL, 0.053 g, 0.51 mmol) was added slowly over a well stirred suspension in dioxane (16 mL) of **3** (2.5 g, 5.09 mmol) and a-cyanoacetic acid (0.52 g, 6.1 mmol) cooled in a water bath. The reaction mixture was left to reach room temperature and after two days the reaction was concluded. The solvent was evaporated almost to dryness and 150 mL of water were added. The solid was filtered off and washed with water, dried and washed with dichloromethane and hot ethyl acetate.

Yield: 62%. Mp: Decomposes at 197 ºC. ^{1}H NMR (300 MHz, DMSO-d6), δ, ppm: 8.28 (s, 1H), 8.13 (d, *J* = 7.6 Hz, 2H), 7.95-7.78 (m, 4H), 7.08 (d, *J* = 8.6 Hz, 2H), 3.48-3.40 (m, 4H), 2.67-2.59 (m, 4H), 2.48-2.40 (m, 2H), 1.57-1.44 (m, 2H), 1.39-1.20 (m, 22H), 0.91-0.82 (m, 3H).

IR (neat, KBr), cm^{-1}: 2922, 2852, 1701, 1596, 1510, 1386, 1237, 1139.

•4'-{2-cyano-3-{4-[4-(4-n-tetradecylpiperazin-1-yl)phenylazo]phenyl}acryloyloxy}-3-[4-(4-n-tetradecyloxybenzoyloxy)benzoyloxy] biphenyl (A)

The acid chloride of **4** was prepared using 0.36 g (0.58 mmol) of **4**, oxalyl chloride (0.10 mL, 0.15 g, 1.16 mmol), 60 mL of dry THF and 5 drops of dimethylformamide. The mixture was stirred under argon atmosphere and room temperature for 15 hours, the solvent was evaporated and the solid dried with a vacuum pump. Without further purification it was put into reaction with **5** (0.30 g, 0.48 mmol), triethylamine (0.10 mL, 0.07 g, 0.67 mmol), and 55 mL of dry THF. After four days of reaction it was heated to 60º C for three days more in order to increase the yield. The solvent was evaporated and the solid purified by half-pressure chromatography on silica gel with dichloromethane as solvent and increasing polarity with a mixture dichloromethane-ethanol (100:1) to elute the product. The compound was recrystallized twice from ethyl acetate. Yield: 41%. Mp: C 147.3 ºC Col 164.8 ºC Is

^{1}H NMR (300 MHz, $CDCl_3$), δ, ppm: 8.44 (s, 1H), 8.31 (d, *J* = 8.7 Hz, 2H), 8.21 (d, *J* = 8.7 Hz, 2H), 8.16 (d, *J* = 8.8 Hz, 2H), 7.98 (d, *J* = 8.6 Hz, 2H), 7.92 (d, *J* = 9.0 Hz, 2H), 7.67 (d, *J* = 8.6 Hz, 2H), 7.55-7.49 (m, 2 H), 7.47-7.44 (m, 1H), 7.39 (d, *J* = 8.7 Hz, 2H), 7.33 (d, *J* = 8.6 Hz, 2H), 7.24-7.21 (m, 1H), 7.03-6.93 (m, 4H), 4.06 (t, *J* = 6.5 Hz, 2 Hz), 3.50-3.38 (m, 4H), 2.65-2.55 (m, 4H), 2.44-2.32 (m, 2H), 1.89-1.76 (m, 2H), 1.49-1.13 (m, 46 H), 0.88 (t, *J* = 6.6 Hz, 6H).

^{13}C NMR (300 MHz, $CDCl_3$), δ, ppm: 164.5, 163.8, 161.4, 156.0, 155.7, 155.4, 153.8, 151.3, 150.1, 145.2, 141.8, 138.6, 132.7, 132.6, 132.4, 131.9, 129.9, 129.9, 128.4, 126.8, 125.6, 124.7, 123.7, 123.2, 122.2, 121.7, 120.9, 120.8, 120.5, 115.5, 114.4, 114.0, 68.4, 58.8, 52.9, 47.5, 31.9, 29.8, 29.7, 29.6, 29.5, 29.4, 29.1, 27.6, 26.9, 26.0, 22.7, 14.1.

IR (neat, KBr), cm^{-1}: 2922, 2851, 1736, 1603, 1591, 1510, 1255, 1195, 1159, 1140.

Elemental Analysis: Calculated $C_{74}H_{91}N_5O_7$: 76.45% C, 7.89% H, 6.02% N, experimental: 76.74% C, 7.86% H, 6.04% N.

MS (MALDI +, ditranol): m/z: 1162.7 (M)$^+$, 514.7, 372.3.

UV-vis (CH_2Cl_2, $1.86\cdot10^{-5}$ M): λ_{max}: 264 nm (ε: $55.17\cdot10^3$ M^{-1}cm^{-1}), λ_{max}: 332 nm (ε: $18.14\cdot10^3$ M^{-1}cm^{-1}), λ_{max}: 485 nm (ε: $35.41\cdot10^3$ M^{-1}cm^{-1}).

- ***1-phenyl-4-(n-tetradecyl)piperazine (6)***

1-*n*-bromotetradecane (16.8 mL, 18.0 g, 63 mmol) was added dropwise over a mixture of phenylpiperazine (10 mL, 9.43 g, 57.0 mmol), and potassium carbonate (8.485 g, 57 mmol) in dry acetone (100 mL), stirred and heated under argon atmosphere at reflux temperature. After 16 hours the reaction mixture was cooled to room temperature and poured over 250 mL of water. The product was extracted with dichloromethane (3x100 mL) and the organic layer was dried with anhydrous sodium sulphate, the solvent evaporated and the solid purified by half-pressure chromatography on silica gel using a mixture dichloromethane-ethanol (100:1) as solvent. Yield: 83%. Mp: 63 ºC.

^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 7.29-7.23 (m, 2H), 6.96-6.91 (m, 2H), 6.85 (tt, *J*1 = 1 Hz, *J*2 = 7.2 Hz, 1H), 3.23-3.19 (m, 4H), 3.63-3.58(m, 4H), 2.41-2.35 (m, 2H), 1.58-1.47 (m, 2H), 1.35-1.21 (m, 22H), 0.88 (t, *J* = 6.8 Hz, 3H).

IR (neat, KBr), cm^{-1}: 2916, 2849, 1603, 1504, 1469, 1243, 1157.

- ***Sodium 2-nitro-5-[4-(4-n-tetradecylpiperazin-1-yl)phenylazo]benzoate (7)***

A suspension of 5-amino-2-nitrobenzoic acid (1.07 g, 5.58 mmol) in a mixture H_2O-HCl (5:1) (3.5 mL), was cooled in an ice-water bath and a solution of sodium nitrite (0.40 g, 5.58 mmol) in 1 mL of water was added dropwise. After 15 minutes compound **6** (5.58 mmol) and sodium acetate (0.95 g) were added using 1 mL of a mixture of HCl-H_2O (1:5). The reaction mixture was stirred for six hours in the ice-water bath and fifteen hours more at room temperature. Then, the mixture was diluted with water and basified with saturated solution of sodium carbonate in order to obtain the sodium salt of the acid, which was filtered off, washed with water, dried and washed with hexane. Yield: 39%. Mp: decomposes at 219 ºC.

^{1}H NMR (300 MHz, DMSO-d6), δ, ppm: 7.92-7.90 (m, 1H), 7.84 (d, *J* = 9.0 Hz, 2H), 7.76-7.73 (m, 2H), 7.09 (d, *J* = 9.3 Hz, 2H), 3.35 (4H)*, 2.50 (4H)*, 2.38-2.23 (m, 2H), 1.35-1.18 (m, 2H), 1.17-1.09 (m, 22H), 0.85 (t, *J* = 6.8 Hz, 3H). (*: Isochronal signal with water and DMSO, detected by COSY).

IR (neat, KBr), cm^{-1}: 2920, 2850, 1600, 1575, 1525, 1509, 1379, 1348, 1153.

- ***4-bencyloxyphenyl 4-[4-(n-tetradecyloxy)benzoyloxy]benzoate (9)***

A mixture of 0.49 g of 4-bencyloxyphenol (2.42 mmol), 1.0 g of compound **8** (2.20 mmol) and 0.03 mg of DMAP (0.22 mmol) in 40 mL of dry dichloromethane, was cooled in an ice-water bath and 0.55 g of DCC (2.64 mmol) were added under an argon atmosphere. After 30 min, the reaction mixture was allowed to stir at room temperature overnight. The precipitate was filtered off, the solvent was evaporated and the solid was washed with hot ethanol. Yield: 76%. Mp: C 112 ºC SmC 163 ºC N 189 ºC Is.

^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm**:** 8.27 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 8.9 Hz, 2H), 7.47-7.32 (m, 7H), 7.14 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 5.08 (s, 2H), 4.05 (t, *J* = 6.5 Hz, 2H), 1.87-1.78 (m, 2H), 1.52-1.43 (m, 2H), 1.42-1.22 (m, 20H), 0.88 (t, *J* = 6.8 Hz, 3H).

IR (neat, KBr), cm^{-1}: 2916, 2849, 1740, 1608, 1512, 1285, 1250, 1199.

- ***4-hydroxyphenyl 4-[4-(n-tetradecyloxy)benzoyloxy]benzoate (10)***

To a mixture of the benzyl ether **9** (1.01 g, 1.57 mmol) and cyclohexene (12 mL) in ethanol absolute (70 mL), $Pd(OH)_2/C$ (20%, 0. 10 g) was added under an argon atmosphere. The mixture was heated under reflux for 16 h, filtered through a pad of Celite® and washed with THF. The solvent was evaporated and the resulting solid was purified by half-pressure chromatography on silica gel using first dichloromethane as solvent and increasing polarity with a mixture DCM-AcEt (10:1). Yield: 49%. Mp: C 149 ºC SmC 178 ºC N 191 ºC Is.

^{1}H NMR (400 MHz, $CDCl_3$), δ, ppm: 8.25 (d, *J* = 8.7 Hz, 2H), 8.15 (d, *J* = 8.8 Hz, 2H), 7.37 (d, *J* = 8.7 Hz, 2H), 7.08 (d, *J* = 8.8 Hz, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 6.83 (d, *J* = 8.9 Hz, 2H), 4.07 (t, *J* = 6.5 Hz, 2H), 1.90-1.78 (m, 2H), 1.57-1.22 (m, 22H), 0.90 (t, *J* = 6.7 Hz, 3H).

IR (neat, KBr), cm^{-1}: 3456, 3414, 2934, 2849, 1741, 1607, 1515, 1296, 1286, 1256, 1199.

- ***4-{4-[4-(n-tetradecyloxy)benzoyloxy]benzoyloxy}phenyl 2-nitro-5-[4-(4-n-tetradecylpiperazin-1-yl)phenylazo]benzoate (B)***

Oxalyl chloride (0.12 mL, 0.18 g, 1.39 mmol) was added to a suspension of the sodium salt **7** (0.40 g, 0.70 mmol) in 30 mL of dry dichloromethane with 5 drops of dimethylformamide. The mixture was stirred under argon atmosphere at room temperature for 15 hours, then it was evaporated and the solid dried with a vacuum pump. The acid chloride obtained (the dried solid), without further purification, was put into reaction with compound **10** (0.32 g, 0.58 mmol), triethylamine (0.11 mL, 0.08 g, 0.81 mmol), and 50 mL of dry dichloromethane. After 16 hours of reaction, the solvent was evaporated and the solid purified by half-pressure chromatography on silica gel with a mixture dichloromethane-ethanol (100:1) as solvent and finally it was recrystallized twice from ethyl acetate. Yield: 32%. Mp: C 158.1 ºC Is.

^{1}H NMR (400 MHz, CD_2Cl_2), δ, ppm: 8.31-8.27 (m, 3H), 8.21 (d, *J* = 8.7 Hz, 1H), 8.15 (d, *J* = 8.9 Hz, 2H), 8.11 (dd, *J*1 = 8.7 Hz, *J*2 = 2.1 Hz, 1H), 7.93 (d, *J* = 9.2 Hz, 2H), 7.43-7.28 (m, 6H), 7.04-6.92 (m, 4H), 4.05 (t, *J* = 6.5 Hz, 2H), 3.55-3.40 (m, 4H), 2.69-2.53 (m, 4H), 2.46-2.34 (m, 2H), 1.89-1.77 (m, 2H), 1.60-1.18 (m, 46H), 0.88 (t, *J* = 6.6 Hz, 6H).

^{13}C NMR (400 MHz, $CDCl_3$), δ, ppm: 164.3, 164.3, 163.8, 155.5, 154.2, 148.8, 148.0, 146.5, 144.8, 132.4, 131.9, 129.0, 126.7, 126.1, 125.7, 122.8, 122.8, 122.4, 122.2, 120.9, 114.4, 113.8, 68.4, 58.8, 52.9, 47.3, 31.9, 29.7, 29.6, 29.4, 29.1, 27.6, 26.9, 26.0, 22.7, 14.2.

IR (neat, KBr), cm^{-1}: 2921, 2850, 1765, 1731, 1722, 1599, 1505, 1351, 1230, 1164.

Elemental Analysis: Calculated $C_{65}H_{85}N_5O_9$: 72.26% C, 7.93% H, 6.48% N, experimental: 72.10% C, 7.88% H, 6.41% N.

MS (MALDI +, ditranol): 1080.7 $(M+H)^+$, 522.4, 372.3.

UV-vis (CH_2Cl_2, $1.14 \cdot 10^{-5}$ M): λ_{max}: 272 nm (ε: $47.52 \cdot 10^3$ M^{-1}cm^{-1}), λ_{max}: 480 nm (ε: $29.93 \cdot 10^3$ M^{-1}cm^{-1}).

3. Experimental data corresponding to compound A.

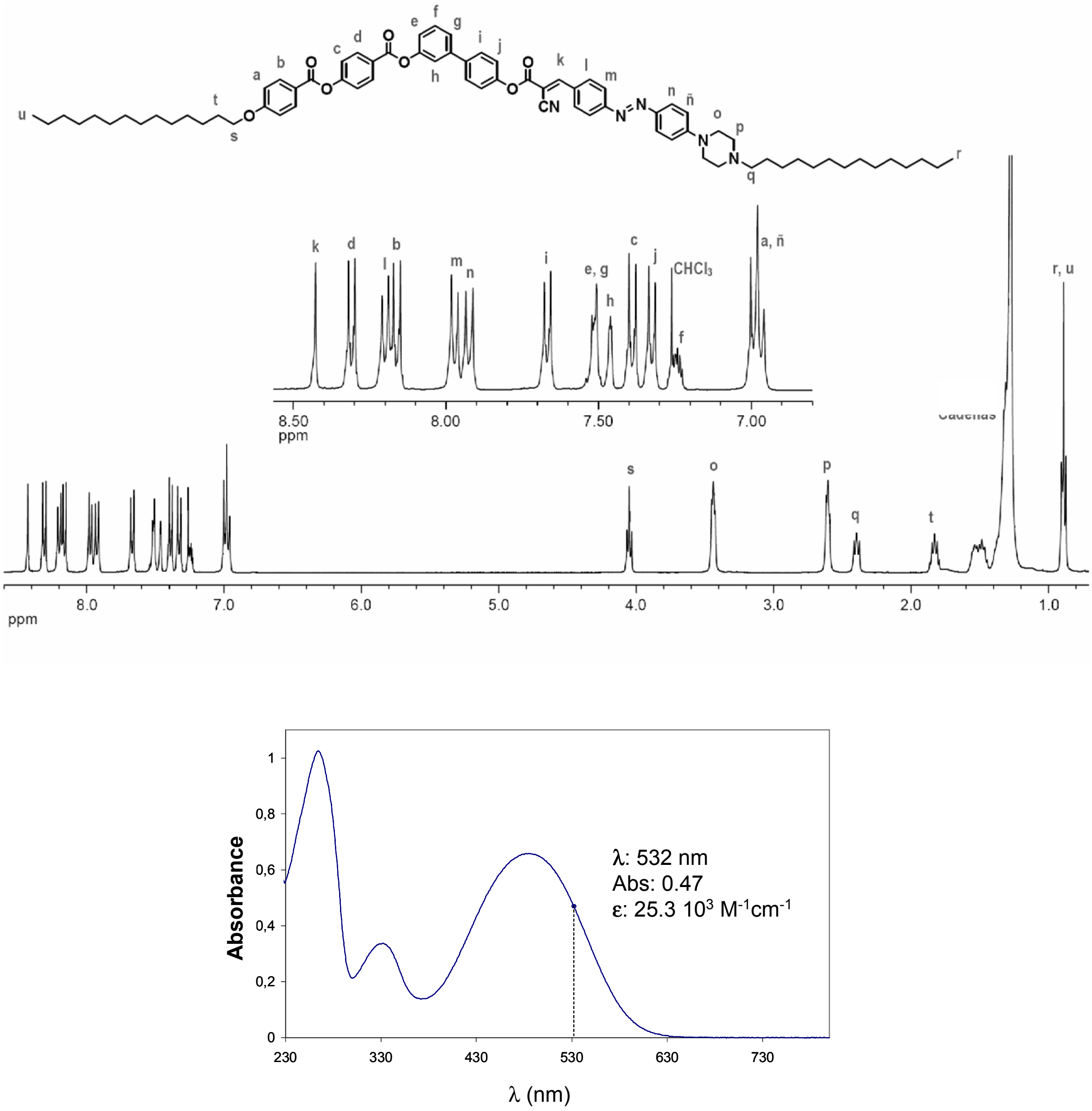

Figure S1: *^{1}H NMR (400 MHz, CDCl$_3$) spectrum and UV-Vis absorption spectrum in 1.86·10^{-5} M dichloromethane solution of compound **A**.*

4. Experimental data of compound B.

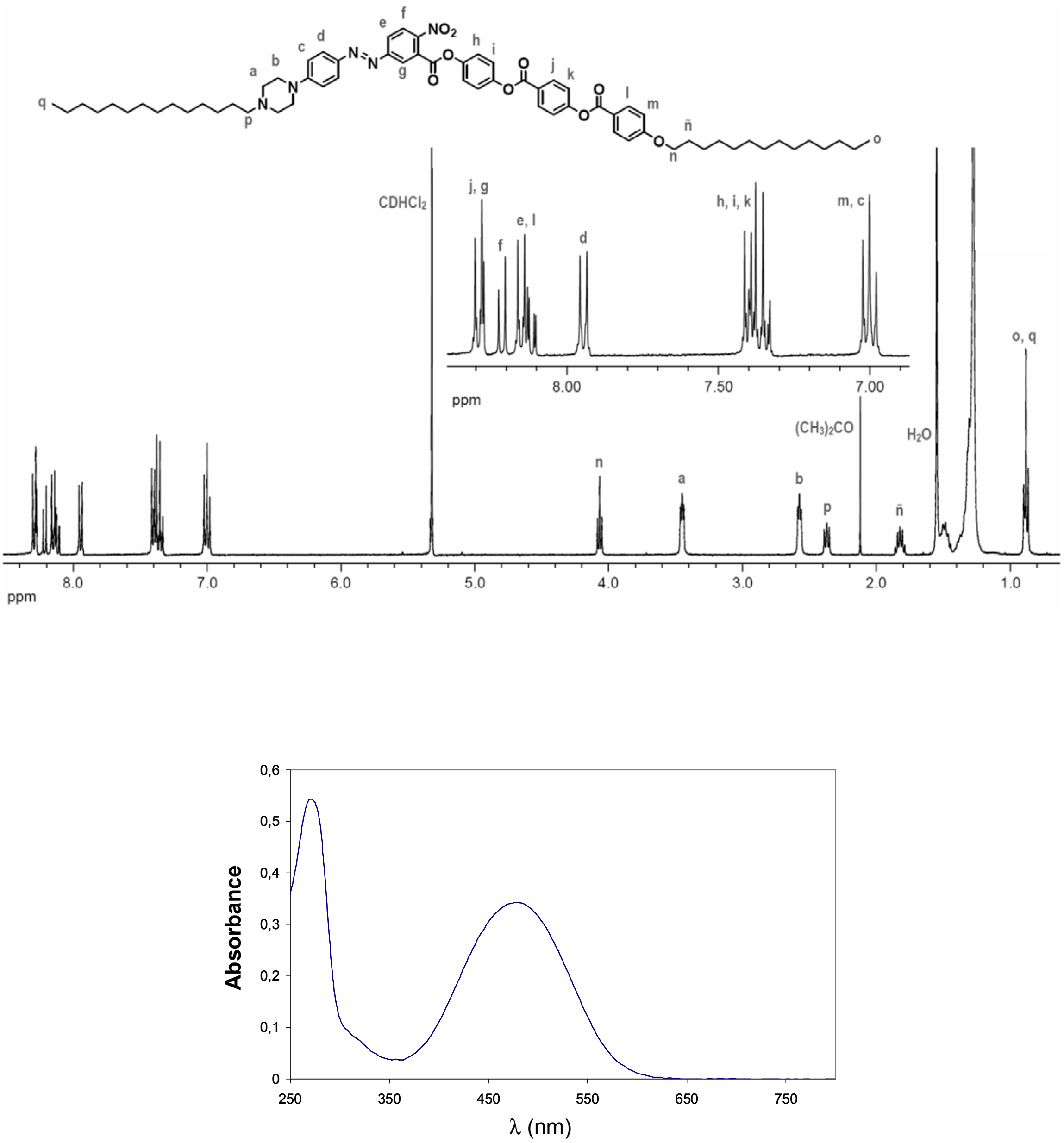

Figure S2: *^{1}H NMR (400 MHz, CD_2Cl_2) spectrum and UV-Vis absorption spectrum in $1.14{\cdot}10^{-5}$ M dichloromethane solution of compound **B**.*

5. Experimental data of the mixture A + C.

Table S1: X-ray study of the 50% mol mixture **A** + **C**

XRD data at 140 ºC

Material	Mesophase	d (Å)	Miller indexes (*hkl*)	Smectic spacing (Å)
A + C	SmCP	42.5	(001)	42.3
		21.1	(002)	

6. Second harmonic generation measurements

According to the theory for absorbing SHG, if we neglect the absorption of the fundamental incident light, the SH power is given by[6]

$$P^{2\omega} \propto d_{eff}^2 L^2 e^{-\alpha L/2} \frac{sin^2\left(\frac{2\pi\delta n}{\lambda}\right) + sinh^2\left(\frac{\alpha L}{4}\right)}{\left(\frac{2\pi\delta n}{\lambda}\right)^2 + \left(\frac{\alpha L}{4}\right)^2}, \qquad \text{(S1)}$$

where d_{eff} is the second order susceptibility effective component for a given experimental configuration of fields and sample orientation, L is the sample thickness, δn the index mismatch between the fundamental and the SH wave, λ is the fundamental wavelength and α the absorption coefficient at $\lambda/2$. To obtain an absolute value for the nonlinear coefficients a y-cut quartz (d_{11}=0.4 pmV^{-1}) was used for calibration. Also the Fresnel correction was taken into account. For the determination of α, an extrapolation was made from the data of a solution 1.86x10^{-5} M (see Fig. S1). The value of α obtained for the measured mixture is 2.52 μm^{-1}.

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[6] Herman, W. N., Hayden, L. M. *J. Opt. Soc. Am. B,* **1995**, *12*, 416

At 1064 nm the SHG study was carried out using an experimental geometry where the fundamental wave was polarized along the macroscopic polarization **P**. Accordingly the nonlinear d coefficient was determined. Measurements were performed on 5 cells of adequate thicknesses and a simultaneous fit was made for d and δn using equation (S1). The best fit gives a nonlinear coefficient d=24 pmV^{-1} and an index mismatch $\delta n = 0.1$, see Fig S3. This implies, by extrapolating to the pure A compound, d=48 pmV^{-1}.

Using the model proposed in Ref. 7 where the SHG response of a bent-core material depends only on an effective value of the hyperpolarizability along the wings of the bent-core molecule we can also estimate D. For perfect molecular order we have:

$$\frac{D}{d} = \tan^2\left(\frac{\phi}{2}\right), \tag{S2}$$

where ϕ is the bending angle of the molecule (~120º). This gives a nonlinear coefficient D=140 pmV^{-1}.

For the measurements at 1600 nm the sample preparation and experimental configuration were the same as for the measurement at 1064 nm. Cells of different thicknesses (5.5, 9.8 and 18 μm) were used in the experiment. We used two cells for each thickness in order to check the experimental reproducibility. Measurements were carried out on the same mixture (50% mol of compounds A and C) at normal incidence in two different polarization configurations, i.e., fundamental light polarized parallel (p) or perpendicular (s) to the electric field direction, and second harmonic light always parallel (p) to the electric field. SHG intensity vs. thickness curves were fitted to expression (S1) for α=0 (perfect transparency for the SH signal). Figures S4a-b shows the experimental results for pp and sp configurations respectively. Solid lines represent the best fits that correspond to coefficient values d=4

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[7] F. Araoka, B. Park, Y. Kinoshita, K. Ishikawa, H. Takezoe, J. Thisayukta, J. Watanabe, *Jpn. J. Appl. Phys.* **1999**, *38*, 3526

pmV^{-1} and $D\sin^2\theta = 2.5$ pmV^{-1} respectively. The molecular tilt was optically determined to be about 30-35°. By extrapolating to the pure **A** compound D~17 pmV^{-1} and d~8pmV^{-1} values were estimated.

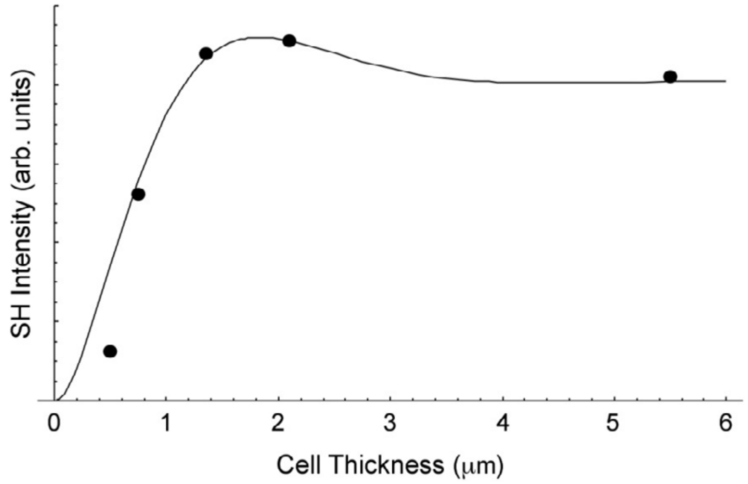

Figure S3: *Fits to eq. (S1) of the SHG intensity experimental results (black dots) for an absorption coefficient* $\alpha = 2.52\ \mu m^{-1}$ *at the SHG wavelength 532 nm in a 50% molar mixture of compounds A and C. Cells 0.5, 0.8, 1.4, 2.1, 5.5* μm *thick were used. Since for high absorption SHG signal quickly saturates, very thin cells are needed. The obtained parameters are* $\delta n = 0.1$ *and* $d = 24\ pmV^{-1}$.

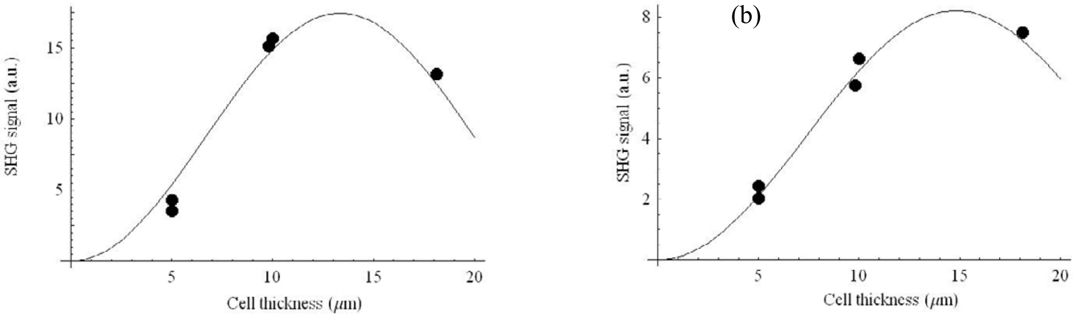

Figure S4: *Fits to eq. (S1) of the SHG intensity experimental results (black dots) for* $\alpha = 0$ *at* $\lambda = 1600$ *nm in a 50% molar mixture of compounds A and C. Cells 5.5, 9.8 and 18* μm *thick were used. (a) pp polarization configuration,* $\delta n = 0.03$ *and* $d = 4\ pmV^{-1}$*, (b) sp polarization configuration,* $\delta n = 0.03$ *and* $d_{eff} = D\sin^2\theta = 2.5\ pmV^{-1}$.