Supporting Information to accompany:

Novel NLO-phores with Proaromatic Donor and Acceptor Groups

Raquel Andreu, Javier Garín,* Jesús Orduna, Rafael Alcalá, and Belén Villacampa

Departamento de Química Orgánica and Departamento de Física de la Materia Condensada, ICMA,
Universidad de Zaragoza-CSIC, E-50009 Zaragoza, Spain.

Experimental Section

General Remarks: Infrared measurements were carried out in nujol mulls using a Perkin-Elmer FTIR 1600 spectrometer. — Melting points were obtained on an Olympus BH-Z polarizing microscope equipped with a hot stage and are uncorrected. — ^1H - and ^{13}C -NMR spectra were recorded on a Bruker ARX300 or a Varian Unity-300 spectrometers operating at 300 MHz and 75 MHz respectively; δ values are given in ppm (relative to TMS) and J values in Hz. — EI Mass spectra were recorded with a VG Autospec at 70 eV. — Accurate mass measurements were obtained by narrow-range voltaje scanning at 10000 resolution (measured as peak width at 5% height) using perfluorokerosene as reference compound and were corrected to an accuracy of ± 10 ppm of the theoretical value.— Electronic spectra were recorded with a UV-Vis-NIR Cary 500 Scan spectrophotometer.— Cyclic voltammetry measurements were performed with a μ -Autolab ECO-Chemie potentiostat, using a glassy carbon working electrode, Pt counter electrode, and Ag/AgCl reference electrode. The experiments were carried out under argon, in CH_2Cl_2 , with Bu_4NPF_6 as supporting electrolyte (0.1 mol L^{-1}). Scan rate was 100 mV s^{-1} . Molecular orbital calculations were performed on Intel Pentium III and Pentium IV based computers running under Windows XP. HF and DFT calculations were performed with the gaussian 98w program.¹ Processing of the results of molecular orbital calculations was achieved with the MOLEKEL-4.3 program.² EFISH measurements were taken with a non-linear optics spectrometer from SOPRA S.A. The fundamental light source at $1.907 \mu\text{m}$ was the first Stokes peak of a hydrogen Raman cell pumped by the $1.064 \mu\text{m}$ light of a Q-switched Nd:YAG laser (Quantel YG 781, 10 pps, 8 ns, pulse). That light was passed through a linear polarizer and focused on the EFISH cell. The

¹ Gaussian 98, Revision A.9, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, Jr., J. A.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Baboul, A. G.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Andres, J. L.; Gonzalez, C.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. Gaussian, Inc., Pittsburgh PA, 1998.

² Portmann, S.; Lüthi, H. P. *Chimia* **2000**, *54*, 766.

polarizing dc electric field (parallel to the light polarization) used in this cell was 6 kV. The output light from the cell was passed through an interference filter to select the second harmonic light (0.954 μm) which was finally detected with a R642 photomultiplier from Hamamatsu.

Compounds **2**,³ **4a-c**⁴ and **6**⁵ were prepared as previously described.

1,3-Diethyl-5-(1,3-dithiol-2-ylidene)-2-thiobarbituric acid (**3**)

To a stirred solution of EtONa (4.31 mmol) in absolute ethanol (20 mL) was added 1,3-diethylthiobarbituric acid (**1**) (750 mg, 3.75 mmol). The mixture was refluxed during 30 minutes. Then, 2-methylthio-1,3-dithiolium iodide (**2**) (1.035 g, 3.75 mmol) was added, and refluxing was continued for 4-5 hours. The mixture was cooled to room temperature and ethanol was evaporated. Water was added and product was extracted with CH_2Cl_2 (3x100 mL). The extracts were dried over MgSO_4 , evaporated and purified by chromatography (silica gel) using CH_2Cl_2 as eluent, to give a yellow solid (290 mg, 26%).

M.p. 278°C. — IR (Nujol) ν (cm^{-1}): 1627 (C=O), 1105 (C=S). — ^1H NMR (CDCl_3 , 300 MHz): δ = 7.60 (s, 2H), 4.65 (q, J = 6.9 Hz, 4H), 1.35 (t, J = 6.9 Hz, 6H). — ^{13}C NMR (CDCl_3 , 75 MHz): δ = 180.3, 177.1, 158.9, 127.8, 101.5, 43.4, 12.3. — MS (EI^+) m/z (%): 300 (M^+ , 100), 267 (45), 212 (23), 143 (27), 142 (25), 69 (21).

General procedure for **5a-b**:

A 150 mg (0.75 mmol) sample of 1,3-diethylthiobarbituric acid (**1**) was added to a solution of 1 mmol of the corresponding aldehyde (**4a**, **4b**) in 10 mL of absolute ethanol. The solution was stirred under argon atmosphere with exclusion of light for 25 minutes at 80-90°C and for 4 hours at room temperature. Then, the precipitated solid was filtered, washed with cold ethanol and ether and dried.

1,3-Diethyl-5-[2-(4,5-dimethyl-[1,3]-dithiol-2-ylidene)-ethylidene]-2-thiobarbituric acid (**5a**).

Purple solid (138 mg, 52 %)

M.p. 234-238°C. — IR (Nujol) ν (cm^{-1}): 1642 (C=O), 1520 (C=C). — ^1H NMR (CDCl_3 , 300 MHz): δ = 8.18 (d, J = 13.8 Hz, 1H), 8.14 (d, J = 13.8 Hz, 1H), 4.54 (q, J = 6.80 Hz, 4H), 2.22 (s, 3H), 2.21 (s, 3H), 1.28 (t, J = 6.80 Hz, 6H). — ^{13}C NMR (CDCl_3 , 75 MHz): δ = 178.48, 161.50, 160.88, 147.91, 130.56, 129.86, 111.29, 103.61, 43.42, 42.83, 14.13, 13.85, 13.41, 12.48. — MS

³ Challenger, F.; Mason, E. A.; Holdsworth, E. C.; Emmott, R. *J. Chem. Soc.* **1953**, 292.

⁴ a) Yoshida, Z.; Kawase, T.; Awaji, H.; Sugimoto, I.; Sugimoto, T.; Yoneda, S. *Tetrahedron Lett.* **1983**, 24, 3469.

b) Nguyen, T.-T.; Gouriou, Y.; Sallé, M.; Frère, P.; Jubault, M.; Gorgues, A.; Toupet, L.; Riou, A. *Bull. Soc. Chim. Fr.* **1996**, 133, 301.

⁵ Brooker, L. G. S.; Craig, A. C.; Heseltine, D. W.; Jenkins, P. W.; Lincoln, L. L. *J. Am. Chem. Soc.* **1965**, 87, 2443.

(EI⁺) m/z (%): 354 (M⁺,100), 321 (75), 266 (70), 225 (25), 142 (57), 114 (46), 84 (34), 66 (33), 57 (40).

1,3-Diethyl-5-[4-(4,5-dimethyl-[1,3]-dithiol-2-ylidene)-but-2-enylidene]-2-thiobarbituric acid (5b). Dark blue solid (114 mg, 52 %)

M.p. 238°C. — IR (Nujol) ν (cm⁻¹): 1651 (C=O), 1533 (C=C), 1190 (C=S). — ¹H NMR (CDCl₃, 300 MHz): δ = 8.03 (d, J = 12.91 Hz, 1H), 7.74 (t, J = 13.30 Hz, 1H), 7.19 (t, J = 13.81 Hz, 1H), 6.46 (d, J = 12.19 Hz, 1H), 4.53 (q, J = 6.90 Hz, 4H), 2.13 (s, 3H), 2.10 (s, 3H), 1.27 (t, J = 6.90 Hz, 3H), 1.26 (t, J = 6.90 Hz, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ = 178.65, 162.67, 161.37, 160.34, 157.50, 151.47, 127.76, 127.20, 123.28, 112.38, 108.78, 43.46, 42.90, 13.77, 13.34, 12.48. — MS (EI⁺) m/z (%): 380 (M⁺,100), 347 (30), 292 (21), 249 (22), 194 (45). — HRMS (EI⁺) m/z: calculated for C₁₇H₂₀N₂O₂S₃: 380.0687; found: 380.0702.

1,3-diethyl-5-[3-(4,5-dimethyl-[1,3]-dithiol-2-ylidenemethyl)-5,5-dimethyl-2-cyclohexen-1-ylidene]-2-thiobarbituric acid (8)

To a solution of 4,5-dimethyl-2-methylthio-1,3-dithiolium tetrafluoroborate (**7**) (264 mg, 1 mmol) in pyridine (5 mL) was added 1,3-diethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-2-thiobarbituric acid (**6**) (320 mg, 1 mmol) and triethylamine (0.4 mL). The mixture was refluxed with exclusion of light for 30 minutes, cooled, and the solvents distilled. The crude product was dissolved in CH₂Cl₂, washed with HCl 1N (3x100 mL) and water (2x100 mL). The organic layer was dried over MgSO₄, evaporated and purified by chromatography (silica gel) using CH₂Cl₂ as eluent, giving a dark blue solid (157 mg, 35%).

M.p. 143-145°C. — IR (Nujol) ν (cm⁻¹): 1626 (C=O), 1524 (C=C), 1150 (C=S). — ¹H NMR (CDCl₃, 300 MHz): δ = 8.27 (s, 1H), 6.50 (s, 1H), 4.53 (q, J = 6.95 Hz, 4H), 3.03 (s, 2H), 2.35 (s, 2H), 2.15 (s, 3H), 2.12 (s, 3H), 1.28 (t, J = 6.95 Hz, 6H), 1.02 (s, 6H). — ¹³C NMR (CDCl₃, 75 MHz): δ = 177.64, 170.51, 161.22, 158.06, 156.32, 128.79, 128.50, 123.68, 114.47, 107.25, 44.37, 43.56, 43.41, 32.08, 29.68, 28.53, 14.11, 13.78, 12.86, 12.62. — MS (EI⁺) m/z (%): 448 (M⁺,100), 415 (51), 360 (28).

General procedure for **9a**, **9c**:

To a stirred solution of corresponding aldehyde (**4a**, **4c**) (0.5 mmol) and 1,3-diethyl-5-(3,5,5-trimethyl-2-cyclohexen-1-ylidene)-2-thiobarbituric acid (**6**) (160 mg, 0.5 mmol) in toluene (10 mL) was added a drop of piperidine. The mixture was refluxed under argon atmosphere with exclusion of light for 2-4 hours (TLC monitoring). After evaporation of the solvent, the crude product was purified by chromatography (silica gel).

1,3-diethyl-5-{3-[(4,5-dimethyl-[1,3]-dithiol-2-ylidene)-propenyl]-5,5-dimethyl-2-cyclohexen-1-ylidene}-2-thiobarbituric acid (9a)

Chromatography eluent: hexane/Et₂O (2:1).

Green solid (47 mg, 20%)

M.p. 173-176°C. — IR (Nujol) ν (cm⁻¹): 1641 (C=O), 1568 (C=C), 1167 (C=S). — ¹H NMR (CDCl₃, 300 MHz): δ = 8.32 (s, 1H), 6.72 (dd, J = 14.26 Hz, J' = 11.21 Hz, 1H), 6.32 (d, J = 14.26 Hz, 1H), 6.22 (d, J = 11.21 Hz, 1H), 4.53 (q, J = 6.70 Hz, 4H), 3.07 (s, 2H), 2.36 (s, 2H), 2.04 (s, 3H), 2.01 (s, 3H), 1.30 (t, J = 6.70 Hz, 6H). — MS (EI⁺) m/z (%): 474 (M⁺, 30), 386 (30), 355 (50), 339 (65), 131 (77). — HRMS (EI⁺) m/z : calculated for C₂₄H₃₀N₂O₂S₃: 474.1469; found: 474.1471.

1,3-diethyl-5-{3-[(4,5-dimethyl-[1,3]-dithiol-2-ylidene)-hepta-1,3,5-trienyl]-5,5-dimethyl-2-cyclohexen-1-ylidene}-2-thiobarbituric acid (9c)

Purified by repeated column chromatography (eluent: hexane/AcOEt (11:1)).

Green solid (26 mg, 10%)

MS (EI⁺) m/z (%): 526 (M⁺, 32), 207 (78), 131 (100).

1,3-diethyl-5-[3-(2-tetrathiafulvalenylvinyl)-5,5-dimethyl-2-cyclohexen-1-ylidene]-2-thiobarbituric acid (13)

The product was prepared analogously to **9a** and **9c**, but using formyltetrathiafulvalene⁶ and one drop of piperidine in toluene (1:1). Reaction time was 24 hours, and additional drops of catalyst solution were added as necessary.

Chromatography eluent: hexane/AcOEt (10:1).

Green solid (67 mg, 25%)

M.p. 155-159°C. — IR (Nujol) ν (cm⁻¹): 1654 (C=O), 1500 (C=C), 1106 (C=S). — ¹H NMR (CDCl₃, 300 MHz): δ = 8.29 (s, 1H), 6.76 (d, J = 15.62 Hz, 1H), 6.56 (s, 1H), 6.35-6.29 (m, 3H), 4.53-4.45 (m, 4H), 3.04 (s, 2H), 2.30 (s, 2H), 1.32-1.24 (m, 6H), 1.01 (s, 6H). — MS (EI⁺) m/z (%): 534 (M⁺, 15), 146 (100), 103 (49), 76 (62), 57 (73).

⁶ Garín, J.; Orduna, J.; Uriel, S.; Moore, A. J.; Bryce, M. R.; Wegener, S.; Yufirt, D. S.; Howard, J. A. K. *Synthesis* **1994**, 489.