Supporting Material

Rhodanine dyes for dye-sensitized solar cells :

spectroscopy, energy levels and photovoltaic performance

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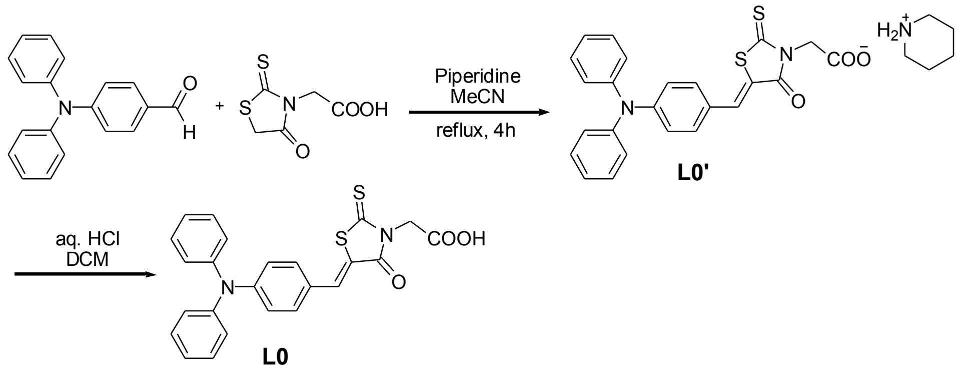
S1. Experimental

S1.1 Synthesis methodology. All reactions were carried out under N_2 with the use of standard inert atmosphere and Schlenk techniques. Solvents were dried by standard procedures. The microwave heating was performed with a Smith Creator^{TM} single mode cavity from Personal Chemistry AB, Uppsala, Sweden, equipped with magnetic stirrer and automatic temperature control. ^1H and ^{13}C NMR spectra were recorded on Bruker 500 and 400 MHz instruments using the residual signals δ 7.26 ppm and δ 77.0 ppm from $CDCl_3$, and 2.50 ppm and 39.4 ppm from DMSO, as internal references for ^1H and ^{13}C respectively. HR-MS were performed using a Q-Tof Micro (Micromass Inc., Manchester, England) mass spectrometry equipped with Z-spray ionization source.



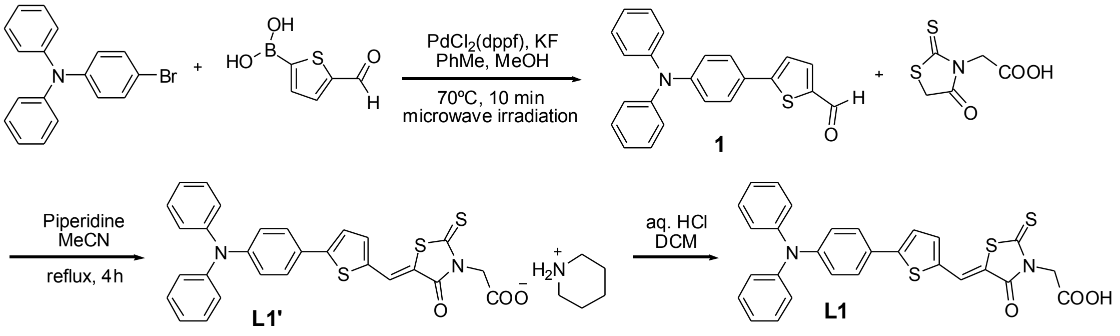
L0

4-(diphenylamino)phenyl-rodanine-3-acetic acid – piperidine salt (L0')

A 50 mL acetonitrile solution of 4-Diphenylamino-benzaldehyde (0.5 g, 1.83 mmol), rhodanine-3-acetic acid (0.35 g, 1.83 mmol) and piperidine (0.312 g, 3.66 mmol) was refluxed for 4 h under nitrogen atmosphere. The formed precipitate was collected by filtration, washed with acetonitrile and dried under vacuum, to yield a orange solid, **L0'** (0.43 g, 44 %). mp 213-215ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.69 (s, 1H), 7.33 (m, 6H), 7.14 (m, 6H), 7.01 (d, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 193.4, 171.5, 167.9, 150.2, 146.2, 132.9, 132.2, 129.8, 126.0, 125.6, 124.9, 120.5, 119.3, 47.7, 44.1, 22.6, 22.5. HR-MS (Q-Tof) m/z: 445.0687 $[M-C_5H_{12}N]^-$ calcd. for $C_{30}H_{21}N_2O_3S_3$ ($M-C_5H_{12}N$): 445.0681.

4-(diphenylamino)phenyl-rodanine-3-acetic acid (L0)

L0' (0.43 g, 0.81 mmol) was dissolved in DCM (300 mL) and washed with aq HCl (1 M, 300 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered. Solvent removal by rotary evaporation yielded the final product **L0**, as a red solid. (0.38 g, 99 %). mp 240-242ºC. ^{1}H NMR (500 MHz, DMSO-d_6): δ 7.76 (s, 1H), 7.53 (d, J = 8.9 Hz, 2H), 7.42 (d, J = 8.4 Hz, 4H), 7.23 (t, J = 8.4 Hz, 2H), 7.19(d, J = 8.4 Hz, 4H) 6.92 (d, J = 8.9 Hz, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 192.8, 167.3, 166.4, 150.1, 145.4, 133.9, 132.8, 129.9, 126.1, 125.3, 124.4, 119.2, 117.3, 44.9. HR-MS (Q-Tof) m/z: 445.0674 $[M-H]^-$ calcd. for $C_{30}H_{21}N_2O_3S_3$ (M-H): 445.0681.



L1

5-[4-(diphenylamino)phenyl]thiophene-2-carbaldehyde (1)

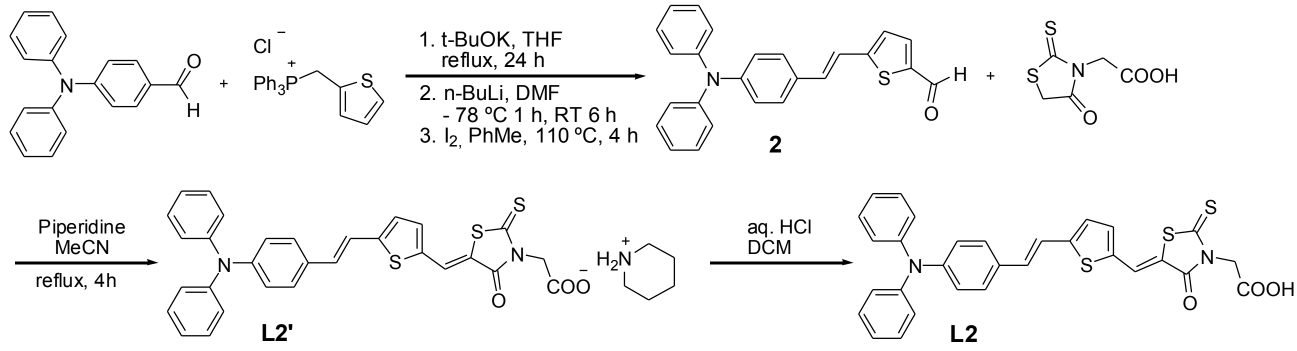
To a solution of 4-Bromo-N,N-diphenylaniline (200 mg 0.617 mmol) and $PdCl_2$(dppf) (51 mg 0.06 mmol) in dry toluene (2 mL) was added a solution of 5-formylthiophene-2-yl-2-boronic acid (192 mg, 1.23 mmol) and K_2CO_3 (426 mg, 3.10 mmol) in dry methanol (2 mL). The mixture was heated by microwave irradiation at 70 °C for 10 min. The reaction was quenched by the addition of water (30 mL) and extracted with DCM (3 × 30 mL). The combined organic extract was dried over anhydrous $NaSO_4$ and filtered. Solvent removal by rotary evaporation followed by column chromatography over silica gel using DCM/hexane (80/20) yielded a yellow oil (165 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$): 9.85 (s, 1 H), 7.69 (d, 1 H), 7.51 (d, 2 H), 7.29 (m, 5 H), 7.13 (d, 4H), 7.08 (t, 2H), 7.05 (d, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): 182.6, 154.6, 149.1, 147.0, 141.3, 137.7, 129.5, 127.2, 126.1, 125.2, 123.9, 122.8, 122.3.

5-[4-(diphenylamino)phenyl]thiophene-2-rodanine-3-aceticacid – piperidine salt (L1')

A 30 mL acetonitrile solution of 5-(4-N,N-diphenylaniline)thiophene-2-carbaldehyde (0.1 g, 0.28 mmol,), rhodanine-3-acetic acid (54 mg, 0.28 mmol) and piperidine (48 mg, 0.56 mmol) was refluxed for 4 h under nitrogen atmosphere. The formed precipitate was collected by filtration, washed with acetonitrile and dried under vacuum, to yield a dark orange solid **L1'** (76 mg, 44 %), mp 209-210ºC. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.83 (s, 1H), 7.48 (d, 2H), 7.34 (d, 1H), 7.28 (m, 5H), 7.08 (m 8H), 4.67 (s, 2H), 2.93 (t, 4H), 1.70 (m, 4H), 1.55 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 192.6, 171.5, 167.4, 152.7, 148.8, 147.0, 136.1, 135.6, 129.5, 126.8, 126.3, 125.4, 125.1, 123.8, 123.6, 122.6 120.1, 47.8, 44.2, 22.6, 22.5. HR-MS (Q-Tof) m/z: 527.0547 $[M-C_5H_{12}N]^-$ calcd. For $C_{30}H_{21}N_2O_3S_3$ $(M-C_5H_{12}N)$: 527.0558

5-[4-(diphenylamino)phenyl]thiophene-2-rodanine-3-aceticacid (L1)

L1’ (76 mg, 0.12 mmol) was dissolved in DCM (50 mL) and washed with aq HCl (1 M, 50 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered. Solvent removal by rotary evaporation yielded the final product, as a dark purple solid, **L1** (65 mg, 99 %). mp >270ºC. ^1H NMR (500 MHz, DMSO-d_6): δ 8.14 (s, 1H), 7.81 (d, *J* = 4.01 Hz, 1H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.64 (d, *J* = 4.1, 1H), 7.36 (t, J = 7.4 Hz, 4H), 7.13 (t, J = 7.4 Hz, 2H), 7.10 (d, J = 7.4 Hz, 4H), 6.97 (d, J = 8.8 Hz, 2H), 4.72 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 191.8, 167.2, 165.9, 152.5, 148.3, 146.3, 138.4, 135.2, 129.7, 127.1, 126.9, 125.5, 124.9, 124.7, 124.0, 121.8, 117.7, 45.1. HR-MS (Q-Tof) m/z: 527.0565 $[M-H]^-$ calcd. For $C_{30}H_{21}N_2O_3S_3$ (M-H): 527.0558.



L2

5-[2-(4-Diphenylamino-phenyl)-vinyl]-thiophene[1]

4-Diphenylamino-benzaldehyde (2 g, 7.37 mmol) and t-BuOK (0.99 g, 8.84 mmol) was dissolved in THF (22 mL) and stirred at ambient temperature under nitrogen atmosphere for 1 h. 2-thienylmethyl triphenylphosphonium chloride (4.05 g, 10.2 mmol) was dissolved in THF and added drop wise to the solution. The reaction mixture was stirred for 1 h at ambient temperature, whereupon the mixture was heated to reflux for 24 h. The reaction mixture was allowed to cool to ambient temperature and a molar excess of water was added. The mixture was concentrated by rotary evaporator and the water phase was extracted with DCM. The organic phase was dried over $MgSO_4$, filtered through a plug of silica gel (DCM) and a crude intermediate was obtained (2.65 g, 7.52 mmol). The crude product was used directly in the next step without further purification.

5-[2-(4-Diphenylamino-phenyl)-vinyl]-thiophene-2-carbaldehyde[1] (2)

5-[2-(4-Diphenylamino-phenyl)-vinyl]-thiophene (2.65 g, 7.52 mmol) was dissolved in THF (20 mL) and the solution was cooled to -78 ºC under nitrogen atmosphere. n-Butyl Lithium (3.3 mL, 2.5 M hexane solution) was added drop wise over 10 min and the mixture was stirred at -78 ºC for 1 h. The mixture was allowed to warm to 0 ºC and stirred for 30 min. The mixture was once again cooled to -78 ºC and DMF (0.64 ml, 8.27 mmol) was added. The reaction mixture was allowed to warm to ambient temperature and stirred for 2 h. The reaction was quenched by the addition of aqueous HCl (10 %, 100

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[1] Hu, Z. Y.; Fort, A.; Barzoukas, M.; Jen, A. K. Y.; Barlow, S.; Marder, S. R. *Journal Of Physical Chemistry B* **2004,** 108, (25), 8626-8630.

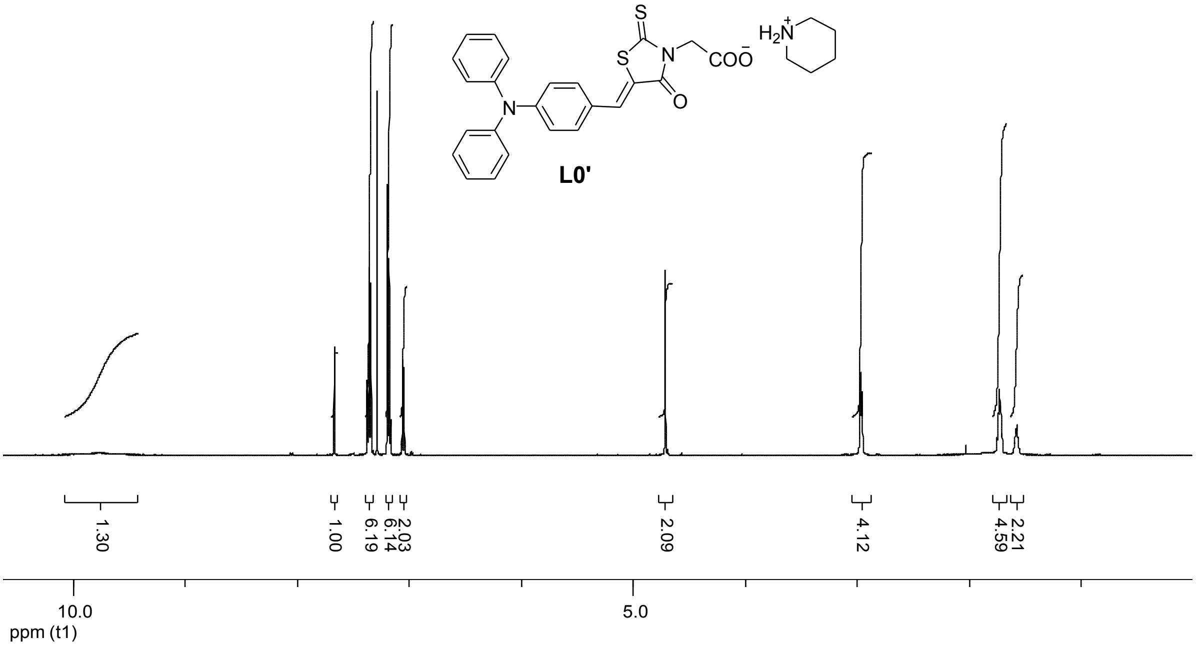
mL) and extracted with DCM (3 × 30 mL). The combined organic extract was dried over anhydrous $MgSO_4$ and filtered. Solvent removal by rotary evaporation and column chromatography over silica gel using hexane/DCM mixture (1:1) yielded an orange solid (1.1 g, 39%). ^{1}H NMR (400 MHz, $CDCl_3$): 9.85 (s, 1 H), 7.67 (d, 1 H), 7.40-7.15 (m, 6 H), 7.16-7.05 (m, 11 H). ^{13}C NMR (100 MHz, $CDCl_3$): 182.8, 153.6, 148.9, 147.6, 141.4, 137.8, 133.0, 130.0, 128.3, 126.3, 125.4, 124.0, 123.7, 123.0, 119.1.

3-{5-[4-(diphenylamino)styryl]thiophen-2-yl}-2-cyanoacrylic acid – piperidine salt (L2')

A 50 mL acetonitrile solution of 5-(4-(diphenylamino)styryl)thiophene-2-carbaldehyde (0.12 g, 0.316 mmol), rhodanine3-acetic acid (60 mg, 0.316mmol) and piperidine (54 mg, 0.632 mmol) was refluxed for 4 h under nitrogen atmosphere. The formed precipitate was collected by filtration, washed with acetonitrile and dried under vacuum, to yield a red solid, **L2'** (82 mg, 51 %). mp 210-211ºC (dec). ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.81 (s, 1H), 7.34 (d, 2H), 7.27 (m, 5H), 7.06 (m, 11H), 4.67 (s, 2H), 2.93 (t, 4H), 1.70 (m, 4H), 1.55 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): 192.6, 171.5, 167.4, 151.7, 148.4, 147.2, 136.0, 135.3, 131.4, 129.7, 129.4, 127.8, 127.1, 125.2, 125.0, 123.6, 122.7, 120.5 118.8, 47.8, 44.2, 22.6, 22.5. HR-MS (Q-Tof) m/z: 553.0711 $[M-C_5H_{12}N]^-$ calcd. for $C_{30}H_{21}N_2O_3S_3$ $(M-C_5H_{12}N)$: 553.0714.

3-{5-[4-(diphenylamino)styryl]thiophen-2-yl}-2-cyanoacrylic acid (L2)

L2' (82 mg, 0.13 mmol) was dissolved in DCM (50 mL) and washed with aq HCl (1 M, 50 mL). The organic phase was dried over anhydrous $MgSO_4$ and filtered. Solvent removal by rotary evaporation yielded the final product as a dark purple solid, **L2** (69 mg, 97 %). mp 235-236ºC. ^{1}H NMR (500 MHz, DMSO-d_6): δ 8.13 (s, 1H), 7.76 (d, *J* = 4.0 Hz, 1H), 7.55 (d, *J* = 8.7 Hz, 2H), 7.41 (d, *J* = 16.1 Hz, 1H), 7.37 (d, *J* = 4.0 Hz, 1H), 4.35 (t, *J* = 7.4 Hz, 4H), 7.32 (d; *J* = 16.1 Hz, 1H), 7.11 (t, *J* = 7.4 Hz, 2H) 7.07 (d, *J* = 7.4 Hz, 4H) 6.93 (d, *J* = 8.7, 2H) 4.72 (s, 2H). ^{13}C NMR (125 MHz, DMSO-d_6): 191.7, 167.2, 165.9, 152.2, 147.6, 146.6, 138.0, 135.2, 131.4, 129.6, 129.6, 128.1, 127.9, 126.8, 124.6, 123.7, 121.9, 119.1, 117.8, 45.1. HR-MS (Q-Tof) m/z: 553.0721 $[M-H]^-$ calcd. for $C_{30}H_{21}N_2O_3S_3$ (M-H): 553.0714.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S
N
COO$^-$
O
N
$H_2\overset{+}{N}$
L0'
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6.14
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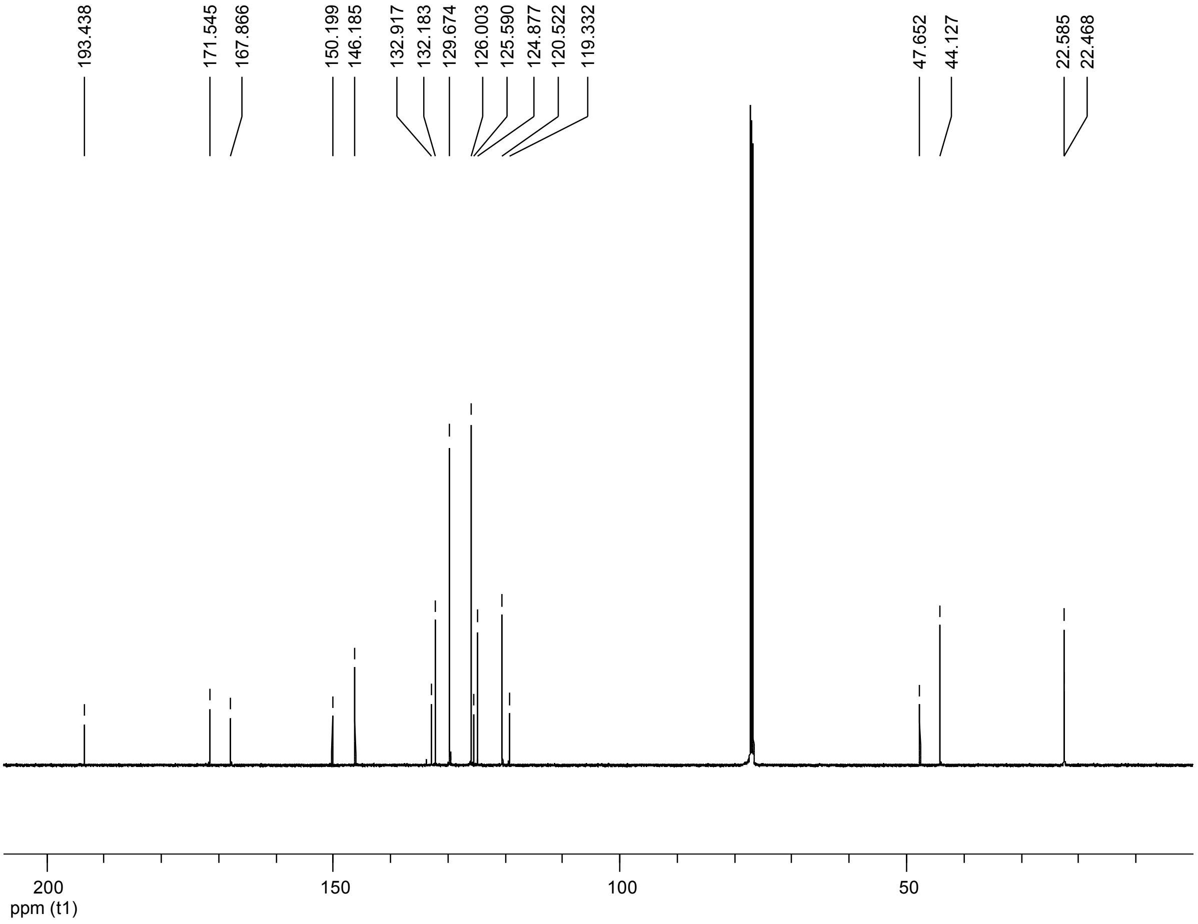
2.09
4.12
4.59
2.21
10.0
5.0
ppm (t1)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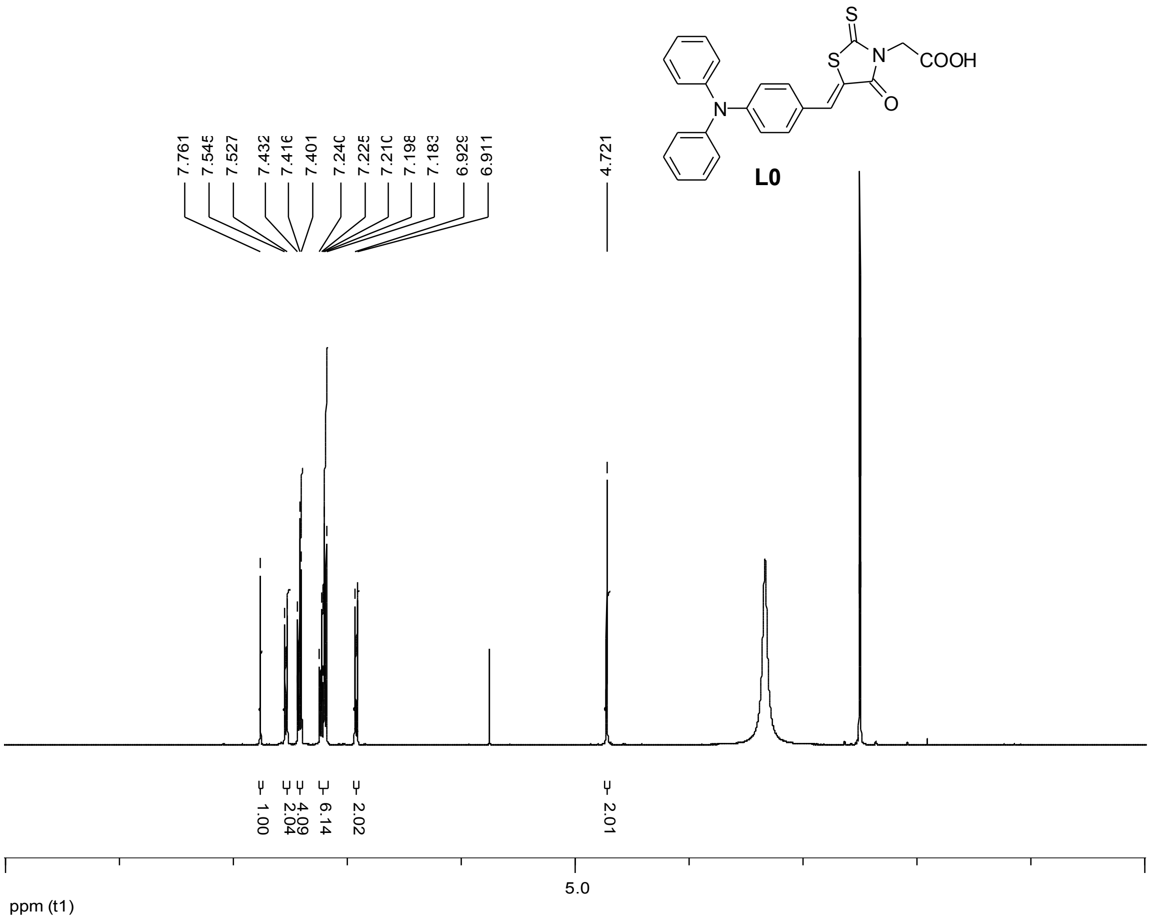
150
100
50
ppm (t1)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7.198
7.183
6.929
6.911
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4.09
6.14
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2.01
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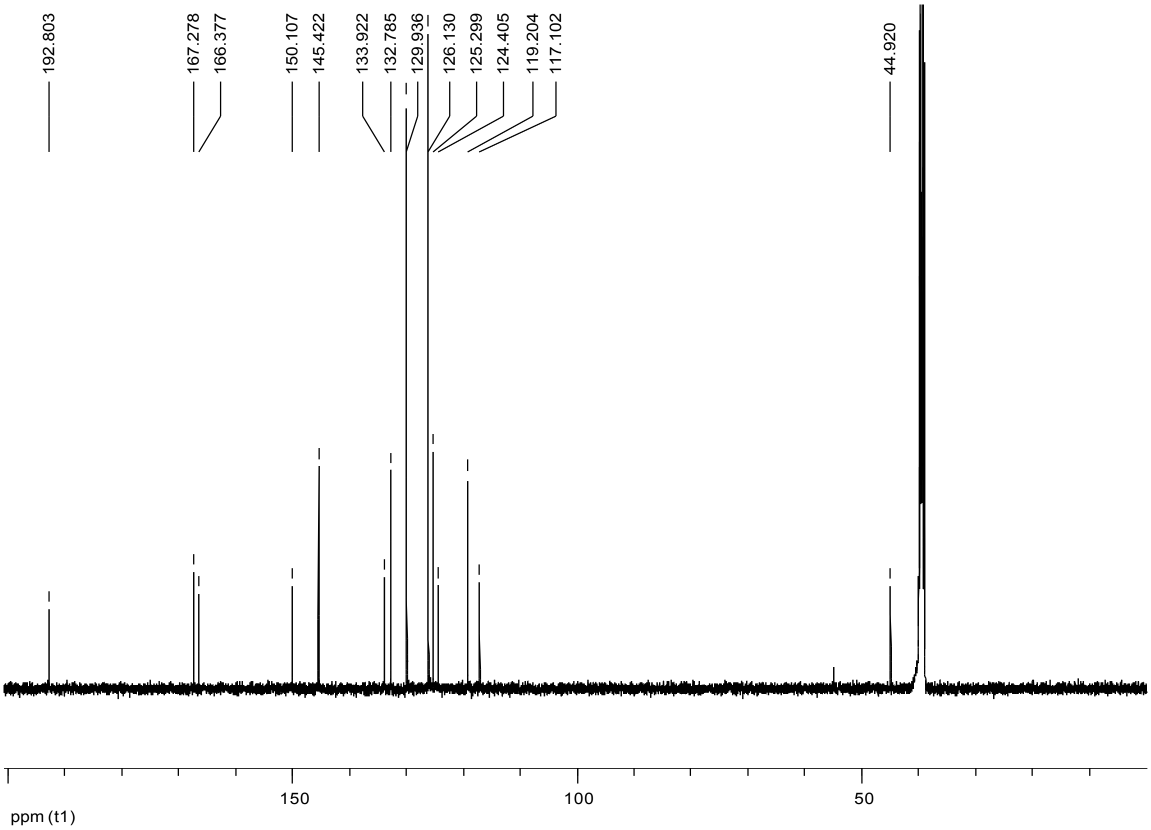
ppm (t1)

L0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150
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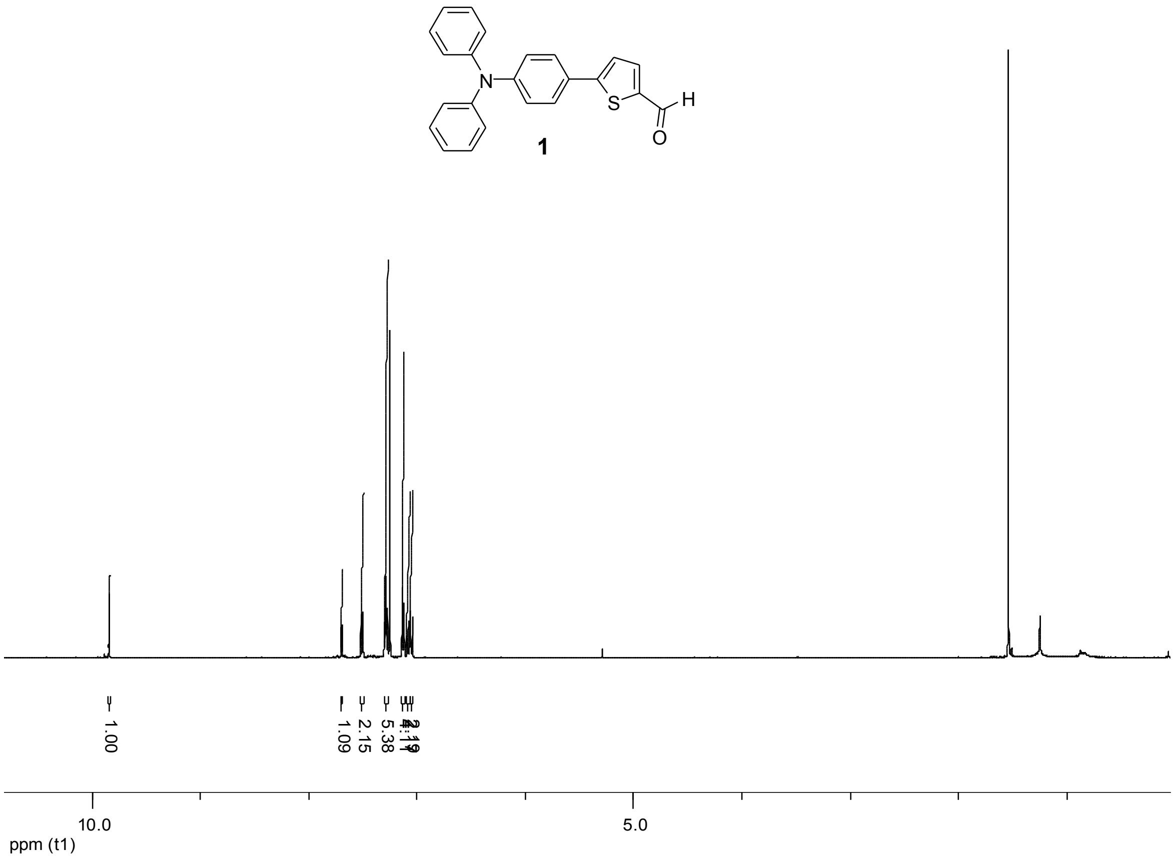
50
ppm (t1)

N
S
H
O

1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2.19
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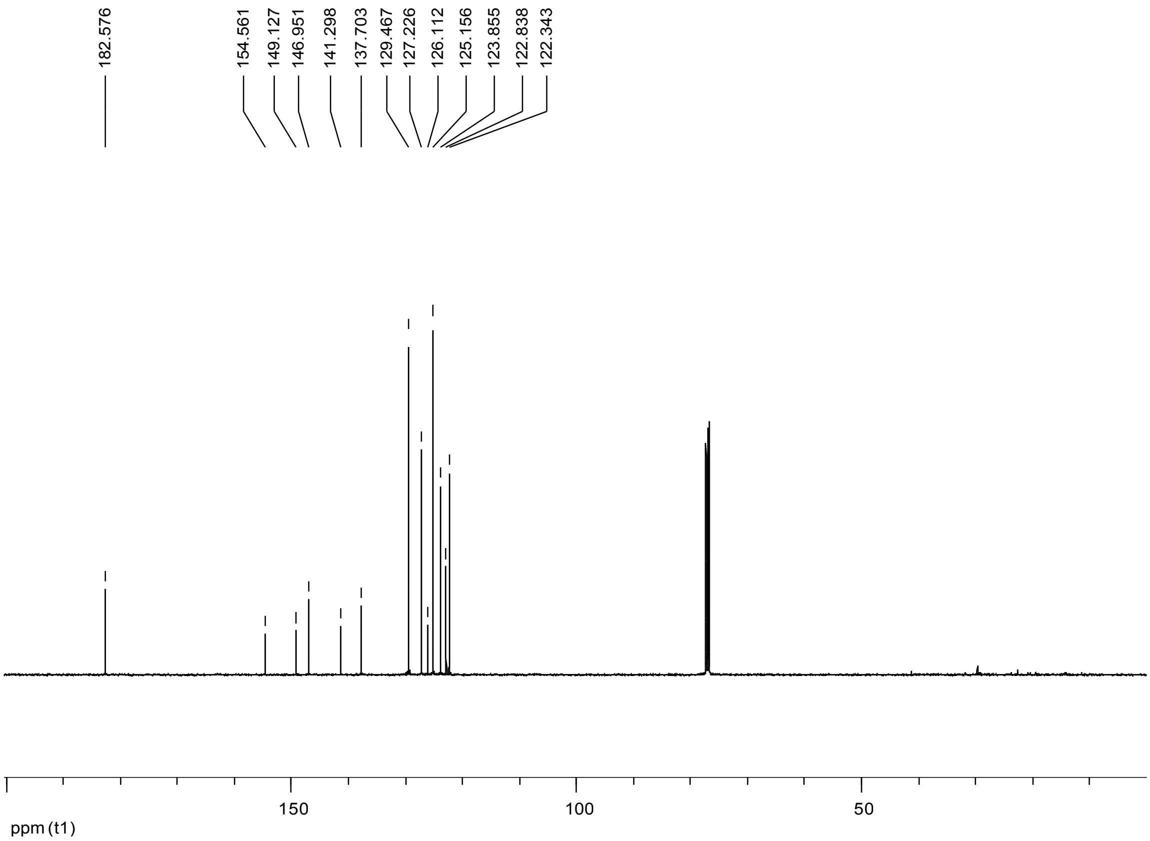
ppm (t1)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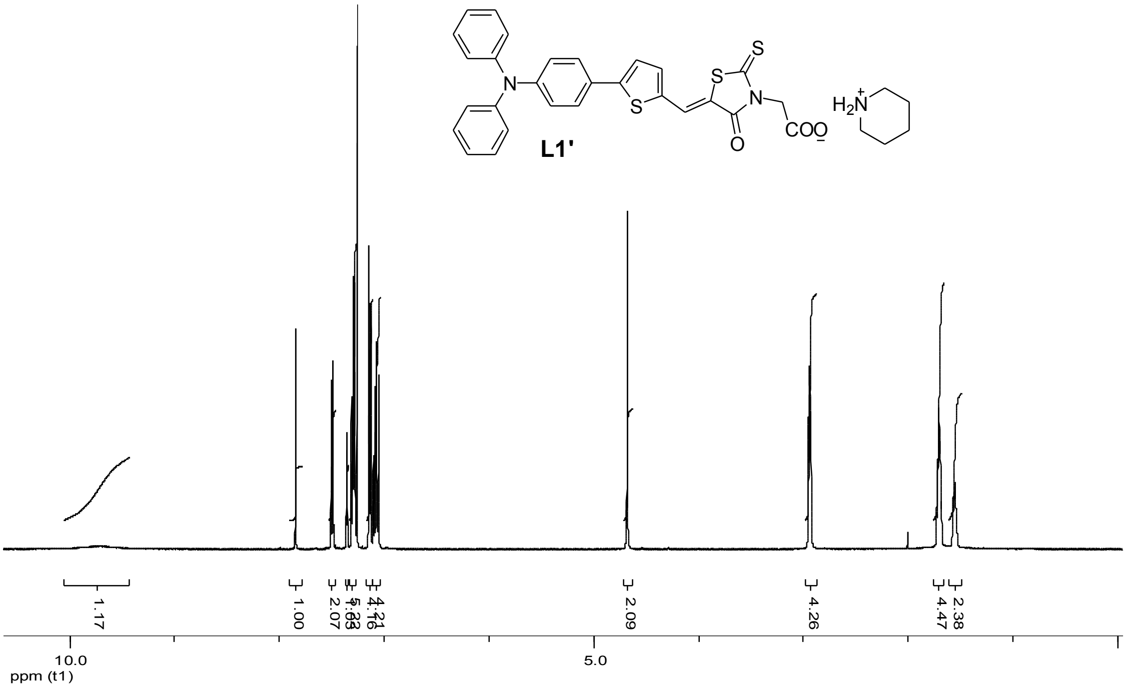
ppm (t1)


L1'
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S
S
S
N
O
COO
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2.09
4.26
4.47
2.38
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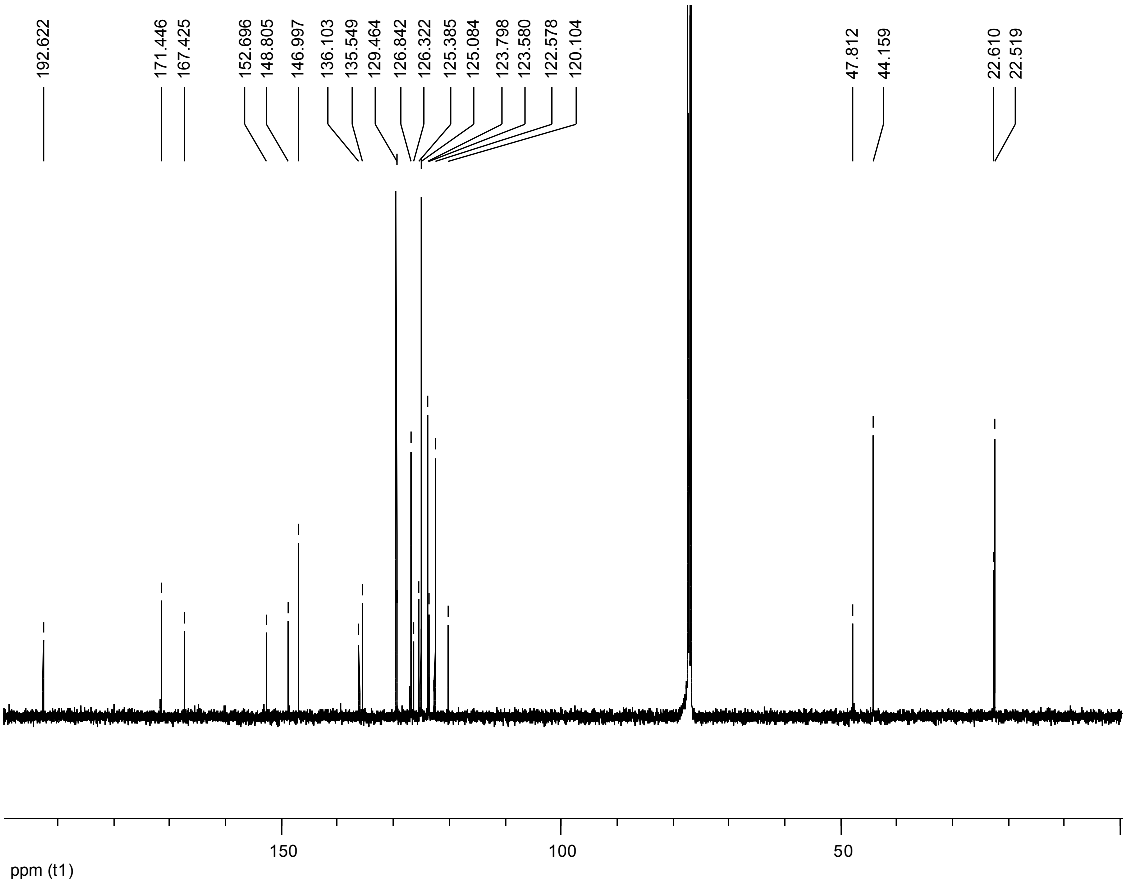
5.0
ppm (t1)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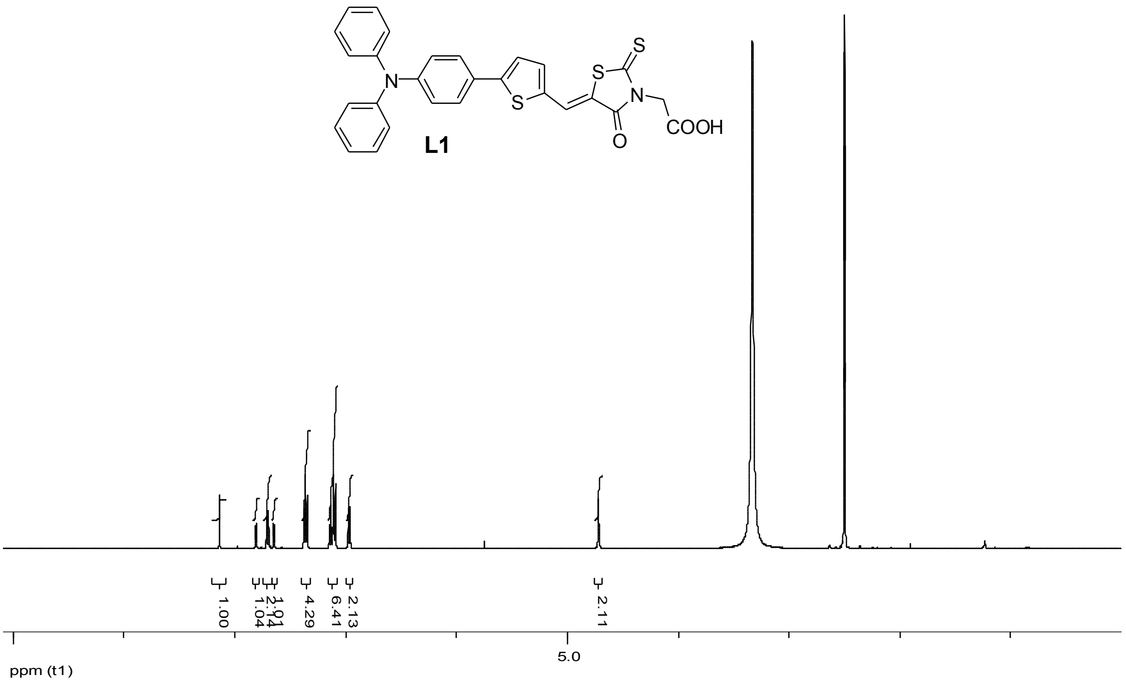
ppm (t1)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O
N
S
L1
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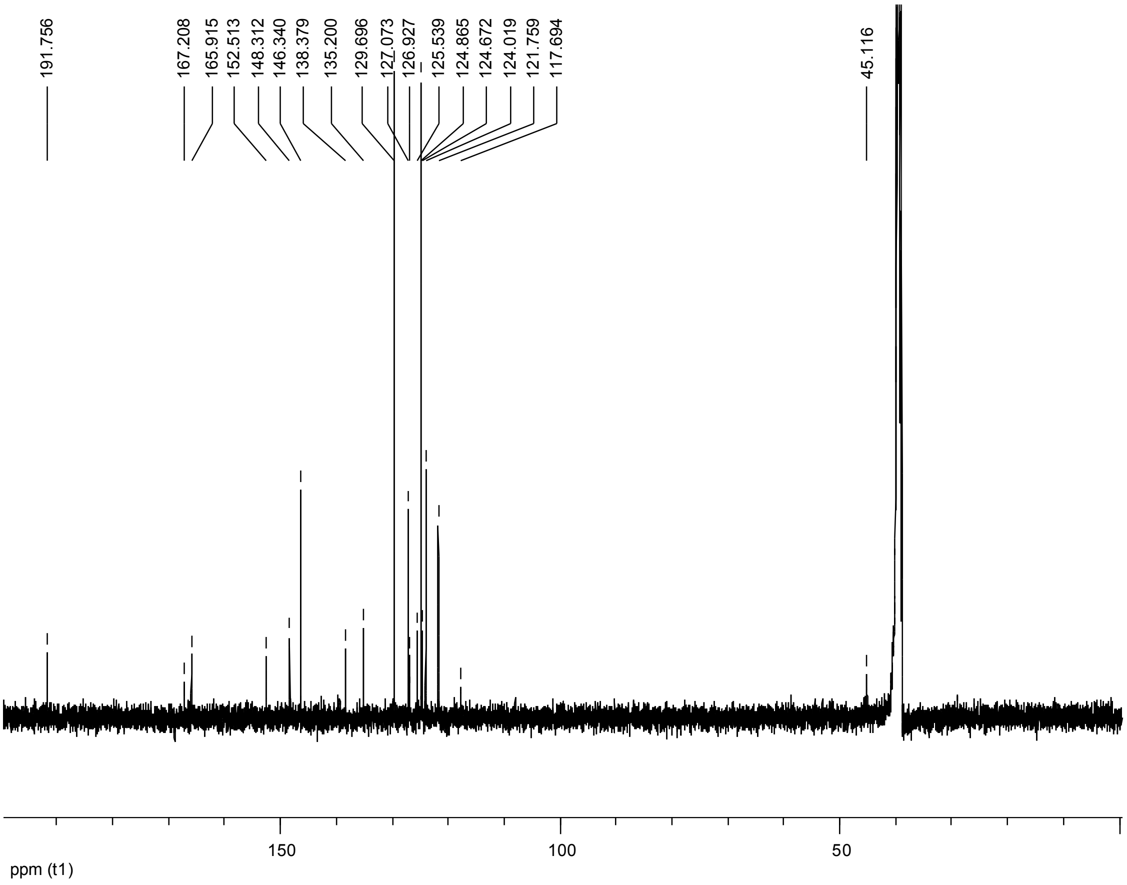
ppm (t1)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124.019
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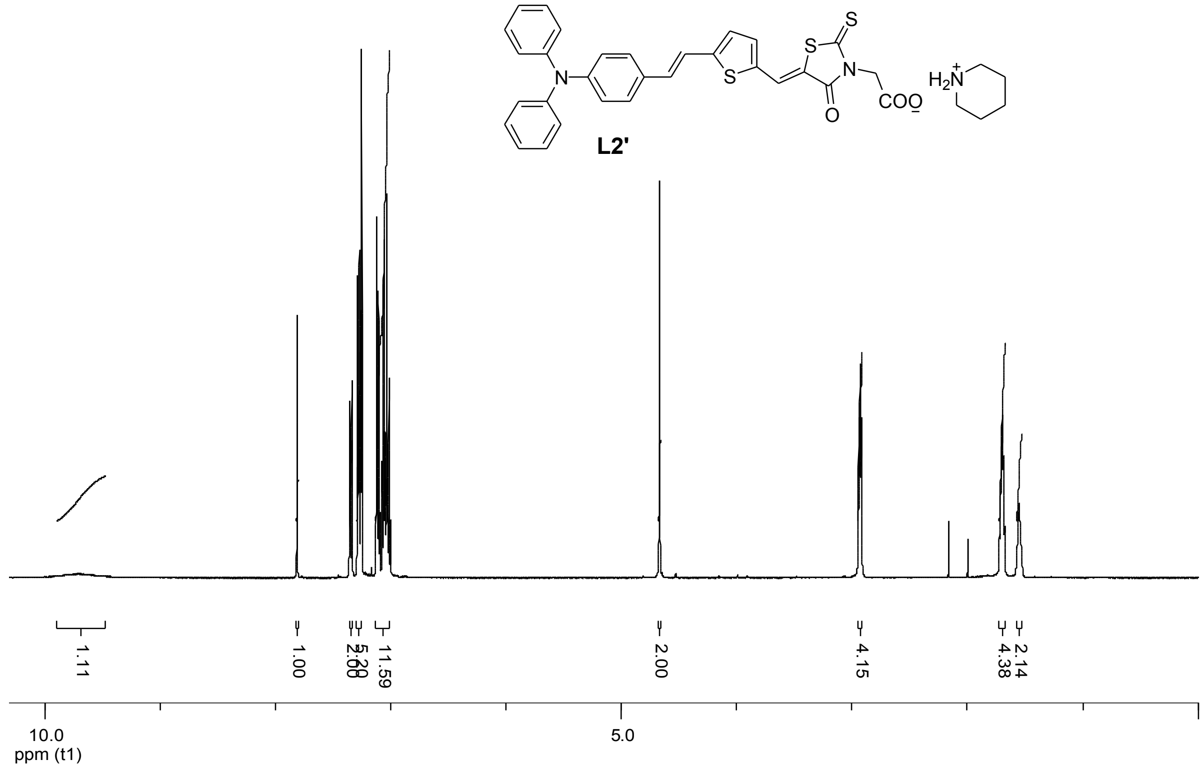
ppm (t1)


S
N
S
S
N
O
COO−
H2N+
L2'
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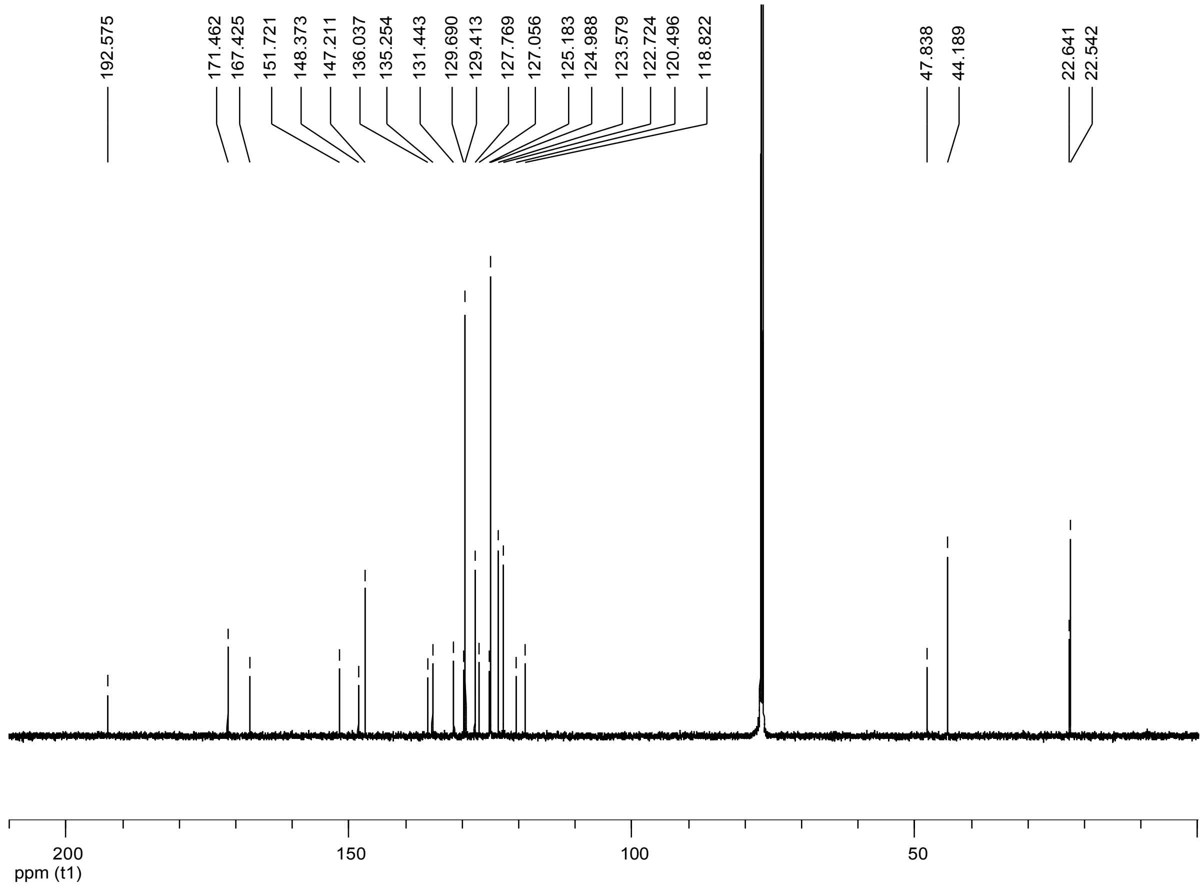
5.0
ppm (t1)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125.183
124.988
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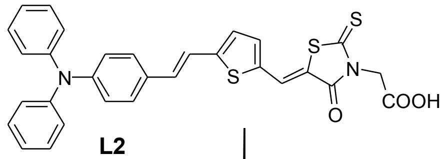
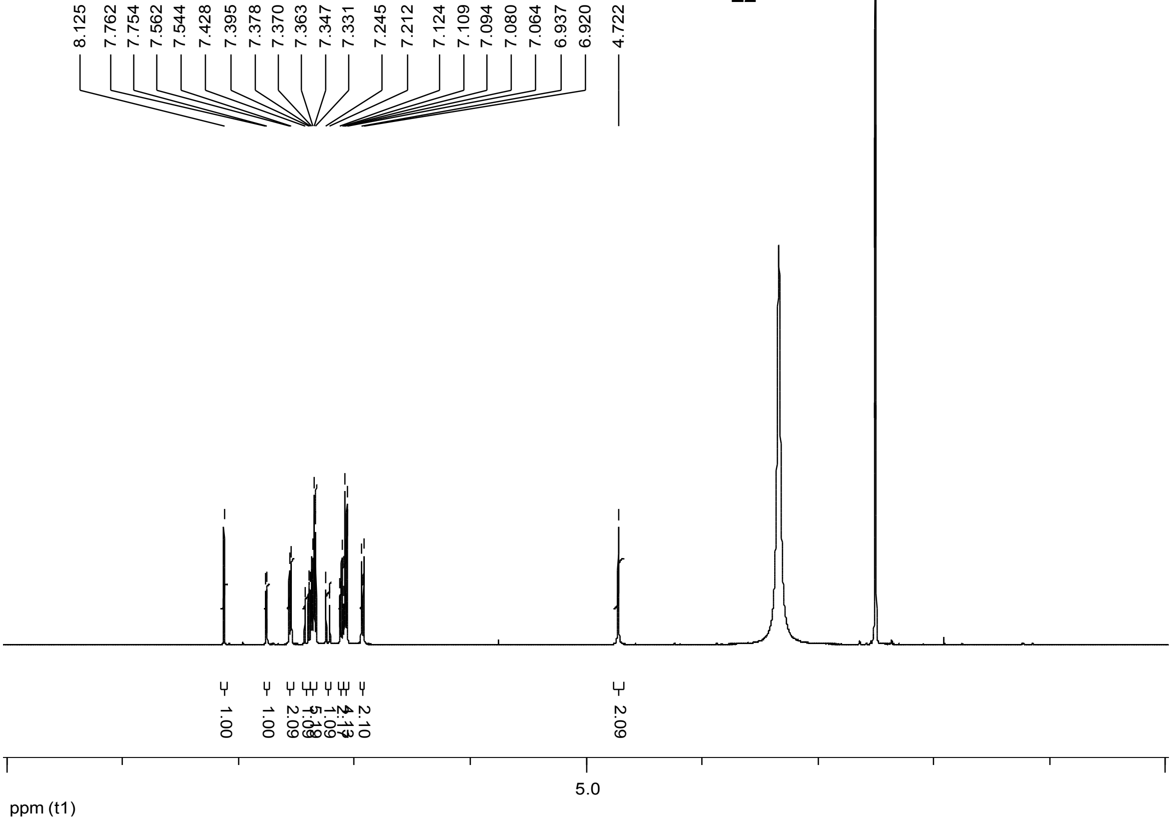
50
ppm (t1)


N
S
S
S
N
O
COOH

L2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7.347
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7.212
7.124
7.109
7.094
7.080
7.064
6.937
6.920
4.722
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1.09
2.17
4.13
2.10
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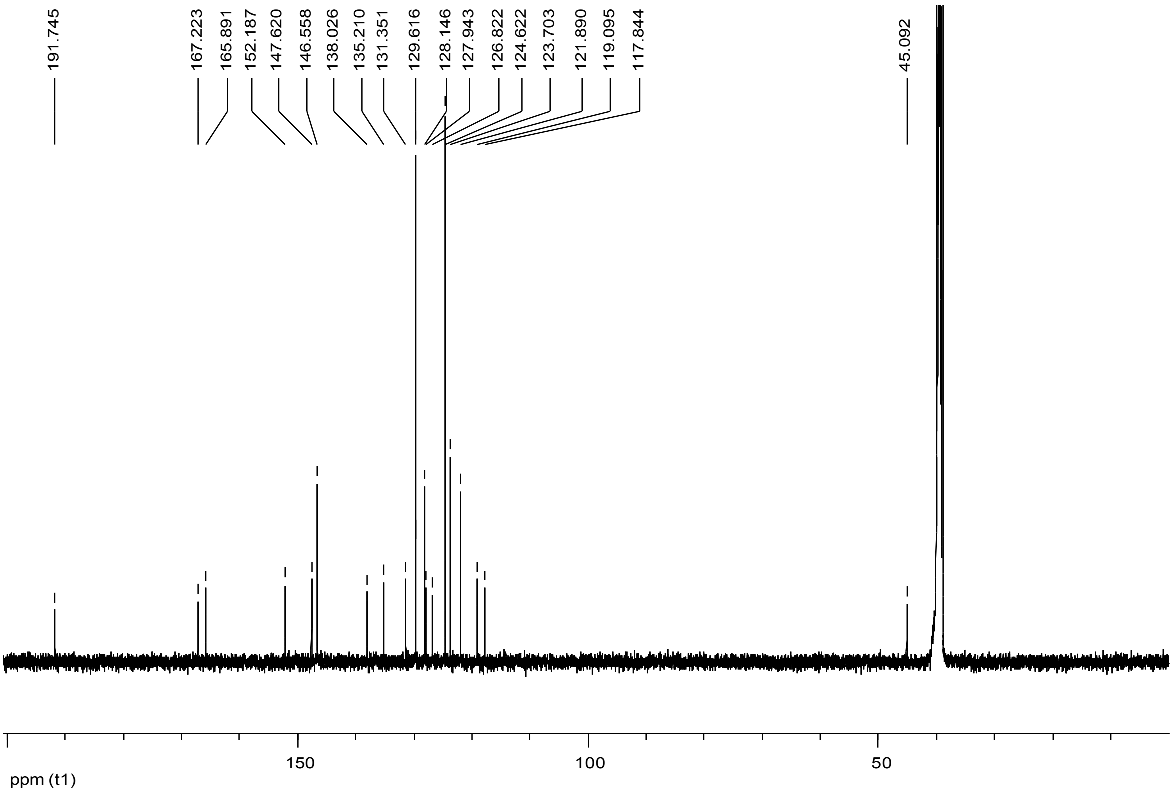
ppm (t1)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128.146
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126.822
124.622
123.703
121.890
119.095
117.844
45.092
150
100
50
ppm (t1)

S1.2 Materials

Screen printed nanostructured TiO_2 photoelectrodes were prepared by IVF Industrial Research and Development Corporation using a TiO_2 paste from ECN, The Netherlands.[2] Fluorine doped SnO_2 conducting glass TEC 8 (Pilkington) was used both for working and counter electrodes and was cleaned in ethanol in an ultrasonic bath prior to use. All solvents and chemicals used in this work were of reagent grade and used without further purification.

S1.3 Preparation of Dye-Sensitized TiO_2 Electrodes

Preparation of dye sensitized solar cells were done by the following procedure; screen printed TiO_2 electrodes were sintered at 450 °C for 45 min and cooled down to 80-100°C before immersion into 500 μM acetonitrile dye solutions for 12-14 hours in room temperature. After completion of the dye sensitization, the electrode was immersed in 99% acetonitrile for a couple of minutes and subsequently dried in air flow.

S1.4 Photovoltaic Measurements

The sandwich type two electrode electrochemical cell used for photovoltaic measurements is composed of a working electrode consisting of a dye-sensitized, 9-11 μm thick porous TiO_2 electrode, 50 μm Surlyn frame and a liquid electrolyte, a counter electrode consisting of FTO, fluorine doped tin oxide that was thermally platinized by depositing 15 μL 5 mM H_2PtCl_6 in iso-propanol and heated at 380˚C for 15 min. The area of the TiO_2 film electrodes was 0.48 cm^2. The electrolyte consisted of 0.5 M LiI, 0.05 M I_2 in acetonitrile with and without 0.5 M 4-*tert*-butylpyridine (4-TBP), unless indicated otherwise. A Xenon lamp with a Schott Tempax 113 filter was used to simulate sunlight (AM 1.5) and was calibrated to $1000 W m^{-2}$ with a reference silicon diode. The DSCs were masked to 0.63 cm^2, a mask somewhat larger than the active surface area, to capture both the direct and the diffuse light in accordance to the discussion of Ito et al.[3]

The redox potential of the I^-/I_3^- electrolyte was determined as follows: a reference electrode was constructed from a small tube with a porous plug at the bottom which was filled with the redox electrolyte. A Pt wire was immersed in the solution. This assembly was placed in a electrochemical cell with a Pt working electrode, a Pt counter electrode and an electrolyte containing ca. 10 mM ferrocene and 0.1 M $TBAPF_6$ in MeCN. The formal potential of the Fc^+/Fc couple was determined to be +0.33 V vs. the I^-/I_3^- reference. As the $E^{0'}$ (Fc^+/Fc) in MeCN is given to be +0.630 V vs NHE,[2] the redox potential of the I^-/I_3^- electrolyte is calculated to be 0.30 V vs NHE.

S1.5 Experimental techniques

The UV-Visible spectra of the dyes in solution and adsorbed on TiO_2 films were recorded on a HR-2000 Ocean Optics, fiber optics spectrophotometer. The IPCE was recorded using a computerized set-up consisting of a xenon arc lamp (300 W Cermax, ILC Technology), followed by a 1/8 m monochromator (CVI Digikrom CM 110). The data collection was done with a Keithley 2400 source/meter, and a Newport 1830-C power meter with 818-UV detector head. Differential pulse voltammetry was performed with a CH Instruments 660 Potentiostat using 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in acetonitrile (Fluka > 99.9%) as supporting electrolyte. A platinum working electrode, platinum counter electrode and a Ag/Ag^+ reference electrode were used. The system was internally calibrated with ferrocene/ferrocenium

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[2] Pavlishchuk, V. V.; Addison, A. W., *Inorg. Chim. Acta.* 2000, 298, (1), 97-102.

(Fc/Fc^+). Electron lifetimes and transport times in the complete dye sensitized solar cell device were measured in a system using a red-light emitting diode (Luxeon Star 1W, λ_{max}= 640 nm) as light source. Voltage and current traces were recorded using a 16-bit resolution data acquisition board (DAQ National Instruments) in combination with a current amplifier (Stanford Research Systems SR570) and a custom-made system using electromagnetic relay switches. The relation between potential and charge was investigated by combining the voltage decay and charge extraction methods. Extraction charge measurements were performed in the following way; the solar cell was illuminated for 5 s under open-circuit conditions, then the light was shut off and the voltage was let to decay to a voltage V. The cell was then short-circuited at the same time the current was measured under 10 s and then integrated to obtain Q_{oc} (V). Electron lifetimes were determined by monitoring the transient voltage responses after a small light intensity modulation (square wave modulation, <10% intensity of 0.5 Hz), and the step response was recorded by the DAQ board. The voltage response was well fitted to first-order decay, and time constants were hence obtained. Samples for Photoelectron spectroscopy (PES) measurements (sensitized electrodes and dye powder) were prepared as follows; the TiO_2 electrodes were sensitized in the same way as for DSC preparation and dye powder was pressed on F: SnO_2 substrates. The experiment was performed on a Scienta ESCA-300 spectrometer, using monochromatic AlK_α radiation (1487eV) and with an electron take off angle of 90°. Also, TiO_2 sensitized electrodes were investigated by PES using a Scienta SES-200 analyzer and synchrotron radiation at BLI411 at the Swedish national laboratory MAX-lab, Lund. In these measurements the electron take off angle was either 70° or 80° and the electron take off direction was collinear with the e-vector of the incident photon beam. The PES spectra were energy calibrated by setting the Ti2p substrate signal to 458.56eV.[4, 5]

S1.6 Computational Methods and Procedure

The Gaussian 03 program suite[6] was used for all electronic structure calculations. Optimized geometries have been computed at the B3LYP/6-31G (d) and PBE1PBE/6-31G (d) levels of theory. PBE1PBE refer to the 1997 hybrid exchange-correlation functional of Perdew, Burke and Ernzerhof.[7] Electronic absorption spectra were calculated at the optimized geometries using time-dependent density functional theory (TDDFT) with the same exchange-correlation functionals but with the larger 6-31+G* basis set. The diffuse functions of the basis set have a negligible influence on geometries of ground state neutral and cationic molecules, but can have a significant effect on excitation energies and oscillatory strengths due to the more diffuse electron density of the excited states. The TDDFT method is known to perform well for computing valence-excited states of regular molecules but often underestimates the energies of charge-transfer (CT) states.[8] In addition, the error generally increases with the distance between the negative and positive charge of the CT state. This is an effect of the lack of self-interaction correction in pure DFT functionals, and the error is reduced in hybrid functionals, like the B3LYP and PBE1PBE, which contains 20 and 25% Hartree-Fock exchange, respectively. However, for extended π-systems, such as the dyes of this study, the error may still be substantial. We have therefore also calculated excitation energies using time-dependent Hartree-Fock theory (TDHF) at the HF/6-31+G (d) level. The TDHF method generally underestimates excitation energies, due to the lack of electron correlation treatment, but the excitation energies has a correct distance-dependence for CT-states.[8] Solvation energies of neutral and oxidized dyes have been computed at the B3LYP/6-31G(d) level using the recent implementation of the polarizable continuum model (PCM)[9] in Gaussian 03. The cavity was defined by overlapping spheres centered at the nuclei, and the radii of the spheres were taken as defined in the UAKS parameterization of Gaussian 03. The solvent parameters were those defined for acetonitrile. Oxidation potentials versus NHE have been calculated using the following equation;

$$E^{o}_{D^{+}/D} = \mathrm{IP} + \frac{1}{F}\left(\Delta G^{o}_{sol}(D^{+}) - \Delta G^{o}_{sol}(D)\right) + C \qquad [1]$$

The parameters $\Delta G^{o}_{sol}(D^{+})$ and $\Delta G^{o}_{sol}(D)$ are the computed PCM solvation energies of the oxidized dye and neutral dye, respectively. The IP is the adiabatic ionization potential of the dye, which is calculated from the DFT computed electronic energies of the oxidized and neutral dyes. Thus, in calculating the oxidation potential we do not consider the change in zero point energy and thermal energy of the dye upon oxidation. Also the change in entropy due to the change in thermal motions of the dye is omitted. However, these effects are likely to be small as there are very small changes in the internal geometry of the dye upon oxidation. For the constant C a value of -4.49 V is used, which has been calculated from the absolute potential of the standard calomel electrode (= -4.74 V)[10, 11] and the conversion factor between the standard calomel electrode and the NHE electrode in acetonitrile (0.25 V).[12]

The reorganization energy of the dye upon oxidation has been computed using the following equation

$$\begin{aligned}\lambda &= F(\mathrm{IP^{*}\text{-}IP}) + \left(\Delta G^{*}_{sol}(D^{+}{*}) - \Delta G^{o}_{sol}(D^{+})\right) = \\ &\left(E(D^{+}{*}) - E(D^{+})\right) + \left(\Delta G^{*}_{sol}(D^{+}{*}) - \Delta G^{o}_{sol}(D^{+})\right)\end{aligned} \qquad [2]$$

where IP* is the vertical ionization energy and $\Delta G^{*}_{sol}(D^{+}{*})$ is the PCM solvation energy computed from the dielectric constant at infinite frequency and at the geometry of the neutral/unoxidized dye. The expressions $E(D^{+}{*})$ and $E(D^{+})$ are the DFT computed electronic energies of the oxidized dye at the geometries of the neutral and oxidized dye, respectively. The first part of the equation (within the first parentheses) essentially corresponds to the inner sphere reorganization energy and the second part, the outer sphere reorganization energy, according to Marcus theory. It should be noted that λ_o only considers the reorganization of the dye upon oxidation; the effect of the coupling with the electron acceptor is neglected.

S2. Results

S2.1.1 PES, measurements on S2p

Generally, the S2p spectrum of a sulfur atom show a doublet ($S2p_{1/2}$ and $S2p_{3/2}$) with a spin-orbit split of 1.18 eV and an intensity ratio of 0.5. The spectrum of L0 can be deconvoluted reasonably well using two such doublets shifted about 1.9 eV with the double bonded sulphur at lower binding energy as expected from the sulphur in the rhodanine moiety. However, the intensity ratios of the two peaks differ substantially from one, see Figure S1. Following the previous discussion, this can partly be explained by the surface sensitivity of the measurements and a molecular orientation with the carboxylate group attaching the surface. Apart from the two sulphurs in the rhodanine unit, both L1 and L2 also contain sulphur in the thiophene unit. The S2p spectra of L1 and L2 are rather similar supporting the conclusion that the molecular surface structures are similar, see Figure S1.

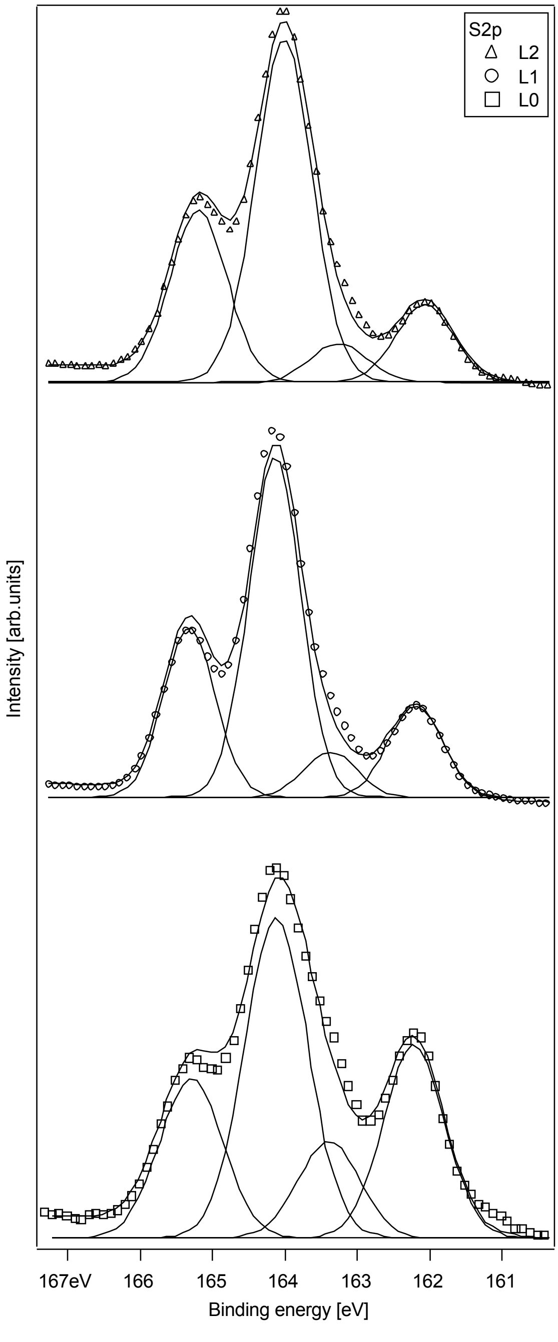

Figure S1. The S2p PES spectra for the different dyes adsorbed on TiO_2. The spectra were measured with a photon energy of 454 eV.

S2.1.2 Photoinduced absorption

The PIA differential spectrum of the L2 oxidized dye is shown in Figure S2 and shows a positive absorption at 690 nm and 760 nm. Similar spectral features are observed for the oxidized L1 dye and for the oxidized L0 dye only a bleach is observed in the 500 nm region. As confirmed by PIA experiments all three dyes can inject electrons in the CB of

TiO_2, i.e. they become oxidized after electronic excitation of the dye. For all three dyes the spectra of the oxidized dye were no longer visible in the presence of redox electrolyte, with and without 4-TBP.

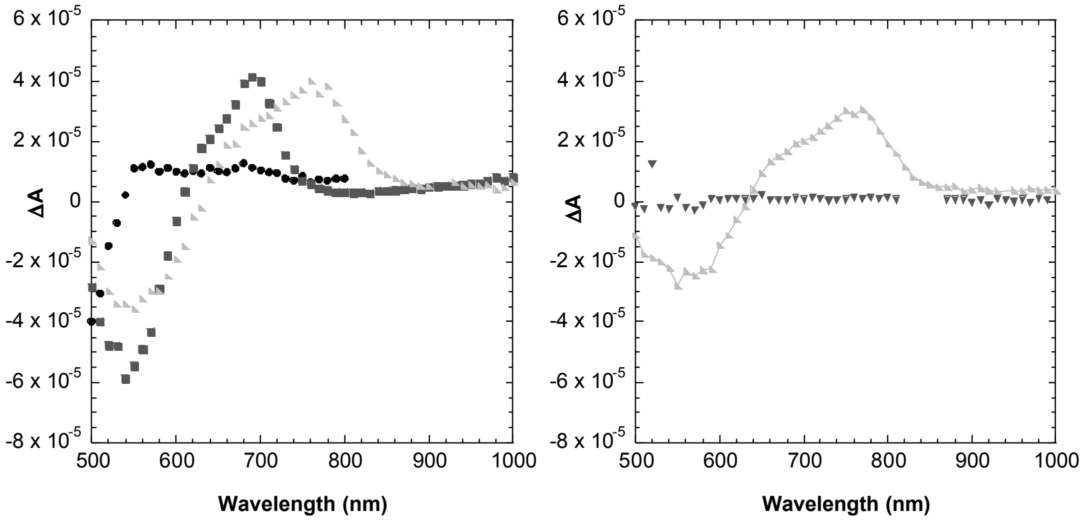

Figure S2. Photoinduced absorption spectra, excitation wavelength 450 nm with a frequency of 10 Hz, (left) L0, L1 and L2 sensitized nanostructured TiO_2 film in air (right) L2 sensitized nanostructured TiO_2 film with (▼) and without (▶) redox couple.

S2.1.3 Differences in charge collection efficiency

The relation between the lifetimes and transport times vs. the illumination intensity for DSC based on L0, L1 and L2, respectively, with the 0.5 M LiI, 0.05 M I_2 electrolyte is depicted in Figure S3. Transport times were found to be shorter compared to electron lifetimes, but the difference between the two decreases noticeably in the order L0, L1 and L2, suggesting greater recombination losses for the L2 dye during charge collection. The charge collection efficiency can be estimated as follows:

$$\eta_{cc} = 1 - \tau_{tr} / \tau_e$$

where τ_{tr} is the electron transport time and τ_e the electron lifetime. Using the data of Fig. S3 at the higher light intensities η_{cc} values of 0.91, 0.94 and 0.65 are calculated for L0, L1 and L2, respectively. I should be noted, however, that τ_e was measured at open-circuit conditions. For a good calculation of η_{cc} under short-circuit conditions (as in the IPCE measurement), at correction should be made. Additional charge extraction measurement under short-circuit condition were performed; using this charge, electron lifetimes can be estimated using Figure 8b. Using these values, η_{cc} is estimated to be 1.0 , 1.0, and 0.9 for L0, L1 and L2, respectively.

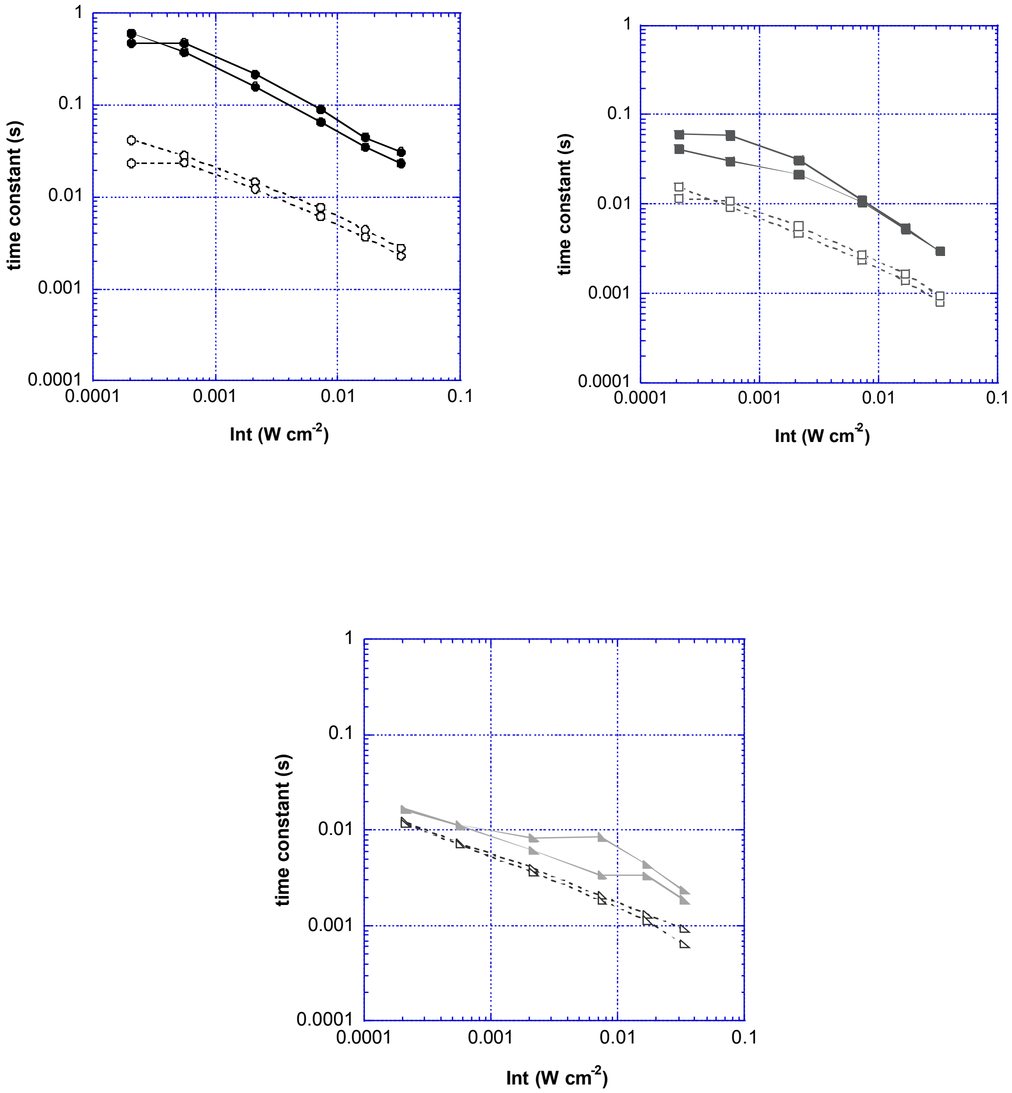

Figure S3. Electron lifetime (——) and electron transport time (------) as function of light intensity. Time constants were determined using time-resolved small modulation techniques. Solar cells based on i) L0 (●) **ii)** L1(■) and iii) L2(▶) dyes, respectively, with 0.5 M LiI, 0.05 M I_2 in acetonitrile.

S2.2 The effect of 4-TBP on the charge collection efficiency

The effect of 4-TBP on the charge collection efficiency for the solar cell device was further studied. The reaction that is more likely to be affected by the presence of 4-TBP is the overall recombination process of conduction band electrons, mainly to triiodide.
It is well known that the electron lifetime is dependent on the light intensity, i.e. the number of electrons in the TiO_2. Thus a relevant measurement is how the lifetime varies with the accumulated charge in the TiO_2 for DSC based on electrolytes with and without 4-TBP. The electron lifetime versus the extracted charge was plotted for L2 based DSCs in Figure S4 (left). At light intensities > 0.3 sun the electron lifetime did not differ

significantly with and without the additive, i.e. the 4-TBP does not show a blocking effect in the present system.

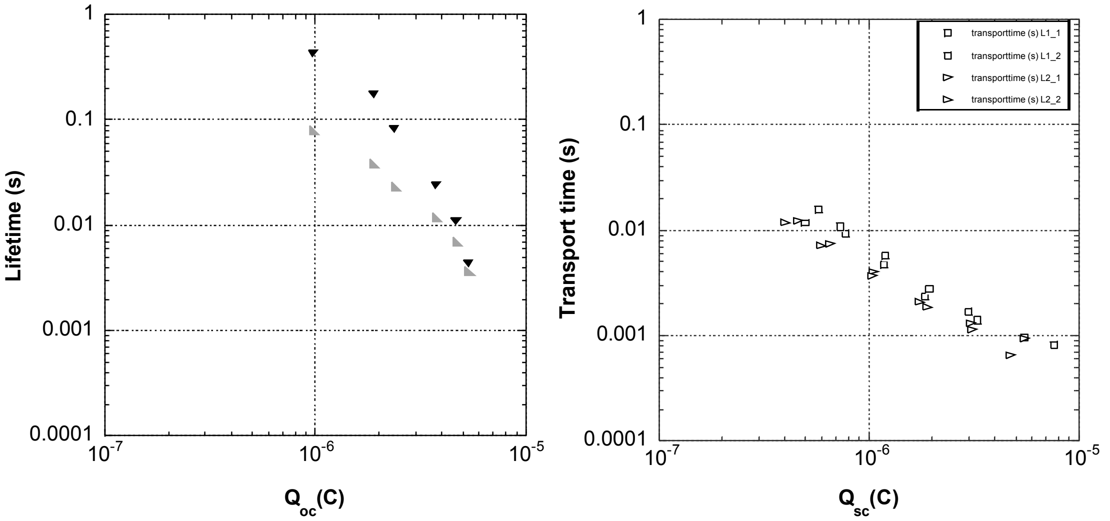

Figure S4. (left) Electron lifetime as function of extracted charge, time constants were determined using time-resolved small modulation techniques, in dye sensitized solar cells based on L1 with electrolyte 1 **(▼)** 0.5 M LiI, 0.05 M I_2, 0.5 M 4-TBP and 2 **(▶)** 0.5 M LiI, 0.05 M I_2 in acetonitrile, respectively.(right) Transport time as a function of short-circuit charge density for L2 (triangles) and L1 (squares).

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