Structural modulation of internal charge transfer in small molecular donors for organic solar cells.

Antoine Leliège, C-H. Le Régent, Magali Allain, Philippe Blanchard* and Jean Roncali*

LUNAM, University of Angers, CNRS UMR 6200, MOLTECH-Anjou, Group Linear Conjugated Systems, 2Bd Lavoisier, 49045 Angers, France

Electronic Supplementary Information

1. Experimental conditions

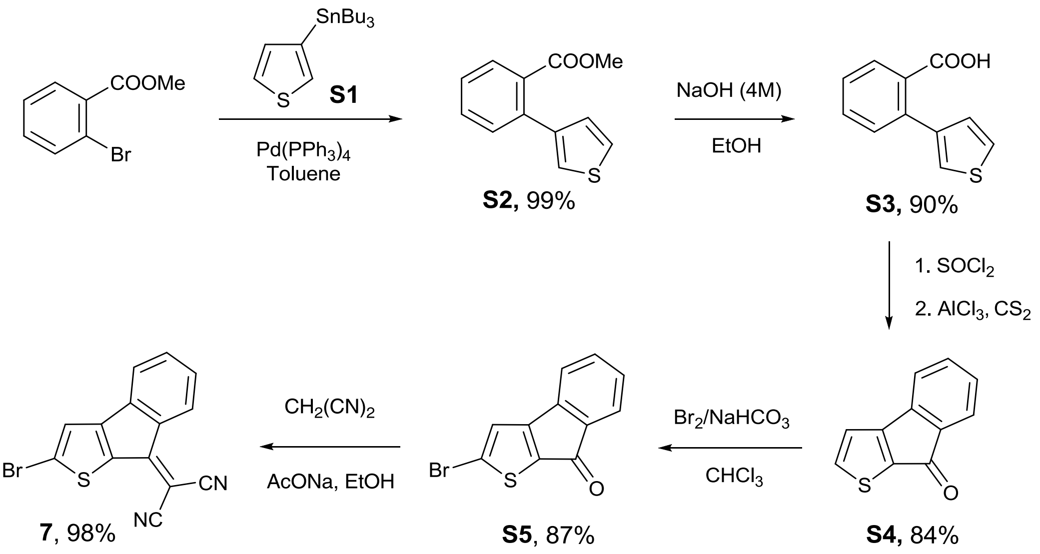
NMR spectra were recorded with a Bruker AVANCE III 300 (^{1}H, 300 MHz and ^{13}C, 75 MHz) or Bruker AVANCE DRX 500 (^{1}H, 500 MHz and ^{13}C, 125 MHz). Chemical shifts are given in ppm relative to TMS. Infrared spectra were recorded on a Bruker spectrometer Vertex 70 and UV-Vis spectra with a Perkin Elmer Lambda 19 spectrometer. Melting points are uncorrected.

Matrix Assisted Laser Desorption/Ionization was performed on MALDI-TOF MS BIFLEX III Bruker Daltonics spectrometer using dithranol as matrix.

Cyclic voltammetry was performed in dichloromethane solutions purchased from SDS (HPLC grade). Tetrabutylammonium hexafluorophosphate (0.1 M as supporting electrolyte) were purchased from Acros and used without purification. Solutions were deaerated by nitrogen bubbling prior to each experiment which was run under a nitrogen atmosphere. Experiments were done in a one-compartment cell equipped with a platinum working microelectrode (∅ = 2 mm) and a platinum wire counter electrode. An Ag/AgNO$_3$ (0.01 M in CH$_3$CN) electrode was used as reference and checked against the ferrocene/ferricinium couple (Fc/Fc$^+$) before and after each experiment. Then the potentials were expressed relative to SCE reference electrode (E_{ox} (Ferrocene) = 0.405 V/SCE). Electrochemical experiments were carried out with a Biologic SP-150 potentiostat with positive feedback compensation. Elemental analyses were performed with a thermo-electron instrument. Column chromatography purifications were carried out on Acros silica gel Si 60 (35-70 µm). DSC and TGA were performed with TA Instruments.

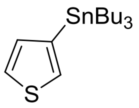
2. Synthesis and analytical data

4-Bromo-*N*,*N*-diphenylaniline, 2-(tributylstannyl)thiophene, 3-bromothiophene and methyl 2-bromobenzoate were purchased from Aldrich. The new derivative **7** was prepared according to Scheme S1. The synthesis of the intermediate compound **S4** has been previously described using other procedures.[1-3]



Scheme S1

3-Tributylstannylthiophene (S1)

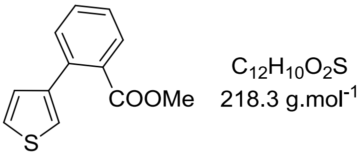


$C_{16}H_{30}SSn$
373.2 g.mol^{-1}

In a 100 mL three-necked round bottom flask, a solution of *n*-BuLi 1.6 M in hexane (24.4 mL, 39 mmol, 1.1 equiv.) was added slowly to a solution of 3-bromothiophene (5.79 g, 35.5 mmol) in anhydrous Et_2O (40 mL) cooled to -78°C under a N_2 atmosphere. After 0.5 h of stirring at -78°C, a white precipitate was observed and 96% pure Bu_3SnCl (10.5 mL, 38.7 mmol, 1.1 equiv.) was added slowly. The reaction mixture was then allowed to reach room temperature. After addition of Et_2O (50 mL), the mixture was washed with a saturated aqueous solution of NH_4Cl, dried over $MgSO_4$ and concentrated to dryness. The residue was dissolved in EtOAc (100 mL) and treated with a saturated aqueous solution of NaF (20 mL). The resulting white precipitate was filtered off and the filtered solution was washed with a saturated aqueous solution of NaCl (50 mL) and finally dried over $MgSO_4$ to give colorless oil (9.89 g, 75% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.45 (dd, 1H, ^3J=4.7Hz, ^4J=2.5Hz); 7.34 (dd, 1H,

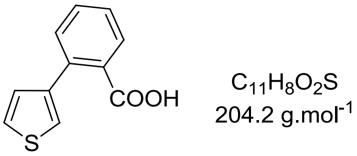
^{4}J=2.4Hz, ^{4}J=1.1Hz); 7.16 (dd, 1H, ^{3}J=4.8Hz, ^{4}J=0.8Hz); 1.50-1.57 (m, 6H); 1.28-1.37 (m, 6H); 0.96-1.12 (m, 6H); 0.89 (t, 9H, ^{3}J=7.4Hz).

Methyl 2-(thien-3-yl)benzoate (S2)



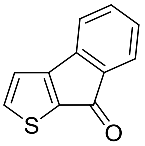
In a 100 mL three-necked round bottom flask equipped with a condenser, a mixture of stannyl compound **S1** (9.89 g, 26.5 mmol, 1.1 equiv.) and methyl 2-bromobenzoate (5.12 g, 23.8 mmol) in toluene (50 mL) was degassed with N_2 for 10 min before addition of $Pd(PPh_3)_4$ (0.54 g, 0.47 mmol, 2% mol.). The reaction mixture was refluxed for 24 h under a N_2 atmosphere. After evaporation of the solvent, the residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/Petroleum ether 1:1) to give **S2** as colorless oil (5.16 g, 99% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.77 (dd, 1H, ^{3}J=7.7Hz, ^{4}J=1.2Hz); 7.50 (m, 1H, ^{3}J=7.5Hz, ^{4}J=1.4Hz); 7.42 (dd, 1H, ^{3}J=7.5Hz, ^{4}J=1.1Hz); 7.39 (m, 1H, ^{3}J=7.6Hz, ^{4}J=1.6Hz); 7.34 (dd, 1H, ^{3}J=5.0Hz, ^{4}J=3.0Hz, $H_{thioph.}$); 7.25 (dd, 1H, ^{4}J=3.0Hz, ^{4}J=1.2Hz, $H_{thioph.}$); 7.09 (dd, 1H, ^{3}J=5.0Hz, ^{4}J=1.2Hz, $H_{thioph.}$); 3.72 (s, 3H). IR (neat): $\tilde{\nu}$ = 1717 cm^{-1} (C=O). EI MS: 217.9 [M$^+$]. These data are consistent with the literature data.[3]

2-(Thien-3-yl)benzoic acid (S3)[4]



In a 100 mL three-necked round bottom flask equipped with a condenser, a 4 M solution of NaOH (30 mL) was added to a solution of **S2** (3.47 g, 15.8 mmol) in EtOH (30 mL). The mixture was warmed and stirred at 90°C for 2 h. The mixture was cooled to 0°C before dropwise addition of concentrated HCl (10 mL). At room temperature, the mixture was diluted with Et_2O (100 mL), washed with water (2 x 100 mL) and dried to dryness affording pure compound **S3** as yellowish solid (2.93 g, 90% yield). M. p. 90-91°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 11.0 (br. s, 1H); 7.93 (d, 1H, ^{3}J=7.6Hz); 7.55 (t, 1H, ^{3}J=7.5Hz); 7.43-7.40 (m, 2H); 7.33 (dd, 1H, ^{4}J=3.0Hz, ^{3}J=4.9Hz, $H_{thioph.}$); 7.27 (dd, 1H, ^{4}J=3.0Hz, ^{4}J=1.3Hz, $H_{thioph.}$); 7.13 (dd, 1H, ^{3}J=4.9Hz, ^{4}J=1.2Hz, $H_{thioph.}$). EI MS: 203.9 [M$^+$].

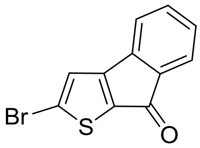
8*H*-Indeno[2,1-*b*]thiophen-8-one (S4)[1-3]



$C_{11}H_6OS$
186.2 g.mol^{-1}

A mixture of acid **S3** (2.93 g, 14.3 mmol) and thionyl chloride (5 mL, 68.5 mmol) was stirred overnight at 45°C under N_2 atmosphere. After evaporation of the excess of thionyl chloride under vacuum, the resulting brown oil was directly engaged in the next reaction. Under a N_2 atmosphere, a solution of this oil dissolved in CS_2 (35 mL) was added dropwise over a period of 5 min through a dropping funnel to a 250 mL three-necked round bottom flask containing a suspension of $AlCl_3$ (4.4 g, 33 mmol, 2.3 equiv.) in CS_2 (50 mL) under stirring. The reaction mixture was then refluxed for 6 h. At room temperature, this mixture was poured into a mixture of ice (100 mL) and concentrated HCl (20 mL). After separation, the organic phase was concentrated and diluted with Et_2O (50 mL). The aqueous phase was extracted with Et_2O (2 x 100 mL). All organic phases were gathered and washed with a saturated aqueous solution of NaCl, dried over $MgSO_4$ and concentrated to dryness. A purification by column chromatography on silica gel (eluent: CH_2Cl_2) gave **S4** as yellow solid (2.25 g, 84% yield). M. p. 106-110°C. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.74 (d, 1H, ^{3}J=4.6Hz, $H_{thioph.}$); 7.47 (d, 1H, ^{3}J=7.0Hz); 7.33 (m, 1H, ^{3}J=7.5Hz, ^{4}J=1.2Hz); 7.17 (d, 1H, ^{3}J=7.2Hz); 7.16 (m, 1H, ^{3}J=7.6Hz, ^{4}J=1.2Hz); 7.12 (d, 1H ^{3}J=4.7Hz, $H_{thioph.}$). IR (neat): $\tilde{\nu}$ = 1726 cm^{-1}; 1687 cm^{-1} (C=O). EI MS: 185.7 [M$^+$].

2-Bromo-8H-indeno[2,1-*b*]thiophen-8-one (S5)

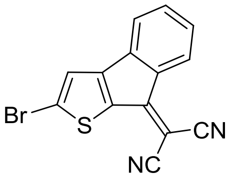


$C_{11}H_5BrOS$
265,1

Br_2 (0.19 mL, 3.70 mmol) was added dropwise to a mixture of ketone **S4** (0.5 g, 2.68 mmol) and $NaHCO_3$ (241 mg, 2.87 mmol) in $CHCl_3$ (20 mL) cooled to 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 7 h. Water (100 mL) was added and the mixture was extracted by CH_2Cl_2 (3 x 25 mL). The organic phases were washed with a saturated aqueous solution of $NaHCO_3$ (100 mL), water (2 x 100 mL), dried over $MgSO_4$ and concentrated. The residue was purified by column chromatography on silica gel (eluent: CH_2Cl_2/Petroleum ether 1:1) to lead to **S5** as yellow-orange powder (0.62 g, 87% yield). M. p. 135-136°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.47 (ddd, 1H, J=7.2Hz, J=1.2Hz, J=0.7Hz); 7.34

(td, 1H, J=7.2Hz, J=1.2Hz); 7.19 (td, 1H, J=7.2Hz, J=1.0Hz); 7.17 (s, 1H); 7.13 (ddd, 1H, J=7.2Hz, J=0.9Hz, J=0.7Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 184.7 ; 157.7 ; 139.2 ; 136.8 ; 136.5 ; 133.9 ; 128.8 ; 128.1 ; 124.5 ; 123.6 ; 119.9. UV-Vis (CH_2Cl_2) λ_{max}/nm: 408 (ε=800 L mol^{-1} cm^{-1}). IR (neat): $\tilde{\nu}$ = 1726 cm^{-1}; 1685 cm^{-1} (C=O). EI MS: 263.6/266.0 [M$^+$]. Anal. Calcd. for $C_{11}H_5BrOS$: C, 49.83; H, 1.90; found: C, 49.76; H, 2.06.

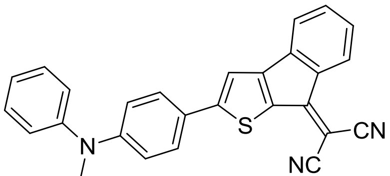
2-(2-Bromo-8H-indeno[2,1-*b*]thiophen-8-ylidene)malononitrile (7)



$C_{14}H_5BrN_2S$
313,2

Malononitrile (124 mg, 1.88 mmol) was added to a solution of **S5** (250 mg, 0.94 mmol) and CH_3COONa (100 mg, 1.22 mmol) in EtOH (10 mL). The reaction mixture was refluxed for 1.5 h and cooled with an ice bath. The precipitate was recovered by filtration and was washed with EtOH (2 x 10 mL) to give compound **7** as brown powder (290 mg, 98% yield). M. p. 254-258°C. ^{1}H NMR (300 MHz, CD_2Cl_2) δ: 8.12 (d, 1H, J=7.7Hz); 7.39 (td, 1H, J=7.5Hz, J=1Hz); 7.29 (d, 1H, J=7.4Hz); 7.27 (s, 1H); 7.24 (td, 1H, J=7.6Hz, J=1.3Hz). ^{13}C NMR (75 MHz, CD_2Cl_2) δ: 157.9 ; 154.4 ; 138.2 ; 136.7 ; 136.1 ; 134.1 ; 129.0 ; 128.8 ; 127.1 ; 124.1 ; 121.4 ; 114.2 ; 113.0 ; 74.0. EI MS: 311.7 [M$^+$]. Anal. Calcd. for $C_{14}H_5BrN_2S$: C, 53.69; H, 1.61; N, 8.95; found: C, 53.23; H, 1.61; N, 8.83. IR (neat): $\tilde{\nu}$ = 2220 cm^{-1} (C≡N).

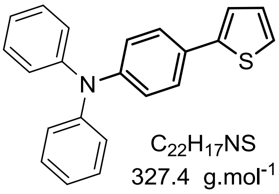
2-(2-(4-(Diphenylamino)phenyl)-8H-indeno[2,1-*b*]thiophen-8-ylidene)malononitrile (2)



$C_{32}H_{19}N_3S$
477.6 g.mol^{-1}

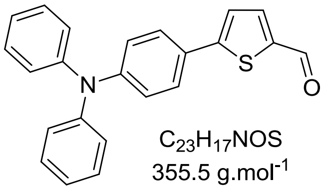
Under argon atmosphere and using a Schlenk flask protected from light, *n*-BuLi 2.5 M in hexane (0.50 mL, 1.25 mmol) was added dropwise to a solution of 4-bromo-*N*,*N*-diphenylaniline (250 mg, 0.77 mmol) in anhydrous THF (15 mL) cooled to -78°C. The reaction mixture was stirred at this temperature for 0.5 h before addition of Bu_3SnCl (0.25 mL, 0.92 mmol). After 5 min at -78°C, the mixture was allowed to warm to room temperature and then stirred for 2 h. After dilution with Et_2O (50 mL), the organic phase was washed with a saturated aqueous solution of NaF (100 mL), water (2 x 100 mL), dried over $MgSO_4$ and evaporated affording *N*,*N*-diphenyl-4-(tri-*n*-butylstannyl)aniline **6**[5]as a light yellow oil which was directly used in the next Stille reaction. A mixture of the stannyl derivative **6** and compound **7** (240 mg, 0.77 mmol) in toluene (10 mL) in a Schlenk flask was degassed with argon during 15 min before addition of $Pd(PPh_3)_4$ (50 mg, 0.04 mmol). The reaction mixture was refluxed for 12 h under an argon atmosphere. After addition of water (30 mL), the mixture was extracted with toluene (30 mL). The organic phase was washed with a saturated aqueous solution of NH_4Cl (30 mL) and water (3 x 30 mL), dried over $MgSO_4$ and evaporated. The residue was purified twice by column chromatography on silica gel (eluent: dichloromethane) to give **2** as blue solid (320 mg, 87% yield). M. p. 249-251°C. ^1H NMR (300 MHz, CD_2Cl_2) δ: 8.07 (d, 1H, J=7.6Hz); 7.55 (d, 2H, J=8.8Hz); 7.40-7.27 (m, 7H); 7.21 (m, 1H, J=7.3Hz, J=1.7Hz); 7.19-7.09 (m, 6H) ; 7.04 (d, 2H, J=8.8Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ: 161.5 ; 157.5 ; 156.3 ; 149.9 ; 146.8 ; 138.2 ; 138.1 ; 133.2 ; 132.8 ; 129.7 ; 128.4 ; 127.2 ; 126.3 ; 125.9 ; 125.6 ; 124.4 ; 121.9 ; 120.8 ; 114.7 ; 114.4 ; 113.5 ; 70.7. UV-Vis (CH_2Cl_2) λ_{max}/nm: 610 (ε=16200 L mol^{-1} cm^{-1}). IR (neat): $\tilde{\nu}$ = 2219 cm^{-1} (C≡N). EI MS: 477.1 [M^+]. HRMS (M+H): for $C_{32}H_{20}N_3S$ 478.13724, found 478.13720. Anal. Calcd. for $C_{32}H_{19}N_3S$: C, 80.48; H, 4.01; N, 8.80; S, 6.71; found: C, 80.08; H, 3.99; N, 8.72; S, 6.61.

N,*N*-diphenyl-4-(thien-2-yl)aniline (4)[5]



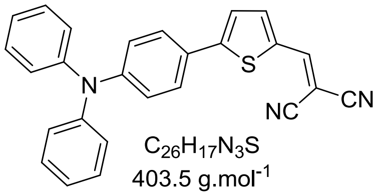
A mixture of 4-bromo-*N*,*N*-diphenylaniline **5** (2 g, 6.16 mmol) and 2-(tributylstannyl)thiophene (3.44 g, 9.24 mmol) in toluene (100 mL) was placed in a Schlenk flask and degassed with argon during 15 min before addition of tetrakis(triphenylphosphine)palladium(0) (400 mg, 0.35 mmol) as catalyst. The reaction mixture was refluxed for 20 h under an argon atmosphere. After evaporation of the solvent, the residue was dissolved in dichloromethane (200 mL) and the solution was washed with water (2 x 200 mL), dried over $MgSO_4$ and evaporated to dryness. Purification by column chromatography on silica gel (eluent: dichloromethane/hexane 1:9) gave **4** as slightly yellow solid (1.05 g, 52% yield). ^1H NMR (300 MHz, CD_2Cl_2) δ: 7.48 (d, 2H, ^3J=8.8Hz); 7.31-7.22 (m, 6H); 7.13-7.01 (m, 9H).

5-(4-(Diphenylamino)phenyl)thiophene-2-carbaldehyde (3)



Under a N_2 atmosphere, $POCl_3$ (0.2 mL, 2.01 mmol) was added to a solution of *N*,*N*-diphenyl-4-(thiophen-2-yl)aniline **4** (600 mg, 1.83 mmol) and anhydrous DMF (0.2 mL, 2.51 mmol) in 1,2-dichloroethane (30 mL). The mixture was refluxed for 15 h under a N_2 atmosphere and cooled to room temperature. A saturated aqueous solution of sodium acetate (40 mL) and CH_2Cl_2 (20 mL) were added and the mixture was further stirred for 6 h. After extraction with CH_2Cl_2 (2 x 75 mL), the combined organic phases were washed with water (3 x 100 mL), dried over $MgSO_4$ and concentrated. The product was purified by column chromatography on silica gel (eluent: CH_2Cl_2) affording **3** as yellow solid (480 mg, 74% yield). M. p. 88-90°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 9.85 (s, 1H); 7.70 (d, 1H, J=4.0Hz); 7.52 (d, 2H, J=9.0Hz); 7.34-7.27 (m, 5H); 7.17-7.04 (m, 8H). UV-Vis (CH_2Cl_2) λ_{max}/nm: 408 (ε=28700 L mol^{-1} cm^{-1}). IR (neat): $\tilde{\nu}$ = 1659 cm^{-1} (C=O). MALDI-TOF MS: 355.2 [M$^+$]. These data are consistent with the literature data.[6]

2-((5-(4-(Diphenylamino)phenyl)thiophen-2-yl)methylene)malononitrile (1)



Two drops of Et_3N were added to a mixture of compound **3** (200 mg, 0.56 mmol) and malononitrile (74 mg, 1.12 mmol) in $CHCl_3$ (15 mL). The reaction mixture was refluxed for 14 h. The solvent was evaporated under vacuum and the crude product was triturated with hot EtOH (15 mL), filtered and washed with EtOH (15 mL) to give **1** as red-brown powder (170 mg, 75% yield). M. p. 127-129°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 7.74 (s, 1H); 7.68 (d, 1H, J=8.9Hz); 7.53 (d, 2H, J=8.9 Hz); 7.36-7.27 (m, 5H); 7.18-7.09 (m, 6H); 7.05 (d, 2H, J=8.8Hz). UV-Vis (CH_2Cl_2) λ_{max}/nm: 501 (ε=33900 L mol^{-1} cm^{-1}). IR (neat): $\tilde{\nu}$ = 2220 cm^{-1} (C≡N). MALDI-TOF MS: 403.2 [M$^+$]. These data are consistent with the literature data.[6]

References:

1. D.W.H. MacDowell and T.B. Patrick, *J. Org. Chem.*, 1967, **32**, 2441-2445.
2. M. A. Campo and R. C. Larock, *J. Org. Chem.*, 2002, **67**, 5616-5620.
3. M. Bancerz, L. A. Huck, W. J. Leigh, G. Mladenova, K. Najafian, X. Zeng and E. Lee-Ruff, *J. Phys. Org. Chem.*, 2010, **23**, 1202-1213.
4. J. Zhang, J. Aszodi, C. Chartier, N. L'hermite and J. Weston, *Tetrahedron Lett.*, 2001, **42**, 6683-6686.
5. A. Leliège, P. Blanchard, T. Rousseau and J. Roncali, *Org. Lett.*, 2011, **13**, 3098-3101.
6. C. Sissa, V. Parthasarathy, D. Drouin-Kucma, M. H. V. Werts, M. Blanchard-Desce and F. Terenziani, *Phys. Chem. Chem. Phys.*, 2010, **12**, 11715-11727.

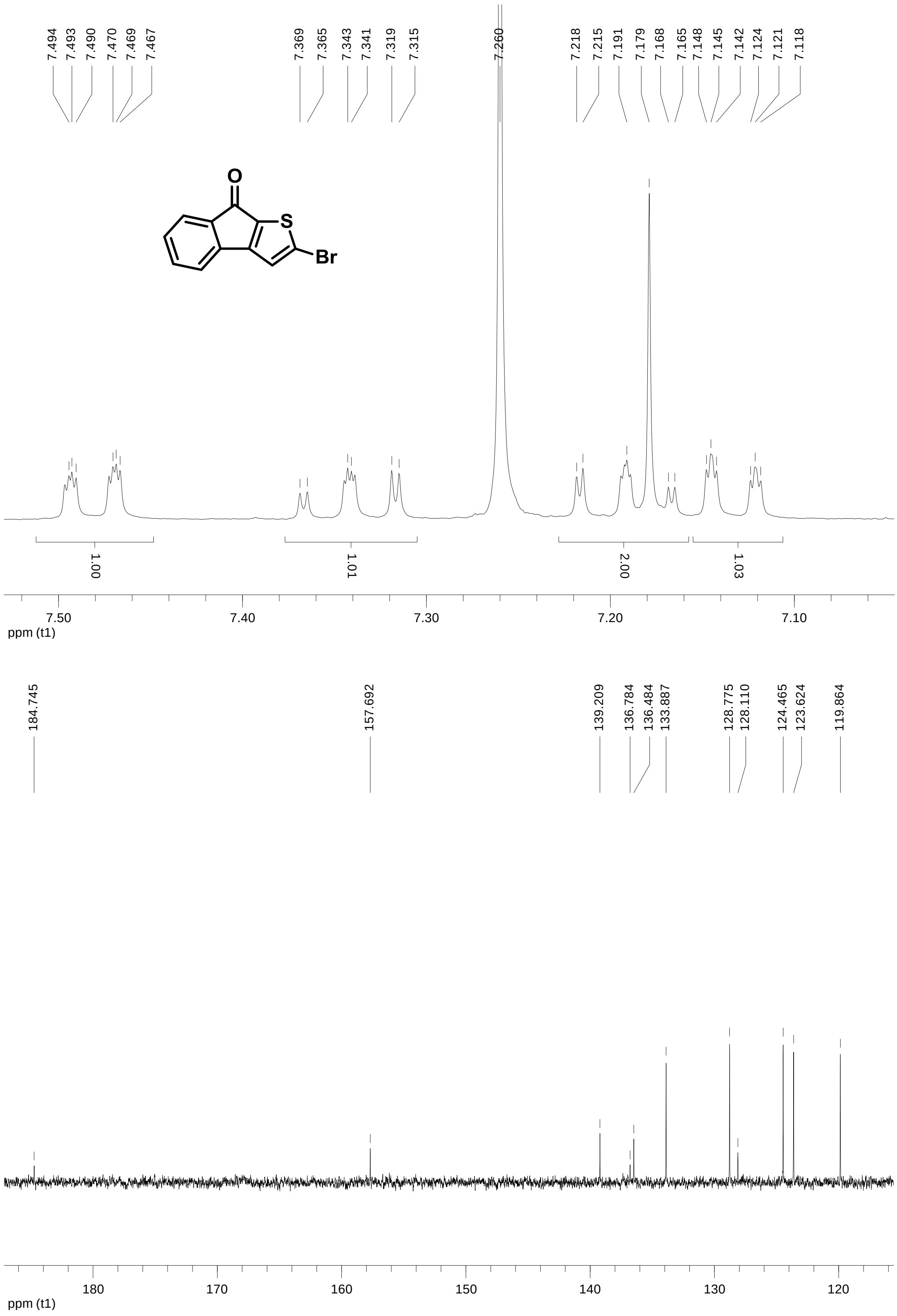


Fig. S1. ^{1}H NMR (300 MHz, top) and ^{13}C NMR (75 MHz, bottom) spectra of **S5** in $CDCl_3$ at 20°C.

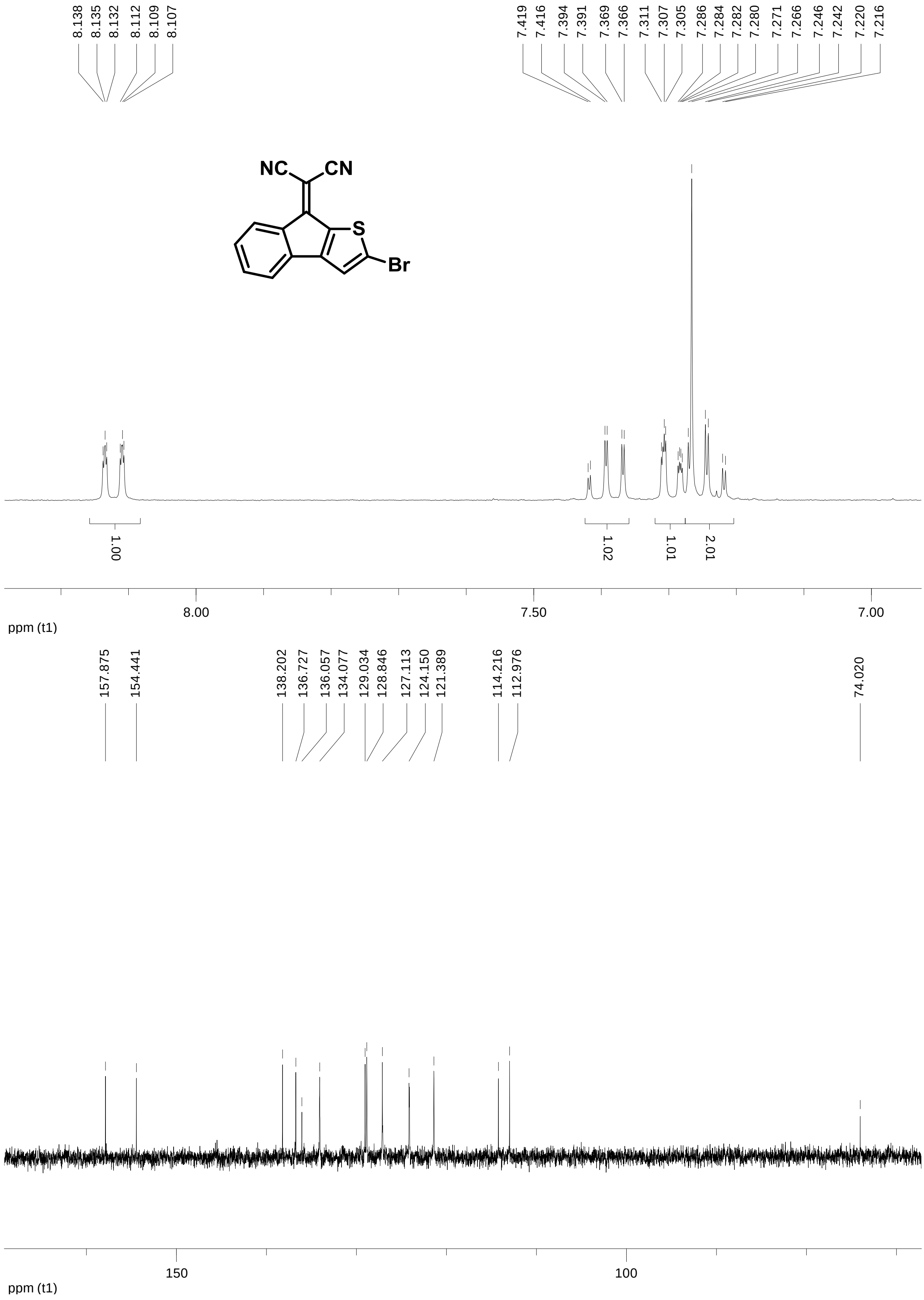


Fig. S2. ^{1}H NMR (300 MHz, top) and ^{13}C NMR (75 MHz, bottom) spectra of **7** in CD_2Cl_2 at 20°C.

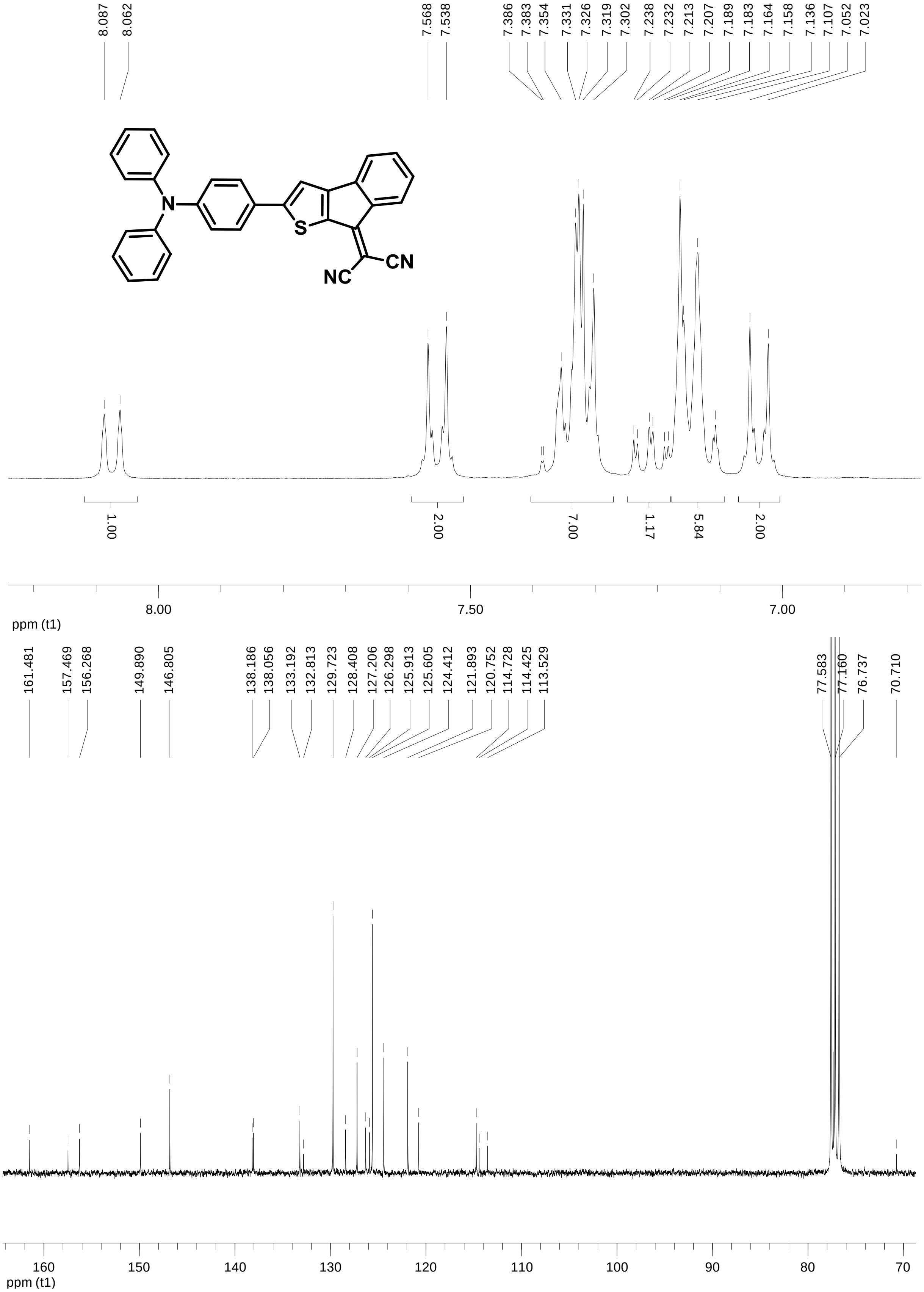


Fig. S3. ^{1}H NMR (300 MHz, top) spectrum of **2** in CD_2Cl_2 at 20°C and ^{13}C NMR (75 MHz, bottom) spectrum of **2** in $CDCl_3$ at 20°C.

3. Cyclic Voltammetry and UV-Visible spectroscopy

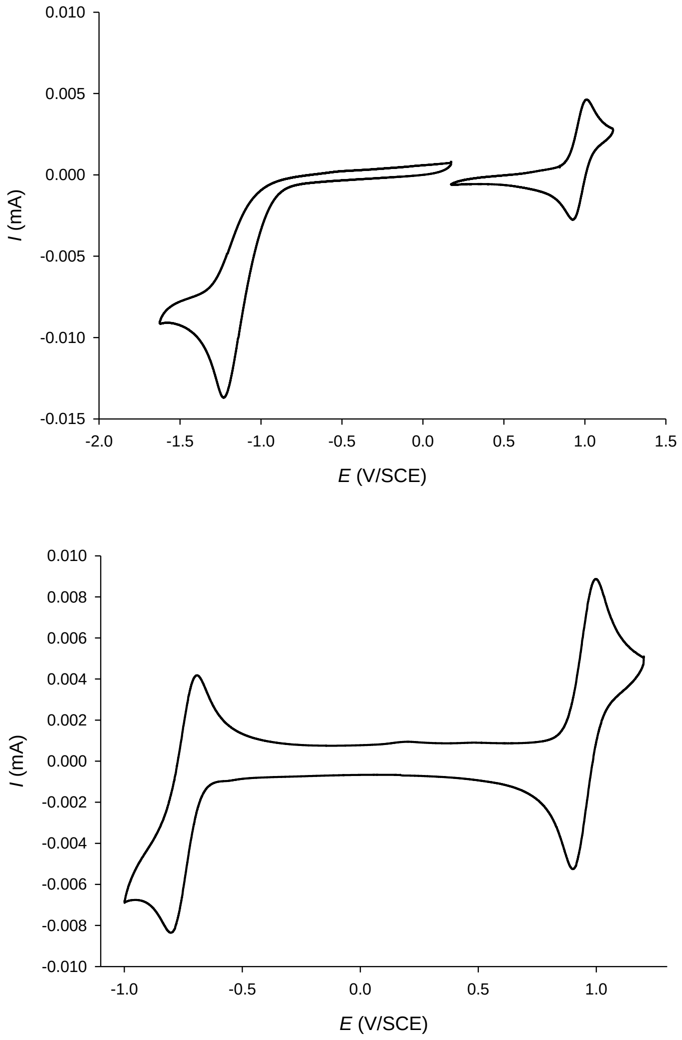
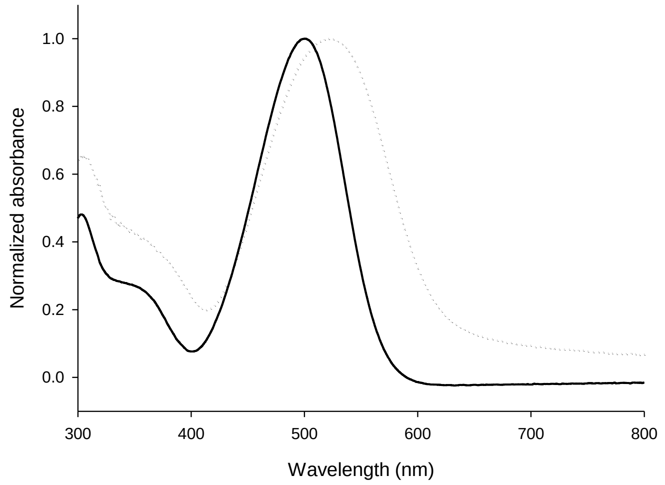


Fig. S4. Cyclic voltammograms of **1** (0.5 mM, top) and **2** (1 mM, bottom) in 0.1M Bu_4NPF_6/CH_2Cl_2, scan rate 100 mV.s^{-1}, Pt working electrode, SCE ref.



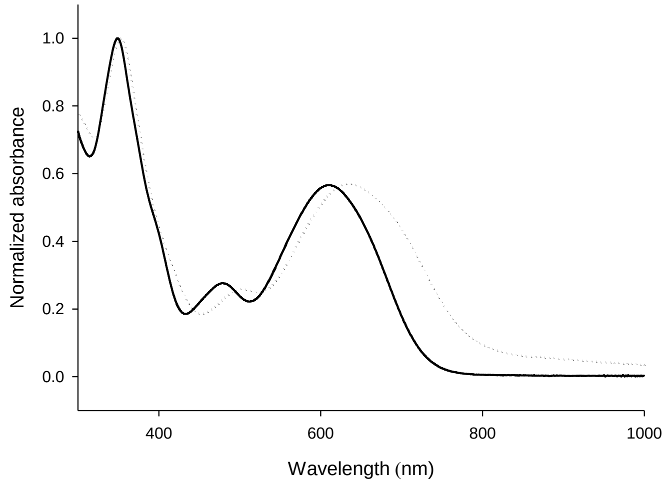


Fig. S5. Normalized absorption spectra in CH_2Cl_2 (solid line) and of a spun-casted thin film on glass (dotted line) for compounds **1** (top) and **2** (bottom).

4. Crystallographic structure of compound 2 (CCDC-884845)

X-ray single-crystal diffraction data were collected at 293K on a BRUKER-NONIUS KappaCCD diffractometer, equipped with a graphite monochromator utilizing MoKα radiation (λ = 0.71073Å). The structure was solved by direct methods using SIR92 (Altomare et al., 1993) and refined on F^2 by full-matrix least-squares method, using SHELXL97 (G.M. Sheldrick, 1998). All non-H atoms were refined anisotropically and the H atoms were found by Fourier difference synthesis. Absorption was corrected by SADABS program ((Bruker AXS area detector scaling and absorption correction, v2008/1, Sheldrick, G.M., (2008)).

Table 1. Crystal data and structure refinement for compound **2**.

Identification code	AL211
Empirical formula	C32 H19 N3 S
Formula weight	477.56
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions	a = 6.8928(6) Å alpha = 96.347(6) deg.
	b = 9.1948(8) Å beta = 95.242(7) deg.
	c = 20.413(1) Å gamma = 100.897(8) deg.
Volume	1254.24(17) $Å^3$
Z, Calculated density	2, 1.265 Mg/m^3
Absorption coefficient	0.155 mm^{-1}
F(000)	496
Crystal size	0.29 x 0.1 x 0.04 mm
Theta range for data collection	2.28 to 29.05 deg.
Limiting indices	-9<=h<=9, -11<=k<=12, -27<=l<=27
Reflections collected / unique	38182 / 6586 [R(int) = 0.0688]
Completeness to theta = 29.05	98.1 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.746 and 0.687
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6586 / 0 / 401
Goodness-of-fit on F^2	1.117
Final R indices [I>2sigma(I)]	R1 = 0.0617, wR2 = 0.0967 [3742 Fo]
R indices (all data)	R1 = 0.1401, wR2 = 0.1183
Largest diff. peak and hole	0.206 and -0.301 $e.A^{-3}$

Table 2. Atomic coordinates and equivalent isotropic displacement parameters for compound **2**.

U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
C(1)	0.3098(3)	0.1549(2)	0.07550(9)	0.0342(5)
C(2)	0.2896(3)	0.2149(2)	0.01637(10)	0.0376(5)
C(3)	0.2479(3)	0.1047(2)	-0.03864(9)	0.0334(4)
C(4)	0.2338(3)	-0.0387(2)	-0.02255(9)	0.0329(4)
C(5)	0.1867(3)	-0.1468(2)	-0.08109(9)	0.0328(4)
C(6)	0.1638(3)	-0.2989(2)	-0.08445(10)	0.0379(5)
C(7)	0.1081(3)	-0.4002(2)	-0.14490(11)	0.0443(5)
C(8)	0.2005(4)	-0.3635(2)	-0.02522(12)	0.0491(6)
C(9)	0.1730(3)	-0.0573(2)	-0.13752(9)	0.0346(5)
C(10)	0.2126(3)	0.0953(2)	-0.11128(9)	0.0373(5)
C(11)	0.2136(4)	0.2039(3)	-0.15243(11)	0.0532(6)
C(12)	0.1756(4)	0.1606(3)	-0.22102(12)	0.0621(7)
C(13)	0.1380(4)	0.0114(3)	-0.24663(12)	0.0580(7)
C(14)	0.1355(4)	-0.0995(3)	-0.20520(11)	0.0478(6)
C(15)	0.3573(3)	0.2362(2)	0.14252(9)	0.0352(5)
C(16)	0.3780(3)	0.1635(3)	0.19862(11)	0.0465(6)
C(17)	0.4307(4)	0.2436(3)	0.26142(11)	0.0495(6)
C(18)	0.4654(3)	0.3989(2)	0.27052(10)	0.0437(5)
C(19)	0.4421(3)	0.4719(3)	0.21517(10)	0.0448(5)
C(20)	0.3887(3)	0.3920(2)	0.15265(10)	0.0416(5)
C(21)	0.6650(4)	0.4167(2)	0.37692(10)	0.0497(6)
C(22)	0.8425(4)	0.3932(3)	0.35602(14)	0.0652(7)
C(23)	0.9717(6)	0.3335(4)	0.39538(19)	0.0884(10)
C(24)	0.9236(8)	0.2971(4)	0.4557(2)	0.0972(13)
C(25)	0.7489(8)	0.3208(4)	0.47747(15)	0.0908(12)
C(26)	0.6154(5)	0.3800(3)	0.43805(12)	0.0663(8)
C(27)	0.5081(4)	0.6263(3)	0.35281(10)	0.0522(6)
C(28)	0.6595(5)	0.7283(3)	0.39263(13)	0.0712(8)
C(29)	0.6358(8)	0.8732(4)	0.41109(16)	0.0965(12)
C(30)	0.4673(8)	0.9195(4)	0.38960(16)	0.1012(13)
C(31)	0.3170(7)	0.8197(4)	0.34960(15)	0.0854(10)
C(32)	0.3359(5)	0.6733(3)	0.33174(13)	0.0642(7)
N(1)	0.5301(3)	0.4773(2)	0.33498(8)	0.0542(5)
N(2)	0.0626(3)	-0.4818(2)	-0.19275(10)	0.0620(6)
N(3)	0.2373(4)	-0.4115(2)	0.02267(12)	0.0786(7)
S(1)	0.27463(8)	-0.03876(6)	0.06194(2)	0.03667(15)
H(2)	0.308(3)	0.318(2)	0.0143(10)	0.043(6)
H(11)	0.238(3)	0.309(3)	-0.1328(11)	0.063(7)
H(12)	0.180(4)	0.237(3)	-0.2507(13)	0.075(8)
H(13)	0.111(4)	-0.015(3)	-0.2936(13)	0.074(8)
H(14)	0.106(3)	-0.201(2)	-0.2235(10)	0.043(6)
H(16)	0.356(3)	0.054(3)	0.1933(11)	0.055(7)
H(17)	0.446(3)	0.188(2)	0.2989(11)	0.052(6)
H(19)	0.466(3)	0.577(2)	0.2206(10)	0.041(6)
H(20)	0.376(3)	0.446(2)	0.1171(11)	0.052(6)
H(22)	0.876(4)	0.427(3)	0.3143(13)	0.077(8)
H(23)	1.101(5)	0.321(4)	0.3782(16)	0.113(13)
H(24)	1.023(5)	0.257(4)	0.4791(17)	0.114(12)

H(25)	0.701(5)	0.295(3)	0.5161(17)	0.107(11)
H(26)	0.495(4)	0.401(3)	0.4510(13)	0.079(10)
H(28)	0.782(4)	0.692(3)	0.4049(13)	0.080(9)
H(29)	0.744(5)	0.938(4)	0.4350(17)	0.118(13)
H(30)	0.456(5)	1.020(4)	0.4031(16)	0.112(11)
H(31)	0.195(5)	0.847(3)	0.3359(15)	0.096(11)
H(32)	0.235(4)	0.605(3)	0.3059(12)	0.064(8)

Table 3. Bond lengths [A] for compound **2**.

C(1)-C(2)	1.388(3)
C(1)-C(15)	1.462(3)
C(1)-S(1)	1.738(2)
C(2)-C(3)	1.396(3)
C(2)-H(2)	0.94(2)
C(3)-C(4)	1.382(3)
C(3)-C(10)	1.471(3)
C(4)-C(5)	1.437(3)
C(4)-S(1)	1.7220(19)
C(5)-C(6)	1.371(3)
C(5)-C(9)	1.494(3)
C(6)-C(8)	1.428(3)
C(6)-C(7)	1.436(3)
C(7)-N(2)	1.144(3)
C(8)-N(3)	1.143(3)
C(9)-C(14)	1.380(3)
C(9)-C(10)	1.411(3)
C(10)-C(11)	1.374(3)
C(11)-C(12)	1.399(3)
C(11)-H(11)	0.98(2)
C(12)-C(13)	1.380(3)
C(12)-H(12)	0.98(3)
C(13)-C(14)	1.394(3)
C(13)-H(13)	0.95(3)
C(14)-H(14)	0.94(2)
C(15)-C(20)	1.396(3)
C(15)-C(16)	1.398(3)
C(16)-C(17)	1.386(3)
C(16)-H(16)	0.98(2)
C(17)-C(18)	1.391(3)
C(17)-H(17)	0.98(2)
C(18)-C(19)	1.389(3)
C(18)-N(1)	1.418(3)
C(19)-C(20)	1.382(3)
C(19)-H(19)	0.94(2)
C(20)-H(20)	0.93(2)
C(21)-C(22)	1.378(4)
C(21)-C(26)	1.384(3)
C(21)-N(1)	1.437(3)
C(22)-C(23)	1.376(4)
C(22)-H(22)	0.97(3)
C(23)-C(24)	1.365(5)
C(23)-H(23)	1.01(3)
C(24)-C(25)	1.368(5)
C(24)-H(24)	0.95(4)
C(25)-C(26)	1.393(5)
C(25)-H(25)	0.92(3)
C(26)-H(26)	0.94(3)
C(27)-C(32)	1.387(4)
C(27)-C(28)	1.392(3)
C(27)-N(1)	1.418(3)
C(28)-C(29)	1.387(4)
C(28)-H(28)	0.98(3)
C(29)-C(30)	1.363(5)
C(29)-H(29)	0.92(4)

C(30)-C(31)	1.380(5)
C(30)-H(30)	0.95(3)
C(31)-C(32)	1.388(4)
C(31)-H(31)	0.95(3)
C(32)-H(32)	0.92(2)

Table 4. Bond angles [deg] for compound **2**.

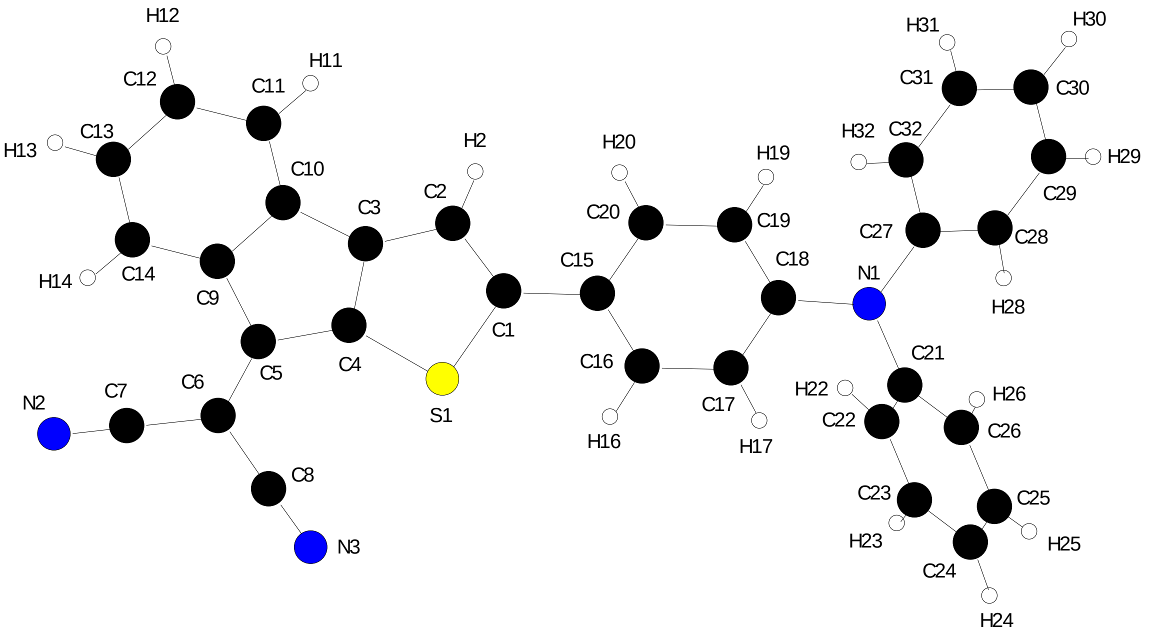
C(2)-C(1)-C(15)	127.27(18)
C(2)-C(1)-S(1)	111.58(15)
C(15)-C(1)-S(1)	121.14(14)
C(1)-C(2)-C(3)	112.01(19)
C(1)-C(2)-H(2)	123.1(12)
C(3)-C(2)-H(2)	124.9(12)
C(4)-C(3)-C(2)	113.76(18)
C(4)-C(3)-C(10)	108.07(16)
C(2)-C(3)-C(10)	138.17(19)
C(3)-C(4)-C(5)	110.99(17)
C(3)-C(4)-S(1)	111.39(14)
C(5)-C(4)-S(1)	137.61(16)
C(6)-C(5)-C(4)	127.38(18)
C(6)-C(5)-C(9)	127.50(17)
C(4)-C(5)-C(9)	105.11(16)
C(5)-C(6)-C(8)	119.33(18)
C(5)-C(6)-C(7)	124.00(19)
C(8)-C(6)-C(7)	116.66(18)
N(2)-C(7)-C(6)	179.4(3)
N(3)-C(8)-C(6)	177.2(3)
C(14)-C(9)-C(10)	120.29(19)
C(14)-C(9)-C(5)	131.51(19)
C(10)-C(9)-C(5)	108.18(16)
C(11)-C(10)-C(9)	120.75(19)
C(11)-C(10)-C(3)	131.61(19)
C(9)-C(10)-C(3)	107.64(16)
C(10)-C(11)-C(12)	118.8(2)
C(10)-C(11)-H(11)	119.0(13)
C(12)-C(11)-H(11)	122.2(13)
C(13)-C(12)-C(11)	120.4(2)
C(13)-C(12)-H(12)	120.3(15)
C(11)-C(12)-H(12)	119.3(15)
C(12)-C(13)-C(14)	121.2(2)
C(12)-C(13)-H(13)	118.4(15)
C(14)-C(13)-H(13)	120.4(15)
C(9)-C(14)-C(13)	118.6(2)
C(9)-C(14)-H(14)	121.4(13)
C(13)-C(14)-H(14)	119.9(13)
C(20)-C(15)-C(16)	117.19(19)
C(20)-C(15)-C(1)	120.57(18)
C(16)-C(15)-C(1)	122.22(19)
C(17)-C(16)-C(15)	121.1(2)
C(17)-C(16)-H(16)	119.5(13)
C(15)-C(16)-H(16)	119.3(13)
C(16)-C(17)-C(18)	121.0(2)
C(16)-C(17)-H(17)	118.0(13)

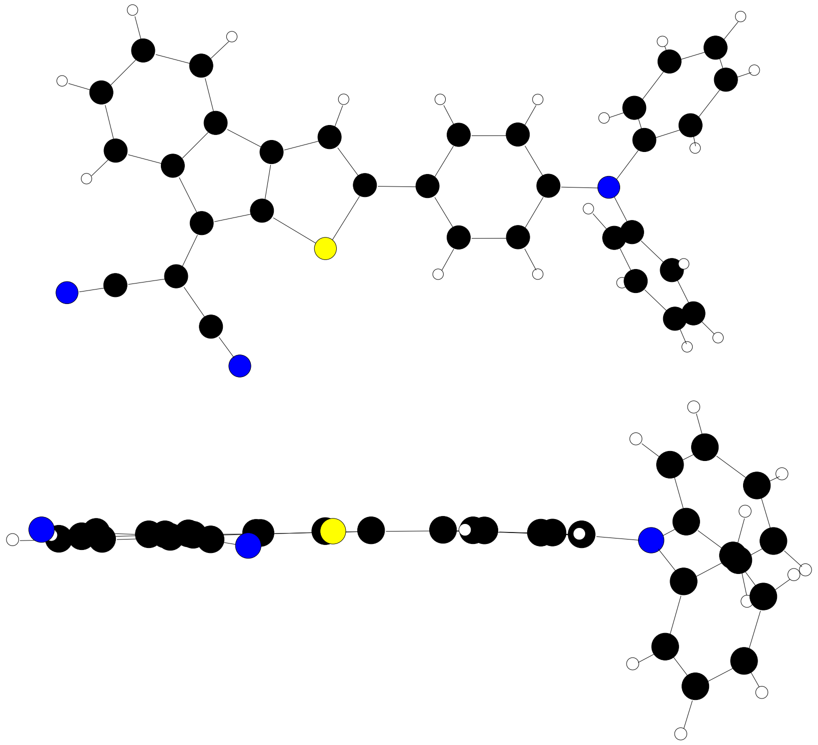
C(18)-C(17)-H(17)	121.0(13)
C(19)-C(18)-C(17)	118.28(19)
C(19)-C(18)-N(1)	122.3(2)
C(17)-C(18)-N(1)	119.40(19)
C(20)-C(19)-C(18)	120.7(2)
C(20)-C(19)-H(19)	120.1(12)
C(18)-C(19)-H(19)	119.2(12)
C(19)-C(20)-C(15)	121.8(2)
C(19)-C(20)-H(20)	117.5(14)
C(15)-C(20)-H(20)	120.7(13)
C(22)-C(21)-C(26)	120.0(3)
C(22)-C(21)-N(1)	120.1(2)
C(26)-C(21)-N(1)	119.9(3)
C(23)-C(22)-C(21)	120.7(3)
C(23)-C(22)-H(22)	122.0(16)
C(21)-C(22)-H(22)	117.2(16)
C(24)-C(23)-C(22)	119.6(4)
C(24)-C(23)-H(23)	123.0(19)
C(22)-C(23)-H(23)	117.4(19)
C(23)-C(24)-C(25)	120.5(3)
C(23)-C(24)-H(24)	113(2)
C(25)-C(24)-H(24)	126(2)
C(24)-C(25)-C(26)	120.7(3)
C(24)-C(25)-H(25)	127(2)
C(26)-C(25)-H(25)	113(2)
C(21)-C(26)-C(25)	118.5(3)
C(21)-C(26)-H(26)	117.3(17)
C(25)-C(26)-H(26)	124.1(17)
C(32)-C(27)-C(28)	118.5(3)
C(32)-C(27)-N(1)	121.2(2)
C(28)-C(27)-N(1)	120.3(3)
C(29)-C(28)-C(27)	120.1(3)
C(29)-C(28)-H(28)	123.6(17)
C(27)-C(28)-H(28)	116.3(16)
C(30)-C(29)-C(28)	121.2(3)
C(30)-C(29)-H(29)	122(2)
C(28)-C(29)-H(29)	116(2)
C(29)-C(30)-C(31)	119.2(3)
C(29)-C(30)-H(30)	119(2)
C(31)-C(30)-H(30)	122(2)
C(30)-C(31)-C(32)	120.6(4)
C(30)-C(31)-H(31)	121.0(19)
C(32)-C(31)-H(31)	118.3(19)
C(27)-C(32)-C(31)	120.4(3)
C(27)-C(32)-H(32)	118.5(16)
C(31)-C(32)-H(32)	121.1(16)
C(27)-N(1)-C(18)	122.45(18)
C(27)-N(1)-C(21)	118.62(17)
C(18)-N(1)-C(21)	117.03(18)
C(4)-S(1)-C(1)	91.26(9)

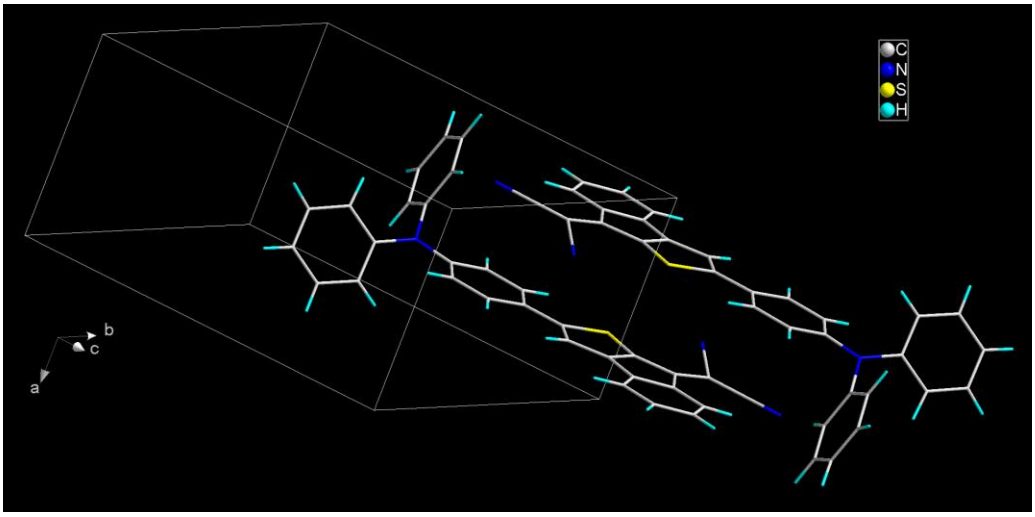
Table 5. Anisotropic displacement parameters for compound **2**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

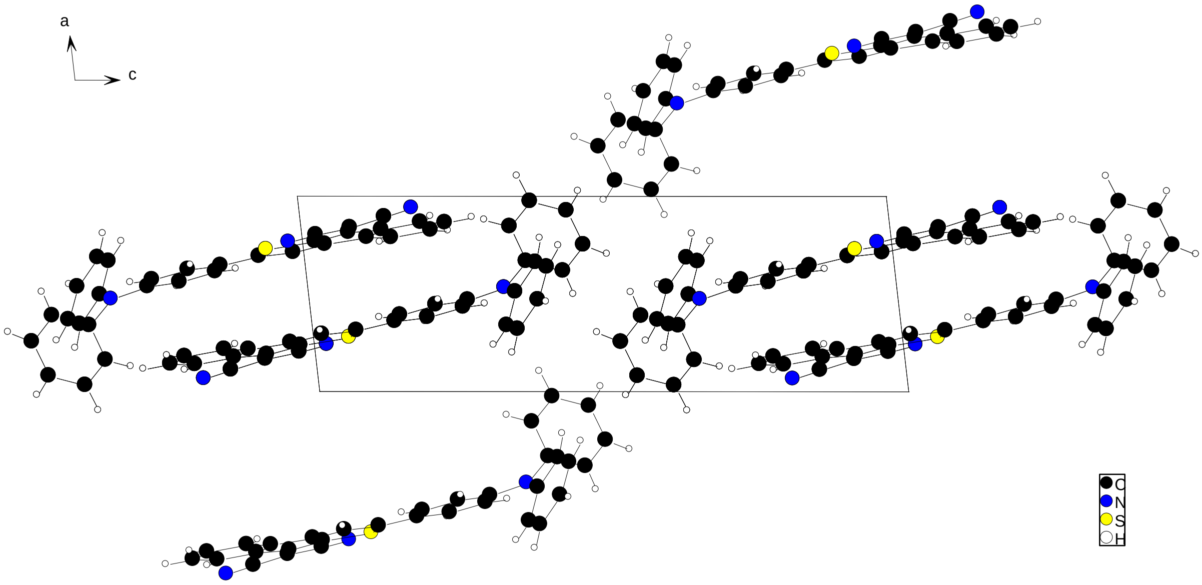
	U11	U22	U33	U23	U13	U12
C(1)	0.0271(11)	0.0378(11)	0.0357(11)	0.0008(9)	0.0014(8)	0.0050(8)
C(2)	0.0408(13)	0.0334(12)	0.0372(11)	0.0021(9)	0.0024(9)	0.0067(9)
C(3)	0.0293(11)	0.0378(11)	0.0328(10)	0.0019(9)	0.0025(8)	0.0079(8)
C(4)	0.0282(11)	0.0384(11)	0.0316(10)	0.0028(9)	0.0028(8)	0.0072(8)
C(5)	0.0268(11)	0.0352(11)	0.0352(10)	-0.0003(8)	0.0021(8)	0.0065(8)
C(6)	0.0332(12)	0.0415(12)	0.0378(11)	0.0014(9)	0.0004(9)	0.0083(9)
C(7)	0.0440(14)	0.0396(12)	0.0483(13)	0.0006(11)	0.0013(10)	0.0107(10)
C(8)	0.0559(15)	0.0321(12)	0.0552(15)	0.0027(11)	-0.0015(12)	0.0045(10)
C(9)	0.0313(11)	0.0401(11)	0.0327(10)	0.0034(9)	0.0038(8)	0.0086(9)
C(10)	0.0367(12)	0.0408(12)	0.0336(11)	0.0040(9)	0.0028(9)	0.0068(9)
C(11)	0.0740(18)	0.0419(14)	0.0407(13)	0.0066(11)	0.0001(12)	0.0065(12)
C(12)	0.089(2)	0.0570(16)	0.0391(13)	0.0159(12)	0.0000(13)	0.0090(14)
C(13)	0.0783(19)	0.0627(17)	0.0308(12)	0.0057(12)	-0.0003(12)	0.0121(13)
C(14)	0.0566(15)	0.0459(14)	0.0377(12)	-0.0027(11)	0.0002(11)	0.0098(11)
C(15)	0.0278(11)	0.0437(12)	0.0323(10)	0.0005(9)	-0.0004(8)	0.0066(9)
C(16)	0.0542(15)	0.0421(13)	0.0406(12)	0.0020(10)	-0.0007(10)	0.0083(11)
C(17)	0.0632(16)	0.0525(15)	0.0298(11)	0.0059(10)	-0.0056(11)	0.0090(12)
C(18)	0.0462(14)	0.0500(13)	0.0303(11)	-0.0037(9)	-0.0030(9)	0.0070(10)
C(19)	0.0539(15)	0.0391(13)	0.0375(12)	-0.0015(10)	0.0000(10)	0.0064(11)
C(20)	0.0473(14)	0.0453(13)	0.0306(11)	0.0032(10)	0.0004(10)	0.0083(10)
C(21)	0.0647(17)	0.0484(13)	0.0297(11)	-0.0029(10)	-0.0084(11)	0.0064(11)
C(22)	0.0644(19)	0.0794(19)	0.0460(15)	0.0004(14)	-0.0093(14)	0.0117(15)
C(23)	0.080(3)	0.101(3)	0.076(2)	-0.0083(19)	-0.026(2)	0.026(2)

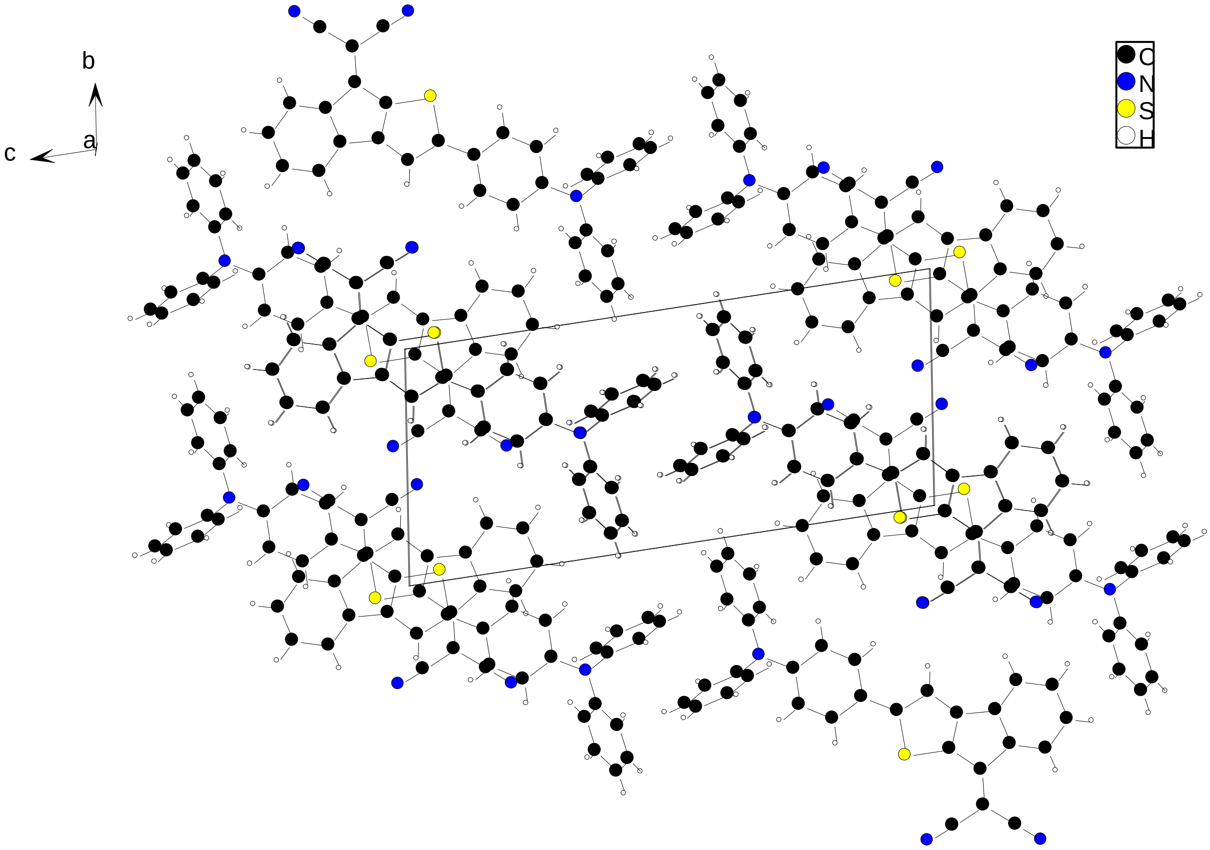
C(24)	0.127(4)	0.074(2)	0.079(3)	-0.0016(18)	-0.053(3)	0.028(2)
C(25)	0.153(4)	0.072(2)	0.0366(16)	0.0133(14)	-0.017(2)	0.005(2)
C(26)	0.090(2)	0.0654(18)	0.0363(14)	-0.0004(12)	0.0017(14)	0.0042(16)
C(27)	0.0744(18)	0.0488(14)	0.0289(11)	-0.0009(10)	-0.0002(11)	0.0078(12)
C(28)	0.093(2)	0.0573(17)	0.0518(16)	-0.0016(13)	-0.0136(15)	0.0015(16)
C(29)	0.157(4)	0.0514(19)	0.062(2)	-0.0028(15)	-0.022(2)	-0.004(2)
C(30)	0.190(4)	0.053(2)	0.0585(19)	-0.0004(16)	-0.004(2)	0.032(2)
C(31)	0.130(3)	0.075(2)	0.0574(18)	0.0018(16)	-0.0010(19)	0.047(2)
C(32)	0.084(2)	0.0607(17)	0.0453(14)	-0.0050(13)	-0.0003(14)	0.0184(16)
N(1)	0.0729(14)	0.0544(12)	0.0313(10)	-0.0073(8)	-0.0096(9)	0.0176(10)
N(2)	0.0756(15)	0.0504(12)	0.0554(13)	-0.0100(10)	-0.0015(11)	0.0154(11)
N(3)	0.113(2)	0.0525(13)	0.0654(15)	0.0188(12)	-0.0100(14)	0.0077(13)
S(1)	0.0378(3)	0.0402(3)	0.0308(3)	0.0033(2)	0.0001(2)	0.0073(2)






C
N
S
H
b
c
a


a
c
C
N
S
H


b
c
a
C
N
S
H

5. Details on the fabrication of organic solar cells based on compounds 1 and 2

The PEDOT:PSS Baytron®PH500 suspension used to apply smoothing and hole conducting layers was received from HC Stark. As electrodes, indium-tin-oxide (ITO) coated glasses (PGO, sheet resistance ≤ 10 Ω/□) and evaporated Al films (ca. 100 nm thick) were used. The ITO electrodes were cleaned in ultrasonic baths (deconnex, water, acetone and absolute ethanol) then dried under vacuum at 100°C for 10 min and further subjected to UV-ozone treatment for 15 min and modified by a spin-cast layer of Baytron (filtered through a 0.45 µm membrane just prior of casting at 5000 rpm), which was then dried at 130 °C for 15 min. Devices with ITO/Baytron/**1** or **2**/C_{60}/Al structures were prepared by spin-casting a 10 mg.mL^{-1} solution of **1** or **2** in $CHCl_3$ (using 6000 rpm for 3s and then 10000 rpm for 9s) followed by high vacuum evaporation of C_{60} (30 nm) (99%+ purchased from MER Corporation). The 35 nm thickness of the donor layer of **1** and **2** was determined by measuring the thickness of a reference thick layer (typically ca. 80-100 nm) using a profilometer Dektak 6M stylus (Veeco) and further extrapolation by comparing the optical density of their absorption maxima. The cells were completed by evaporation of Al through a round shadow mask (devices area of 0.28 cm^2). After preparation, the solar cells were stored and characterized in a glove-box under an argon atmosphere. The *J-V* curves were recorded in dark and under illumination using a Keithley 236 source-measure unit and a homemade acquisition program. The light source was an AM1.5 Solar Constant 575 PV simulator (Steuernagel Lichttecknik, equipped with a metal halogenide lamp) and its intensity was measured by a broad-band power meter (13PEM001, Melles Griot). The devices were illuminated through the ITO electrode side. The efficiency values reported in this work are not corrected, neither for the possible solar simulator spectral mismatch nor for the reflection/absorbance of the glass/ITO/Baytron coated electrodes. IPCE spectra were recorded with a Perkin Elmer 7225 lock-in amplifier under monochromatic illumination at a chopping frequency of 210 Hz. The light from a W lamp was dispersed by an Acton SpectraPro150. Electronic absorption spectra were recorded with a Perkin Elmer Lambda 950 spectrophotometer.

6. TGA and DSC Analysis

Thermogravimetric analyses and differential scanning calorimetry were performed on a TGA Q500 and a DSC Q20 instruments from TA INSTRUMENTS.

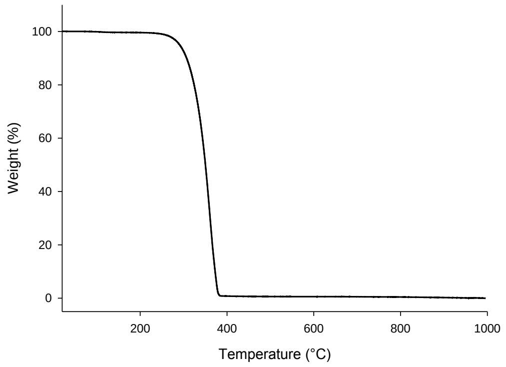


Figure S6. TGA curve of compound **1** under N_2 with a heating rate of 10 °C/min.

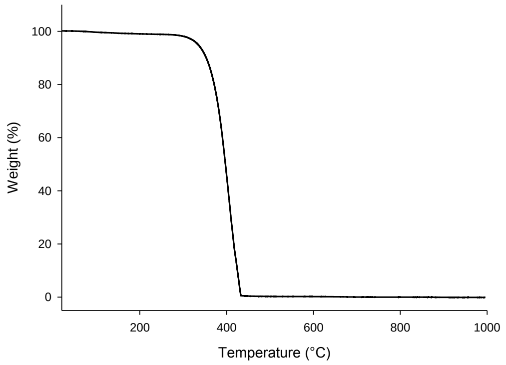


Figure S7. TGA curve of compound **2** under N_2 with a heating rate of 10 °C/min.

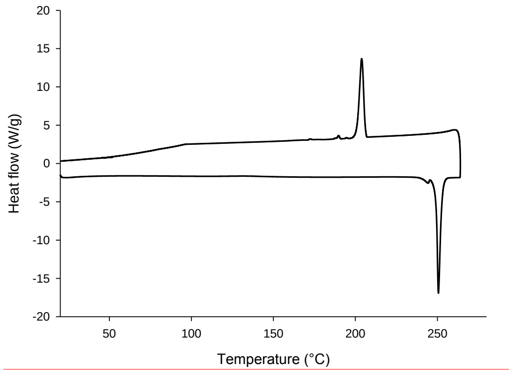


Figure S8. DSC curve of compound **2** under N_2 with a heating rate of 10 °C/min.