

Dithieno[2,3-*d*;2',3'-*d'*]benzo[1,2-*b*;4,5-*b'*]dithiophene Based Organic Sensitizers for Dye-Sensitized Solar Cells

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Contents

General methods	S2
DSSCs Device Fabrication	S2
Synthetic details	S3
Reported organic dyes containing coplanar fused π -spacers (Figure S1)	S8
Cyclic voltammograms of DTBDT1 and DTBDT2 (Figure S2)	S8
NMR and HRMS spectra (Figures S3-S17)	S9
References	S16

General methods

^1H NMR and ^{13}C NMR spectra were recorded in deuterated solvents such as CD_2Cl_2 and $\text{DMSO}-d_6$ using a Bruker DPX 250 spectrometer, with the solvent proton or carbon signal as an internal standard. Field desorption (FD) mass spectra were obtained using a VG instrument ZAB 2-SE-FPD. High-resolution mass spectra were recorded on a Bruker Reflex II-TOF Spectrometer using a 337 nm nitrogen laser with TCNQ as matrix. UV–vis absorption spectra were recorded at room temperature using a Perkin-Elmer Lambda 9 spectrophotometer. Fluorescence spectra were recorded on a SPEX-Fluorolog II (212) spectrometer. CV measurements were carried out on a computer-controlled GSTAT12 in a three-electrode cell in a DCM solution of Bu_4NPF_6 (0.1 M) with a scan rate of 100 mV/s at room temperature. Density functional theory (DFT) calculations have been performed using the Gaussian 03 program (Frisch, M. J. et al.)¹ with the B3LYP hybrid functional (Becke 3-Parameter, Lee, Yang and Parr),^{2,3} and a basis set 6-31G* for the ground state geometry optimization.

DSSCs Device Fabrication

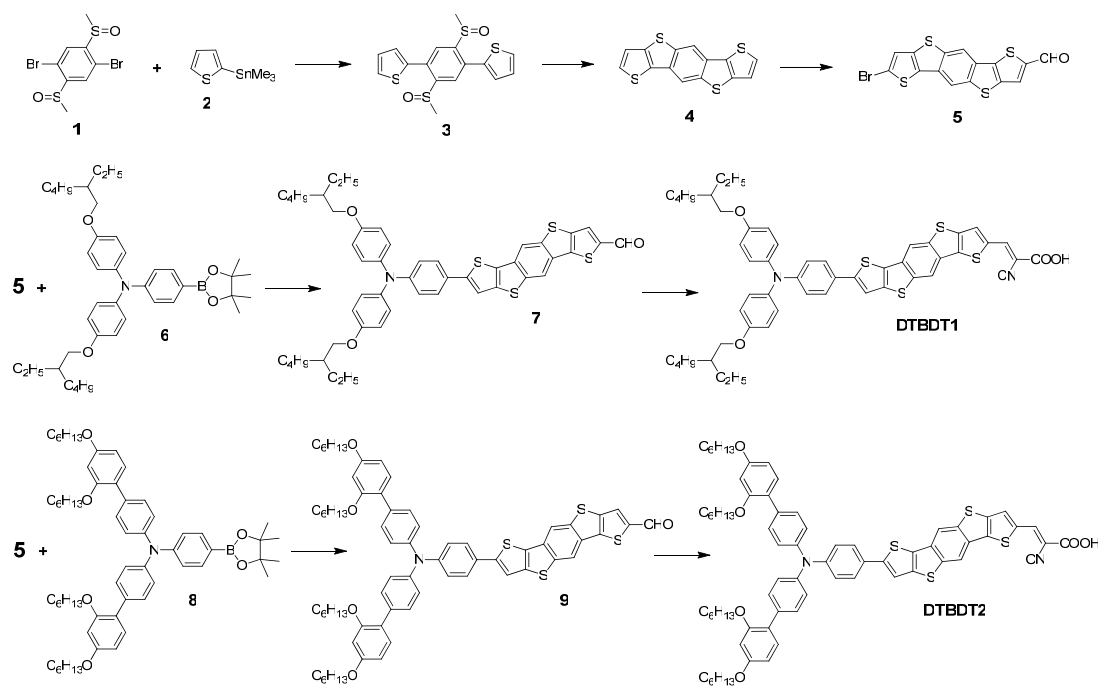
DSSCs were fabricated by screen printing TiO_2 paste (23 nm particle size) on fluorine doped SnO_2 (FTO) glass to form a mesoporous transparent TiO_2 layer of 5 μm thickness. This photoanode was completed by a subsequent deposition of a 3 μm thick 400 nm particle sized TiO_2 scattering layer. After sintering at 500 $^\circ\text{C}$ for 30 min, the TiO_2 films were soaked in 0.1 mM organic dye in THF/ethanol (1:1 v/v) for 12 h in dark. The cells were finished by sealing the sensitized photoanode to a carbon

counter electrode with a 15 μm Surlyn film, followed by electrolyte injection composed of 0.2 M Co(II)(bpy)₃TFSI, 0.05 M Co(III)(bpy)₃TFSI, 0.1 M LiTFSI, and 0.2 M *tert*-butylpyridine in acetonitrile. The photovoltaic performance was measured at 100 mW/cm² under AM 1.5G conditions.

Synthetic details

All reagents and chemicals were purchased from Aldrich, Alfa Aesar, and Acros and used for synthesis without further purification unless otherwise specified. The synthesis of the two DTBDT-based organic dyes was depicted in Scheme S1.

Compounds **1**,⁴ **6**,⁵ and **8**⁶ were prepared according to literature procedures.



Scheme S1. Synthetic routes for DTBDT-based organic dyes.

Compound 3

Compounds **1** (2.16 g, 6.0 mmol), **2** (5.60 g, 15.0 mmol) and anhydrous DMF (60 mL) were placed in a dry three-neck flask and the resulting mixture was bubbled with argon for 15 min. Pd(PPh₃)₂Cl₂ (0.21 g, 0.3 mmol) was then added, and the reaction

mixture was heated to 90 °C overnight. DMF was removed under vacuum then the residue was dissolved in DCM and washed with aqueous KF and water. The organic layer was separated and dried with MgSO₄. After removal of the solvent, the crude product was purified by a column chromatography on silica gel with DCM as eluent to give the title compound (1.88 g, 85%) as a white solid. ¹H NMR (250 MHz, DMSO-*d*₆) δ 8.03 (s, 2H), 7.85 (dd, 2H, J = 5.1 Hz), 7.44 (dd, 2H, J = 3.6 Hz), 7.27-7.24 (m, 2H), 2.61 (s, 6H). ¹³C NMR (62.5 MHz, DMSO-*d*₆) δ 147.70, 136.81, 131.73, 129.10, 129.05, 128.52, 125.61, 41.47. FD-MS: 365.7. HRMS (ESI⁺): m/z calcd 366.9955, found 366.9958 (Figure S12).

Compound 4

To a flask which was charged with compound **3** (1.83 g, 5.0 mmol) was slowly added Eaton's reagent (10 mL) at 0 °C. The mixture was stirred at room temperature under dark for 48 h. The dark-green mixture was then poured into ice water to form a yellow transparent solution, indicating that the sulfonium salt was soluble in water. The aqueous solution was heated to 70 °C and stirred for 1h, during which period white precipitate was gradually formed. The solid was filtered and washed with water and methanol. The crude product was further purified by recrystallization in hexane/DCM mixture to afford unsubstituted DTBDT **4** (1.36 g, 90%) as a white solid. ¹H NMR (250 MHz, CDCl₃) δ 8.30 (s, 2H), 7.54 (d, 2H, J = 5.2 Hz), 7.34 (d, 2H, J = 5.2 Hz). ¹³C NMR (62.5 MHz, CDCl₃) δ 140.42, 138.37, 133.89, 130.14, 128.17, 120.57, 115.70. FD-MS: 302.1. HRMS (ESI⁺): m/z calcd 302.9431, found 302.9433 (Figure S13).

Compound 5

To a solution of compound **4** (1.30 g, 4.3 mmol) in chloroform (100 mL) was added in portions *N*-bromosuccinimide (0.77 g, 4.3 mmol), and the mixture was stirred at room temperature overnight. Then, water was added to quench the reaction and the mixture was extracted with chloroform. The organic phase was washed with sodium bicarbonate and water and dried with MgSO_4 . After removal of the solvent, the residue was dried in vacuum and then added to a mixture of DMF (0.31 g, 4.3 mmol) and 1,2-dichloroethane (50 mL). POCl_3 (0.66 g, 4.3 mmol) was slowly added by a syringe to the reaction mixture which was heated to 80 °C and stirred overnight. Saturated sodium acetate solution (20 mL) was added and the mixture was stirred for an additional hour. Organic phase was separated and poured into hexane (100 mL). The precipitate was filtered and successively washed with hexane and methanol. The crude product was dried in vacuum and then used directly for next step without further purification because of the limitation of solubility. The title compound **5** was detected by FD-MS with a molecular weight of 408.5 (calcd 409.4).

Compound 7

A mixture of compound **5** (0.41 g, 1.0 mmol), pinacol ester **6** (0.94 g, 1.5 mmol), K_2CO_3 (0.69 g, 5.0 mmol) and Aliquat 336 (40 mg, 0.1 mmol) in toluene (15 mL) and water (2.5 mL) was purged with argon for 10 min, and then $\text{Pd}(\text{PPh}_3)_4$ (58 mg, 0.05 mmol) was added and the mixture was heated with stirring at 90 °C for 12 h. The cooled solution was extracted with toluene, and the organic layer was washed with brine and dried over MgSO_4 . The crude product was purified by column

chromatography on silica gel with hexane/DCM (1/3, v/v) to give title compound as an orange solid (0.54 g, 65%). ^1H NMR (250 MHz, CD_2Cl_2) δ 9.96 (s, 1H), 8.38 (s, 1H), 8.23 (s, 1H), 7.98 (s, 1H), 7.49 (d, 2H, $J = 8.7$ Hz), 7.41 (s, 1H), 7.10 (d, 4H, $J = 8.8$ Hz), 6.92-6.85 (m, 6H), 3.85 (d, 4H, $J = 5.6$ Hz), 1.77-1.67 (m, 2H), 1.49-1.26 (m, 16H), 0.97-0.88 (m, 12H). Measurements of ^{13}C NMR spectrum of compound **7** were attempted in commonly used deuterated solvents but no satisfied one was obtained. δ . FD-MS: 830.0. HRMS (ESI+): m/z calcd 830.2830, found 830.2833 (Figure S14).

Compound 9

The preparation of compound **9** is identical with that of compound **7**. Instead of **6**, pinacol ester **8** was employed. The product was obtained as an orange-red solid (0.68 g, 60%). ^1H NMR (250 MHz, CD_2Cl_2) δ 9.95 (s, 1H), 8.36 (s, 1H), 8.23 (s, 1H), 7.96 (s, 1H), 7.59 (d, 2H, $J = 8.7$ Hz), 7.50 (d, 4H, $J = 8.7$ Hz), 7.46 (s, 1H), 7.27 (d, 2H, $J = 9.0$ Hz), 7.19-7.16 (m, 6H), 6.55-6.52 (m, 4H), 4.01-3.95 (m, 8H), 1.84-1.70 (m, 8H), 1.51-1.28 (m, 24H), 0.95-0.86 (m, 12H). ^{13}C NMR (62.5 MHz, CDCl_3) δ 183.27, 160.20, 157.42, 149.34, 148.74, 145.86, 145.73, 142.35, 141.63, 141.10, 140.71, 138.66, 134.29, 132.57, 131.93, 131.17, 130.74, 130.04, 129.12, 127.78, 127.03, 124.64, 123.33, 122.98, 117.56, 115.57, 115.51, 105.86, 100.59, 68.82, 68.57, 32.03, 31.90, 29.71, 29.53, 26.19, 26.14, 23.05, 23.01, 14.25, 14.23. FD-MS: 1125.8. HRMS (ESI+): m/z calcd 1126.4606, found 1126.4634 (Figure S15).

DTBDT1

To a solution of compound **7** (0.42 g, 0.5 mmol) and cyanoacetic acid (0.13 g, 1.5 mmol) in chloroform (15 mL) was added piperidine (0.34 g, 4.0 mmol) under argon.

The mixture was refluxed with stirring overnight and then 2 M HCl (10 mL) was added. The resulting mixture was extracted with DCM, and the organic layer was washed with brine and dried over MgSO₄. After removal of the solvent, the crude product was purified by a column chromatography on silica gel with DCM/methanol (12/1, v/v) as eluent to afford target dye DTBDT1 (0.31 g, 70%) as a deep-red solid. ¹H NMR (250 MHz, DMSO-*d*₆) δ 8.67 (s, 1H), 8.53 (s, 1H), 8.19 (s, 1H), 8.06 (s, 1H), 7.71 (s, 1H), 7.56 (d, 2H, J = 4.3 Hz), 7.09 (d, 4H, J = 4.4 Hz), 6.95 (d, 4H, J = 4.4 Hz), 6.85 (d, 2H, J = 4.3 Hz), 3.89 (d, 4H, J = 2.9 Hz), 1.73-1.68 (m, 2H), 1.51-1.27 (m, 16H), 0.95-0.89 (m, 12H). No satisfied ¹³C NMR spectrum was obtained for this compound due to its aggregation in commonly used deuterated solvents. High-temperature (100 °C in DMSO-*d*₆) ¹³C NMR spectrum was also measured but a satisfied spectrum cannot still be obtained. HRMS (ESI+): m/z calcd 896.2810, found 896.2788 (Figure S16).

DTBDT2

The preparation of dye DTBDT2 is identical with that of DTBDT1. Instead of **7**, compound **9** was employed. The target product was obtained as an dark-red solid (0.40 g, 67%). ¹H NMR (250 MHz, DMSO-*d*₆) δ 8.77 (s, 1H), 8.65 (s, 1H), 8.15 (s, 1H), 8.08 (s, 1H), 7.89 (s, 1H), 7.70 (d, 2H, J = 8.6 Hz), 7.48 (d, 4H, J = 8.5 Hz), 7.25 (d, 2H, J = 8.3 Hz), 7.12-7.08 (m, 6H), 6.62-6.56 (m, 4H), 4.01-3.98 (m, 8H), 1.77-1.60 (m, 8H), 1.54-1.24 (m, 26H), 0.92-0.79 (m, 12H). No satisfied ¹³C NMR spectrum was obtained for this compound, as stated for DTBDT1. HRMS (ESI+): m/z calcd 1192.4586, found 1192.4585 (Figure S17).

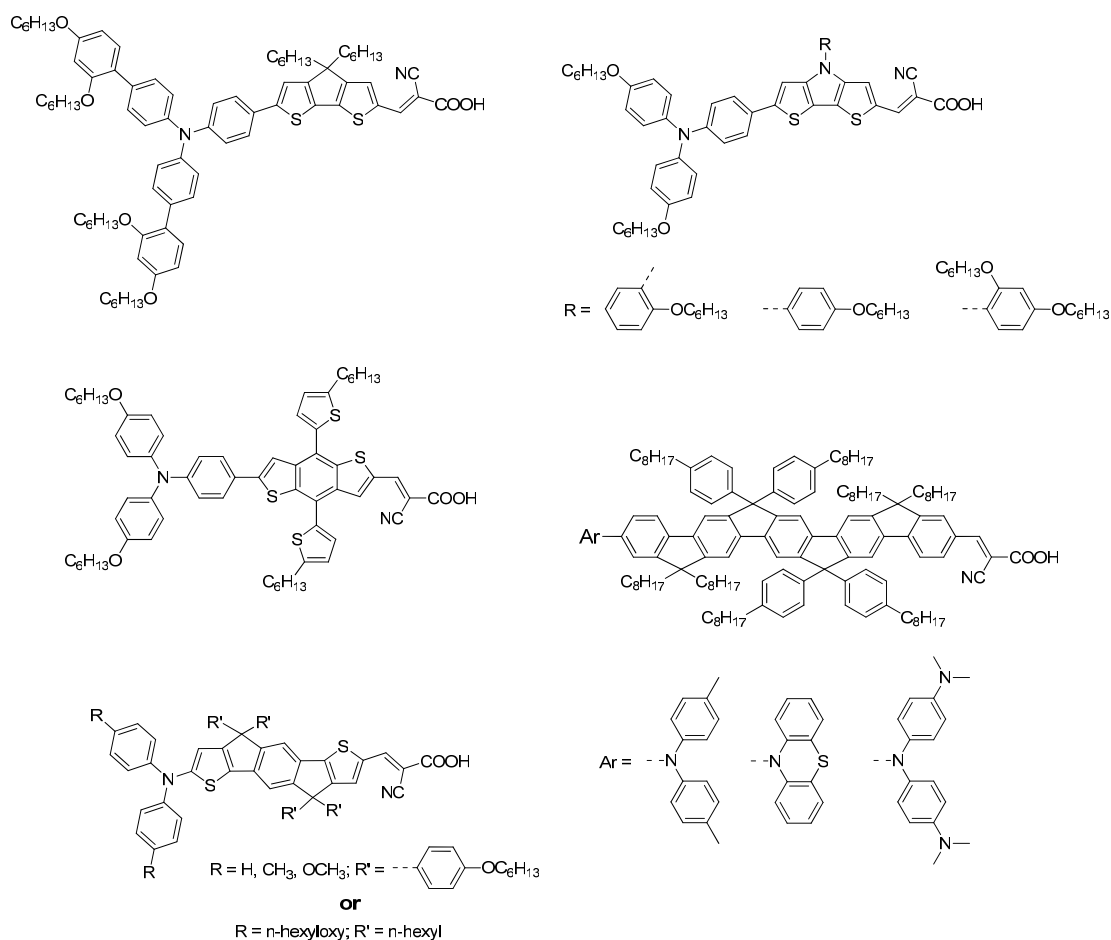


Figure S1. Examples of reported organic sensitizers containing coplanar fused π -spacers.

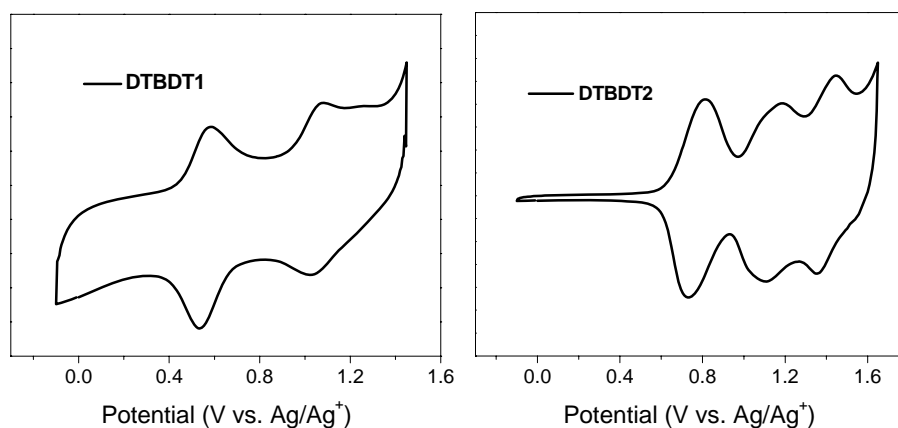


Figure S2. Cyclic voltammograms of DTBDT1 and DTBDT2 in DCM with 0.1 M Bu₄NPF₆ as supporting electrolyte, Ag/Ag⁺ as reference electrode, Pt disk as working electrode, Pt wire as counter electrode, and Fc/Fc⁺ as an internal standard that can be converted to NHE by addition of 630 mV.⁷ The scan rate is 100 mV/s.

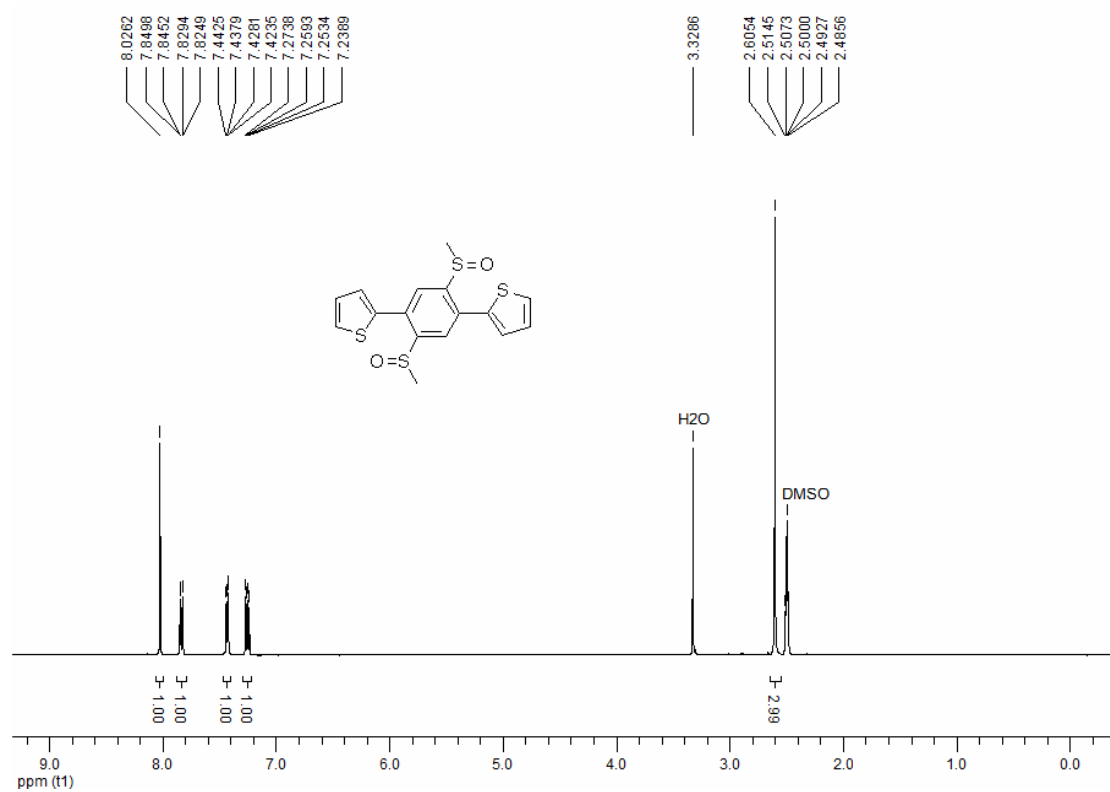


Figure S3. ¹H NMR spectrum of compound **3**.

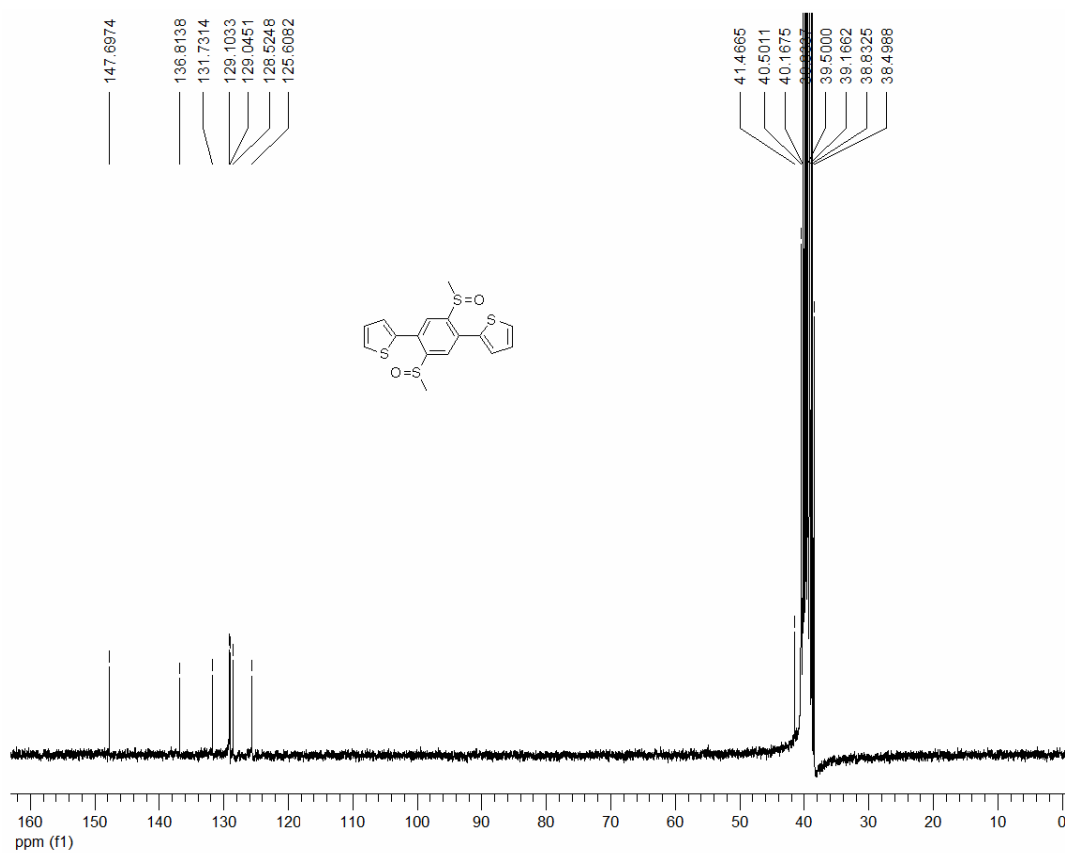


Figure S4. ¹³C NMR spectrum of compound **3**.

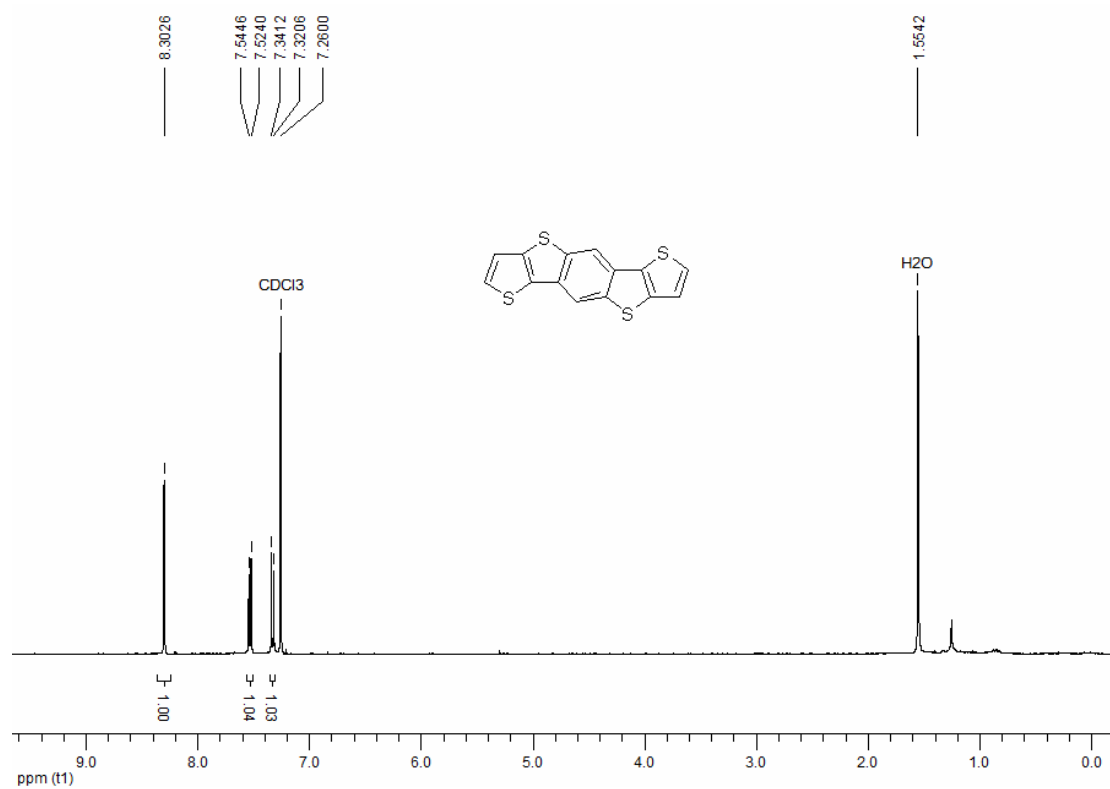


Figure S5. ¹H NMR spectrum of compound **4**.

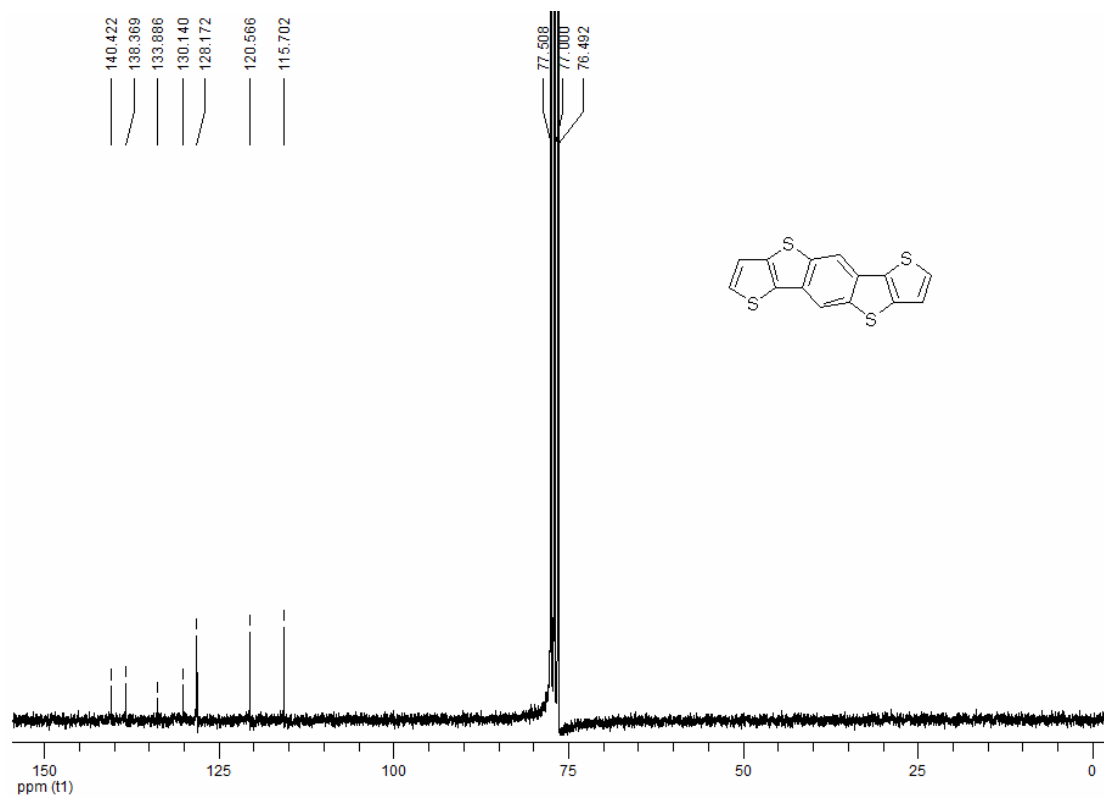


Figure S6. ¹³C NMR spectrum of compound **4**.

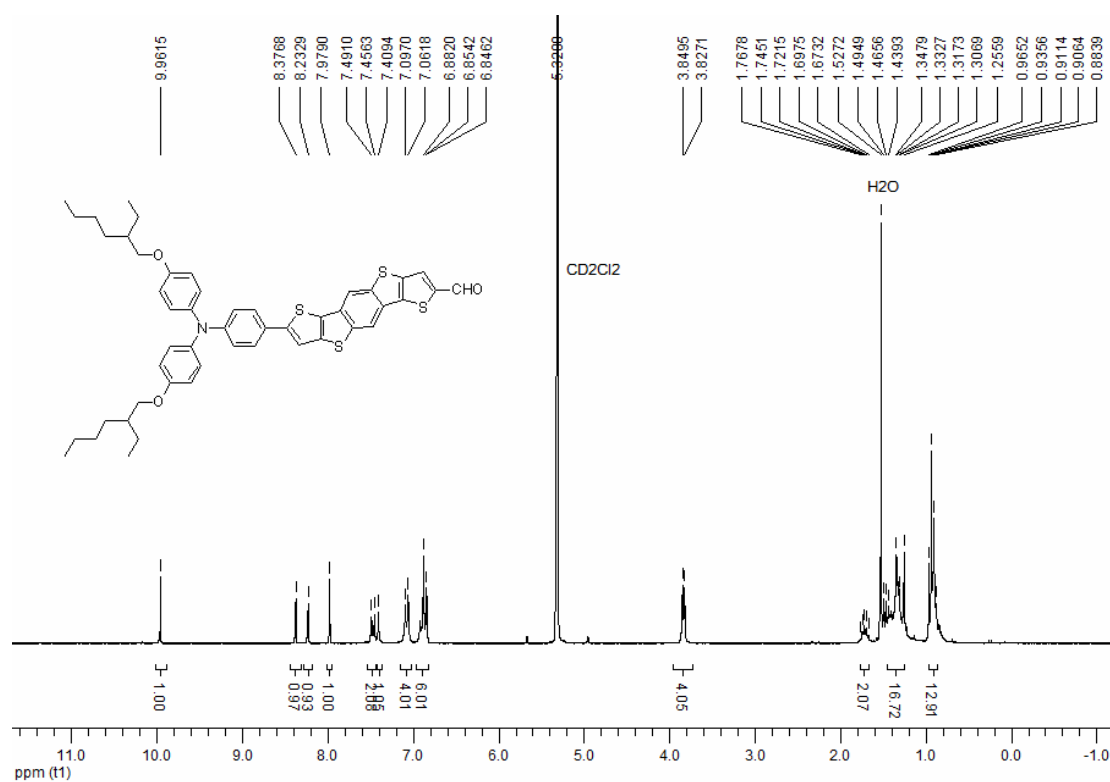


Figure S7. ^1H NMR spectrum of compound **7**.

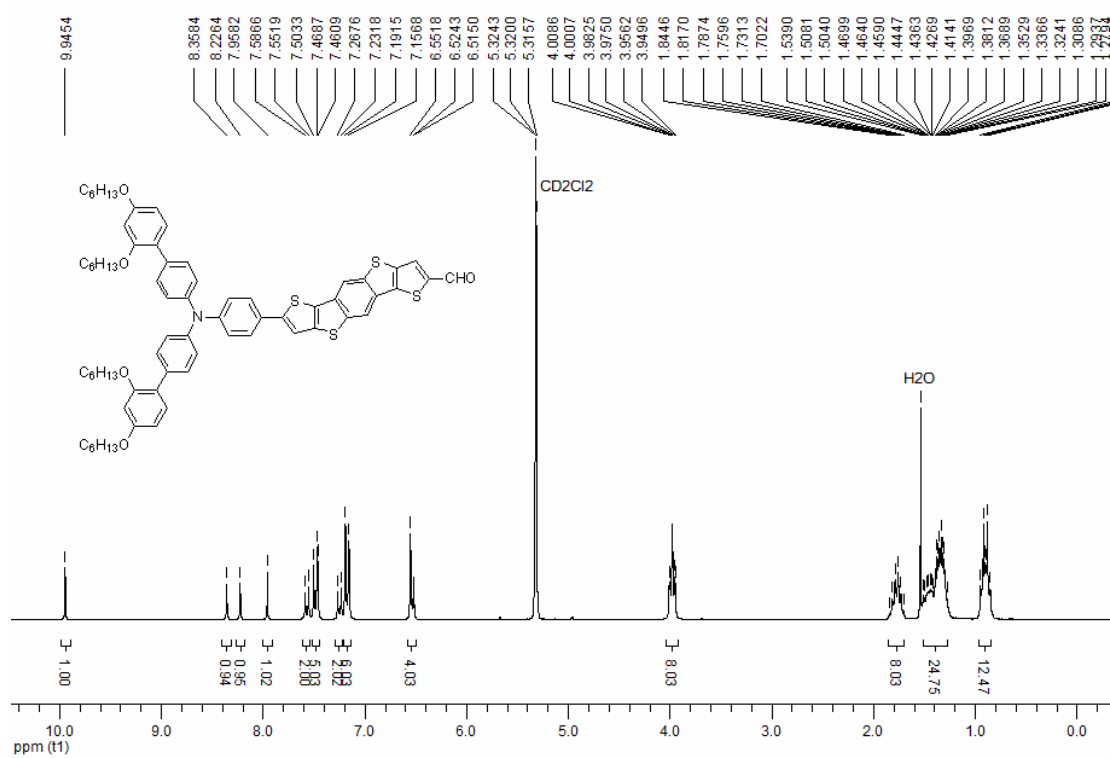


Figure S8. ^1H NMR spectrum of compound **9**.

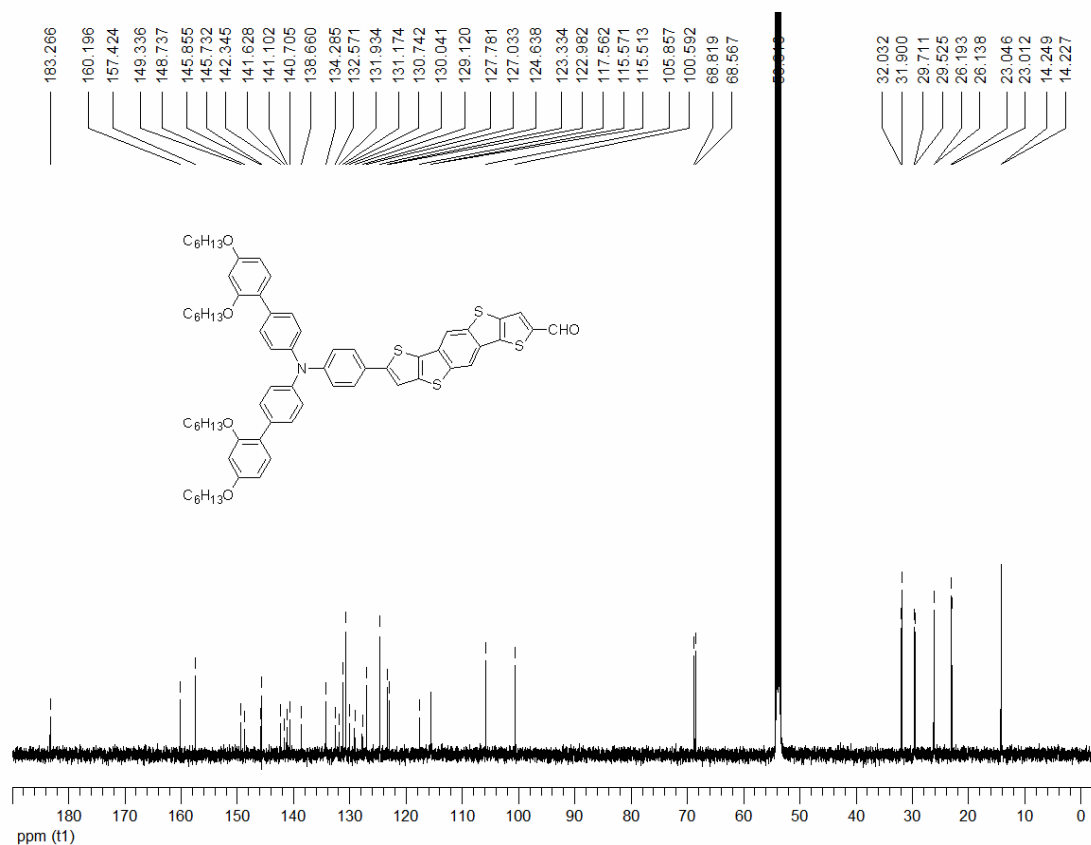
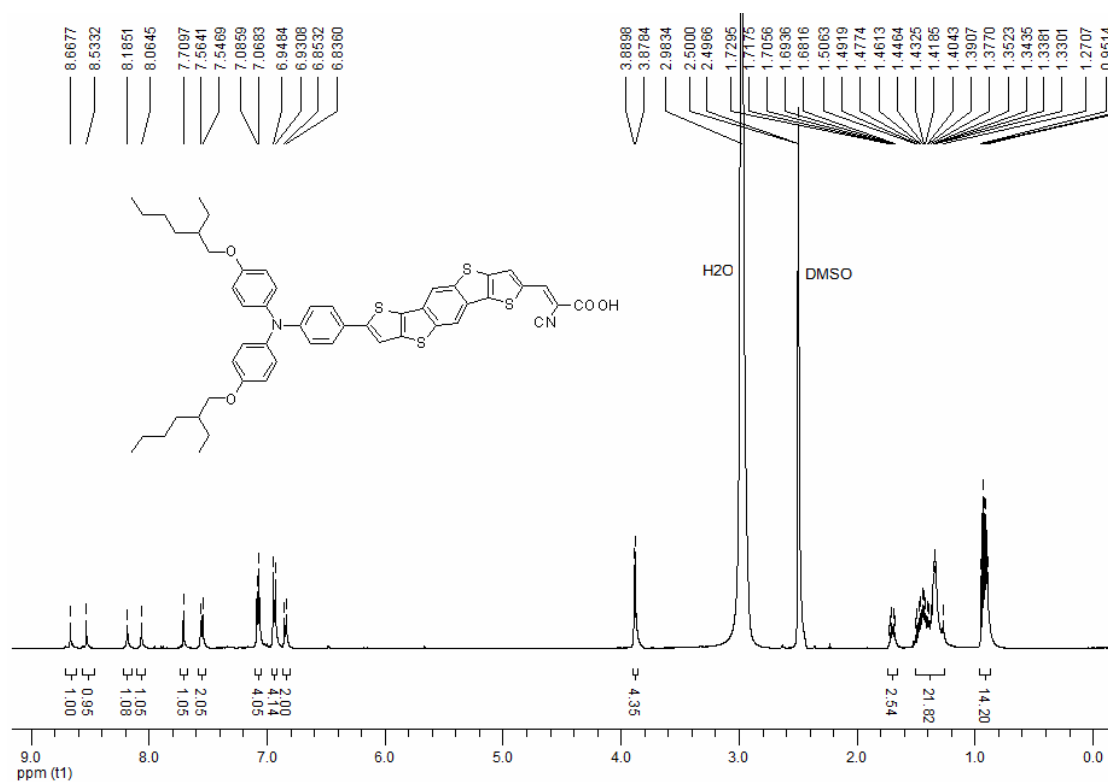


Figure S9. ¹³C NMR spectrum of compound **9**.



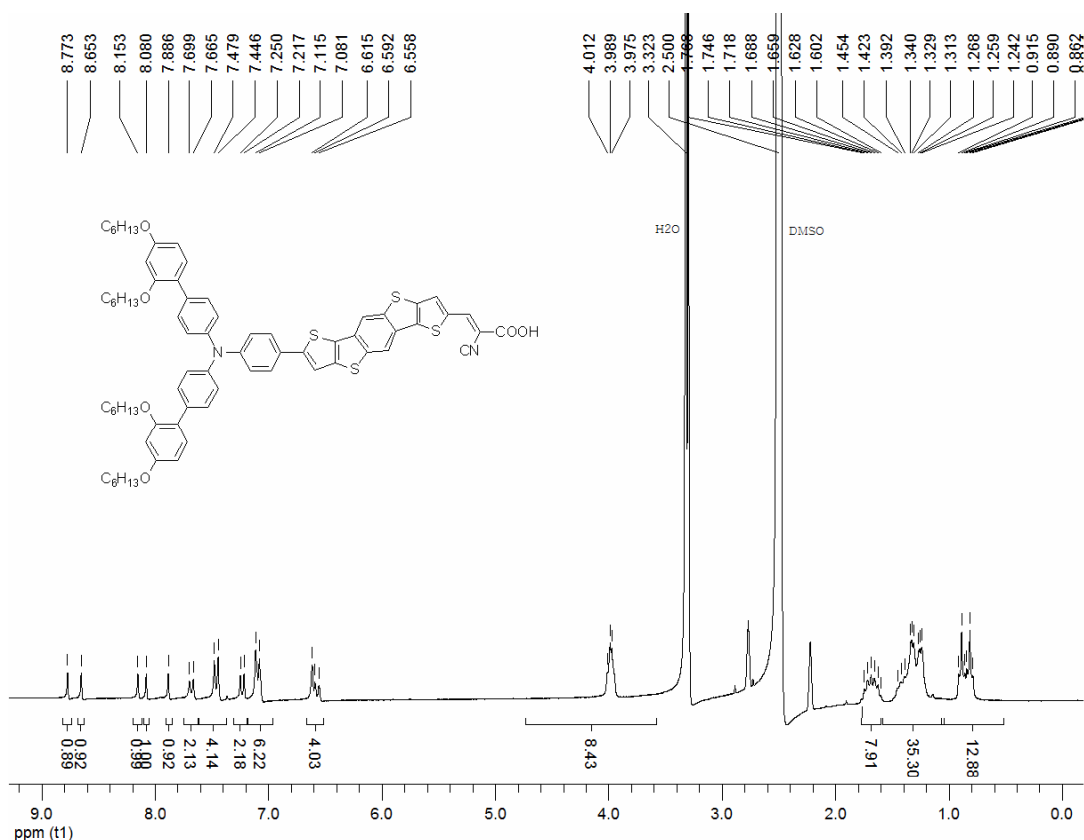


Figure S11. ^1H NMR spectrum of dye DTBDT2.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

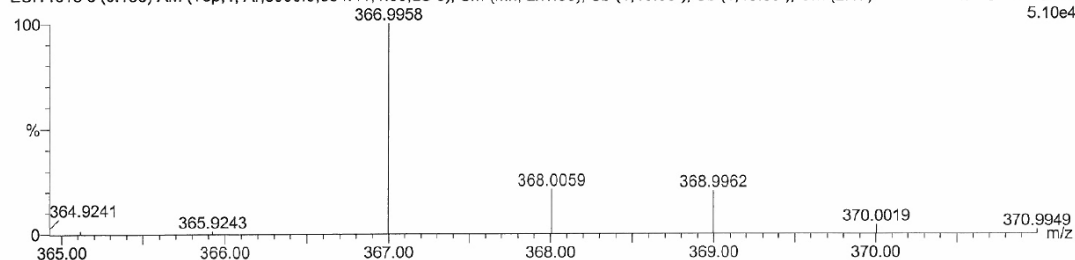
Monoisotopic Mass, Odd and Even Electron Ions

44 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

An, D3, Muellen

ESI14615 6 (0.156) AM (Top,4, Ar,8000.0,354.41,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Sb (1,40.00); Cm (2:17)

1: TOF MS ES+
5.10e4



Minimum:
Maximum:

200.0 10.0 -1.5
50.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
366.9958	366.9955	0.3	0.8	9.5	1	C16 H15 O2 S4

Figure S12. High-resolution mass spectrum of compound 3.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

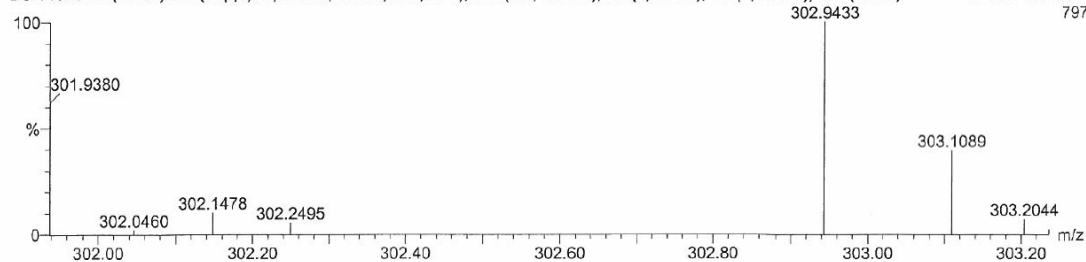
Monoisotopic Mass, Odd and Even Electron Ions

13 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

An, D4, Muellen

ESI14616 23 (0.582) AM (Top,4, Ar,8000.0,354.41,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Sb (1,40.00); Cm (23:27)

1: TOF MS ES+
797



Minimum:				-1.5		
Maximum:	200.0	10.0		50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
302.9433	302.9431	0.2	0.8	11.5	1	C14 H7 S4

Figure S13. High-resolution mass spectrum of compound 4.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

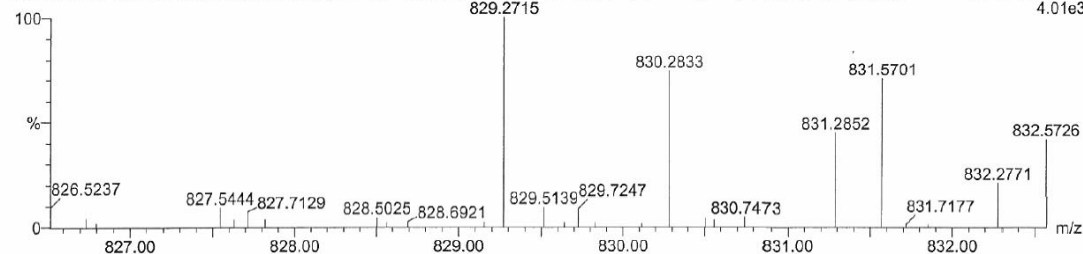
Monoisotopic Mass, Odd and Even Electron Ions

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An, D7, Muellen

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1: TOF MS ES+
4.01e3



Minimum:				-1.5		
Maximum:	200.0	10.0		50.0		
Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
830.2833	830.2830	0.3	0.4	24.5	1	C49 H52 N O3 S4

Figure S14. High-resolution mass spectrum of compound 7.

Elemental Composition Report

Page 1

Single Mass Analysis

Tolerance = 10.0 PPM / DBE: min = -1.5, max = 50.0

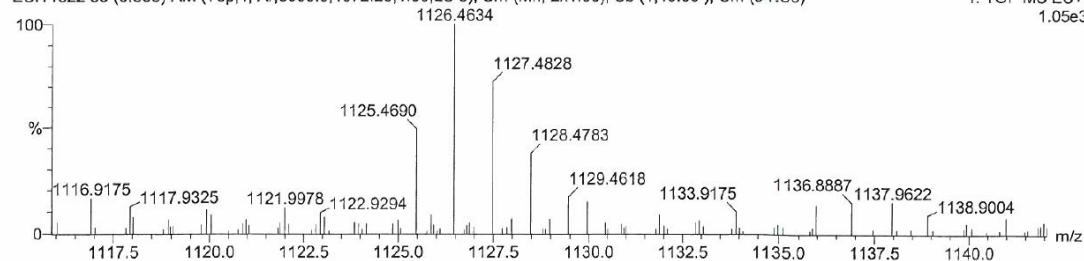
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

299 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

An, D9, Muellen

ESI14622 36 (0.898) AM (Top,4, Ar,8000.0,1072.25,1.00,LS 5); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (34:56)

1: TOF MS ES+
1.05e3Minimum:
Maximum:200.0 10.0
-1.5 50.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
1126.4634	1126.4606	2.8	2.5	32.5	1	C69 H76 N O5 S4

Figure S15. High-resolution mass spectrum of compound 9.

Elemental Composition Report

Page 1

Single Mass Analysis (displaying only valid results)

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 200.0

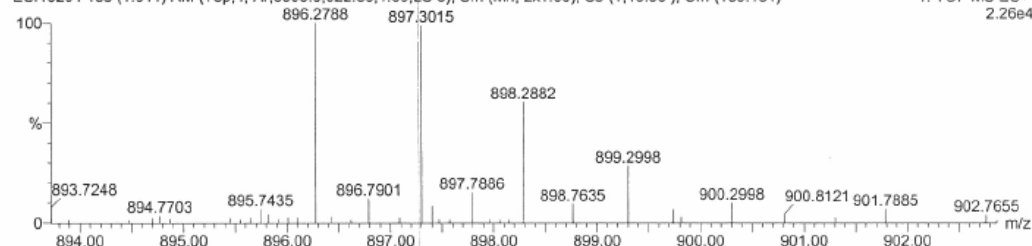
Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

25 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

An, DTBDT1, Muellen

ESI13204 135 (1.644) AM (Top,4, Ar,8000.0,922.36,1.00,LS 6); Sm (Mn, 2x1.00); Sb (1,40.00); Cm (130:184)

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2.26e4Minimum:
Maximum:200.0 20.0
-1.5 200.0

Mass	Calc. Mass	mDa	PPM	DBE	Score	Formula
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Figure S16. High-resolution mass spectrum of dye DTBDT1.

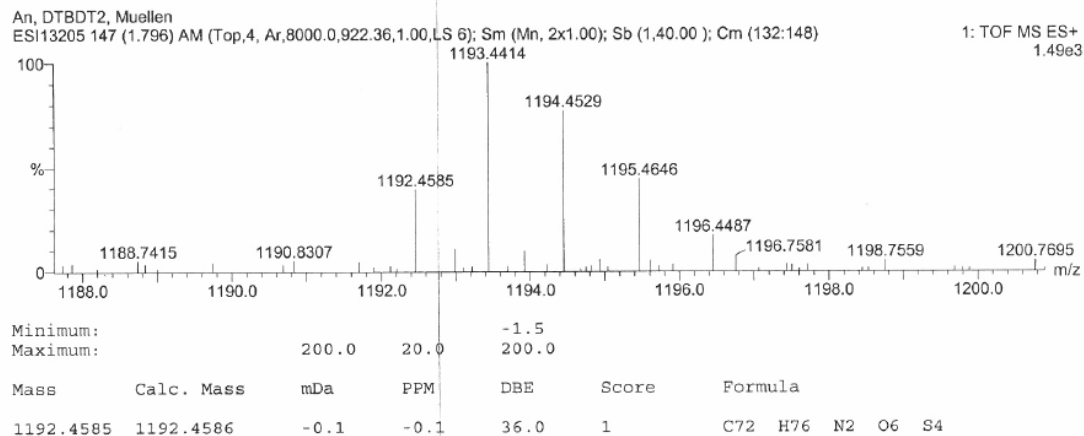
Single Mass Analysis (displaying only valid results)

Tolerance = 20.0 PPM / DBE: min = -1.5, max = 200.0

Isotope cluster parameters: Separation = 1.0 Abundance = 1.0%

Monoisotopic Mass, Odd and Even Electron Ions

18 formula(e) evaluated with 1 results within limits (up to 50 closest results for each mass)

**Figure S17.** High-resolution mass spectrum of dye **DTBBDT2**.**References**

- (1) Gaussian 03, Revision B.04: Frisch, M. J. et al. Gaussian, Inc., Pittsburgh PA, 2003.
- (2) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- (3) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B.*, 1988, **37**, 785.
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- (5) D. H. Lee, M. J. Lee, H. M. Song, B. J. Song, K. D. Seo, M. Pastore, C. Anselmi, S. Fantacci, F. De Angelis, M. K. Nazeeruddin and H. K. Kim, *Dyes and Pigments*, 2011, **91**, 192.
- (6) H. N. Tsao, C. Yi, T. Moehl, J.-H. Yum, S. M. Zakeeruddin, M. K. Nazeeruddin and M. Grätzel, *ChemSusChem*, 2011, **4**, 591.
- (7) J.-H. Chen, C.-H. Tsai, S.-A. Wang, Y.-Y. Lin, T.-W. Huang, S.-F. Chiu, C.-C. Wu and K.-T. Wong, *J. Org. Chem.*, 2011, **76**, 8977.