Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

For

New EDOT-SQ systems for electrochromic applications

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CONTENTS:

1. Additional emission spectra of EDOT derivatives

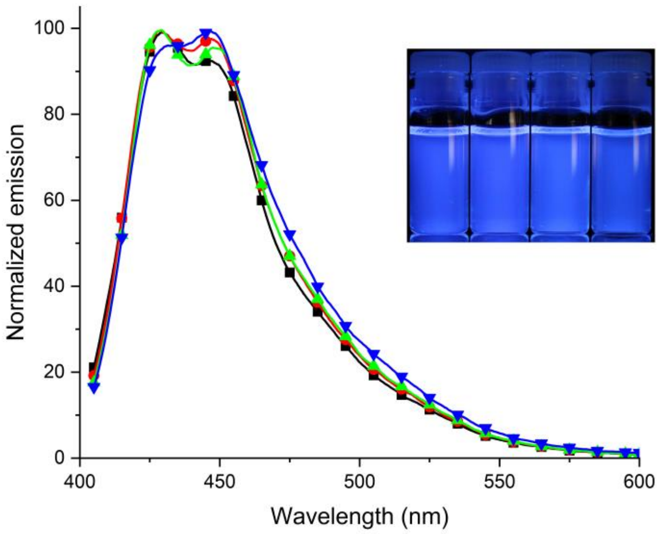


Figure S1. Emission spectra of **EDOT-SQ_I** in toluene (■), THF (●), $CHCl_3$ (▲) and acetone (▲) when excited at the absorption maxima.

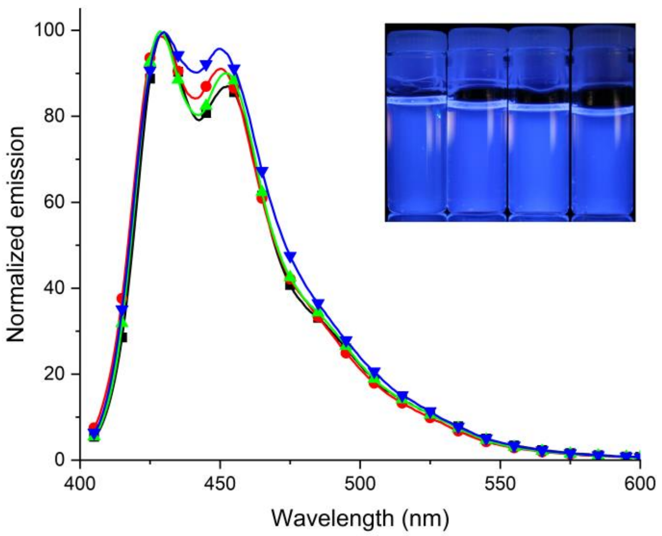


Figure S2. Emission spectra of **EDOT-DDSQ_I** in toluene (■), THF (●), $CHCl_3$ (▲) and acetone (▲) when excited at the absorption maxima.

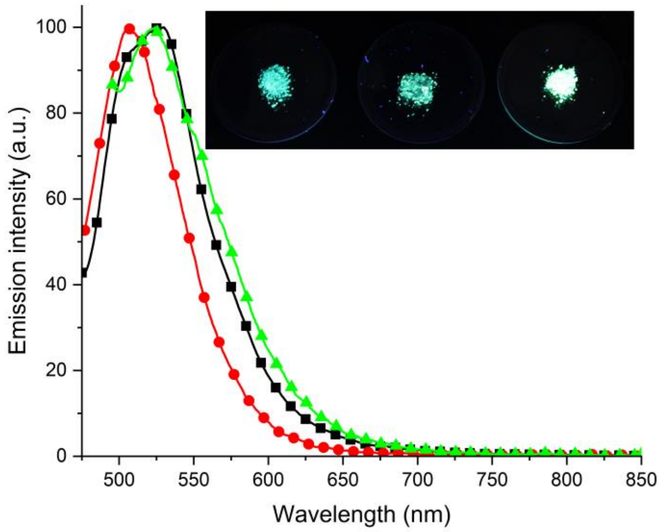


Figure S3. Normalized emission spectra of **EDOT-SQ_I** (■) **EDOT-SQ_II** (●) and **EDOT-DDSQ-I** (▲) in the solid state. Insert: the photograph showing the emission in the solid state of **EDOT-SQ_I**, **EDOT-DDSQ-I** and **EDOT-SQ_II** (from left to right).

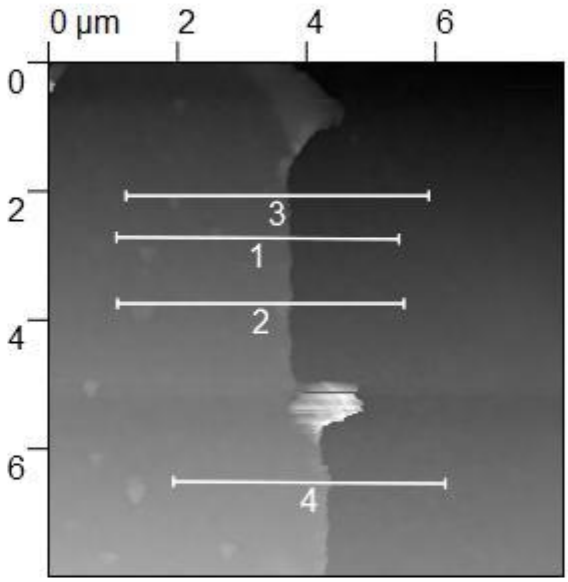
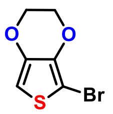
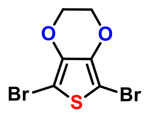
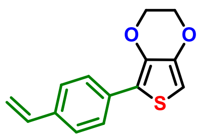
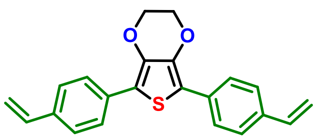


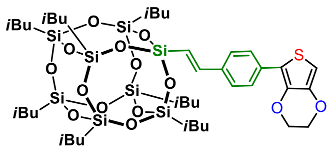
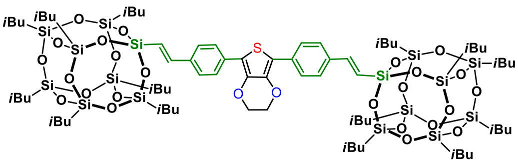
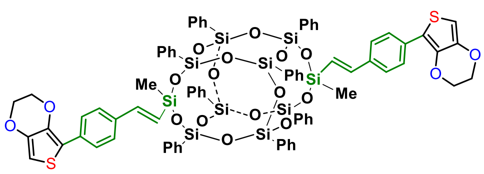
Figure S4. AFM micrograph of **EDOT-DDSQ_I** polymer deposited on ITO electrode showing the step between the ITO and polymer surface.

2. Analytical data of EDOT derivatives

2.1. Analytical data of EDOTs

 EDOT_Br_I	Light yellow solid, isolated yield: 70%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 4.18-4.21 (m, 2H, -CH_2-CH_2-), 4.25-4.28 (m, 2H, -CH_2-CH_2-), 6.34 (s, 1H, S-CH); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 64.5 (OCH_2), 65.0 (OCH_2), 87.0, 99.6, 140.0, 141.1; MS m/z (rel. intensity): 45.00 (31), 57.10 (21), 69.10 (38), 85.10 (35), 97.10 (15), 141.00 (52), 220.10 (86), 221.00 (11), 222.00 (100, M^+). These data are accordance with the literature.[1]
 EDOT_Br_II	Light yellow solid, isolated yield: 81%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 4.27 (s, 4H, -CH_2-CH_2-); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 65.10 (OCH_2), 85.67, 139.84; MS m/z (rel. intensity): 84.10 (11), 95.10 (61), 123.10 (21), 125.00 (20). 139.10 (15), 163.10 (13), 165.00 (14), 274.10 (11), 298.20 (41), 299.99 (100, M^+). These data are accordance with the literature.[2]
 EDOT_I	Yellow oil, isolated yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 4.15-4.19 (m, 2H, -CH_2-CH_2-), 4.20-4.28 (m, 2H, -CH_2-CH_2-), 5.16 (d, 1H, J_{HH} = 10.9 Hz, -CH=CH_2), 5.67 (d, 1H, J_{HH} = 17.6 Hz, -CH=CH_2), 6.22 (s, 1H, S-CH), 6.63 (dd, 1H, J_{HH} = 17.6, 10.9 Hz, -CH=CH_2), 7.32 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-), 7.60 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 64.43 (OCH_2), 64.76 (OCH_2), 97.63, 99.61, 113.42, 125.98, 126.40, 132.67, 135.77, 136.46, 138.25, 142.26; MS m/z (rel. intensity): 56.98 (24), 69.10 (35), 76.04 (28), 84.02 (35), 103.05 (28), 141.00 (19), 217.03 (15), 244.06 (100, M^+).
 EDOT_II	Yellow oil, isolated yield: 95%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 4.30 (s, 4H, -CH_2-CH_2-), 5.17 (d, 2H, J_{HH} = 10.9 Hz, -CH=CH_2), 5.69 (d, 2H, J_{HH} = 17.5 Hz, -CH=CH_2), 6.64 (dd, 2H, J_{HH} = 17.5, 10.9 Hz, -CH=CH_2), 7.34 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-), 7.65 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 64.58 (OCH_2), 113.49, 126.06, 126.45, 132.42, 135.82, 136.46, 138.80; MS m/z (rel. intensity): 56.98 (19), 69.10 (32), 76.10 (29), 84.11 (31), 103.09 (27), 139.90 (19), 243.08 (26), 346.06 (100, M^+).

2.2. Analytical data of EDOT-SQ systems

 EDOT-SQ_I	Yellow solid, isolated yield: 96%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.60-0.68 (m, 14H, CH_2), 0.93 – 1.02 (m, 42H, CH_3), 1.83-1.93 (m, 7H, CH), 4.23-4.28 (m, 2H, -CH_2-CH_2-), 4.29 – 4.34 (m, 2H, -CH_2-CH_2-), 6.12 (d, 1H, J_{HH} = 19.2 Hz, =CH), 6.31 (s, 1H, SCH), 7.16 (d, 1H, J_{HH} = 19.2 Hz, =CH), 7.43 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-), 7.69 (d, 2H, J_{HH} = 8.4 Hz, -C_6H_4-); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 22.44 (CH_2), 22.50 (CH_2), 23.85 (CH), 23.86 (CH), 25.70 (CH_3), 64.42 (OCH_2), 64.76 (OCH_2), 97.63, 117.18, 118.01, 125.90, 127.02, 129.70, 133.50, 135.73, 138.45, 142.25, 147.55; ^{29}Si NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -67.40, -67.83 (core), -79.90 (*Si*CH=).
 EDOT-SQ_II	Yellow solid, isolated yield: 93%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.64-0.70 (m, 28H, CH_2), 0.98-1.01 (m, 84H, CH_3), 1.87-1.95 (m, 14H, CH), 4.41 (s, 4H, -CH_2-CH_2-), 6.16 (d, 2H, J_{HH} = 19.2 Hz, =CH), 7.19 (d, 2H, J_{HH} = 19.2 Hz, =CH), 7.47 (d, 4H, J_{HH} = 8.4 Hz, -C_6H_4-), 7.76 (d, 4H, J_{HH} = 8.4 Hz, -C_6H_4-); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) 22.45 (CH_2), 22.51 (CH_2), 23.85 (CH), 23.87 (CH), 25.71 (CH_3), 64.57 (OCH_2), 115.47, 118.11, 126.00, 126.75, 127.06, 128.51, 133.20, 135.83, 139.01, 147.51; ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -67.40, -67.83, -67.85 (core), -79.76 (*Si*CH=).
 EDOT-DDSQ_I	Yellow solid, isolated yield: 94%; ^{1}H NMR (400 MHz, $CDCl_3$, 296K): δ (ppm) 0.45 (s, 6H, SiCH_3), 4.12-4.49 (m, 8H, -CH_2-CH_2-), 6.42 (d, 2H, J_{HH} = 19.2 Hz, =CH), 6.92-6.99, 7.04-7.13, 7.15-7.25, 7.27-7.33, 7.34-7.39, 7.44-7.48, 7.54-7.63 (m, 50H, -C_6H_4-, -C_6H_5 and =CH); ^{13}C NMR (100 MHz, $CDCl_3$, 296K): δ (ppm) -0.72 (SiCH_3), 64.46 (OCH_2), 64.78 (OCH_2), 97.81, 123.57, 125.88, 125.97, 126.81, 127.02, 127.08, 127.51, 127.55, 127.59, 127.79, 128.38, 130.21, 130.26, 130.35, 132.02, 134.00, 134.12, 146.17; ^{29}Si NMR (79 MHz, $CDCl_3$, 296K): δ (ppm) -30.03 (*Si*CH=), -76.98, -78.14 (core).

3. NMR spectra of EDOT derivatives

3.1. NMR spectra of EDOTs

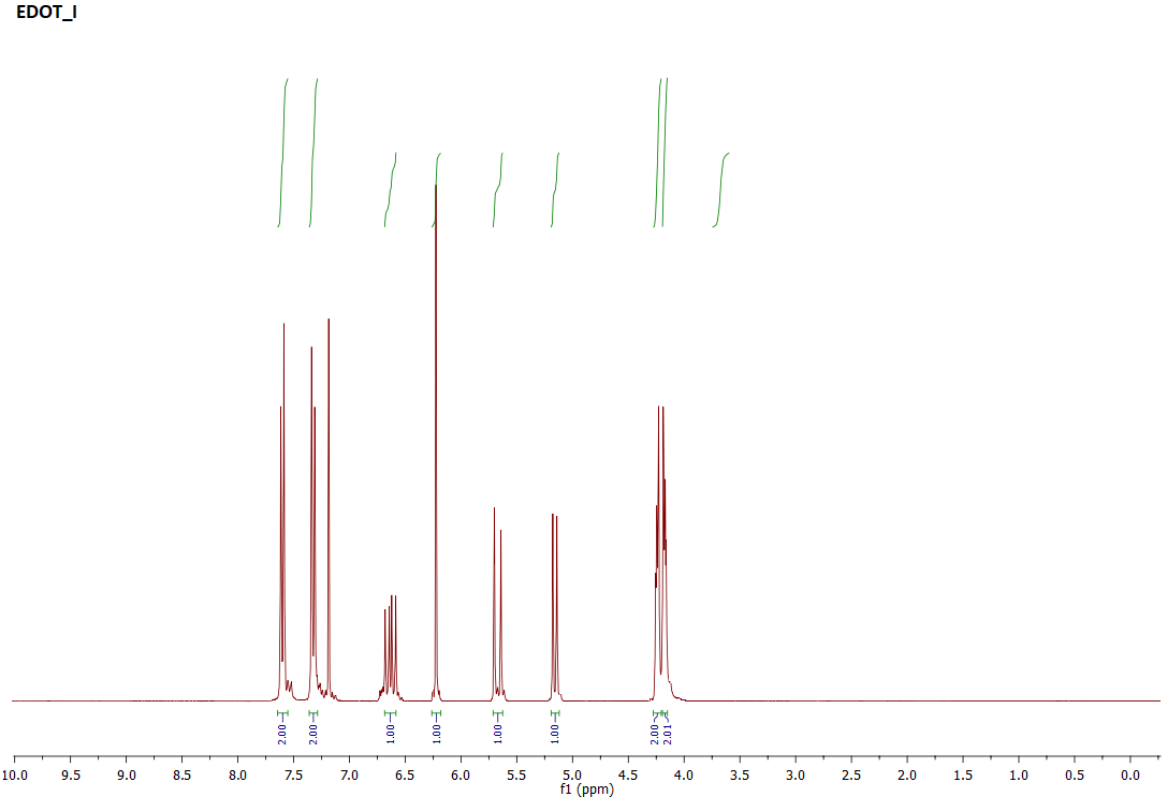


Figure S5. ^{1}H NMR (400 MHz, $CDCl_3$) of **EDOT_I**

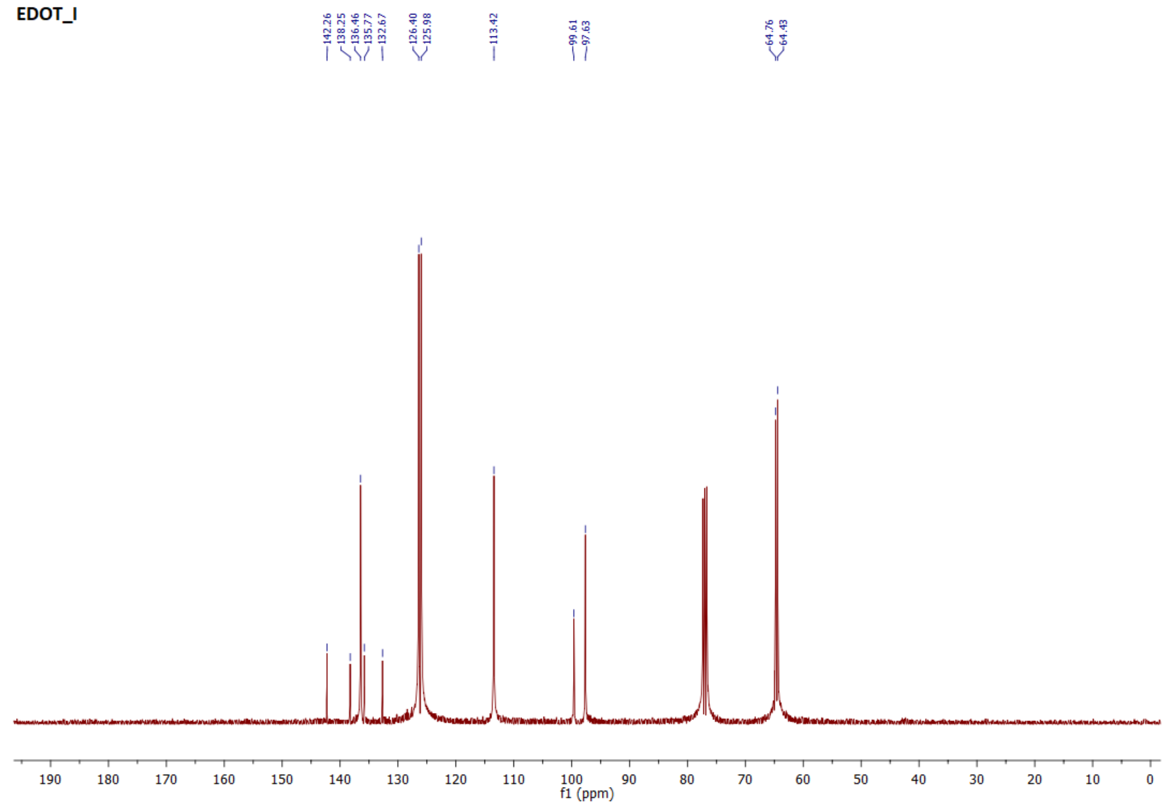


Figure S6. ^{13}C NMR (101 MHz, $CDCl_3$) of olefin **EDOT_I**

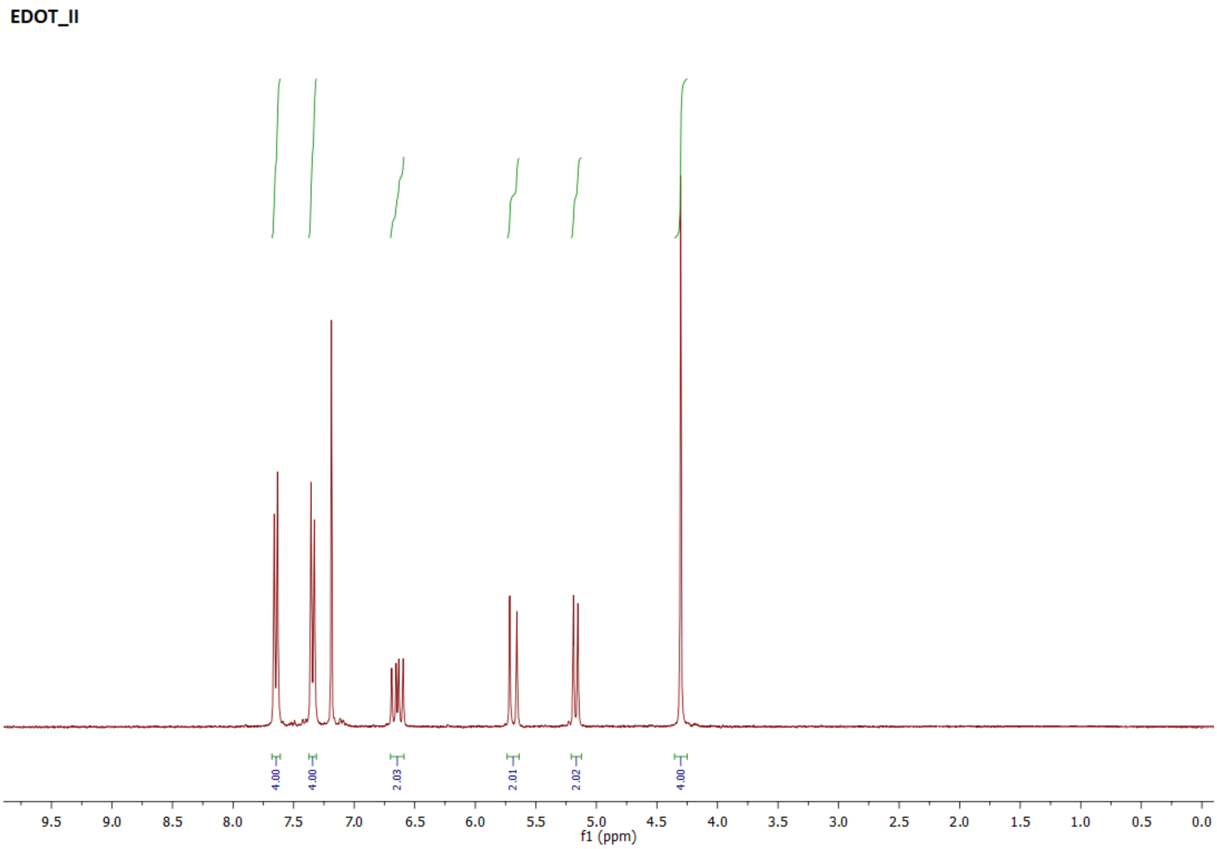


Figure S7. ^{1}H NMR (400 MHz, $CDCl_3$) of **EDOT_II**

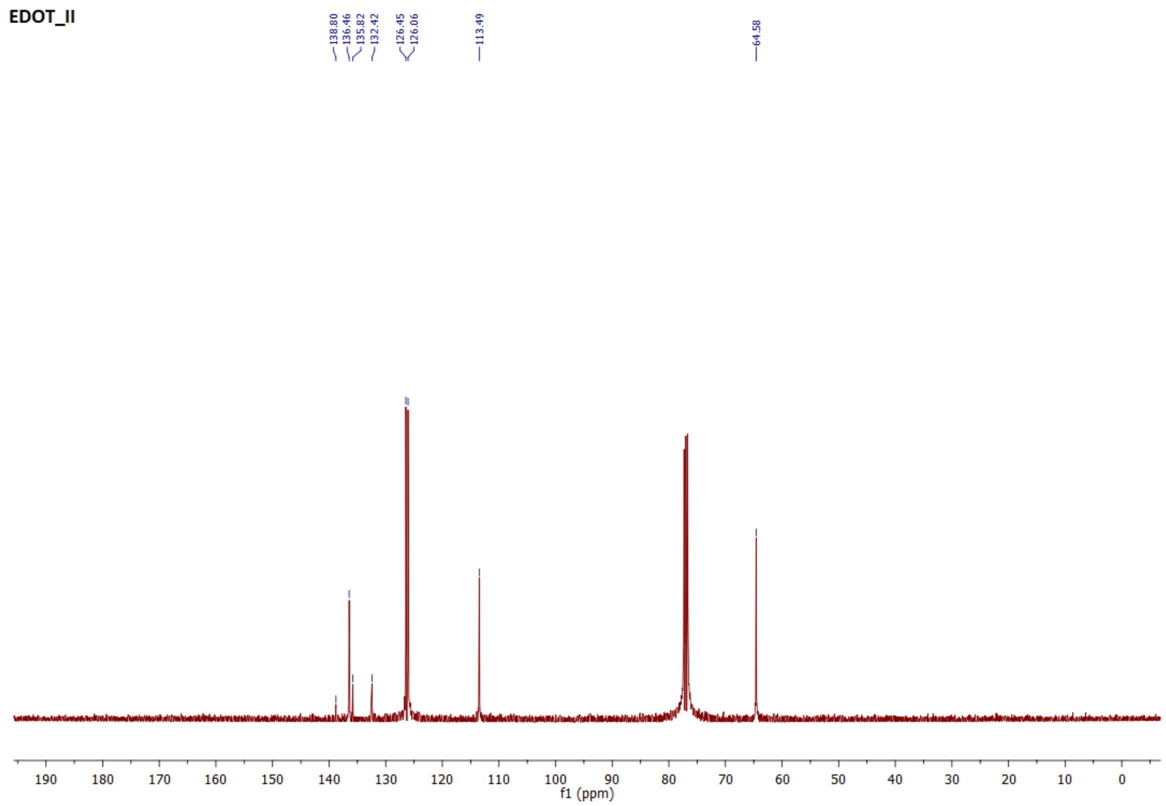


Figure S8. ^{13}C NMR (101 MHz, $CDCl_3$) of olefin **EDOT_II**

3.2. NMR spectra of EDOT-SQ systems

EDOT-SQ_I

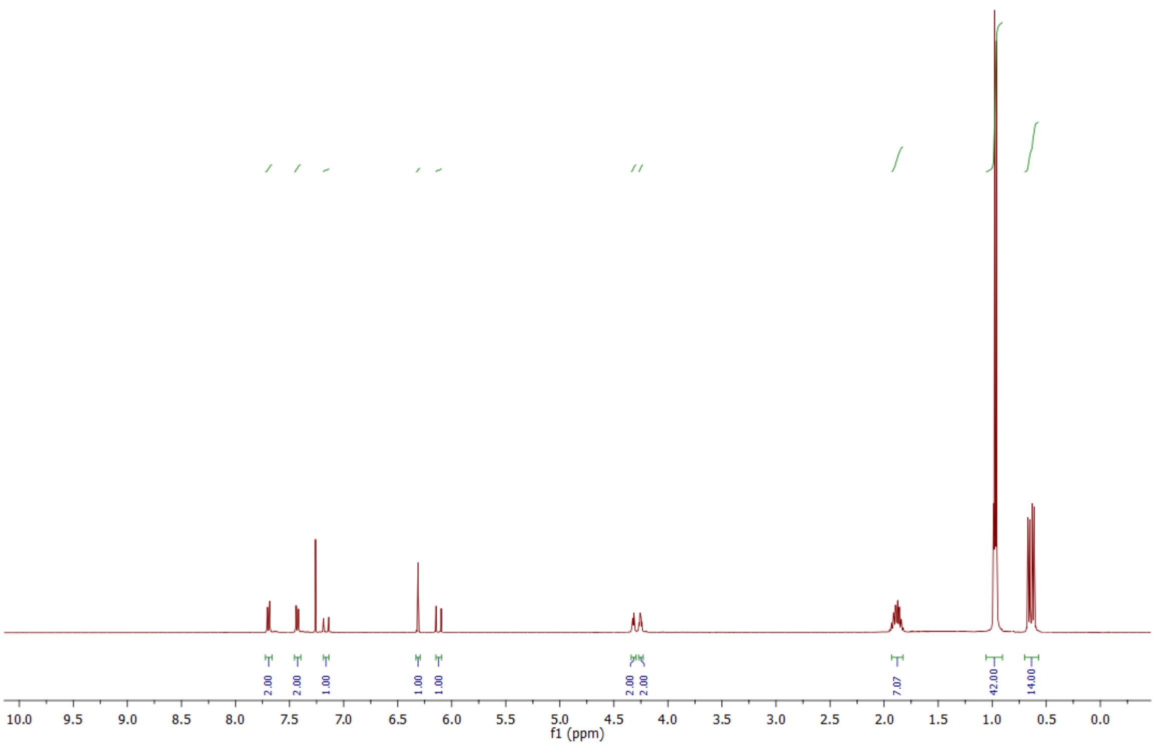


Figure S9. ^{1}H NMR (400 MHz, $CDCl_3$) of **EDOT-SQ_I**

EDOT-SQ_I

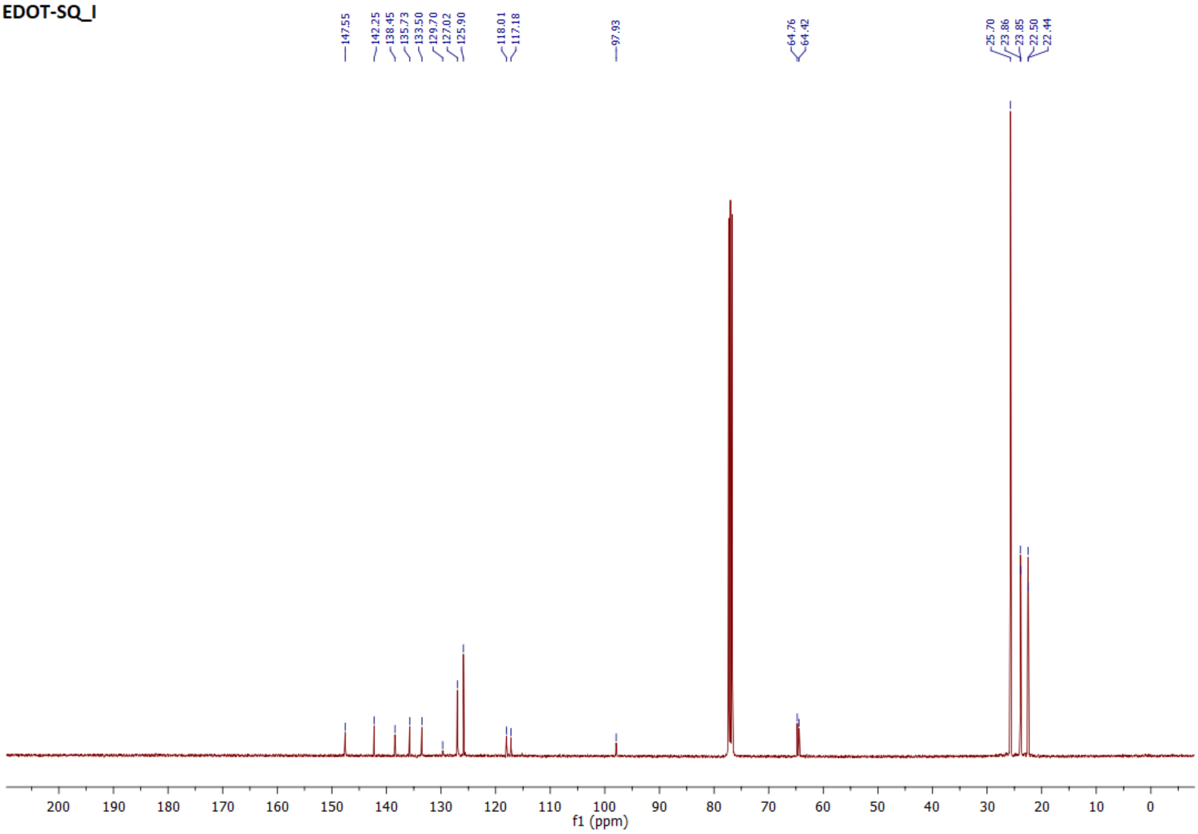


Figure S10. ^{13}C NMR (101 MHz, $CDCl_3$) of **EDOT-SQ_I**

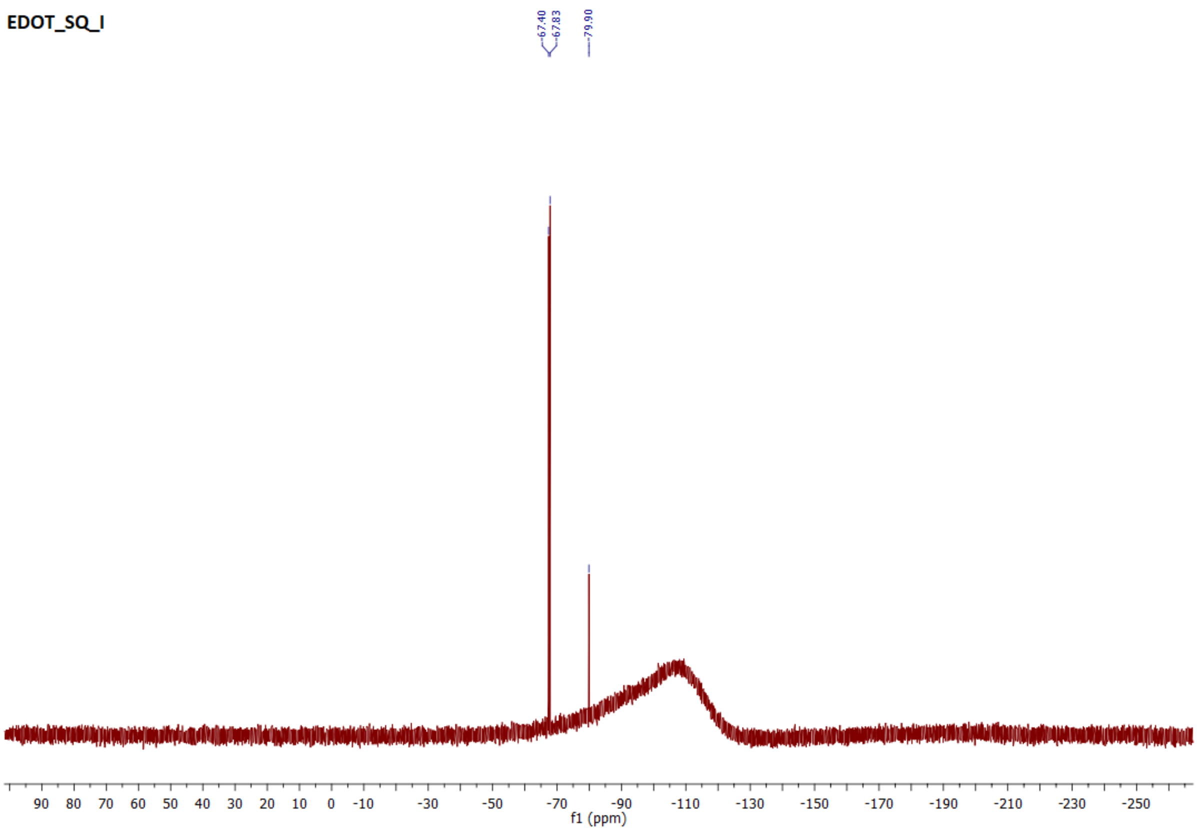


Figure S11. ^{29}Si NMR (79 MHz, $CDCl_3$) of **EDOT-SQ_I**

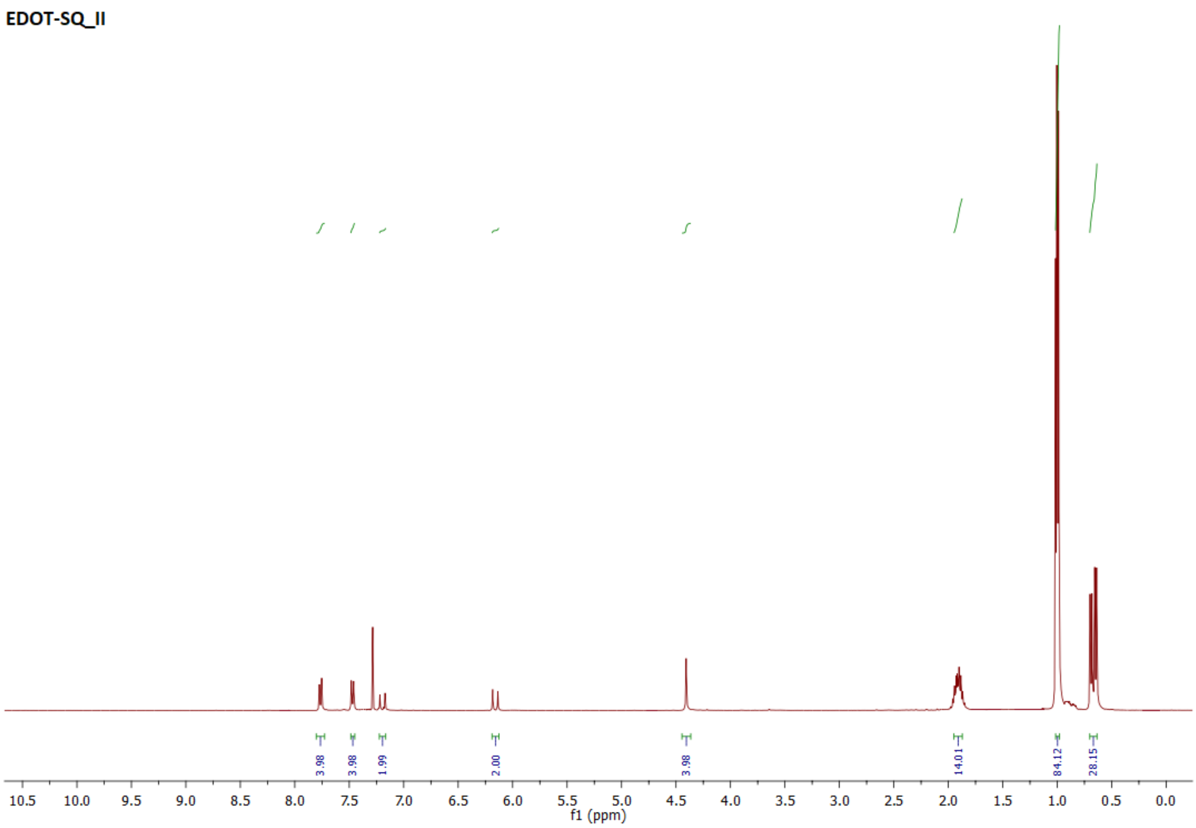


Figure S12. ^{1}H NMR (400 MHz, $CDCl_3$) of product **EDOT-SQ_II**

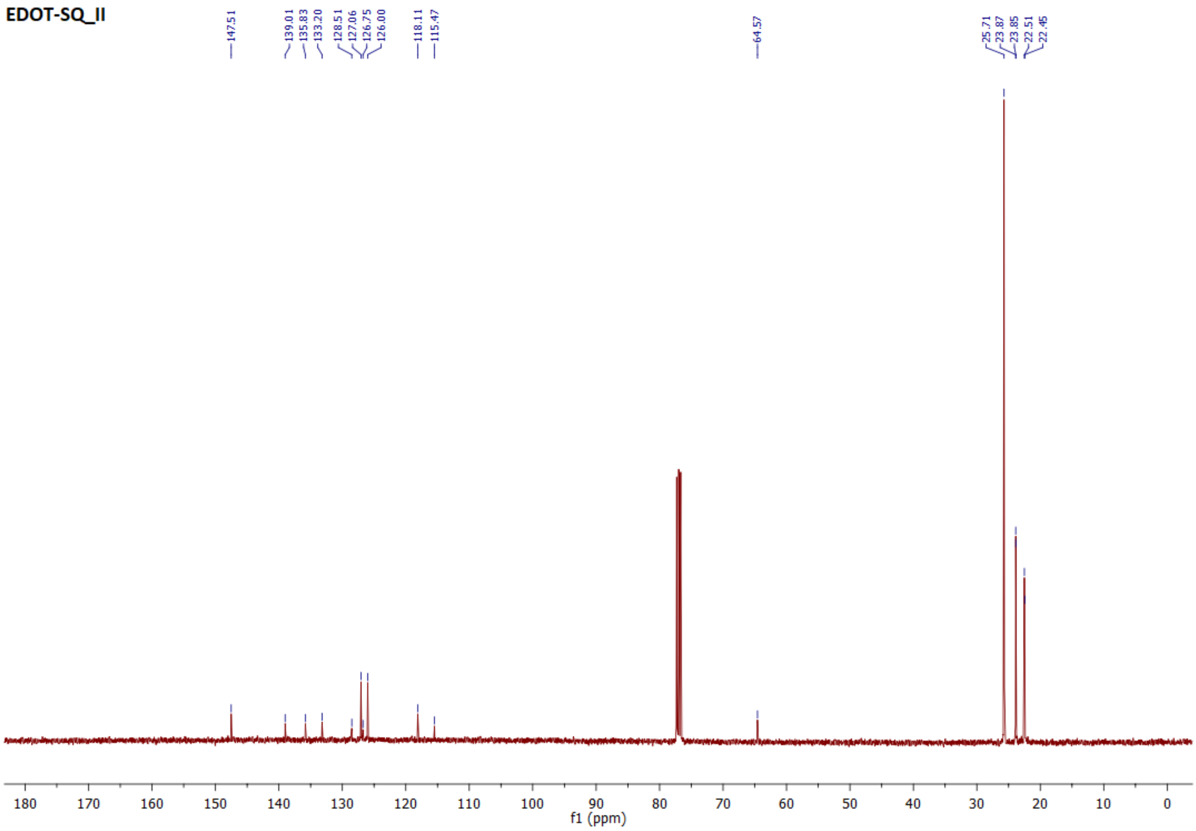


Figure S13. ^{13}C NMR (101 MHz, $CDCl_3$) of **EDOT-SQ_II**

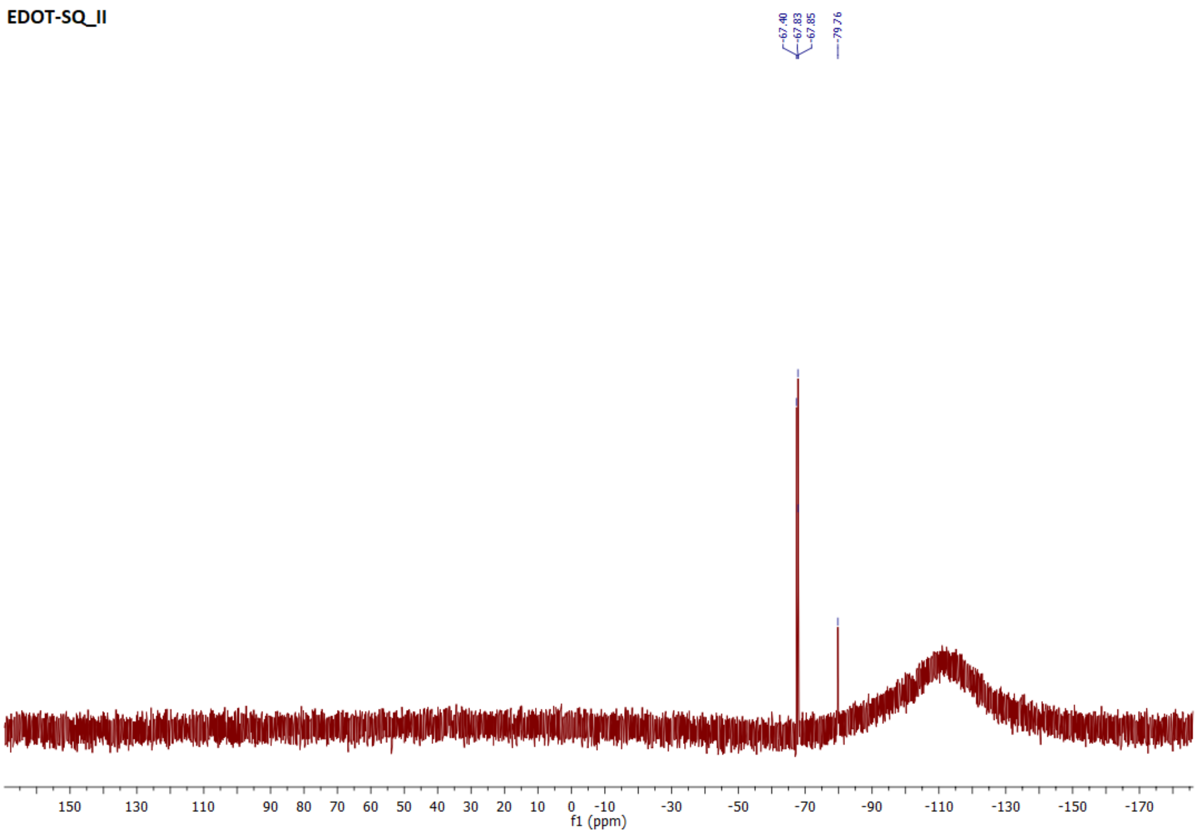


Figure S14. ^{29}Si NMR (79 MHz, $CDCl_3$) of **EDOT-SQ_II**

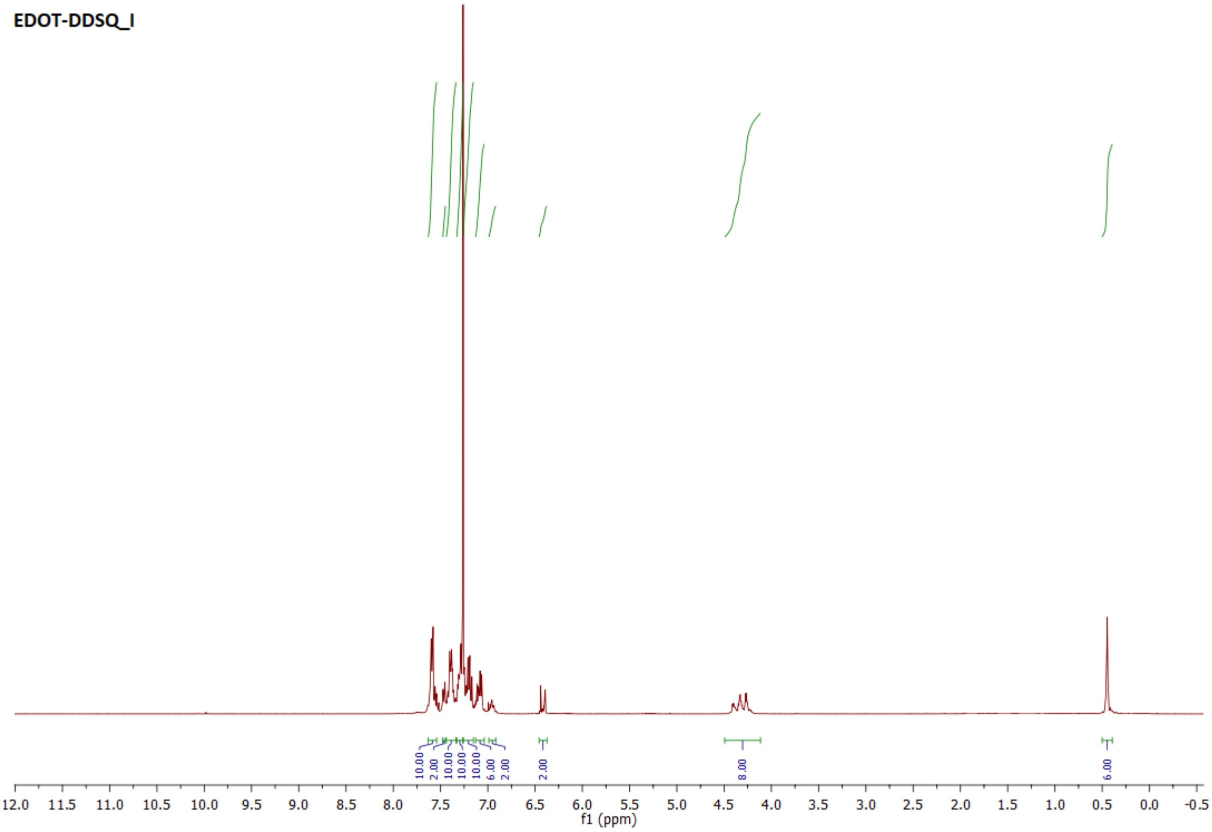


Figure S15. ^{1}H NMR (400 MHz, $CDCl_3$) of product **EDOT-DDSQ_I**

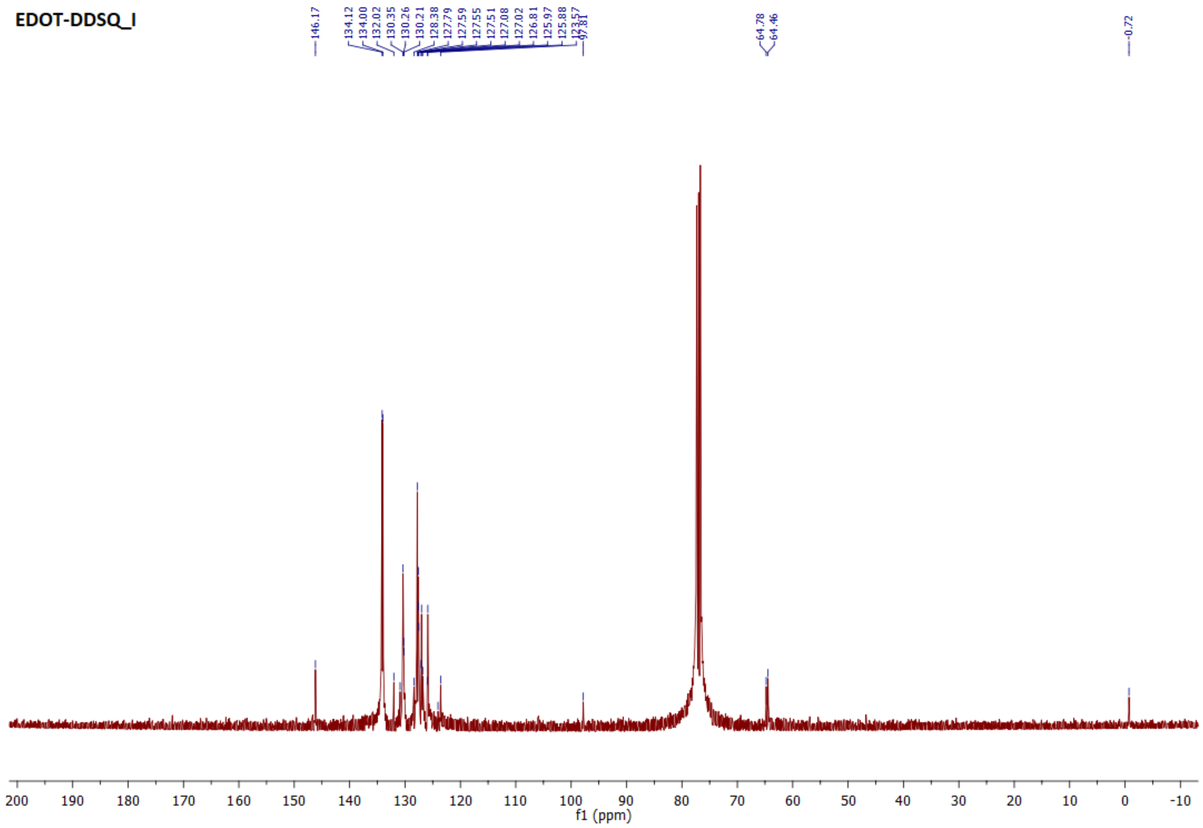


Figure S16. ^{13}C NMR (101 MHz, $CDCl_3$) of product **EDOT-DDSQ_I**

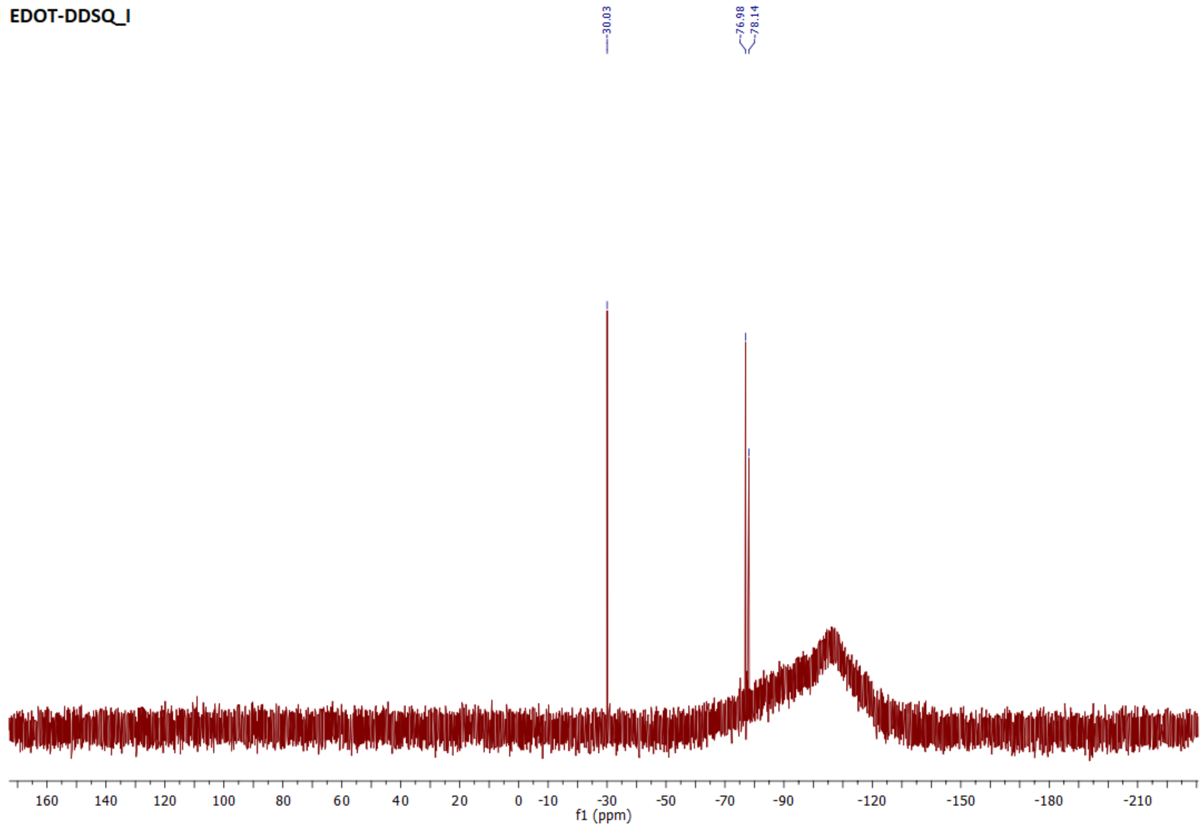


Figure S17. ^{29}Si NMR (79 MHz, $CDCl_3$) of product **EDOT-DDSQ_I**

4. References

[1] X. Yin, Z. Li, J. Jin, C. Tusy, J. Xia, *Facile synthesis of poly(3,4-ethylenedioxythiophene) by acid-assisted polycondensation of 5-bromo-2,3-dihydro-thieno[3,4-b][1,4]dioxine, Synth. Met.,* 2013, **175**, 97.

[2] J. J. Apperloo, L. Bert Groenendaal, H. Verheyen, M. Jayakannan, R. A. J. Janssen, A. Dkhissi, D. Beljonne, R. Lazzaroni, J.-L. Brédas, *Optical and Redox Properties of a Series of 3,4-Ethylenedioxythiophene Oligomers, Chem. Eur. J.*, 2002, **8**, 2384.