Electronic Supplementary Material (ESI) for RSC Advances.


# Electronic Supporting Information

## Synthesis and Structure-property Investigation of Multi-arm Oligothiophenes

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## 1. $^{1}H$, $^{13}C$ NMR and mass spectra

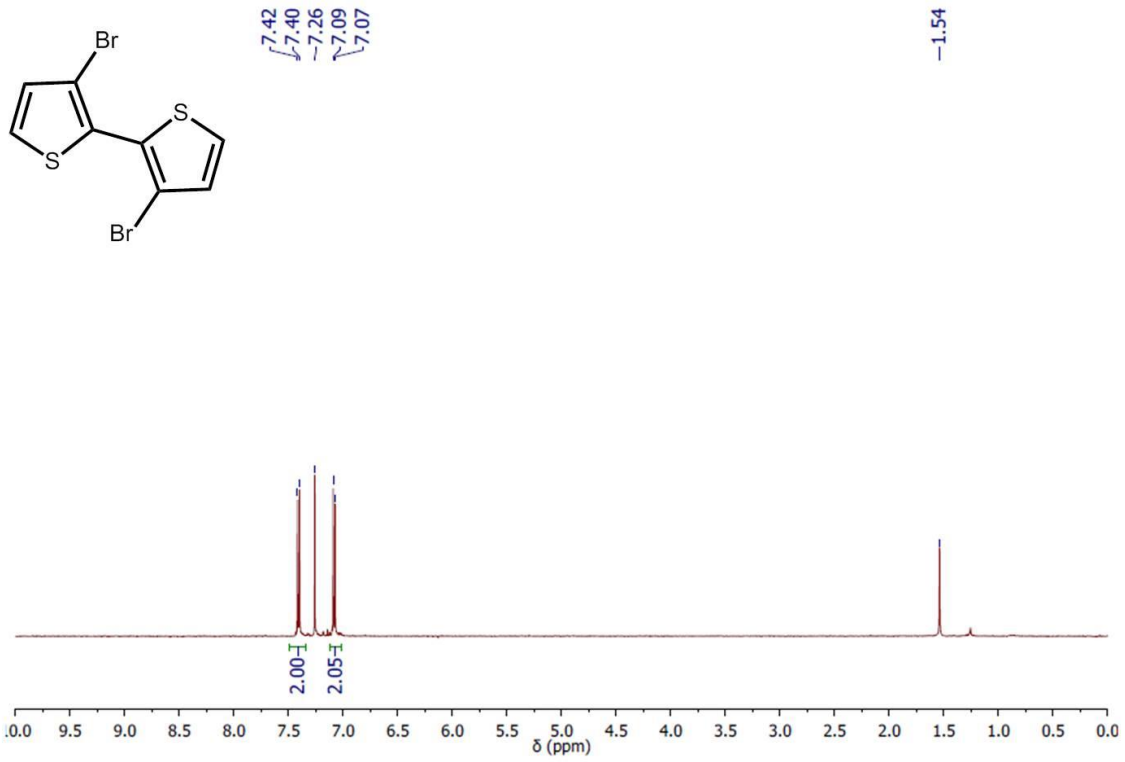



***Figure S1.*** $^{1}H$ NMR spectrum of compound **1** in $CDCl_3$.

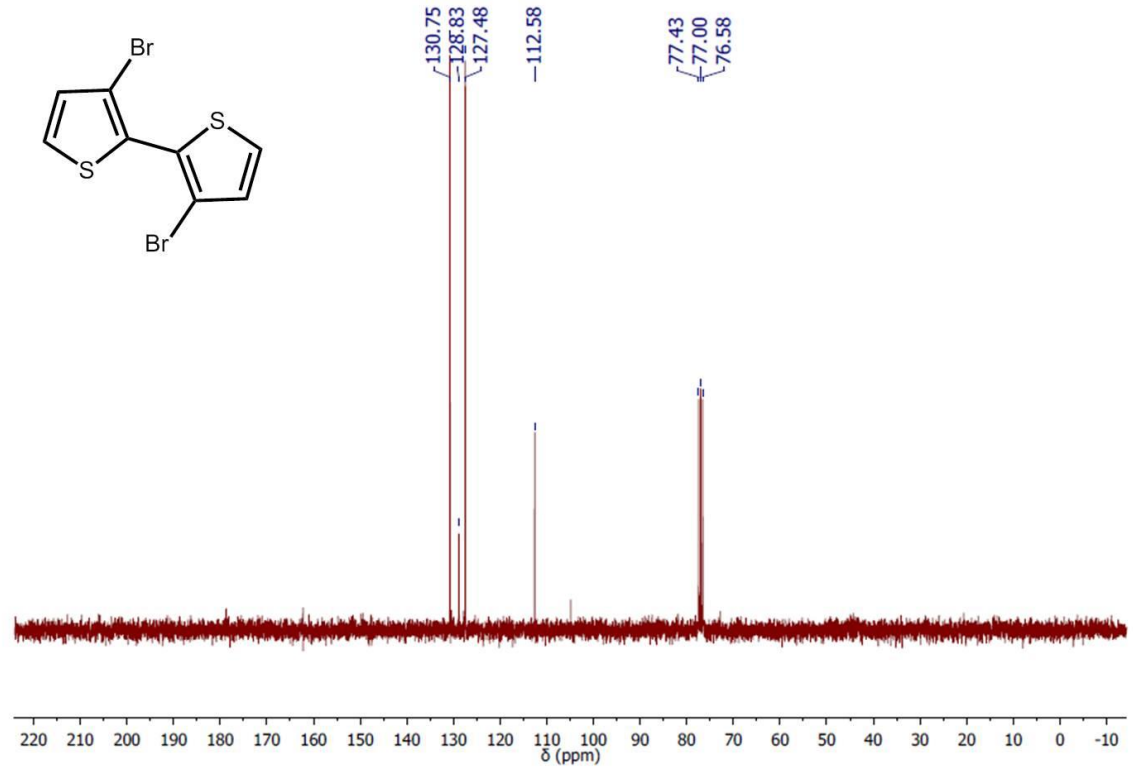


***Figure S2.*** $^{13}$C NMR spectrum of compound **1** in $CDCl_3$.

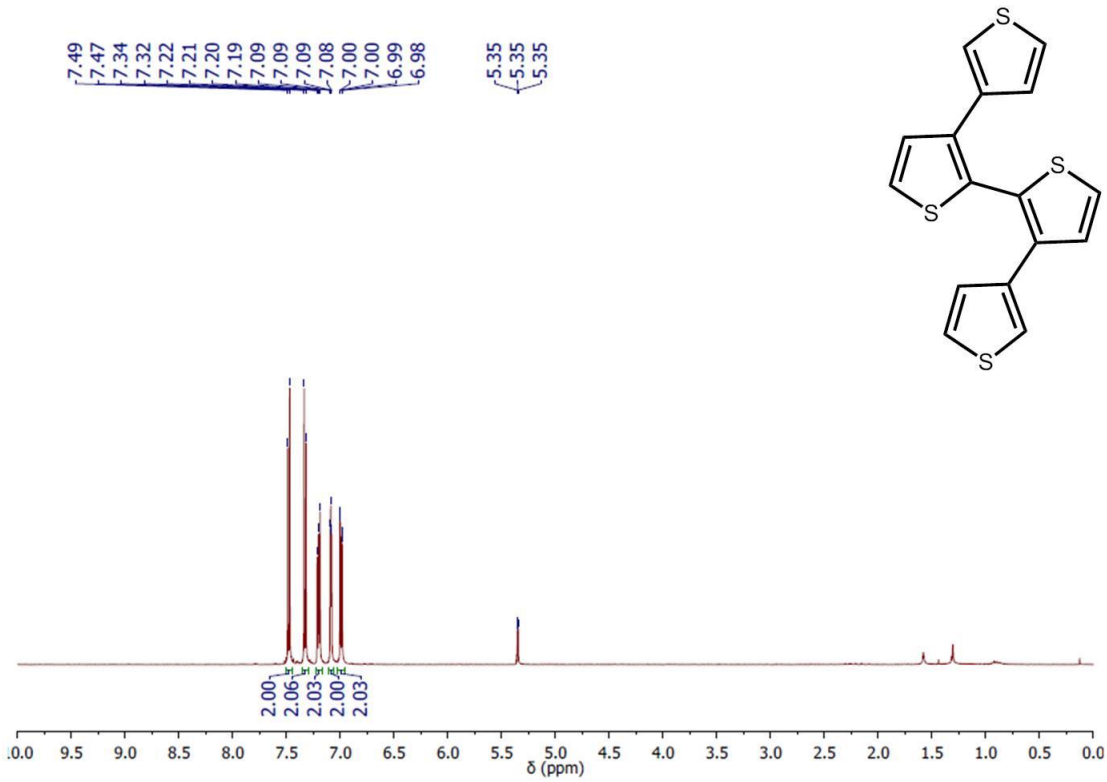



***Figure S3.*** $^{1}$H NMR spectrum of compound **2** in $CD_2Cl_2$.

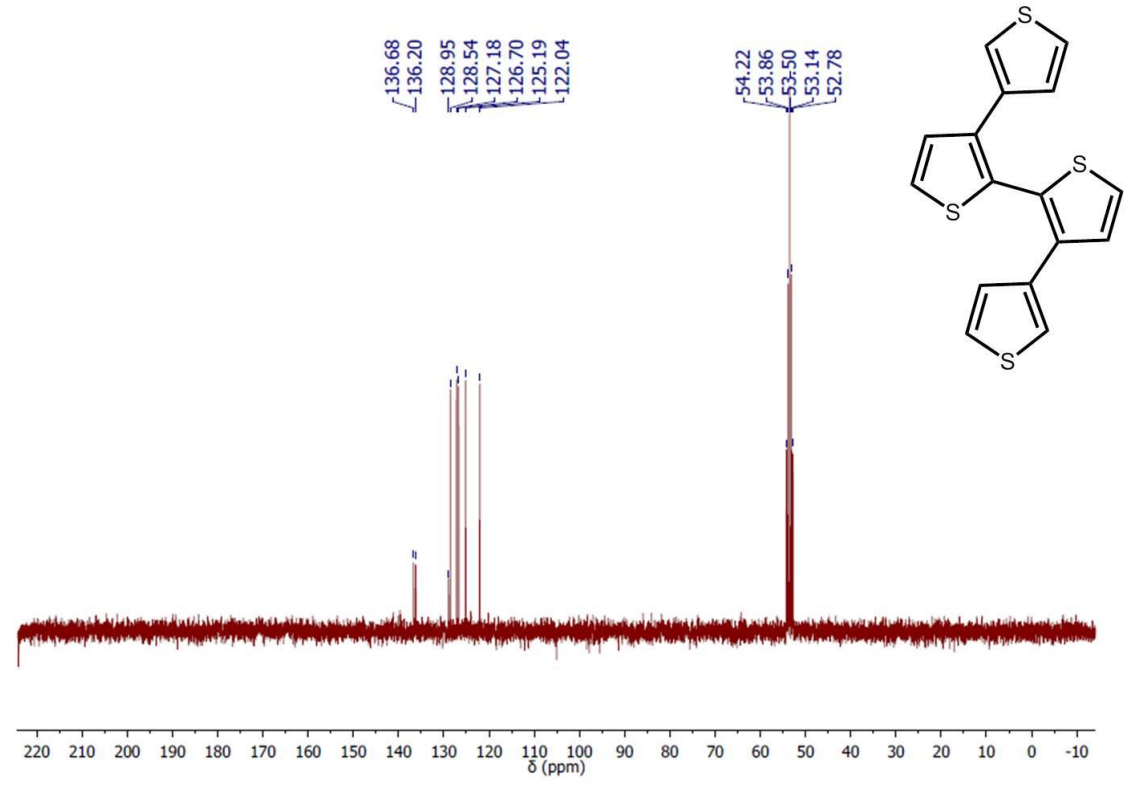



***Figure S4.*** $^{13}$C NMR spectrum of compound **2** in $CD_2Cl_2$.

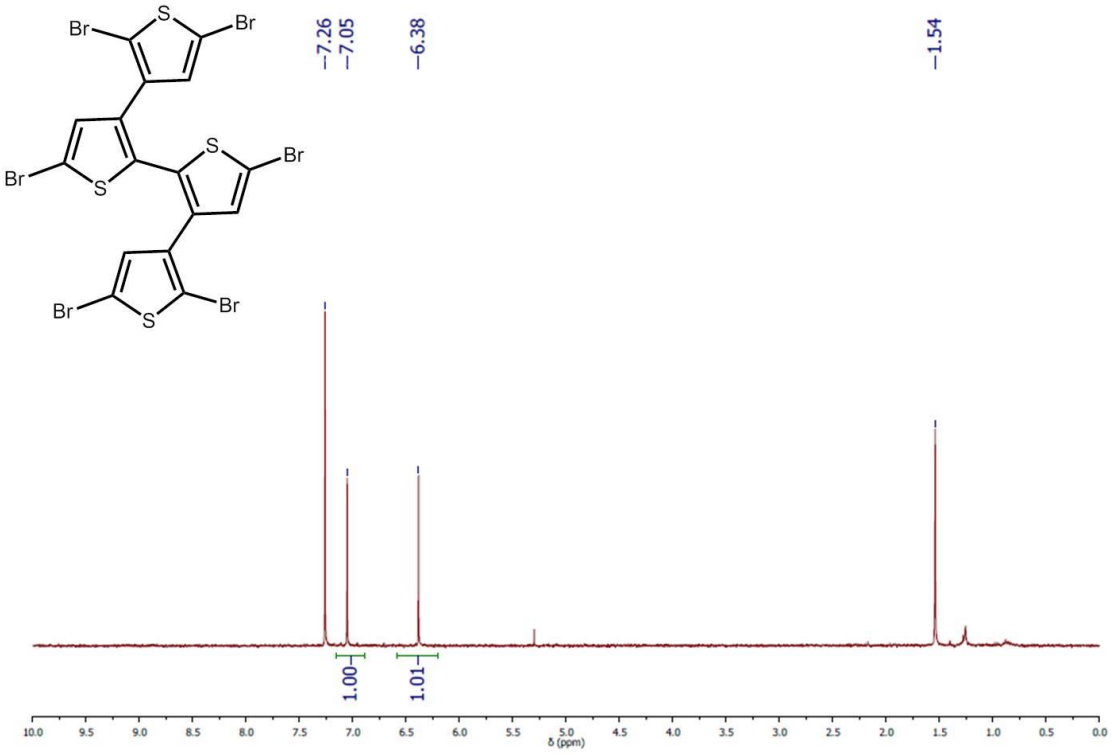



***Figure S5.*** $^{1}$H NMR spectrum of compound **3** in $CDCl_3$.

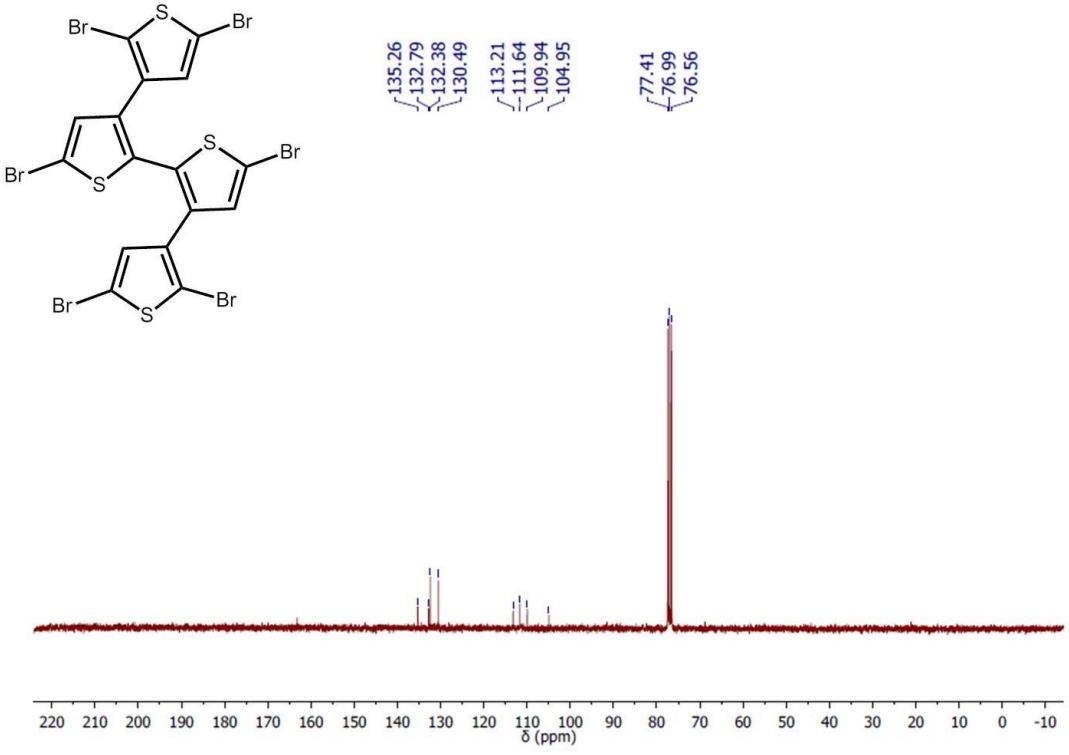



***Figure S6.*** $^{13}$C NMR spectrum of compound **3** in $CDCl_3$.

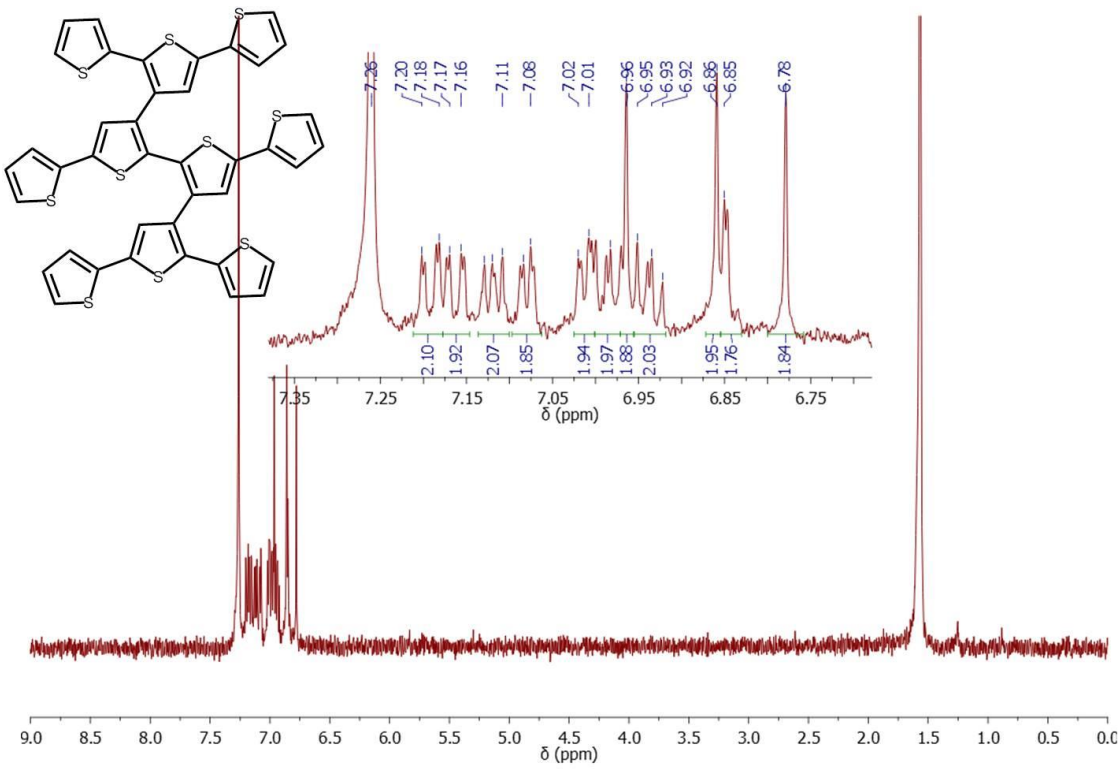



***Figure S7.*** $^{1}$H NMR spectrum of **SCT-1** in $CDCl_3$.

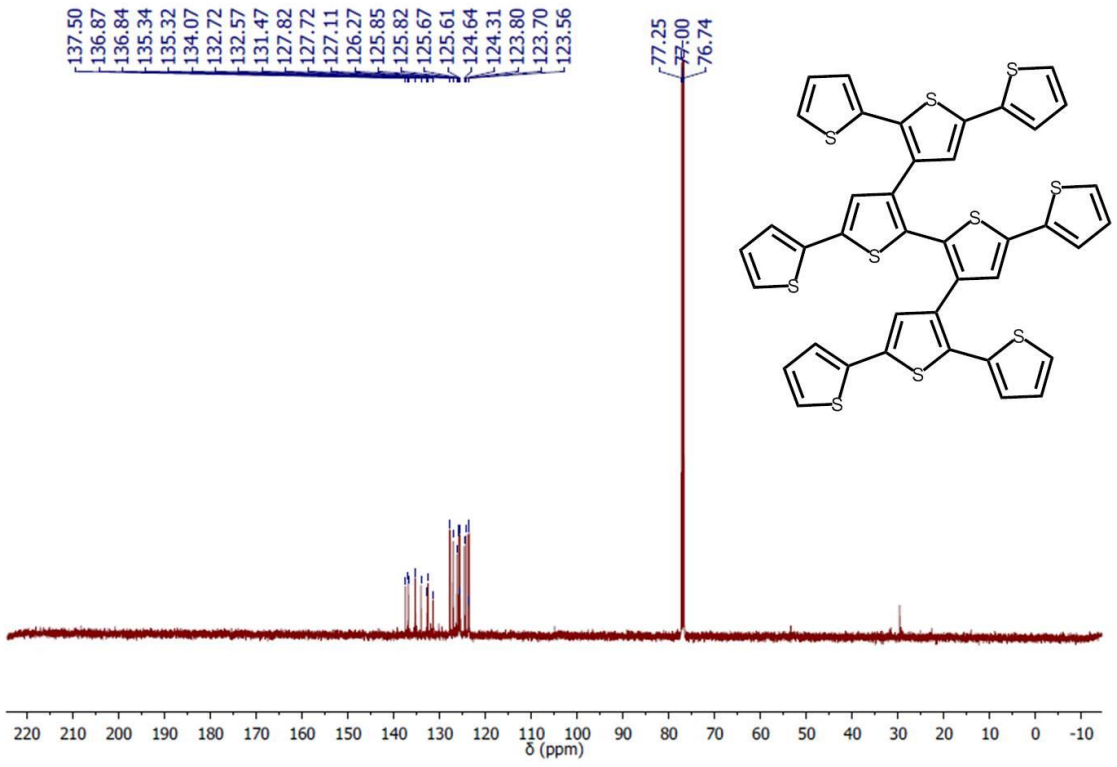



***Figure S8.*** $^{13}$C NMR spectrum of **SCT-1** in $CDCl_3$.

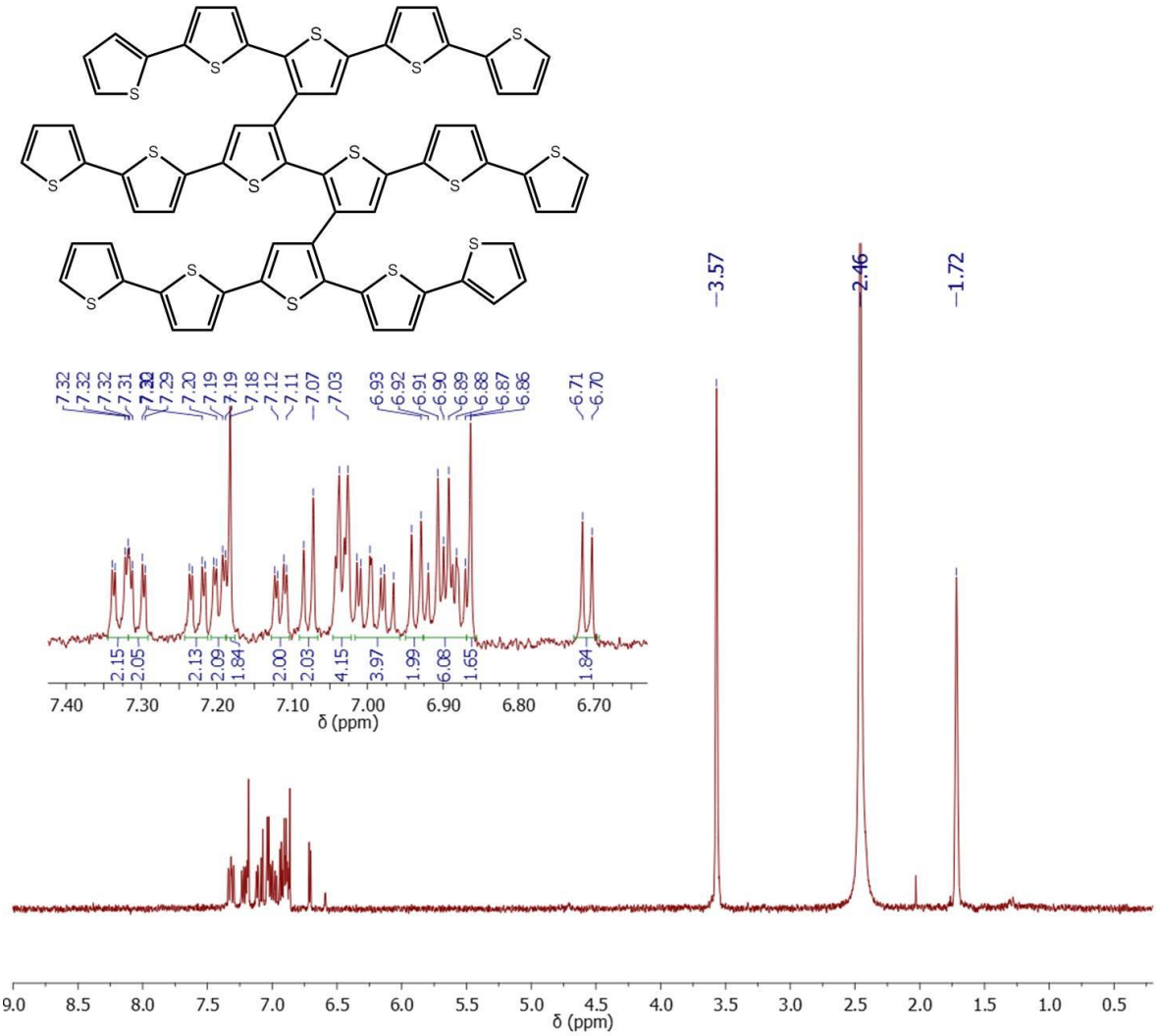



***Figure S9.*** $^{1}$H NMR spectrum of **SCT-2** in THF-d8.

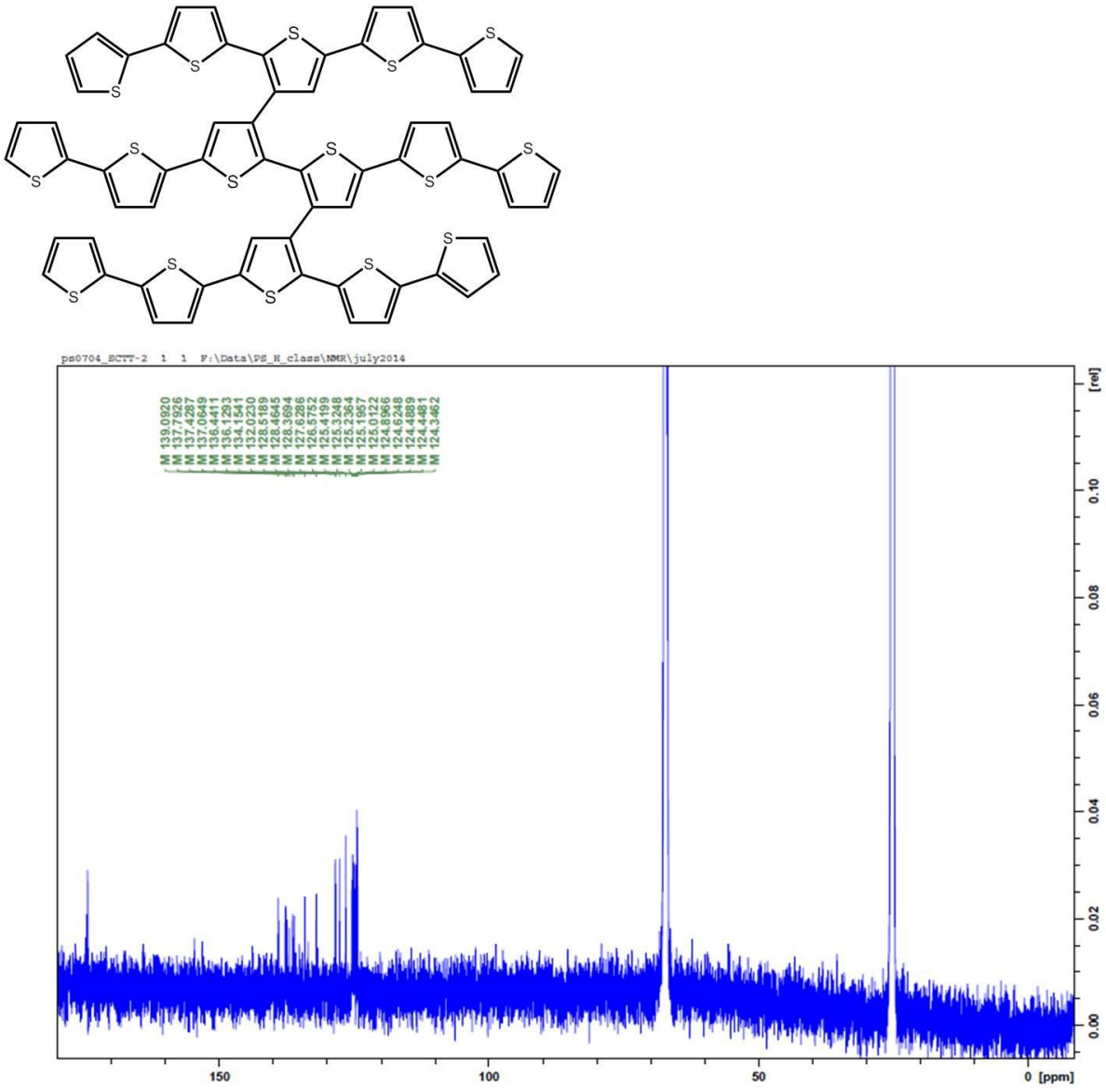



***Figure S10.*** $^{13}$C NMR spectrum of **SCT-2** in THF-d8.

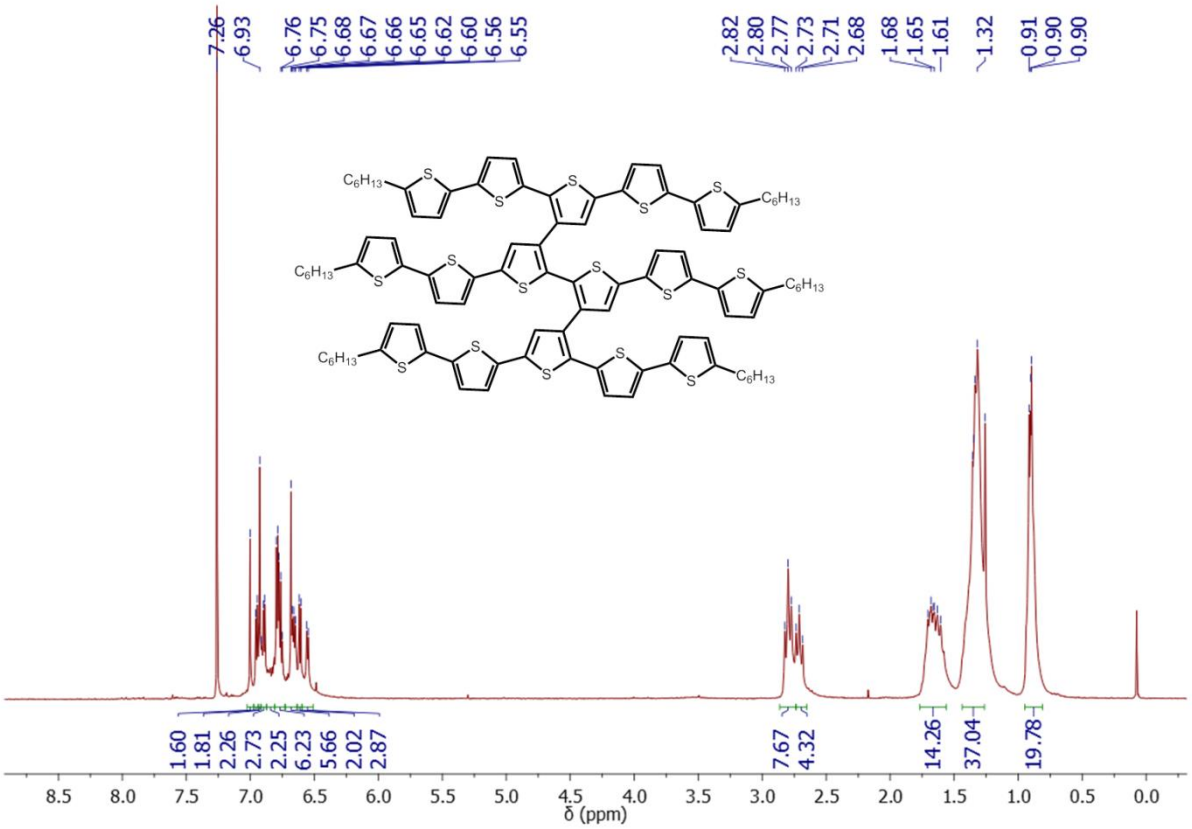



***Figure S11.*** $^{1}$H NMR spectrum of **SCT-3** in $CDCl_3$.

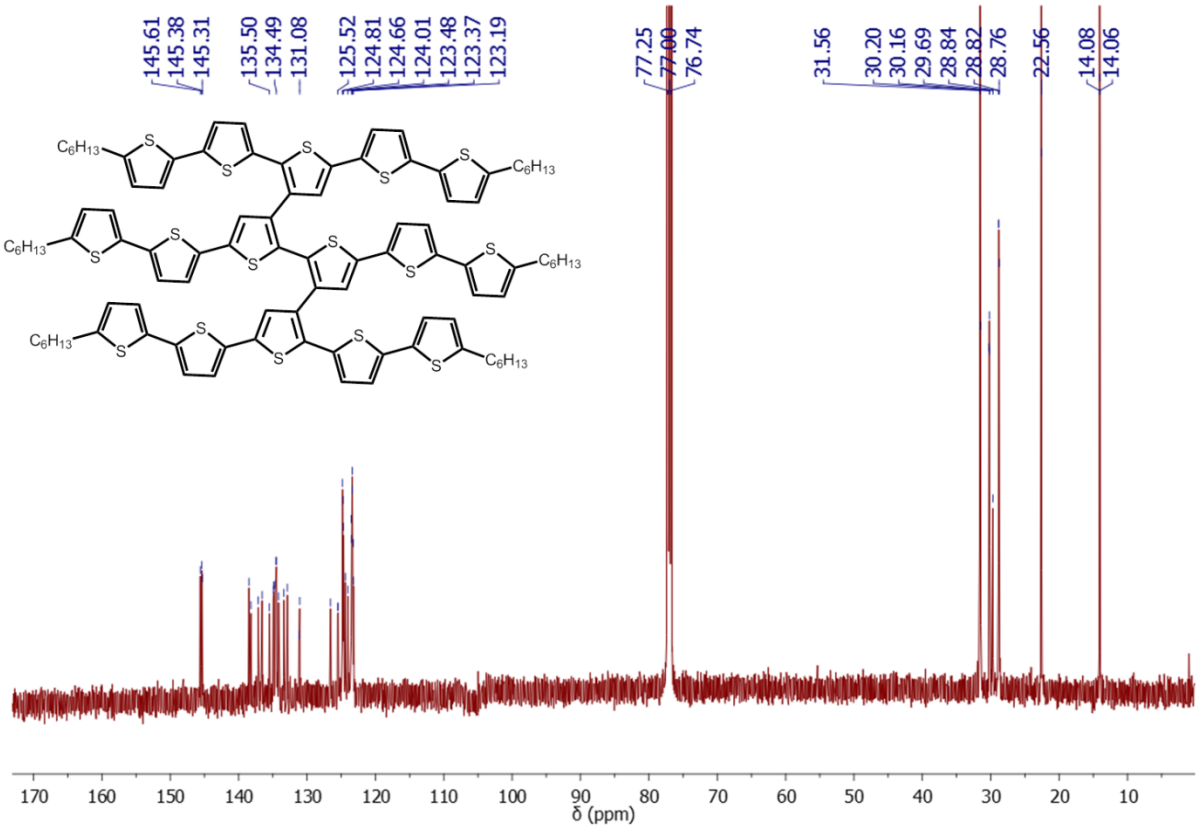



***Figure S12.*** $^{13}$C NMR spectrum of **SCT-3** in $CDCl_3$.

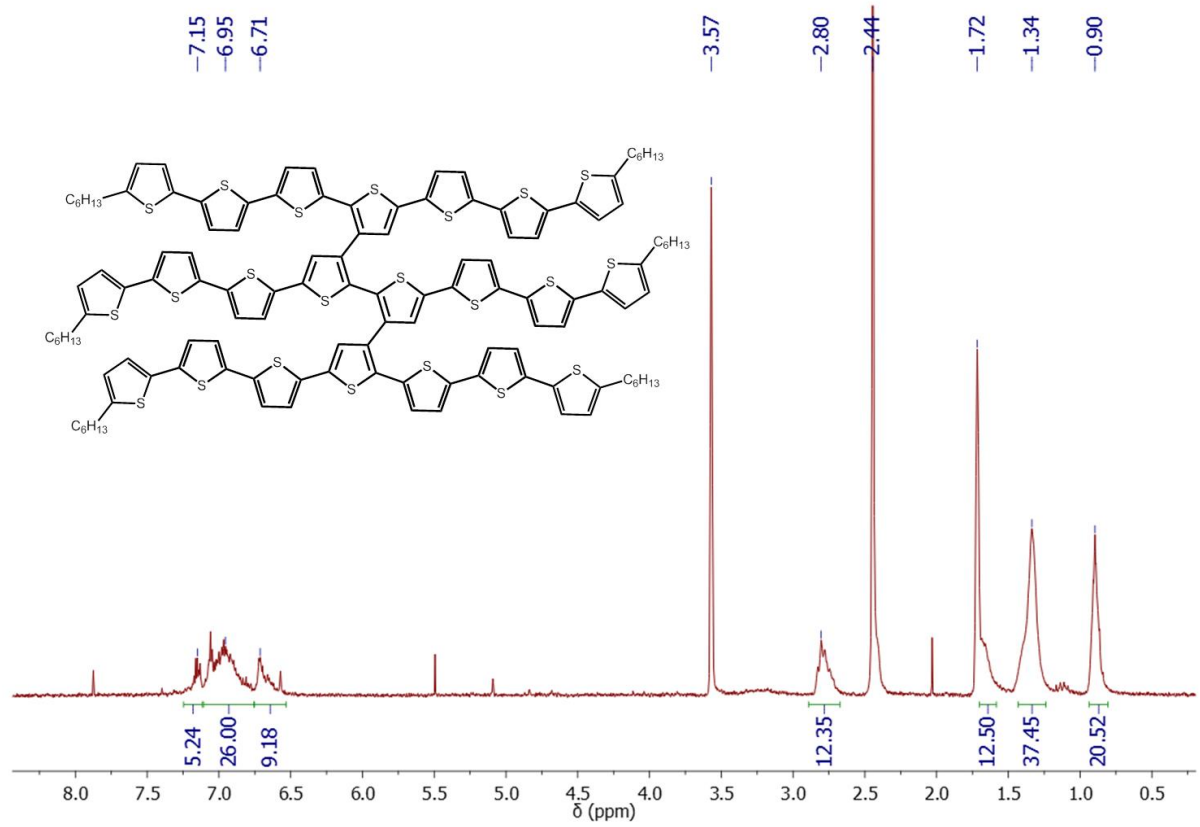
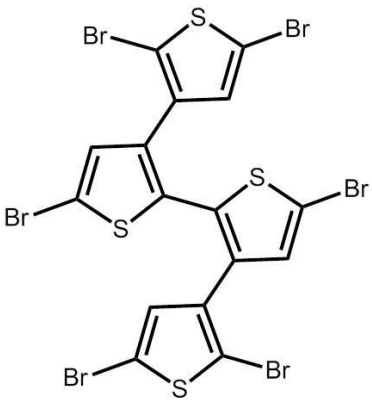
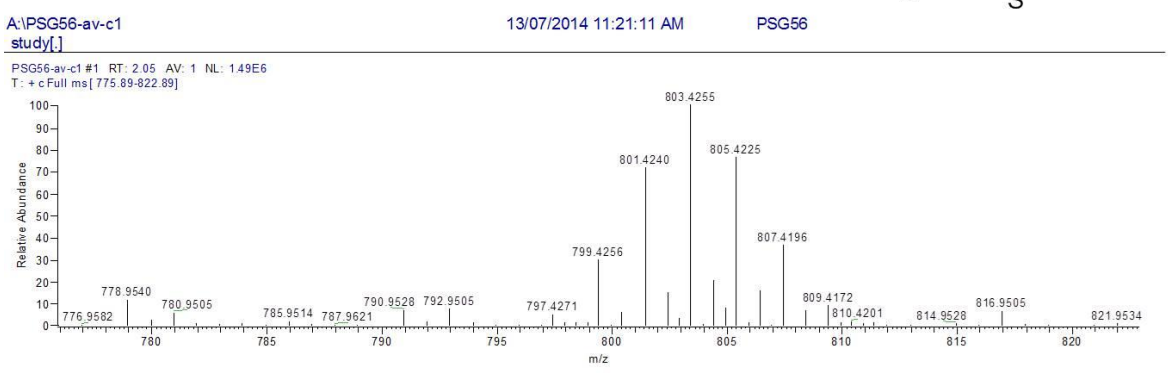



***Figure S13.*** $^{1}$H NMR spectrum of **SCT-4** in THF-d8.

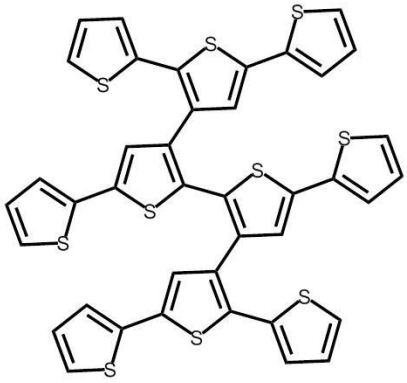


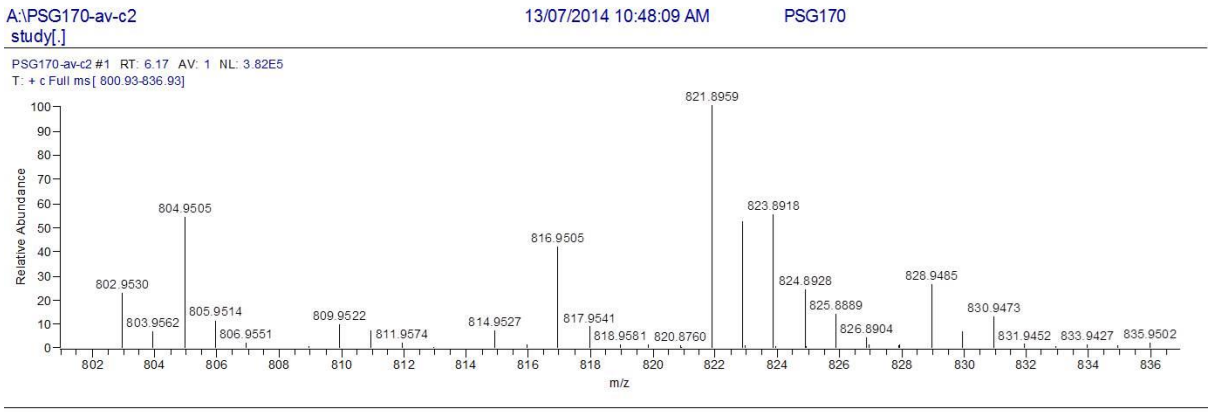




PSG56-av-c1#1 RT: 2.05
T: + c Full ms [ 775.89-822.89]
m/z= 797.07-809.63

| m/z | Intensity | Relative | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|---|---|---|---|---|---|---|
| 797.4271 | 69985.0 | 4.71 | 797.4296 | -3.11 | 12.0 | $C_{16}H_4{}^{79}Br_6{}^{32}S_4$ |
| 799.4256 | 444023.0 | 29.86 | 799.4276 | -2.45 | 12.0 | $C_{16}H_4{}^{79}Br_5{}^{81}Br_1{}^{32}S_4$ |
| 801.4240 | 1070471.0 | 71.98 | 801.4255 | -1.85 | 12.0 | $C_{16}H_4{}^{79}Br_4{}^{81}Br_2{}^{32}S_4$ |
| 802.4313 | 225287.0 | 15.15 | 802.4333 | -2.57 | 11.5 | $C_{16}H_5{}^{79}Br_4{}^{81}Br_2{}^{32}S_4$ |
| 803.4255 | 1487095.0 | 100.00 | 803.4235 | 2.56 | 12.0 | $C_{16}H_4{}^{79}Br_3{}^{81}Br_3{}^{32}S_4$ |
| 804.4264 | 302729.0 | 20.36 | 804.4313 | -6.07 | 11.5 | $C_{16}H_5{}^{79}Br_3{}^{81}Br_3{}^{32}S_4$ |
| 805.4225 | 1135433.0 | 76.35 | 805.4214 | 1.38 | 12.0 | $C_{16}H_4{}^{79}Br_2{}^{81}Br_4{}^{32}S_4$ |
| 807.4196 | 543993.0 | 36.58 | 807.4194 | 0.26 | 12.0 | $C_{16}H_4{}^{79}Br_1{}^{81}Br_5{}^{32}S_4$ |

***Figure S14.*** High resolution EI-MS spectrum of compound **3**.



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m/z= 821.55-822.87

| m/z | Intensity | Relative | Theo. Mass | Delta (ppm) | RDB equiv. | Composition |
|---|---|---|---|---|---|---|
| 821.8959 | 381718.0 | 100.00 | 821.8929 | 3.69 | 30.0 | $C_{40}H_{22}{}^{32}S_{10}$ |

***Figure S15.*** High resolution EI-MS spectrum of **SCT-1**.

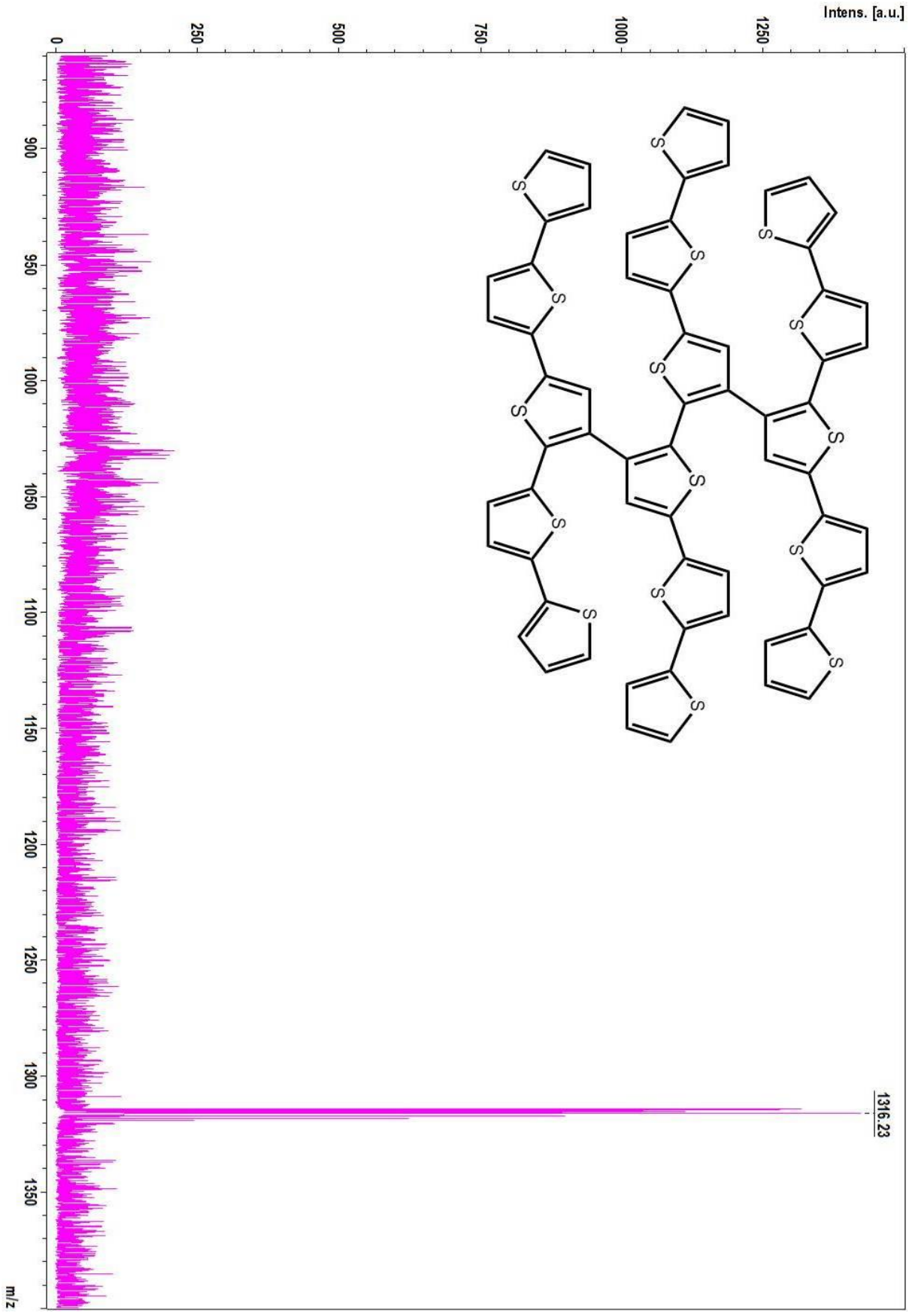



***Figure S16.*** MALDI-TOF spectrum of **SCT-2**.

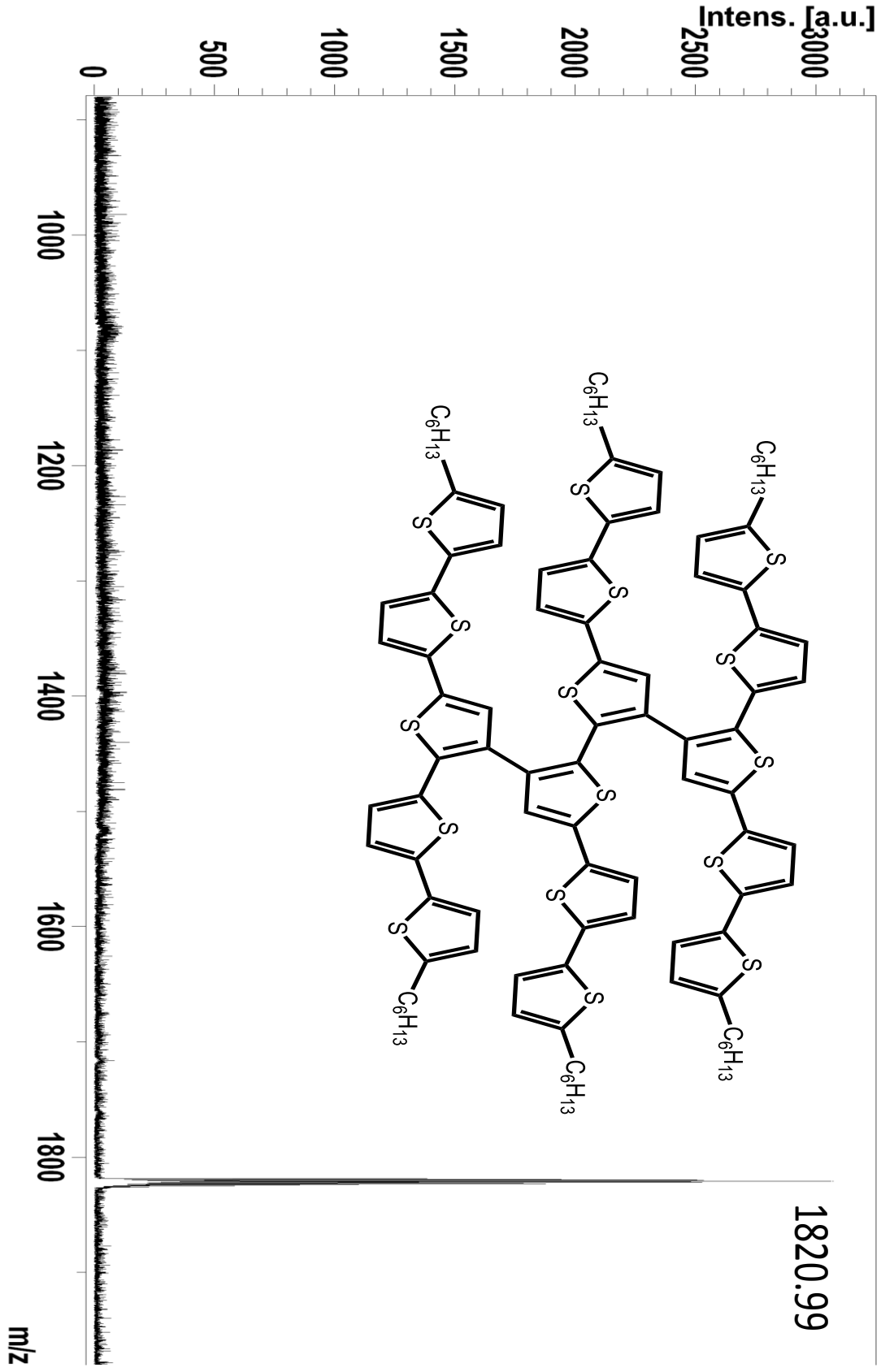



***Figure S17.*** MALDI-TOF spectrum of **SCT-3**.

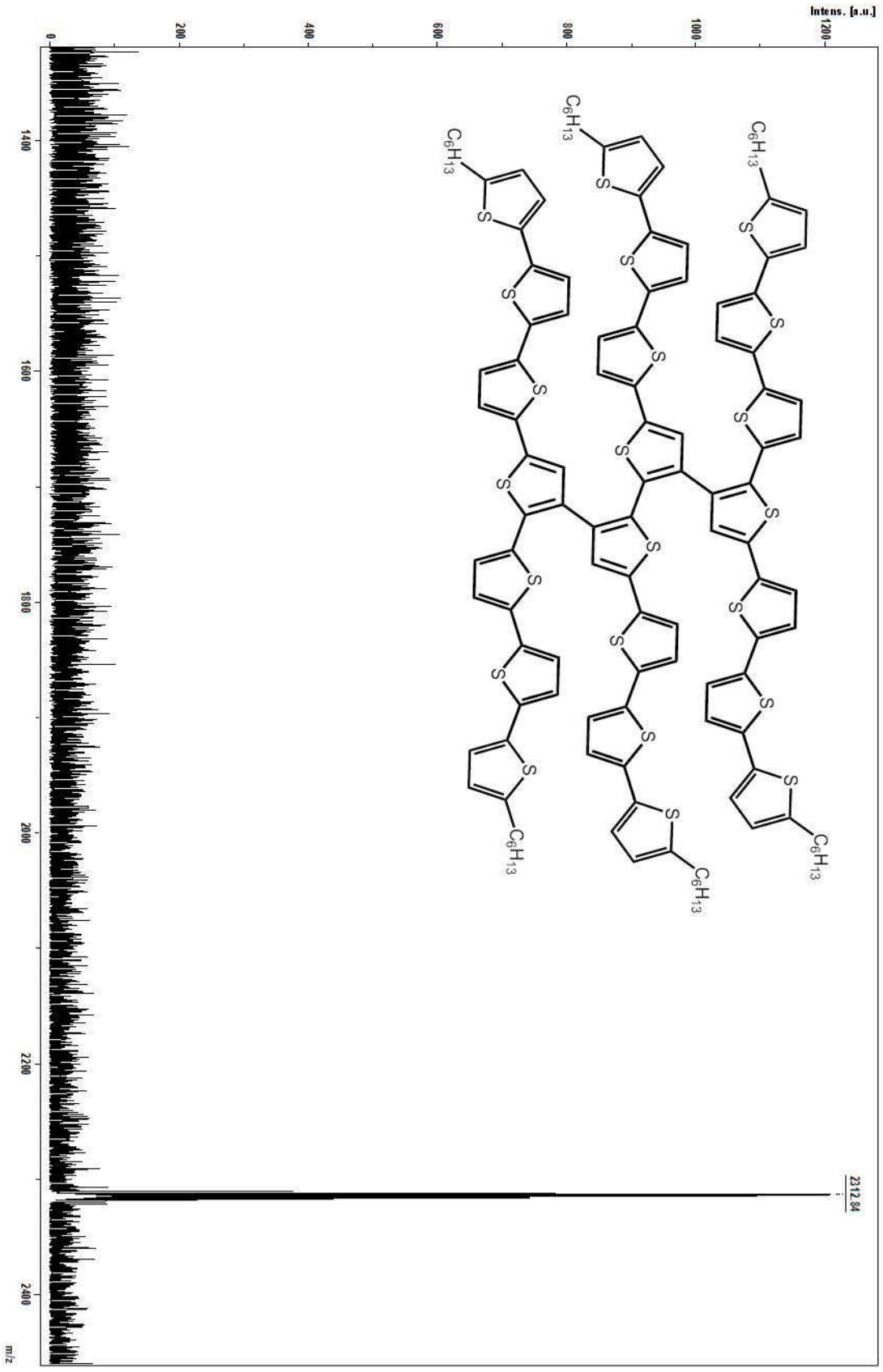
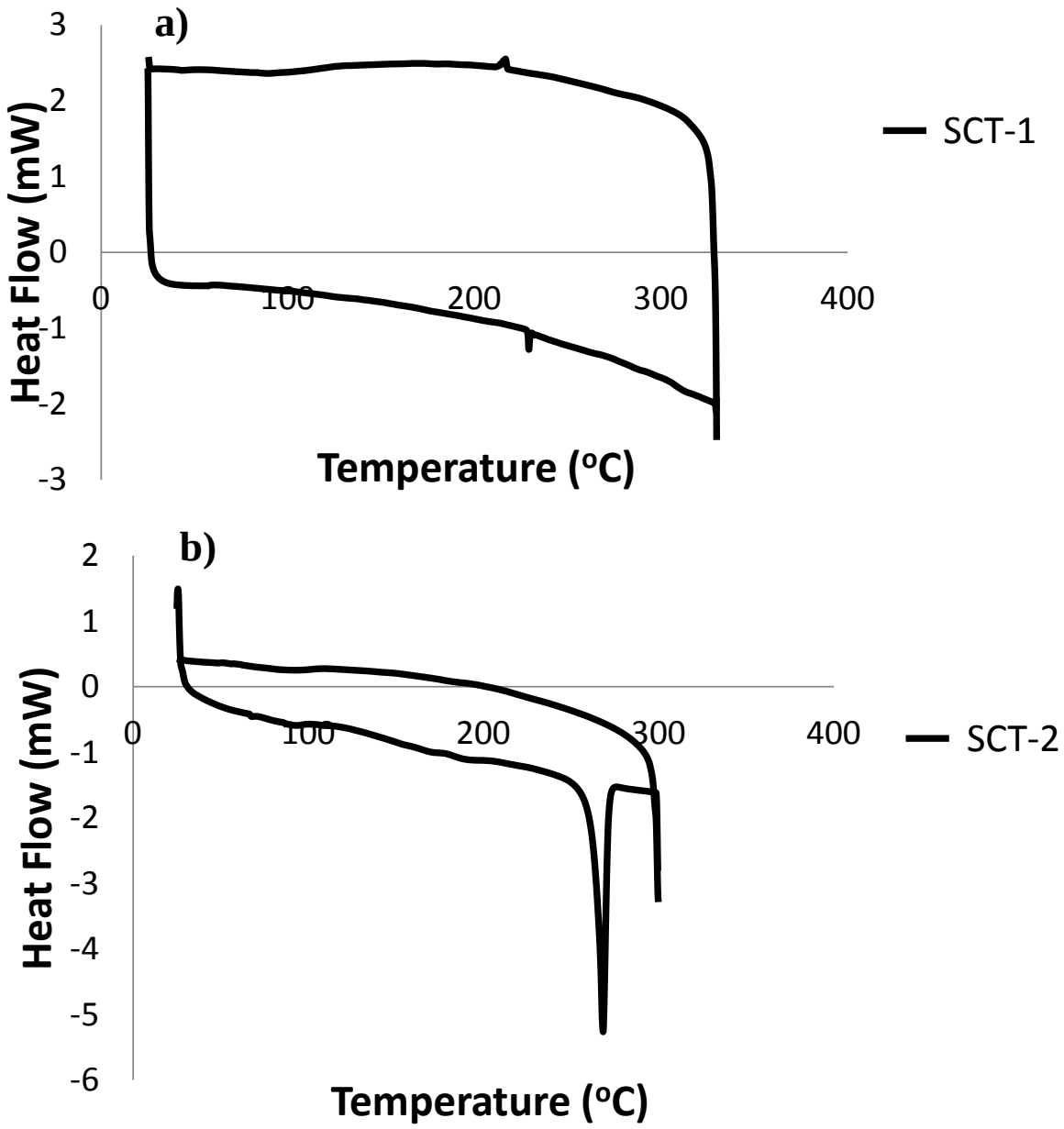



***Figure S18.*** MALDI-TOF spectrum of **SCT-4**.

## 2.DSC results


a)
3
2
1
0
-1
-2
-3
0
100
200
300
400
Heat Flow (mW)
Temperature (°C)
SCT-1
b)
2
1
0
-1
-2
-3
-4
-5
-6
0
100
200
300
400
Heat Flow (mW)
Temperature (°C)
SCT-2

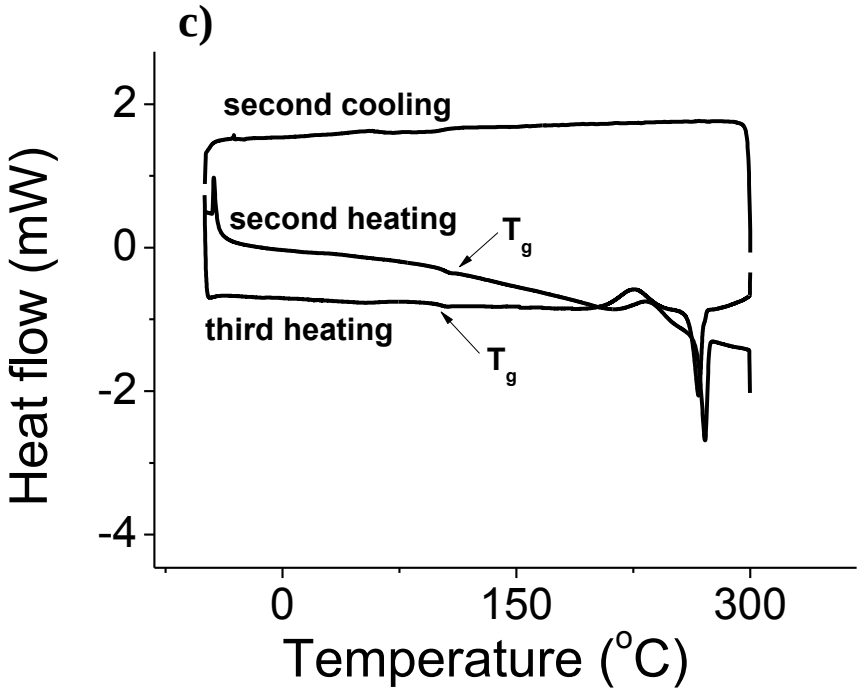



***Figure S19.*** DSC curves of (**a**) **SCT-1** recorded at heating rate of 5 °C $min^{-1}$; (**b**) **SCT-2** (first heating, 10 °C $min^{-1}$) and (**c**) **SCT-2** (second heating and third heating, 5 °C $min^{-1}$)

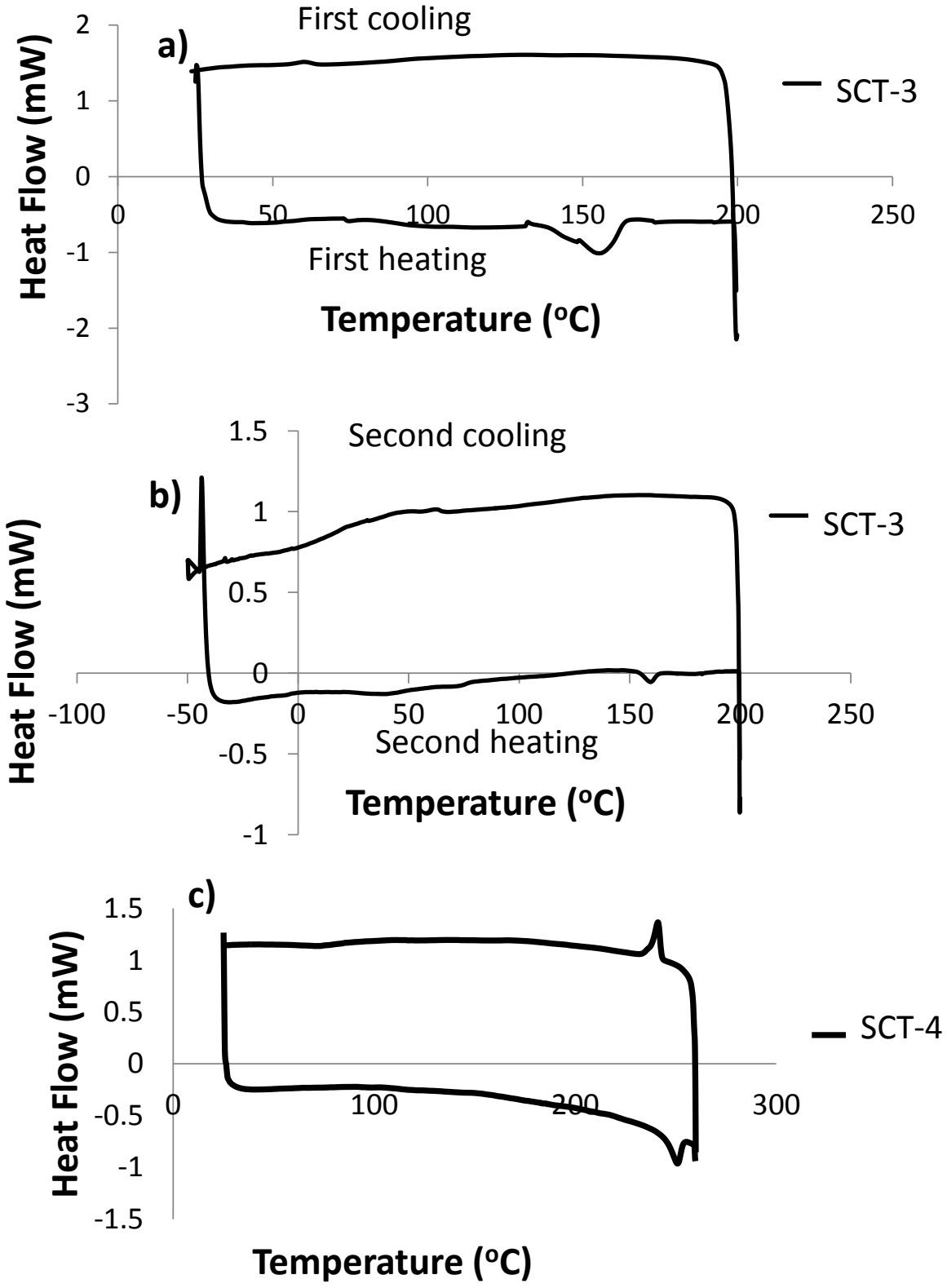



***Figure S20.*** DSC curves of **SCT-3** for (a) first heating and (b) second heating; (c) **SCT-4** recorded at heating rate of 5 °C $min^{-1}$ under nitrogen atmosphere.

**3. Optimized structures and frontier orbital plots of SCTs from DFT calculation at B3LYP/6-31G(d) level using Gaussian09.[1]**

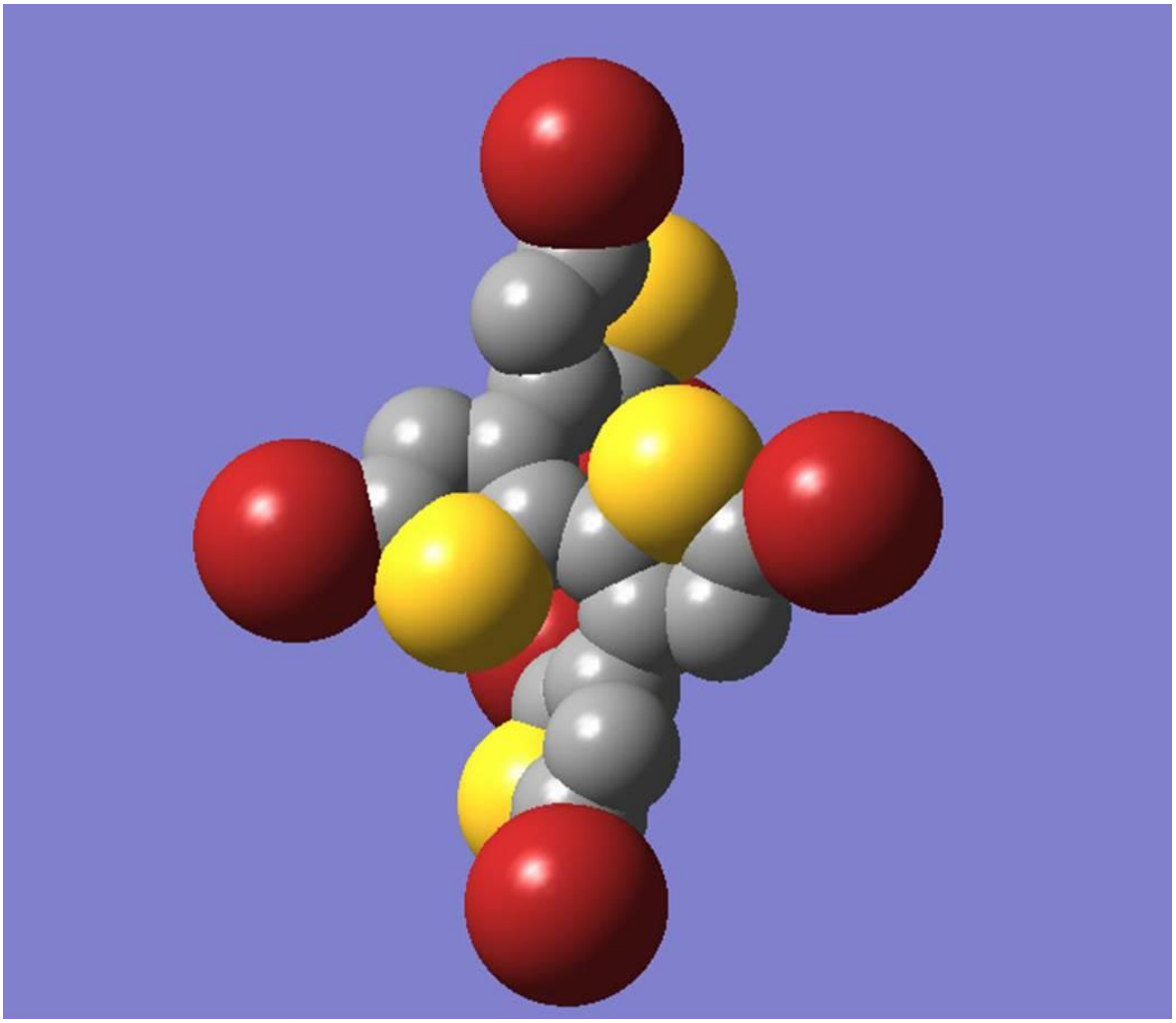


***Figure S21.*** Optimized structure of **3** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

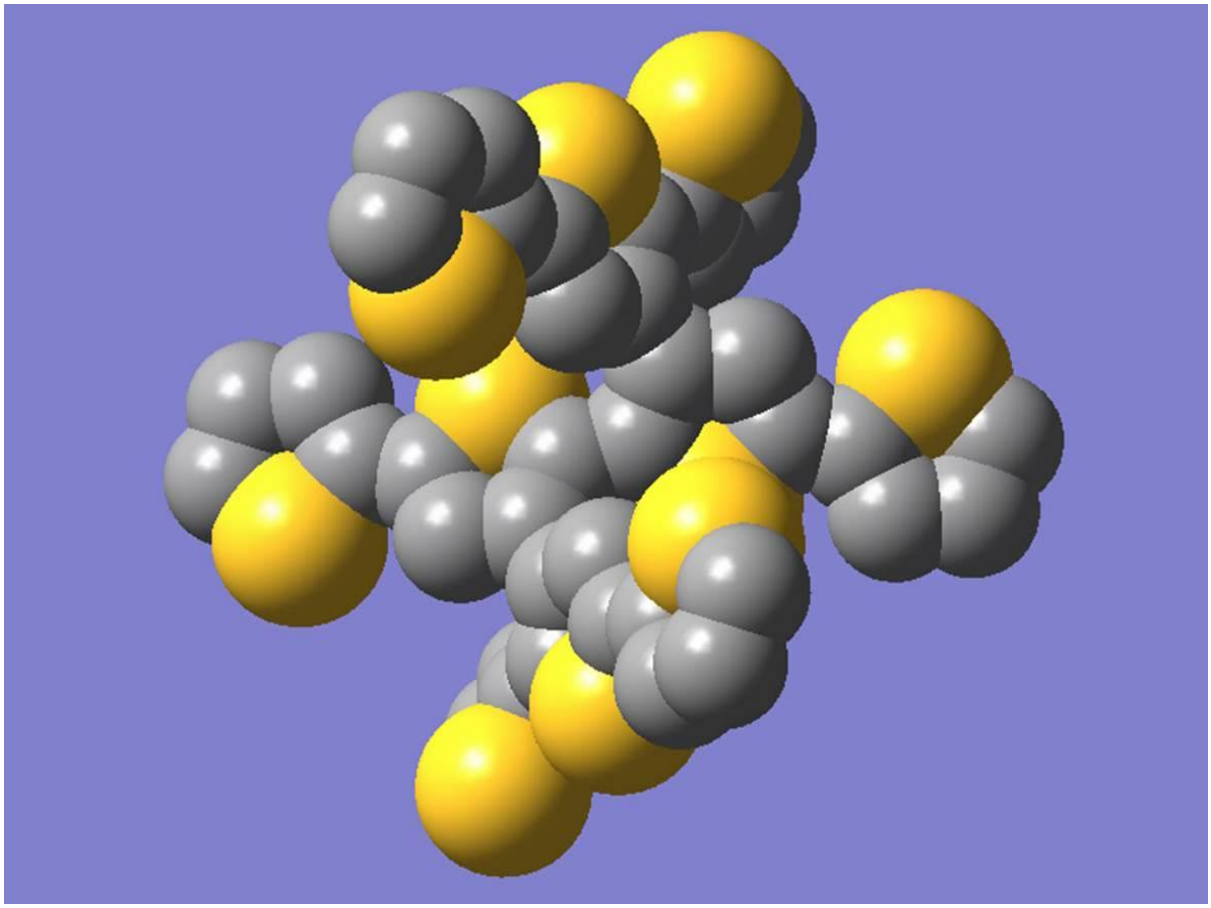


***Figure S22.*** Optimized structure of **SCT-1** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

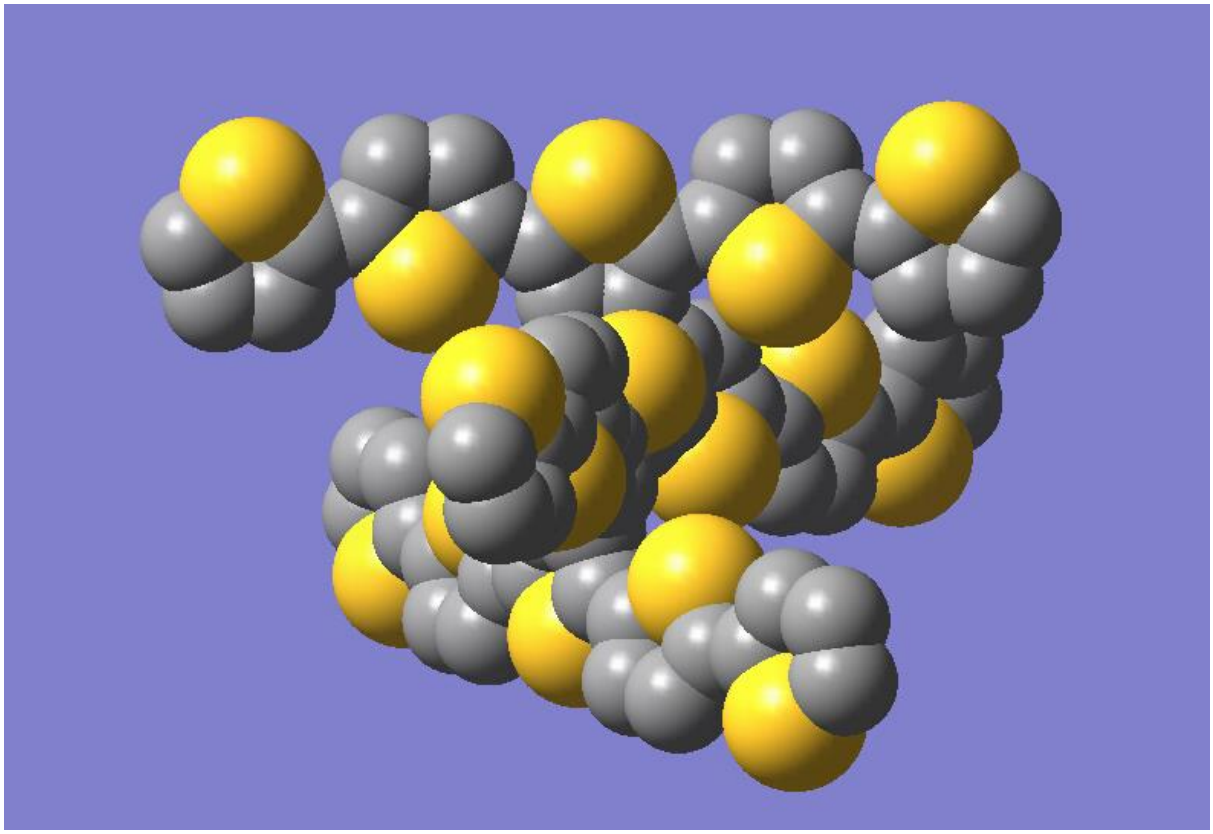


***Figure S23.*** Optimized structure of **SCT-2** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

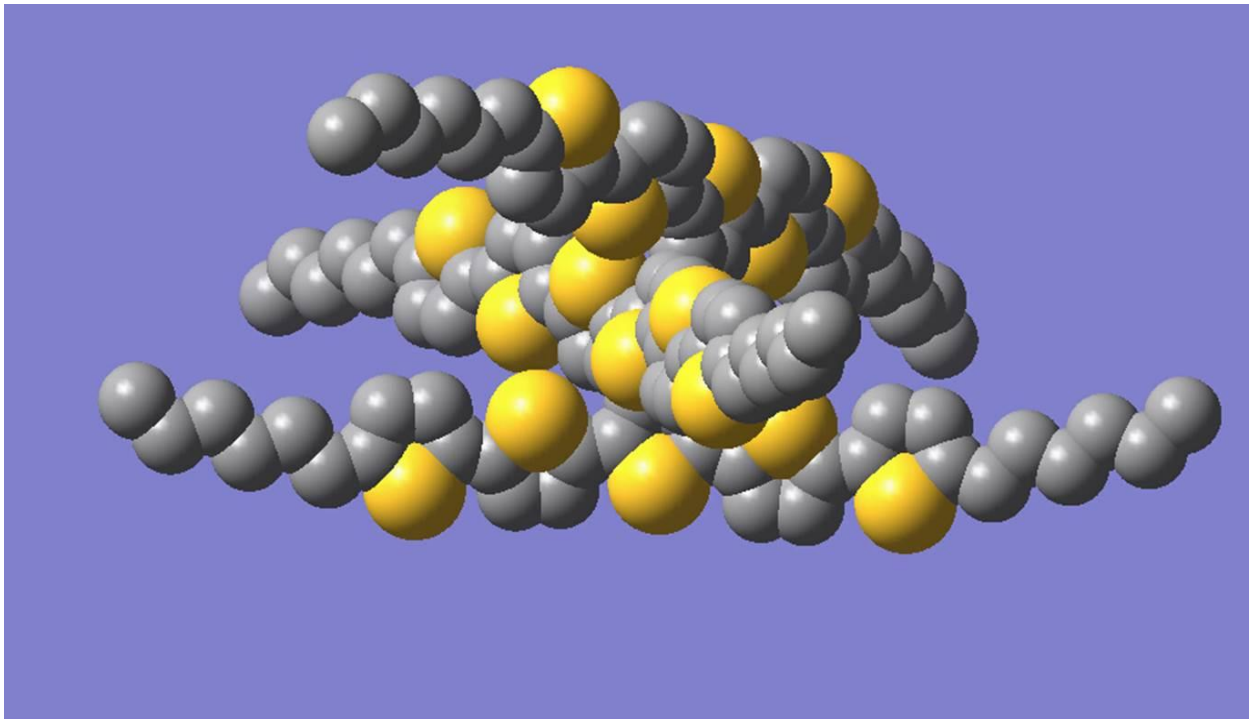


***Figure S24.*** Optimized structure of **SCT-3** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

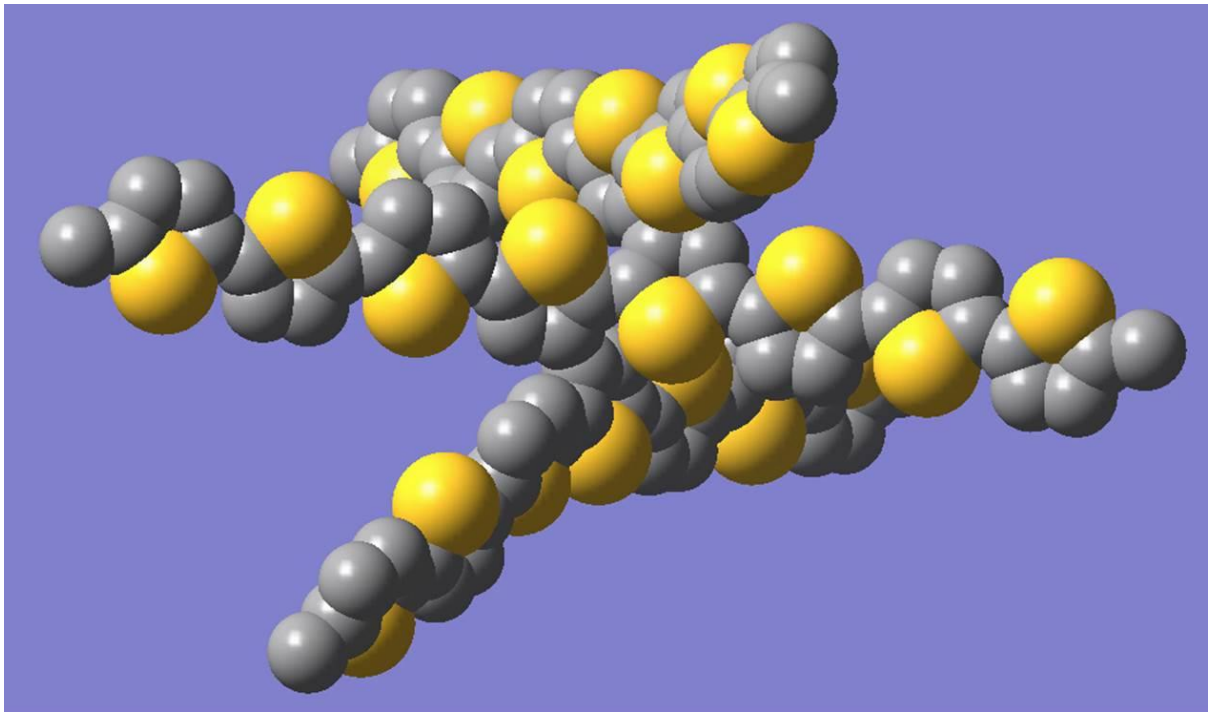


***Figure S25.*** Optimized structure of **SCT-4** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

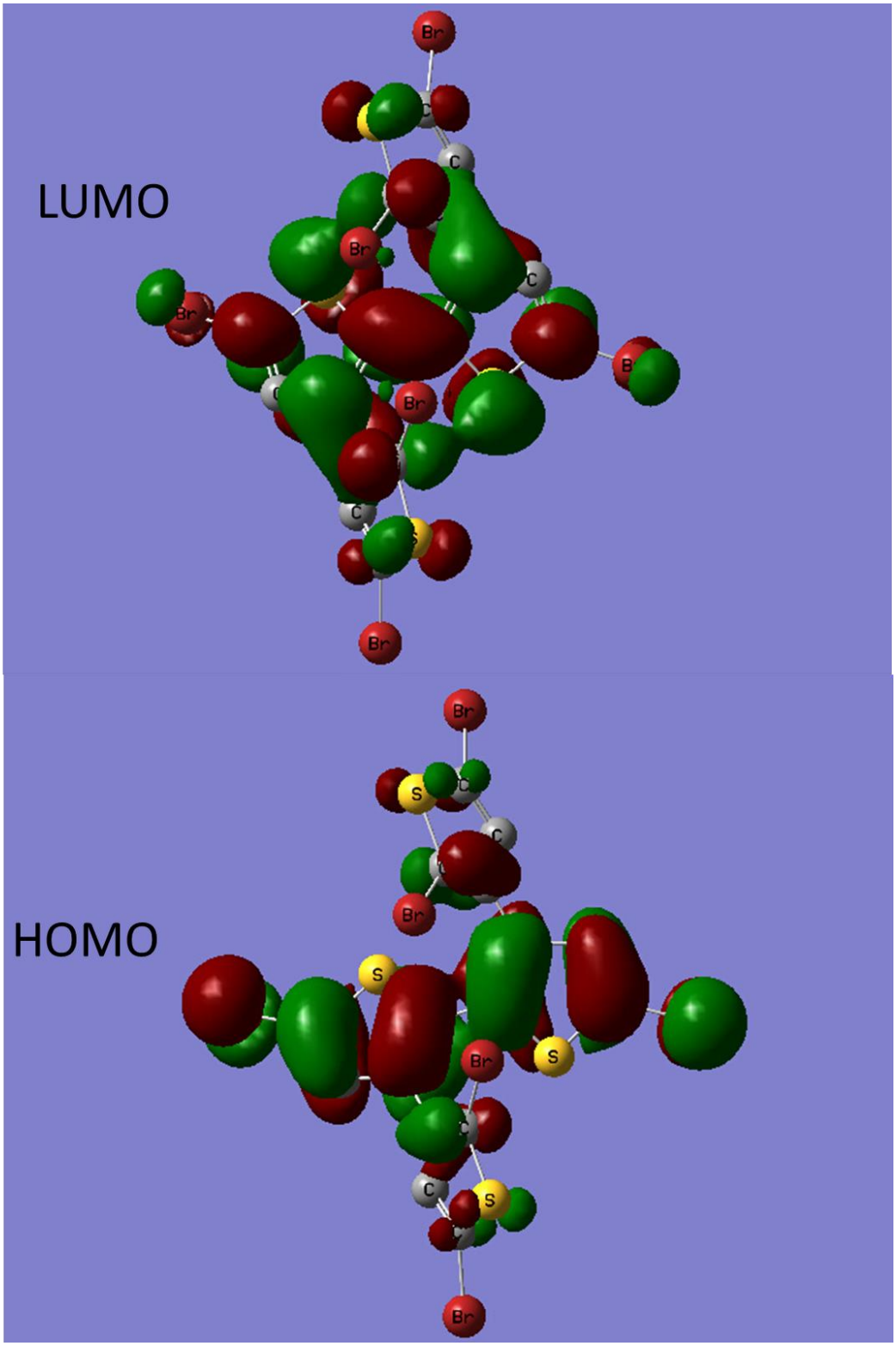



***Figure S26.*** Frontier orbitals of compound **3** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

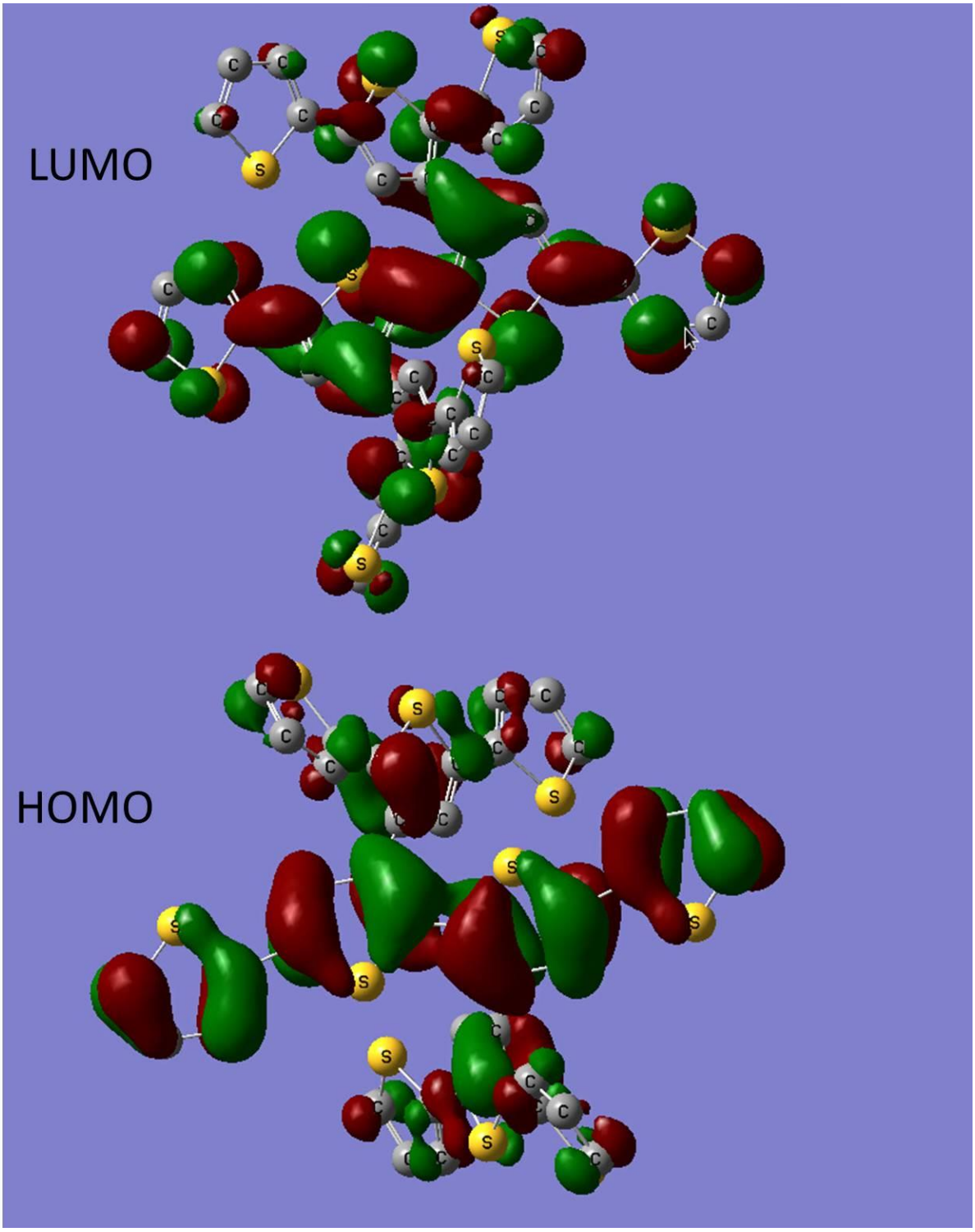



***Figure S27.*** Frontier orbitals of **SCT-1** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

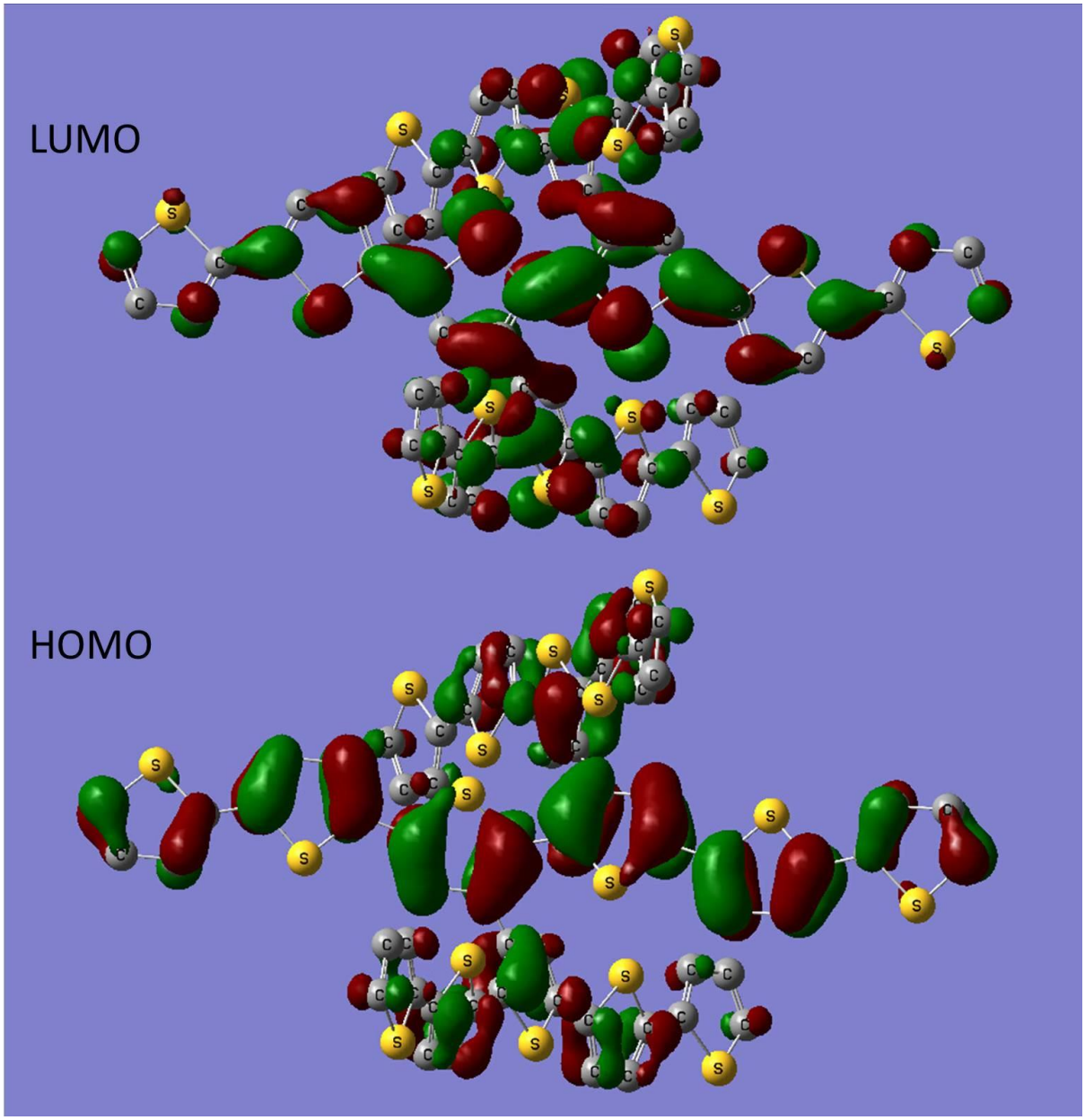



***Figure S28.*** Frontier orbitals of **SCT-2** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

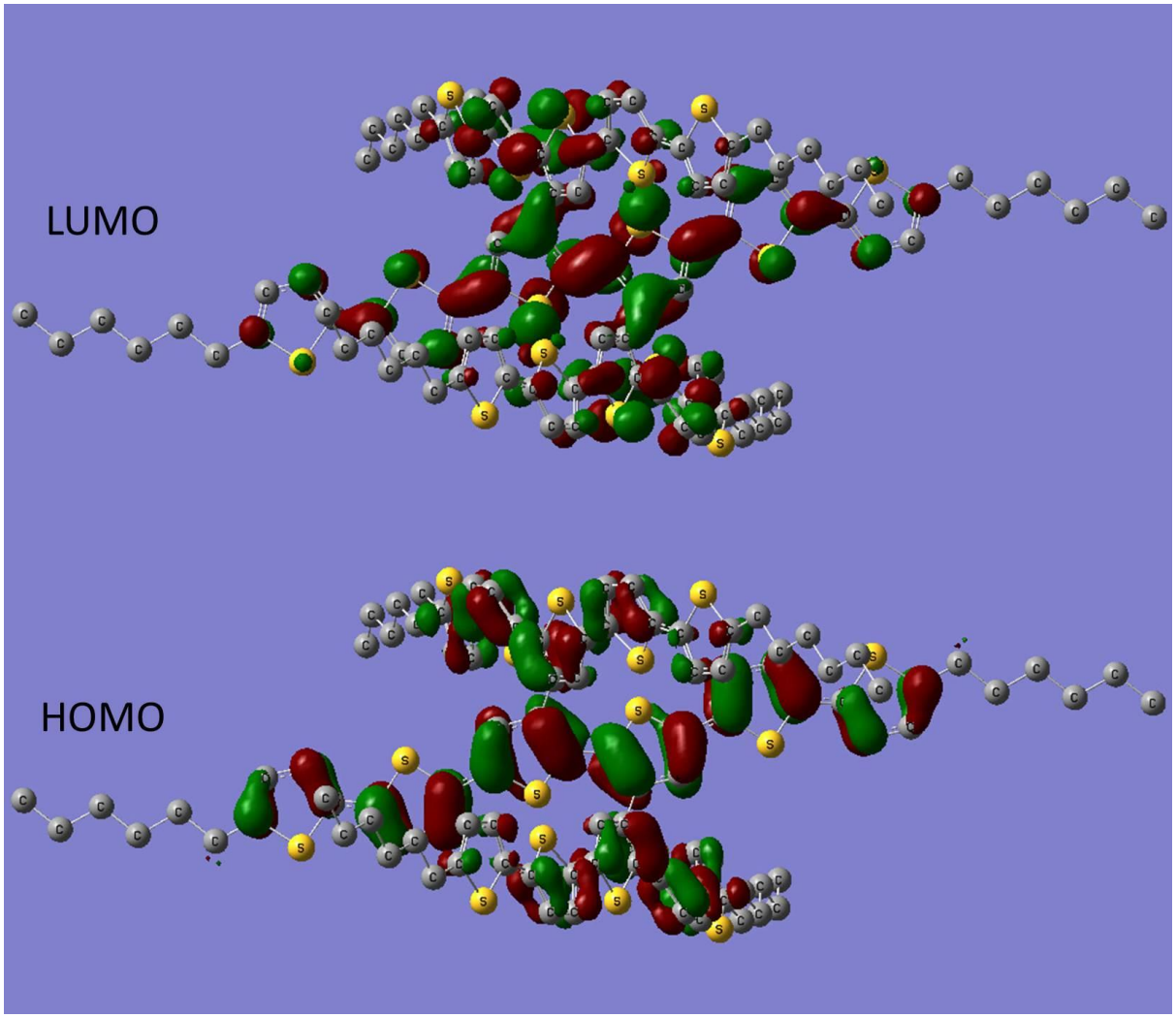



***Figure S29.*** Frontier orbitals of **SCT-3** obtained from DFT calculation at B3LYP/6-31G (d) level with omitted hydrogen atoms for better clarity.

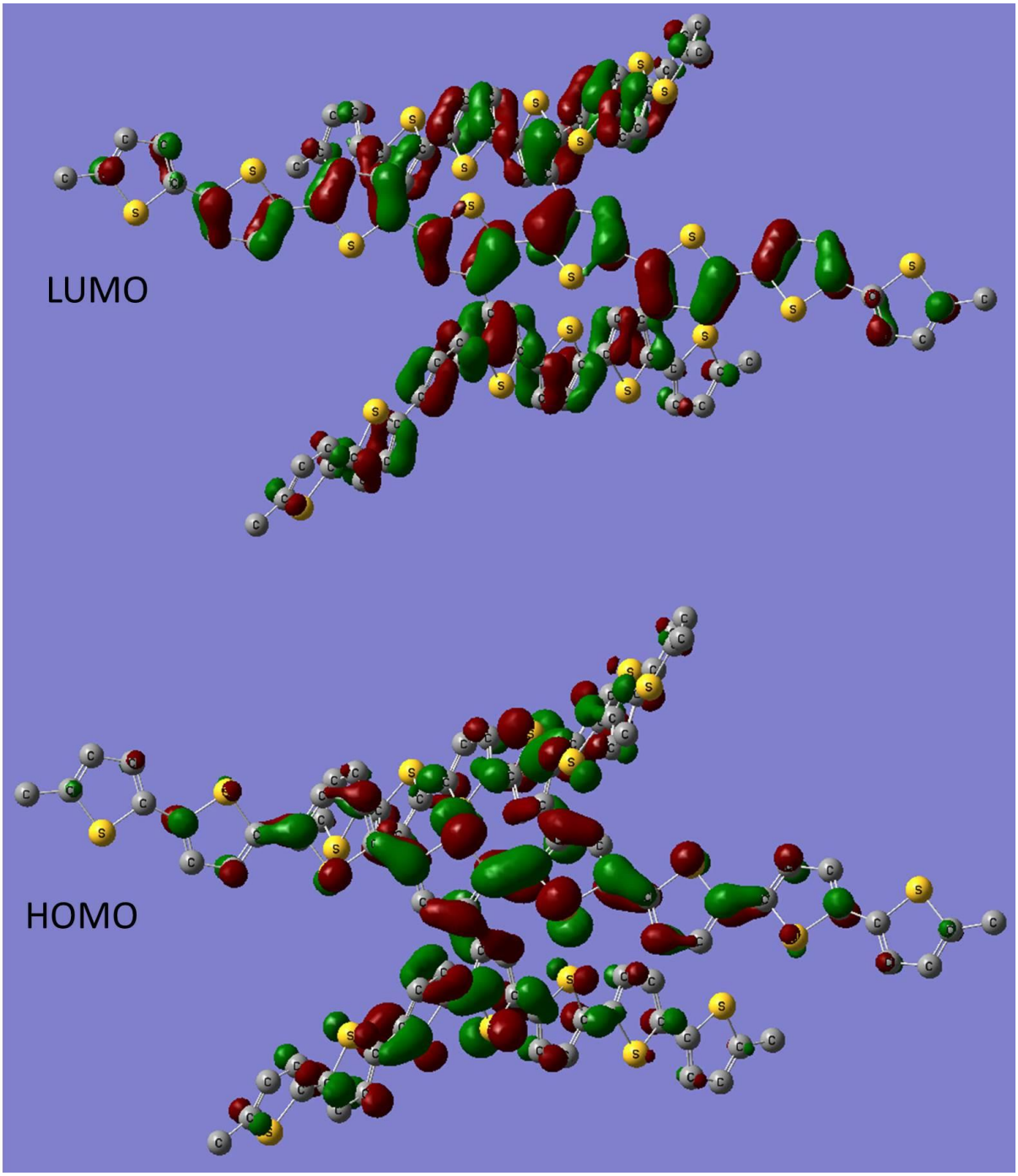



***Figure S30.*** Frontier orbitals of **SCT-4** obtained from DFT calculation at B3LYP/6-31G(d) level with omitted hydrogen atoms for better clarity.

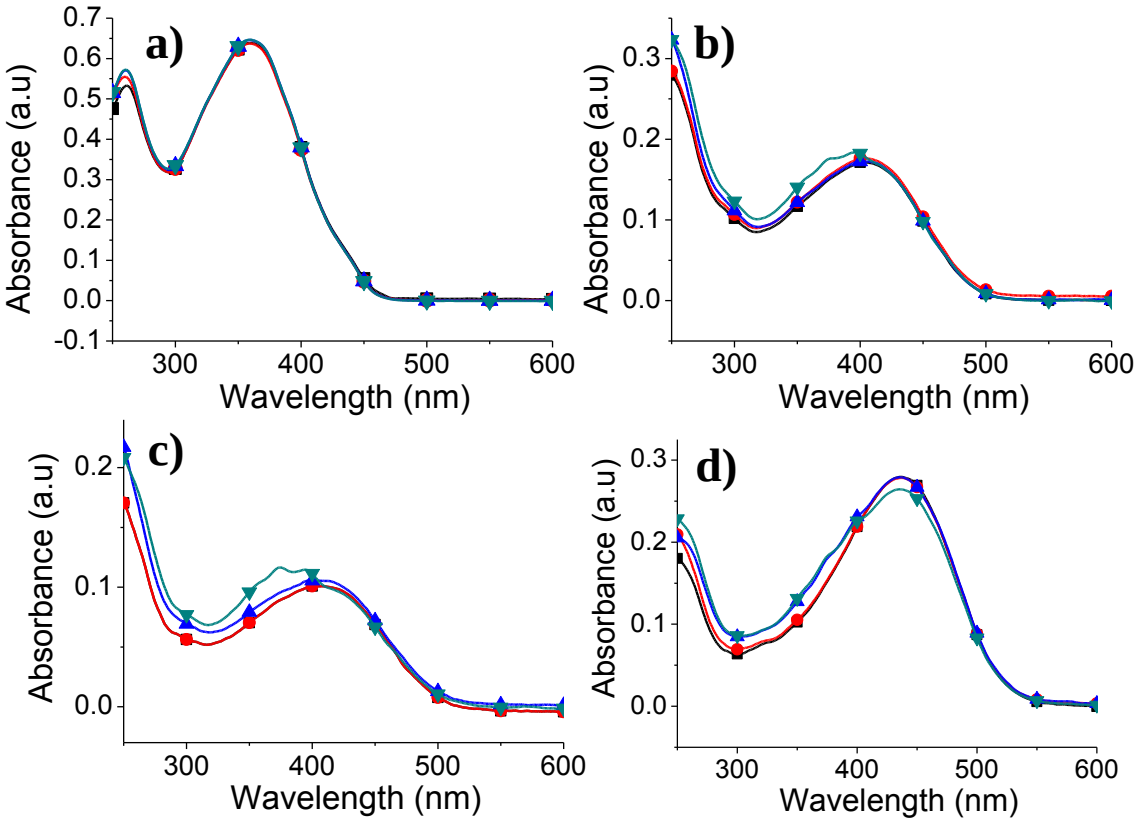



***Figure S31.*** Absorption spectra of **SCT-1** (a), **SCT-2** (b), **SCT-3** (c), and **SCT-4** (d) before light irradiation (-■-), 6 hours (-●-), 12 hours (-▲-), and 24 hours (-▼-) after light irradiation in dilute THF.

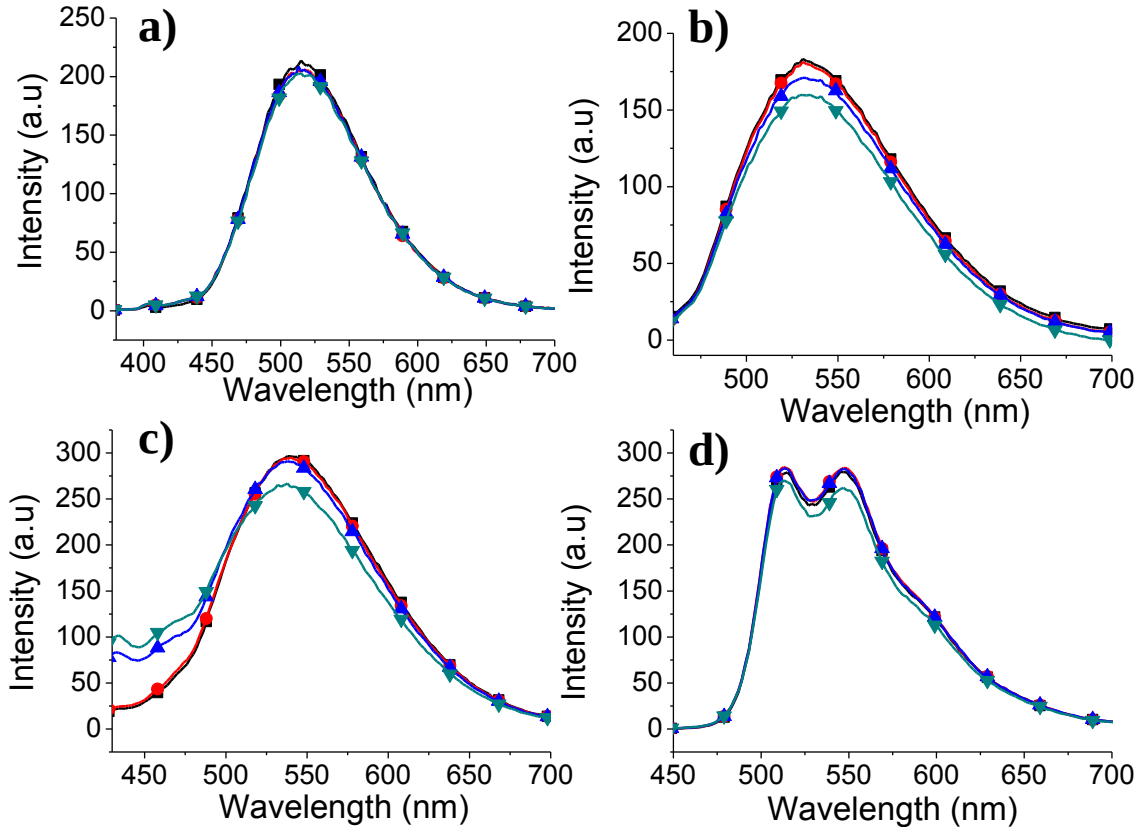



***Figure S32.*** Emission spectra of **SCT-1** (a), **SCT-2** (b), **SCT-3** (c), and **SCT-4** (d) before light irradiation (-■-), 6 hours (-●-), 12 hours (-▲-), and 24 hours (-▼-) after light irradiation in dilute THF.

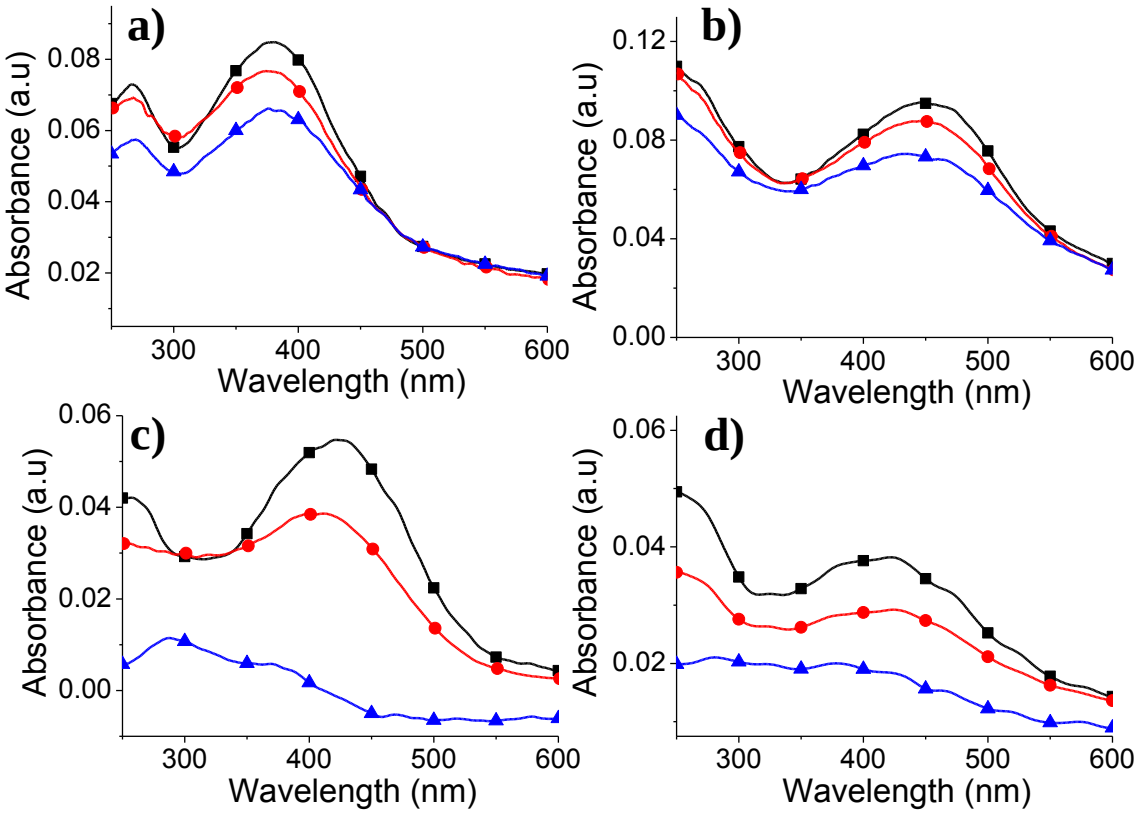



***Figure S33.*** Absorption spectra of **SCT-1** (a), **SCT-2** (b), **SCT-3** (c), and **SCT-4** (d) thin films before light irradiation (-■-), 12 hours (-●-), and 24 hours (-▲-) after light irradiation. The **SCTs** thin films were prepared by spin casting the **SCTs** solution in THF at room temperature.

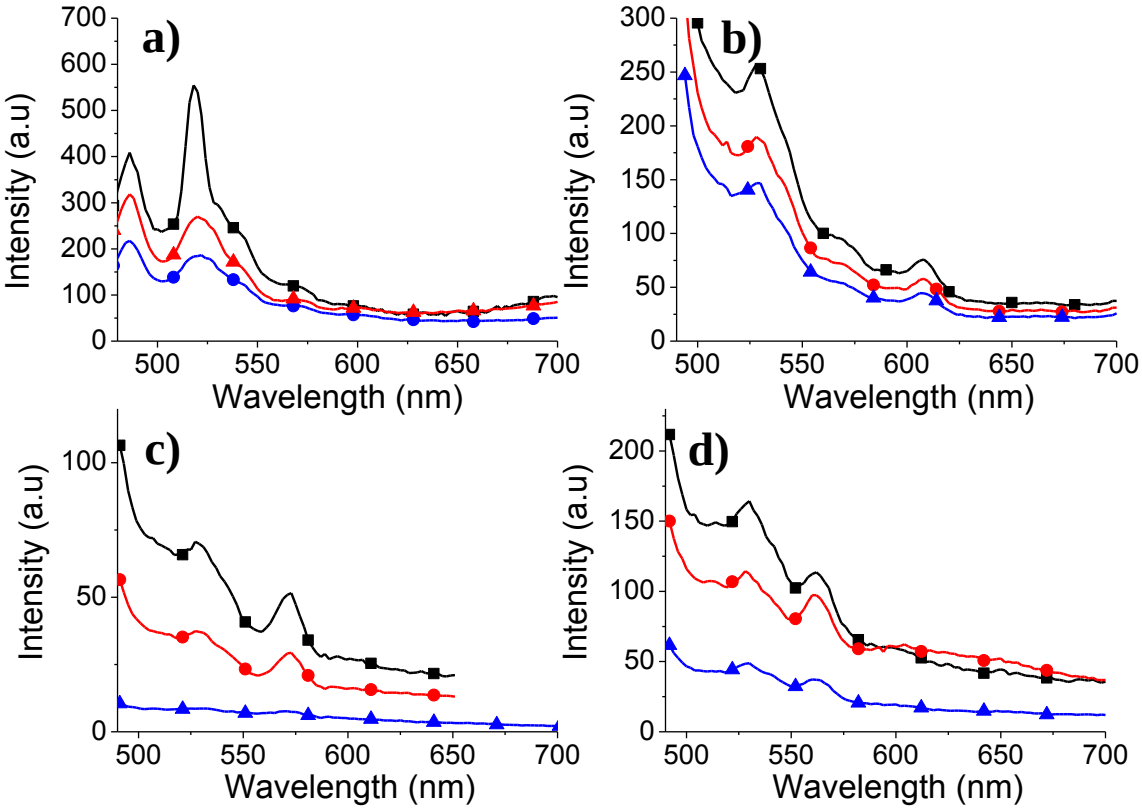



***Figure S34.*** Emission spectra of **SCT-1** (a), **SCT-2** (b), **SCT-3** (c), and **SCT-4** (d) thin films before light irradiation (-■-), 12 hours (-●-), and 24 hours (-▲-) after light irradiation. The **SCTs** thin films were prepared by spin casting the **SCTs** solution in THF at room temperature.

**4. Absorption and emission spectra of SCTs in presence of Pb(II) and Cd(II) ions.**

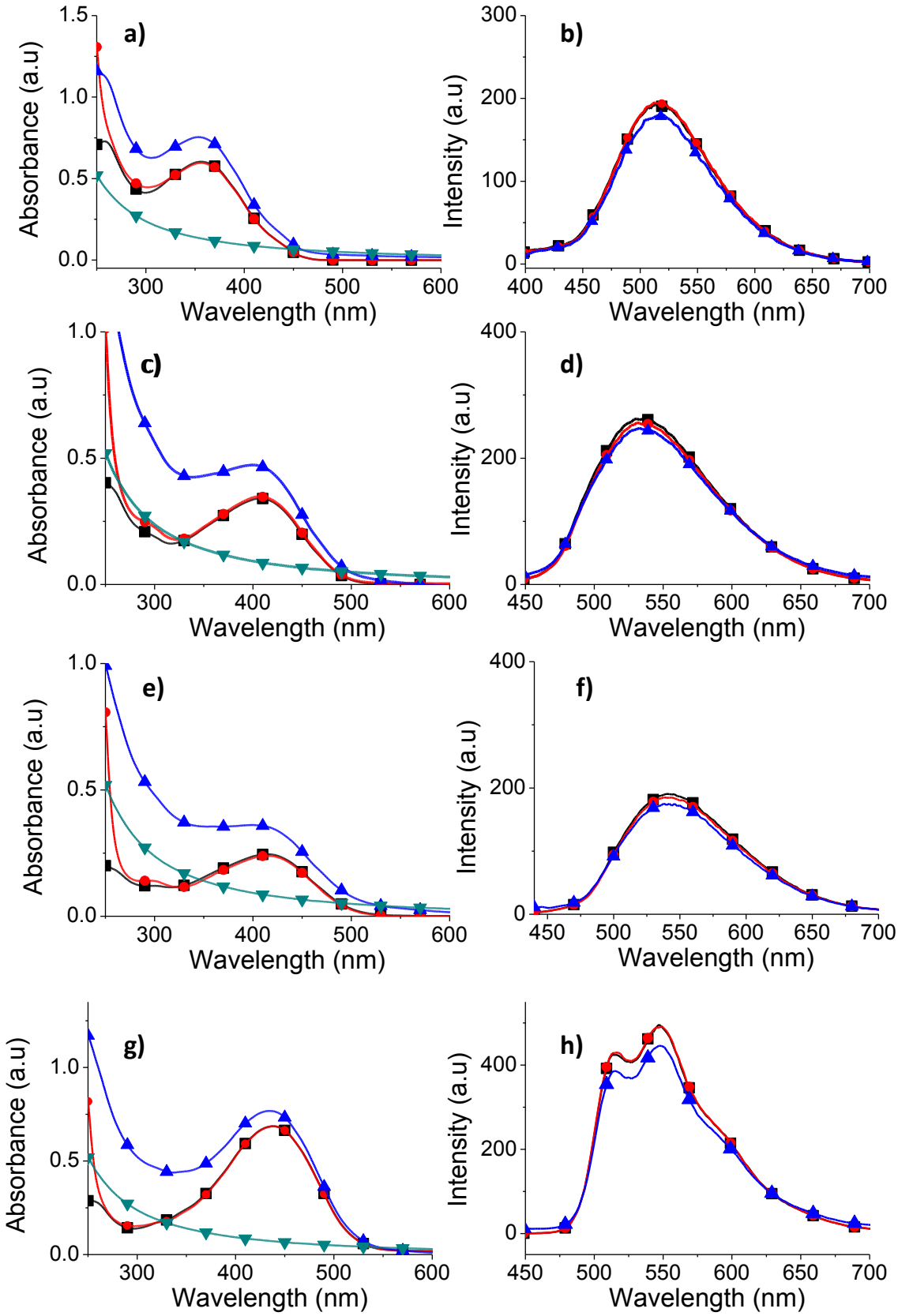



***Figure S35.*** Absorption and emission spectra of **SCT-1** (a, b), **SCT-2** (c, d), **SCT-3** (e, f) and **SCT-4** (g, h) in presence of Pb(II) and Cd(II) ions; SCTs in THF (-■-), in presence of 1 x $10^{-}$

$^{3}$ M $Pb(NO_3)_2$ aqueous solution (-●-), and in presence of 1 x $10^{-3}$ M $Cd(CH_3CO_2)_2$ aqueous solution (-▲-). The absorption spectra of 1 x $10^{-3}$ M $Cd(CH_3CO_2)_2$ in THF was shown (-▼-). The concentrations of **SCT-1**, **SCT-2**, **SCT-3**, and **SCT-4** are 1.5 x $10^{-5}$ M, 3.4 x $10^{-6}$ M, 2.4 x $10^{-6}$ M, and 4.7 x $10^{-6}$ M, respectively.

**5. Absorption spectra of SCT-4 at pH 1 - 6**

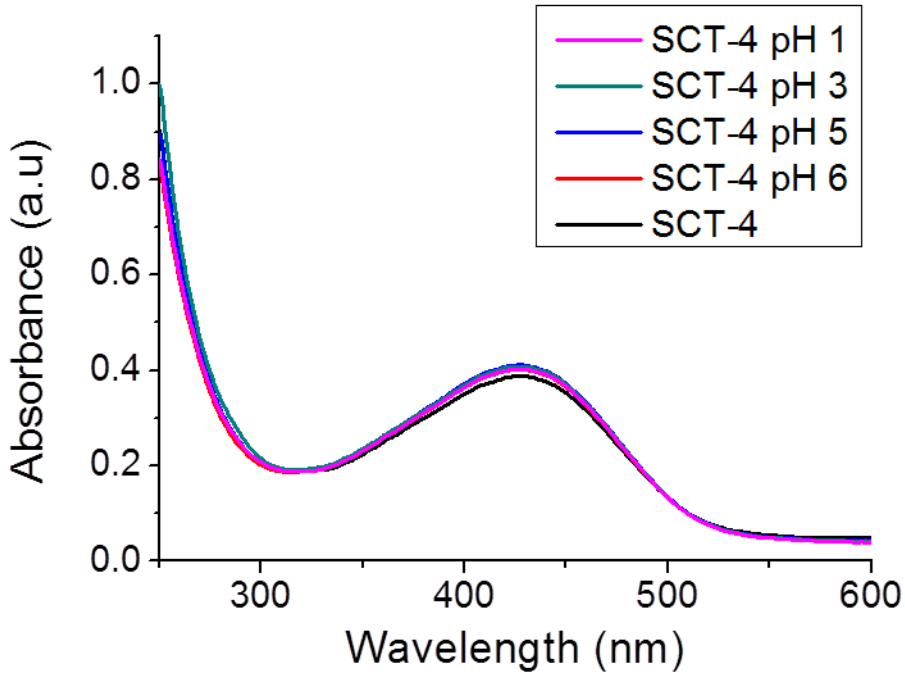



***Figure S36.*** Uv-visible absorption of **SCT-4** at different acidic pH (pH 1 – 6) in THF and appropriate amounts of dilute HCl was added to get the desired pH.

**6. SEM micrographs on SCT/Hg(II) and SCT/TCNQ complexes**

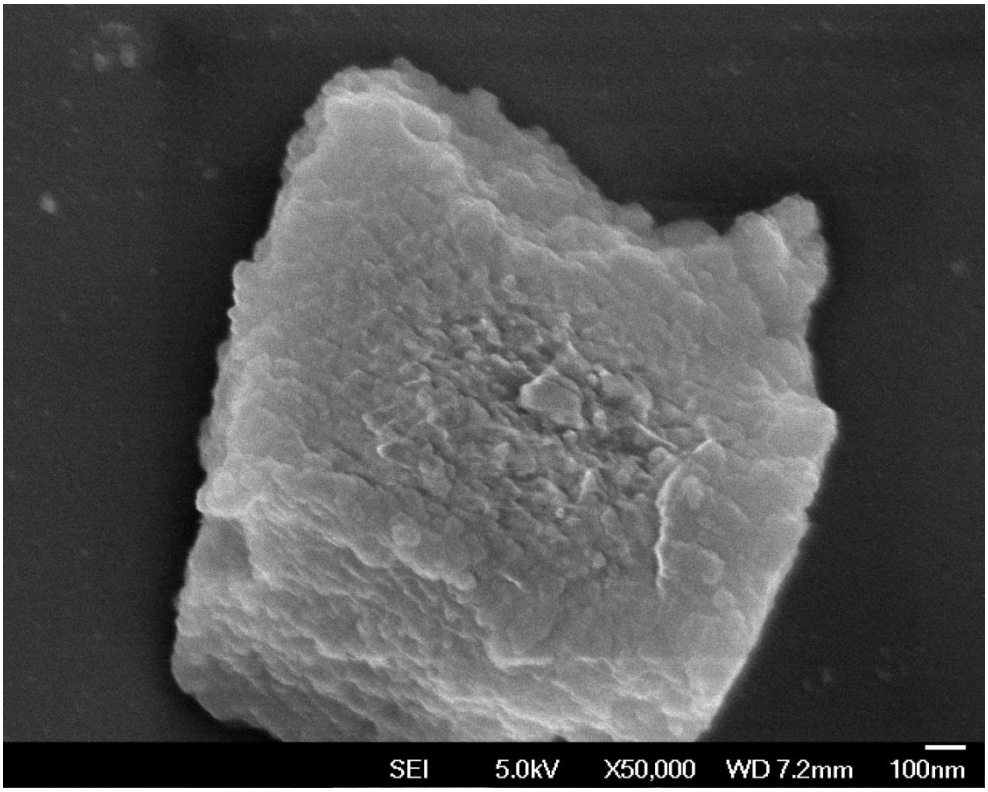



***Figure S37.*** SEM micrograph on the Hg(II)-**SCT**s precipitate by dropcasting on the glass substrate and dried under ambient condition before examination by FESEM.

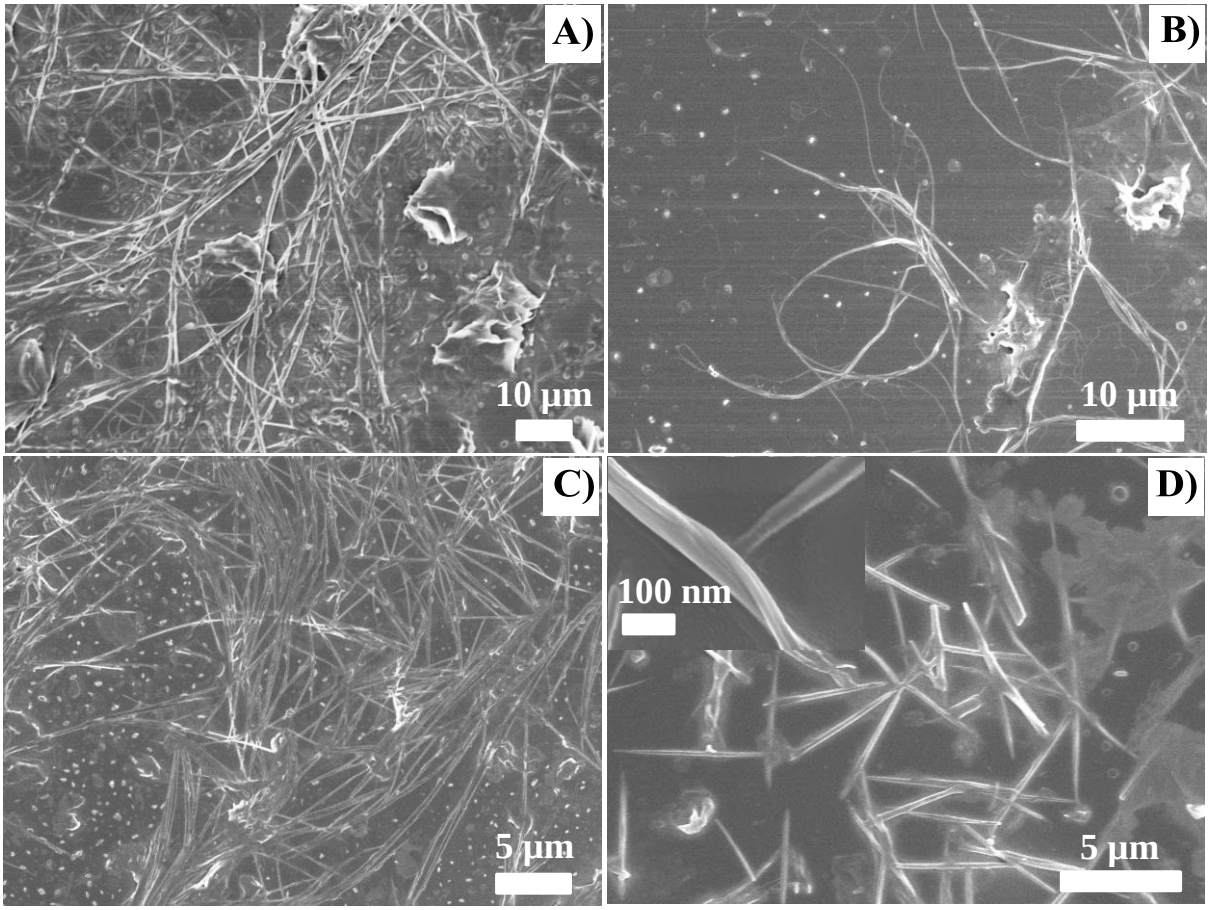



**Figure S38** Field emission SEM micrographs (a) **SCT-1**, (b) **SCT-2**, (c) **SCT-3** and (d) **SCT-4** with TCNQ; inset: magnified image on the SCT-4/TCNQ needle. The samples were prepared by dropcasting SCTs-TCNQ in THF on glass substrate and dried at ambient temperature prior to FESEM examination.

## 7. Theoretical calculations on HOMO energy levels of SCTs.

***Table S1*.** Summary of electrochemical properties and of **SCT-1**, **SCT-2**, **SCT-3** and **SCT-4**.

| | HOMO [a] (eV) | LUMO [b] (eV) | HOMO [c] (eV) | LUMO [c] (eV) | $E_g$ [c] (eV) |
|---|---|---|---|---|---|
| **SCT-1** | -5.28 | -2.55 | -5.05 | -1.80 | 3.25 |
| **SCT-2** | -5.26 | -2.78 | -4.83 | -2.07 | 2.76 |

| | | | | | |
|---|---|---|---|---|---|
| **SCT-3** | -5.22 | -2.77 | -4.64 | -1.91 | 2.74 |
| **SCT-4** | -5.07 | -2.75 | -4.65 | -2.13 | 2.52 |

[a] Electrochemical HOMO = -($E^{ox}$ +4.8) eV, where $E^{ox}$ were determined from the onset potentials of first oxidation peak calibrated with ferrocene/ferocenium ion redox couple in thin film. [b] LUMO = HOMO + optical band gap. [c] Theoretical calculations using DFT.

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