**ELECTRONIC SUPPORTING INFORMATION (ESI)**

**Table S1.** Crystal data and structure refinement details for **4,4'-DDS-S** and **3,3'-DDS-S**.

| **Compound** | **4,4'-DDS-S** | **3,4'-DDS-S** |
|---|---|---|
| Empirical formula | $C_{24}H_{28}N_4O_{12}S_4$ | $C_{24}H_{28}N_4O_{12}S_4$ |
| Formula weight | 692.74 | 692.74 |
| Temperature/K | 100(2) | 100(2) |
| Crystal system | monoclinic | monoclinic |
| Space group | $P2_1$ | $P2_1/c$ |
| $a$/Å | 10.6218(4) | 30.1122(18) |
| $b$/Å | 9.6697(4) | 11.7047(5) |
| $c$/Å | 14.1442(5) | 8.0292(3) |
| $\alpha$/° | 90 | 90 |
| $\beta$/° | 106.322(4) | 96.307(5) |
| $\gamma$/° | 90 | 90 |
| Volume/Å$^3$ | 1394.20(9) | 2812.8(2) |
| $Z$ | 2 | 4 |
| $\rho_{calc}$g/cm$^3$ | 1.650 | 1.636 |
| $\mu$/mm$^{-1}$ | 3.787 | 3.754 |
| $F$(000) | 720.0 | 1440.0 |
| Crystal size/mm$^3$ | 0.29 × 0.17 × 0.11 | 0.23 × 0.17 × 0.03 |
| Radiation | Cu$K\alpha$ ($\lambda$ = 1.54184) | Cu$K\alpha$ ($\lambda$ = 1.54184) |
| 2$\Theta$ range for data collection/° | 6.512 to 134.11 | 5.906 to 134.154 |
| Index ranges | -12 ≤ $h$ ≤ 12,<br>-11 ≤ $k$ ≤ 11,<br>-16 ≤ $l$ ≤ 16 | -35 ≤ $h$ ≤ 35,<br>-13 ≤ $k$ ≤ 7,<br>-9 ≤ $l$ ≤ 7 |
| Reflections collected | 10111 | 10170 |
| Independent reflections | 4882 [$R_{int}$ = 0.0250,<br>$R_{sigma}$ = 0.0295] | 5010 [$R_{int}$ = 0.0443,<br>$R_{sigma}$ = 0.0629] |
| Data/restraints/parameters | 4882/15/433 | 5010/12/433 |
| Goodness-of-fit on $F^2$ | 1.063 | 1.057 |
| Final $R$ indexes [$I$>=2σ ($I$)] | $R_1$ = 0.0329,<br>w$R_2$ = 0.0881 | $R_1$ = 0.0573,<br>w$R_2$ = 0.1344 |
| Final $R$ indexes [all data] | $R_1$ = 0.0365,<br>w$R_2$ = 0.0919 | $R_1$ = 0.0832,<br>w$R_2$ = 0.1485 |
| Largest diff. peak/hole / e Å$^{-3}$ | 0.36/-0.56 | 0.54/-0.41 |
| Flack parameter | -0.011(10) | – |

**Table S2.** Bond lengths for **4,4'-DDS-S**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| C1B | C2B | 1.394(5) | C3A | C4A | 1.382(5) |
| C1B | C6B | 1.393(5) | C4A | C5A | 1.389(5) |
| C1B | S7B | 1.770(4) | C4A | N16A | 1.459(5) |
| C2B | C3B | 1.380(5) | C5A | C6A | 1.387(5) |
| C3B | C4B | 1.385(5) | C8A | C9A | 1.392(5) |
| C4B | C5B | 1.387(5) | C8A | C13A | 1.395(5) |
| C4B | N16B | 1.460(5) | C8A | S7A | 1.777(4) |
| C5B | C6B | 1.387(5) | C9A | C10A | 1.389(5) |
| C8B | C9B | 1.385(5) | C10A | C11A | 1.384(5) |
| C8B | C13B | 1.398(5) | C11A | C12A | 1.386(5) |
| C8B | S7B | 1.769(4) | C11A | N17A | 1.459(5) |
| C9B | C10B | 1.385(5) | C12A | C13A | 1.385(5) |
| C10B | C11B | 1.382(5) | O14A | S7A | 1.439(3) |
| C11B | C12B | 1.391(5) | O15A | S7A | 1.443(3) |

| | | | | | |
|---|---|---|---|---|---|
| C11B | N17B | 1.457(4) | O19B | S18B | 1.484(3) |
| C12B | C13B | 1.377(5) | O20B | S18B | 1.479(3) |
| O14B | S7B | 1.440(3) | O21B | S18B | 1.484(3) |
| O15B | S7B | 1.446(3) | O22B | S18B | 1.473(3) |
| C1A | C2A | 1.396(5) | O19A | S18A | 1.480(2) |
| C1A | C6A | 1.389(5) | O20A | S18A | 1.488(3) |
| C1A | S7A | 1.762(4) | O21A | S18A | 1.462(3) |
| C2A | C3A | 1.382(5) | O22A | S18A | 1.493(3) |

**Table S3.** Values of the valence angles for **4,4'-DDS-S**.

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C2B | C1B | S7B | 119.1(3) | C3A | C4A | N16A | 118.1(3) |
| C6B | C1B | C2B | 121.3(3) | C5A | C4A | N16A | 119.8(3) |
| C6B | C1B | S7B | 119.4(3) | C6A | C5A | C4A | 119.0(3) |
| C3B | C2B | C1B | 119.1(3) | C5A | C6A | C1A | 119.1(3) |
| C2B | C3B | C4B | 119.4(3) | C9A | C8A | C13A | 122.0(3) |
| C3B | C4B | C5B | 121.8(3) | C9A | C8A | S7A | 118.8(3) |
| C3B | C4B | N16B | 118.3(3) | C13A | C8A | S7A | 119.0(3) |
| C5B | C4B | N16B | 119.8(3) | C10A | C9A | C8A | 118.9(3) |
| C4B | C5B | C6B | 119.0(3) | C11A | C10A | C9A | 119.0(3) |
| C5B | C6B | C1B | 119.2(3) | C10A | C11A | C12A | 122.0(3) |
| C9B | C8B | C13B | 122.1(3) | C10A | C11A | N17A | 118.8(3) |
| C9B | C8B | S7B | 118.5(3) | C12A | C11A | N17A | 119.2(3) |
| C13B | C8B | S7B | 119.2(3) | C13A | C12A | C11A | 119.5(3) |
| C8B | C9B | C10B | 118.8(3) | C12A | C13A | C8A | 118.4(3) |
| C11B | C10B | C9B | 119.2(3) | C1A | S7A | C8A | 107.84(17) |
| C10B | C11B | C12B | 121.8(3) | O14A | S7A | C1A | 107.47(16) |
| C10B | C11B | N17B | 119.5(3) | O14A | S7A | C8A | 107.21(16) |
| C12B | C11B | N17B | 118.6(3) | O14A | S7A | O15A | 119.78(16) |
| C13B | C12B | C11B | 119.3(3) | O15A | S7A | C1A | 106.92(16) |
| C12B | C13B | C8B | 118.6(3) | O15A | S7A | C8A | 107.13(16) |
| C8B | S7B | C1B | 107.62(18) | O20B | S18B | O19B | 108.35(15) |
| O14B | S7B | C1B | 107.36(16) | O20B | S18B | O21B | 109.07(15) |
| O14B | S7B | C8B | 107.38(16) | O21B | S18B | O19B | 109.77(15) |
| O14B | S7B | O15B | 119.76(16) | O22B | S18B | O19B | 109.23(15) |
| O15B | S7B | C1B | 107.28(16) | O22B | S18B | O20B | 110.81(16) |
| O15B | S7B | C8B | 106.93(16) | O22B | S18B | O21B | 109.58(15) |
| C2A | C1A | S7A | 119.0(3) | O19A | S18A | O20A | 109.29(15) |
| C6A | C1A | C2A | 121.5(3) | O19A | S18A | O22A | 107.60(16) |
| C6A | C1A | S7A | 119.5(3) | O20A | S18A | O22A | 108.46(15) |
| C3A | C2A | C1A | 119.1(3) | O21A | S18A | O19A | 111.34(15) |
| C2A | C3A | C4A | 119.3(3) | O21A | S18A | O20A | 110.35(14) |
| C3A | C4A | C5A | 121.9(3) | O21A | S18A | O22A | 109.72(16) |

**Table S4.** Values of torsion angles for **4,4'-DDS-S**.

| A | B | C | D | Angle/° | A | B | C | D | Angle/° |
|---|---|---|---|---|---|---|---|---|---|
| C1B | C2B | C3B | C4B | -1.1(5) | C1A | C2A | C3A | C4A | -1.3(5) |
| C2B | C1B | C6B | C5B | -3.1(6) | C2A | C1A | C6A | C5A | -2.0(5) |
| C2B | C1B | S7B | C8B | -100.0(3) | C2A | C1A | S7A | C8A | -92.8(3) |
| C2B | C1B | S7B | O14B | 15.3(3) | C2A | C1A | S7A | O14A | 22.5(3) |
| C2B | C1B | S7B | O15B | 145.3(3) | C2A | C1A | S7A | O15A | 152.3(3) |
| C2B | C3B | C4B | C5B | -2.2(6) | C2A | C3A | C4A | C5A | -0.9(6) |
| C2B | C3B | C4B | N16B | 174.3(4) | C2A | C3A | C4A | N16A | 174.8(3) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C3B | C4B | C5B | C6B | 2.9(6) | C3A | C4A | C5A | C6A | 1.7(6) |
| C4B | C5B | C6B | C1B | -0.2(6) | C4A | C5A | C6A | C1A | -0.3(5) |
| C6B | C1B | C2B | C3B | 3.8(6) | C6A | C1A | C2A | C3A | 2.8(5) |
| C6B | C1B | S7B | C8B | 85.1(3) | C6A | C1A | S7A | C8A | 91.1(3) |
| C6B | C1B | S7B | O14B | -159.6(3) | C6A | C1A | S7A | O14A | -153.6(3) |
| C6B | C1B | S7B | O15B | -29.7(3) | C6A | C1A | S7A | O15A | -23.8(3) |
| C8B | C9B | C10B | C11B | 0.1(5) | C8A | C9A | C10A | C11A | 0.8(6) |
| C9B | C8B | C13B | C12B | 3.0(6) | C9A | C8A | C13A | C12A | 3.2(6) |
| C9B | C8B | S7B | C1B | 95.3(3) | C9A | C8A | S7A | C1A | 100.3(3) |
| C9B | C8B | S7B | O14B | -20.0(3) | C9A | C8A | S7A | O14A | -15.1(3) |
| C9B | C8B | S7B | O15B | -149.7(3) | C9A | C8A | S7A | O15A | -144.9(3) |
| C9B | C10B | C11B | C12B | 3.3(6) | C9A | C10A | C11A | C12A | 3.1(6) |
| C9B | C10B | C11B | N17B | -173.8(3) | C9A | C10A | C11A | N17A | -174.5(4) |
| C10B | C11B | C12B | C13B | -3.6(6) | C10A | C11A | C12A | C13A | -3.9(6) |
| C11B | C12B | C13B | C8B | 0.5(6) | C11A | C12A | C13A | C8A | 0.7(5) |
| C13B | C8B | C9B | C10B | -3.3(6) | C13A | C8A | C9A | C10A | -3.9(6) |
| C13B | C8B | S7B | C1B | -89.4(3) | C13A | C8A | S7A | C1A | -84.3(3) |
| C13B | C8B | S7B | O14B | 155.3(3) | C13A | C8A | S7A | O14A | 160.3(3) |
| C13B | C8B | S7B | O15B | 25.6(3) | C13A | C8A | S7A | O15A | 30.5(3) |
| N16B | C4B | C5B | C6B | -173.6(4) | N16A | C4A | C5A | C6A | -174.0(3) |
| N17B | C11B | C12B | C13B | 173.5(3) | N17A | C11A | C12A | C13A | 173.7(3) |
| S7B | C1B | C2B | C3B | -171.1(3) | S7A | C1A | C2A | C3A | -173.3(3) |
| S7B | C1B | C6B | C5B | 171.7(3) | S7A | C1A | C6A | C5A | 174.0(3) |
| S7B | C8B | C9B | C10B | 171.9(3) | S7A | C8A | C9A | C10A | 171.3(3) |
| S7B | C8B | C13B | C12B | -172.2(3) | S7A | C8A | C13A | C12A | -172.1(3) |

**Table S5.** Bond lengths for **3,3'-DDS-S**.

| **Atom** | **Atom** | **Length/Å** | **Atom** | **Atom** | **Length/Å** |
|---|---|---|---|---|---|
| C1A | C2A | 1.376(6) | C9A | C10A | 1.380(6) |
| C1A | C6A | 1.385(6) | C9B | C10B | 1.384(5) |
| C1A | S7A | 1.777(4) | C10A | C11A | 1.389(6) |
| C1B | C2B | 1.398(6) | C10A | N17A | 1.442(6) |
| C1B | C6B | 1.387(6) | C10B | C11B | 1.397(6) |
| C1B | S7B | 1.780(4) | C10B | N17B | 1.449(5) |
| C2A | C3A | 1.393(6) | C11A | C12A | 1.395(6) |
| C2B | C3B | 1.387(6) | C11B | C12B | 1.375(6) |
| C3A | C4A | 1.385(6) | C12A | C13A | 1.389(6) |
| C3A | N16A | 1.447(5) | C12B | C13B | 1.394(6) |
| C3B | C4B | 1.389(6) | O14A | S7A | 1.442(3) |
| C3B | N16B | 1.464(6) | O14B | S7B | 1.438(3) |
| C4A | C5A | 1.379(6) | O15A | S7A | 1.435(3) |
| C4B | C5B | 1.398(6) | O15B | S7B | 1.433(3) |
| C5A | C6A | 1.401(6) | O19B | S18B | 1.480(3) |
| C5B | C6B | 1.390(6) | O20B | S18B | 1.494(3) |
| C8A | C9A | 1.394(6) | O21B | S18B | 1.494(3) |
| C8A | C13A | 1.385(6) | O22B | S18B | 1.454(3) |
| C8A | S7A | 1.781(4) | O19A | S18A | 1.493(3) |
| C8B | C9B | 1.388(6) | O20A | S18A | 1.451(3) |
| C8B | C13B | 1.392(6) | O21A | S18A | 1.477(3) |
| C8B | S7B | 1.777(4) | O22A | S18A | 1.501(3) |

**Table S6.** Values of valence angles for **3,3'-DDS-S**.

| **Atom** | **Atom** | **Atom** | **Angle/°** | **Atom** | **Atom** | **Atom** | **Angle/°** |
|---|---|---|---|---|---|---|---|

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C2A | C1A | C6A | 122.0(4) | C9B | C10B | N17B | 119.4(4) |
| C2A | C1A | S7A | 118.4(3) | C11B | C10B | N17B | 119.7(4) |
| C6A | C1A | S7A | 119.3(3) | C10A | C11A | C12A | 119.6(4) |
| C2B | C1B | S7B | 117.4(3) | C12B | C11B | C10B | 119.5(4) |
| C6B | C1B | C2B | 121.8(4) | C13A | C12A | C11A | 120.3(4) |
| C6B | C1B | S7B | 120.6(3) | C11B | C12B | C13B | 120.8(4) |
| C1A | C2A | C3A | 118.8(4) | C8A | C13A | C12A | 118.8(4) |
| C3B | C2B | C1B | 118.6(4) | C8B | C13B | C12B | 118.7(4) |
| C2A | C3A | N16A | 118.1(4) | C1A | S7A | C8A | 100.28(19) |
| C4A | C3A | C2A | 120.5(4) | O14A | S7A | C1A | 108.28(19) |
| C4A | C3A | N16A | 121.4(4) | O14A | S7A | C8A | 108.04(19) |
| C2B | C3B | C4B | 120.7(4) | O15A | S7A | C1A | 108.04(19) |
| C2B | C3B | N16B | 117.9(4) | O15A | S7A | C8A | 109.7(2) |
| C4B | C3B | N16B | 121.3(4) | O15A | S7A | O14A | 120.56(18) |
| C5A | C4A | C3A | 119.8(4) | C8B | S7B | C1B | 103.20(19) |
| C3B | C4B | C5B | 119.8(4) | O14B | S7B | C1B | 106.96(19) |
| C4A | C5A | C6A | 120.6(4) | O14B | S7B | C8B | 108.00(18) |
| C6B | C5B | C4B | 120.5(4) | O15B | S7B | C1B | 109.3(2) |
| C1A | C6A | C5A | 118.2(4) | O15B | S7B | C8B | 107.84(18) |
| C1B | C6B | C5B | 118.7(4) | O15B | S7B | O14B | 120.20(18) |
| C9A | C8A | S7A | 116.4(3) | O19B | S18B | O20B | 108.44(19) |
| C13A | C8A | C9A | 121.7(4) | O19B | S18B | O21B | 108.40(17) |
| C13A | C8A | S7A | 121.4(3) | O20B | S18B | O21B | 107.10(17) |
| C9B | C8B | C13B | 121.4(4) | O22B | S18B | O19B | 111.45(18) |
| C9B | C8B | S7B | 118.6(3) | O22B | S18B | O20B | 110.98(19) |
| C13B | C8B | S7B | 119.9(3) | O22B | S18B | O21B | 110.32(18) |
| C10A | C9A | C8A | 118.5(4) | O19A | S18A | O22A | 106.30(18) |
| C10B | C9B | C8B | 118.7(4) | O20A | S18A | O19A | 110.00(17) |
| C9A | C10A | C11A | 120.9(4) | O20A | S18A | O21A | 112.32(18) |
| C9A | C10A | N17A | 118.1(4) | O20A | S18A | O22A | 110.85(18) |
| C11A | C10A | N17A | 120.8(4) | O21A | S18A | O19A | 108.45(17) |
| C9B | C10B | C11B | 120.9(4) | O21A | S18A | O22A | 108.70(17) |

**Table S7.** Values of torsion angles for **3,3'-DDS-S**.

| **A** | **B** | **C** | **D** | **Angle/°** | **A** | **B** | **C** | **D** | **Angle/°** |
|---|---|---|---|---|---|---|---|---|---|
| C1A | C2A | C3A | C4A | 1.6(6) | C9A | C8A | S7A | O14A | -38.6(4) |
| C1A | C2A | C3A | N16A | -176.3(4) | C9A | C8A | S7A | O15A | -171.9(3) |
| C1B | C2B | C3B | C4B | -1.9(6) | C9A | C10A | C11A | C12A | 0.2(7) |
| C1B | C2B | C3B | N16B | 174.1(3) | C9B | C8B | C13B | C12B | -0.3(6) |
| C2A | C1A | C6A | C5A | 1.1(6) | C9B | C8B | S7B | C1B | -62.4(4) |
| C2A | C1A | S7A | C8A | -66.9(4) | C9B | C8B | S7B | O14B | 50.6(4) |
| C2A | C1A | S7A | O14A | 46.2(4) | C9B | C8B | S7B | O15B | -178.1(3) |
| C2A | C1A | S7A | O15A | 178.3(3) | C9B | C10B | C11B | C12B | 0.9(6) |
| C2A | C3A | C4A | C5A | 1.1(6) | C10A | C11A | C12A | C13A | 1.9(7) |
| C2B | C1B | C6B | C5B | 0.7(6) | C10B | C11B | C12B | C13B | -1.3(6) |
| C2B | C1B | S7B | C8B | 81.5(3) | C11A | C12A | C13A | C8A | -1.5(7) |
| C2B | C1B | S7B | O14B | -32.3(4) | C11B | C12B | C13B | C8B | 1.0(6) |
| C2B | C1B | S7B | O15B | -163.9(3) | C13A | C8A | C9A | C10A | 3.2(6) |
| C2B | C3B | C4B | C5B | 0.9(6) | C13A | C8A | S7A | C1A | -97.8(4) |
| C3A | C4A | C5A | C6A | -2.7(6) | C13A | C8A | S7A | O14A | 149.0(3) |
| C3B | C4B | C5B | C6B | 1.0(7) | C13A | C8A | S7A | O15A | 15.8(4) |
| C4A | C5A | C6A | C1A | 1.7(6) | C13B | C8B | C9B | C10B | -0.1(6) |
| C4B | C5B | C6B | C1B | -1.8(7) | C13B | C8B | S7B | C1B | 115.4(4) |

| | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| C6A | C1A | C2A | C3A | -2.7(6) | C13B | C8B | S7B | O14B | -131.5(3) |
| C6A | C1A | S7A | C8A | 107.2(4) | C13B | C8B | S7B | O15B | -0.2(4) |
| C6A | C1A | S7A | O14A | -139.8(3) | N16A | C3A | C4A | C5A | 178.9(4) |
| C6A | C1A | S7A | O15A | -7.6(4) | N16B | C3B | C4B | C5B | -175.0(4) |
| C6B | C1B | C2B | C3B | 1.1(6) | N17A | C10A | C11A | C12A | -174.5(4) |
| C6B | C1B | S7B | C8B | -93.5(4) | N17B | C10B | C11B | C12B | 178.5(4) |
| C6B | C1B | S7B | O14B | 152.7(3) | S7A | C1A | C2A | C3A | 171.2(3) |
| C6B | C1B | S7B | O15B | 21.1(4) | S7A | C1A | C6A | C5A | -172.8(3) |
| C8A | C9A | C10A | C11A | -2.7(6) | S7A | C8A | C9A | C10A | -169.1(3) |
| C8A | C9A | C10A | N17A | 172.1(4) | S7A | C8A | C13A | C12A | 170.8(3) |
| C8B | C9B | C10B | C11B | -0.2(6) | S7B | C1B | C2B | C3B | -173.9(3) |
| C8B | C9B | C10B | N17B | -177.8(4) | S7B | C1B | C6B | C5B | 175.5(3) |
| C9A | C8A | C13A | C12A | -1.2(6) | S7B | C8B | C9B | C10B | 177.8(3) |
| C9A | C8A | S7A | C1A | 74.6(3) | S7B | C8B | C13B | C12B | -178.2(3) |

**Table S8.** Values of geometrical parameters of the hydrogen bonds identified in the crystal of **4,4'-SDD-S**.

| D−H | A | d(D−H) [Å] | d(H···A) [Å] | d(D···A) [Å] | <(D−H···A) [ °] |
|---|---|---|---|---|---|
| N16B−H16A | O19B | 0.88(4) | 1.88(4) | 2.733(4) | 163(4) |
| N16B−H16B | O19A | 0.87(2) | 2.54(2) | 3.362(5) | 158(3) |
| N16B−H16B | O22A | 0.87(2) | 2.19(4) | 2.921(4) | 142(3) |
| N16B−H16C | O20B$^{i}$ | 0.87(3) | 1.84(3) | 2.683(5) | 163(4) |
| N16A−H16D | O22A$^{ii}$ | 0.87(4) | 1.92(3) | 2.740(4) | 156(4) |
| N16A−H16E | O21B$^{iii}$ | 0.87(3) | 1.94(3) | 2.805(4) | 169(4) |
| N16A−H16F | O19A | 0.87(4) | 1.90(4) | 2.748(4) | 165(4) |
| N17B−H17A | O20B$^{iv}$ | 0.88(3) | 2.46(3) | 3.042(4) | 124(3) |
| N17B−H17A | O21B$^{iv}$ | 0.88(3) | 2.05(3) | 2.871(4) | 155(4) |
| N17B−H17B | O20A$^{v}$ | 0.88(3) | 1.95(3) | 2.812(4) | 166(3) |
| N17B−H17C | O19B$^{vi}$ | 0.88(4) | 2.47(4) | 3.088(4) | 128(3) |
| N17B−H17C | O22B$^{vi}$ | 0.88(4) | 1.94(4) | 2.775(4) | 159(4) |
| N17A−H17D | O19A$^{vii}$ | 0.88(4) | 2.55(4) | 3.209(5) | 133(3) |
| N17A−H17D | O20A$^{vii}$ | 0.88(4) | 1.98(4) | 2.809(4) | 156(4) |
| N17A−H17E | O19B$^{iv}$ | 0.88(2) | 1.91(3) | 2.732(4) | 155(3) |
| N17A−H17F | O22A$^{iv}$ | 0.87(2) | 1.97(3) | 2.766(5) | 153(4) |
| C2A−H2A | O15B | 0.93 | 2.50 | 3.343(5) | 152 |
| C5A−H5A | O22B$^{iii}$ | 0.93 | 2.58 | 3.213(5) | 126 |
| C5B−H5B | O19A | 0.93 | 2.49 | 3.309(5) | 147 |
| C6B−H6B | O15A$^{viii}$ | 0.93 | 2.50 | 3.388(5) | 161 |
| C10A−H10A | O20B$^{iv}$ | 0.93 | 2.58 | 3.501(5) | 169 |
| C10B−H10B | O21A$^{v}$ | 0.93 | 2.57 | 3.175(5) | 123 |

Symmetry codes: (i) $-x+1, y-1/2, -z+1$; (ii) $-x, y+1/2, -z+1$; (iii) $x-1, y, z$; (iv) $x, y, z+1$; (v) $x+1, y, z+1$; (vi) $-x+1, y-1/2, -z+2$; (vii) $-x, y+1/2, -z+2$; (viii) $-x, y-1/2, -z+2$.

**Table S9.** Values of geometrical parameters of the S−O···π contacts in the crystal of **4,4'-SDD-S**.

| D−X | *Cg*I | d(X···*Cg*I) [Å] | <(D−X···*Cg*I) [ °] | d(D···*Cg*I) [Å] |
|---|---|---|---|---|
| S7A−O14A | 1$^{vii}$ | 3.651(3) | 89.44(11) | 3.9116(18) |
| S7B−O14B | 3$^{ix}$ | 3.811(3) | 92.44(12) | 4.1306(18) |
| S7B−O14B | 4$^{ix}$ | 3.690(3) | 91.59(12) | 3.9983(18) |
| S7A−O15A | 1$^{vii}$ | 3.515(3) | 94.86(12) | 3.9116(18) |
| S7A−O15A | 2$^{vii}$ | 3.861(3) | 93.72(11) | 4.2085(18) |
| S7B−O15B | 3$^{ix}$ | 3.818(3) | 92.05(13) | 4.1306(18) |
| S7B−O15B | 4$^{ix}$ | 3.700(3) | 91.12(13) | 3.9983(18) |

*Cg*1, *Cg*2, *Cg*3 and *Cg*4 denote the geometric centers of gravity of aromatic rings defined by the C1A−C6A, C8A−C13A, C1B−C6B and C8B−C13B atoms, respectively.
Symmetry codes: (vii) $-x, y+1/2, -z+2$; (ix) −x + 1, y + ½, −z +2.

**Table S10.** Values of geometrical parameters of the hydrogen bonds identified in the crystal of **3,3'-SDD-S**.

| D−H | A | d(D−H) [Å] | d(H···A) [Å] | d(D···A) [Å] | <(D−H···A) [ °] |
|---|---|---|---|---|---|

| | | | | | |
|---|---|---|---|---|---|
| N16A−H16A | O19B | 0.87(3) | 2.24(5) | 2.828(5) | 125(3) |
| N16A−H16A | O20B | 0.87(3) | 2.31(3) | 3.165(5) | 170(5) |
| N16A−H16B | O19A$^{i}$ | 0.87(2) | 1.86(3) | 2.723(4) | 169(5) |
| N16A−H16C | O19A | 0.88(4) | 1.85(4) | 2.725(5) | 177(3) |
| N16B−H16D | O19A | 0.87(3) | 2.36(5) | 3.034(5) | 135(4) |
| N16B−H16D | O22A | 0.87(3) | 2.35(3) | 3.141(5) | 151(4) |
| N16B−H16E | O22A$^{ii}$ | 0.88(3) | 1.95(3) | 2.795(5) | 163(4) |
| N16B−H16F | O19B | 0.87(4) | 1.84(4) | 2.687(5) | 163(4) |
| N17A−H17A | O20B$^{iii}$ | 0.87(3) | 1.98(4) | 2.828(5) | 163(4) |
| N17A−H17A | O21B$^{iii}$ | 0.87(3) | 2.51(5) | 3.054(5) | 121(4) |
| N17A−H17B | O20B | 0.87(3) | 2.02(3) | 2.829(5) | 153(4) |
| N17A−H17C | O21A$^{ii}$ | 0.87(4) | 1.86(4) | 2.731(5) | 177(4) |
| N17B−H17D | O21A$^{i}$ | 0.87(3) | 2.46(5) | 2.983(5) | 119(4) |
| N17B−H17D | O22A$^{i}$ | 0.87(3) | 1.96(3) | 2.828(5) | 175.6(19) |
| N17B−H17E | O21B$^{iv}$ | 0.87(4) | 1.91(4) | 2.761(4) | 166(4) |
| N17B−H17F | O21B | 0.87(3) | 1.92(3) | 2.782(4) | 170(4) |
| C2A−H2A | O20A$^{ii}$ | 0.93 | 2.50 | 3.357(5) | 154 |
| C4B−H4B | O22A | 0.93 | 2.59 | 3.209(6) | 124 |
| C5A−H5A | O14A$^{v}$ | 0.93 | 2.38 | 3.088(5) | 133 |
| C9B−H9B | O21B | 0.93 | 2.50 | 3.178(5) | 130 |
| C12A−H12A | O15A$^{vi}$ | 0.93 | 2.58 | 3.420(6) | 150 |
| C12B−H12B | O14B$^{v}$ | 0.93 | 2.48 | 3.149(5) | 129 |

Symmetry codes: (i) $x, -y + 1/2, z + 1/2$; (ii) $x, -y + 1/2, z - 1/2$; (iii) $x, -y + 3/2, z - 1/2$; (iv) $x, -y + 3/2, z + 1/2$; (v) $x, y, z + 1$; (vi) $x - 1, y + 1/2, -z + 1/2$.

**Table S11.** Values of geometrical parameters of the S−O···π contacts in the crystal of **3,3'-SDD-S**.

| **D−X** | ***Cg*I** | **d(X···*Cg*I) [Å]** | **<(D−X···*Cg*I) [ °]** | **d(D···*Cg*I) [Å]** |
|---|---|---|---|---|
| S7A−O14A | 1$^{ii}$ | 3.195(4) | 136.51(16) | 4.3562(19) |
| S7B−O14B | 4$^{iii}$ | 3.143(3) | 141.31(14) | 4.3593(19) |

*Cg*1 and *Cg*4 denote the geometric centers of gravity of aromatic rings defined by the C1A−C6A and C8B−C13B atoms, respectively. Symmetry codes: (ii) $x, -y + 1/2, z - 1/2$; (iii) $x, -y + 3/2, z - 1/2$.

**Table S12.** Attribution of the IR and Raman frequencies of the different functional groups for investigated compounds.

| **4,4'-DDS-S** | | **3,3'-DDS-S** | **Attribution** |
|---|---|---|---|
| **IR (cm$^{-1}$)** | **Raman (cm$^{-1}$)** | **IR (cm$^{-1}$)** | |
| 3470 | - | 3563 | ν(CH) |
| 3070 | - | 3056 | ν(CH) |
| 2862 | - | 2865 | ν(CH) |
| 2604 | - | 2597 | ν(N-H.. O) |
| 2137 | - | 2134 | ν(N-H.. O) |
| 1936 | - | 1934 | ν(N-H.. O) |
| 1626 | - | 1623 | $\delta_{as}(NH_3)$ |
| 1602 | 1603 | 1597 | $\delta_{as}(NH_3)$ |
| 1579 | - | 1564 | $\delta_{s}(NH_3)$ |
| 1497 | 1501 | 1501 | $\nu$(C=C) |
| 1482 | - | 1498 | ν(C=C) |
| 1425 | - | 1444 | $\delta$(C-C-H) |
| 1310 | - | 1318 | ν(C-S) |
| 1297 | 1220 | 1219 | $\nu_{as}(SO_2)$, $\nu$(C-C) |
| 1234 | 1193 | 1206 | ν(C-C), ν(C-N) |
| 1134 | 1153 | 1151 | $\nu_s$(S=O), ν(C-N), $\delta$(CH) |
| 1092 | - | 1091 | $\delta$(C-C-H) |
| 1072 | 1072 | 1077 | $\nu_3(SO_4)$ |
| 1057,1036 | - | 1040 | ν(C-N) |
| 1000 | - | 1002 | ν(C-C), $\delta$(H-N-C) |
| - | 974 | 970 | $\delta_{as}(C\text{-}C\text{-}C)_{Ar}$ |
| 963 | 963 | 965 | $\nu_1$ $(SO_4)$, $\delta_{as}$ $(C\text{-}C\text{-}C)_{Ar}$ |
| 827 | 829-810 | 820 | ν(CH) |
| 708 | - | 697 | $\nu$(C-S) |

| | | | |
|---|---|---|---|
| 684 | - | 678 | $\nu$(C-S), $\delta$(O-S-C) |
| 632 | 633 | 637 | $\nu$(C-S),$\delta$(C-C-C)$_{Ar}$ |
| 616-550 | 613 | 618 | $\nu_4(SO_4)$, $\delta$(C-C-C) $_{Ar}$ |
| 490 | 493 | 485 | $\nu_s(SO_2)$, $\delta$(C-N) |
| 455 | 455 | 458 | $\nu_2(SO_4)$, $\delta$(C-C-C)$_{Ar}$ |
| - | 293 | | $\nu(SO_2)$ |
| - | 288-201 | | Network translation |
| - | 193-118 | | Network translation |

**Table S13.** Attribution of the chemical shifting for the **4,4'-DDS-S**.

| $\delta$ **(ppm)** | **C-atoms** | |
|---|---|---|
| 124,30 | **C of type 1** | |
| 126,32 | | C5A, C3A, C10A, C12A, C5B, C3B, C10B, C12B |
| 131,29 | **C of type 2** | C6A, C2A, C9A, C13A, |
| 132,55 | | C6B, C2B, C9B, C13B |
| 137,14 | **C of type 3** | C1A, C8A, C9B, C8B |
| 140,35 | | |
| 141,58 | | |
| 152,33 | **C of type 4** | C4A, C11A, C4B, C11B |

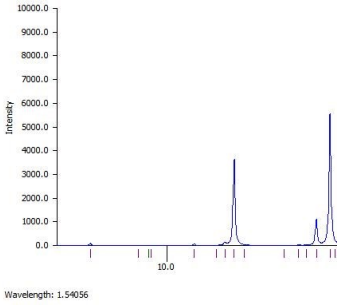


**Figure S1.** Simulated PXRD pattern for **4,4'-DDS-S.**

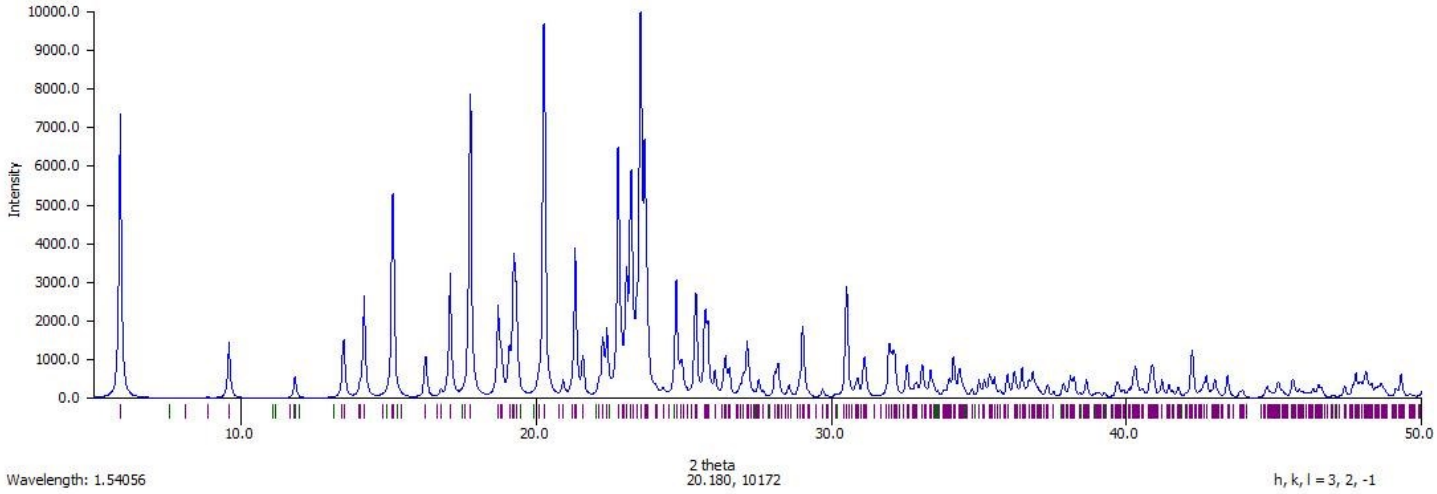


**Figure S2.** Simulated PXRD pattern for **3,3'-DDS-S**.

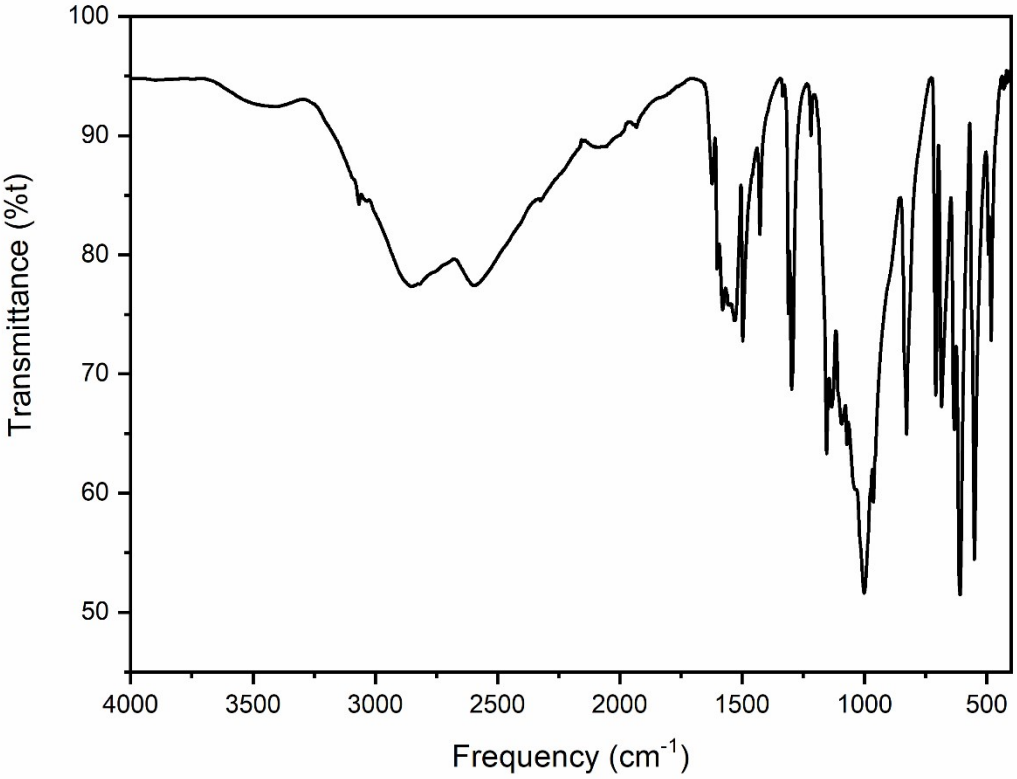


**Figure S3.** The Infrared spectrum recorded for **4,4'-DDS-S**.

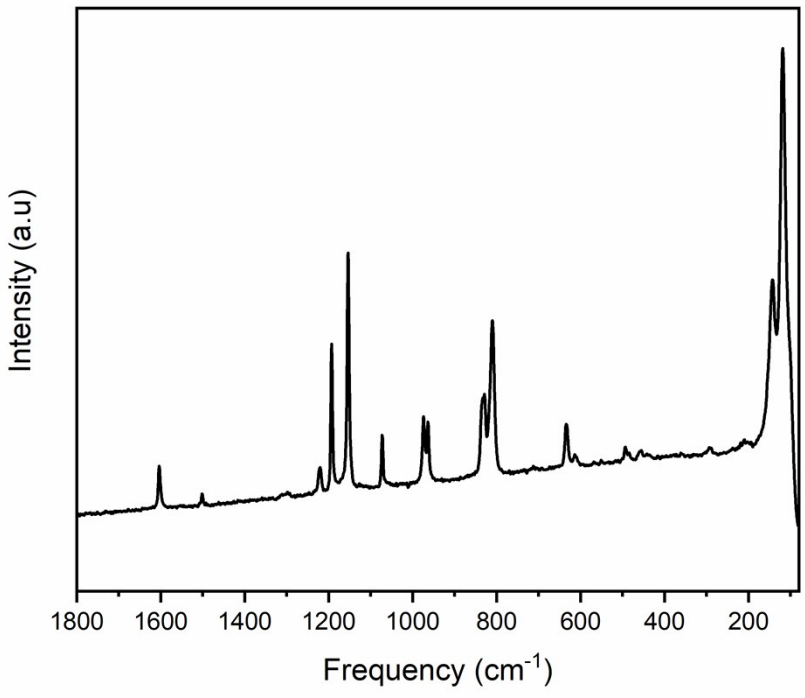


**Figure S4.** The Raman spectrum recorded for the **4,4'-DDS-S**.

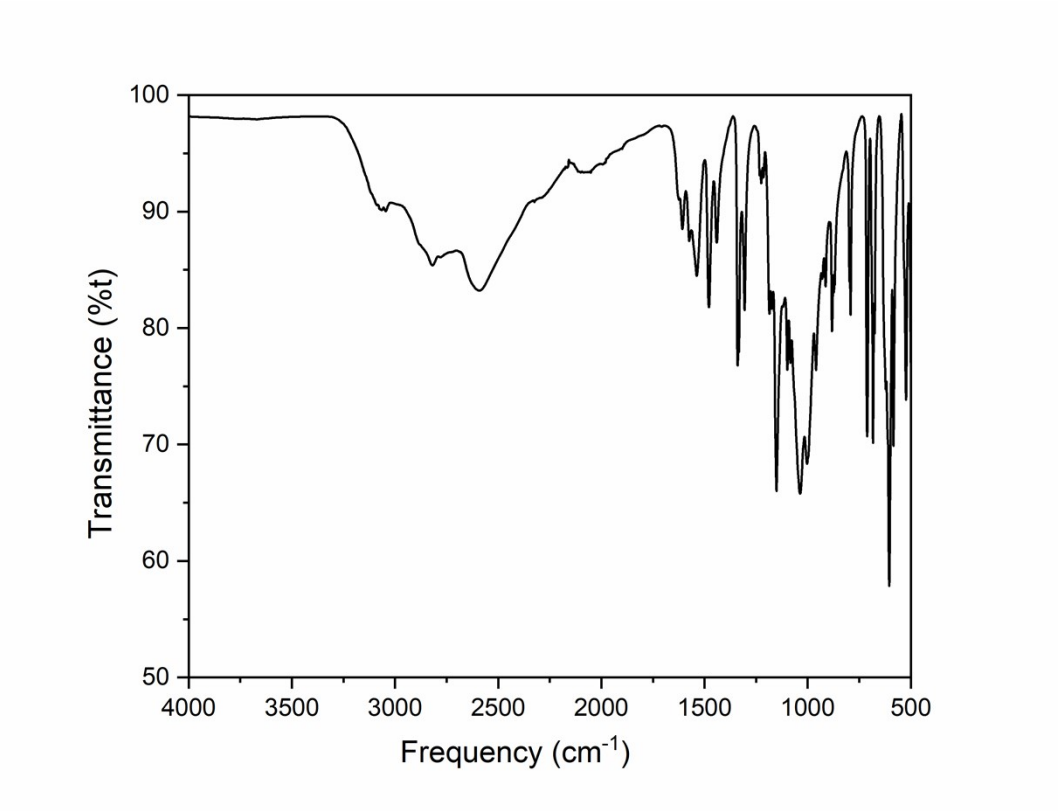


**Figure S5.** The Infrared spectrum recorded for **3,3'-DDS-S**.

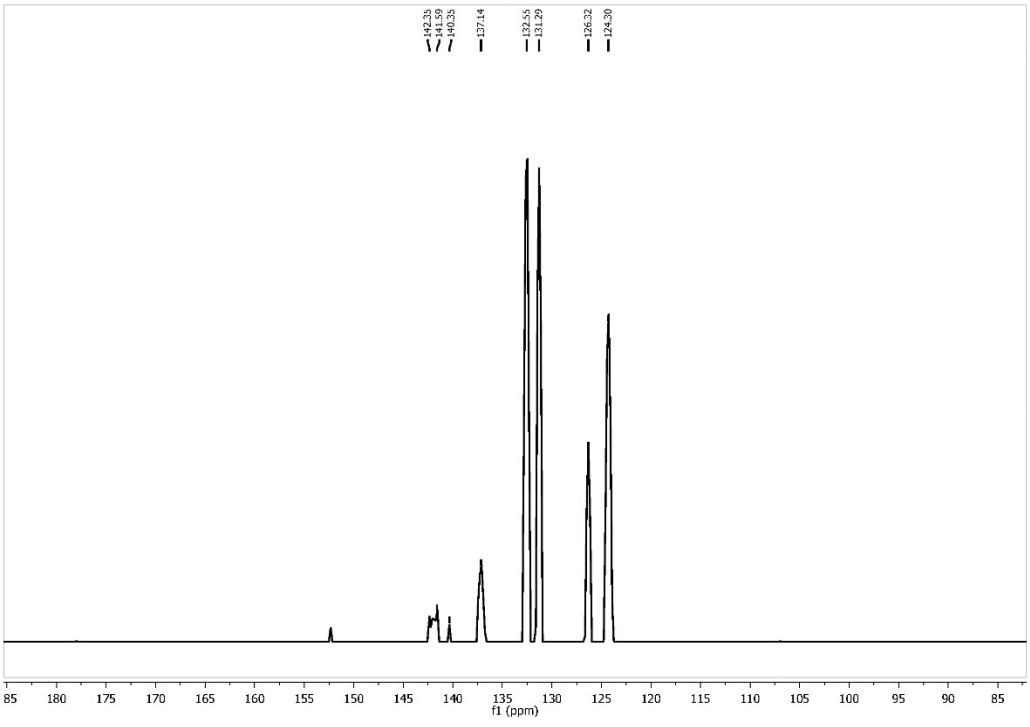


**Figure S6.** NMR $^{13}C$ MASS spectrum recorded for **4,4'-DDS-S**.

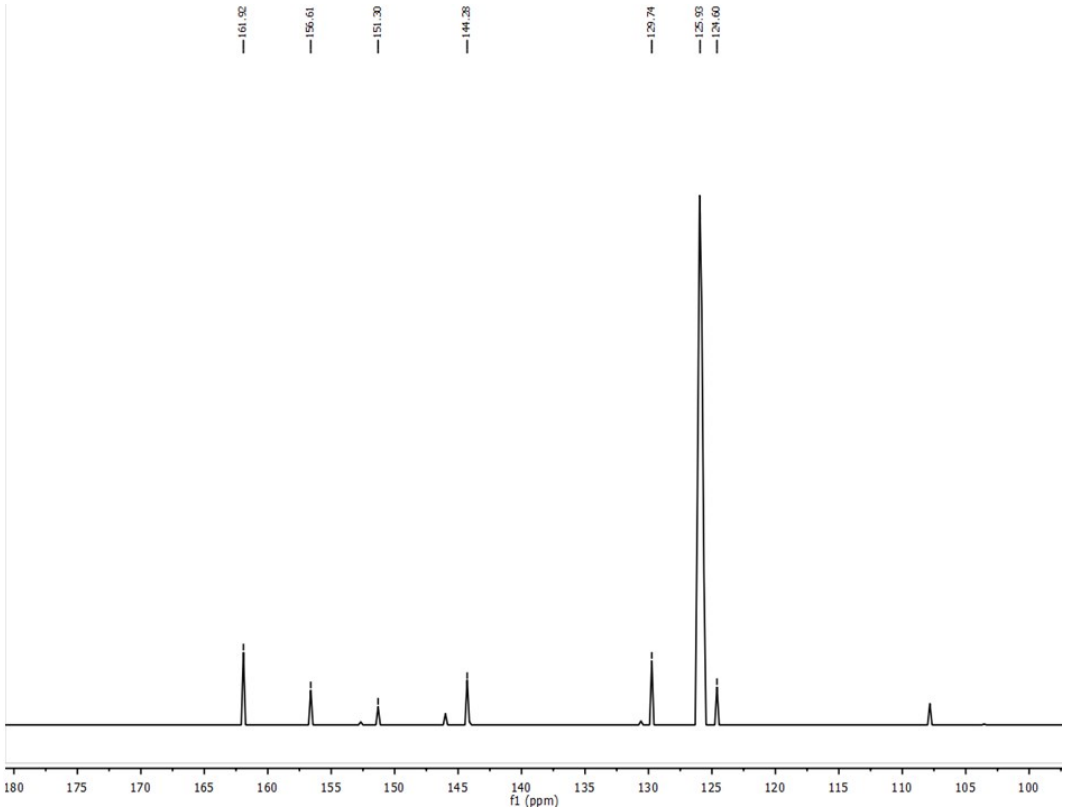


**Figure S7.** NMR $^{13}C$ MASS spectrum recorded for **3,3'-DDS-S**.

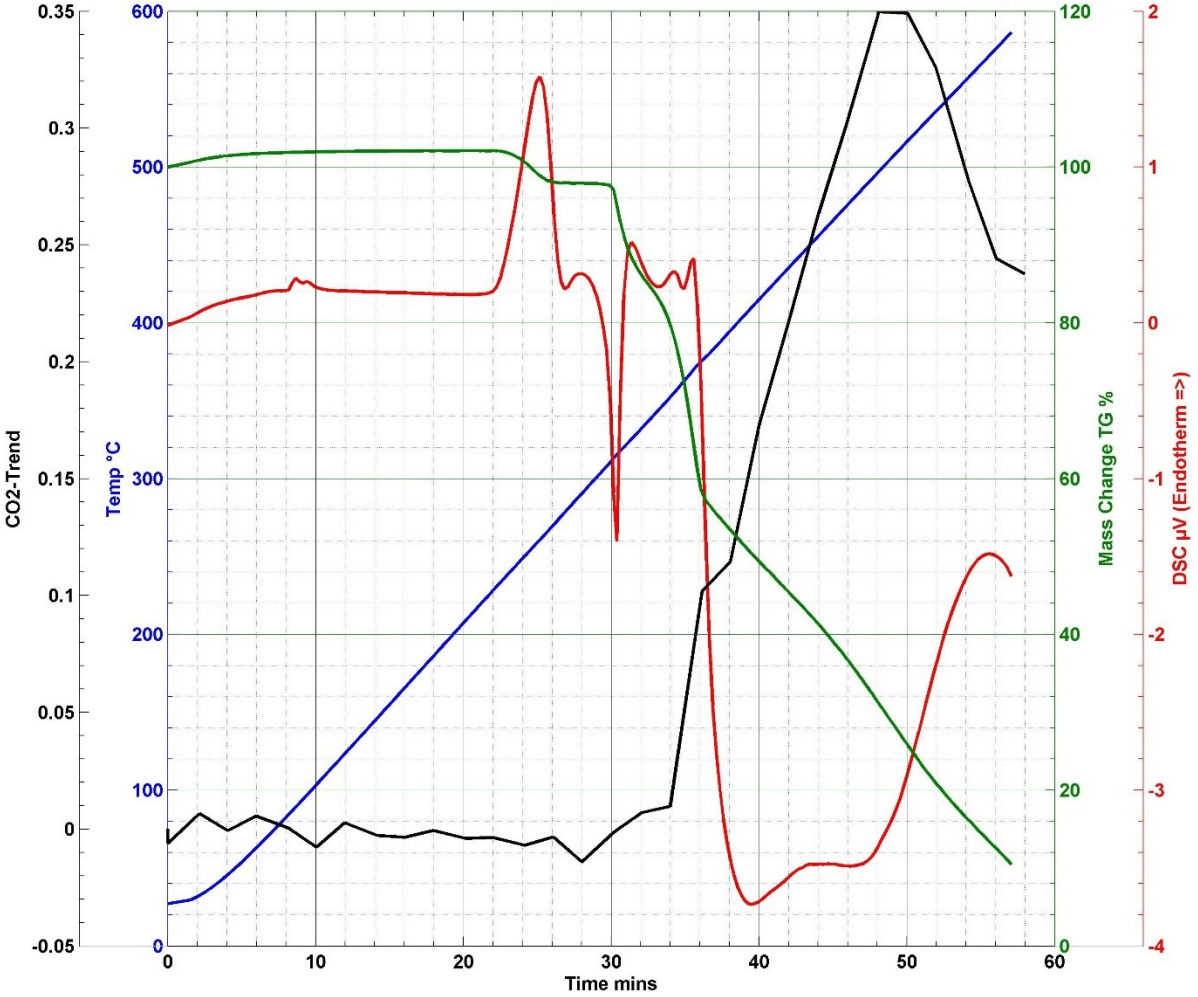


**Figure S8.** TGA-DSC of $CO_2$ gas releasing curves recorded for **4,4'-DDS-S.**

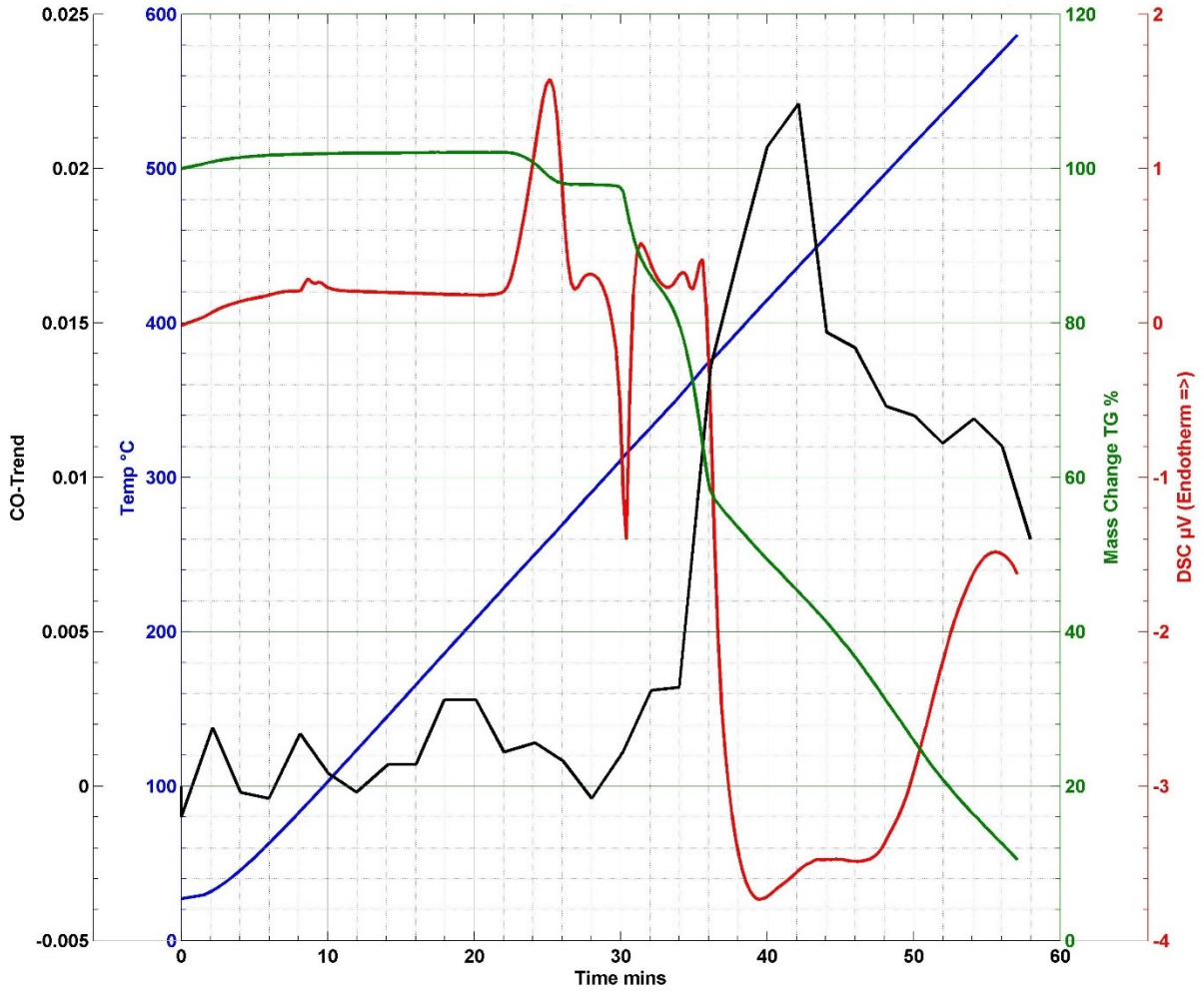


**Figure S9.** TGA-DSC of CO gas releasing curves recorded for **4,4'-DDS-S.**

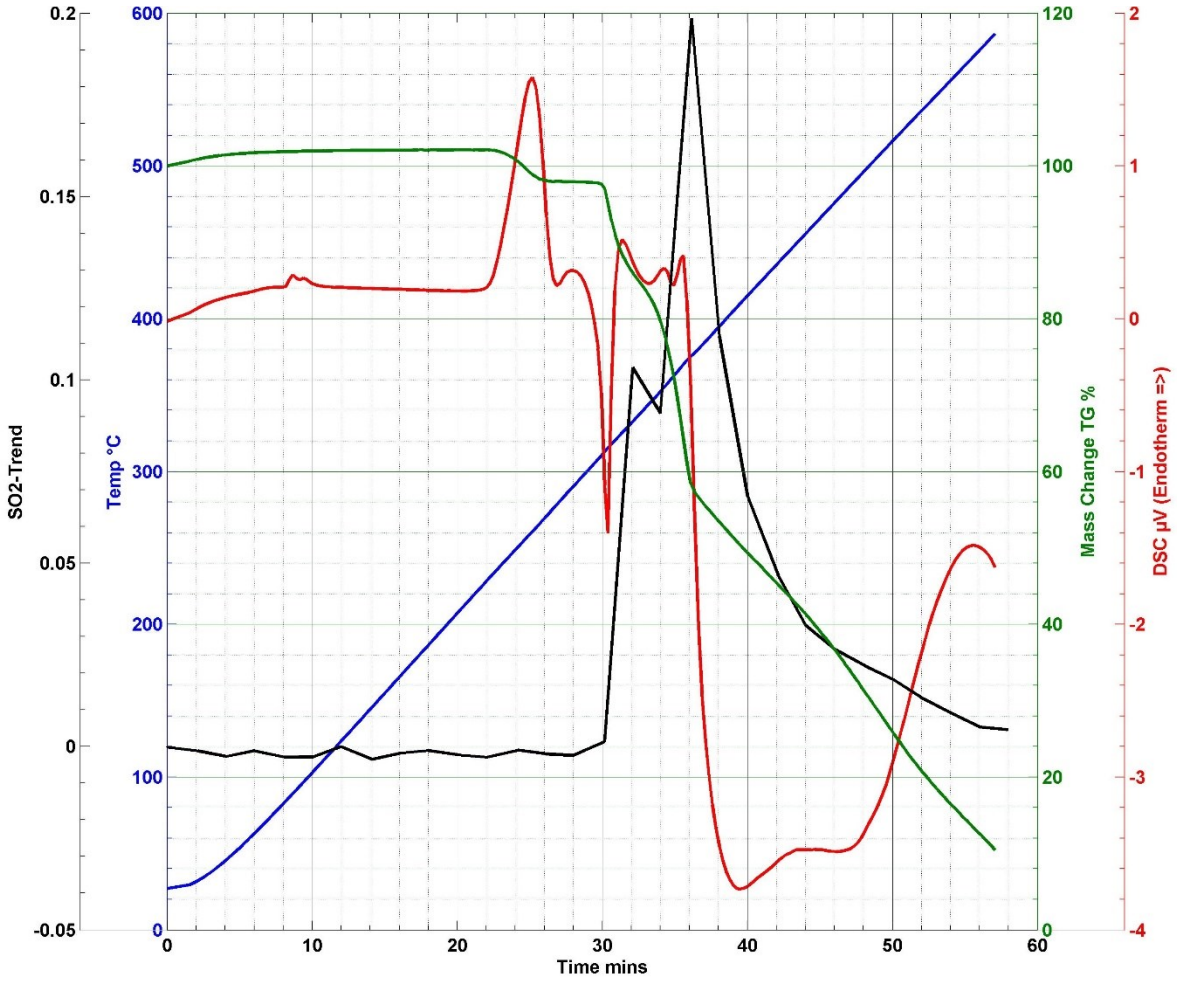


**Figure S10.** TGA-DSC of $SO_2$ gas releasing curves recorded for **4,4'-DDS-S.**

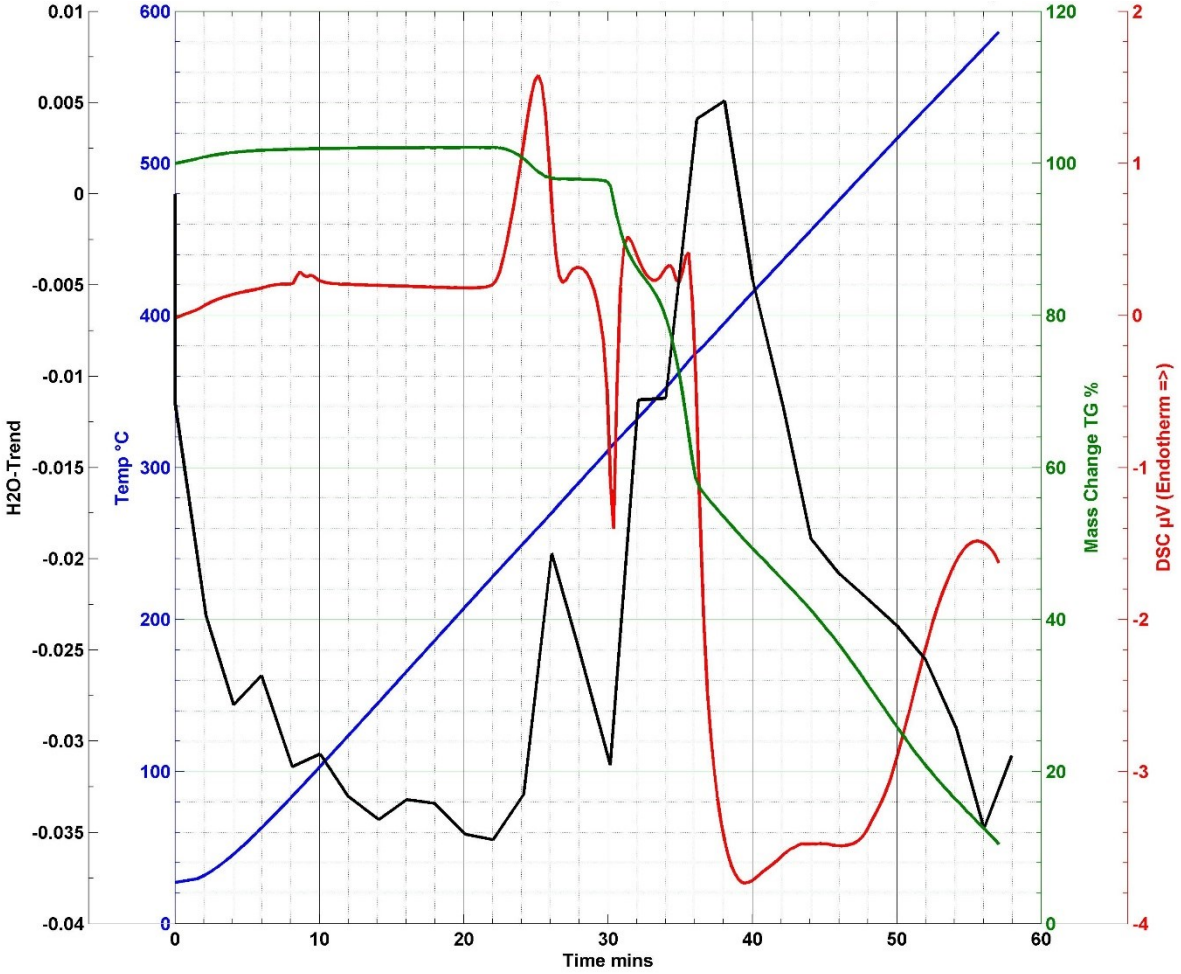


**Figure S11.** TGA-DSC of $H_2O$ gas releasing curves recorded for **4,4'-DDS-S.**

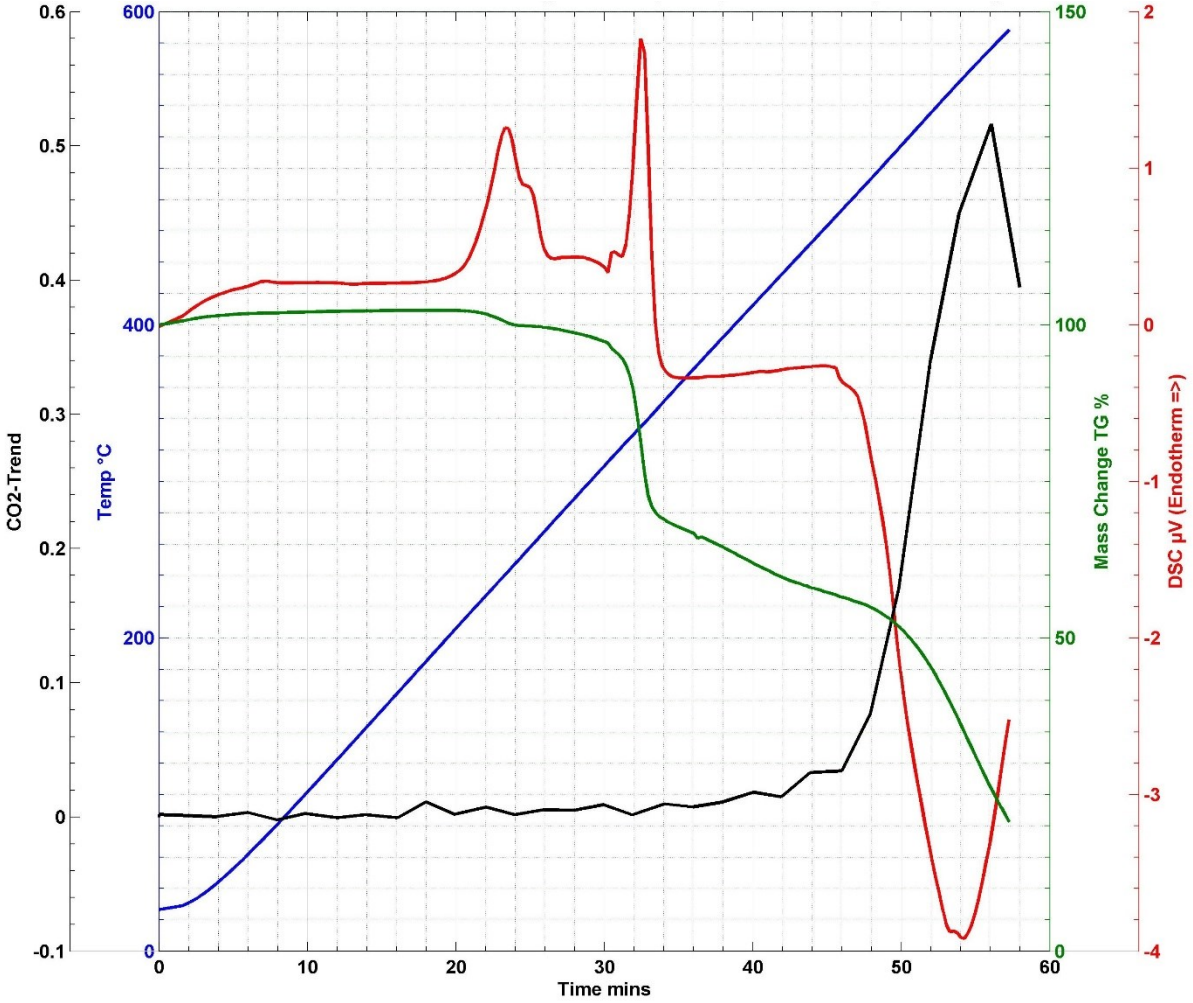


**Figure S12.** TGA-DSC of $CO_2$ gas releasing curves recorded for **3,3'-DDS-S.**

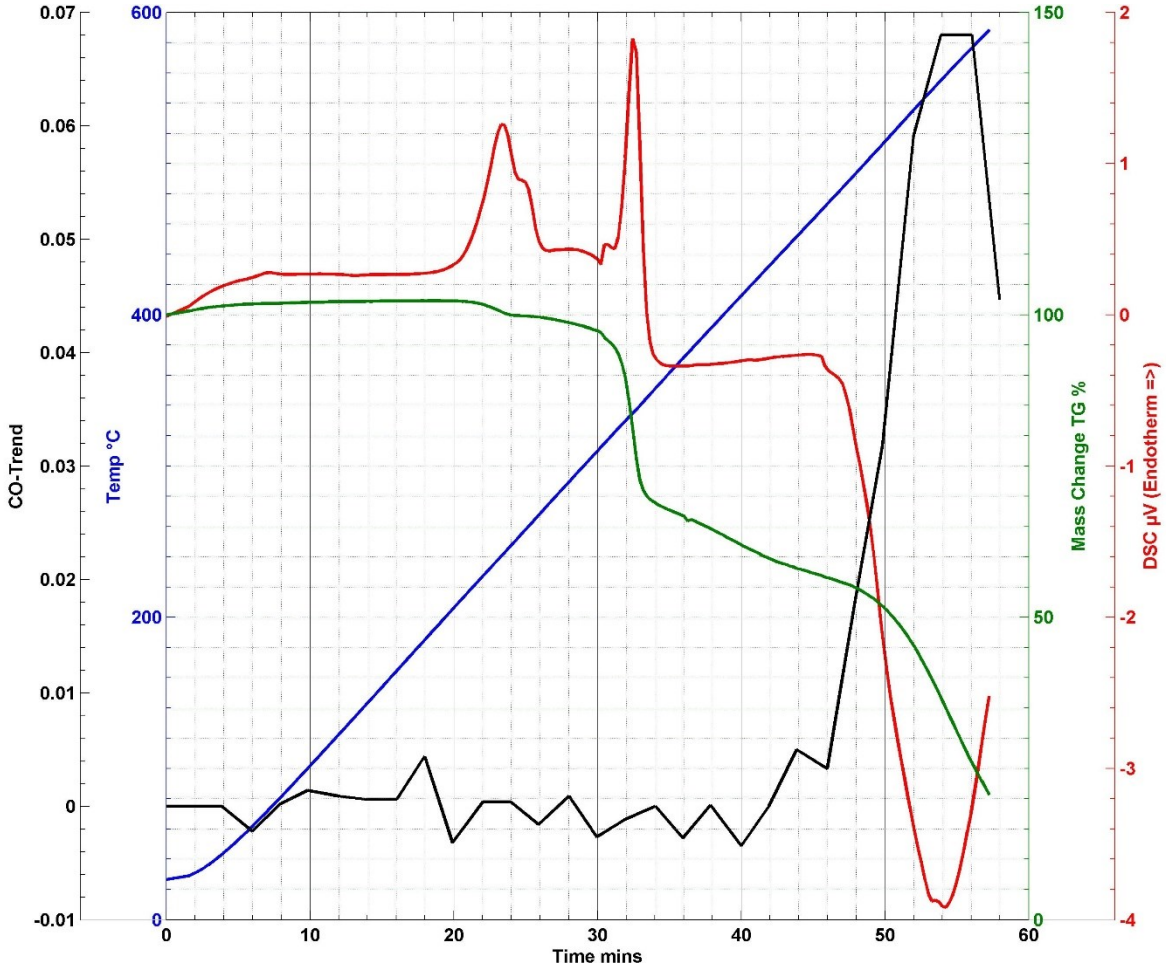


**Figure S13.** TGA-DSC of CO gas releasing curves recorded for **3,3'-DDS-S.**

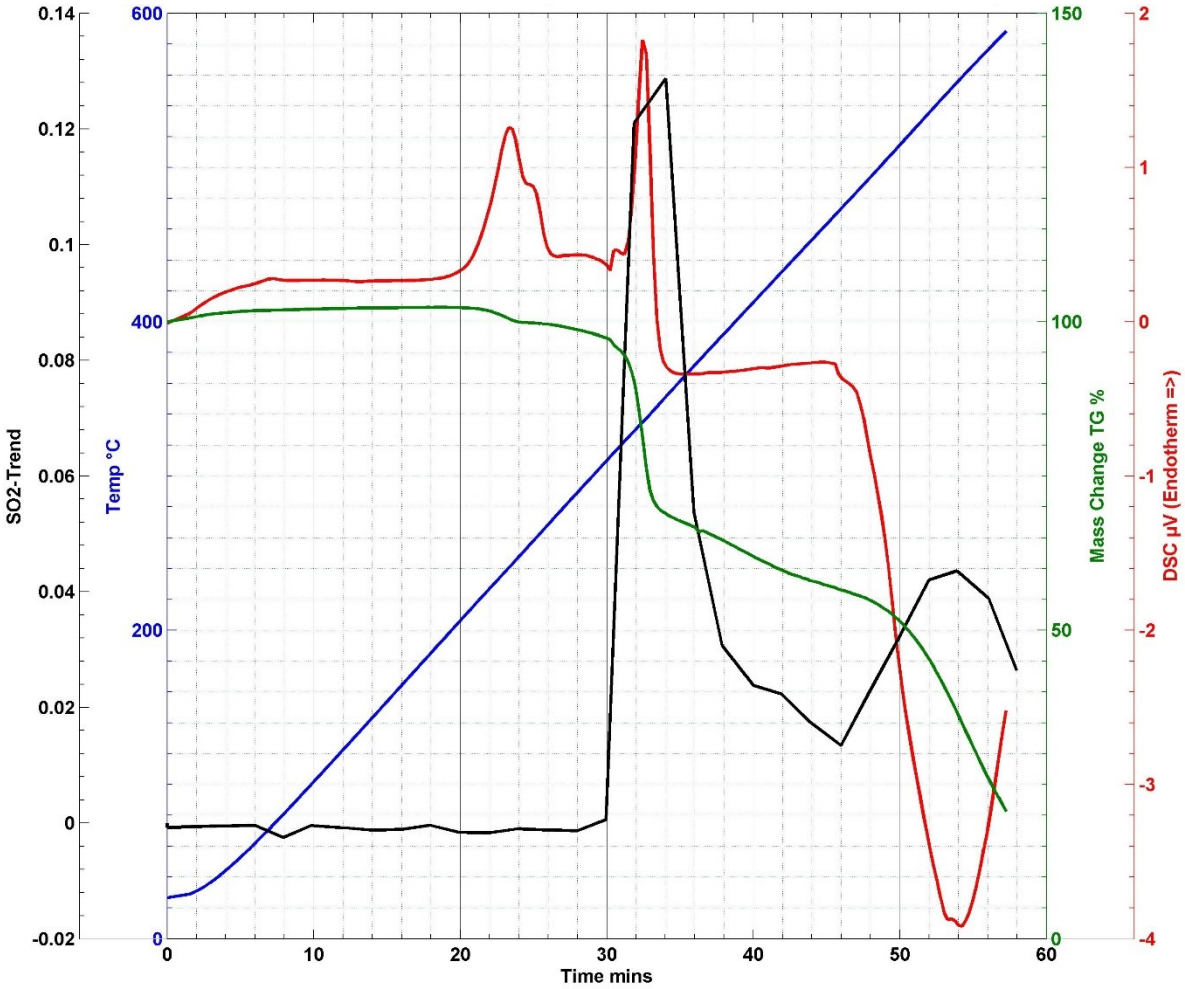


**Figure S14.** TGA-DSC of $SO_2$ gas releasing curves recorded for **3,3'-DDS-S.**

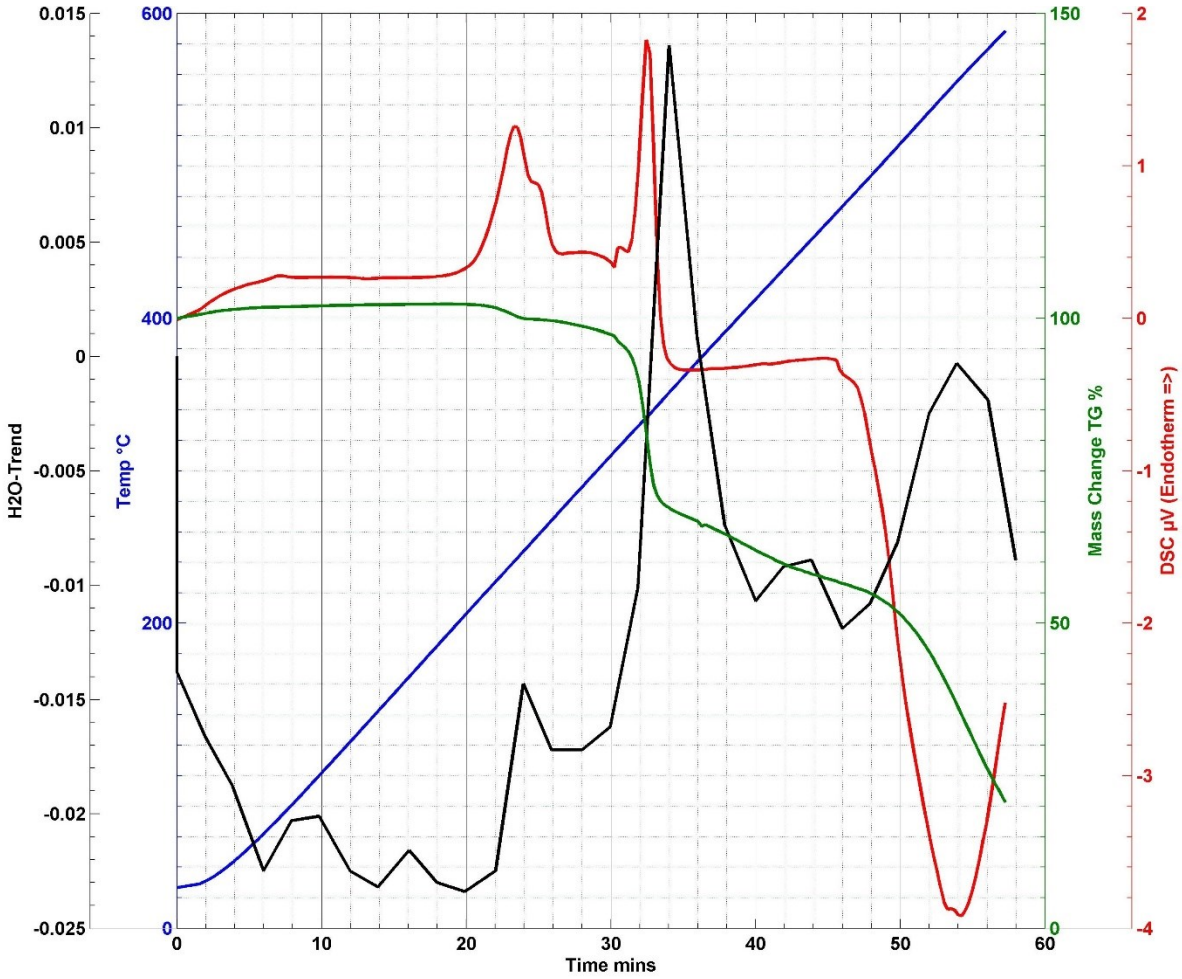


**Figure S15.** TGA-DSC of $H_2O$ gas releasing curves recorded for **3,3'-DDS-S.**

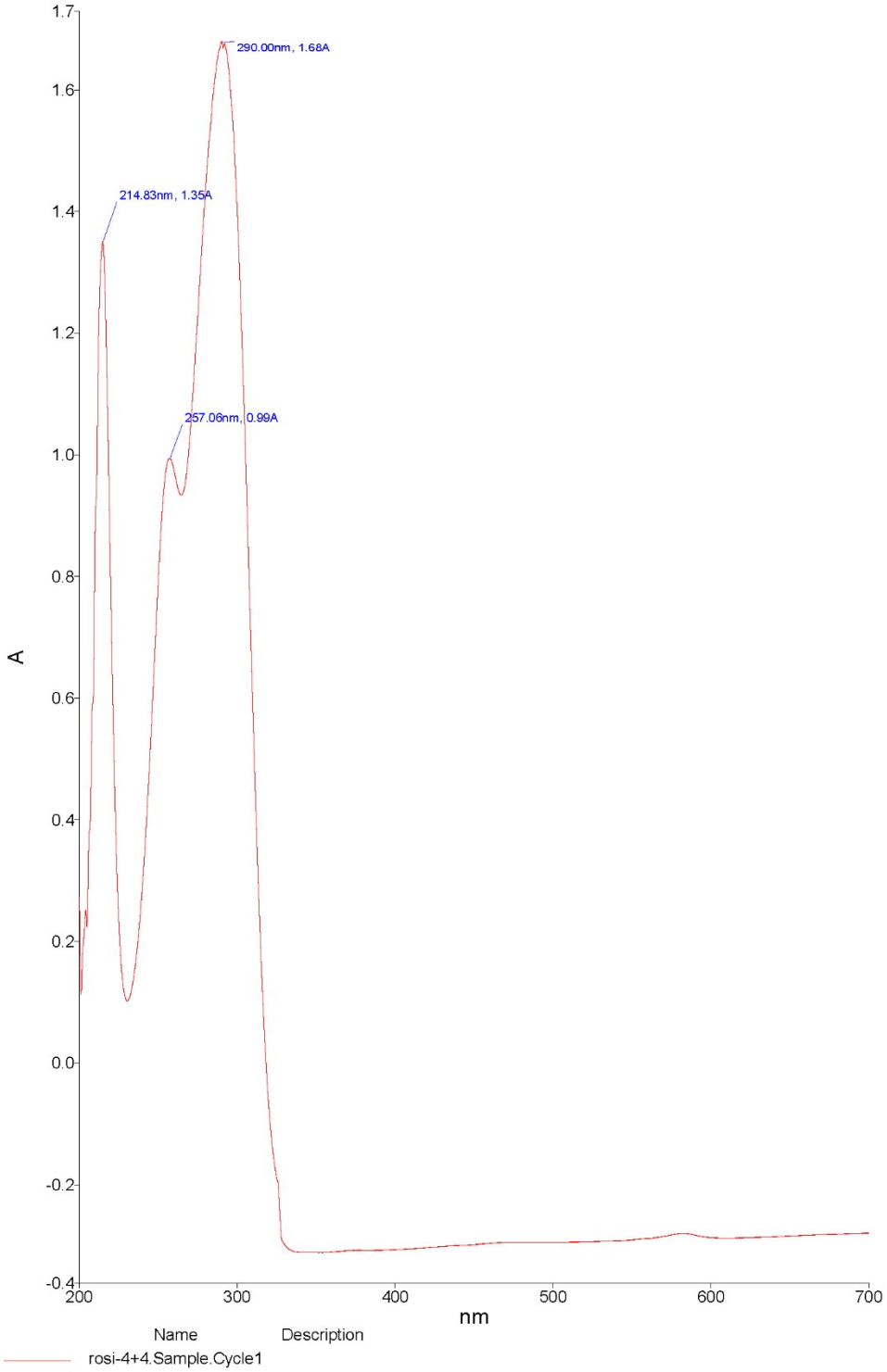


**Figure S16.** The UV-Vis spectrum recorded for **4,4'-DDS-S**.

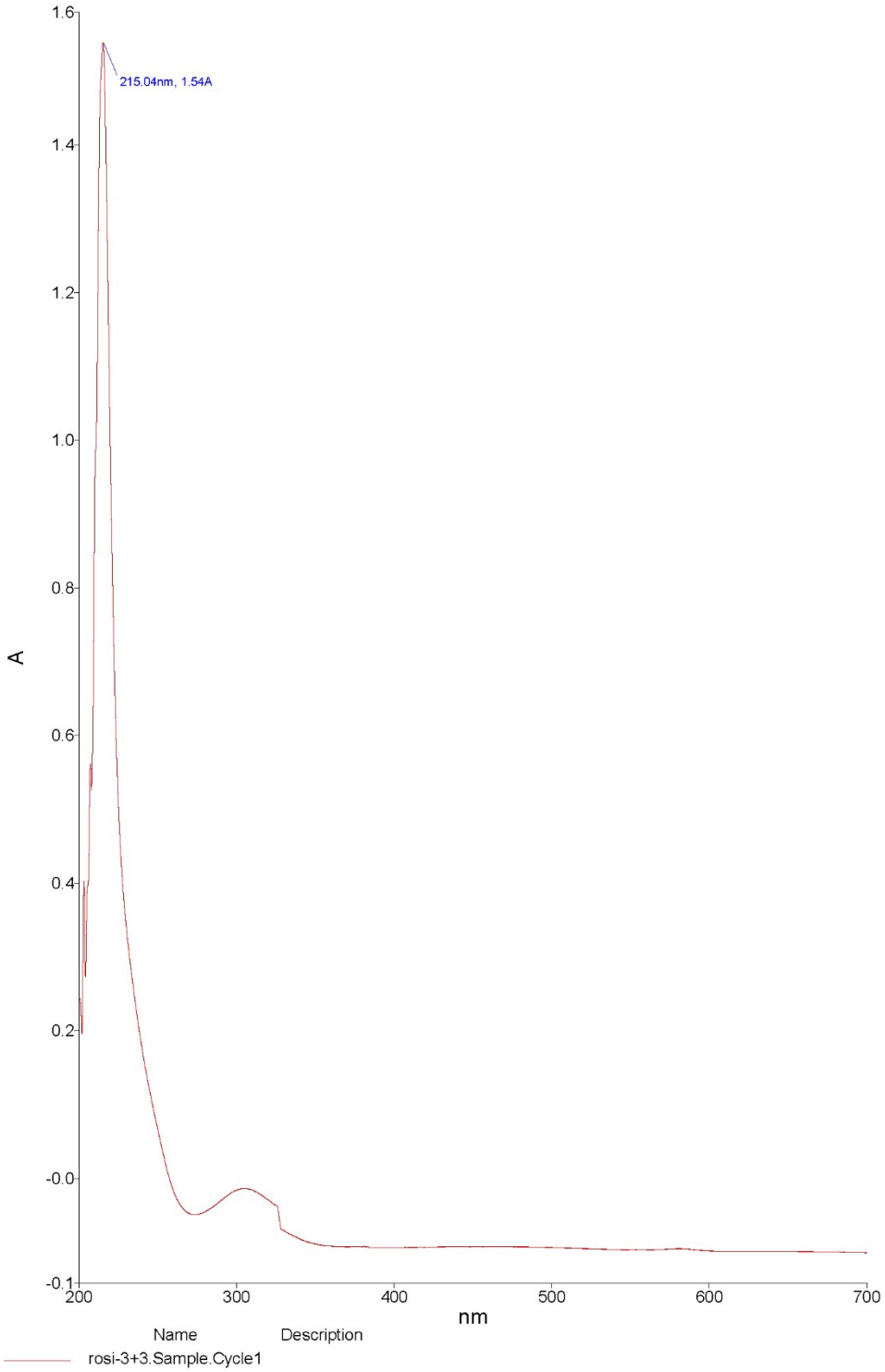


**Figure S17.** The UV-Vis spectrum recorded for **3,3'-DDS-S**.