SUPPORTING INFORMATION

Conducting chiral nickel(II) bis(dithiolene) complexes: structural and electron transport modulation with the charge and the number of stereogenic centres

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Experimental section

**General comments.** Reactions of complexation were carried out under Argon atmosphere using the Schlenk technique. All compounds were obtained as single crystals and characterized by X-ray diffraction measurement. Elemental analysis were recorded using Flash 2000 Fisher Scientific Thermo Electron analyzer.

**Synthesis of (rac)-1**

(rac)-5,6-dihydro-5-methyl-1,3-dithiolo[4,5-b][1,4]dithiine-2-thione ((rac)-1): This compound was synthesized according to our procedure previously reported.

Reference: N. Mroweh, P. Auban-Senzier, N. Vanthuyne, E. Canadell and N. Avarvari, *J. Mater. Chem. C*, 2019, 7, 12664–12673.

**Synthesis of (rac)-2**

5,6-Dihydro-5,6-dimethyl-1,3-dithiolo[4,5-b][1,4]dithiin-2-thione ((rac)-2): The trithione 2‘ has been prepared according to the literature procedure: N.Svenstrup and J. Becher, *Synthesis*, 1995, 215–235. Then, for the preparation of (rac)-2, we have modified the procedure briefly described in: G. C. Papavassiliou, G. A. Mousdis and A. Papadima, *Z. Naturforsch. B*, 2000, 55, 231–232. Trithione 2‘ (2 g, 0.01 mol) was added into a closed vessel containing 140 mL of toluene. Gaseous trans-2-butene (0.02 mol) has been pumped into this vessel and the mixture was refluxed for two hours at 110 °C. The solvent was then evaporated using rotary evaporator, and the crude product purified by column chromatography using petroleum spirit/dichloromethane 8/2 as eluent to afford a yellowish solid (2 g, 70%). The spectral data for (rac)-2 thus obtained match those reported in the literature: F. Pop, P. Auban-Senzier, A. Frąckowiak, K. Ptaszyński, I. Olejniczak, J. D. Wallis, E. Canadell and N. Avarvari, *J. Am. Chem. Soc.*, 2013, 135, 17176–17186.
Chiral HPLC

Analytical chiral HPLC separation for compound (rac)-1

![](image)

- The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

| Column       | Mobile Phase              | t1  | k1  | t2  | k2  | α   | Rs  |
|--------------|----------------------------|-----|-----|-----|-----|-----|-----|
| Chiralpak IF | Heptane / dichloromethane (80/20) | 12.14 | 3.12 | 13.20 | 3.48 | 1.12 | 2.39 |

Fig. S1 Analytical chiral HPLC separation for compound (rac)-1.

| RT [min] | Area | Area% | Capacity Factor | Enantioselectivity | Resolution (USP) |
|----------|------|-------|-----------------|--------------------|-------------------|
| 12.14    | 2945 | 49.94 | 3.12            |                    |                   |
| 13.20    | 2952 | 50.06 | 3.48            | 1.12               | 2.39              |
Semi-preparative separation for compound (rac)-1:

- Sample preparation: About 250 mg of compound (rac)-1 are dissolved in 8 mL of dichloromethane.
- Chromatographic conditions: Chiralpak IF (250 x 10 mm), hexane / dichloromethane (80/20) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
- Injections (stacked): 270 times 30 μL, every 5 minutes.
- First fraction: 95 mg of the first eluted ((-, CD 254nm)-enantiomer) with ee > 99%
- Second fraction: 72 mg of the second eluted ((+, CD 254 nm)-enantiomer) with ee > 98%
- Chromatograms of the collected fractions:

![Chromatogram](image1)

![Chromatogram](image2)

**Fig. S2** Chiral HPLC separation for compound (S)-1.

| RT [min] | Area | Area% |
|----------|------|-------|
| 12.27    | 1464 | 99.51 |
| 13.29    | 7    | 0.49  |
| Sum      | 1471 | 100.00|
**Optical rotations**

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp (589 nm), a halogen lamp (578 nm and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

| \( \lambda \) (nm) | \((S)\)-1 first eluted on Chiralpak IF \([\alpha]_{25}^{25} (\text{CH}_2\text{Cl}_2, c = 0.085)\) | \((R)\)-1 second eluted on Chiralpak IF \([\alpha]_{25}^{25} (\text{CH}_2\text{Cl}_2, c = 0.088)\) |
|---------------------|-------------------------------------------------|-------------------------------------------------|
| 589                 | -48                                             | +48                                             |
| 578                 | -45                                             | +45                                             |
| 546                 | -18                                             | +18                                             |
Analytical chiral HPLC separation for compound (rac)-2

![Chemical structure](image)

- The sample is dissolved in dichloromethane, injected on the chiral column, and detected with an UV detector at 254 nm and a circular dichroism detector at 254 nm. The flow-rate is 1 mL/min.

| Column       | Mobile Phase           | t1     | k1  | t2     | k2  | α    | Rs   |
|--------------|------------------------|--------|-----|--------|-----|------|------|
| Chiralpak ID | Heptane / dichloromethane (90/10) | 11.09 (-) | 2.76 | 12.15 (+) | 3.12 | 1.13 | 2.18 |

![HPLC chromatogram](image)

**Fig. S4** Analytical chiral HPLC separation for compound (rac)-2.

| RT [min] | Area | Area% | Capacity Factor | Enantioselectivity | Resolution (USP) |
|----------|------|-------|-----------------|--------------------|------------------|
| 11.09    | 1847 | 49.89 | 2.76            |                    |                  |
| 12.15    | 1856 | 50.11 | 3.12            | 1.13               | 2.18             |
Semi-preparative separation for compound (rac)-2:

- Sample preparation: About 312 mg of compound (rac)-2 are dissolved in 10 mL of dichloromethane.
- Chromatographic conditions: Chiralpak ID (250 x 10 mm), hexane / dichloromethane (90/10) as mobile phase, flow-rate = 5 mL/min, UV detection at 254 nm.
- Injections (stacked): 200 times 50 µL, every 4.8 minutes.
- First fraction: 134 mg of the first eluted with ee > 96 %
- Second fraction: 135 mg of the second eluted with ee > 94.5%
- Intermediate: 35 mg
- Chromatograms of the collected fractions:

![Chromatogram](image)

**Fig. S5** Chiral HPLC separation for compound (S,S)-2.

| RT [min] | Area   | Area% |
|----------|--------|-------|
| 10.47    | 25327  | 98.08 |
| 11.94    | 497    | 1.92  |
| Sum      | 25824  | 100.00|
Fig. S6 Chiral HPLC separation for compound \((R,R)\)-2.

| RT [min] | Area  | Area% |
|----------|-------|-------|
| 11.04    | 2149  | 2.66  |
| 11.71    | 78616 | 97.34 |
| Sum      | 80766 | 100.00|

**Optical rotations**

Optical rotations were measured on a Jasco P-2000 polarimeter with a sodium lamp (589 nm), a halogen lamp (578 nm and 546 nm), in a 10 cm cell, thermostated at 25°C with a Peltier controlled cell holder.

| \(\lambda\) (nm) | \((S,S)\)-2 first eluted on Chiralpak ID \([\alpha]_{25}^{25}\) (CH\(_2\)Cl\(_2\), c =0.07) | \((R,R)\)-2 second eluted on Chiralpak ID \([\alpha]_{25}^{25}\) (CH\(_2\)Cl\(_2\), c =0.07) |
|-----------------|-------------------------------------------------|-------------------------------------------------|
| 589             | - 371                                           | + 365                                           |
| 578             | - 400                                           | + 393                                           |
| 546             | - 560                                           | + 553                                           |
**Electronic Circular Dichroism (ECD) and UV-Visible spectroscopy**

ECD and UV spectra were measured on a JASCO J-815 spectrometer equipped with a JASCO Peltier cell holder PTC-423 to maintain the temperature at 25.0 ± 0.2°C. A CD quartz cell of 1 mm of optical pathlength was used. The CD spectrometer was purged with nitrogen before recording each spectrum, which was baseline subtracted. The baseline was always measured for the same solvent and in the same cell as the samples. The spectra are presented without smoothing and further data processing.

**Compound 1**

(S)-1, first eluted on Chiralpak IF: green solid line, concentration = 1.25 mmol.L⁻¹ in acetonitrile.

(R)-1, second eluted on Chiralpak IF: red dotted line, concentration = 1.25 mmol.L⁻¹ in acetonitrile.

Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.

![CD spectra](image1)

**Fig. S7** CD (top) and UV-Vis (bottom) spectra of (S)-1 (green line) and (R)-1 (red dotted line).
**Compound 2**

(S,S)-2, first eluted on Chiralpak ID: green solid line, concentration = 0.815 mmol.L⁻¹ in acetonitrile.
(R,R)-2, second eluted on Chiralpak ID: red dotted line, concentration = 0.816 mmol.L⁻¹ in acetonitrile.

Acquisition parameters: 0.1 nm as intervals, scanning speed 50 nm/min, band width 2 nm, and 3 accumulations per sample.

**Fig. S8** CD (top) and UV-Vis (bottom) spectra of (S,S)-2 (green line) and (R,R)-2 (red dotted line).
DFT and TD-DFT calculations

Compound (R)-1, axial conformation

Fig. S9 Two views of the optimized geometry of axial (R)-1 together with the atom numbering scheme.

| Total molecular energy | -2222.32542 hartrees |
|------------------------|----------------------|
| HOMO number            | 61                   |
| LUMO+1 energies        | -0.86 eV             |
| LUMO energies          | -1.92 eV             |
| HOMO energies          | -5.99 eV             |
| HOMO-1 energies        | -6.60 eV             |

Geometry optimization specific results
Converged nuclear repulsion energy 1133.85712 Hartrees

Frequency and Thermochemistry specific results
Number of negative frequencies 0

- Sum of electronic and zero-point energy -2222.21604 Hartrees
- Sum of electronic and thermal energies at 298.15 K -2222.20453 Hartrees
- Enthalpy at 298.15 K -2222.20458 Hartrees
- Gibbs free energy at 298.15 K -2222.25506 Hartrees
- Entropy at 298.15 K 0.00017 Hartrees

Calculated mono-electronic excitations

| E.S. | Symmetry | nm | cm^{-1} | f | R | Lambda | dCT | qCT Excitation description in % |
|------|----------|----|---------|---|---|---------|-----|---------------------------------|
| 1    | Singlet-A | 410 | 24357   | 0.001 | 28.812 | 0.47 | 114.73 | 0.50 | 60->62 (95) 61->62 (4) |
| 2    | Singlet-A | 360 | 27722   | 0.118 | -37.983 | 0.60 | 295.20 | 0.61 | 59->62 (2) 60->62 (3) 61->62 (92) |
| 3    | Singlet-A | 324 | 30829   | 0.001 | -2.759 | 0.49 | 47.82 | 0.74 | 61->63 (96) 61->64 (2) |
| 4    | Singlet-A | 287 | 34796   | 0.032 | 34.485 | 0.64 | 185.28 | 0.50 | 58->62 (6) 61->63 (2) 61->64 (85) 61->66 (2) |
| 5    | Singlet-A | 272 | 36669   | 0.001 | 0.405 | 0.36 | 265.62 | 0.78 | 58->62 (6) 60->63 (90) |
| 6    | Singlet-A | 271 | 36836   | 0.001 | 2.048 | 0.47 | 237.26 | 0.72 | 59->65 (2) 61->65 (94) |
| 7    | Singlet-A | 261 | 38225   | 0.104 | 10.730 | 0.60 | 276.27 | 0.54 | 59->62 (91) 60->69 (3) |
| 8    | Singlet-A | 254 | 39273   | 0.011 | 11.562 | 0.38 | 281.40 | 0.56 | 58->62 (70) 60->63 (4) 60->64 (6) 61->66 (12) |
| 9    | Singlet-A | 249 | 40111   | 0.003 | 13.038 | 0.23 | 446.32 | 0.84 | 58->62 (2) 60->63 (2) 60->64 (90) |
| 10   | Singlet-A | 237 | 42095   | 0.037 | 2.387 | 0.50 | 168.68 | 0.52 | 58->62 (9) 59->63 (18) 59->64 (11) 61->64 (5) 61->66 (42) 61->67 (6) |
| 11   | Singlet-A | 236 | 42322   | 0.008 | -39.742 | 0.42 | 2.36 | 0.68 | 58->62 (2) 58->65 (2) 59->63 (75) 61->66 (12) |
| 12   | Singlet-A | 228 | 43828   | 0.000 | 1.029 | 0.45 | 179.35 | 0.72 | 57->63 (2) 58->63 (86) 59->65 (5) |
| Atom and N° | Hirshfeld charge | CM5 charge | Mulliken charge |
|------------|------------------|------------|----------------|
| C 11       | -0.258           | -0.112     | -0.319         |
| S 12       | -0.182           | -0.199     | -0.136         |
| C 8        | -0.169           | -0.058     | -0.329         |
| S 5        | +0.126           | +0.099     | +0.225         |
Fig. S10 HOMO, LUMO, HOMO-1 and LUMO+1 (from top to bottom, two views each) of axial (R)-1.

Fig. S11 Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) of axial (R)-1. The excited electron and hole regions are indicated by respectively blue and white surfaces.
**Fig. S12** Calculated UV-vis absorption spectrum of axial (R)-1 with a gaussian broadening (FWHM = 3000 cm⁻¹).

**Fig. S13** Calculated CD spectrum of axial (R)-1 with a gaussian broadening (FWHM = 3000 cm⁻¹).
Compound (S)-1, axial conformation

Fig. S14 Two views of the optimized geometry of axial (S)-1 together with the atom numbering scheme.

Total molecular energy
-2222.32542 hartrees

HOMO number 61
LUMO energies
-1.92 eV
LUMO+1 energies
-0.86 eV
HOMO energies
-5.99 eV
HOMO-1 energies
-6.60 eV

Geometry optimization specific results
Converged nuclear repulsion energy 1133.84361 Hartrees

Frequency and Thermochemistry specific results
Number of negative frequencies 0
Sum of electronic and zero-point energy -2222.21604 Hartrees
Sum of electronic and thermal energies at 298.15 K -2222.20453 Hartrees
Enthalpy at 298.15 K -2222.20358 Hartrees
Gibbs free energy at 298.15 K -2222.25507 Hartrees
Entropy at 298.15 K 0.00017 Hartrees

Calculated mono-electronic excitations

| E.S. | Symmetry | nm  | cm-1 | f     | R    | Lambda dCT | qCT Excitation description in % |
|------|----------|-----|------|-------|------|-------------|---------------------------------|
| 1    | Singlet-A| 410 | 24357| 0.001 | -28.811 | 0.47 114.74 | 0.75 60->62 (95) 61->62 (4) |
| 2    | Singlet-A| 360 | 27722| 0.118 | 37.985  | 0.60 295.21 | 0.61 59->62 (2) 60->62 (3) 61->62 (92) |
| 3    | Singlet-A| 324 | 30830| 0.001 | 2.748   | 0.49 47.95  | 0.74 61->63 (96) 61->64 (2) |
| 4    | Singlet-A| 287 | 34797| 0.032 | -34.477 | 0.64 185.39 | 0.50 58->62 (6) 61->63 (2) 61->64 (85) 61->66 (2) |
| 5    | Singlet-A| 272 | 36669| 0.001 | -0.413  | 0.36 265.52 | 0.78 58->62 (6) 60->63 (90) |
| 6    | Singlet-A| 271 | 36839| 0.001 | -2.046  | 0.47 237.16 | 0.72 59->65 (2) 61->65 (94) |
| 7    | Singlet-A| 261 | 38225| 0.104 | -10.729 | 0.60 276.25 | 0.54 59->62 (91) 60->69 (3) |
| 8    | Singlet-A| 254 | 39274| 0.011 | -11.579 | 0.38 281.63 | 0.56 58->62 (70) 60->63 (4) 60->64 (6) 61->66 (12) |
| 9    | Singlet-A| 249 | 40113| 0.003 | -13.039 | 0.23 446.36 | 0.84 58->62 (2) 60->63 (2) 60->64 (90) |
| 10   | Singlet-A| 237 | 42098| 0.036 | -2.670  | 0.50 167.87 | 0.52 58->62 (9) 59->63 (19) 59->64 (11) 61->64 (5) 61->66 (42) 61->67 (6) |
| 11   | Singlet-A| 236 | 42324| 0.008 | 40.039  | 0.42 2.42  | 0.68 58->62 (2) 58->65 (2) 59->63 (75) 61->66 (12) |
| 12   | Singlet-A| 228 | 43829| 0.000 | -1.027  | 0.45 179.51 | 0.72 57->63 (2) 58->63 (86) 59->65 (5) |
| Atom and N° | Hirshfeld charge | CM5 charge | Mulliken charge |
|-------------|------------------|------------|-----------------|
| C 10        | -0.258           | -0.112     | -0.319          |
| S 12        | -0.182           | -0.199     | -0.136          |
| C 7         | -0.149           | -0.058     | -0.329          |
| H 13        | +0.120           | +0.060     | +0.189          |
| S 5         | +0.126           | +0.099     | +0.221          |
**Fig. S15** HOMO, LUMO, HOMO-1 and LUMO+1 (from top to bottom, two views each) of axial (S)-1.

**Fig. S16** Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) of axial (S)-1. The excited electron and hole regions are indicated by respectively blue and white surfaces.
Fig. S17 Calculated UV-vis absorption spectrum of axial (S)-1 with a gaussian broadening (FWHM = 3000 cm\(^{-1}\)).

Fig. S18 Calculated CD spectrum of axial (S)-1 with a gaussian broadening (FWHM = 3000 cm\(^{-1}\)).
Compound (R)-1, equatorial conformation

Fig. S19 Two views of the optimized geometry of equatorial (R)-1 together with the atom numbering scheme.

Total molecular energy -2222.32580 hartrees
HOMO number 61
LUMO+1 energies -0.84 eV
LUMO energies -1.91 eV
HOMO energies -5.97 eV
HOMO-1 energies -6.59 eV

Geometry optimization specific results
Converged nuclear repulsion energy 1119.80388 Hartrees

Frequency and Thermochemistry specific results
Number of negative frequencies 0
Sum of electronic and zero-point energy -2222.21652 Hartrees
Sum of electronic and thermal energies at 298.15 K -2222.20492 Hartrees
Enthalpy at 298.15 K -2222.20397 Hartrees
Gibbs free energy at 298.15 K -2222.25571 Hartrees
Entropy at 298.15 K 0.00017 Hartrees

Calculated mono-electronic excitations

| E.S. | Symmetry | nm | cm⁻¹ | f | R | Lambda dCT | qCT Excitation description in % |
|------|----------|----|------|---|---|------------|--------------------------------|
| 1    | Singlet-A | 409 | 24400 | 0.001 | -28.348 | 0.47 | 115.68 | 0.7560→62 (95) 61→62 (3) |
| 2    | Singlet-A | 361 | 27680 | 0.119 | 36.575 | 0.60 | 295.95 | 0.6159→62 (2) 60→62 (3) 61→62 (92) |
| 3    | Singlet-A | 323 | 30888 | 0.001 | 3.038 | 0.51 | 28.77 | 0.7061→63 (91) 61→64 (7) |
| 4    | Singlet-A | 290 | 34448 | 0.031 | -33.464 | 0.62 | 180.54 | 0.5258→62 (4) 61→63 (7) 61→64 (81) 61→66 (3) |
| 5    | Singlet-A | 271 | 36775 | 0.001 | -0.329 | 0.35 | 286.22 | 0.7958→62 (7) 60→63 (85) 60→64 (5) |
| 6    | Singlet-A | 269 | 37061 | 0.001 | 0.024 | 0.48 | 237.11 | 0.7359→65 (2) 61→65 (94) |
| 7    | Singlet-A | 261 | 38234 | 0.101 | -8.291 | 0.58 | 300.47 | 0.5459→62 (90) |
| 8    | Singlet-A | 255 | 39146 | 0.004 | -7.164 | 0.41 | 247.21 | 0.5558→62 (66) 59→64 (2) 60→63 (3) 60→64 (4) 61→66 (19) |
| 9    | Singlet-A | 249 | 40032 | 0.001 | -6.364 | 0.25 | 458.99 | 0.8560→63 (6) 60→64 (87) 61→66 (2) |
| 10   | Singlet-A | 239 | 41673 | 0.058 | 26.572 | 0.48 | 160.14 | 0.4758→62 (19) 59→64 (7) 61→64 (7) 61→66 (3) |
| 11   | Singlet-A | 235 | 42396 | 0.000 | 2.728 | 0.42 | 16.49 | 0.7559→63 (91) 59→64 (3) |
| 12   | Singlet-A | 227 | 44036 | 0.001 | -1.031 | 0.46 | 174.60 | 0.6957→63 (2) 58→63 (83) 58→64 (2) 59→65 (4) |
| 13   | Singlet-A | 224 | 44591 | 0.022 | -10.314 | 0.49 | 201.81 | 0.6858→64 (5) 59→63 (2) 59→64 (78) 61→66 (9) |
| 14   | Singlet-A | 220 | 45346 | 0.014 | -0.023 | 0.31 | 470.47 | 0.6760→65 (49) 61→67 (40) |
| 15   | Singlet-A | 220 | 45416 | 0.039 | 6.899 | 0.34 | 453.94 | 0.6660→65 (44) 61→67 (43) 61→68 (4) |

Atomic charges population analysis. Selection of the most charged atoms based on Hirshfeld analysis

| Atom and N° | Hirshfeld charge | CM5 charge | Mulliken charge |
|-------------|-----------------|------------|----------------|
|   | C 12 | S 10 | C 5  | S 9  |
|---|------|------|------|------|
| C 12 | -0.250 | -0.104 |      |      |
| S 10 | -0.182 | -0.199 |      |      |
| C 5  | -0.148 | -0.060 |      |      |
| H 11 | +0.119 | +0.062 |      |      |
| S 9  | +0.126 | +0.099 |      |      |

-0.386
-0.136
-0.363
+0.168
+0.220
**Fig. S20** HOMO, LUMO, HOMO-1 and LUMO+1 (from top to bottom, two views each) of equatorial (R)-1.

**Fig. S21** Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) of equatorial (R)-1. The excited electron and hole regions are indicated by respectively blue and white surfaces.
**Fig. S22** Calculated UV-vis absorption spectrum of equatorial (R)-1 with a gaussian broadening (FWHM = 3000 cm⁻¹).

**Fig. S23** Calculated CD spectrum of equatorial (R)-1 with a gaussian broadening (FWHM = 3000 cm⁻¹).
**Compound (S)-1, equatorial conformation**

Fig. S24 Two views of the optimized geometry of equatorial (S)-1 together with the atom numbering scheme.

| Total molecular energy | -2222.32580 hartrees |
|------------------------|-----------------------|
| HOMO number            | 61                    |
| LUMO+1 energies        |                       |
| LUMO energies          | -0.84 eV              |
| HOMO energies          | -1.91 eV              |
| Geometry optimization specific results |
| Converged nuclear repulsion energy | 1119.80413 Hartrees |

**Frequency and Thermochemistry specific results**

| Number of negative frequencies |
|-------------------------------|
| 0                             |
| Sum of electronic and zero-point energy | -2222.21652 Hartrees |
| Sum of electronic and thermal energies at 298.15 K | -2222.20492 Hartrees |
| Enthalpy at 298.15 K          | -2222.20397 Hartrees |
| Gibbs free energy at 298.15 K | -2222.25572 Hartrees |
| Entropy at 298.15 K           | 0.00017 Hartrees     |

| Calculated mono-electronic excitations | Excitation description in % |
|----------------------------------------|-----------------------------|
| E.S. | Symmetry | nm | cm⁻¹ | f | R | Lambda | dCT | qCT |                           |
|------|----------|----|------|---|---|--------|-----|-----|---------------------------|
| 1    | Singlet-A | 409| 24401| 0.001| 28.338| 0.47 | 115.69 | 0.75 | 60->62 (95) 61->62 (3)    |
| 2    | Singlet-A | 361| 27680| 0.119| -36.548| 0.60 | 295.97 | 0.61 | 59->62 (2) 60->62 (3) 61->62 (92) |
| 3    | Singlet-A | 323| 30889| 0.001| -3.041| 0.51 | 28.80 | 0.70 | 61->63 (91) 61->64 (7)    |
| 4    | Singlet-A | 290| 34451| 0.031| 33.450| 0.62 | 180.5 | 0.52 | 58->62 (4) 61->63 (7) 61->64 (81) 61->66 (3) |
| 5    | Singlet-A | 271| 36776| 0.001| 0.327| 0.35 | 286.15 | 0.79 | 58->62 (7) 60->63 (85) 60->64 (5) |
| 6    | Singlet-A | 269| 37062| 0.001| -0.050| 0.48 | 237.26 | 0.73 | 59->65 (2) 61->65 (94)    |
| 7    | Singlet-A | 261| 38234| 0.101| 8.278| 0.58 | 300.5 | 0.54 | 59->62 (90)               |
| 8    | Singlet-A | 255| 39146| 0.004| 7.175| 0.41 | 247.3 | 0.55 | 58->62 (66) 59->64 (2) 60->63 (3) 60->64 (4) 61->66 (19) |
| 9    | Singlet-A | 249| 40034| 0.001| 6.361| 0.25 | 458.98 | 0.85 | 60->63 (6) 60->64 (87) 61->66 (2) |
| 10   | Singlet-A | 239| 41673| 0.058| -26.543| 0.48 | 160.3 | 0.47 | 58->62 (19) 59->64 (6) 61->64 (7) 61->66 (55) |
| 11   | Singlet-A | 235| 42397| 0.000| -2.733| 0.42 | 16.56 | 0.75 | 59->63 (91) 59->64 (3)    |
| 12   | Singlet-A | 227| 44037| 0.001| 1.038| 0.46 | 174.6 | 0.69 | 57->63 (2) 58->63 (83) 58->64 (2) 59->65 (4) |
| 13   | Singlet-A | 224| 44593| 0.022| 10.311| 0.49 | 201.7 | 0.66 | 58->64 (5) 59->63 (2) 59->64 (78) 61->66 (9) |
| 14   | Singlet-A | 220| 45346| 0.013| 0.048| 0.32 | 464.48 | 0.67 | 60->65 (47) 61->67 (42)   |
| 15   | Singlet-A | 220| 45416| 0.040| -6.913| 0.33 | 460.6 | 0.67 | 60->65 (46) 61->67 (41) 61->68 (4) |

**Atomic charges population analysis. Selection of the most charged atoms based on Hirshfeld analysis**

| Atom and N° | Hirshfeld charge | CMS5 charge | Mulliken charge |
|-------------|------------------|-------------|-----------------|
| C 11        | -0.250           | -0.104      | -0.386          |
| S 10        | -0.182           | -0.199      | -0.136          |
| C 6         | -0.148           | -0.060      | -0.363          |
| H 12        | +0.119           | +0.062      | +0.168          |
Fig. S25 HOMO, LUMO, HOMO-1 and LUMO+1 (from top to bottom, two views each) of equatorial (S)-1.

Fig. S26 Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) of equatorial (S)-1. The excited electron and hole regions are indicated by respectively blue and white surfaces.
Fig. S27 Calculated UV-vis absorption spectrum of equatorial \((S)-1\) with a gaussian broadening \((\text{FWHM} = 3000 \text{ cm}^{-1})\).

Fig. S28 Calculated CD spectrum of equatorial \((S)-1\) with a gaussian broadening \((\text{FWHM} = 3000 \text{ cm}^{-1})\).
Compound (R,R)-2, axial conformation

Fig. S29 Two views of the optimized geometry of axial (R,R)-2 together with the atom numbering scheme.

Total molecular energy -2261.60481 hartrees
HOMO number 65
LUMO+1 energies -0.83 eV
LUMO energies -1.89 eV
HOMO energies -5.96 eV
HOMO-1 energies -6.57 eV

Geometry optimization specific results
Converged nuclear repulsion energy 1275.57674 Hartrees

Frequency and Thermochemistry specific results
Number of negative frequencies 0
Sum of electronic and zero-point energy -2261.46753 Hartrees
Sum of electronic and thermal energies at 298.15 K -2261.45455 Hartrees
Enthalpy at 298.15 K -2261.45361 Hartrees
Gibbs free energy at 298.15 K -2261.50809 Hartrees
Entropy at 298.15 K 0.00018 Hartrees

Calculated mono-electronic excitations

| E.S. | Symmetry | nm | cm⁻¹ | f | R | λ | dCT | qCT | Excitation description in % |
|------|----------|----|------|---|---|---|-----|-----|-------------------------------|
| 1    | Singlet-A | 410| 24359 | 0.001 | 28.177 | 0.47 | 116.18 | 0.76 | 64->66 (95) 65->66 (3) |
| 2    | Singlet-A | 360| 27727 | 0.121 | -36.643 | 0.60 | 297.24 | 0.61 | 63->66 (2) 64->66 (3) 65->66 (92) |
| 3    | Singlet-A | 324| 30860 | 0.001 | -2.202 | 0.48 | 53.29 | 0.75 | 65->67 (98) |
| 4    | Singlet-A | 281| 35564 | 0.028 | 29.191 | 0.65 | 141.86 | 0.61 | 62->66 (10) 65->68 (83) 65->70 (2) |
| 5    | Singlet-A | 272| 36777 | 0.002 | -3.800 | 0.24 | 522.67 | 0.87 | 64->69 (95) |
| 6    | Singlet-A | 272| 36757 | 0.001 | 0.749 | 0.48 | 243.17 | 0.55 | 63->66 (92) 64->73 (3) |
| 7    | Singlet-A | 261| 38248 | 0.108 | -9.202 | 0.61 | 277.20 | 0.55 | 63->66 (92) 64->73 (3) |
| 8    | Singlet-A | 254| 39229 | 0.015 | 19.696 | 0.40 | 293.81 | 0.57 | 62->66 (70) 64->67 (6) 64->68 (2) 65->68 (4) 65->70 (11) |
| 9    | Singlet-A | 245| 40651 | 0.001 | 10.564 | 0.22 | 442.16 | 0.88 | 64->68 (95) |
| 10   | Singlet-A | 236| 42198 | 0.026 | 20.334 | 0.47 | 101.66 | 0.60 | 62->66 (5) 63->67 (46) 63->68 (5) 65->68 (4) 65->70 (29) 65->71 (3) 65->72 (2) |
| 11   | Singlet-A | 235| 42373 | 0.021 | -59.950 | 0.46 | 93.10 | 0.61 | 62->66 (4) 62->69 (3) 63->67 (48) 63->68 (3) 65->68 (4) 65->70 (27) 65->71 (4) |
| 12   | Singlet-A | 229| 43664 | 0.000 | 1.034 | 0.45 | 183.53 | 0.74 | 61->67 (2) 62->67 (89) 63->69 (4) |
| 13   | Singlet-A | 226| 44078 | 0.005 | 6.765 | 0.47 | 371.54 | 0.66 | 65->70 (12) 65->71 (40) 65->72 (42) |
| 14   | Singlet-A | 222| 44926 | 0.043 | -3.800 | 0.24 | 522.67 | 0.87 | 64->69 (95) |
| 15   | Singlet-A | 219| 45542 | 0.026 | 35.839 | 0.51 | 212.65 | 0.64 | 63->68 (85) 65->70 (7) 65->71 (3) |
Atomic charges population analysis. Selection of the most charged atoms based on Hirshfeld analysis

| Atom and N° | Hirshfeld charge | CM5 charge | Mulliken charge |
|-------------|------------------|------------|----------------|
| C 4         | -0.262           | -0.113     | -0.297         |
| C 7         | -0.261           | -0.113     | -0.297         |
| S 20        | -0.183           | -0.201     | -0.138         |
Fig. S30 HOMO, LUMO, HOMO-1 and LUMO+1 (from top to bottom, two views each) of axial (R,R)-2.

Fig. S31 Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) of axial (R,R)-2. The excited electron and hole regions are indicated by respectively blue and white surfaces.
Fig. S32 Calculated UV-vis absorption spectrum of axial $(R,R)$-2 with a gaussian broadening (FWHM = 3000 cm$^{-1}$).

Fig. S33 Calculated CD spectrum of axial $(R,R)$-2 with a gaussian broadening (FWHM = 3000 cm$^{-1}$).
Compound (S,S)-2, axial conformation

Fig. S34 Two views of the optimized geometry of axial (S,S)-2 together with the atom numbering scheme.

- Total molecular energy: -2261.60481 hartrees
- HOMO number: 65
- LUMO+1 energies: -0.83 eV
- LUMO energies: -1.89 eV
- HOMO energies: -5.96 eV
- HOMO-1 energies: -6.57 eV

Geometry optimization specific results
- Converged nuclear repulsion energy: 1275.57484 Hartrees

Frequency and Thermochemistry specific results
- Number of negative frequencies: 0
- Sum of electronic and zero-point energy: -2261.46753 Hartrees
- Sum of electronic and thermal energies at 298.15 K: -2261.45455 Hartrees
- Enthalpy at 298.15 K: -2261.45361 Hartrees
- Gibbs free energy at 298.15 K: -2261.50808 Hartrees
- Entropy at 298.15 K: 0.00018 Hartrees

Calculated mono-electronic excitations

| E.S. | Symmetry | nm  | cm⁻¹  | f   | R   | Lambda | dCT  | qCT  | Excitation description in % |
|------|----------|-----|-------|-----|-----|--------|------|------|-----------------------------|
| 1    | Singlet-A| 410 | 24359 | 0.001 | -28.178 | 0.47  | 116.18 | 0.76 | 64->66 (95) 65->66 (3)   |
| 2    | Singlet-A| 360 | 27727 | 0.121 | 36.643 | 0.60  | 297.24 | 0.61 | 63->66 (2) 64->66 (3) 65->66 (92) |
| 3    | Singlet-A| 324 | 30860 | 0.001 | 2.203  | 0.48  | 53.30  | 0.75 | 65->67 (98)    |
| 4    | Singlet-A| 281 | 35564 | 0.028 | -29.194 | 0.65  | 141.86 | 0.47 | 62->66 (10) 65->68 (83) 65->70 (2) |
| 5    | Singlet-A| 272 | 36677 | 0.002 | -2.098 | 0.36  | 264.32 | 0.79 | 62->66 (6) 64->67 (91) |
| 6    | Singlet-A| 272 | 36757 | 0.001 | -0.749 | 0.48  | 243.17 | 0.74 | 63->69 (2) 65->69 (95) |
| 7    | Singlet-A| 261 | 38248 | 0.108 | -8.650 | 0.61  | 277.20 | 0.55 | 63->66 (92) 64->73 (3) |
| 8    | Singlet-A| 254 | 39229 | 0.015 | -19.695 | 0.40  | 293.79 | 0.57 | 62->66 (70) 64->67 (6) 64->68 (2) 65->68 (4) 65->70 (11) |
| 9    | Singlet-A| 245 | 40651 | 0.001 | -10.563 | 0.22  | 442.16 | 0.88 | 64->68 (95) |
| 10   | Singlet-A| 236 | 42197 | 0.026 | -20.320 | 0.47  | 101.77 | 0.60 | 62->66 (5) 63->67 (46) 63->68 (5) 65->68 (4) 65->70 (29) 65->71 (3) 65->72 (2) |
| 11   | Singlet-A| 236 | 42372 | 0.021 | 59.934 | 0.46  | 92.96  | 0.61 | 62->66 (4) 62->69 (3) 63->67 (48) 63->68 (3) 65->68 (4) 65->70 (27) 65->71 (4) |
| 12   | Singlet-A| 229 | 43664 | 0.000 | -1.033 | 0.45  | 183.52 | 0.74 | 61->67 (2) 62->67 (89) 63->69 (4) |
| 13   | Singlet-A| 226 | 44078 | 0.005 | -6.765 | 0.47  | 371.53 | 0.66 | 65->70 (12) 65->71 (40) 65->72 (42) |
| 14   | Singlet-A| 222 | 44926 | 0.043 | 3.801  | 0.24  | 522.67 | 0.87 | 64->69 (95) |
Atomic charges population analysis. Selection of the most charged atoms based on Hirshfeld analysis

| Atom and N° | Hirshfeld charge | CMS charge | Mulliken charge |
|-------------|------------------|------------|-----------------|
| C 4         | -0.262           | -0.113     | -0.297          |
| C 7         | -0.261           | -0.113     | -0.297          |
| S 20        | -0.183           | -0.201     | -0.138          |
**Fig. S35** HOMO, LUMO, HOMO-1 and LUMO+1 (from top to bottom, two views each) of axial (S,S)-2.

**Fig. S36** Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) of axial (S,S)-2. The excited electron and hole regions are indicated by respectively blue and white surfaces.
**Fig. S37** Calculated UV-vis absorption spectrum of axial (S,S)-2 with a gaussian broadening (FWHM = 300 cm\(^{-1}\)).

**Fig. S38** Calculated CD spectrum of axial (S,S)-2 with a gaussian broadening (FWHM = 3000 cm\(^{-1}\)).
**Compound (R,R)-2, equatorial conformation**

![Image of molecular structure](image)

**Fig. S39** Two views of the optimized geometry of equatorial (R,R)-2 together with the atom numbering scheme.

| Total molecular energy | -2261.60306 hartrees |
|------------------------|-----------------------|
| HOMO number            | 65                    |
| LUMO+1 energies        | -0.79 eV              |
| LUMO energies          | -1.87 eV              |
| HOMO energies          | -5.91 eV              |
| HOMO-1 energies        | -6.56 eV              |
| Geometry optimization specific results |
| Converged nuclear repulsion energy | 1250.94798 Hartrees |
| Frequency and Thermochemistry specific results |
| Number of negative frequencies | 1 |
| Sum of electronic and zero-point energy | -2261.46578 Hartrees |
| Sum of electronic and thermal energies at 298.15 K | -2261.45359 Hartrees |
| Enthalpy at 298.15 K   | -2261.45264 Hartrees  |
| Gibbs free energy at 298.15 K | -2261.50459 Hartrees |
| Entropy at 298.15 K    | 0.00017 Hartrees      |

### Calculated mono-electronic excitations

| E.S. | Symmetry | # | cm⁻¹ | λ | R | dCT | qCT | Excitation description in % |
|------|----------|---|------|---|---|-----|-----|-------------------------------|
| 1    | Singlet-A | 409 | 24405 | 0.002 | -32.603 | 0.47 | 113.54 | 0.75 64->66 (95) 65->66 (4) |
| 2    | Singlet-A | 364 | 27408 | 0.118 | 41.495 | 0.59 | 299.73 | 0.62 63->66 (2) 64->66 (4) 65->66 (92) |
| 3    | Singlet-A | 324 | 30778 | 0.001 | 3.388  | 0.54 | 11.68  | 0.67 65->67 (85) 65->68 (13) |
| 4    | Singlet-A | 293 | 34015 | 0.027 | -37.842 | 0.61 | 148.50 | 0.54 62->66 (3) 65->67 (12) 65->68 (75) 65->70 (4) |
| 5    | Singlet-A | 271 | 36853 | 0.001 | 0.037 | 0.35 | 302.05 | 0.78 62->66 (8) 64->67 (79) 64->68 (10) |
| 6    | Singlet-A | 267 | 37413 | 0.003 | -2.359 | 0.47 | 217.55 | 0.71 63->69 (2) 65->69 (92) |
| 7    | Singlet-A | 262 | 38152 | 0.105 | -7.408 | 0.60 | 267.28 | 0.53 63->66 (90) 64->72 (2) |
| 8    | Singlet-A | 257 | 38818 | 0.000 | -0.373 | 0.43 | 155.07 | 0.53 62->66 (55) 63->68 (2) 64->67 (4) 64->68 (2) 65->70 (32) |
| 9    | Singlet-A | 249 | 40113 | 0.001 | -0.632 | 0.27 | 449.38 | 0.84 64->67 (10) 64->68 (83) 65->70 (3) |
| 10   | Singlet-A | 242 | 41172 | 0.089 | 24.023 | 0.46 | 73.36  | 0.46 62->66 (30) 63->68 (2) 64->67 (3) 65->68 (7) 65->70 (46) |
| 11   | Singlet-A | 236 | 42359 | 0.000 | -3.931 | 0.44 | 20.42  | 0.75 63->67 (88) 63->68 (8) |
| 12   | Singlet-A | 226 | 44058 | 0.001 | 0.961  | 0.48 | 158.46 | 0.69 61->67 (2) 62->67 (82) 62->68 (5) 63->69 (4) |
| 13   | Singlet-A | 224 | 44460 | 0.017 | -10.787 | 0.48 | 191.10 | 0.67 63->67 (6) 63->68 (82) 65->70 (5) |
| 14   | Singlet-A | 223 | 44733 | 0.007 | 1.325  | 0.48 | 329.22 | 0.89 65->71 (91) 65->73 (3) |
| 15   | Singlet-A | 217 | 45900 | 0.020 | -0.945 | 0.48 | 119.36 | 0.61 62->68 (67) 62->70 (2) 63->69 (7) 64->69 (13) |

### Atomic charges population analysis. Selection of the most charged atoms based on Hirshfeld analysis

| Atom and N° | Hirshfeld charge | CM5 charge | Mulliken charge |
|-------------|------------------|------------|-----------------|
| C 14        | -0.251           | -0.105     | -0.43           |
| C 13        | -0.251           | -0.105     | -0.43           |
| S 12        | -0.184           | -0.201     | -0.138          |
| S 5         | +0.126           | +0.099     | +0.219          |
**Fig. S40** HOMO, LUMO, HOMO-1 and LUMO+1 (from top to bottom, two views each) of equatorial \((R,R)\)-2.

**Fig. S41** Representation of the Electron Density Difference \((S1-S0\text{ left})\) and \((S2-S0\text{ right})\) of equatorial \((R,R)\)-2. The excited electron and hole regions are indicated by respectively blue and white surfaces.
**Fig. S42** Calculated UV-vis absorption spectrum of equatorial $(R,R)$-$2$ with a gaussian broadening (FWHM = 3000 cm$^{-1}$).

**Fig. S43** Calculated CD spectrum of equatorial $(R,R)$-$2$ with a gaussian broadening (FWHM = 3000 cm$^{-1}$).
Compound (S,S)-2, equatorial conformation

Fig. S44 Two views of the optimized geometry of equatorial (S,S)-2 together with the atom numbering scheme.

Total molecular energy -2261.60307 hartrees
HOMO number 65
LUMO+1 energies -0.79 eV
LUMO energies -1.87 eV

HOMO energies -5.91 eV
HOMO-1 energies -6.56 eV

Geometry optimization specific results
Converged nuclear repulsion energy 1250.99903 Hartrees

Frequency and Thermochemistry specific results
Number of negative frequencies 1
Sum of electronic and zero-point energy -2261.46578 Hartrees
Sum of electronic and thermal energies at 298.15 K -2261.45359 Hartrees
Enthalpy at 298.15 K -2261.45265 Hartrees
Gibbs free energy at 298.15 K -2261.50460 Hartrees
Entropy at 298.15 K 0.00017 Hartrees

Calculated mono-electronic excitations

| E.S. | Symmetry | cm-1 | f | R | Lambda | dCT | qCT | Excitation description in % |
|------|----------|------|---|---|--------|-----|-----|----------------------------|
| 1    | Singlet-A | 0.002 | 31.979 | 0.47 | 113.91 | 0.75 | 64->66 (95) 65->66 (4) |
| 2    | Singlet-A | 0.119 | -40.618 | 0.59 | 299.96 | 0.62 | 63->66 (2) 64->66 (4) 65->66 (92) |
| 3    | Singlet-A | 0.001 | -3.323 | 0.53 | 14.24 | 0.68 | 65->67 (85) 65->68 (12) |
| 4    | Singlet-A | 0.028 | 37.420 | 0.61 | 150.16 | 0.53 | 62->66 (3) 65->67 (12) 65->68 (76) 65->70 (3) |
| 5    | Singlet-A | 0.001 | -0.060 | 0.35 | 299.29 | 0.78 | 62->66 (8) 64->67 (80) 64->68 (10) |
| 6    | Singlet-A | 0.003 | 0.998 | 0.46 | 246.52 | 0.70 | 65->69 (89) 65->70 (3) |
| 7    | Singlet-A | 0.104 | 7.602 | 0.60 | 268.58 | 0.53 | 63->66 (90) 64->72 (2) |
| 8    | Singlet-A | 0.000 | 0.839 | 0.43 | 162.46 | 0.53 | 62->66 (55) 63->68 (2) 64->67 (4) 64->68 (2) 65->70 (31) |
| 9    | Singlet-A | 0.001 | 0.803 | 0.27 | 450.10 | 0.84 | 64->67 (9) 64->68 (83) 65->70 (3) |
| 10   | Singlet-A | 0.068 | -23.019 | 0.46 | 83.72 | 0.47 | 62->66 (30) 63->68 (2) 64->67 (3) 65->68 (7) 65->69 (2) 65->70 (45) |
| 11   | Singlet-A | 0.000 | 3.430 | 0.44 | 18.33 | 0.75 | 63->67 (88) 63->68 (8) |
| 12   | Singlet-A | 0.001 | -0.341 | 0.48 | 154.37 | 0.69 | 61->67 (2) 62->67 (80) 62->68 (4) 63->68 (2) 63->69 (4) |
| 13   | Singlet-A | 0.016 | 10.492 | 0.49 | 177.80 | 0.68 | 62->67 (2) 62->68 (3) 63->67 (6) 63->68 (79) 65->70 (5) |
| 14   | Singlet-A | 0.006 | -1.288 | 0.48 | 329.81 | 0.69 | 65->71 (91) 65->73 (3) |
| 15   | Singlet-A | 0.015 | 1.084 | 0.44 | 149.20 | 0.58 | 62->68 (62) 63->69 (5) 64->69 (16) |

Atomic charges population analysis. Selection of the most charged atoms based on Hirshfeld analysis

| Atom and N° | Hirshfeld charge | CMS charge | Mulliken charge |
|-------------|-----------------|------------|----------------|
|     |   |   |     |
|-----|---|---|-----|
| C 13 | -0.251 | -0.105 | -0.431 |
| C 14 | -0.251 | -0.105 | -0.430 |
| S 12 | -0.184 | -0.201 | -0.138 |
| S 5  | +0.126 | +0.098 | +0.222 |
**Fig. S45** HOMO, LUMO, HOMO-1 and LUMO+1 (from top to bottom, two views each) of equatorial (S,S)-2.

**Fig. S46** Representation of the Electron Density Difference (S1-S0 left) and (S2-S0 right) of equatorial (S,S)-2. The excited electron and hole regions are indicated by respectively blue and white surfaces.
**Fig. S47** Calculated UV-vis absorption spectrum of equatorial (S,S)-2 with a gaussian broadening (FWHM = 3000 cm\(^{-1}\)).

**Fig. S48** Calculated CD spectrum of equatorial (S,S)-2 with a gaussian broadening (FWHM = 3000 cm\(^{-1}\)).
Table S1 Crystallographic data for (S,S)-, (R,R)- and (rac)-dm-ddt-thione 2

| Empirical formula | C₇H₈S₅ | C₇H₈S₅ | C₇H₈S₅ |
|-------------------|---------|---------|---------|
| Fw                | 252.43  | 252.43  | 252.43  |
| Crystal color     | Yellow  | Yellow  | Yellow  |
| Crystal size (mm³)| 0.40*0.07*0.03 | 0.40*0.04*0.02 | 0.11*0.08*0.06 |
| Temperature (K)   | 150     | 150     | 150     |
| Wavelength (Å)    | 1.54154 | 1.54184 | 1.54184 |
| Crystal system, Z | Monoclinic, 4 | Monoclinic, 4 | Monoclinic, 4 |
| Space group       | P₂₁     | P₂₁     | P₂₁/n   |
| a (Å)             | 7.4413(2) | 7.4434(2) | 13.2577 (9) |
| b (Å)             | 15.6747(4) | 15.6819(4) | 5.9544 (4) |
| c (Å)             | 8.6991(2) | 8.7048(2) | 13.8006 (8) |
| α (°)             | 90      | 90      | 90      |
| β (°)             | 92.916(2) | 92.980(2) | 106.797 (7) |
| γ (°)             | 90      | 90      | 90      |
| V (Å³)            | 1013.35(4) | 1014.71(4) | 1042.96 (12) |
| ρ(calc) (g.cm⁻³)  | 1.655   | 1.652   | 1.608   |
| μ(CuKα) (mm⁻¹)    | 10.060  | 10.046  | 9.774   |
| θ range (°)       | 5.091–73.592 | 5.088–73.415 | 4.073–72.898 |
| Data collected    | 6956    | 7411    | 3768    |
| Data unique       | 3887    | 3915    | 2027    |
| Data observed     | 3670    | 3581    | 1624    |
| R(int)            | 0.0508  | 0.0561  | 0.0468  |
| Nb of parameters / restraints | 217/1 | 217/1 | 129/0 |
| Flack parameter   | 0.07(5) | -0.08(3) | -       |
| R1(Fobs, I > 2σ(I)) | 0.0449  | 0.0419  | 0.0444  |
| wR2(F²) all data | 0.1378  | 0.1153  | 0.1188  |
| S(F²)c all data   | 1.077   | 1.055   | 1.015   |
Fig. S49 View of the structures of $S,S$-dm-dddt-thione (top left) and $R,R$-dm-dddt-thione (top right) in the $bc$ plane and $rac$-dm-dddt-thione in the $ac$ plane (bottom). Color code: C (black), H (cyan), S (yellow).
Table S2 Crystallographic data for (TBA)[Ni(S-me-dddt)$_2$], (TBA)[Ni(R-me-dddt)$_2$], (TBA)[Ni(S-me-dddt)(R-me-dddt)] and (TBA)[Ni(S-me-dddt)(R-me-dddt)] obtained by scrambling experiment

|                        | (TBA) [Ni(S-me-dddt)$_2$] | (TBA) [Ni(R-me-dddt)$_2$] | (TBA) [Ni(S-me-dddt)(R-me-dddt)] | (TBA) [Ni(S-me-dddt)(R-me-dddt)] scrambl
|------------------------|-----------------------------|-----------------------------|-----------------------------------|-----------------------------------------|
| Empirical formula      | C$_{26}$H$_{48}$NNiS$_8$    | C$_{26}$H$_{48}$NNiS$_8$    | C$_{26}$H$_{48}$NNiS$_8$          | C$_{26}$H$_{48}$NNiS$_8$              |
| Fw                     | 689.84                      | 689.84                      | 689.84                            | 689.84                                 |
| Crystal color          | Green                       | Green                       | Green                             | Green                                  |
| Crystal size (mm$^3$)  | 0.05*0.03*0.02              | 0.10*0.03*0.02              | 0.12*0.08*0.02                    | 0.12*0.06*0.03                        |
| Temperature (K)        | 150                         | 150                         | 150                               | 150                                    |
| Wavelength (Å)         | 1.54184                     | 1.54154                     | 1.54184                           | 1.54184                                |
| Crystal system, Z      | Triclinic, 2                | Triclinic, 2                | Triclinic, 2                      | Triclinic, 2                           |
| Space group            | P1                          | P1                          | P-1                               | P-1                                    |
| a (Å)                  | 9.3775 (4)                  | 9.3629 (7)                  | 9.3679 (7)                        | 9.3679 (7)                             |
| b (Å)                  | 13.5118 (4)                 | 13.5340 (7)                 | 13.5115 (10)                      | 13.5115 (10)                           |
| c (Å)                  | 13.7352 (5)                 | 13.7348 (7)                 | 13.8074 (9)                       | 13.8074 (9)                            |
| α (°)                  | 83.682 (3)                  | 83.774 (4)                  | 83.771 (6)                        | 83.771 (6)                             |
| β (°)                  | 77.681 (3)                  | 77.788 (5)                  | 76.905 (6)                        | 76.905 (6)                             |
| γ (°)                  | 87.481 (3)                  | 87.427 (5)                  | 87.281 (6)                        | 87.281 (6)                             |
| V (Å$^3$)              | 1689.57 (11)                | 1690.59 (18)                | 1691.7 (2)                        | 1691.7 (2)                             |
| ρ$_{calc}$ (g.cm$^{-3}$)| 1.356                       | 1.355                       | 1.354                             | 1.360                                  |
| μ(CuKα) (mm$^{-1}$)    | 5.571                       | 5.567                       | 5.564                             | 5.589                                  |
| θ range (°)            | 3.292–73.696                | 3.286–74.116                | 3.291–73.612                      | 3.298–73.189                           |
| Data collected         | 28197                       | 27719                       | 12886                             | 26519                                  |
| Data unique            | 12527                       | 12475                       | 6561                              | 6435                                   |
| Data observed          | 9826                        | 8028                        | 4648                              | 5140                                   |
| R(int)                 | 0.0376                      | 0.0566                      | 0.0387                            | 0.0449                                 |
| Nb of parameters / restraints | 649/47                     | 649/78                      | 346/27                            | 346/34                                 |
| Flack parameter        | 0.105 (18)                  | 0.12 (3)                    | -                                 | -                                      |
| R1(F), I > 2σ(I)       | 0.0705                      | 0.0744                      | 0.0824                            | 0.1046                                 |
| wR2(F$^2$), all data  | 0.2060                      | 0.2255                      | 0.2421                            | 0.3208                                 |
| S(F$^2$), all data    | 1.063                       | 1.059                       | 1.069                             | 1.136                                  |

$^a$R1(F) = Σ||F$_{0}$| - |Fc||/Σ|F$_{0}$|; $^b$wR2(F$^2$) = [Σw(F$_{0}^2$-F$_{C}^2$)$^2$/ΣwF$_{0}^4$]$^{1/2}$; $^c$S(F$^2$) = [Σw(F$_{0}^2$-F$_{C}^2$)$^2$/(n+r-p)]$^{1/2}$.
Fig. S50 Structure of (TBA)[Ni(S-me-dddt)$_2$] (a), (TBA)[Ni(R-me-dddt)$_2$] (b) and (TBA)[Ni(S-me-dddt)(R-me-dddt)] (c) with atom label.
Fig. S51 Highlighting axial and equatorial positions of the methyl substituents from two consecutive *trans* isomers in (TBA)[Ni(S-me-dddt)₂] (a), (TBA)[Ni(R-me-dddt)₂] (b) and (TBA)[Ni(S-me-dddt)(R-me-dddt)] (c). The resulting C–H⋯S intermolecular interactions are represented in orange dashed lines. Color code: C (black), H (cyan), S (yellow), Ni (green).
Table S3 Crystallographic data for (TBA)[Ni(\(S,S\)-dm-dddt)\((R,R\)-dm-dddt)]]

|                          | (TBA) [Ni(\(S,S\)-dm-dddt)\((R,R\)-dm-dddt)] | (TBA) [Ni(\(S,S\)-dm-dddt)\((R,R\)-dm-dddt)] |
|--------------------------|-----------------------------------------------|-----------------------------------------------|
| Empirical formula        | \(C_{28}H_{52}NNiS_8\)                      | \(C_{28}H_{52}NNiS_8\)                      |
| Fw                       | 717.89                                        | 717.89                                        |
| Crystal color            | Green                                         | Green                                         |
| Crystal size (\(\text{mm}^3\)) | 0.28*0.25*0.08                                | 0.28*0.25*0.08                               |
| Temperature (K)          | 297                                           | 297                                           |
| Wavelength (Å)           | 1.54184                                       | 1.54184                                       |
| Crystal system, Z        | Triclinic, 2                                  | Triclinic, 2                                  |
| Space group              | \(P-1\)                                       | \(P-1\)                                       |
| a (Å)                    | 9.9746 (3)                                    | 9.9129 (2)                                    |
| b (Å)                    | 12.8587 (4)                                   | 12.6872 (4)                                   |
| c (Å)                    | 15.4306 (5)                                   | 15.3643 (5)                                   |
| α (°)                    | 81.684 (3)                                    | 81.603 (3)                                    |
| β (°)                    | 80.287 (3)                                    | 80.128 (2)                                    |
| γ (°)                    | 69.560 (3)                                    | 68.888 (3)                                    |
| V (Å\(^3\))              | 1820.05 (11)                                  | 1768.45 (10)                                  |
| \(\rho_{\text{calc}}\) (g cm\(^{-3}\)) | 1.310                                         | 1.348                                         |
| \(\mu\) (CuK\(\alpha\)) (mm\(^{-1}\)) | 5.192                                         | 5.343                                         |
| \(\theta\) range (°)    | 2.918–73.509                                  | 2.932–76.323                                  |
| Data collected           | 12621                                         | 29990                                         |
| Data unique              | 7089                                          | 7142                                          |
| Data observed            | 6001                                          | 6981                                          |
| R(int)                   | 0.0334                                        | 0.0336                                        |
| Nb of parameters / restraints | 382/2                                     | 382/7                                         |
| Flack parameter          | -                                             | -                                             |
| \(R1(F)_a\) / \(I > 2\sigma(I)\) | 0.0516                                        | 0.0451                                        |
| \(wR2(F)^b\) all data   | 0.1639                                        | 0.1268                                        |
| \(S(F)^c\) all data     | 1.055                                         | 0.995                                         |

\(R1(F)_a = \Sigma ||F_0|| - |F_c||/\Sigma |F_0|; \) \(wR2(F)^b = [\Sigma w(F_0^2 - F_c^2)/\Sigma wF_0^4]^{1/2}; \) \(S(F)^c = [\Sigma w(F_0^2 - F_c^2)^2/(n+r-p)]^{1/2}.\)
Fig. S52 View of the structure of \((TBA)\text{[Ni}(S,S\text{-dm-dddt})\text{]}(R,R\text{-dm-dddt})\).
Table S4 Crystallographic data for (TMA)[Ni(S,S-dm-dddt)_2], (TMA)[Ni(R,R-dm-dddt)_2] and (TMA)[Ni(S,S-dm-dddt)(R,R-dm-dddt)]

|                              | (TMA) [Ni(S,S-dm-dddt)_2] | (TMA) [Ni(R,R-dm-dddt)_2] | (TMA) [Ni(S,S-dm-dddt)(R,R-dm-dddt)] |
|------------------------------|---------------------------|---------------------------|--------------------------------------|
| **Empirical formula**        | C_{16}H_{28}NNiS_8        | C_{16}H_{28}NNiS_8        | C_{16}H_{28}NNiS_8                   |
| **Fw**                       | 549.58                    | 549.58                    | 549.58                               |
| **Crystal color**            | Green                     | Green                     | Green                                |
| **Crystal size (mm³)**       | 0.2*0.17*0.09             | 0.28*0.25*0.12            | 0.15*0.11*0.05                       |
| **Temperature (K)**          | 150                       | 150                       | 150                                  |
| **Wavelength (Å)**           | 1.54184                   | 1.54184                   | 1.54184                              |
| **Crystal system, Z**        | Monoclinic, 4             | Monoclinic, 4             | Monoclinic, 4                        |
| **Space group**              | I2                        | I2                        | I2/a                                 |
| **a (Å)**                    | 17.5736 (4)               | 17.5730 (5)               | 27.1336 (11)                         |
| **b (Å)**                    | 9.9714 (2)                | 9.9665 (2)                | 9.9785 (3)                           |
| **c (Å)**                    | 15.7038 (4)               | 15.7025 (5)               | 15.7836 (7)                          |
| **α (°)**                    | 90                        | 90                        | 90                                   |
| **β (°)**                    | 119.990 (3)               | 119.996 (4)               | 145.935 (3)                          |
| **γ (°)**                    | 90                        | 90                        | 90                                   |
| **V (Å³)**                   | 2383.39 (11)              | 2381.80 (14)              | 2393.70 (19)                         |
| **ρ(calc) (g.cm⁻³)**         | 1.532                     | 1.533                     | 1.525                                |
| **μ(CuKα) (mm⁻¹)**           | 7.745                     | 7.750                     | 7.712                                |
| **θ range (°)**              | 3.091–72.063              | 3.091–71.946              | 5.303–73.476                         |
| **Data collected**           | 10593                     | 10384                     | 4853                                 |
| **Data unique**              | 4505                      | 4411                      | 2329                                 |
| **Data observed**            | 4450                      | 4371                      | 2084                                 |
| **R(int)**                   | 0.0186                    | 0.0188                    | 0.0266                               |
| **Nb of parameters / restraints** | 226/14                      | 231/1                      | 138/0                                |
| **R1(F), a I > 2σ(I)**       | 0.022 (10)                | 0.038 (10)                | -                                    |
| **wR2(F²), b all data**      | 0.0301                    | 0.0295                    | 0.0387                               |
| **S(F²), c all data**        | 0.0856                    | 0.0846                    | 0.1147                               |

\[ R1(F) = \frac{\sum|F_o| - |F_c|}{\sum|F_o|}; \quad \text{b} \quad wR2(F²) = \frac{\sum w(F_o² - F_c²)}{\sum wF_o}{²}^{1/2}; \quad \text{c} \quad S(F²) = \sqrt{\frac{\sum w(F_o² - F_c²)}{n+r-p}}{²}. \]
Fig. S53 Structures of (TMA)[Ni(S,S-dm-dddt)]_2 (a), (TMA)[Ni(R,R-dm-dddt)]_2 (b) and (TMA)[Ni(S,S-dm-dddt)(R,R-dm-dddt)] (c) with atom label.
Fig. S54 Structures of (TMA)[Ni(S,S-dmdtt)₂] (a) and (TMA)[Ni(R,R-dmdtt)₂] (b) in the ab plane (top) and bc plane (bottom). Color code: C (black), H (cyan), N (blue), S (yellow), Ni (green).
**Fig. S55** Distance between planes of complexes in \((TMA)[Ni(S,S\text{-}dm\text{-}dddt)](R,R\text{-}dm\text{-}dddt)]\). Color code: C (black), H (cyan), S (yellow), Ni (green).

**Fig. S56** Intermolecular S···S interactions below 4.50 Å between neighbouring complexes in \((TMA)[Ni(S,S\text{-}dm\text{-}dddt)]_2\), \((TMA)[Ni(R,R\text{-}dm\text{-}dddt)]_2\) (top) and \((TMA)[Ni(S,S\text{-}dm\text{-}dddt)](R,R\text{-}dm\text{-}dddt)]\) (bottom).
Table S5 Crystallographic data for [Ni(S-me-dddt)₂], [Ni(R-me-dddt)₂] and [Ni(S-me-dddt)(R-me-dddt)]

| Empirical formula                  | [Ni(S-me-dddt)₂] | [Ni(R-me-dddt)₂] | [Ni(S-me-dddt)(R-me-dddt)] |
|------------------------------------|------------------|------------------|-----------------------------|
| Fw                                 | 447.39           | 447.39           | 447.39                      |
| Crystal color                      | Black            | Black            | Black                       |
| Crystal size (mm³)                 | 0.12*0.04*0.02   | 0.27*0.06*0.03   | 0.28*0.08*0.04              |
| Temperature (K)                    | 150              | 150              | 150                         |
| Wavelength (Å)                     | 1.54184          | 1.54184          | 1.54184                     |
| Crystal system, Z                  | Monoclinic, 2    | Monoclinic, 2    | Monoclinic, 2               |
| Space group                        | P2₁              | P2₁              | P2₁/c                       |
| a (Å)                              | 5.2529 (2)       | 5.2567 (6)       | 5.2521 (2)                  |
| b (Å)                              | 15.0859 (4)      | 15.0900 (19)     | 15.1161 (5)                 |
| c (Å)                              | 10.1409 (3)      | 10.1421 (12)     | 10.1483 (3)                 |
| α (°)                              | 90               | 90               | 90                          |
| β (°)                              | 90.135 (3)       | 90.093 (11)      | 90.181 (4)                  |
| γ (°)                              | 90               | 90               | 90                          |
| V (Å³)                             | 803.61 (4)       | 804.51 (17)      | 805.68 (5)                  |
| ρcalc (g.cm⁻³)                     | 1.849            | 1.847            | 1.844                       |
| μ(CuKα) (mm⁻¹)                     | 11.306           | 11.293           | 11.277                      |
| θ range (°)                        | 4.360–73.517     | 4.359–74.843     | 5.250–73.106                |
| Data collected                     | 7587             | 5115             | 4209                        |
| Data unique                        | 2969             | 3010             | 1476                        |
| Data observed                      | 2777             | 2679             | 1426                        |
| R(int)                             | 0.0292           | 0.0486           | 0.0531                      |
| Nb of parameters / restraints      | 172/1            | 172/1            | 88/0                        |
| Flack parameter                    | 0.05 (3)         | 0.15 (6)         | -                           |
| R1(F), a I > 2σ(l)                 | 0.0363           | 0.0647           | 0.0631                      |
| wR2(F²), b all data                | 0.0963           | 0.1802           | 0.1709                      |
| S(F²), c all data                  | 1.127            | 1.076            | 1.144                       |

\(^a\) R1(F) = Σ||F₀| - |Fc||Σ|F₀|; \(^b\) wR2(F²) = [Σw(F₀²-F_c²)²]/Σw(F₀⁴)\(^{1/2}\); \(^c\) S(F²) = [Σw(F₀²-F_c²)²/(n+r-p)]\(^{1/2}\).
Fig. S57 Structures of \([\text{Ni}(S\text{-me-dddt})_2]\) (a), \([\text{Ni}(R\text{-me-dddt})_2]\) (b) and \([\text{Ni}(S\text{-me-dddt})(R\text{-me-dddt})]\) (c) with atom label.
Fig. S58 “In plane” intermolecular C–H···S interactions between neighbouring complexes in [Ni(S-me-dddt)$_2$]. Color code: C (black), H (cyan), S (yellow), Ni (green). Different colours are used to discriminate each interaction.

Fig. S59 “In plane” intermolecular C–H···S interactions between neighbouring complexes in [Ni(R-me-dddt)$_2$]. Color code: C (black), H (cyan), S (yellow), Ni (green). Different colours are used to discriminate each interaction.
**Fig. S60** “In plane” intermolecular C-H···S interactions between neighbouring complexes in \([\text{Ni}(S\text{-me-dddt})(R\text{-me-dddt})]\). Color code: C (black), H (cyan), S (yellow), Ni (green). Different colours are used to discriminate each interaction.

**Fig. S61** “Out-of-plane” intermolecular S···S interactions between neighbouring complexes in (a) \([\text{Ni}(S\text{-me-dddt})_2]\), (b) \([\text{Ni}(R\text{-me-dddt})_2]\) and (c) \([\text{Ni}(S\text{-me-dddt})(R\text{-me-dddt})]\). Color code: C (black), H (cyan), S (yellow), Ni (green).
Table S6 Crystallographic data for [Ni(S,S-dm-dddt)$_2$], [Ni(R,R-dm-dddt)$_2$] and [Ni(S,S-dm-dddt)(R,R-dm-dddt)]

|                          | [Ni(S,S-dm-dddt)$_2$] | [Ni(R,R-dm-dddt)$_2$] | [Ni(S,S-dm-dddt)(R,R-dm-dddt)] |
|--------------------------|-----------------------|-----------------------|-------------------------------|
| Empirical formula        | C$_{12}$H$_{16}$NiS$_8$ | C$_{12}$H$_{16}$NiS$_8$ | C$_{12}$H$_{16}$NiS$_8$ |
| Fw                       | 475.44                | 475.44                | 475.44                        |
| Crystal color            | Black                 | Black                 | Black                         |
| Crystal size (mm$^3$)    | 0.12*0.04*0.02        | 0.20*0.15*0.13        | 0.20*0.20*0.16                |
| Temperature (K)          | 150                   | 293                   | 150                           |
| Wavelength (Å)           | 1.54184               | 0.71073               | 1.54184                       |
| Crystal system, Z        | Triclinic, 1          | Triclinic, 1          | Triclinic, 1                  |
| Space group              | P1                    | P1                    | P-1                           |
| a (Å)                    | 6.9052 (3)            | 6.9784 (4)            | 6.9552 (7)                    |
| b (Å)                    | 7.7527 (3)            | 7.8994 (6)            | 7.8717 (8)                    |
| c (Å)                    | 9.1468 (3)            | 9.2170 (5)            | 9.1681 (9)                    |
| α (°)                    | 70.732 (4)            | 70.105 (6)            | 69.989 (9)                    |
| β (°)                    | 76.045 (3)            | 75.451 (5)            | 74.837 (8)                    |
| γ (°)                    | 76.463 (4)            | 75.277 (4)            | 72.895 (9)                    |
| V (Å$^3$)                | 442.17 (3)            | 454.44 (5)            | 443.49 (8)                    |
| ρcalc (g.cm$^{-3}$)      | 1.785                 | 1.737                 | 1.780                         |
| μ (mm$^{-1}$)            | 10.315 (CuKα)         | 1.975 (MoKα)          | 10.284 (CuKα)                 |
| θ range (°)             | 5.206–72.040          | 3.63–29.99            | 5.22–73.76                    |
| Data collected           | 5909                  | 10223                 | 2933                          |
| Data unique              | 3083                  | 4578                  | 1716                          |
| Data observed            | 3010                  | 3728                  | 1644                          |
| R(int)                   | 0.0174                | 0.0241                | 0.0199                        |
| Nb of parameters / restraints | 190/3                | 190/3                 | 115/0                         |
| Flack parameter          | 0.038 (11)            | 0.017 (12)            | -                             |
| R1(F)$^a$ I > 2σ(I)      | 0.0212                | 0.0267                | 0.0371                        |
| wR2(F$^2$)$^b$, all data| 0.0575                | 0.0610                | 0.1108                        |
| S(F$^2$)$^c$, all data   | 1.049                 | 1.019                 | 1.141                         |

$^a$R1(F) = Σ||F$_o$| - |F$_c$||Σ|F$_o$|; $^b$wR2(F$^2$) = [Σw(F$_o^2$-F$_c^2$)$^2$]/ΣwF$_o^4$]$^{1/2}$; $^c$S(F$^2$) = [Σw(F$_o^2$-F$_c^2$)$^2$/(n-r-p)]$^{1/2}$.
Fig. S62 Structures of [Ni(S,S-dm-ddddt)₂] (a), [Ni(R,R-dm-ddddt)₂] (b) and [Ni(S,S-dm-ddddt)(R,R-dm-ddddt)] (c) with atom label.
Fig. S63 View of the crystal packing in [Ni(S,S-dm-dddt)]$_2$ (a), [Ni(R,R-dm-dddt)]$_2$ (b) and [Ni(S,S-dm-dddt)(R,R-dm-dddt)] (c).
Band structure calculations

Fig. S64 DFT band structure for the neutral solids [Ni(S-me-lddt)] (a) and [Ni(S-me-lddt)(R-me-lddt)] (b). Γ = (0, 0, 0), X = (a*/2, 0, 0), Y = (0, b*/2, 0), Z = (0, 0, c*/2), M = (a*/2, b*/2, 0), P = (0, b*/2, c*/2), N = (a*/2, 0, c*/2) and R = (α*/2, b*/2, c*/2). The dashed line refers to the highest occupied level.
Fig. S65 Extended Hückel band structure for the neutral solids [Ni(R-me-dddt)]\(_2\) (a) [Ni(S-me-dddt)]\(_2\) (b) and [Ni(S-me-dddt)(R-me-dddt)] (c) as well as for the parent system [Ni(dddt)]\(_2\) (d). \(\Gamma = (0, 0, 0), X = (a*/2, 0, 0), Y = (0, b*/2, 0), Z = (0, 0, c*/2), M = (a*/2, b*/2, 0), P = (0, b*/2, c*/2), R = (a*/2, b*/2, c*/2)\) and \(N = (a*/2, 0, c*/2)\). The dashed line refers to the highest occupied level.
Fig. S66 DFT band structure for the neutral solids [Ni(S,S-dm-dddt)$_2$] (a) and [Ni(S,S-dm-dddt)(R,R-dm-dddt)]. $\Gamma$ = (0, 0, 0), $X$ = $(a*/2, 0, 0)$, $Y$ = $(0, b*/2, 0)$, $Z$ = $(0, 0, c*/2)$, $M$ = $(a*/2, b*/2, 0)$, $P$ = $(0, b*/2, c*/2)$, $Q$ = $(a*/2, 0, c*/2)$, $R$ = $(a*/2, b*/2, c*/2)$ and $S$ = $(-a*/2, 0, c*/2)$. The dashed line refers to the highest occupied level.
Fig. S67 DFT band structure for the ferromagnetic (FM) (a, c) and antiferromagnetic (AF) (b, d) states of (TMA)[Ni(R,R-dm-dddt)] and (TMA)[Ni(S,S-dm-dddt)(R,R-dm-dddt)], respectively. Spin up and spin down bands are shown in red and blue, respectively. The FM state is calculated using the crystallographic cell (a, b, c) containing 4 complexes and \( \Gamma = (0, 0, 0) \), Y = (0, \( b^*/2 \), 0), Z = (0, 0, \( c^*/2 \)), R = (\( a^*/2 \), \( b^*/2 \), \( c^*/2 \)) and X (\( a^*/2 \), 0, 0). The AFM state is calculated using a double cell (\( a' = a \), \( b' = 2b \) and \( c' = c \)) containing 8 complexes and \( \Gamma = (0, 0, 0) \), Y = (0, \( b'^*/2 \), 0), Z = (0, 0, \( c'^*/2 \)), R = (\( a'^*/2 \), \( b'^*/2 \), \( c'^*/2 \)) and X (\( a'^*/2 \), 0, 0). The dashed line refers to the highest occupied level. In (b and d) the spin up and spin down bands are identical although located in spatially different but equivalent sites so that only the blue bands are visible.