ESI

Chemo-chromism in an orthogonal dabco-based Co(II) network
assembled by methanol-coordination and hydrogen bond formation

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1. Structural SC-XRD analysis
2. Magnetic measurement
3. P-XRD analysis
4. FTIR
5. UV-VIS-NIR spectra
6. NMR
7. GC-MS
1. Structural SC-XRD analysis

**Figure S1-1.** Bond and inter atomic distances in 1 for NCS ligand (left) and hydrogen bond (right) at 120 K.

**Figure S1-2.** Crystal structure of 1-pink (C: white, N: blue, O: red, S: yellow, Co: green) of bc plane. H-atoms and disordering of dabco(c) are omitted for clarifying illustrations.
Figure S1-3. ORTEP view of structure
Figure S1-3. Diffraction patterns taken before (left) and after (right) incubation for 450 minutes at 90 degree using same single crystal with same angles (axis).
2. Magnetic measurement

Magnetic measurements were performed using a Quantum Design SQUID magnetometer. The temperature dependence of the molar magnetic susceptibility was measured between 2 and 350 K in an external field of 5,000 Oe. Powder samples were fixed in polyvinylidene chloride foils for measurements.

Line fitting was done by using MagSaki free soft* for a model of Co(II) mono-nuclear, axially distorted octahedral. Axial splitting parameter: \( \Delta \), spin-orbit coupling constant: \( \lambda \) (\(-172\) cm\(^{-1}\) for Co(II)) and orbital reduction factor: \( \kappa \) were estimated to \( \Delta = -533\) cm\(^{-1}\), \( \lambda = -142\) cm\(^{-1}\), \( \kappa = 0.75\). Further details on magnetic behaviour at the low temperature phase will be reported by us in elsewhere.

![Graph showing magnetic susceptibility vs temperature](image)

**Figure S2-1.** Temperature dependence of magnetic susceptibility (up) and scheme of electronic states (down).

3. P-XRD analysis

Unit cell parameters of as grown and incubated sample (Figure S3-1 and -2) were estimated by Lebail method (A. Le Bail, H. Duroy and J.L. Fourquet, Mat. Res. Bull. 23 (1988) 447-452.)

Figure S3-1. Whole pattern fitting of p-XRD pattern of as grown sample.

Figure S3-2. Whole pattern fitting of p-XRD pattern of sample after heating in vacuumed condition; (iv) in main text.
Figure S3-3. P-XRD of as-grown 1-pink (pink), 1-blue (blue) and sample after treating methanol to 1-blue (green). Diffraction patterns were recoded using RIGAKU SmartLab.
Figure S3-4. Comparison of powder pattern of as grown 1-pink and 1-blue.

Figure S3-5. P-XRD of 1-pink after grinding (1-blue(a)). Since peaks were observed, base line is appeared due to low intensities of diffractions.
4. FTIR

**Figure S4-1.** FTIR spectra of as-grown 1-blue and after thermal treatment.

**Figure S4-2.** FT–IR spectra of well ground samples of 1-pink.

**Table S4-1.** List of FTIR peak of NCS moiety

<table>
<thead>
<tr>
<th></th>
<th>1-pink</th>
<th>1-blue</th>
<th>&gt; SCN</th>
<th>-NCS-</th>
<th>-SCN</th>
<th>-NCS</th>
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<tr>
<td>$\nu$(C–N)/ cm$^{-1}$</td>
<td>2079</td>
<td>2067</td>
<td>2200-2140</td>
<td>&gt;2100</td>
<td>2130-2085</td>
<td>2100-2050</td>
</tr>
<tr>
<td>$\nu$(C–S)/ cm$^{-1}$</td>
<td>840</td>
<td>837</td>
<td>800-750</td>
<td>760-700</td>
<td>870-820</td>
<td></td>
</tr>
</tbody>
</table>

5. UV-VIS-NIR spectra

![UV-VIS-NIR spectra diagram](image)

**Figure S5-1.** Diffusion-reflection spectra and peak assignments of 1-pink with Tanabe-Sugano diagram.

$v_1: ^4T_{2g} \rightarrow ^4T_{1g} \quad 8-10 \text{ km}^{-1} \quad \sim 10 \text{ km}^{-1}$

$v_2: ^4A_{2g} \rightarrow ^4T_{1g} \quad v_2/v_1 \sim 2 \text{ (weak)} \quad \sim 20 \text{ km}^{-1}$

$v_3: ^4T_{1g}(P) \rightarrow ^4T_{1g} \text{ visible region} \quad \sim 22 \text{ km}^{-1}$
A compound 1-blue(a) was prepared by grading samples for 40 min and desorption of methanol was validated by IR measurement (Figure S4-2). P-XRD showed very weak intensity because of amorphous state (Figure S3-5). Treatments by methanol were performed by dropping 15 μL of methanol to 1-blue(a) (0.01 g). Color of powder 1-blue(a) was changed to pink by this methanol treatment. Spectra of 1-pink, 1-blue and 1-blue(a) as well as 1-blue and 1-blue (a) after methanol treatments were shown in figure S5-2.

Figure S5-2. Diffusion-reflection spectra of compounds.
6. NRM

Figure S6-1. $^1$H-NMR of chloroform solution of mixture of methanol and $n$-butanol, $n$-butanol, methanol, after treatment of 1-blue, before treatment of 1-blue, and controlled experiment with this order from up to down.
7. GC-MS

Time development of the GC-MS was characterized at 90 °C. Desorption of methanol was almost finished after 90 mints of incubation.

Figure S7-1. Time development of the GC-MS was characterized at 90 °C.