Electronic Supplementary Information (ESI)

Evolution of Spin-Crossover Transition in Hybrid Crystals Involving Cationic iron Complexes [Fe(III)(3-OMesal₂-trien)]⁺ and Anionic Gold Bis(dithiolene) Complexes Au(dmit)₂ and Au(dddt)₂.

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1. Synthesis:

[Fe(3-OMe-sal₂-trien)][Au(dmit)₂] (1).

Figure S1 displays the thermogram of [Fe(3-OMe-sal₂-trien)][Au(dmit)₂] (1). A weight loss of 30.08% was observed in the temperature range 120-350°C with DSC endothermic peak at 268.0°C, which is assigned to the melting of 1 and exothermic peak at 277.7°C, which is assigned to the decomposition of the complex (Figure SC). As this takes place, the ions with m/z 18 (H₂O), 17 (HO), 13 (CH) and 26 (CN) relating to the fragments of molecule are observed in the mass spectrum. Figure SD displays the P-XDR 1 in 20 from 5° to 45°.

![Thermogravimetric analysis of [Fe(3-OMe-sal₂-trien)][Au(dmit)₂] (1).](image-url)

Fig. S1. Thermogravimetric analysis of [Fe(3-OMe-sal₂-trien)][Au(dmit)₂] (1).
Fig. S2. Powder X-ray diffractogram for [Fe(3-OMe-sal:-trien)][Au(dmit)2]: experimental (line) and simulation (dots).
Figure S3 displays the thermogram of [Fe(3-OMe-sal-trien)][Au(dddt)_2]·CH$_3$CN (2).

Fig. S3. The thermogravimetric analysis of [Fe(3-OMe-sal-trien)][Au(dddt)_2]·CH$_3$CN (2).

Fig.S4. Powder X-ray diffractogram for [Fe(3-OMe-sal-trien)][Au(dddt)_2]·CH$_3$CN: experimental (line) and simulation (dots).
Crystal shapes

Fig. S5. Single crystals of [Fe(3-OMesal-trien)][Au(dmit)$_2$] (left) and [Fe(3-OMesal-trien)][Au(dddt)$_2$] (right).

Fig. S6. Polycrystalline sample of [Fe(3-OMe-Sal-trien)][Au(dddt)$_2$] * CH$_3$CN
2. Electron-probe X-ray microanalysis (EPMA).

EPMA of the salt crystals was performed with a Zeiss Supra-25 analytical field emission electron microscope equipped with a Gemini electron optical column at magnification varying from 600 to 6200 depending on the sample and the electron beam energy of 9.7-20 keV. The depth of beam penetration into the sample was 1-3 μm.

3. Powder X-Ray Diffraction (P-XRD) was measured using a Siemens D500 powder diffractometer with linear detector at room temperature (CuKα - radiation, λ = 1.5406 Å, step = 0.02°, singlecrystal cuvette). Powder patterns are used as a fingerprint for identification of the crystalline phase presented in a material.

4. Crystal structure determination

X-ray single crystal diffraction studies were carried out on an Oxford Diffraction Gemini-R diffractometer with Atlas CCD detector [λ(MoKα) = 0.71073 Å, graphite monochromator, ω-scan mode]. The structures were solved by the direct method and refined by the full-matrix least-squares technique against \( F^2 \) in the anisotropic approximation for all non-hydrogen atoms using SHELX-2016 program [1]. Hydrogen atoms were refined isotropically in a rigid model. Table 1 contains unit cell parameters and details of data collection and structure refinement. CCDC 1868121-1, 1868120-1, 1868123-2, 1868122-2 contain supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

5. Thermogravimetric analysis

The thermogravimetric analysis was performed in argon atmosphere with a heating rate 5.0 °C min⁻¹ using a NETZSCH STA 409 C Luxx thermal analyzer, interfaced to a QMS 403 Aelos mass spectrometer, which allows simultaneous thermogravimetry (TG), differential scanning calorimetry (DSC) and mass-spectrometry measurements.

6. Magnetic SQUID measurements

Magnetic measurements were performed by using a Quantum Design MPMS-5-XL and MPMS-1 SQUID magnetometers. Static magnetic susceptibility \( \chi(T) \) was measured on polycrystalline samples at the magnetic field \( H = 100 \) Oe, while warming and cooling regimes. The temperature range of measurements was 2–300 K. Field dependences of the magnetization \( M(H) \) were obtained at 2.0 K during several scans over the field range ~50 kOe to +50 kOe. The samples had been cooled down to 2.0 K in the magnetic field \( H = 40 \) kOe. The measurements were performed while decreasing the field value over the sign reversal to -50 kOe and further increasing it to +50 kOe.

Thermocycling procedure in Fig. 11 corresponds to a series of three subsequent at warming \( \chi(T)\uparrow \) and cooling \( \chi(T)\downarrow \) cycles shown as black, blue and purple color data points (○, ○, ○) and respective solid lines guided by mean free path approximation. Solid red line is a reference curve for fresh crystals from Fig. 1.

References