

Supporting Information for

## Photochromism and photomagnetism in three cyano-bridged 3d-4f heterobimetallic viologen frameworks

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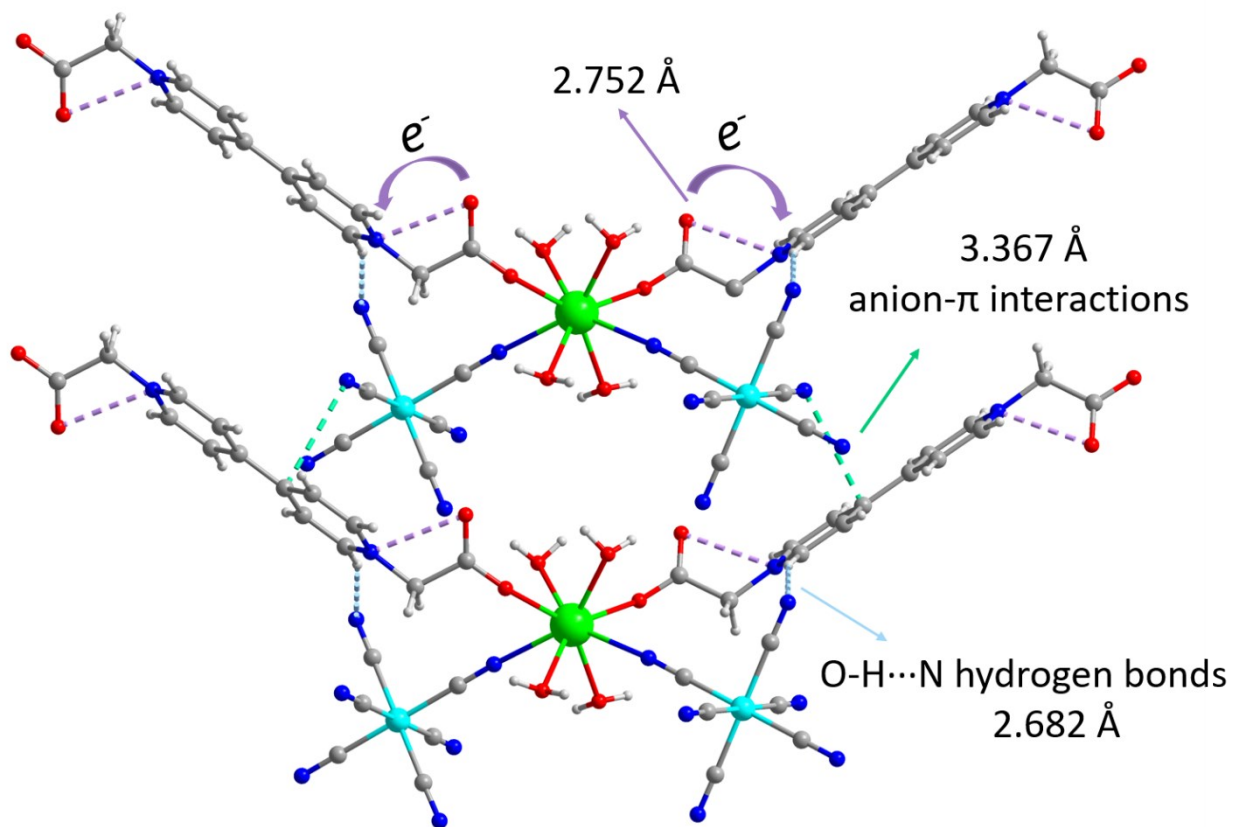
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1. The additional crystal figure for the compound.



**Fig. S1.** The weak intermolecular O-H...N hydrogen bonds interactions and anion- $\pi$  interactions electron transfer orientation diagrams between  $[\text{Co}(\text{CN})_6]^{3-}$  and Bcbpy ligands.

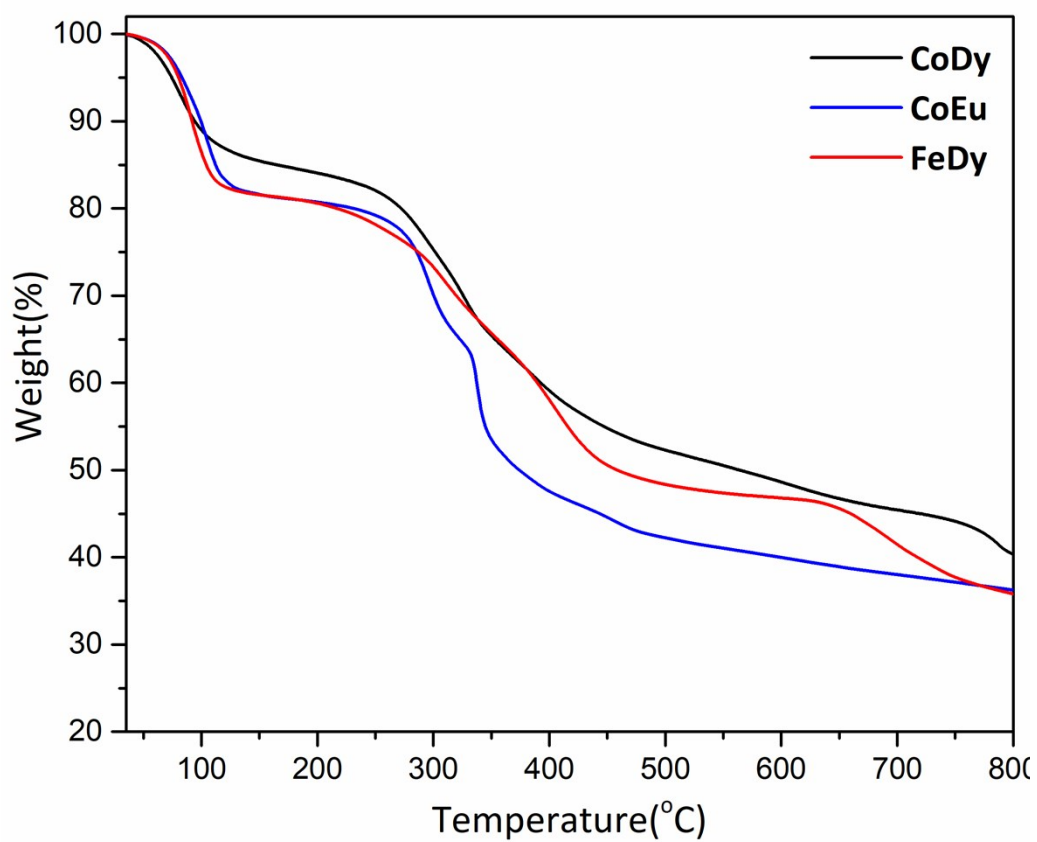
## 2. Crystal data and structure refinement

Crystal data for the hybrids were collected on a Rigaku Saturn 724 CCD diffractometer with Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at 295 K and reduction were performed by using the program CrysAlisPro.<sup>1</sup> The structures were solved by the direct method and different Fourier syntheses. All calculations were performed by full-matrix least-squares methods on F<sup>2</sup> by using the SHELXTL program<sup>2</sup>, all non-hydrogen atoms were refined with anisotropic thermal parameters and the hydrogen atoms were fixed at calculated positions and refined by a riding mode. Details of the crystal parameter data collection and refinement for hybrid **CoDy**, **CoEu**, and **FeDy** are summarized in Table 1. Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 2040867-2040869 and 2061512 for **CoDy**, **CoEu**, **FeDy**, and **CoEu-a (after irradiation)** which can be obtained free of charge from the Cambridge Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Table 1.** Crystallographic Data and Structural Refinements Parameters for **CoDy**, **CoEu**, **FeDy** and **CoEu-a**.

Complex	<b>CoDy</b>	<b>CoEu</b>	<b>FeDy</b>	<b>CoEu-a</b>
Empirical formula	<b>C<sub>20</sub>H<sub>33.06</sub>CoDyN<sub>8</sub>O<sub>13</sub></b>	<b>C<sub>21.4</sub>H<sub>36.2</sub>CoEuN<sub>8</sub>O<sub>13</sub></b>	<b>C<sub>21.04</sub>H<sub>32.66</sub>DyFeN<sub>8</sub>O<sub>13</sub></b>	<b>C<sub>21</sub>H<sub>29.57</sub>CoEuN<sub>8</sub>O<sub>12</sub></b>
Formula weight	815.03	824.47	824.04	796.98
Temperature/K	293(2)	293(2)	285(5)	293(2)
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>c</i>
a/ $\text{\AA}$	19.882(3)	19.8318(8)	19.7891(9)	19.8265(12)
b/ $\text{\AA}$	8.0889(7)	8.1069(2)	8.1030(3)	8.1126(4)
c/ $\text{\AA}$	20.090(2)	20.1876(7)	20.1878(9)	20.1853(9)
$\alpha$ / $^\circ$	90	90	90	90
$\beta$ / $^\circ$	108.912(14)	108.793(4)	108.704(5)	108.862(6)
$\gamma$ / $^\circ$	90	90	90	90
Volume/ $\text{\AA}^3$	3056.5(7)	3072.62(19)	3066.2(2)	3072.3(3)
Z	4	4	4	4
$\rho_{\text{calc}}/\text{cm}^3$	1.771	1.782	1.785	1.723
$\mu/\text{mm}^{-1}$	3.041	2.637	2.965	2.632
2 $\theta$ range for data collection/ $^\circ$	4.286 to 58.944	4.262 to 58.584	5.478 to 59.098	4.264 to 50.05
Reflections collected	11720	13625	13783	12033
R <sub>int</sub>	0.0915	0.0346	0.0261	0.2015
Data/restraints/parameters	2705/0/188	3568/522/289	3552/165/304	2715/165/279
Goodness-of-fit on F <sup>2</sup>	0.976	1.163	1.074	1.088
Final R indexes [ $I \geq 2\sigma(I)$ ]	R <sub>1</sub> = 0.0555	R <sub>1</sub> = 0.0310	R <sub>1</sub> = 0.0230	R <sub>1</sub> = 0.0562
Final R indexes [all data]	R <sub>1</sub> = 0.1035	R <sub>1</sub> = 0.0379	R <sub>1</sub> = 0.0266	R <sub>1</sub> = 0.0729
Largest diff. peak/hole / e $\text{\AA}^{-3}$	1.10/-1.49	1.15/-0.68	0.46/-0.48	1.47/-1.16

### 3. Thermo-gravimetric analysis (TG)



**Figure S2.** The TG curves of **CoDy**, **CoEu**, and **FeDy** under  $N_2$  atmosphere with a heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

#### 4. X-ray powder diffraction analysis

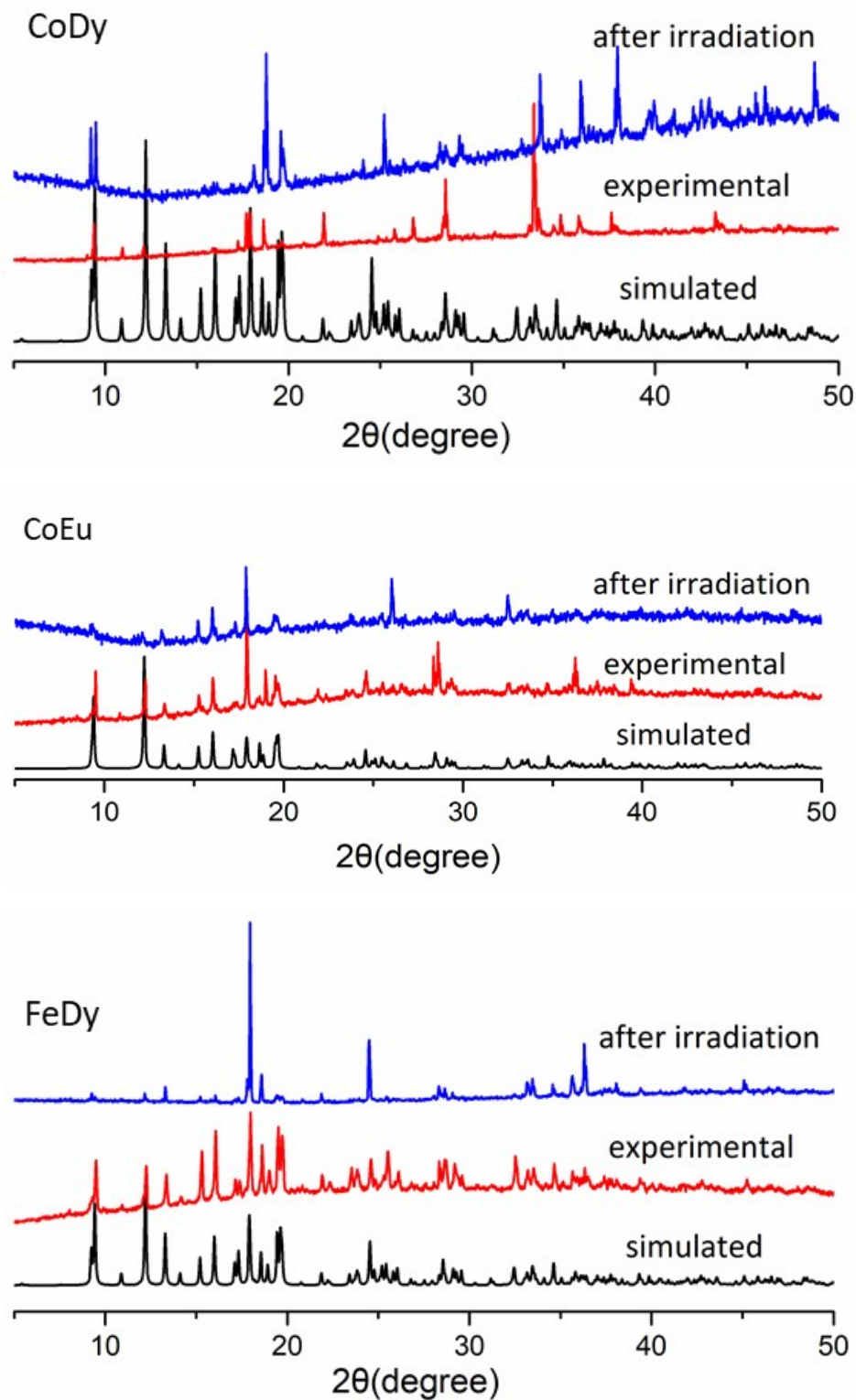


Figure S3. PXRD patterns of CoDy, CoEu, and FeDy after the irradiation for 15 min.

## 5. Mössbauer spectra of FeDy

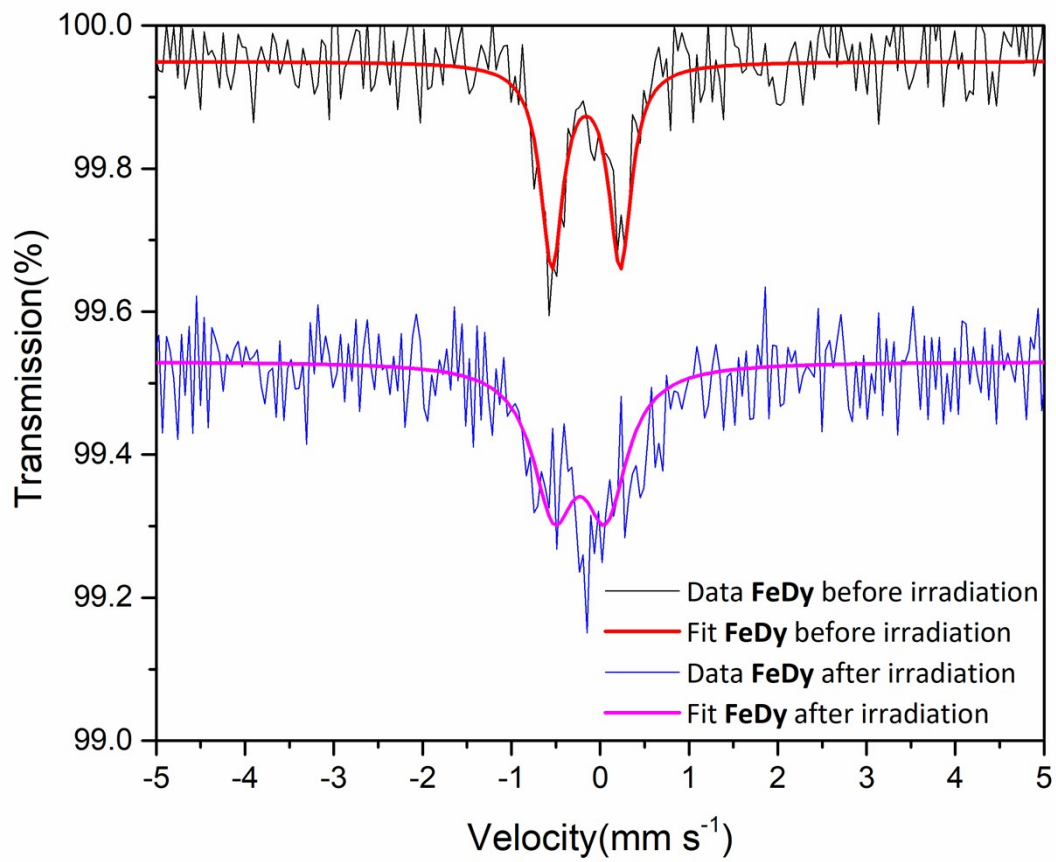


Figure S4. Mössbauer spectra of FeDy before and after irradiation recorded at room temperature.

## 6. Luminescent behaviors of compounds CoEu

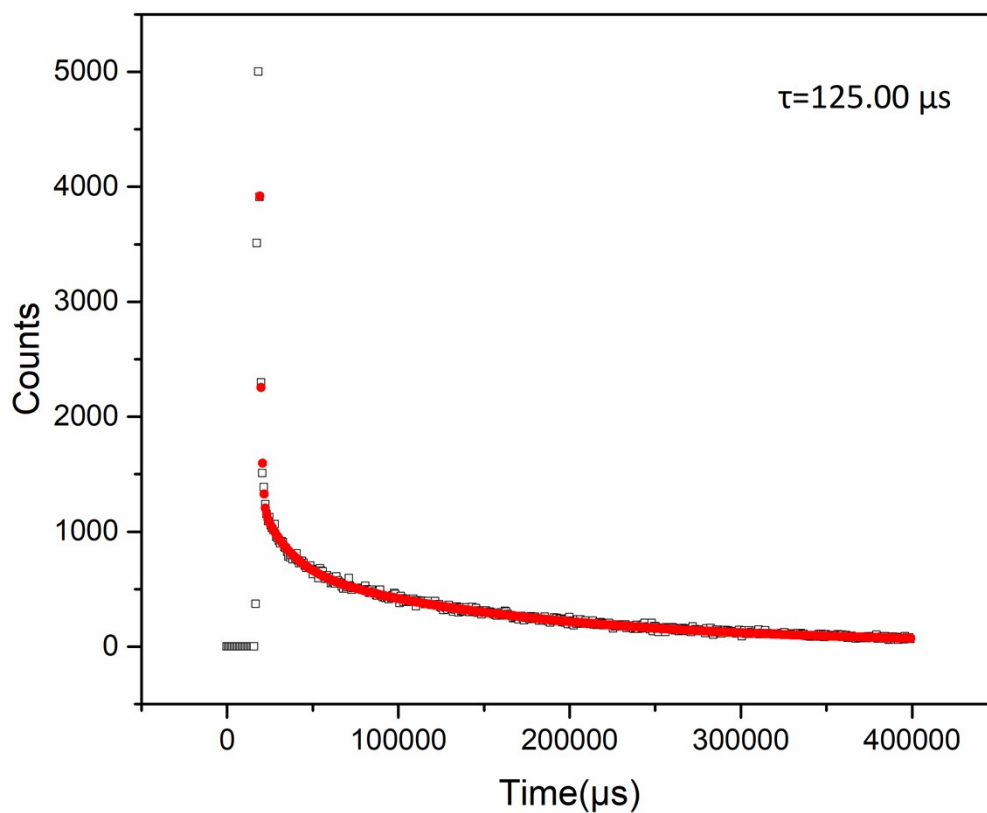


Figure S5. Luminescence decays of compound CoEu under ambient conditions.

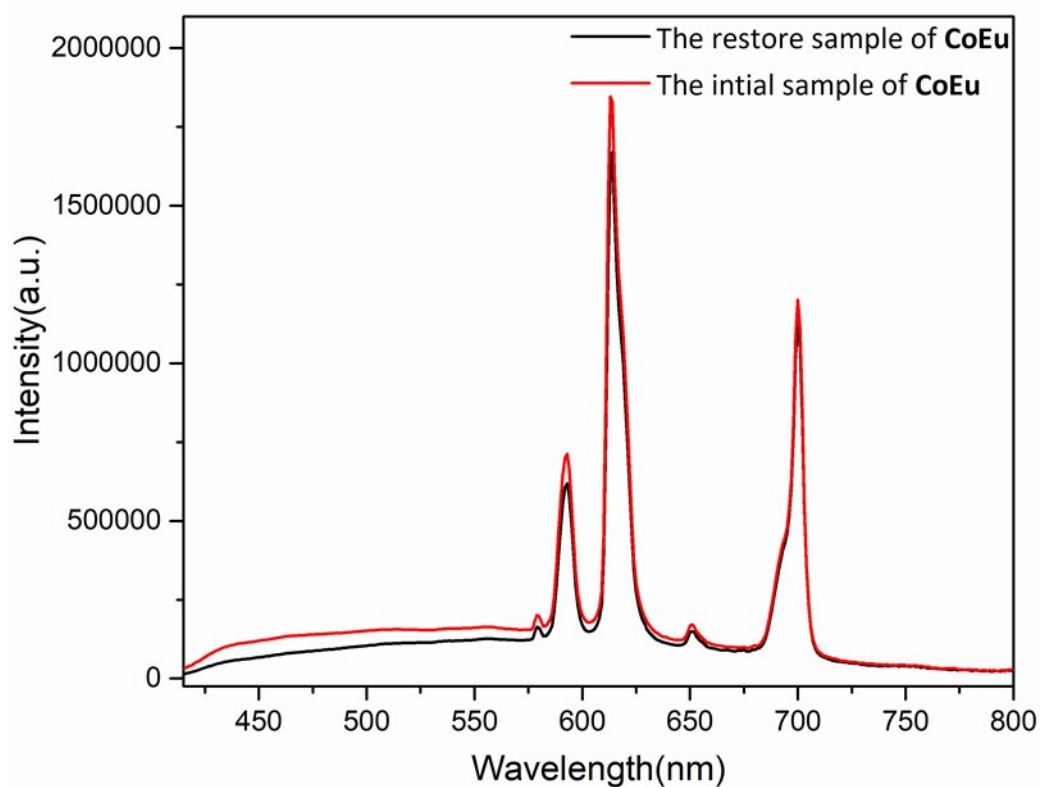


Figure S6. The luminescence emission of the original sample and the restored sample.

## Reference

S1 *CrysAlisPro* 2012, Version 1.171.36.31; Agilent Technologies.

S2 (a) O.V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, & H. Puschmann, *J. Appl. Cryst.* 2009, **42**, 339-341.; (b) G. M. Sheldrick, *Acta Cryst. C.* 2015, **71**, 3-8.