

**Novel 3D anionic heterometallic frameworks based on trinuclear Co^{II} and
trinuclear Ln^{III} motifs: displaying slow magnetic relaxation and selective
adsorption of methylene blue**

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Table S1 Selected bond lengths (Å) and angles (°) for CoEu (1)

| | | | |
|--------------|-----------|--------------|-----------|
| Eu1-O9A | 2.291(12) | Eu1-O9 | 2.291(12) |
| Eu1-O1B | 2.322(6) | Eu1-O1C | 2.322(6) |
| Eu1-O6D | 2.430(6) | Eu1-O6E | 2.430(6) |
| Eu1-O21 | 2.452(13) | Eu2-O7F | 2.297(6) |
| Eu2-O10G | 2.309(11) | Eu2-O2H | 2.355(5) |
| Eu2-O5I | 2.417(5) | Eu2-O12 | 2.430(6) |
| Eu2-O3D | 2.486(6) | Eu2-O4D | 2.508(5) |
| Eu2-O11 | 2.576(6) | | |
| Co1-O14 | 2.065(11) | Co1-O13 | 2.111(12) |
| Co1-N2 | 2.152(6) | Co1-N2B | 2.152(6) |
| Co1-N10B | 2.194(15) | Co1-N10 | 2.194(15) |
| Co2-O15 | 2.027(11) | Co2-O13 | 2.100(11) |
| Co2-N6 | 2.126(8) | Co2-N6B | 2.126(8) |
| Co2-N3 | 2.126(6) | Co2-N3B | 2.126(6) |
| Co3-O17 | 2.054(9) | Co3-O13 | 2.054(10) |
| Co3-N11B | 2.074(15) | Co3-O18 | 2.090(9) |
| Co3-N7 | 2.111(12) | Co3-O16 | 2.120(9) |
| O9A-Eu1-O9 | 153.2(7) | O9A-Eu1-O1B | 85.7(4) |
| O9-Eu1-O1B | 83.4(4) | O9A-Eu1-O1C | 83.4(4) |
| O9-Eu1-O1C | 85.7(4) | O1B-Eu1-O1C | 131.5(3) |
| O9A-Eu1-O6D | 95.0(3) | O9-Eu1-O6D | 105.7(4) |
| O1B-Eu1-O6D | 75.18(19) | O1C-Eu1-O6D | 152.7(2) |
| O9A-Eu1-O6E | 105.7(4) | O9-Eu1-O6E | 95.0(3) |
| O1B-Eu1-O6E | 152.7(2) | O1C-Eu1-O6E | 75.18(19) |
| O6D-Eu1-O6E | 79.1(3) | O9A-Eu1-O21 | 56.3(5) |
| O9-Eu1-O21 | 97.2(5) | O1B-Eu1-O21 | 61.0(4) |
| O1C-Eu1-O21 | 73.9(4) | O6D-Eu1-O21 | 127.4(4) |
| O6E-Eu1-O21 | 145.7(4) | O21A-Eu1-O21 | 43.4(7) |
| O7F-Eu1-O10G | 74.0(4) | O7F-Eu2-O2H | 150.1(2) |
| O10G-Eu2-O2H | 94.9(3) | O7F-Eu2-O5I | 80.8(3) |
| O10G-Eu2-O5I | 117.0(4) | O2H-Eu2-O5I | 79.9(2) |
| O7F-Eu2-O12 | 129.3(2) | O10G-Eu2-O12 | 78.8(4) |

| | | | |
|--------------|-----------|--------------|------------|
| O2H-Eu2-O12 | 73.0(2) | O5I-Eu2-O12 | 149.8(2) |
| O7F-Eu2-O3D | 127.7(2) | O10G-Eu2-O3D | 156.2(3) |
| O2H-Eu2-O3D | 70.48(18) | O5I-Eu2-O3D | 79.8(2) |
| O12-Eu2-O3D | 78.9(2) | O7F-Eu2-O4D | 78.0(2) |
| O10G-Eu2-O4D | 142.5(3) | O2H-Eu2-O4D | 121.21(19) |
| O5I-Eu2-O4D | 81.9(2) | O12-Eu2-O4D | 100.9(3) |
| O3D-Eu2-O4D | 51.41(18) | O7F-Eu2-O11 | 78.6(2) |
| O10G-Eu2-O11 | 74.7(4) | O2H-Eu2-O11 | 126.0(2) |
| O5I-Eu2-O11 | 152.2(2) | O12-Eu2-O11 | 53.0(2) |
| O3D-Eu2-O11 | 98.3(2) | O4D-Eu2-O11 | 75.7(2) |
| O14-Co1-O13 | 179.5(5) | O14-Co1-N2 | 92.8(3) |
| O13-Co1-N2 | 87.6(3) | O14-Co1-N2B | 92.8(3) |
| O13-Co1-N2B | 87.6(3) | N2-Co1-N2B | 87.4(3) |
| O14-Co1-N10B | 99.1(4) | O13-Co1-N10B | 80.6(4) |
| N2-Co1-N10B | 83.1(5) | N2B-Co1-N10B | 165.1(5) |
| O14-Co1-N10 | 99.1(4) | O13-Co1-N10 | 80.6(4) |
| N2-Co1-N10 | 165.1(5) | N2B-Co1-N10 | 83.1(5) |
| N10B-Co1-N10 | 103.8(9) | O15-Co2-O13 | 179.2(5) |
| O15-Co2-N6 | 90.1(3) | O13-Co2-N6 | 90.4(3) |
| O15-Co2-N6B | 90.1(3) | O13-Co2-N6B | 90.4(3) |
| N6-Co2-N6B | 94.5(4) | O15-Co2-N3 | 92.9(3) |
| O13-Co2-N3 | 86.6(3) | N6-Co2-N3 | 88.8(3) |
| N6B-Co2-N3 | 175.6(3) | O15-Co2-N3B | 92.9(3) |
| O13-Co2-N3B | 86.6(3) | N6-Co2-N3B | 175.6(3) |
| N6B-Co2-N3B | 88.8(3) | N3-Co2-N3B | 87.8(3) |
| O17-Co3-O13 | 107.7(4) | O17-Co3-N11B | 170.8(6) |
| O13-Co3-O11B | 80.4(5) | O17-Co3-O18 | 89.8(6) |
| O13-Co3-O18 | 96.0(5) | N11B-Co3-O18 | 84.9(6) |
| O17-Co3-N7 | 86.6(5) | O13-Co3-N7 | 88.4(4) |
| N11B-Co3-N7 | 98.1(6) | O18-Co3-N7 | 175.0(6) |
| O17-Co3-O16 | 75.8(7) | O13-Co3-O16 | 175.5(6) |
| N11B-Co3-O16 | 96.4(7) | O18-Co3-O16 | 86.8(7) |
| N7-Co3-O16 | 89.0(7) | | |

Symmetry codes: A: $-x+1, y, -z+2$; B: $x, -y+1, z$; C: $-x+1, -y+1, -z+2$; D: $-x+1/2, y+1/2, -z+1$; E: $x+1/2, y+1/2, z+1$; F: $x+1/2, y+1/2, z$; G: $-x+1, y, -z+1$; H: $x, -y+1, z-1$; I: $-x+1/2, y+1/2, -z$.

Table S2 Selected bond lengths (Å) and angles (°) for CoGd (2)

| | | | |
|---------|-----------|----------|-----------|
| Gd1-O9A | 2.260(17) | Gd1-O9 | 2.260(17) |
| Gd1-O1B | 2.359(11) | Gd1-O1C | 2.359(11) |
| Gd1-O6D | 2.376(12) | Gd1-O6E | 2.376(12) |
| Gd1-O21 | 2.54(3) | Gd2-O10F | 2.284(19) |

| | | | |
|--------------|-----------|--------------|-----------|
| Gd2-O7G | 2.306(11) | Gd2-O2H | 2.351(11) |
| Gd2-O5I | 2.389(11) | Gd2-O12 | 2.409(13) |
| Gd2-O3D | 2.488(12) | Gd2-O4D | 2.496(11) |
| Gd2-O11 | 2.537(12) | Co1-O13 | 2.03(2) |
| Co1-O14 | 2.09(2) | Co1-N2 | 2.156(13) |
| Co1-N2B | 2.156(13) | Co1-N10 | 2.16(2) |
| Co1-N10B | 2.16(2) | Co2-O15 | 2.059(18) |
| Co2-N6 | 2.123(14) | Co2-N6B | 2.123(14) |
| Co2-N3B | 2.135(12) | Co2-N3 | 2.135(12) |
| Co2-O13 | 2.16(2) | Co3-N11B | 2.08(3) |
| Co3-O13 | 2.05(2) | Co3-O17 | 2.083(10) |
| Co3-O18 | 2.092(10) | Co3-O16 | 2.104(10) |
| Co3-N7 | 2.20(3) | | |
| O9A-Gd1-O9 | 157.3(12) | O9A-Gd1-O1B | 90.2(7) |
| O9-Gd1-O1B | 80.4(6) | O9A-Gd1-O1C | 80.4(6) |
| O9-Gd1-O1C | 90.2(7) | O1B-Gd1-O1C | 130.9(6) |
| O9A-Gd1-O6D | 98.0(6) | O9-Gd1-O6D | 99.8(7) |
| O1B-Gd1-O6D | 76.4(4) | O1C-Gd1-O6D | 152.4(4) |
| O9A-Gd1-O6E | 99.8(7) | O9-Gd1-O6E | 98.0(6) |
| O1B-Gd1-O6E | 152.4(4) | O1C-Gd1-O6E | 76.4(4) |
| O6D-Gd1-O6E | 76.8(6) | O9A-Gd1-O21 | 66.1(11) |
| O9-Gd1-O21 | 91.2(11) | O1B-Gd1-O21 | 62.7(12) |
| O1C-Gd1-O21 | 69.5(12) | O6D-Gd1-O21 | 135.1(12) |
| O6E-Gd1-O21 | 144.7(12) | O21A-Gd1-O21 | 26.9(18) |
| O10F-Gd2-O7G | 74.2(7) | O10F-Gd2-O2H | 93.7(6) |
| O7G-Gd2-O2H | 149.8(5) | O10F-Gd2-O5I | 112.0(7) |
| O7G-Gd2-O5I | 78.9(5) | O2H-Gd2-O5I | 80.5(4) |
| O10F-Gd2-O12 | 79.9(7) | O7G-Gd2-O12 | 129.4(5) |
| O2H-Gd2-O12 | 73.1(4) | O5I-Gd2-O12 | 151.8(4) |
| O10F-Gd2-O3D | 155.9(7) | O7G-Gd2-O3D | 128.2(4) |
| O2H-Gd2-O3D | 70.5(4) | O5I-Gd2-O3D | 84.0(5) |
| O12-Gd2-O3D | 78.1(5) | O10F-Gd2-O4D | 143.1(6) |
| O7G-Gd2-O4D | 77.0(4) | O2H-Gd2-O4D | 122.3(4) |
| O5I-Gd2-O4D | 84.1(5) | O12-Gd2-O4D | 101.6(5) |
| O3D-Gd2-O4D | 52.7(4) | O10F-Gd2-O11 | 76.8(6) |
| O7G-Gd2-O11 | 78.9(4) | O5H-Gd2-O11 | 126.0(4) |
| O5I-Gd2-O11 | 152.6(4) | O12-Gd2-O11 | 52.9(4) |
| O3D-Gd2-O11 | 97.4(4) | O4D-Gd2-O11 | 75.4(4) |
| O13-Co1-O14 | 178.0(9) | O13-Co1-N2 | 89.2(6) |
| O14-Co1-N2 | 92.2(6) | O13-Co1-N2B | 89.2(6) |
| O14-Co1-N2B | 92.2(6) | N2-Co1-N2B | 88.4(7) |
| O13-Co1-N10 | 81.7(6) | O14-Co1-N10 | 97.0(7) |
| N2-Co1-N10 | 168.6(7) | N2B-Co1-N10 | 84.7(8) |
| O13-Co1-N10B | 81.7(6) | O14-Co1-N10B | 97.0(7) |

| | | | |
|--------------|-----------|--------------|-----------|
| N2-Co1-N10B | 84.7(8) | N2B-Co1-N10B | 168.6(7) |
| N10-Co1-N10B | 100.6(13) | O15-Co2-N6 | 90.2(6) |
| O15-Co2-N6B | 90.2(6) | N6-Co2-N6B | 95.3(8) |
| O15-Co2-N3B | 92.9(6) | N6-Co2-N3B | 174.8(5) |
| O6B-Co2-N3B | 88.8(6) | O15-Co2-N3 | 92.9(6) |
| N6-Co2-N3 | 88.8(6) | N6B-Co2-N3 | 174.8(5) |
| N3B-Co2-N3 | 86.9(7) | O15-Co2-O13 | 178.8(8) |
| N6B-Co2-O13 | 90.6(6) | N3B-Co2-O13 | 86.2(6) |
| N3-Co2-O13 | 86.2(6) | N11B-Co3-O13 | 79.3(9) |
| N11B-Co3-O17 | 175.2(9) | O13-Co3-O17 | 105.4(8) |
| N11B-Co3-O18 | 81.4(12) | O13-Co3-O18 | 91.9(10) |
| O17-Co3-O18 | 98.0(10) | N11B-Co3-O16 | 93.3(13) |
| O13-Co3-O16 | 171.1(11) | O17-Co3-O16 | 82.0(12) |
| O18-Co3-O16 | 91.9(13) | N11B-Co3-N7 | 101.3(13) |
| O13-Co3-N7 | 90.9(9) | O17-Co3-N7 | 79.0(9) |
| O18-Co3-N7 | 176.4(12) | O16-Co3-N7 | 85.7(13) |

Symmetry codes: A: $-x+1, y, -z+2$; B: $x, -y+1, z$; C: $-x+1, -y+1, -z+2$; D: $-x+1/2, y+1/2, -z+1$; E: $x+1/2, y+1/2, z+1$; F: $x+1/2, y+1/2, z$; G: $-x+1, y, -z+1$; H: $x, -y+1, z-1$; I: $-x+1/2, y+1/2, -z$.

Table S3 Selected bond lengths (Å) and angles (°) for CoTb (**3**)

| | | | |
|-------------|-----------|-------------|-----------|
| Tb1-O9A | 2.221(7) | Tb1-O9 | 2.221(7) |
| Tb1-O1B | 2.294(5) | Tb1-O1C | 2.294(5) |
| Tb1-O6D | 2.319(5) | Tb1-O6E | 2.319(5) |
| Tb1-O21 | 2.460(12) | Tb2-O10F | 2.247(8) |
| Tb2-O7G | 2.284(5) | Tb2-O2H | 2.298(4) |
| Tb2-O5I | 2.332(5) | Tb2-O12 | 2.377(5) |
| Tb2-O3D | 2.452(5) | Tb2-O4D | 2.468(5) |
| Tb2-O11 | 2.503(5) | Co1-O14 | 2.062(9) |
| Co1-O13 | 2.073(8) | Co1-N2B | 2.146(5) |
| Co1-N2 | 2.146(5) | Co1-N10 | 2.202(18) |
| Co1-N10B | 2.202(18) | Co2-O13 | 2.083(8) |
| Co2-O15 | 2.083(10) | Co2-N6 | 2.098(7) |
| Co2-N6B | 2.098(7) | Co2-N3B | 2.110(5) |
| Co2-N3 | 2.110(5) | Co3-O13 | 2.029(7) |
| Co3-N7 | 2.039(9) | Co3-N11B | 2.054(14) |
| Co3-O17 | 2.097(9) | Co3-O18 | 2.096(8) |
| Co3-O16 | 2.112(9) | | |
| O9A-Tb1-O9 | 159.1(5) | O9A-Tb1-O1B | 87.7(4) |
| O9-Tb1-O1B | 84.1(3) | O9A-Tb1-O1C | 84.1(3) |
| O9-Tb1-O1C | 87.7(4) | O1B-Tb1-O1C | 133.6(3) |
| O9A-Tb1-O6D | 97.6(2) | O9-Tb1-O6D | 98.9(4) |
| O1B-Tb1-O6D | 75.50(18) | O1C-Tb1-O6D | 150.8(2) |

| | | | |
|--------------|------------|--------------|------------|
| O9A-Tb1-O6E | 98.9(4) | O9-Tb1-O6E | 97.6(2) |
| O1B-Tb1-O6E | 150.81(19) | O1C-Tb1-O6E | 75.50(18) |
| O6D-Tb1-O6E | 75.5(2) | O9A-Tb1-O21 | 69.1(5) |
| O9-Tb1-O21 | 90.2(5) | O1B-Tb1-O21 | 60.5(4) |
| O1C-Tb1-O21 | 74.0(4) | O6D-Tb1-O21 | 133.9(4) |
| O6E-Tb1-O21 | 148.1(4) | O10F-Tb2-O7G | 74.2(3) |
| O10F-Tb2-O2H | 92.3(3) | O7G-Tb2-O2H | 149.85(18) |
| O10F-Tb2-O5I | 111.9(3) | O7G-Tb2-O5I | 80.1(2) |
| O2H-Tb2-O5I | 80.23(18) | O10F-Tb2-O12 | 80.7(3) |
| O7G-Tb2-O12 | 129.5(2) | O2H-Tb2-O12 | 72.33(19) |
| O5I-Tb2-O12 | 150.4(2) | O10F-Tb2-O3D | 156.6(3) |
| O7G-Tb2-O3D | 127.83(19) | O2H-Tb2-O3D | 71.60(17) |
| O5I-Tb2-O3D | 82.7(2) | O12-Tb2-O3D | 78.2(2) |
| O10F-Tb2-O4D | 144.2(3) | O7G-Tb2-O4D | 77.48(18) |
| O2H-Tb2-O4D | 122.69(17) | O5I-Tb2-O4D | 83.94(19) |
| O12-Tb2-O4D | 101.4(2) | O3D-Tb2-O4D | 51.85(16) |
| O10F-Tb2-O11 | 78.7(3) | O7G-Tb2-O11 | 79.6(2) |
| O2H-Tb2-O11 | 124.87(18) | O5I-Tb2-O11 | 153.43(19) |
| O12-Tb2-O11 | 52.57(19) | O3D-Tb2-O11 | 96.39(19) |
| O4D-Tb2-O11 | 75.0(2) | O14-Co1-O13 | 177.5(4) |
| O14-Co1-N2B | 95.1(3) | O13-Co1-N2B | 86.7(2) |
| O14-Co1-N2 | 95.1(3) | O13-Co1-N2 | 86.7(2) |
| N2B-Co1-N2 | 87.0(3) | O14-Co1-N10 | 99.3(4) |
| O13-Co1-N10 | 79.2(3) | N2B-Co1-N10 | 83.1(5) |
| N2-Co1-N10 | 163.2(5) | O14-Co1-N10B | 99.3(4) |
| O13-Co1-N10B | 79.2(3) | N2B-Co1-N10B | 163.2(5) |
| N2-Co1-N10B | 83.1(5) | N10-Co1-N10B | 103.0(10) |
| O13-Co2-O15 | 178.1(4) | O13-Co2-N6 | 90.5(3) |
| O15-Co2-N6 | 90.8(3) | O13-Co2-N6B | 90.5(3) |
| O15-Co2-N6B | 90.8(3) | N6-Co2-N6B | 93.8(4) |
| O13-Co2-N3B | 86.8(2) | O15-Co2-N3B | 91.8(3) |
| N6-Co2-N3B | 176.2(3) | N6B-Co2-N3B | 88.8(3) |
| O13-Co2-N3 | 86.8(2) | O15-Co2-N3 | 91.8(3) |
| N6-Co3-N3 | 88.8(3) | N6B-Co3-N3 | 176.2(3) |
| N3B-Co2-N3 | 88.4(3) | O13-Co3-N7 | 94.9(4) |
| O13-Co3-N11B | 78.3(5) | N7-Co3-N11B | 97.2(6) |
| O13-Co3-O17 | 106.2(4) | N7-Co3-O17 | 82.1(5) |
| O11B-Co3-O17 | 175.5(5) | O13-Co3-O18 | 97.1(4) |
| N7-Co3-O18 | 166.4(6) | N11B-Co3-O18 | 91.3(6) |
| O17-Co3-O18 | 88.6(6) | O13-Co3-O16 | 177.1(7) |
| N7-Co3-O16 | 85.6(7) | N11B-Co3-O16 | 98.7(8) |
| O17-Co3-O16 | 76.7(7) | O18-Co3-O16 | 82.7(7) |

Symmetry codes: A: -x+1, y, -z+2; B: x, -y+1, z; C: -x+1, -y+1, -z+2; D: -x+1/2, y+1/2, -z+1; E: x+1/2, y+1/2, z+1; F: x+1/2, y+1/2, z; G: -x+1, y, -z+1; H: x, -y+1, z-

1; I: -x+1/2, y+1/2, -z.

Table S4 Selected bond lengths (Å) and angles (°) for CoDy (4)

| | | | |
|--------------|-----------|---------------|-----------|
| Dy1-O9 | 2.237(11) | Dy1-O9A | 2.237(11) |
| Dy1-O1B | 2.308(12) | Dy1-O1C | 2.308(12) |
| Dy1-O6D | 2.315(12) | Dy1-O6E | 2.315(12) |
| Dy1-O21 | 2.473(19) | Dy2-O10F | 2.278(12) |
| Dy2-O7G | 2.270(11) | Dy2-O2H | 2.315(10) |
| Dy2-O5I | 2.371(11) | Dy2-O12 | 2.372(11) |
| Dy2-O4E | 2.426(11) | Dy2-O3E | 2.463(11) |
| Dy2-O11 | 2.528(10) | Co1-O13 | 2.046(19) |
| Co1-O14 | 2.153(19) | Co1-N2 | 2.162(13) |
| Co1-N2B | 2.162(13) | Co1-N10B | 2.19(3) |
| Co1-N10 | 2.19(3) | Co2-O13 | 2.09(2) |
| Co2-O15 | 2.08(2) | Co2-N6 | 2.107(13) |
| Co2-N6B | 2.107(13) | Co2-N3 | 2.112(12) |
| Co2-N3B | 2.112(12) | Co3-N11B | 2.04(3) |
| Co3-O13 | 2.079(17) | Co3-O17 | 2.090(9) |
| Co3-O18 | 2.086(10) | Co3-O16 | 2.106(10) |
| Co3-N7 | 2.16(2) | | |
| O9-Dy1-O9A | 167.1(10) | O9-Dy1-O1B | 84.3(5) |
| O9A-Dy1-O1B | 90.9(7) | O9-Dy1-O1C | 90.9(7) |
| O9A-Dy1-O1C | 84.3(5) | O1B-Dy1-O1C | 136.6(6) |
| O9-Dy1-O6D | 98.0(4) | O9A-Dy1-O6D | 92.2(7) |
| O1B- Dy1-O6D | 148.9(4) | O1C-Dy1-O6D | 74.5(4) |
| O9-Dy1-O6E | 92.2(7) | O9A-Dy1-O6E | 98.0(4) |
| O1B-Dy1-O6E | 74.5(4) | O1C-Dy1-O6E | 148.9(4) |
| O6D-Dy1-O6E | 74.5(6) | O9-Dy1-O21 | 89.3(9) |
| O9A-Dy1-O21 | 77.8(9) | O1B-Dy1-O21 | 65.3(11) |
| O1C-Dy1-O21 | 71.5(10) | O6D-Dy1-O21 | 145.3(11) |
| O6E-Dy1-O21 | 139.4(10) | O21A- Dy1-O21 | 13.4(14) |
| O10F-Dy2-O7G | 75.7(5) | O10F-Dy2-O2H | 89.3(6) |
| O7G-Dy2-O2H | 147.7(4) | O10F-Dy2-O5I | 106.3(6) |
| O7G-Dy2-O5I | 78.3(5) | O2H-Dy2-O5I | 78.9(4) |
| O10F-Dy2-O12 | 81.7(6) | O7G-Dy2-O12 | 130.4(4) |
| O2H-Dy2-O12 | 73.5(4) | O5I-Dy2-O12 | 151.1(4) |
| O10F-Dy2-O4E | 145.5(6) | O7G-Dy2-O4E | 77.3(4) |
| O2H-Dy2-O4E | 124.5(4) | O5I-Dy2-O4E | 88.7(4) |
| O12-Dy2-O4E | 100.1(5) | O10F-Dy2-O3E | 155.6(5) |
| O7G-Dy2-O3E | 128.4(4) | O2H-Dy2-O3E | 71.2(4) |
| O5I-Dy2-O3E | 84.6(5) | O12-Dy2-O3E | 78.9(5) |
| O4E-Dy2-O3E | 53.8(4) | O10F-Dy2-O11 | 77.2(6) |
| O7G-Dy2-O11 | 78.5(4) | O2H-Dy2-O11 | 126.4(4) |

| | | | |
|--------------|-----------|--------------|-----------|
| O5I-Dy2-O11 | 154.7(4) | O12-Dy2-O11 | 53.5(4) |
| O4E-Dy2-O11 | 76.6(4) | O3E-Dy2-O11 | 102.3(4) |
| O13-Co1-O14 | 179.3(9) | O13-Co1-N2 | 87.5(6) |
| O14-Co1-N2 | 92.0(6) | O13-Co1-N2B | 87.5(6) |
| O14-Co1-N2B | 92.0(6) | N2-Co1-N2B | 86.1(7) |
| O13-Co1-N10B | 81.1(7) | O14-Co1-N10B | 99.4(7) |
| N2-Co1-N10B | 83.8(10) | N2B-Co1-N10B | 165.0(10) |
| O13-Co1-N10 | 81.1(7) | O14-Co1-N10 | 99.4(7) |
| O2-Co1-N10 | 165.0(10) | N2B-Co1-N10 | 83.8(10) |
| N10B-Co1-N10 | 103.8(18) | O13-Co2-O15 | 178.1(8) |
| O13-Co2-N6 | 90.5(6) | O15-Co2-N6 | 90.8(6) |
| O13-Co2-N6B | 90.5(6) | O15-Co2-N6B | 90.8(6) |
| N6-Co2-N6B | 95.2(8) | O13-Co2-N3 | 86.5(5) |
| O15-Co2-N3 | 92.1(6) | N6-Co2-N3 | 88.9(5) |
| N6B-Co2-N3 | 175.0(6) | O13-Co2-N3B | 86.5(5) |
| O15-Co2-N3B | 92.1(6) | N6-Co2-N3B | 175.0(6) |
| N6B-Co2-N3B | 88.9(5) | N3-Co2-N3B | 86.9(7) |
| N11B-Co3-O13 | 80.7(9) | N11B-Co3-O17 | 173.6(12) |
| O13-Co3-O17 | 105.2(7) | N11B-Co3-O18 | 85.6(13) |
| O13-Co3-O18 | 94.6(8) | O17-Co3-O18 | 91.3(10) |
| N11B-Co3-O16 | 95.6(13) | O13-Co3-O16 | 175.8(10) |
| O17-Co3-O16 | 78.6(11) | O18-Co3-O16 | 87.0(13) |
| N11B-Co3-N7 | 99.5(14) | O13-Co3-N7 | 89.0(8) |
| O17-Co3-N7 | 83.3(9) | O18-Co3-N7 | 174.2(10) |
| O16-Co3-N7 | 89.7(12) | | |

Symmetry codes: A: $-x+1, y, -z+2$; B: $x, -y+1, z$; C: $-x+1, -y+1, -z+2$; D: $-x+1/2, y+1/2, -z+1$; E: $x+1/2, y+1/2, z+1$; F: $x+1/2, y+1/2, z$; G: $-x+1, y, -z+1$; H: $x, -y+1, z-1$; I: $-x+1/2, y+1/2, -z$.

Table S5 Selected bond lengths (Å) and angles (°) for CoHo (5)

| | | | |
|---------|-----------|----------|-----------|
| Ho1-O9A | 2.223(13) | Ho1-O9 | 2.223(13) |
| Ho1-O1B | 2.277(12) | Ho1-O1C | 2.277(12) |
| Ho1-O6D | 2.302(13) | Ho1-O6E | 2.302(13) |
| Ho1-O21 | 2.43(2) | Ho2-O10F | 2.26(4) |
| Ho2-O7G | 2.276(13) | Ho2-O2H | 2.304(12) |
| Ho2-O5I | 2.364(12) | Ho2-O12 | 2.389(12) |
| Ho2-O4D | 2.433(12) | Ho2-O3D | 2.450(13) |
| Ho2-O11 | 2.519(11) | Co1-O13 | 2.07(2) |
| Co1-O14 | 2.10(2) | Co1-N2B | 2.158(14) |
| Co1-N2 | 2.158(14) | Co1-N10B | 2.15(3) |
| Co1-N10 | 2.15(3) | Co2-O15 | 2.041(19) |
| Co2-O13 | 2.06(2) | Co2-N6 | 2.110(16) |

| | | | |
|--------------|-----------|--------------|-----------|
| Co2-N6B | 2.110(16) | Co2-N3B | 2.126(14) |
| Co2-N3 | 2.126(14) | Co3-N11B | 2.08(3) |
| Co3-O17 | 2.087(10) | Co3-O13 | 2.09(2) |
| Co3-O16 | 2.099(10) | Co3-O18 | 2.097(10) |
| Co3-N7 | 2.19(2) | | |
| O9A-Ho1-O9 | 166.5(8) | O9A-Ho1-O1B | 90.0(5) |
| O9-Ho1-O1B | 85.0(5) | O9A-Ho1-O1C | 85.0(5) |
| O9-Ho1-O1C | 90.0(5) | O1B-Ho1-O1C | 136.2(6) |
| O9A-Ho1-O6D | 98.6(5) | O9-Ho1-O6D | 92.2(5) |
| O1B-Ho1-O6D | 75.3(4) | O1C-Ho1-O6D | 148.5(5) |
| O9A-Ho1-O6E | 92.2(5) | O9-Ho1-O6E | 98.6(5) |
| O1B-Ho1-O6E | 148.5(5) | O1C-Ho1-O6E | 75.3(4) |
| O6D-Ho1-O6E | 73.4(7) | O9A-Ho1-O21 | 79.4(12) |
| O9-Ho1-O21 | 87.2(12) | O1B-Ho1-O21 | 64.3(12) |
| O1C-Ho1-O21 | 72.0(12) | O6D-Ho1-O21 | 139.4(12) |
| O6E-Ho1-O21 | 146.7(13) | O21A-Ho1-O21 | 11.3(19) |
| O10F-Ho2-O7G | 75.8(17) | O10F-Ho2-O2H | 89.5(14) |
| O7G-Ho2-O2H | 147.3(5) | O10F-Ho2-O5I | 106.1(12) |
| O7G-Ho2-O5I | 77.4(5) | O2H-Ho2-O5I | 79.1(4) |
| O10F-Ho2-O12 | 79.2(16) | O7G-Ho2-O12 | 130.2(5) |
| O2H-Ho2-O12 | 73.1(5) | O5I-Ho2-O12 | 151.7(5) |
| O10F-Ho2-O4D | 145.1(13) | O7G-Ho2-O4D | 76.7(5) |
| O2H-Ho2-O4D | 124.9(5) | O5I-Ho2-O4D | 88.2(5) |
| O12-Ho2-O4D | 103.2(6) | O10F-Ho2-O3D | 155.0(17) |
| O7G-Ho2-O3D | 128.6(5) | O2H-Ho2-O3D | 71.9(5) |
| O5I-Ho2-O3D | 86.9(5) | O12-Ho2-O3D | 79.6(5) |
| O4D-Ho2-O3D | 53.9(4) | O10F-Ho2-O11 | 77.3(9) |
| O7G-Ho2-O11 | 78.6(5) | O2H-Ho2-O11 | 126.9(4) |
| O5I-Ho2-O11 | 154.0(4) | O12-Ho2-O11 | 54.1(4) |
| O4D-Ho2-O11 | 76.5(4) | O3D-Ho2-O11 | 100.4(4) |
| O13-Co1-O14 | 179.9(8) | O13-Co1-N2B | 87.5(6) |
| O14-Co1-N2B | 92.6(6) | O13-Co1-N2 | 87.5(6) |
| O14-Co1-N2 | 92.6(6) | O2B-Co1-N2 | 86.2(8) |
| O13-Co1-N10B | 82.1(7) | O14-Co1-N10B | 97.9(7) |
| N2B-Co1-N10B | 166.6(9) | N2-Co1-N10B | 85.0(9) |
| O13-Co1-N10 | 82.1(7) | O14-Co1-N10 | 97.9(7) |
| N2B-Co1-N10 | 85.0(9) | N2-Co1-N10 | 166.6(9) |
| O10B-Co1-N10 | 101.8(15) | O15-Co2-O13 | 178.8(9) |
| O15-Co2-N6 | 90.9(6) | O13-Co2-N6 | 89.9(6) |
| O15-Co2-N6B | 90.9(6) | O13-Co2-N6B | 89.9(6) |
| N6-Co2-N6B | 96.2(9) | O15-Co2-N3B | 92.1(6) |
| O13-Co2-N3B | 87.0(6) | N6-Co2-N3B | 174.6(6) |
| N6B-Co2-N3B | 88.2(6) | O15-Co2-N3 | 92.1(6) |

| | | | |
|--------------|-----------|--------------|-----------|
| O13-Co2-N3 | 87.0(6) | N6-Co2-N3 | 88.2(6) |
| N6B-Co2-N3 | 174.6(6) | N3B-Co2-N3 | 87.3(9) |
| N11B-Co3-O17 | 172.0(12) | N11B-Co3-O13 | 82.1(9) |
| O17-Co3-O13 | 105.2(8) | N11B-Co3-O16 | 95.4(13) |
| O17-Co3-O16 | 77.5(12) | O13-Co3-O16 | 176.7(11) |
| N11B-Co3-O18 | 86.7(12) | O17-Co3-O18 | 89.0(10) |
| O13-Co3-O18 | 97.9(8) | O16-Co3-O18 | 84.0(12) |
| N11B-Co3-N7 | 99.7(13) | O17-Co3-N7 | 84.2(9) |
| O13-Co3-N7 | 86.4(8) | O16-Co3-N7 | 92.1(12) |
| O18-Co3-N7 | 172.8(11) | | |

Symmetry codes: A: $-x+1, y, -z+2$; B: $x, -y+1, z$; C: $-x+1, -y+1, -z+2$; D: $-x+1/2, y+1/2, -z+1$; E: $x+1/2, y+1/2, z+1$; F: $x+1/2, y+1/2, z$; G: $-x+1, y, -z+1$; H: $x, -y+1, z-1$; I: $-x+1/2, y+1/2, -z$.

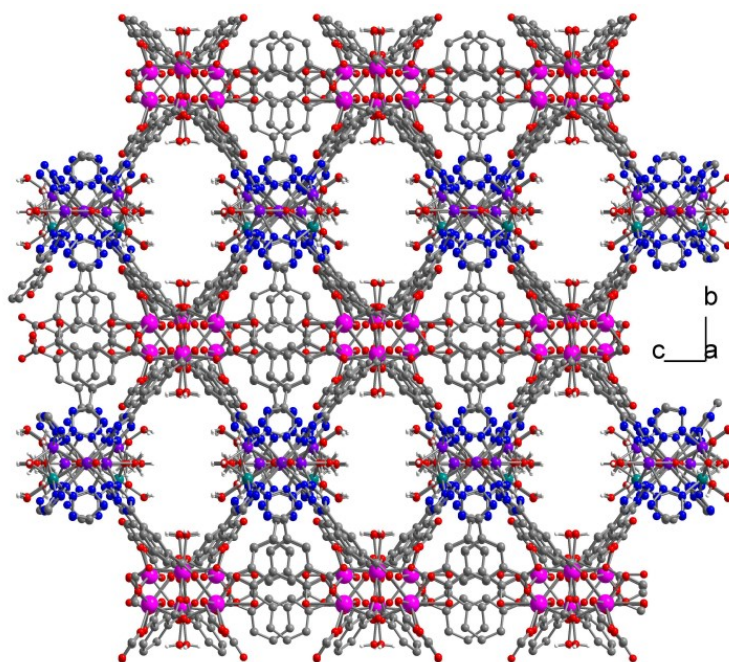


Fig. S1 3D structure of CoDy (4) along the *a*-axis.

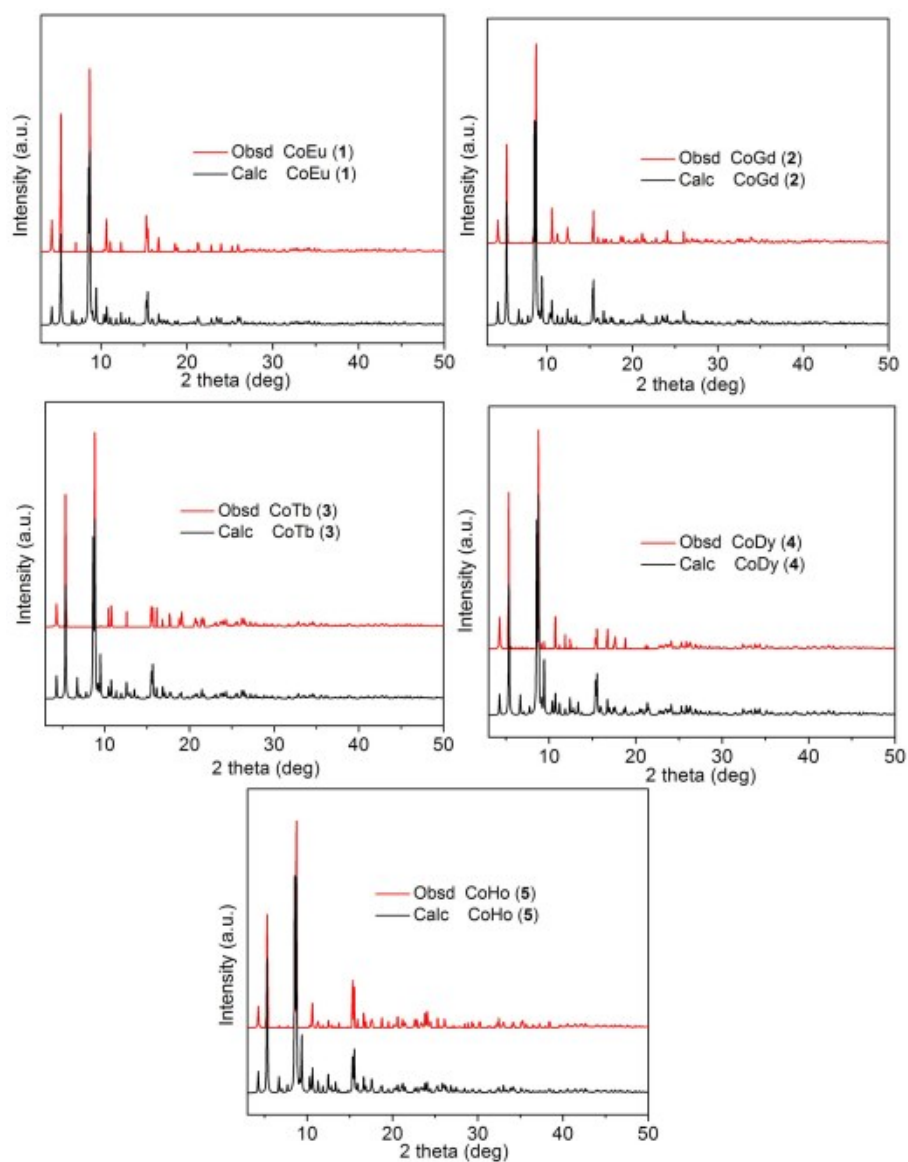


Fig. S2 PXR D patterns of CoLn (1-5) (black line) simulated from the single-crystal data, (red line) for the as-synthesized sample.

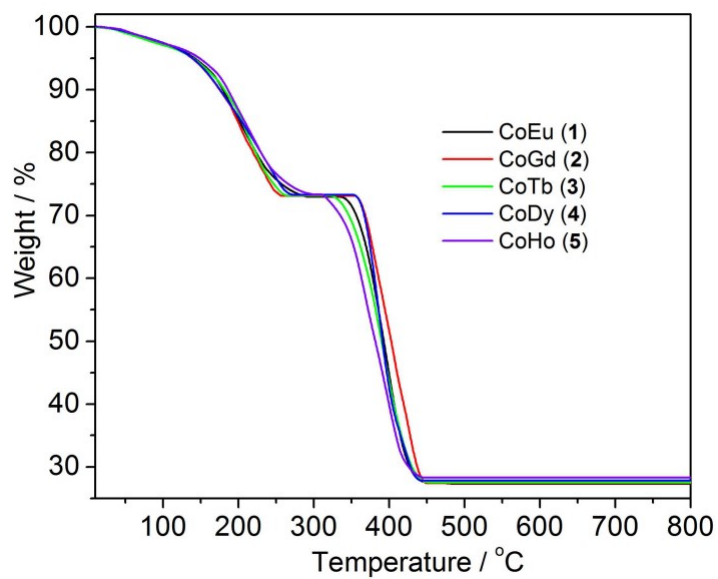


Fig. S3 TGA plots of CoLn (1-5).

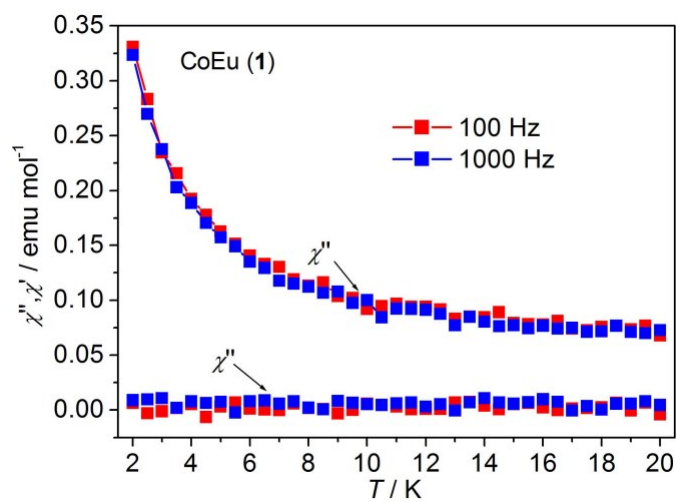


Fig. S4 In-phase (shown as χ') and out-of-phase (χ'') ac susceptibility signals of CoEu (1) oscillating at the indicated frequencies at $H_{ac} = 2.0$ Oe and $H_{dc} = 0$.

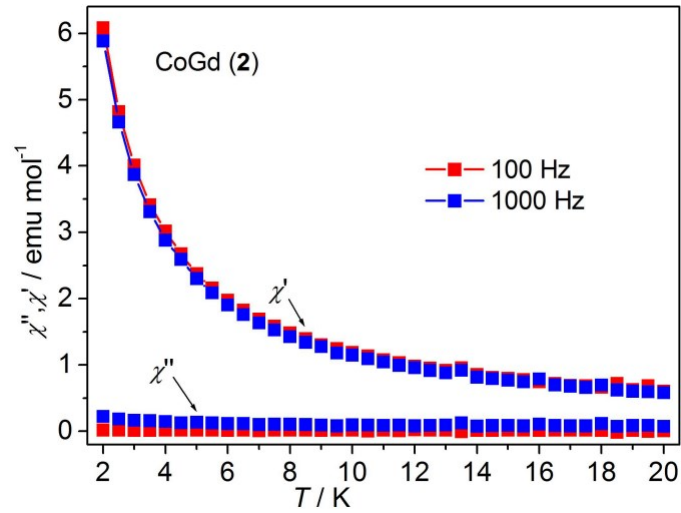


Fig. S5 In-phase (shown as χ') and out-of-phase (χ'') ac susceptibility signals of CoGd (2) oscillating at the indicated frequencies at $H_{\text{ac}} = 2.0$ Oe and $H_{\text{dc}} = 0$.

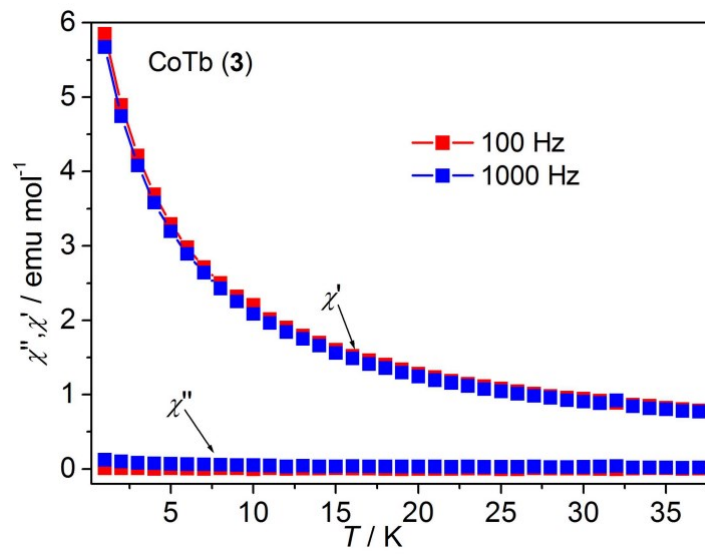


Fig. S6 In-phase (shown as χ') and out-of-phase (χ'') ac susceptibility signals of CoTb (3) oscillating at the indicated frequencies at $H_{\text{ac}} = 2.0$ Oe and $H_{\text{dc}} = 0$.

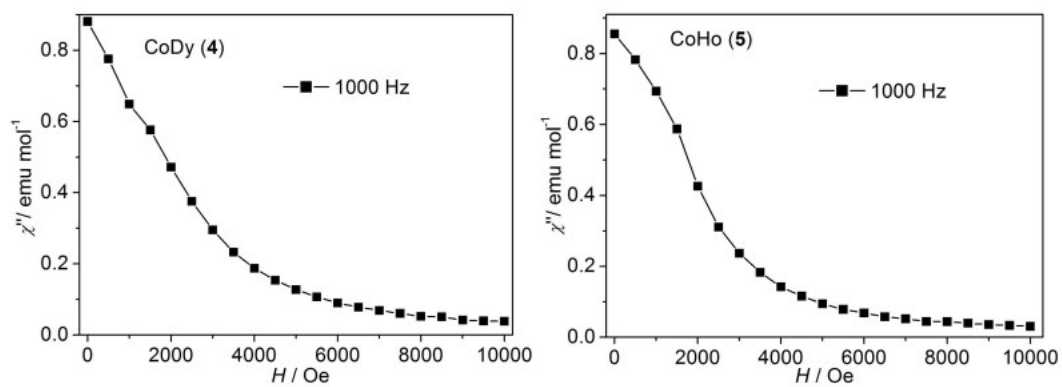


Fig. S7 The out-of-phase (χ'') ac susceptibility for CoDy (**4**) and CoHo (**5**) (2 K, $f = 1000$ Hz) under the applied static field from 0-10000 Oe.

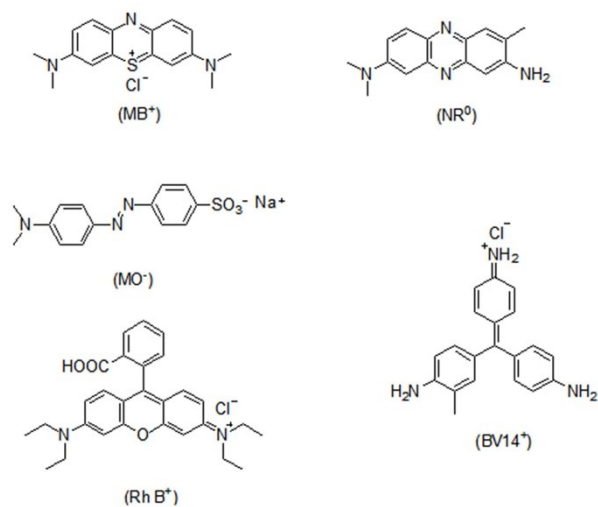


Fig. S8 Chemical structures of dyes used in this study.

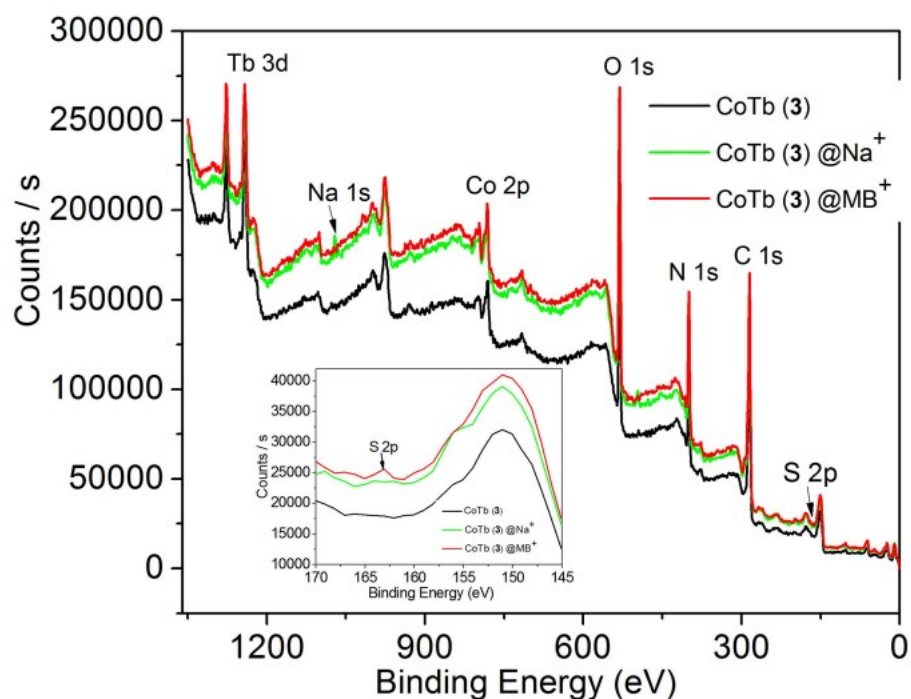


Fig. S9 Comparison of the XPS spectra of CoTb (3) (black), CoTb (3)@MB⁺ (red) and CoTb (3)@Na⁺ (green).

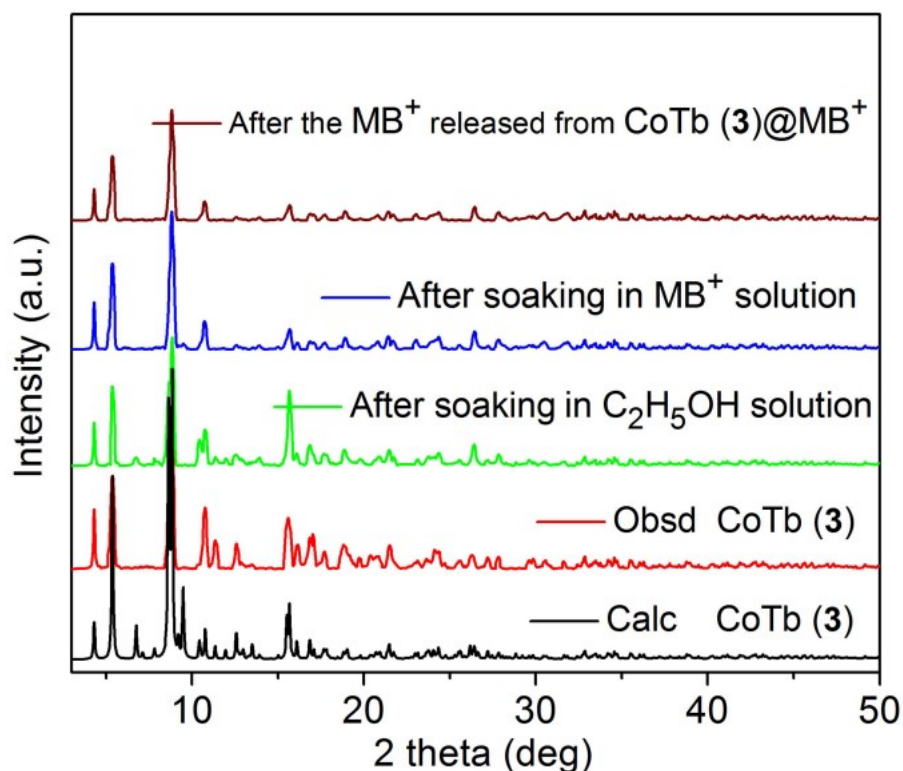


Fig. S10 The powder X-ray diffraction patterns of simulated CoTb (3), as-synthesized CoTb (3), CoTb (3) immersed in EtOH solutions and after the absorption and desorption of MB⁺, respectively.