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# The Photocatalysis from a series of polyoxoazocobaltate high-nuclearity nanoclusters

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**Table S1.** Selected bond distances (Å) and angles (°) for compounds **2**–**3**.

| Compound **2** | | | |
|---|---|---|---|
| Co(1)–O(7) | 1.985(13) | Co(2)–O(22) | 2.009(10) |
| Co(1)–O(22) | 1.997(12) | Co(2)–O(19) | 2.024(10) |
| Co(1)–O(24) | 2.011(11) | Co(2)–O(21) | 2.037(11) |
| Co(1)–O(25) | 2.053(11) | Co(2)–N(13) | 2.073(17) |
| Co(1)–N(15) | 2.109(16) | Co(2)–O(20) | 2.078(10) |
| Co(1)–O(1) | 2.400(11) | Co(2)–O(1) | 2.452(12) |
| Co(3)–O(18) | 1.989(11) | Co(4)–O(12) | 2.004(11) |
| Co(3)–O(16) | 1.997(11) | Co(4)–O(14) | 2.016(12) |
| Co(3)–O(17) | 2.024(12) | Co(4)–O(15) | 2.037(11) |
| Co(3)–O(19) | 2.027(11) | Co(4)–O(16) | 2.081(12) |
| Co(3)–N(11) | 2.149(16) | Co(4)–N(8) | 2.293(17) |
| Co(3)–O(2) | 2.405(11) | Co(4)–O(2) | 2.450(10) |
| Co(5)–O(5) | 2.014(11) | Co(6)–O(5) | 2.005(12) |
| Co(5)–O(13) | 2.031(11) | Co(6)–O(8) | 2.058(11) |
| Co(5)–O(9) | 2.042(11) | Co(6)–O(7) | 2.058(12) |
| Co(5)–O(12) | 2.045(11) | Co(6)–O(6) | 2.065(10) |
| Co(5)–N(3) | 2.110(18) | Co(6)–N(1) | 2.165(16) |
| Co(5)–O(3) | 2.426(12) | Co(6)–O(3) | 2.369(11) |
| Co(7)–O(13) | 1.993(12) | Co(8)–O(11) | 1.990(12) |

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|---|---|---|---|
| Co(7)–O(28) | 2.029(12) | Co(8)–O(23) | 2.010(11) |
| Co(7)–O(15) | 2.074(11) | Co(8)–O(17) | 2.011(12) |
| Co(7)–O(26) | 2.110(11) | Co(8)–O(14) | 2.044(12) |
| Co(7)–N(23) | 2.1(6) | Co(8)–N(9) | 2.169(18) |
| Co(7)–O(4) | 2.424(10) | Co(8)–O(2) | 2.511(11) |
| Co(9)–O(21) | 2.033(12) | Co(10)–O(9) | 1.996(11) |
| Co(9)–O(24) | 2.043(11) | Co(10)–O(10) | 2.000(11) |
| Co(9)–O(23) | 2.058(11) | Co(10)–O(6) | 2.016(10) |
| Co(9)–O(10) | 2.075(12) | Co(10)–O(11) | 2.065(11) |
| Co(9)–N(17) | 2.200(16) | Co(10)–N(5) | 2.128(15) |
| Co(9)–O(1) | 2.469(11) | Co(10)–O(3) | 2.459(11) |
| Co(11)–N(19) | 2.055(16) | Co(12)–O(19) | 2.081(11) |
| Co(11)–O(7) | 2.089(11) | Co(12)–O(20) | 2.097(11) |
| Co(11)–N(2) | 2.125(18) | Co(12)–O(18) | 2.100(11) |
| Co(11)–O(25) | 2.135(12) | Co(12)–N(22) | 2.11(4) |
| Co(11)–O(8) | 2.162(11) | Co(12)–N(12) | 2.127(16) |
| Co(11)–N(16) | 2.218(19) | Co(12)–N(14) | 2.150(17) |
| Co(13)–O(25) | 1.984(11) | Co(15)–O(12) | 2.125(11) |
| Co(13)–O(27) | 2.020(12) | Co(15)–O(15) | 2.128(12) |
| Co(13)–O(26) | 2.034(12) | Co(15)–O(13) | 2.140(11) |
| Co(13)–O(8) | 2.051(12) | Co(15)–N(4) | 2.224(19) |
| Co(13)–N(20) | 2.181(15) | Co(15)–N(7) | 2.23(2) |
| Co(13)–O(4) | 2.495(10) | Co(15)–S(24) | 2.398(13) |
| Co(16)–O(6) | 2.055(11) | Co(17)–O(10) | 2.104(10) |
| Co(16)–O(5) | 2.077(11) | Co(17)–O(23) | 2.141(12) |
| Co(16)–O(9) | 2.081(11) | Co(17)–N(6) | 2.148(18) |
| Co(16)–S(2) | 2.488(6) | Co(17)–O(11) | 2.162(11) |
| Co(16)–S(6) | 2.503(6) | Co(17)–N(18) | 2.20(2) |
| Co(16)–S(4) | 2.529(7) | Co(17)–S(10) | 2.381(7) |
| Co(18)–O(20) | 1.989(11) | Co(19)–O(28) | 2.056(11) |

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|---|---|---|---|
| Co(18)–O(28) | 2.006(12) | Co(19)–O(26) | 2.137(12) |
| Co(18)–N(21) | 2.0(6) | Co(19)–O(27) | 2.152(11) |
| Co(18)–O(18) | 2.057(11) | Co(19)–O(29) | 2.171(16) |
| Co(18)–O(27) | 2.065(11) | Co(19)–N(24) | 2.33(6) |
| Co(18)–O(4) | 2.440(11) | Co(19)–S(22) | 2.36(3) |
| Co(20)–O(22) | 2.079(11) | Co(14)–O(17) | 2.036(12) |
| Co(20)–O(21) | 2.082(11) | Co(14)–O(16) | 2.095(11) |
| Co(20)–O(24) | 2.096(13) | Co(14)–O(14) | 2.111(12) |
| Co(20)–S(14) | 2.502(7) | Co(14)–N(10) | 2.31(2) |
| Co(20)–S(16) | 2.511(6) | Co(14)–S(12) | 2.511(7) |
| Co(20)–S(18) | 2.564(7) | | |
| O(7)–Co(1)–O(22) | 177.1(5) | O(22)–Co(2)–O(19) | 175.5(5) |
| O(7)–Co(1)–O(24) | 95.8(5) | O(22)–Co(2)–O(21) | 82.4(4) |
| O(22)–Co(1)–O(24) | 82.7(5) | O(19)–Co(2)–O(21) | 96.6(4) |
| O(7)–Co(1)–O(25) | 84.1(5) | O(22)–Co(2)–N(13) | 97.5(6) |
| O(22)–Co(1)–O(25) | 97.1(5) | O(19)–Co(2)–N(13) | 86.9(5) |
| O(24)–Co(1)–O(25) | 177.0(5) | O(21)–Co(2)–N(13) | 94.2(6) |
| O(7)–Co(1)–N(15) | 87.7(7) | O(22)–Co(2)–O(20) | 97.9(4) |
| O(22)–Co(1)–N(15) | 94.9(7) | O(19)–Co(2)–O(20) | 82.9(4) |
| O(24)–Co(1)–N(15) | 91.9(6) | O(21)–Co(2)–O(20) | 177.8(5) |
| O(25)–Co(1)–N(15) | 91.1(6) | N(13)–Co(2)–O(20) | 87.9(5) |
| O(7)–Co(1)–O(1) | 95.4(4) | O(22)–Co(2)–O(1) | 80.4(4) |
| O(22)–Co(1)–O(1) | 82.0(4) | O(19)–Co(2)–O(1) | 95.2(4) |
| O(24)–Co(1)–O(1) | 81.5(4) | O(21)–Co(2)–O(1) | 80.0(4) |
| O(25)–Co(1)–O(1) | 95.5(4) | N(13)–Co(2)–O(1) | 174.1(5) |
| N(15)–Co(1)–O(1) | 173.0(6) | O(20)–Co(2)–O(1) | 97.9(4) |
| O(18)–Co(3)–O(16) | 101.0(5) | O(12)–Co(4)–O(14) | 97.7(5) |
| O(18)–Co(3)–O(17) | 174.5(5) | O(12)–Co(4)–O(15) | 81.9(5) |
| O(16)–Co(3)–O(17) | 82.7(5) | O(14)–Co(4)–O(15) | 175.6(5) |
| O(18)–Co(3)–O(19) | 81.5(4) | O(12)–Co(4)–O(16) | 173.9(4) |

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|---|---|---|---|
| O(16)–Co(3)–O(19) | 177.5(5) | O(14)–Co(4)–O(16) | 80.6(5) |
| O(17)–Co(3)–O(19) | 94.8(5) | O(15)–Co(4)–O(16) | 99.3(5) |
| O(18)–Co(3)–N(11) | 89.8(6) | O(12)–Co(4)–N(8) | 88.2(7) |
| O(16)–Co(3)–N(11) | 95.4(6) | O(14)–Co(4)–N(8) | 94.3(7) |
| O(17)–Co(3)–N(11) | 93.9(6) | O(15)–Co(4)–N(8) | 90.1(7) |
| O(19)–Co(3)–N(11) | 84.1(5) | O(16)–Co(4)–N(8) | 97.8(7) |
| O(18)–Co(3)–O(16) | 101.0(5) | O(12)–Co(4)–O(14) | 97.7(5) |
| O(18)–Co(3)–O(17) | 174.5(5) | O(12)–Co(4)–O(15) | 81.9(5) |
| O(16)–Co(3)–O(17) | 82.7(5) | O(14)–Co(4)–O(15) | 175.6(5) |
| O(18)–Co(3)–O(19) | 81.5(4) | O(12)–Co(4)–O(16) | 173.9(4) |
| O(16)–Co(3)–O(19) | 177.5(5) | O(14)–Co(4)–O(16) | 80.6(5) |
| O(5)–Co(5)–O(13) | 98.2(5) | O(5)–Co(6)–O(8) | 96.1(5) |
| O(5)–Co(5)–O(9) | 81.5(4) | O(5)–Co(6)–O(7) | 177.1(4) |
| O(13)–Co(5)–O(9) | 176.7(5) | O(8)–Co(6)–O(7) | 85.2(5) |
| O(5)–Co(5)–O(12) | 174.2(5) | O(5)–Co(6)–O(6) | 81.6(4) |
| O(13)–Co(5)–O(12) | 84.0(5) | O(8)–Co(6)–O(6) | 177.4(5) |
| O(9)–Co(5)–O(12) | 95.9(4) | O(7)–Co(6)–O(6) | 97.1(5) |
| O(5)–Co(5)–N(3) | 95.5(6) | O(5)–Co(6)–N(1) | 95.2(6) |
| O(13)–Co(5)–N(3) | 89.5(6) | O(8)–Co(6)–N(1) | 89.4(6) |
| O(9)–Co(5)–N(3) | 93.8(6) | O(7)–Co(6)–N(1) | 87.4(6) |
| O(12)–Co(5)–N(3) | 89.8(6) | O(6)–Co(6)–N(1) | 92.1(6) |
| O(5)–Co(5)–O(13) | 98.2(5) | O(5)–Co(6)–O(8) | 96.1(5) |
| O(5)–Co(5)–O(9) | 81.5(4) | O(5)–Co(6)–O(7) | 177.1(4) |
| O(13)–Co(5)–O(9) | 176.7(5) | O(8)–Co(6)–O(7) | 85.2(5) |
| O(5)–Co(5)–O(12) | 174.2(5) | O(5)–Co(6)–O(6) | 81.6(4) |
| O(13)–Co(5)–O(12) | 84.0(5) | O(8)–Co(6)–O(6) | 177.4(5) |
| O(13)–Co(7)–O(28) | 175.2(5) | O(11)–Co(8)–O(17) | 174.7(5) |
| O(13)–Co(7)–O(15) | 84.1(5) | O(23)–Co(8)–O(17) | 94.8(5) |
| O(28)–Co(7)–O(15) | 93.2(5) | O(11)–Co(8)–O(14) | 96.9(5) |
| O(13)–Co(7)–O(26) | 99.1(5) | O(23)–Co(8)–O(14) | 177.0(5) |

| | | | |
|---|---|---|---|
| O(28)–Co(7)–O(26) | 83.4(5) | O(17)–Co(8)–O(14) | 83.1(5) |
| O(15)–Co(7)–O(26) | 176.5(5) | O(11)–Co(8)–N(9) | 100.3(7) |
| O(13)–Co(7)–N(23) | 96(10) | O(23)–Co(8)–N(9) | 94.1(6) |
| O(28)–Co(7)–N(23) | 88(10) | O(17)–Co(8)–N(9) | 84.9(7) |
| O(15)–Co(7)–N(23) | 93(10) | O(14)–Co(8)–N(9) | 87.8(7) |
| O(26)–Co(7)–N(23) | 88(10) | O(11)–Co(8)–O(2) | 96.8(4) |
| O(13)–Co(7)–O(28) | 175.2(5) | O(11)–Co(8)–O(17) | 174.7(5) |
| O(13)–Co(7)–O(15) | 84.1(5) | O(23)–Co(8)–O(17) | 94.8(5) |
| O(28)–Co(7)–O(15) | 93.2(5) | O(11)–Co(8)–O(14) | 96.9(5) |
| O(13)–Co(7)–O(26) | 99.1(5) | O(23)–Co(8)–O(14) | 177.0(5) |
| O(28)–Co(7)–O(26) | 83.4(5) | O(17)–Co(8)–O(14) | 83.1(5) |
| O(21)–Co(9)–O(24) | 81.1(5) | O(9)–Co(10)–O(10) | 175.6(4) |
| O(21)–Co(9)–O(23) | 98.8(5) | O(9)–Co(10)–O(6) | 81.3(4) |
| O(24)–Co(9)–O(23) | 177.3(4) | O(10)–Co(10)–O(6) | 97.0(5) |
| O(21)–Co(9)–O(10) | 174.1(4) | O(9)–Co(10)–O(11) | 98.2(5) |
| O(24)–Co(9)–O(10) | 97.3(5) | O(10)–Co(10)–O(11) | 83.3(4) |
| O(23)–Co(9)–O(10) | 82.6(4) | O(6)–Co(10)–O(11) | 178.1(4) |
| O(21)–Co(9)–N(17) | 98.3(6) | O(9)–Co(10)–N(5) | 94.9(6) |
| O(24)–Co(9)–N(17) | 94.2(6) | O(10)–Co(10)–N(5) | 89.3(6) |
| O(23)–Co(9)–N(17) | 88.5(6) | O(6)–Co(10)–N(5) | 93.9(5) |
| O(10)–Co(9)–N(17) | 87.5(6) | O(11)–Co(10)–N(5) | 88.0(5) |
| O(21)–Co(9)–O(24) | 81.1(5) | O(9)–Co(10)–O(10) | 175.6(4) |
| O(21)–Co(9)–O(23) | 98.8(5) | O(9)–Co(10)–O(6) | 81.3(4) |
| O(24)–Co(9)–O(23) | 177.3(4) | O(10)–Co(10)–O(6) | 97.0(5) |
| O(21)–Co(9)–O(10) | 174.1(4) | O(9)–Co(10)–O(11) | 98.2(5) |
| O(24)–Co(9)–O(10) | 97.3(5) | O(10)–Co(10)–O(11) | 83.3(4) |
| N(19)–Co(11)–O(7) | 164.1(6) | O(19)–Co(12)–O(20) | 81.0(4) |
| N(19)–Co(11)–N(2) | 104.0(7) | O(19)–Co(12)–O(18) | 77.6(4) |
| O(7)–Co(11)–N(2) | 86.5(6) | O(20)–Co(12)–O(18) | 78.9(4) |
| N(19)–Co(11)–O(25) | 87.2(6) | O(19)–Co(12)–N(22) | 156(2) |

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|---|---|---|---|
| O(7)–Co(11)–O(25) | 79.7(4) | O(20)–Co(12)–N(22) | 84.4(18) |
| N(2)–Co(11)–O(25) | 161.1(6) | O(18)–Co(12)–N(22) | 82(2) |
| N(19)–Co(11)–O(8) | 86.5(6) | O(19)–Co(12)–N(12) | 85.0(6) |
| O(7)–Co(11)–O(8) | 81.9(4) | O(20)–Co(12)–N(12) | 162.5(6) |
| N(2)–Co(11)–O(8) | 87.7(6) | O(18)–Co(12)–N(12) | 87.8(6) |
| O(25)–Co(11)–O(8) | 77.7(5) | N(22)–Co(12)–N(12) | 105.0(15) |
| N(19)–Co(11)–O(7) | 164.1(6) | O(19)–Co(12)–O(20) | 81.0(4) |
| N(19)–Co(11)–N(2) | 104.0(7) | O(19)–Co(12)–O(18) | 77.6(4) |
| O(7)–Co(11)–N(2) | 86.5(6) | O(20)–Co(12)–O(18) | 78.9(4) |
| N(19)–Co(11)–O(25) | 87.2(6) | O(19)–Co(12)–N(22) | 156(2) |
| O(7)–Co(11)–O(25) | 79.7(4) | O(20)–Co(12)–N(22) | 84.4(18) |
| O(25)–Co(13)–O(27) | 98.4(5) | O(12)–Co(15)–O(15) | 77.1(4) |
| O(25)–Co(13)–O(26) | 173.5(4) | O(12)–Co(15)–O(13) | 79.5(4) |
| O(27)–Co(13)–O(26) | 80.7(5) | O(15)–Co(15)–O(13) | 79.4(5) |
| O(25)–Co(13)–O(8) | 83.8(5) | O(12)–Co(15)–N(4) | 86.3(6) |
| O(27)–Co(13)–O(8) | 172.8(4) | O(15)–Co(15)–N(4) | 160.3(6) |
| O(26)–Co(13)–O(8) | 96.3(5) | O(13)–Co(15)–N(4) | 87.3(6) |
| O(25)–Co(13)–N(20) | 86.9(6) | O(12)–Co(15)–N(7) | 86.9(7) |
| O(27)–Co(13)–N(20) | 101.7(6) | O(15)–Co(15)–N(7) | 88.7(8) |
| O(26)–Co(13)–N(20) | 99.5(6) | O(13)–Co(15)–N(7) | 163.6(8) |
| O(8)–Co(13)–N(20) | 85.2(6) | N(4)–Co(15)–N(7) | 101.1(8) |
| O(25)–Co(13)–O(4) | 91.8(4) | O(12)–Co(15)–S(24) | 174.6(5) |
| O(27)–Co(13)–O(4) | 81.1(4) | O(15)–Co(15)–S(24) | 105.6(5) |
| O(26)–Co(13)–O(4) | 81.7(4) | O(13)–Co(15)–S(24) | 105.4(5) |
| O(8)–Co(13)–O(4) | 92.0(4) | N(4)–Co(15)–S(24) | 91.9(6) |
| N(20)–Co(13)–O(4) | 177.0(6) | N(7)–Co(15)–S(24) | 88.5(7) |
| O(6)–Co(16)–O(5) | 80.1(4) | O(10)–Co(17)–O(23) | 79.9(4) |
| O(6)–Co(16)–O(9) | 78.3(4) | O(10)–Co(17)–N(6) | 84.9(6) |
| O(5)–Co(16)–O(9) | 79.1(4) | O(23)–Co(17)–N(6) | 160.1(6) |
| O(6)–Co(16)–S(2) | 95.0(3) | O(10)–Co(17)–O(11) | 78.6(4) |

| | | | |
|---|---|---|---|
| O(5)–Co(16)–S(2) | 93.8(3) | O(23)–Co(17)–O(11) | 77.8(4) |
| O(9)–Co(16)–S(2) | 170.9(4) | N(6)–Co(17)–O(11) | 86.7(6) |
| O(6)–Co(16)–S(6) | 94.5(3) | O(10)–Co(17)–N(18) | 88.6(7) |
| O(5)–Co(16)–S(6) | 170.5(4) | O(23)–Co(17)–N(18) | 85.9(7) |
| O(9)–Co(16)–S(6) | 92.2(3) | N(6)–Co(17)–N(18) | 106.7(7) |
| S(2)–Co(16)–S(6) | 94.4(2) | O(11)–Co(17)–N(18) | 160.7(7) |
| O(6)–Co(16)–S(4) | 171.5(4) | O(10)–Co(17)–S(10) | 177.6(4) |
| O(5)–Co(16)–S(4) | 93.4(4) | O(23)–Co(17)–S(10) | 98.1(3) |
| O(9)–Co(16)–S(4) | 95.1(4) | N(6)–Co(17)–S(10) | 97.2(5) |
| S(2)–Co(16)–S(4) | 91.0(2) | O(11)–Co(17)–S(10) | 102.4(4) |
| S(6)–Co(16)–S(4) | 91.1(2) | N(18)–Co(17)–S(10) | 89.9(6) |
| O(20)–Co(18)–O(28) | 175.3(5) | O(28)–Co(19)–O(26) | 82.1(5) |
| O(20)–Co(18)–N(21) | 87(10) | O(28)–Co(19)–O(27) | 80.6(4) |
| O(28)–Co(18)–N(21) | 95(10) | O(26)–Co(19)–O(27) | 75.5(5) |
| O(20)–Co(18)–O(18) | 82.5(4) | O(28)–Co(19)–O(29) | 162.9(6) |
| O(28)–Co(18)–O(18) | 93.4(5) | O(26)–Co(19)–O(29) | 91.5(6) |
| N(21)–Co(18)–O(18) | 87(10) | O(27)–Co(19)–O(29) | 113.3(6) |
| O(20)–Co(18)–O(27) | 100.0(5) | O(28)–Co(19)–N(24) | 78.9(14) |
| O(28)–Co(18)–O(27) | 84.0(5) | O(26)–Co(19)–N(24) | 79.4(14) |
| N(21)–Co(18)–O(27) | 96(10) | O(27)–Co(19)–N(24) | 149.4(16) |
| O(18)–Co(18)–O(27) | 175.9(5) | O(29)–Co(19)–N(24) | 84.3(15) |
| O(20)–Co(18)–O(4) | 99.2(4) | O(28)–Co(19)–S(22) | 94.9(7) |
| O(28)–Co(18)–O(4) | 78.7(4) | O(26)–Co(19)–S(22) | 173.5(8) |
| N(21)–Co(18)–O(4) | 173(10) | O(27)–Co(19)–S(22) | 98.3(7) |
| O(18)–Co(18)–O(4) | 94.8(4) | O(29)–Co(19)–S(22) | 92.9(8) |
| O(27)–Co(18)–O(4) | 81.6(4) | N(24)–Co(19)–S(22) | 105.8(15) |
| O(22)–Co(20)–O(21) | 79.7(4) | O(17)–Co(14)–O(16) | 80.1(4) |
| O(22)–Co(20)–O(24) | 78.8(5) | O(17)–Co(14)–O(14) | 80.9(5) |
| O(21)–Co(20)–O(24) | 78.7(5) | O(16)–Co(14)–O(14) | 78.1(5) |
| O(22)–Co(20)–S(14) | 95.2(4) | O(17)–Co(14)–N(10) | 80.3(7) |

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|---|---|---|---|
| O(21)–Co(20)–S(14) | 94.1(4) | O(16)–Co(14)–N(10) | 156.0(7) |
| O(24)–Co(20)–S(14) | 171.3(4) | O(14)–Co(14)–N(10) | 85.3(7) |
| O(22)–Co(20)–S(16) | 93.9(3) | O(17)–Co(14)–S(12) | 93.5(4) |
| O(21)–Co(20)–S(16) | 171.9(4) | O(16)–Co(14)–S(12) | 96.2(4) |
| O(24)–Co(20)–S(16) | 95.2(4) | O(14)–Co(14)–S(12) | 172.6(4) |
| S(14)–Co(20)–S(16) | 91.4(2) | N(10)–Co(14)–S(12) | 98.6(6) |
| O(22)–Co(20)–S(18) | 170.6(4) | S(14)–Co(20)–S(18) | 90.0(2) |
| O(21)–Co(20)–S(18) | 92.2(3) | S(16)–Co(20)–S(18) | 93.7(2) |
| O(24)–Co(20)–S(18) | 95.1(4) | | |
| Compound **3** | | | |
| Co(1)–O(6) | 2.031(11) | Co(2)–O(9) | 2.054(11) |
| Co(1)–O(8) | 2.057(12) | Co(2)–O(10) | 2.060(11) |
| Co(1)–O(7) | 2.069(10) | Co(2)–O(5) | 2.076(10) |
| Co(1)–O(5) | 2.095(9) | Co(2)–O(11) | 2.091(10) |
| Co(1)–N(7) | 2.132(13) | Co(2)–N(30) | 2.131(12) |
| Co(3)–N(25) | 2.155(14) | Co(2)–O(1) | 2.442(10) |
| Co(3)–O(16) | 2.057(10) | Co(4)–O(11) | 2.042(11) |
| Co(3)–O(18) | 2.095(10) | Co(4)–O(16) | 2.056(11) |
| Co(3)–O(17) | 2.099(11) | Co(4)–O(12) | 2.095(11) |
| Co(3)–O(15) | 2.118(11) | Co(4)–O(13) | 2.122(11) |
| Co(5)–N(22) | 2.160(17) | Co(4)–N(27) | 2.175(13) |
| Co(5)–O(17) | 2.043(10) | Co(6)–O(9) | 2.053(9) |
| Co(5)–O(28) | 2.073(10) | Co(6)–O(23) | 2.068(9) |
| Co(5)–O(19) | 2.083(9) | Co(6)–O(6) | 2.074(10) |
| Co(5)–O(14) | 2.090(10) | Co(6)–O(25) | 2.090(10) |
| Co(7)–N(19) | 2.171(12) | Co(6)–N(10) | 2.101(16) |
| Co(7)–O(18) | 2.012(10) | Co(8)–O(23) | 2.052(10) |
| Co(7)–O(21) | 2.028(12) | Co(8)–O(21) | 2.059(11) |
| Co(7)–O(20) | 2.057(9) | Co(8)–O(24) | 2.098(10) |
| Co(7)–O(19) | 2.065(11) | Co(8)–O(22) | 2.111(10) |

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|---|---|---|---|
| Co(9)–O(3) | 2.449(10) | Co(8)–N(13) | 2.150(14) |
| Co(9)–O(22) | 2.044(11) | Co(11)–O(26) | 2.059(10) |
| Co(9)–O(20) | 2.048(10) | Co(11)–O(28) | 2.061(11) |
| Co(9)–O(7) | 2.088(10) | Co(11)–O(8) | 2.068(11) |
| Co(9)–O(26) | 2.089(11) | Co(11)–O(27) | 2.078(10) |
| Co(9)–N(1) | 2.172(12) | Co(11)–N(4) | 2.161(15) |
| Co(12)–O(22) | 2.085(10) | Co(13)–O(24) | 2.061(9) |
| Co(12)–O(20) | 2.114(11) | Co(13)–O(13) | 2.064(10) |
| Co(12)–O(21) | 2.137(10) | Co(13)–O(15) | 2.095(11) |
| Co(12)–N(20) | 2.223(14) | Co(13)–O(25) | 2.103(11) |
| Co(12)–S(10) | 2.492(6) | Co(13)–S(12) | 2.543(6) |
| Co(12)–S(2) | 2.501(5) | Co(15)–S(22) | 2.531(4) |
| Co(14)–O(19) | 2.155(10) | Co(15)–O(5) | 2.126(12) |
| Co(14)–O(17) | 2.159(10) | Co(15)–O(6) | 2.129(10) |
| Co(14)–O(18) | 2.166(12) | Co(15)–O(9) | 2.157(10) |
| Co(14)–N(26) | 2.192(14) | Co(15)–N(8) | 2.297(13) |
| Co(14)–N(23) | 2.237(17) | Co(15)–S(8) | 2.497(6) |
| Co(14)–S(14) | 2.529(5) | Co(17)–S(20) | 2.485(5) |
| Co(16)–O(26) | 2.151(11) | Co(17)–O(10) | 2.129(9) |
| Co(16)–O(8) | 2.163(10) | Co(17)–O(12) | 2.131(10) |
| Co(16)–O(7) | 2.165(11) | Co(17)–N(34) | 2.170(16) |
| Co(16)–N(5) | 2.183(16) | Co(17)–O(11) | 2.173(11) |
| Co(16)–N(2) | 2.215(13) | Co(17)–N(31) | 2.220(14) |
| Co(16)–S(6) | 2.489(5) | Co(19)–N(14) | 2.315(14) |
| Co(18)–O(16) | 2.085(11) | Co(19)–N(16) | 2.044(16) |
| Co(18)–O(13) | 2.147(11) | Co(19)–O(23) | 2.110(10) |
| Co(18)–O(15) | 2.147(10) | Co(19)–O(25) | 2.153(10) |
| Co(18)–O(29) | 2.150(14) | Co(19)–O(24) | 2.198(11) |
| Co(18)–N(28) | 2.257(13) | Co(19)–N(11) | 2.271(16) |
| Co(18)–S(18) | 2.524(6) | Co(10)–O(27) | 2.468(11) |

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|---|---|---|---|
| Co(20)–O(27) | 2.130(11) | Co(10)–O(14) | 2.053(11) |
| Co(20)–O(14) | 2.135(11) | Co(10)–O(12) | 2.057(10) |
| Co(20)–O(28) | 2.143(10) | Co(10)–O(10) | 2.084(10) |
| Co(20)–S(16) | 2.513(6) | Co(10)–N(33) | 2.192(15) |
| Co(20)–S(24) | 2.565(5) | O(11)–Co(2)–O(1) | 97.9(4) |
| Co(20)–S(4) | 2.658(5) | N(30)–Co(2)–O(1) | 173.1(4) |
| O(6)–Co(1)–O(8) | 175.7(4) | O(9)–Co(2)–O(10) | 177.7(4) |
| O(6)–Co(1)–O(7) | 94.3(4) | O(9)–Co(2)–O(5) | 84.7(4) |
| O(8)–Co(1)–O(7) | 84.7(4) | O(10)–Co(2)–O(5) | 93.5(4) |
| O(6)–Co(1)–O(5) | 84.6(4) | O(9)–Co(2)–O(11) | 98.0(4) |
| O(8)–Co(1)–O(5) | 96.4(4) | O(10)–Co(2)–O(11) | 83.9(4) |
| O(7)–Co(1)–O(5) | 178.6(4) | O(5)–Co(2)–O(11) | 177.3(5) |
| O(6)–Co(1)–N(7) | 87.3(5) | O(9)–Co(2)–N(30) | 95.6(5) |
| O(8)–Co(1)–N(7) | 96.9(5) | O(10)–Co(2)–N(30) | 85.8(5) |
| O(7)–Co(1)–N(7) | 95.6(4) | O(5)–Co(2)–N(30) | 91.6(4) |
| O(5)–Co(1)–N(7) | 85.2(4) | O(11)–Co(2)–N(30) | 89.0(4) |
| O(6)–Co(1)–O(1) | 78.4(4) | O(9)–Co(2)–O(1) | 83.1(4) |
| O(17)–Co(3)–N(25) | 84.9(5) | O(10)–Co(2)–O(1) | 95.3(4) |
| O(15)–Co(3)–N(25) | 95.7(5) | O(5)–Co(2)–O(1) | 81.6(4) |
| O(16)–Co(3)–O(18) | 173.9(4) | O(11)–Co(4)–O(16) | 174.5(4) |
| O(16)–Co(3)–O(17) | 92.4(4) | O(11)–Co(4)–O(12) | 83.6(4) |
| O(18)–Co(3)–O(17) | 83.0(4) | O(16)–Co(4)–O(12) | 92.3(4) |
| O(16)–Co(3)–O(15) | 83.8(4) | O(11)–Co(4)–O(13) | 99.8(4) |
| O(18)–Co(3)–O(15) | 100.8(4) | O(16)–Co(4)–O(13) | 84.2(4) |
| O(17)–Co(3)–O(15) | 176.1(4) | O(12)–Co(4)–O(13) | 176.5(4) |
| O(16)–Co(3)–N(25) | 93.2(5) | O(11)–Co(4)–N(27) | 98.2(5) |
| O(18)–Co(3)–N(25) | 90.4(4) | O(16)–Co(4)–N(27) | 85.7(5) |
| O(19)–Co(5)–N(22) | 88.1(5) | O(12)–Co(4)–N(27) | 93.4(5) |
| O(14)–Co(5)–N(22) | 94.7(5) | O(13)–Co(4)–N(27) | 86.2(5) |
| O(17)–Co(5)–O(28) | 177.8(5) | O(9)–Co(6)–O(23) | 174.9(4) |

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|---|---|---|---|
| O(17)–Co(5)–O(19) | 82.2(4) | O(9)–Co(6)–O(6) | 83.3(4) |
| O(28)–Co(5)–O(19) | 98.1(4) | O(23)–Co(6)–O(6) | 92.9(4) |
| O(17)–Co(5)–O(14) | 96.2(4) | O(9)–Co(6)–O(25) | 100.2(4) |
| O(28)–Co(5)–O(14) | 83.3(4) | O(23)–Co(6)–O(25) | 83.2(4) |
| O(19)–Co(5)–O(14) | 176.8(5) | O(6)–Co(6)–O(25) | 173.8(4) |
| O(17)–Co(5)–N(22) | 88.0(5) | O(9)–Co(6)–N(10) | 95.9(5) |
| O(28)–Co(5)–N(22) | 94.1(5) | O(23)–Co(6)–N(10) | 87.6(5) |
| O(20)–Co(7)–N(19) | 85.8(4) | O(6)–Co(6)–N(10) | 92.3(5) |
| O(19)–Co(7)–N(19) | 101.8(5) | O(25)–Co(6)–N(10) | 92.5(5) |
| O(18)–Co(7)–O(21) | 95.1(4) | O(23)–Co(8)–O(21) | 174.4(4) |
| O(18)–Co(7)–O(20) | 176.9(4) | O(23)–Co(8)–O(24) | 83.6(4) |
| O(21)–Co(7)–O(20) | 84.6(4) | O(21)–Co(8)–O(24) | 97.0(4) |
| O(18)–Co(7)–O(19) | 84.8(4) | O(23)–Co(8)–O(22) | 97.1(4) |
| O(21)–Co(7)–O(19) | 175.1(4) | O(21)–Co(8)–O(22) | 82.4(4) |
| O(20)–Co(7)–O(19) | 95.2(4) | O(24)–Co(8)–O(22) | 179.3(4) |
| O(18)–Co(7)–N(19) | 97.2(4) | O(23)–Co(8)–N(13) | 89.9(5) |
| O(21)–Co(7)–N(19) | 83.1(5) | O(21)–Co(8)–N(13) | 95.7(5) |
| O(22)–Co(9)–O(3) | 82.1(4) | O(24)–Co(8)–N(13) | 88.2(4) |
| O(20)–Co(9)–O(3) | 79.5(4) | O(22)–Co(8)–N(13) | 91.6(5) |
| O(22)–Co(9)–O(20) | 82.4(4) | O(26)–Co(11)–O(28) | 96.6(4) |
| O(22)–Co(9)–O(7) | 98.8(4) | O(26)–Co(11)–O(8) | 82.2(4) |
| O(20)–Co(9)–O(7) | 178.6(4) | O(28)–Co(11)–O(8) | 178.2(4) |
| O(22)–Co(9)–O(26) | 176.3(4) | O(26)–Co(11)–O(27) | 176.7(4) |
| O(20)–Co(9)–O(26) | 94.4(4) | O(28)–Co(11)–O(27) | 83.3(4) |
| O(7)–Co(9)–O(26) | 84.3(4) | O(8)–Co(11)–O(27) | 97.9(4) |
| O(22)–Co(9)–N(1) | 96.4(5) | O(26)–Co(11)–N(4) | 88.0(5) |
| O(20)–Co(9)–N(1) | 91.9(4) | O(28)–Co(11)–N(4) | 94.3(5) |
| O(7)–Co(9)–N(1) | 88.7(4) | O(8)–Co(11)–N(4) | 87.1(5) |
| O(26)–Co(9)–N(1) | 85.6(5) | O(27)–Co(11)–N(4) | 95.3(5) |
| O(7)–Co(9)–O(3) | 99.9(4) | O(13)–Co(13)–S(12) | 94.3(3) |

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|---|---|---|---|
| O(26)–Co(9)–O(3) | 95.5(4) | O(15)–Co(13)–S(12) | 89.6(3) |
| N(1)–Co(9)–O(3) | 171.4(4) | O(25)–Co(13)–S(12) | 98.5(3) |
| O(22)–Co(12)–O(20) | 79.9(4) | O(24)–Co(13)–O(13) | 172.8(4) |
| O(22)–Co(12)–O(21) | 81.2(4) | O(24)–Co(13)–O(15) | 101.2(4) |
| O(20)–Co(12)–O(21) | 80.6(4) | O(13)–Co(13)–O(15) | 79.0(4) |
| O(22)–Co(12)–N(20) | 158.5(4) | O(24)–Co(13)–O(25) | 81.2(4) |
| O(20)–Co(12)–N(20) | 84.5(5) | O(13)–Co(13)–O(25) | 97.6(4) |
| O(21)–Co(12)–N(20) | 81.7(4) | O(15)–Co(13)–O(25) | 171.4(4) |
| O(22)–Co(12)–S(10) | 98.7(3) | O(24)–Co(13)–S(12) | 92.9(3) |
| O(20)–Co(12)–S(10) | 172.1(3) | O(6)–Co(15)–S(8) | 90.6(3) |
| O(21)–Co(12)–S(10) | 91.5(3) | O(9)–Co(15)–S(8) | 100.7(3) |
| N(20)–Co(12)–S(10) | 94.7(4) | N(8)–Co(15)–S(8) | 94.0(4) |
| O(22)–Co(12)–S(2) | 94.7(3) | O(5)–Co(15)–S(22) | 92.7(3) |
| O(20)–Co(12)–S(2) | 91.9(3) | O(6)–Co(15)–S(22) | 170.4(3) |
| O(21)–Co(12)–S(2) | 172.0(3) | O(9)–Co(15)–S(22) | 92.0(3) |
| N(20)–Co(12)–S(2) | 100.5(4) | N(8)–Co(15)–S(22) | 105.5(3) |
| S(10)–Co(12)–S(2) | 96.01(17) | S(8)–Co(15)–S(22) | 95.54(17) |
| O(19)–Co(14)–O(17) | 78.0(4) | O(5)–Co(15)–O(6) | 81.5(4) |
| O(19)–Co(14)–O(18) | 79.1(4) | O(5)–Co(15)–O(9) | 81.0(4) |
| O(17)–Co(14)–O(18) | 80.0(4) | O(6)–Co(15)–O(9) | 79.6(4) |
| O(19)–Co(14)–N(26) | 157.9(5) | O(5)–Co(15)–N(8) | 81.9(5) |
| O(17)–Co(14)–N(26) | 84.5(5) | O(6)–Co(15)–N(8) | 81.4(4) |
| O(18)–Co(14)–N(26) | 84.8(5) | O(9)–Co(15)–N(8) | 156.0(4) |
| O(19)–Co(14)–N(23) | 83.8(5) | O(5)–Co(15)–S(8) | 171.5(3) |
| O(17)–Co(14)–N(23) | 88.0(5) | O(12)–Co(17)–N(31) | 160.2(4) |
| O(18)–Co(14)–N(23) | 160.8(5) | N(34)–Co(17)–N(31) | 102.1(5) |
| N(26)–Co(14)–N(23) | 109.1(6) | O(11)–Co(17)–N(31) | 86.2(5) |
| O(19)–Co(14)–S(14) | 101.3(3) | O(10)–Co(17)–S(20) | 178.0(3) |
| O(17)–Co(14)–S(14) | 176.2(3) | O(12)–Co(17)–S(20) | 98.3(3) |
| O(18)–Co(14)–S(14) | 96.2(3) | N(34)–Co(17)–S(20) | 96.0(4) |

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|---|---|---|---|
| N(26)–Co(14)–S(14) | 95.3(4) | O(11)–Co(17)–S(20) | 98.6(3) |
| N(23)–Co(14)–S(14) | 95.6(4) | N(31)–Co(17)–S(20) | 97.5(3) |
| O(26)–Co(16)–O(8) | 78.0(4) | O(10)–Co(17)–O(12) | 79.8(4) |
| O(26)–Co(16)–O(7) | 81.1(4) | O(10)–Co(17)–N(34) | 84.7(5) |
| O(8)–Co(16)–O(7) | 79.9(4) | O(12)–Co(17)–N(34) | 88.1(5) |
| O(26)–Co(16)–N(5) | 88.2(5) | O(10)–Co(17)–O(11) | 80.3(4) |
| O(8)–Co(16)–N(5) | 82.3(5) | O(12)–Co(17)–O(11) | 79.7(4) |
| O(7)–Co(16)–N(5) | 160.8(5) | N(34)–Co(17)–O(11) | 162.1(5) |
| O(26)–Co(16)–N(2) | 83.4(4) | O(10)–Co(17)–N(31) | 84.2(4) |
| O(8)–Co(16)–N(2) | 159.6(4) | O(23)–Co(19)–N(11) | 88.7(5) |
| O(7)–Co(16)–N(2) | 89.1(5) | O(25)–Co(19)–N(11) | 87.6(5) |
| N(5)–Co(16)–N(2) | 105.4(6) | O(24)–Co(19)–N(11) | 162.1(5) |
| O(26)–Co(16)–S(6) | 174.8(3) | N(16)–Co(19)–N(14) | 93.3(6) |
| O(8)–Co(16)–S(6) | 103.3(3) | O(23)–Co(19)–N(14) | 83.0(5) |
| O(7)–Co(16)–S(6) | 94.1(3) | O(25)–Co(19)–N(14) | 159.8(5) |
| N(5)–Co(16)–S(6) | 97.0(4) | O(24)–Co(19)–N(14) | 88.3(5) |
| N(2)–Co(16)–S(6) | 94.6(4) | N(11)–Co(19)–N(14) | 104.0(5) |
| O(16)–Co(18)–O(13) | 82.9(4) | N(16)–Co(19)–O(23) | 174.0(5) |
| O(16)–Co(18)–O(15) | 82.4(4) | N(16)–Co(19)–O(25) | 101.8(5) |
| O(13)–Co(18)–O(15) | 76.0(4) | O(23)–Co(19)–O(25) | 80.7(4) |
| O(16)–Co(18)–O(29) | 171.8(5) | N(16)–Co(19)–O(24) | 95.3(6) |
| O(13)–Co(18)–O(29) | 96.7(5) | O(23)–Co(19)–O(24) | 79.8(4) |
| O(15)–Co(18)–O(29) | 105.5(5) | O(25)–Co(19)–O(24) | 77.1(4) |
| O(16)–Co(18)–N(28) | 80.9(5) | N(16)–Co(19)–N(11) | 96.8(6) |
| O(13)–Co(18)–N(28) | 85.9(5) | O(14)–Co(10)–O(12) | 98.4(4) |
| O(15)–Co(18)–N(28) | 156.6(5) | O(14)–Co(10)–O(10) | 177.3(4) |
| O(29)–Co(18)–N(28) | 90.9(5) | O(12)–Co(10)–O(10) | 82.6(4) |
| O(16)–Co(18)–S(18) | 96.6(3) | O(14)–Co(10)–N(33) | 94.3(5) |
| O(13)–Co(18)–S(18) | 173.1(3) | O(12)–Co(10)–N(33) | 86.6(5) |
| O(15)–Co(18)–S(18) | 97.1(3) | O(10)–Co(10)–N(33) | 88.2(5) |

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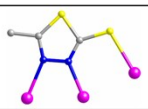
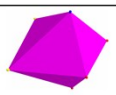
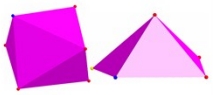
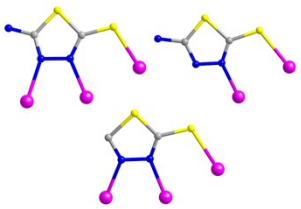
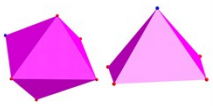
|---|---|---|---|
| O(29)–Co(18)–S(18) | 84.7(4) | O(14)–Co(10)–O(27) | 80.2(4) |
| N(28)–Co(18)–S(18) | 100.9(4) | O(12)–Co(10)–O(27) | 99.4(4) |
| O(27)–Co(20)–O(14) | 81.2(4) | O(10)–Co(10)–O(27) | 97.2(4) |
| O(27)–Co(20)–O(28) | 80.1(4) | N(33)–Co(10)–O(27) | 172.4(5) |
| O(14)–Co(20)–O(28) | 80.6(4) | S(16)–Co(20)–S(4) | 95.51(18) |
| O(27)–Co(20)–S(16) | 172.8(3) | S(24)–Co(20)–S(4) | 91.70(18) |
| O(14)–Co(20)–S(16) | 94.0(3) | O(27)–Co(20)–S(4) | 88.8(3) |
| O(28)–Co(20)–S(16) | 93.9(3) | O(14)–Co(20)–S(4) | 169.0(3) |
| O(27)–Co(20)–S(24) | 94.2(3) | O(28)–Co(20)–S(4) | 93.3(3) |
| O(14)–Co(20)–S(24) | 93.5(3) | S(16)–Co(20)–S(24) | 91.47(19) |
| O(28)–Co(20)–S(24) | 172.3(3) | | |

**Table S2.** The substituent groups of the organic ligands, the coordination modes of the organic ligands and $Co^{II}$ ions in compounds **1**–**3**.

| Compounds | Substituent groups | Organic ligands | Metal ions |
|---|---|---|---|
| **1** | **-$CH_3$** |  |  |
| **2** | **None** |  |  |
| **3** | **-$NH_2$** |  |  |

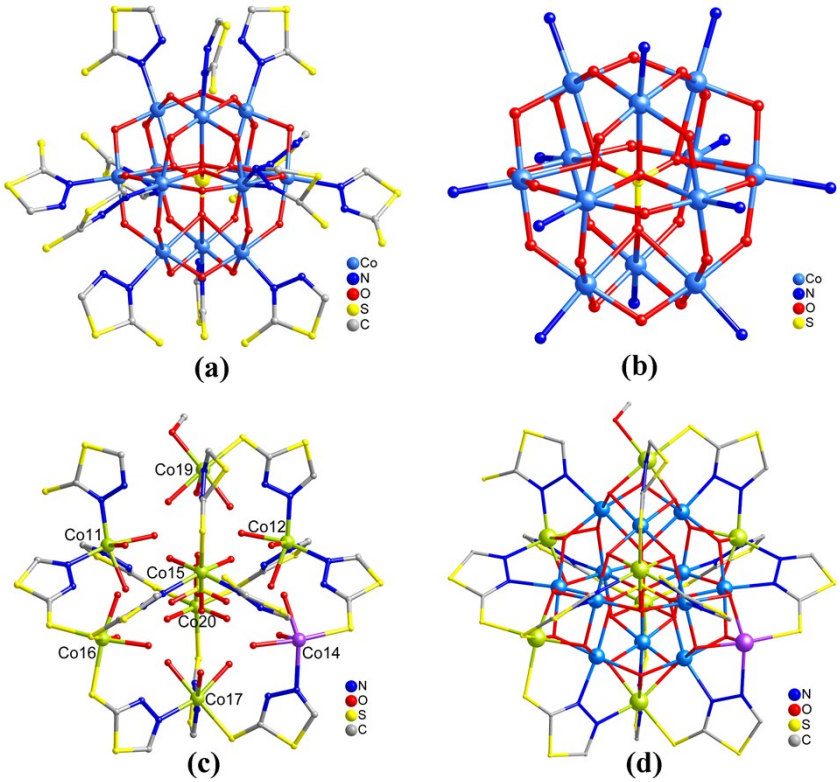



**Fig. S1.** (a) The α-Keggin-type skeleton based on $Co^{II}$ ions and MT ligands in compound **2**; (b) The α-Keggin polyoxoazocobaltate core of compound **2**; (c) The coordination environments from eight peripheral $Co^{II}$ ions of compound **2**; (d) Stick view of homometallic high-nuclearity cluster of compound **2**.

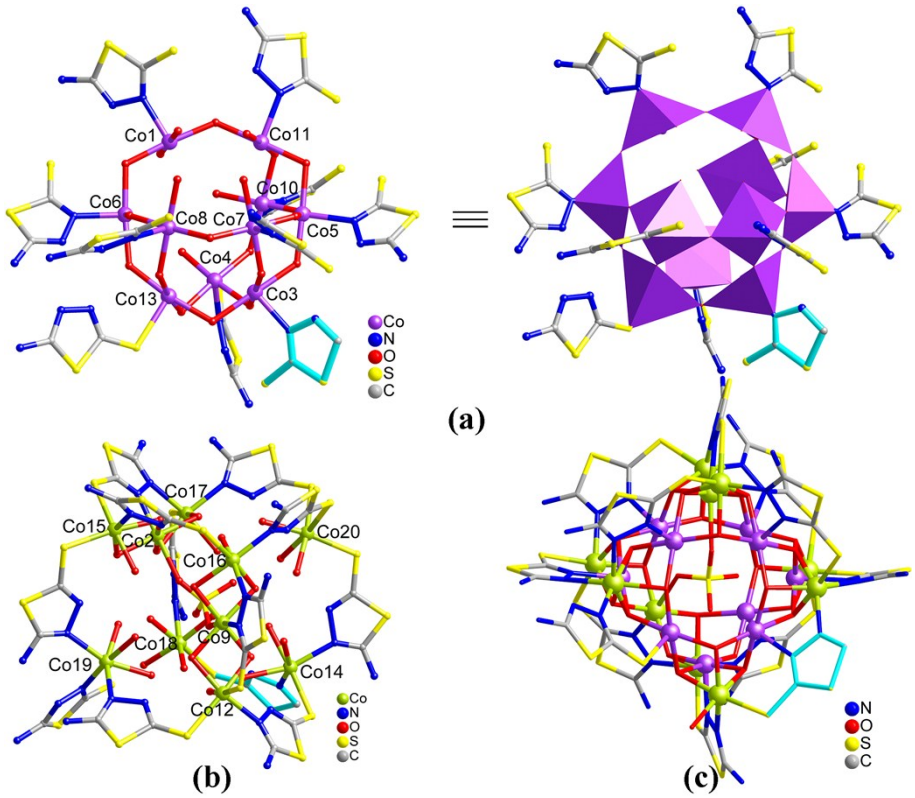



**Fig. S2.** (a) The semi-open $\{Co_{10}\}$ metallic cluster in compound **3**; (b) The coordination environments from ten peripheral $Co^{II}$ ions of compound **3**; (d) Stick view of high-nuclearity nanoscale cluster of compound **3**.

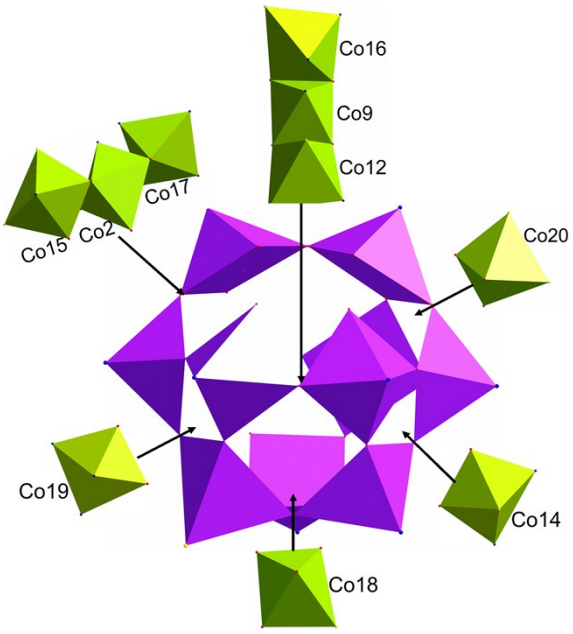



**Fig S3.** The structural distribution of the ten peripheral $Co^{II}$ ions for the $\{Co_{10}\}$ core in

compound **3**.

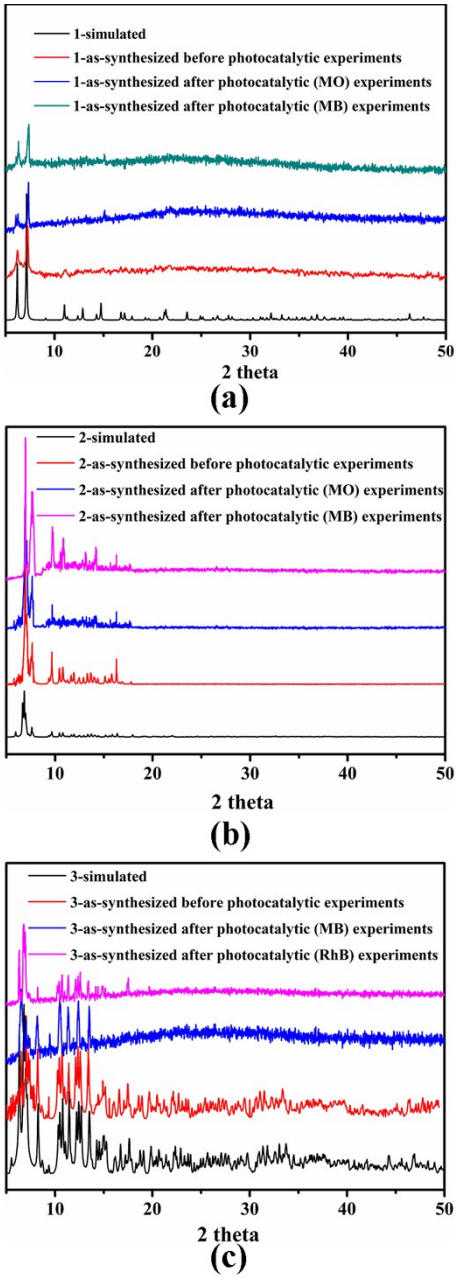



**Fig. S4.** The simulated, as-synthesized and as-synthesized after photocatalytic experiments powder X–ray diffraction patterns for compounds **1**–**3**.

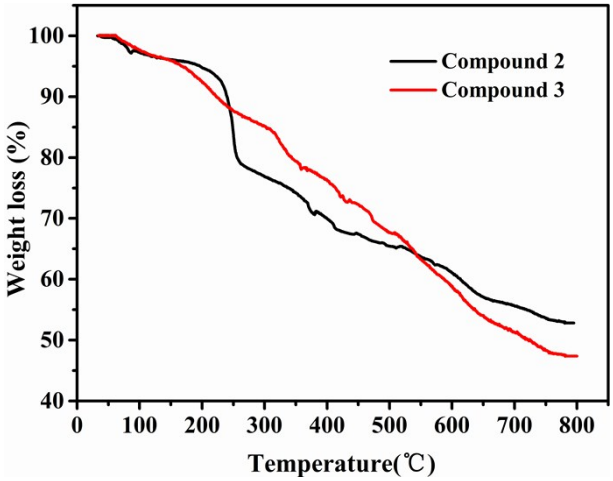



**Fig. S5.** The TG curves of compounds **1**–**3**.

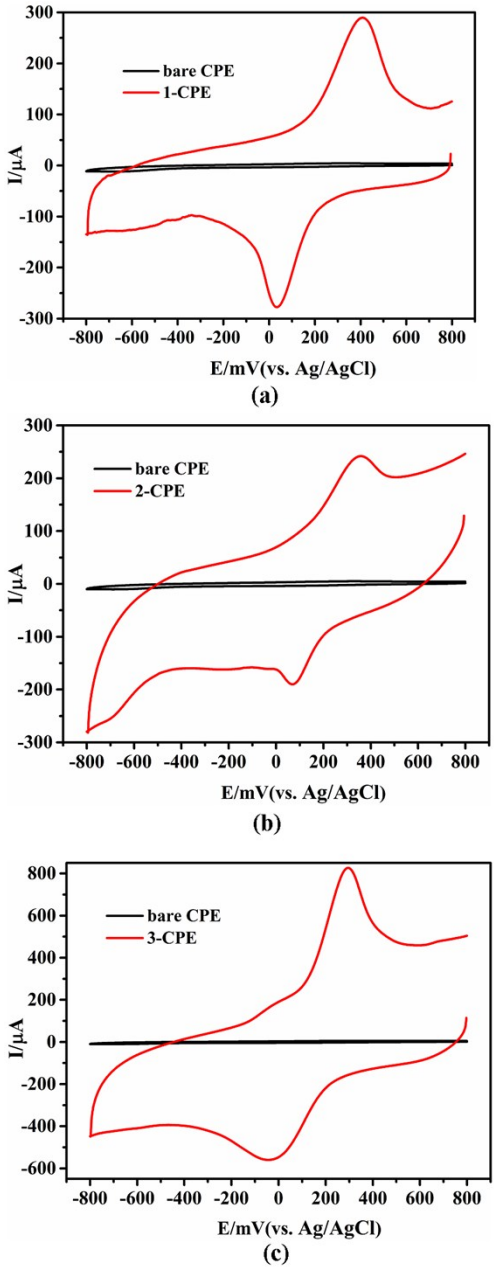



**Fig. S6.** Cyclic voltammograms of **1**–, **2**– and **3**–CPE (+800 to –800mV) in 0.01 M $H_2SO_4$ + 0.5 M $Na_2SO_4$ aqueous solution for compounds **1**–**3**. Scan rate: 100 $mVs^{-1}$.

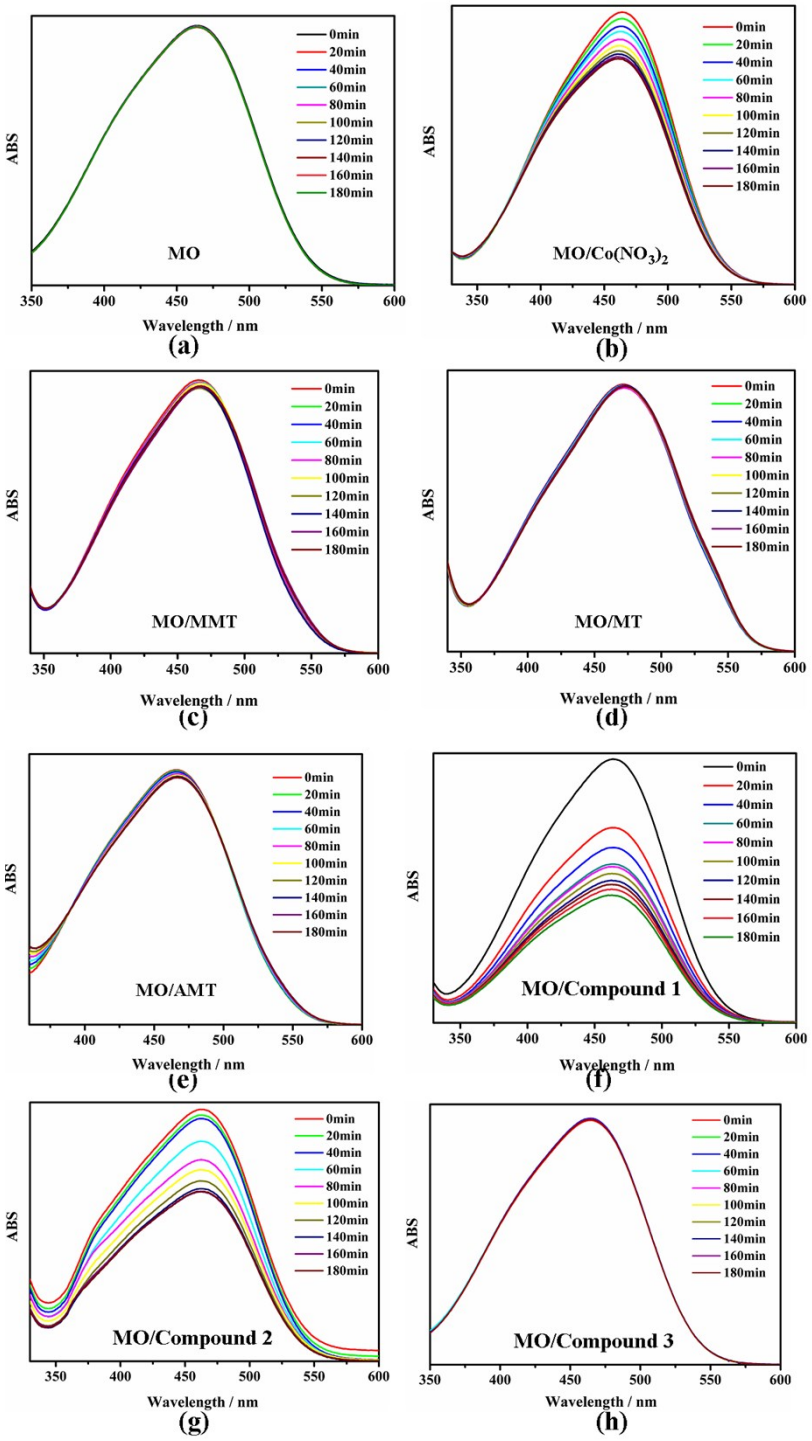
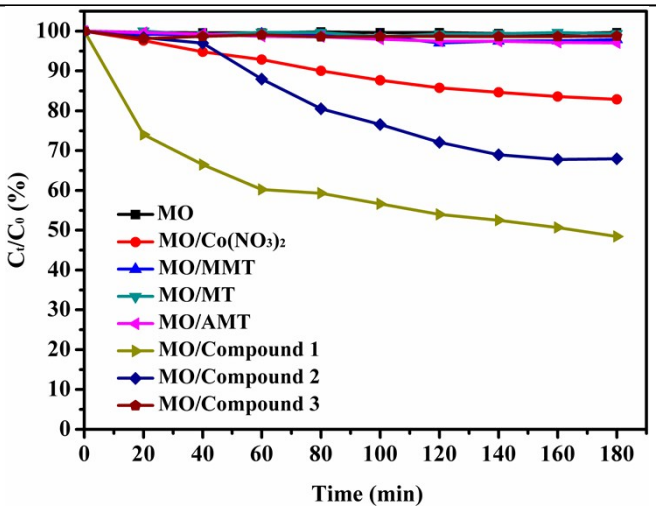
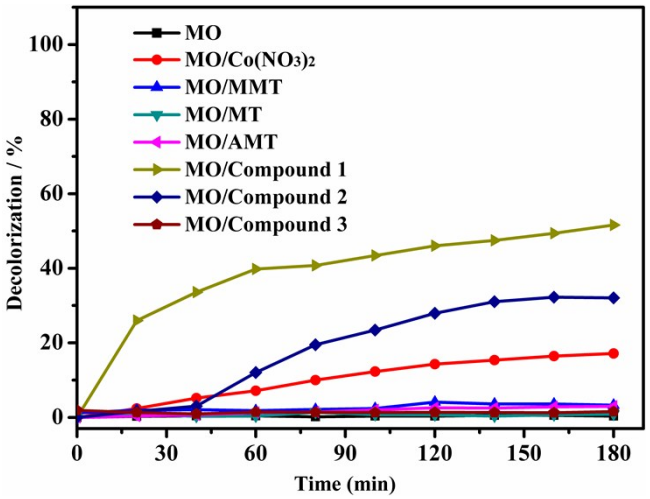



**Fig. S7.** Absorption spectra of the MO solution during the decomposition reaction under visible-light irradiation in the presence of (a) MO; (b) MO/$Co(NO_3)_2$; (c) MO/MMT; (d) MO/MT; (e) MO/AMT; (f) MO/Compound **1**; (g) MO/Compound **2**; (h) MO/Compound **3**.




**(a)**




**(b)**

**Fig. S8.** (a) Photocatalytic decomposition rates of MO solution under visible-light irradiation with the use of compounds **1**–**3**, $Co(NO_3)_2$, MMT, MT, AMT and no crystal in the same conditions; (b) Decolorization rates of MO in different reaction systems.

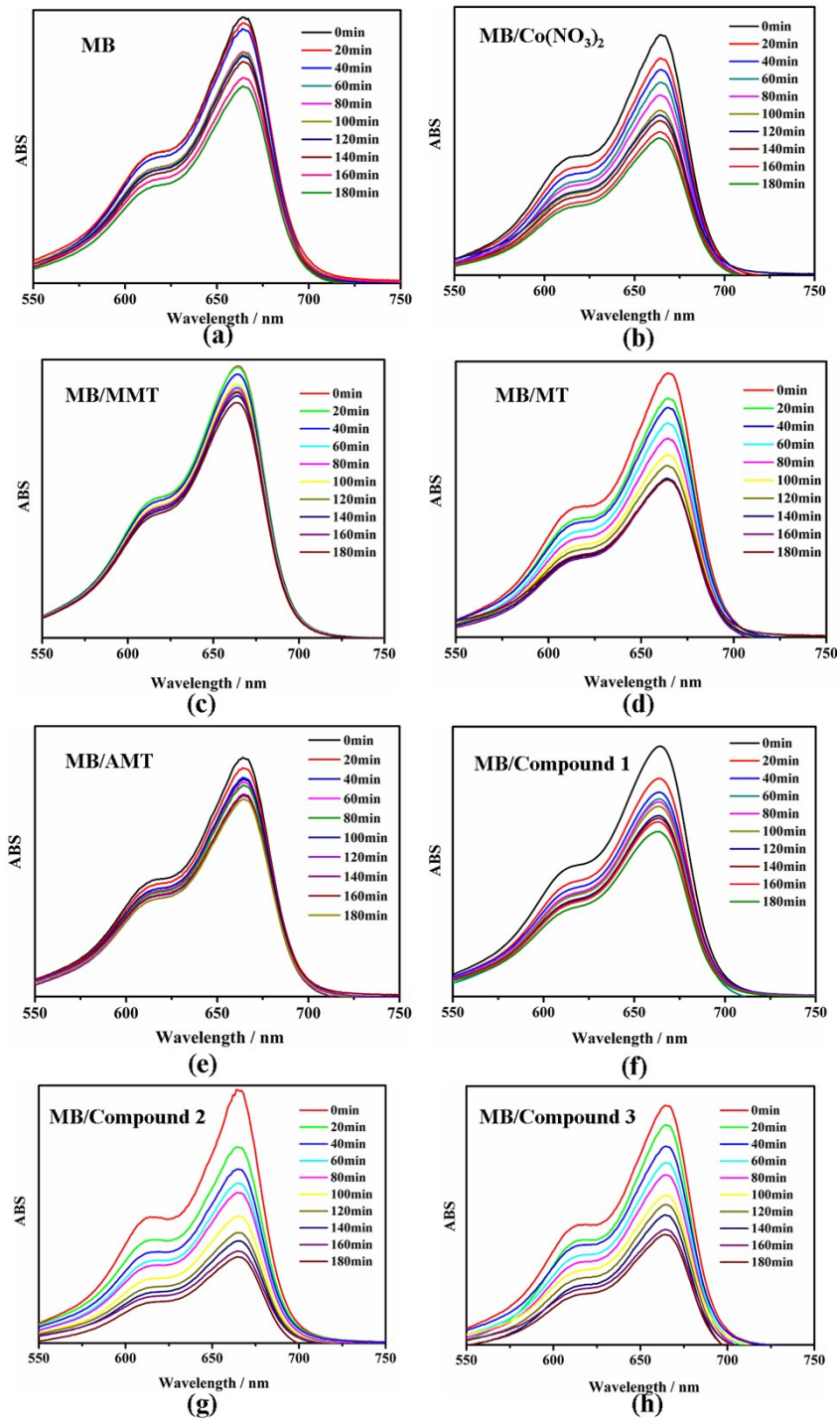
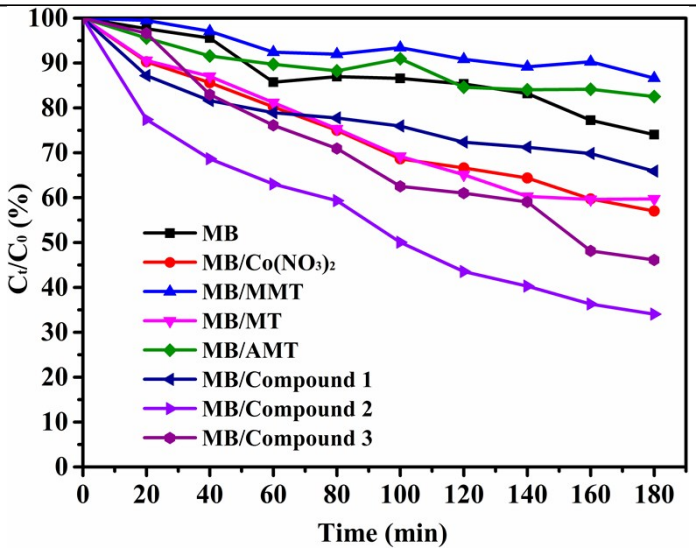
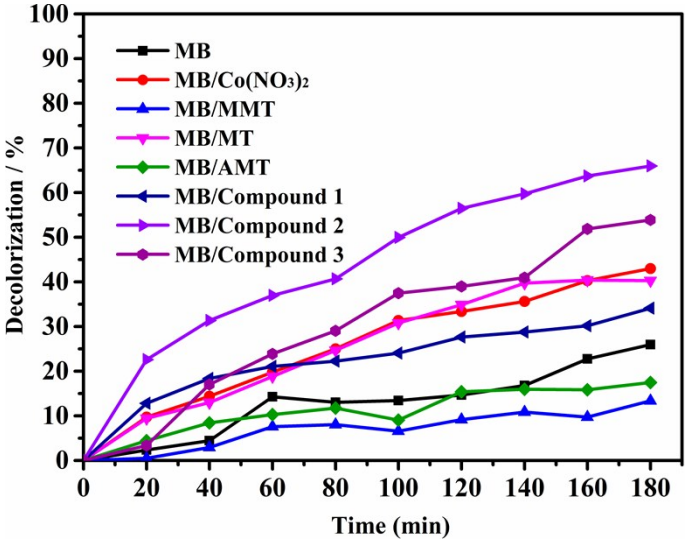



**Fig. S9.** Absorption spectra of the MB solution during the decomposition reaction under visible-light irradiation in the presence of (a) MB; (b) MB/$Co(NO_3)_2$; (c) MB/MMT; (d) MB/MT; (e) MB/AMT; (f) MB/Compound **1**; (g) MB/Compound **2**; (h) MB/Compound **3**.




**(a)**




**(b)**

**Fig. S10.** (a) Photocatalytic decomposition rates of MB solution under visible-light irradiation with the use of compounds **1**–**3**, $Co(NO_3)_2$, MMT, MT, AMT and no crystal in the same conditions; (b) Decolorization rates of MB in different reaction systems.

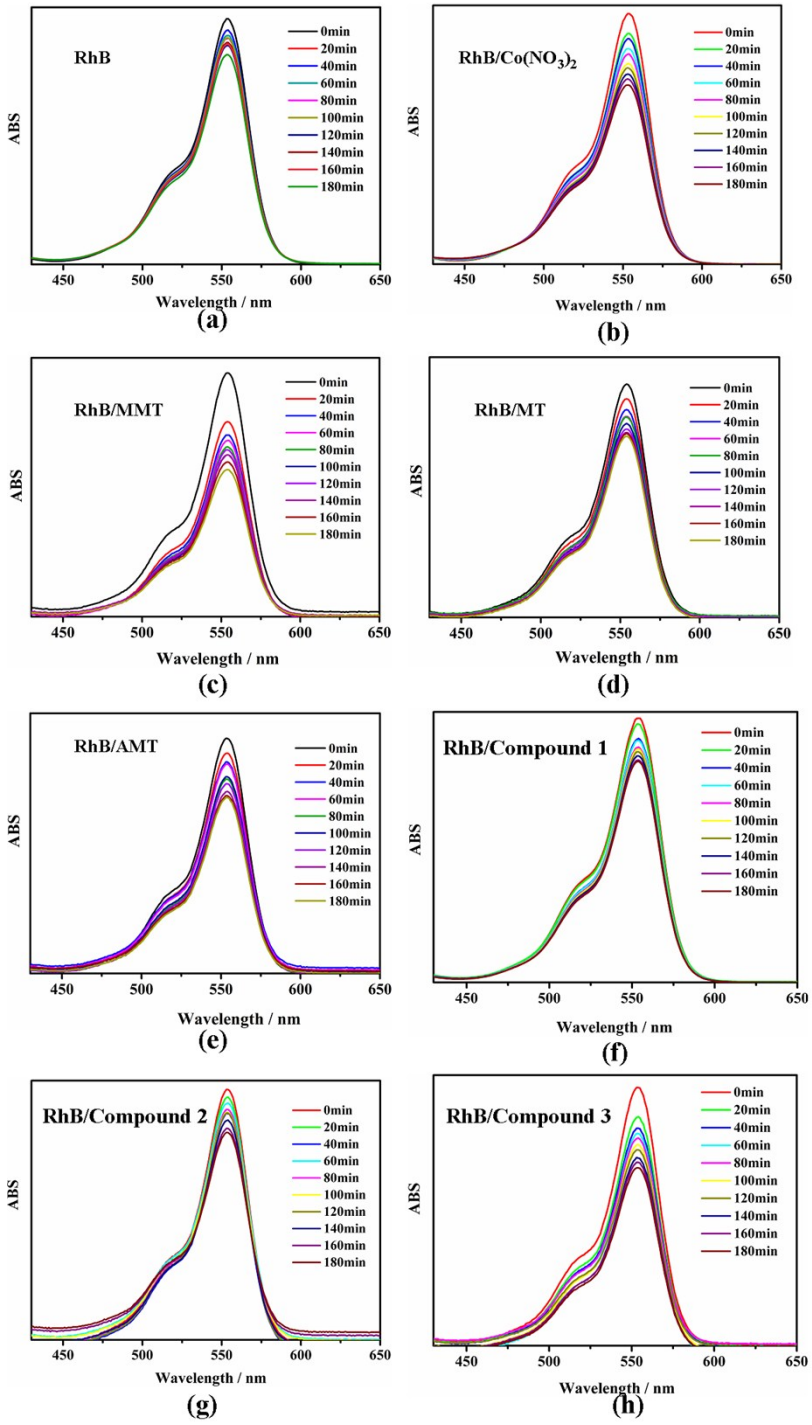
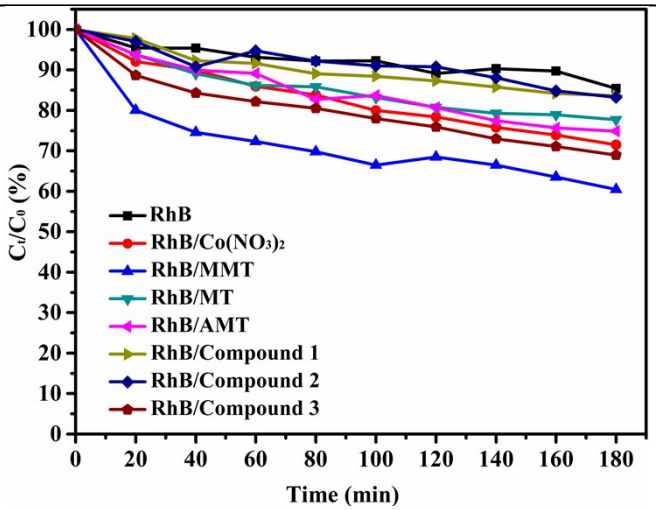
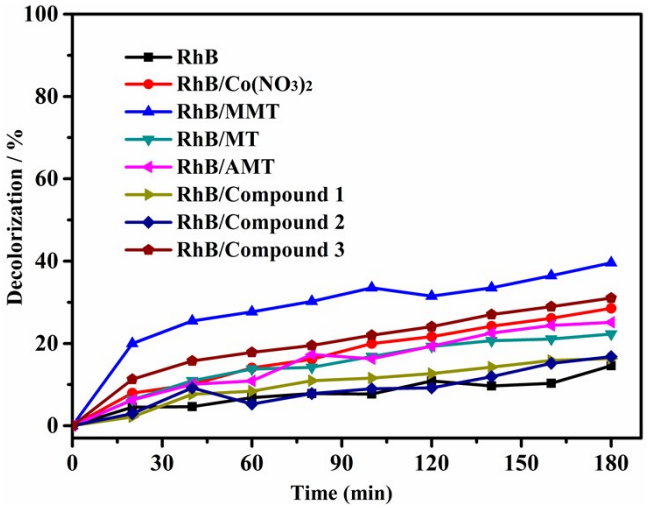



**Fig. S11.** Absorption spectra of the RhB solution during the decomposition reaction under visible-light irradiation in the presence of (a) RhB; (b) RhB/$Co(NO_3)_2$; (c) RhB/MMT; (d) RhB/MT; (e) RhB/AMT; (f) RhB/Compound **1**; (g) RhB/Compound **2**; (h) RhB/Compound **3**.




**(a)**




**(b)**

**Fig. S12.** (a) Photocatalytic decomposition rates of RhB solution under visible-light irradiation with the use of compounds **1**–**3**, $Co(NO_3)_2$, MMT, MT, AMT and no crystal in the same conditions; (b) Decolorization rates of RhB in different reaction systems.