# Electronic Supplementary Information

## First structurally characterized self-assembly of bipodal *N*-thiophosphorylated bis-thiourea with $Co^{II}$: Magnetic properties and thermal decomposition

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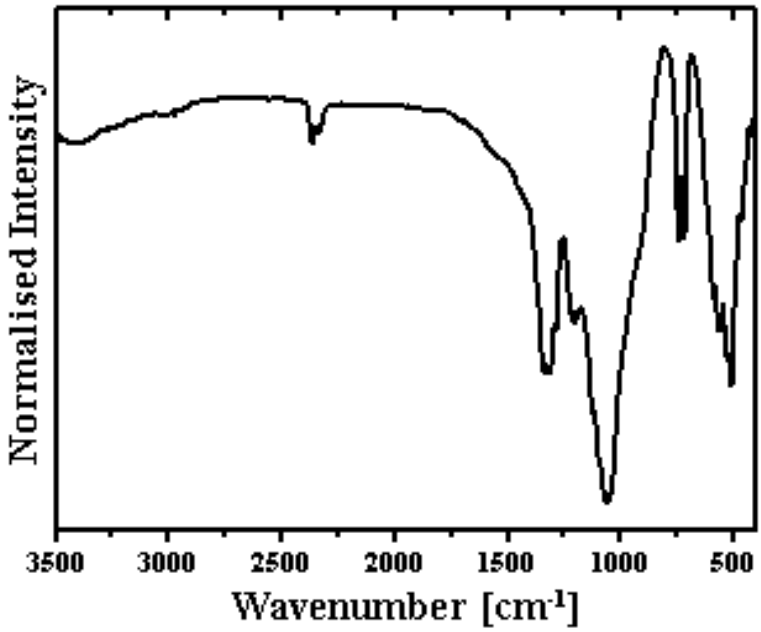


**Fig. S1** Normalised IR spectrum of $[CoPS_3]_2$ obtained from annealing of **$[Co_2L_2]$** at 900 °C.

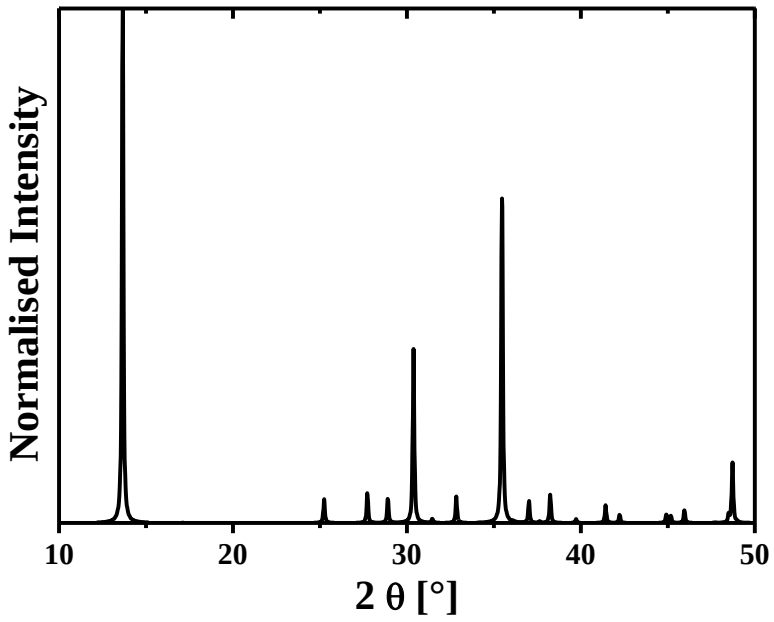


**Fig. S2** Normalised PXRD diffractogram of $[CoPS_3]_2$ obtained after annealing **[$Co_2L_2$]** at 900 °C.

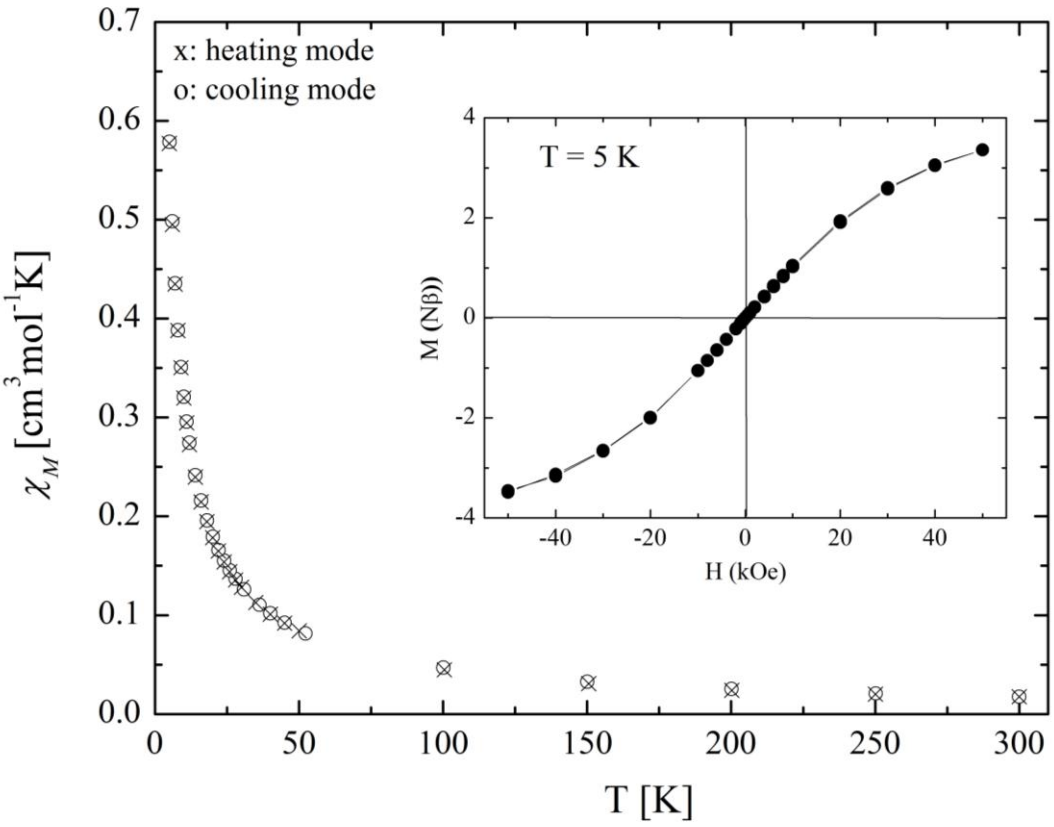


**Fig. S3** $\chi_M$ *vs. T* plot in both heating and cooling modes over the temperature range 5–300 K for **[$Co_2L_2$].** The inset shows the magnetization *vs.* field hysteresis loop at 5 K for **[$Co_2L_2$].**

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

| | | | | | |
|---|---|---|---|---|---|
| *Bond lengths* | | | | | |
| S(1)–P(2) | 1.9228(6) | O(7)–C(8) | 1.469(2) | C(4)–C(6) | 1.506(3) |
| P(2)–O(3) | 1.5811(13) | N(11)–C(12) | 1.476(2) | C(8)–C(9) | 1.499(3) |
| P(2)–O(7) | 1.5797(13) | N(11)–C(13)a | 1.463(2) | C(8)–C(10) | 1.498(3) |
| P(2)–N(11) | 1.6521(14) | C(4)–C(5) | 1.499(3) | C(12)–C(13) | 1.514(3) |
| O(3)–C(4) | 1.474(2) | | | | |
| *Bond angles* | | | | | |
| S(1)–P(2)–O(3) | 115.46(5) | P(2)–O(3)–C(4) | 119.97(11) | O(3)–C(4)–C(6) | 108.08(16) |
| S(1)–P(2)–O(7) | 116.11(5) | P(2)–O(7)–C(8) | 121.39(11) | C(5)–C(4)–C(6) | 112.85(16) |
| S(1)–P(2)–N(11) | 114.27(5) | P(2)–N(11)–C(12) | 118.00(11) | O(7)–C(8)–C(9) | 106.90(16) |
| O(3)–P(2)–O(7) | 100.76(7) | P(2)–N(11)–C(13)a | 121.09(11) | O(7)–C(8)–C(10) | 107.19(16) |
| O(3)–P(2)–N(11) | 104.86(7) | C(12)–N(11)–C(13)a | 111.97(13) | C(9)–C(8)–C(10) | 114.4(2) |
| O(7)–P(2)–N(11) | 103.67(7) | O(3)–C(4)–C(5) | 107.97(16) | N(11)–C(12)–C(13) | 109.67(14) |

**Table S2.** Selected bond lengths (Å) and angles (°) for **[$Co_2L_2$]**

| | | | | | |
|---|---|---|---|---|---|
| *Bond lengths* | | | | | |
| Co(1)–S(2) | 2.3090(16) | P(24)–O(30) | 1.560(3) | N(18)–C(21) | 1.351(6) |
| Co(1)–S(14) | 2.2794(15) | P(24)–N(23) | 1.596(4) | N(23)–C(21) | 1.298(6) |
| Co(1)–S(22)a | 2.2788(15) | O(4)–C(5) | 1.407(8) | C(5)–C(6) | 1.465(11) |
| Co(1)–S(25)a | 2.3236(16) | O(8)–C(9) | 1.463(6) | C(5)–C(7) | 1.506(10) |
| S(2)–P(3) | 1.997(2) | O(26)–C(27) | 1.465(6) | C(9)–C(10) | 1.491(9) |
| S(14)–C(13) | 1.746(4) | O(30)–C(31) | 1.449(6) | C(9)–C(11) | 1.473(10) |
| S(22)–C(21) | 1.760(5) | N(12)–C(13) | 1.321(5) | C(16)–C(17) | 1.516(7) |
| S(25)–P(24) | 1.991(2) | N(15)–C(13) | 1.328(6) | C(19)–C(20) | 1.505(6) |
| P(3)–O(4) | 1.553(4) | N(15)–C(16) | 1.460(6) | C(27)–C(28) | 1.482(9) |
| P(3)–O(8) | 1.560(3) | N(15)–C(20) | 1.473(5) | C(27)–C(29) | 1.462(11) |
| P(3)–N(12) | 1.584(4) | N(18)–C(17) | 1.452(5) | C(31)–C(32) | 1.479(10) |
| P(24)–O(26) | 1.568(3) | N(18)–C(19) | 1.449(6) | C(31)–C(33) | 1.474(9) |
| *Bond angles* | | | | | |
| S(2)–Co(1)–S(14) | 107.50(6) | O(26)–P(24)–O(30) | 102.26(18) | O(8)–C(9)–C(11) | 106.7(5) |
| S(2)–Co(1)–S(22)a | 99.52(6) | O(26)–P(24)–N(23) | 109.1(2) | C(10)–C(9)–C(11) | 113.6(6) |
| S(2)–Co(1)–S(25)a | 123.40(6) | O(30)–P(24)–N(23) | 105.5(2) | S(14)–C(13)–N(12) | 124.0(3) |
| S(14)–Co(1)–S(22)a | 123.41(5) | P(3)–O(4)–C(5) | 122.4(4) | S(14)–C(13)–N(15) | 117.4(3) |
| S(14)–Co(1)–S(25)a | 99.16(5) | P(3)–O(8)–C(9) | 123.7(3) | N(12)–C(13)–N(15) | 118.6(4) |
| S(22)a–Co(1)–S(25)a | 105.86(6) | P(24)–O(26)–C(27) | 125.4(3) | N(15)–C(16)–C(17) | 111.8(3) |
| Co(1)–S(2)–P(3) | 98.42(7) | P(24)–O(30)–C(31) | 122.1(3) | N(18)–C(17)–C(16) | 109.2(4) |
| Co(1)–S(14)–C(13) | 104.67(15) | P(3)–N(12)–C(13) | 129.8(3) | N(18)–C(19)–C(20) | 109.2(3) |
| C(21)–S(22)–Co(1)a | 98.44(16) | C(13)–N(15)–C(16) | 121.7(3) | N(15)–C(20)–C(19) | 110.2(4) |
| P(24)–S(25)–Co(1)a | 98.22(7) | C(13)–N(15)–C(20) | 125.7(4) | S(22)–C(21)–N(18) | 117.2(3) |
| S(2)–P(3)–O(4) | 107.06(17) | C(16)–N(15)–C(20) | 112.5(4) | S(22)–C(21)–N(23) | 124.6(4) |
| S(2)–P(3)–O(8) | 111.87(14) | C(17)–N(18)–C(19) | 110.7(4) | N(18)–C(21)–N(23) | 118.2(4) |
| S(2)–P(3)–N(12) | 121.01(17) | C(17)–N(18)–C(21) | 121.1(4) | O(26)–C(27)–C(28) | 107.7(5) |
| O(4)–P(3)–O(8) | 102.2(2) | C(19)–N(18)–C(21) | 124.7(4) | O(26)–C(27)–C(29) | 108.7(5) |
| O(4)–P(3)–N(12) | 106.0(2) | P(24)–N(23)–C(21) | 126.7(4) | C(28)–C(27)–C(29) | 110.7(6) |
| O(8)–P(3)–N(12) | 107.0(2) | O(4)–C(5)–C(6) | 113.9(6) | O(30)–C(31)–C(32) | 109.6(5) |
| S(25)–P(24)–O(26) | 112.80(14) | O(4)–C(5)–C(7) | 106.4(6) | O(30)–C(31)–C(33) | 108.8(5) |
| S(25)–P(24)–O(30) | 108.98(14) | C(6)–C(5)–C(7) | 112.5(6) | C(32)–C(31)–C(33) | 111.9(6) |
| S(25)–P(24)–N(23) | 116.97(17) | O(8)–C(9)–C(10) | 105.9(5) | | |

**Table S3.** Selected bond lengths (Å) and angles (°) for **2**

| | | | | | |
|---|---|---|---|---|---|
| *Bond lengths* | | | | | |
| N(6)–C(5) | 1.480(4) | N(6)–C(7) | 1.486(4) | C(5)–C(7)a | 1.516(4) |
| *Bond angles* | | | | | |
| C(5)–N(6)–C(7) | 111.3(2) | N(6)–C(5)–C(7)a | 109.6(2) | N(6)–C(7)–C(5)a | 110.2(2) |

**Table S4.** Hydrogen bond lengths (Å) and angles (°) for **2**[a]

| D–H···A | *d*(D–H) | *d*(H···A) | *d*(D···A) | ∠(DHA) |
|---|---|---|---|---|
| N(6)–H(6A)···O(4)#1 | 0.92 | 1.78 | 2.695(3) | 172 |
| N(6)–H(6B)···O(3) | 0.92 | 1.77 | 2.685(2) | 171 |

[a] Symmetry transformations used to generate equivalent atoms: #1 1 + *x*, *y*, *z*