

## **Supporting Information**

### **The substituent guest effect on four-step spin-crossover behavior**

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## Supporting Information

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**Table S1.** Selected structural parameters for **1·1.5F<sub>n</sub>aph** at different temperatures.

| Parameter                       | 100(2)                                                   | 168(2)                                                                                                               | 195(2)                                                   | 226(2)                                                   | 298(2)                                                   |
|---------------------------------|----------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|----------------------------------------------------------|
| <Fe–N> <sup>a</sup>             | 1.967(7)                                                 | <Fe1–N>1.977(6)<br><Fe2–N>1.981(6)<br><Fe3–N>1.977(6)<br><Fe4–N>2.131(6)                                             | <Fe1–N>1.979(7)<br><Fe2–N>2.155(7)                       | 2.121(3)                                                 | 2.174(2)                                                 |
| Ag <sup>⋯</sup> Ag <sup>b</sup> | 3.2087(11)<br>3.0041(11)                                 | 3.0083(7)<br>3.2238(7)<br>3.2316(7)<br>3.0203(7)                                                                     | 3.0312(10)<br>3.2507(11)                                 | 3.2604(5)<br>3.0512(5)                                   | 3.2903(6)<br>3.0723(6)                                   |
| Fe <sup>⋯</sup> Fe <sup>c</sup> | 14.1295(16)                                              | 14.1141(13)<br>14.1153(13)<br>14.2520(13)<br>14.2563(13)                                                             | 14.2571(18)<br>14.2618(18)                               | 14.3340(9)                                               | 14.4461(10)                                              |
| Fe <sup>⋯</sup> Fe <sup>d</sup> | 10.1751(25)<br>10.2141(25)<br>10.2820(15)<br>10.3033(15) | 10.2173(14)<br>10.2937(11)<br>10.3115(14)<br>10.4669(11)<br>10.3141(11)<br>10.1747(14)<br>10.3478(14)<br>10.4489(11) | 10.3305(18)<br>10.3712(18)<br>10.4608(16)<br>10.4817(16) | 10.4141(17)<br>10.4620(17)<br>10.5619(23)<br>10.5805(23) | 10.5093(17)<br>10.5587(17)<br>10.6554(27)<br>10.6696(27) |
| ΣFe <sup>e</sup>                | 7.7(3)                                                   | ΣFe1 7.2(2)<br>ΣFe2 9.0(2)<br>ΣFe3 8.7(2)<br>ΣFe4 14.1(2)                                                            | ΣFe1 6.9(3)<br>ΣFe2 14.8(3)                              | 12.87(11)                                                | 13.96(11)                                                |
| Fe–N–C <sup>f</sup>             | 174.6(7)                                                 | Fe1–N–C 174.9(6)<br>Fe2–N–C 175.6(6)<br>Fe3–N–C 175.3(6)<br>Fe4–N–C 172.1(6)                                         | Fe1–N–C 175.5(7)<br>Fe2–N–C 172.1(7)                     | 173.1(3)                                                 | 172.7(3)                                                 |
| ∠ <sup>g</sup>                  | 84.14(2)<br>84.23(2)<br>95.63(2)                         | Fe1: 83.394(9)<br>Fe2: 84.734(9)<br>Fe3: 83.306(9)                                                                   | 83.85(1)<br>83.95(1)<br>95.91(1)                         | 83.662(4)<br>83.803(4)                                   | 83.846(4)<br>84.014(4)                                   |

|                             |                           |                                                                                                                                      |                                                                |                         |                         |
|-----------------------------|---------------------------|--------------------------------------------------------------------------------------------------------------------------------------|----------------------------------------------------------------|-------------------------|-------------------------|
|                             | 96.01(2)                  | Fe4:83.306(9)                                                                                                                        | 96.29(1)                                                       | 96.066(5)<br>96.469(5)  | 95.880(5)<br>96.261(5)  |
| dihedral angle <sup>h</sup> | 16.5(3)/8.5 (3); 12.9 (3) | Fe1O1: 16.3(2)/7.0 (2); 13.5(2)<br>Fe2O2: 16.1(2)/8.4(2);12.3(2)<br>Fe3O3: 16.2(3)/7.1(2);13.2(3)<br>Fe4O4: 16.6 (3)/7.6 (3);13.8(2) | Fe1O1:15.8(3)/6.5(4);13.8 (3)<br>Fe2O2:16.1(3)/8.3(3);13.0 (3) | 16.2(1)/6.6(1);13.9 (1) | 16.09(9)/6.3(1);14.0(1) |
| dihedral angle <sup>i</sup> | 9.2 (3)                   | Fe1: 8.8(2)<br>Fe2: 9.7(2)<br>Fe3: 9.8(4)<br>Fe4: 11.1(3)                                                                            | Fe1: 8.5(3)<br>Fe2: 11.6(3)                                    | 10.9(1)                 | 10.98(9)                |

<sup>a</sup>The average Fe–N bond lengths (Å); <sup>b</sup>The argentophilic interactions (Å); <sup>c</sup>The Fe···Fe distance (Å) linked by dpoda; <sup>d</sup>The Fe···Fe distance (Å) linked by [Ag(CN)<sub>2</sub>]<sup>−</sup>; <sup>e</sup>Octahedral distortion parameters (°); <sup>f</sup>Average Fe–N–C angles within Hofmann layer; <sup>g</sup>The acute angle between neighboring Fe(II) sites within the Hofmann layer; <sup>h</sup>In the dpoda ligand, the dihedral angles between the oxadiazole and each pyridine ring as well as the dihedral angle between the pyridine rings; <sup>i</sup>The dihedral angle between the up and down pyridine rings coordinated to Fe(II) site.

**Table S2.**  $\pi \cdots \pi$  interactions for **1·1.5Fnaph** at different temperatures.

| <b>100 K</b>                                                                                                                                                                                                                                                                                                                                                      | $\theta^b$ | $Z^c$  | $d^d$  | $r^e$  | $\alpha^f$ | $l^g$  |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------|--------|--------|--------|------------|--------|
| Fnaph1 and oda1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                      | 2.492      | 3.7976 | 3.2068 | 2.0343 |            |        |
| Fnaph1 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 9.325      | 3.7513 | 3.2003 | 1.9571 |            |        |
| Fnaph2 and oda1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                      | 2.065      | 3.4058 | 3.2757 | 0.9323 |            |        |
| Fnaph2 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 9.595      | 3.6781 | 3.3309 | 1.5600 |            |        |
| Fnaph3 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 83.675     | 4.9254 | 4.7674 | 1.2375 | 131.100    | 3.1136 |
| <b>226 K</b>                                                                                                                                                                                                                                                                                                                                                      | $\theta^b$ | $Z^c$  | $d^d$  | $r^e$  | $\alpha^f$ | $l^g$  |
| Fnaph1 and oda1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                      | 2.586      | 3.9560 | 3.2699 | 2.2266 |            |        |
| Fnaph1 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 7.710      | 3.8660 | 3.2776 | 2.0502 |            |        |
| Fnaph2 and oda1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                      | 2.352      | 3.4894 | 3.3391 | 1.0131 |            |        |
| Fnaph2 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 7.914      | 3.6902 | 3.3646 | 1.5156 |            |        |
| Fnaph3 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 82.183     | 5.1351 | 4.8772 | 1.6069 | 134.716    | 3.2757 |
| <b>298 K</b>                                                                                                                                                                                                                                                                                                                                                      | $\theta^b$ | $Z^c$  | $d^d$  | $r^e$  | $\alpha^f$ | $l^g$  |
| Fnaph1 and oda1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                      | 2.596      | 3.9826 | 3.3066 | 2.2198 |            |        |
| Fnaph1 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 7.527      | 3.8957 | 3.3110 | 2.0527 |            |        |
| Fnaph2 and oda1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                      | 2.389      | 3.5351 | 3.3805 | 1.0340 |            |        |
| Fnaph2 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 7.720      | 3.7305 | 3.4069 | 1.5198 |            |        |
| Fnaph3 and py1 <sup>a</sup>                                                                                                                                                                                                                                                                                                                                       | 82.685     | 5.1697 | 4.9195 | 1.5888 | 135.468    | 3.3134 |
| <sup>a</sup> Fnaph1: C17-C26, F1-F2, x, y, z; Fnaph2: C17-C26, F1-F2, x, 1-y, $\frac{1}{2}+z$ ; Fnaph3: C27-C31, F3, 1-x, 1-y, 1-z; oxadiazole(oda1): N6-N7, C10-C11, O1, x, y, z; py1: C12-C16, N8, x, y, z.                                                                                                                                                     |            |        |        |        |            |        |
| <b>195 K L1-O1</b>                                                                                                                                                                                                                                                                                                                                                | $\theta^b$ | $Z^c$  | $d^d$  | $r^e$  | $\alpha^f$ | $l^g$  |
| Fnaph1 and oda1 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                      | 2.827      | 3.9293 | 3.2460 | 2.2142 |            |        |
| Fnaph1 and py1 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                       | 7.139      | 3.8157 | 3.2516 | 1.9967 |            |        |
| Fnaph2 and oda1 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                      | 2.620      | 3.4664 | 3.3189 | 1.000  |            |        |
| Fnaph2 and py1 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                       | 7.553      | 3.6896 | 3.3475 | 1.5516 |            |        |
| Fnaph3 and py1 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                       | 85.643     | 5.0635 | 4.8877 | 1.3227 | 135.452    | 3.1825 |
| <b>195 K L2-O2</b>                                                                                                                                                                                                                                                                                                                                                |            |        |        |        |            |        |
| Fnaph4 and oda2 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                      | 3.146      | 3.8511 | 3.2442 | 2.0751 |            |        |
| Fnaph4 and py2 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                       | 9.851      | 3.8297 | 3.2521 | 2.0225 |            |        |
| Fnaph5 and oda2 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                      | 2.690      | 3.4566 | 3.3223 | 0.9542 |            |        |
| Fnaph5 and py2 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                       | 9.888      | 3.6890 | 3.3574 | 1.5286 |            |        |
| Fnaph6 and py2 <sup>h</sup>                                                                                                                                                                                                                                                                                                                                       | 80.308     | 5.0745 | 4.8160 | 1.5990 | 131.407    | 3.2615 |
| <sup>h</sup> Fnaph1: C17-C26, F1, x, y, z; Fnaph2: C48-C57, F3, 1-x, 1-y, 2-z; Fnaph3: C27-C31, F2, -x, 2-y, 1-z; Fnaph4: C48-C57, F3, x, y, z; Fnaph5: C17-C26, F1, 1-x, 1-y, 1-z; Fnaph6: C58-C62, F4, 2-x, -y, 2-z; oxadiazole(oda1): N6-N7, C10-C11, O1, x, y, z; oda2: N14-N15, C40-C41, O2, x, y, z; py1: C12-C16, N8, x, y, z; py2: C43-C47, N16, x, y, z. |            |        |        |        |            |        |
| <b>168 K L1-O1</b>                                                                                                                                                                                                                                                                                                                                                | $\theta^b$ | $Z^c$  | $d^d$  | $r^e$  | $\alpha^f$ | $l^g$  |
| Fnaph1 and oda1 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                      | 2.255      | 3.8709 | 3.2286 | 2.1354 |            |        |
| Fnaph1 and py1 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 8.037      | 3.7821 | 3.2258 | 1.9745 |            |        |
| Fnaph2 and oda1 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                      | 1.546      | 3.4365 | 3.2878 | 1.0000 |            |        |
| Fnaph2 and py1 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 7.997      | 3.6940 | 3.3502 | 1.5562 |            |        |
| Fnaph3 and py1 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 86.177     | 4.9903 | 4.8601 | 1.1325 | 134.727    | 3.1041 |
| <b>168 K L2-O2</b>                                                                                                                                                                                                                                                                                                                                                |            |        |        |        |            |        |
| Fnaph4 and oda2 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                      | 2.609      | 3.8262 | 3.2290 | 2.0526 |            |        |
| Fnaph4 and py2 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 9.382      | 3.7770 | 3.2417 | 1.9293 |            |        |
| Fnaph5 and oda2 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                      | 2.301      | 3.4340 | 3.3046 | 0.9338 |            |        |
| Fnaph5 and py2 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 9.694      | 3.6948 | 3.3338 | 1.5929 |            |        |
| Fnaph6 and py2 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 83.514     | 4.9119 | 4.7562 | 1.2269 | 132.670    | 3.0664 |
| <b>168 K L3-O3</b>                                                                                                                                                                                                                                                                                                                                                |            |        |        |        |            |        |
| Fnaph7 and oda3 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                      | 2.806      | 3.8270 | 3.2196 | 2.0688 |            |        |
| Fnaph7 and py3 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 8.762      | 3.7769 | 3.2261 | 1.9640 |            |        |
| Fnaph8 and oda3 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                      | 2.501      | 3.4378 | 3.3003 | 0.9625 |            |        |
| Fnaph8 and py3 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 8.930      | 3.6723 | 3.3394 | 1.5278 |            |        |
| Fnaph9 and py3 <sup>i</sup>                                                                                                                                                                                                                                                                                                                                       | 82.297     | 4.9716 | 4.7643 | 1.4207 | 131.713    | 3.1674 |

| <b>168 K L4-O4</b>            |        |        |        |        |         |        |
|-------------------------------|--------|--------|--------|--------|---------|--------|
| Fnaph10 and oda4 <sup>i</sup> | 2.467  | 3.8094 | 3.2364 | 2.0093 |         |        |
| Fnaph10 and py4 <sup>i</sup>  | 8.571  | 3.7951 | 3.2344 | 1.9853 |         |        |
| Fnaph11 and oda4 <sup>i</sup> | 2.525  | 3.4363 | 3.3039 | 0.9447 |         |        |
| Fnaph11 and py4 <sup>i</sup>  | 9.292  | 3.6740 | 3.3459 | 1.5176 |         |        |
| Fnaph12 and py4 <sup>i</sup>  | 80.374 | 5.0794 | 4.8046 | 1.6481 | 130.345 | 3.2865 |

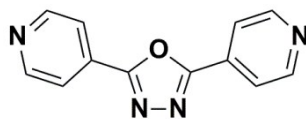
<sup>i</sup>Fnaph1: C17-C26, F1, x, y, z; Fnaph2: C110-C119, F7, 1-x, 2-y, 1-z; Fnaph3: C27-C31, F2, -x, 2-y, -z; Fnaph4: C48-C57, F3, x, y, z; Fnaph5: C79-C88, F5, 1-x, -y, -z; Fnaph6: C58-C62, F4, 1-x, 1-y, -z; Fnaph7: C79-C88, F5, x, y, z; Fnaph8: C48-C57, F3, 1-x, -y, 1-z; Fnaph9: C89-C93, F6, 1-x, -1-y, 1-z; Fnaph10: C110-C119, F7, x, y, z; Fnaph11: C17-C26, F1, 1-x, 2-y, -z; Fnaph12: C120-C124, F8, 2-x, 2-y, 1-z; oxadiazole(oda1): N6-N7, C10-C11, O1, x, y, z; oda2: N14-N15, C41-C42, O2, x, y, z; oda3: N22-N23, C72-C73, O3, x, y, z; oda4: N30-N31, C103-C104, O4, x, y, z; pyl: C12-C16, N8, x, y, z; py2: C43-C47, N16, x, y, z; py3: C74-C78, N24, x, y, z; py4: C105-C109, N32, x, y, z;.

<sup>b</sup>The dihedral angle between two aromatic rings (°); <sup>c</sup>The distance between the centroids of aromatic rings (Å); <sup>d</sup>The perpendicular distance between two aromatic rings (Å); <sup>e</sup>The offset distance between two aromatic rings (Å); <sup>f</sup>The angle of  $\pi$ -H $\cdots$  $\pi$  (°), in which the H atom have <sup>g</sup>the shortest distance of H-to-ring center (Å).

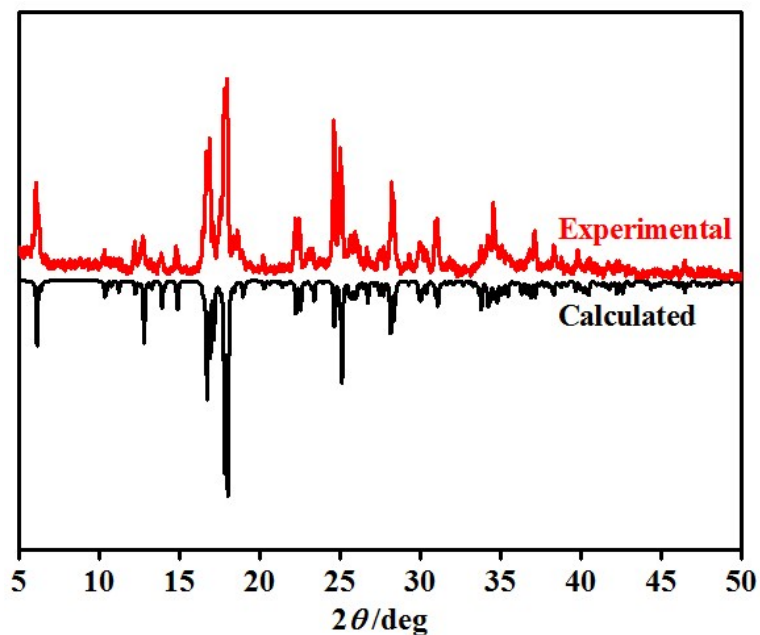
**Table S3.** F...Ag interactions for **1·1.5Fnaph** at different temperatures.

| <i>T</i> (K)     | F  | Ag  | Symm. Codes <sup>a</sup> | Distance (Å) |
|------------------|----|-----|--------------------------|--------------|
| 100 <sup>b</sup> | F1 | Ag4 | 1/2+x,1/2+y,z            | 3.3247       |
|                  | F2 | Ag2 | 1/2-x,1/2-y,-z           | 3.2266       |
|                  | F3 | Ag3 | 1/2-x,1/2-y,-z           | 2.8105       |
| 168 <sup>c</sup> | F1 | Ag2 | 1-x,1-y,-z               | 3.3291       |
|                  | F2 | Ag6 | 1-x,1-y,-z               | 2.9423       |
|                  | F3 | Ag2 | 1-x,-y,1-z               | 3.2738       |
|                  | F4 | Ag1 | 1-x,-y,1-z               | 2.9211       |
|                  | F5 | Ag8 | 2-x,-y,1-z               | 3.2476       |
|                  | F6 | Ag1 | 1-x,-1-y,1-z             | 2.8649       |
|                  | F7 | Ag8 | 2-x,1-y,2-z              | 3.3060       |
|                  | F8 | Ag5 | x,1+y,z                  | 3.1014       |
| 195 <sup>d</sup> | F1 | Ag1 | 1-x,1-y,1-z              | 3.3678       |
|                  | F2 | Ag3 | -1+x,1+y,-1+z            | 3.2155       |
|                  | F3 | Ag1 | 1-x,-y,2-z               | 3.3509       |
|                  | F4 | Ag3 | 2-x,-y,2-z               | 3.1835       |
| 226 <sup>b</sup> | F1 | Ag4 | 1/2+x,1/2+y,z            | 3.5117       |
|                  | F2 | Ag2 | 1/2-x,1/2-y,-z           | 3.4332       |
|                  | F3 | Ag3 | 1/2-x,1/2-y,-z           | 2.9647       |
| 298 <sup>b</sup> | F1 | Ag4 | 1/2+x,1/2+y,z            | 3.5647       |
|                  | F2 | Ag2 | 1/2-x,1/2-y,-z           | 3.4856       |
|                  | F3 | Ag3 | 1/2-x,1/2-y,-z           | 2.9871       |

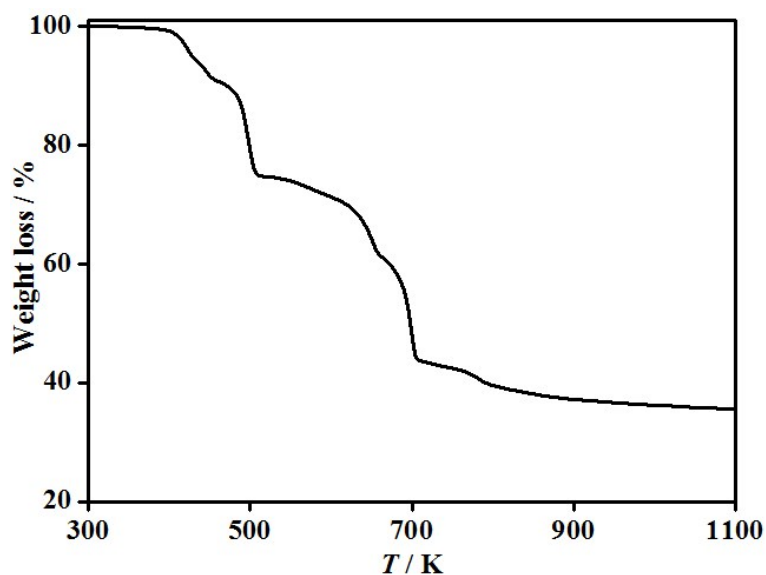
<sup>a</sup>Symmetry codes for Ag atoms; <sup>b</sup>The F1 and F2 atom are disordered with a ratio of F1:F2 = 30:70, while the F3 atom is disordered with a half occupation; <sup>c</sup>The F2, F4, F6 and F8 atoms are disordered with a half occupation; <sup>d</sup>The F2 and F4 atoms are disordered with a half occupation.



**Scheme S1.** The bent pillar ligand 2,5-di-(pyridyl)-1,3,4-oxadiazole (dpoda).

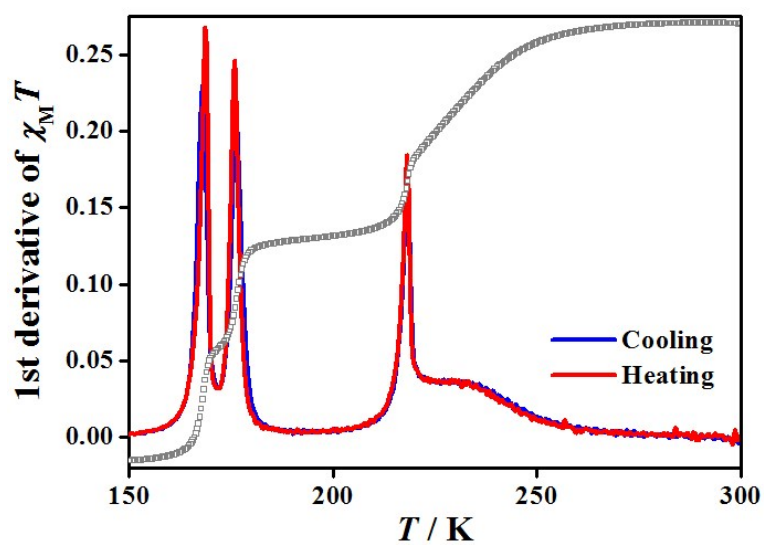


**Figure S1.** Powder X-ray diffraction data of **1·1.5Fnaph** at room temperature.

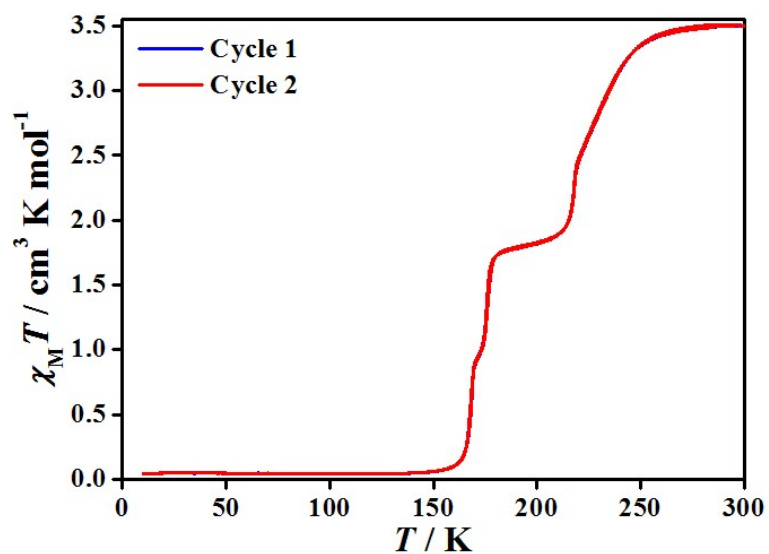


**Figure S2.** Thermogravimetric analyses of **1·1.5Fnaph**. The weight loss of Fnaph guest is 25.32%, which is close to the weight percent of 1.4 Fnaph (25.50%).

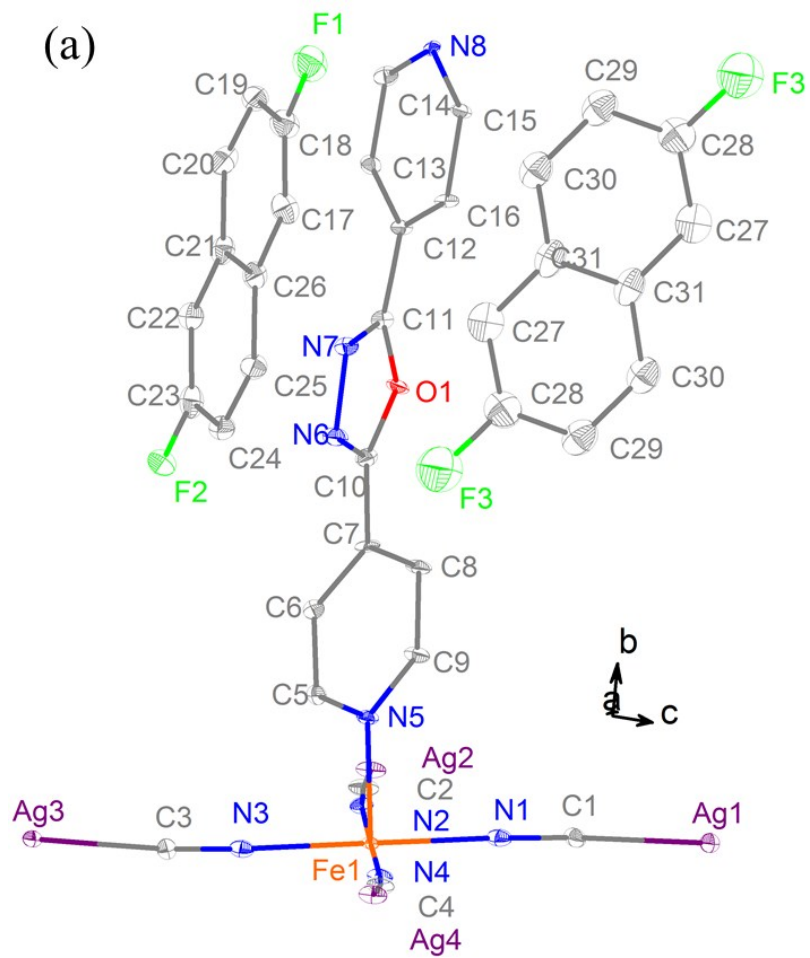




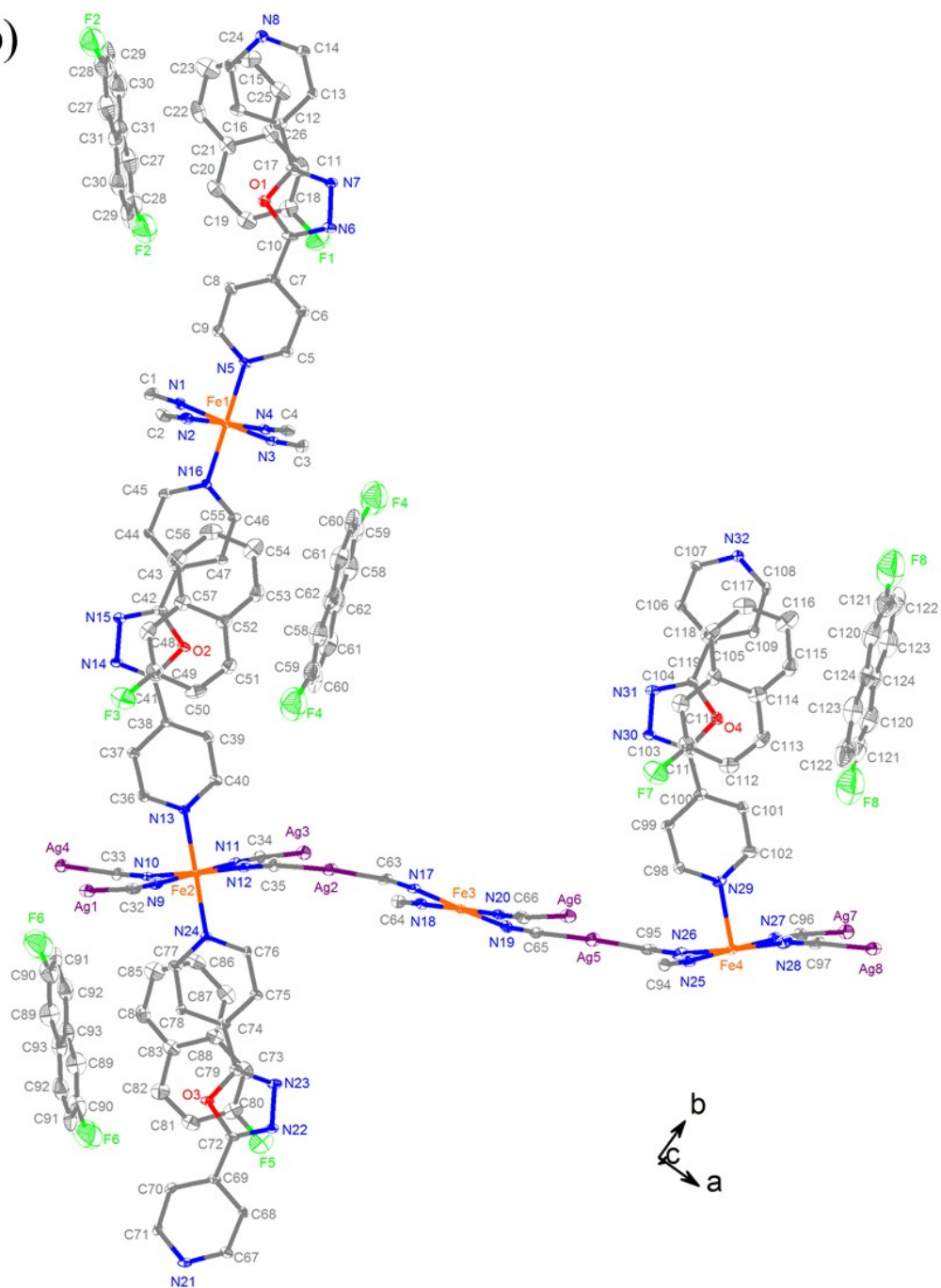
**Figure S3.** The first order differentiation of  $\chi_M T$  versus  $T$  plot for **1·1.5Fnaph** on cooling (blue) and heating (red).



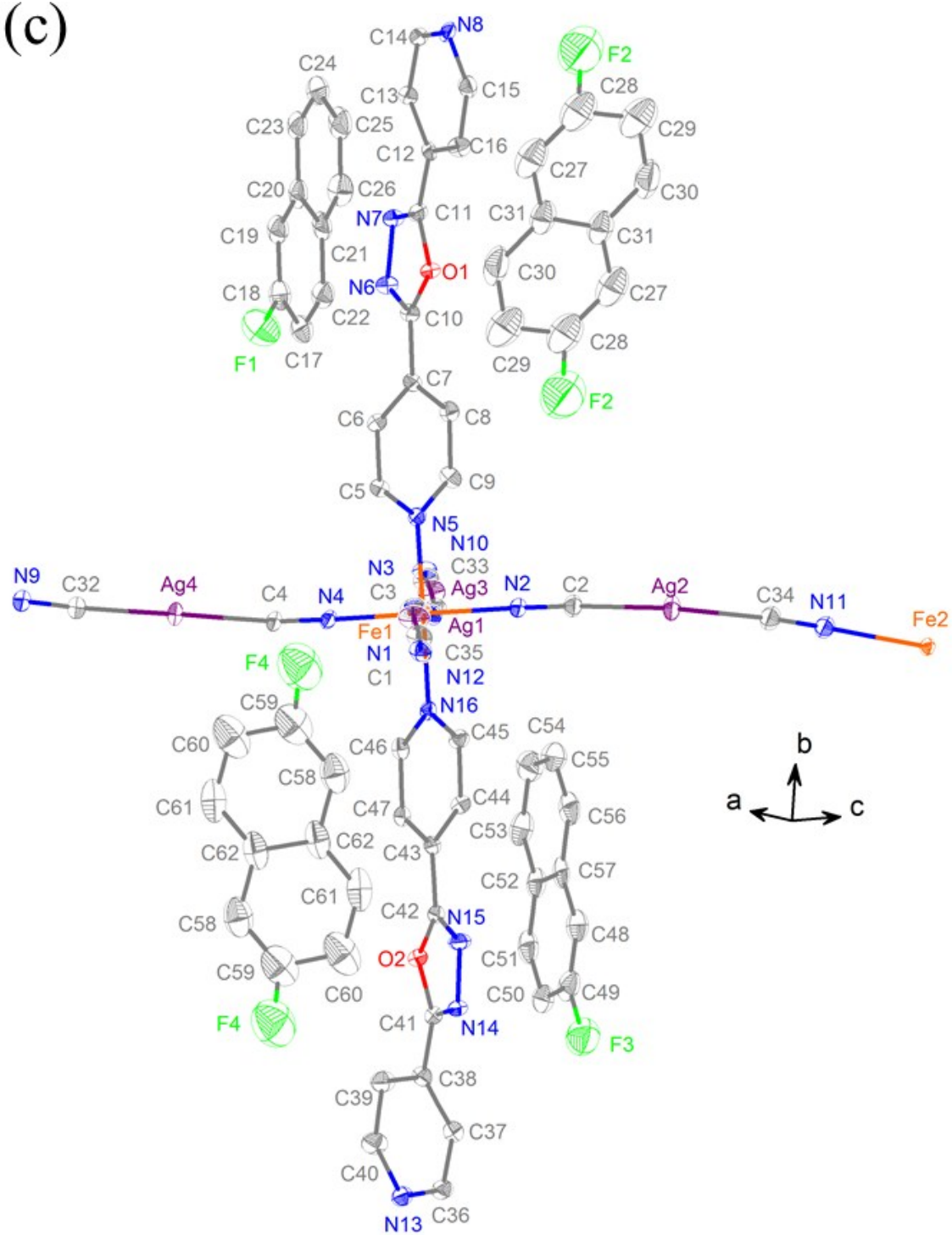
**Figure S4.** Magnetic susceptibility data with two sequential cycles for **1·1.5Fnaph** at  $2 \text{ K min}^{-1}$ .

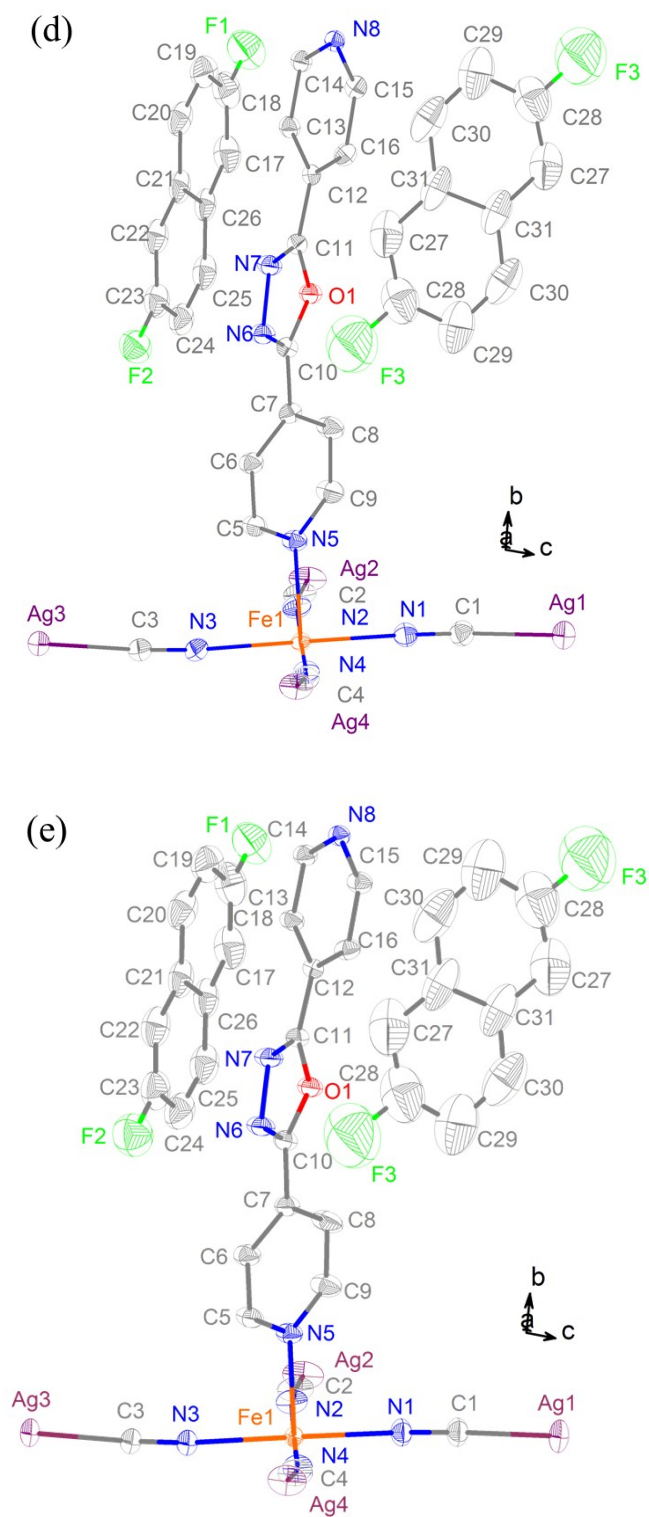


(b)

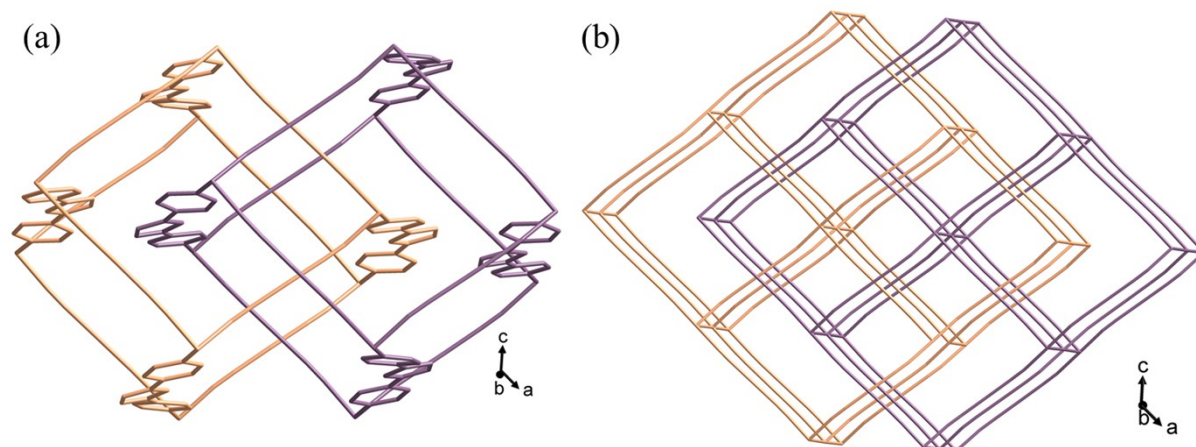


(c)

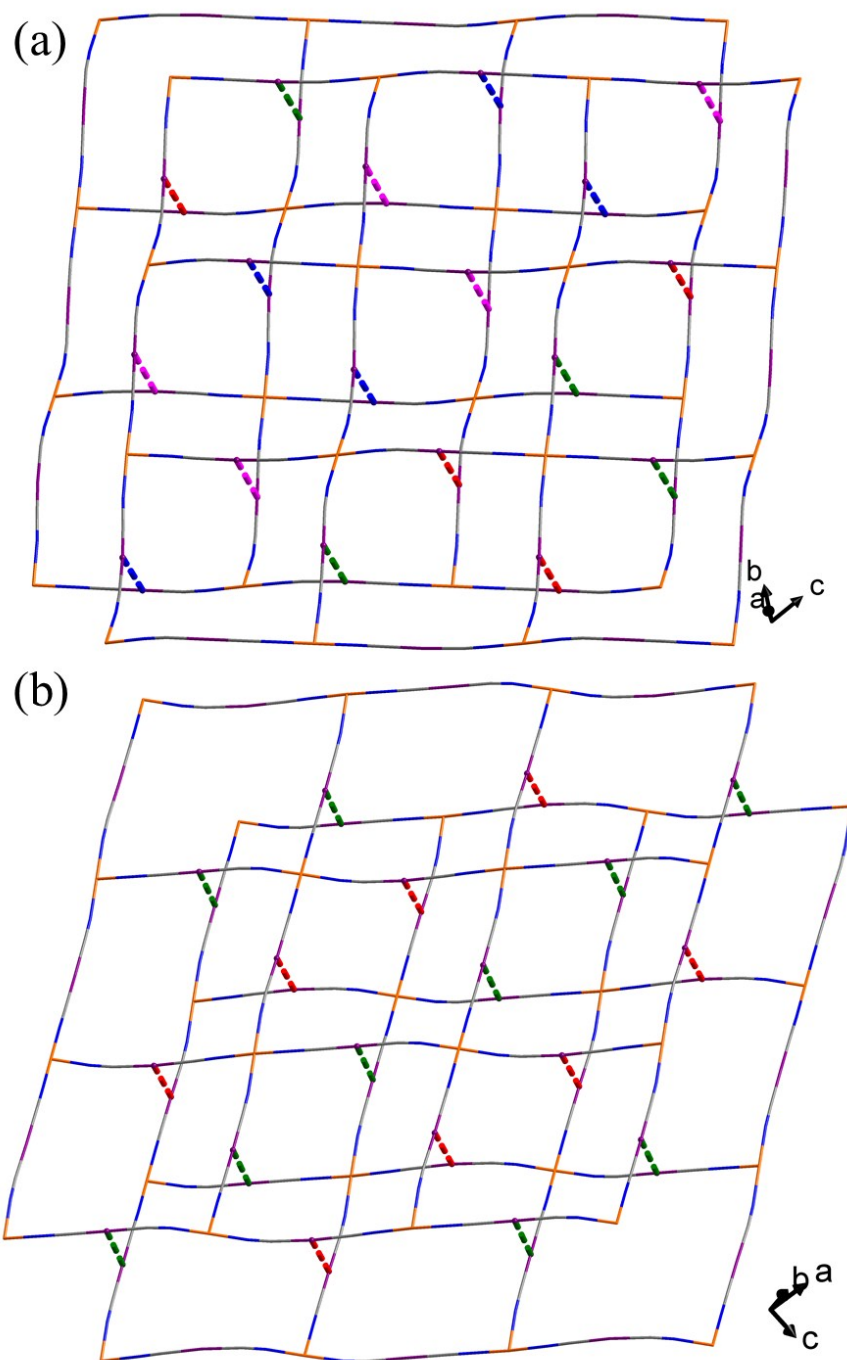




**Figure S5.** Asymmetric unit of **1·1.5Fnaph** at 100 K (a), 168 K (b), 195 K (c), 226 K (d) and 298 K (e). Thermal ellipsoids are drawn at the 30 % probability. Hydrogen atoms are omitted for clarity.

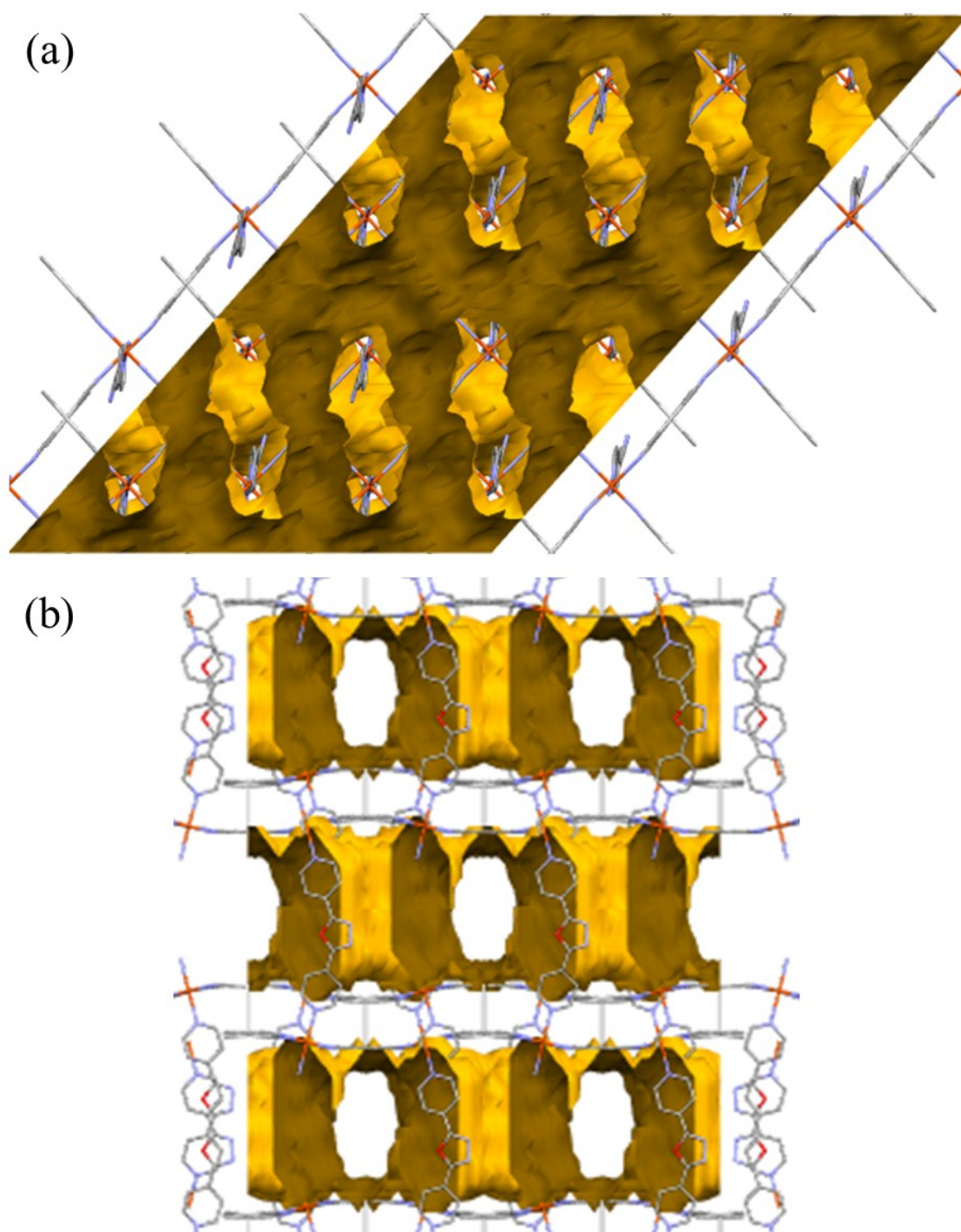


**Figure S6.** Structural illustration of two-fold interpenetrated frameworks and the **pcu** topological network of **1·1.5Fnaph**.



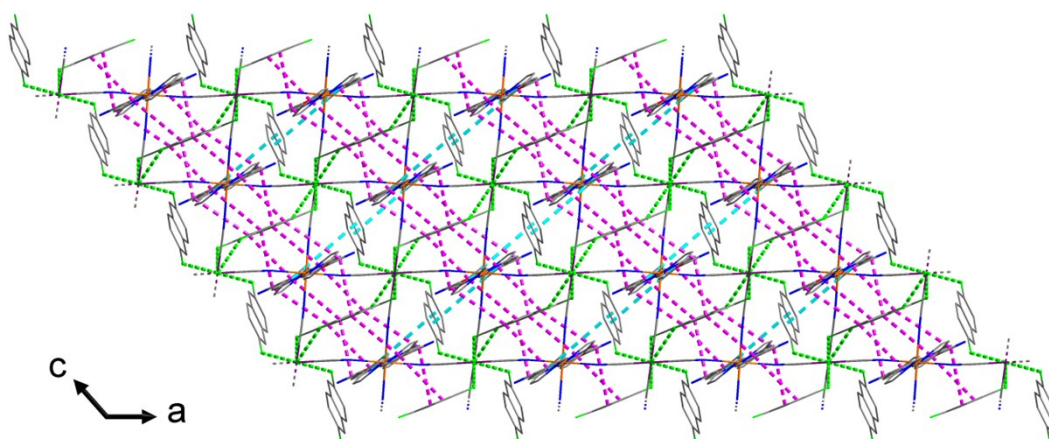
**Figure S7.** The argentophilic interactions in  $1 \cdot 1.5\text{Fnaph}$ : (a) four sets of  $\text{Ag} \cdots \text{Ag}$  interactions at 168 K: 3.2316 Å (green), 3.2238 Å (violet), 3.0203 Å (blue), 3.0083 Å (red); (b) structural illustration of two sets (red and green) of  $\text{Ag} \cdots \text{Ag}$  interactions.



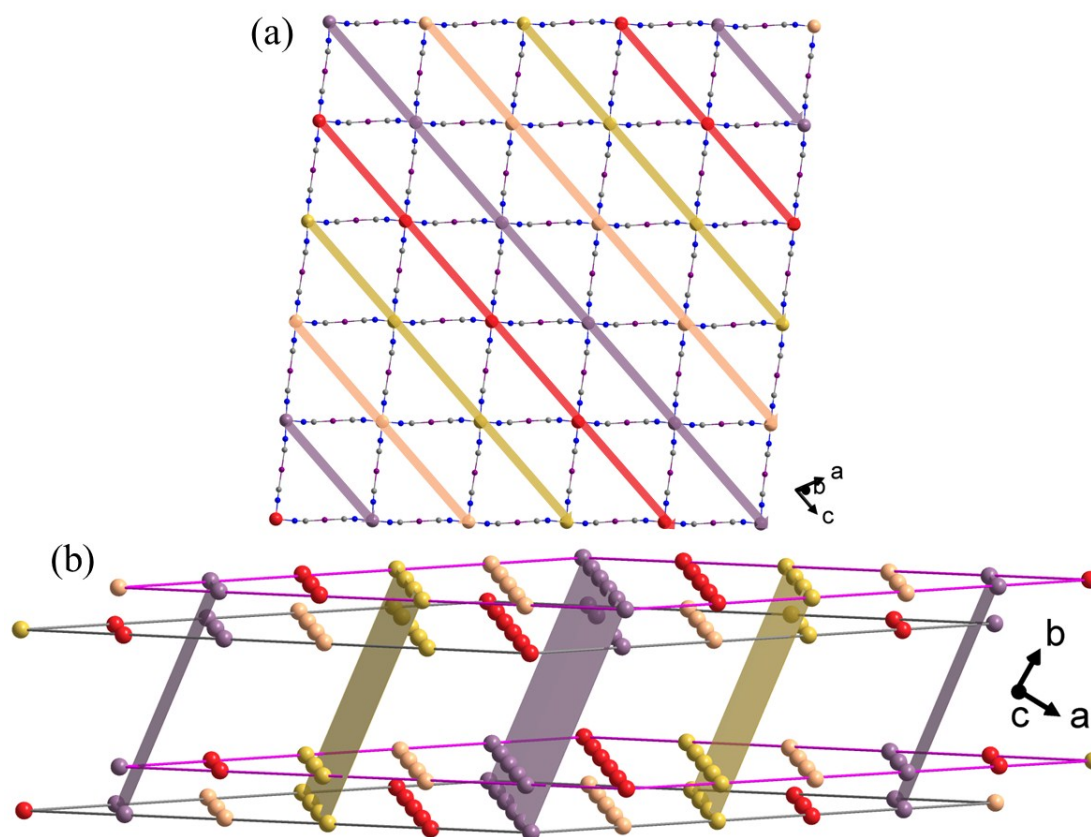


**Figure S8.** (a) 2D pore along the *ac* plane in **1·1.5Fnaph** and (b) the view along the *c* axis.



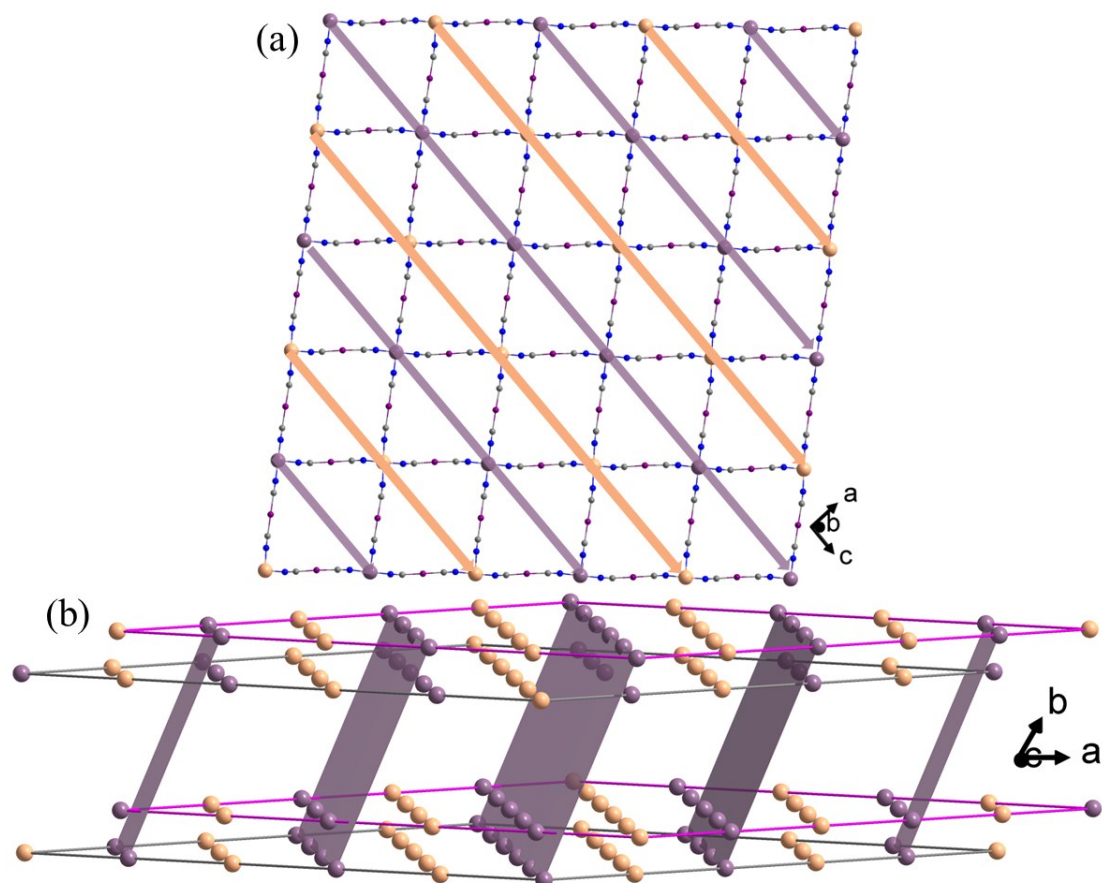


**Figure S9.** Offset face-to-face  $\pi\cdots\pi$  interactions (pink dash lines), edge-to-face  $\pi\cdots\pi$  interactions (turquoise dashed lines) and F $\cdots$ Ag interactions (green dashed lines) in **1·1.5Fnaph** along the  $b$  axis. The F atoms are disordered over two positions.

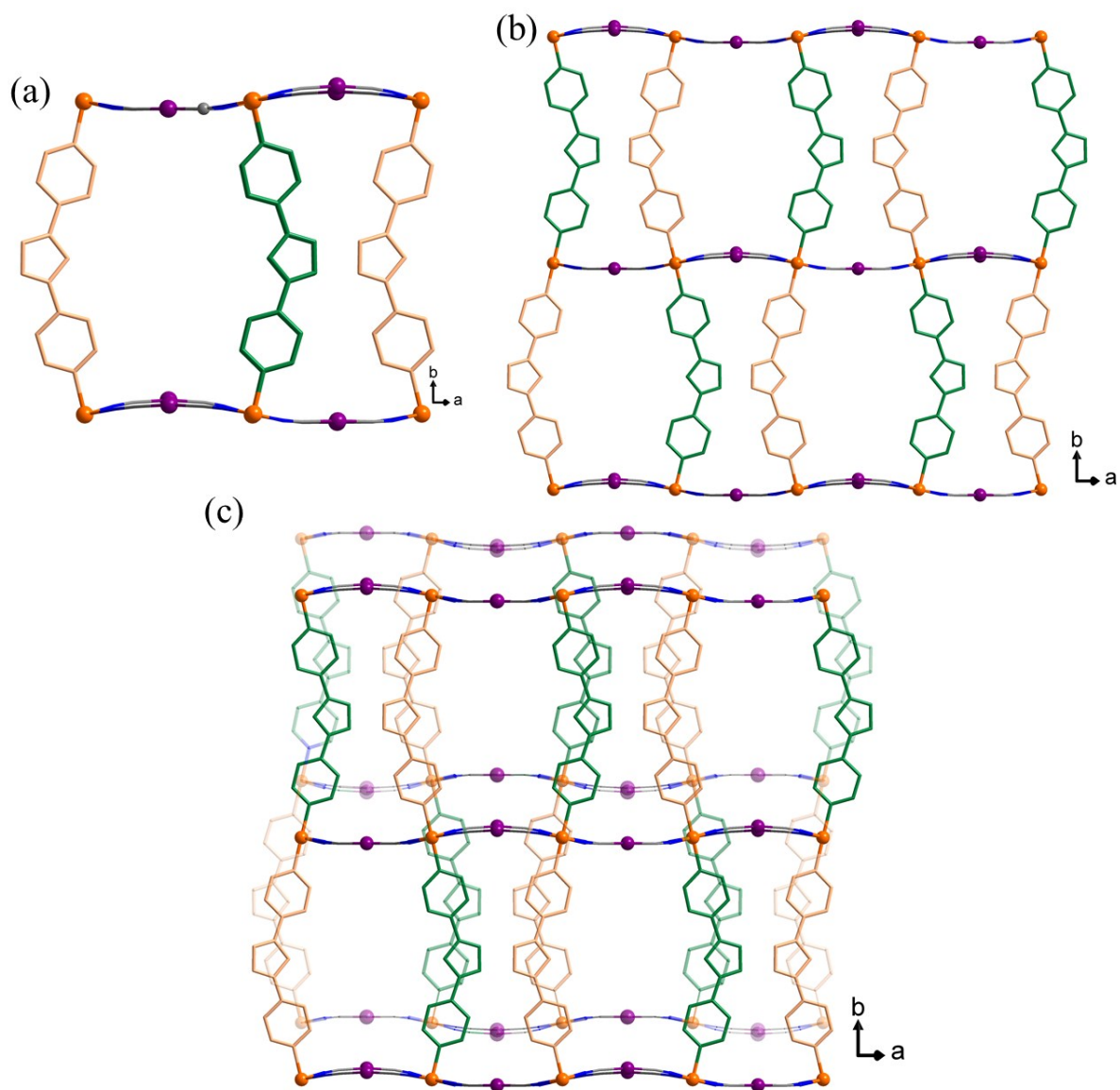


**Figure S10.** (a) Ordered arrangement of Fe1 (red), Fe2 (violet), Fe3 (pink) and Fe4 (yellow) sites within one Hofmann layer for **1·1.5Fnaph**, showing the same Fe(II) ions along the  $c$ -axis at 168 K. (b) View of twofold-interpenetrated framework for **1·1.5Fnaph**, showing the same Fe2 (violet) and Fe4 (yellow) ions along the  $bc$  plane, respectively. The Hofmann-type layers from two sets of 3D frameworks are

represented by violet and grey squares, respectively. The pillar ligands connected the same colored squares are omitted for clarity.



**Figure S11.** (a) Ordered arrangement of Fe1 (violet) and Fe2 (pink) ions within one Hofmann layer for  $1 \cdot 1.5\text{Fnaph}$ , showing the same Fe(II) ions along the  $c$ -axis at 195K. (b) View of twofold-interpenetrated 3D framework for  $1 \cdot 1.5\text{Fnaph}$ , showing the ordered arrangements of Fe1 and Fe2 ions in the whole 3D framework. The Hofmann-type layers from two sets of 3D frameworks are represented by violet and grey squares, respectively. The pillar ligands connected the same colored squares are omitted for clarity. The LS Fe1 ions are marked by the violet blocks.



**Figure S12.** The orientations of the dpoda ligands within one cubic (a), one set of 3D framework (b) and twofold-interpenetrated 3D framework (c) in  $1 \cdot 1.5\text{Fnaph}$  at 100 K. The opposite orientations of the dpoda ligands are marked by pink and green, respectively.