Electronic Supporting Information

Heterobimetallic cyanide-bridged $Fe^{III}(\mu$-CN)M^{II} complexes (M = Mn and Cu). Synthesis, structure and magnetism†

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Figures:

Fig. S1 ^{1}H NMR spectra of (*a*) L^1 and (*b*) L^2 in $CDCl_3$.

Fig. S2 Perspective view of metal coordination environment in $[Fe^{III}(Tp)(CN)_2(\mu$–CN)-$Mn^{II}Cl(L^1)]$•3DMF•$3H_2O$ (**1**) (both PART 1 and PART 2).

Fig. S3 Perspective view of metal coordination environment in $[Fe^{III}(Tp)(CN)_2(\mu$–CN)Mn^{II}Cl-$(L^2)]$•DMF (**2**) with modelled DMF molecules (both PART 1 and PART 2).

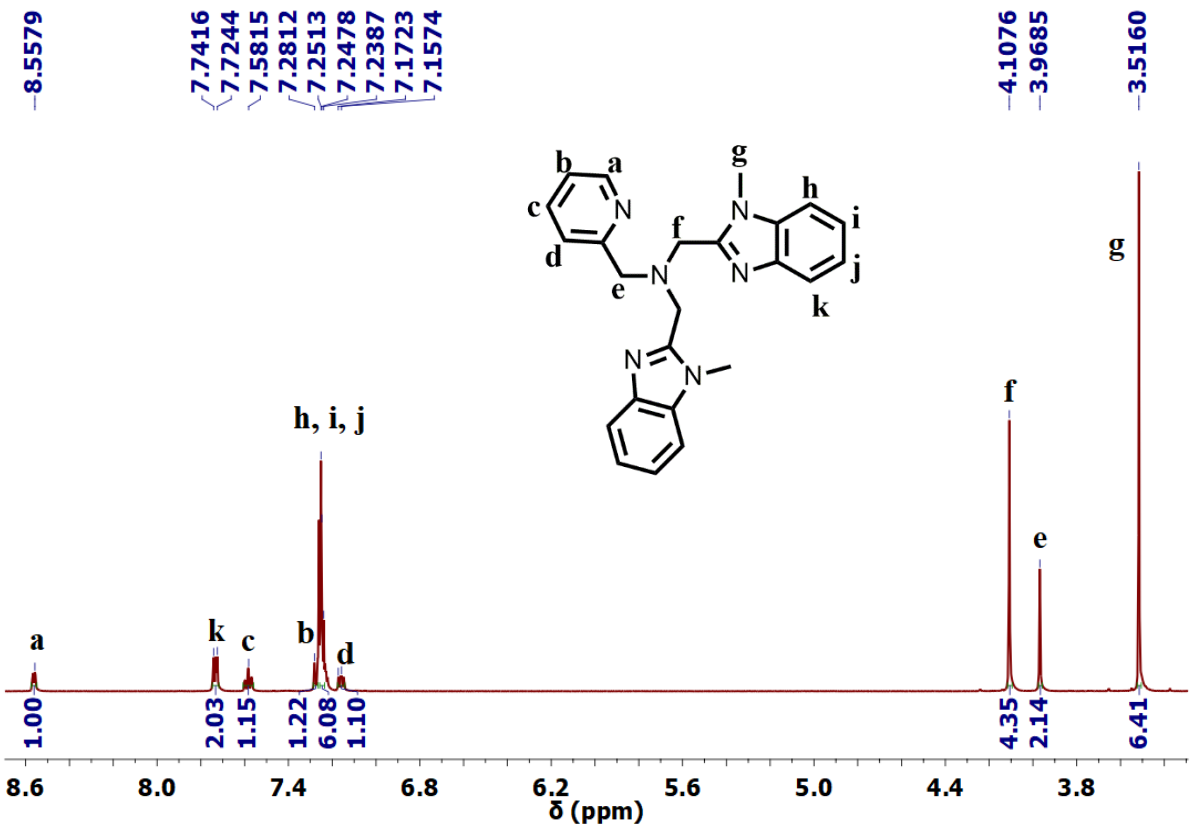
Fig. S4 Perspective view of metal coordination environment in $[Fe^{III}(Tp)(CN)_2(\mu$–CN)-$Cu^{II}(L^1)](ClO_4)$•$2CH_3OH$ (**3**) (both PART 1 and PART 2).

Fig. S5 XPRD spectra of (*a*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Mn^{II}Cl(L^1)]$•3DMF•$3H_2O$ (**1**), (*b*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Mn^{II}Cl(L^2)]$•DMF (**2**), (*c*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Cu^{II}(L^1)](ClO_4)$-•$2CH_3OH$ (**3**) and (*d*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Cu^{II}(L^2)](ClO_4)$•$2CH_3CN$ (**4**).

Fig. S6 IR spectra (in KBr) of (*a*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Mn^{II}Cl(L^1)]$•3DMF•$3H_2O$ (**1**), (*b*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Mn^{II}Cl(L^2)]$•DMF (**2**), (*c*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Cu^{II}(L^1)](ClO_4)$-•$2CH_3OH$ (**3**) and (*d*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Cu^{II}(L^2)](ClO_4)$•$2CH_3CN$ (**4**).

Fig. S7 Electronic spectrum in CH_3CN of (*a*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Mn^{II}Cl(L^1)]$-•3DMF•$3H_2O$ (**1**), (*b*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Mn^{II}Cl(L^2)]$•DMF (**2**), (*c*) $[Fe^{III}(Tp)(CN)_2$-$(\mu$–CN)$Cu^{II}(L^1)](ClO_4)$•$2CH_3OH$ (**3**) and (*d*) $[Fe^{III}(Tp)(CN)_2(\mu$–CN)$Cu^{II}(L^2)]$-(ClO_4)•$2CH_3CN$ (**4**).

(*a*)



(*b*)

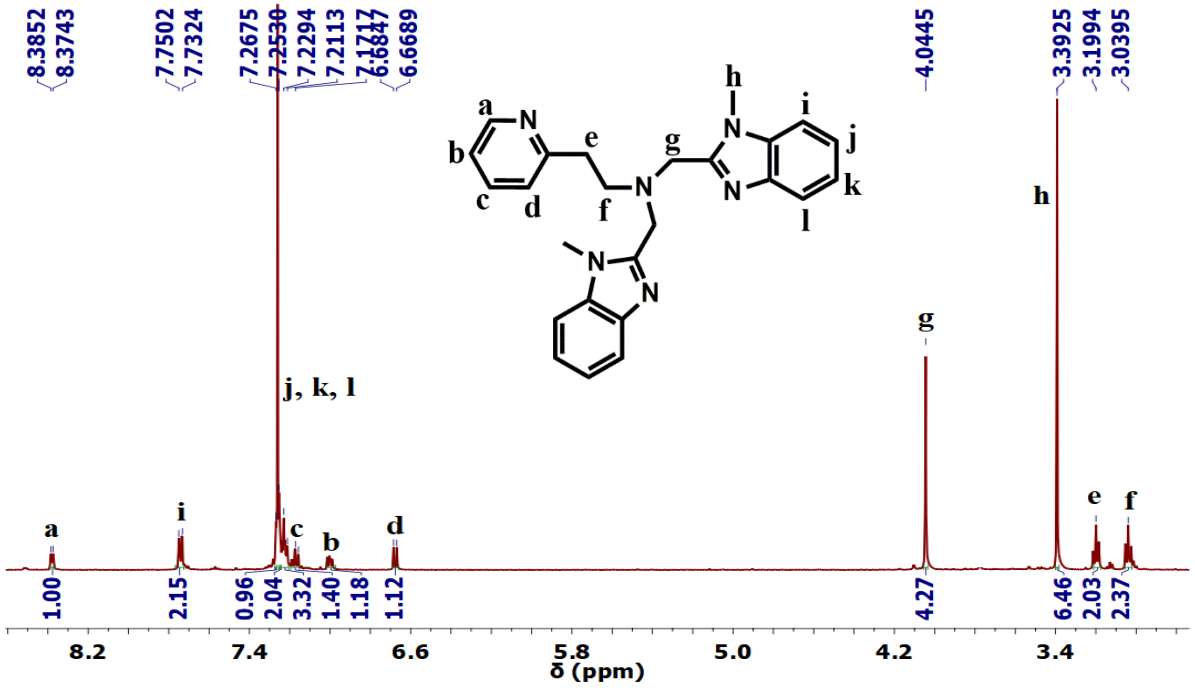


Fig. S1 ^{1}H NMR spectra of (*a*) L^{1} and (*b*) L^{2} in $CDCl_3$.

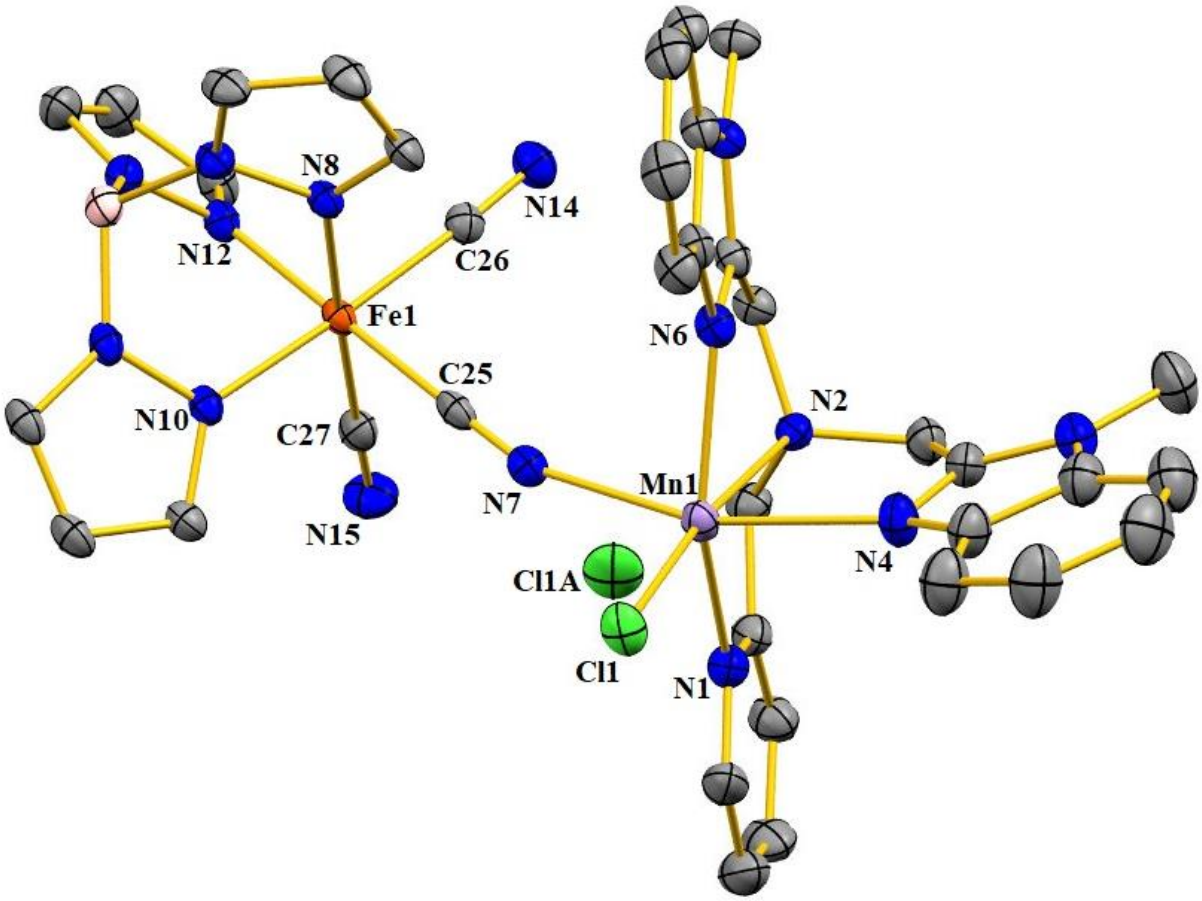


Fig. S2 Perspective view of metal coordination environment in [Fe^{III}(Tp)$(CN)_2$(μ–CN)-Mn^{II}Cl(L^1)]•3DMF•3H_2O (**1**) with split chloride ions (both PART 1 and PART 2). Only donor atoms are labelled. All hydrogen atoms are excluded for clarity. All the solvent molecules in the formula unit are masked.

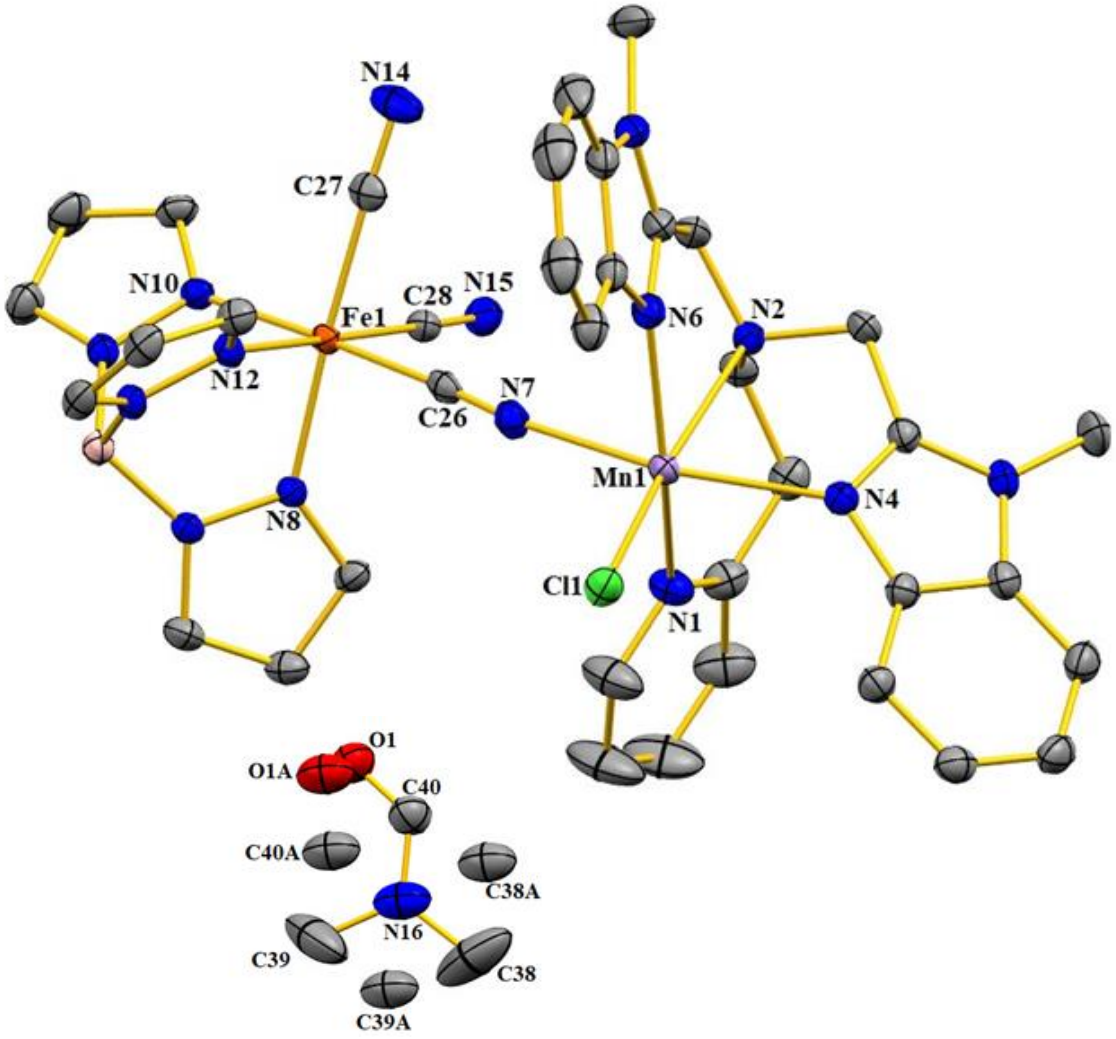


Fig. S3 Perspective view of metal coordination environment in [Fe^{III}(Tp)$(CN)_2$(μ–CN)Mn^{II}Cl-(L^2)]•DMF (**2**) with modelled DMF molecule (both PART 1 and PART 2). Only donor atoms are labelled. All hydrogen atoms are excluded for clarity.

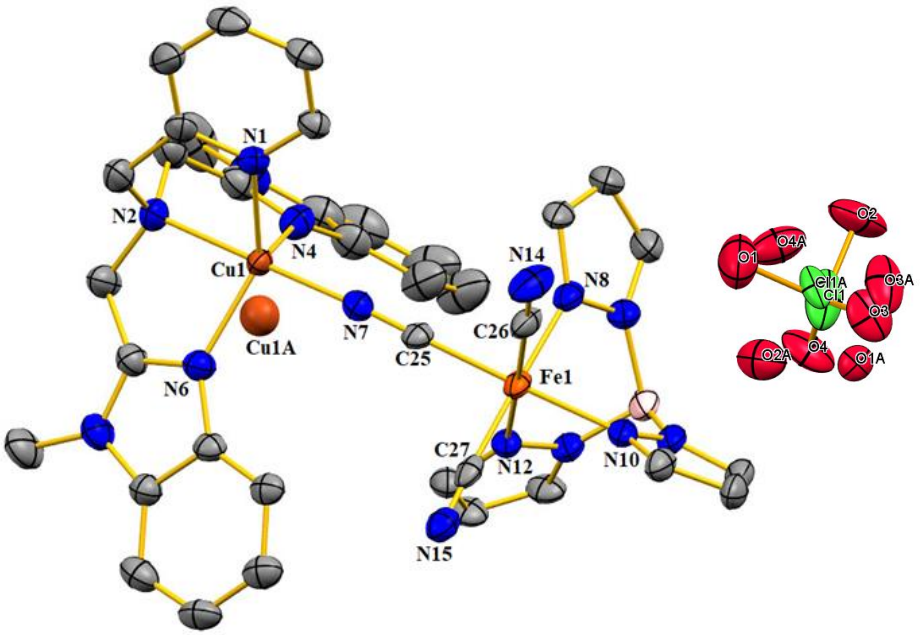
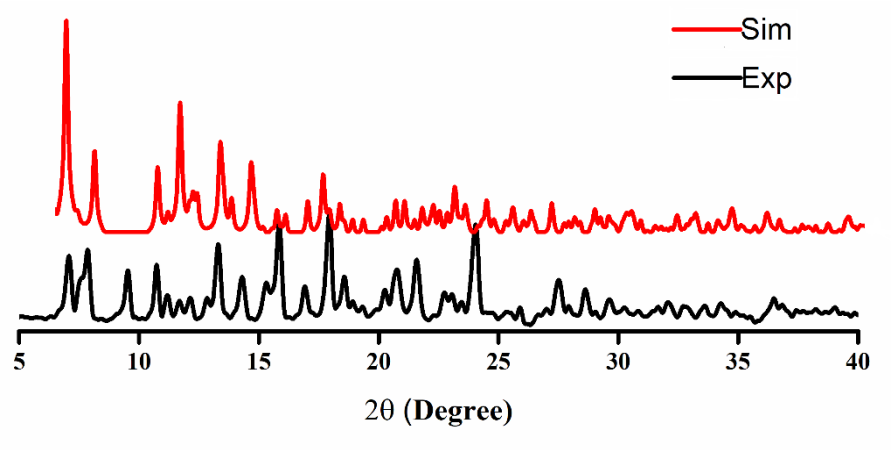
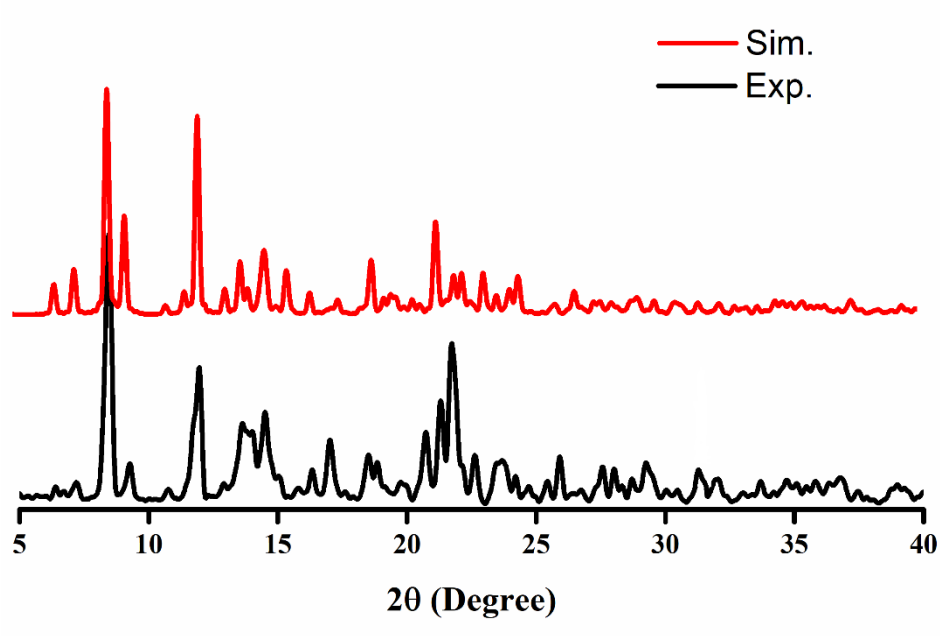


Fig. S4 Perspective view of metal coordination environment in $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)\text{-}Cu^{II}(L^1)](ClO_4)\bullet 2CH_3OH$ (**3**) with split copper centres and modelled perchlorate ion (both PART 1 and PART 2). Only donor atoms are labelled. All hydrogen atoms and solvent molecules are excluded for clarity.

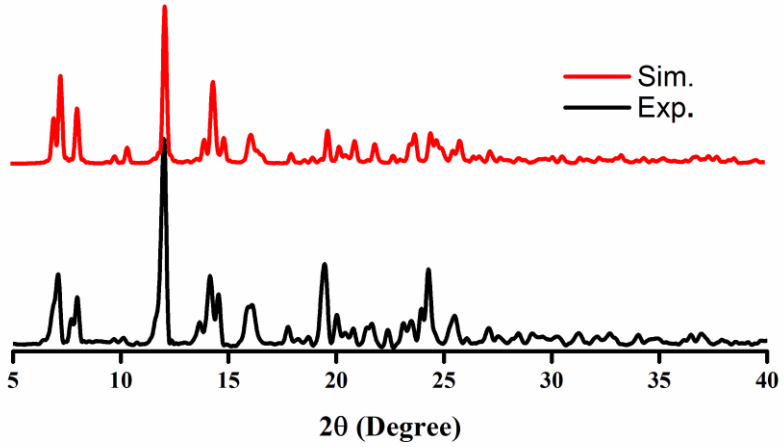
(*a*)


Sim
Exp
5
10
15
20
25
30
35
40
2θ (Degree)

(*b*)


Sim.
Exp.
5
10
15
20
25
30
35
40
2θ (Degree)

(*c*)



(*d*)

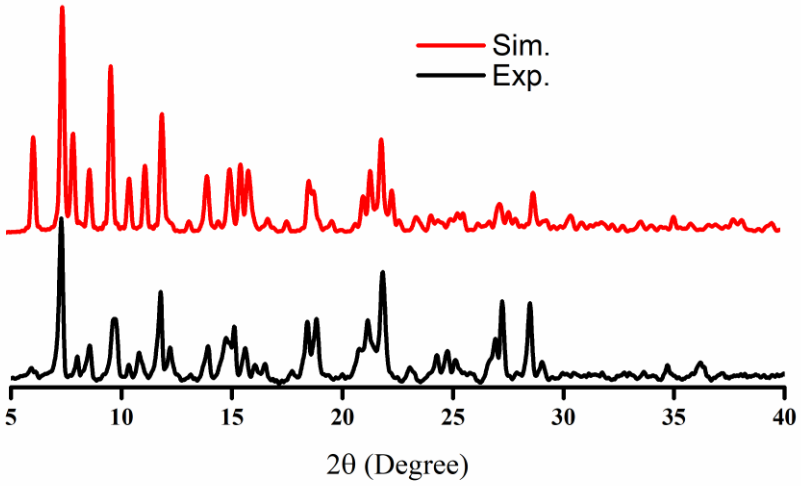
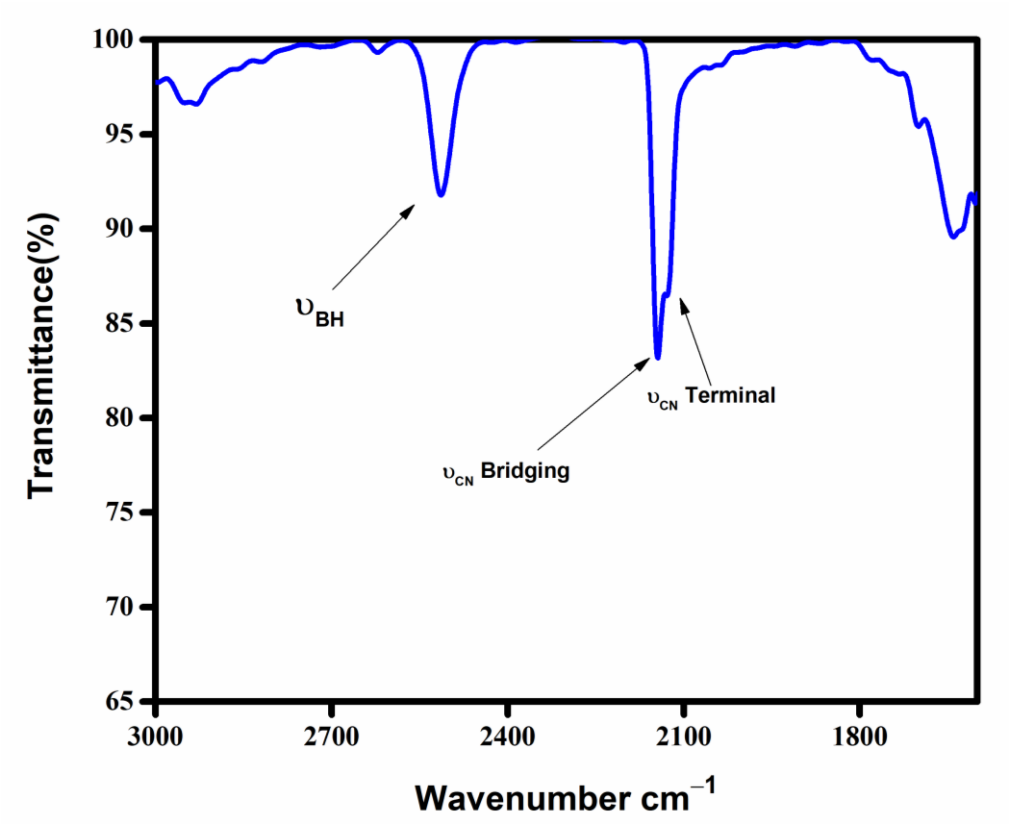
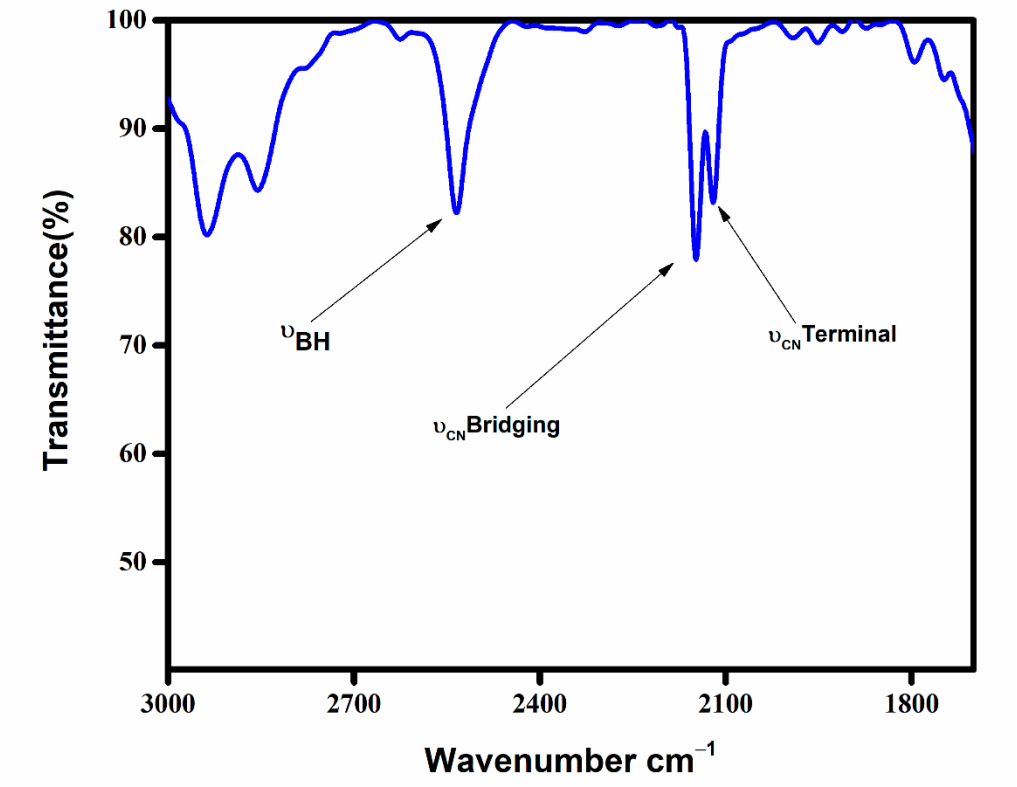


Fig. S5 XPRD spectra of (*a*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Mn^{II}Cl(L^1)]\bullet 3DMF\bullet 3H_2O$ (**1**), (*b*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Mn^{II}Cl(L^2)]\bullet DMF$ (**2**), (*c*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Cu^{II}(L^1)](ClO_4)\text{-}\bullet 2CH_3OH$ (**3**) and (*d*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Cu^{II}(L^2)](ClO_4)\bullet 2CH_3CN$ (**4**).

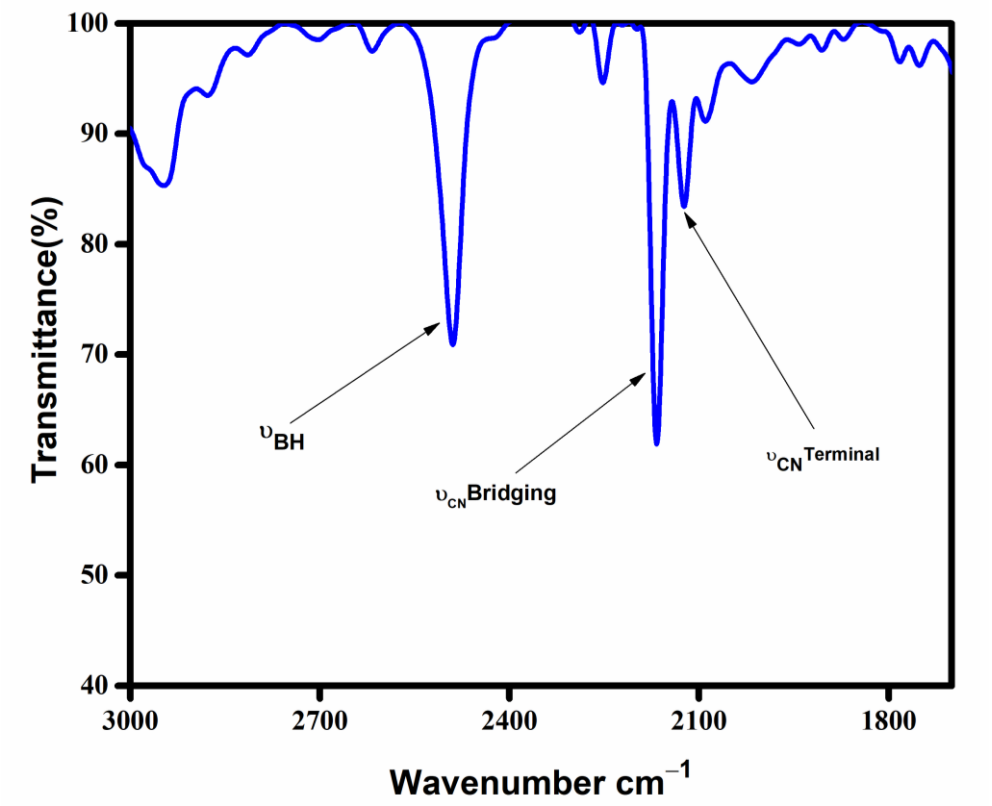
(*a*)


100
95
90
85
80
75
70
65
Transmittance(%)
υBH
υCN Terminal
υCN Bridging
3000
2700
2400
2100
1800
Wavenumber cm−1

(*b*)


100
90
80
70
60
50
Transmittance(%)
υBH
υCN Terminal
υCN Bridging
3000
2700
2400
2100
1800
Wavenumber cm−1

(*c*)



(*d*)

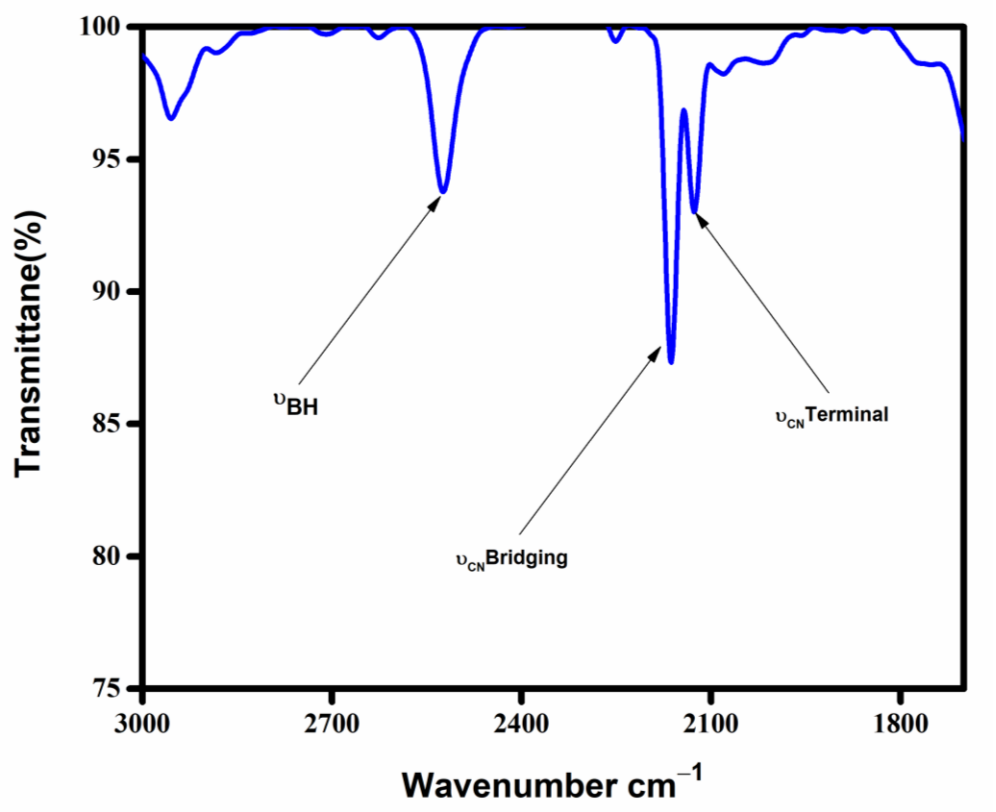
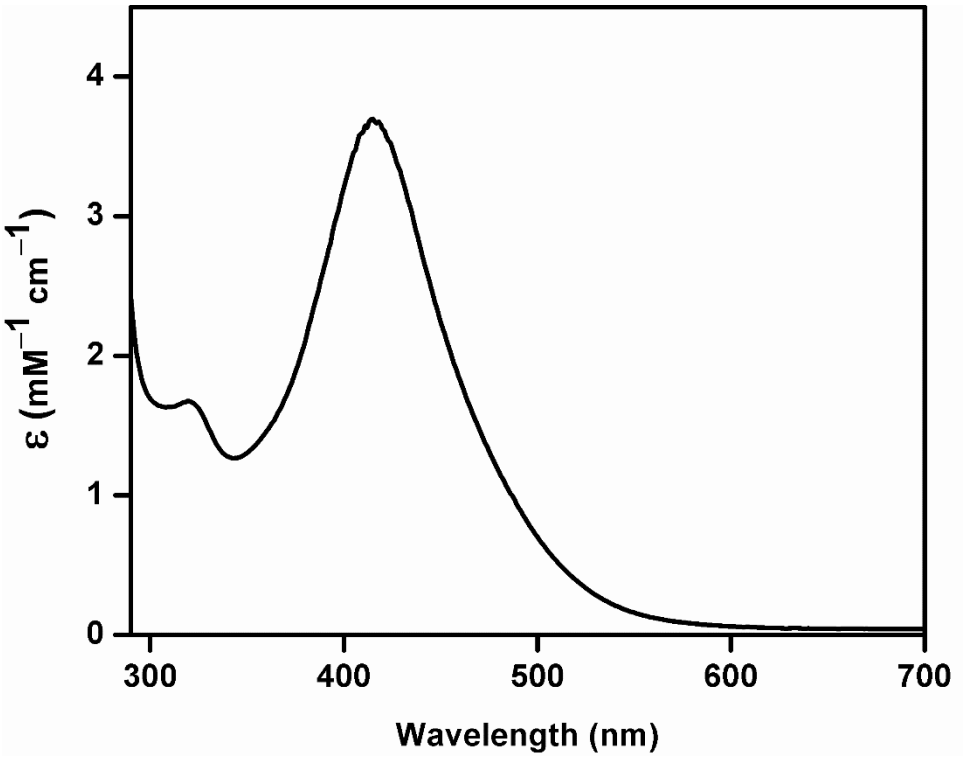
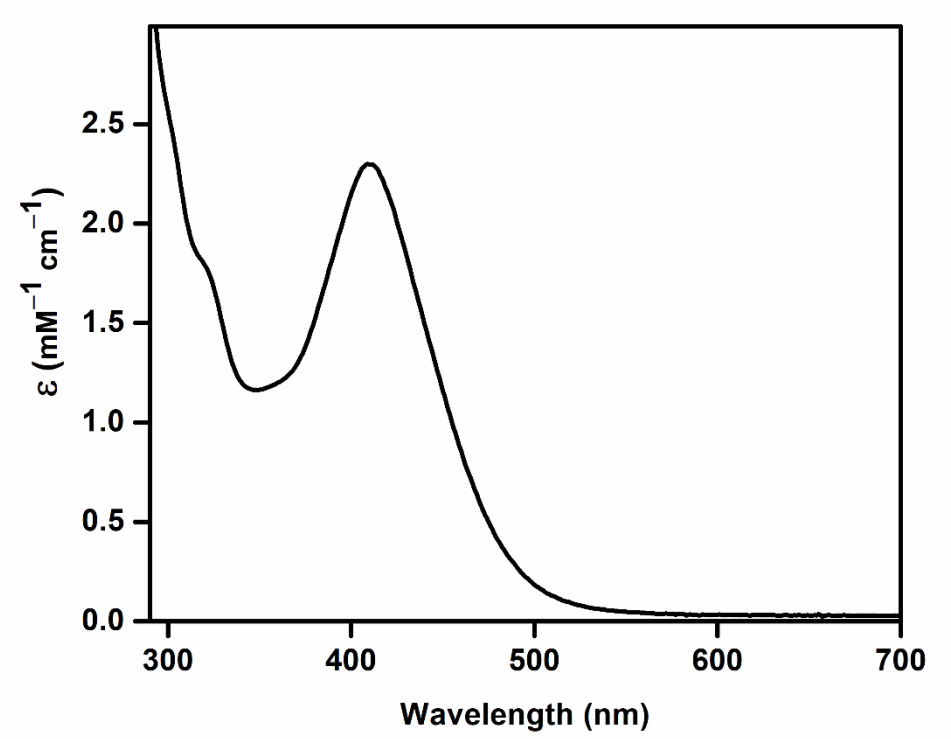


Fig. S6 Selected portion of IR spectra (in KBr) of (*a*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Mn^{II}Cl(L^1)]$-•3DMF•$3H_2O$ (**1**), (*b*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Mn^{II}Cl(L^2)]$•DMF (**2**), (*c*) $[Fe^{III}(Tp)(CN)_2$-$(\mu\text{–}CN)Cu^{II}(L^1)](ClO_4)$•$2CH_3OH$ (**3**) and (*d*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Cu^{II}(L^2)](ClO_4)$-•$2CH_3CN$ (**4**).

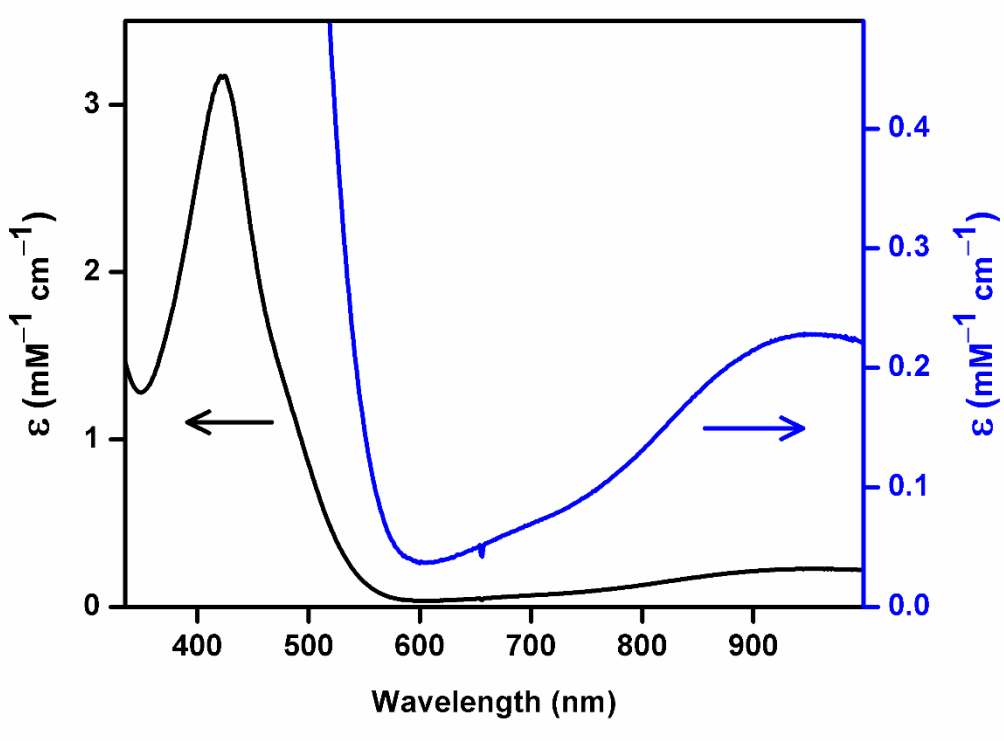
(*a*)


ε (mM^{-1} cm^{-1})
0
1
2
3
4
300
400
500
600
700
Wavelength (nm)

(*b*)


ε (mM^{-1} cm^{-1})
0.0
0.5
1.0
1.5
2.0
2.5
300
400
500
600
700
Wavelength (nm)

(*c*)



(*d*)

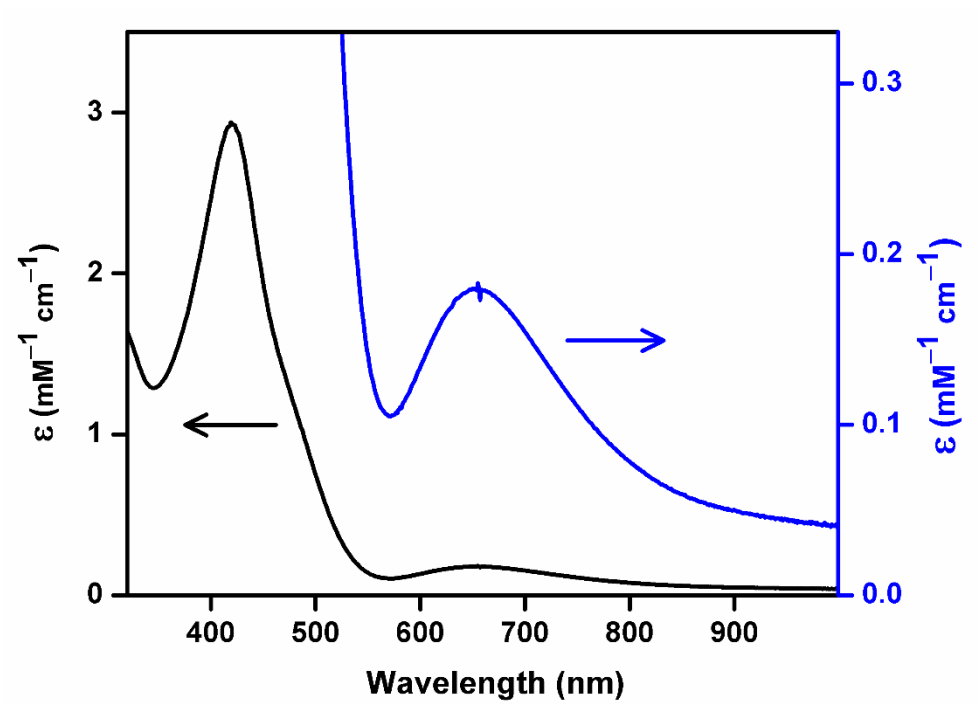


Fig. S7 Electronic spectra in CH_3CN of (*a*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Mn^{II}Cl(L^1)]\bullet 3DMF\bullet 3H_2O$ (**1**), (*b*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Mn^{II}Cl(L^2)]\bullet DMF$ (**2**), (*c*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Cu^{II}(L^1)](ClO_4)\bullet 2CH_3OH$ (**3**) and (*d*) $[Fe^{III}(Tp)(CN)_2(\mu\text{–}CN)Cu^{II}(L^2)](ClO_4)\bullet 2CH_3CN$ (**4**).