

Electronic supplementary information (ESI)

(18 pages)

Axial zero-field splitting in mononuclear Co(II) 2-N

substituted N-Confused porphyrin:

Co(2-NC₃H₅-21-Y-CH₂C₆H₄CH₃-NCTPP)Cl (Y = *o*, *m*, *p*)

and Co(2-NC₃H₅-21-CH₂C₆H₅-NCTPP)Cl

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Contents

1. Fig. S1. X-ray structure of 1	S2
2. Fig. S2. X-ray structure of 3	S3
3. Fig. S3. X-ray structure of 7	S4
4. Fig. S4. X-ray structure of 8	S5
5. Fig. S5. X-ray structure of 9	S6
6. Fig. S6. X-ray structure of 10	S7
7. Fig. S7. UV-Vis spectra of 1	S8
8. Fig. S8. UV-Vis spectra of 3	S8
9. Fig. S9. UV-Vis-NIR spectra of 7	S9
10. Fig. S10. UV-Vis-NIR spectra of 8	S10
11. Fig. S11. UV-Vis-NIR spectra of 9	S11
12. Fig. S12. UV-Vis-NIR spectra of 10	S12
13. Fig. S13. SQUID diagram of 7	S13
14. Fig. S14. SQUID diagram of 8	S13
15. Fig. S15. SQUID diagram of 9	S14
16. Fig. S16. SQUID diagram of 10	S14
17. Fig. S17. ¹ H NMR spectra for 3	S15
18. Table S1. X-ray, ¹ H (599.93 MHz) and ¹³ C (150.87 MHz) NMR chemical shifts of the N(4)-CH(19)(Ar) [or N(4) ⁺ =CH(19)(Ar)] fragment in CDCl ₃ at 293 K for 1 – 3, 7 – 10	S16
19. Derivation of D _{xx} , D _{yy} , D _{zz} and D	S17

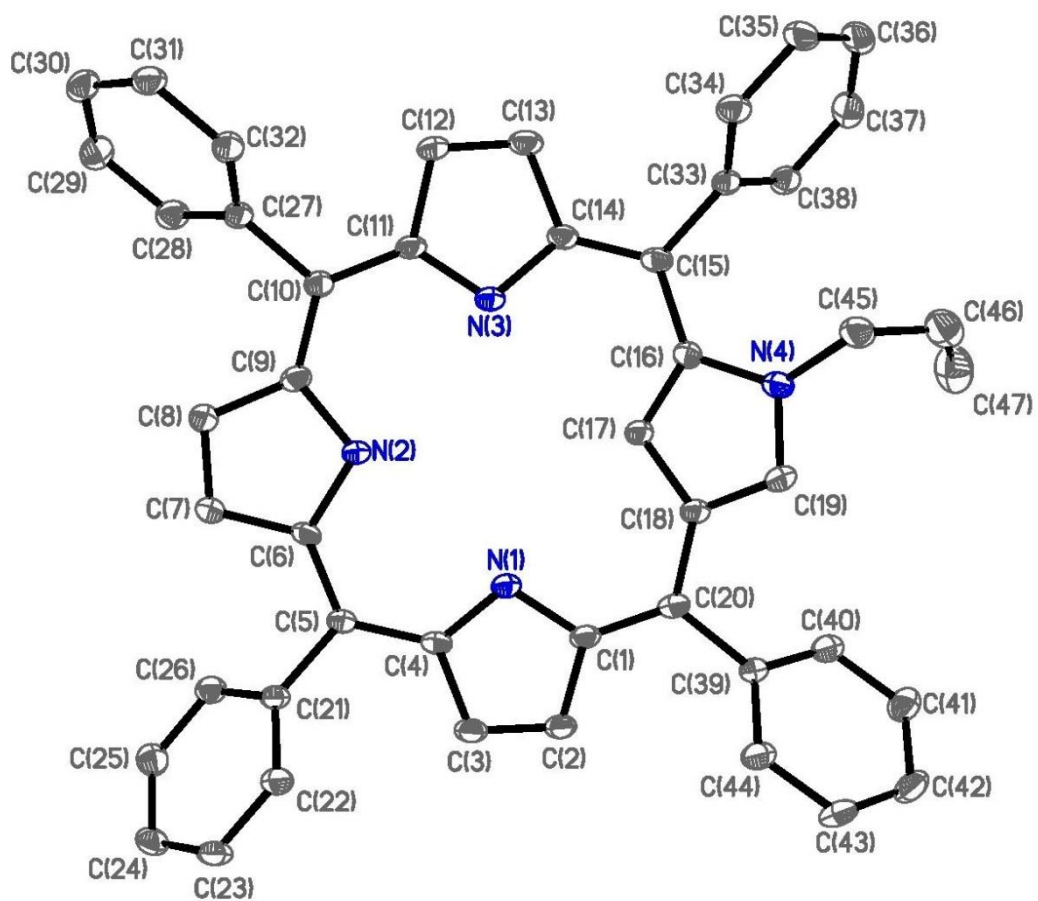


Fig. S1. X-ray structure of 1.

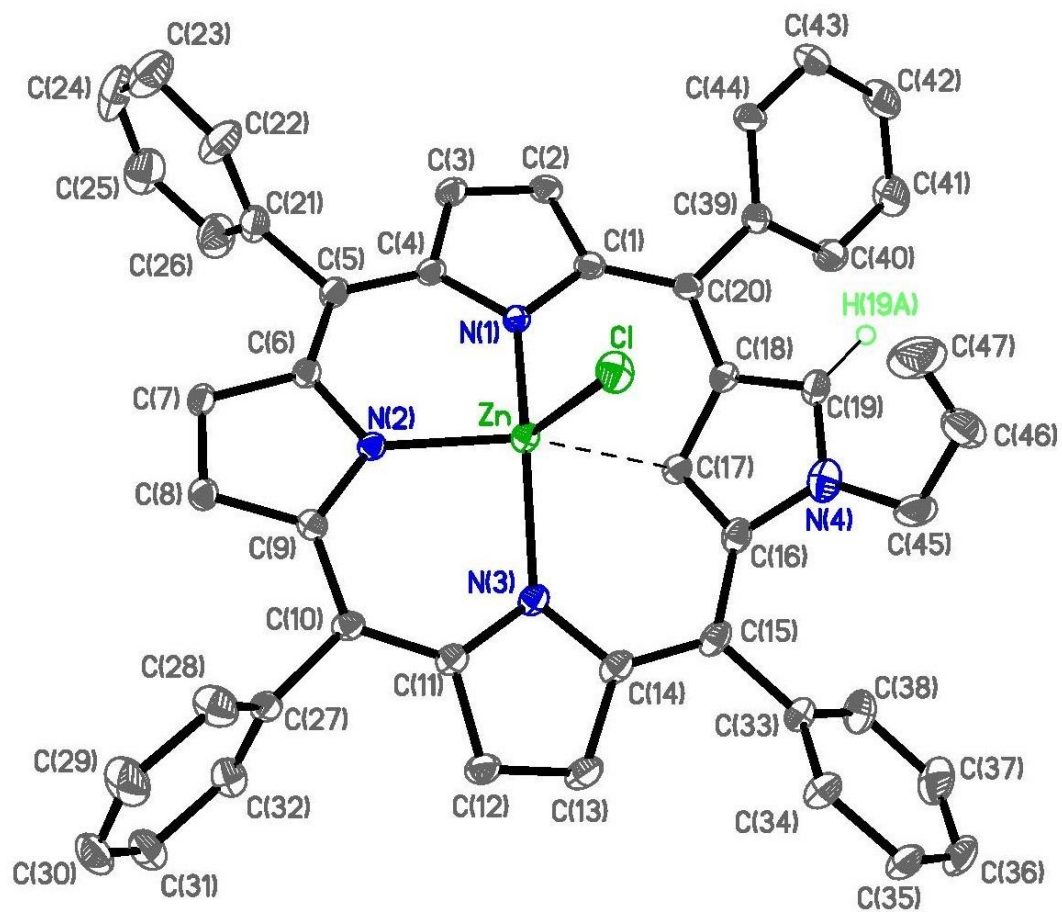


Fig. S2. X-ray structure of 3.

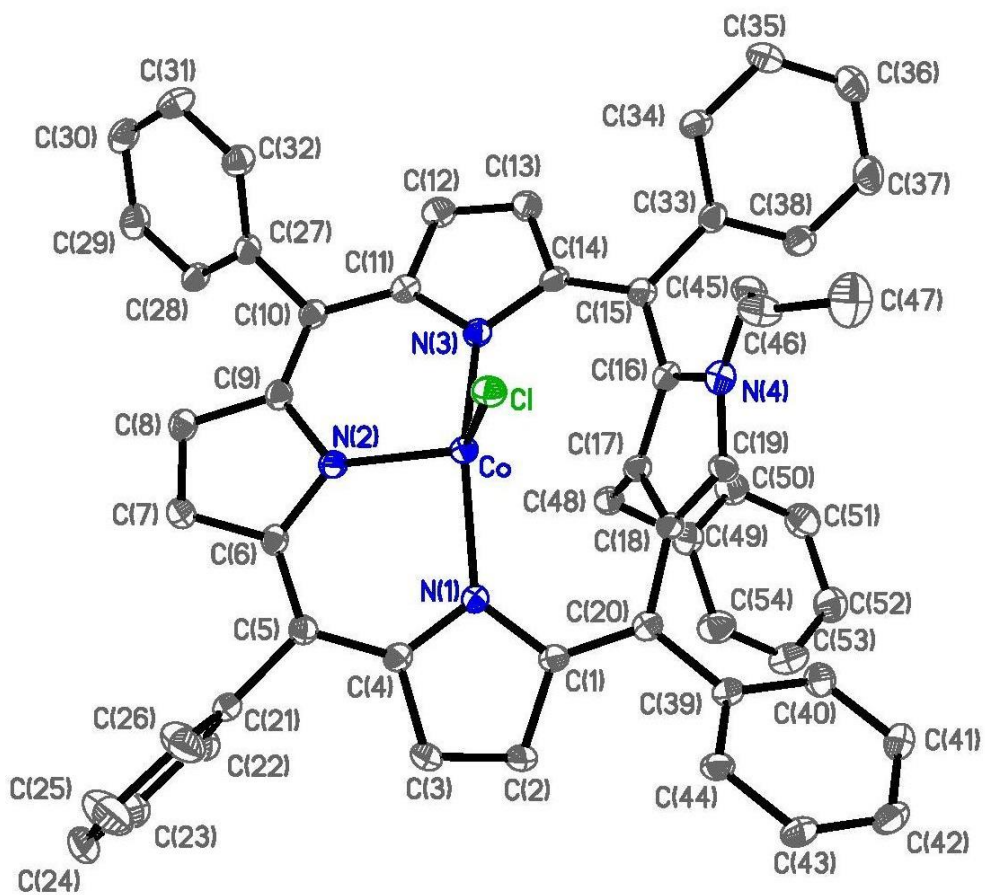


Fig. S3. X-ray structure of 7.

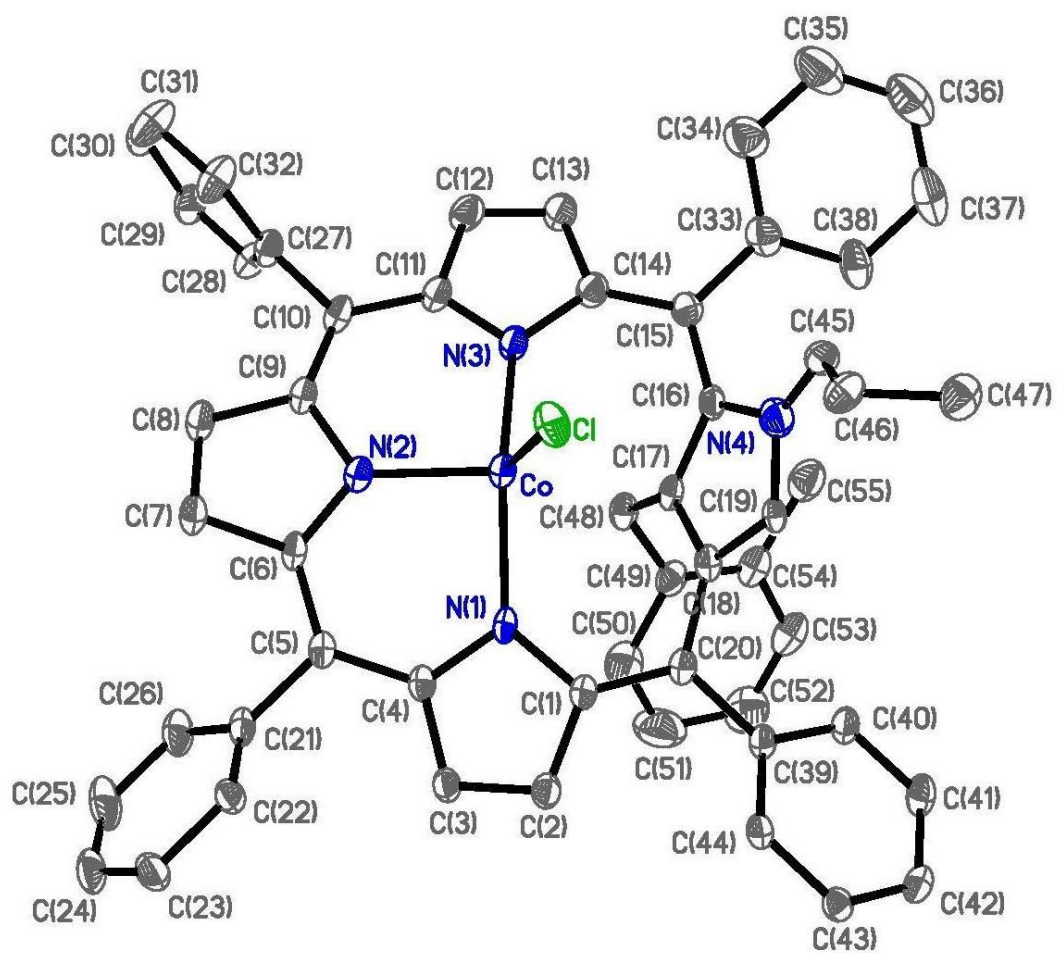


Fig. S4. X-ray structure of **8**.

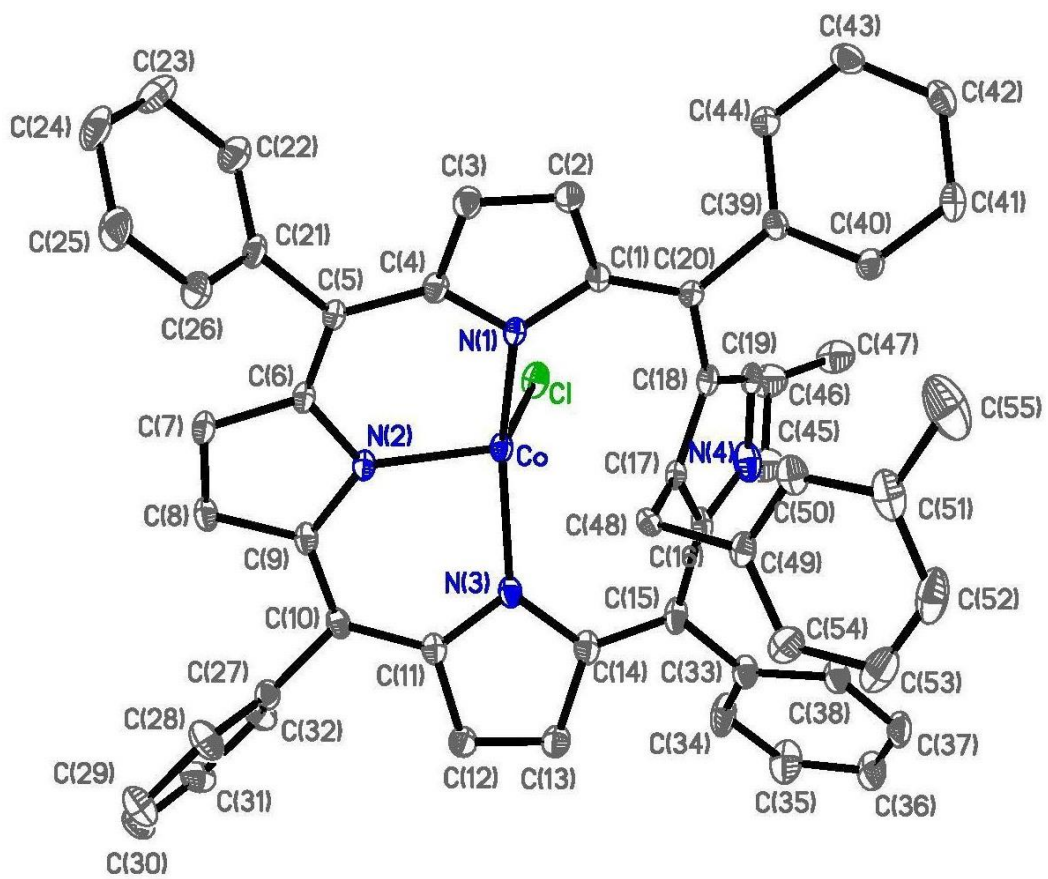


Fig. S5. X-ray structure of **9**.

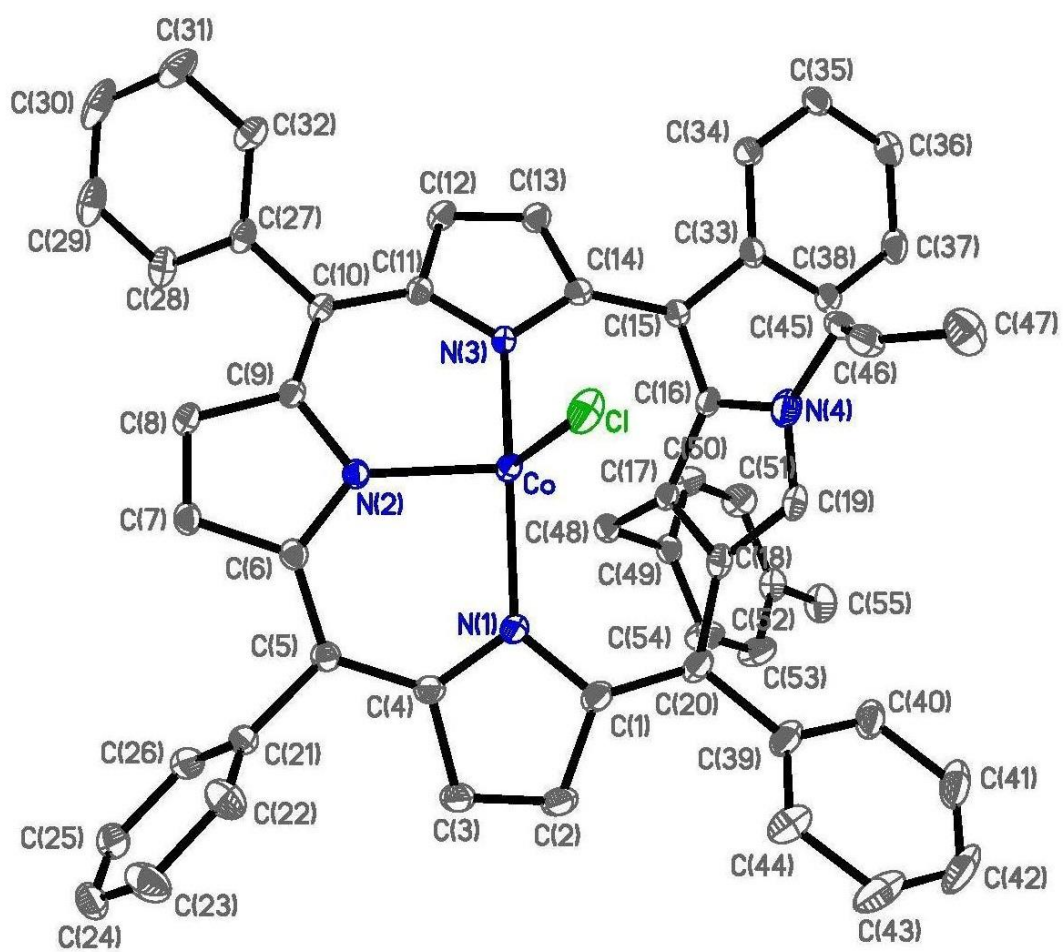


Fig. S6. X-ray structure of 10.

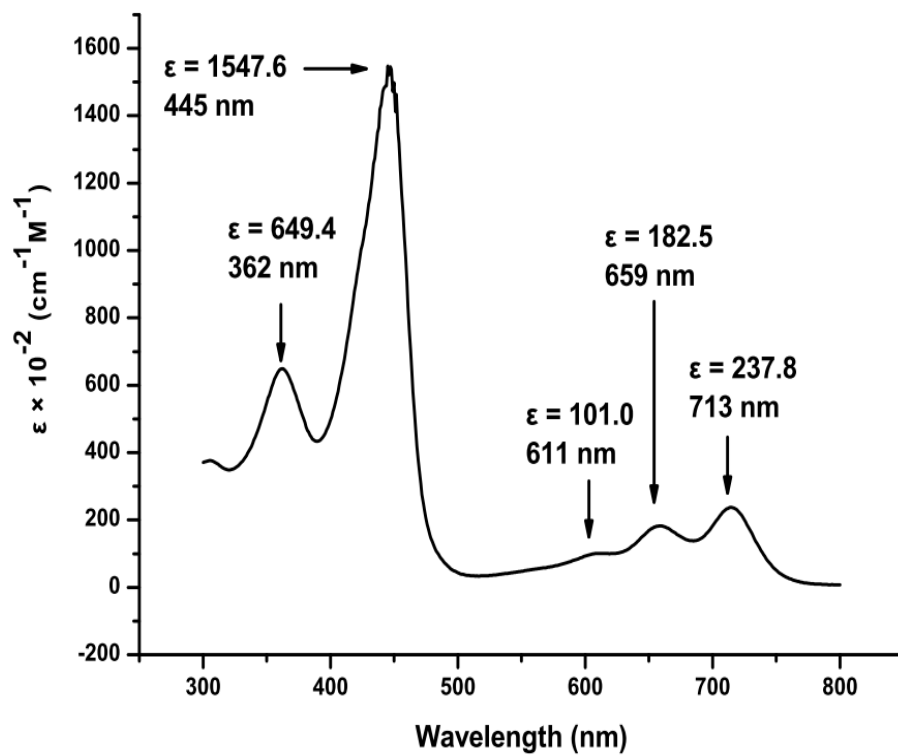


Fig. S7. UV-Vis spectra of **1** in CH₂Cl₂ at 300 K (300 – 800 nm).

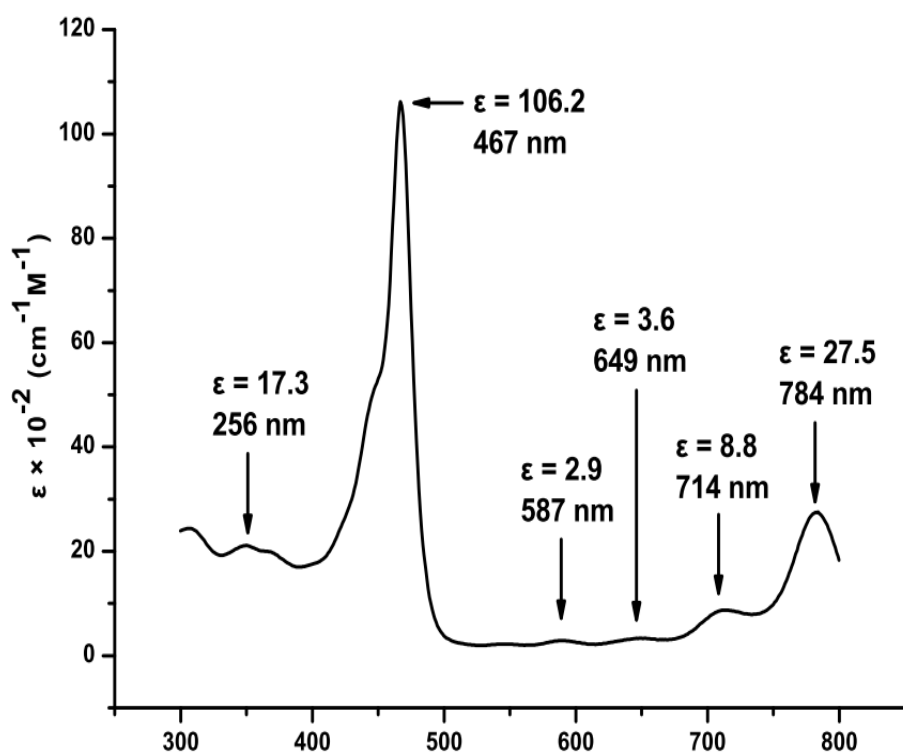


Fig. S8. UV-Vis spectra of **3** in CH₂Cl₂ at 300 K (300 – 800 nm).

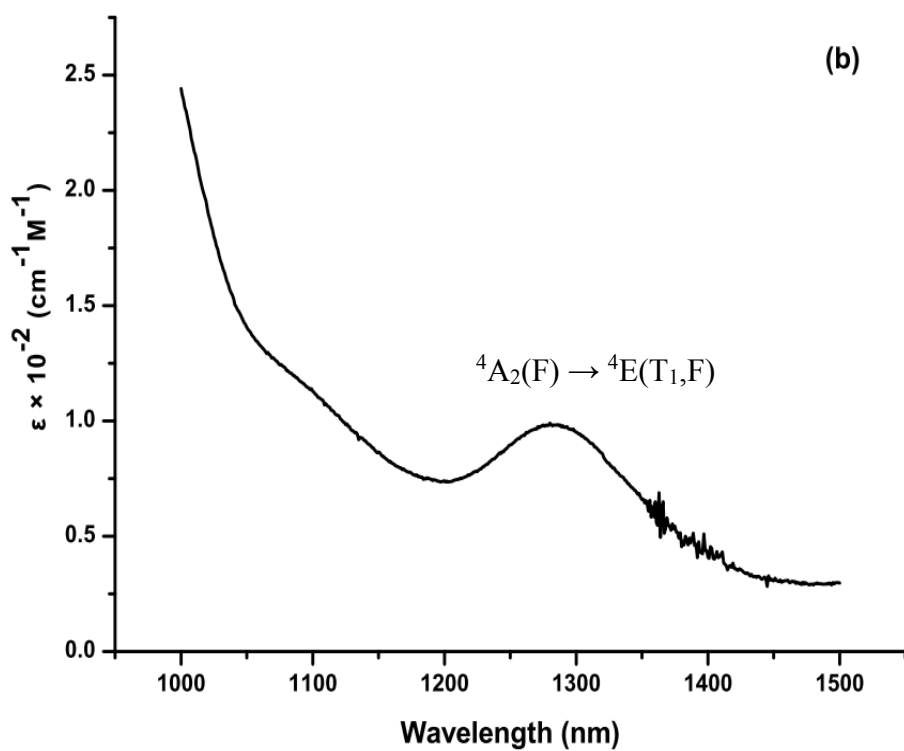
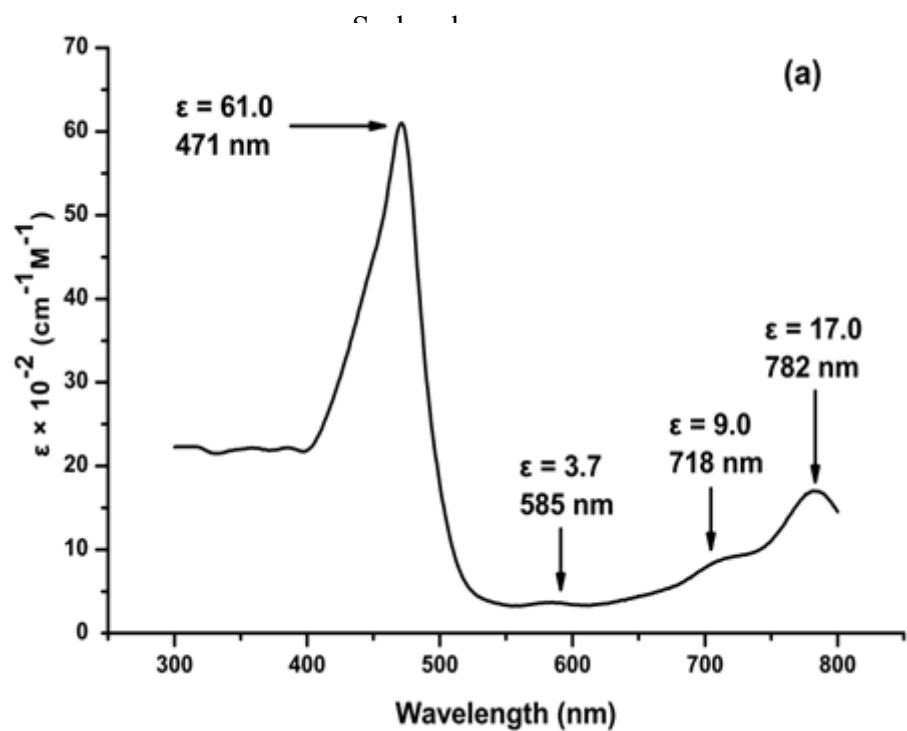


Fig. S9. UV-Vis-NIR spectra of **7** in CDCl_3 at 300 K : (a) 300 – 800 nm (b) 1000 – 1500 nm

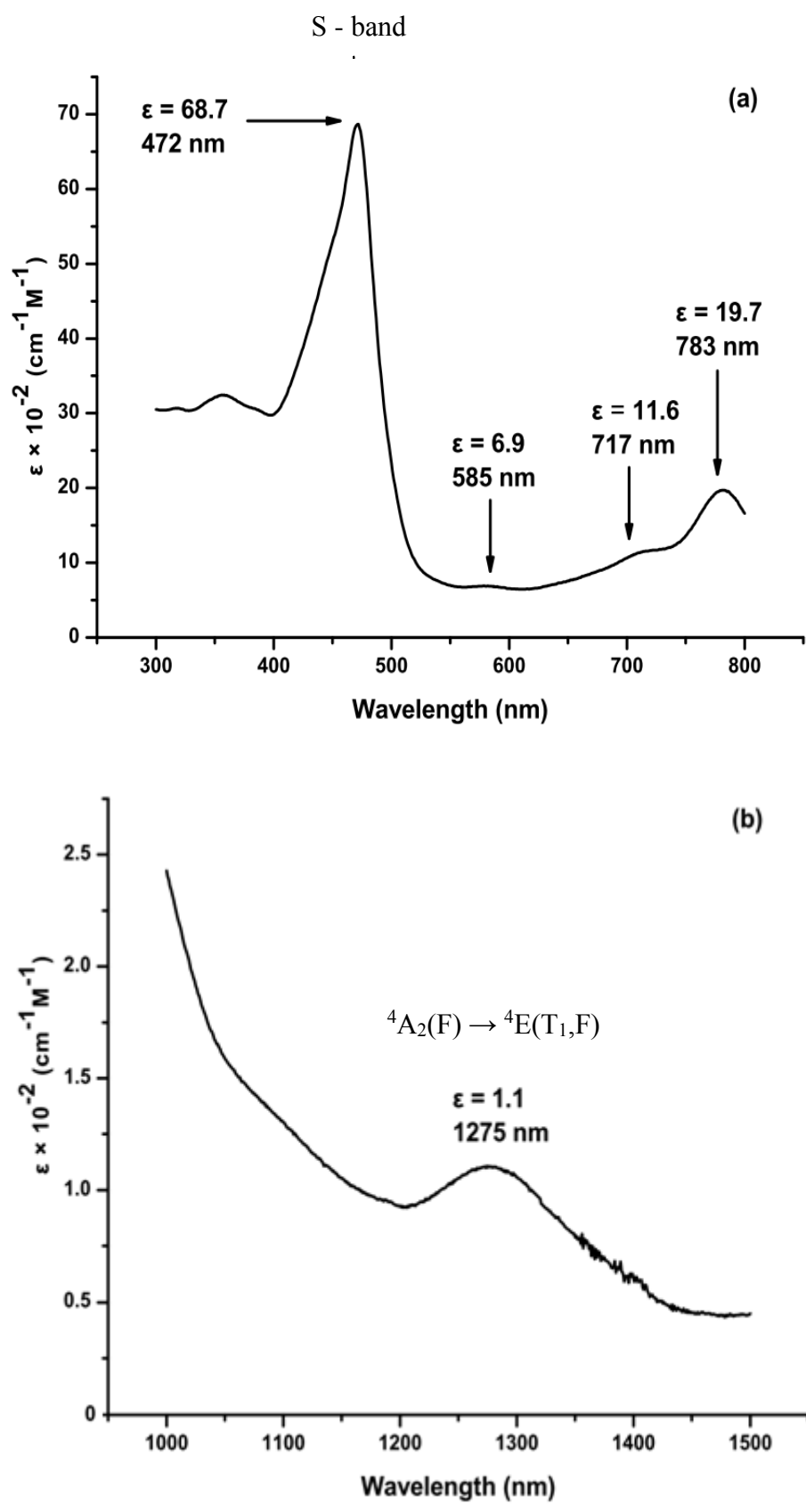


Fig. S10. UV-Vis-NIR spectra of **8** in CDCl_3 at 300 K : (a) 300 – 800 nm (b) 1000 – 1500 nm

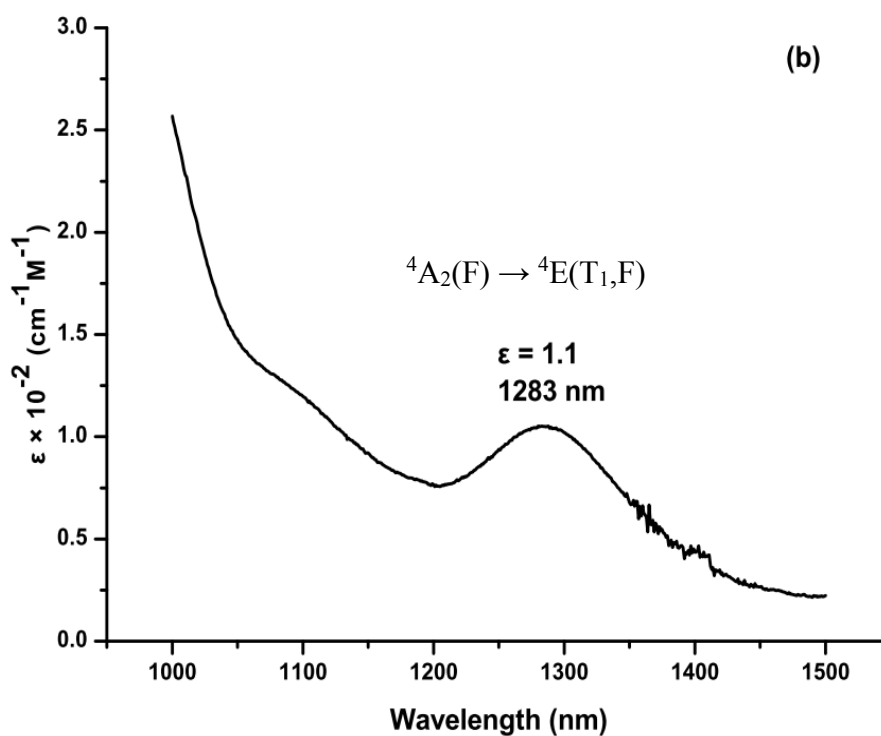
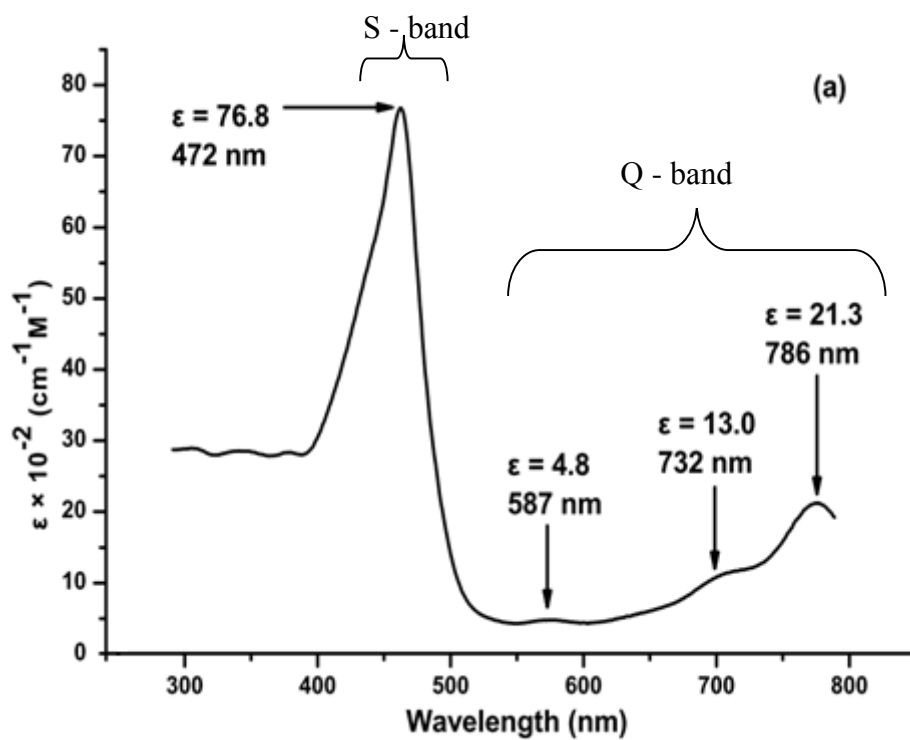


Fig. S11. UV-Vis-NIR spectra of **9** in CDCl_3 at 300 K : (a) 300 – 800 nm (b) 1000 – 1500 nm

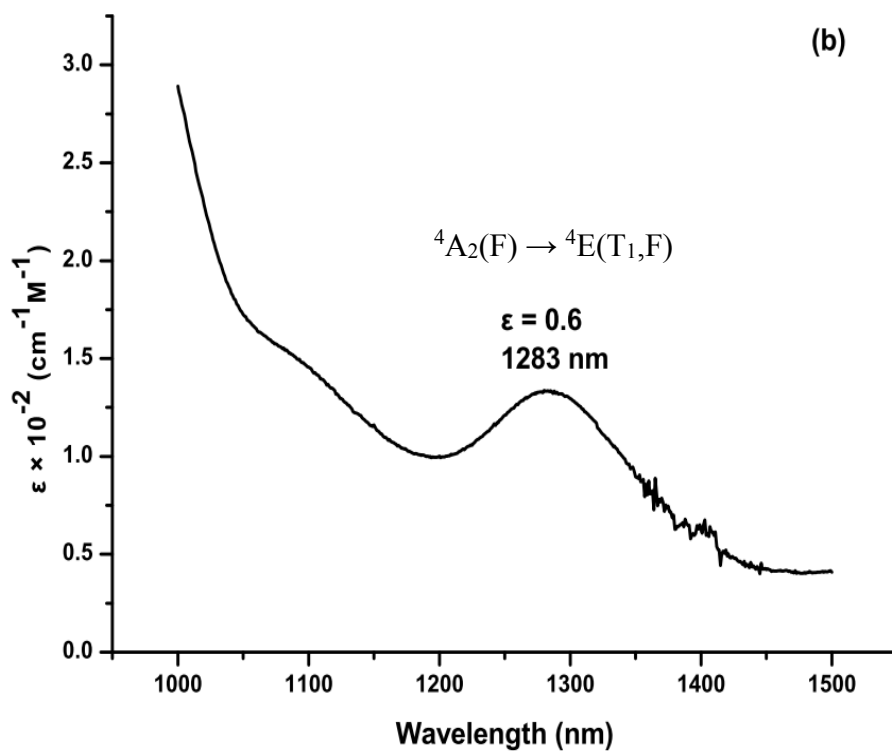
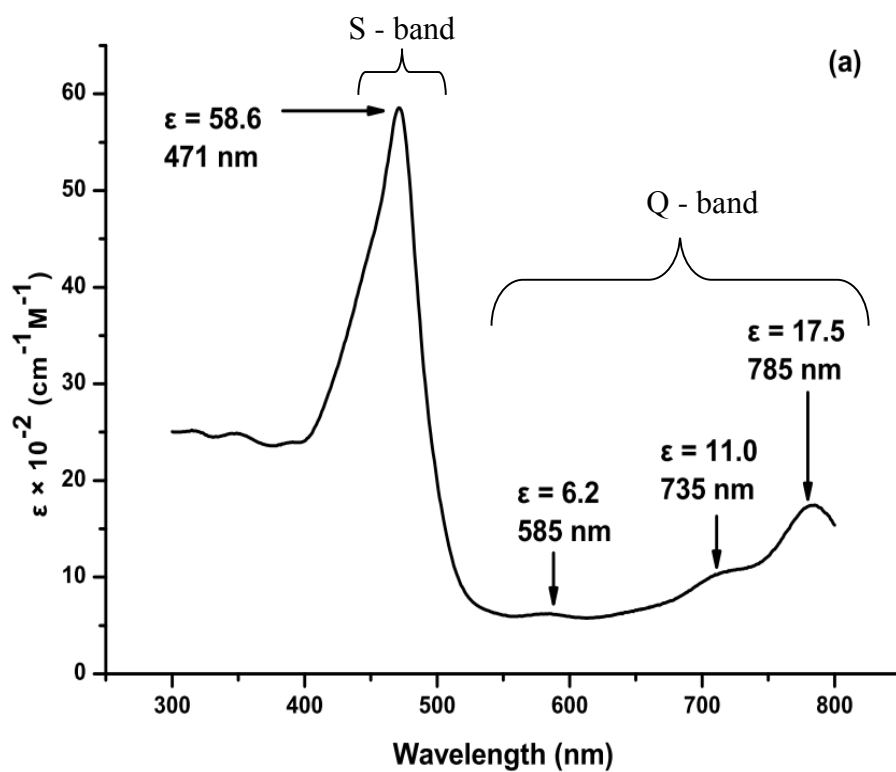


Fig. S12. UV-Vis-NIR spectra of **10** in CDCl_3 at 300 K : (a) 300 – 800 nm (b) 1000 – 1500 nm

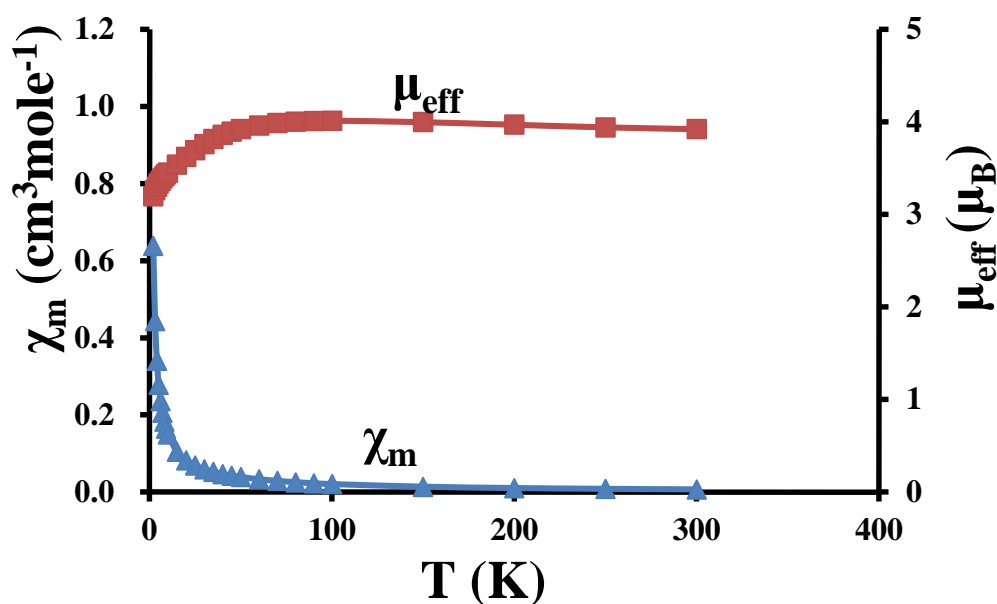


Fig. S13. Temperature variation of the molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) for the powder sample of **7** in the range of 2-300 K.

($g_{\text{av}} = 2.0$, $|D| = 35.6 \text{ cm}^{-1}$, $R = 0.602 \%$)

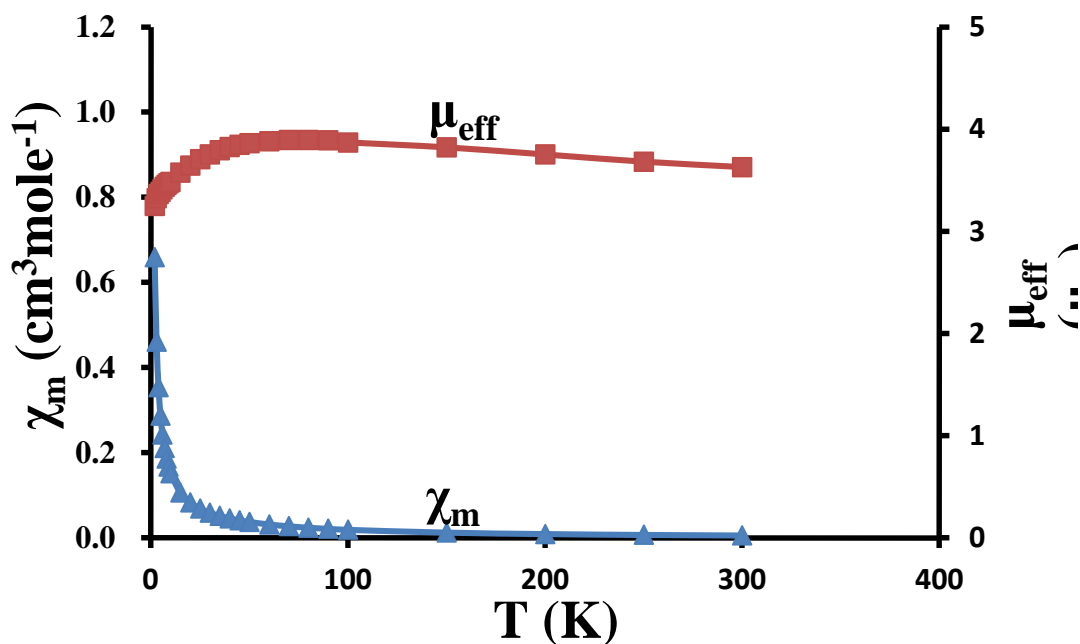


Fig. S14. Temperature variation of the molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) for the powder sample of **8** in the range of 2-300 K.

($g_{\text{av}} = 2.42$, $|D| = 30.7 \text{ cm}^{-1}$, $R = 0.719 \%$)

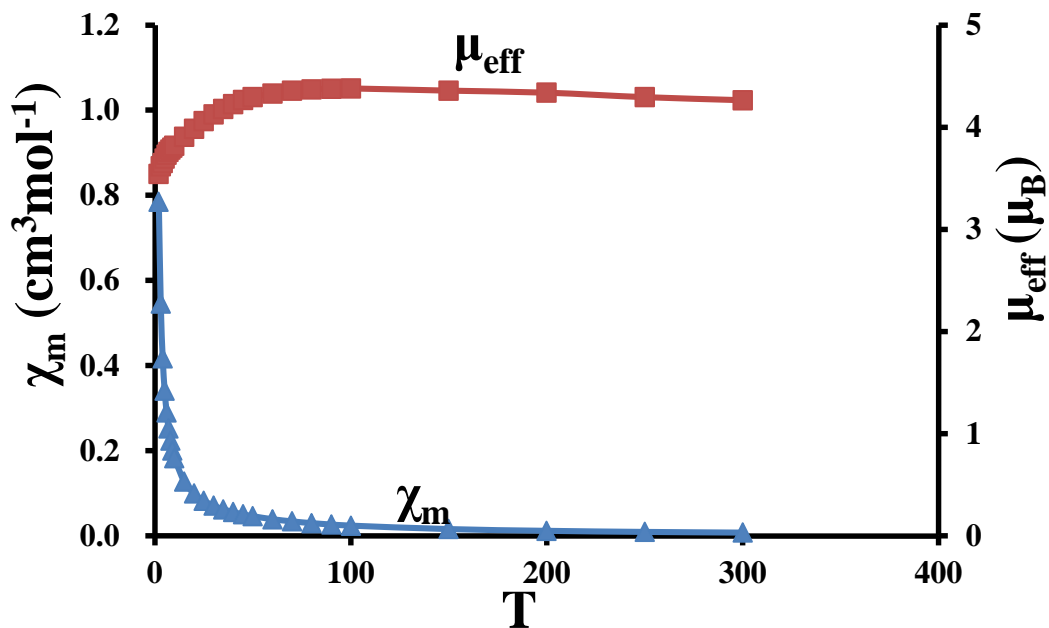


Fig. S15. Temperature variation of the molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) for the powder sample of **9** in the range of 2-300 K.

($g_{\text{av}} = 2.10$, $|D| = 42.0 \text{ cm}^{-1}$, $R = 0.588 \%$)

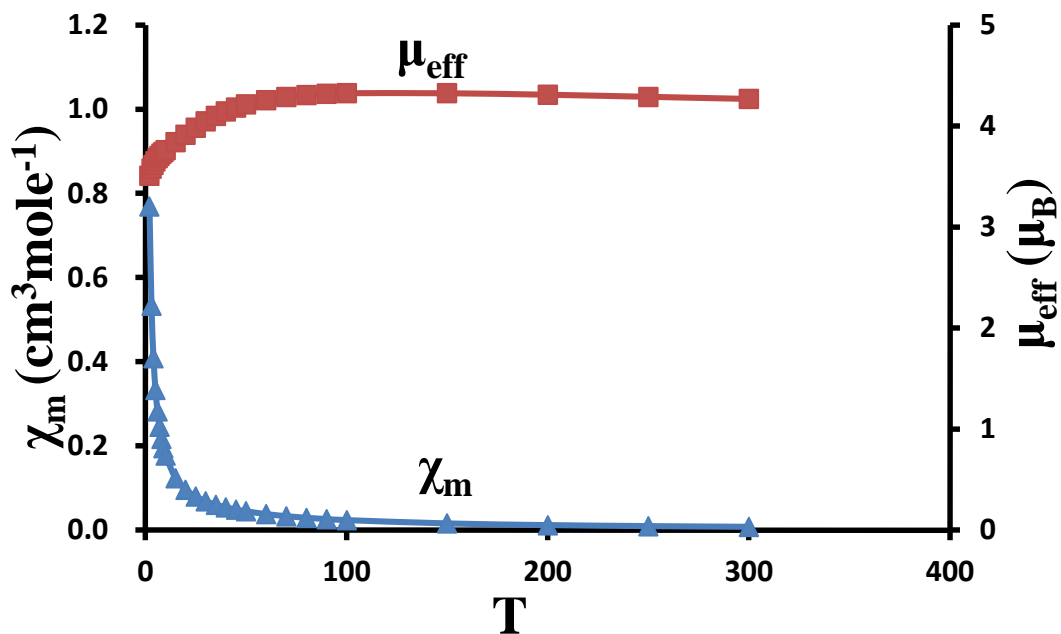
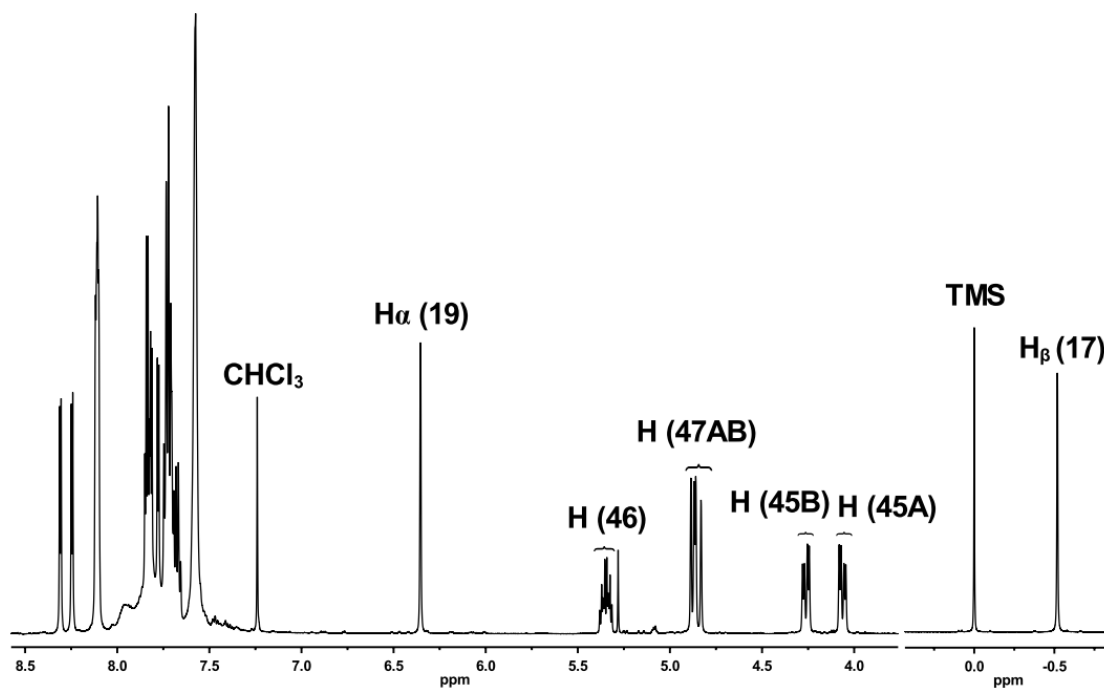


Fig. S16. Temperature variation of the molar magnetic susceptibility (χ_m) and effective magnetic moment (μ_{eff}) for the powder sample of **10** in the range of 2-300 K.

($g_{\text{av}} = 2.09$, $|D| = 46.9 \text{ cm}^{-1}$, $R = 0.574 \%$)

(a)



(b)

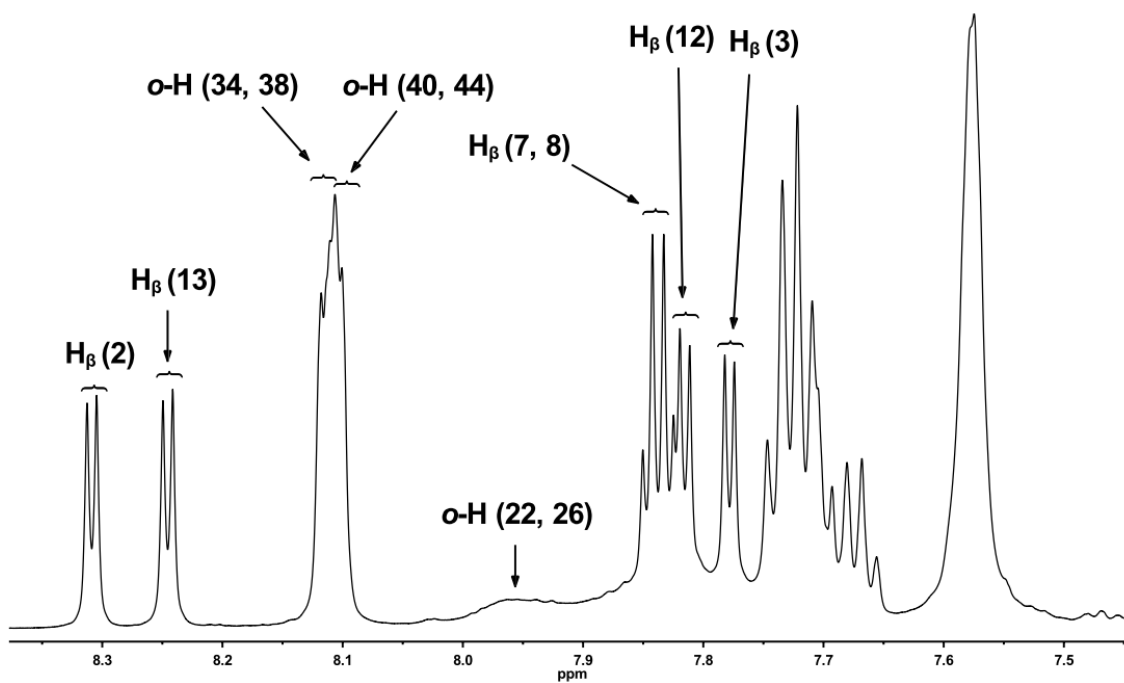


Fig. S17. ^1H NMR spectra for **3** at 599.93 MHz in CDCl_3 at 293 K: (a) entire spectrum; (b) expansion of the region of 7.4–8.4 ppm of (a). Chemical shifts are in ppm from TMS at 0 ppm.

Table S1. X-ray, ^1H (599.93 MHz) and ^{13}C (150.87 MHz) NMR chemical shifts of the N(4)-CH(19)(Ar) [or N(4)⁺=CH(19)(Ar)] fragment in CDCl₃ at 293 K for **1** – **3**, **7** – **10**.

Compound	δ (^1H) (ppm)		δ (^{13}C) (ppm) ^c		X-ray dihedral angle φ ($^\circ$) ^d				X-ray Coordination Geometry ^e	Major canonical form ^f
	[CH(17)] ^a	[CH(19)]	[CH(17)]	[CH(19)]	N(1)	N(2)	N(3)	C(17)		
1 (2-NC ₃ H ₅ NCTPPH)	1.41(s)	7.25(s)	105.8(s)	134.9(s)	6.9	10.3	11.0	24.4	-	-
2 (Mn ³⁺)	-	-	-	-	7.7	8.2	8.3	8.8	DSBP	Dipolar
3 (Zn ²⁺)	-0.53(d)	6.34(d)	74.6(s)	119.8(s)	15.2	10.1	12.4	48.4	DT	Covalent
	(1.8) ^b	(1.8)								
7 (Co ²⁺ -benzyl)	-	-	-	-	10.9	2.0	11.6	56.4	DT	Covalent
8 (Co ²⁺ - <i>o</i> -xylyl)	-	-	-	-	19.2	5.5	17.1	60.5	DT	Covalent
9 (Co ²⁺ - <i>m</i> -xylyl)	-	-	-	-	16.5	5.3	16.1	56.2	DT	Covalent
10 (Co ²⁺ - <i>p</i> -xylyl)	-	-	-	-	17.6	1.8	18.9	58.3	DT	Covalent

^a s = singlet, d = doublet. ^b 4J (^1H - ^1H) coupling constant in Hz. ^c Broad band ^{13}C . ^d The dihedral angles between the plane defined by N(1) N(2) N(3) and the pyrrole planes [N(1), N(2), N(3), C(17)], respectively. ^e DSBP = distorted square-based pyramid, DT = distorted tetrahedron. ^f Resonance contributors for dipolar form and covalent form.

§ Derivation of D_{xx} , D_{yy} , D_{zz} and D :

The ZFS parameters (D and E) are calculated from the elements of the diagonalized \mathbf{D} tensor (see eq S1) :

$$D = D_{zz} - \frac{1}{2} (D_{xx} + D_{yy}) \quad ; \quad E = \frac{1}{2} (D_{xx} - D_{yy}) \dots \dots \dots (S1)$$

In a highly qualitative nature and we restrict our attention to the metal d-based molecular orbitals (Fig. 4), the general expressions for D_{kl} of distorted tetrahedral Co^{2+} complexes (7-10, $S = \frac{3}{2}$) with local C_{2v} symmetry from the contributions of the excited states with the same spin as the ground states reduce to equations (S2) – (S4) for D_{xx} , D_{yy} and D_{zz} :

$$1. D_{xx} = -\frac{\zeta_{eff}^2}{9} \left\{ \frac{\langle d_{yz} | \hat{l}_x | d_{xy} \rangle \langle d_{xy} | \hat{l}_x | d_{yz} \rangle}{\varepsilon_{xy} - \varepsilon_{yz}} + \frac{\langle d_{xz} | \hat{l}_x | d_{x^2-y^2} \rangle \langle d_{x^2-y^2} | \hat{l}_x | d_{xz} \rangle}{\varepsilon_{x^2-y^2} - \varepsilon_{xz}} + \frac{\langle d_{xz} | \hat{l}_x | d_{z^2} \rangle \langle d_{z^2} | \hat{l}_x | d_{xz} \rangle}{\varepsilon_{z^2} - \varepsilon_{xz}} \right\} = -\frac{\zeta_{eff}^2}{9} \left(\frac{1}{\varepsilon_{xy} - \varepsilon_{yz}} + \frac{1}{\varepsilon_{x^2-y^2} - \varepsilon_{xz}} + \frac{3}{\varepsilon_{z^2} - \varepsilon_{xz}} \right) \dots \dots \dots (S2)$$

$$2. D_{yy} = -\frac{\zeta_{eff}^2}{9} \left\{ \frac{\langle d_{xz} | \hat{l}_y | d_{xy} \rangle \langle d_{xy} | \hat{l}_y | d_{xz} \rangle}{\varepsilon_{xy} - \varepsilon_{xz}} + \frac{\langle d_{yz} | \hat{l}_y | d_{z^2} \rangle \langle d_{z^2} | \hat{l}_y | d_{yz} \rangle}{\varepsilon_{z^2} - \varepsilon_{yz}} + \frac{\langle d_{yz} | \hat{l}_y | d_{x^2-y^2} \rangle \langle d_{x^2-y^2} | \hat{l}_y | d_{yz} \rangle}{\varepsilon_{x^2-y^2} - \varepsilon_{yz}} \right\} = -\frac{\zeta_{eff}^2}{9} \left(\frac{1}{\varepsilon_{xy} - \varepsilon_{xz}} + \frac{1}{\varepsilon_{x^2-y^2} - \varepsilon_{yz}} + \frac{3}{\varepsilon_{z^2} - \varepsilon_{yz}} \right) \dots \dots \dots (S3)$$

$$3. D_{zz} = 0 \dots \dots \dots (S4)$$

$$\text{Hence, } D = D_{zz} - \frac{1}{2} (D_{xx} + D_{yy}) = \frac{\zeta_{eff}^2}{9} \left(\frac{1}{\Delta_1} + \frac{1}{\Delta_3} + \frac{3}{\Delta_2} \right) \dots \dots \dots (S5)$$

where

$$E = 0 \dots \dots \dots (S6)$$

$$\Delta_1 = \varepsilon(d_{xy}) - \varepsilon(d_{xz}) \doteq \varepsilon(d_{xy}) - \varepsilon(d_{yz})$$

$$\Delta_2 = \varepsilon(d_z^2) - \varepsilon(d_{xz}) \doteq \varepsilon(d_z^2) - \varepsilon(d_{yz})$$

$$\Delta_3 = \varepsilon(d_{x^2-y^2}) - \varepsilon(d_{xz}) \doteq \varepsilon(d_{x^2-y^2}) - \varepsilon(d_{yz})$$

Ref.

1' J. Cirera, E. Ruiz, S. Alvarez, F. Neese and J. Kortus, *Chem. Eur. J.* 2009, **15**, 4078-4087.

2' S. Gomez-Coca, E. Cremades, N. Aliaga-Alcalde and E. Ruiz, *J. Am. Chem. Soc.* 2013, **135**, 7010-7018.

3' S. Gomez-Coca, D. Aravena, R. Morales and E. Ruiz, *Coord. Chem. Rev.* 2015, **289-290**, 379-392.

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