Supporting Information

A cobalt(II) spin-crossover compound with partially charged TCNQ radicals and an anomalous conducting behavior

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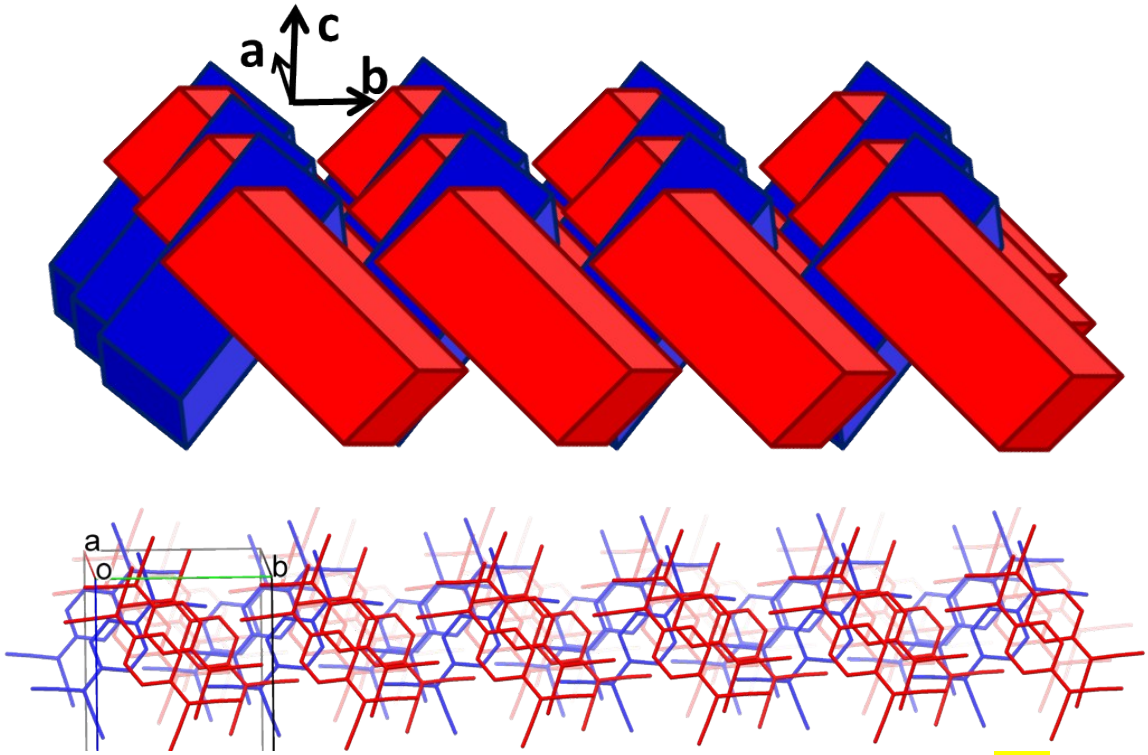


Figure S1. Stacking patterns of the TCNQ triads in the crystal structure. The blue and red triads are related by one set of screw axes along the a axis and two sets of glide planes parallel to the ab and ac planes, respectively. The $[Co(terpy)_2]^{2+}$ units and acetonitrile molecules are omitted for clarity.

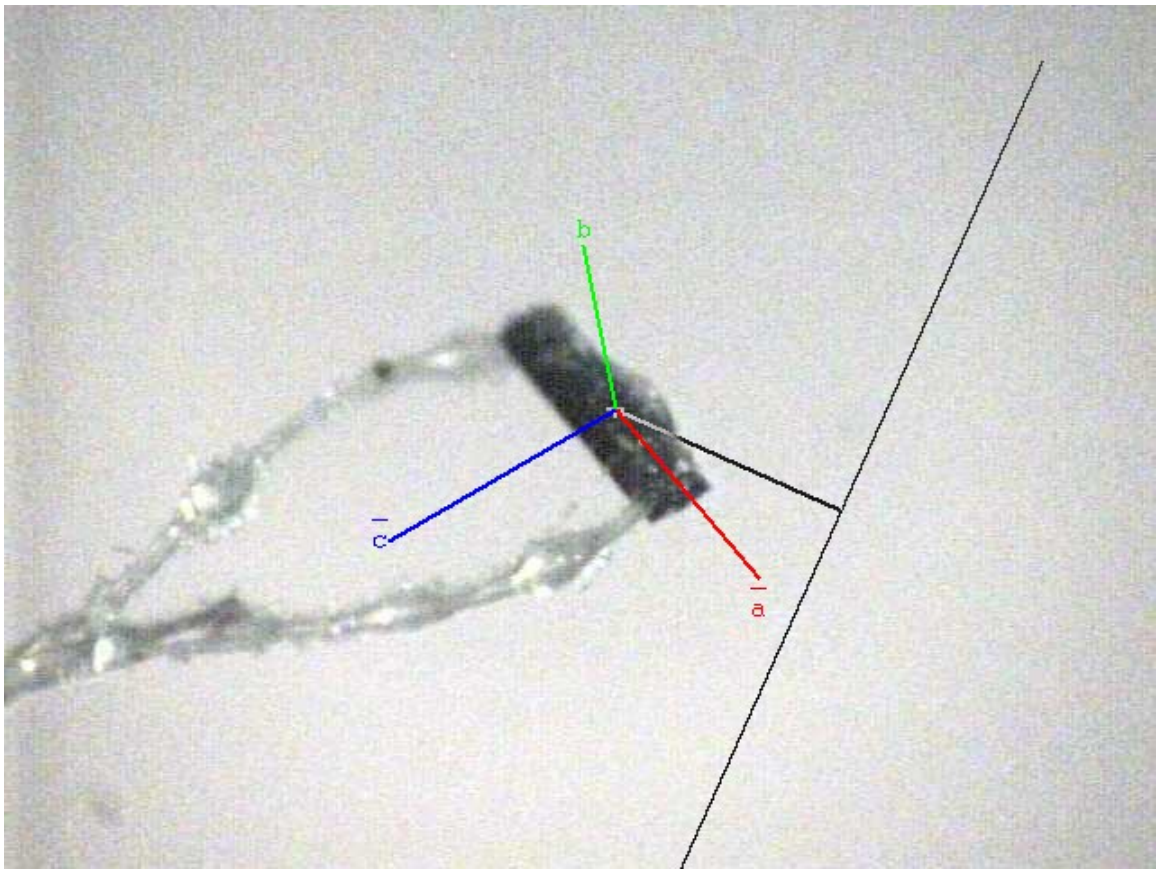


Figure S2. Face index of a single crystal of $[Co(terpy)_2](TCNQ)_3 \bullet CH_3CN$. The long direction of the thin needle crystals is along the stacking direction (a axis) of the TCNQ triads.

Table S1. Co-N bond distances (in Å) at different temperatures.

Temperature	100 K	130 K	150 K	180 K	190 K	300 K
Co1-N1	1.867(3)	1.862(4)	1.874(5)	1.862(6)	1.868(4)	1.878(5)
Co1-N3	1.980(4)	1.975(4)	1.981(5)	1.983(6)	1.989(4)	2.001(5)
Co1-N2	1.978(4)	1.969(4)	1.982(5)	1.982(6)	1.991(4)	2.000(5)
Co1-N4	1.920(3)	1.923(4)	1.921(5)	1.910(6)	1.921(4)	1.909(5)
Co1-N5	2.153(4)	2.149(5)	2.151(5)	2.135(7)	2.149(4)	2.131(5)
Co1-N6	2.162(3)	2.154(4)	2.163(5)	2.145(6)	2.142(4)	2.141(4)

Table S2. Selected bond angles (in degree) in the Co(II) coordination sphere at different temperatures.

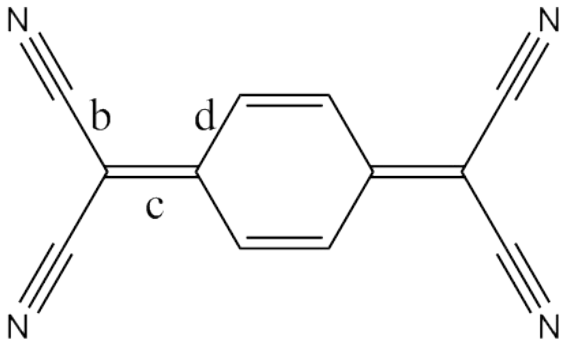
Temperature	100 K	130 K	150 K	180 K	190 K	300 K
N1-Co1-N2	81.53(15)	81.35(19)	81.61(19)	81.0(3)	81.79(17)	80.92(19)
N1-Co1-N3	81.99(15)	81.79(18)	81.7(2)	81.7(3)	81.24(17)	81.42(19)
N2-Co1-N3	163.36(13)	163.02(17)	163.24(19)	162.5(2)	162.94(16)	162.26(18)
N4-Co1-N5	79.19(15)	79.49(18)	79.5(2)	79.2(3)	78.91(19)	79.1(2)
N4-Co1-N6	78.84(15)	78.8(2)	78.8(2)	79.3(3)	79.25(18)	78.7(2)
N5-Co1-N6	158.01(14)	158.22(18)	158.3(2)	158.5(3)	158.15(18)	157.9(2)

Table S3. Pertinent crystallographic data for $[Co(terpy)_2](TCNQ)_3 \bullet CH_3CN$ at different temperatures.

Temperature	100 K	130 K	150 K	180 K	190 K	300 K
Empirical formula	$C_{68}H_{37}CoN_{19}$	$C_{68}H_{37}N_{19}Co$	$C_{68}H_{37}N_{19}Co$	$C_{68}H_{37}CoN_{19}$	$C_{68}H_{37}CoN_{19}$	$C_{68}CoN_{19}H_{37}$
Formula weight	1179.09	1179.09	1179.09	1179.09	1179.09	1179.09
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
Space group	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$	$Pna2_1$
a/Å	18.9411(10)	18.967(3)	19.087(7)	18.969(6)	19.074(6)	19.2853(15)
b/Å	8.6917(4)	8.6864(12)	8.742(3)	8.681(3)	8.705(3)	8.7270(7)
c/Å	33.5158(17)	33.532(5)	33.634(12)	33.397(10)	33.611(10)	33.589(3)
α/°	90	90	90	90	90	90
β/°	90	90	90	90	90	90
γ/°	90	90	90	90	90	90
Volume/Å^3	5517.7(5)	5524.8(13)	5613(3)	5499(3)	5581(3)	5653.1(8)
Z	4	4	4	4	4	4
ρ_{calc}g/cm^3	1.419	1.418	1.395	1.424	1.403	1.385
μ/mm^{-1}	0.376	0.376	0.370	0.377	0.372	0.367
F(000)	2420.0	2420.0	2420.0	2420.0	2420.0	2420.0
Crystal size/mm^3	0.149 × 0.038 × 0.02	0.25 × 0.15 × 0.008	0.31 × 0.06 × 0.008	0.25 × 0.15 × 0.008	0.3 × 0.12 × 0.008	0.237 × 0.035 × 0.015
Radiation	Synchrotron (λ = 0.41328 Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073 Å)	MoKα (λ = 0.71073)	MoKα (λ = 0.71073)	Synchrotron (λ = 0.51800 Å)
2Θ range for data collection/°	4.3 to 58.26	4.294 to 52.044	4.268 to 49.708	2.438 to 53.008	4.27 to 52.042	2.424 to 52.798
Index ranges	-25 ≤ h ≤ 25, -11 ≤ k ≤ 7, -45 ≤ l ≤ 45	-23 ≤ h ≤ 23, -10 ≤ k ≤ 10, -41 ≤ l ≤ 41	-22 ≤ h ≤ 22, -10 ≤ k ≤ 10, -39 ≤ l ≤ 39	-23 ≤ h ≤ 23, -10 ≤ k ≤ 10, -41 ≤ l ≤ 41	-23 ≤ h ≤ 23, -10 ≤ k ≤ 10, -41 ≤ l ≤ 41	-24 ≤ h ≤ 24, -10 ≤ k ≤ 6, -41 ≤ l ≤ 42
Reflections collected	77611	54108	50404	56984	55562	73630
Independent reflections	14467 [R_{int} = 0.1046, R_{sigma} = 0.1007]	10889 [R_{int} = 0.1147, R_{sigma} = 0.1092]	9665 [R_{int} = 0.1488, R_{sigma} = 0.1256]	11364 [R_{int} = 0.1606, R_{sigma} = 0.1625]	11002 [R_{int} = 0.0928, R_{sigma} = 0.0735]	11144 [R_{int} = 0.1130, R_{sigma} = 0.0977]
Data/restraints/parameters	14467/1/795	10889/1/795	9665/1/795	11364/1/795	11002/1/795	11144/1/795
Goodness-of-fit on F^2	1.010	0.872	0.864	0.845	1.018	1.044
Final R indexes [I>=2σ (I)]	R_1 = 0.0507, wR_2 = 0.1083	R_1 = 0.0451, wR_2 = 0.0783	R_1 = 0.0450, wR_2 = 0.0713	R_1 = 0.0508, wR_2 = 0.0868	R_1 = 0.0475, wR_2 = 0.0710	R_1 = 0.0482, wR_2 = 0.1173
Final R indexes [all data]	R_1 = 0.0796, wR_2 = 0.1243	R_1 = 0.0854, wR_2 = 0.0888	R_1 = 0.0838, wR_2 = 0.0817	R_1 = 0.1258, wR_2 = 0.1240	R_1 = 0.0799, wR_2 = 0.0829	R_1 = 0.0757, wR_2 = 0.1483
Largest diff. peak/hole / e Å^{-3}	0.49/-0.59	0.32/-0.59	0.22/-0.43	0.29/-0.30	0.23/-0.36	0.60/-0.53
Flack parameter	0.486(16)	0.437(18)	0.370(19)	0.38(2)	0.489(18)	0.46(2)

$R_1 = \Sigma||F_o| - |F_c||/ \Sigma|F_o|$. $wR_2 = [\Sigma w(|F_o| - |F_c|)^2/|\Sigma w(F_o)^2]^{1/2}$. $w = 0.75/(\sigma^2(F_o)+0.00010F_o^2)$

Table S4. The charges (ρ) of different TCNQ species in $[Co(terpy)_2](TCNQ)_3 \bullet CH_3CN$ at various temperatures estimated from the Kistenmacher's formula (b, c and d are average C-C bond distances as depicted below).[1]



Temperature	TCNQ	b	c	d	ρ	Triad
100 K	A	1.424	1.423	1.420	-1.01	-2.23
	B	1.424	1.413	1.425	-0.83	
	C	1.434	1.394	1.438	-0.39	
130 K	A	1.422	1.420	1.417	-1.01	-2.05
	B	1.430	1.411	1.425	-0.76	
	C	1.437	1.388	1.437	-0.29	
150 K	A	1.427	1.420	1.427	-0.90	-1.81
	B	1.432	1.417	1.434	-0.78	
	C	1.452	1.388	1.442	-0.14	
180 K	A	1.412	1.404	1.414	-0.87	-1.90
	B	1.420	1.407	1.416	-0.84	
	C	1.428	1.373	1.429	-0.19	
190 K	A	1.427	1.410	1.419	-0.80	-1.89
	B	1.428	1.409	1.424	-0.75	
	C	1.433	1.388	1.435	-0.33	
300 K	A	1.417	1.417	1.414	-1.03	-2.27
	B	1.416	1.412	1.419	-0.92	
	C	1.433	1.385	1.429	-0.33	

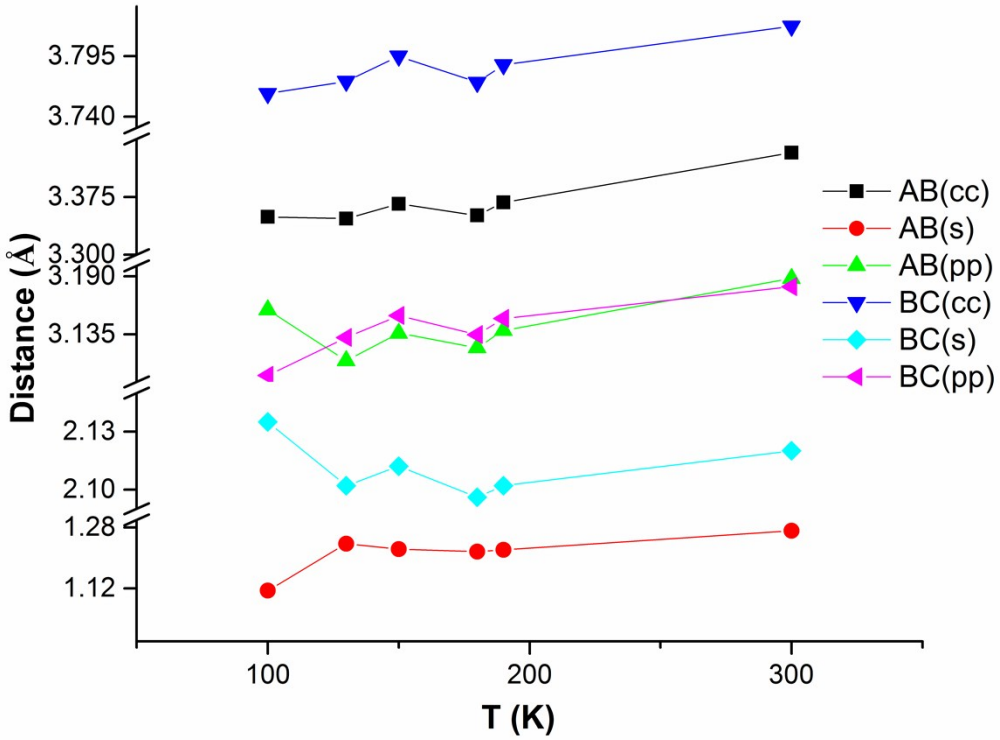


Figure S3. Temperature dependence of the π-π stacking distances of the TCNQ species with *cc* for centroid-centroid distances, *s* for shift distances and *pp* for plane-plane distances.

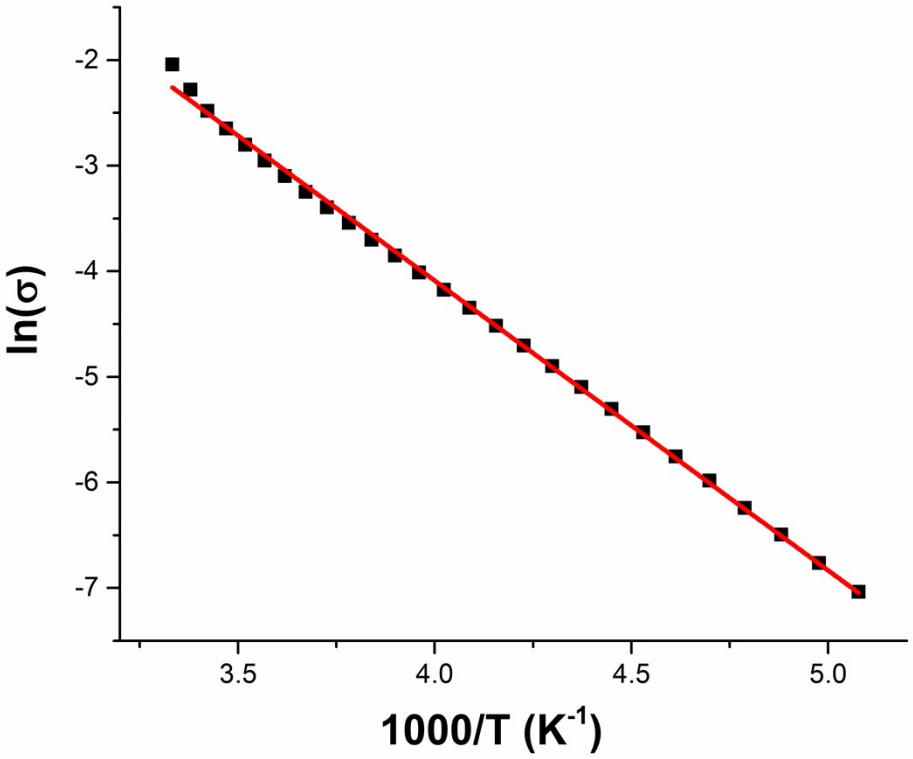


Figure S4. Arrhenius plot of the conductivity data from 195 to 300 K (the red line is a linear fit of the data).

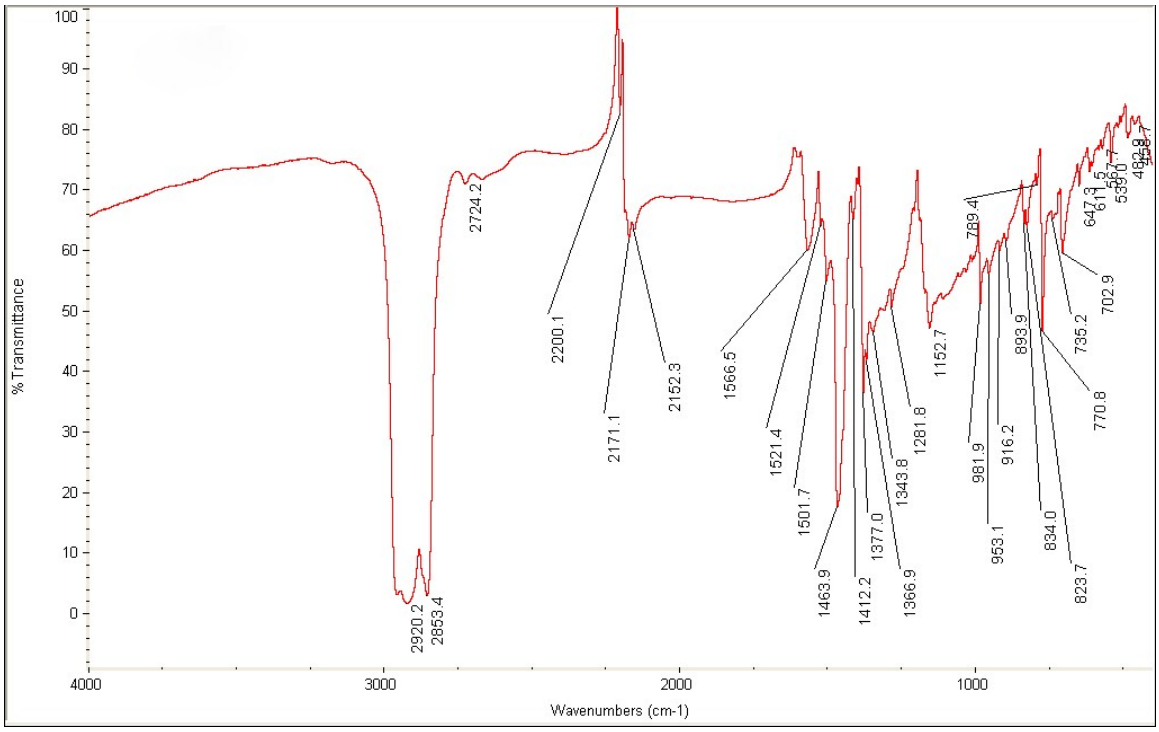


Figure S5. IR spectrum of $[Co(terpy)_2](TCNQ)_3 \bullet CH_3CN$ in Nujol mulls at room temperature. The bands at 2920, 2853, 2724, 1464, 1377 cm^{-1} are from the Nujol background.

References

1. Kistenmacher, T. J.; Emge, T. J.; Bloch, A. N.; Cowan, D. O. *Acta Crystallographica Section B* **1982**, *38*, 1193.