Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information for:

Benzoquinone-Bridged Co_2 complex with different magnetic anisotropy Induced by Solvent Molecules

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Experimental section.

Preparation of compounds and Physical Measurements All manipulations are performed under a nitrogen atmosphere with the use of standard Schlenk techniques unless otherwise stated. Acetonitrile were dried by distilling over calcium hydride under a nitrogen atmosphere. Methanol was dried by distilling over magnesium. The compound tris(2-pyridylmethyl)amine (TPyA) was synthesized as previously described[1]. All other reagents were available commercially and used without further purification. Elemental analyses (C, H, N) was carried out on Vario MICRO elemental analyzer. Infrared (IR) spectra were recorded on a Perkin-Elmer Spectrum One spectrophotometer with KBr pellet. The DC Magnetic susceptibilities were measured with a Quantum Design MPMS-XL SQUID suscepto-meter under an applied magnetic field of 1 kOe in the 2-300 K range. Diamagnetic corrections were made using Pascal's constants. The single crystal data for complexes **1·2CH$_3$CN** and **1·3H$_2$O** were collected on a Saturn724 + CCD diffractometer equipped with graphitemonochromatic Mo Kα (λ = 0.71073 Å) radiation by using an ω-scan model technique at 293 K. All the structures were solved using SHELXL-97 and refined by the full-matrix least-squares techniques on F^2 with SHELXL-97.

[(TPyA)CoII(BA^{2-})CoII(TPyA)](ClO$_4$)$_2$·2MeCN (1·2CH$_3$CN). TPyA (291 mg, 1.00mmol) was dissolved in MeOH (10 mL), and this solution was added dropwise with stirring to a solution of Co(ClO$_4$)$_2$·6H$_2$O (366 mg,1.00 mmol) in MeOH (10 mL). The resulting brown solution was stirred for 10 min at ambient temperature and then was treated with a solution of H$_2$Ba (149mg,0.500mmol) to give a dark red mixture. To this mixture was added triethylamine (1.40ml,1.00mmol), and the solution was heated to reflux for 30 min, Lots of red microcrystals precipitated and were filtered, washed with MeOH(5ml)three times,then the microcrystals(yield: 332.2 mg, 55.4%) were dissolved in MeCN(8ml).A portion of diethyl ether(10ml) was carefully layered onto the red solution to give a dark red crystals after3 day. Elemental analysis calculated for $Co_2Br_2Cl_2O_{12}N_{10}C_{46}H_{42}$: C 43.32, H 3.32, N 10.98%. Found: C 43.22, H 3.20, N 10.76%.

[(TPyA)CoII(BA^{2-})CoII(TPyA)](ClO$_4$)$_2$·4H$_2$O (1·3H$_2$O). A 10.0 ml methanol solution of 0.5 mmol Co(ClO$_4$)$_2$·6H$_2$O and 0.5 mmol TPyA was placed at the bottom of a test tube, and a 15.0 ml methanol solution of H$_2$Ba (75mg,0.25mmol) and triethylamine (0.7ml,0.5mmol) was layered on the solution. Crystallization required several weeks and gave crystals in 43% yield(126.6 mg). Elemental analysis calculated for $Co_2Br_2Cl_2O_{16}N_8C_{42}H_{44}$: C 39.86, H 3.5, N 8.85%. Found: C 39.04, H 3.54, N 8.71%.

Table S1. Crystallographic data for compounds **1·2CH_3CN** and **1·3H_2O**

	1·2CH_3CN	**1·3H_2O**
Empirical formula	C_{46} H_{42} Br_2 Cl_2 Co_2 N_{10} O_{12}	C_{42} H_{36} Br_2 Cl_2 Co_2 N_8 O_{14}
Color and Habit	Dark red Prism	Dark red Prism
Crystal Size (mm)	0.433×0.322 ×0.211	0.534×0.422 ×0.122
Crystal system	Monoclinic	Monoclinic
Space group	P 2_1/c	C2/c
a (A)	11.368(5)	26.891(6)
b (A)	16.766(7)	11.090(3)
c (A)	13.510(6)	16.954(4)
alpha (deg.)	90	90
beta (deg.)	129.213(19)	92.458(4)
gamma (deg.)	90	90
Volume(A^3)	2574.1(19)	5051(2)
Z	2	4
Formula weight	1275.54	1225.37
Density(cal.)(Mg/m^3)	1.646	1.611
Absorption coefficient(mm^-1)	2.371	2.415
F(000)	1284	2456
Reflections measured	22049	21090
Independent reflections	5868 (Rint = 0.0337)	5793 (Rint = 0.0334)
Observed Reflection	5040 (>2sigma(I))	4622 (>2sigma(I))
Parameter/Restraints/Data(obs.)	335 / 0 / 5040	311 / 24 / 4622
Final R indices (obs.)	R1 = 0.0402, wR2 = 0.1022	R1 = 0.0577, wR2 = 0.1970
R indices (all)	R1 = 0.0486, wR2 = 0.1075	R1 = 0.0668, wR2 = 0.2078
Goodness-of-fit	0.998	0.974

Table S2. Bond lengths (Å) for compound **1·2CH$_3$CN** and **1·3H$_2$O**

	1·2CH$_3$CN	**1·3H$_2$O**
Co(1)-O(1)	2.0261(19)	2.024(3)
Co(1)-N(3)	2.075(2)	2.024(3)
Co(1)-N(2)	2.102(2)	2.126(4)
Co(1)-N(4)	2.106(3)	2.106(4)
Co(1)-N(1)	2.240(2)	2.250(3)
Co(1)-O(2)	2.298(2)	2.315(3)
O(1)-C(1)	1.272(3)	1.287(5)
O(2)-C(2)	1.243(3)	1.233(4)
Co(1)···Co(1a)$_{intra}$	8.137(1)	8.138(1)
Co(1)···Co(1a)inter	6.997(2)	6.832(1)
O(7)···H···O(3)		2.971(3)
O(8)···H···O(3a)		2.992(1)
O(7)···H···O(8)		2.901(2)

Table S3. Angles (deg.) for compound **1·2CH$_3$CN** and **1·3H$_2$O**

	1·2CH$_3$CN	**1·3H$_2$O**
O(1)-Co(1)-N(3)	114.08(9)	117.93(14)
O(1)-Co(1)-N(2)	88.25(9)	87.45(13)
N(3)-Co(1)-N(2)	98.06(10)	100.19(13)
O(1)-Co(1)-N(4)	100.87(10)	98.56(13)
N(3)-Co(1)-N(4)	135.38(10)	133.04(14)
N(2)-Co(1)-N(4)	110.31(10)	110.53(14)
O(1)-Co(1)-N(1)	161.65(8)	159.17(13)
N(3)-Co(1)-N(1)	78.32(9)	78.02(14)
N(2)-Co(1)-N(1)	76.24(9)	75.98(14)
N(4)-Co(1)-N(1)	76.03(10)	76.15(13)
O(1)-Co(1)-O(2)#1	74.20(7)	73.79(11)
N(3)-Co(1)-O(2)#1	82.41(9)	82.18(12)
N(2)-Co(1)-O(2)#1	160.74(8)	159.58(13)
N(4)-Co(1)-O(2)#1	81.37(9)	80.82(13)
N(1)-Co(1)-O(2)#1	122.36(8)	124.06(12)

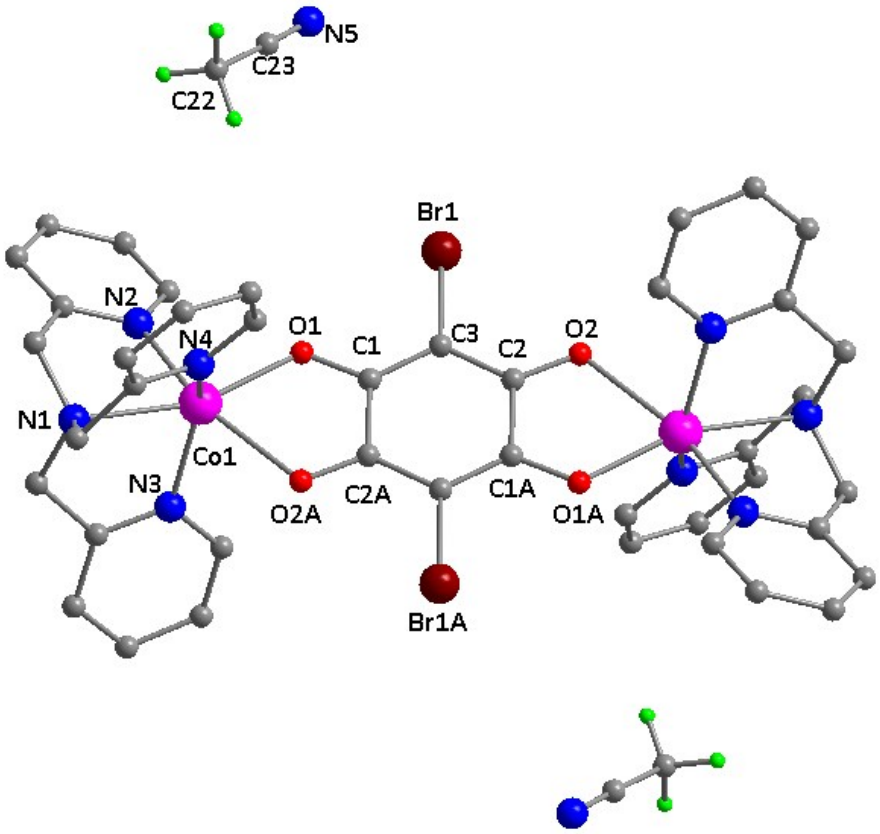

Figure S1. X-ray crystal structure of **1·2CH_3CN** with solvent molecule, pink, dark red, red, blue , gray and green spheres represent Co, Br, O, N, C and H atoms, respectively. H atoms in the molecule are omitted for clarity.

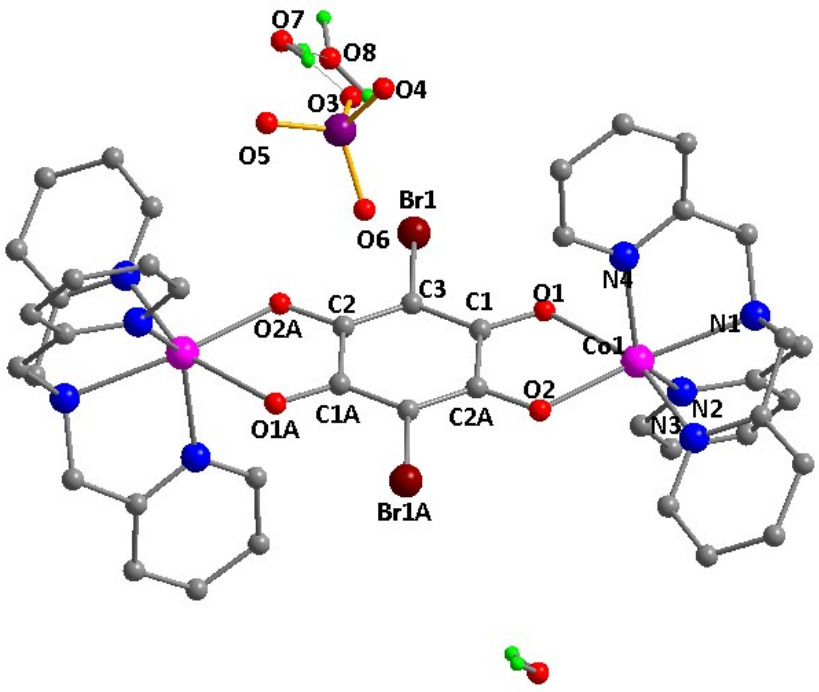

Figure S2. X-ray crystal structure of **1·3H$_2$O** with solvent molecule at 293K, pink, dark red, red, blue , gray and green spheres represent Co, Br, O, N, C and H atoms, respectively. H atoms in the molecule are omitted for clarity.

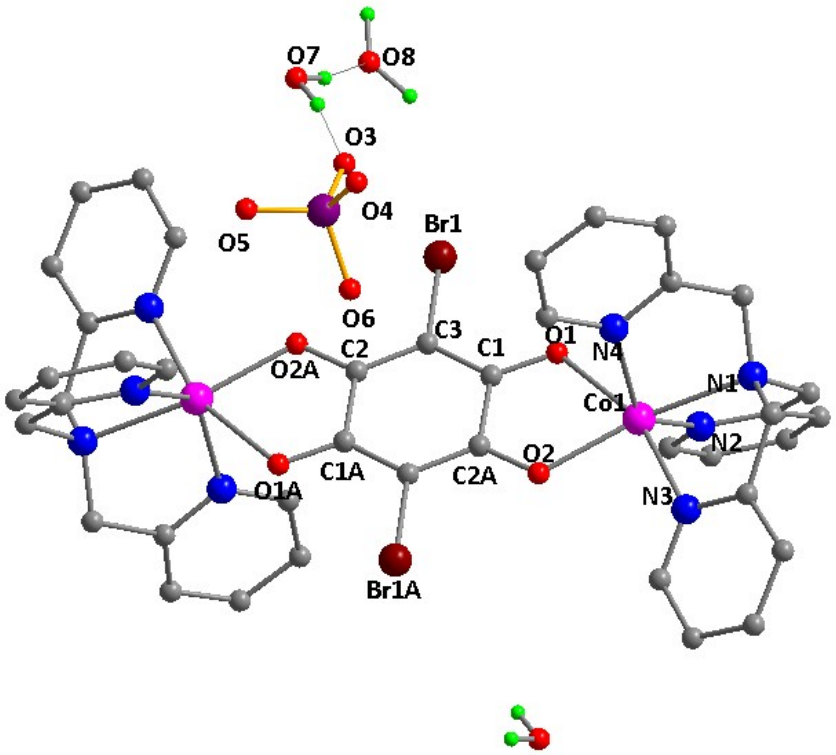

Figure S3. X-ray crystal structure of **1·3H$_2$O** with hydrogen bonds (lines of dashes) at 123K, pink, dark red, red, blue , gray, violet and green spheres represent Co, Br, O, N, C, Cl and H atoms, H atoms in the molecule are omitted for clarity.

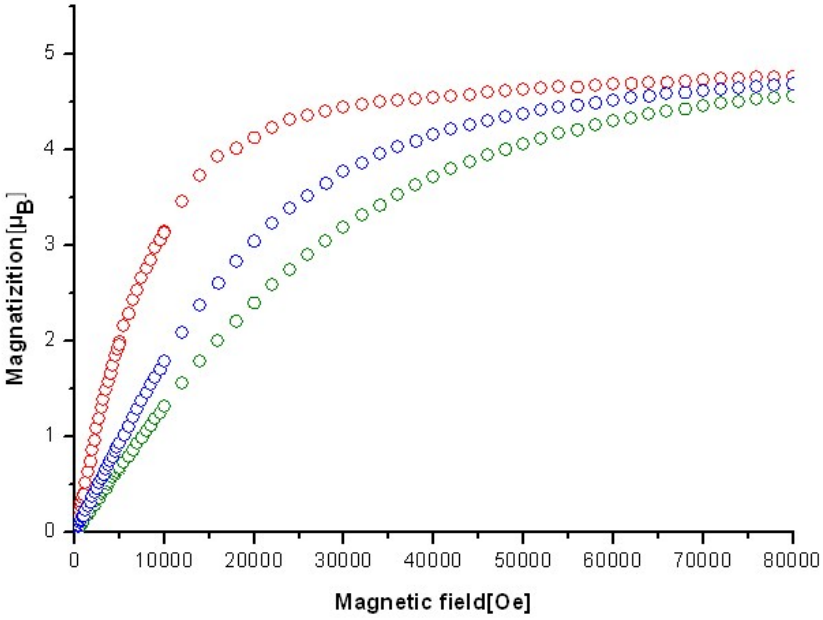

Figure S4. Isothermal field-dependent magnetizations for compound **1·2CH$_3$CN** at 2K (red), 5K (blue), 7K (green).

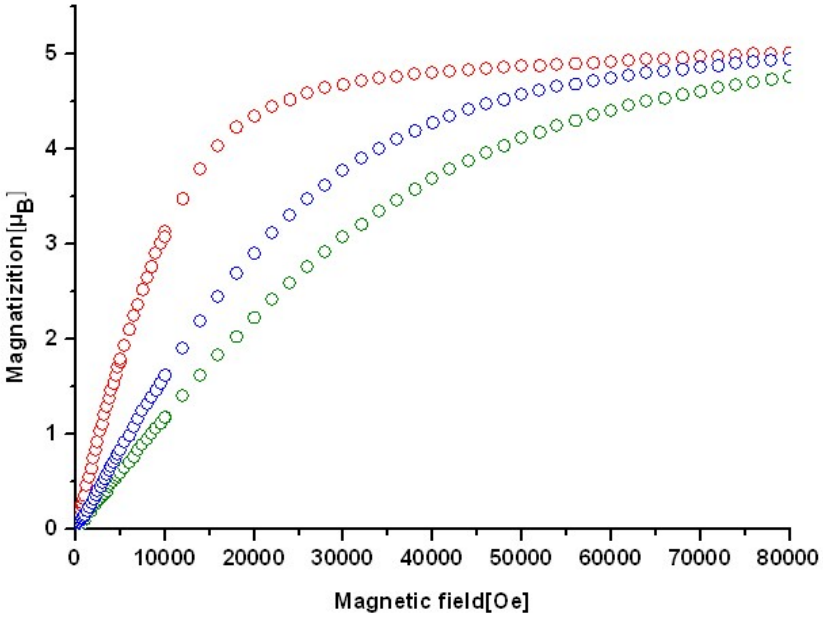

Figure S5. Isothermal field-dependent magnetizations for compound **1·3H$_2$O** at 2K (red), 5K (blue), 7K (green).

1. Z. Tyeklar, R. R. Jacobson, N. Wei, N. N. Murthy, J. Zubieta and K. D. Karlin, *J. Am. Chem. Soc.*, 1993, **115**, 2677-2689.