Supporting Information

Experimental Section

Materials and Physical Measurements: All of the starting materials employed were commercially available and used as received without further purification. The rhodamine 6G derivative H_2L ligand was synthesized following previously reported procedures.[12] Elemental analyses (C, H, N) were conducted using a Perkin-Elmer 240 elemental analyzer. The Fourier transform infrared (FT-IR) spectra were obtained in the range of 4000–400 cm^{-1} as KBr pellets on a Bruker VECTOR 22 spectrometer. Powder X-ray diffraction (PXRD) patterns were obtained at room temperature with a Phillips XPERT PRO with Cu Kα irradiation (λ = 1.5418 A). TGA-DTG measurement was performed on a PE Diamond TG/DTA unit under air atmosphere at a rate of 10 °C min^{-1} in the temperature range of 30 °C − 700 °C. The magnetic susceptibility and magnetization measurements were performed on a Quantum Design SQUID magnetometer MPMS-XL 7 operating between 1.8 and 300 K for dc-applied fields ranging from 0 to 5 T. Microcrystalline samples were dispersed in Vaseline to avoid torquing of the crystallites. The sample mulls were contained in a calibrated gelatin capsule held at the center of a drinking straw that was fixed at the end of the sample rod. The ac susceptibility measurements were performed under an oscillating ac field of 3.5 Oe and frequencies ranging from 0.1 to 1500 Hz.

Synthesis of $[Co^{II}_{12}(L)_6(OH)_6(Ac)_6]\cdot 2DMF$ (1): A mixture of $Co(Ac)_2\cdot H_2O$ (14.9 mg, 0.06 mmol), H_2L (11.5 mg, 0.02 mmol), water (0.5 mL), DMF (2 mL) and CH_3CN (2 mL) was stirred for 10 min in air. It was then transferred and sealed in a 25 mL Teflon-lined reactor which was heated in an oven at 110 °C for 3 days and then cooled to room temperature at a rate of 5 °C/ h^{-1}. After the mixture was slowly cooled to room temperature, orange-red rod-shaped crystals of **1** (55 mg) were separated in a 56% yield (based on H_2L). Anal. Calcd for $Co_{12}C_{222}H_{218}N_{26}O_{50}$: C, 56.05; H, 4.62; N, 7.65. Found: C, 55.58; H, 4.70; N, 7.52. FT-IR spectra (KBr pellet, cm^{-1}): 3438(m), 1670(m), 1621(s), 1557(m), 1518(m), 1471(w), 1422(m), 1359(m), 1271(w), as shown in Figure S1.

X-ray data collection and structure determination: Single crystal X-ray diffraction analysis of **1** was carried out on a Bruker SMART APEX CCD diffractometer[19] using graphite-monochromatized Mo Kα radiation (λ = 0.71073 Å) at room temperature using the ω-scan technique. The structures were solved by direct methods with SHELXS-97[20] and refined by the full-matrix least-squares method on F^2 with anisotropic thermal parameters for all non-H atoms (SHELXL-97).[21] The empirical absorption corrections were applied by the SADABS program.[22] No satisfactory disorder model for some of the included solvent could be achieved, and therefore the SQUEEZE program implemented in PLATON was used to remove its electron density.[23] The crystallographic data and selected bond lengths and angles for **1** are listed in Tables S1 and S2.

[19] *SMART and SAINT. Area Detector Control and Integration Software*; Siemens Analytical X-Ray Systems, Inc.: Madison, WI, 1996.

[20] Sheldrick, G. M. *SHELXS-97: Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1997.

[21] Sheldrick, G. M. *SHELXL-97, Program for the Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 1997.

[22] Sheldrick, G. M. *SADABS Siemens Area Correction Absorption Program*; University of Göttingen: Göttingen, Germany, 1994.

[23] Spek, A. L. *Implemented as the PLATON Procedure, a Multipurpose Crystallographic Tool*; Utrecht University: Utrecht, The Netherlands, 1998.

Table S1. Crystallographic data and structure refinement parameters for **1**

Empirical formula	$C_{222}H_{218}Co_{12}N_{26}O_{50}$
Formula weight	4757.38
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Triclinic
Space group	P-1
a (Å)	17.7558(5)
b (Å)	21.8506(8)
c (Å)	21.8517(7)
α / deg	60.483(4)
β / deg	81.896(2)
γ / deg	68.780(3)
V / Å3	6870.0(4)
Z	1
Density (calcd) (Mg m-3)	1.150
F (000)	2446
Crystal size (mm^3)	0.34 × 0.32 × 0.29
Reflections	56108
Independent	25559 [R(int) = 0.0421]
Data / restraints / parameters	25559 / 1697 / 1429
GOF on F^2	0.966
Final *R* indices [$I > 2\sigma(I)$]	R1 = 0.0597, wR2 = 0.1563
R indices (all data)	R1 = 0.0977, wR2 = 0.1775
Largest diff peak and hole (e $Å^{-3}$)	0.877 and -0.480

Table S2. Selected bond lengths (Å) and angles [deg] for **1**

Co(1)-O(2)	2.048(2)	Co(4)-O(13)	2.043(3)
Co(1)-O(16)	2.079(2)	Co(4)-O(17)	2.073(2)
Co(1)-N(1)	2.082(3)	Co(4)-N(10)	2.072(3)
Co(1)-O(22)	2.116(3)	Co(4)-O(20)	2.121(3)
Co(1)-O(14)	2.123(3)	Co(4)-O(9)	2.131(3)
Co(1)-O(1)	2.158(3)	Co(4)-O(12)	2.166(3)
Co(2)-O(18)#1	2.007(2)	Co(5)-O(17)	1.997(2)
Co(2)-O(2)	2.031(2)	Co(5)-O(8)	2.027(2)
Co(2)-O(16)	2.038(2)	Co(5)-O(18)	2.041(2)
Co(2)-O(3)	2.069(2)	Co(5)-O(9)	2.080(2)
Co(2)-O(21)	2.203(3)	Co(5)-O(23)	2.195(3)
Co(2)-O(19)	2.225(3)	Co(5)-O(21)#1	2.229(3)
Co(3)-O(16)	2.008(2)	Co(6)-O(8)	2.043(3)
Co(3)-O(13)	2.027(2)	Co(6)-N(6)	2.065(3)
Co(3)-O(17)	2.044(2)	Co(6)-O(18)	2.079(2)
Co(3)-O(14)	2.070(3)	Co(6)-O(24)	2.112(3)
Co(3)-O(19)	2.173(2)	Co(6)-O(3)#1	2.118(2)
Co(3)-O(23)	2.197(2)	Co(6)-O(7)	2.138(3)
Co(1)-Co(2)	2.9627(7)	Co(5)-Co(6)	2.9420(7)
Co(3)-Co(4)	2.9609(7)		
O(2)-Co(1)-O(16)	85.40(9)	O(13)-Co(4)-O(17)	85.57(10)
O(2)-Co(1)-N(1)	85.20(11)	O(13)-Co(4)-N(10)	84.77(10)
O(16)-Co(1)-N(1)	170.04(11)	O(17)-Co(4)-N(10)	168.77(11)
O(2)-Co(1)-O(22)	88.87(11)	O(13)-Co(4)-O(20)	88.10(11)
O(16)-Co(1)-O(22)	89.24(10)	O(17)-Co(4)-O(20)	88.72(9)
N(1)-Co(1)-O(22)	93.83(12)	N(10)-Co(4)-O(20)	96.66(11)
O(2)-Co(1)-O(14)	97.48(10)	O(13)-Co(4)-O(9)	98.33(11)
O(16)-Co(1)-O(14)	76.99(9)	O(17)-Co(4)-O(9)	77.18(9)
N(1)-Co(1)-O(14)	101.03(11)	N(10)-Co(4)-O(9)	98.58(9)
O(22)-Co(1)-O(14)	164.25(10)	O(20)-Co(4)-O(9)	163.93(10)
O(2)-Co(1)-O(1)	162.22(11)	O(13)-Co(4)-O(12)	160.19(10)
O(16)-Co(1)-O(1)	111.59(10)	O(17)-Co(4)-O(12)	112.58(10)
N(1)-Co(1)-O(1)	78.10(11)	N(10)-Co(4)-O(12)	77.84(11)
O(22)-Co(1)-O(1)	86.22(10)	O(20)-Co(4)-O(12)	84.58(10)
O(14)-Co(1)-O(1)	91.71(10)	O(9)-Co(4)-O(12)	93.64(11)
O(2)-Co(1)-Co(2)	43.21(7)	O(13)-Co(4)-Co(3)	43.11(7)
O(16)-Co(1)-Co(2)	43.43(6)	O(17)-Co(4)-Co(3)	43.63(7)
N(1)-Co(1)-Co(2)	127.84(9)	N(10)-Co(4)-Co(3)	127.62(9)
O(22)-Co(1)-Co(2)	80.59(7)	O(20)-Co(4)-Co(3)	79.91(8)

O(14)-Co(1)-Co(2)	94.18(7)	O(9)-Co(4)-Co(3)	94.70(7)
O(1)-Co(1)-Co(2)	151.34(7)	O(12)-Co(4)-Co(3)	151.36(7)
O(18)#1-Co(2)-O(2)	164.09(10)	O(17)-Co(5)-O(8)	163.66(10)
O(18)#1-Co(2)-O(16)	106.61(9)	O(17)-Co(5)-O(18)	106.78(10)
O(2)-Co(2)-O(16)	86.89(9)	O(8)-Co(5)-O(18)	87.53(10)
O(18)#1-Co(2)-O(3)	80.47(9)	O(17)-Co(5)-O(9)	80.05(10)
O(2)-Co(2)-O(3)	85.53(10)	O(8)-Co(5)-O(9)	85.34(10)
O(16)-Co(2)-O(3)	171.86(10)	O(18)-Co(5)-O(9)	172.67(9)
O(18)#1-Co(2)-O(21)	80.20(10)	O(17)-Co(5)-O(23)	80.50(9)
O(2)-Co(2)-O(21)	93.30(10)	O(8)-Co(5)-O(23)	93.57(10)
O(16)-Co(2)-O(21)	83.68(10)	O(18)-Co(5)-O(23)	84.06(10)
O(3)-Co(2)-O(21)	93.76(10)	O(9)-Co(5)-O(23)	94.63(10)
O(18)#1-Co(2)-O(19)	102.03(10)	O(17)-Co(5)-O(21)#1	101.10(10)
O(2)-Co(2)-O(19)	88.63(10)	O(8)-Co(5)-O(21)#1	89.13(10)
O(16)-Co(2)-O(19)	78.67(9)	O(18)-Co(5)-O(21)#1	78.84(9)
O(3)-Co(2)-O(19)	104.10(10)	O(9)-Co(5)-O(21)#1	102.76(10)
O(21)-Co(2)-O(19)	162.12(9)	O(23)-Co(5)-O(21)#1	162.57(10)
O(18)#1-Co(2)-Co(1)	146.43(7)	O(17)-Co(5)-Co(6)	147.02(8)
O(2)-Co(2)-Co(1)	43.64(7)	O(8)-Co(5)-Co(6)	43.93(7)
O(16)-Co(2)-Co(1)	44.53(7)	O(18)-Co(5)-Co(6)	44.95(6)
O(3)-Co(2)-Co(1)	127.43(8)	O(9)-Co(5)-Co(6)	127.72(7)
O(21)-Co(2)-Co(1)	79.70(7)	O(23)-Co(5)-Co(6)	79.84(7)
O(19)-Co(2)-Co(1)	89.61(6)	O(21)#1-Co(5)-Co(6)	90.34(7)
O(16)-Co(3)-O(13)	164.41(10)	O(8)-Co(6)-N(6)	85.77(11)
O(16)-Co(3)-O(17)	107.14(9)	O(8)-Co(6)-O(18)	86.09(9)
O(13)-Co(3)-O(17)	86.74(10)	N(6)-Co(6)-O(18)	171.86(2)
O(16)-Co(3)-O(14)	79.76(10)	O(8)-Co(6)-O(24)	88.91(11)
O(13)-Co(3)-O(14)	85.98(10)	N(6)-Co(6)-O(24)	89.41(12)
O(17)-Co(3)-O(14)	172.19(10)	O(18)-Co(6)-O(24)	90.28(10)
O(16)-Co(3)-O(19)	80.56(10)	O(8)-Co(6)-O(3)#1	96.22(11)
O(13)-Co(3)-O(19)	94.44(10)	N(6)-Co(6)-O(3)#1	103.36(11)
O(17)-Co(3)-O(19)	83.15(9)	O(18)-Co(6)-O(3)#1	77.69(9)
O(14)-Co(3)-O(19)	94.60(10)	O(24)-Co(6)-O(3)#1	166.52(11)
O(16)-Co(3)-O(23)	100.97(10)	O(8)-Co(6)-O(7)	164.26(12)
O(13)-Co(3)-O(23)	88.33(10)	N(6)-Co(6)-O(7)	79.09(12)
O(17)-Co(3)-O(23)	79.43(9)	O(18)-Co(6)-O(7)	109.02(10)
O(14)-Co(3)-O(23)	103.16(10)	O(24)-Co(6)-O(7)	86.70(11)
O(19)-Co(3)-O(23)	162.18(10)	O(3)#1-Co(6)-O(7)	91.46(10)
O(16)-Co(3)-Co(4)	147.50(7)	O(8)-Co(6)-Co(5)	43.50(11)
O(13)-Co(3)-Co(4)	43.53(7)	N(6)-Co(6)-Co(5)	128.08(9)
O(17)-Co(3)-Co(4)	44.41(7)	O(18)-Co(6)-Co(5)	43.91(7)
O(14)-Co(3)-Co(4)	127.88(7)	O(24)-Co(6)-Co(5)	81.01(7)
O(19)-Co(3)-Co(4)	80.41(7)	O(3)#1-Co(6)-Co(5)	94.13(7)

O(23)-Co(3)-Co(4)	89.68(7)	O(7)-Co(6)-Co(5)	149.62(8)

Symmetry operation for #1: -x, -y, -z

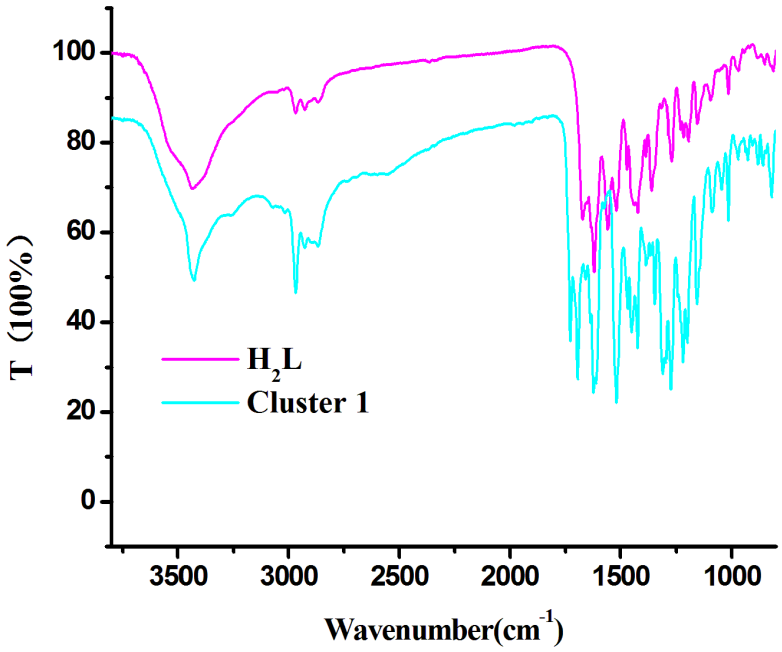

Fig. S1. FT-IR spectra of **1**

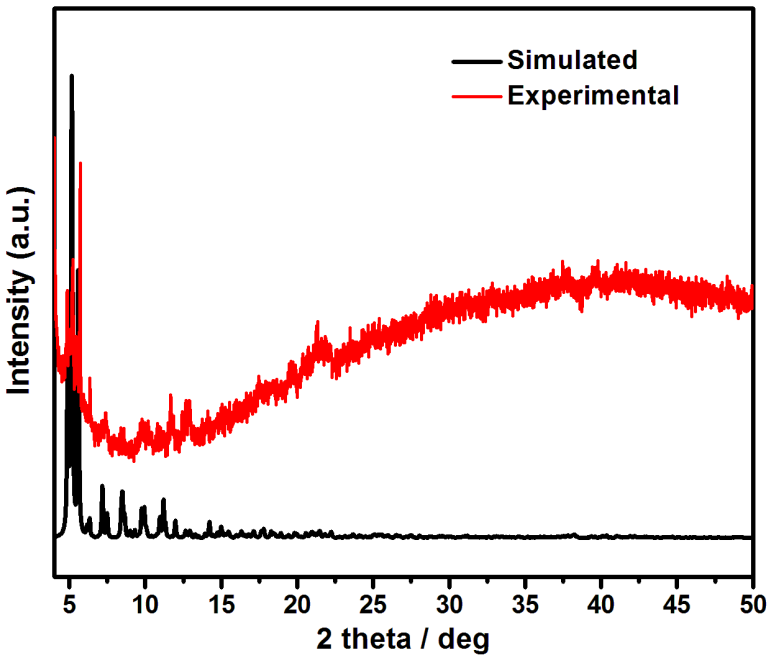

Fig. S2. Powder X-ray diffraction (PXRD) spectra of **1**

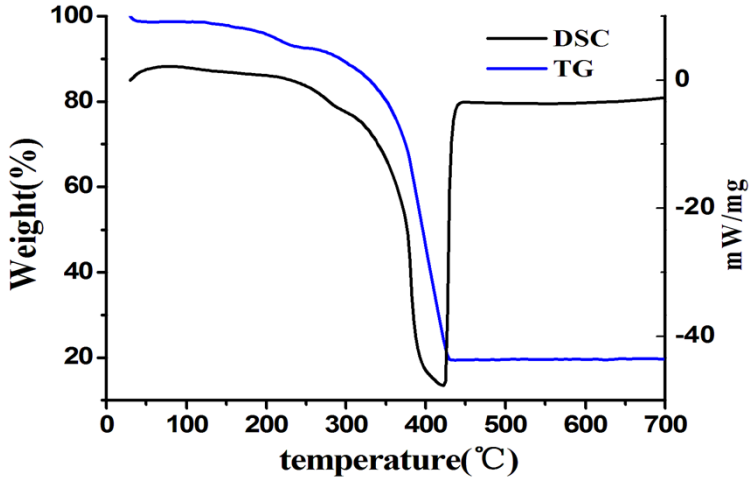

Fig. S3. The result of TG-DSC of **1**