Electronic Supplementary Material (ESI) for Dalton Transactions.

Electronic Supplementary Information for

Syntheses, structures, and properties of six cobalt(II) complexes based on a tripodal tris(4-(1*H*-1,2,4-triazol-1-yl)phenyl)amine ligand

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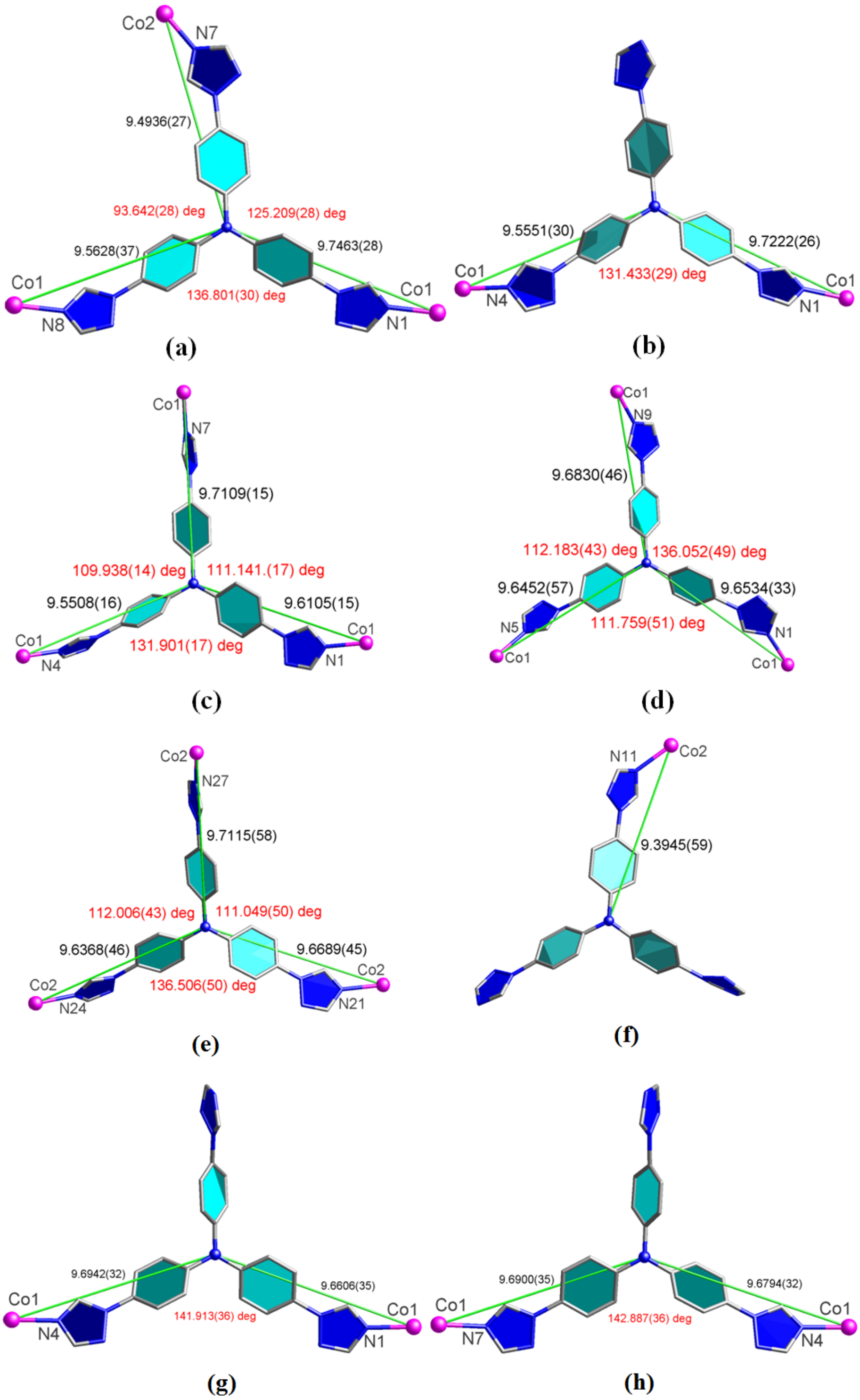
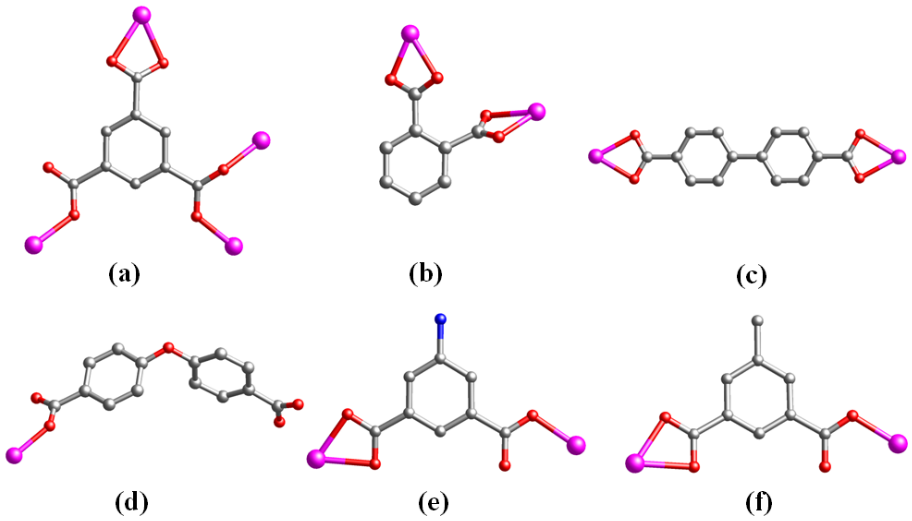
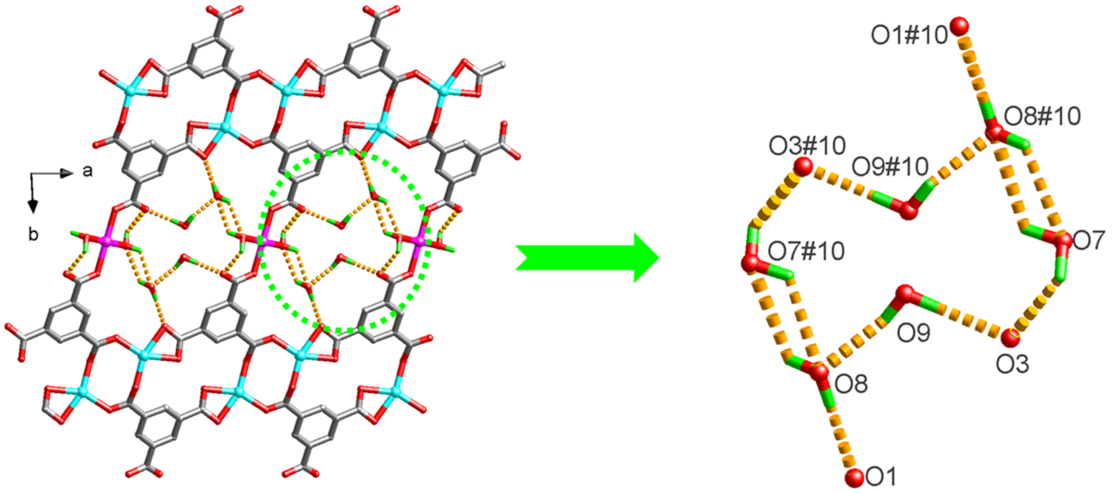


Fig S1. The conformation of TTPA ligand

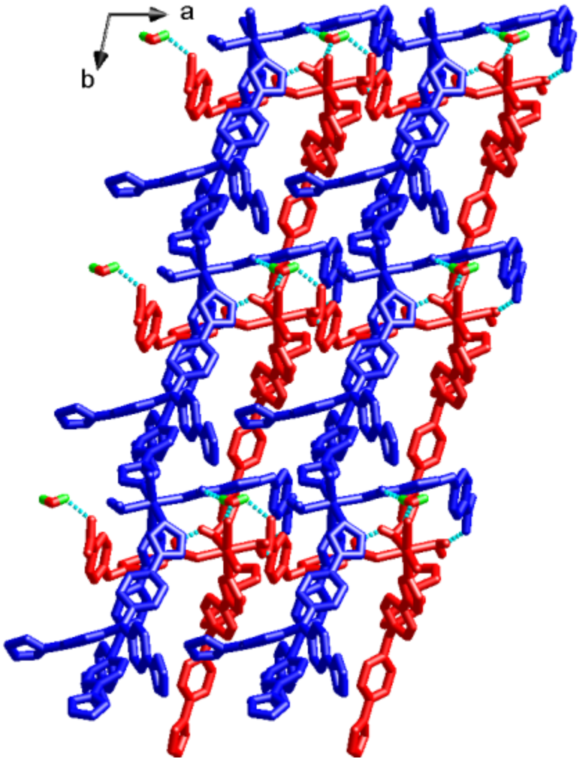

(a) (b) (c)

(d) (e) (f)

Fig S2. The coordination modes of auxiliary ligands in complexes **1-6**



(a)



(b)

Fig S3. (a) Perspective view of the 2D layer exists O-H···O hydrogen bonding interactions (yellow dashed lines) in **2**. (b) Perspective view of the ···ABAB··· stacking 3D framework by O-H···O hydrogen bonding interactions (turquoise dashed lines) in **4**.

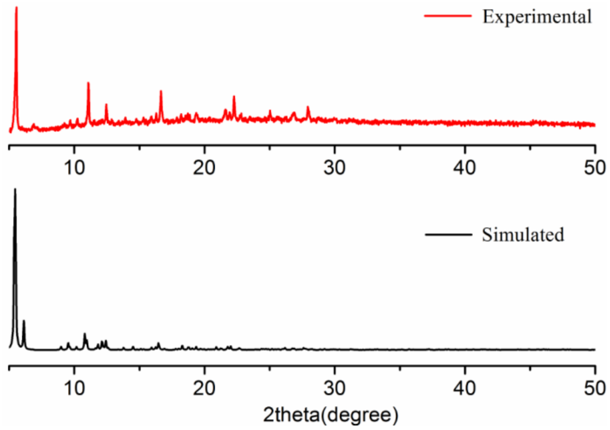


Fig S4. Powder X-ray diffraction patterns of complex **1**

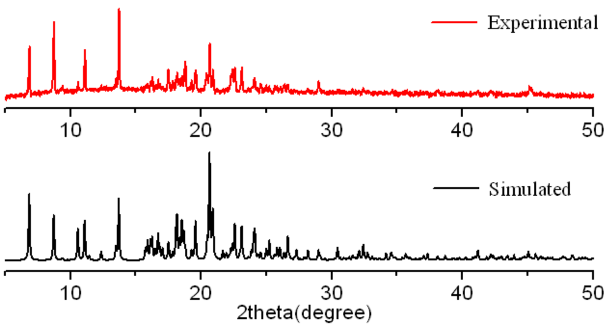


Fig S5. Powder X-ray diffraction patterns of complex **2**

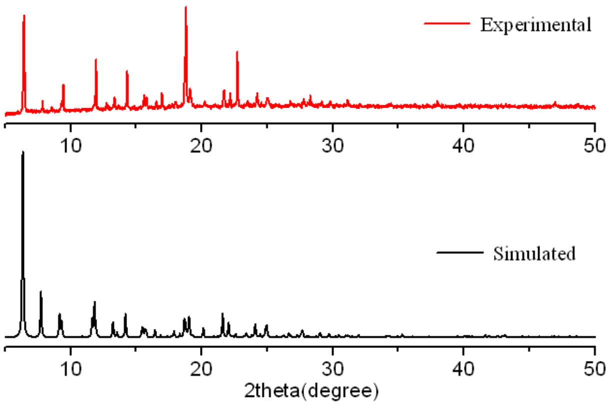


Fig S6. Powder X-ray diffraction patterns of complex **3**

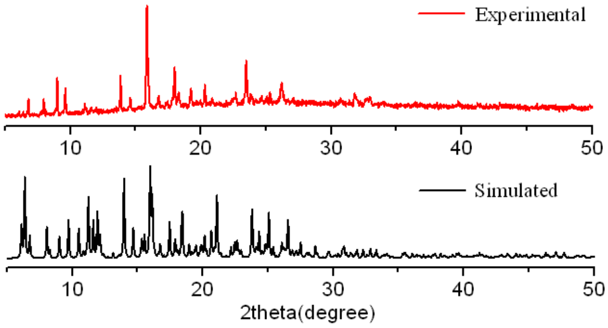


Fig S7. Powder X-ray diffraction patterns of complex **4**

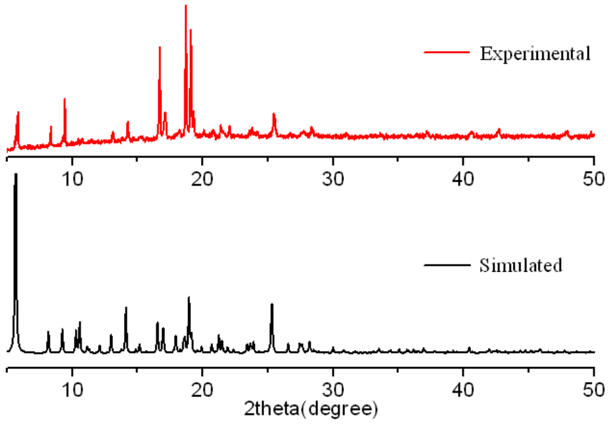


Fig S8. Powder X-ray diffraction patterns of complex **5**

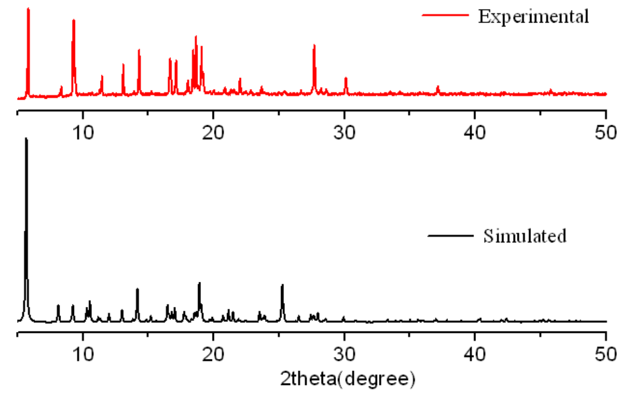
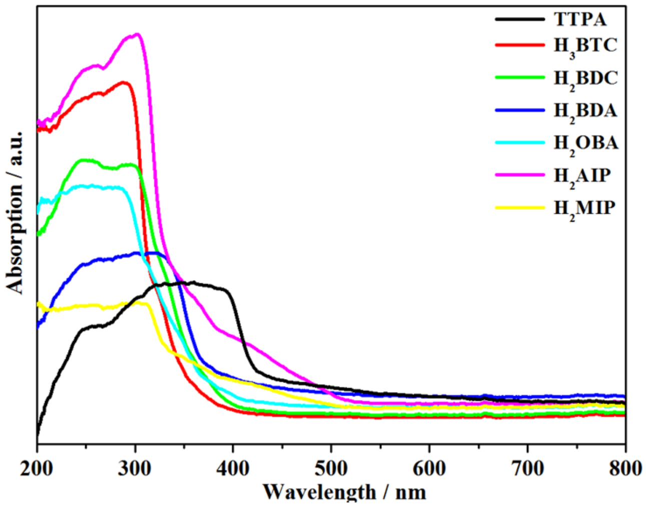
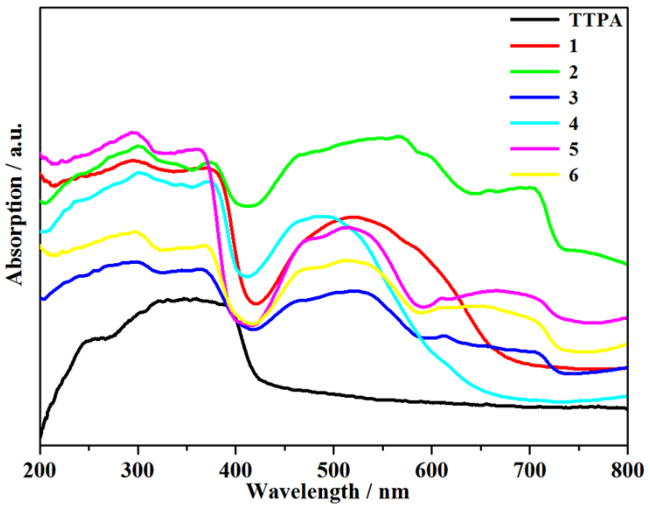


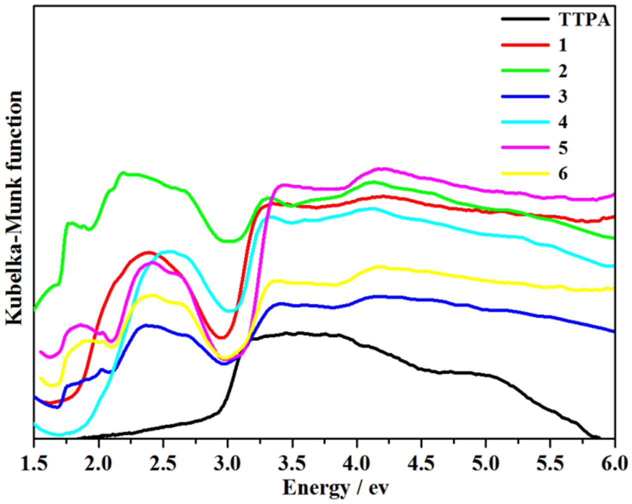
Fig S9. Powder X-ray diffraction patterns of complex **6**



(a)



(b)



(c)

Fig S10. (a) and (b) UV-vis absorbance spectra of TTPA ligand, auxiliary ligands and complexes **1-6** at room temperature. (c) Plot of Kubelka-Munk as a function of energy of TTPA ligand and complexes **1-6**.

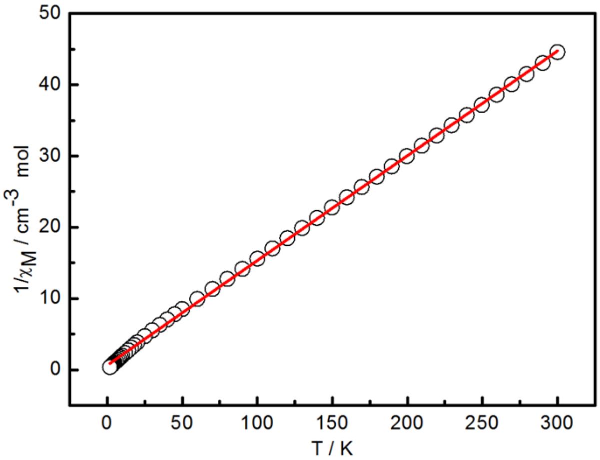


Fig S11. Temperature dependence of $1/\chi_{\mathrm{M}}$ versus T for complex **1**. The open points are the experimental data, the solid red line results from a fit of the data to the theoretical equations.

Materials and methods

All chemicals and solvents except TTPA ligand were of reagent-grade quality from commercial sources and were used without further purification. The triangular ligand tris(4-(1H-1,2,4-triazol-1-yl)phenyl)amine (TTPA) was prepared by the copper-catalyzed carbon-nitrogen bond cross-coupling reaction between tris(4-bromophenyl)amine and 1,2,4-triazole using Ullmann condensation methods based on previous literature with proper modifications.[S1] NMR spectra were recorded on a Bruker NMR 500 DRX spectrometer. The IR absorption spectra of these complexes were recorded in the range of 400-4000 cm^{-1} by means of a Nicolet (Impact 410) spectrometer with KBr pellets. Element analyses (C, H, N) were carried out on a Perkin-Elmer model 240C analyzer. PXRD measurements were performed on a Bruker D8 Advance X-ray diffractometer using Cu-$K\alpha$ radiation (0.15418 nm), in which the X-ray tube was operated at 40 kV and 30 mA. Thermogravimetric analysis was performed on a Perkin Elmer thermogravimetric analyzer from room temperature to 700 °C with a heating rate of 20 K·min^{-1} under N_2 atmosphere. Solid-state UV-vis absorbance spectra were obtained at room temperature using Shimadzu UV-3600 double monochromator spectrophotometer, and $BaSO_4$ was used as a 100% reflectance standard for all materials. Temperature dependent magnetic susceptibility data for crystalline samples **1** were obtained on a MPMS XL-7 SQUID magnetometer under an applied field of 2000 Oe in the temperature range of 1.8−300 K.

Synthesis of tris(4-(1*H*-1,2,4-triazol-1-yl)phenyl)amine (TTPA)

A mixture of tris(4-bromophenyl)amine (20.0 mmol, 9.64 g), 1,2,4-triazole (200.0 mmol, 13.80 g), CuI (1 mmol, 0.19 g), 18-crown-6 (2.0 mmol, 0.53 g), and K_2CO_3 (200.0 mmol, 27.6 g) was suspended in 100 mL of DMF. The mixture in a 250-mL two-necked round-bottom flask under N_2 was refluxed at 160 °C for 2 days and then cooled to room temperature. Solvent was removed by distillation under a vacuum, and the reaction mixture was added into 200 mL H_2O. The deposit was filtered and washed with water and dried in vacuum to obtain light blue powder. Then the crude product was separated by column chromatography ($CH_3COOCH_3CH_2/CH_3OH$ = 10:1) to afford white crystalline powder (yield: ~81%, 7.22g, based on tris(4-bromophenyl)amine). ^1H NMR (500 MHz, DMSO-d_6), δ (ppm): 9.24 (s, 3H), 8.23 (s, 3H), 7.84 (d, J = 9.0 Hz, 6H), 7.27 (d, J = 9.0 Hz, 6H). Anal. Calcd for $C_{24}H_{18}N_{10}$: C, 64.56; H, 4.06; N, 31.37. Found: C, 64.61; H, 4.00; N, 31.28. IR (KBr, cm^{-1}): 3384w, 3110w, 1611w, 1570m, 1517vs, 1433m, 1402m, 1276s, 1217m, 1178w, 1146m, 1053m, 982s, 955m, 835m, 706m, 673m, 542w. MS (ESI), m/z (%): 447.75 for

$C_{24}H_{19}N_{10}^+$. (Fig S12-S14)

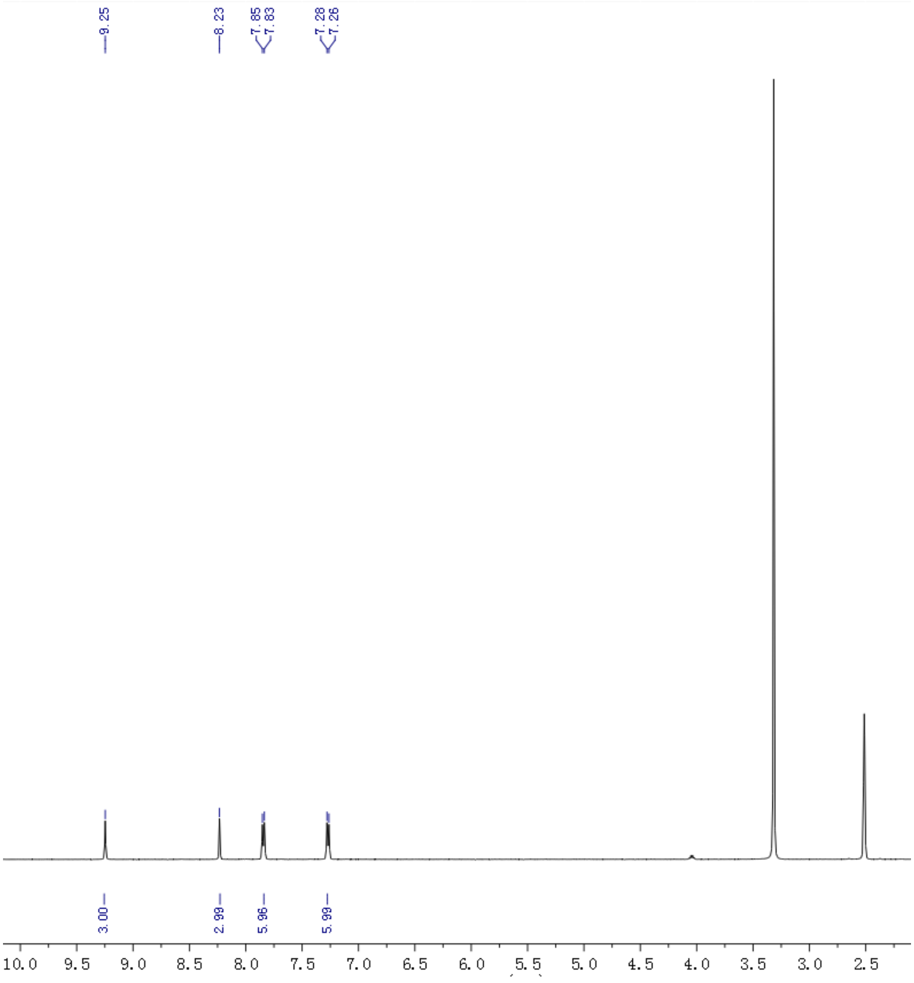


Fig S12. The ^{1}H NMR spectra of TTPA

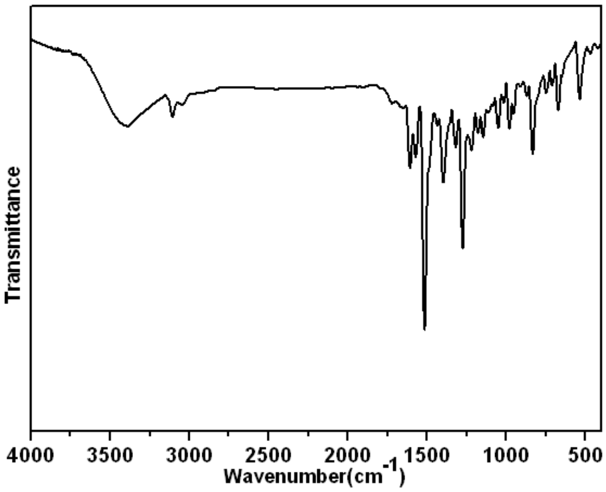


Fig S13. FT-IR spectroscopy of TTPA

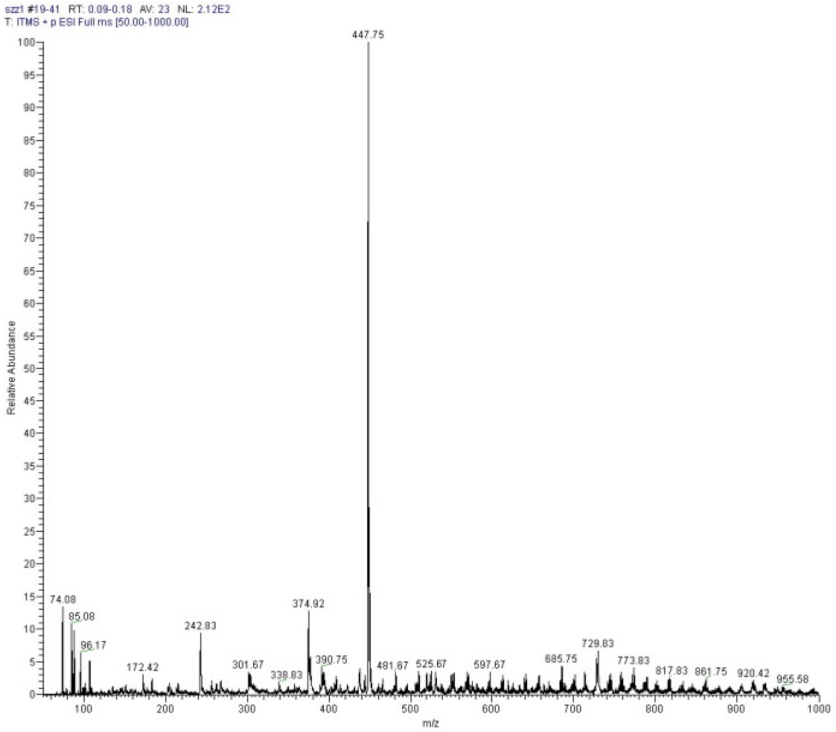


Fig S14. The EI-MS scheme of TTPA

Crystal structure determination

Single crystals of **1**-**6** were prepared by the methods described in the synthetic procedure. Their crystal structures were determined by single-crystal X-ray analyses. Data collections were performed using a Bruker Smart Apex CCD diffractometer with Mo-*Kα* radiation with an *φ*–*ω* mode (λ = 0.71073 Å). But, only data collection of complex **4** was collected at low temperature to get better diffraction data. The structures were solved with direct methods using the SHELXTL program[S2] and refined anisotropically with SHELX2014 using full-matrix least-squares procedures. During the structural refinement, in the structures of complex **3**, the occupancy probabilities of the oxygen atoms of the guest water molecules determined by structure refinements are as follows: 0.3 (O2W), 0.3 (O3W), 0.4 (O4W), respectively. In the structure of complexes **5** and **6**, two disordered carbon atoms (C5', C6' for **5**; C23', C24' for **6**) and three nitrogen atoms (N7', N8', N9' for **5**; N8', N9', N10' for **6**) of one uncoordinated triazole ring from TTPA ligand were restrained in order to obtain reasonable thermal parameters. In the crystal X-ray structure analysis, some residual electron densities of complexes **1** and **3**-**6** were observed within the pores, and assignment to specific molecules cannot be made. They were removed by the SQUEEZE routine in PLATON.

Preparation of the complexes 1-6

Synthesis of {[$Co_{1.5}$(TTPA)(BTC)(H_2O)]$_2$·13H_2O}$_n$ (1). A mixture of TTPA (22.3 mg, 0.05 mmol), H_3BTC (21.0 mg, 0.1 mmol), and $Co(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.1 mmol) was dissolved in 8 mL of DMF/CH_3CN/H_2O (2:4:2, v/v/v). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 85 °C for 3 days and then cooled to room temperature over 24 h. Purple block-shaped crystals of **1** were obtained, dried in air and collected in 47% yield (based on Co(II) salt). Elemental analysis calcd. for $C_{66}H_{72}N_{20}O_{27}Co_3$ (%): C, 45.19; H, 4.14; N, 15.97. Found: C, 45.23; H, 4.29; N, 15.88. IR (KBr, cm^{-1}): 3386s, 1659s, 1612s, 1519vs, 1431s, 1366s, 1277s, 1144w, 1100w, 1049w, 976w, 834w, 714m, 672m, 541w (Fig S15).

Synthesis of [Co(TTPA)(PA)]$_n$ (2). A mixture of TTPA (11.2 mg, 0.025 mmol), H_2PA (16.6 mg, 0.1 mmol), and $Co(CH_3COO)_2 \cdot 4H_2O$ (24.9 mg, 0.1 mmol) was dissolved in 6 mL of DMF/H_2O (1:5, v/v). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 90 °C for 3 days and then cooled to room temperature over 24 h. Purple block-shaped crystals of **2** were obtained, dried in air and collected in 45% yield (based on Co(II) salt). Elemental analysis calcd. for $C_{32}H_{22}CoN_{10}O_4$ (%): C, 57.41; H, 3.31; N, 20.92. Found: C, 57.38; H, 3.43; N, 20.88. IR (KBr, cm^{-1}): 3393s, 3086m, 1606w, 1515vs, 1401s, 1275s, 1139m, 972w, 828w, 744w, 707w, 668w, 545w (Fig S16).

Synthesis of {[Co(TTPA)(BDA)$_{0.5}$(NO_3)]·3H_2O}$_n$ (3). A mixture of TTPA (11.2 mg, 0.025 mmol), H_2BDA (24.2 mg, 0.1 mmol), and $Co(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.1 mmol) was dissolved in 6 mL of DMF/ H_2O (1:5, v/v). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 90 °C for 3 days and then cooled to room temperature over 24 h. Purple block-shaped crystals of **3** were obtained, dried in air and collected in 38% yield (based on Co(II) salt). Elemental analysis calcd. for $C_{31}H_{28}N_{11}O_8Co$ (%): C, 50.21; H, 3.80; N, 20.78.

Found: C, 50.33; H, 3.69; N, 20.68. IR (KBr, cm^{-1}): 3393vs, 1608s, 1522s, 1391s, 1316s, 1279s, 1141m, 1050w, 978w, 834w, 766w, 551w (Fig S17).

Synthesis of {[$Co_2(TTPA)_3(OBA)_2(H_2O)_3$]·$2CH_3CN$·$4H_2O$}$_n$ (4). A mixture of TTPA (22.3 mg, 0.05 mmol), H_2OBA (18.1 mg, 0.1 mmol), and $Co(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.1 mmol) was dissolved in 6 mL of DMF/CH_3CN/H_2O (1:1:4, v/v/v). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 95 °C for 3 days and then cooled to room temperature over 24 h. Red block-shaped crystals of **4** were obtained, dried in air and collected in 45% yield (based on Co(II) salt). Elemental analysis calcd. for $C_{104}H_{90}Co_2N_{32}O_{17}$ (%): C, 57.35; H, 4.17; N, 20.58. Found: C, 57.58; H, 4.05; N, 20.24. IR (KBr, cm^{-1}): 3105s, 1669m, 1598s, 1517vs, 1379s, 1327m, 1307m, 1280s, 1235s, 1148s, 1049m, 1011w, 977s, 875m, 833s, 786m, 726w, 672s, 650m, 540m (Fig S18).

Synthesis of {[Co(TTPA)(AIP)(H_2O)]·$2H_2O$}$_n$ (5) and {[Co(TTPA)(MIP)(H_2O)]·$2H_2O$}$_n$ (6). A mixture of TTPA (22.3 mg, 0.05 mmol), $Co(NO_3)_2 \cdot 6H_2O$ (29.1 mg, 0.1 mmol), H_2AIP (18.1 mg, 0.1 mmol) or H_2MIP (0.1 mmol, 18.0 mg) was dissolved in 6.5 mL of DMF/H_2O (3.5:3, v/v). The final mixture was placed in a Teflon vessel (15 mL) under autogenous pressure and heated at 100 °C for 3 days and then cooled to room temperature over 24 h. Purple block-shaped crystals of **5** and **6** were obtained, dried in air and collected in 48% and 40% yield (based on Co(II) salt), respectively. Elemental analysis calcd. for $C_{32}H_{29}N_{11}O_7Co$ (%): C, 52.04; H, 3.96; N, 20.86. Found: C, 52.12; H, 3.89; N, 20.74. IR (KBr, cm^{-1}): 3420m, 3120m, 1609m, 1518s, 1436m, 1378s, 1326m, 1279s, 1146m, 1051m, 979w, 833w, 778w, 730w, 673w, 546w for **5** (Fig S19). Elemental analysis calcd. for $C_{33}H_{30}N_{10}O_7Co$ (%): C, 53.74; H, 4.10; N, 18.99. Found: C, 53.61; H, 4.02; N, 19.09. IR (KBr, cm^{-1}): 3417m, 3120m, 1607m, 1518s, 1436m, 1378s, 1326m, 1278s, 1146w, 1051w, 979m, 833w, 778w, 730w, 672w, 546w for **6** (Fig S20).

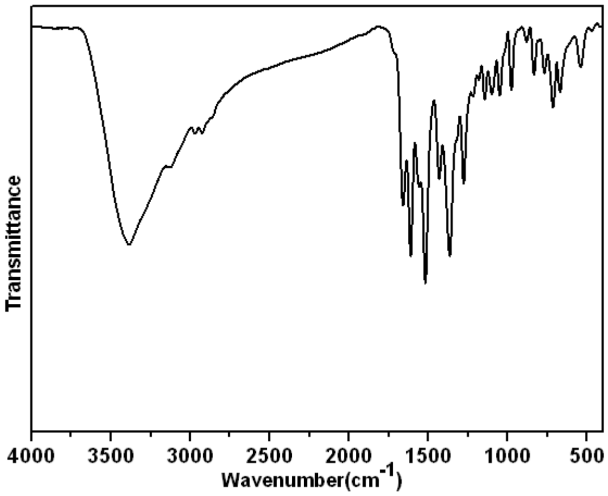


Fig S15. IR spectra of complex **1**

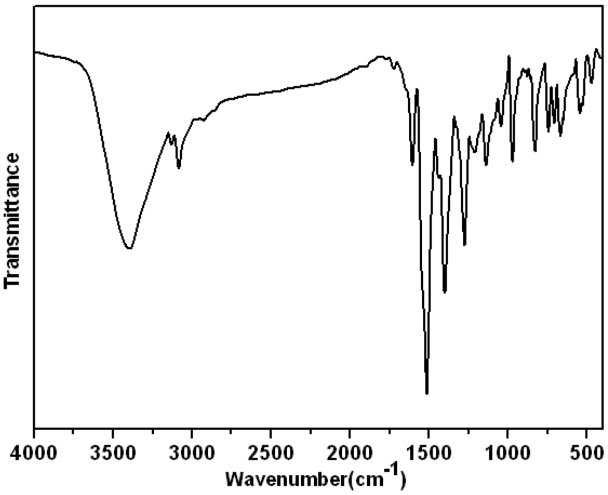


Fig S16. IR spectra of complex **2**

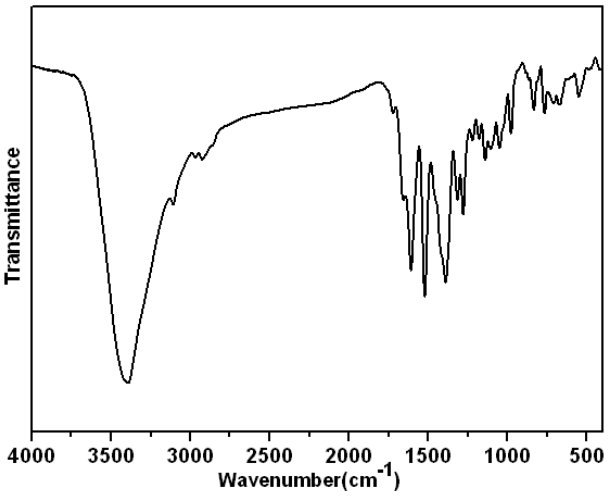


Fig S17. IR spectra of complex **3**

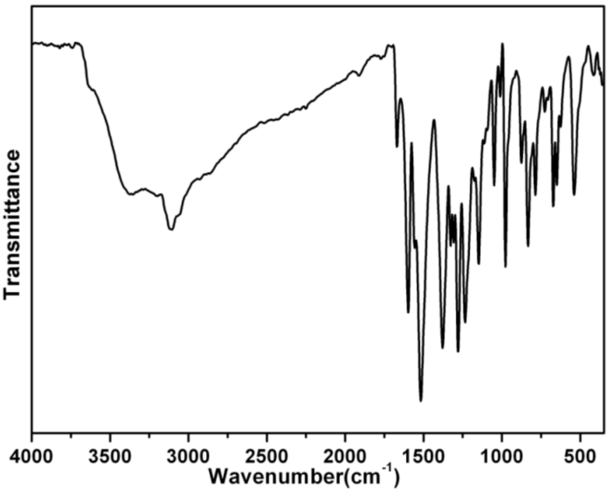


Fig S18. IR spectra of complex **4**

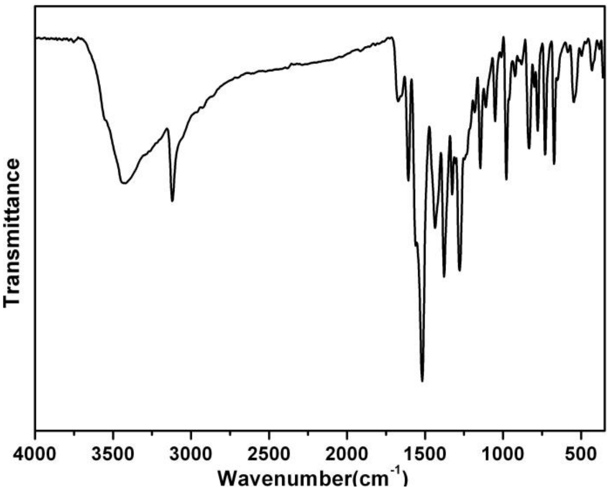


Fig S19. IR spectra of complex **5**

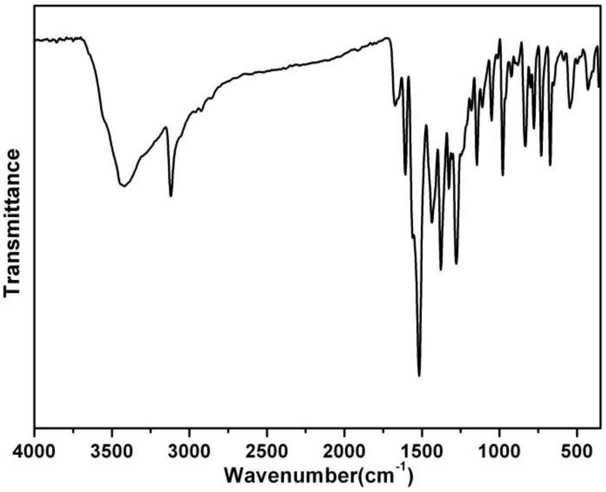


Fig S20. IR spectra of complex **6**

Table S1. Selected bond lengths (Å) and angles (°) for complexes **1-6**

Complex **1**			
Co(1)-O(5)#1	2.0235(19)	Co(2)-O(4)	2.0744(19)
Co(1)-O(6)#2	2.051(2)	Co(2)-O(4)#4	2.0744(19)
Co(1)-N(1)	2.121(3)	Co(2)-N(7)#5	2.120(3)
Co(1)-N(8)#3	2.131(3)	Co(2)-N(7)#6	2.120(3)
Co(1)-O(2)	2.164(2)	Co(2)-O(7)	2.138(3)
Co(1)-O(1)	2.224(2)	Co(2)-O(7)#4	2.138(3)
O(5)#1-Co(1)-O(6)#2	108.22(8)	O(4)-Co(2)-O(4)#4	180.000(1)
O(5)#1-Co(1)-N(1)	89.78(9)	O(4)-Co(2)-N(7)#5	89.74(10)
O(6)#2-Co(1)-N(1)	86.47(10)	O(4)#4-Co(2)-N(7)#5	90.26(10)
O(5)#1-Co(1)-N(8)#3	90.05(9)	O(4)-Co(2)-N(7)#6	90.26(10)
O(6)#2-Co(1)-N(8)#3	93.27(9)	O(4)#4-Co(2)-N(7)#6	89.75(10)
N(1)-Co(1)-N(8)#3	179.63(10)	N(7)#5-Co(2)-N(7)#6	179.997(1)
O(5)#1-Co(1)-O(2)	98.90(8)	O(4)-Co(2)-O(7)	93.02(9)
O(6)#2-Co(1)-O(2)	152.87(8)	O(4)#4-Co(2)-O(7)	86.98(9)
N(1)-Co(1)-O(2)	93.00(9)	N(7)#5-Co(2)-O(7)	89.84(11)
N(8)#3-Co(1)-O(2)	87.35(9)	N(7)#6-Co(2)-O(7)	90.17(11)
O(5)#1-Co(1)-O(1)	158.42(8)	O(4)-Co(2)-O(7)#4	86.98(9)
O(6)#2-Co(1)-O(1)	92.97(8)	O(4)#4-Co(2)-O(7)#4	93.02(9)
N(1)-Co(1)-O(1)	87.42(9)	N(7)#5-Co(2)-O(7)#4	90.17(11)
N(8)#3-Co(1)-O(1)	92.87(9)	N(7)#6-Co(2)-O(7)#4	89.83(11)
O(2)-Co(1)-O(1)	59.93(7)	O(7)-Co(2)-O(7)#4	179.998(1)
Complex **2**			
Co(1)-O(2)	2.035(3)	Co(1)-N(1)	2.091(3)
Co(1)-O(3)#1	2.064(3)	Co(1)-O(4)#1	2.226(2)
Co(1)-N(4)	2.089(3)	Co(1)-O(1)	2.332(2)

O(2)-Co(1)-O(3)#1	107.16(11)	N(4)-Co(1)-O(4)#1	89.01(10)
O(2)-Co(1)-N(4)	103.99(12)	N(1)-Co(1)-O(4)#1	87.47(10)
O(3)#1-Co(1)-N(4)	140.35(11)	O(2)-Co(1)-O(1)	59.52(9)
O(2)-Co(1)-N(1)	91.18(11)	O(3)#1-Co(1)-O(1)	89.36(9)
O(3)#1-Co(1)-N(1)	106.45(11)	N(4)-Co(1)-O(1)	85.78(10)
N(4)-Co(1)-N(1)	96.72(11)	N(1)-Co(1)-O(1)	150.09(10)
O(2)-Co(1)-O(4)#1	167.00(11)	O(4)#1-Co(1)-O(1)	122.43(9)
O(3)#1-Co(1)-O(4)#1	61.03(9)		

Complex **3**

Co(1)-N(4)#1	2.109(2)	Co(1)-O(3)	2.140(2)
Co(1)-N(7)#2	2.121(3)	Co(1)-O(1)	2.186(2)
Co(1)-N(1)	2.126(3)	Co(1)-O(2)	2.228(2)
N(4)#1-Co(1)-N(7)#2	95.40(11)	N(1)-Co(1)-O(1)	85.64(9)
N(4)#1-Co(1)-N(1)	91.50(10)	O(3)-Co(1)-O(1)	127.88(11)
N(7)#2-Co(1)-N(1)	173.07(10)	N(4)#1-Co(1)-O(2)	90.56(9)
N(4)#1-Co(1)-O(3)	82.36(11)	N(7)#2-Co(1)-O(2)	89.11(10)
N(7)#2-Co(1)-O(3)	90.53(11)	N(1)-Co(1)-O(2)	91.45(10)
N(1)-Co(1)-O(3)	89.77(11)	O(3)-Co(1)-O(2)	172.84(10)
N(4)#1-Co(1)-O(1)	149.53(10)	O(1)-Co(1)-O(2)	59.26(8)
N(7)#2-Co(1)-O(1)	88.72(10)		

Complex **4**

Co(1)-O(2W)	2.041(4)	Co(2)-O(6)	2.039(3)
Co(1)-O(1)	2.064(4)	Co(2)-O(3W)	2.097(3)
Co(1)-O(1W)	2.094(4)	Co(2)-N(24)#3	2.122(5)
Co(1)-N(5)#1	2.132(4)	Co(2)-N(27)#4	2.153(4)
Co(1)-N(1)	2.143(5)	Co(2)-N(21)	2.176(5)
Co(1)-N(9)#2	2.159(5)	Co(2)-N(11)	2.198(4)

O(2W)-Co(1)-O(1)	176.97(17)	O(6)-Co(2)-O(3W)	173.79(16)
O(2W)-Co(1)-O(1W)	92.29(16)	O(6)-Co(2)-N(24)#3	100.12(16)
O(1)-Co(1)-O(1W)	90.66(15)	O(3W)-Co(2)-N(24)#3	85.60(16)
O(2W)-Co(1)-N(5)#1	93.64(16)	O(6)-Co(2)-N(27)#4	84.70(14)
O(1)-Co(1)-N(5)#1	83.47(15)	O(3W)-Co(2)-N(27)#4	92.88(14)
O(1W)-Co(1)-N(5)#1	173.05(16)	N(24)#3-Co(2)-N(27)#4	90.25(16)
O(2W)-Co(1)-N(1)	87.74(17)	O(6)-Co(2)-N(21)	87.63(15)
O(1)-Co(1)-N(1)	91.36(18)	O(3W)-Co(2)-N(21)	86.62(15)
O(1W)-Co(1)-N(1)	93.52(18)	N(24)#3-Co(2)-N(21)	172.18(16)
N(5)#1-Co(1)-N(1)	90.35(17)	N(27)#4-Co(2)-N(21)	89.38(16)
O(2W)-Co(1)-N(9)#2	86.81(18)	O(6)-Co(2)-N(11)	93.71(14)
O(1)-Co(1)-N(9)#2	94.20(18)	O(3W)-Co(2)-N(11)	88.21(14)
O(1W)-Co(1)-N(9)#2	84.41(18)	N(24)#3-Co(2)-N(11)	94.71(16)
N(5)#1-Co(1)-N(9)#2	92.29(17)	N(27)#4-Co(2)-N(11)	175.00(19)
N(1)-Co(1)-N(9)#2	174.08(18)	N(21)-Co(2)-N(11)	85.81(16)
Complex **5**			
Co(1)-O(4)#1	2.050(2)	Co(1)-O(2)	2.140(3)
Co(1)-O(1W)	2.084(2)	Co(1)-N(1)	2.143(2)
Co(1)-N(4)#2	2.128(3)	Co(1)-O(1)	2.289(2)
O(4)#1-Co(1)-O(1W)	123.52(10)	N(4)#2-Co(1)-O(2)	87.07(10)
O(4)#1-Co(1)-N(4)#2	88.43(11)	N(1)-Co(1)-O(2)	91.81(10)
O(1W)-Co(1)-N(4)#2	93.35(11)	O(4)#1-Co(1)-O(1)	150.60(9)
O(4)#1-Co(1)-N(1)	89.75(10)	O(1W)-Co(1)-O(1)	85.69(10)
O(1W)-Co(1)-N(1)	88.65(10)	N(4)#2-Co(1)-O(1)	93.44(11)
N(4)#2-Co(1)-N(1)	177.82(10)	N(1)-Co(1)-O(1)	87.57(10)
O(4)#1-Co(1)-O(2)	91.97(9)	O(2)-Co(1)-O(1)	58.89(9)
O(1W)-Co(1)-O(2)	144.51(10)		

Complex **6**			
Co(1)-O(4)#1	2.041(2)	Co(1)-N(7)#2	2.135(3)
Co(1)-O(5)	2.081(3)	Co(1)-O(2)	2.156(3)
Co(1)-N(4)	2.128(3)	Co(1)-O(1)	2.269(2)
O(4)#1-Co(1)-O(5)	120.64(11)	N(4)-Co(1)-O(2)	87.42(11)
O(4)#1-Co(1)-N(4)	88.29(11)	N(7)#2-Co(1)-O(2)	90.81(11)
O(5)-Co(1)-N(4)	93.81(12)	O(4)#1-Co(1)-O(1)	151.72(10)
O(4)#1-Co(1)-N(7)#2	89.85(11)	O(5)-Co(1)-O(1)	87.52(11)
O(5)-Co(1)-N(7)#2	88.74(11)	N(4)-Co(1)-O(1)	92.71(12)
N(4)-Co(1)-N(7)#2	177.36(11)	N(7)#2-Co(1)-O(1)	88.04(11)
O(4)#1-Co(1)-O(2)	92.96(10)	O(2)-Co(1)-O(1)	58.89(9)
O(5)-Co(1)-O(2)	146.40(11)		

Symmetry codes: #1: − *x* + 2, − *y* + 1, − *z* + 1; #2: *x* − 1, *y*, *z*; #3: *x*, *y*, *z* + 1; #4; − *x* + 3, − *y*,− *z* + 1; #5: − *x* + 3, − *y* + 1, − *z*; #6: *x*, *y* − 1, *z* + 1 for **1**; #1: *x* − 1/2, − *y* + 3/2, − *z* + 2 for **2**; #1: − *x*, *y* + 1,– *z* + 1/2; #2: *x* + 1/2, − *y* + 3/2, *z* + 1/2 for **3**; #1: *x*, *y* + 1, *z*; #2: *x*, *y* + 1, *z* + 1; #3: *x*, *y* − 1, *z* – 1; #4: *x*, *y* − 1, *z* for **4**; #1: *x* + 1, *y*, *z*; #2: *x*, *y* − 1, *z* − 1 for **5**; #1: *x* − 1, *y*, *z*; #2: *x*, *y* − 1, *z* − 1 for **6**.

Table S2. Hydrogen bonding distances (Å) and angles (°) for complexes **1** and **3-6**

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
Complex **1**				
O(7)-H(7A)···O(3)	0.96	2.23	2.688	108.02
O(7)-H(7B)···O(8) #10	0.96	2.41	2.996	118.93
O(8)-H(8A)···O(1)	0.85	2.02	2. 865	179.88
O(8)-H(8B)···O(7) #10	0.85	2.50	2.996	118.40
O(9)-H(9A)···O(3)	0.85	1.86	2.709	179.40
O(9)-H(9B)···O(8)	0.85	2.03	2.713	137.04
Complex **3**				
O1W-H1WA···O1	0.85	1.97	2.821	179.40

O1W-H1WB···O2#6	0.85	2.10	2.862	149.26
Complex **4**				
O1W-H1WB···O2	0.85	1.99	2.640	132.37
O1W-H1WC···O4W#2	0.85	1.88	2.671	154.91
O2W-H2WA···O4#5	0.85	1.97	2.598	130.18
O2W-H2WC···O8#1	0.85	1.86	2.643	152.71
O3W-H3WA···O3#4	0.85	2.09	2.693	118.10
O3W-H3WB···O9#6	0.85	1.66	2.634	173.83
O4W-H4WD···O7	0.85	1.98	2.832	179.78
O4W-H4WC···O3#7	0.85	2.24	2.773	121.22
Complex **5**				
O1W-H1WA···O3#1	0.85	2.53	3.054	121.25
O1W-H1WB···O3#6	0.85	2.11	2.692	125.82
O2W-H2WB···O1	0.85	1.99	2.795	157.32
Complex **6**				
O5-H(5A)···O3#1	0.85	2.50	3.045	122.30
O5-H(5B)···O3#6	0.85	2.11	2.700	126.68
O6-H(6A)···O1#7	0.85	2.43	2.819	108.23
O6-H(6B)···O1#8	0.85	2.25	2.936	138.29

Symmetry codes: #10: $-x+2, -y, -z+1$ for **1**; #6: $-x+1/2, y-1/2, -z+1/2$ for **3**; #1: $x, y+1, z$; #2: $x, y+1, z+1$; #4: $x, y-1, z$; #5: $x+1, y, z+1$; #6: $x-1, y, z-1$; #7: $x+1, y-1, z$ for **4**; #1: $x+1, y, z$; #6: $-x, -y+1, z+1$ for **5**; #1: $x-1, y, z$; #5: $-x+2, y, -z+1$; #6: $x-1, y+1, z$; #7: $-x+1, -y+1, -z+1$ for **6**.

Table S3. Crystal structure affected by organic ligands in complexes **1-6**

complex	**Connectivity of TTPA**	**Connectivity of aromatic carboxylate**	**dimensions**	**topology**
1	3	3	3D	new topology
2	2	2	3D	**dia**
3	3	2	3D	**fsc**
4	3 / 1	1	3D stacked by 2D	**hcb**
5	2	2	3D stacked by 2D	**sql**
6	2	2	3D stacked by 2D	**sql**

References

S1. X. Q. Yao, D. P. Cao, J. S. Hu, Y. Z. Li, Z. J. Guo, H. G. Zheng, *Cryst. Growth Des.* 2011, **11**, 231.

S2. Bruker 2000, SMART (Version 5.0), SAINT-plus (Version 6), SHELXTL(Version 6.1), and SADABS (Version 2.03); Bruker AXS Inc.: Madison, WI.