Dinuclear Cobalt Complexes with Redox Active Biphenyl Bridging Ligand $[Co_2(BP)(tqa)_2](PF_6)_2$ (H_4BP = 4,4'-*bis*(3-*tert*-butyl-1,2-catechol), tqa = *tris*(2-quinolylmethyl)amine): Structure and Magnetic Properties

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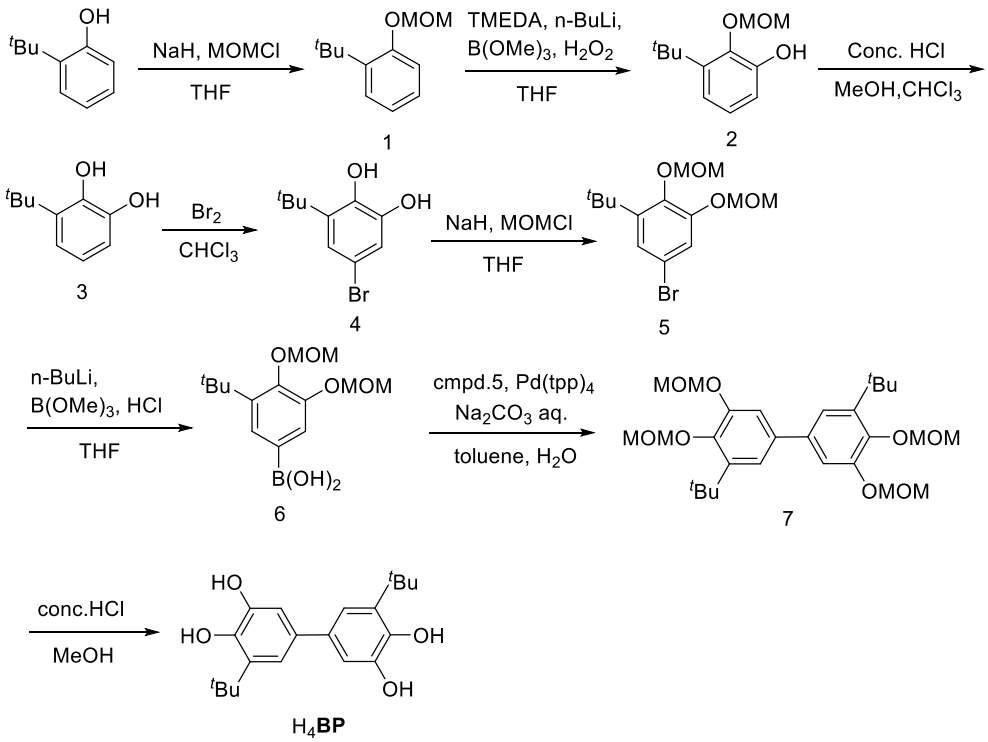
Experimental

Synthesis H_4BP:



Scheme S1 Synthesis of H_4BP

Synthesis of 4,4'-*bis*(3-*tert*-butyl-1,2-catechol) (H_4BP)

*Bis*catechol (H_4BP) was synthesized according to Scheme S1. Toluene (40 mL) solution of *tetrakis*(triphenylphosphine)palladium(0) (1 mol%, 58.69 mg) and compound **5**[1] (1.693 g, 5.08 mmol) was added to the water/ethanol (10/40 mL)

solution of sodium carbonate (21.0 mmol, 2.226 g) and compound **6** (1.281 g, 4.29 mmol) under an Ar atmosphere. The resultant solution was stirred and refluxed at 110°C overnight. The reaction mixture was cooled to room temperature and filtered. The obtained solution was extracted by toluene (50 mL×3) and washed by brine solution (100 mL×1). The obtained organic layer was dried over with sodium sulfate and concentrated under vacuum. The resultant crude product was purified by column chromatography (silica gel: 250 mL, hexane: ethyl acetate = 10:1→ 3:1) and compound **7** was obtained as orange oil (1.444 g, 2.85 mmol, yields 68%).

Compound **7** (1.444 g, 2.85 mmol) was dissolved in methanol (30 mL) in a 100 mL flask. Conc. HCl (2 mL) was added and stirred for 3 hours at room temperature. After that, saturated $NaHCO_3$ aq. (50 mL) was added. This solution was extracted with diethyl ether (50 mL). This obtained water phase was neutralized used 1M-HCl and extracted with diethyl ether 50 mL and combined former obtained organic phase. The combined organic phase was washed with brine solution (100 mL) and dried over with Na_2SO_4 and concentrated under reduced pressure. Obtained brown powder washed with hexane (100 mL), so H_4BP was obtained as pale brown powder without further purification (0.641 g, 1.96 mmol, yields 69%). ^{1}H-NMR (400 MHz, CD_3OD, ppm, Figure S1) 1.41(s, 9H), 6.82(d, 1H), 6.84(d, 1H).

(Reference)

1. Y. Suenaga, Y. Umehata, Y. Hirano, T. Minematsu, C. G. Pierpont, *Inorg. Chim. Acta*, 2008, **361**, 2941-2949.

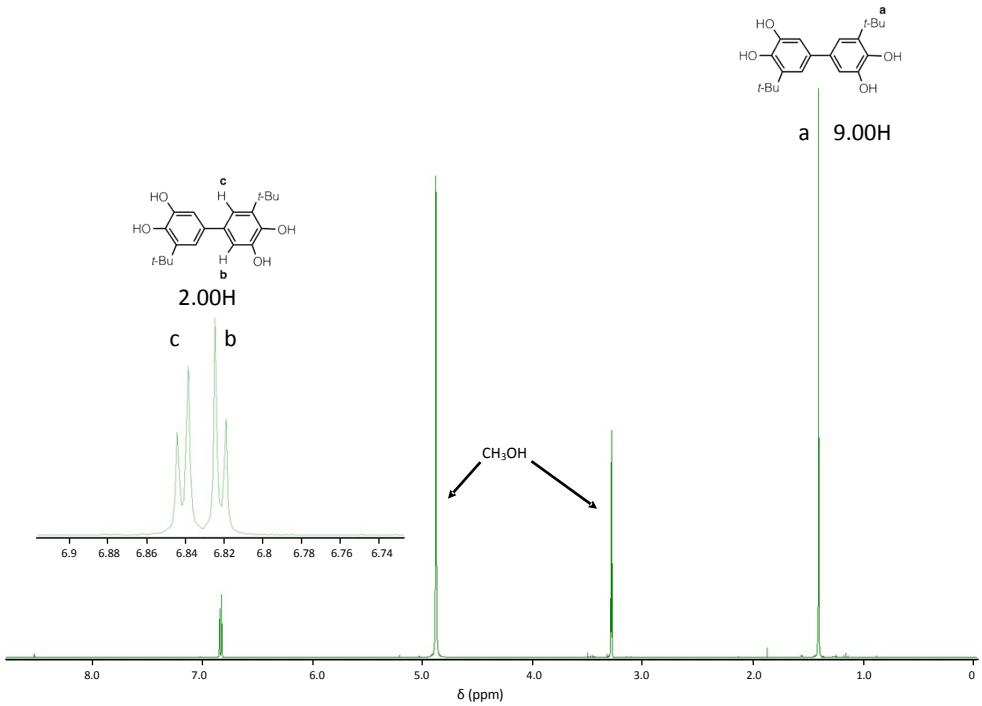


Figure S1. ^{1}H-NMR spectrum in CD_3OD of H_4BP

ESI-MS of $[Co_2(BP)(tpa)_2](PF_6)_2$ (1):

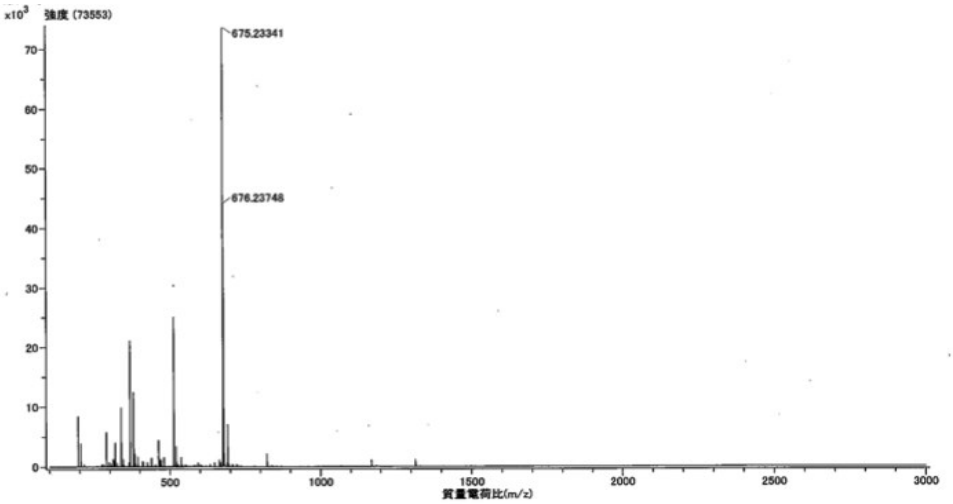


Figure S2. ESI-MS spectrum of $[Co_2(BP)(tpa)_2](PF_6)_2$ (1)

ESI-MS of $[Co_2(BP)(tpa)_2](PF_6)_3$ (2):

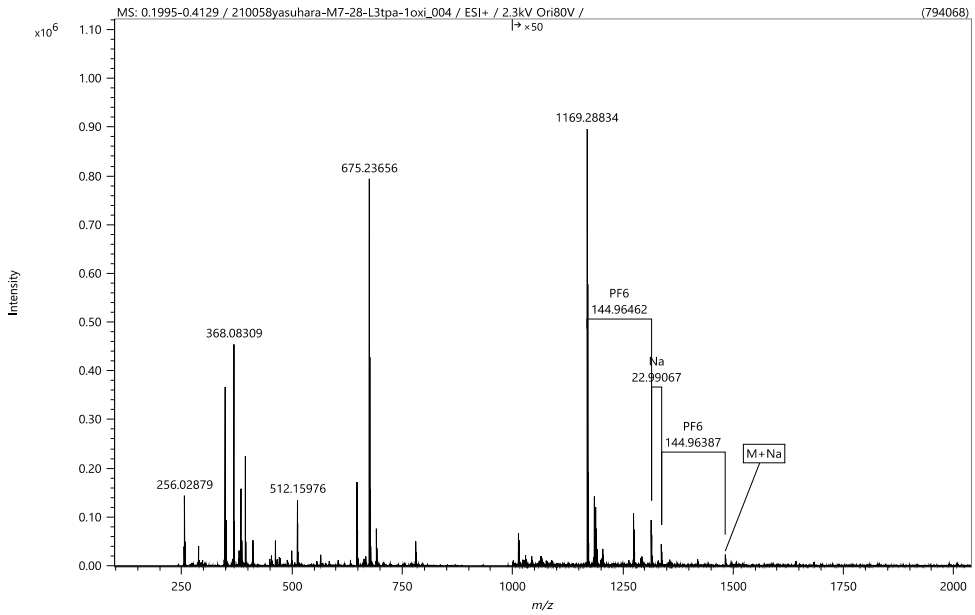


Figure S3. ESI-MS spectrum of $[Co_2(BP)(tpa)_2](PF_6)_3$ (2)

ESI-MS of $[Co_2(BP)(bpqa)_2](PF_6)_2$ (3):

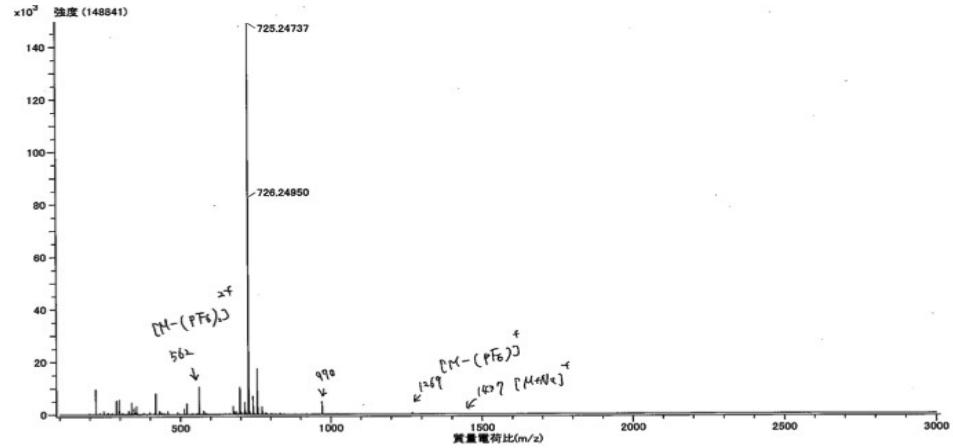


Figure S4. ESI-MS spetrum of $[Co_2(BP)(bpqa)_2](PF_6)_2$ (3)

ESI-MS of $[Co_2(BP)(pbqa)_2](PF_6)_2$ (4):

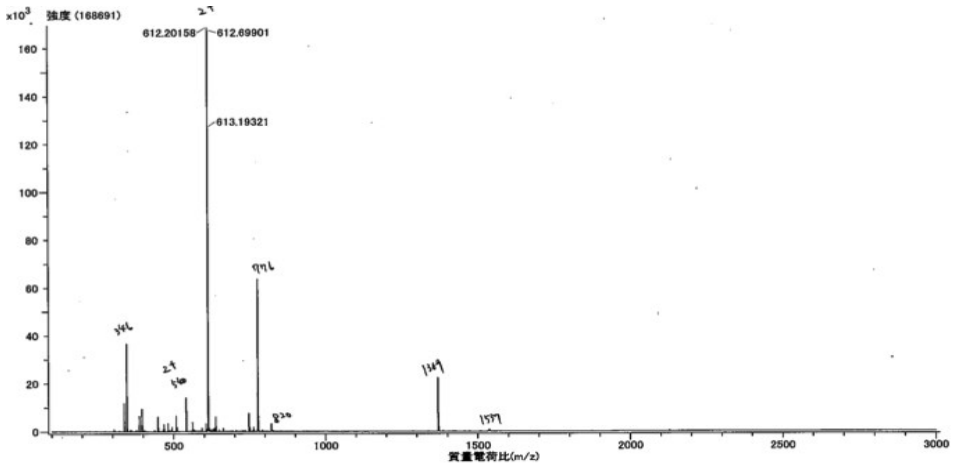


Figure S5. ESI-MS spectrum of $[Co_2(BP)(pbqa)_2](PF_6)_2$ (4)

ESI-MS of $[Co_2(BP)(tqa)_2](PF_6)_2$ (5):

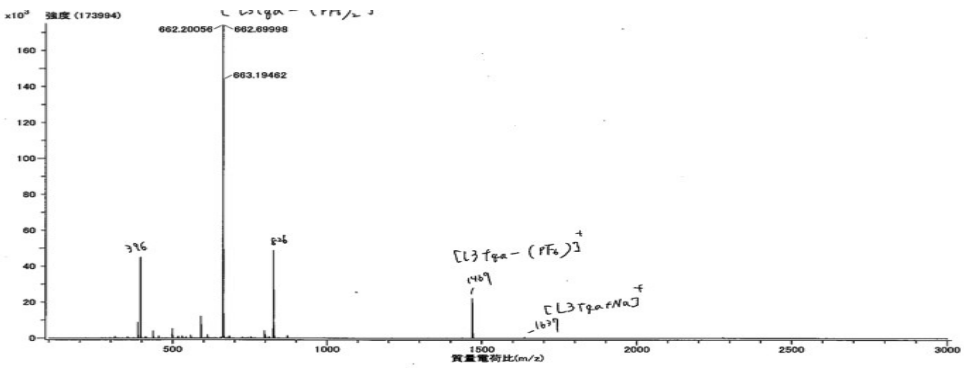


Figure S6. ESI-MS spectrum of $[Co_2(BP)(tqa)_2](PF_6)_2$ (5)

IR spectra

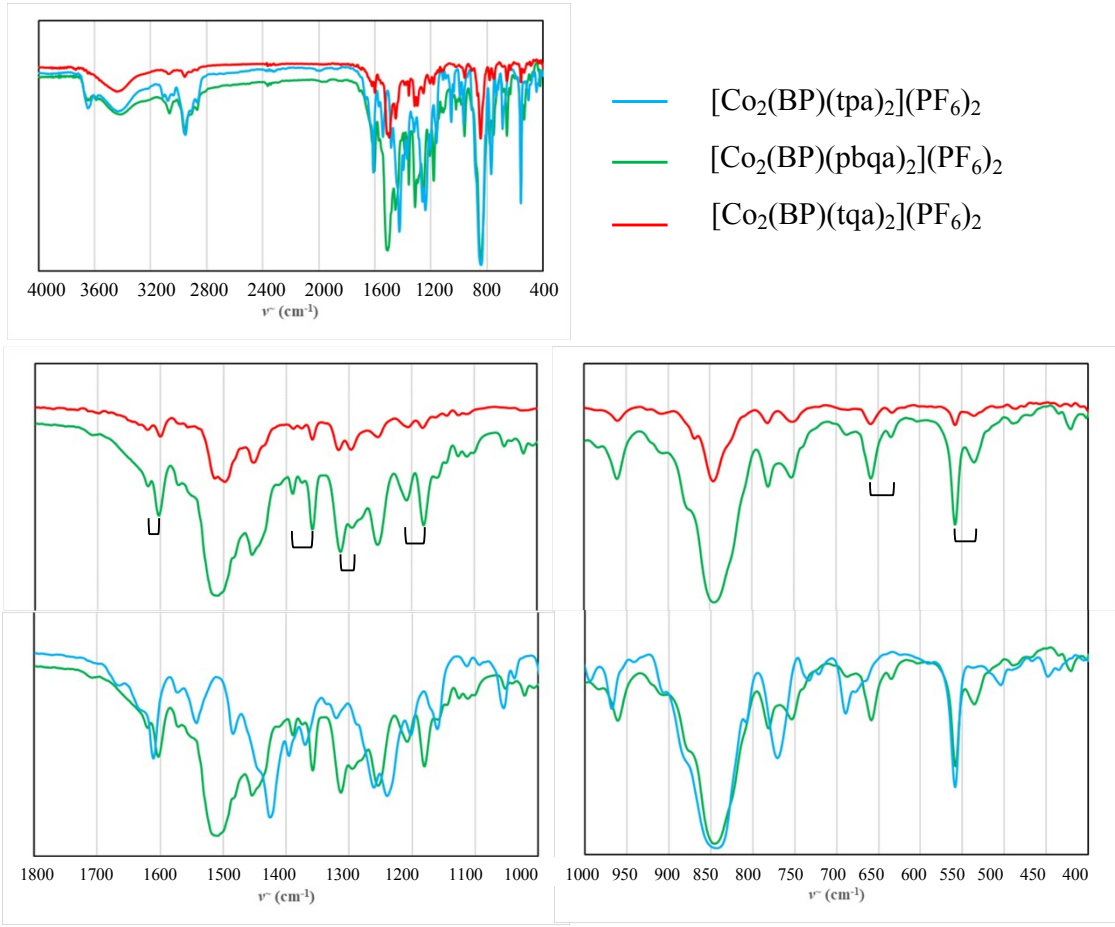


Figure S7. IR spectra of dinuclear Co comolexes.

UV-Vis-NIR spectra

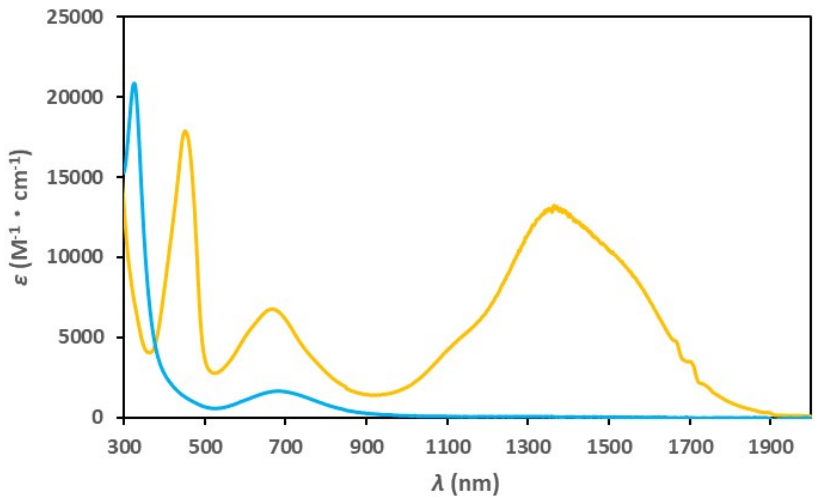


Figure S8. UV-Vis-NIR spectra of dinuclear Co complexes. blue line: $[Co_2(BP)(tpa)_2](PF_6)_2$ (1), yellow line: $[Co_2(BP)(tpa)_2](PF_6)_3$ (2) in acetonitrile solution at room temperature.

EPR spectrum for complex (2)

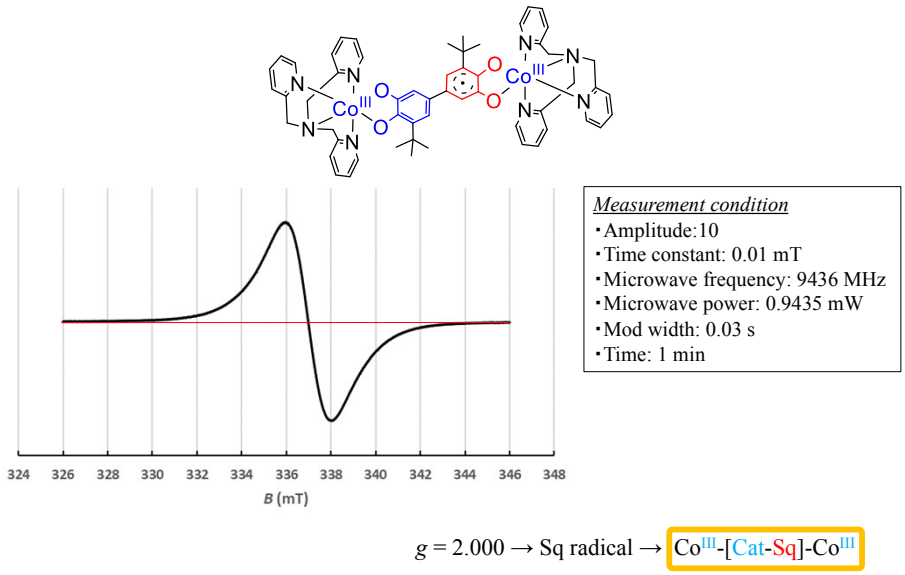


Figure S9. EPR spectrum of $[Co_2(BP)(tpa)_2](PF_6)_3$ (2) at room temperature.

IVCT parameters

Table S1. Mixed-valence and IVCT parameters for complex (2)

	$\Delta diox$	H_{AB1}	H_{AB2}	H_{AB3} limit	$2H_{AB1}/\nu_{max}$	$2H_{AB2}/\nu_{max}$	Γ	MV Class
	mV	cm^{-1}	cm^{-1}	cm^{-1}				
Complex (2)	377	1218	362	3645	0.33	0.10	0.47	II-III
Complex (5a)*)	175	184	1990	2820	0.07	0.71	-0.85	II-III
Pd complex**)	365	1530	3290	3710	>0.41	0.89	0.52	II-III

*) G. K. Gransbury, *et al.*, *J. Am. Chem. Soc.*, 2020, **142**, 10692-10704.

**) A. L. Poddel'sky, *et al., Russ. J. Coord. Chem.*, 2012, 38, 284-294.

Analysis of verious temperatute in UV-Vis-NIR spectra

The thermal variation of the fraction of *hs*Co^{II}(Sq) species determined by spectral deconvolution appears to sigmoidal profile (Figure S10).

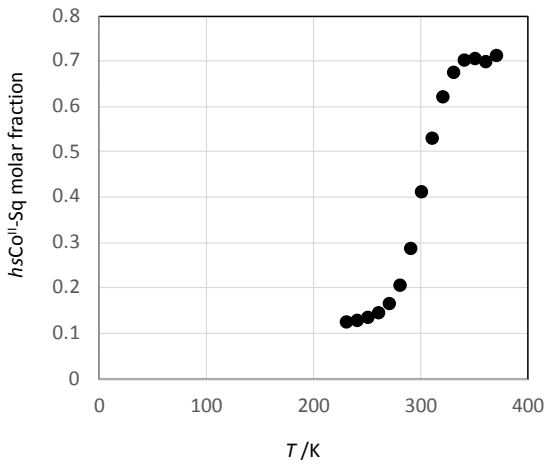


Figure S10. Temperature dependence of the molar fraction of *hs*Co^{II}-Sq for $[Co_2(BP)(bpqa)_2](PF_6)_2$ (3).

Cyclic voltammetry

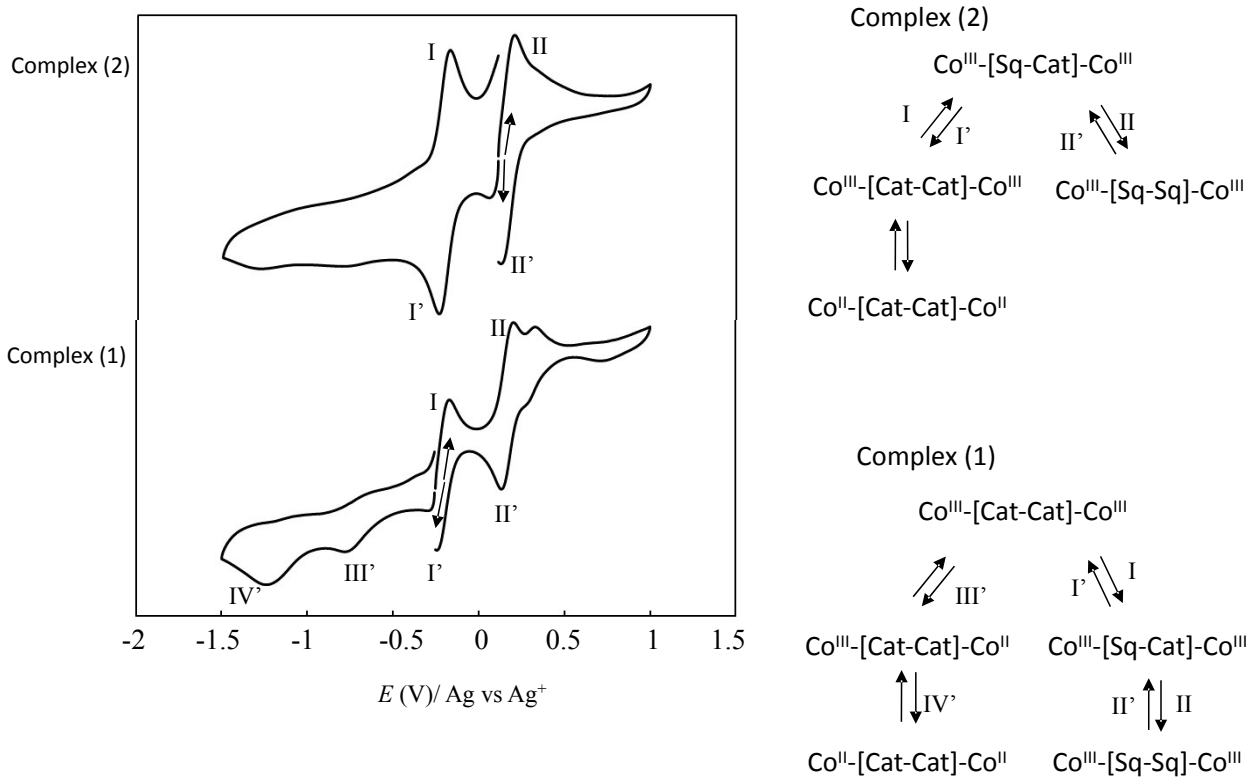


Figure S11. Cyclic voltammogram of complex(1) and (2) in acetonitrile solution at room temperature.

Table S2. Cyclic voltammetry for dinuclear Co complexes in CH_3CN

Complex	Rest potential /V	$E_{1/2}$ (V)/ΔE_p(mV)			
		I/I'	II/II'	III'	IV'
(1)	-0.25	-0.194 (73)	0.169 (54)	～-0.8	～-1.3
(2)	0.108	-0.203 (68)	0.174 (85)	–	–

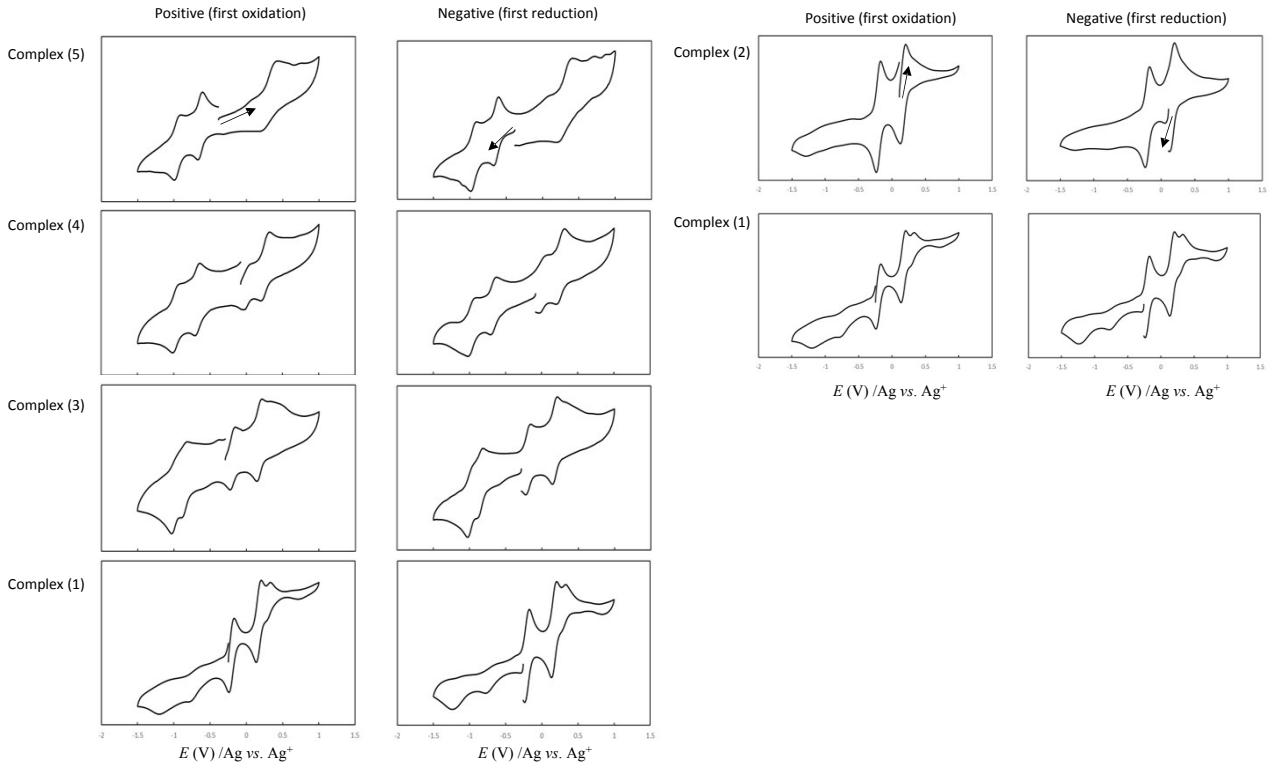


Figure S12. Cyclic voltammerty of these complexes in acetonitrile at room temperature.

Crystallography

Table S3. Crystallographic data for $[Co_2(BP)(tqa)_2](PF_6)_2$ (5) and $[Co_2(BP)(pbqa)_2](PF_6)_2$ (4)

	$[Co_2(BP)(tqa)_2](PF_6)_2$ (5)	$[Co_2(BP)(pbqa)_2](PF_6)_2$ (4)
Chemical formula	$C_{80}H_{70}Co_2N_8O_4F_{12}P_2 \cdot 3(C_3H_6O)$	$C_{72}H_{66}Co_2N_8O_4F_{12}P_2 \cdot 2(C_3H_6O)$
Formula weight	1963.70	1863.59
Crystal system	monoclinic	monoclinic
Space group	*P 21/m*	*P 21/m*
Lattice Parameters		
a/Å	9.2480(3)	9.1110(4)
b/Å	41.0134(12)	41.1206(10)
c/Å	12.2659(5)	12.1350(3)
β/°	103.376(4)	102.590(3)
Unit Cell Volume		
V/Å^3	4526.2(3)	4437.1(3)
Z	2	2
μ(Mo-Kα)/cm^{-1}	0.71073	0.71073
No. reflections measured	10397	10309
No. observed reflections	6921	8386
[$I > 2\sigma(I)$]		
R1	0.0636	0.1069
*WR*2	0.1717	0.2344
T/K	100	100
GOF	1.009	1.128
Max/Min residual electron densities	0.562/-0.529	0.709/-0.428
Measurement	Rigaku XtaLAB P200	Rigaku XtaLAB P200
Programs systems	SHELXL 2018	SHELXL 2018
Structure determination	Olex 2	Olex 2
CCDC deposition number	2067474	2067516

$R=\Sigma||Fo|-|Fc||/\Sigma|Fo|$, $Rw=[\Sigma\omega(Fo^2-Fc^2)^2/\Sigma\omega(Fo^2)^2]^{1/2}$

Table S4. Selected distances (Å) and angles (°) for $[Co_2(BP)(pbqa)_2](PF_6)_2$ (**4**)

Bond	Distances (Å)	Bond	Distances (Å)
Co1-O1	2.145(3)	**Co1-O2**	1.973(3)
Co1-N1	2.141(4)	**Co1-N2**	2.166(5)
Co1-N3	2.164(5)	**Co1-N4**	2.139(3)
C1-O2	1.300(6)	**C6-O1**	1.256(5)
C1-C2	1.380(6)	**C2-C3**	1.400(6)
C3-C4	1.436(6)	**C4-C5**	1.359(6)
C5-C6	1.446(6)	**C6-C1**	1.467(6)
Bond	**Angles (°)**	**Bond**	**Angles (°)**
O1-Co1-O2	79.3(1)	**O2-Co1-N4**	104.5 (1)
N4-Co1-N1	82.8(1)	**N1-Co1-O1**	93.3(1)
N2-Co1-N3	156.1(2)		

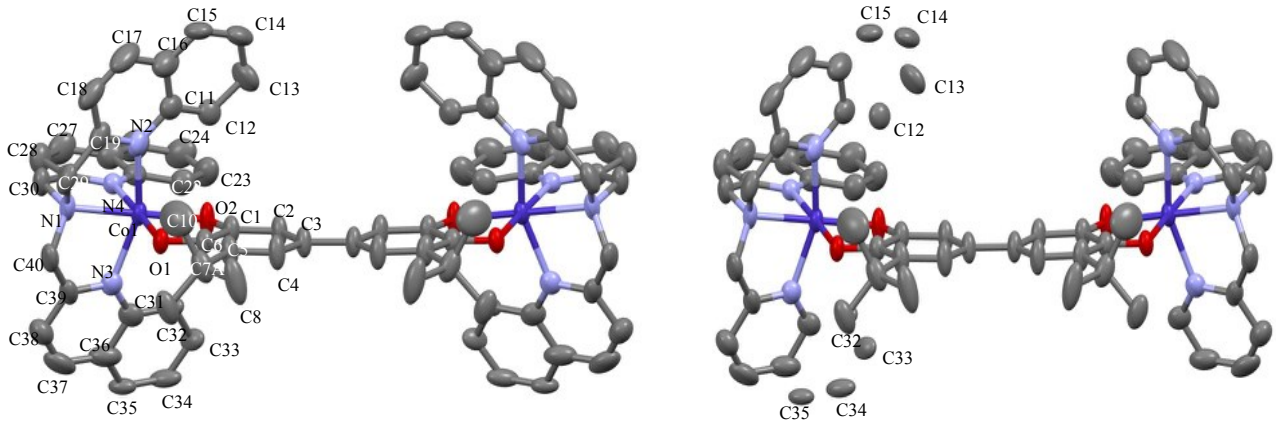


Figure S13. Perspective view of the complex cation in $[Co_2(BP)(pbqa)_2](PF_6)_2$ (**4**) showing 50% thermal ellipsoids. Hydrogen atoms and the PF_6 anions are omitted for the sake of clarity. Right: drawing the disorder axal quinoline rings (C12~C15 and C32~C35) due to structual rearrengement of complex.

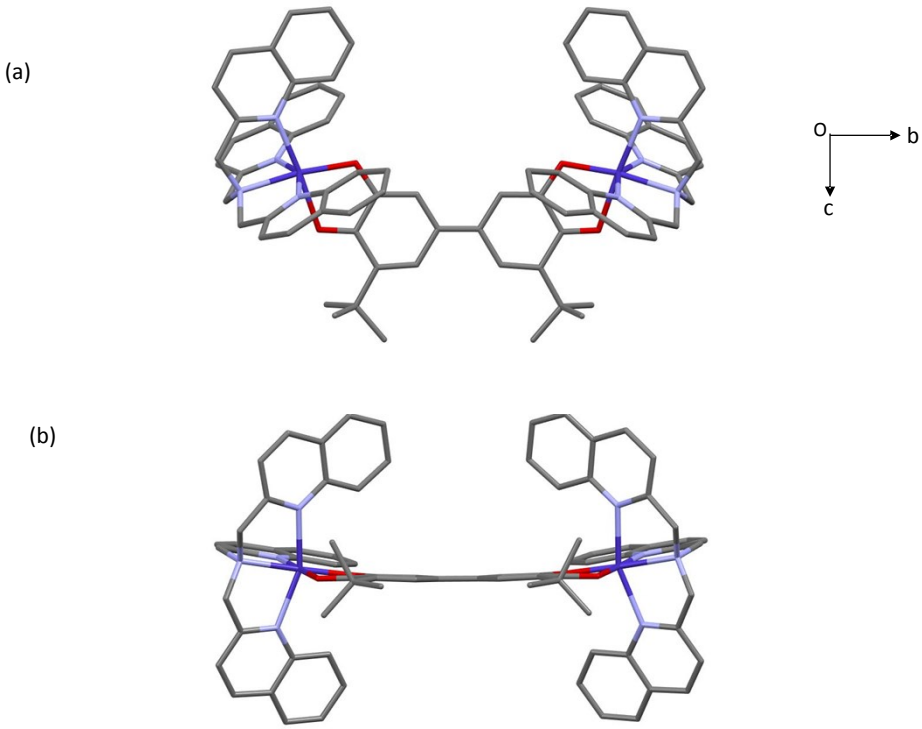


Figure S14. Crystal structure of $[Co_2(BP)(pbqa)_2](PF_6)_2$ (**4**). Hydrogen atoms and the PF_6 anions are omitted for the sake of clarity. (a) top view (b) side view.

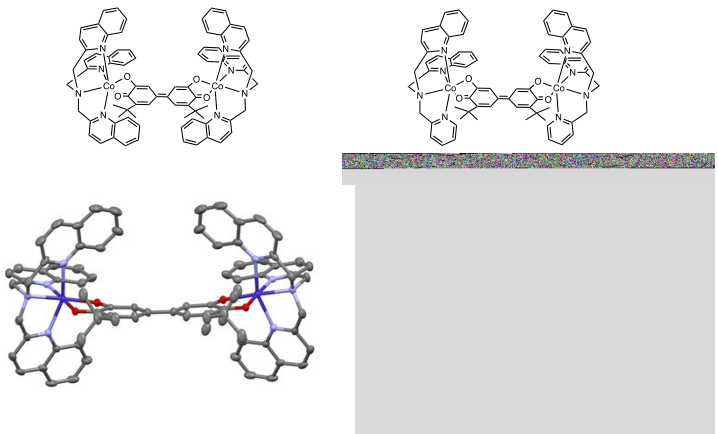


Figure S15. Compared of $[Co_2(BP)(tqa)_2](PF_6)_2$ (**5**) (left) and $[Co_2(BP)(pbqa)_2](PF_6)_2$ (**4**) (right).

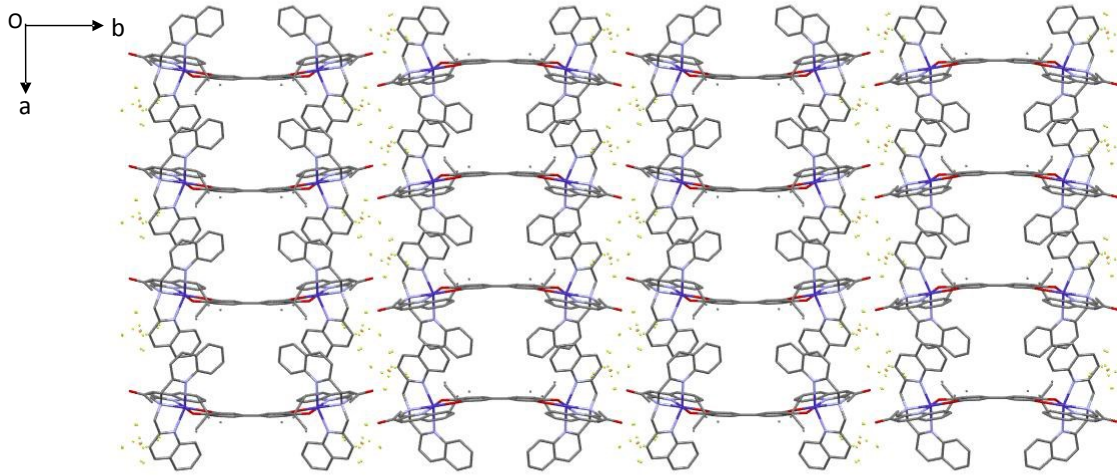


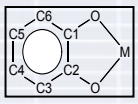
Figure S16. Crystal packing structure of $[Co_2(BP)(tqa)_2](PF_6)_2$ (**5**). The upper and lower bent di-nuclear cobalt complexes's structure layers are alternative arranged, and acetone and PF_6^- counter anions are pretend between the layers.

Metrical oxidation state (MOS) calculation

For complex (**4**), dioxolene C-C and C-O bond lengths are correlated to the ligand oxidation state, such that a least-squares fit enables assignment of an apparent metrical oxidation state (MOS, Brown). Catecholate ligands have a MOS of around -0.947 and are characterized as having shorter C-O bonds and longer C-C bonds. Complex (**4**) is assigned Co^{II}-[Sq-Sq]-Co^{II} in the solid state. To determine the Co oxidation state, we used the Co-O, Co-N_{amine}, and Co-N_{qn} bond lengths and octahedral distortion parameter. The calculated Σ index (98.3, $\Sigma = \sum_{i=1}^{12} |90 - \alpha_i|$ where α_i are the 12 *cis*-O/N-Co-O/N angles about the cobalt atom.) represents the distortion of a coordination environment from an ideal polyhedron. Co(II) has long metal-ligand bonds and distorted octahedral geometries compared to Co(III).

Table S5. MOS values for complex (4)

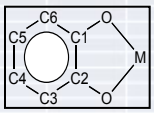
Instructions for using the Metrical Oxidation State Calculator:



Enter the measured bond distances in the appropriate columns C-G according to the numbering scheme at left.
The two C-O distances are averaged in cell C, the C2-C3 and C1-C6 distances are averaged in cell E, and the C3-C4 and C5-C6 distances are averaged in cell F.
Then enter a guess for the oxidation state of the ligand into column I. Copy the formulas from line 12, columns J-Q,
and use Solver to minimize the value in column O by varying the value in column I. The metrical oxidation state will be
in column I, and its esd in column Q.

Compound	Metal	C-O average	C1-C2	C2-C3 avg	C3-C4 avg	C4-C5	Calc. MOS	Calc C-O	Calc C1-C2	Calc C2-C3	Calc C3-C4	Calc C4-C5	sum of sqs	rmsd	esd
BEFXUF	Co II	1.278	1.467	1.413	1.3795	1.436	-0.9465749	1.2820923	1.46272441	1.42736454	1.36742924	1.43188427	0.00040401	0.00898899	0.08586416
pbqs	C1-O	1.3													
	C2-O	1.256													
	C2-C3	1.38													
	C3-C4	1.4													
	C4-C5	1.436													
	C5-C6	1.359													
	C1-C2	1.467													
	C1-C6	1.446													

Table S6. MOS values for complex (5)



Instructions for using the Metrical Oxidation State Calculator:

Enter the measured bond distances in the appropriate columns C-G according to the numbering scheme at left.
The two C-O distances are averaged in cell C, the C2-C3 and C1-C6 distances are averaged in cell E, and the C3-C4 and C5-C6 distances are averaged in cell F.
Then enter a guess for the oxidation state of the ligand into column I. Copy the formulas from line 12, columns J-Q,
and use Solver to minimize the value in column O by varying the value in column I. The metrical oxidation state will be
in column I, and its esd in column Q.

Compound	Metal	C-O average	C1-C2	C2-C3 avg	C3-C4 avg	C4-C5	Calc. MOS	Calc C-O	Calc C1-C2	Calc C2-C3	Calc C3-C4	Calc C4-C5	sum of sqs	rmsd	esd
BEFXUF	Co II	1.269	1.491	1.413	1.3855	1.437	-0.7799543	1.27052883	1.47493213	1.4331796	1.36362195	1.43963213	0.00115331	0.01518754	0.14106985
tqa	C1-O	1.293													
	C2-O	1.245													
	C2-C3	1.372													
	C3-C4	1.42													
	C4-C5	1.437													
	C5-C6	1.351													
	C1-C2	1.491													
	C1-C6	1.454													

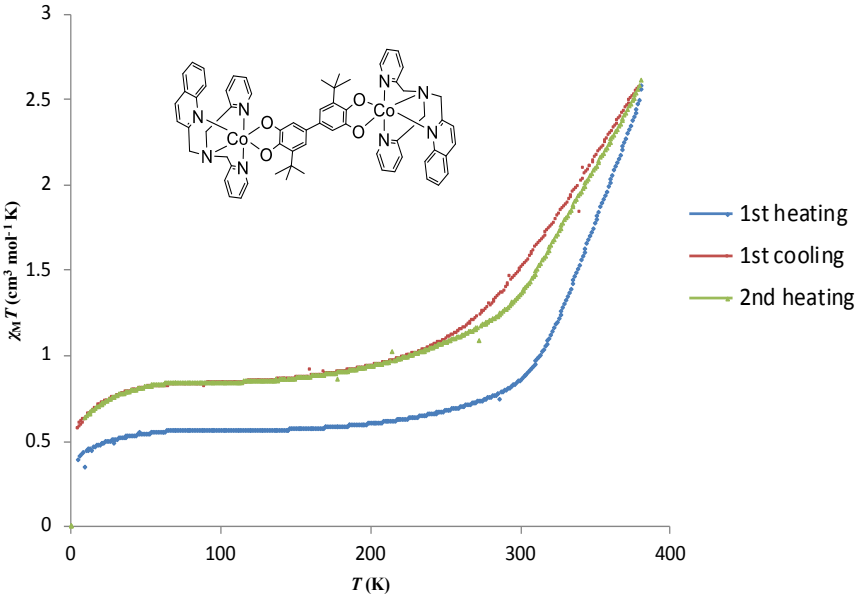


Figure S17. Magnetic susceptibility of $[Co_2(BP)(bpqa)_2](PF_6)_2$ (3). Repeated data for heating and coolimg for samples.