Electronic Supplementary Information

Synthesis, characterization and third order nonlinear optical properties of *trans*-A_2B-tpye cobalt corroles

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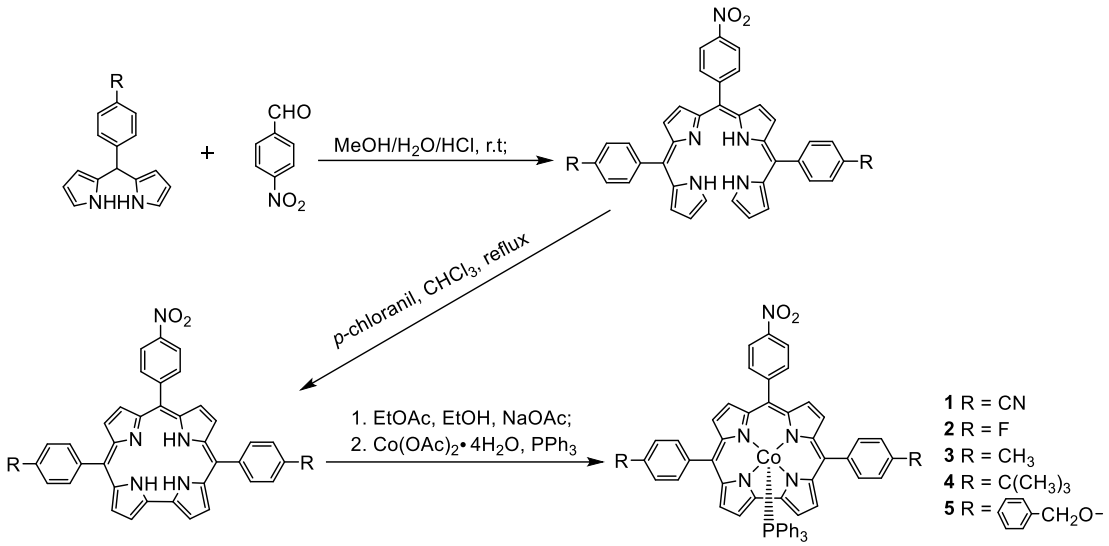
Materials. Reagents and solvents (Sinopharm or Aldrich) were of the highest grade available and were used without further purification, except for CH_2Cl_2, which was distilled under reduced pressure prior to use from P_2O_5. Tetra-n-butylammonium perchlorate (TBAP), as supporting electrolyte, was recrystallized from ethyl alcohol, and dried under vacuum at 40 °C for at least 1 week prior to use.

Physical Measurements. IR spectra (KBr pellets) were recorded on AVATAR-370 spectrometer. ^{1}HNMR spectra were recorded in a $CDCl_3$ solution at 400 MHz using a Bruker Advance 400 spectrometer at 25 ^{o}C. Chemical shifts (ppm) were determined with TMS as the internal reference. MALDI-TOF mass spectra were carried out on a Bruker BIFLEX III ultrahigh resolution Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometer with α-cyano-4-hydroxycinnamic acid as matrix. The fluorescence spectrum was recorded on a CaryEclipse fluoresence spectrophotometer.

Electrochemistry. Cyclic voltammetry was carried out at 298 K using a CHI-730C Electrochemical Workstation. A homemade three-electrode cell was used for cyclic voltammetric measurements and consisted of a glassy carbon working electrode, a platinum counter electrode and a homemade saturated calomel reference electrode (SCE). The SCE was separated from the bulk of the solution by a fritted glass bridge of low porosity which contained the solvent/supporting electrolyte mixture. All potentials are referenced to the SCE. High purity N_2 was used to deoxygenate the solution and a stream of nitrogen gas was kept over the solution during each electrochemical experiment.



Scheme S1. Synthetic route for compounds [Cor(*p*-RPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) **1-5**.

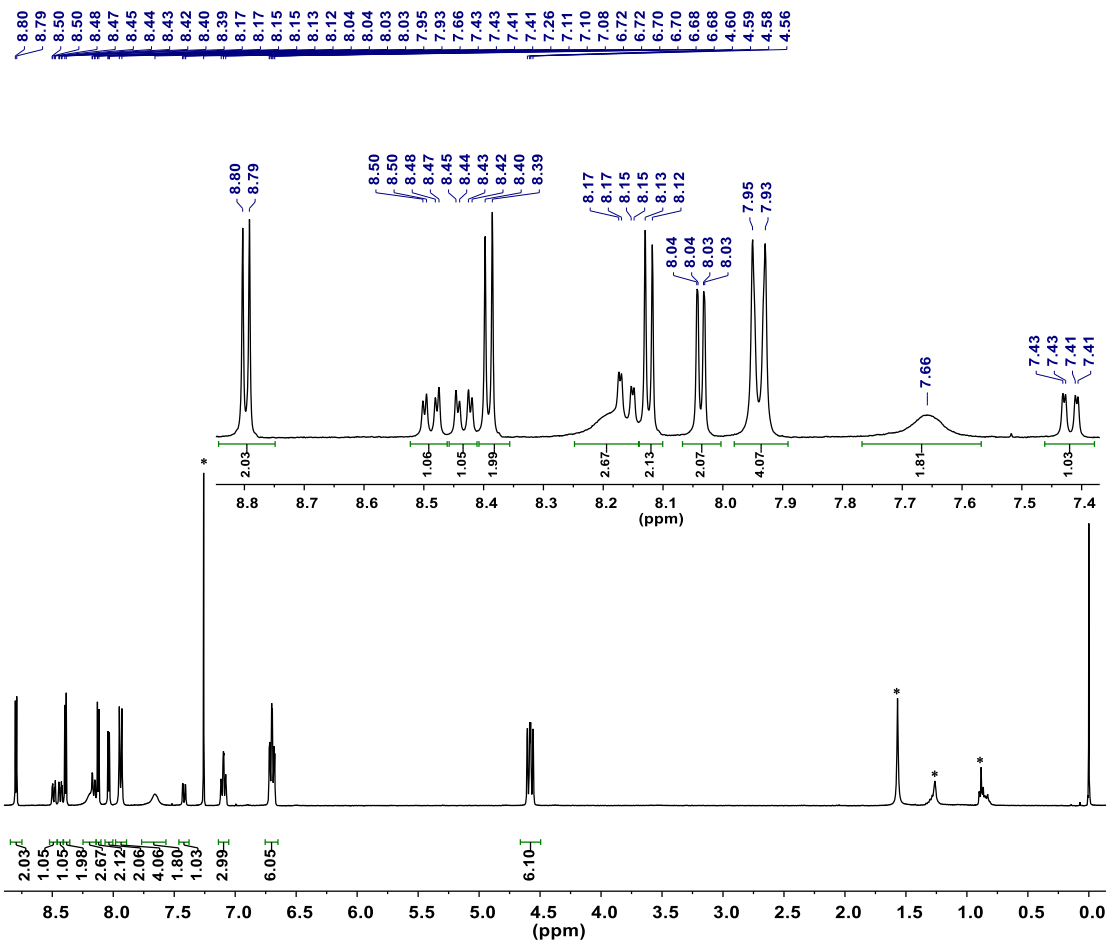


Fig. S1. ^{1}H NMR spectrum of [Cor(*p*-CNPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) (**1**) (* 7.26 ppm is the solvent peak of $CDCl_3$, 1.56 ppm is the peak of H_2O, 0.88 and 1.26 ppm are solvent peaks from *n*-hexane).

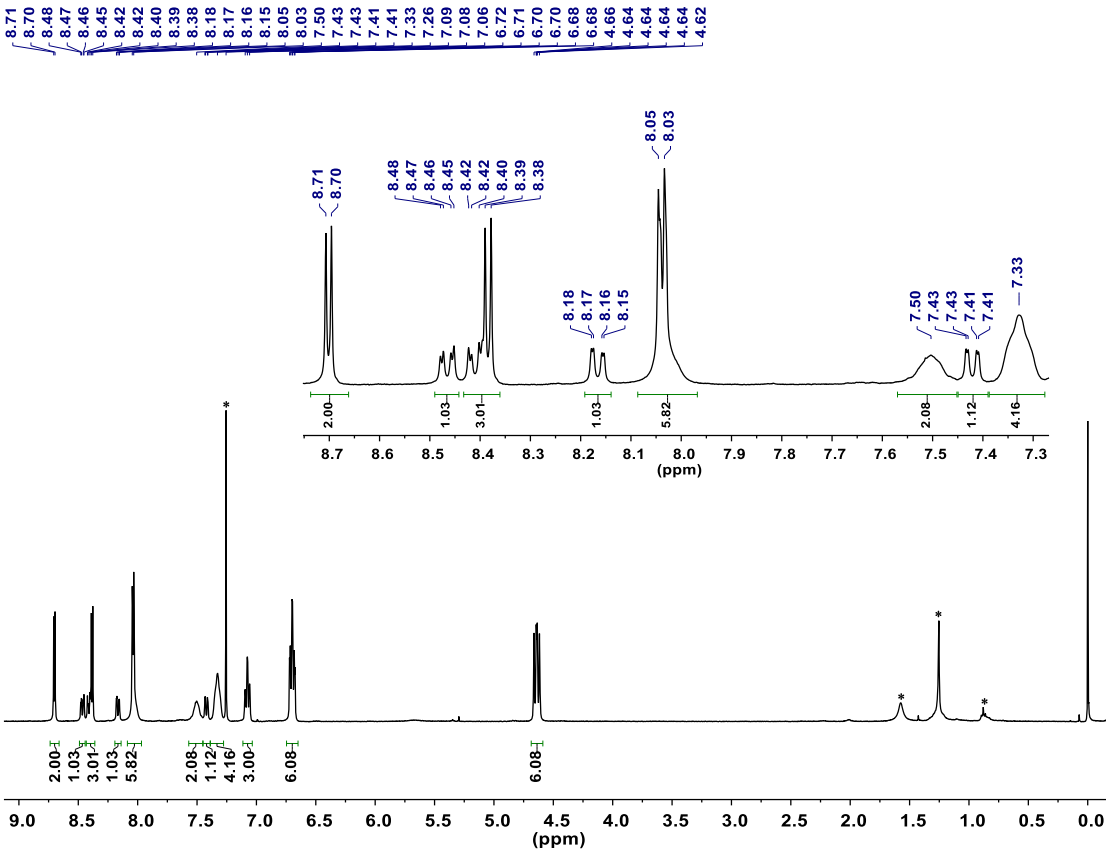


Fig. S2. ^{1}H NMR spectrum of [Cor(*p*-FPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) (**2**) (* 7.26 ppm is the solvent peak of CDCl$_3$, 1.56 ppm is the peak of H$_2$O, 0.88 and 1.26 ppm are solvent peaks from *n*-hexane).

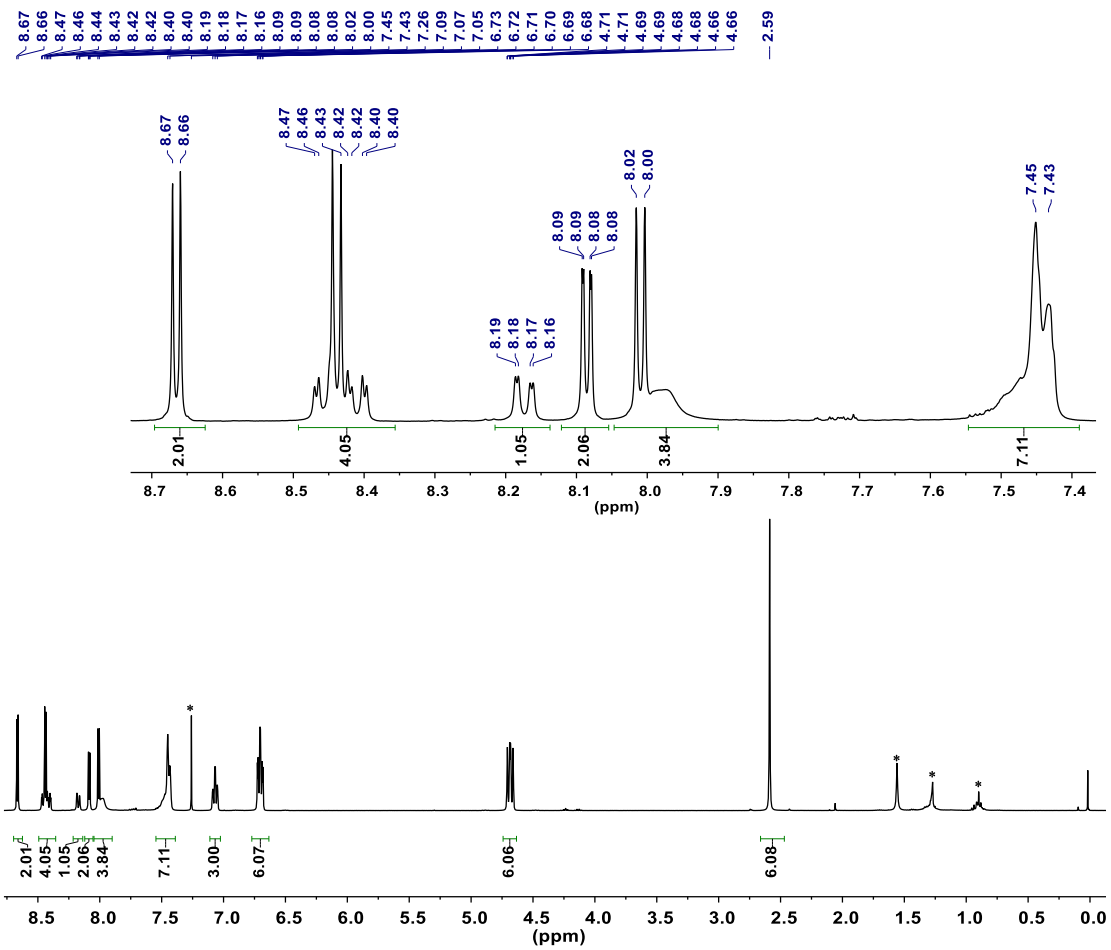


Fig. S3. ^{1}H NMR spectrum of [Cor(*p*-$CH_3Ph)_2$(*p*-NO_2Ph)]Co(PPh_3) (**3**) (* 7.26 ppm is the solvent peak of $CDCl_3$, 1.56 ppm is the peak of H_2O, 0.88 and 1.26 ppm are solvent peaks from *n*-hexane).

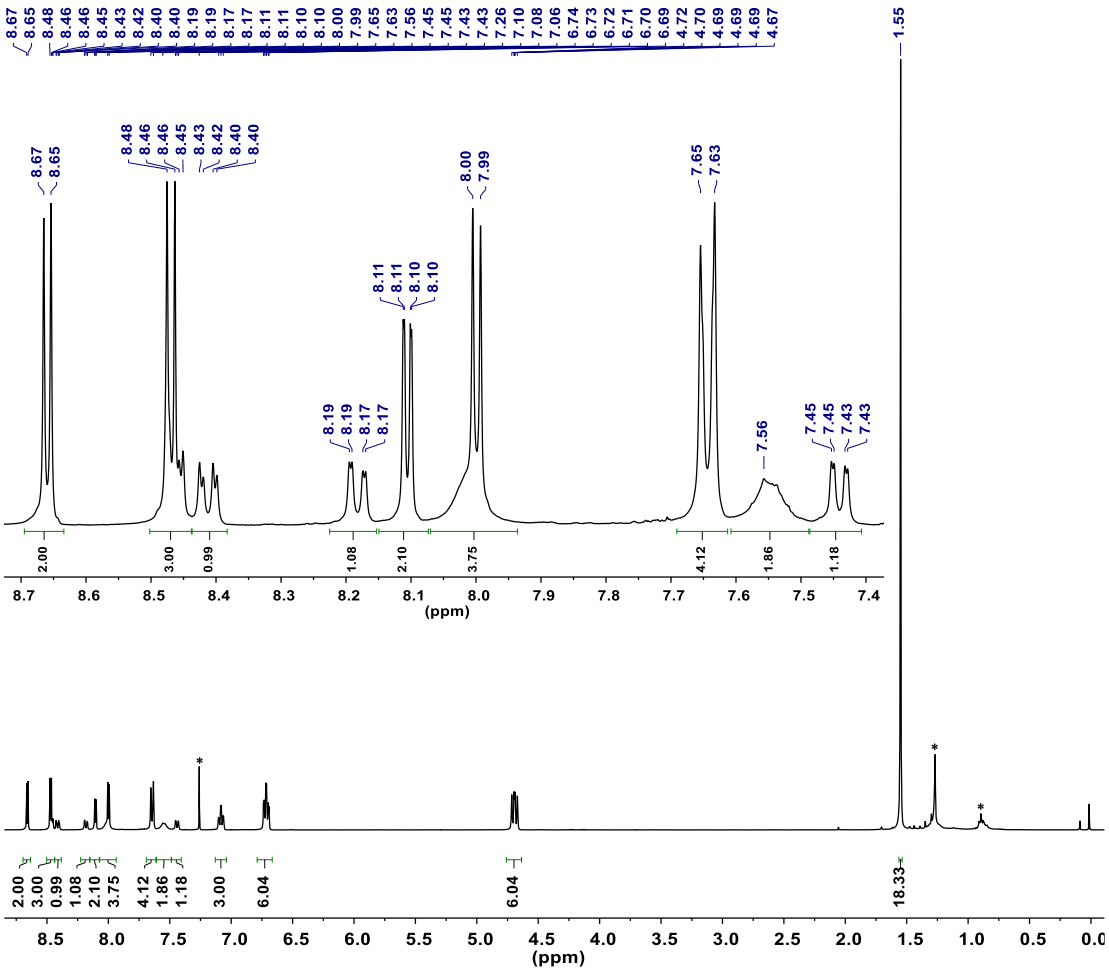


Fig. S4. ^{1}H NMR spectrum of [Cor(*p*-$C(CH_3)_3Ph)_2$(*p*-NO_2Ph)]Co(PPh_3) (**4**) (* 7.26 ppm is the solvent peak of $CDCl_3$, 0.88 and 1.26 ppm are solvent peaks from *n*-hexane).

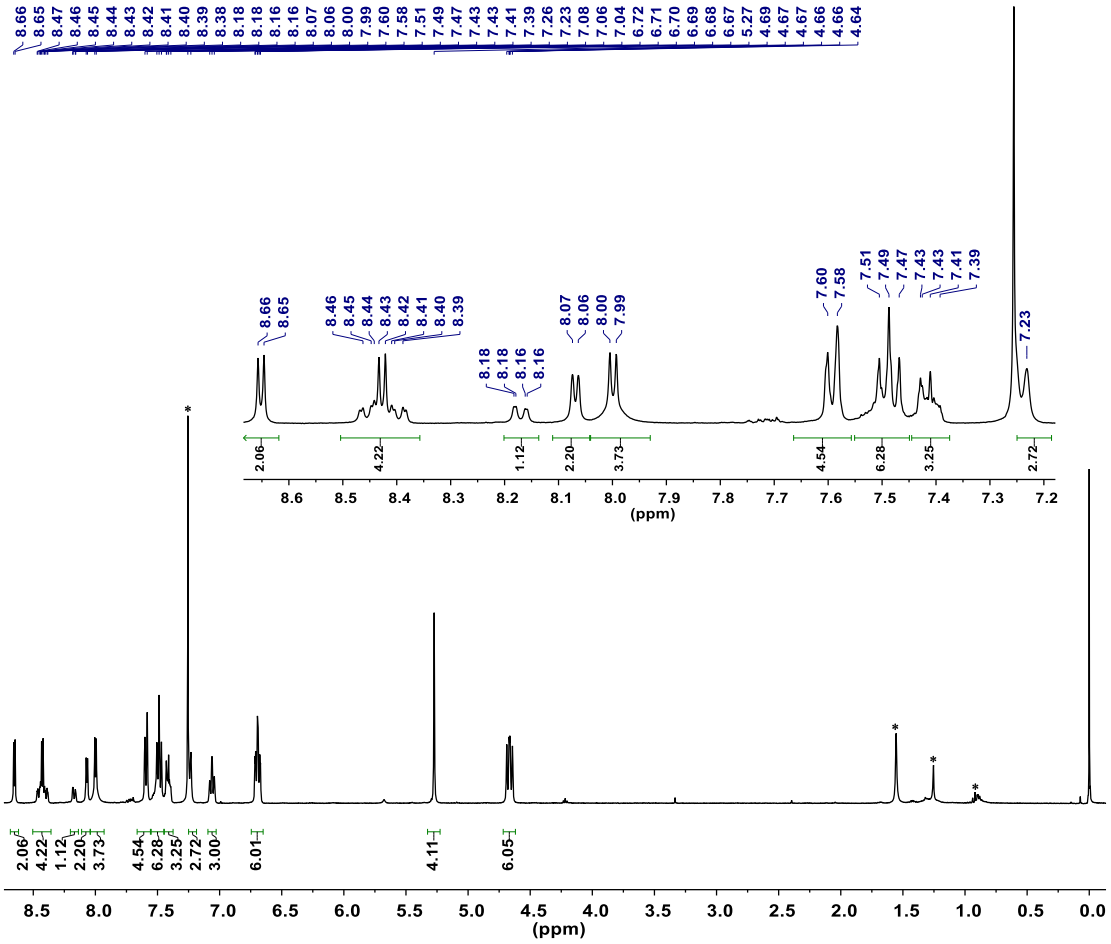


Fig. S5. ^{1}H NMR spectrum of [Cor(*p*-$PhCH_2OPh$)$_2$(*p*-NO_2Ph)]Co(PPh_3) (**5)** (* 7.26 ppm is the solvent peak of $CDCl_3$, 1.56 ppm is the peak of H_2O, 0.88 and 1.26 ppm are solvent peaks from *n*-hexane).

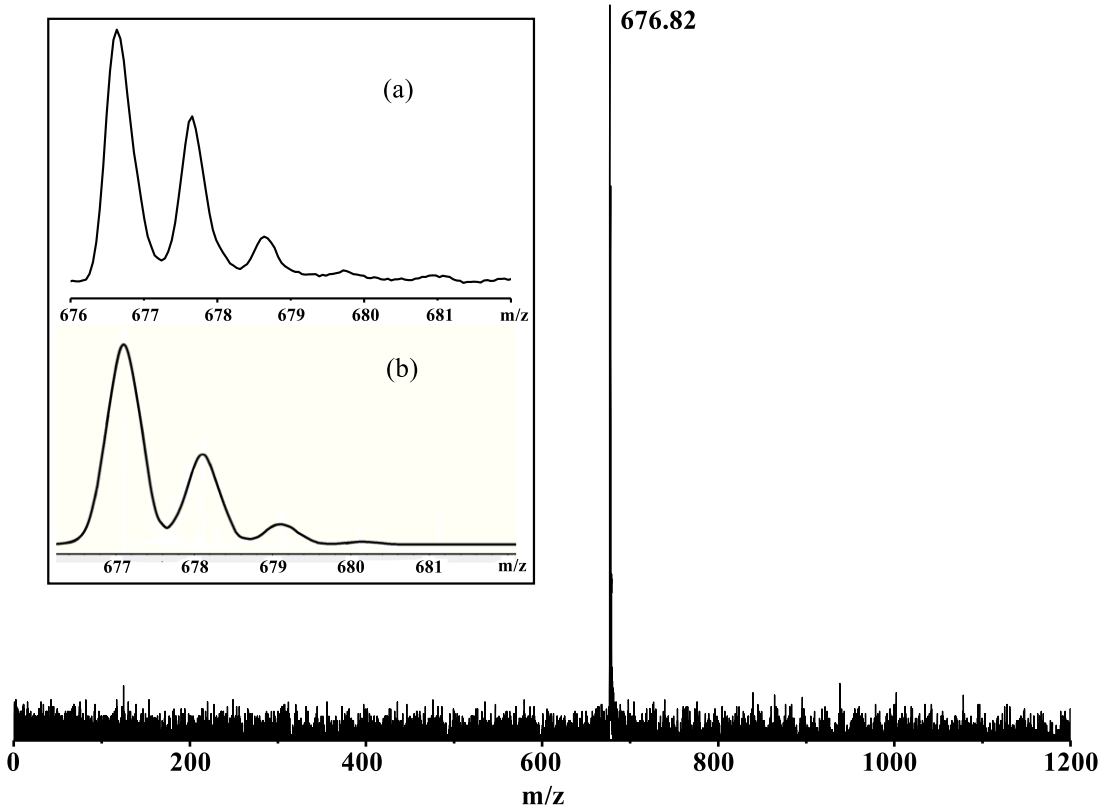


Fig. S6. MALDI-TOF mass spectrum of [Cor(*p*-CNPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) (**1**). The inset shows experimental (a) and simulated isotopic pattern (b) for the molecular ion of compound **1**.

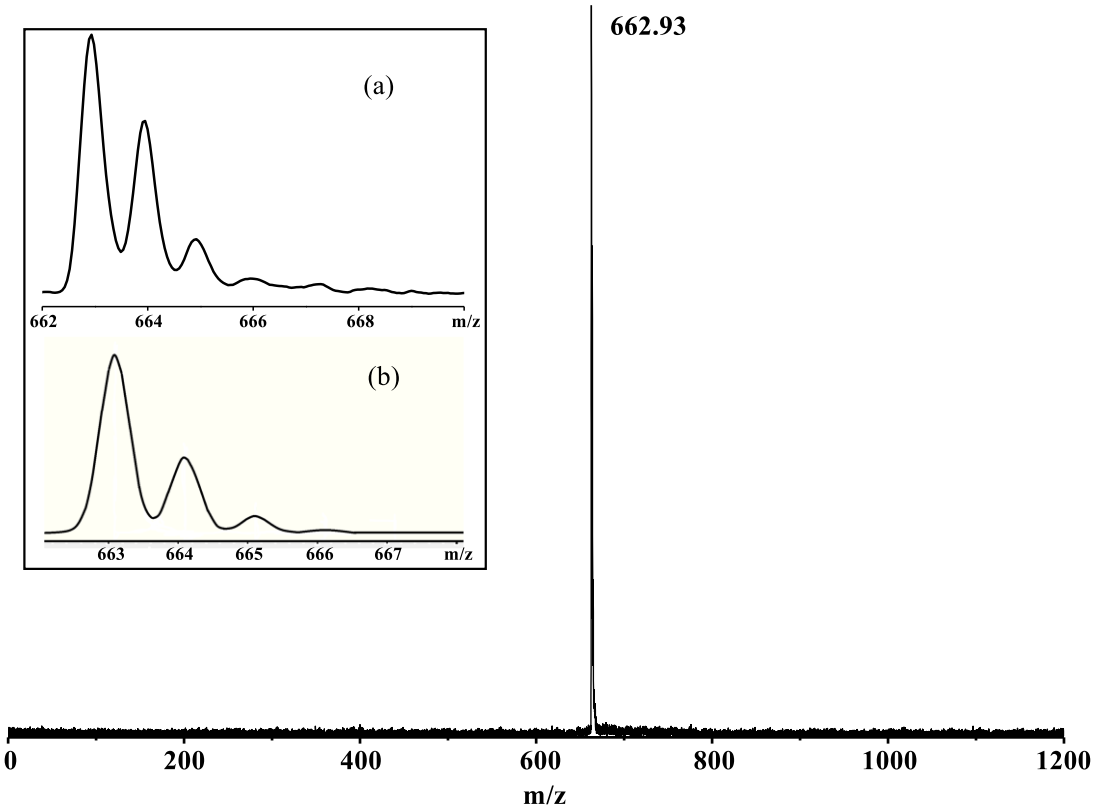


Fig. S7. MALDI-TOF mass spectrum of [Cor(*p*-FPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) (**2**). The inset shows experimental (a) and simulated isotopic pattern (b) for the molecular ion of compound **2**.

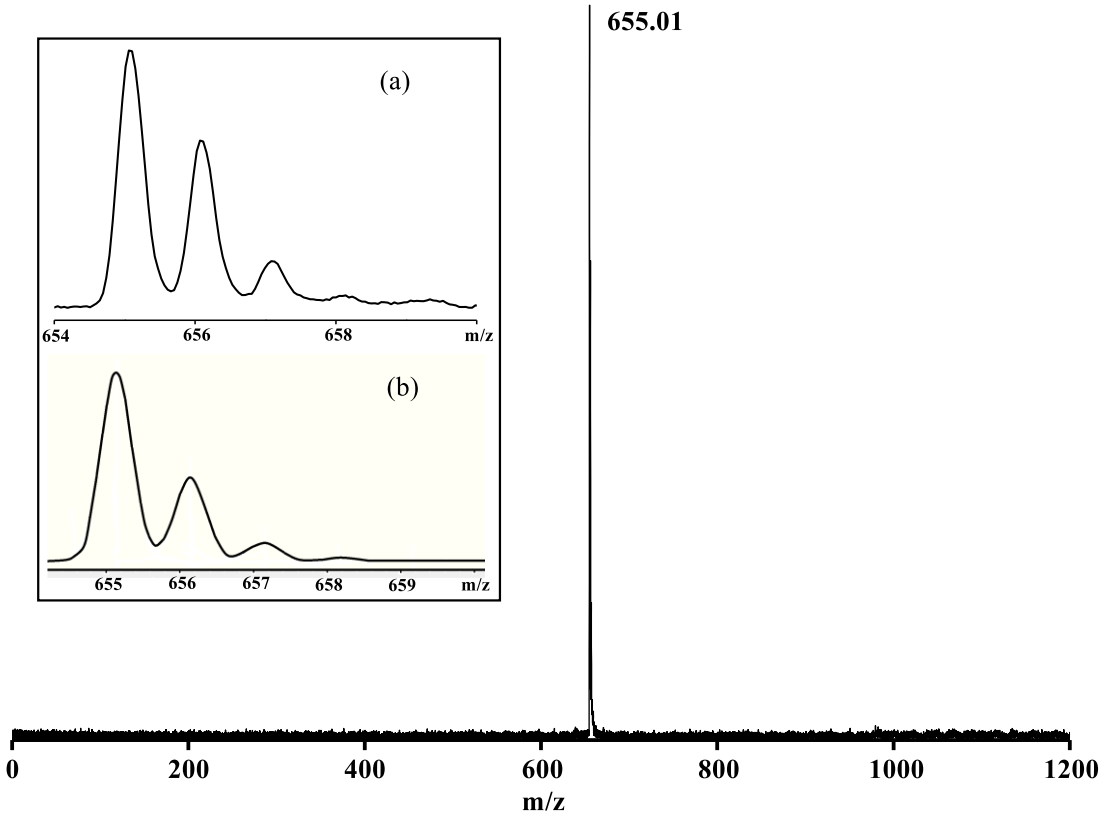


Fig. S8. MALDI-TOF mass spectrum of [Cor(*p*-$CH_3Ph)_2$(*p*-NO_2Ph)]Co(PPh_3) (**3)**. The inset shows experimental (a) and simulated isotopic pattern (b) for the molecular ion of compound **3**.

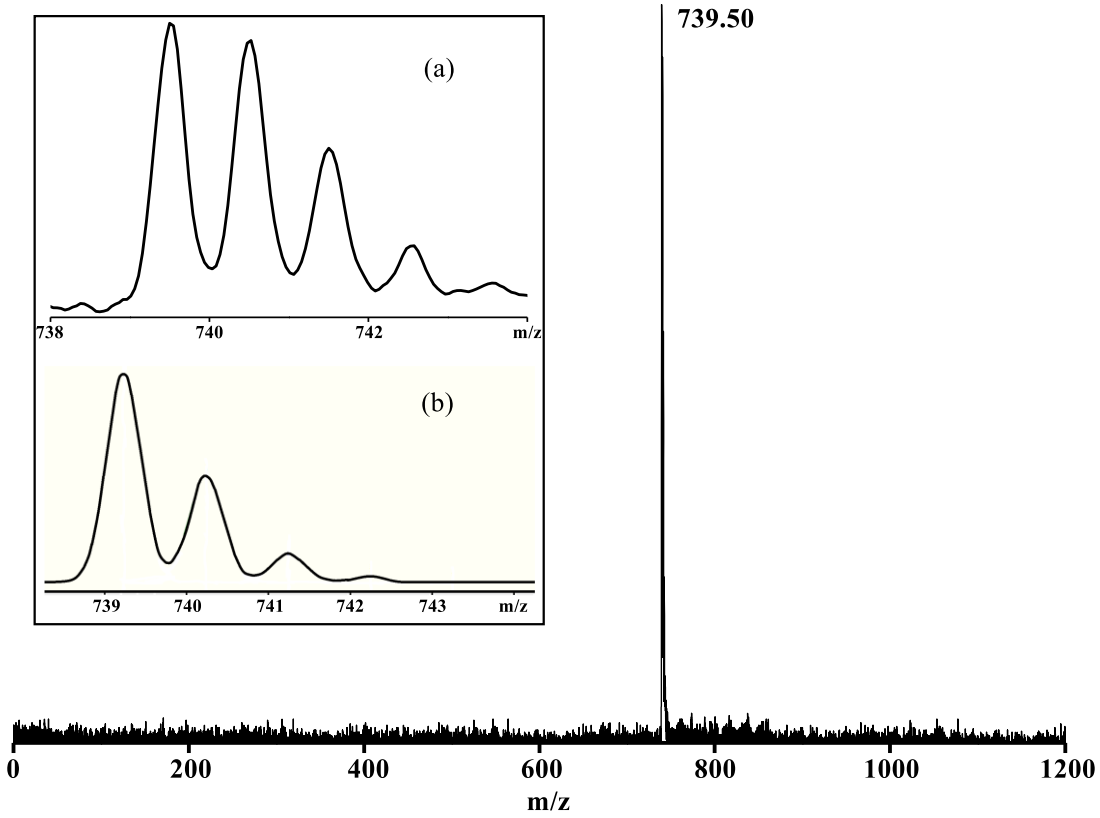


Fig. S9. MALDI-TOF mass spectrum of [Cor(*p*-C(CH_3)$_3$Ph)$_2$(*p*-NO_2Ph)]Co(PPh_3) (**4**). The inset shows experimental (a) and simulated isotopic pattern (b) for the molecular ion of compound **4**.

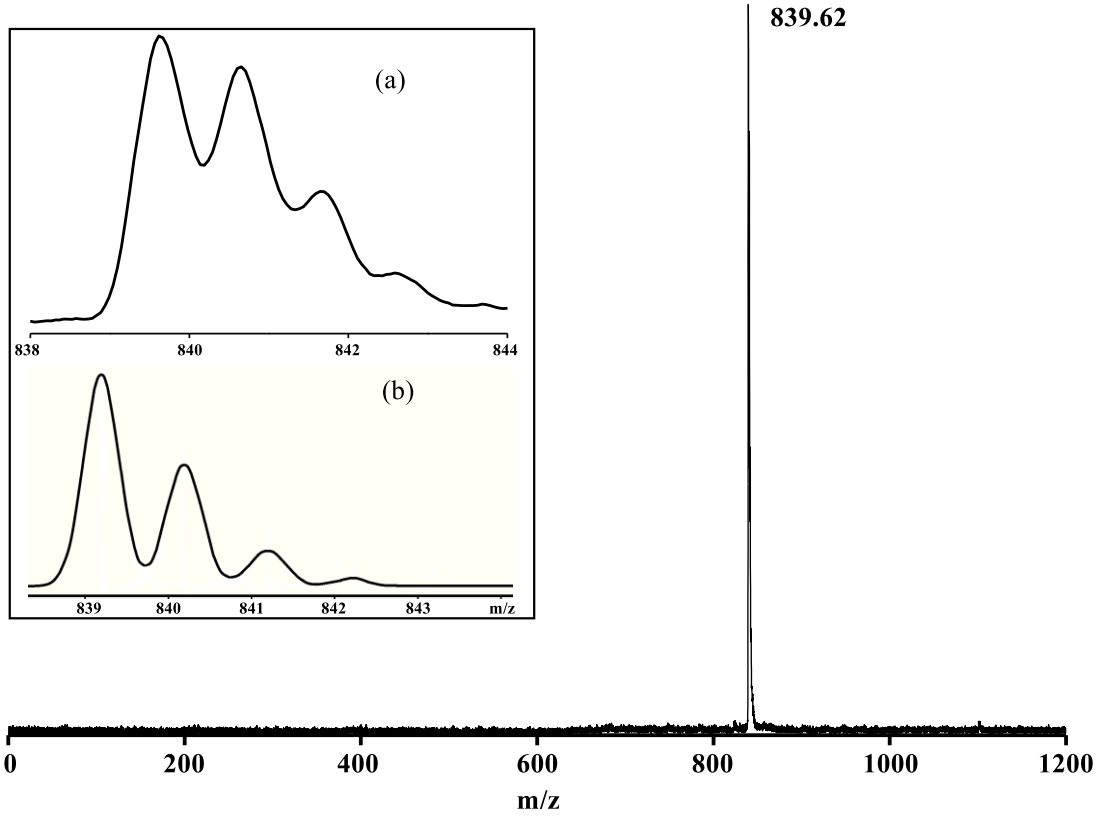


Fig. S10. MALDI-TOF mass spectrum of [Cor(*p*-PhCH$_2$OPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) (**5**). The inset shows experimental (a) and simulated isotopic pattern (b) for the molecular ion of compound **5**.

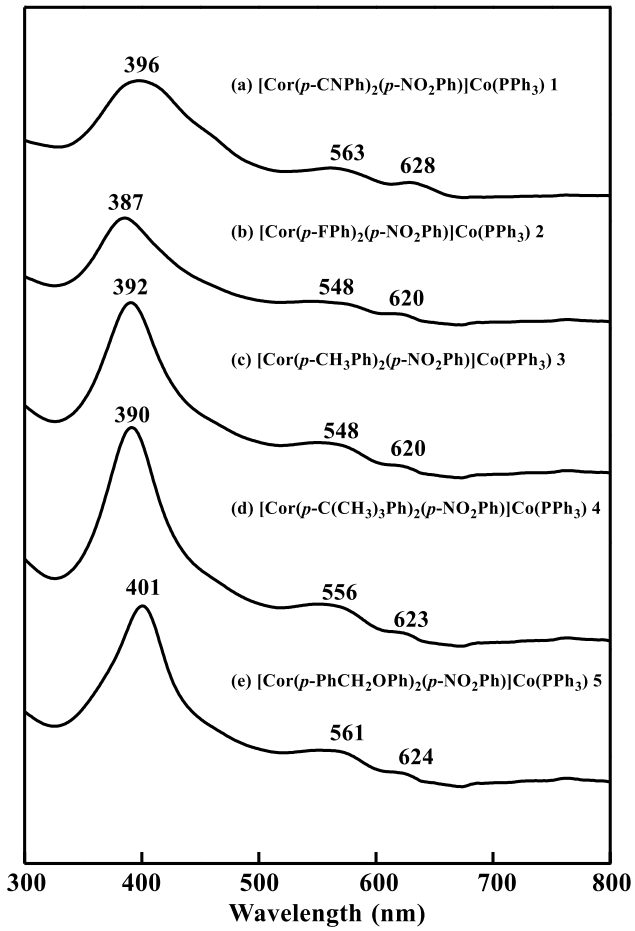


Fig. S11. Electronic absorption spectra of compounds [Cor(*p*-RPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) (**1-5)** in DMF.

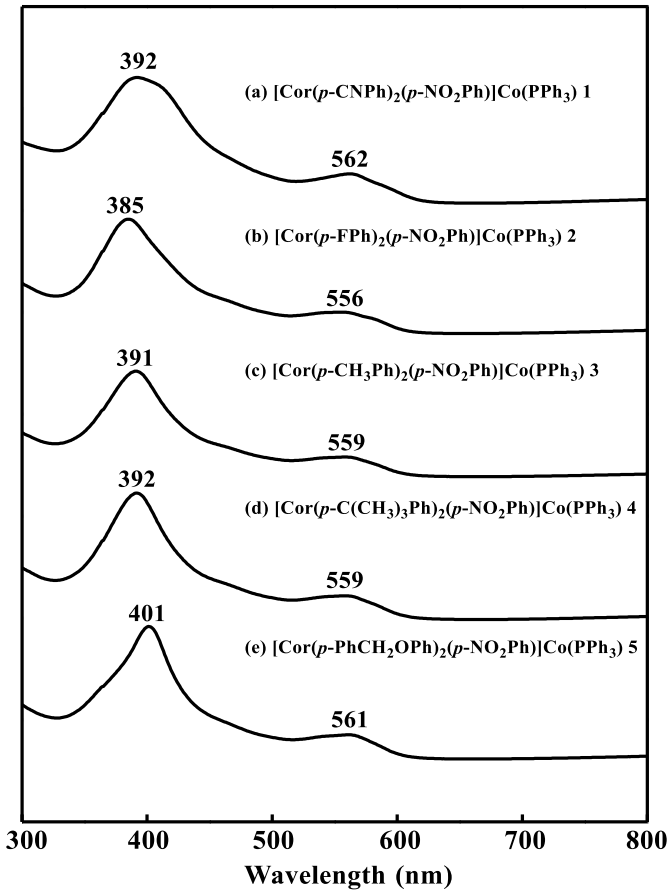


Fig. S12. Electronic absorption spectra of compounds [Cor(*p*-RPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) (**1-5)** in DMA.

Table S1. Electronic absorption data for [Cor(p-RPh)$_2$(p-NO_2Ph)]Co(PPh_3) (**1-5**) in CH_2Cl_2, DMF and DMA.

Solvent	R	λ_{max} / [nm, ε x 10^{-5} (L mol^{-1} cm^{-1})]		
CH_2Cl_2	CN	392 (1.0715)	568 (0.2258)	
	F	386 (1.4355)	553 (0.2792)	
	CH_3	391 (0.9249)	560 (0.1414)	
	$C(CH_3)_3$	393 (0.8006)	556 (0.1534)	
	$PhCH_2O$	403 (1.7869)	569 (0.2604)	
DMF	CN	396 (0.5440)	563 (0.1398)	628 (0.0720)
	F	387 (0.4811)	548 (0.0885)	620 (0.0297)
	CH_3	392 (0.8067)	548 (0.1344)	620 (0.0271)
	$C(CH_3)_3$	390 (1.0095)	556 (0.1647)	623 (0.0309)
	$PhCH_2O$	401 (0.8260)	561 (0.1305)	624 (0.0229)
DMA	CN	392 (0.6253)	562 (0.1527)	
	F	385 (0.5651)	556 (0.1094)	
	CH_3	391 (0.5214)	559 (0.1003)	
	$C(CH_3)_3$	392 (0.6250)	559 (0.1215)	
	$PhCH_2O$	401 (0.6552)	561 (0.1243)	

Table S2. Characteristic IR bands (cm^{-1}) of corrole for [Cor(*p*-RPh)$_2$(*p*-NO_2Ph)]Co(PPh_3) (**1-5**) with 2 cm^{-1} resolution.

CN	F	CH_3	$C(CH_3)_3$	$PhCH_2O$	Assignment
413w	418w				C-C-C out-of-plane wag of phenyl
458w	459w			457w	Coupling the Pyrrole in plane bending and C-C-C out-of-plane wag of phenyl
499w	499w	499w	499w	499w	Pyrrole in-plane rotation
521s	522s	519s	521s	520s	Pyrrole in plane bending
576w	576w	576w	585w	575w	C(10-*meso*)-C(Pyrrole) out-of-plane bending
618w	616w	616w	618w	618w	C-C-C in plane deformation of phenyl groups
695s	694s	693s	695s	695s	C-H out-of-plane wag of the Pyrrole
714s	721s	719s	716s	714s	C-H out-of-plane wag of the Pyrrole
747m	747m	747m	742m	746m	C-H out-of-plane wag of the phenyl groups
			749a		C-H out-of-plane wag of the phenyl groups
786m	786m	784m	785m	785m	Pyrrole in-plane deformation
		807m			Pyrrole in-plane bending
820s	820s	820s	821s	822s	Pyrrole in-plane bending
846w	845w	845m	845m	845m	Coupling of Pyrrole stretching and the out of plane C-H wag
881w	880w	880w	881w	880w	C-H in-plane bending of the Pyrrole
985m	986m	985m	985m	985m	Coupling the breathing vibration of the phenyl groups and the corrole skeleton
1013s	1016s	1017s	1018s	1015s	Coupling C-H in plane bending of phenyl groups and porrole breathing
1053m	105s	1052m	1052m	1050m	C-H bending of the Pyrrole
1088w	1088w	1088w	1088w	1088w	C-H in plane bending of the phenyl groups
1109w	1109w	1109w	1109w	1109w	Phenyl groups in plane breathing
1190w	1160s	1184w	1190w		C-H bending of the Pyrrole
				1172s	Ar-O-C stretching (*sym*)
	1221s				C-F stretching
1226w	1229s	1226w	1226w	1224w	Coupling of the C(10-*meso*)-C(phenyl groups) stretching and Pyrrole in plane bending

1249w	1250w	1248w	1249w		Coupling the C(5, 15-*meso*)-C(phenyl groups) stretching and Pyrrole stretching
				1242s	Ar-O-C stretching (*asym*)
1319w	1316m	1318w	1319w	1316w	Pyrrole stretching
1345vs	1343vs	1341vs	1340vs	1342s	Coupling the stretch of pyrrole, C-C stretching and symmetric N=O stretching
1435w	1435m	1435m	1432m	1433m	C-C stretching of the Pyrrole
1507w	1507w	1507s	1506w	1506vs	Coupling of Pyrrole stretching and asymmetric N=O stretching
1521s	1520s	1521s	1520s	1517s	Coupling of the C(5,15-*meso*)-C(Pyrrole) stretching and Pyrriole in plane bending
	1540w	1540w	1540w	1542w	Coupling of Benzene stretching and asymmetric N=O stretching
1600s	1593m	1593m	1596m	1592m	Benzene stretching
				1601m	Benzene stretching
2225s					C≡N stretching
		2853m	2850m		C-H stretching (-CH_3-, *sym*)
				2883br	C-H stretching (-CH_2-, *sym*)
		2920s	2921s		C-H stretching (-CH_3-, *asym*)
		2953a	2959s		C-H stretching (-CH_3-, *asym*)
				2970s	C-H stretching (-CH_2-, *asym*)
3062w	3058w	3054w	3058w	3060w	aromatic C-H stretching

[a] Shulder band.

Table S3. Half-wave and peak potentials (V *vs* SCE) for the oxidations and reductions of [Cor(*p*-RPh)$_2$(*p*-NO$_2$Ph)]Co(PPh$_3$) (**1-5**) in CH_2Cl_2 containing 0.1 M TBAP.

Compound	R	Oxidation			Readuction		
		$E_{1/2}(2)$	$E_{1/2}(1)$	$\triangle E$(2-1)	$E_p(1)$	$E_{1/2}(NO_2Ph)$	$E_p(2)$
1	CN	1.04	0.65	0.39	-0.53	-1.06	-1.53
2	F	0.95	0.57	0.38	-0.66	-1.13	-1.64
3	CH_3	0.93	0.53	0.4	-0.70	-1.15	-1.69
4	$C(CH_3)_3$	0.91	0.53	0.38	-0.73	-1.14	-1.70
5	$PhCH_2O$	0.87	0.52	0.35	-0.72	-1.14	-1.69

Scan rate 100 mV/s.