Supporting Information

Electrochemistry and Spectroelectrochemistry of Cobalt Porphyrins with π-Extended and/or Highly Electron-Withdrawing Pyrrole Substituents. *In-situ* Electrogeneration of σ-bonded Complexes

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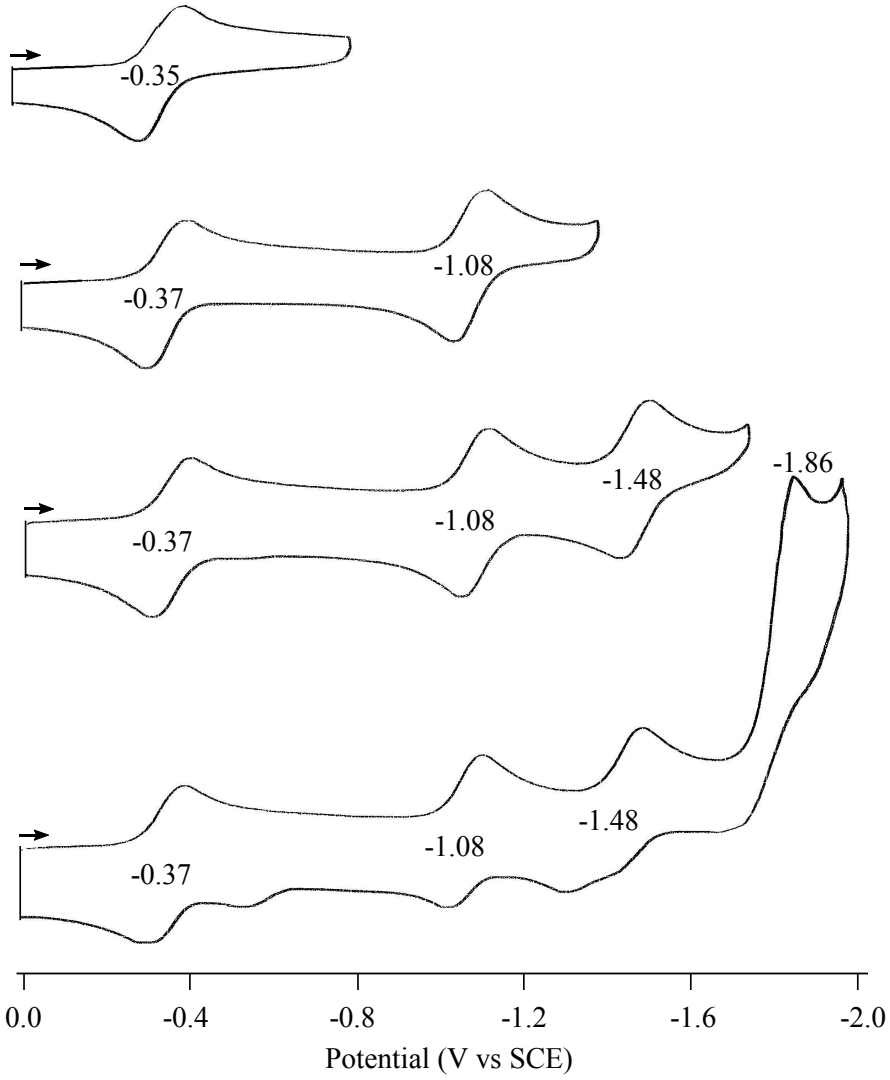

Figure S1. Cyclic voltammograms illustrating stepwise reduction of TPP(NO_2)$(PE)_6$Co **9** in PhCN with 0.1 M TBAP. Scan rate = 0.1V/s. The forth reduction at E_p = -1.86 V is assigned to a reduction involving the NO2 substituent on the porphyrin.

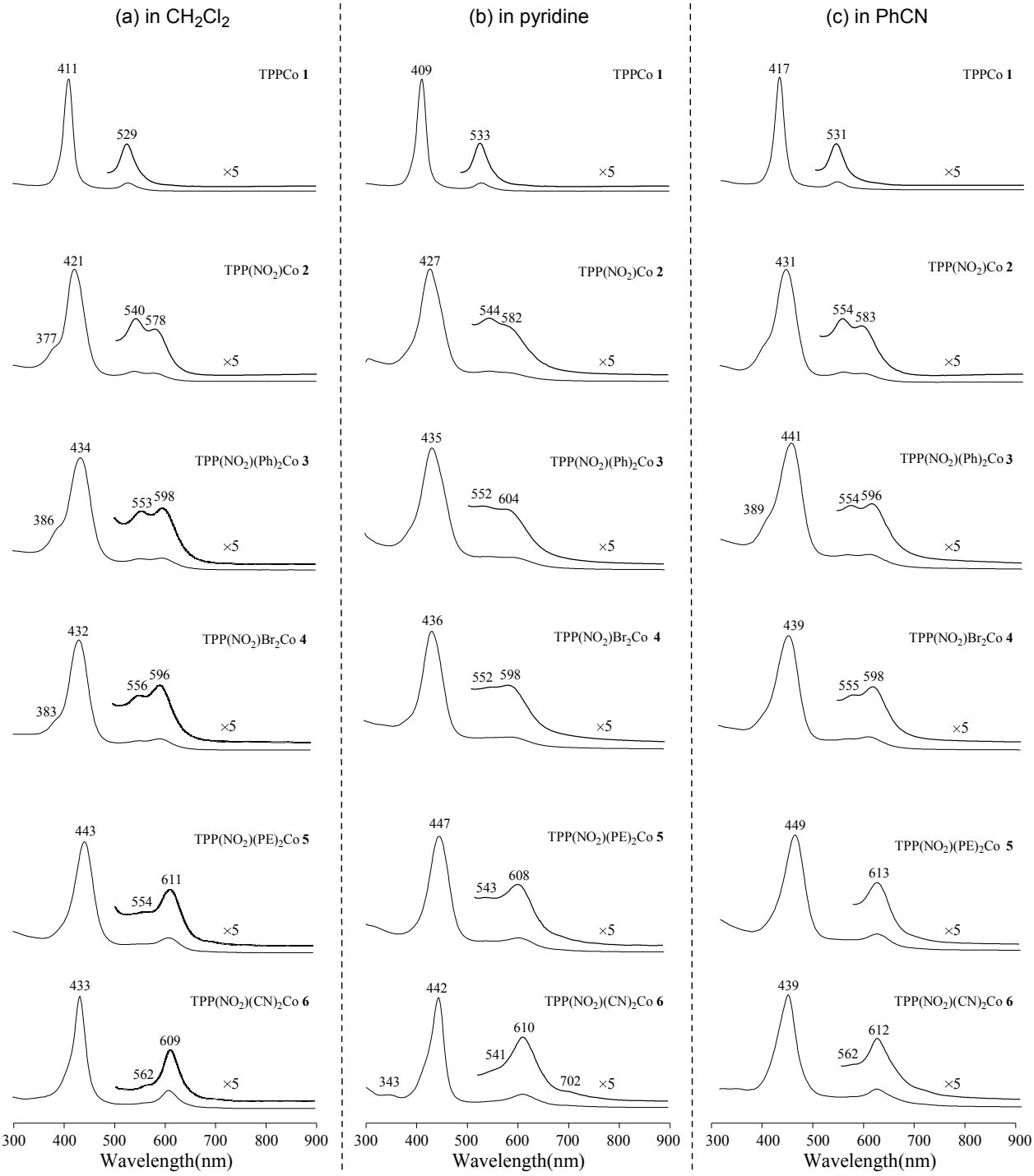

Figure S2. UV-vis spectra for TPPCo **1** and $TPP(NO_2)(Y)_2Co$ derivatives **2**-**6** in (a) CH_2Cl_2, (b) pyridine and (c) PhCN.

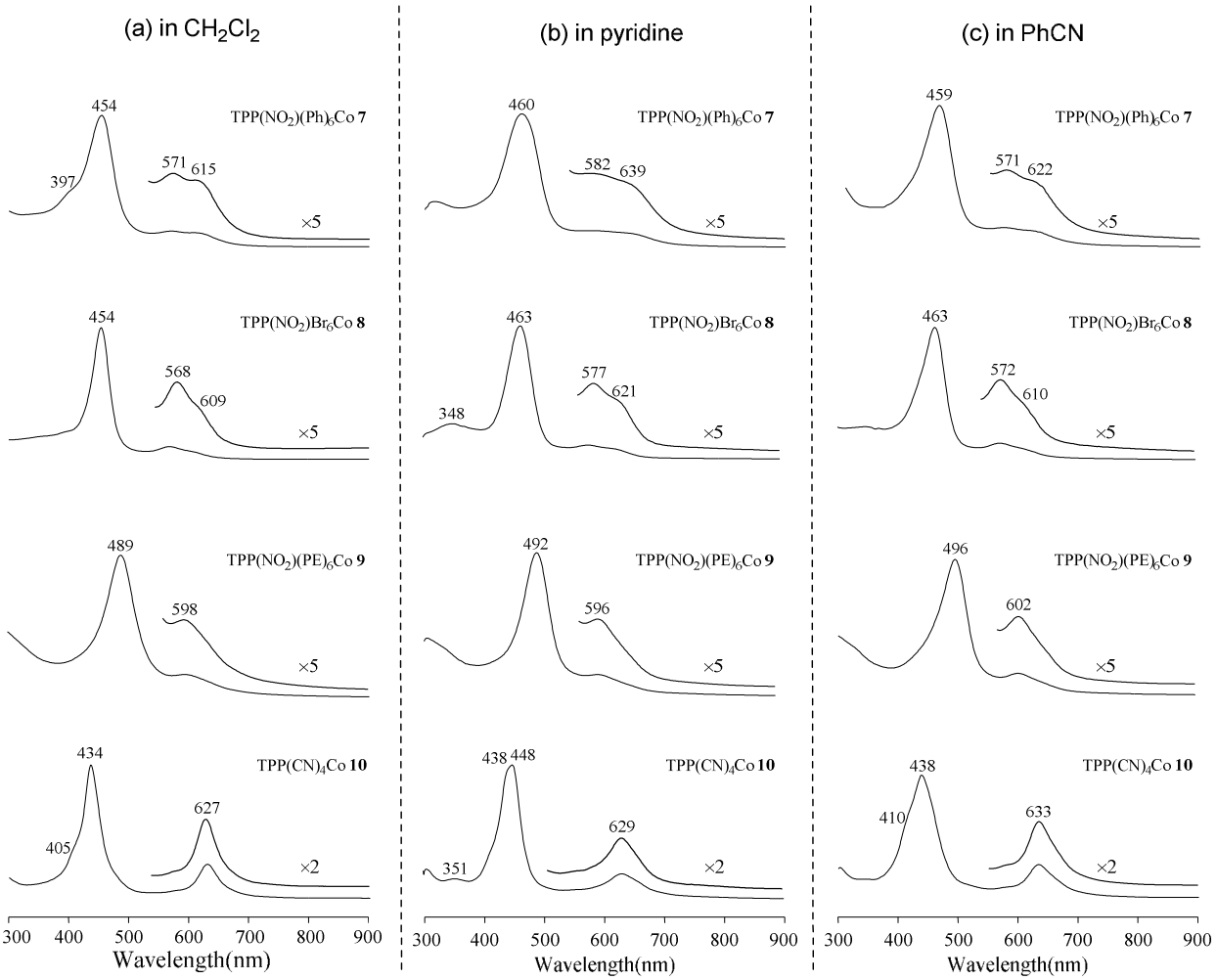

Figure S3. UV-vis spectra for $TPP(NO_2)(Y)_6Co$ derivatives **7-10** in (a) CH_2Cl_2, (b) pyridine and (c) PhCN.

Table S1. UV-Visible Spectral Data for investigated Co(II) series compound in CH_2Cl_2, Pyridine and benzonitrile.

Solvent	Compound	Soret band , λ (nm) ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1})	Q band region , λ (nm) ($\varepsilon \times 10^{-4}$ M^{-1} cm^{-1})	
CH_2Cl_2	TPPCo **1**	411 (21.0)	528 (1.3)	
	$TPP(NO_2)Co$ **2**	377 (s), 421 (9.9)	540 (0.9)	578 (0.8)
	$TPP(NO_2)(Ph)_2Co$ **3**	386 (s), 434 (11.2)	553 (1.1)	598 (1.2)
	$TPP(NO_2)Br_2Co$ **4**	383 (s), 432 (12.5)	556 (1.1)	596 (1.3)
	$TPP(NO_2)(PE)_2Co$ **5**	443 (11.6)	554 (1.0)	611 (1.7)
	$TPP(NO_2)(CN)_2Co$ **6**	433 (18.4)	609 (2.9)	
	$TPP(NO_2)(Ph)_6Co$ **7**	397 (s), 455 (14.3)	571 (1.7)	615 (1.5)
	$TPP(NO_2)Br_6Co$ **8**	454 (14.0)	568 (1.5)	609 (0.9)
	$TPP(NO_2)(PE)_6Co$ **9**	488 (9.7)	597 (1.3)	
	$TPP(CN)_4Co$ **10**	405 (s), 435 (14.3)	627 (3.7)	
Pyridine	TPPCo **1**	409 (18.0)	533 (1.0)	
	$TPP(NO_2)Co$ **2**	427 (10.4)	544 (0.9)	582 (0.8)
	$TPP(NO_2)(Ph)_2Co$ **3**	435 (8.9)	552 (0.9)	604 (0.8)
	$TPP(NO_2)Br_2Co$ **4**	436 (13.1)	552 (1.3)	598 (1.4)
	$TPP(NO_2)(PE)_2Co$ **5**	447 (12.9)	543 (1.1)	608 (1.4)
	$TPP(NO_2)(CN)_2Co$ **6**	442 (15.5)	541 (0.7)	610 (1.7)
	$TPP(NO)_2(Ph)_6Co$ **7**	460 (6.8)	582 (0.9)	639 (0.8)
	$TPP(NO)_2Br_6Co$ **8**	463 (8.1)	577 (1.0)	621 (0.8)
	$TPP(NO)_2(PE)_6Co$ **9**	492 (7.5)	596 (1.3)	
	$TPP(CN)_4Co$ **10**	438 (12.0), 448 (12.5)	629 (3.7)	
PhCN	TPPCo **1**	417 (23.6)	531 (1.5)	
	$TPP(NO)_2Co$ **2**	383 (s), 431 (12.2)	554 (1.2)	583 (1.1)
	$TPP(NO)_2(Ph)_2Co$ **3**	389 (s), 441 (7.2)	554 (1.0)	596 (1.1)
	$TPP(NO)_2Br_2Co$ **4**	439 (14.0)	555 (1.5)	598 (1.7)
	$TPP(NO)_2(PE)_2Co$ **5**	449 (10.8)	613 (1.7)	
	$TPP(NO)_2(CN)_2Co$ **6**	439 (9.3)	562 (1.1)	612 (1.7)
	$TPP(NO)_2(Ph)_6Co$ **7**	459 (8.1)	571 (1.3)	622 (1.1)
	$TPP(NO)_2Br_6Co$ **8**	463 (7.5)	572 (0.8)	610 (0.6)
	$TPP(NO)_2(PE)_6Co$ **9**	496 (12.2)	602 (2.1)	
	$TPP(CN)_4Co$ **10**	410 (s), 438 (6.7)	633 (1.7)	

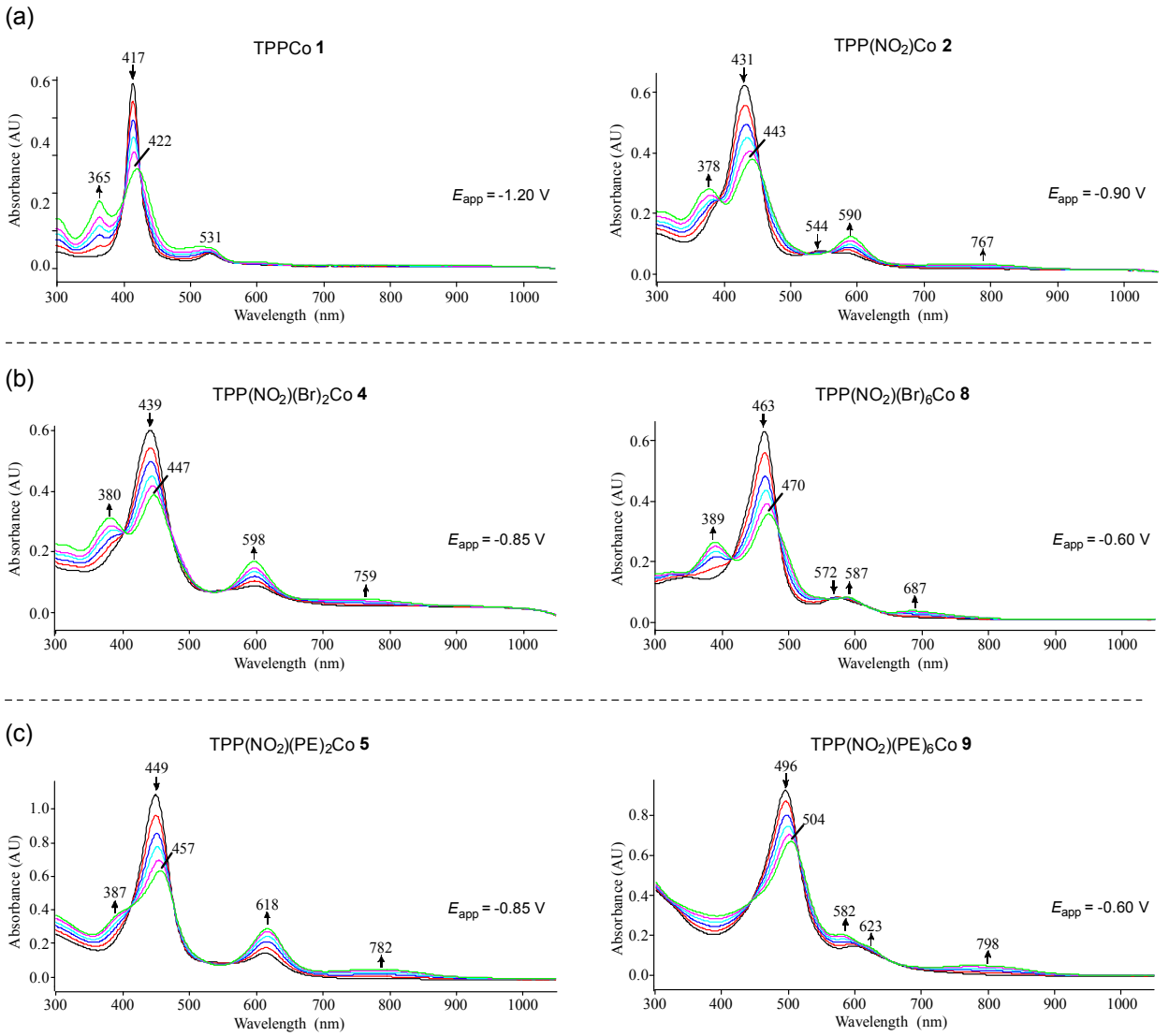

Figure S4. Spectral changes during the first one-electron reduction of selected porphyrins in PhCN containing 0.1 M TBAP. (a) reference compounds **1** and **2**, (b) di- and hexabromo porphyrins **4** and **8** and (c) di and hexa-PE porphyrins **5** and **9**.

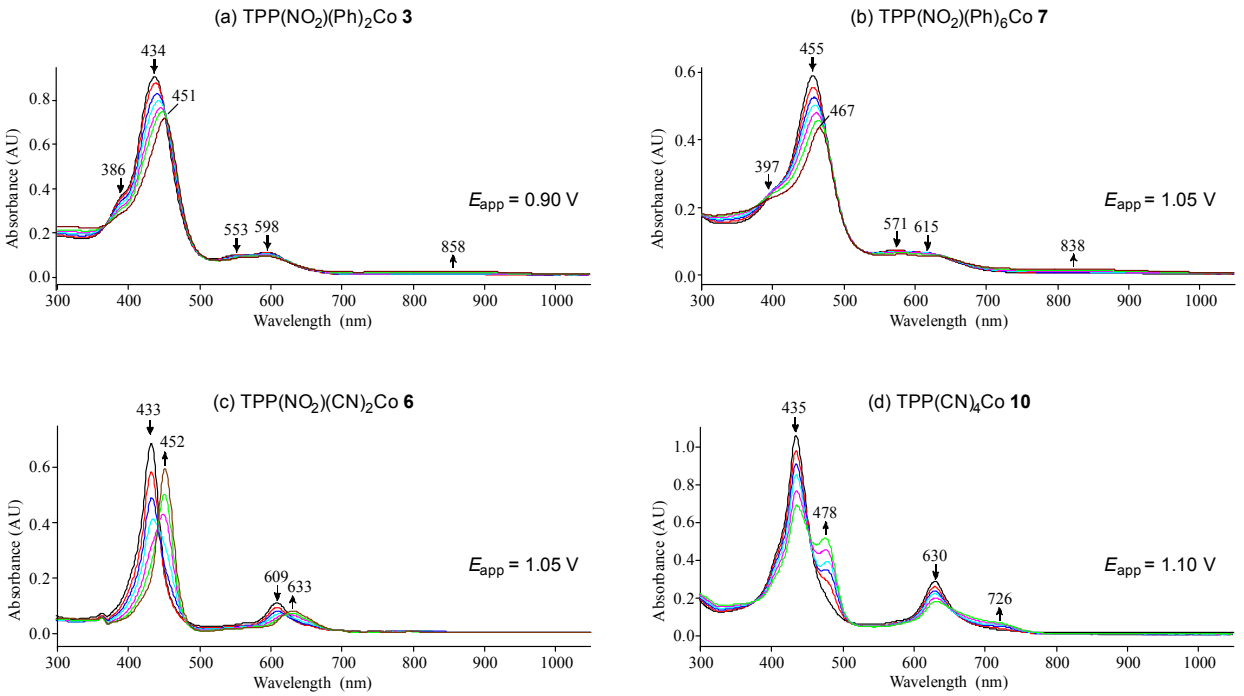

Figure S5. Spectral changes of first oxidation in CH_2Cl_2 obtained for (a) TPP$(NO_2)(Ph)_2$Co **3**, (b) TPP$(NO_2)(Ph)_2$Co **7**, (c) TPP$(NO_2)(CN)_2$Co **6**, and (d) TPP$(CN)_4$Co **10**, with 0.1M TBAP.

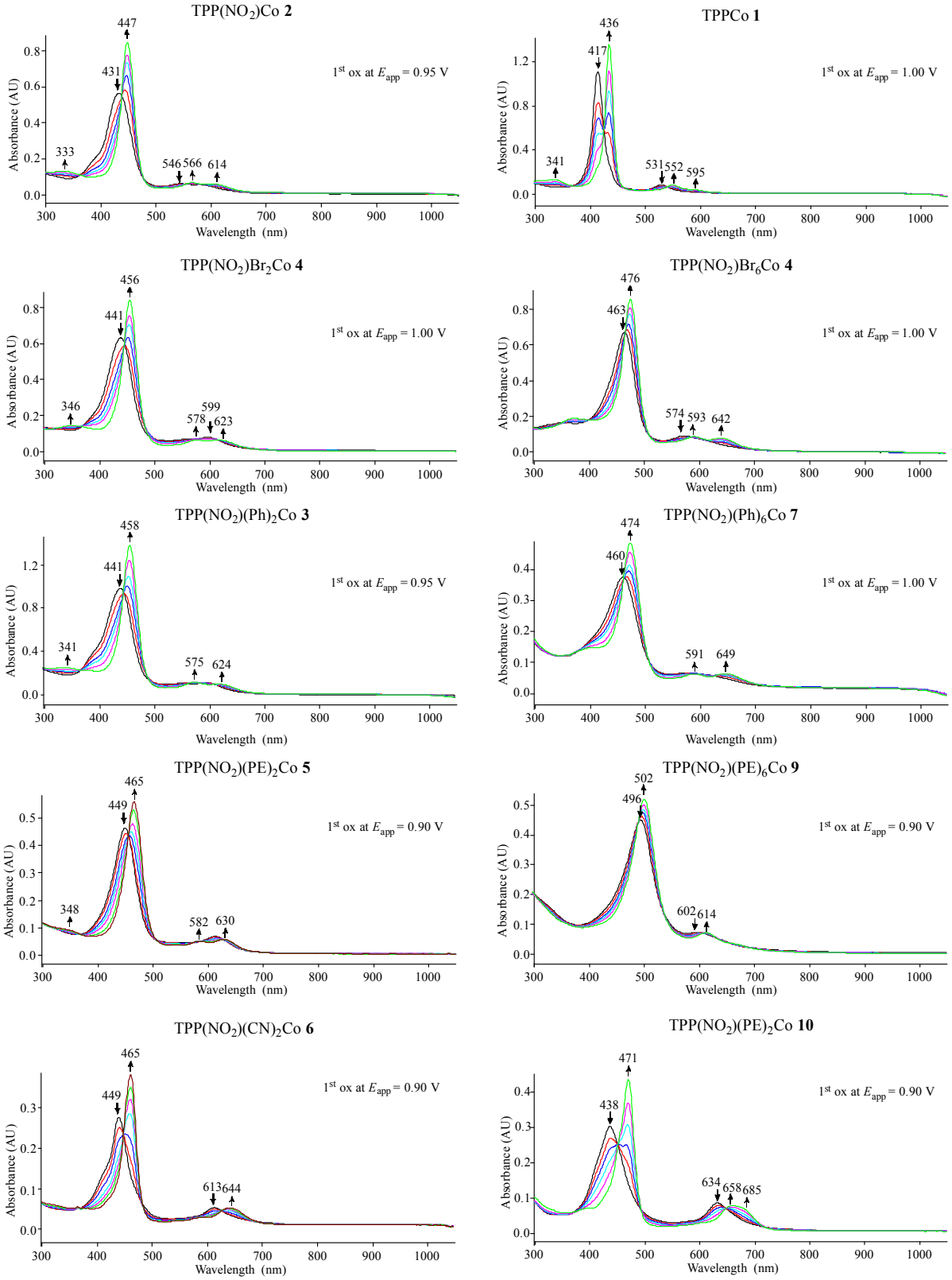

Figure S6. UV-visible spectra changes in PhCN obtained during first controlled potential oxidation of investigated *β*-substituted cobalt porphyrins with 0.1M TBAP.

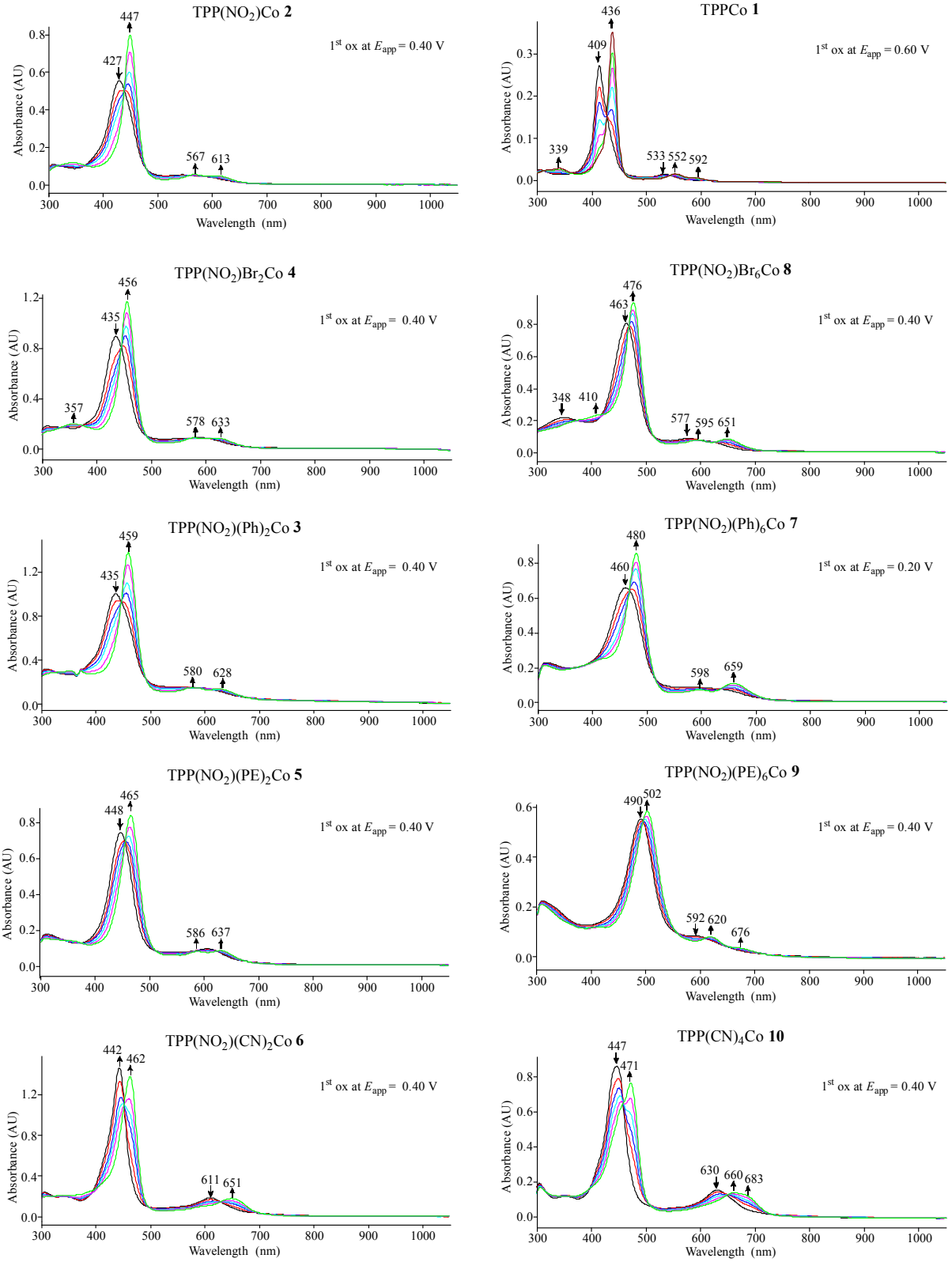

Figure S7 UV-visible spectra changes in pyridine obtained during first controlled potential oxidation of investigated *β*-substituted cobalt porphyrins with 0.1M TBAP.

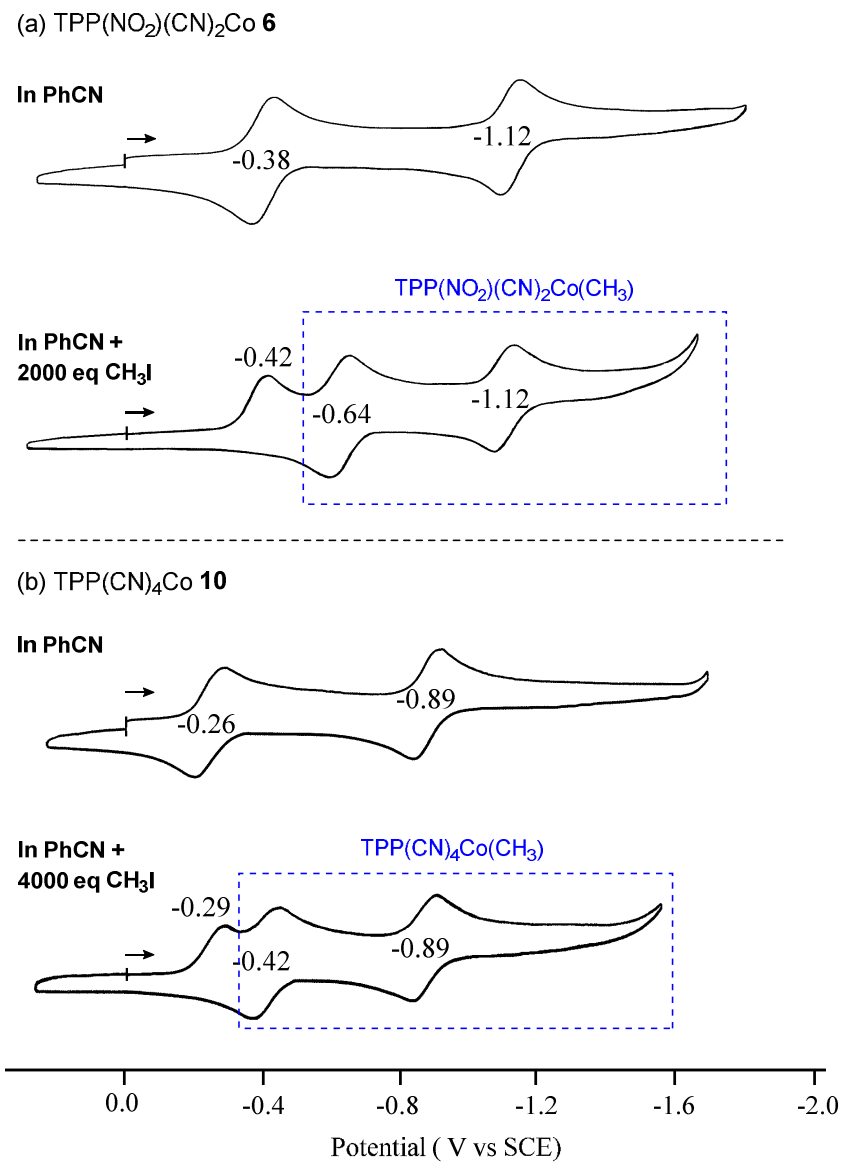

Figure S8: Cyclic voltammograms of (a) $TPP(NO_2)(CN)_2Co$ **6** and (b) $TPP(CN)_4Co$ **10** in PhCN, 0.1 M TBAP before and after addition of CH_3I to solution. The three electrode reactions within the box correspond to reduction of the electrogenerated $PorCo(CH_3)$ complexes in solution.

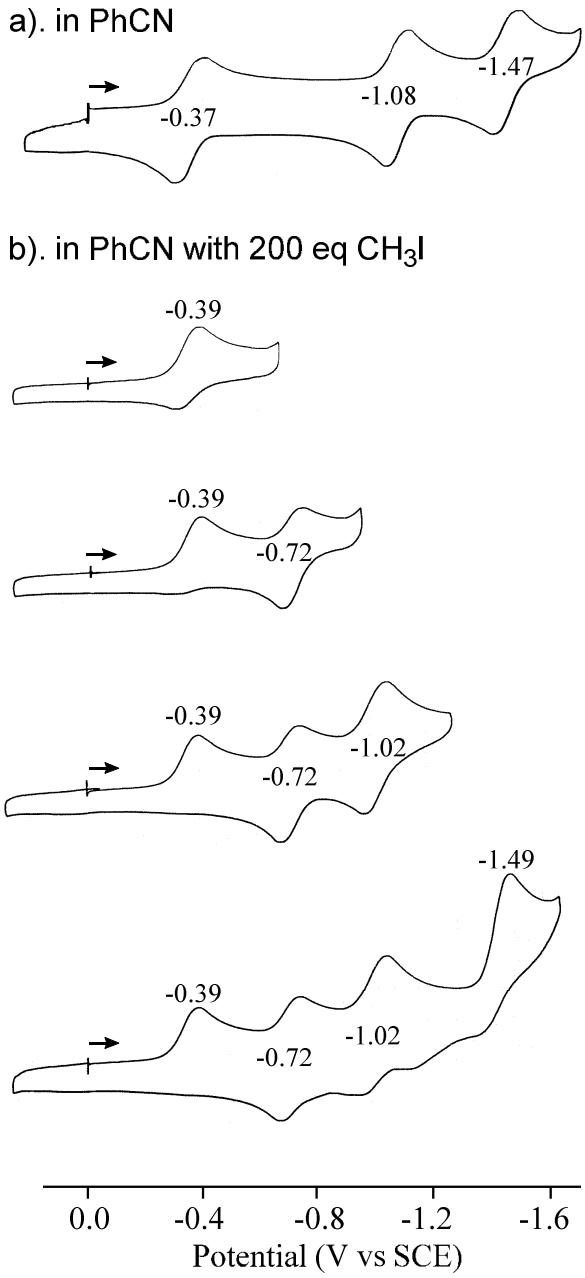

Figure S9. Cyclic voltammograms of $TPP(NO_2)(PE)_6Co$ **9** in PhCN containing 0.1 M TBAP (a) before and (b) after addition of 200 eq. CH_3I to solution. Scan rate = 0.1 V/s.

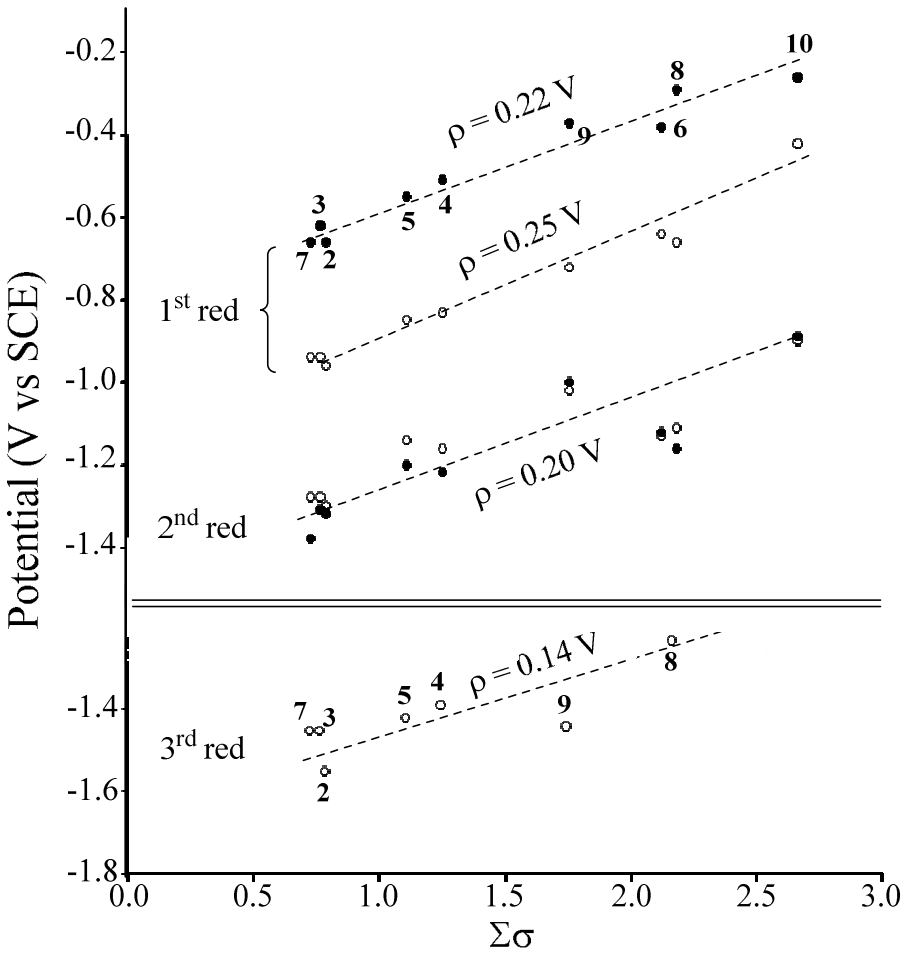

Figure S10. Plots of half-wave potentials for first two or three reductions of $PorCo^{II}$ (●) and electrosynthesized $PorCo(CH_3)$ (○) compounds **2**-**10** vs the sum of Hammett constants for the β-pyrrole substituents. The value of ρ are defined by Equation X in the text.

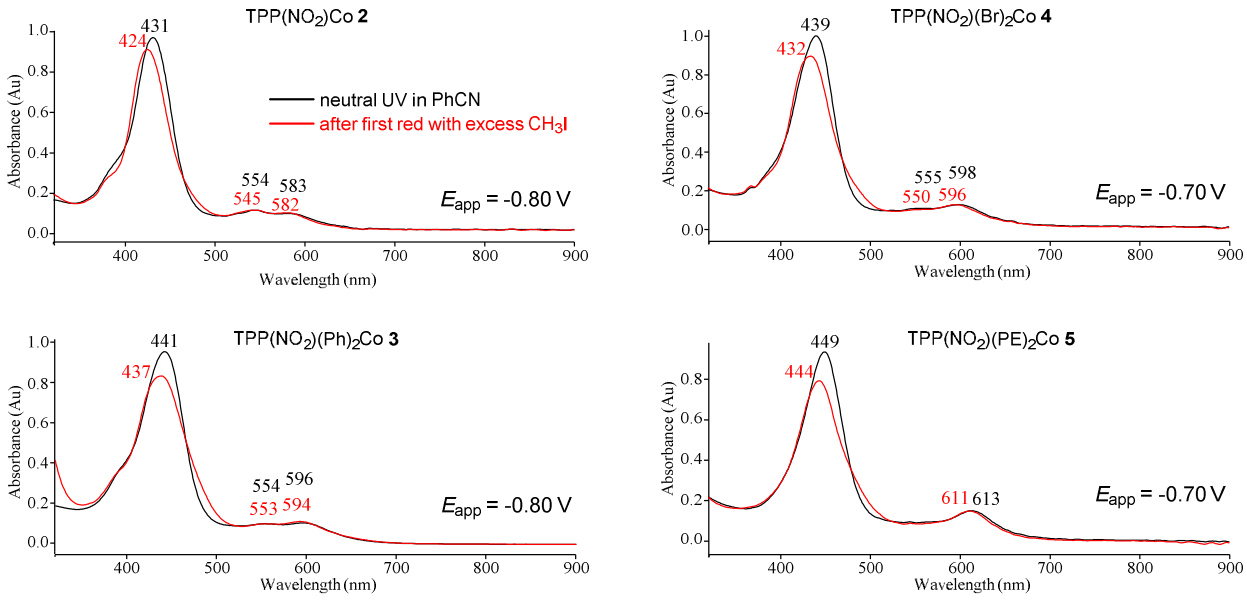

Figure S11. UV-visible spectral changes obtained during controlled potential reduction of investigated porphyrins in PhCN containing 0.1 M TBAP before and after addition of excess CH_3I to solution.

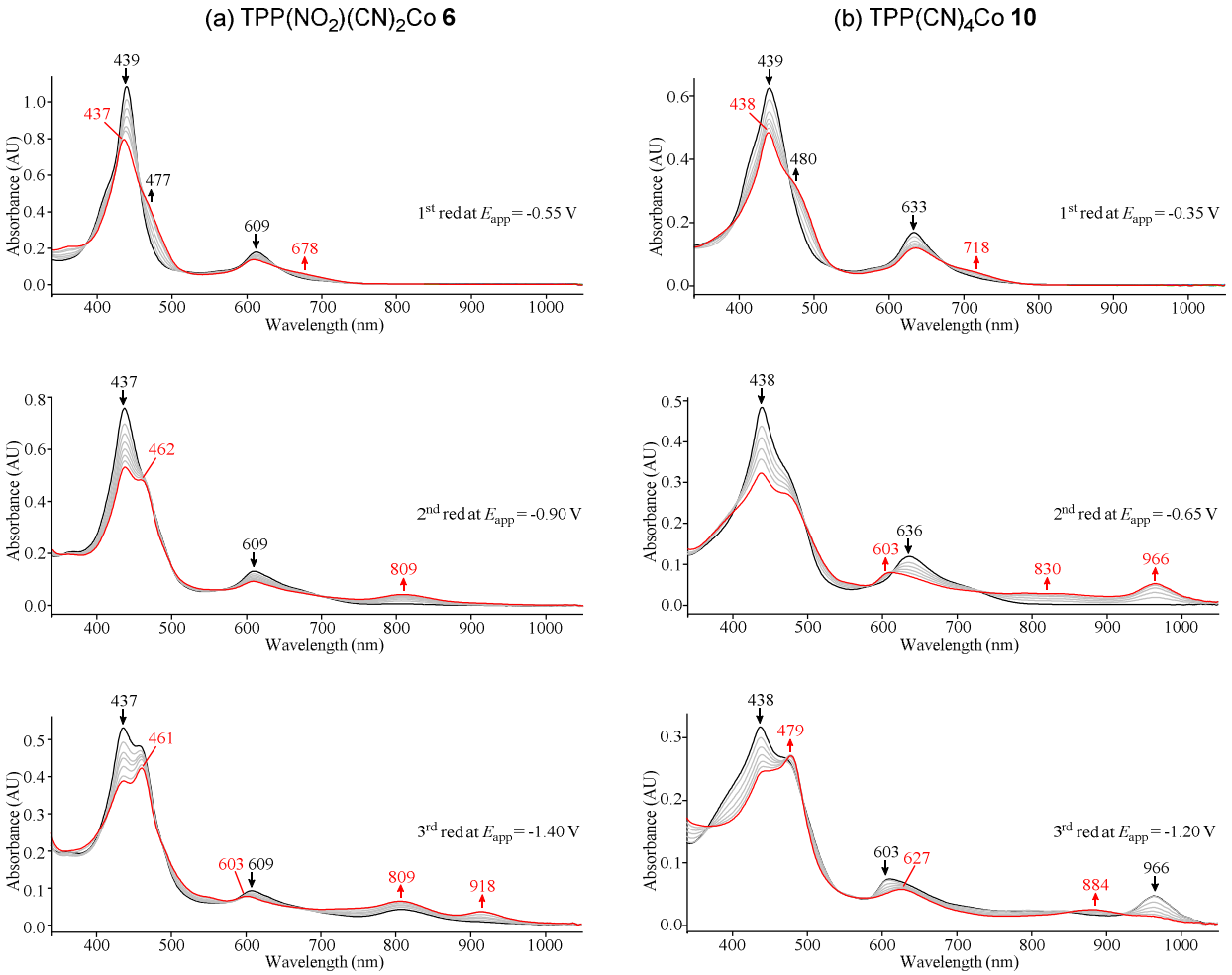

Figure S12. UV-visible spectral changes obtained during controlled potential reductions of (a)TPP$(NO_2)(CN)_2$Co **6** and (b)TPP$(CN)_4$Co **10** in PhCN containing 0.1 M TBAP before and after addition of excess CH_3I to solution.

Table S2. Spectral data for reduction of PorCo(CH_3) compounds **1-10** in PhCN, 0.1M TBAP.

Macrocycle	Por[Co^{III}-CH_3]	Por[Co^{III}-CH_3]$^-$
TPPCo **1**	**410**, 529	**410**, 461, 602, 782
TPP(NO_2) **2**	**424**, 545, 582	
TPP(NO_2)($Ph)_2$ **3**	**437**, 553, 594	
TPP(NO_2)Br_2 **4**	**432**, 550, 596	
TPP(NO_2)($PE)_2$ **5**	**444**, 611	**446,** 583, 633, 740
TPP(NO_2)($CN)_2$ **6**	**437**, 603, 678	**437**, 462, 609, 809
TPP(NO_2)($Ph)_6$ **7**	**454**, 568, 609	
TPP(NO_2)Br_6 **8**	**455**, 568, 609	**455**, 669, 856
TPP(NO_2)($PE)_6$ **9**	**490**, 602	**490**, 713, 911
TPP($CN)_4$ **10**	**438**, 633, 718	**438**, **670**, 603 830, 966