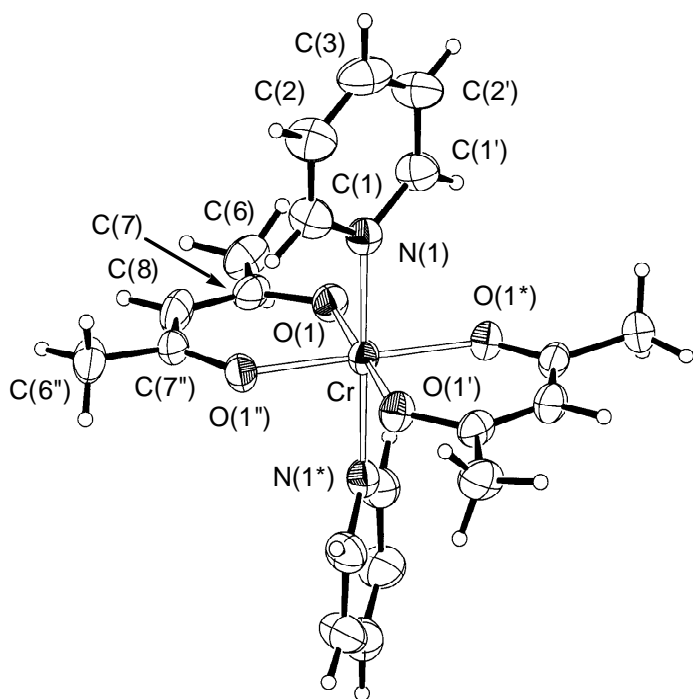
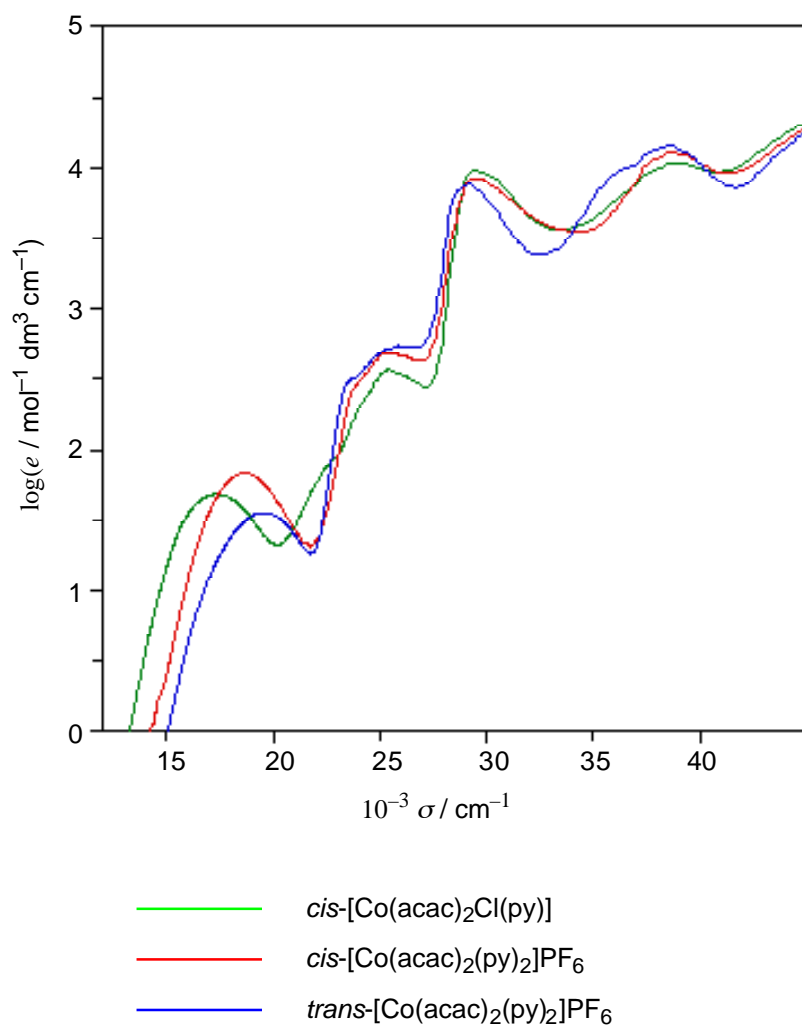


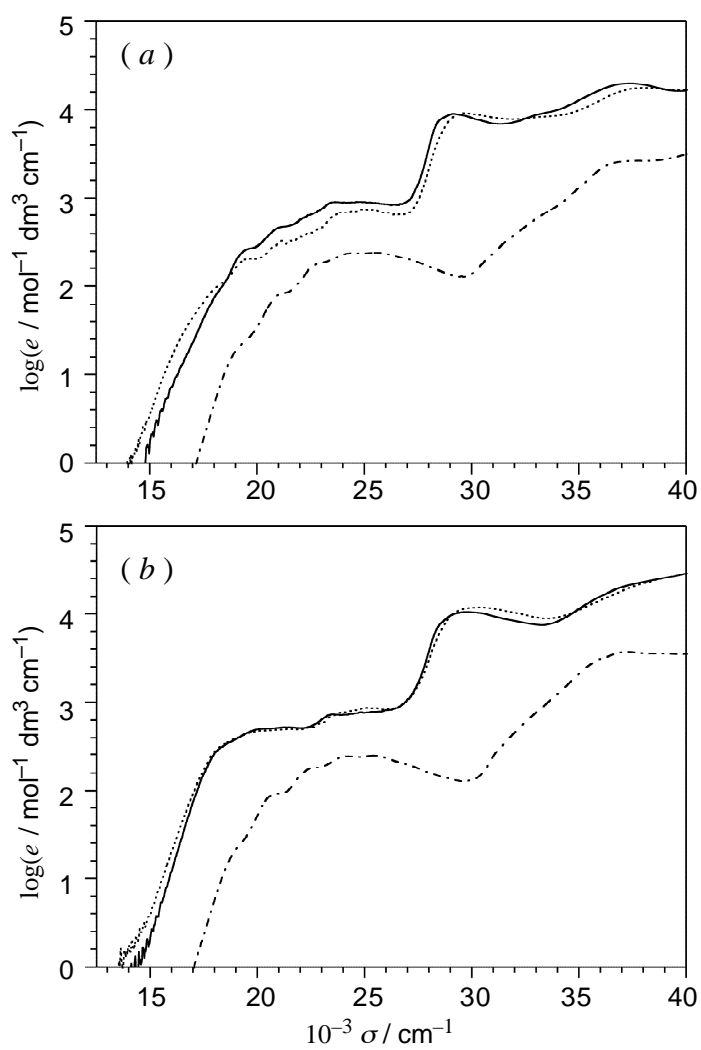
**Figure S1.**  $^2\text{H}$  NMR spectra (in  $\text{CH}_3\text{CN}$ , 76.75 MHz, 300K) of (a) *mN3*, (b) *mN4*, (c) *mI3*, and (d) *mI4*.



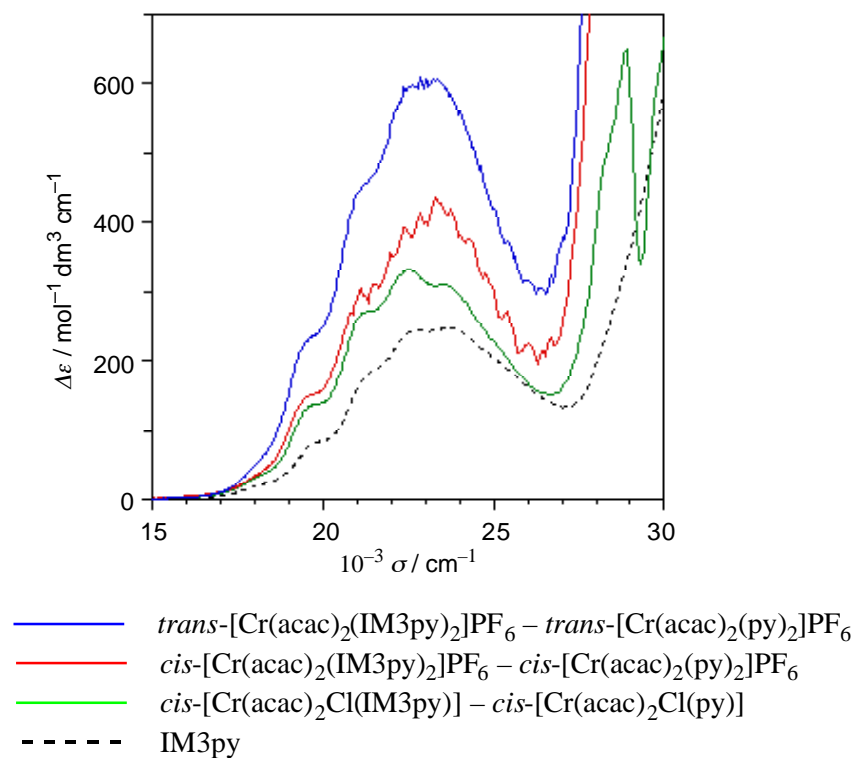
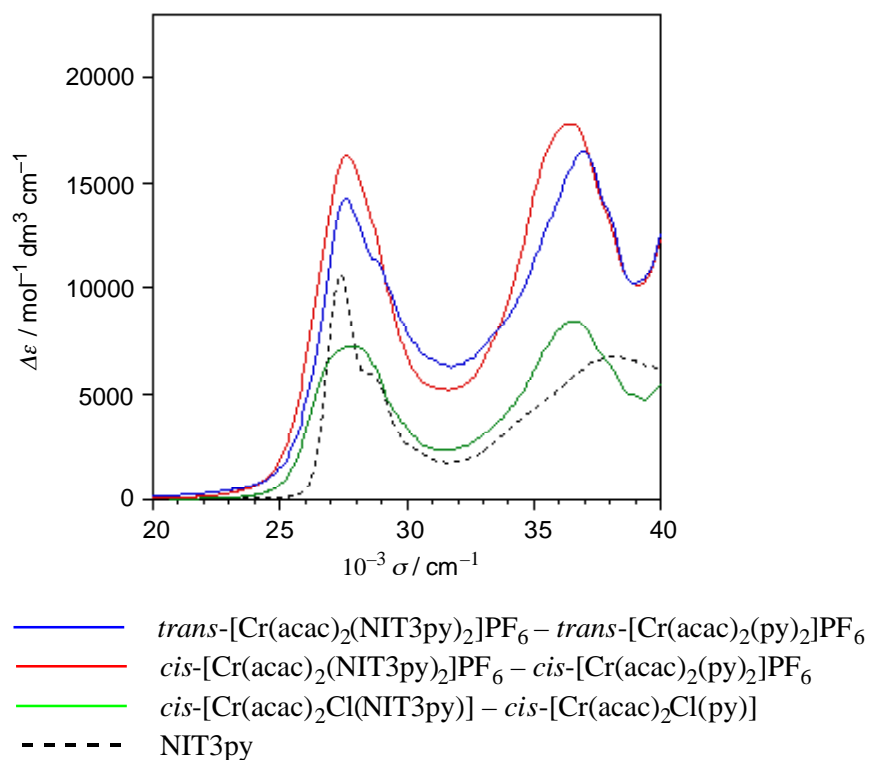
**Figure S2.** ORTEP (10% probability level) of  $trans\text{-}[\text{Cr}(\text{acac})_2(\text{py})_2]^+$  in *tpy*. Selected bond lengths (Å): Cr–O(1) 1.950(2), Cr–N(1) 2.080(5).



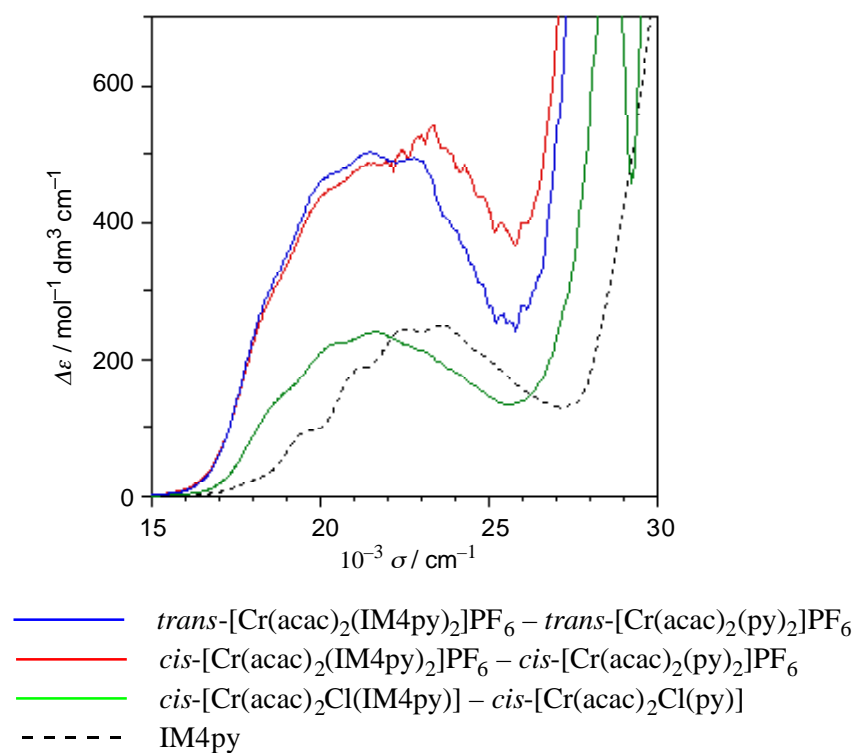
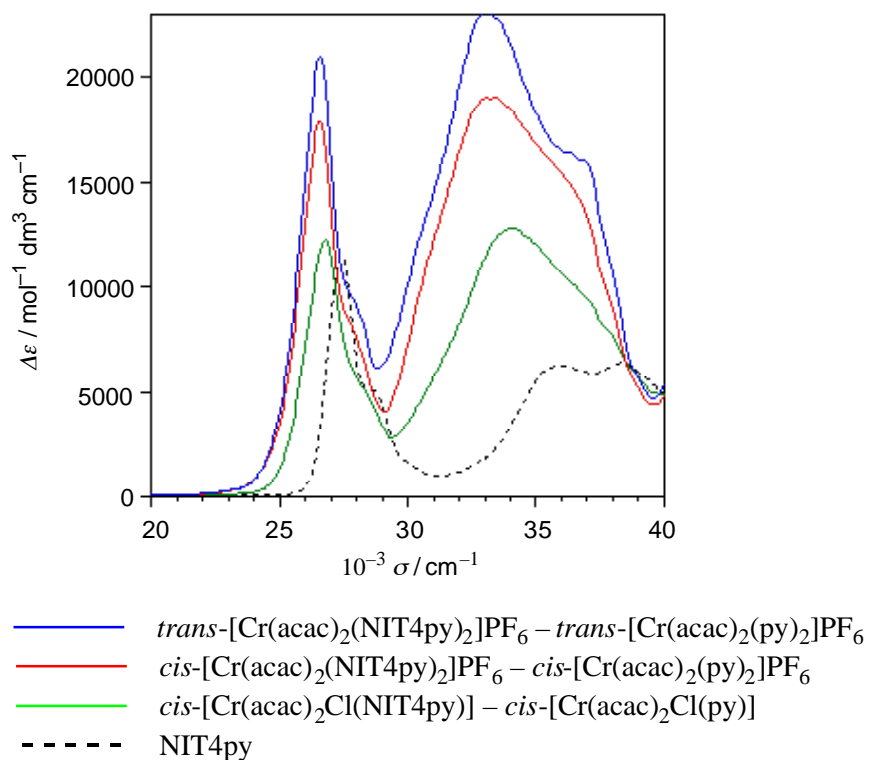
**Figure S3.** Absorption spectra of pyridine complexes.



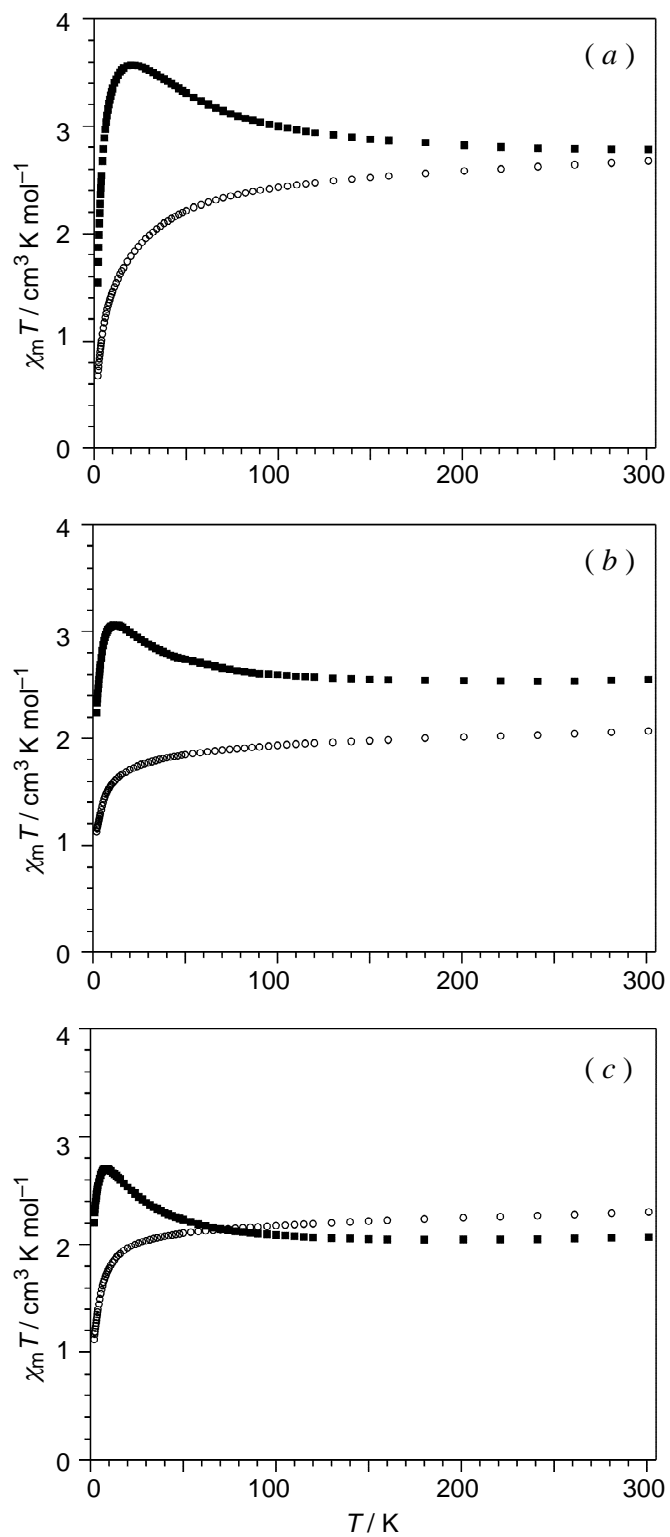
**Figure S4.** UV-vis absorption spectra of (a) *tI3* (—), *cI3* (·····), and IM3py (— · — ·); (b) *tI4* (—), *cI4* (·····), and IM4py (— · — ·) in acetonitrile at room temperature.



**Figure S5.** The difference absorption spectra of the NIT3py and IM3py complexes from the corresponding pyridine complexes.



**Figure S6.** The difference absorption spectra of the NIT4py and IM4py complexes from the corresponding pyridine complexes.



**Figure S7.** Temperature dependence of the magnetic susceptibilities in the form of  $\chi_m T$  vs.  $T$  for (a) **tN3** (O) and **tN4** (■), (b) **cI3** (O) and **cI4** (■), and (c) **tI3** (O) and **tI4** (■).