

Supporting Information Available for**“Separated” versus “Contact” Ion-Pair Structures in Solution from their Crystalline States:
Dynamic Effects on Dinitrobenzenide as a Mixed-Valence Anion.**

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Crystallization details and physical properties of ion pair salts (Table S1); thermodynamics of the CIP₁/CIP₂ isomerization of K(L_{E4})⁺DNB⁻ (Figure S1); temperature-dependent ESR spectrum of K(L_{E3})⁺DNB⁻ (Figure S2); dynamic ESR simulation of alternating line-broadening for K(L_{E3})⁺DNB⁻ (Figure S3); simulation of low-temperature ESR spectrum of K(L_{E3})⁺DNB⁻ as superposition of CIP and SIP ion-pairs (Figure S4); simulation of low-temperature ESR spectrum of K(L_{E4})⁺DNB⁻ as superposition of CIP and SIP ion-pairs (Figure S5); temperature-dependent ESR spectrum of K(L_{E2})⁺DNB⁻ (Figure S6); temperature-dependent ESR spectrum of K(L_{E2})⁺DNB-d₄⁻ (Figure S7); temperature-dependent electronic spectrum of K(L_{E2})⁺DNB⁻ (Figure S8); and IR spectra of crystalline ion-pair salts (Figure S9).

Table S1. Crystallization and physical properties of ion-pair salts.

Ion Pair	solvents	Solution color	Crystal color	Crystal shape
$K(L_C)^+ DNB^-$	THF/hexane	Yellow green	Dark green	Needle plate (single)
$K(L_{E1})_2^+ DNB^-$	THF	Yellow green	Dark green	Needle (single)
$K(L_{E2})^+ DNB^-$	THF/hexane	green	green	Thin plate (poly)
$K(L_{E3})^+ DNB^-$	THF/hexane	Green	Dark green	Needle (single)
$K(L_{E4})^+ DNB^-$	THF/hexane	Green	Dark green	Hemisphere (poly)
$[K(L_{E2})^+]_2 DNB^{2-}$	THF	brown	brown	Needle (single)

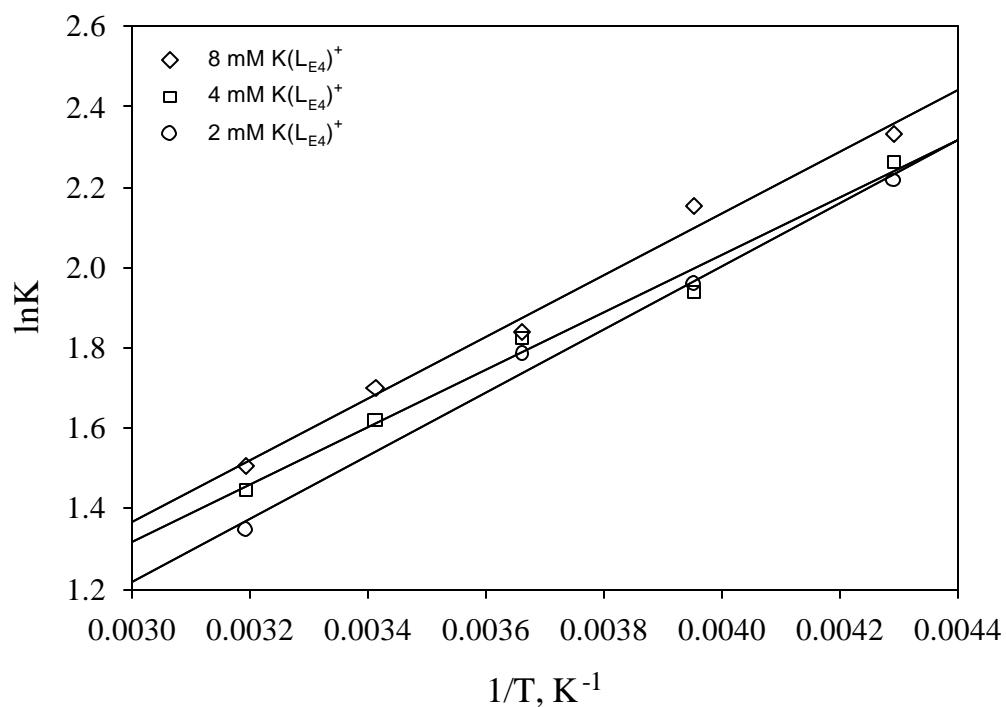


Figure S1. Thermodynamics of temperature-dependent equilibrium between isomeric contact ion pairs of $\text{K}(\text{L}_{\text{E}4})^+\text{DNB}^\bullet$ in THF: $\text{CIP}_1 \xrightleftharpoons{\text{K}_{\text{iso}}} \text{CIP}_2$, with $\Delta\text{H}_{\text{iso}} = -1.5 \text{ kcal mol}^{-1}$ and $\Delta\text{S}_{\text{iso}} = -2 \text{ e.u.}$

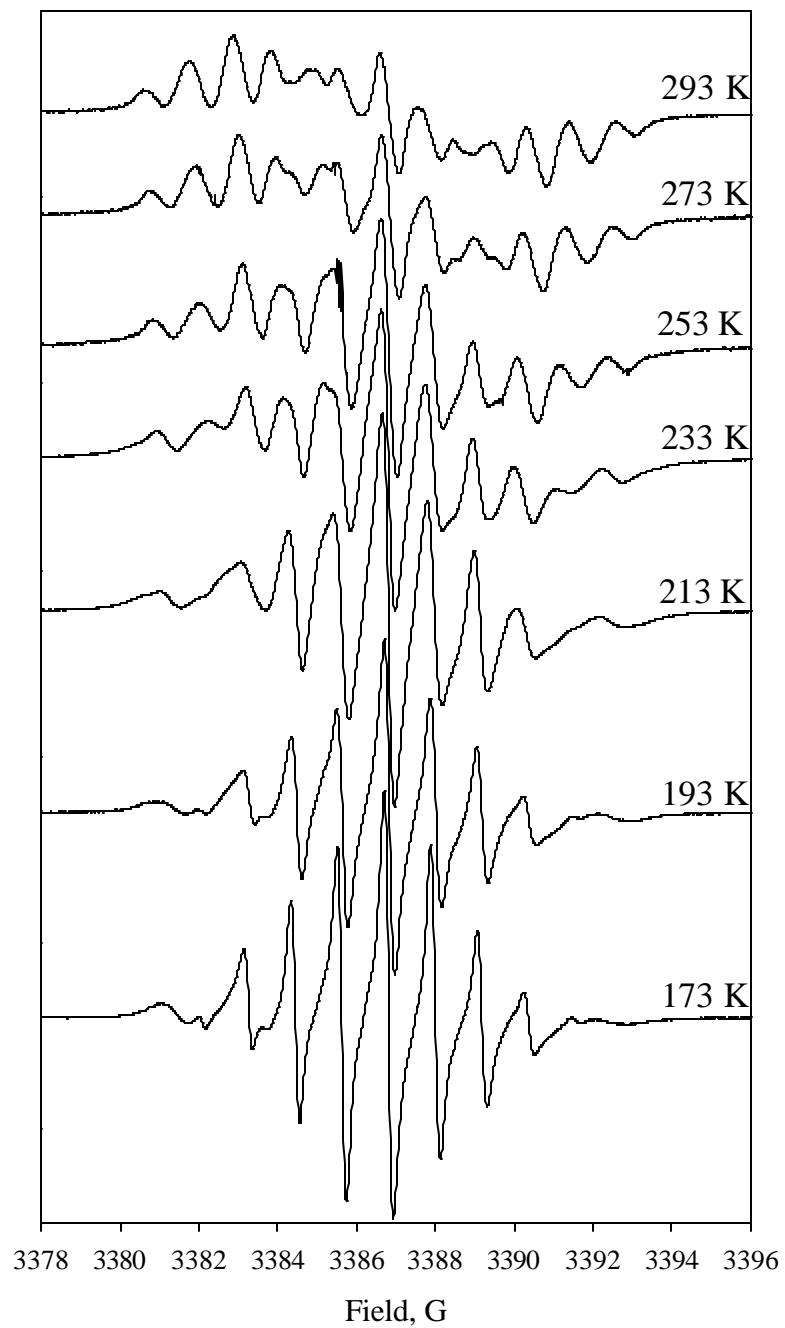


Figure S2. Temperature dependence of the ESR spectrum of $\text{K}(\text{L}_{\text{E}3})^+\text{DNP}^-$ in THF solution.

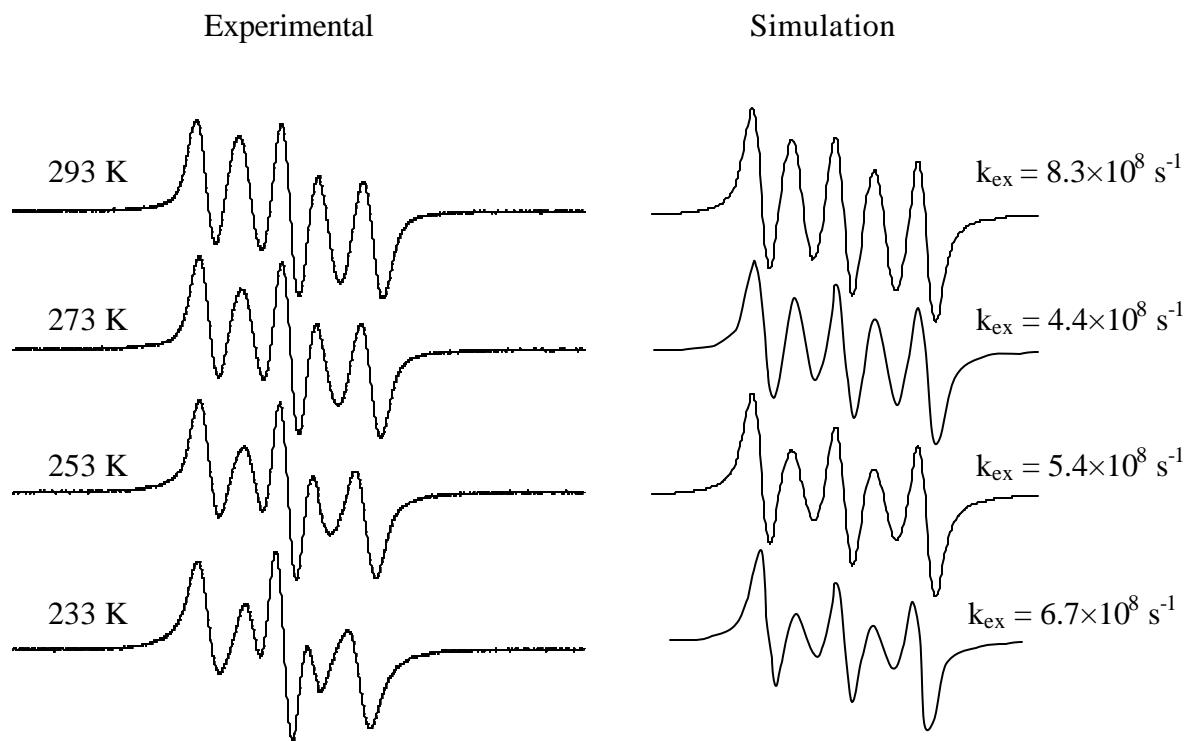


Figure S3. Dynamic ESR simulation (with rate constant presented on the right side) of the alternating linebroadening in the temperature-dependent ESR spectrum of $\text{K}(\text{L}_{\text{E}3})^+\text{DNB}^-$ in THF solution.

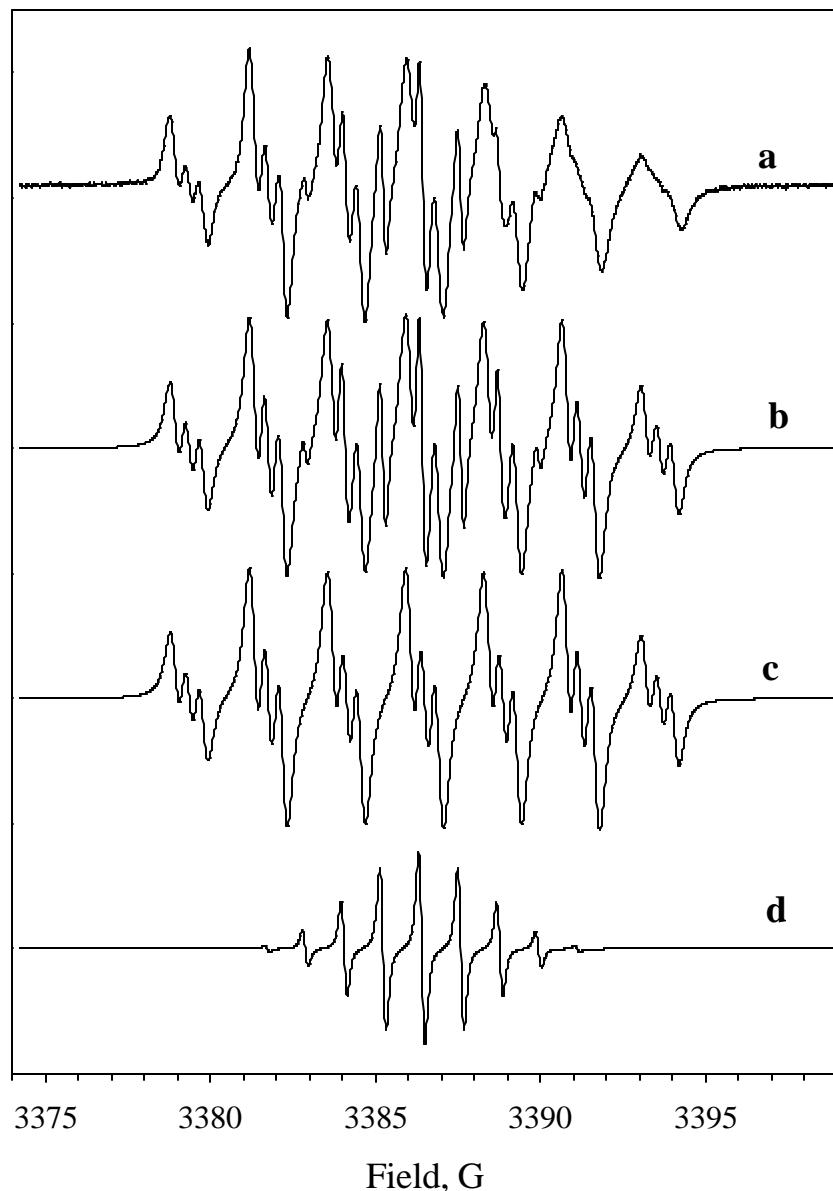


Figure S4. ESR spectrum of $\text{K}(\text{L}_{\text{E}4})^+\text{DNB}^-$ in THF at $-100\text{ }^\circ\text{C}$ (a) and its simulation (b) by the addition of two components: CIP (c) and SIP (d)

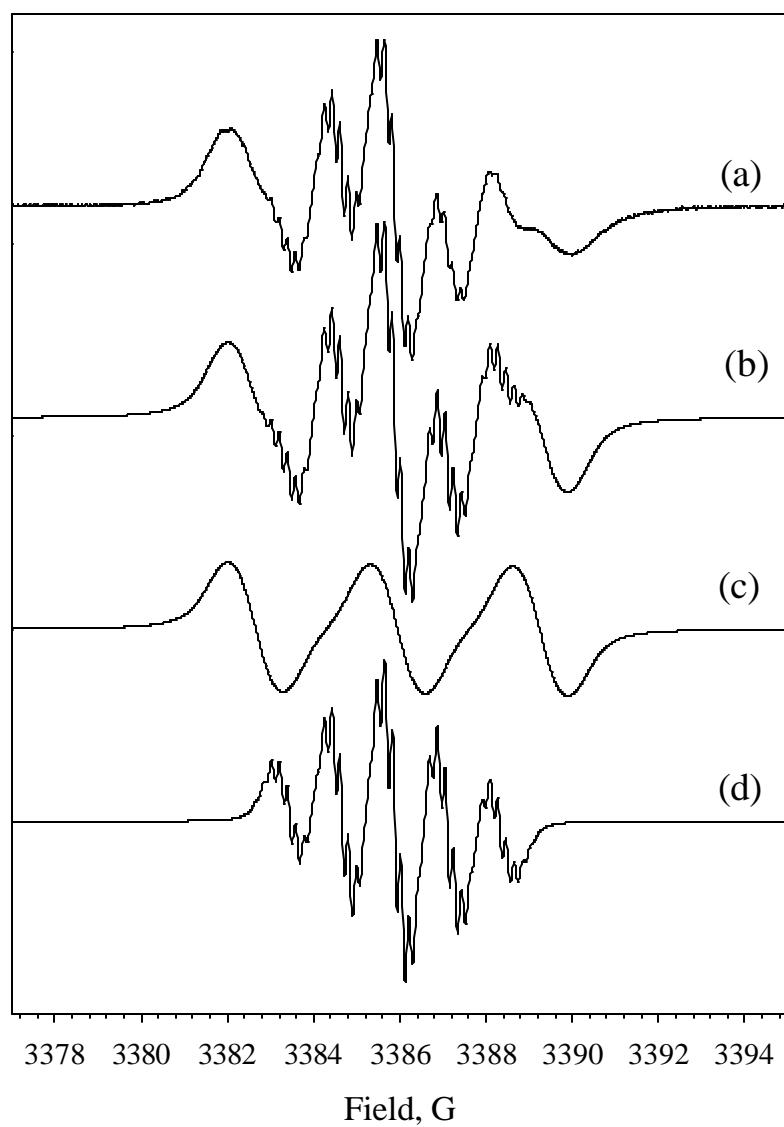


Figure S5. ESR spectrum of $\text{K}(\text{L}_{\text{E}3})^+\text{DNB-d4}$ in THF at $-100\text{ }^\circ\text{C}$ (a) and its simulation (b) by the addition of two components of CIP (c) and SIP (d)

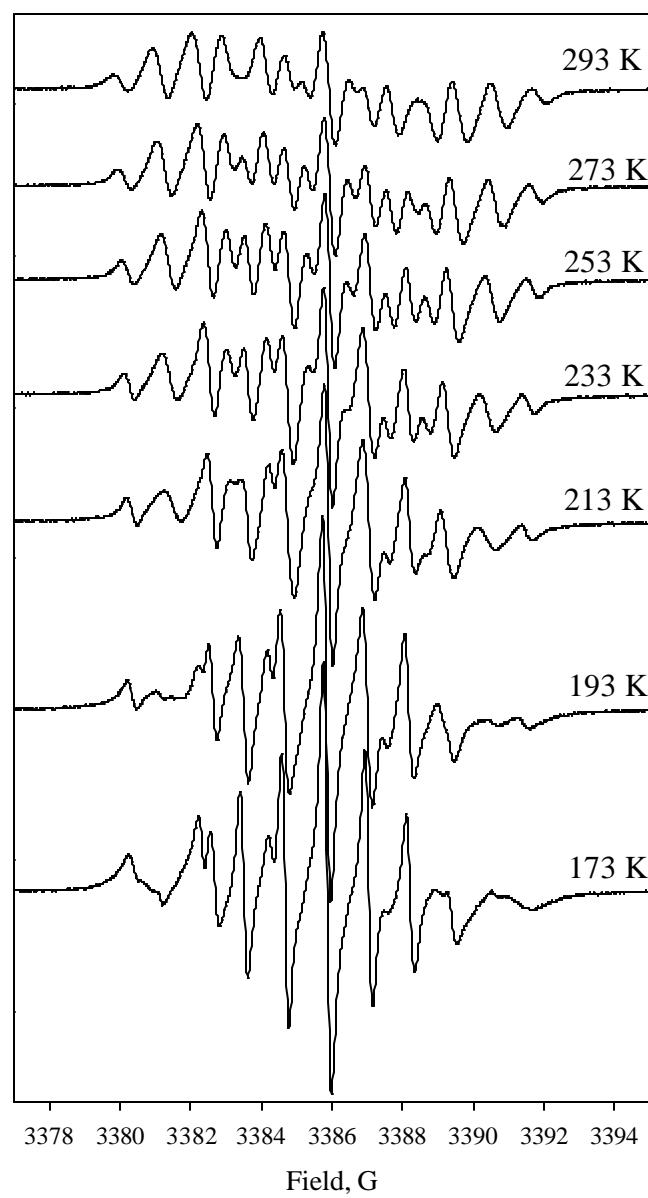


Figure S6. Temperature dependence of the ESR spectrum of $\text{K}(\text{L}_{\text{E}2})^+\text{DNB}^-$ in THF solution.

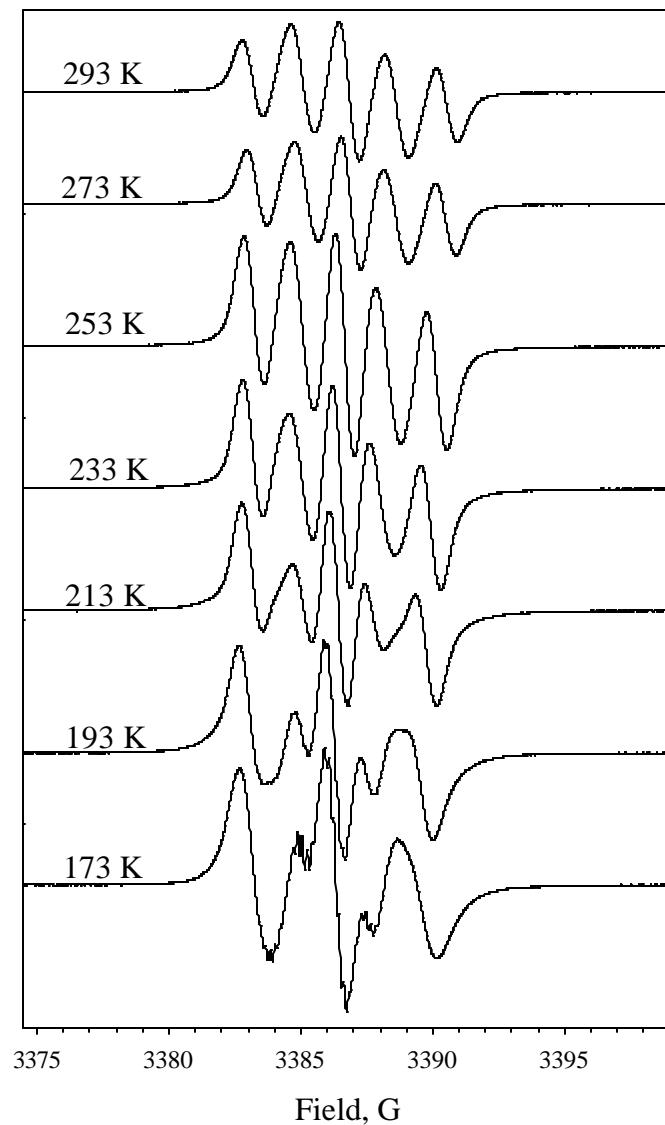


Figure S7. Temperature dependence of the ESR spectrum of
1 mM $\text{K}(\text{L}_{\text{E}2})^+$ DNB-d₄⁻ in THF

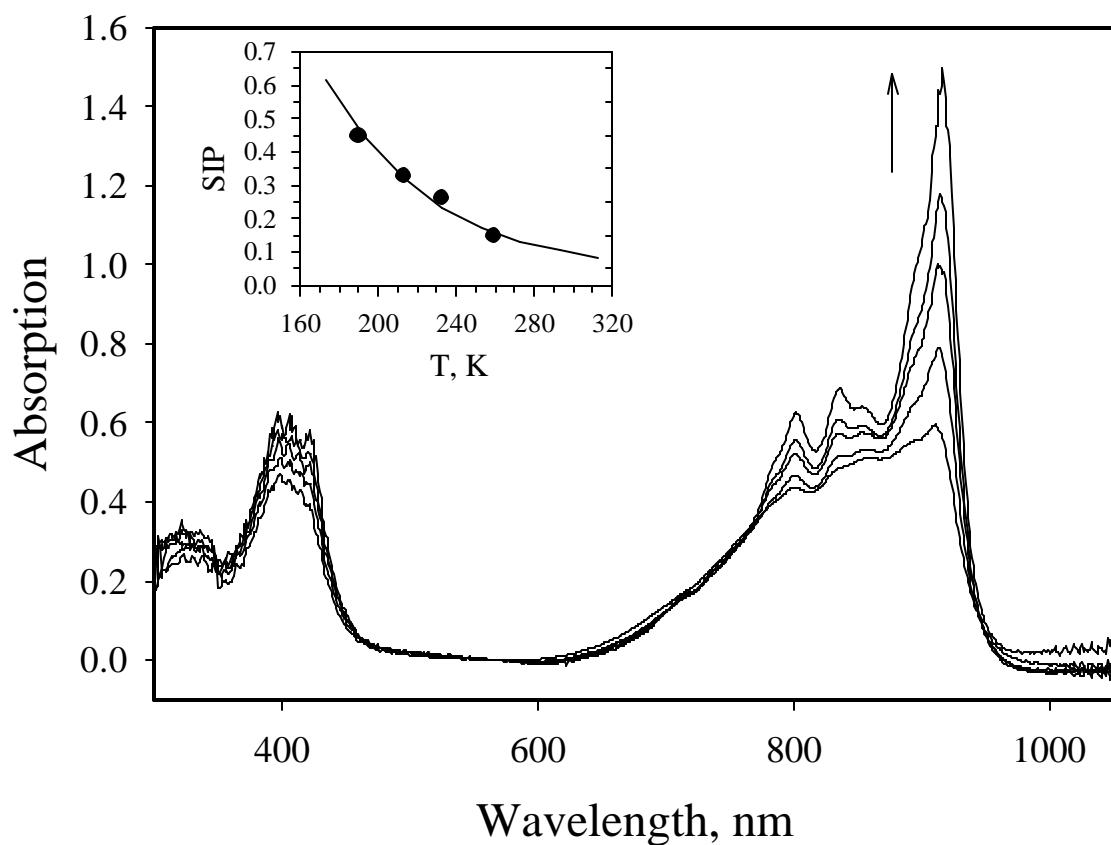


Figure S8. Temperature-dependent UV-NIR spectrum of $\text{K}(\text{L}_{\text{E}2})^+ \text{DNB}^-$ in THF measured at (bottom- to-top): 295, 259, 233, 213 and 190 K to reflect the $\text{SIP} \rightleftharpoons \text{CIP}$ interchange in eq 3. Inset: Fraction of SIP fitted with $\Delta H = -2.2 \text{ kcal/mol}$ and $\Delta S = -12 \text{ e.u}$ (inset).

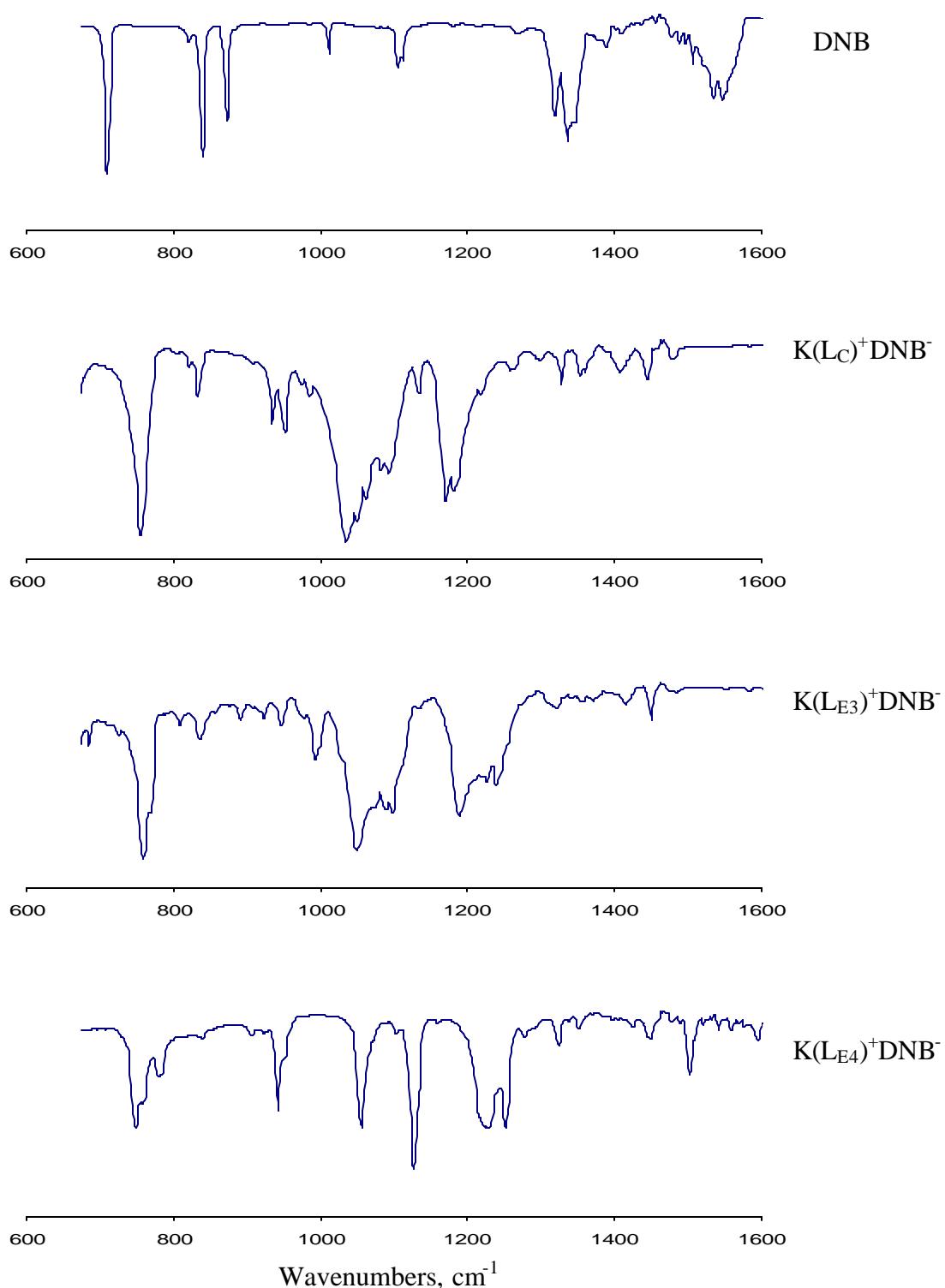


Figure S9. Solid-state (reflectance) IR spectra of dinitrobenzenide ion-pair salts (showing significant shifts of the symmetric and asymmetric NO_2 -stretching frequencies in comparison with those at 1330 and 1530 cm^{-1} of the neutral acceptor).