Supporting Information

The Class II/III Transition Electron Transfer on an Infrared Vibrational Time Scale for *N,N′*-Diphenyl-1,4-phenylenediamine Structures

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Bloch equation treatment

The effects of exchange between the N-H and $N^{+\bullet}$–H should be treated according to ref. 16.

First, the simple exchange rate in NMR spectra is described as follows,

$$\mathrm{A} \underset{k_\mathrm{B}}{\overset{k_\mathrm{A}}{\rightleftharpoons}} \mathrm{B} \quad (1)$$

$$\frac{\mathrm{d[A^*]}}{\mathrm{dt}} = -k_\mathrm{A}[\mathrm{A^*}] \quad (2)$$

where [A*] is the concentration of A. The relation between the rate constant and the existence ratio is as follows,

$$\mathrm{p_A} + \mathrm{p_B} = 1 \quad (3)$$

$$\mathrm{p_A} \cdot k_\mathrm{A} = \mathrm{p_B} \cdot k_\mathrm{B} \quad (4)$$

where p_A and p_B are the fractional populations in sites A and B. Finally, the bandshape of the super exchange is as follows

$$v = -C_0 \frac{\left\{ P\left[1 + \tau\left(\frac{p_B}{T_{2A}} + \frac{p_A}{T_{2B}} \right) \right] + QR \right\}}{P^2 + R^2} \quad (5)$$

$$\delta\nu = \nu_A - \nu_B, \Delta\nu = 0.5(\nu_A + \nu_B) - \nu$$

$$P = \tau\left[\frac{1}{T_{2A}T_{2B}} - 4\pi^2\Delta\nu^2 1 + \pi^2(\delta\nu)^2 \right] + \frac{p_A}{T_{2A}} + \frac{p_B}{T_{2B}}$$

$$Q = \tau[2\pi\Delta\nu - \pi\delta\nu(p_A - p_B)]$$

$$R = 2\pi\Delta\nu\left[1 + \tau\left(\frac{1}{T_{2A}} + \frac{1}{T_{2B}} \right) \right] + \pi\delta\nu\tau\left(\frac{1}{T_{2B}} + \frac{1}{T_{2A}} \right) + \pi\delta\nu(p_A - p_B)$$

$$\tau = \frac{p_A}{k_B} = \frac{p_B}{k_A}$$

where $\tau_A = \frac{1}{k_A}$, and $\tau_B = \frac{1}{k_B}$ are the lifetimes, $W_A = \frac{1}{\pi T_{2A}}$, and $W_B = \frac{1}{\pi T_{2B}}$ are the bandwidths as a single Lorentzian without super exchange, and ν_A and ν_B are the chemical shifts. The arbitrary bandshape of the coalescent NMR spectra was obtained as v vs ν by the determination of k_A (and/or k_B). and generally, the Eyring equation holds between *k* and *T*.

However, in our case of the IR spectra, the magnitude and bandwidth of the N–H and the $N^{+\bullet}$–H vibration signals are different. Moreover, the shapes of the spectra are not in accord with the simple Lorentzian function but are according to the Voigt function which convolutes Lorentzian and Gaussian due to the solution.

First, we treat the magnitude difference as the difference in the existence ratio ($p_A \neq p_B$), and second, the IR spectra shapes are treated according to the peak position and the bandwidth of the Voigt function as the Lorentzian function of Bloch-type equation analysis.

However, only under these conditions, it is difficult to fit the Bloch-type equation to the experimental spectra

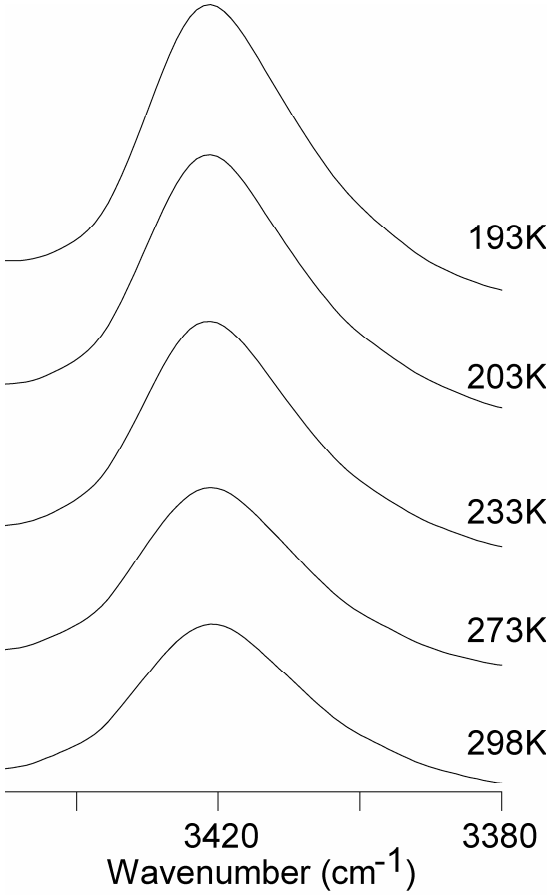
exactly. The suitable k_A (and k_b) at an arbitrary temperature are calculated beforehand using the Eyring equation when the experimental spectra at all temperatures at the same time are best fits. The Eyring plots and the estimation of $\Delta G^{\ddagger}$ are shown in SI Figure 3 and SI Table 5.

SI Table 1 Fitting parameters for Figure 5a (PDA) using Voigt function obtained from Igor Pro 4.08J

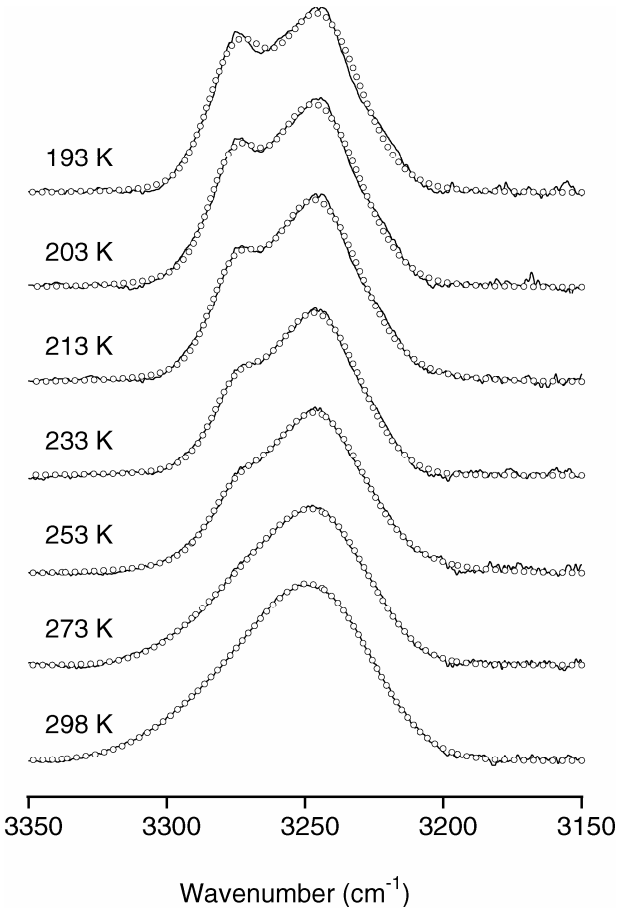
Potential (V)	0	0.2	0.3	0.5	0.7	0.8
Amplitude	0.0113	0.0051	0	0	0	0
Position	3420	3420				
Width (cm^{-1})	15.9	16.8				
V Shape	0.143	0.798				
Amplitude	0.0046	0.0026	0.0027	0	0	0
Position	3371	3369	3367			
Width (cm^{-1})	22.766	15.145	12.249			
V Shape		0.1158	5.18			
Amplitude	0	0.0230	0.0405	0.0325	0.0137	0
Position		3249	3247	3247	3248	
Width (cm^{-1})		38.2	40.7	38.7	37.6	
V Shape		0.709	0.216	0.467	0.000	
Amplitude	0	0.0032	0.0082	0.0047	0.0049	0
Position		3185	3186	3187	3191	
Width (cm^{-1})		10.2	12.5	10.9	20.2	
V Shape		0.001	0.000	0.012	1.54	

SI Table 2 Fitting parameters for Figure 5b (PDA-Br) using 2 kinds of Voigt function obtained from Igor Pro 4.08J

Potential (V)	0	0.5	0.55	0.6	1
Amplitude	0.0154	0.0058	0.0041	0.0040	0
Position	3401	3401	3396	3393	
Width (cm^{-1})	18.5	17.5	19.1	10.4	
V Shape	0.267	0.079	0.289	165	
Amplitude	0	0.0127	0.0163	0.0179	0.0011
Position		3320	3322	3321	3323
Width (cm^{-1})		21.7	23.3	22.0	15.9
V Shape		0.000	0.074	0.000	0.370



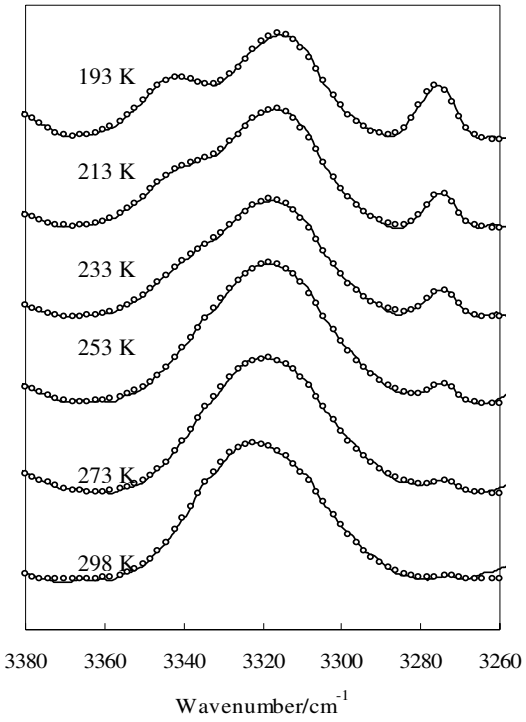
SI Figure 1 Variable temperature of IR-spectra for N–H stretching vibration of PDA in the neutral state.



SI Figure 2 Variable temperature of IR-Spectra for $PDA^{+\bullet}$. — Measurement, ° fitting curve using 2 kinds of Voigt function.

SI Table 3 Fitting parameters for SI Figure 1 using 2 kinds of Voigt function obtained from Igor Pro 4.08J

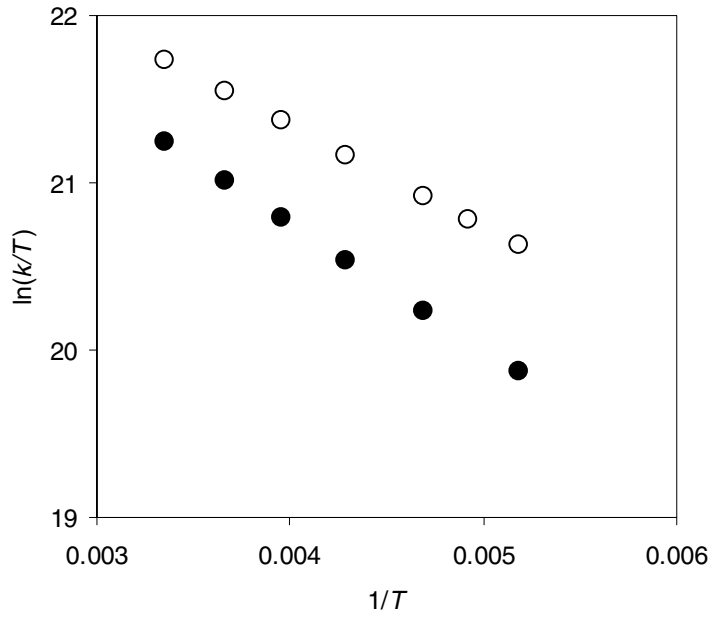
Temp (K)	193	203	213	233	253	273	298
Amplitude	0.0268	0.0270	0.0487	0.0236	0.0251	0.0176	0.0220
Position	3245	3246	3246	3246	3246	3242	3244
Width	22.4	23.4	14.5	22.4	27.4	24.4	28.1
Voigt Shape	0.144	0.107	0.268	0	0.344	0.033	0.021
Amplitude	0.0193	0.0175	0.0137	0.0119	0.0084	0.0117	0.0101
Position	3276	3276	3276	3275	3276	3269	3276
Width	15.2	14.7	13.8	15.1	16.1	29.0	32.5
Voigt Shape	0.207	0.559	0.358	0.578	0.509	0	0



SI Figure 3 Variable temperature of IR-Spectra for PDA-$Br^{+\bullet}$. — Measurement, ° fitting curve using 4 kinds of Voigt function.

SI Table 4 Fitting parameters for SI Figure 2 using 4 kinds of Voigt function obtained from Igor Pro 4.08J

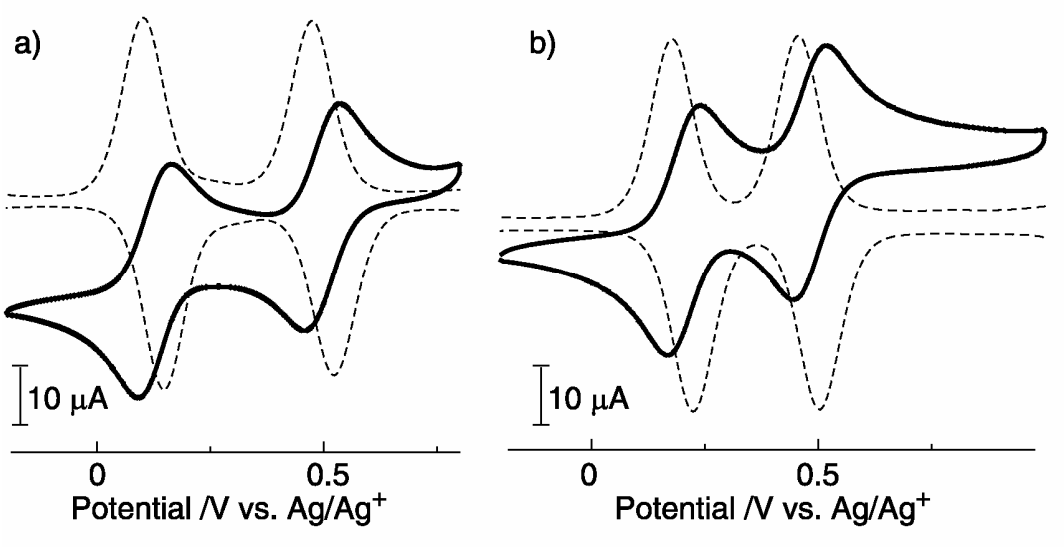
Temp (K)	193	213	233	253	273	298
Amplitude	0.0064	0.0039	0.0029	0.0019	0.0013	0.0006
Position	3276	3275	3275	3274	3274	3273
Width	6.1	5.2	5.1	4.4	4.0	2.1
Voigt Shape	0.018	0	0.003	0.063	0.910	11.428
Amplitude	0.0116	0.0130	0.0137	0.0171	0.0150	0.0119
Position	3316	3316	3317	3316	3314	3315
width	14.6	15.6	17.9	21.1	20.7	17.9
Voigt Shape	0.005	0	0.264	0.532	0.865	0.003
Amplitude	0.0072	0.0058	0.0043	0.0035	0.0069	0.0075
Position	3343	3341	3339	3334	3329	3331
width	13.3	13.8	13.1	13.0	14.3	14.6
Voigt Shape	0.487	0.188	0.001	0	0.001	0
Amplitude	0.0027	0.0014	0.0013	0.0024	0.0028	0.0010
Position	3381	3381	3381	3384	3384	3384
width	6.9	6.6	6.8	9.7	12.5	5.5
Voigt Shape	0.001	0	0.003	0.001	0.008	0.033



SI Figure 4 Eyring plot of ln(*k*/T) vs 1/*T* for (°) $PDA^{+\bullet}$ and (•) $PDA\text{-}Br^{+\bullet}$, yielding $\Delta G^{\ddagger}$ = 420 and 522(cm^{-1}), respectively.

SI Table 5 Fitting parameters for Bloch-type equation

	$PDA^{+\bullet}$	$PDA\text{-}Br^{+\bullet}$
T_{2A}	0.030	0.023
T_{2B}	0.015	0.022
ν_A (cm^{-1})	3275	3342.5
ν_B (cm^{-1})	3243	3315.5
P_A	0.28	0.26
P_B	0.72	0.74
$\Delta G^{\ddagger}$ (cm^{-1})	420	522



SI Figure 5 Cyclic voltammograms (solid lines) and relative differential pulse voltammograms (dotted lines) of (a) 1 mM solution of 2,6-DMPDA with 0.63 M trifluoroacetic acid and (b) 1 mM solution of PDA with 0.5 M trifluoroacetic acid. The condition is as follows. Solvent: acetonitrile, Electrode: glassy carbon (0.071 cm^2), Counter electrode: Pt coil, Reference electrode: Ag/Ag^+, Supporting electrolyte: 0.2 M $TBABF_4$, Amplitude: 50 mV.