Understanding the shift in BIP-cyclohexylimine redox potential as a function of the number of benzimidazole moieties

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To understand the shift in the redox potential as the number of benzimidazole units is increased, we can decompose the process into elementary steps of the thermodynamic cycle. A schematic of the different steps is given in Figure 1.

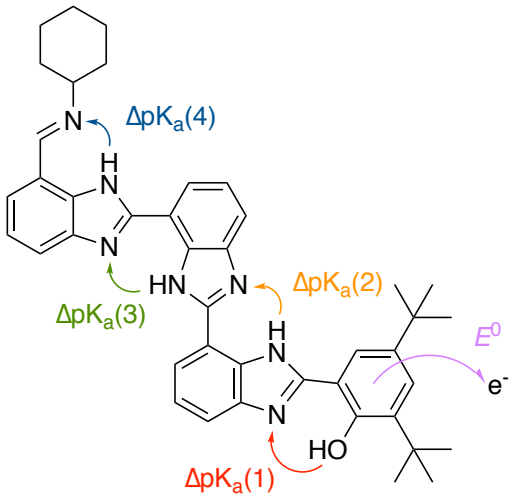

Figure 1. Stepwise decomposition of the different energetic components involved in the E4PT process for tri-BIP-cyclohexylimine.

Mathematically, we can represent the change in redox potential for each intermediate step in the EnPT process as

$$\begin{aligned} E^0(\mathrm{E0PT}) &= E^0 \\ E^0(\mathrm{E1PT}) &= E^0 + \Delta\mathrm{pK_a}(1) \\ E^0(\mathrm{E2PT}) &= E^0 + \Delta\mathrm{pK_a}(1) + \Delta\mathrm{pK_a}(2) \\ E^0(\mathrm{E3PT}) &= E^0 + \Delta\mathrm{pK_a}(1) + \Delta\mathrm{pK_a}(2) + \Delta\mathrm{pK_a}(3) \\ E^0(\mathrm{E4PT}) &= E^0 + \Delta\mathrm{pK_a}(1) + \Delta\mathrm{pK_a}(2) + \Delta\mathrm{pK_a}(3) + \Delta\mathrm{pK_a}(4) \end{aligned} \quad (1)$$

Here E^0 is the redox potential for the reaction $\mathrm{BIP}^+ + e^- \rightarrow \mathrm{BIP}$, with no transfer of protons. Each $\Delta\mathrm{pK}_a$ describes how the redox potential shifts as each intermediate proton is transferred.[1] A summary of the computed results for the members of the BIP-cyclohexylimine series is given below in Table 1.

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[1] In Eq. 1, the $\Delta\mathrm{pK}_a$ s are assumed to be converted to an effective ΔE^0 that is in units of Volts by multiplying by 2.3RT/F.

Table 1. Shifts to redox potential (V vs Fc^+/Fc) as a function of proton transfer for BIP-cyclohexylimines with different numbers of benzimidazole moieties.

All units in Volts	mono-BIP-cyclohexylimine	di-BIP-cyclohexylimine	tri-BIP-cyclohexylimine
E^0	1.11	1.07	1.06
$\Delta pK_a(1)$	-0.4	-0.37	-0.34
$\Delta pK_a(2)$	-0.3	-0.16	-0.19
$\Delta pK_a(3)$	—	-0.24	-0.10
$\Delta pK_a(4)$	—	—	-0.22

What we see is that upon oxidation of the BIP, subsequent proton transfer is thermodynamically favorable. The energetic benefit for each *n* subsequent proton transfer, denoted by $\Delta pK_a(n)$, demonstrates that with each subsequent proton transfer, the overall reaction becomes more thermodynamically favorable. However, there are diminishing energetic returns for each proton transfer, and it appears that with each proton transfer in a given complex, the shift in potential roughly halves. The exception is on the final proton transfer to the imine. With this final proton transfer, the shift in redox potential is given an extra "push". The reason for this favorable shift is perhaps due to the nature of the transfer from benzimidazolium to imine, as well as the cyclohexyl substituent.

The shifts in ΔpK_a tell us that there are limits to the length of the BIP-cyclohexylimine series should we still want to observe full proton transfer. At a certain point, we would expect that the final proton transfer would no longer provide any thermodynamic benefit. This of course, will change upon change of the substituent. A full summary of the computed redox potentials for the BIP-cyclohexylimine series is given in Table 2.

Table 2. Overall redox potentials (V vs Fc^+/Fc) as a function of proton transfer for BIP-cyclohexylimines with different numbers of benzimidazole moieties.

Redox potential (V)	mono-BIP-cyclohexylimine	di-BIP-cyclohexylimine	tri-BIP-cyclohexylimine
$E^0(E0PT)$	1.11	1.07	1.06
$E^0(E1PT)$	0.71	0.70	0.72
$E^0(E2PT)$	**0.41**	0.54	0.53
$E^0(E3PT)$	—	**0.30**[a]	0.43
$E^0(E4PT)$	—	—	**0.21**

[a]Agrees by construction (reference reaction)