

# Mechanisms of Multi-Electron Transfers in *N*-Aryl Expanded Pyridiniums: Establishing their Unusual Versatile Electrophoric Activity

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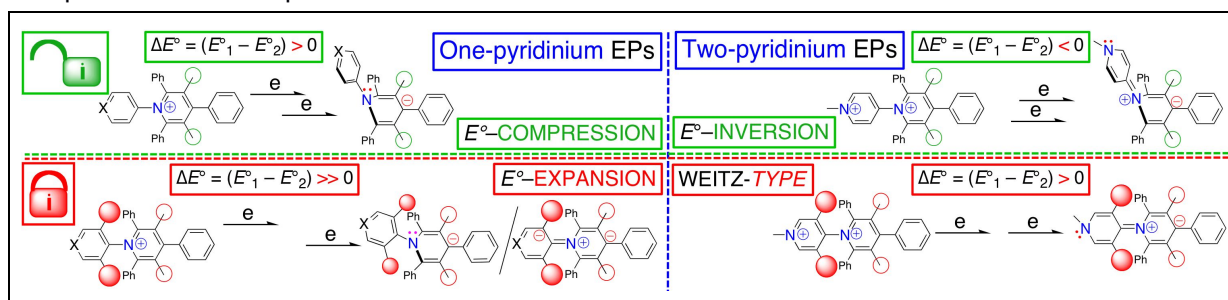
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The study of a series of pyridinium-based electrophores, namely *N*-aryl expanded pyridiniums (EPs),<sup>1a</sup> is presented with the aim of elucidating multifaceted mechanisms underpinning the complex electrophoric activity of these fluxional EP systems.<sup>1b</sup> By kinetic mapping of the first two heterogeneous electron transfers (ETs) of electrophores and computational mapping, at the DFT level, of their electronic and geometrical features in various redox states, it is established that, depending on whether EPs are made of one or two “head-to-tail”-connected pyridinium rings, the nature of the redox-triggered distortions (when allowed) is different, namely, *N*-pyramidalization due to hybridization change in the former case *versus* saddle-shaped distortion originating from conflicting intramolecular interactions in the latter case. When skeletal relaxations are sterically hampered, zwitterionic states and electron delocalization with quinoidal features are promoted as alternative relaxation modes. It follows that “potential compression” is changed to “potential expansion” (*i.e.* a further separation of redox potentials) in single-pyridinium EPs whereas “potential inversion” (*i.e.* single-step two-electron transfer) is changed to stepwise ETs of the Weitz type, for two-pyridinium EPs. Overall, this study establishes EPs as a unique class of electrophores.<sup>2</sup>



1. (a) Fortage, J.; Peltier, C.; Nastasi, F.; Puntoriero, F.; Tuyères, F.; Griveau, S.; Bedioui, F.; Adamo, C.; Ciofini, I.; Campagna, S.; Lainé, P. P. *J.A.C.S.* **2010**, *132*, 16700. (b) Fortage, J.; Peltier, C.; Perruchot, C.; Takemoto, Y.; Teki, Y.; Bedioui, F.; Marvaud, V.; Dupeyre, G.; Pospíšil, L.; Adamo, C.; Hromadová, M.; Ciofini, I.; Lainé, P. P. *J.A.C.S.* **2012**, *134*, 2691.

2. Lachmanová, S.; Dupeyre, G.; Tarábek J.; Perruchot, C.; Ciofini, I.; Hromadová, M.; Pospíšil, L.; Lainé, P. P. *Submitted*.