Due to the tolerance of catalyst **7** in combination with the interesting properties of poly(DCPD), new filled or unfilled thermosets could be prepared, which should find novel applications in the field of electro casting, insulation, and tooling (among others) in the near future. Work to improve catalysts and polymer systems are ongoing.

Experimental Section

The ruthenium and osmium complexes were prepared according to literature procedures [11]. NBE was purchased from Fluka, and DCPD (technical quality, 94%) from Shell and used as received. Viscosimetric measurements were performed on a home-built, real-time viscosimeter. Gel times were recorded on a Brookfield viscosimeter, DSCs on a Mettler DSC30 with a Mettler TC11 controller, TGAs on a Mettler TG50 with a Mettler TC10A controller, and surface roughness on a Form Talysurf S3C-50. Micro hardness was determined on a Fischerscope H100. ^{13}C CP-MAS NMR spectra of a piece of poly(DCPD) that was tightly fitted into the spinner were recorded on a Bruker 400-MHz instrument with a MAS rate of 11 kHz and a pulse delay of 5 s (a pulse delay of 60 s gave an identical result).

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The Amidinium–Carboxylate Salt Bridge as a Proton-Coupled Interface to Electron Transfer Pathways[**]

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Proton motion coupled to electron transfer is a basic energy conversion mechanism. Many proteins and enzymes function by utilizing the energy gathered along a charge-separating network to drive a proton pump, which in turn is manifested in a transmembrane chemical potential that provides the energy for the synthesis of complex biomolecules.[1] Yet some thirty years after Mitchell's initial proposal of proton translocation driven by electron transfer,[2] the mechanistic details of how the electron couples to the proton remain undefined.[1a, 3] To unravel the relationship between the proton and the electron, we have developed the following approach: electron transfer is photoinduced within photoexcitable electron donor–acceptor supramolecule complexes formed from the association of a proton transfer interface.[4] We have concentrated on asymmetric inter-

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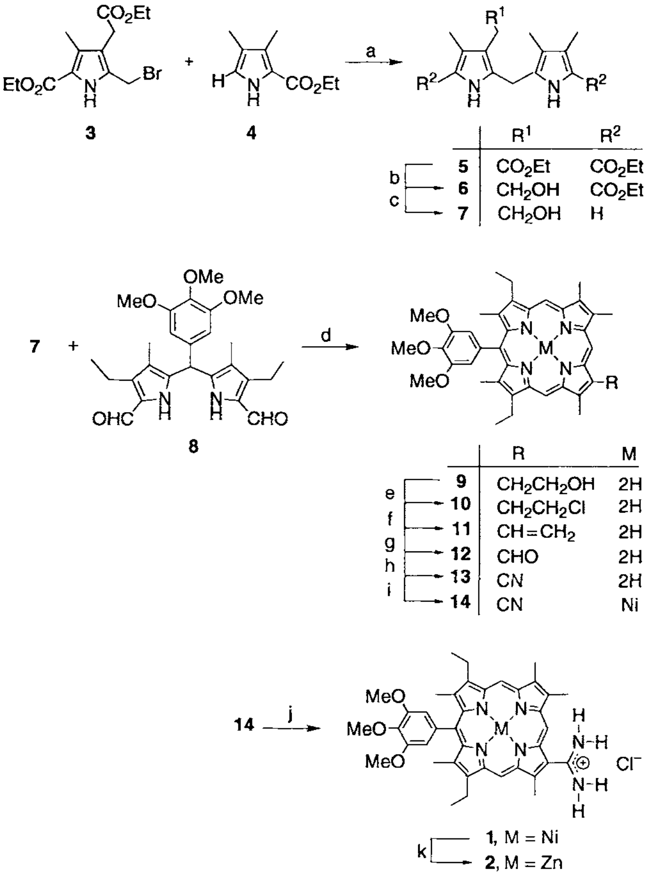
faces such as salt bridges, because they provide an important model for proton-coupled electron transfer (PCET) in biology, where reaction dynamics are modulated by coupling the charge redistribution accompanying both proton *and* electron motion to the surrounding environment.[5] Such is the case for the donor-(salt bridge)-acceptor supramolecule systems. Changes in polarity, charge, and energetics resulting from the transfer of an electron from the donor to the acceptor are augmented by the charge shift accompanying proton displacement within the salt bridge interface.

One attractive salt bridge for PCET studies is the amidinium-carboxylate interface, which models the arginine-aspartate salt bridges important to many biological structures.[6] But unlike the guanidinium-carboxylate interaction of Arg-Asp, amidinium group shows only one specific binding mode for carboxylate, thereby simplifying PCET studies. Though high association constants are characteristic of salt bridge supramolecules, an electron donor-acceptor complex assembled by such noncovalent interactions at the interface has yet to be structurally characterized. We now report the X-ray crystal structure of **1**·benzoate and show that the salt bridge is preserved in solutions of high dielectric constant. The salt bridge is maintained upon replacement of the phenyl ring by the electron-withdrawing 3,5-dinitro phenyl moiety, but with an attenuated association constant. When the porphyrin is made photoexcitable by Zn^{II} substitution of Ni^{II}, we observe an unusually slow rate of electron transfer for the porphyrinatozinc(II)-(amidinium carboxylate)-3,5-dinitrobenzene complex. Electronic spectroscopy indicates that the salt-bridge is strongly coupled to the electron transfer pathway and that it significantly influences the rate of electron transfer.

The syntheses of compounds **1** and **2** are outlined in Scheme 1. Dipyrrylmethane **5**, obtained from acid-catalyzed condensation of bromomethylpyrrole **3** and α-unsubstituted pyrrole **4**, was reduced by diborane (generated in situ by addition of BF_3 to $NaBH_4$) to give dipyrrylmethane **6**, which was then hydrolyzed and decarboxylated by heating with sodium hydroxide in ethylene glycol to give compound **7**. A modified MacDonald condensation[7] between **7** and **8** produced **9** in about 45% yield. Alcohol-derivatized porphyrin **9** was converted into vinyl porphyrin **11** by chlorination and elimination from **10** following standard procedures.[8] The vinyl group was oxidized to aldehyde **12** with osmium tetraoxide followed by sodium periodate. The aldehyde was converted into the nitrile ($\tilde{\nu}_{CN}$ at 2250 cm^{-1}) by heating at reflux with hydroxyamine hydrochloride in formic acid. After nickel complexation, **14** was converted into **1**[9] with Weinreb's reagent ($AlCl(CH_3)(NH_2)$) to deliver the amide.[10] The conversion of the Ni complex into the Zn complex can be accomplished by published procedures.[10]

The formation of the salt bridge is confirmed by X-ray crystallography of **1**·benzoate (Figure 1).[11] The relatively short N to O distances of 2.757(11) and 2.812(11) Å of the salt bridge indicates substantial stability and relatively strong hydrogen bonding ($d_{calcd}(O \cdots H) = 1.800$ and 1.874 Å). These bond lengths are usual for this type of salt bridge; according to a crystal structure analysis of the doubly hydrogen-bonded salt bridge formed between a bicyclic guanidinium unit and a carboxylate group, the N-O length is 2.85(4) and the attendant $O \cdots H$ bond length 1.97(4) Å.[12] An S_4 ruffling of the porphyrin ring is common for Ni^{II} porphyrin complexes and results from the contraction of the metal coordination site owing to the small size and high electrophilicity of the Ni^{II} atom.[13] The amidinium group is rotated by 42° with respect to the plane of the porphyrin ring, defined by the four pyrrole nitrogens (0.016 Å mean deviation from plane).[14] This canting of the



Scheme 1. a) HCl, ethanol, 80%; b) $NaBH_4$, BF_3, THF, 81%; c) NaOH, ethylene glycol, reflux, 95%; d) 1. $HClO_4$, methanol/THF; 2. chloranil, 48%; e) 1. $POCl_3$, DMF; 2. Na_2CO_3, 88%; f) DBU, pyridine, reflux, 95%; g) 1. OsO_4, CH_2Cl_2; 2. H_2S; 3. $NaIO_4$ in pyridine, 78%; h) $NH_2OH \cdot HCl$, formic acid, reflux, 95%; i) $Ni(OAc)_2$, DMF; j) $AlCl(CH_3)(NH_2)$, toluene, 93%; k) 1. concd H_2SO_4; 2. NaOH; 3. $Zn(OAc)_2$ in CH_2Cl_2, 90%.

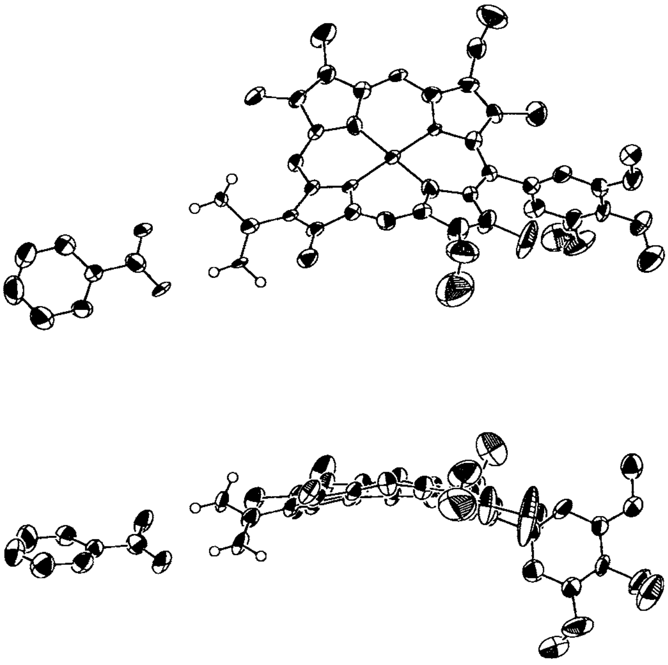


Figure 1. Top and side views of the ORTEP diagrams of the salt-bridged supramolecular assembly **1**·benzoate.

amidinium is not fully compensated by a counter rotation of the carboxylate, and a slight twist of 5.4° is observed within the salt bridge interface (dihedral angle defined by the planes of the CN_2 and CO_2 atoms of the salt bridge).

The amidinium–carboxylate salt bridge is very stable, and it persists in solutions, even when the dielectric constant of the solvent is high. Figure 2 shows the ^1H NMR spectral changes resulting from the association of the Ni^{II} porphyrin to benzoate ions in [D$_6$]DMSO. The chemical shift of the *meso* proton adjacent to the amidinium group at $\delta = 10.0$, and the nearly coincident singlets of two distal *meso* protons (indicated by the arrows) at $\delta = 9.8$, do not vary with addition of benzoate, indicating that π-stacking is not an important association mechanism (the *meso* protons are a sensitive measure of π-stacking in porphyrin systems[15]). As observed previously for the bicyclic guanidinium–carboxylate salt bridge,[12] a signature of salt bridge formation is the concentration-dependent downfield shift of amidinium protons involved in hydrogen bonding (NH_{ax} varies by more than 4 ppm) to carboxylate and the insensitivity of the chemical shift ($\delta < 0.5$) for the amidinium protons external to the salt bridge (NH_{eq}). A linear least-squares fit of chemical shift of the hydrogen-bonded amidinium protons vs. the carboxylate concentration, as described by Wilcox,[16] yields an association constant (K_a) of $1550(9)\,\text{M}^{-1}$ for **1**·benzoate in DMSO. A 1:1 stoichiometry of the complex is established by a Job's plot[17] of the ^1H NMR titration data, which shows that the optimal formation of **1**·benzoate occurs at equimolar concentrations of the amidinium and carboxylate (that is, 0.5 mole fraction). The exceptionally high association of the salt bridge accords well with Jorgensen's classification for two favorable secondary interactions that compose the hydrogen bonded interface,[18] bolstered by the stabilization imparted by the molecular recognition of the negatively charged carboxylate by the positively charged amidinium groups. When the benzoate ion is replaced by the well-known electron acceptor 3,5-dinitrobenzoate (3,5-DNBCOO$^-$), similar behavior is observed. The chemical shifts of the *meso* protons ($\delta = 9.72$) and NH_{eq} ($\delta = 9.96$) exhibit an insignificant shift upon 3,5-DNBCOO$^-$ addition ($\Delta\delta < 0.1$ over 12 mM), while NH_{ax} varies by 2 ppm over the same concentration range. However, we observe a smaller K_a of $267\,\text{M}^{-1}$, which is consistent with a decreased basicity of the carboxylate group conferred by the electron-withdrawing nitro groups, which results in a weaker hydrogen bonding interaction.

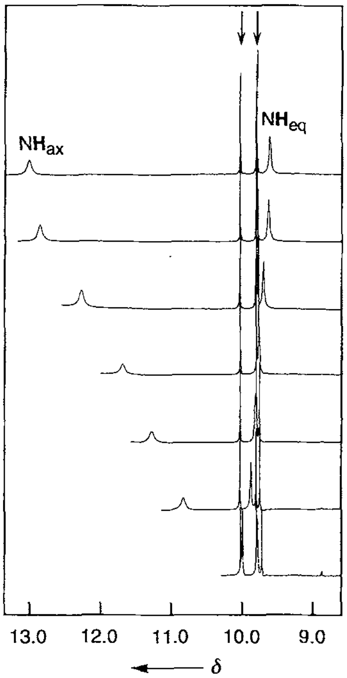


Figure 2. Selected ^1H NMR spectra of **1** (3.63 mM) in the presence of 0.00, 1.39, 2.08, 2.77, 4.16, 7.62, and 13.9 mM (bottom to top) tetrabutylammonium benzoate in [D$_6$]DMSO. The spectral range captures the signals of the amidinium protons internal (NH_{ax}) and external (NH_{eq}) to the salt bridge interface and the three *meso* protons of the porphyrin ring (indicated by arrows).

In less polar solvents the association constant greatly increases. Indeed the binding in CH_2Cl_2 is so high that the association can conveniently be followed by absorption spectroscopy. The Soret and Q-bands of the porphyrin undergo a blue shift immediately upon association of **1** to the carboxylate ion (λ_{max}(**1**) = 406, 530, 574 nm; λ_{max} (**1**·benzoate) = 403, 525, 570 nm; λ_{max} (**1**·3,5-DNBCOO$^-$) = 404, 526, 571 nm). Benesi–Hildebrand fits of these shifts in the absorption maxima with added carboxylate yields K_a of $5.7(11)\times10^6\,\text{M}^{-1}$ and $7.7(11)\times10^5\,\text{M}^{-1}$. As above, the electron-withdrawing nitro groups engender a smaller association constant.

The perturbation of the absorption profile upon salt-bridge formation suggests that the interface is strongly coupled to the porphyrinic chromophore and correspondingly to the electron transfer pathway. When Ni^{II} is replaced by Zn^{II}, the amidinium porphyrin exhibits luminescence, which decays monoexponentially with a lifetime of 1.5 ns (λ_{exc} = 588 nm, λ_{det} = 620 nm) for **2**·benzoate in CH_2Cl_2 at 25 °C. Replacement of the benzoate ion by the 3,5-DNBCOO$^-$ ion results in luminescence quenching, and a unimolecular rate constant of $6.4\times10^7\,\text{s}^{-1}$ is calculated from the decay kinetics. This observation is consistent with electron transfer from the singlet excited state of **2** to 3,5-DNBCOO$^-$ mediated by the amidinium–carboxylate salt bridge. The electron transfer rate constant for **2** is considerably smaller than that of covalently linked Zn^{II} porphyrin donor–acceptor systems. For instance, an electron transfer rate constant of $k = 3\times10^{10}\,\text{s}^{-1}$ is interpolated from Wasielewski's data on Zn^{II}porphyrin-L-quinone (L = rigid polycyclic spacer) systems at driving forces equivalent to **2** ($\Delta G = -0.30$ eV).[19] This considerably faster rate of the covalently tethered donor–acceptor system is further augmented by its longer electron transfer distance (edge-to-edge distance: Zn^{II}porphyrin-L-quinone = 10.5 Å; **2** 7.0 Å) and hence weaker electronic coupling.

The dramatic attenuation in the electron transfer rate constant through the salt bridge may have several origins. First, the electron transfer is in the direction of the permanent dipole of the salt bridge. The presence of an internal electric field contained within the electron transfer pathway will alter the driving force of reaction relative to the isolated constituents.[20] Second, the charge shift of the electron will be stabilized by an accompanying proton shift within the salt bridge. PCET through a salt bridge therefore includes Franck–Condon factors arising from the charge shift of the electron *and* the proton coupling to the polarization of the surrounding environment.[21] Finally, differences in H-bonding strengths of the asymmetric interfaces are manifested in differences in electronic coupling efficiencies.[22] The studies reported herein thus show that salt bridges can be used to form electron transfer networks by self-assembly, and as a constituent of the electron transfer pathway, the salt bridge can profoundly affect the rate of electron transport.

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Corrigendum

In the communication "Synthesis and Structure of the Nanoclusters $[Hg_{32}Se_{14}(SePh)_{36}]$, $[Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4]$, $[P(Et)_2(Ph)C_4H_8OSiMe_3]_5[Cd_{18}I_{17}(PSiMe_3)_{12}]$, and $[N(Et)_3C_4H_8OSiMe_3]_5[Cd_{18}I_{17}(PSiMe_3)_{12}]$" by S. Behrens, M. Bettenhausen, A. C. Deveson, A. Eichhöfer, D. Fenske, A. Lohde, and U. Woggon (*Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 2215–2218), Equation (c) was inadvertently omitted at a late stage of production. Equation (c) should read:

$$[CdCl_2(PPh_3)_2] \xrightarrow[\text{acetone}]{PhSeSiMe_3} [Cd_{32}Se_{14}(SePh)_{36}(PPh_3)_4]$$

0570-0833/97/3619-2127 $ 17.50+.50/0