Ion-Selective Channels Hot Paper

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Supramolecular Gating of Ion Transport in Nanochannels**

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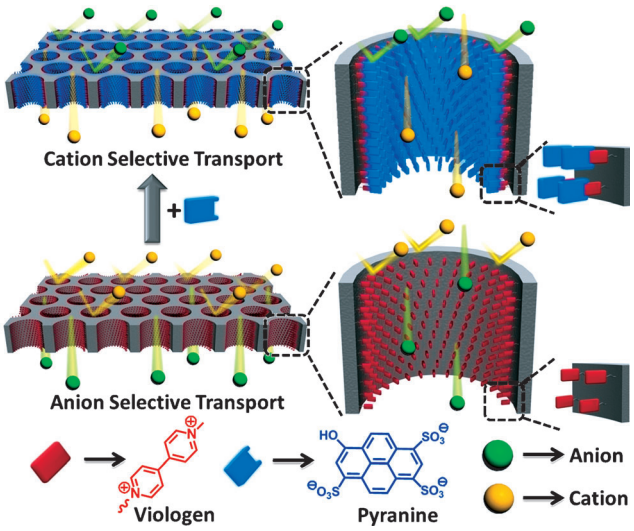
Abstract: *Several covalent strategies towards surface charge-reversal in nanochannels have been reported with the purpose of manipulating ion transport. However, covalent routes lack dynamism, modularity and post-synthetic flexibility, and hence restrict their applicability in different environments. Here, we introduce a facile non-covalent approach towards charge-reversal in nanochannels (< 10 nm) using strong charge-transfer interactions between dicationic viologen (acceptor) and trianionic pyranine (donor). The polarity of ion transport was switched from anion selective to ambipolar to cation selective by controlling the extent of viologen bound to the pyranine. We could also regulate the ion transport with respect to pH by selecting a donor with pH-responsive functional groups. The modularity of this approach further allows facile integration of various functional groups capable of responding to stimuli such as light and temperature to modulate the transport of ions as well as molecules.*

Biological systems employ protein nanochannels to regulate ion transport which is vital for maintaining their integrity and communication with extracellular environment.[1] Design of abiotic analogues to manipulate ion transport through nanochannels has gained tremendous attention in recent years, considering their role in the development of ionic circuits for sensing, switching and amplifying the chemical identities from aqueous environment.[2] Nanochannels with charged surfaces having pore dimensions within the Debye length range, are known to display selective transport properties associated with the surface charge dependent enhancement[3] and depletion phenomenon.[4] Thus, control of surface charge within the nanochannel is critical for effective gating and rectification of ion transport.[5] Manipulation of surface charge in nanochannels of size less than 10 nm is of biological relevance since at physiological salt concentrations the Debye length is in the range of few nanometers. Nanochannels having charge-reversal surfaces would be able to switch the polarity of ion transport from cation selective to anion selective and are ideal candidates for gating and rectification. To achieve charge-reversal, surfaces were often covalently functionalized with pH-[6] or light-responsive[7] functional groups such as aminoacids[8] and spiropyrans.[9] However, the covalent functionalization to a larger extent lacks dynamism, modularity and post-synthetic flexibility and hence, restricts its wider applicability in different environments. On the other hand, non-covalent functionalization, notwithstanding its ability to overcome some of these limitations, has not been successful so far in confined environments (< 10 nm). Since, non-covalent approach largely relies on electrostatic interactions, it is unlikely to attain charge-reversal in confined spaces where the penalty for charge accumulation is high.[10] In order to realize charge-reversal and hence, the control of ion permeation in nanopores/nanochannels through non-covalent approach, one has to overcome the electrostatic repulsion of "like" charges through strong orthogonal interactions. Here, for the first time we report the use of non-covalent, charge-transfer (C-T) based supramolecular motifs to obtain charge-reversal surfaces inside the nanopores and demonstrated their gating ability (Scheme 1). By employing pyranine as the donor and viologen as the acceptor we



Scheme 1. Non-covalent functionalization of viologen modified nanopores with negatively charged donor, pyranine (or coronene tetracarboxylate), to switch the gating properties of the nanopores from anion selective to cation selective.

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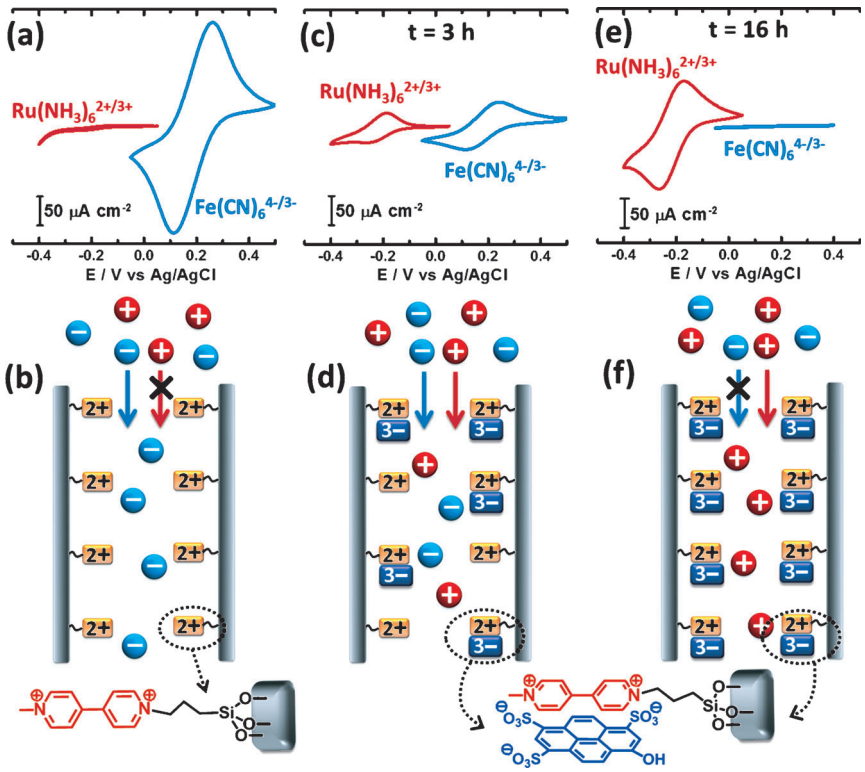

Figure 1. Cyclic voltammograms corresponding to viologen-modified mesoporous silica film (MF-V) deposited on ITO electrode in the presence of 1 mM $[Ru(NH_3)_6]^{3+}$ (red trace) and 1 mM $[Fe(CN)_6]^{3-}$ (blue trace) before (a) and after soaking in 1 mM pyranine solution for 3 h (c) and 16 h (e). The corresponding schematics are given as (b), (d) and (f), respectively. Scan rate: 200 mV s^{-1}, supporting electrolyte: 0.1 M KCl (pH 6).

manipulated the surface charge inside the nanochannels from positive to neutral or negative. pH-responsive switching of ion transport was also achieved through the use of coronene tetracarboxylate as donor.

Mixed charge transfer modules, in which donor and acceptor aromatic molecules are co-facially arranged, have recently emerged as strong supramolecular motifs for the formation of supramolecular polymers[11] and charge-transfer nanostructures.[12] In our previous report, we have shown that the non-covalent C-T interactions between covalently immobilized viologen and free pyranine analogues can be exploited to tune the pore size and philicity of mesoporous silica SBA-15.[13] The unusually strong C-T interactions (binding constant $\approx 10^5\,M^{-1}$) between the positively charged acceptor and negatively charged donor, led us to believe that the surface charge could be controlled non-covalently by using donors of different molecular charges.

To understand the ability of these strong supramolecular motifs in attaining charge-reversal within the confined nanopores (< 10 nm) and their concomitant role in gating of ion transport, cyclic voltammetric studies were carried out over viologen-modified mesoporous silica film prepared on a conducting ITO (indium tin oxide) substrate. The mesoporous silica films, SBA-16, were prepared on ITO[14] substrates by dip-coating a sol of tetraethylorthosilicate in presence of nonionic block-copolymer template, Pluronic F127.[15] The as-synthesized and calcined films were characterized using optical profilometry, TEM and cyclic voltammetry [Figures S1a,b, S2 and S3 in the Supporting Information (SI)]. The walls of the nanopores were covalently functionalized with viologen moieties through an iodopropylsilane method (Figure S4, SI) standardized for the functionalization of SBA-15 nanopores.[13] The TEM images of the viologen-modified mesoporous silica films (MF-V) show retention of mesoporous structure (Figure S1c,d, SI). IR spectroscopy and digestive analysis of the films confirmed the presence of viologen (Figure S5,S6, SI).

The transport across the nanopores of MF-V supported on ITO substrate was investigated separately with 1 mM solutions of $[Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_6]^{3+}$ as anionic and cationic electroactive probes, respectively, using cyclic voltammetry. Electrochemical measurements were carried out in the potential window of −0.40 V to +0.45 V, where there are no interferences from the electroactive acceptor, viologen and the donor, pyranine (Figure S7, SI). Figure 1a shows the cyclic voltammogram for the transport of $[Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_6]^{3+}$ through MF-V at pH 6 with 0.1M KCl as supporting electrolyte. The positively charged pores of the MF-V elicits a strong and highly selective electrochemical response (cathodic current density 185 μA cm^{-2}) for the transport of anionic, $[Fe(CN)_6]^{3-}$ probe (blue trace), and no response to the cationic, $[Ru(NH_3)_6]^{3+}$ (red trace), owing to the unipolar environment inside the nanopores (Figure 1b) of radius in the order of the Debye length range. To reverse the surface charge within the pores, non-covalent interactions between the positively charged viologen (each unit carries two positive charges) and negatively charged pyranine (each unit has three negative charges at pH 6) was used by soaking the MF-V film in 1 mM solution of pyranine (Figure S8, SI). MF-V soaked in pyranine solution for 16 h, shows a strong electrochemical response to cationic probe, $[Ru(NH_3)_6]^{3+}$ and no response for anionic $[Fe(CN)_6]^{3-}$ in the cyclic voltammogram, a complete reversal of ionic transport from anion selective to cation selective indicating charge-reversal inside the nanopores (Figure 1e,f). Furthermore, the peak current density for $[Ru(NH_3)_6]^{3+}$ transport (cathodic current density 96 μA cm^{-2}) is half that of the peak current density observed for $[Fe(CN)_6]^{3-}$ transport (cathodic current density 185 μA cm^{-2}) in MF-V. This can possibly be understood by considering the fact that the transport in nanochannels is governed by the surface charge.[3] On soaking MF-V in pyranine (16 h), the surface charge inside the nanopores is halved as the dicationic viologen moieties become monocationic C-T pairs and hence lead to a decrease in ion transport.

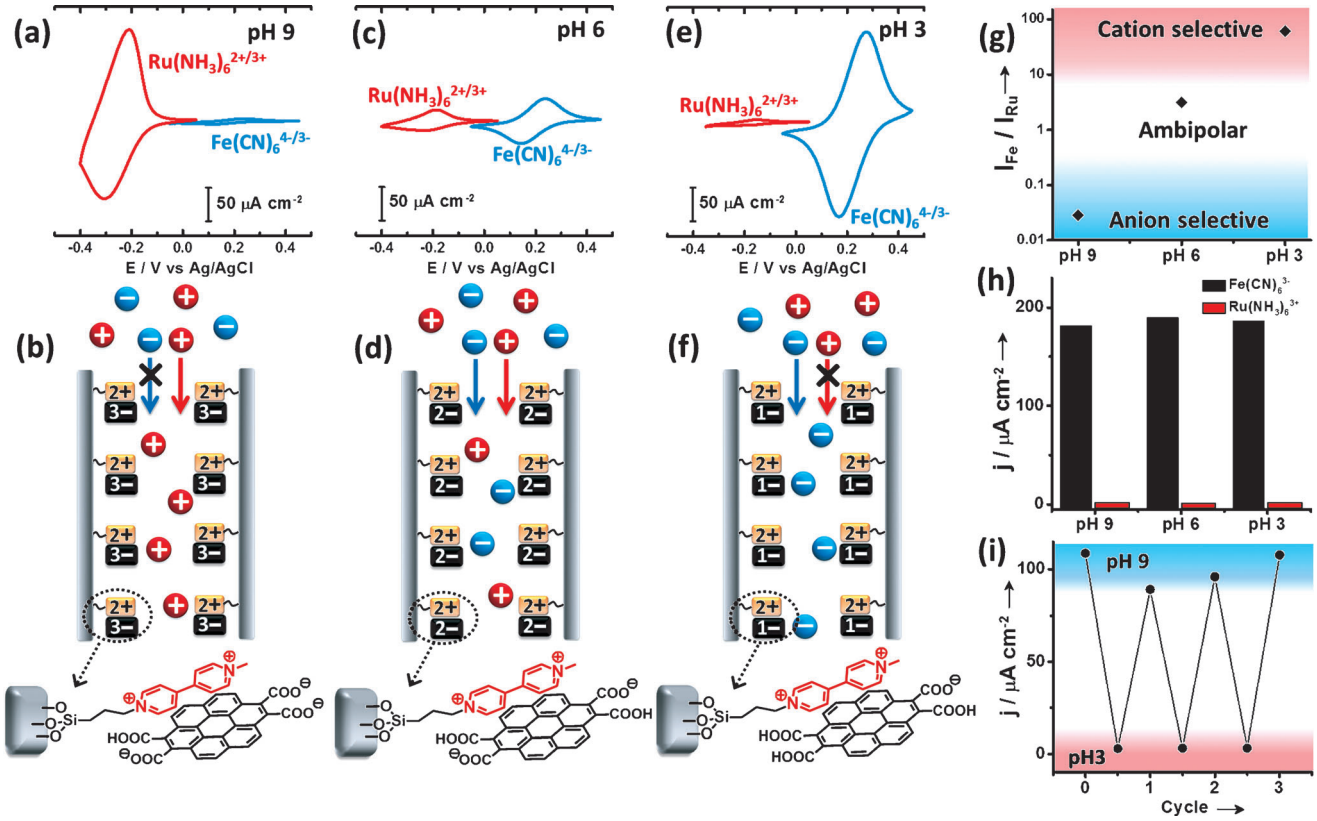

Figure 2. Cyclic voltammograms corresponding to coronene tetracarboxylate bound MF-V deposited on ITO electrode in the presence of 1 mM $[Ru(NH_3)_6]^{3+}$ (red trace) and 1 mM $[Fe(CN)_6]^{3-}$ (blue trace) at different pH conditions: a) 9, c) 6 and e) 3. Scan rate: 200 mVs^{-1}, supporting electrolyte: 0.1 M KCl. The corresponding schematics are given as (b), (d) and (f). g) The ratio of anion to cation current density showing three orders of change with pH. The regimes of different types of ion transport, viz. anion selective, cation selective and ambipolar, are shown in different colors. h) The peak current densities of $[Fe(CN)_6]^{3-}$ and $[Ru(NH_3)_6]^{3+}$ for MF-V show no significant change with variation in pH indicating absence of free silanol groups. i) The switching of peak current density of $[Ru(NH_3)_6]^{3+}$ on exposure to three cycles of pH change showing good reversibility.

It is to be noted that charge-reversal in 1:1 binding would be possible only when, the donor has more number of negative charges than the number of positive charges available with the acceptor. If the charges on both donor and acceptor are equal, 1:1 binding will only lead to charge neutralization. In our case, the dicationic acceptor, viologen and trianionic donor, pyranine would lead to neutralization when two-thirds of the viologen are bound to pyranine. The observation of charge reversal on soaking MF-V in pyranine for 16 h suggests that most of the viologen are bound to pyranine. Moreover, the extent of viologen moieties binding to pyranine inside the nanopores can be controlled by the time of soaking since the binding of pyranine to viologen is diffusion controlled.[13] SBA-16 films used here have a three-dimensional pore network containing pores of diameter 10–11 nm and pore necks of size around 6 nm.[10a] Functionalization with viologen moieties (MF-V) further reduces the pore neck size and hence restricts the diffusion of pyranine. This is in contrast to the fast diffusion observed over viologen-functionalized SBA-15 with relatively large pore size (8 nm).[13] The slow diffusion over MF-V was in turn used to control the surface charge within the pores from positive to neutral (or negative) depending upon the degree of binding of pyranine with time. When the soaking time of MF-V in pyranine solution was reduced to 3 h, the resulting film shows ambipolar transport by allowing both anionic and cationic probes to comparable extent (Figure 1 c,d).[16] This suggests that the surface charge of the nanopores is close to neutrality, implying that roughly two-thirds of the viologen are bound to pyranine.[17] It is worthy to note that an ionic blank (MF-B, Figure S4 in SI) made by functionalizing the pores of mesoporous silica films with dicationic ammonium salt of 1,4-diazabicyclo[2.2.2]octane (DABCO) did not show any reversal of transport behavior on soaking with pyranine (Figure S9, SI). This clearly supports the role of strong supramolecular C-T motifs in reversing the surface charge and polarity of ion transport in a confined environment.

The modular nature of these C-T based supramolecular motifs gives ample flexibility to manipulate the surface charge as they can be functionalized with various moieties which could respond to external stimuli like pH, light, and temperature. For example, donor components having several carboxylic acid groups (with different pK_a values) in the same molecule would offer pH responsive surface charge regulation within the confined nanopores. To integrate pH responsive ion-gating into the system, we have selected coronene

tetracarboxylate (CS) as the donor with four carboxylate groups whose protonation/deprotonation can be modulated with pH (Figure S8 and S10, SI). The MF-V films were soaked in coronene tetracarboxylate solution (1 mM, pH 6) to non-covalently functionalize the pore walls with CS. The ion transport through the nanopores of CS bound MF-V film was investigated at different pH (9, 6 and 3) to understand its pH-responsive transport. The voltammogram recorded at pH 9 shows a very high transport for positively charged $[Ru(NH_3)_6]^{3+}$ probe and a suppression for $[Fe(CN)_6]^{3-}$ transport, implying negatively charged pore walls (Figure 2a). This is understandable as most of the carboxylate groups of CS are not protonated at pH 9 (Figure 2b, S10 in SI), thereby flipping the charge on the pore walls from positive (MF-V) to negative. At pH 6, both positive and negative probes give similar voltammetric response indicating ambipolar transport (Figure 2c) This suggests that at pH 6, probably two of the four carboxylate groups in the donor molecules are protonated, thereby effectively neutralizing the dicationic viologen moieties inside the pores (Figure 2d, S10 in SI). In contrast to pH 9, at pH 3 the transport shows a strong preference to negatively charged $[Fe(CN)_6]^{3-}$, similar to that of MF-V, suggesting that most of the carboxylate groups in the donor are in the protonated form (Figure 2e,f, S10 in SI). On changing the pH from 9 to 3, the electrochemical current density for $[Ru(NH_3)_6]^{3+}$ decreases from 101 $\mu A\,cm^{-2}$ to 3 $\mu A\,cm^{-2}$ while, for $[Fe(CN)_6]^{3-}$ it increases from 3 $\mu A\,cm^{-2}$ to 126 $\mu A\,cm^{-2}$ (Figure S11, SI). The ratio of electrochemical currents for negative and positive redox probes, I_{Fe}/I_{Ru}, which is 0.03 at pH 9 increases to 60 at pH 3, a change nearly three orders in magnitude (Figure 2g). The variation of surface charge with respect to pH by silanol groups[18] is ruled out in our case as the pore surfaces were modified through a surface polymerization approach,[19] which completely coats the surface with a monolayer of silane leaving no free silanol groups. Moreover, separate ion-transport experiments on MF-V with respect to pH did not show any variation in the asymmetry of transport (Figure 2h, S12 in SI) clearly supporting that the origin of pH-responsive ion transport is from the carboxyl functional groups associated with the donor. Thus, by selecting a donor with pH responsive functional groups, we were able to switch the transport between cation selective, anion selective and ambipolar by changing the pH (Figure 2g). To demonstrate the switching ability of the system with pH, we monitored the voltammograms through three cycles of pH which showed good reversibility (Figure 2i, S13 in SI).

In conclusion, we have demonstrated a facile non-covalent approach to attain charge-reversal within the nanopores (< 10 nm) using supramolecular C-T motifs. This non-covalent approach gives a lot of maneuverability to control the surface charge within the confined pores which in turn was exploited to achieve various forms of ion transport, like cation selective, anion selective and ambipolar with respect to extent of donor binding. Furthermore, the functional utility of donors for pH responsive ion transport has also been demonstrated. This in principle opens up the possibility of selecting large variety of donor modules attached with various functional groups which could respond to multiple stimuli such as light, pH, temperature and redox system and hence modulate transport of ions as well as the molecules across the nanochannel.

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