**Supporting Information**

**Highly efficient ion sieving through angstrom-scale channels embedded with supramolecular coordination complexes**

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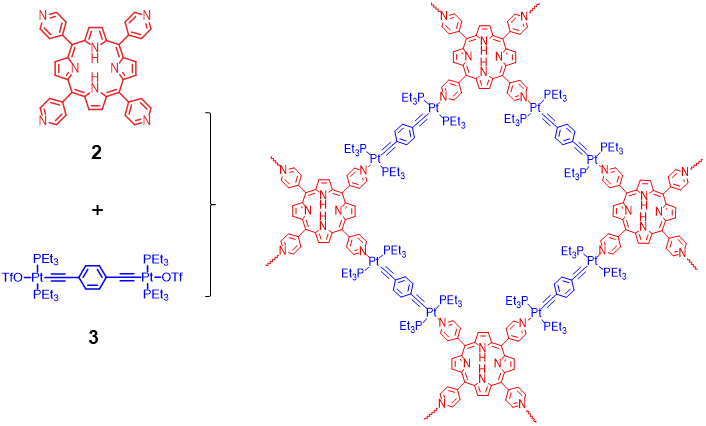
1. Experimental Procedures

**Materials**

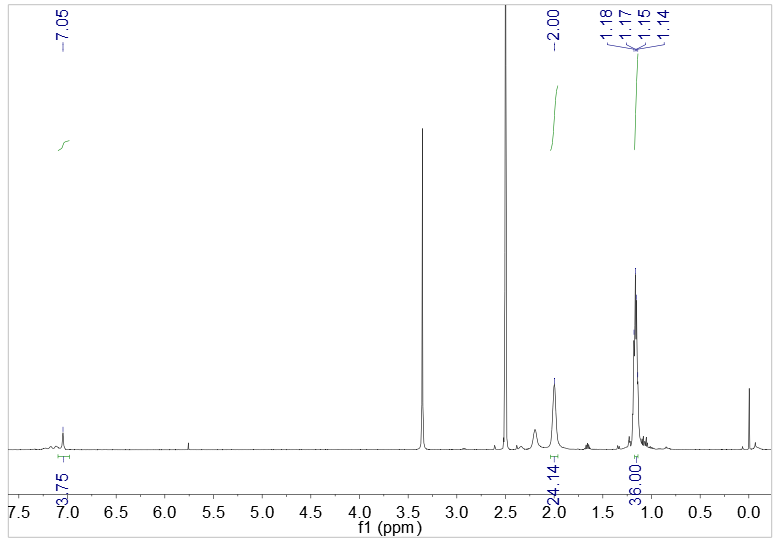
Potassium nitrate (KNO3), sodium nitrate (NaNO3), lithium nitrate (LiNO3), calcium nitrate (Ca(NO3)2), magnesium nitrate (Mg(NO3)2), formic acid (HCOOH), sodium hydroxide (NaOH), dimethyl sulfoxide (DMSO) and ethanol were purchased from Sinopharm Chemical Reagent Shanghai Co., Ltd. (SCRC, China). All electrolyte solutions were formed in MilliQ water. Poly (ethylene terephthalate) (PET, 12 μm thick) membranes were irradiated with heavy ion (Au) of energy 11.4 MeV/nucleon at UNILAC linear accelerator (GSI, Darmatadt, Germany).

1. Synthesis and characterization of SCCs 1

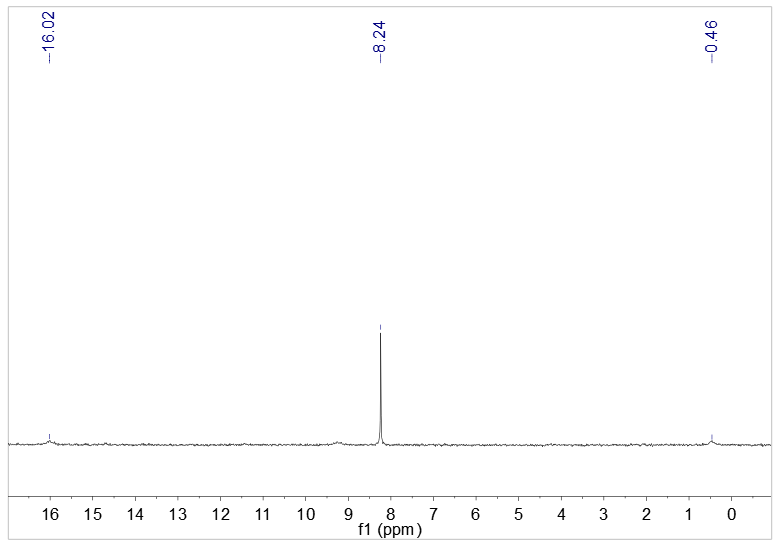
Compounds **3** was prepared according to the literature procedures.1 Compounds **2** (5 mg, 0.008 mmol) and **3** (20.76 mg, 0.016 mmol) were in dimethyl sulfoxide (3 mL) dissolved in a vial, and reacted at room temperature for 24 h. The resulting solution was added with toluene and diethyl ether to precipitate the product, separated and dried under vacuum (15.8mg, 61.3%).



**Scheme S1.** The synthesis SCCs **1**.



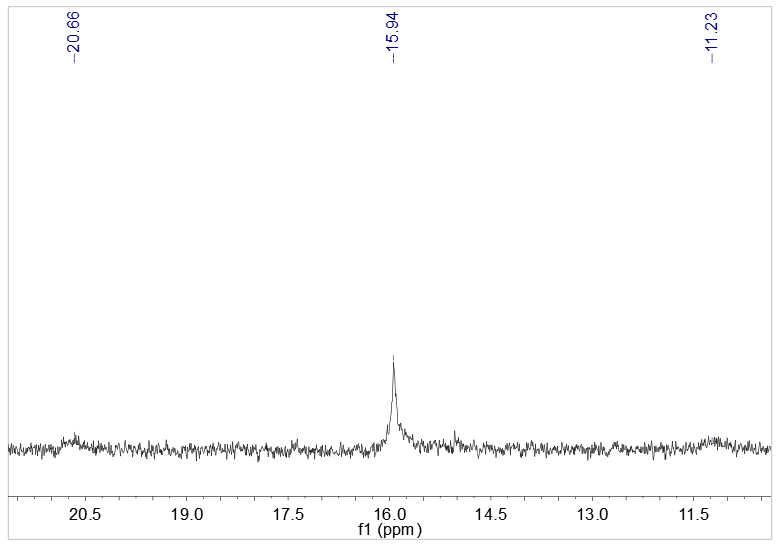
**Figure S1.** 1H NMR spectrum (DMSO-*d6*, 400 MHz, 298 K) recorded for ligand **3**.



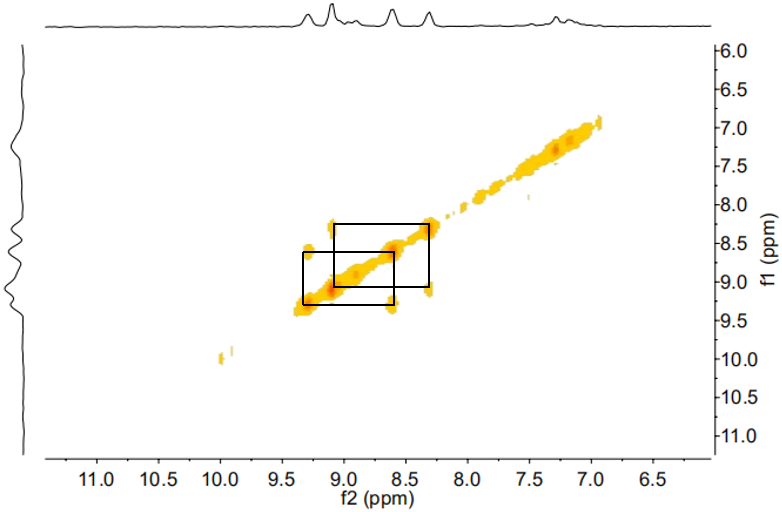
**Figure S2.** 31P NMR spectrum (DMSO-*d6*, 121.4 MHz, 298 K) recorded for ligand **3**.



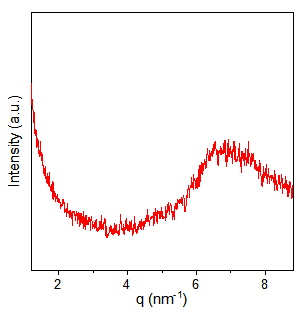
**Figure S3.** 1H NMR spectrum (DMSO-*d6*, 400 MHz, 298 K) recorded for SCCs **1**.



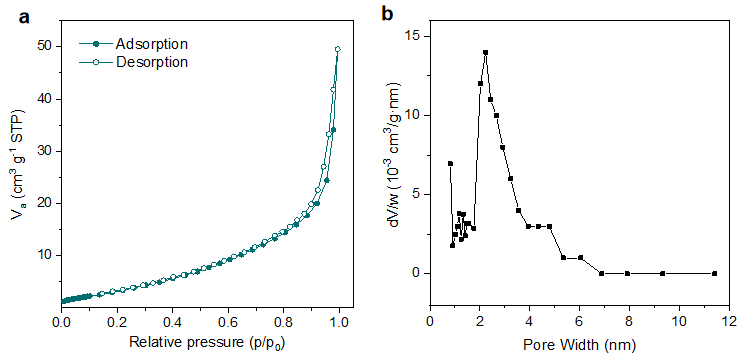
**Figure S4.** 31P NMR spectrum (DMSO-*d6*, 121.4 MHz, 298 K) recorded for SCCs **1**.



**Figure S5.** 2D COSY NMR spectrum (DMSO-*d6*, 400 MHz, 298 K) recorded for SCCs **1**.

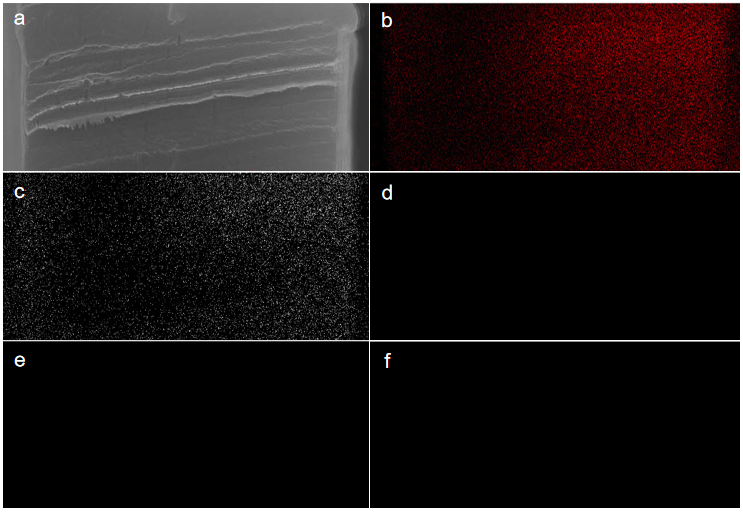


**Figure S6.** Small angle x-ray scattering pattern of SCCs **1**. The *d*-spacing corresponding to the peak at 7 nm-1 is ~0.9 nm.

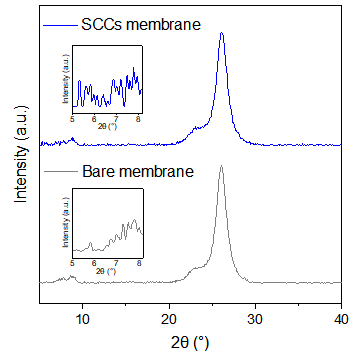


**Figure S7.** N2 adsorption-desorption isotherms (**a**) and pore size distribution profiles (**b**) of SCCs **1** at 77K.

1. The characterization of membranes

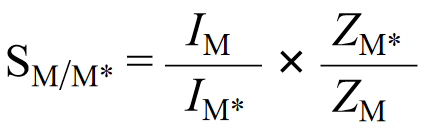


**Figure S8.** EDS mapping of cross section of bare membrane. **a,** SEM image of cross section of bare membrane. **b-f,** the cross-sectional images of SEM and C, O, P, S and Pt mapping of bare membrane, respectively.

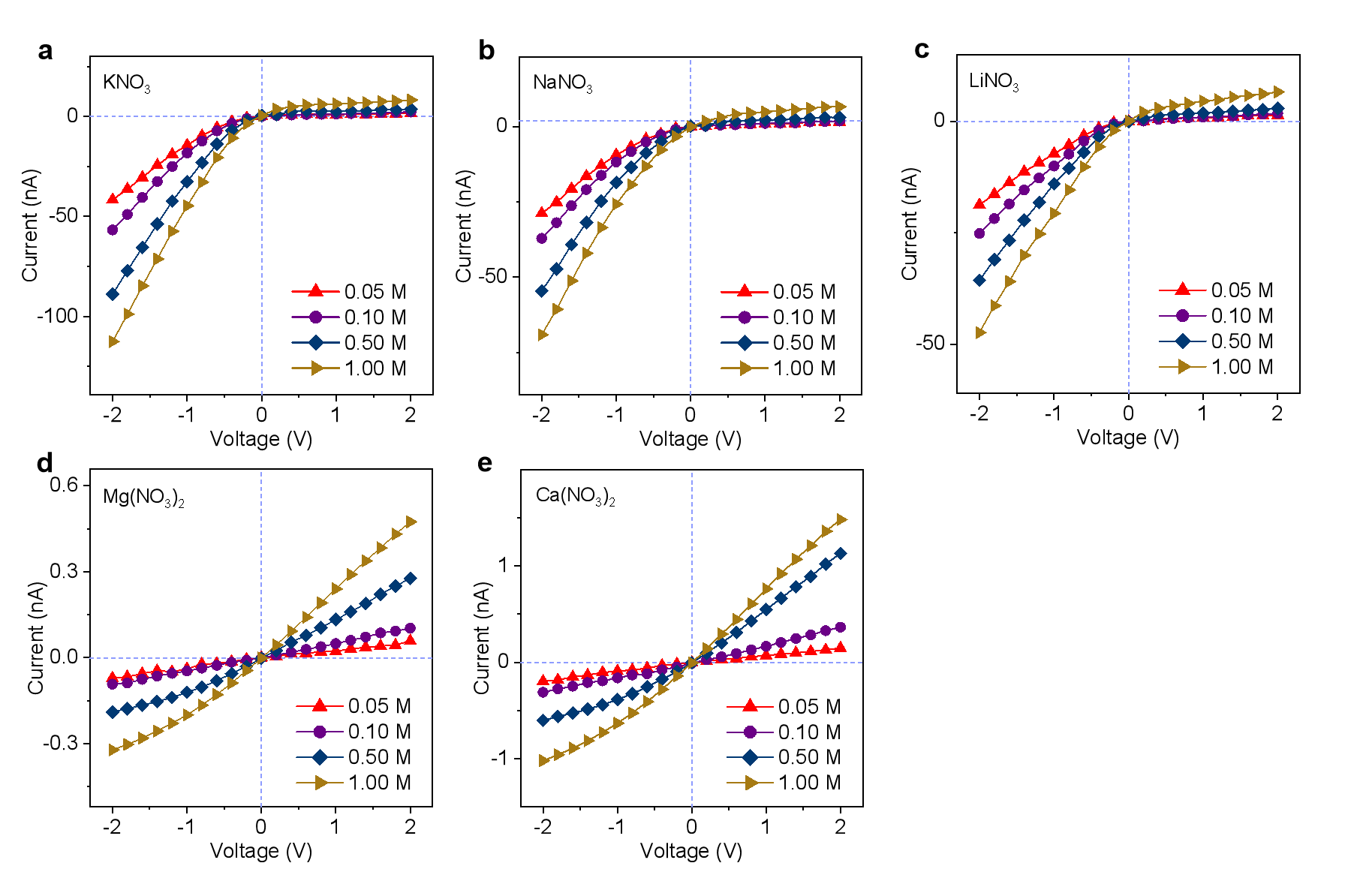


**Figure S9.** XRD patterns of the bare membrane and the SCCs membrane, the inserts are XRD patterns of 2θ values between 5 and 8 degree.

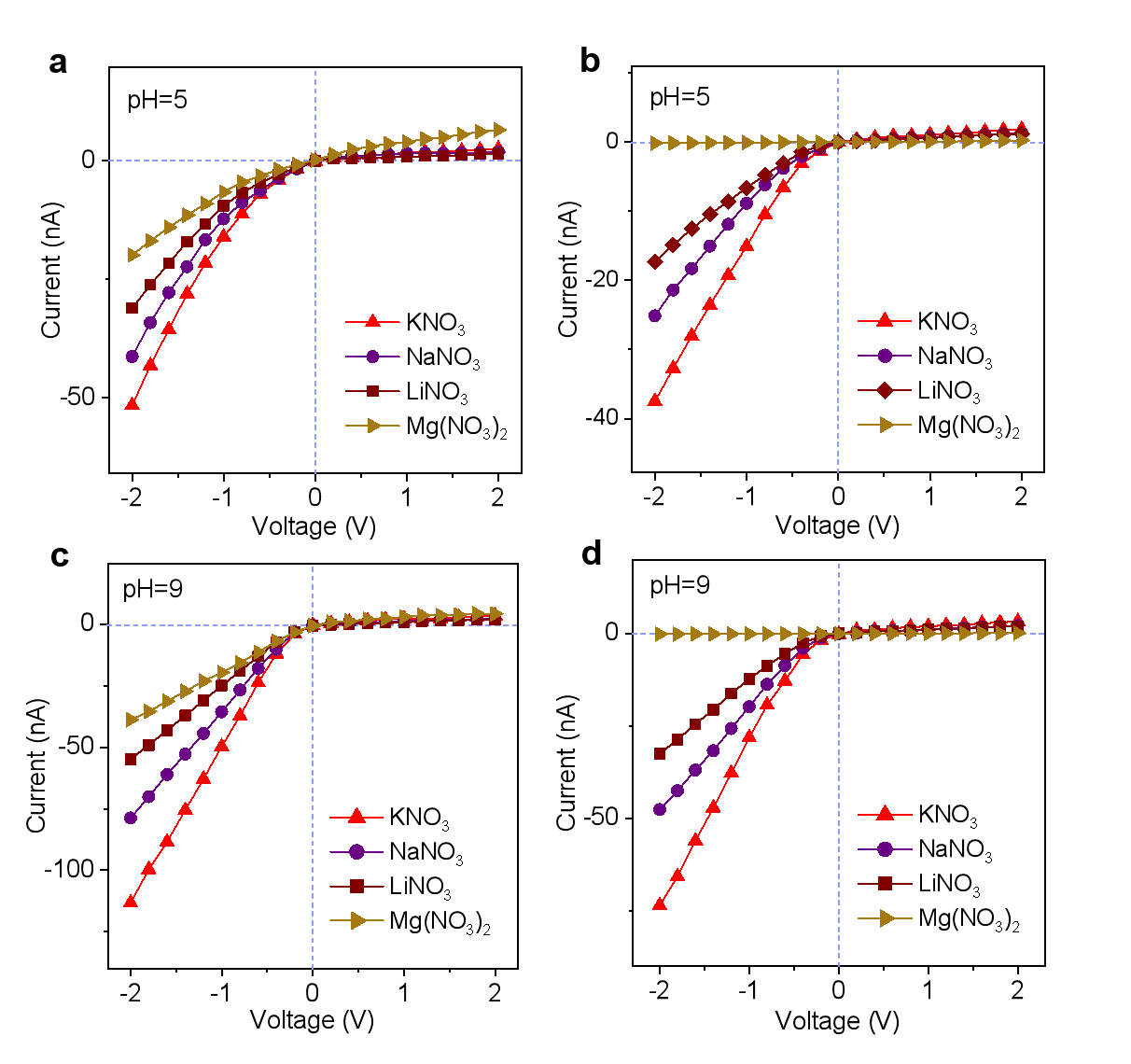
1. **Ion selectivity of cations based on ion currents**

 (S1)

The ion selectivity (SM/M\*) of metal ions is calculated from the transmembrane ion currents. According to the equation, *I*M and *I*M\* are the corresponding current values of metal ions M and M\* at the same transmembrane voltage in channel, respectively. *Z*M and *Z*M\* are the corresponding valences of metal ions.



**Figure S10.** I‒V curves of the SCCs 1 based hybrid membrane for KNO3 (**a**), NaNO3 (**b**), LiNO3 (**c**), Mg(NO3)2 (**d**) and Ca(NO3)2 (**e**) with concentration from 0.05 M to 1.00 M, respectively.

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**Figure S11. a,c**.I-V curves of the bare channel at pH values of 5 (**a**) and 9 (**c**), respectively; **b,d**. I-V curves of the SCCs channel at pH values of 5 (**b**) and 9 (**d**), respectively. (Notably, the concentration of Ca2+ in aqueous solution is very low in alkaline environment, and that is why we didn't test the effect of pH on Ca2+ transport in channel).

**Table S1. Monovalent/divalent metal ion selectivity (K+/Mg2+) and K+ conductivity of various artificial channels.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Artificial channel** | **Thickness (μm)** | **Ion selectivity (K+/Mg2+)** | **K+ conductivity**  **(S m-1)** | **Driving force** | **Ref.** |
| SCCs | 12 | 1015.5 | 27.88 | U=2V | This work |
| MOF (UIO-66) | 12 | 822.3 | 1.9 | U=1V | 9 |
| PSS/MOF (HKUST-1) | 8 | 27.1 | 5.6×10-4 | U=0.4V | 10 |
| PET | 2 | 134.6 | 0.19 | U=10V | 11 |
| Graphene | 6×10-4 | 4 | 1.14 | U=0.15V | 12 |
| FRGO | 2.16 | 120 | n/a | ΔC | 13 |
| Graphene oxide (GO) | 0.2 | 90.3 | n/a | ΔC | 14 |
| MoS2 | 6.5×10-4 | 1.3 | 17.8 | U=0.8V | 15 |
| Graphite/MoS2 | 7 | 2.3 | 1.2 | U=0.2V | 16 |
| MXene (Ti3C2) | 1.5 | 5.9 | n/a | ΔC | 17 |
| GO/MXene | ~4.3 | 1.7 | n/a | U=0.04V | 18 |

1. Density functional theory (DFT) simulations

Binding energy of metal ions and porphyrin groups on the SCC **1** was examined by DFT simulations. The primary simulation structures of ligand **2** containing porphyrin groups were constructed by material Studio 8.0, and the five metal ions were added in the center of porphyrin groups, respectively. Then the final simulation structures that to be DFT calculated were obtained through geometric optimization. The resulting simulation structures were calculated at B3LYP/LANL2DZ levels using Gaussian 09. Moreover, it is necessary to calculated the energy of the metal ions without any interaction with the ligand **2**. Finally, the binding energies were calculated by comparing the energy difference between the two DFT simulation results. As a result, the calculated binding energy order of metal ions with the porphyrin groups on the SCC 1 is K+ (−1.293 eV) < Na+ (−2.012 eV) < Li+ (−3.192 eV) < Ca2+ (−6.985 eV) < Mg2+ (−11.197 eV) (Table S1). Negative values of binding energy demonstrate that it is favorable to the binding of metal ions with porphyrin groups. The high binding energy of divalent metal ions with porphyrin groups reveal their low mobility in the SCCs channel.

# Table S2. Properties of the metal ions.

|  |  |  |  |
| --- | --- | --- | --- |
| **Electrolyte species** | **Bare diameter**  **(Å)** | **Hydrated diameter (Å)** | **Hydration energy (KJ mol-1)** |
| K+ | 1.20 | 6.62 | -295 |
| Na+ | 1.90 | 7.16 | -365 |
| Li+ | 2.66 | 7.64 | -475 |
| Ca2+ | 1.98 | 8.24 | -1505 |
| Mg2+ | 1.30 | 8.56 | -1830 |

**Table S3.** **The binding of metal ions with porphyrin groups on the SCCs 1 were examined by DFT** **calculations at B3LYP/LANL2DZ levels using Gaussian 09.**

|  |  |
| --- | --- |
| **Metal ion** | **Binding energy (eV)** |
| K+ | -1.293 |
| Na+ | -2.012 |
| Li+ | -3.192 |
| Ca2+ | -6.985 |
| Mg2+ | -11.197 |

1. Molecular dynamics (MD) simulations

SCC **1** periodic supercell was used as the MD simulation model for the investigation of ion transport (Fig. S13). To describe the flexibility of the framework, we employed the consistent valence force field (CVFF)2 for SCC **1** model. The force model was used for bonded and non-bonded interactions. The non-bonded interactions include van der Waals interactions, which are modelled by the classic 12-6 Lennard Jones (LJ) potential, and Coulombic interaction (equation S2). The particle-particle particle-mesh (PPPM) solver with an accuracy of 1e−4 eV was used to treat the long-range Coulombic interactions.

The atom types in the SCC **1** are marked in Fig. S14. The LJ parameters between different atoms were determined by Lorentz-Berthelot mixing rule3. Table S3 summarizes the LJ parameters and partial charges for different types of atoms. All the LJ interactions were calculated with a cutoff radius of 12.0 Å.

In order to simulate the bonding characteristics of SCC **1**, We must establish a framework model of complex three-dimensional atomic connectivity, including the bond, angle, dihedral and improper interactions (equation S3-S6).

In our MD simulations, we used the TIP3P model for water molecules4. The LJ parameters of electrolyte ions are listed in Table S3. To determine the ion transport mobility, we applied a constant electric field of 0.085 V/Å along the [111] crystal direction in our MD simulations. The electro-kinetic mobility of ions inside the SCC framework was derived from the displacement of ions along the [111] crystal direction under the E-fields.

All the MD simulations were performed with LAMMPS software5. The ion displacements were averaged from 5 independent simulations with different initial configuration. The simulations were conducted in NVT ensemble at 298 K with time step of 2 fs, ran MD simulations for 5 ns under the E-fields. The results of ion drift in the last 3 ns were used to calculate the ion mobility. To prevent the possible drift of the simulated SCC structure, the framework was frozen and the linear momentum was set to zero. Note that the triethyl phosphorous groups as the branched chains of SCC model and the H atoms on the framework were flexible.

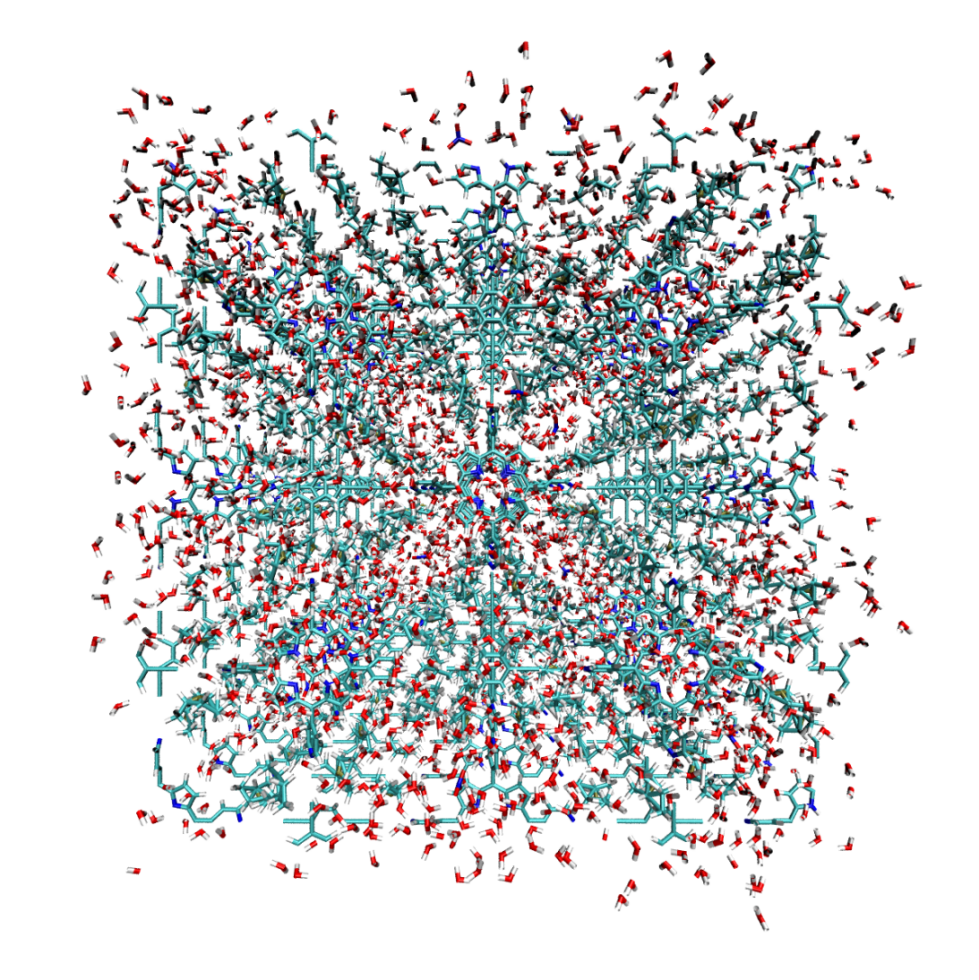
(S2)

(S3)

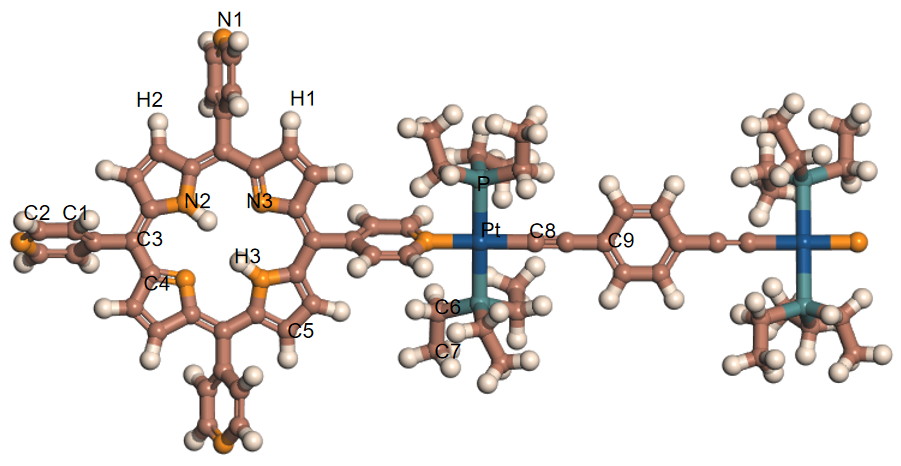
(S4)

(S5)

(S6)

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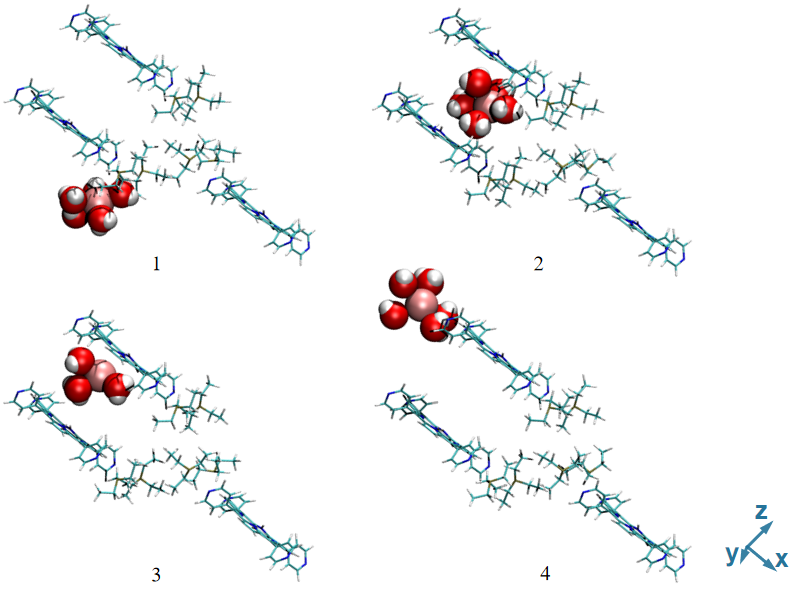
**Figure S12.** periodic supercell of SCCs **1** used as the MD simulation model.



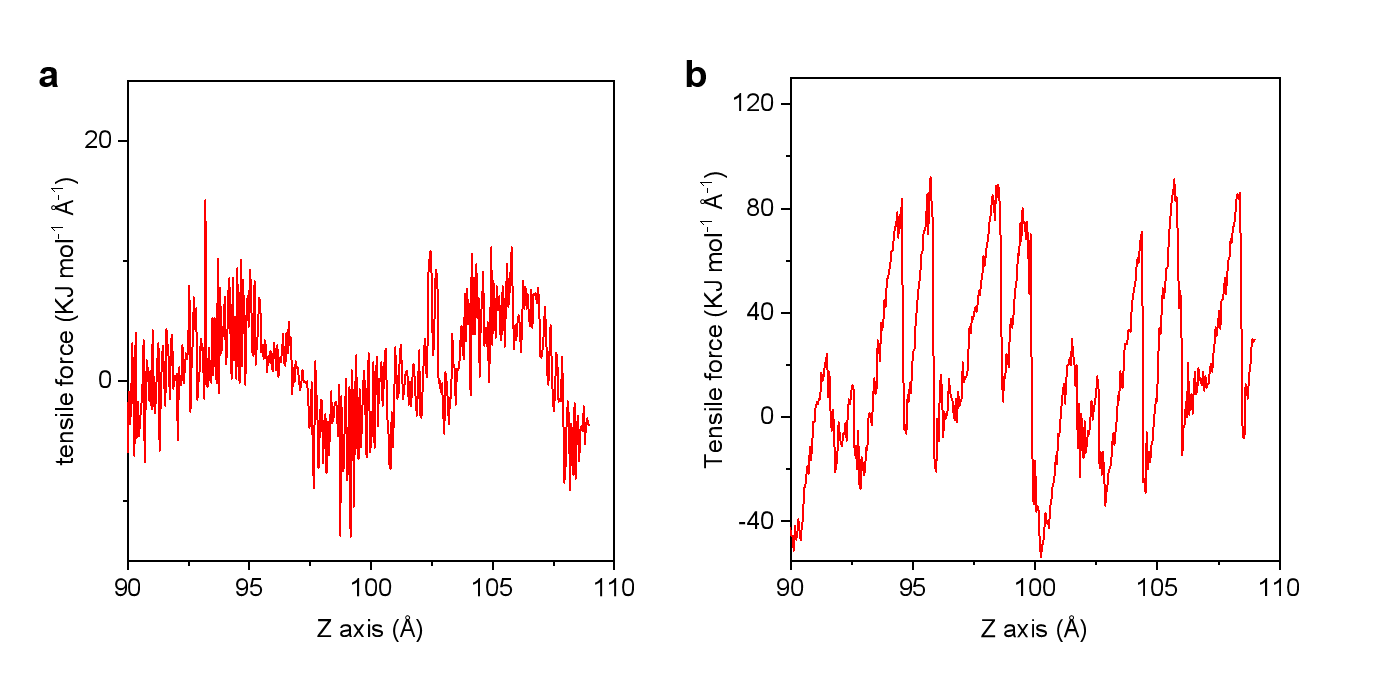
**Figure S13.** Structural connector of SCCs **1** assembled by organic ligand **2** and metal ligand **3**,and the atomic types of the structural model used in MD simulation. Blue ball stands for Pt; cyan ball for P; orange ball for N; light brown ball for C and light magenta ball for H.

1. Potential of Mean Force (PMF) for cation migration

To estimate the energy barrier for different ions transport through the nanochannel, the potential of mean force (PMF) for ions was studied (free energy). The PMF were determined in umbrella sampling (US) calculations. The reaction coordinate going along the center of the nanochannel was partitioned into 20 windows of 1 Å widths. Confinement potentials were introduced in the form of harmonic restraints with a force constant of k = 5 Kcal/(mol·Å2), and each window was run for 1 ns. The weighted histogram analysis method (WHAM)was used to reconstruct the PMF. Monte Carlo bootstrap error analysis was performed with the WHAM algorithm (with num MC trials set to 5). The histograms of the US windows used to reconstruct the PMF were examined and had an appropriate overlap.



**Figure S14.** Side view graphs showing the migration of metal ions along the interlayer slits to better display the way ions pass through the edge of the channel.



**Figure S15.** Tensile force of the K+ (**a**) and Mg2+ (**b**) migrating through the SCCs channel.

# Table S4. Lennard-Jones potential parameters and partial charges of all types of atoms in SCC 1 model.

|  |  |  |  |
| --- | --- | --- | --- |
| **Symbol** | ***σ* (Å)** | ***ε* (kcal/mol)** | ***q* (e)** |
| Pt | 2.542 | 15.718 | 3.943 |
| P | 3.742 | 0.200 | 0.179 |
| N1 | 3.501 | 0.167 | -0.277 |
| N2 | 3.501 | 0.167 | -0.617 |
| N3 | 3.501 | 0.167 | -0.337 |
| C1 | 3.617 | 0.148 | -0.157 |
| C2 | 3.617 | 0.148 | -0.047 |
| C3 | 3.617 | 0.148 | -0.057 |
| C4 | 3.617 | 0.148 | 0.083 |
| C5 | 3.617 | 0.148 | -0.187 |
| C6 | 3.875 | 0.039 | -0.335 |
| C7 | 3.875 | 0.039 | -0.357 |
| C8 | 3.617 | 0.148 | -0.057 |
| C9 | 3.617 | 0.148 | 0.028 |
| H1 | 2.450 | 0.038 | 0.043 |
| H2 | 2.450 | 0.038 | 0.073 |
| H3 | 0.0 | 0.0 | 0.223 |
| K+ [a] | 3.528 | 0.087 | 1 |
| Na+ [a] | 2.822 | 0.047 | 1 |
| Li+ [a] | 1.506 | 0.690 | 1 |
| Ca2+ [b] | 2.723 | 0.048 | 2 |
| Mg2+ [b] | 2.288 | 0.004 | 2 |
| N (NO3-) [c] | 3.150 | 0.170 | 0.794 |
| O (NO3-) [c] | 2.860 | 0.210 | -0.598 |

# [a], [b], [c] take from the previous work for monovalent metal ions6, divalent metal ions7 and nitrate ions8.

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