Electronic Supplementary Material (ESI) for Chemical Communications

S1: Fabrication of SWCNT membranes:

Single-walled CNTs with an average core diameter of ~1.5 nm and length of 5-30 μm were purchased from cheaptubes.com and purified using a two-step filtration method before usage. To describe it briefly, 0.1g SWCNTs were first dispersed in one liter deionized water containing 10 g dodecylbenzenesulfonic acid sodium (Sigma) under horn sonication at 10W, 20% magnitude (Qsonica, LLC.; model: Sonicator S-4000; tip size, 1/8 inch). The solution was then forced through polytetrafluoroethene (PTFE) membrane (Sterlitech Corp.) with a pore size of 20 μm to remove CNT bundles and impurities. SWCNTs were retrieved from the filtered solution using another PTFE membrane with a pore size of 1 μm. Next, the purified SWCNTs were mixed with Epon 862 epoxy resin (Miller Stephenson Chem. Co.), hardener methylhexahydrophthalic anhydride (MHHPA, Broadview Tech. Inc.), catalyst 1-Cyanoethyl-2-ethyl-4-methylimidazole (2E4MZ-CN, Shikoku Chemical, Japan), and 0.1g surfactant Triton-X 100 (Sigma) using a Thinky^{TM} centrifugal shear mixer. As-prepared CNTs-Epoxy composite was cured at 85 ^{o}C according to commercial epoxy procedure before being cut into CNT membranes using a microtome equipped with a glass blade. The membranes (~0.6x0.6 cm^2) were glued over a 3mm diameter hole in polycarbonate plate (1mm thick) to act as a mechanical support. The top of the membrane is in the recess of the hole in polycarbonate and the bottom of the membrane is on the bottom plane of polycarbonate support. Finally, each side of as-prepared SWCNT membranes were treated using water plasma oxidation for 1 minute to remove extra polymeric residuals.

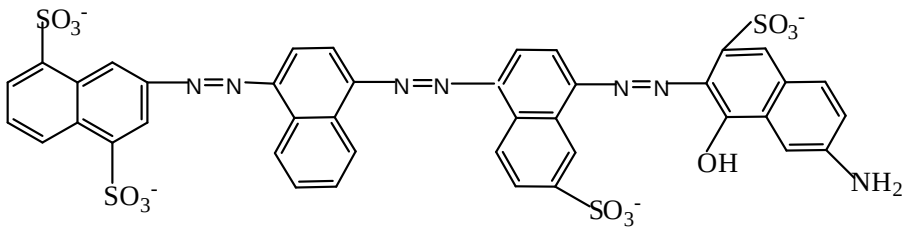
S2: Functionalization of SWCNT membranes:

The as-prepared SWCNT membranes were first flow grafted (FG) with benzoic acid by immersing the top of membranes in 100 mM 4-carboxy phenyl diazonium tetrafluoroborate under a 2 cm DI water column pressure for 12 hours at the bottom of the membrane using U-tube fittings diagrammed in S6. In the next step, Direct Blue 71 dye was coupled to benzoic acid via one step carbodiimide chemistry under flow grafting with a 2 cm water column pressure: 10 mg of ethyl-(N',N'-dimethylamino)propylcarbodiimide hydrochloride (EDC) and 5 mg N-hydroxysulfosuccinimide (Sulfo-NHS) were dissolved into 4 ml of 50 mM Direct Blue 71 (dye, Aldrich) in 0.1 (M) 2-(N-morpholino)ethanesulfonic acid (MES) buffer for 12 h at ambient temperature. Pd/Au (30nm) is sputter deposited on the bottom of membrane to give electrical contact to CNT membrane and act as effective working electrode.

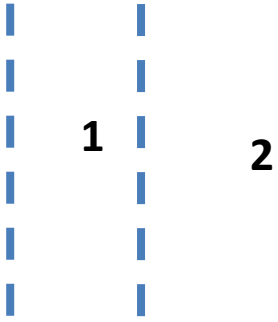
S3: Figure shows (a) 4-carboxy phenyl diazonium tetrafluoroborate; (b) of Direct Blue Dye 71 and (c) Schematic of SWCNT membrane functionalization.

(a)

(b)



(c)



S4: Estimation of SWCNT membrane pore area:

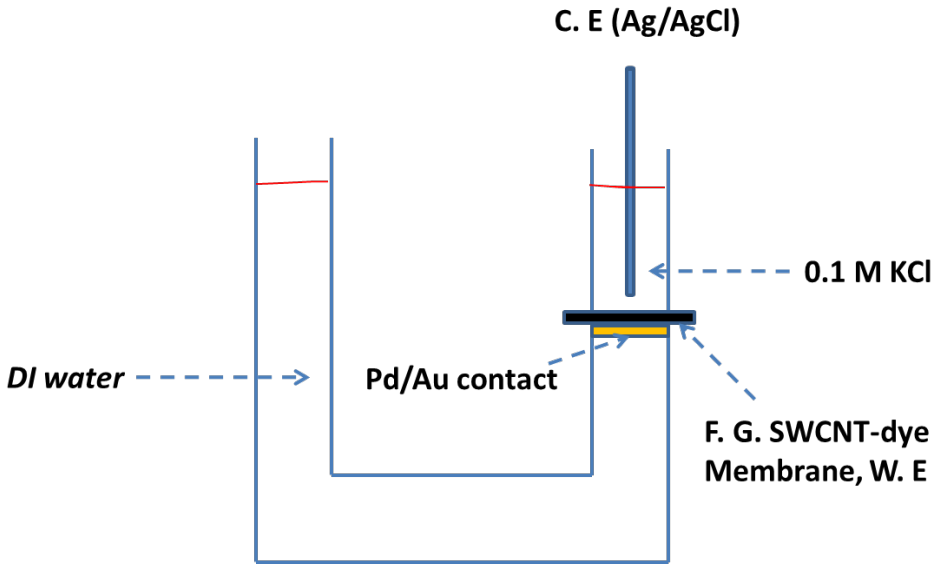
Pore area of SWCNT membrane was calculated by ionic current using the following equations:

$$A_p = (M * l)/(\mu EM * C * E) \qquad (1)$$

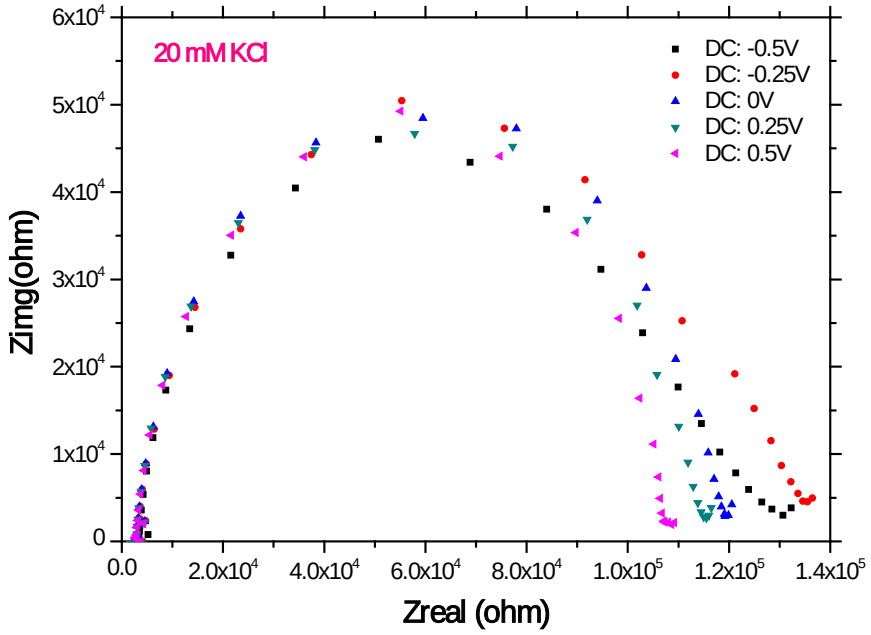
$$M = I * t^{+}/(e * N) \qquad (2)$$

where A_p is membrane pore area; M is electrophoretic molar flow rate of K^+ ions through SWCNT membrane; l is membrane thickness (5 μm); C is the concentration of KCl solution (100 mM); μ_{EM} is experimentally measured K^+ electrophoretic mobility of 0.1 M in SWCNTs (~8x-10^{-08} m^2/s-V,)[38] and E is the applied voltage (-0.4V). I stands for ionic current; t^+ is K^+ transport number (0.5); e is elementary charge and N is Avogadro constant.

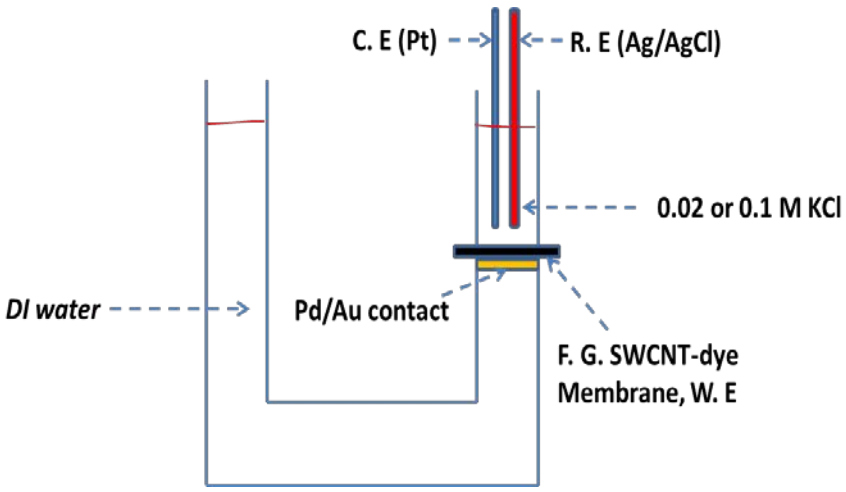
S5: Schematic of the ionic rectification setup using F.G. SWCNT-dye membrane. Working electrode (W.E) is SWCNT membrane coated with 30 nm thick Pd/Au film; Reference Electrode (R.E) is Ag/AgCl electrode. Constant potential was provided using a Princeton Scientific Model 263A Potentiostat. Counter electrode is a sintered Ag/AgCl electrode purchased from IVM Company, and working electrode is SWCNT membrane coated with a layer of 30 nm thick Au/Pd film. The membrane area is ~0.07 cm^2. All chemicals were purchased from Sigma Aldrich without further purification.



S6: (a) EIS Nyquist plots of unmodified SWCNT membrane using 20 mM KCl. (b) Experimental setup for the EIS measurements. Experimental conditions: Working Electrode (W.E): F. G. SWCNTs–dye; Reference Electrode (R.E): Ag/AgCl; Counter Electrode (R.E): Pt; AC magnitude:10 mV; DC magnitude: -0.5, -0.25, 0, 0.25, 0.5 V; frequency: 100 kHz to 0.2 Hz. Platinum wire, Ag/AgCl and F.G. SWCNTs–dye membrane were used as counter, reference and working electrodes, respectively.



(a)



(b)

S7: Schematic of the experimental setup used to measure the mass transport of caffeine through S.G. SWCNT-dye membranes, applying various biases (-400, 0, +100 mV). Working electrode (W.E) is F.G. SWCNT-dye membrane coated with 30 nm thick Pd/Au film; Reference Electrode (R.E) is Ag/AgCl electrode.