Supporting Information

Experimental section

Starting materials

$Fe(NO_3)_3 \cdot 9H_2O$ (99%), $Cu(NO_3)_2 \cdot 3H_2O$ (99%), citric acid (99%), malic acid (99%) and tartaric acid (99%) were purchased from Sigma-Aldrich. NaOH (99%) and NaCl (99.5%) were supplied by Merck. Ethanol (99%) was obtained from Acros Organics. All the chemicals above were used as received. DI water from a Milli-Q (Millipore, USA) system was used in all experiments.

Synthesis of complexes

$Na_5[Fe(C_6H_4O_7)_2]$ (**Fe-CA**) $Fe(NO_3)_3 \cdot 9H_2O$ (10 mmol, 4 g) and citric acid (20 mmol, 3.84 g) in DI water (30 mL) were stirred overnight at 50 °C. Then NaOH (1.0 M) was added stepwise to pH ~ 8. The resultant solution was stirred further for 3 h and then concentrated to ~10 mL under vacuum. Cold ethanol was added to precipitate the product. It was then purified 3 times from H_2O/EtOH. The resultant yellow solid $Na_5[Fe(C_6H_4O_7)_2] \cdot 2H_2O$ was dried under vacuum (yield > 95%) and ready for characterization and performance tests. Elemental analysis: calcd: C 24.7, H 2.1, O 43.9%; found: C 25.1, H 2.0, O 43.5%.

The synthesis procedures of **Cu-CA**, **Cu-MA**, **Fe-MA**, **Cu-TA** and **Fe-TA** are similar to those of **Fe-CA**. Calcd for **Cu-CA** ($Na_2[Cu(C_6H_4O_7)(H_2O)]$): C 22.8, H 1.9, O 40.6%; found: C 23.1, H 1.8, O 40.2%. Calcd for **Cu-MA** ($Na[CuC_4H_3O_5)(H_2O)]$): C 20.4, H 2.1, O 40.8%; found: C 20.7, H 1.9, O 40.2%. Calcd for **Fe-MA**($Na_3[Fe(C_4H_3O_5)_2] \cdot H_2O$): C 23.7, H 2.0, O 43.5%; found: C 24.0, H 1.9, O 43.3%. Calcd for **Cu-TA** ($CuC_4H_4O_6$): C

22.7, H 1.9, O 45.4%; found: C 23.1, H 1.9, O 45.2%. Calcd for **Fe-TA** ($Na_3[Fe(C_4H_3O_6)_2]$): C 22.9, H 1.4, O 45.8%; found: C 23.3, H 1.3, O 45.5%.

Characterization of complexes

FTIR measurements were conducted through a Perkin-Elmer FT-IR Spectrometer Spectrum 2000 in the range of 4000 to 400 cm^{-1} to determine the functional groups of complexes. The spectra were obtained by the solid KBr method. The weight loss of complexes was measured by TGA with a TGA 2050 themogravimetric analyzer (TA Instruments, New Castle, DE) during thermal oxidation. The measurement was conducted under air from 30 to 600 ^{o}C at a heating rate of 10 ^{o}C/min.

Relative viscosity of the complex solutions

The relative viscosity of the complex solutions, η_r, compared to DI water is calculated using equation (1):

$$\eta_r = \frac{\eta}{\eta_0} = \frac{t\rho}{t_0\rho_0} \quad (1)$$

where t (s) is the elution time of the complex solution measured by a AVS 360 inherent viscosity meter, ρ (g·mL^{-1}) is the density of the complex solution measured by a DMA 35 potable density meter, and t_0 (s) and ρ_0 (g·mL^{-1}) are the elution time and density of DI water, respectively.

FO process

FO experiments were carried out through a lab-scale circulating set-up as depicted elsewhere.[1,2] Commercial HTI flat sheet membranes (Batch No. 060327-3, Hydration Technologies Inc., OR, USA) and self-made hollow fiber membranes made of cellulose acetate (CA)[3] were used in FO. For the flat sheet membranes, a crossflow permeation cell was designed in frame configuration with a rectangular channel on both sides of the

membrane. Feed and draw solutions flowed co-currently through their respective cell channels at the velocity of 6.4 $cm \cdot s^{-1}$. For the hollow fiber membrane measurement, the flow velocities were 10 $mL \cdot min^{-1}$ and 300 $mL \cdot min^{-1}$ at the lumen and shell sides, respectively. The temperatures of both the feed and draw solutions were maintained at 25 ± 0.5 ºC. Draw solutions were prepared from synthesized complexes. DI water was used as the feed solution and operated under the pressure retarded osmosis (PRO) (draw solution against the selective layer of membrane) mode unless otherwise stated. The water flux, J_v, ($L \cdot m^{-2} \cdot hr^{-1}$, abbreviated as LMH) is calculated from the volume change of the feed solution using equation (2).

$$J_v = \Delta V/(A\Delta t) \quad (2)$$

where ΔV (L) is the volume change of the feed solution over a predetermined time Δt (hr) and A is the effective membrane surface area (m^2). The reverse solute flux, J_s (gMH), in FO refers to the draw solute permeating from the draw solution to the feed side. Since the complexes dissociate and are conductive in their aqueous solutions, the concentration of draw solutes permeating to the feed solution was obtained through the conversion of its electrical conductivity measured using a calibrated conductivity meter (Oakton Instruments, Vernon Hills, IL). The value of J_s was determined from the increase in the feed conductivity:

$$J_s = \frac{(C_t V_t) - (C_0 V_0)}{\Delta t} \frac{1}{A_m} \quad (3)$$

where C_0 ($mol \cdot L^{-1}$) and V_0 (L) are the initial salt concentration and the initial volume of the feed, respectively, while C_t ($mol \cdot L^{-1}$) and V_t (L) are the salt concentration and the volume of the feed over a predetermined time Δt (h), respectively.

The pH values of draw solutions were determined using a pH meter (Horiba pH meter D-54, Japan). The draw solution osmotic pressure of complex was measured using a model 3250 osmometer (Advanced Instruments, Inc.).

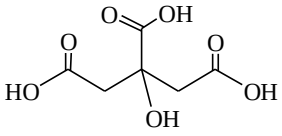
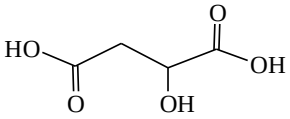
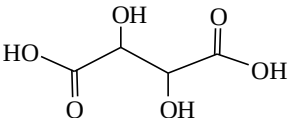
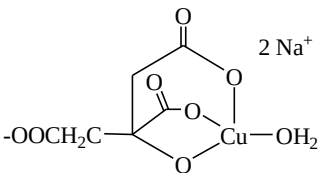
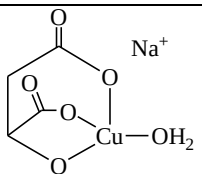
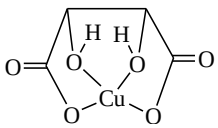
Regeneration of complex draw solutes

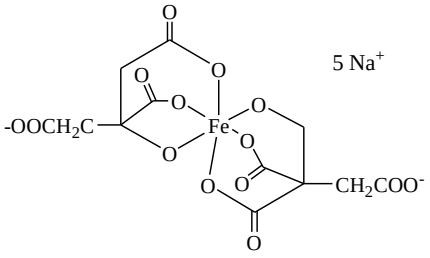
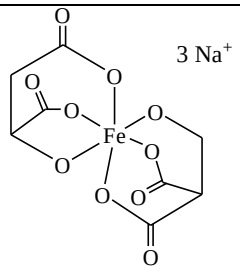
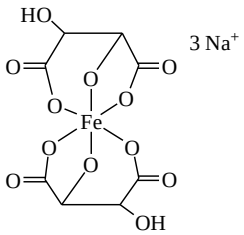
After the FO test, the diluted complex solution was re-concentrated through a pressure-driven process. A thin-film polyamide NF membrane (NE2540-70) was used for the Fe-CA regeneration under a gas pressure of 10-bar. When using DI water as the feed, the pure water permeability of the NF membrane was 16.8 LMH/bar calculated by equation (2) under 10-bar. The salt rejection of the system gives an indication of the percentage of the draw solute that is retained by the membrane and is calculated by equation (4):

$$R = (1 - \frac{C_P}{C_F}) x 100\% \quad (4)$$

where R is the salt rejection, C_P (mol·L^{-1}) is the solute concentration in the permeate, and C_F (mol·L^{-1}) is the solute concentration in the feed solution.

Table S1 Structures and molecules of hydroacid complexes and their precursors

Hydroxy acid	 Citric acid (CA)	 Malic acid (MA)	 Tartaric acid (TA)
Cupric complex	 Cu-CA ($Na_2[Cu(C_6H_4O_7)(H_2O)]$)	 Cu-MA ($Na[CuC_4H_3O_5)(H_2O)]$)	 Cu-TA ($CuC_4H_4O_6$)

Ferric complex	 Fe-CA ($Na_5[Fe(C_6H_4O_7)_2]\cdot 2H_2O$)	 Fe-MA ($Na_3[Fe(C_4H_3O_5)_2]\cdot H_2O$)	 Fe-TA ($Na_3[Fe(C_4H_3O_6)_2]$)

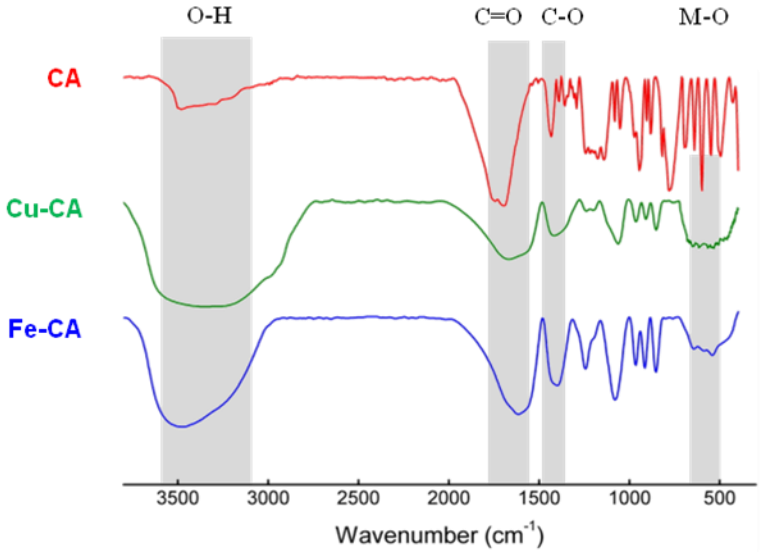
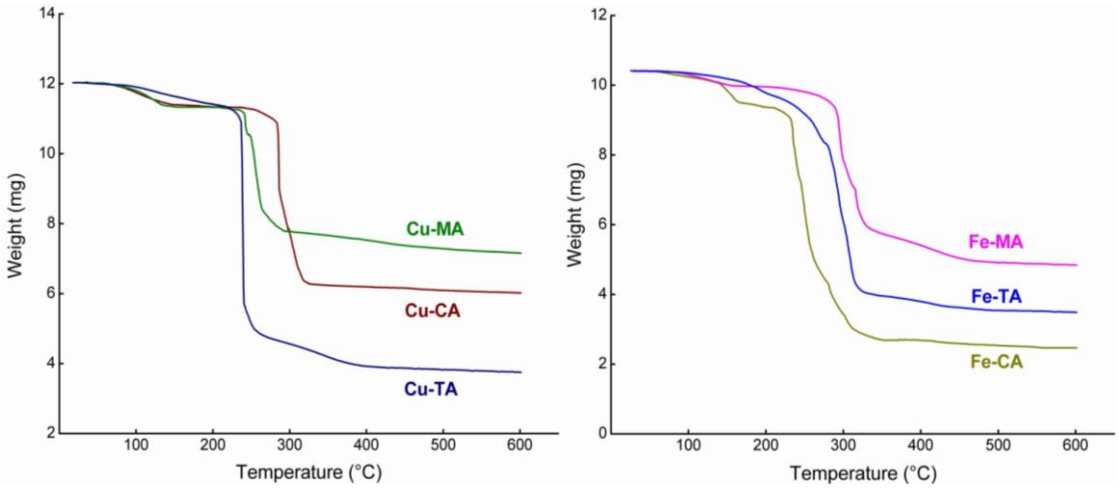


Fig. S1 FTIR spectra of CA and its complexes

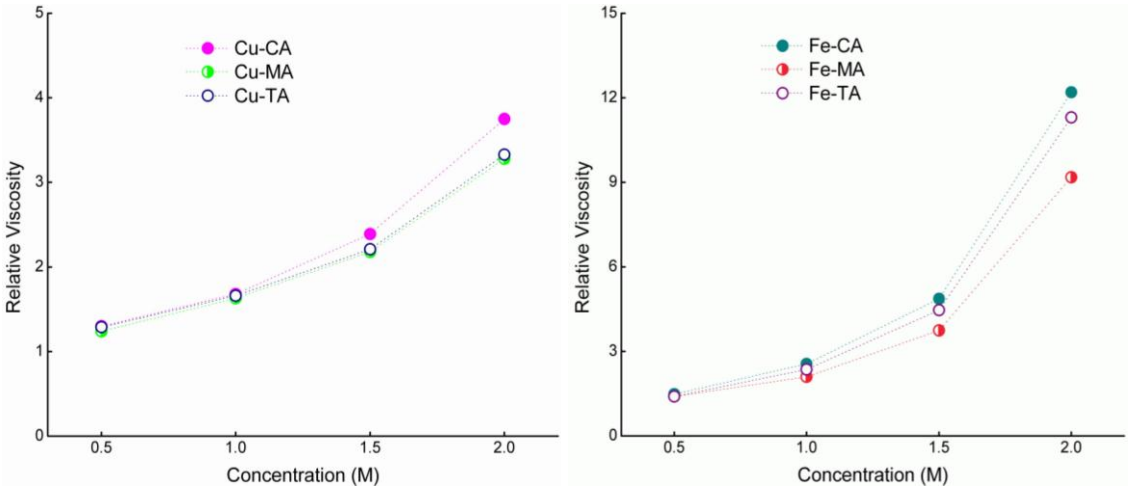


(a) (b)

Fig. S2 TGA spectra: (a) cupric complexes; (b) ferric complexes

Table S2 Weight loss of hydroacid complexes in TGA measurements

Sample	Decomposition stage	Observed weight loss (%)	Calculated weight loss (%)
Cu-CA	I (H_2O)	5.9	5.7
	II (organic ligand)	50.9	49.4
Cu-MA	I (H_2O)	7.8	7.6
	II (organic ligand)	46.9	45.4
Cu-TA	organic ligand	65.2	62.4
Fe-CA	I (H_2O)	6.4	6.2
	II (organic ligand)	56.0	53.5
Fe-MA	I (H_2O)	4.2	4.4
	II (organic ligand)	55.1	52.8
Fe-TA	organic ligand	61.1	58.7



(a) (b)

Fig. S3 Relative viscosity comparison of (a) cupric complexes; (b) ferric complexes

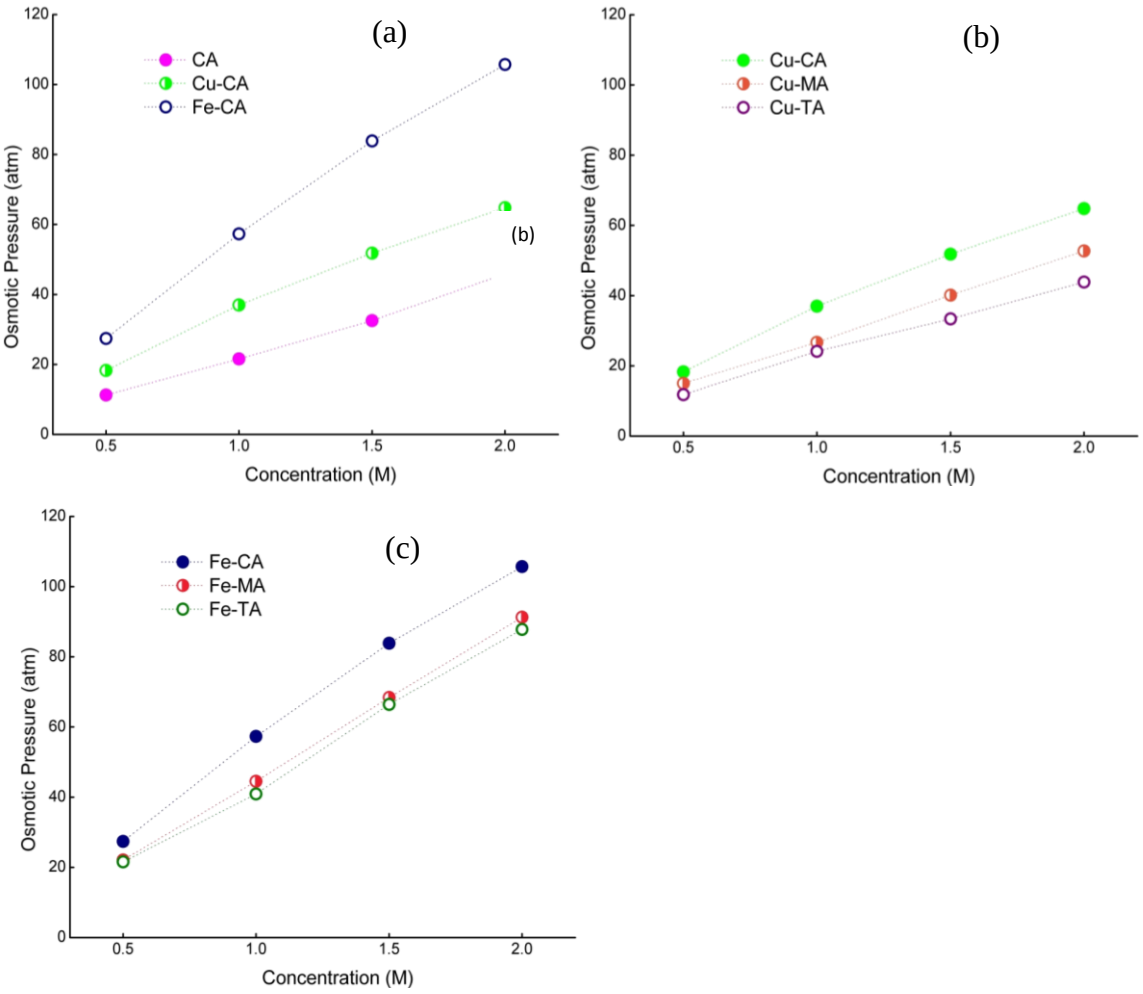


Fig. S4 Osmotic pressure comparison of (a) CA and its complexes; (b) cupric complexes; (c) ferric complexes

References

1 K. Y. Wang, R. C. Ong and T. S. Chung, *Ind. Eng. Chem. Res.*, 2010, **49**, 4824.

2 J. C. Su, Q. Yang, J. F. Teo and T. S. Chung, *J. Membr. Sci.*, 2010, **355**, 36.

3 J. C. Su and T. S. Chung, *J. Membr. Sci.*, 2011, **376**, 214.