Supporting Information

Experimental section

Starting materials

$Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (99%), $Na_2Cr_2O_7{\cdot}2H_2O$ (99.5%), $H_2C_2O_4$ (98%), H_2O_2 (30 wt.% in H_2O) and Bovine Serum Albumin (BSA, 96%) were purchased from Sigma-Aldrich. NaOH (99%) and NaCl (99.5%) were supplied by Merck. Ethanol (EtOH, 99%) was obtained from Acros Organics. All the chemicals above were used as received. DI water from a Milli-Q (Millipore, USA) system was utilized in all experiments.

Syntheses of complexes

$Na_3[Fe(C_2O_4)_3]$ (Na-Fe-OA) $Fe(NH_4)_2(SO_4)_2{\cdot}6H_2O$ (25.5 mmol, 10 g) was added into a 250 mL breaker containing 50 mL DI water at 40°C. 50 mL of 1 M $H_2C_2O_4$ was added to this solution and a yellow precipitate of iron (II) oxalate (FeC_2O_4) formed instantly. After constantly stirring for 30 minutes, 3.15 g of $H_2C_2O_4$ (35 mmol) and 36 mL of 2 M NaOH were added to the FeC_2O_4 suspension. After stirring for 10 minutes, 4 mL of 30 % H_2O_2 was added dropwise. The mixture was heated to boil until no more bubble came out. 16 mL of 1 M $H_2C_2O_4$ was then added slowly with constant stirring. A clean green solution was achieved. The resultant solution was stirred for further 30 minutes and then concentrated to ~ 30 mL through a rotary evaporator. Cold EtOH was added to precipitate the product. It was then purified 3 times from H_2O/EtOH. Green powder of $Na_3[Fe(C_2O_4)_3]{\cdot}4H_2O$ was obtained after vacuum drying (yield > 95%). The product was ready for characterization and performance tests. Elemental analysis: calcd: C 15.2, H 1.7, O 53.9 %; found: C 15.5, H 1.9, O 55.1%.

$Na_3[Cr(C_2O_4)_3]$ (Na-Cr-OA) NaOH (182 mmol, 7.3 g) and $H_2C_2O_4$ (90 mmol, 8.1 g) in 200 mL DI water were stirred for 30 minutes at 40 °C. Then $H_2C_2O_4$ (318 mmol, 28.6 g) was added into the solution, followed by the addition of $Na_2Cr_2O_7{\cdot}2H_2O$ (45 mmol, 13.4 g) in small portions under constant stirring. The resultant violet solution was stirred for further 2 hours and then concentrated to ~ 50 mL through a rotary evaporator. Cold EtOH was added to precipitate the product. It was then purified 3 times from H_2O/EtOH. Violet powder of $Na_3[Cr(C_2O_4)_3]{\cdot}4H_2O$ was obtained after vacuum drying (yield > 95%). The product was ready for characterization and performance tests. Elemental analysis: calcd: C 15.2, H 2.1, O 57.3%; found: C 15.4, H 2.0, O 57.8%.

Characterization of complexes

FTIR spectra was recorded by a Perkin-Elmer FT-IR Spectrometer Spectrum 2000 in the range of 4000 to 400 cm^{-1} to determine the functional groups of oxalic acid complexes (OACs). A solid KBr method was used to obtain the FTIR spectra. TGA with a TGA 2050 themogravimetric analyzer (TA Instruments, New Castle, DE) was used to measure the composition of OACs. The TGA experiments were conducted under nitrogen atmosphere from 30 to 700 ^oC at a heating rate of 10 ^oC/min.

Crystallographic studies

X-ray single crystals of Na-Fe-OA and Na-Cr-OA were grown by slow evaporation of H_2O from their concentrated aqueous solutions. The diffraction experiments were carried out on a Bruker SMART CCD diffractometer using Mo-Ka radiation (l = 0.71073 A˚).

The program SMART[1] was used to collect frames of data, indexing reflections and determination of lattice parameters, and SHELXTL[2] for space group and structure determination, refinements, graphics, and report of structure. The structures were refined by full-matrix least squares on *F*2 with anisotropic thermal parameters for non-hydrogen atoms and all hydrogen atoms were placed in idealized positions.

Relative viscosity of the OACs solutions

The relative viscosities (η_r) of Na-Fe-OA and Na-Cr-OA at various concentrations, compared to that of DI water, were 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 conducted using a lab-scale FO set-up as described elsewhere.[3] For comparison, two types of thin-film composite (TFC) FO membranes fabricated on polyethersulfone (PES) supports were employed. They were denoted as TFC-PES$_1$[4] and TFC-PES$_2$[5] (the membrane of TFC-PES$_{water/NMP/PEG}$ in ref 5) because different dope compositions and spinning conditions were employed in fabricating the PES substrates. Their spinning and TFC formation conditions have been described elsewhere.[4,5] Each module contains 5 pieces of hollow fibers with a length of 20 cm each. During FO

experiments, the feed and draw solutions flowed co-currently. The flow rates at the lumen and shell sides were 10 mL·min^{-1} (0.054 m·s^{-1}) and 300 mL·min^{-1} (0.2 m·s^{-1}), respectively. The pressures at two channel inlets were below 0.07 bar (1.0 psi). Both the feed and draw solutions were maintained at 25 ± 0.5 ºC during experiments. Draw solutions with a volume of 80 mL were prepared from Na-Fe-OA and Na-Cr-OA. The feed solution is either 500 mL DI water or protein solution. Two testing modes, viz., pressure retarded osmosis (PRO) (draw solution facing the TFC selective layer) and FO (draw solution facing the PES porous layer), were used. All data were obtained from 3 parallel tests. The water permeation flux, J_w, (L·m^{-2}·hr^{-1}, abbreviated as LMH) was acquired from the volume change of the feed solution using equation (2).

$$J_w = \frac{\Delta V}{A_m \Delta t} \tag{2}$$

where ΔV (L) is the feed volume change over a predetermined time Δt (h) and A_m is the effective membrane surface area (m^2). The reverse solute flux, J_s (g·m^{-2}·hr^{-1}, abbreviated as gMH), describes the amount of the draw solute diffusing from the draw solution to the feed. As both Na-Fe-OA and Na-Cr-OA are conductive in their aqueous solutions, their concentrations in feed solutions were attained by a calibrated conductivity meter (Oakton Instruments, Vernon Hills, IL). The value of J_s was determined from the increase of the feed conductivity:

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

where C_0 (g·L^{-1}) and V_0 (L) are the initial solute concentration and the initial feed volume, respectively, while C_t (g·L^{-1}) and V_t (L) are the solute concentration and the feed volume after a predetermined time Δt (h), respectively. The specific reverse solute flux

(J_s/J_w, $g \cdot L^{-1}$), defined as the ratio of the reverse solute flux (J_s, gMH) to the water flux (J_w, LMH), is used to estimate the draw solute lost when treating per liter of the feed solution during FO experiments. The pH values of draw solutions were determined using a pH meter (Horiba pH meter D-54, Japan). The osmotic pressures of complex solutions were measured using a model 3250 osmometer (Advanced Instruments, Inc.).

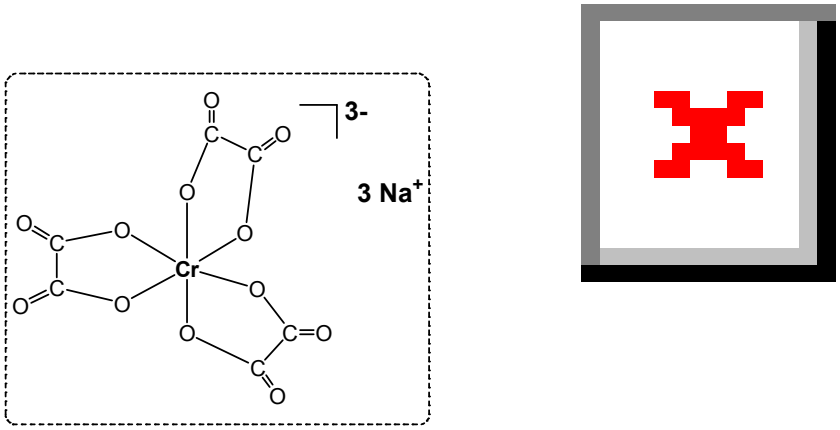
A Bovine Serum Albumin (BSA) aqueous solution was used as the model protein solution in this work. In the protein enrichment experiments, a 200 ppm BSA solution of 500 mL was utilized as the feed solution using the TFC-PES_2 membrane under the PRO mode. The possible change of protein structure after FO experiments was investigated by circular dichroism (CD) spectra. The enrichment percentage ($(C_t - C_0) / C_0$) is defined as the ratio of the protein concentration increment, ($C_t - C_0$), to the initial protein concentration C_0. It is used to estimate the protein enrichment efficiency.

Regeneration of complex draw solutes

After the FO experiment, the draw solution is diluted as a result of water transportation from the feed to the draw solution. The diluted draw solution was re-concentrated via a pressure-driven NF process in this study. A thin-film polyamide NF membrane (NE2540-70) was used under a 10-bar pressure. The pure water permeability of the NF membrane was 16.8 LMH/bar calculated by equation (2) when DI water used as the feed under 10 bars. The solute rejection, indicative of the percentage of the OA complex retained by the membrane, is calculated by equation (4):

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

where R is the solute 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.



(a) (b)

Fig. S1 (a) Proposed structure of Na-Cr-OA, (b) X-ray single crystal structure of Na-Cr-OA

Table S1 Selected bond lengths [Å] and angles [◦] of Na-Fe-OA and Na-Cr-OA

Na-Fe-OA		Na-Cr-OA	
bond lengths [Å]			
Fe1-O1	2.011(1)	Cr1-O1	1.973(2)
Fe1-O2	1.996(1)	Cr1-O2	1.972(2)
Fe1-O5	2.002(1)	Cr1-O5	1.958(2)
Fe1-O6	2.033(1)	Cr1-O6	1.970(2)
Fe1-O9	2.032(1)	Cr1-O9	1.983(2)
Fe1-O10	1.999(1)	Cr1-O10	1.961(2)
C1-O3	1.225(2)	C1-O3	1.219(3)
C2-O4	1.228(2)	C2-O4	1.224(3)
C3-O7	1.229(2)	C3-O7	1.219(3)
C4-O8	1.226(2)	C4-O8	1.220(3)
C5-O11	1.232(2)	C5-O11	1.222(3)

C6-O12	1.218(2)	C6-O12	1.222(3)
angles [◦]			
O2-Fe1-O1	81.08(5)	O2-Cr1-O1	82.50(6)
O5-Fe1-O6	80.70(5)	O5-Cr1-O6	83.15(6)
O10-Fe1-O9	80.19(5)	O10-Cr1-O9	82.35(6)
O5-Fe1-O1	94.81(6)	O1-Cr1-O9	170.52(7)
O1-Fe1-O6	164.81(6)	O6-Cr1-O2	172.25(7)
O1-Fe1-O9	97.28(6)	O5-Cr1-O10	172.53(6)
O10-Fe1-O1	92.38(6)	O5-Cr1-O1	95.42(7)
O2-Fe1-O5	103.27(6)	O6-Cr1-O1	91.53(6)
O2-Fe1-O6	85.82(6)	O10-Cr1-O1	89.19(6)
O2-Fe1-O9	89.47(6)	O5-Cr1-O2	92.46(7)
O2-Fe1-O10	167.02(6)	O2-Cr1-O9	93.78(6)
O5-Fe1-O9	163.66(6)	O10-Cr1-O2	93.96(7)
O10-Fe1-O5	88.38(6)	O5-Cr1-O9	93.44(6)
O9-Fe1-O6	90.22(6)	O6-Cr1-O9	92.86(6)
O10-Fe1-O6	101.93(6)	O10-Cr1-O6	90.87(6)

Table S2 Crystal data and structure refinement of Na-Fe-OA and Na-Cr-OA

Complex	Na-Fe-OA	Na-Cr-OA
Chemical formula	$C_6H_6FeNa_3O_{17}$	$C_6H_{10}CrNa_3O_{17}$
Formula weight	474.93 g/mol	475.11 g/mol
Temperature	100(2) K	100(2) K
Crystal size	0.140 x 0.340 x 0.470 mm	0.260 x 0.460 x 0.600 mm
Crystal system	monoclinic	monoclinic
Space group	C 1 2/c 1	C 1 2/c 1
a (Å)	17.4212(9)	17.255(2)
b (Å)	12.5545(7)	12.464(1)
c (Å)	14.9217(8)	15.123(2)
α (◦)	90	90
β (◦)	101.047(2)	100.454(2)

γ (◦)	90	90
V (Å^3)	3203.1(3)	3198.4(6)
Z,	8	8
Dcalc (g cm^{-3})	1.970	1.973
Absorption coefficient (mm^{-1})	1.115	0.889
θ range (◦)	2.31 to 28.28	2.03 to 27.50
Reflections collected	21361	11192
Independent reflections	3978 [R(int) = 0.0247]	3685 [R(int) = 0.0239]
Max. and min. transmission	0.7485 and 0.6062	0.7457 and 0.6542
Final R indices [I > 2σ (I)] R_1, wR_2	R1 = 0.0367, wR2 = 0.1137	R1 = 0.0361, wR2 = 0.0863
R indices (all data) R_1, wR_2	R1 = 0.0373, wR2 = 0.1144	R1 = 0.0407, wR2 = 0.0883
Largest diff peak and hole (eÅ^{-3})	1.425 and -0.870	0.934 and -0.493

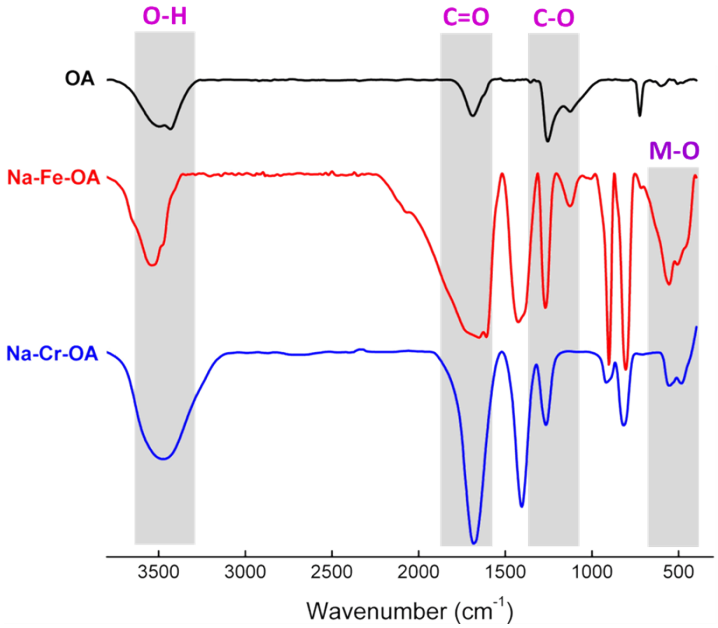


Fig. S2 FTIR spectra comparison among OA, Na-Fe-OA and Na-Cr-OA

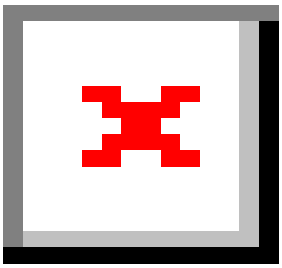


Fig. S3 Spectra of TGA measurements of Na-Fe-OA and Na-Cr-OA

Table S3 Weight losses in the 1st and 2nd stages of OACs in TGA measurements

Sample	Decomposition stage	Observed weight loss (%)	Calculated weight loss (%)
Na-Fe-OA	I (H_2O)	18.8 ± 0.5	18.1
	II (organic ligand)	46.2 ± 1.0	45.5
Na-Cr-OA	I (H_2O)	18.5 ± 0.3	18.9
	II (organic ligand)	46.0 ± 0.7	45.5

(a) (b)

Fig. S4 A comparison of relative viscosity among (a) OA, Na-Fe-OA and Na-Cr-OA; (b) OACs, Na-Fe-CA[6] and PAA-Na[7]

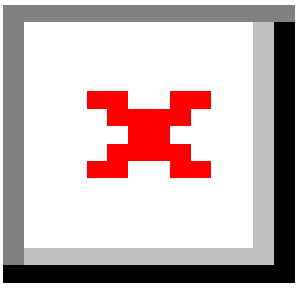


Fig. S5 A comparison of osmotic pressures among OA, Na-Fe-OA and Na-Cr-OA

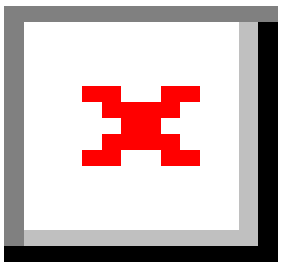


Fig. S6 BSA concentration vs. time ((TFC-PES_2 membrane, 1 M Na-Cr-OA and 1 M NaCl as respective draw solutions, PRO mode)

References

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