Supporting Information

Probing the Speciation of Quaternary Ammonium Polybromides by Voltammetric Tribromide Titration

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Table of Contents

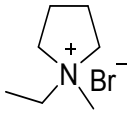
Experimental Section

Chemicals: All reagents and solvents were purchased from commercial vendors and used without further purification. All solutions were prepared with deionized Milli-Q water.

Instruments and measurements: ^{1}H and ^{13}C NMR spectra were recorded on a 500 MHz spectrometer (Varian VNMRS 500) and LC-MS spectra were recorded using ESI mode (Hewlett Packard Series 1100 and Agilent Technologies 6130). IVIUM compactstat (IVIUM technologies, Netherlands) was used for all electrochemical measurements. Three electrodes were used in an electrochemical cell; Pt ultramicroelectrodes (radius: a = 5 μm) as working electrodes, Ag wire as a quasi-reference electrode, and Pt wire as a counter electrode. All electrodes were purchased and used from CH Instruments.

Synthesis and Characterization of QBrs:

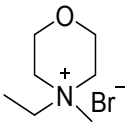
***N*-Methyl-*N*-ethyl pyrrolidinium bromide (MEPBr)[1]**



[CAS No. 69227-51-6]

1-Methylpyrrolidine (8.5 g, 100 mmol), bromoethane (8.9 mL, 120 mmol) and ethyl acetate (20 mL) was added in a 100 mL round bottom flask. Then the mixture was stirred at room temperature for 6 h. The solid product was filtered, washed with ethyl acetate 3 times, and dried in vacuum to give the desired product as white solid (18.6 g, 96%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.52 – 3.35 (m, 6H), 2.97 (d, J = 2.0 Hz, 3H), 2.07 (dd, J = 5.3, 4.0 Hz, 4H), 1.31 – 1.24 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 63.26, 58.63, 47.31, 21.49, 9.40. MS (EI) m/z = 114 (M^+).

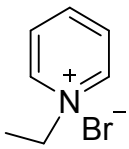
N-Methyl-N-ethyl-morpholinium bromide (MEMBr)[2]



[CAS No. CAS 65756-41-4]

4-Methylmorpholine (17.5 mL, 160 mmol), bromoethane (23.5 mL, 320 mmol), ethyl acetate (20 mL) was added in a 100 mL round bottom flask and the reaction mixture was refluxed at 40 ℃ for 72 h. After cooled at room temperature, the solid product was filtered, washed with ethyl acetate for 3 times, and dried in vacuum to give the desired product as white solid (24.3 g, 72%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.92 (t, J = 9.1 Hz, 4H), 3.52 (dd, J = 14.6, 7.3 Hz, 2H), 3.44 – 3.36 (m, 4H), 3.10 (d, J = 5.9 Hz, 3H), 1.25 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 60.25, 59.70, 58.84, 45.79, 7.37. MS (EI) m/z = 130 (M^+).

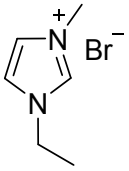
1-Ethylpyridinium bromide (EPyBr)[3]



[CAS No. 1906-79-2]

To a solution of pyridine (40.3 mL, 500 mmol) in ethyl acetate (40 mL) was added dropwise ethyl bromide (74 mL, 1.0 mol) in ice-bath. Then the mixture was stirred at 30 ℃ for 72 h. The solid product was filtered, washed with ethyl acetate for 3 times, and dried in vacuum to give the desired product as white solid (59 g, 63%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.11 (d, J = 5.8 Hz, 2H), 8.60 (t, J = 7.8 Hz, 1H), 8.16 (t, J = 6.9 Hz, 2H), 4.63 (q, J = 7.3 Hz, 2H), 1.54 (t, J = 7.3 Hz, 3H); ^{13}C NMR (126 MHz, DMSO-d_6) δ 146.09, 145.25, 128.76, 57.02, 17.05; MS (EI) m/z = 108.1 (M^+)

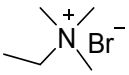
1-Ethyl-3-methylimidazolium bromide bromide (EMIBr)[4]



[CAS 65039-08-9]

1-Methylimidazole (24 mL, 300 mmol), bromoethane (30 mL, 400 mmol), ethyl acetate (20 mL) was added in a 100 ml round bottom flask. Then the mixture was stirred at room temperature for 72 h. The solid product was filtered, washed with ethyl acetate 3 times and dried in vacuum to give the desired product as white solid (56 g, 98%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 9.16 (s, 1H), 7.81 – 7.78 (m, 1H), 7.72 – 7.69 (m, 1H), 4.20 (q, J = 7.3 Hz, 2H), 3.85 (s, 3H), 1.46 – 1.37 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 136.71, 123.94, 122.40, 44.53, 36.19, 15.64. MS (EI) m/z = 111 (M^+).

Ethyltrimethyl ammonium bromide (ETMABr)[5]



[CAS 2650-77-3]

Trimethylamine (28 % in water; 50 mL, 215 mmol), bromoethane (35 mL, 322.5 mmol), ethyl acetate (50 mL) was added in a 100 ml round bottom flask. Then the mixture was stirred at room temperature for 72 h. The aqueous phase was collected and water was removed under vacuum to give the crude product. The crude product was washed with ethyl acetate 3 times and dried in vacuum to give the desired product as white solid (34.6 g, 96%).^{1}H NMR (500 MHz, DMSO-d_6) δ 3.42 – 3.26 (m, 2H), 3.02 (d, J = 2.3 Hz, 9H), 1.33 – 1.18 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 61.06, 51.93, 8.61. MS (EI) m/z = 88 (M^+).

Preparation of QBr_{2n+1}-WMS formed from QBr and bromine (Br_2) in acidic aqueous solution

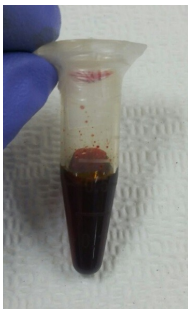
QBr (2 mmol) was dissolved in 20 mL of 0.5 M H_2SO_4 aqueous solution followed by addition of bromine (Br_2) in various equivalents (0.5 ~ 12 equiv.). The mixture was stirred at room temperature for 20 h under Ar atmosphere. Then, QBr_{2n+1}-WMS was separated from the aqueous phase by centrifugation and it was further used for electro-analysis and Raman spectroscopy analysis.

① Bromine was added to QBr in 0.5 M H_2SO_4 aqueous solution.

② The mixture was stirred for 20 h at r.t. under Ar.

③ Two phases are formed after being stirred; aqueous phase (top) and organic phase (bottom)

④ The organic phase was separated by centrifugation



⑤ The organic phase was collected in Eppendorf tube.

Supporting figures

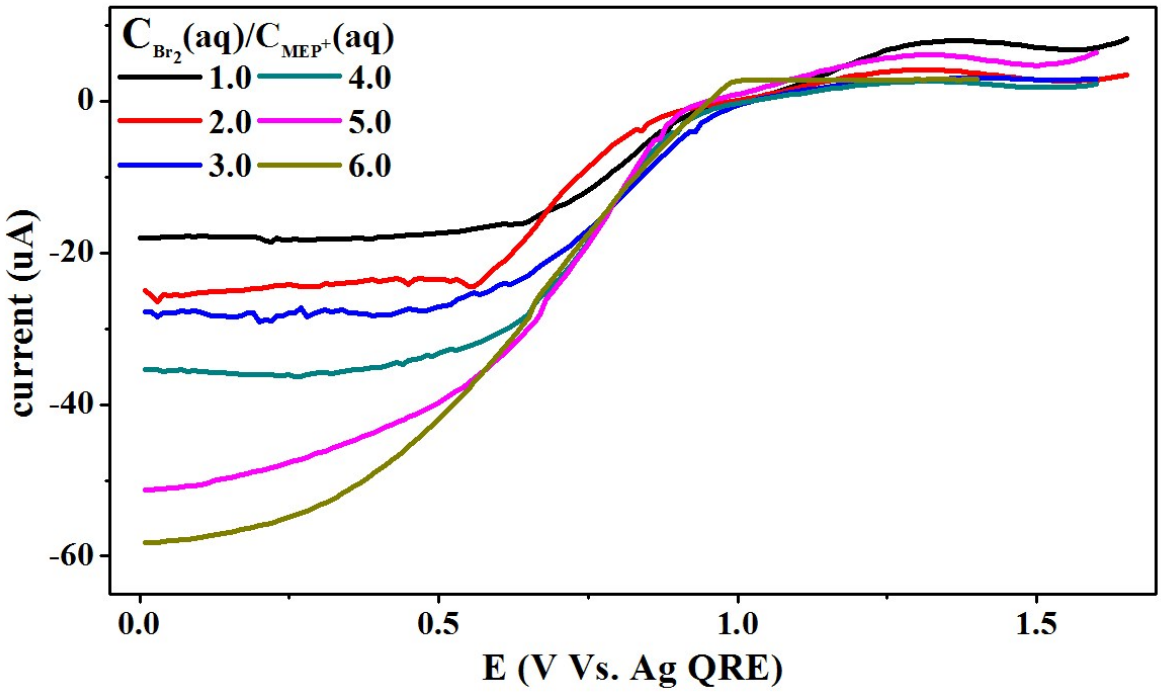


Figure S1. LSVs of $MEPBr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with various $C_{Br_2(aq)}/C_{MEP^+(aq)}$.

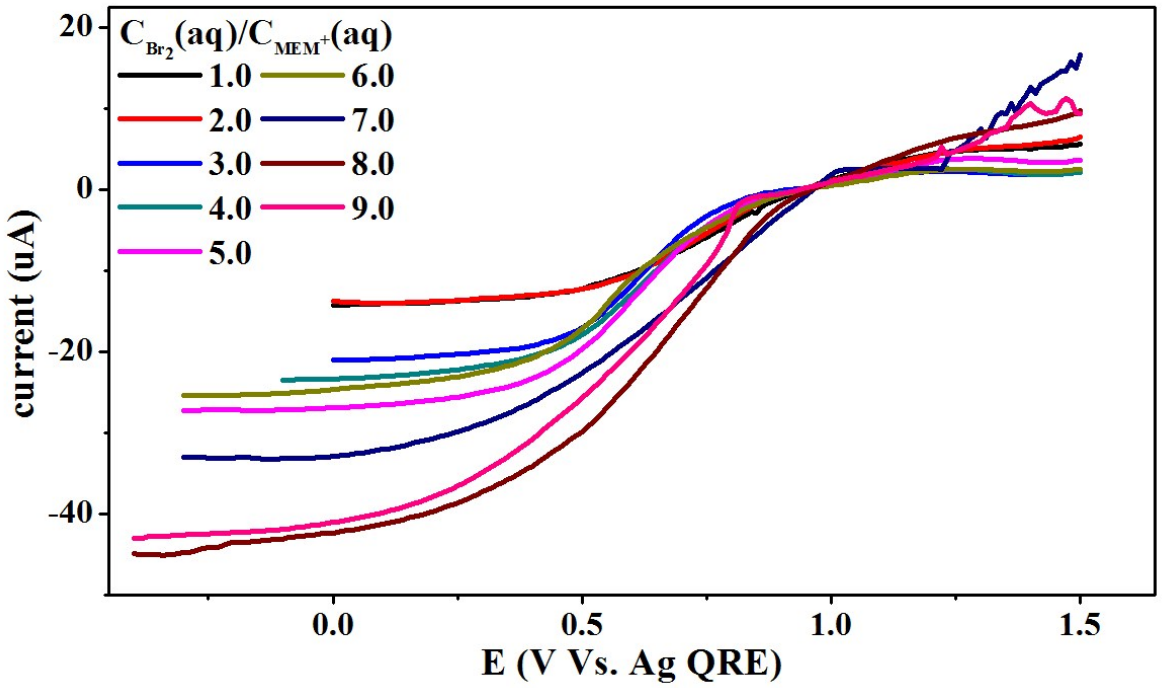


Figure S2. LSVs of $MEMBr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with various $C_{Br_2(aq)}/C_{MEM^+(aq)}$.

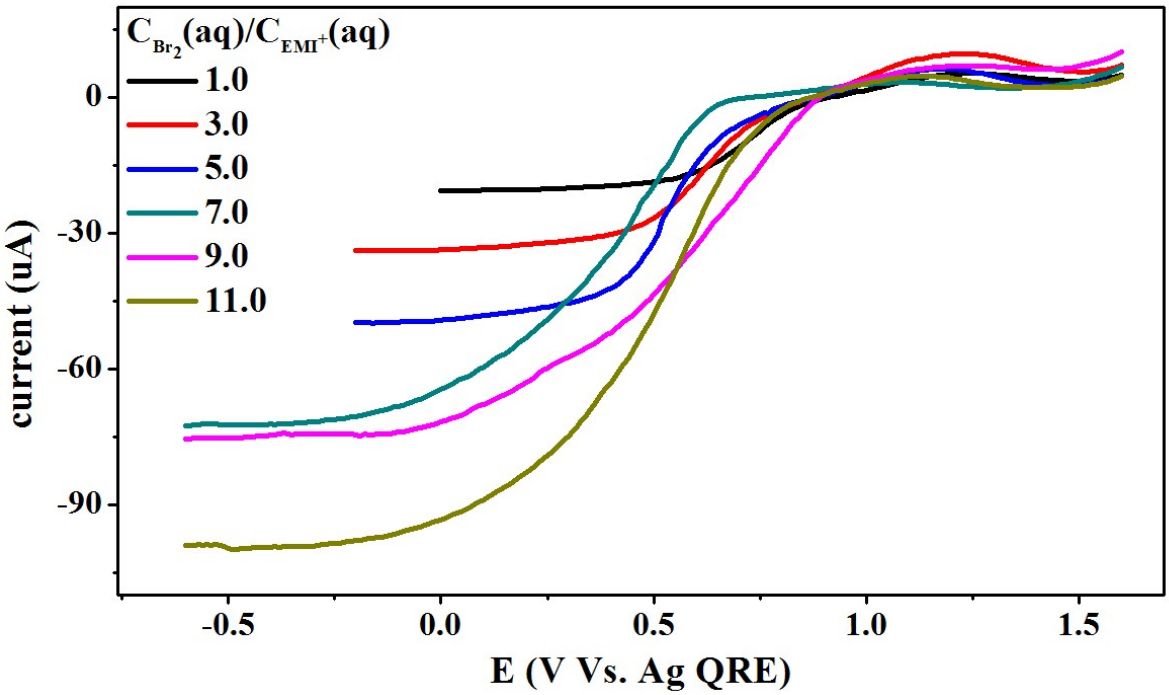


Figure S3. LSVs of $EMIBr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with various $C_{Br_2(aq)}/C_{EMI^+(aq)}$.

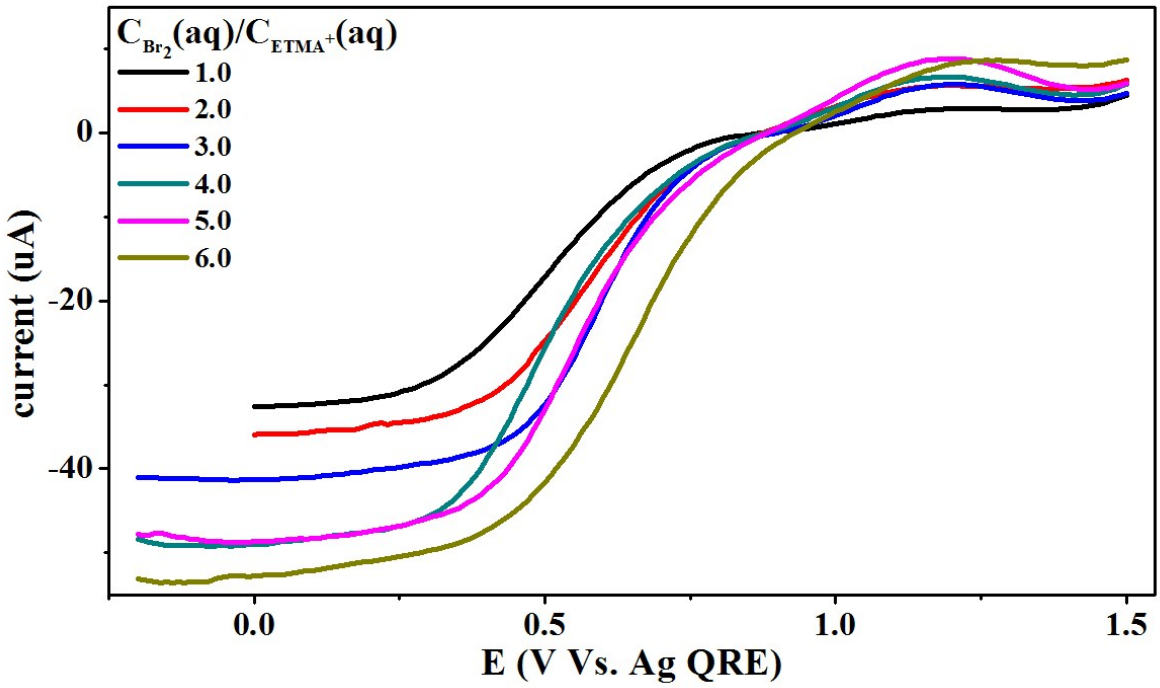


Figure S4. LSVs of $ETMABr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with various $C_{Br_2(aq)}/C_{ETMA^+(aq)}$.

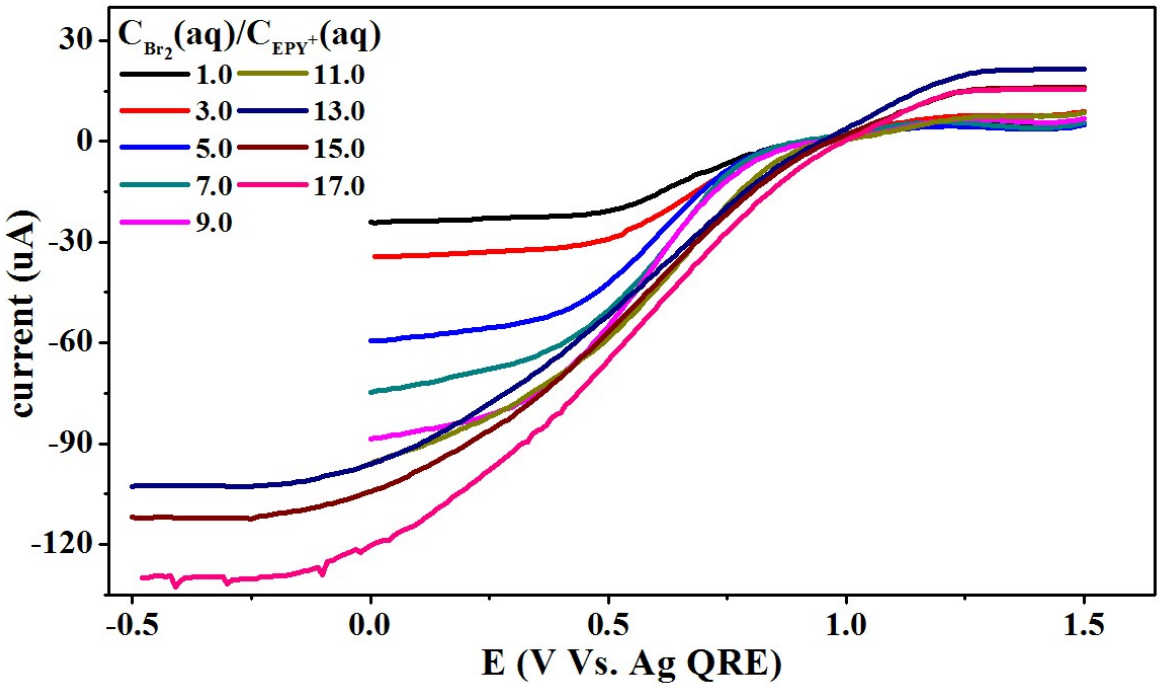


Figure S5. LSVs of $EPyBr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with various $C_{Br_2(aq)}/C_{EPy^+(aq)}$.

Raman spectroscopic analyses of QBr_{2n+1}-WMSs

Figure S6-10 shows the normalized Raman spectra from QBr_{2n+1}-WMSs. The observed Raman spectroscopic features were similar in QBr_{2n+1}-WMSs with different Q^+; the small peak at 158 cm^{-1} is attributed to the symmetrical stretch of Br_3^-, while the large peak at 260 cm^{-1} with the shoulder at 204 cm^{-1} could be associated with mixed Br_{2n+1}^- ($n \geq 2$).[6] However, the broad peak at 260 cm^{-1} was not resolved for the all QBr_{2n+1}-WMSs, and thus, it was difficult to obtain accurate QBr_{2n+1} speciation from the Raman spectra. This enforces the importance of the electrochemical analysis for the QBr_{2n+1} speciation, suggested in this main article.

In the QBr_{2n+1}-WMSs prepared from 0.5 M H_2SO_4 solutions with higher $C_{Br_2(aq)}/C_{Q^+(aq)}$, the peak from Br_3^- decreased and was hardly observed at $C_{Br_2(aq)}/C_{MEP^+(aq)} \geq 5$, indicating that the fraction of Br_3^- would decrease while Br_{2n+1}^- with the highest order of n would become predominant in QBr_{2n+1}-WMS (Figure 2). Also, the peak at 260 cm^{-1} was shifted to bigger values and its shoulder at 204 cm^{-1} disappeared as $C_{Br_2(aq)}/C_{Q^+(aq)}$ increased, which would result from the existence of more Br_2 in QBr_{2n+1}-WMS.[7]

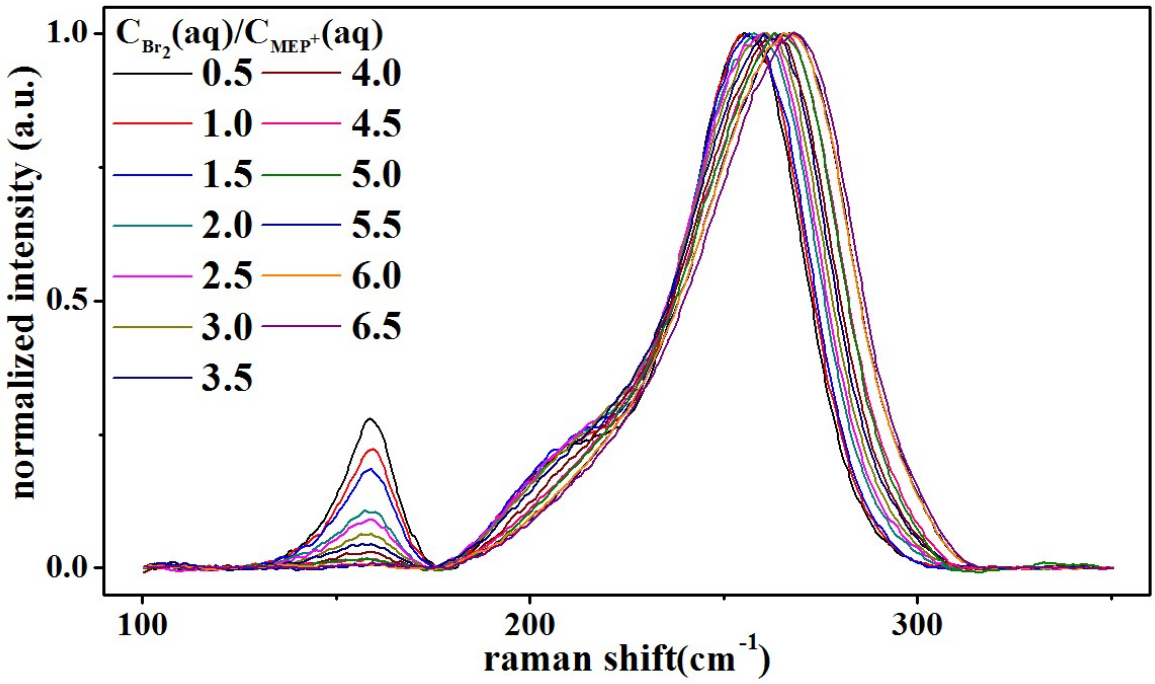


Figure S6. Raman spectrums (RSs) of $MEPBr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with different $C_{Br_2(aq)}/C_{MEP^+(aq)}$.

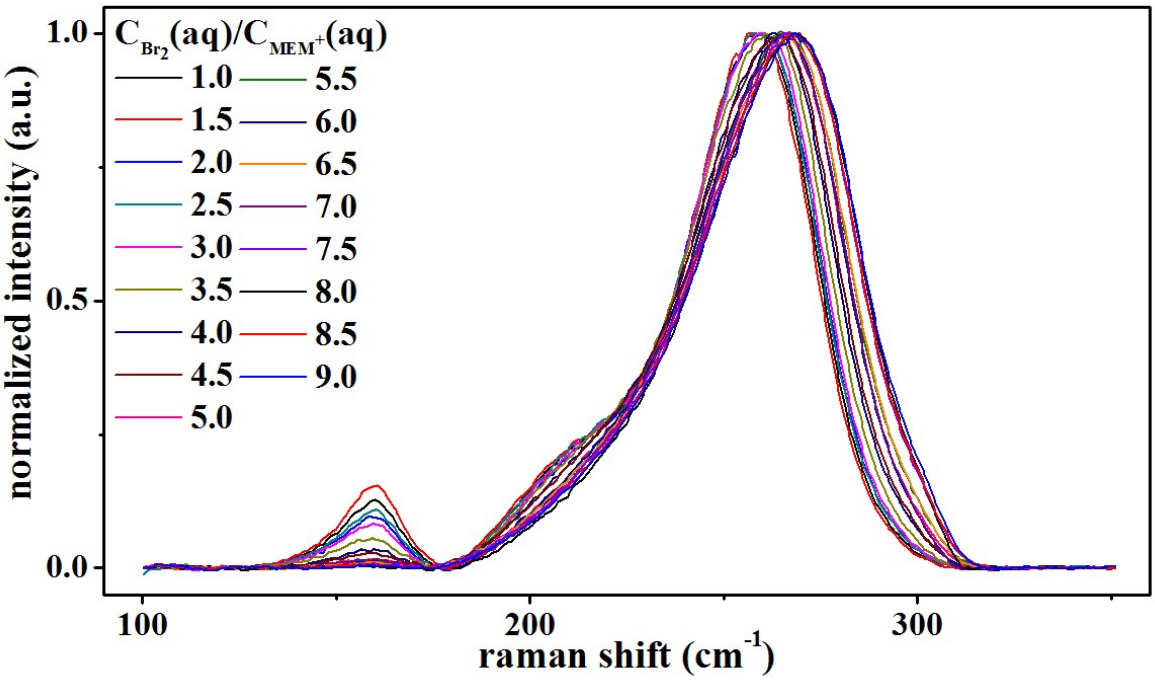


Figure S7. RSs of $MEMBr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with different $C_{Br_2(aq)}/C_{MEM^+(aq)}$.

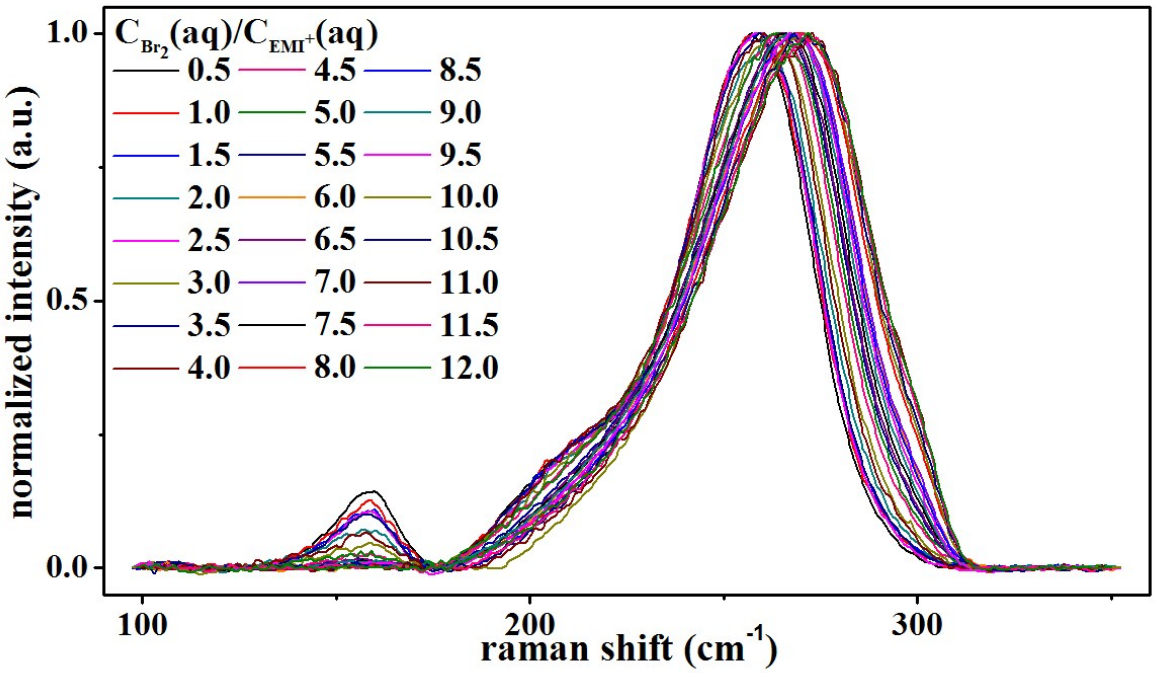


Figure S8. RSs of $EMIBr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with different $C_{Br_2(aq)}/C_{EMI^+(aq)}$.

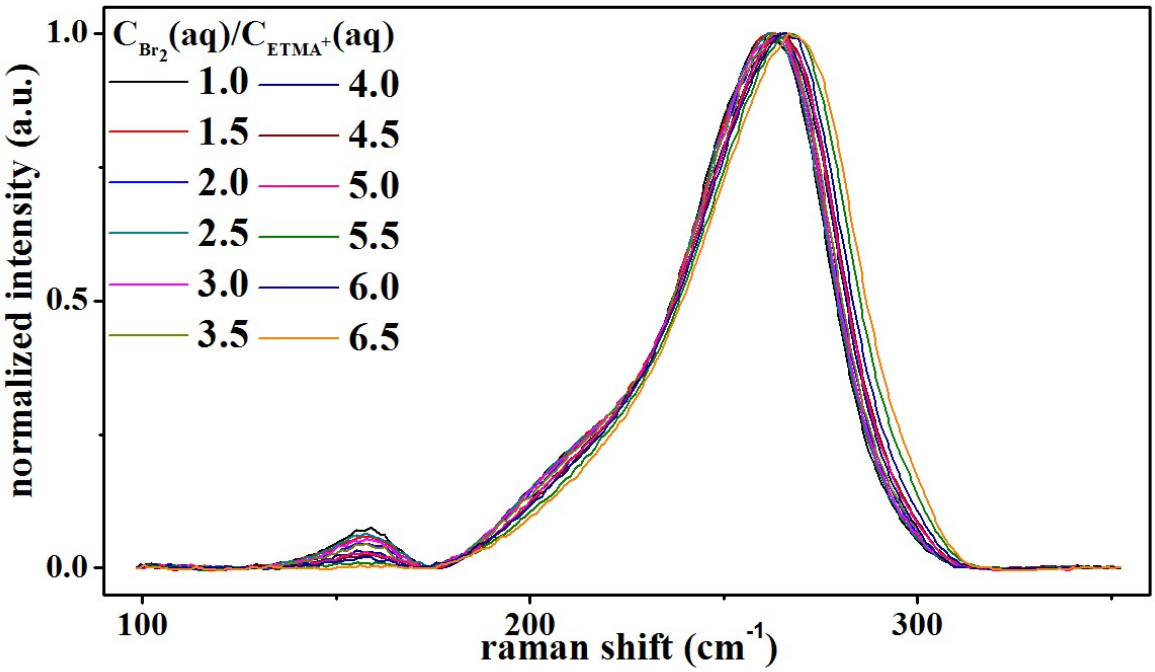


Figure S9. RSs of $ETMABr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with different $C_{Br_2(aq)}/C_{ETMA^+(aq)}$.

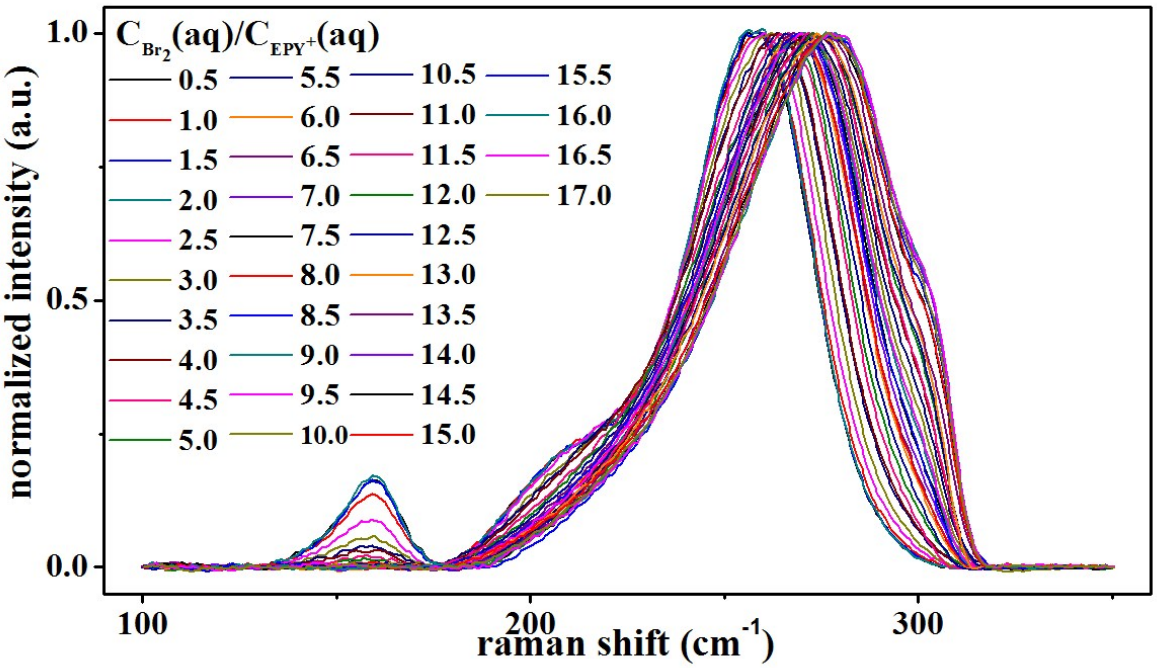


Figure S10. RSs of $EPyBr_{2n+1}$-WMSs prepared from 0.5 M H_2SO_4 solutions with different $C_{Br_2(aq)}/C_{EPy^+(aq)}$.

Supporting table

Table S1. $K^{`}_{eq(n)}$ in QBr_{2n+1}-WMSs with different Q^+.

$K^{`}_{eq(n)}$ in QBr_{2n+1}-WMS	Q^+ in QBr_{2n+1}-WMS				
	MEP^+	MEM^+	EPy^+	EMI^+	$ETMA^+$
$K^{`}_{eq(2)}$	97.05	53.44	98.15	142.94	146.89
$K^{`}_{eq(3)}$	175.39	97.05	186.04	210.62	182.73
$K^{`}_{eq(4)}$		128.12	237.04	310.65	
$K^{`}_{eq(5)}$			319.52		

Table S2. C_{Br^-} in each QBr_{2n+1}-WMS with different Q^+ estimated by the LSV at the highest $C_{Br_2}(aq)/C_{Q^+}(aq)$ before the solidification of the corresponding QBr_{2n+1}-WMS.

$C_{Br_2}(aq)/C_{Q^+}(aq)$	$I_{ss,ox}$ (μA)	$C_{Br^-(org)}$ (M)
$C_{Br_2}(aq)/C_{MEP^+}(aq) =$ 6.0	2.91	14
$C_{Br_2}(aq)/C_{MEM^+}(aq) =$ 9.0	4.94	24
$C_{Br_2}(aq)/C_{EPy^+}(aq) =$ 17.0	15.5	74
$C_{Br_2}(aq)/C_{EMI^+}(aq) =$ 11.0	2.98	14
$C_{Br_2}(aq)/C_{ETMA^+}(aq) =$ 6.0	8.66	42

References

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