Supporting Information

Time transient electrochemical monitoring of tetraalkylammonium polybromide solid particle formation: observation of ionic liquid-to-solid transition

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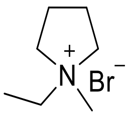
Synthesis and Characterization of QBrs and TBrs

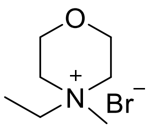
Note S1. Synthetic mechanism for *N*-Methyl-*N*-ethyl pyrrolidinium bromide (MEPBr)



[CAS No. 69227-51-6]

1-Methylpyrrolidine (8.5 g, 100 mmol), bromoethane (8.9 mL, 120 mmol) and ethyl acetate (20 mL) were added to a 100 mL round bottom flask. The mixture was stirred at room temperature for 6 h. The solid product was filtered, washed with ethyl acetate three times, and dried in a vacuum to yield a 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 (125 MHz, DMSO-d_6) δ 63.26, 58.63, 47.31, 21.49, 9.40; MS (EI) m/z = 114 (M$^+$).

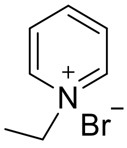
Note S2. Synthetic mechanism for *N*-Methyl-*N*-ethyl-morpholinium bromide (MEMBr)



[CAS No. CAS 65756-41-4]

4-Methylmorpholine (17.5 mL, 160 mmol), bromoethane (23.5 mL, 320 mmol), ethyl acetate (20 mL) were added to a 100 mL round bottom flask, and the reaction mixture refluxed at 40 ℃ for 72 h. After it cooled to room temperature, the solid product was filtered, washed three times with ethyl acetate, and dried in a vacuum to yield a 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 (125 MHz, DMSO-d_6) δ 60.25, 59.70, 58.84, 45.79, 7.37; MS (EI) m/z = 130 (M$^+$).

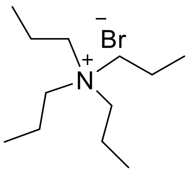
Note S3. Synthetic mechanism for 1-Ethylpyridinium bromide (EPyBr)



[CAS No. 1906-79-2]

To a solution of pyridine (40.3 mL, 500 mmol) in ethyl acetate (40 mL), bromoethane (74 mL, 1.0 mol) was added dropwise in ice-bath. The mixture was stirred at 30 ℃ for 72 h. The solid product was filtered, washed three times with ethyl acetate, and dried in a vacuum to yield a 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 (125 MHz, DMSO-d_6) δ 146.09, 145.25, 128.76, 57.02, 17.05; MS (EI) m/z = 108.1 (M^+).

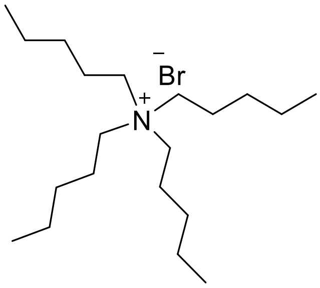
Note S4. Synthetic mechanism for Tetrapropylammonium bromide (TProABr)



[CAS No. 1941-30-6]

Tripropylamine (15.0 mL, 80 mmol), 1-bromopropane (11.0 mL, 120 mmol), and ethanol (50 mL) were added to a 250 mL round bottom flask, and the reaction mixture was refluxed at 80 ℃ for 48 h. After cooling to room temperature, the reaction mixture was concentrated to give a crude solid product. The crude product was washed with EtOAc and dried in a vacuum to yield a white solid (11.8 g, 55%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.18 – 3.08 (m, 8H), 1.72 – 1.49 (m, 8H), 0.87 (t, J = 7.3 Hz, 12H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 59.75 (s), 15.31 (s), 11.00 (s); MS (EI) m/z = 186.2 (M^+).

Note S5. Synthetic mechanism for Tetrapentylammonium bromide (TPABr)



[CAS No. 866-97-7]

1-Bromopentane (10 mL, 80 mmol), tripentylamine (46 mL 160 mmol), and ethanol (50 mL) were added to a 250 mL round bottom flask, and the reaction mixture was refluxed at 80 ℃ for 72 h. After cooling to room temperature, the reaction mixture was concentrated to give a crude solid product. The crude product was washed with EtOAc and dried in a vacuum to yield a white solid (13.4 g, 50%). ^{1}H NMR (500 MHz, DMSO-d_6) δ 3.23 – 3.10 (m, 8H), 1.66 – 1.48 (m, 8H), 1.48 – 1.15 (m, 16H), 0.87 (t, J = 7.2 Hz, 12H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 58.15 (s), 28.40 (s), 22.03 (s), 21.28 (s), 14.18 (s); MS (EI) m/z = 298.3 (M^+).

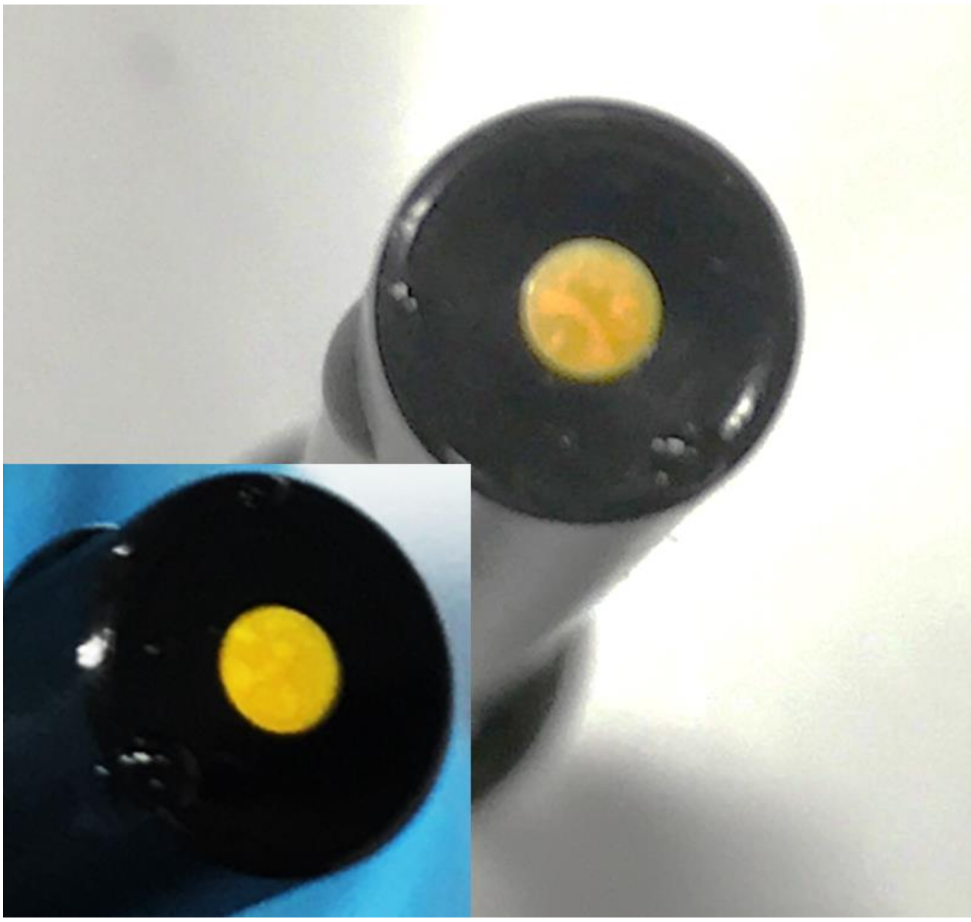
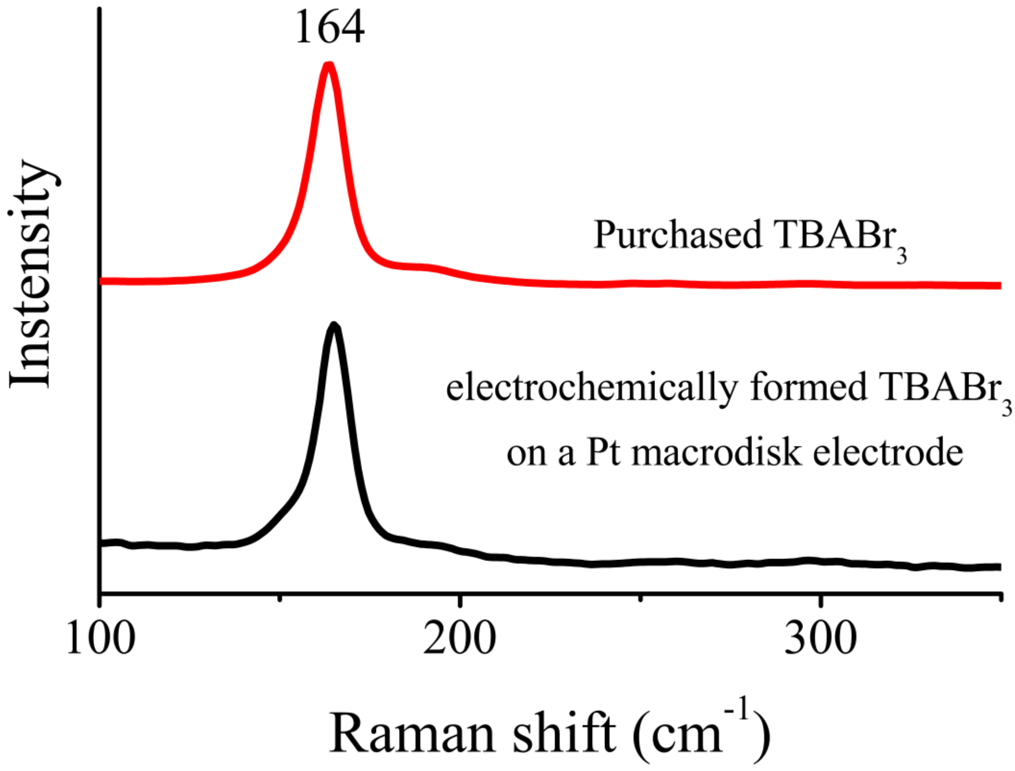


Figure S1. The photograph of precipitated $TBABr_3$ on a Pt macro disk electrode with a radius of 1 mm after a potential of 1.5 V was applied for 1000 s in a 0.5 M H_2SO_4 aqueous solution with C_{TBABr} = 50 mM.



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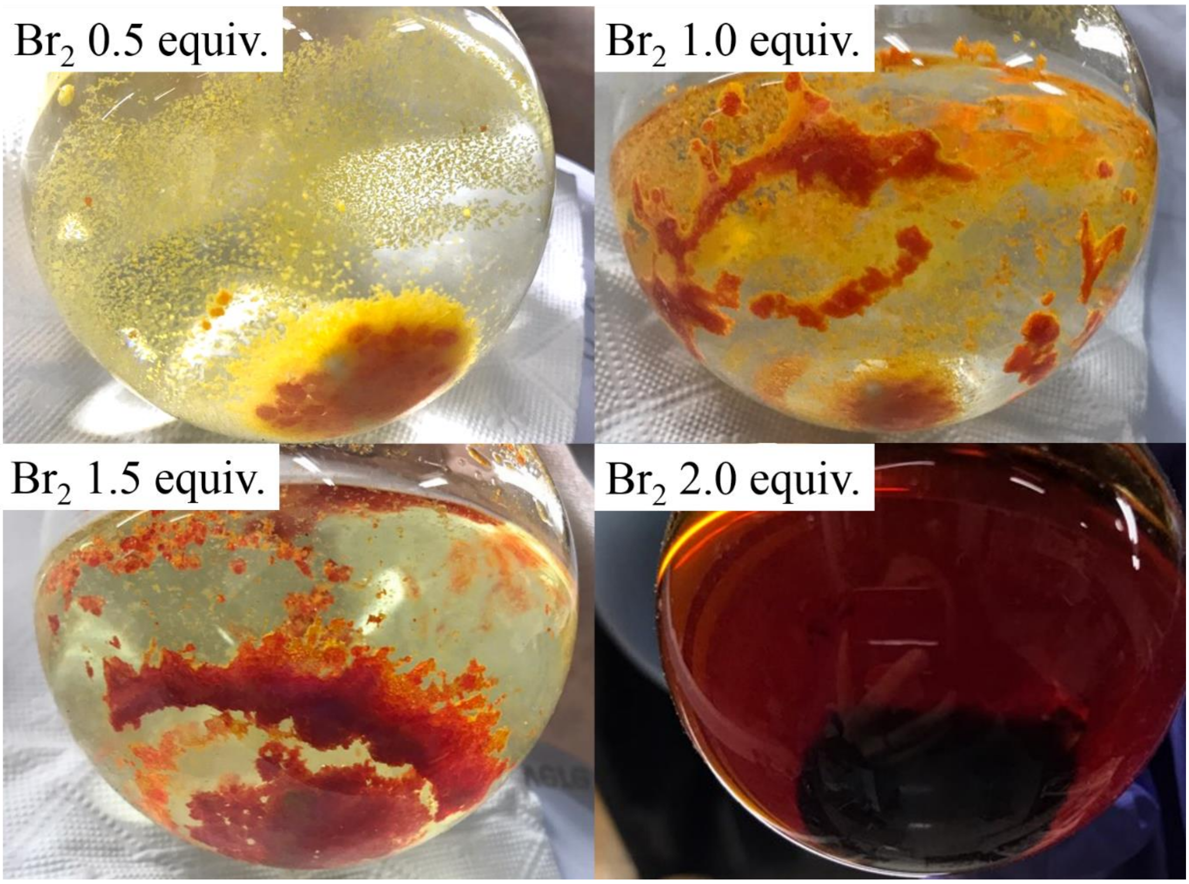

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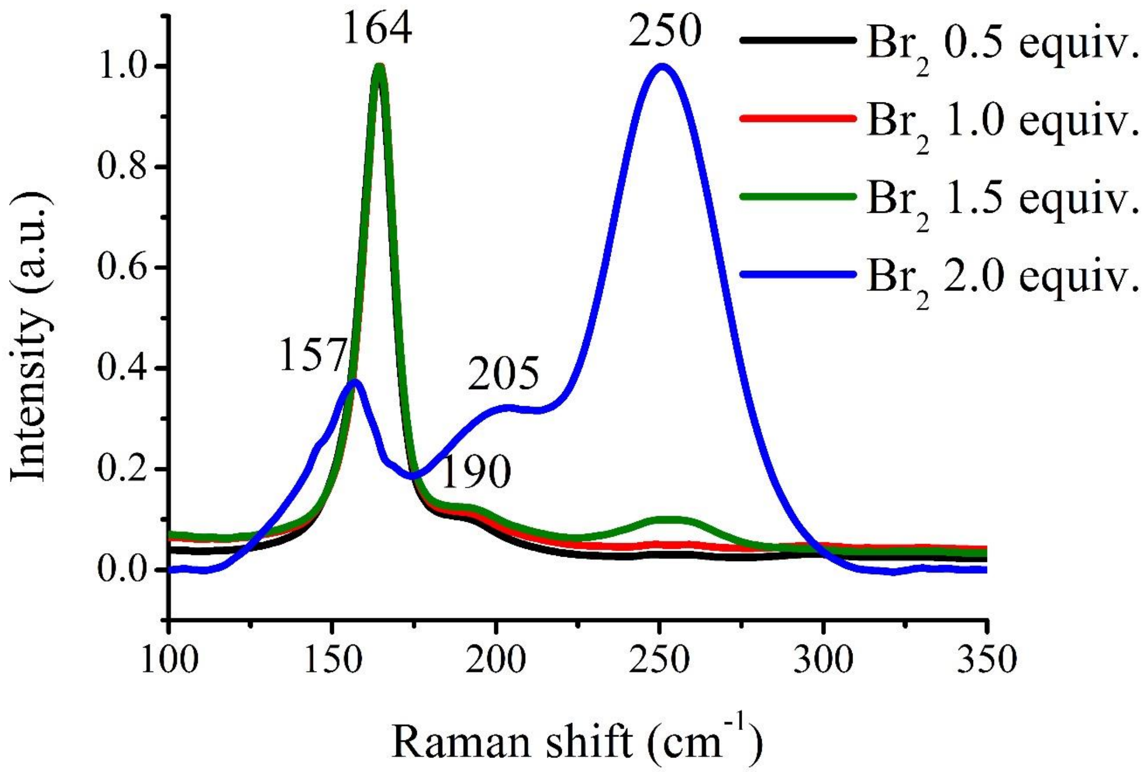
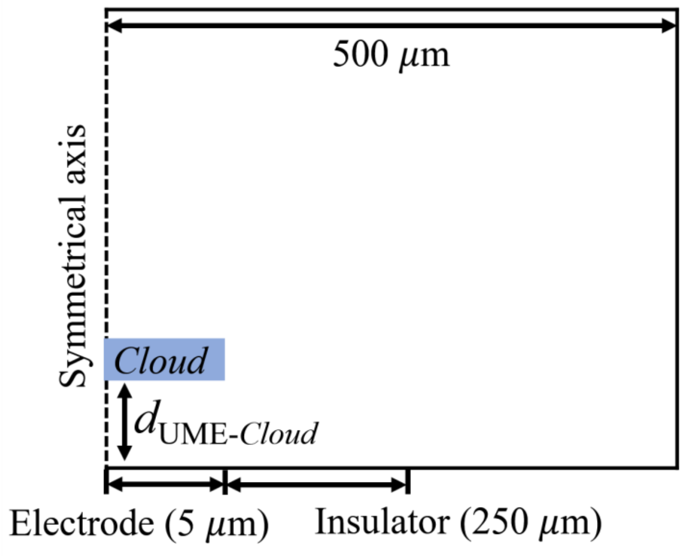


Figure S4. The Raman spectra obtained from TBr_{2n+1}, which were chemically synthesized by adding Br_2 to TBr aqueous solutions to have different ratios of $C_{Br_2(aq)}$ to $C_{Br^-(aq)}$.



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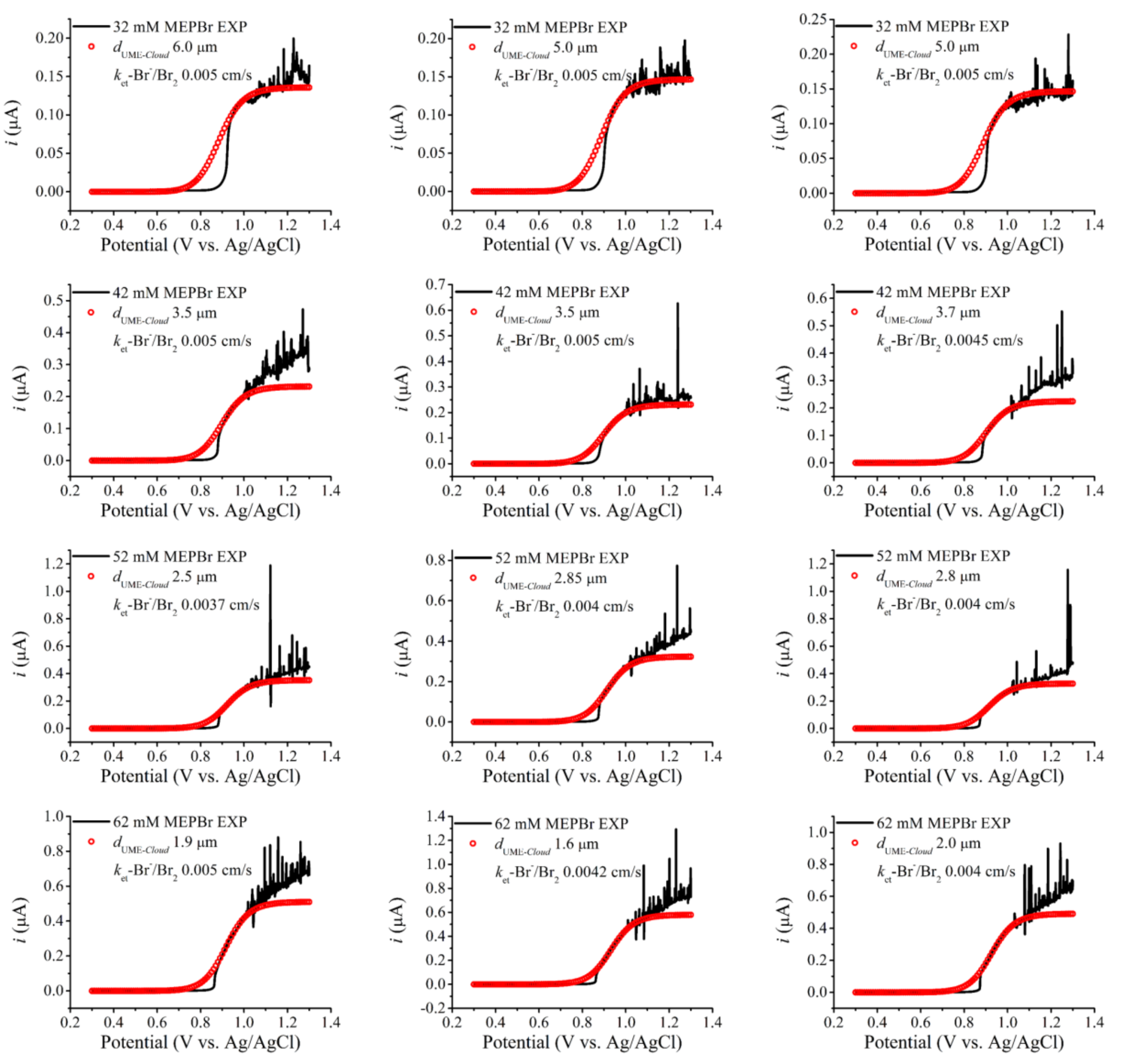
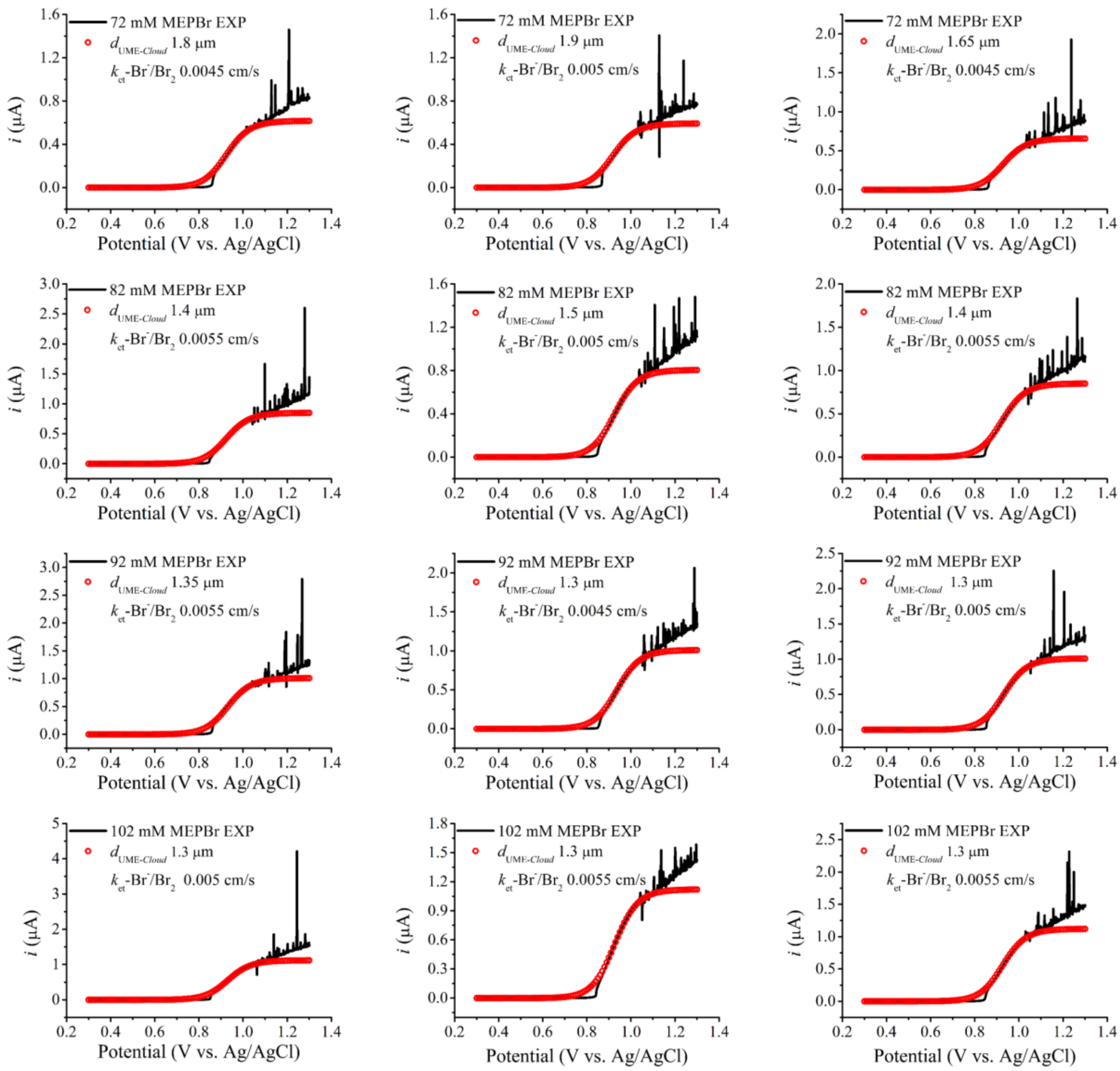


Figure S6. The linear sweep voltammograms (LSVs, black) measured in 0.5 M H_2SO_4 aqueous solutions containing various concentrations of MEPBr (32, 42, 52, and 62 mM), and the corresponding simulation results (red) based on the *Cloud* model for the estimation of k_{et}-Br^{-}/Br_2.



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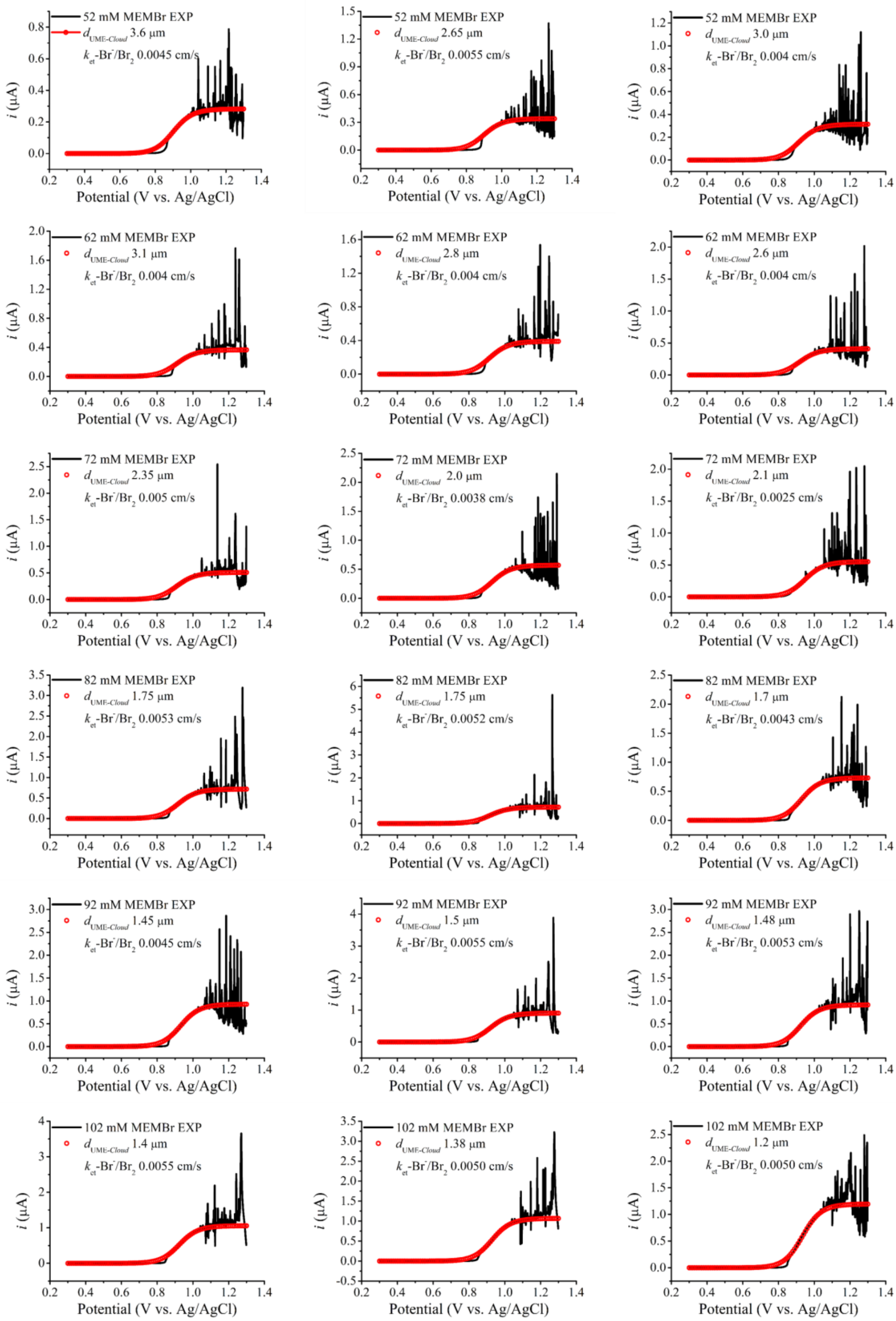
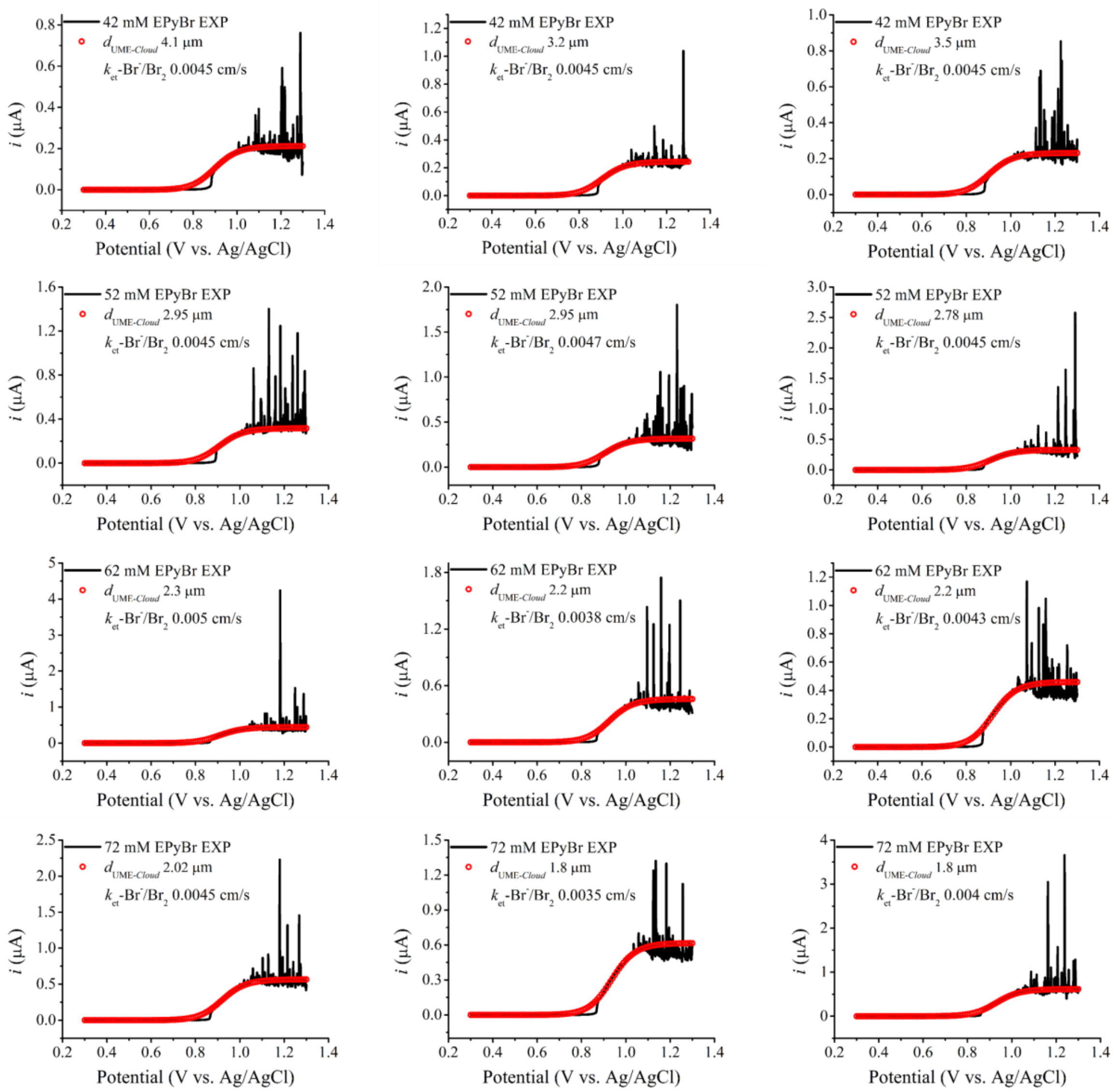


Figure S8. The LSVs (black) measured in 0.5 M H_2SO_4 aqueous solutions containing various concentrations of MEMBr (52, 62, 72, 82, 92, and 102 mM), and the corresponding simulation results (red) based on the *Cloud* model for the estimation of k_{et}-Br^-/Br_2.



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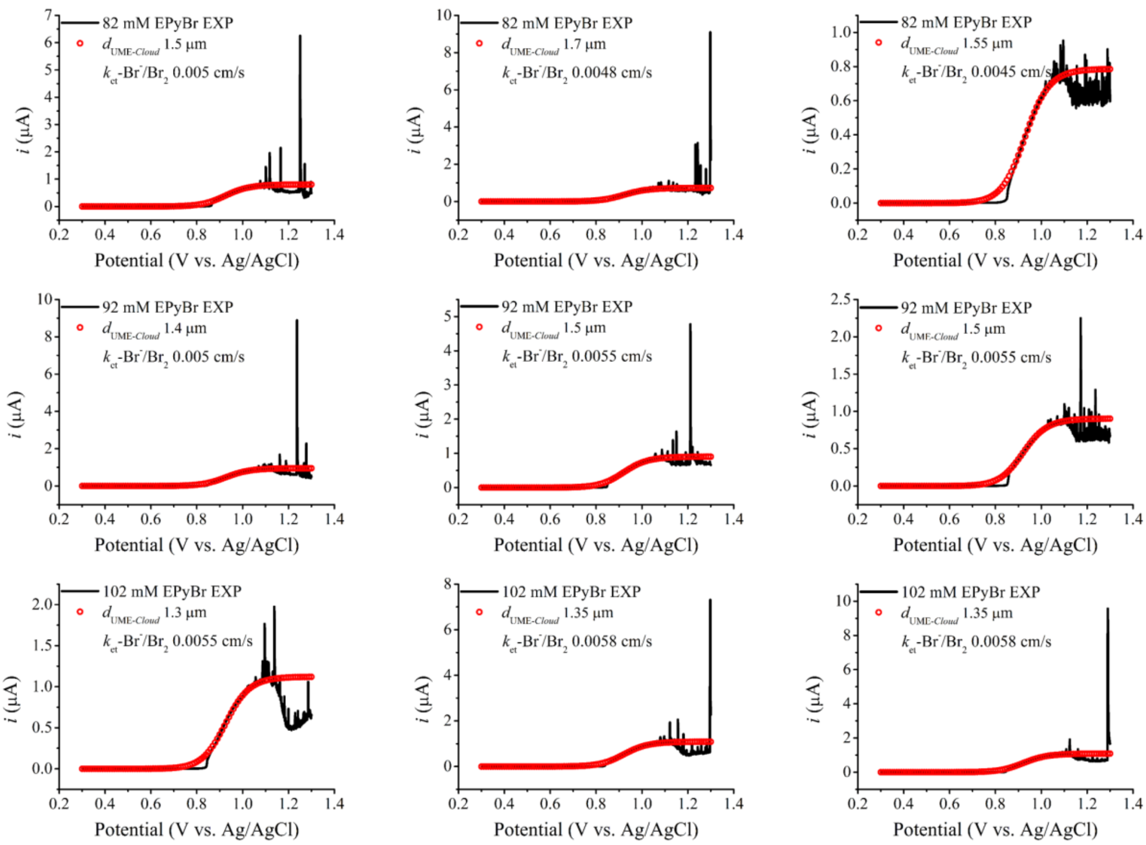

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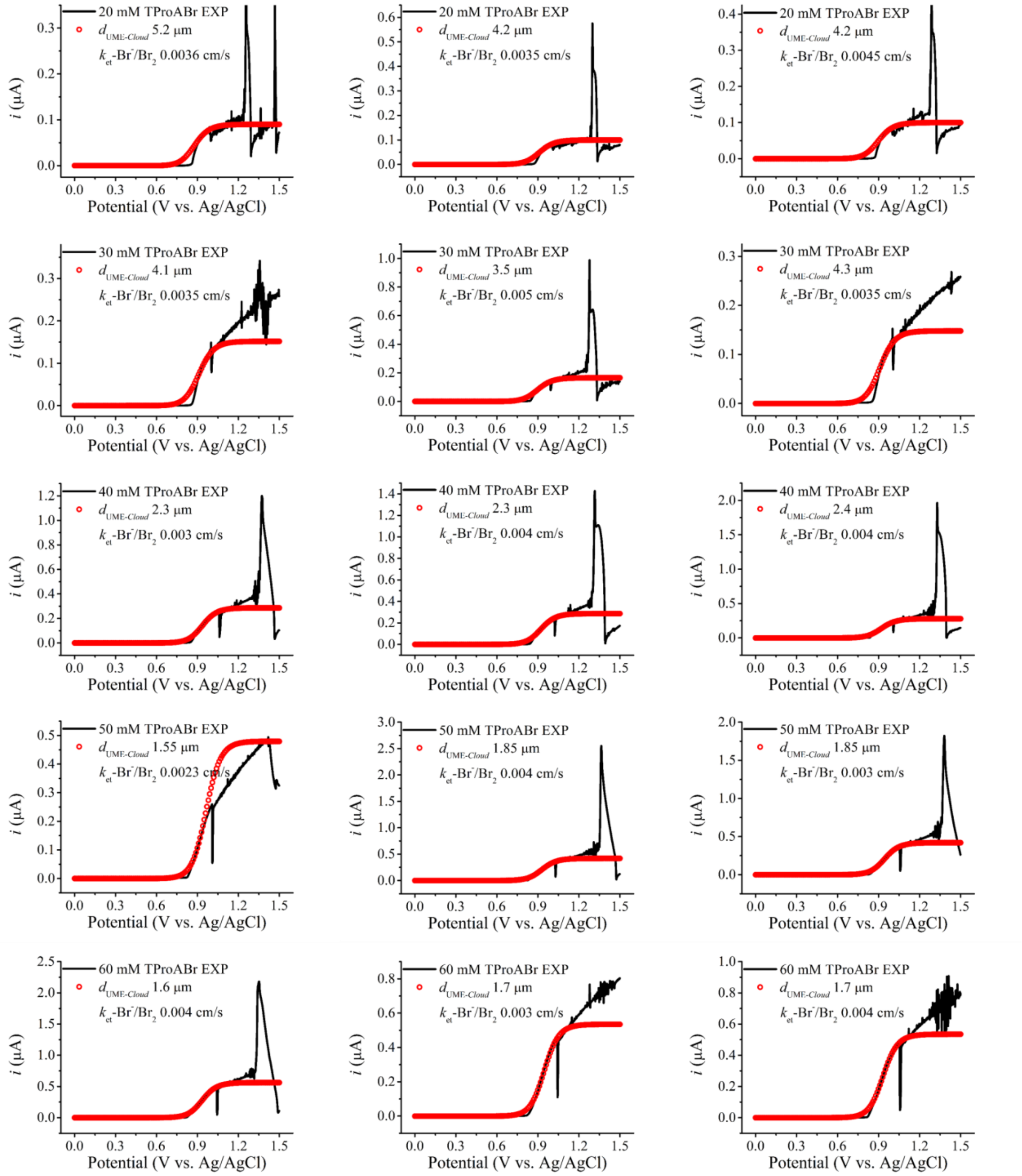

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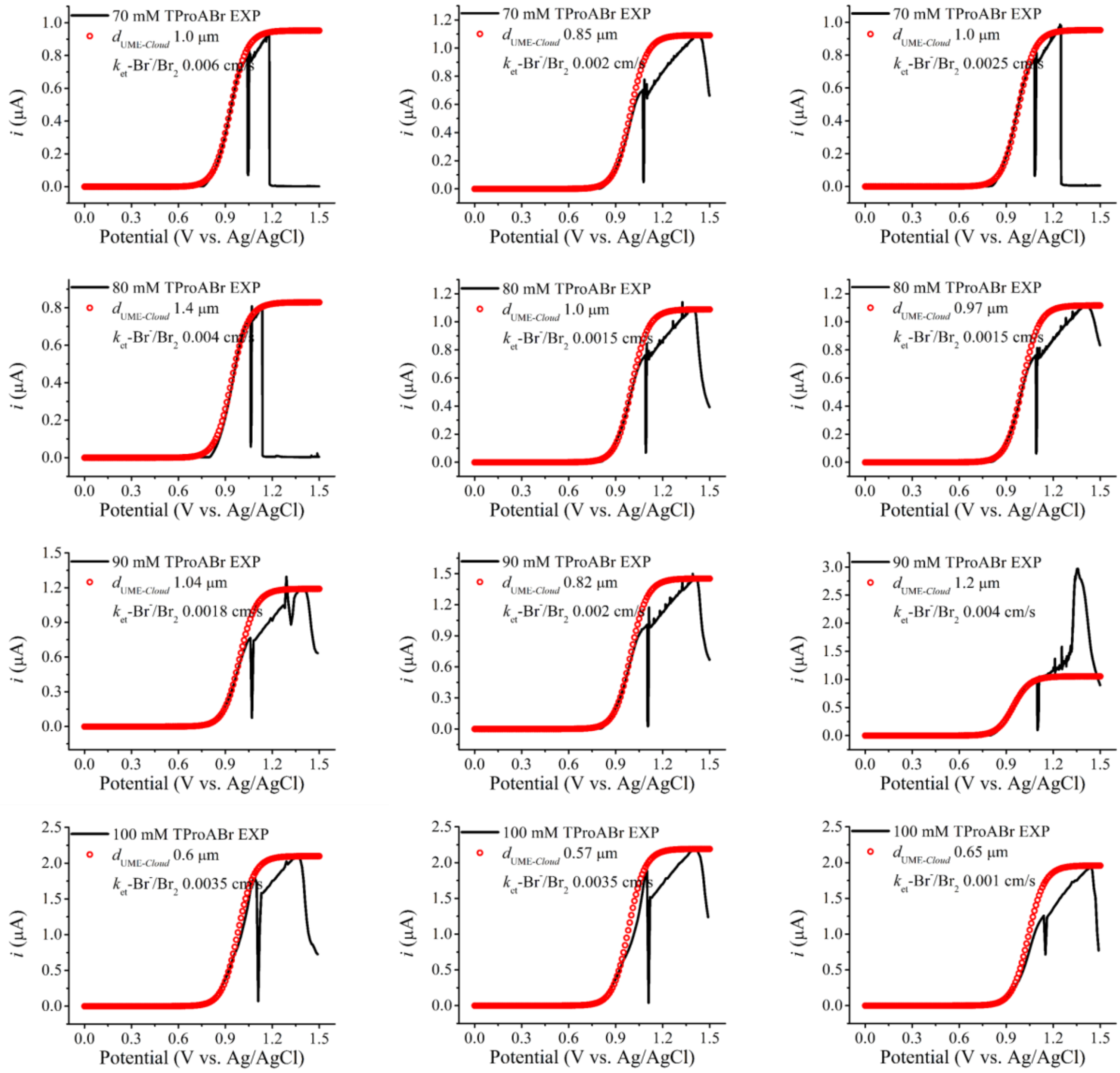

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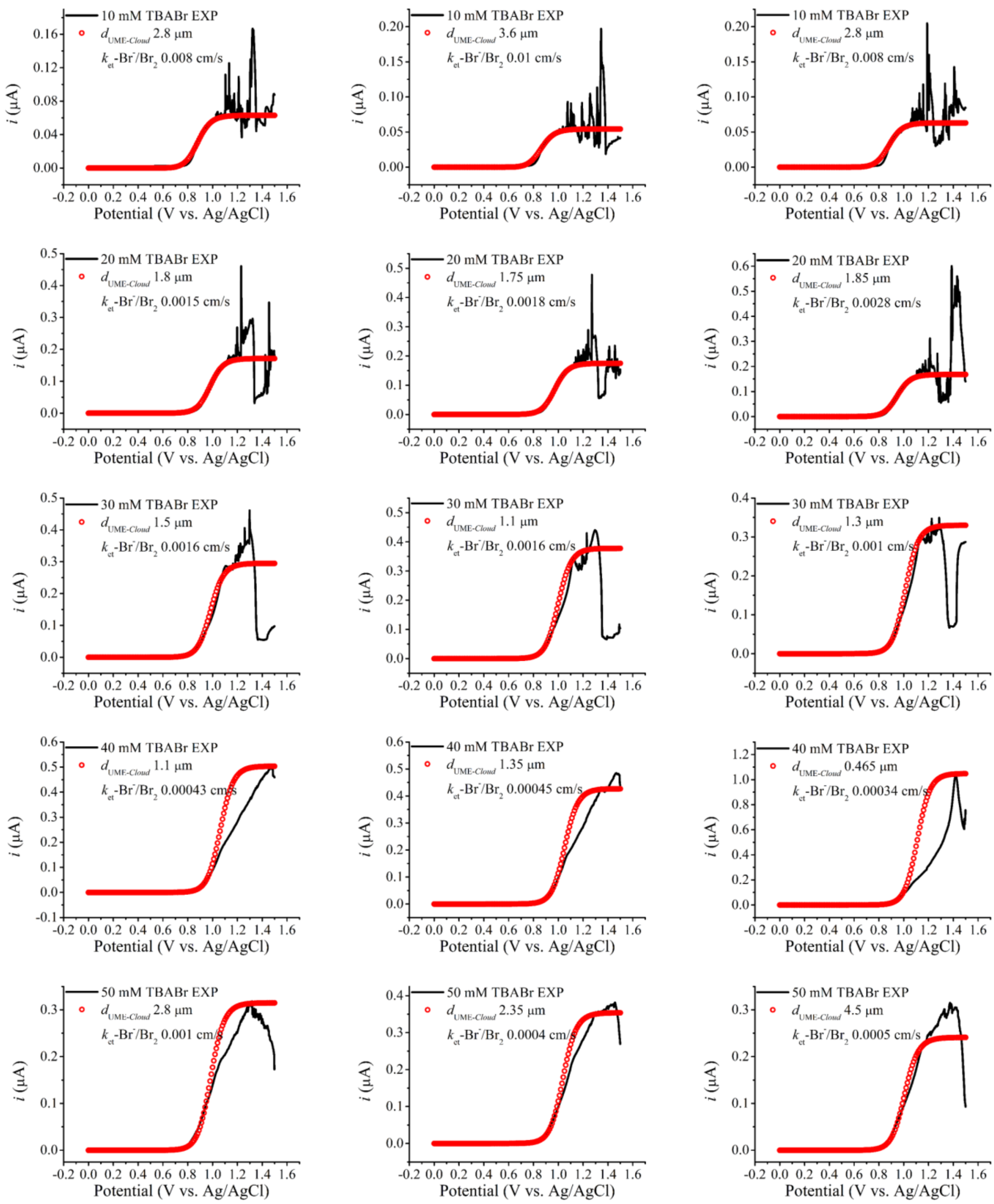

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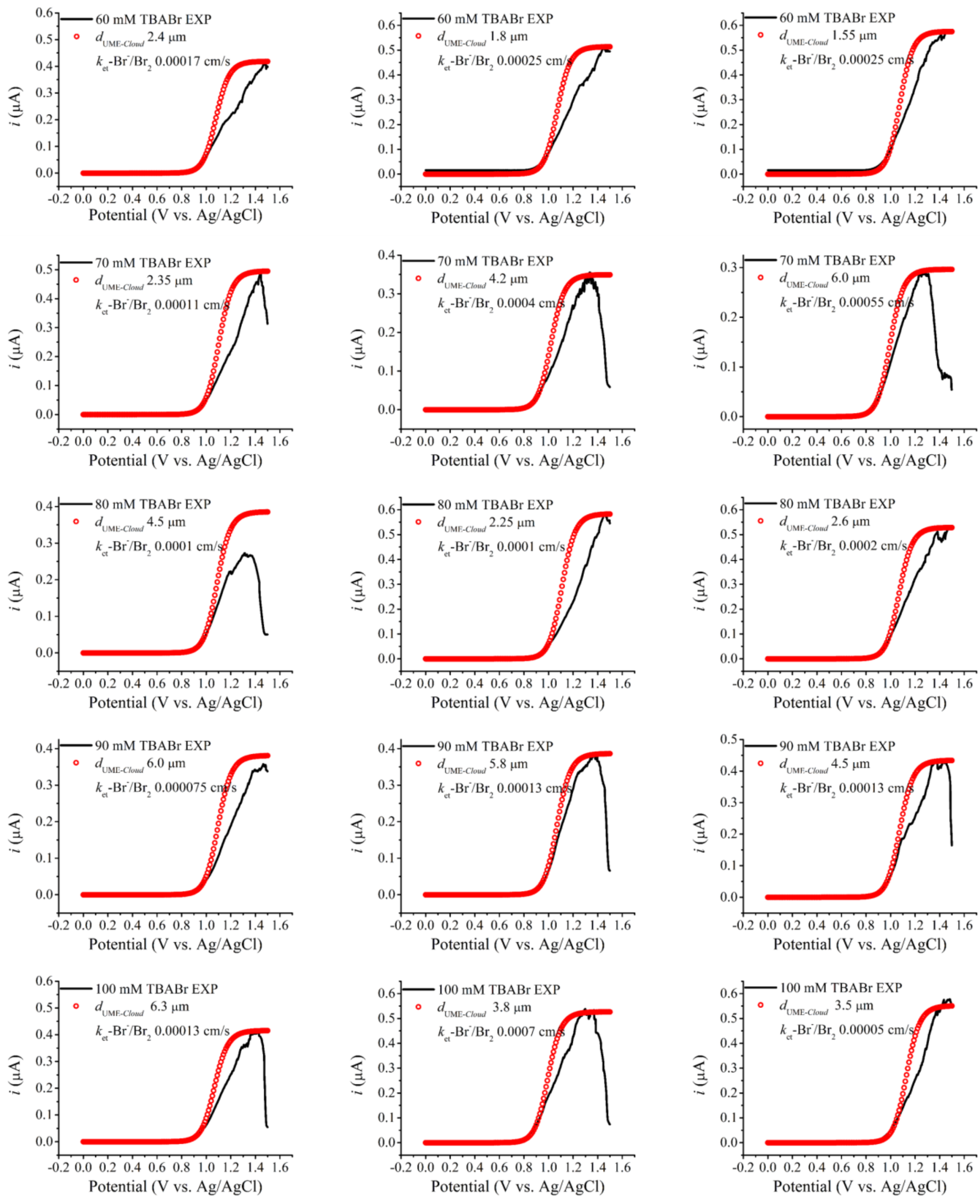

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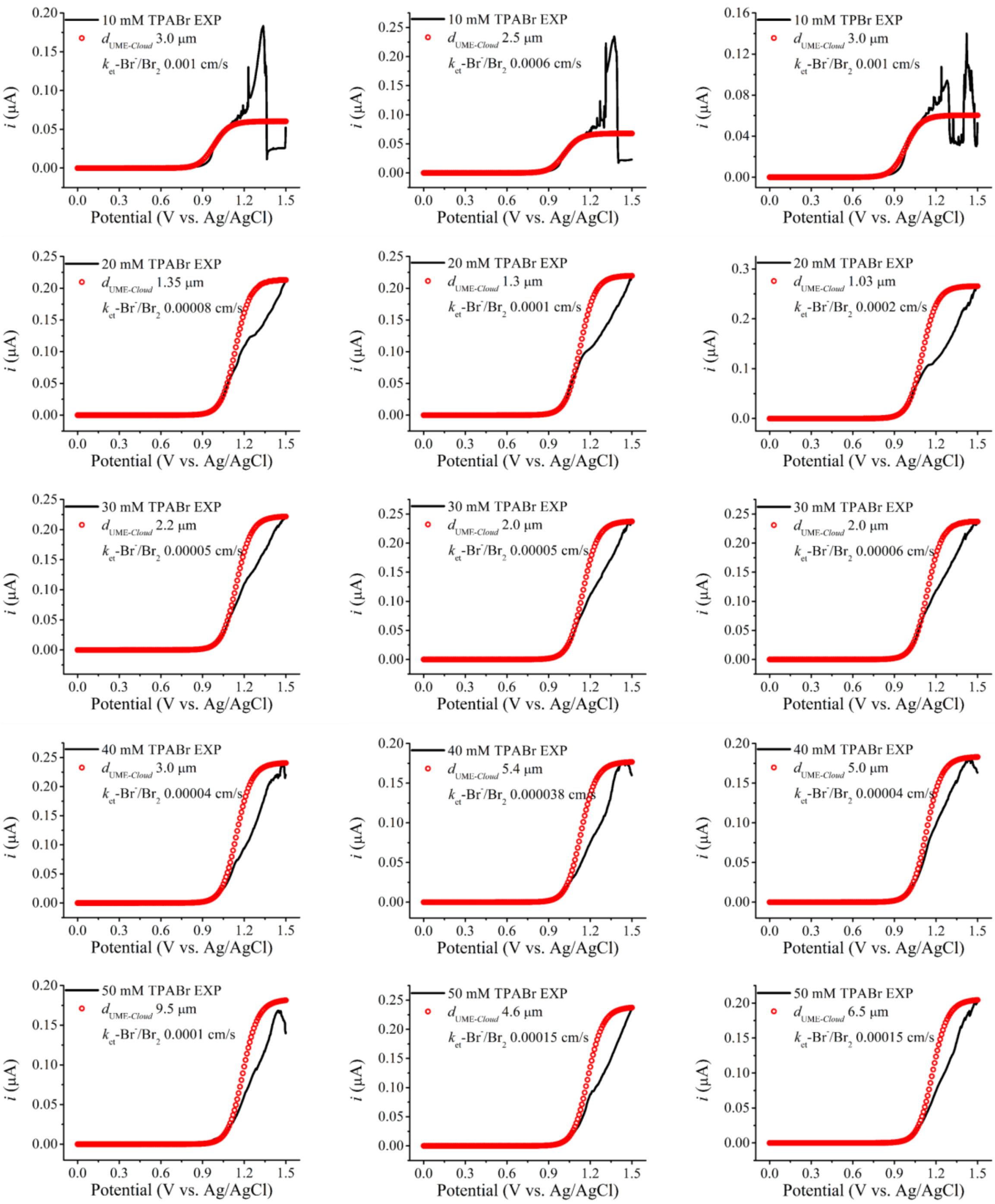


Figure S15. The LSVs (black) measured in 0.5 M H_2SO_4 aqueous solutions containing various concentrations of TPABr (10, 20, 30, 40, and 50 mM), and the corresponding simulation results (red) based on the *Cloud* model for the estimation of k_{et}-Br^-/Br_2.

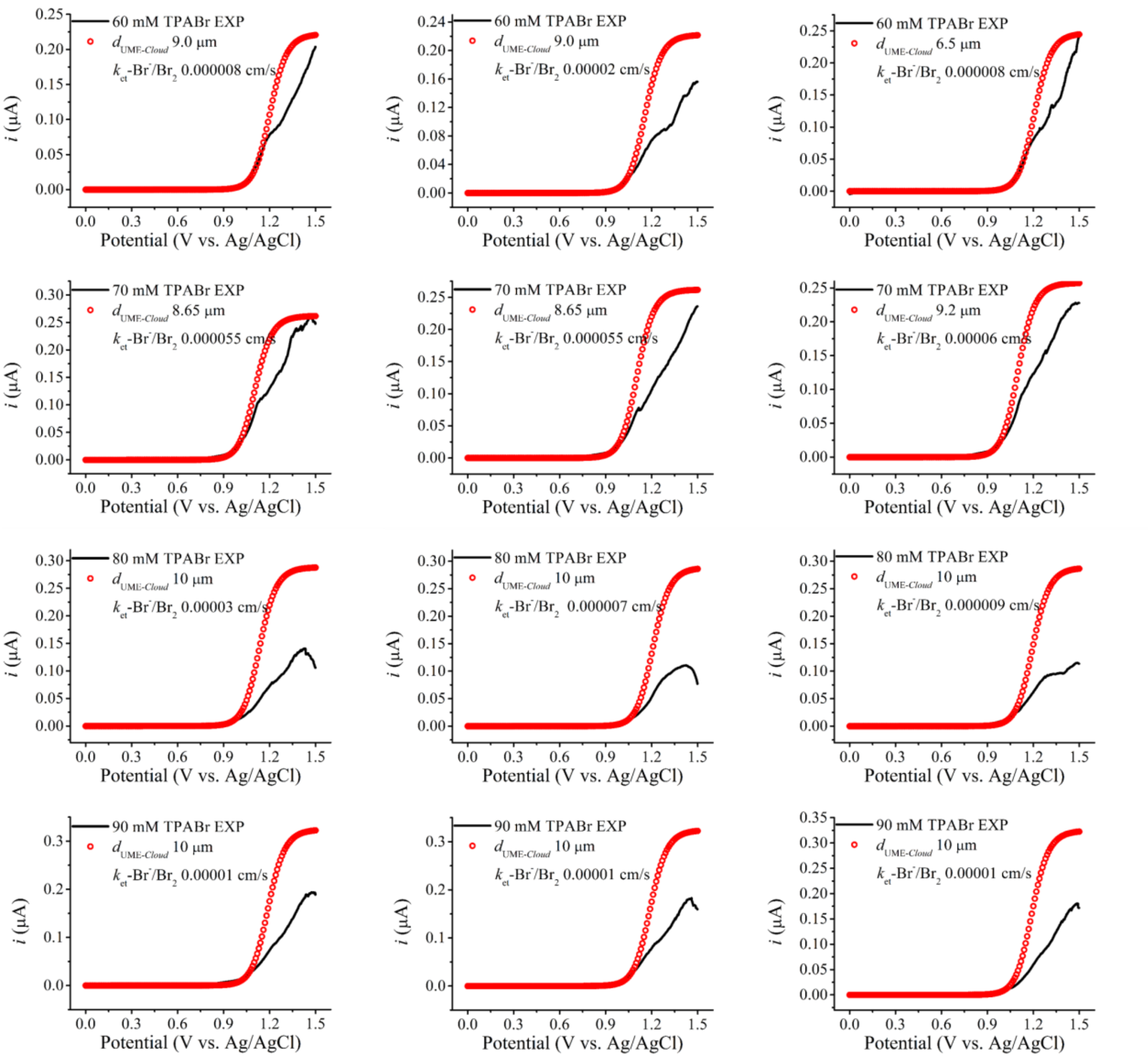
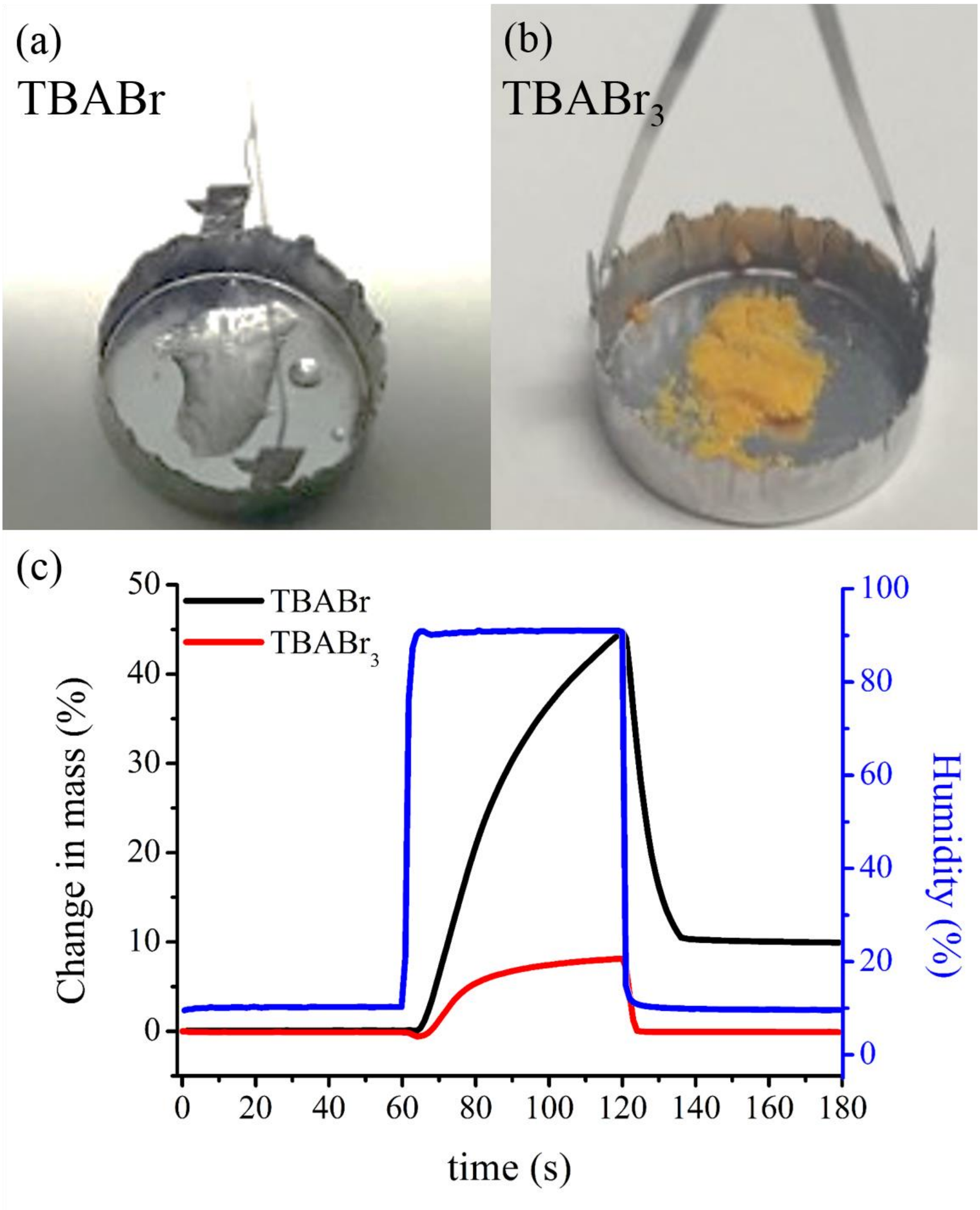


Figure S16. The LSVs (black) measured in 0.5 M H_2SO_4 aqueous solutions containing various concentrations of TPABr (60, 70, 80, and 90 mM), and the corresponding simulation results (red) based on the *Cloud* model for the estimation of k_{et}-Br^-/Br_2.



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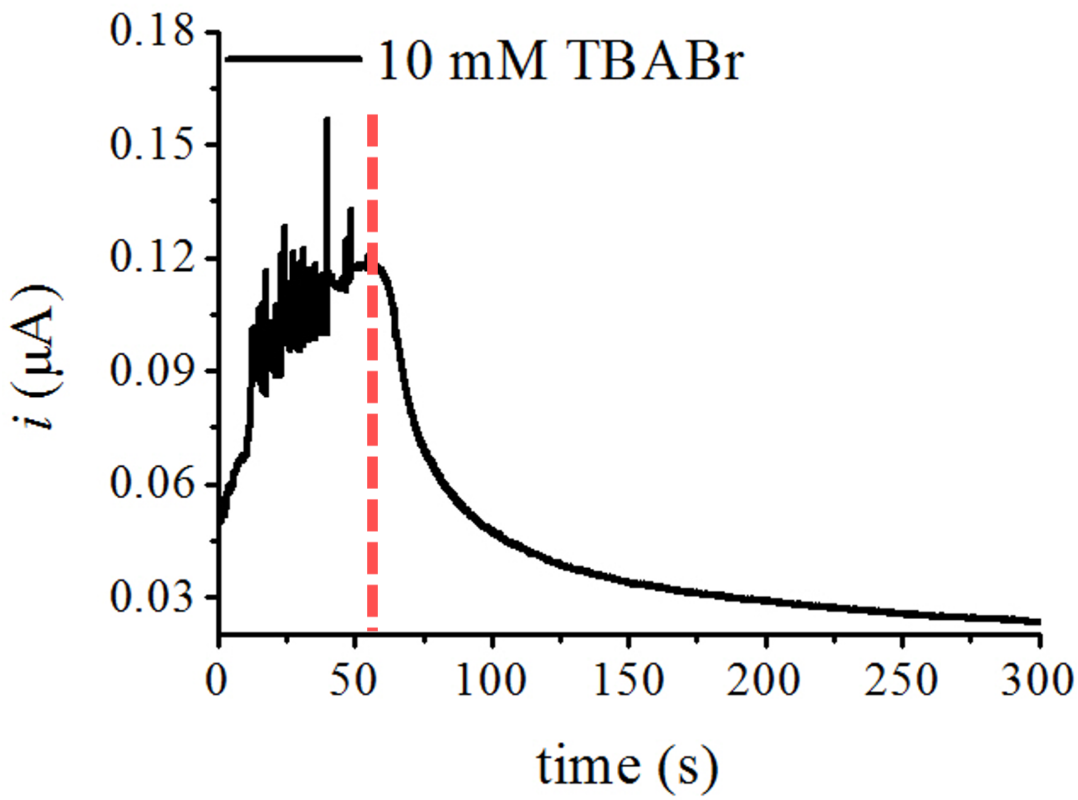

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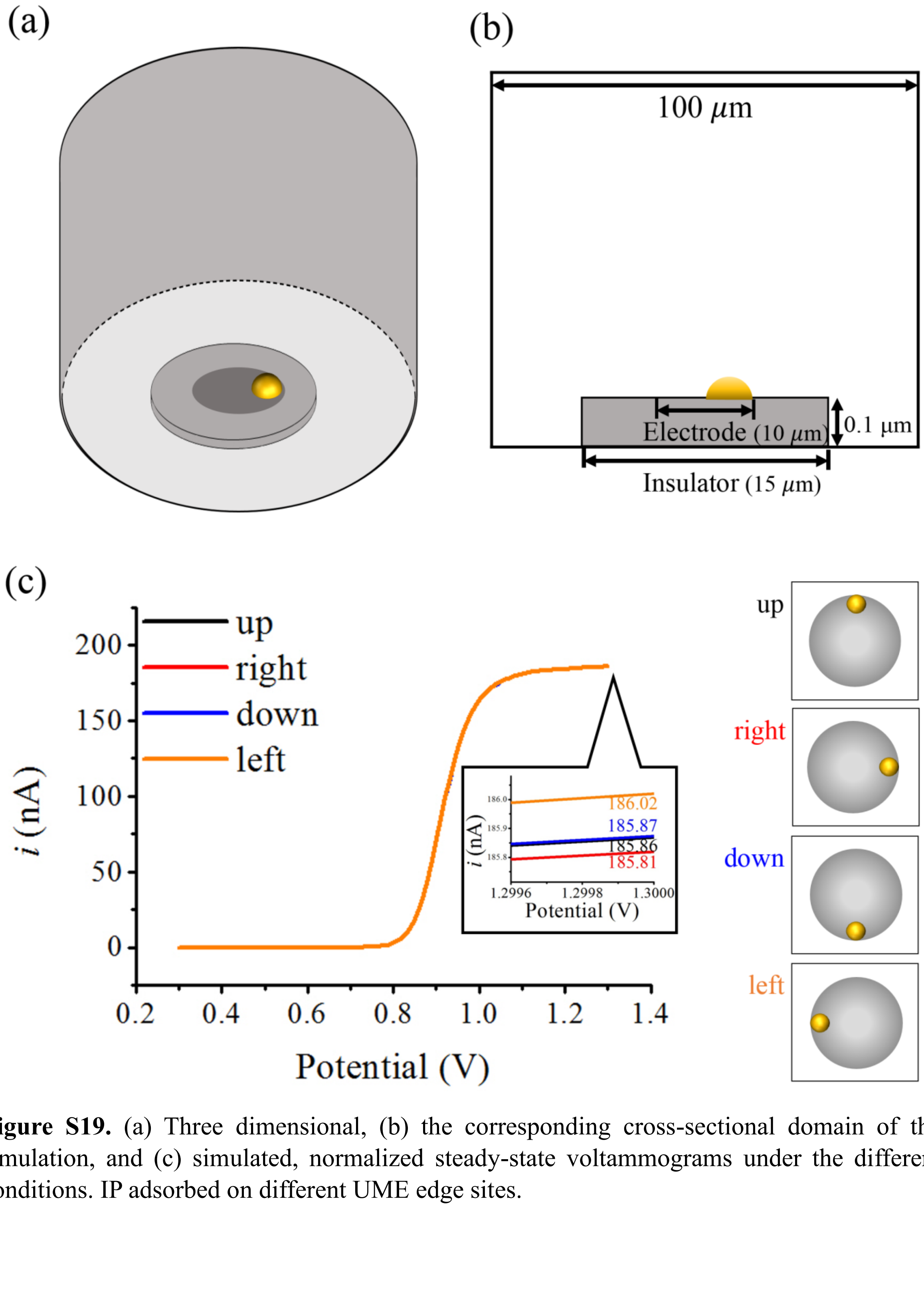

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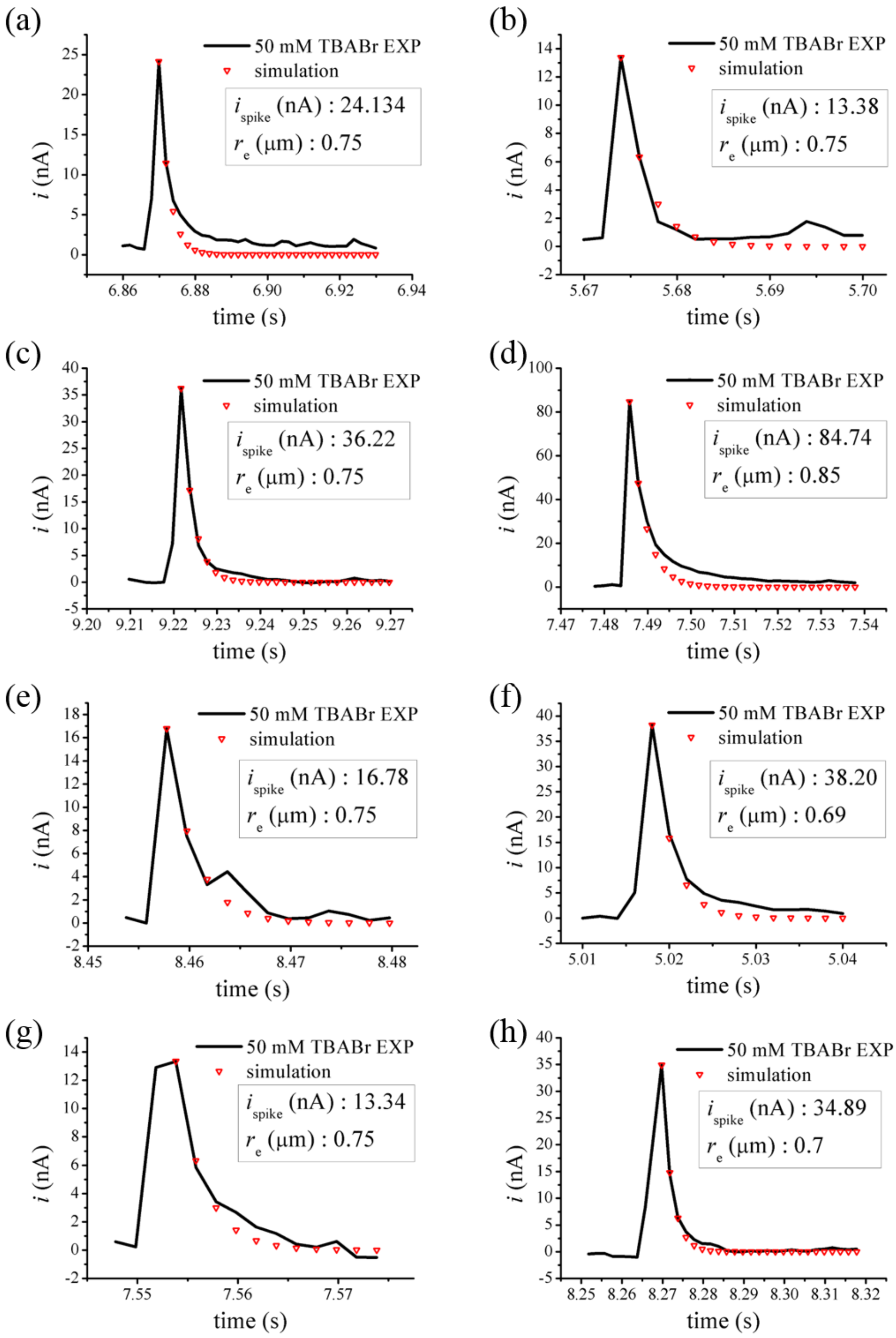

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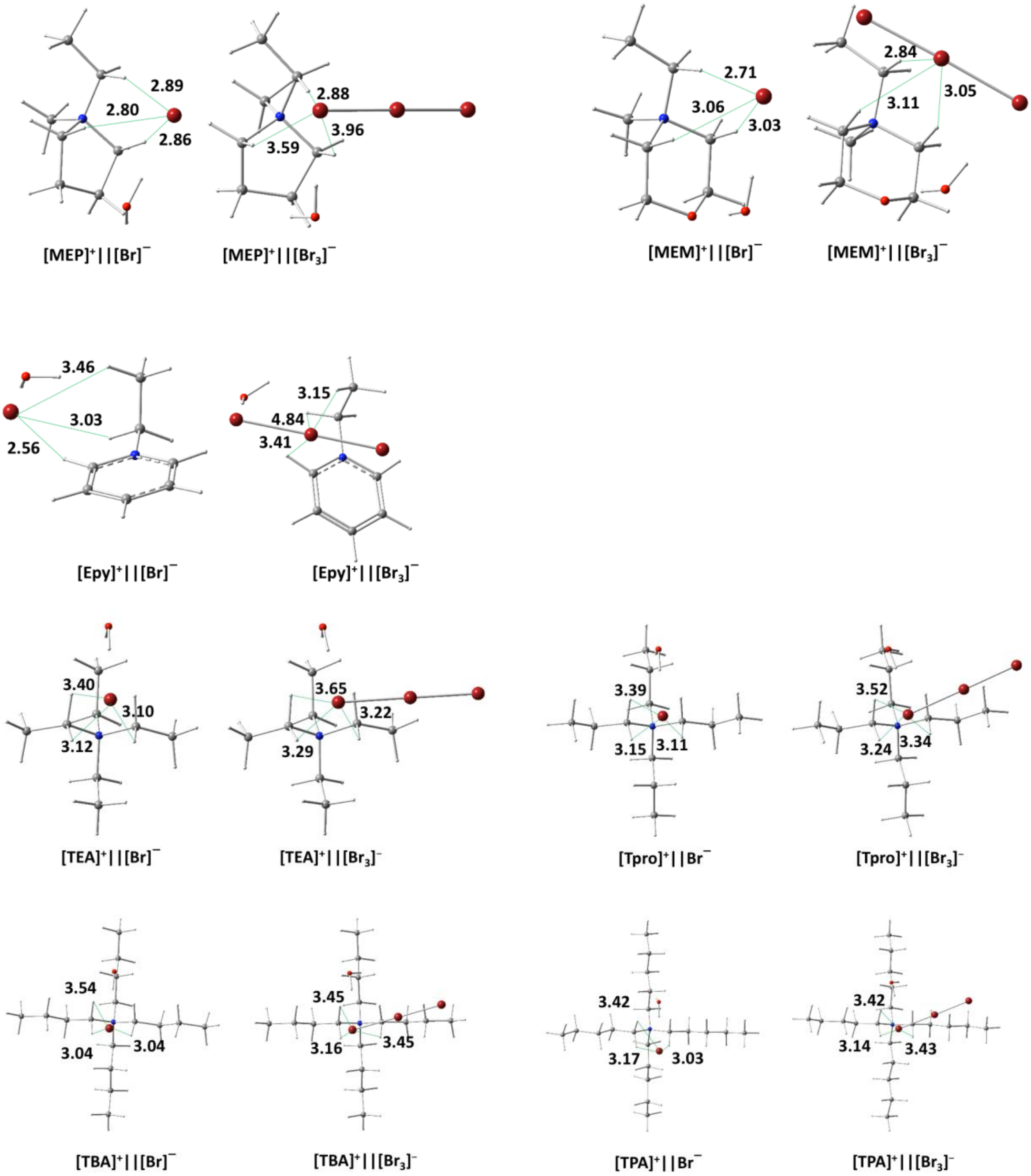

Figure S21. DFT-optimized structures for the solvent-separated ion pairs of IL cations with H···Br distance in Å.

Tables

Table S1. Reactions, corresponding parameters, relevant time-dependent diffusion and chemical equations, and initial concentration of the chemical species using finite element analysis (Figure S5).

Reactions in *aq.* phase	Parameters			
	k_{et} on Pt UME	k_{et} on *Cloud*	E_{eq}	α
$Br\cdot + e^- \leftrightharpoons Br^-$	variable (cm/s)	0.1 (cm/s)	0.76 (V)	0.5
$2Br\cdot \rightarrow Br_2$	$k_{f1} = 500\ (M^{-1}s^{-1})$			
$Br_2 + e^- \leftrightharpoons Br_2^{-\cdot}$	0.1 (cm/s)	0.1 (cm/s)	0.72 V	0.5
H_{Cloud}	0.56 (V)			
$d_{UME\text{-}Cloud}$	variable			

The relevant time-dependent diffusion equations

(1) $\frac{\partial C_{Br\cdot}}{\partial t} = D_{Br\cdot}\left[\frac{\partial^2 C_{Br\cdot}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{Br\cdot}}{\partial r} + \frac{\partial^2 C_{Br\cdot}}{\partial z^2}\right] - \frac{1}{2}k_{f1}C_{Br\cdot}{}^2$

(2) $\frac{\partial C_{Br^-}}{\partial t} = D_{Br^-}\left[\frac{\partial^2 C_{Br^-}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{Br^-}}{\partial r} + \frac{\partial^2 C_{Br^-}}{\partial z^2}\right]$

(3) $\frac{\partial C_{Br_2}}{\partial t} = D_{Br_2}\left[\frac{\partial^2 C_{Br_2}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{Br_2}}{\partial t} + \frac{\partial^2 C_{Br_2}}{\partial z^2}\right] + \frac{1}{2}k_{f1}C_{Br\cdot}{}^2$

(4) $\frac{\partial C_{Br_2^{-\cdot}}}{\partial t} = D_{Br_2^{-\cdot}}\left[\frac{\partial^2 C_{Br_2^{-\cdot}}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{Br_2^{-\cdot}}}{\partial t} + \frac{\partial^2 C_{Br_2^{-\cdot}}}{\partial z^2}\right]$

The initial condition, completing the definition of the problem

t = 0, all r, z; $C_{Br\cdot} = 0$, $= variable, C_{Br_2,Br_2^{-\cdot}} = 0,$

$D_{Br\cdot,Br^-} = 1.58 \times 10^{-5}$, $D_{Br_2} = 1.18 \times 10^{-5}$, $D_{Br_2^{-\cdot}} = 1.00 \times 10^{-5}$ cm^2/s

Table S2. Reactions, corresponding parameters, relevant time-dependent diffusion and chemical equations, and initial concentrations of chemical species using finite element analysis (Figure 5).

Reactions in aq. Phase	Parameters
$1/2Br\cdot + e^- \leftrightharpoons Br^-$	$k_{et} = 0.1$ cm/s E_{eq} 0.9 V, $\alpha = 0.5$
The relevant time-dependent diffusion equations	
(1) $\frac{\partial C_{Br\cdot}}{\partial t} = D_{Br\cdot}\left[\frac{\partial^2 C_{Br\cdot}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{Br\cdot}}{\partial r} + \frac{\partial^2 C_{Br\cdot}}{\partial z^2}\right]$ (2) $\frac{\partial C_{Br^-}}{\partial t} = D_{Br^-}\left[\frac{\partial^2 C_{Br^-}}{\partial r^2} + \frac{1}{r}\frac{\partial C_{Br^-}}{\partial r} + \frac{\partial^2 C_{Br^-}}{\partial z^2}\right]$	
The initial condition, completing the definition of the problem	
t = 0, all r, z; $C_{Br\cdot} = 0, C_{Br^-} = 50 \times 10^{-3}\ M, D_{Br\cdot,Br^-} = 1.58\text{x}10^{-5}$	

Table S3. The tabulated Cartesian coordinates of the optimized geometries associated with Figure S21.

$[MEP]^+ \Vert [Br]^-$				$[MEP]^+ \Vert [Br_3]^-$			
28				30			
C	-1.101704	-0.291425	1.066920	C	-1.957739	-1.799544	1.158100
N	-1.597483	0.271320	-0.232244	C	-1.521831	-0.342583	1.246288
C	-1.110369	-0.736667	-1.235302	N	-1.519414	0.134420	-0.175862
C	-1.276991	-2.093998	-0.552525	C	-0.922920	-1.030457	-0.914028
C	-1.380995	-1.782963	0.956938	C	-1.515860	-2.268320	-0.247117
C	-1.016341	1.616420	-0.537651	C	-0.673121	1.353455	-0.372830
C	-1.426753	2.694773	0.439019	C	-1.184184	2.578287	0.349256
C	-3.082044	0.314597	-0.251754	C	-2.907715	0.369363	-0.652022
Br	2.545677	0.199526	-0.380497	O	1.844402	-2.247935	1.305986
H	-1.676476	-0.610175	-2.151131	Br	2.961777	0.498267	-1.241498
H	-0.062266	-0.508832	-1.405531	H	-1.144946	-0.921076	-1.969177
H	-0.033520	-0.087718	1.094330	H	0.150574	-0.975896	-0.757119
H	-1.603253	0.203342	1.889063	H	-0.497032	-0.253188	1.597526
H	-0.662321	-2.339434	1.546630	H	-2.171017	0.289509	1.838762
H	-2.373674	-2.014027	1.329194	H	-1.490177	-2.372490	1.952175
H	-0.418737	-2.717537	-0.780288	H	-3.032876	-1.885177	1.272009
H	-2.166536	-2.605512	-0.903604	H	-0.761488	-3.045530	-0.196939
H	-1.340255	1.856991	-1.546431	H	-2.359580	-2.651133	-0.810225
H	0.061787	1.475468	-0.533246	H	-0.629735	1.514853	-1.446394
H	-3.434295	0.868562	0.609212	H	0.317015	1.089247	-0.014866
H	-3.393435	0.797525	-1.171726	H	-3.398559	1.063199	0.018446
H	-3.465148	-0.698175	-0.219078	H	-2.855036	0.776464	-1.655891
H	-0.914779	3.609261	0.150313	H	-3.442759	-0.572763	-0.662336
H	-2.494961	2.888375	0.416226	H	-0.457041	3.372292	0.198279
H	-1.127430	2.451226	1.454823	H	-2.138269	2.919112	-0.040614
H	2.183130	-1.768969	0.740017	H	-1.272832	2.404567	1.418274
O	2.030256	-2.611669	1.213522	H	2.067401	-1.305767	1.297639
H	1.381952	-3.077747	0.679035	H	0.901586	-2.283237	1.488642
				Br	2.849653	1.014498	1.353430
				Br	2.996272	-0.005320	-3.673083

$[MEM]^+ \Vert [Br]^-$				$[MEM]^+ \Vert [Br_3]^-$			
29				31			
C	-4.092369	-1.473305	0.797060	O	-3.415770	-2.760470	0.227522
C	-3.328115	-0.313780	0.204124	C	-3.995305	-1.533877	0.659447
N	-1.858590	-0.379228	0.506765	C	-3.223534	-0.353548	0.117217
C	-1.366049	-1.733207	0.092334	N	-1.769818	-0.395416	0.493503
C	-2.191069	-2.839282	0.708441	C	-1.226919	-1.742281	0.118047
O	-3.564246	-2.717699	0.348705	C	-2.070065	-2.861969	0.679237
C	-1.197396	0.691005	-0.326624	C	-1.077692	0.681865	-0.303775
C	0.298614	0.796351	-0.144886	C	0.395031	0.841615	-0.007477
C	-1.597475	-0.120739	1.947653	C	-1.596541	-0.124178	1.946678
H	-2.207423	-0.769882	2.559207	O	-4.557290	-3.329692	-2.304284
H	-1.689976	1.616535	-0.041646	Br	-2.123496	-0.773521	-3.769547
H	-1.447706	0.454524	-1.357701	H	-2.246379	-0.766402	2.523452
H	-0.551141	-0.311095	2.150586	H	-1.620939	1.595971	-0.082191
H	-1.845449	0.915835	2.148815	H	-1.234102	0.423351	-1.346287
H	-0.330595	-1.826980	0.398573	H	-0.564877	-0.313914	2.214370

H	-1.440989	-1.765492	-0.993353
H	-2.098950	-2.858696	1.793935
H	-1.838148	-3.784633	0.310842
H	-4.096642	-1.452196	1.885935
H	-5.117096	-1.413072	0.446627
H	-3.411023	-0.330696	-0.881020
H	-3.697297	0.631226	0.590566
H	0.644430	1.568481	-0.828170
H	0.577282	1.094885	0.860699
H	0.810068	-0.125872	-0.404329
Br	-2.310353	-0.619998	-3.688808
H	-3.186959	-2.576754	-2.854266
O	-3.553251	-3.378479	-2.433160
H	-3.649222	-3.135347	-1.501098

H	-1.854413	0.914471	2.121843
H	-0.211823	-1.815081	0.490548
H	-1.225133	-1.784389	-0.968537
H	-2.052605	-2.875253	1.768399
H	-1.674465	-3.801769	0.310719
H	-4.055058	-1.523406	1.746248
H	-5.001065	-1.492113	0.254009
H	-3.261139	-0.359389	-0.969754
H	-3.628792	0.581751	0.490676
H	0.771412	1.603342	-0.685847
H	0.575708	1.179819	1.007817
H	0.955382	-0.069425	-0.193165
H	-4.568215	-2.477070	-2.758685
H	-4.070645	-3.169375	-1.482130
Br	0.341504	-1.243417	-3.587130
Br	-4.672334	-0.274630	-3.841565

$[EPy]^+$ ‖ $[Br]^-$

22

C	-2.269876	2.068039	0.102172
N	-0.931335	2.091235	0.134284
C	-0.212050	0.961163	0.165207
C	-0.834631	-0.262334	0.150240
C	-2.219690	-0.311508	0.112683
C	-2.942970	0.868413	0.089752
C	-0.229927	3.392359	0.226612
C	0.067476	3.727119	1.671911
Br	-3.346153	5.541363	0.686499
H	-2.728591	-1.261709	0.100928
H	-0.236811	-1.157100	0.168709
H	0.858076	1.079239	0.196939
H	-2.762098	3.031180	0.090753
H	-4.019176	0.872277	0.063245
H	0.676422	3.302690	-0.360996
H	-0.884591	4.134143	-0.216405
H	0.692417	2.960736	2.124715
H	0.594565	4.676641	1.710579
H	-0.856856	3.822620	2.235976
H	-3.553830	3.905237	2.302995
O	-3.657093	3.187422	2.959457
H	-2.825240	2.707015	2.936727

$[EPy]^+$ ‖ $[Br_3]^-$

24

C	-2.006349	-1.255693	-1.235842
C	-1.947975	-0.906559	0.092573
N	-2.833149	-0.044459	0.606851
C	-3.772519	0.530025	-0.156687
C	-3.875463	0.216430	-1.489028
C	-2.983830	-0.692206	-2.036686
C	-2.717371	0.350141	2.029118
C	-1.828352	1.566086	2.173747
Br	1.200357	0.700439	-0.535907
Br	-0.510760	2.299577	-1.429404
Br	2.934924	-1.004861	0.419875
H	-3.049574	-0.955107	-3.079991
H	-4.644517	0.681360	-2.081118
H	-4.429035	1.224848	0.339732
H	-1.217930	-1.303965	0.778475
H	-1.288839	-1.956822	-1.626081
H	-3.723093	0.544858	2.383138
H	-2.316166	-0.505727	2.559114
H	-2.249504	2.416098	1.643554
H	-1.744095	1.814677	3.228373
H	-0.835733	1.366047	1.776627
H	1.146000	-1.266310	2.015461
O	0.424197	-1.430421	2.641229
H	0.094389	-0.559378	2.879959

$[TEA]^+$ ‖ $[Br]^-$

33

C	-1.162903	-1.849283	3.324085
C	-1.791625	-1.019897	2.229156
N	-0.826859	-0.457818	1.220759
C	-0.064771	-1.555735	0.526062
C	-0.917248	-2.574027	-0.193580
C	-1.658359	0.333096	0.246694

$[TEA]^+$ ‖ $[Br_3]^-$

35

C	-1.177666	-1.750357	3.387676
C	-1.818360	-0.951396	2.276364
N	-0.863167	-0.420957	1.239868
C	0.183701	0.462500	1.866229
C	-0.347123	1.648268	2.637062
C	-0.110238	-1.541519	0.569734

C	-0.886429	0.988524	-0.874886	C	-0.965488	-2.559860	-0.147996
C	0.210949	0.408915	1.884275	C	-1.699605	0.344513	0.248518
C	-0.333435	1.591297	2.650620	C	-0.935930	0.951785	-0.906310
O	2.821534	0.556485	-1.028753	Br	3.600087	-1.461522	1.832199
H	0.786933	-0.246351	2.526436	O	2.891972	0.513366	-0.871337
H	0.881813	0.731692	1.097013	H	0.777311	-0.180860	2.504900
H	-2.320105	-0.169728	2.645213	H	0.822807	0.788477	1.054624
H	-2.507168	-1.606168	1.663884	H	-2.338826	-0.087545	2.673471
H	0.612674	-1.062662	-0.160820	H	-2.542215	-1.551699	1.737665
H	0.553388	-2.022612	1.283578	H	0.579196	-1.067426	-0.119559
H	-2.397231	-0.355853	-0.146662	H	0.482630	-2.010874	1.345155
H	-2.183806	1.075973	0.836079	H	-2.449303	-0.350927	-0.110434
H	-0.478390	-1.270891	3.937379	H	-2.209721	1.112983	0.817425
H	-1.970261	-2.196725	3.964224	H	-0.465015	-1.163843	3.960269
H	-0.647683	-2.722812	2.935807	H	-1.974836	-2.053708	4.061711
H	-0.386824	0.263204	-1.511554	H	-0.692743	-2.650891	3.022208
H	-1.607031	1.524464	-1.487801	H	-0.452720	0.200339	-1.524563
H	-0.162066	1.711751	-0.509654	H	-1.661099	1.473056	-1.526436
H	-0.977646	1.291833	3.472162	H	-0.198838	1.679998	-0.579135
H	0.521480	2.113646	3.073808	H	-0.946910	1.350606	3.491918
H	-0.865585	2.290982	2.012740	H	0.516641	2.192749	3.011234
H	-0.236639	-3.284126	-0.657549	H	-0.920208	2.326593	2.012225
H	-1.561418	-3.127531	0.483261	H	-0.287756	-3.293775	-0.578931
H	-1.519359	-2.130470	-0.981171	H	-1.637709	-3.085485	0.523701
H	1.871271	0.697043	-1.031096	H	-1.537386	-2.120930	-0.960235
H	3.004152	-0.000219	-0.242878	H	1.942021	0.594142	-0.993628
Br	3.559218	-1.303218	1.573854	H	3.002271	-0.069068	-0.105620
				Br	2.958160	-3.457728	0.244769
				Br	2.317000	-5.342629	-1.260262

$[TPro]^+ \parallel [Br]^-$				$[TPro]^+ \parallel [Br_3]^-$			
45				47			
C	-1.179947	-1.832186	3.352245	C	-1.336377	-1.783341	3.411284
C	-1.794601	-1.022848	2.230585	C	-1.889708	-0.919275	2.297988
N	-0.829684	-0.459389	1.223399	N	-0.895842	-0.452439	1.268485
C	0.208608	0.405228	1.886929	C	-1.684325	0.331970	0.253203
C	-0.314347	1.609610	2.638378	C	-0.887198	0.924031	-0.889770
C	-0.066806	-1.557065	0.529310	C	0.176977	0.397531	1.896703
C	-0.902198	-2.593426	-0.190340	C	-0.281983	1.671746	2.572883
C	-1.660268	0.333068	0.250764	C	-0.183953	-1.616635	0.628574
C	-0.903159	0.991106	-0.882927	C	-1.075588	-2.644936	-0.034484
O	2.808039	0.536214	-1.044195	Br	3.540905	-3.086330	-0.104483
Br	3.571555	-1.312451	1.556484	Br	3.424831	-4.675275	-2.022831
H	0.771996	-0.246868	2.544960	Br	3.643530	-1.389121	1.904990
H	0.893086	0.715140	1.104687	O	2.795186	0.714196	-0.654390
H	-2.342443	-0.177387	2.634216	H	0.694327	-0.239821	2.605141
H	-2.496353	-1.630098	1.667984	H	0.877950	0.632547	1.104069
H	0.606455	-1.066258	-0.164955	H	-2.341865	-0.022356	2.707896
H	0.558703	-2.021061	1.284198	H	-2.659749	-1.456685	1.754136
H	-2.405757	-0.350850	-0.141908	H	0.504451	-1.191877	-0.094998
H	-2.180393	1.082443	0.838771	H	0.413712	-2.075549	1.409938
H	-0.507429	-1.216136	3.944094	H	-2.444680	-0.340971	-0.128302
C	-2.302200	-2.355541	4.240029	H	-2.190600	1.117194	0.805698
H	-0.609046	-2.668327	2.955919	H	-0.567873	-1.251683	3.966869

H	-0.397557	0.244436	-1.491906
C	-1.893908	1.761086	-1.746908
H	-0.153270	1.677779	-0.495311
H	-1.010447	1.308001	3.417508
C	0.871959	2.331207	3.266422
H	-0.835165	2.287395	1.966107
C	0.042581	-3.572532	-0.877084
H	-1.535604	-3.132356	0.510334
H	-1.543981	-2.127042	-0.934014
H	1.859421	0.687176	-1.033307
H	2.996976	-0.017197	-0.257257
H	-0.516864	-4.343542	-1.399735
H	0.671152	-3.056317	-1.600554
H	0.691798	-4.056284	-0.149445
H	0.542929	3.217809	3.801444
H	1.390187	1.681109	3.969017
H	1.583910	2.638560	2.502140
H	-1.383159	2.242086	-2.576481
H	-2.651111	1.093413	-2.153785
H	-2.396740	2.530443	-1.163933
H	-1.897909	-2.930876	5.068278
H	-2.884840	-1.532350	4.649675
H	-2.973892	-2.998124	3.673933

C	-2.481507	-2.145227	4.349324
H	-0.894576	-2.691953	3.009566
H	-0.385556	0.141441	-1.455341
C	-1.844823	1.673750	-1.807791
H	-0.130405	1.610888	-0.517655
H	-0.973203	1.456136	3.384056
C	0.950771	2.377140	3.126431
H	-0.784597	2.326814	1.865491
C	-0.196813	-3.719290	-0.662387
H	-1.742418	-3.100308	0.693939
H	-1.686548	-2.183237	-0.806270
H	1.935149	0.456075	-0.998916
H	3.000757	0.061763	0.031671
H	-0.809125	-4.478470	-1.142085
H	0.467263	-3.291148	-1.409669
H	0.424201	-4.202781	0.088778
H	-2.125060	-2.766531	5.166223
H	-2.929567	-1.248409	4.773146
H	-3.257009	-2.693148	3.817328
H	-1.306626	2.115137	-2.642030
H	-2.601166	1.000772	-2.207160
H	-2.350616	2.471867	-1.267707
H	0.674486	3.308024	3.613749
H	1.459756	1.748001	3.854481
H	1.653392	2.605258	2.326426

$[TBA]^+ \| [Br]^-$

57

H	-0.124849	-5.802726	0.425086
C	-0.008638	-5.035742	-0.337252
C	-0.054954	-3.642761	0.269601
C	0.108209	-2.560924	-0.793391
C	0.042093	-1.206981	-0.121845
N	0.246773	-0.013197	-1.017462
C	0.077832	1.196999	-0.136660
C	0.201779	2.538691	-0.823815
C	0.052675	3.641773	0.218774
C	0.170452	5.022254	-0.406921
H	0.062572	5.805235	0.340225
C	-0.745217	-0.006615	-2.147528
C	-2.201719	0.023434	-1.738183
C	-3.072097	0.016478	-2.989875
C	-4.551458	0.049946	-2.641027
H	-5.168528	0.043248	-3.536650
C	1.610643	-0.037307	-1.654302
C	2.785311	-0.046336	-0.699122
C	4.083006	-0.060939	-1.499470
C	5.297699	-0.073233	-0.585233
H	6.222855	-0.082345	-1.156846
Br	-1.451338	0.056932	3.141252
O	1.845674	-0.044643	3.071275
H	-0.888392	1.094593	0.344569
H	0.823583	1.105542	0.644593
H	-0.505695	0.858767	-2.756767

$[TBA]^+ \| [Br_3]^-$

59

H	-2.986168	3.437724	2.137248
C	-1.901879	3.465921	2.052990
C	-1.373336	2.206542	1.386213
C	0.145358	2.234647	1.258173
C	0.608524	0.964416	0.578959
N	2.097401	0.831824	0.386417
C	2.307045	-0.494579	-0.293999
C	3.737230	-0.866130	-0.617099
C	3.739314	-2.213396	-1.332044
C	5.148970	-2.654578	-1.691162
H	5.143768	-3.615014	-2.201444
C	2.823665	0.889141	1.704123
C	2.401373	-0.134461	2.735577
C	3.254673	0.039868	3.987204
C	2.868528	-0.957179	5.067992
H	3.478046	-0.828540	5.959576
C	2.646861	1.962490	-0.442321
C	2.075843	2.093953	-1.837354
C	2.718077	3.287676	-2.534757
C	2.175031	3.461986	-3.944073
H	2.636176	4.311002	-4.443343
O	-0.136431	-0.554589	-3.061715
Br	-0.797181	-2.722371	-0.515091
Br	-2.784718	-1.022718	-0.213133
Br	-4.659536	0.597964	0.062448
H	1.858732	-1.240563	0.352179

H	-0.535891	-0.892800	-2.737882	H	1.716338	-0.462110	-1.202234
H	0.798244	-1.135415	0.651277	H	3.877919	0.779054	1.472522
H	-0.915032	-1.063447	0.367296	H	2.675196	1.892924	2.088155
H	1.632803	-0.918033	-2.287431	H	0.164409	0.879060	-0.407603
H	1.657283	0.832824	-2.300881	H	0.298616	0.092756	1.145690
H	-2.423211	0.917518	-1.157738	H	2.467852	2.868798	0.126082
H	-2.451640	-0.843291	-1.128531	H	3.720232	1.809737	-0.487592
H	2.758828	-0.925690	-0.057069	H	2.531200	-1.147171	2.357727
H	2.775681	0.836410	-0.061340	H	1.353784	-0.006448	3.002463
H	-0.570885	2.662661	-1.580787	H	0.997490	2.245833	-1.803881
H	1.169957	2.642843	-1.311117	H	2.272183	1.198076	-2.424183
H	-0.684690	-2.669669	-1.531588	H	4.336299	-0.943730	0.288545
H	1.061536	-2.704911	-1.299362	H	4.198338	-0.122665	-1.264919
H	2.137044	-0.039322	2.155794	H	0.584401	2.327419	2.250173
H	0.867029	-0.014287	3.038646	H	0.434817	3.110442	0.679891
H	0.734534	-3.533658	1.013420	H	-0.030952	0.322035	-2.680636
H	-1.002407	-3.494423	0.787736	H	-0.358260	-1.129346	-2.313662
H	-0.913530	3.539007	0.712722	H	-1.819495	2.092723	0.399235
H	0.816735	3.514103	0.985895	H	-1.672261	1.328388	1.958068
H	4.094892	-0.938042	-2.146382	H	4.305008	-0.084849	3.724314
H	4.113576	0.814846	-2.147550	H	3.137594	1.057020	4.361072
H	-2.816562	0.877204	-3.607934	H	2.531922	4.188136	-1.949703
H	-2.848209	-0.874971	-3.575739	H	3.798116	3.144518	-2.566868
H	-0.805378	-5.162285	-1.068601	H	3.267561	-2.958981	-0.691758
H	0.940972	-5.202576	-0.843290	H	3.130986	-2.139106	-2.233980
H	5.303775	0.807298	0.055322	H	-1.486463	3.576296	3.053645
H	5.286327	-0.953887	0.055076	H	-1.629559	4.349803	1.477927
H	1.140022	5.144072	-0.887404	H	1.824593	-0.831208	5.350680
H	-0.599314	5.167813	-1.163222	H	2.999337	-1.978021	4.712535
H	-4.822611	-0.814131	-2.036435	H	5.623818	-1.925669	-2.346038
H	-4.791100	0.946418	-2.071409	H	5.761062	-2.750475	-0.795690
				H	2.366863	2.571973	-4.541419
				H	1.098680	3.625653	-3.922325

[TPA]$^+$ || [Br]$^-$
69

C	3.429571	-1.114473	-2.238758
C	2.371168	-0.874997	-1.168571
C	1.097875	-0.395566	-1.832016
N	-0.016189	-0.006213	-0.899127
C	-1.176258	0.389088	-1.771755
C	-2.432274	0.822586	-1.046098
C	-3.520595	1.129942	-2.067772
C	-0.381726	-1.145073	0.014812
C	-0.900226	-2.394328	-0.662276
C	-1.178493	-3.449150	0.402585
C	0.400963	1.127617	0.000121
C	0.931348	2.364555	-0.690954
C	1.199419	3.433255	0.363041
O	-2.299852	0.864108	2.763510
Br	0.707812	-0.209352	3.541611
H	0.505656	-1.360090	0.598987
H	-1.119416	-0.755765	0.707910
H	0.697894	-1.168143	-2.480851

[TPA]$^+$ || [Br_3]$^-$
71

C	-3.323618	-3.646363	-1.228777
C	-2.373458	-2.576984	-0.702466
C	-2.563039	-1.308132	-1.505061
N	-1.750757	-0.120281	-1.059121
C	-0.280897	-0.447597	-1.005928
C	0.343928	-0.845839	-2.325189
C	1.782946	-1.289482	-2.092362
C	-2.028304	0.973676	-2.053790
C	-1.346001	2.295783	-1.778487
C	-1.701268	3.285465	-2.881226
C	-2.127911	0.301158	0.335605
C	-3.568090	0.710480	0.551668
C	-3.729070	1.152539	2.002348
O	0.327181	2.785316	1.418032
Br	0.597798	-0.279666	2.920197
Br	2.836744	-0.076105	1.562149
Br	4.958770	0.155575	0.263798
H	-1.866690	-0.527328	0.983683

H	1.294575	0.478635	-2.444285	H	-1.468727	1.123833	0.586913
H	-0.471679	1.375584	0.592938	H	-3.599491	-0.989495	-1.470626
H	1.136243	0.721916	0.686763	H	-2.308274	-1.481192	-2.545256
H	-0.817415	1.188593	-2.411784	H	0.212038	0.431354	-0.601953
H	-1.384413	-0.469519	-2.401632	H	-0.176038	-1.241495	-0.274109
H	2.196863	-1.803329	-0.627409	H	-1.726060	0.585807	-3.020847
H	2.743926	-0.138189	-0.459231	H	-3.105756	1.102242	-2.071953
H	-2.248376	1.715899	-0.451292	H	-2.580842	-2.408388	0.352723
H	-2.787052	0.038155	-0.378832	H	-1.351340	-2.940690	-0.790497
H	-0.171962	-2.786859	-1.369988	H	-0.263496	2.174967	-1.747125
H	-1.821097	-2.189551	-1.205777	H	-1.668354	2.705027	-0.822554
H	1.858515	2.147756	-1.218594	H	-4.246745	-0.117267	0.355093
H	0.215275	2.751351	-1.414102	H	-3.842337	1.536017	-0.102787
H	-2.388953	0.850920	1.807002	H	-0.205437	-1.664780	-2.786085
H	-1.392399	0.544066	2.949937	H	0.338034	-0.006893	-3.019344
C	1.752494	4.714631	-0.240432	H	0.381069	2.637129	0.469165
H	0.273251	3.653344	0.897081	H	0.460709	1.912475	1.816424
H	1.905174	3.045574	1.099887	C	2.482420	-1.655776	-3.392076
C	-1.727584	-4.737065	-0.190845	H	2.338756	-0.496260	-1.590812
H	-0.257738	-3.664324	0.947563	H	1.791461	-2.148183	-1.418383
H	-1.890689	-3.051365	1.128045	C	-3.170829	-4.963223	-0.483631
C	-4.805863	1.603149	-1.407162	H	-4.352294	-3.293953	-1.136803
H	-3.164013	1.896304	-2.758141	H	-3.135459	-3.807025	-2.291727
H	-3.724291	0.236451	-2.660370	C	-1.058341	4.644915	-2.653610
C	4.732790	-1.634474	-1.652158	H	-1.379581	2.887722	-3.845127
H	3.050698	-1.830065	-2.970611	H	-2.785584	3.400591	-2.929015
H	3.619185	-0.182321	-2.773674	C	-5.150955	1.586884	2.320153
C	2.014890	5.774574	0.818489	H	-3.443926	0.332344	2.663745
H	2.676255	4.488427	-0.773724	H	-3.042818	1.976700	2.206931
H	1.046124	5.095343	-0.978783	C	3.900683	-2.151800	-3.154748
H	2.414118	6.686694	0.380260	H	1.902980	-2.422361	-3.908060
H	1.095400	6.027154	1.344637	H	2.500052	-0.781769	-4.044186
H	2.731293	5.411643	1.554280	H	4.407180	-2.376623	-4.091002
C	-5.892232	1.910163	-2.426333	H	4.482699	-1.402833	-2.619999
H	-5.153915	0.836580	-0.714072	H	3.893647	-3.057303	-2.549100
H	-4.593880	2.492956	-0.813569	C	-4.121180	-6.028974	-1.007368
H	-6.806350	2.250007	-1.944396	H	-2.140691	-5.308225	-0.577028
H	-5.563906	2.688322	-3.114018	H	-3.352607	-4.794828	0.578252
H	-6.129967	1.024046	-3.013315	H	-4.002829	-6.967393	-0.470037
C	-1.998578	-5.785646	0.877079	H	-5.155924	-5.706619	-0.900008
H	-2.647117	-4.516117	-0.733602	H	-3.938556	-6.219955	-2.063926
H	-1.015799	-5.125884	-0.919711	C	-5.302564	2.017329	3.771079
H	-2.395212	-6.701943	0.445220	H	-5.429549	2.408064	1.659106
H	-1.083174	-6.033496	1.412501	H	-5.832129	0.762911	2.105277
H	-2.720187	-5.414795	1.603772	H	-6.321427	2.329035	3.990749
C	5.787685	-1.863478	-2.723776	H	-5.048029	1.198352	4.442470
H	5.102100	-0.920683	-0.915183	H	-4.638565	2.851067	3.995268
H	4.537737	-2.565871	-1.119903	C	-1.419700	5.638085	-3.747152
H	6.714838	-2.239780	-2.296915	H	-1.375227	5.030060	-1.683884
H	5.436455	-2.586385	-3.458867	H	0.024306	4.522833	-2.606470
H	6.009879	-0.935183	-3.248045	H	-0.950400	6.604836	-3.578269
				H	-1.096780	5.271713	-4.720600
				H	-2.497571	5.789200	-3.787571