Supporting information

Photoelectron Spectroscopy and Theoretical Studies of Anion–π Interactions: Binding Strength and Anion Specificity

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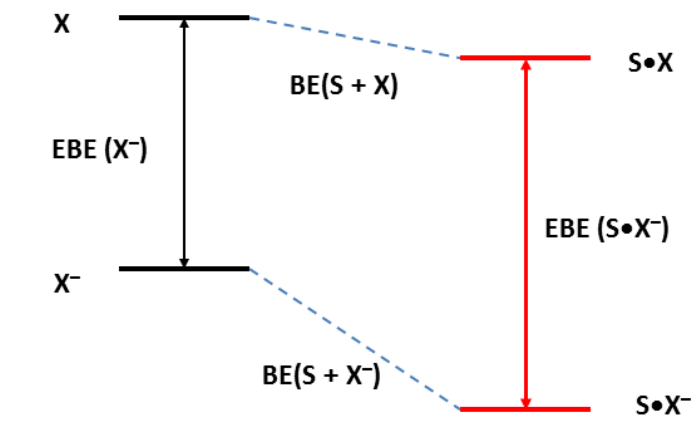


$\Delta EBE = EBE(S\bullet X^-) - EBE\ (X^-) = BE(S + X^-) - BE\ (S + X)$

X^-: Anion; S: Solvent molecule; EBE: Electron binding energy;
BE: Binding Energy between S and X^-.

Figure S1. Schematic depiction of relationship between the increase of electron binding energy of an anion X^- upon interacting with a neutral molecule S, and the binding energy between the anion X^- and the neutral molecule S. In this work, S refers to the π molecule **1**.

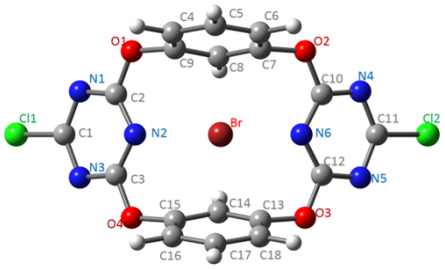
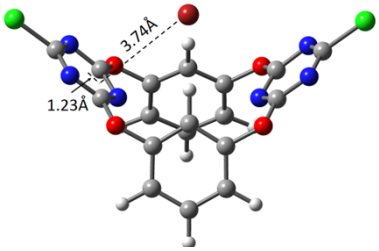
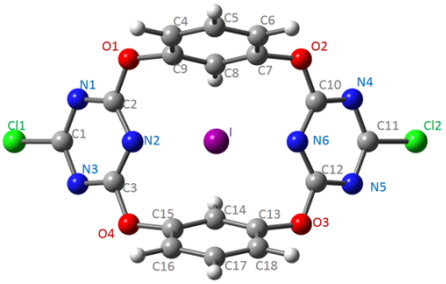
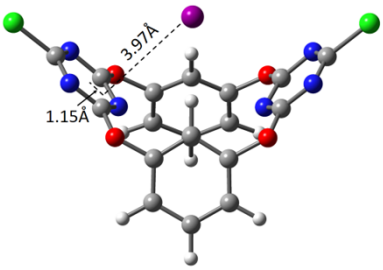
1•Br⁻		
1•I⁻		

Figure S2. Top and side view of ωB97XD/6-311++g(d,p) (for the C, H, O, Cl, N, S atoms) and aug-cc-pvtz-pp (for the I atom) geometries for **1**•Br⁻ and **1**•I⁻.

Table S1. Coordinates of 1•Cl^-, 1•Br^-, 1•I^-, 1•SCN^-, 1•NO_3^-, 1•IO_3^- and 1•SO_4^{2-}

1•Cl^-

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.81880000	1.10677600	-0.07268100
N	-3.82792400	1.18282300	-0.93763900
C	-4.26423300	-0.00021500	-1.30813200
C	-2.81936500	-1.10579600	-0.07075600
N	-2.29008400	0.00080100	0.42140600
N	-3.82845100	-1.18280800	-0.93559500
O	-2.38110900	2.28871000	0.35237000
C	-1.16898000	2.38240600	1.02656000
C	-1.19176300	2.85771200	2.32768200
C	0.00836700	2.12663200	0.34682900
C	0.01532500	3.08879200	2.97548100
H	-2.14245100	3.04727200	2.81051000
C	1.18864600	2.38207600	1.02062200
H	0.00341000	1.70821400	-0.66362400
C	1.21900700	2.85739100	2.32157900
H	0.01804600	3.46161800	3.99344100
H	2.17225000	3.04689300	2.79935600
O	2.39866300	2.28812400	0.34046900
C	2.83877700	1.10653200	-0.07990200
N	2.30200000	0.00011200	0.40516600
C	2.83820500	-1.10719100	-0.07840600
C	4.29733900	-0.00152600	-1.30042500
N	3.85685800	-1.18404500	-0.93296400
N	3.85740400	1.18169300	-0.93455300
O	2.39751500	-2.28801300	0.34345900
O	-2.38227400	-2.28721000	0.35641600
C	-1.16993600	-2.38031200	1.03046300
C	0.00729700	-2.12567000	0.35015100
C	-1.19262700	-2.85405500	2.33214400
C	1.18769000	-2.38068000	1.02395600
H	0.00225600	-1.70851100	-0.66082100
C	0.01454400	-3.08469800	2.97995000
H	-2.14327300	-3.04280400	2.81536600
C	1.21813800	-2.85443200	2.32549700
H	0.01739500	-3.45629500	3.99835900
H	2.17142800	-3.04367900	2.80328700
Cl	-5.60773400	-0.00085500	-2.41933100

Cl	5.65151400	-0.00258600	-2.39830200
Cl	-0.07328400	-0.00148100	-2.32303100

1•Br^-

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
C	2.77991500	-1.10705800	0.18627700
N	3.83916700	-1.18309400	-0.61632900
C	4.29617300	-0.00003400	-0.96238500
C	2.77989800	1.10704200	0.18620400
N	2.21900900	0.00000300	0.64220800
N	3.83916500	1.18304200	-0.61638400
O	2.31689200	-2.28769700	0.58573000
C	1.08477700	-2.36944700	1.22598700
C	1.06787500	-2.80024400	2.54243900
C	-0.07170900	-2.13950800	0.50343600
C	-0.15848200	-3.00928000	3.16081500
H	2.00361900	-2.97270900	3.05969400
C	-1.27300100	-2.36868000	1.14915700
H	-0.03914500	-1.76207000	-0.52065300
C	-1.34192100	-2.79895700	2.46408300
H	-0.19237300	-3.34631100	4.19057700
H	-2.30892100	-2.96952500	2.92080700
O	-2.46018600	-2.28746600	0.42971400
C	-2.89442000	-1.10667900	-0.00168500
N	-2.37060300	0.00002400	0.49692200
C	-2.89440600	1.10672000	-0.00171400
C	-4.32135600	0.00001300	-1.25925000
N	-3.89101200	1.18310200	-0.88046000
N	-3.89101900	-1.18307100	-0.88043700
O	-2.46017200	2.28751200	0.42967000
O	2.31690100	2.28769800	0.58563700
C	1.08479700	2.36947800	1.22591100
C	-0.07169800	2.13953600	0.50337600
C	1.06791300	2.80030200	2.54235400
C	-1.27298100	2.36873300	1.14910400
H	-0.03914600	1.76207300	-0.52070400
C	-0.15843700	3.00936300	3.16073800
H	2.00366300	2.97276900	3.05959600
C	-1.34188500	2.79903700	2.46402100
H	-0.19231400	3.34641700	4.19049300
H	-2.30887900	2.96962400	2.92075100
Cl	5.69957200	-0.00005600	-1.99523600
Cl	-5.64546900	0.00000600	-2.39156200

Br	-0.01366100	-0.00002700	-2.38631300

1•I^-

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
C	2.84873200	0.35635000	-1.10610200
N	3.90234000	-0.45219100	-1.18494800
C	4.35637700	-0.80677900	-0.00264600
C	2.84869500	0.34880200	1.10865100
N	2.28956600	0.81066900	0.00281300
N	3.90225200	-0.46030500	1.18203200
O	2.38312000	0.76141800	-2.28445500
C	1.17148700	1.44206500	-2.34580200
C	1.19266100	2.77997900	-2.70344900
C	-0.00668900	0.74296900	-2.15855100
C	-0.01519500	3.44374700	-2.87836100
H	2.14277900	3.27996400	-2.84532500
C	-1.18921700	1.43460400	-2.34586400
H	-0.00338900	-0.30170400	-1.84800500
C	-1.21886500	2.77235800	-2.70349100
H	-0.01853400	4.49121700	-3.15732100
H	-2.17204200	3.26647600	-2.84535800
O	-2.39655000	0.74629700	-2.28457700
C	-2.85967800	0.33833000	-1.10628700
N	-2.30313200	0.79572000	0.00269200
C	-2.85966100	0.33061200	1.10849000
C	-4.36064300	-0.83359500	-0.00295200
N	-3.90853000	-0.48461500	1.18176700
N	-3.90856400	-0.47635500	-1.18521600
O	-2.39652800	0.73048700	2.28955500
O	2.38303400	0.74593600	2.28969600
C	1.17140600	1.42623300	2.35524600
C	-0.00672200	0.72801900	2.16450400
C	1.19248800	2.76226500	2.71984100
C	-1.18930200	1.41862000	2.35518300
H	-0.00335600	-0.31495300	1.84832300
C	-0.01542900	3.42501700	2.89819600
H	2.14255500	3.26166600	2.86410300
C	-1.21906200	2.75449200	2.71974900
H	-0.01884400	4.47102700	3.18258700
H	-2.17226100	3.24790800	2.86389700
Cl	5.75053200	-1.84977300	-0.00610100
Cl	-5.74900700	-1.88422000	-0.00653500
I	0.00813300	-2.44584000	-0.00769700

1•SCN^-

Atomic Type	Coordinates (Angstroms) X	Y	Z
C	-2.82375100	1.05327400	-0.48771600
N	-3.92530600	0.95061500	-1.22690600
C	-4.48747600	-0.23439200	-1.12949800
C	-2.96273700	-1.03445800	0.23727000
N	-2.30200100	0.11076200	0.27739200
N	-4.09320700	-1.27048900	-0.42161300
O	-2.24959100	2.25315300	-0.52478000
C	-1.10212600	2.47934800	0.23164800
C	-1.24183500	3.11103100	1.45765600
C	0.13233000	2.15979900	-0.29994000
C	-0.10029400	3.43165100	2.17937300
H	-2.23231600	3.34444400	1.82849800
C	1.25065200	2.49711700	0.44602700
H	0.23592700	1.64165800	-1.24923600
C	1.15842300	3.12806400	1.67442500
H	-0.19136700	3.92493100	3.14026600
H	2.06373200	3.37452100	2.21524400
O	2.51595600	2.29383000	-0.08921900
C	2.94562500	1.04563200	-0.27833300
N	2.33363200	0.05581700	0.34720900
C	2.80632200	-1.13789800	0.03635000
C	4.38744900	-0.30200900	-1.24154800
N	3.84914000	-1.39477900	-0.74839600
N	4.01238100	0.94589500	-1.06360600
O	2.24462500	-2.22029700	0.57119200
O	-2.52115100	-2.06267900	0.95784400
C	-1.25594400	-1.99015000	1.52980700
C	-0.13513900	-2.05836900	0.71905300
C	-1.17058200	-1.94239000	2.91032100
C	1.09773400	-2.06780500	1.34348100
H	-0.23517600	-2.09496200	-0.36215400
C	0.08559800	-1.95870200	3.50442800
H	-2.07865100	-1.89605300	3.49868700
C	1.23066000	-2.02254900	2.72241400
H	0.17217700	-1.92128000	4.58430000
H	2.21921100	-2.03777000	3.16445800
Cl	-5.95816200	-0.45292800	-2.03649900
Cl	5.79047200	-0.53565600	-2.24890300
C	0.11047000	-0.71788000	-2.60382400
N	1.11840000	-0.15002300	-2.42399100

S	-1.32020000	-1.52831900	-2.81197200

1•NO_3^-

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
C	-2.81273000	1.10892700	0.03176700
N	-3.91436300	1.18441400	-0.71026000
C	-4.38098900	-0.00025700	-1.03647700
C	-2.81263400	-1.10903700	0.03204500
N	-2.22504000	0.00002200	0.44953200
N	-3.91426900	-1.18480400	-0.70995200
O	-2.33312300	2.28613300	0.42670100
C	-1.13789400	2.32016100	1.13703800
C	-1.19266100	2.54796700	2.50241600
C	0.05945700	2.21285400	0.45292000
C	-0.00315500	2.66322900	3.21097600
H	-2.15537000	2.63234600	2.99136900
C	1.22213500	2.32162400	1.19253300
H	0.07056400	2.02902000	-0.61848200
C	1.21792200	2.54933800	2.55838100
H	-0.02843400	2.84110700	4.28006100
H	2.15786000	2.63275700	3.08989300
O	2.44542200	2.28632600	0.52666100
C	2.92892000	1.10760100	0.14445600
N	2.38230500	0.00022200	0.61468900
C	2.92901400	-1.10724700	0.14478000
C	4.44235100	0.00007300	-1.00568400
N	3.98463200	-1.18366600	-0.66348100
N	3.98452900	1.18387300	-0.66383100
O	2.44561500	-2.28590200	0.52732700
O	-2.33293200	-2.28610300	0.42727800
C	-1.13771100	-2.31985600	1.13764100
C	0.05964500	-2.21262100	0.45352000
C	-1.19248500	-2.54733600	2.50307400
C	1.22231700	-2.32112000	1.19318300
H	0.07076000	-2.02904800	-0.61792600
C	-0.00298400	-2.66233100	3.21168500
H	-2.15519600	-2.63167800	2.99202700
C	1.21809700	-2.54850200	2.55908600
H	-0.02827000	-2.83996200	4.28081100
H	2.15803100	-2.63172000	3.09063600
Cl	-5.83220900	-0.00043500	-2.00629400
Cl	5.84851800	-0.00001600	-2.03817000
N	-0.31454200	-0.00024200	-2.15426200

O	0.91685400	-0.00018600	-1.94469100
O	-0.93165400	1.08035000	-2.24524900
O	-0.93161000	-1.08088800	-2.24492300

1•IO_3^-

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
C	-2.82508300	1.11023400	0.05382900
N	-3.91686000	1.18446800	-0.70436400
C	-4.38250800	-0.00080400	-1.02844100
C	-2.83013900	-1.10868600	0.06333600
N	-2.24215400	0.00128700	0.47706600
N	-3.92576000	-1.18494600	-0.68877600
O	-2.35756100	2.28606400	0.46365800
C	-1.15842100	2.32239200	1.16739500
C	-1.20299000	2.56089000	2.53103800
C	0.03272500	2.20717600	0.47433700
C	-0.00678300	2.67998100	3.22810700
H	-2.16157300	2.65023900	3.02723300
C	1.20253100	2.32274500	1.20115800
H	0.02114400	2.01898900	-0.59635000
C	1.20855900	2.56078600	2.56576700
H	-0.02230300	2.86566800	4.29612500
H	2.15279200	2.64906800	3.08889000
O	2.42089700	2.28882700	0.52735200
C	2.90824700	1.11025800	0.14448100
N	2.35213600	0.00259100	0.60219900
C	2.90635700	-1.10287500	0.13631000
C	4.43131800	0.00634300	-0.99138900
N	3.97512700	-1.17806000	-0.65286000
N	3.97456300	1.18955700	-0.64742100
O	2.41551400	-2.28312600	0.50797000
O	-2.36420400	-2.28322100	0.47882100
C	-1.15968300	-2.32010500	1.17277200
C	0.02665200	-2.20083400	0.47177300
C	-1.19415600	-2.56430900	2.53563500
C	1.20166600	-2.31941000	1.18960600
H	0.00893000	-2.00755800	-0.59732000
C	0.00698200	-2.68562800	3.22376200
H	-2.14928400	-2.65653900	3.03788300
C	1.21732400	-2.56335600	2.55314500
H	-0.00059300	-2.87574100	4.29104700
H	2.16534500	-2.65379600	3.06902600
Cl	-5.81906600	-0.00179200	-2.02340900

Cl	5.84312900	0.00923800	-2.01817000
O	1.44876700	-0.04818600	-2.25591500
O	-0.98493900	1.44634800	-2.35974300
O	-1.06196300	-1.40482100	-2.35302100
I	-0.16714500	-0.00400600	-3.05774300

1•SO_4^{2-}

Atomic	Coordinates (Angstroms)		
Type	X	Y	Z
C	2.93395900	1.01757500	-0.26228700
N	3.96444200	1.04722400	0.58472900
C	4.37076900	-0.15544700	0.90854100
C	2.87285900	-1.18894400	-0.31582400
N	2.39895900	-0.05935800	-0.80583300
N	3.89784200	-1.31678800	0.52872900
O	2.50909900	2.22174400	-0.63917600
C	1.28062800	2.33616400	-1.28588100
C	1.28804100	2.72619200	-2.61711600
C	0.11658000	2.16766200	-0.56054600
C	0.07367700	2.95405800	-3.25276000
H	2.23344700	2.84351600	-3.13379700
C	-1.07383100	2.40332200	-1.22752000
H	0.08514800	1.84455100	0.48813400
C	-1.11971600	2.79424100	-2.55778400
H	0.05661100	3.25430000	-4.29546500
H	-2.08038700	2.96456900	-3.02955000
O	-2.27227100	2.35586700	-0.53133600
C	-2.72802100	1.18000800	-0.09333900
N	-2.21512600	0.06775400	-0.58622000
C	-2.78891500	-1.03246500	-0.13521200
C	-4.28041300	0.09468100	1.00755800
N	-3.86684200	-1.09509000	0.64907000
N	-3.80187700	1.27265900	0.69343900
O	-2.39903200	-2.21422500	-0.61815200
O	2.38215100	-2.34834000	-0.74985300
C	1.14658500	-2.36435600	-1.39284900
C	-0.00337400	-2.15930200	-0.65422000
C	1.12655100	-2.69935300	-2.73886300
C	-1.20774700	-2.30064000	-1.32273100
H	-0.01364400	-1.87864200	0.40711100
C	-0.10122500	-2.83300600	-3.37550700
H	2.06190700	-2.84840200	-3.26557400
C	-1.28084800	-2.63478100	-2.66718600
H	-0.13963700	-3.08905000	-4.42936700

H	-2.25138700	-2.73371300	-3.13911300
Cl	5.77080400	-0.21906500	1.97107300
Cl	-5.73082700	0.11519400	2.01035200
O	1.09900800	-0.06583700	1.64522700
O	-1.02834200	-1.24260200	1.90678900
S	-0.22617900	-0.04859600	2.37821000
O	-0.03086900	-0.08531200	3.84351800
O	-0.96719400	1.20315800	1.95938800

Table S2. The single-point energies of 1•Cl^-, 1•Br^-, 1•I^-, 1•SCN^-, 1•NO_3^-, 1•IO_3^-, 1•SO_4^{2-} and their corresponding neutrals both at the anions' optimized geometries calculated using the ωB97XD and M06-2X functionals.

ωB97XD	anionic	neutral
1·Cl^-	-2700.77896508	-2700.59398107
1·Br^-	-4814.75231481	-4814.58162261
1·I^-	-2536.37337304	-2536.22066882
1·SCN^-	-2731.59758712	-2731.43117043
1·NO_3^-	-2520.85945496	-2520.65639465
1·IO_3^-	-2761.86507828	-2761.64762266
1·SO_4^{2-}	-2939.56042567	-2939.52062566

M06-2X	anion	neutral
1·Cl^-	-2700.72794264	-2700.53764784
1·Br^-	-4814.70983385	-4814.53541321
1·I^-	-2536.16707211	-2536.01643057
1·SCN^-	-2731.55268311	-2731.38236155
1·NO_3^-	-2520.80702768	-2520.58880930
1·IO_3^-	-2761.63187281	-2761.40768208
1·SO_4^{2-}	-2939.50402355	-2939.45410113

Table S3. Electron Density of the Complexes with ρ_{max} Listed in e/a_0^3 ($e/Å^3$). The Density is Plotted in the Plane Cut along two hydrogen in the benzene and the corresponding atom in the anion.

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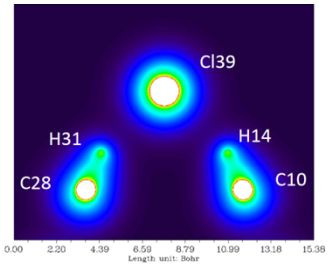
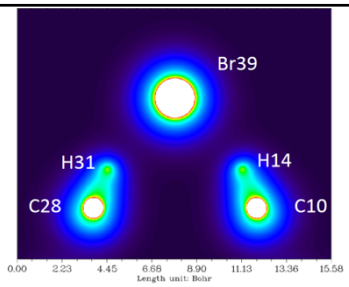
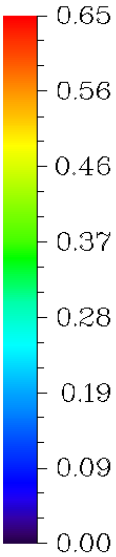
<td> 

1•Cl[–] 0.018 (0.12)</td>
<td> 

1•Br[–] 0.016 (0.11)</td>
<td rowspan="4"> 
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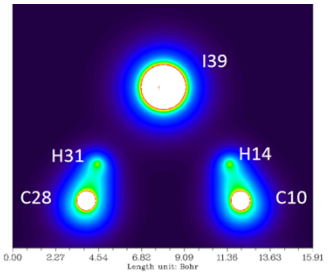
<td> 

1•I[–] 0.013 (0.087)</td>
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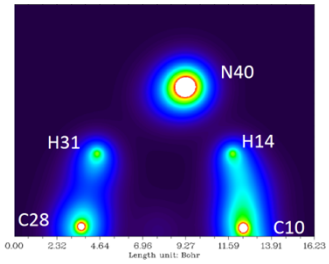
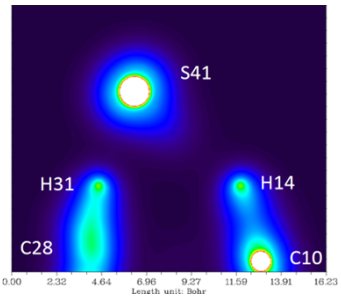
<td> 

1•SCN[–] 0.013 (0.091) for the N-end</td>
<td> 

1•SCN[–] 0.010 (0.070) for the S-end.</td>
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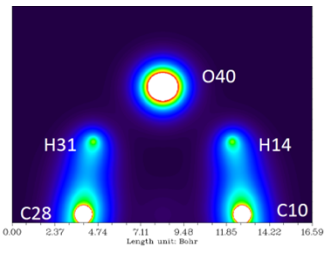
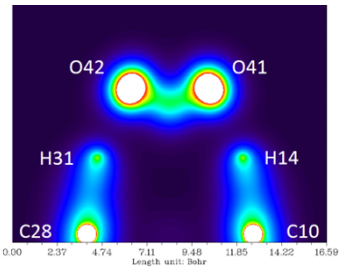
<td> 

1•NO_3^- 0.0088 (0.059)</td>
<td> 

1•NO_3^- 0.019 (0.13)</td>
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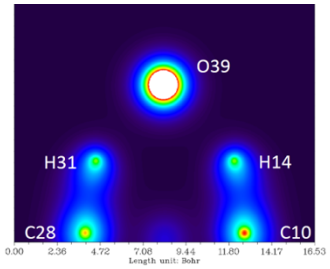
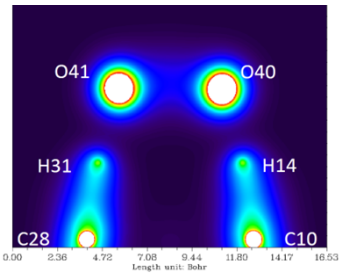
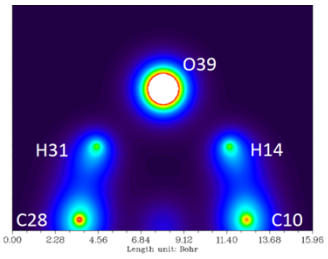
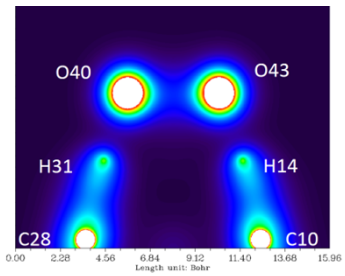
 **1**•IO_3^- 0.0045 (0.031)	 **1**•IO_3^- 0.019 (0.13)	
 **1**•SO_4^{2-} 0.011 (0.074)	 **1**•SO_4^{2-} 0.030 (0.20)	