Supporting Information for

Electrochemical Reduction of Aqueous Imidazolium on Pt (111) by Proton Coupled Electron Transfer

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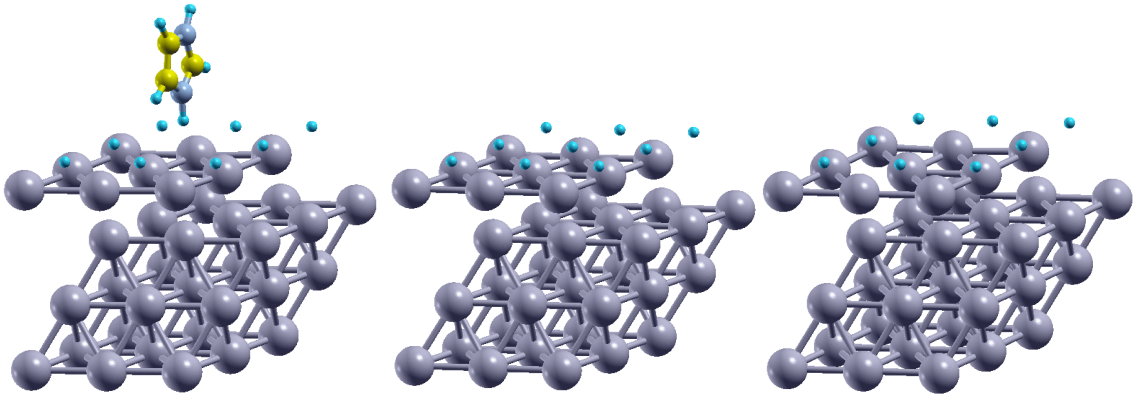
S1 Plane-wave-based DFT calculations

Density functional theory (DFT) calculations were carried out at the gradient-corrected PBE level of theory[1] within the plane-wave pseudopotential scheme as implemented in the Quantum ESPRESSO[2] software package. Ultra-soft pseudopotentials were employed for Pt, C, H, N and O atoms with plane wave kinetic energy cut off values of 40 Ry and 480 Ry for the wavefunctions and the charge densities, respectively. The Pt(111) surface was modeled by a periodically repeating 4 x 4 supercell (11.32 Å x 11.32 Å) in a four-layer slab where the two bottom layers were fixed at the optimized bulk lattice constants. The Monkhorst-Pack type of k-point sampling with a 2 x 2 x 1 was chosen for the slab calculations. Energies obtained via these calculations are in Table ST1 along with images of select structures in Figure SF1.

Table ST1: Electronic energies of optimized structures obtained via plane-wave-based DFT at the PBE level of theory.

	E, Ry	E, kcal/mol
H_2	-2.331166899	-731.4146874
$Pt_{36}H_8$ImH	-3207.245474	-1006288.502
$Pt_{36}H_9$	-3128.668906	-981634.7305
$Pt_{36}H_8$	-3127.477294	-981260.8566



a) $Pt_{36}H_8ImH$ b) $Pt_{36}H_9$ c) $Pt_{36}H_8$

Figure SF1: Optimized structures of supercells employed in plane-wave-based density functional theory calculations.

S2 Cluster DFT calculations

Selected geometries for the cluster calculations were optimized at the PBE level of density functional theory[1] using the Stuttgart RSC 1997 ECP basis set (SDD)[3] for Pt and the 6-31G(d) basis set[4] for all other atoms.

The reduction potential of ImH^+ to H_2 and imidazole was calculated using a larger 6-311+G(2df,p) basis set. The values 4.44 V and 0.242 V were used as the absolute potential of Standard Hydrogen Electrode (SHE) and the potential of Saturated Calomel Electrode (SCE) relative to SHE.[5]

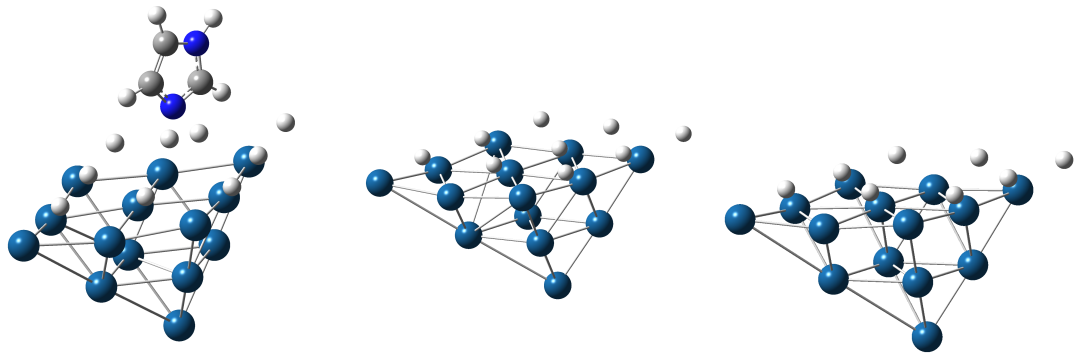
Pyramidal Pt_{14} cluster, the geometry of which was extracted from plane-wave calculations, was used as a model of the Pt surface in cluster calculations. In the calculations, involving Pt_{14} cluster, the four corners of the pyramid, as well as the eight H atoms on the perimeter of the (111) facet were kept frozen.

The grid=ultrafine option (in Gaussian 09)[6] was chosen for integral evaluation and an automatically generated density-fitting basis set was used within the resolution-of-the-identity approximation for the evaluation of Coulomb integrals. The nature of all stationary points was verified by analytic computation of vibrational frequencies, which

were also used for the computation of zero-point vibrational energies and molecular partition functions. Partition functions were further used in the computation of 298 K thermal contributions to free energy employing the usual ideal-gas, rigid-rotator, harmonic oscillator approximation.[7] Solvation effects associated with water as solvent were accounted for by using the SMD aqueous continuum solvation model.[7] The aqueous solvation contribution to the plane-wave-based periodic DFT optimized structures as well as the Gibbs free energy changes for the reactions involving charges species were calculated via generating model clusters with 14 Pt atoms (Figure SF2) and performing single point calculations at the PBE level of density functional theory using SDD basis set for Pt and the 6-31G* basis set for all other atoms (Table ST2). Results of the calculations of the reduction potential of imidazolium are presented in ST3.

Table ST2: Electronic, Zero Point Vibrational, Solvation and Free energies of species calculated at PBE level of theory with the SDD basis set for Pt and the 6-31G(d) basis set for C, H, N and O.

	E, hartree	E, kcal/mol	ΔZPVE, kcal/mol	$-T\Delta S+dG^{298}$, kcal/mol	ΔG_{solv}, kcal/mol
$Pt_{14}H_8ImH$	-1903.205273	-1194279.39	6.48	-5.97	-70.13
ImH^+	-226.3187985	-142017.20			
$[Pt_{14}H_8]^-$	-1676.765141	-1052186.06			
$Pt_{14}H_7$	-1676.033067	-1051726.67	-3.14	3.95	0.81
$Pt_{14}H_9$	-1677.221001	-1052472.11			
H_2	-1.161974863	-729.15			



a) $Pt_{14}H_8ImH$ b) $Pt_{14}H_9$ c) $Pt_{14}H_8$

Figure SF2: Structures of model clusters.

Table ST3: Electronic, Zero Point Vibrational, Solvation and Free energies of species calculated at PBE level of theory with the SDD basis set for Pt and the 6-311+G(2d,f) basis set for C, H, N and O.

	E, hartree	E, kcal/mol	ΔZPVE, kcal/mol	$-T\Delta S+dG^{298}$, kcal/mol	ΔG_{solv}, kcal/mol
ImH^+	-226.3911313	-142062.5856	-5.63	-9.20	54.53
Im	-226.0213653	-141830.554			
H_2	-1.165851906	-731.5831465			

S3 Geometries in Cartesian coordinates

Table ST4: Optimized geometries obtained via plane-wave-based DFT at the PBE level of theory.

H_2

Atom	x (Å)	y (Å)	z (Å)
H	4.884438507	1.77446183	13.73638112
H	5.636382013	1.77446183	13.7363814

$Pt_{36}H_8ImH$

Atom	x (Å)	y (Å)	z (Å)
Pt	5.657426	0.000000	1.000000
Pt	2.828713	4.899474	1.000000
Pt	8.486138	4.899474	1.000000
Pt	0.000000	0.000000	1.000000
Pt	2.828713	-0.000001	1.000000
Pt	1.414356	2.449738	1.000000
Pt	4.243070	2.449738	1.000000
Pt	7.071781	2.449738	1.000000
Pt	5.657426	4.899474	1.000000
Pt	5.657426	3.266316	3.309634
Pt	4.243069	0.816579	3.309634
Pt	7.071783	0.816579	3.309634
Pt	2.828713	3.266315	3.309634
Pt	4.243070	5.716054	3.309634
Pt	8.486138	3.266315	3.309634
Pt	7.071781	5.716054	3.309634
Pt	9.900496	5.716054	3.309634
Pt	1.414357	0.816579	3.309634
Pt	5.656669	1.628075	5.609675
Pt	2.822146	1.629285	5.608643
Pt	4.239003	4.086583	5.608242
Pt	11.310315	6.532202	5.621749
Pt	8.489017	1.630371	5.609341
Pt	9.897966	4.086022	5.621101
Pt	8.486287	6.531292	5.624757
Pt	7.074347	4.085725	5.611464
Pt	5.656417	6.538213	5.611220
Pt	8.475677	4.894062	8.017561
Pt	5.652143	0.004439	8.018132

Pt	2.828833	4.895613	8.005697
Pt	4.267861	2.467935	7.947241
Pt	2.823435	-0.001240	7.990466
Pt	1.410556	2.450868	7.980520
Pt	-0.006271	-0.001790	7.984150
Pt	7.042339	2.464988	7.955231
Pt	5.654504	4.870588	7.960592
H	8.455692	3.242601	8.858779
H	2.858461	3.244351	8.848656
H	4.267844	5.692994	8.854508
H	7.033794	5.699850	8.861774
H	9.895226	5.713137	8.884816
H	1.405594	0.819167	8.857027
H	4.225606	0.860548	8.845509
H	7.070576	0.850498	8.854069
H	5.529268	3.077514	9.845298
C	5.143020	2.018606	11.713530
C	5.197148	2.443928	13.011529
C	5.770770	4.135975	11.680814
N	5.503856	3.081489	10.927280
H	4.881613	1.065524	11.268319
H	4.991536	1.934963	13.942700
H	5.721791	4.378362	13.766261
H	6.074213	5.108244	11.306293
N	5.592295	3.769662	12.966337

$Pt_{36}H_9$

Atom	x (Å)	y (Å)	z (Å)
Pt	5.657426	0.000000	1.000000
Pt	2.828713	4.899474	1.000000
Pt	8.486138	4.899474	1.000000
Pt	0.000000	0.000000	1.000000
Pt	2.828713	-0.000001	1.000000
Pt	1.414356	2.449738	1.000000
Pt	4.243070	2.449738	1.000000
Pt	7.071781	2.449738	1.000000
Pt	5.657426	4.899474	1.000000
Pt	5.657426	3.266316	3.309634
Pt	4.243069	0.816579	3.309634
Pt	7.071783	0.816579	3.309634
Pt	2.828713	3.266315	3.309634
Pt	4.243070	5.716054	3.309634

Pt	8.486138	3.266315	3.309634
Pt	7.071781	5.716054	3.309634
Pt	9.900496	5.716054	3.309634
Pt	1.414357	0.816579	3.309634
Pt	5.648476	1.627909	5.614662
Pt	2.820411	1.628916	5.613332
Pt	4.233504	4.078588	5.614592
Pt	11.305908	6.527952	5.613035
Pt	8.477298	1.628387	5.612778
Pt	9.891214	4.077910	5.613632
Pt	8.476549	6.527965	5.613374
Pt	7.063375	4.078599	5.614379
Pt	5.648384	6.528039	5.612432
Pt	8.469567	4.891267	7.984539
Pt	5.640621	-0.009436	7.982928
Pt	2.811307	4.891464	7.983364
Pt	4.224761	2.440218	7.981777
Pt	2.810842	-0.009206	7.983536
Pt	1.396948	2.440673	7.983597
Pt	-0.016384	-0.008875	7.983977
Pt	7.055019	2.440726	7.981585
Pt	5.640354	4.890037	7.981326
H	8.466921	3.258774	8.865023
H	2.808892	3.258850	8.863733
H	4.227078	5.707182	8.865250
H	7.051771	5.704791	8.865518
H	9.883159	5.708191	8.869353
H	1.396797	0.808347	8.869633
H	4.223525	0.805036	8.863618
H	7.056021	0.806387	8.864674
H	5.638725	3.254079	8.862737

$Pt_{36}H_8$

Atom	x (Å)	y (Å)	z (Å)
Pt	5.657426	0.000000	1.000000
Pt	2.828713	4.899474	1.000000
Pt	8.486138	4.899474	1.000000
Pt	0.000000	0.000000	1.000000
Pt	2.828713	-0.000001	1.000000
Pt	1.414356	2.449738	1.000000
Pt	4.243070	2.449738	1.000000
Pt	7.071781	2.449738	1.000000

Pt	5.657426	4.899474	1.000000
Pt	5.657426	3.266316	3.309634
Pt	4.243069	0.816579	3.309634
Pt	7.071783	0.816579	3.309634
Pt	2.828713	3.266315	3.309634
Pt	4.243070	5.716054	3.309634
Pt	8.486138	3.266315	3.309634
Pt	7.071781	5.716054	3.309634
Pt	9.900496	5.716054	3.309634
Pt	1.414357	0.816579	3.309634
Pt	5.648855	1.626097	5.607086
Pt	2.815299	1.626759	5.608372
Pt	4.231455	4.081006	5.606834
Pt	11.303103	6.527271	5.618058
Pt	8.481079	1.627008	5.609749
Pt	9.891227	4.081908	5.617813
Pt	8.479452	6.527178	5.617886
Pt	7.065336	4.080478	5.608234
Pt	5.648396	6.533472	5.609630
Pt	8.458709	4.886521	8.006899
Pt	5.638785	0.002794	8.006170
Pt	2.819320	4.886301	8.005802
Pt	4.253761	2.458765	7.949807
Pt	2.812112	-0.009625	7.979523
Pt	1.395185	2.444461	7.979422
Pt	-0.020612	-0.009009	7.979840
Pt	7.023120	2.459371	7.954689
Pt	5.639032	4.856860	7.954028
H	8.431571	3.239704	8.865113
H	2.841336	3.240834	8.862807
H	4.256065	5.688866	8.864499
H	7.018854	5.686570	8.864930
H	9.882546	5.708572	8.876030
H	1.395264	0.808557	8.862017
H	4.224541	0.845079	8.863014
H	7.052352	0.846019	8.864860

Table ST5: Geometries of model clusters generated from optimized structures obtained via planewave- based DFT at the PBE/6-31G* level of theory.

$Pt_{14}H_8ImH$

Atom	x (Å)	y (Å)	z (Å)
Pt	5.657427	3.266312	3.309633
Pt	5.656672	1.628095	5.609657
Pt	2.82215	1.629287	5.608638
Pt	4.238982	4.086589	5.608233
Pt	7.074352	4.085719	5.611466
Pt	8.475656	4.894055	8.017497
Pt	5.652135	0.004468	8.018123
Pt	2.828883	4.895575	8.005647
Pt	4.288323	2.478224	7.919713
Pt	2.818029	0.005183	7.777008
Pt	1.413622	2.440823	7.778098
Pt	-0.006273	-0.001789	7.984151
Pt	7.112923	2.402896	7.896963
Pt	5.636927	4.956604	7.899705
H	8.45566	3.242617	8.858802
H	2.858436	3.24431	8.848753
H	4.267847	5.693022	8.854519
H	7.033788	5.699837	8.861816
H	9.895224	5.713134	8.884821
H	1.405643	0.819176	8.857005
H	4.225548	0.860586	8.845503
H	7.07062	0.850435	8.854113
H	5.529282	3.077536	9.845256
C	4.935567	2.791987	11.935775
C	5.548748	3.214031	13.092715
C	6.777725	3.893882	11.348617
N	5.717109	3.225636	10.885681
H	4.02081	2.228236	11.769414
H	5.278438	3.091804	14.137915
H	7.368615	4.337806	13.315494
H	7.555945	4.347618	10.73078
N	6.690842	3.895892	12.696385

ImH^+

Atom	x (Å)	y (Å)	z (Å)
H	2.042685	-0.686985	-0.000053
C	0.689387	0.97857	-0.000032
C	-0.683582	0.982601	0.000092

C	-0.003478	-1.149685	0.000289
N	1.077523	-0.350858	-0.000138
H	1.40688	1.795101	-0.000011
H	-1.396302	1.803268	0.000482
H	-2.046604	-0.674978	-0.000546
H	-0.006816	-2.237156	0.000155
N	-1.079494	-0.344594	-0.000165

$[Pt_{14}H_8]^-$

Atom	x (Å)	y (Å)	z (Å)
Pt	1.801082	-0.221189	3.401429
Pt	0.646573	1.3344	1.346825
Pt	-1.779948	-0.10488	1.621777
Pt	0.648147	-1.497772	1.163188
Pt	3.075295	-0.058184	0.885906
Pt	4.31473	0.112985	-1.729398
Pt	-0.520229	2.882241	-0.816308
Pt	-0.517991	-2.753943	-1.171807
Pt	-0.442708	0.059168	-0.914763
Pt	-2.906449	1.427223	-0.316388
Pt	-2.9042	-1.374832	-0.501171
Pt	-5.363494	0.014693	-0.234792
Pt	1.925396	1.540819	-1.164833
Pt	1.924747	-1.374464	-1.357117
H	3.355404	1.576334	-2.341072
H	-1.435098	-1.265679	-1.790192
H	0.981492	-2.654511	-2.253017
H	3.352182	-1.256653	-2.52857
H	5.80558	0.185233	-2.829726
H	-3.87917	0.081765	-1.340088
H	-1.442357	1.476093	-1.606881
H	0.98772	2.928817	-1.889165

$Pt_{14}H_7$

Atom	x (Å)	y (Å)	z (Å)
Pt	5.657622	3.267784	3.309696
Pt	5.657241	1.63352	5.606083
Pt	2.821267	1.619397	5.614429
Pt	4.24014	4.084585	5.610656
Pt	7.074141	4.086807	5.611629
Pt	8.475903	4.894921	8.016716
Pt	5.651624	0.003657	8.017501
Pt	2.829577	4.893751	8.006139
Pt	4.239503	2.498269	8.037525

Pt	2.796128	0.022205	7.766517
Pt	1.5266	2.510302	7.775507
Pt	-0.00589	-0.001756	7.983501
Pt	7.064299	2.412713	7.919591
Pt	5.622985	4.900428	7.949658
H	8.455253	3.241459	8.858919
H	4.26463	5.700904	8.855393
H	7.033826	5.692839	8.860872
H	9.895205	5.713064	8.884918
H	1.405938	0.825291	8.85205
H	4.226988	0.860163	8.847521
H	7.07085	0.850732	8.8536

$Pt_{14}H_9$

Atom	x (Å)	y (Å)	z (Å)
Pt	1.786413	-0.109954	3.413404
Pt	0.645657	1.377122	1.302794
Pt	-1.784533	-0.051502	1.610641
Pt	0.645874	-1.45952	1.211903
Pt	3.074297	-0.028551	0.901293
Pt	4.329217	0.057358	-1.711372
Pt	-0.510661	2.853792	-0.916751
Pt	-0.506697	-2.791186	-1.087499
Pt	-0.511828	0.030063	-0.914761
Pt	-2.923615	1.423009	-0.329988
Pt	-2.922939	-1.394608	-0.42921
Pt	-5.357383	0.005297	-0.269105
Pt	1.958494	1.530706	-1.222211
Pt	1.961085	-1.449602	-1.32106
H	3.372847	1.500817	-2.3755
H	-1.419026	-1.325576	-1.760056
H	0.999127	-2.726505	-2.163148
H	3.371311	-1.337999	-2.470677
H	5.826198	0.093838	-2.805007
H	-3.866886	0.037407	-1.367587
H	-1.429413	1.421302	-1.665887
H	1.00246	2.865812	-1.982231
H	1.239693	0.061941	-1.980054

H_2

Atom	x (Å)	y (Å)	z (Å)
H	0	0	0.375233
H	0	0	-0.375233

Table ST6: Geometries of model clusters generated from optimized structures obtained via planewave- based DFT at the PBE/6-311+G(2d,f) level of theory.

ImH^+

Atom	x (Å)	y (Å)	z (Å)
H	2.036512	-0.686584	0.000019
C	0.686362	0.975435	-0.000046
C	-0.679998	0.979842	0.000119
C	-0.003811	-1.145246	0.000269
N	1.073961	-0.350743	-0.000132
H	1.400042	1.791766	-0.000067
H	-1.388399	1.800722	0.000474
H	-2.040817	-0.6734	-0.000549
H	-0.007454	-2.230499	0.000182
N	-1.076133	-0.343855	-0.000169

Im

Atom	x (Å)	y (Å)	z (Å)
C	1.143245	-0.268226	-0.00001
C	0.597582	0.995528	0.00005
C	-0.984421	-0.555205	0.000014
N	0.152342	-1.227092	0.00005
H	2.195314	-0.540245	-0.000052
H	1.03637	1.987773	-0.000045
H	-1.477211	1.522203	0.000687
H	-1.982481	-0.986376	-0.000102
N	-0.768117	0.796243	-0.000166

H_2

Atom	x (Å)	y (Å)	z (Å)
H	5.72179114	4.37836247	13.76626095
H	6.32179114	4.37836247	13.76626095

References

(1) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865–3868.

(2) Giannozzi, P.; Baroni, S.; Bonini, N.; Calandra, M.; Car, R.; Cavazzoni, C.; Ceresoli, D.; Chiarotti, G. L.; Cococcioni, M.; Dabo, I.; Corso, A. D.; de Gironcoli, S.; Fabris, S.; Fratesi, G.; Gebauer, R.; Gerstmann, U.; Gougoussis, C.; Kokalj, A.; Lazzeri, M.; Martin-Samos, L.; Marzari, N.; Mauri, F.; Mazzarello, R.; Paolini, S.; Pasquarello, A.; Paulatto, L.; Sbraccia, C.; Scandolo, S.; Sclauzero, G.; Seitsonen, A. P.; Smogunov, A.; Umari, P.; Wentzcovitch, R. M. J. Phys.: Condens. Matter 2009, 21, 395502.

(3) M. Dolg, U. Wedig, H. Stoll, and H. Preuss. *J. Chem. Phys.*, **86** (1987) 866-72.

(4) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. Ab Initio Molecular Orbital Theory; Wiley: New York, 1986.

(5) Trasatti, S. *Pure Appl. Chem.* **1986**, 59, 955.

(5) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J.W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ã.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09 Revision A.1, Gaussian Inc. Wallingford CT 2009. 60

(6) Cramer, C. J. Essentials of Computational Chemistry: Theories and Models, 2nd ed.; John Wiley & Sons: Chichester, 2004. (7) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. J. Phys. Chem. B 2009, 113, 6378–6396. 61