

Supplementary Information

Self-Assembled Films from Chitosan and Poly(Vinyl Sulfonic Acid) on Nafion® for Direct Methanol Fuel Cell

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Table S1. Cartesian coordinates of the (2*S*,3*S*,4*R*,5*R*,6*S*)-5-amino-3,6-dimethoxytetrahydro-2*H*-pyran-2,4-diol / ethenesulfonic acid complex

S	3.12075	-0.32259	-0.35501
O	2.43833	0.99551	-0.29888
O	4.18154	-0.45927	-1.35037
O	2.08115	-1.42840	-0.44044
C	3.86870	-0.59183	1.22643
C	3.86458	0.33415	2.17675
C	-3.37524	0.04273	-0.05757
O	-3.86799	0.54709	1.16346
O	-2.67277	1.01614	-0.77934
C	-1.50738	1.51552	-0.14705
O	-0.97987	2.39963	-1.07677
C	-0.03279	3.31299	-0.53560
C	-0.54568	0.37161	0.15873
C	-1.22292	-0.72846	0.98829
O	-1.46888	-0.27407	2.29499
H	-2.31874	0.19811	2.28608
H	-0.52652	-1.57139	1.06932
C	-2.52111	-1.17735	0.29873
O	-2.27688	-1.85165	-0.92132
C	-1.94412	-3.22039	-0.76843
N	-0.05102	-0.16901	-1.12796
H	4.34723	-1.56238	1.32504
H	4.34874	0.16292	3.13439
H	3.38005	1.29192	2.01085
H	-4.18870	-0.25890	-0.72637
H	-4.38863	1.33990	0.96713
H	-1.76751	2.03796	0.78799
H	0.17027	4.03662	-1.32666
H	0.90246	2.81383	-0.25626
H	-0.45313	3.83900	0.33299
H	0.33359	0.73975	0.69314
H	-3.09566	-1.81418	0.98628
H	-1.85221	-3.63264	-1.77505
H	-2.73869	-3.75445	-0.23066
H	-0.99367	-3.36103	-0.23827
H	0.84325	-0.77970	-0.92940
H	0.23295	0.61666	-1.71950
H	-0.79112	-0.71123	-1.58749

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Table S2. Cartesian coordinates of the (2*S*,3*S*,4*R*,5*R*,6*S*)-5-amino-3,6-dimethoxytetrahydro-2*H*-pyran-2,4-diol / ethenesulfonic acid / methanol complex

O	3.243327	-0.165617	-0.332285
O	2.471604	1.081642	-0.104805
O	4.175056	-0.159943	-1.462748
O	2.284807	-1.347871	-0.385711
C	4.209503	-0.469903	1.121649
C	4.245302	0.382716	2.140177
C	-3.463685	0.061336	-0.187174
O	-4.069292	0.553482	0.989469
O	-2.705015	1.047572	-0.832611
C	-1.602052	1.547249	-0.100063
O	-0.995609	2.437278	-0.974798
C	-0.138575	3.386743	-0.351806
C	-0.662014	0.406947	0.289018
O	-1.406035	-0.706194	1.044388
O	-1.756251	-0.272351	2.336503
H	-2.610963	0.188779	2.287520
H	-0.723255	-1.554116	1.174280
C	-2.633782	-1.154437	0.235746
O	-2.248604	-1.806387	-0.956423
C	-1.994903	-3.195429	-0.813922
N	-0.034212	-0.119217	-0.942211
H	4.779280	-1.394475	1.076319
H	4.864520	0.187439	3.011938
H	3.660561	1.298387	2.118108
H	-4.211705	-0.236669	-0.928613
H	-4.636495	1.304025	0.758119
H	-1.946031	2.069085	0.807284
H	0.133951	4.099741	-1.131489
H	0.773572	2.918623	0.037278
H	-0.667685	3.915278	0.453417
H	0.148320	0.787434	0.917399
H	-3.264932	-1.807414	0.855399
H	-1.600186	-3.537106	-1.771580
H	-2.923916	-3.729865	-0.573768
H	-1.247054	-3.396709	-0.036434
H	0.853413	-0.653313	-0.711344
H	0.243686	0.664207	-1.541660
H	-0.663862	-0.741829	-1.465538
O	0.994739	-2.255910	-2.636649
H	1.605674	-2.427435	-3.898774
H	1.691737	-2.124520	-1.961972
H	0.810775	-2.428242	-4.650488
H	2.145009	-3.383272	-3.963436
H	2.306278	-1.612736	-4.126706

Energy for methanol binding to the (2*S*,3*S*,4*R*,5*R*,6*S*)-5-amino-3,6-dimethoxytetrahydro-2*H*-pyran-2,4-diol / ethenesulfonic acid ionic pair

Geometries were optimized at the PBE0/6-31G* level. Single-point calculations were carried out at the PBE-D level^{1,2} with the TZV(2d,2p) basis set.³⁻⁵ As suggested by Grimme,^{1,2} DFT-D calculations with the triple-zeta basis set include, in a sense, dispersion and BSSE corrections. Single-point calculations were performed with ORCA v2.6rev35.⁶

Table S3. Energies at the PBE-D/TZV(2d,2p) level for the (2*S*,3*S*,4*R*,5*R*,6*S*)-5-amino-3,6-dimethoxytetrahydro-2*H*-pyran-2,4-diol / ethenesulfonic acid ionic pair (E_1), methanol molecule (E_2) and (2*S*,3*S*,4*R*,5*R*,6*S*)-5-amino-3,6-dimethoxytetrahydro-2*H*-pyran-2,4-diol / ethenesulfonic acid / methanol complex (E_3) (energies in ha)

Structure	Ionic pair (E_1)	Methanol (E_2)	Complex (E_3)
Energy / ha	-1408.187629513	-115.630027852	-1523.839762685
$\Delta E = E_3 - (E_2 + E_1) =$	-0.02210532 ha = -13.87 kcal mol ⁻¹		

References

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