Supporting Information

Oxygen reduction catalyzed by a fluorinated free base porphyrin at liquid/liquid interfaces

Imren Hatay,[a,b] Bin Su,[a,f] Manuel A. Méndez,[a] Clémence Corminboeuf,[c] Tony Khoury,[d] Claude P. Gros,[d] Mélanie Bourdillon,[d] Michel Meyer,[d] Jean-Michel Barbe,[d] Mustafa Ersoz,[b] Stanislas Zalis,[e] Zdenec Samec,[e] and Hubert H. Girault*[,a]

[a] Laboratoire d'Electrochimie Physique et Analytique, Ecole Polytechnique Fédérale de Lausanne, Station 6, CH-1015 Lausanne, Switzerland

[b] Department of Chemistry, Selcuk University, 42031 Konya, Turkey

[c] Laboratory for Computational Molecular Design, Ecole Polytechnique Fédérale de Lausanne, BCH-5312, CH-1015 Lausanne, Switzerland

[d] Institut de Chimie Moléculaire de l'Université de Bourgogne, ICMUB (UMR 5260 du CNRS), 9 avenue Alain Savary, BP 47870, 21078 Dijon Cedex, France

[e] J. Heyrovsky Institute of Physical Chemistry of ASCR, v.v.i, Dolejskova 3, 182 23 Prague 8, Czech Republic

[f] Present address: Institute of Microanalytical Systems, Department of Chemistry, Zhejiang University, 310058 Hangzhou, China

*To whom the correspondence should be addressed.
Email: hubert.girault@epfl.ch
Fax: +41 21 6933667

1. Synthesis and Characterization of H_2FAP [S1-S4]

Synthesis of amino-phenyl-pentafluoroporphyrin H_2FAP

Instrumentation. ^1H NMR spectra were recorded on a Bruker DRX-300 AVANCE spectrometer of the "*Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne (PACSMUB)*".; chemical shifts are expressed in ppm relative to chloroform (7.258 ppm). Mass spectra were obtained on a Bruker Daltonics Ultraflex II spectrometer of the "*Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne (PACSMUB)*" in the MALDI/TOF reflectron mode using dithranol as a matrix. Accurate mass measurements (HR-MS) were carried out on a Bruker MicroQTofQ instrument in ESI mode. Both measurements were made at the "*Plateforme d'Analyse Chimique et de Synthèse Moléculaire de l'Université de Bourgogne (PACSMUB)*". UV-visible spectra were recorded on a Varian Cary 1 spectrophotometer.

Chemicals and Reagents. All chemicals and reagents were used as received. Silica gel (Merck; 70-120 mm) was used for column chromatography. Analytical thin layer chromatography was performed using Merck 60 F_{254} silica gel (precoated sheets, 0.2 mm thick). Reactions were monitored by thin-layer chromatography and UV-visible spectroscopy. 5-(pentafluorophenyl)dipyromethane **3** was prepared in 67% yield as described in the literature.[1,2]

Synthesis of 5-(*p*-nitro-phenyl)-10,15,20-tris-pentafluorophenylporphyrin 6

5-(Pentafluorophenyl)dipyrromethane **3** (3.1 g, 9.93 mmol) and pentafluoro-benzaldehyde **2** (0.6 ml, 0.95 g, 4.85 mmol) were dissolved in methanol (500 ml), and a mixture of water (500 ml) and hydrochloric acid (50 ml, 10 M). The reaction mixture was stirred for 4 h and then it was extracted with dichloromethane. The organic layer was washed with water (2 x 100 ml)

and dried over magnesium sulfate, the solvent was removed in vacuo to afford the expected bilane **4**. The bilane **4** and 4-nitro-benzaldehyde **5** (2,02 g, 13.37 mmol) were then dissolved in dichloromethane (800 ml) and TFA (2.7 ml, 35.21 mmol) was added and the reaction mixture was stirred for 14 h. The reaction mixture was then poured in dichloromethane (2000 ml) and DDQ (2.8 g, dissolved in 50 ml of tetrahydrofuran) was added and the mixture was stirred for 6 h. The reaction mixture was then evaporated, purified by filtration over a pad of silica (dichloromethane/heptane; 50:50). The front running brown band was collected and the solvent was removed to afford the 5-(*p*-nitro-phenyl)-10,15,20-tris-pentafluorophenylporphyrin **6** (361 mg, 8%*) as a brown microcrystalline solid. An analytically pure sample was obtained by recrystallization from a chloroform/methanol solution. (HRMS-ESI Found: $[M + Na]^+$ 952.0779. $C_{44}H_{14}F_{15}N_5NaO_2$ requires 952.0800; and Found: $[2 M + Na]^+$ 1881.1683. $C_{88}H_{28}F_{30}N_{10}NaO_4$ requires 1881.1708). λ_{max} (CH_2Cl_2) (log ε): 307 (4.27), 372sh (4.65), 414 (5.58), 475sh (3.51), 508 (4.40), 539 (3.55), 585 (3.88), 639 (2.98) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ -2.87 (2 H, inner NH); 8.41 and 8.69 (4 H, AB quartet, J 8.6 Hz, aryl H); 8.87 (4 H, br s, *β-pyrrolic* H); 8.91 (4 H, br s, *β-pyrrolic* H). Mass spectrum (MALDI-TOF) (m/z): 929.1 ($M^{+\bullet}$ requires 929.1). (*Yield calculated from conversion of pentafluoro-benzaldehyde **2**).

Synthesis of 5-(*p*-amino-phenyl)-10,15,20-tris-pentafluorophenylporphyrin 7

5,10,15-Tris-pentafluorophenyl-20-(*p*-nitro-phenyl)porphyrin **6** (230.0 mg, 0.247 mmol) was dissolved in chloroform (10 ml) and stirred in a hydrochloric acid/ether mixture (1 M, 15 ml) with tin(II) chloride dihydrate (1.12 g, 5.10 mmol) in the dark for 6 h in a similar way to literature method.[3,4] The reaction mixture was poured onto ice (50 g) and when the ice melted, chloroform (20 ml) was added. The organic layer was washed with water (200 ml), sodium hydrogencarbonate solution (10%, 100 ml), water (200 ml). The solvent was then removed

and the crude product was purified by column chromatography over silica (dichloromethane/heptane; 60:40; then dichloromethane 100). The first fraction afforded the unreacted starting material **6** (50 mg, 22%). The second purple band was collected and the solvent was removed to give 5-(*p*-amino-phenyl)-10,15,20-tris-pentafluorophenylporphyrin **7** (167.0 mg, 75%) as a purple microcrystalline solid. (HRMS-ESI Found: $[M + H]^+$ 900.1294. $C_{44}H_{17}F_{15}N_5$ requires 900.1239; and Found: $[2 M + Na]^+$ 1821.2321. $C_{88}H_{32}F_{30}N_{10}Na$ requires 1821.2225). λ_{max} (CH_2Cl_2) (log ε): 308 (4.16), 368sh (4.52), 417 (5.26), 513 (4.20), 549 (3.61), 588 (3.75), 644 (3.07) nm. ^{1}H NMR (300 MHz, $CDCl_3$): δ -2.80 (2 H, inner NH); 5.85 (2 H, br s, NH_2); 7.30 (2 H, d, *J* 7.8 Hz, aryl H); 8.08 (2 H, d, J 8.4 Hz, aryl H); 8.82 (2 H, d, *J* 4.5 Hz, *β-pyrrolic* H); 8.87 (2 H, d, J 4.8 Hz, *β-pyrrolic* H); 8.89 (2 H, d, *J* 5.4 Hz, *β-pyrrolic* H); 9.06 (2 H, d, J 4.8 Hz, *β-pyrrolic* H). Mass spectrum (MALDI-TOF) (m/z): 899.2 ($M^{+\bullet}$ requires 899.1).

2. Cyclic Voltammetry Simulations

Simulated cyclic voltammograms were calculated using Digisim 3.03 assuming the following set of reactions[S5]:

$$A + e^- \rightleftharpoons B \quad E_1^0$$
$$B + e^- \rightleftharpoons C \quad E_2^0$$

These calculations were carried out for different ΔE^0 values and as it can be observed in Figure S-1, the peak potential differences range from approximately 105 to 30 mV. The particular case treated in the manuscript can be describe by the case *b*, in which a peak potential difference of 60 mV is observed and a small ΔE^0 value is then obtained. The value employed in equation 1 for the calculation of the diffusion coefficient can be extracted from the current function of case *c* and corresponds to 0.884.

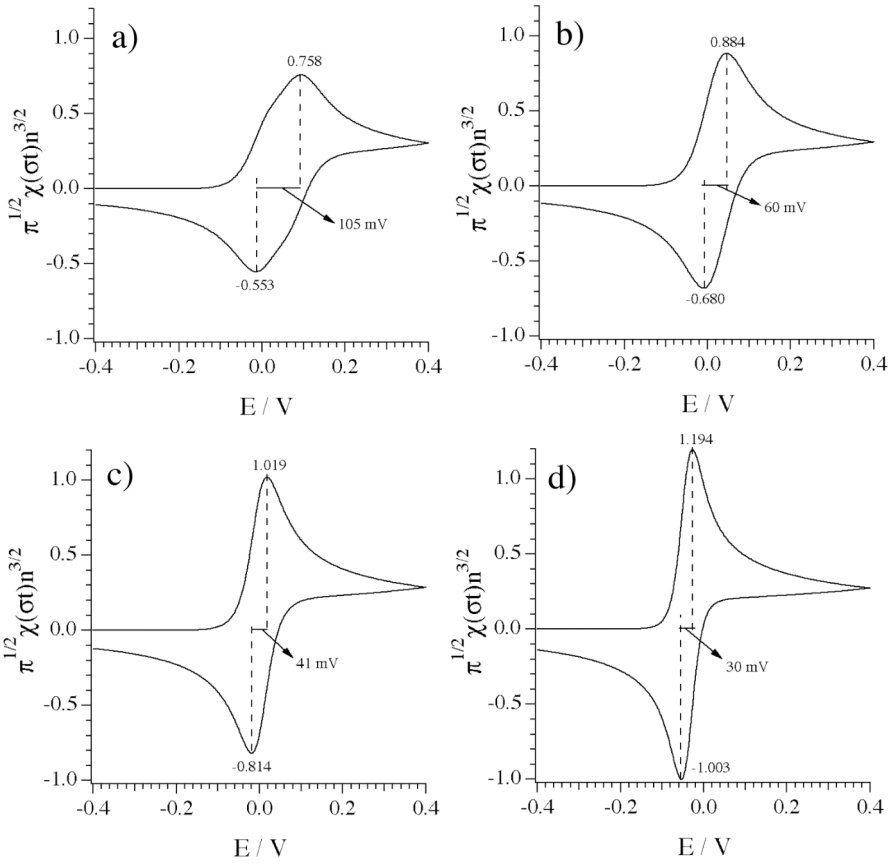

Figure S1. Simulated cyclic voltammograms for standard potential differences, $\Delta E^0 = \left(E_2^0 - E_1^0\right)$ of a) –80, b) –38, c) 0 and d) 80 mV. The peak potential differences are indicated for each case.

To determine the diffusion data, the scan rate dependence of cyclic voltammograms were fiited directly to a Digisim simulation. Smaller concentrations than reported in Figure 2 were used as we have observed that the diffusion coefficient values obtained from scan rate analysis were increasing as the concentration of H_2FAP decreases, hinting that some aggregation of the poprphyrin may take place perhaps by hydrogen binding between the protonated inner iminogroups and the free outer amino group.

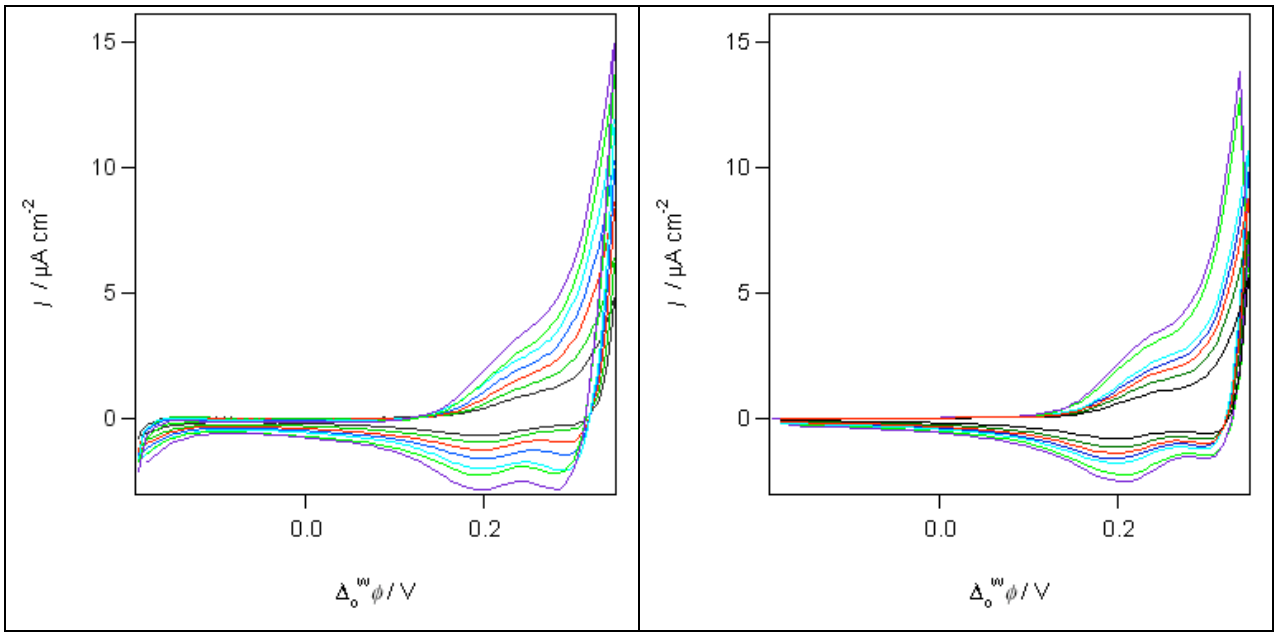

Figure S2. Cyclic voltammograms in the presence of H_2FAP in DCE . Left experimental results : (Scheme 3: x = 20 μM, y = 0, z = 100 mM). Scan rate: 10, 20, 30, 40, 50, 80, and 100 mV s^{-1} from inner to outer, Right : Digisim simulation with the following fixed parameters : Standard ion transfer potential difference (E_2–E_1) = 40 mV, Peak difference = 60 mV, Diffusion Coefficient of protons = 9.0 x 10^{-5} $cm^2 \cdot s^{-1}$, Value obtained for diffusion coefficient of H_2FAP = 8.0 x 10^{-7} $cm^2 \cdot s^{-1}$

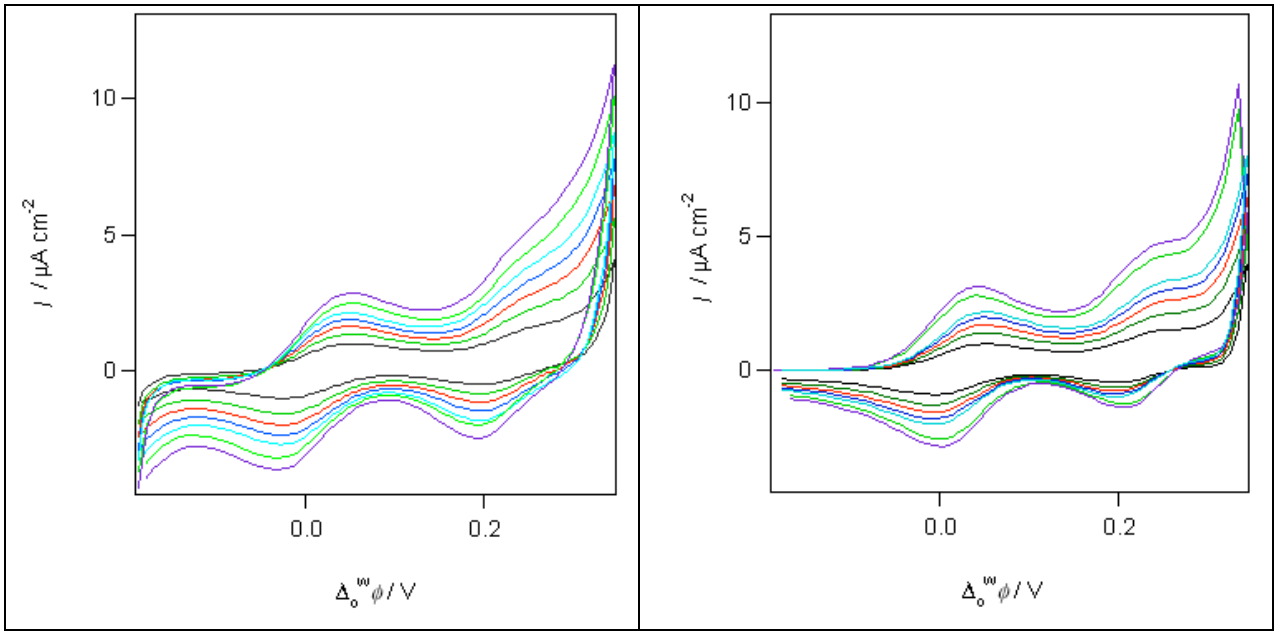

Figure S3. Cyclic voltammograms in the presence of H_2TPP in DCE . Left experimental results : (Scheme 3: x = 20 μM, y = 0, z = 100 mM).Scan rate: 10, 20, 30, 40, 50, 80, and 100 mV s^{-1} from inner to outer, Right : Digisim simulation with the following fixed parameters : Standard ion transfer potential difference (E_2–E_1) = 200 mV. Diffusion Coefficient of protons = 9.0 x 10^{-5} $cm^2 \cdot s^{-1}$. Value obtained for the diffusion coefficient of H_2TPP = 3.4 x 10^{-6} $cm^2 \cdot s^{-1}$

3. Electrochemistry of H_2FAP

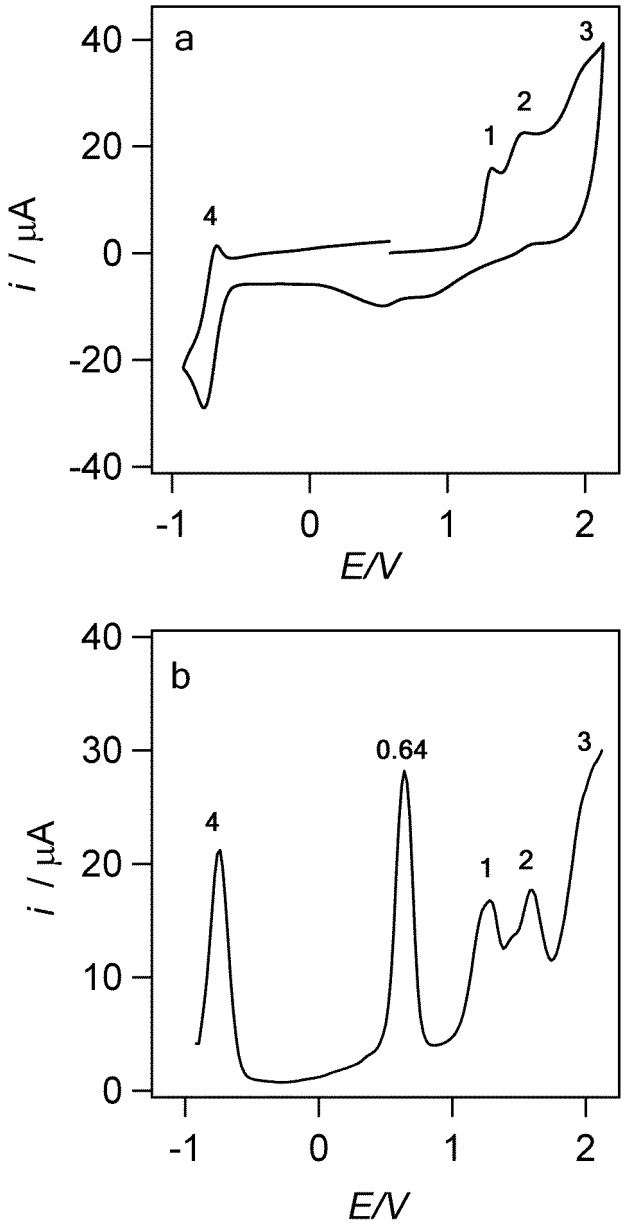

Figure S4. Cyclic voltammograms at a scan rate of 0.1 V s^{-1} (a) and square wave voltammograms with a frequency 8 Hz, potential step 0.01 V and potential amplitude 0.02 V.

Electrochemical measurements of H_2FAP were performed on a potentiostat (PGSTAT 30, Eco-Chemie, Netherlands) in a three-electrode configuration, using a 3 mm-in-diameter Pt electrode, a Pt wire and a Ag wire as the working, counter and quasi-reference electrode, respectively. The concentration of H_2FAP is 1 mM. The supporting electrolyte used was

tetrabutylammonium hexafluorophosphate (TBAPF6, ≥99%) 0.1 M. The solution was bubbled by nitrogen before measurements. The potential scale was calibrated to the normal hydrogen electrode by using ferrocene as the internal reference ($E^0_{Fc^+/Fc}$ = 0.64 V).

The waves 1 (1.30 V) and 2 (1.57 V) are assigned to the first ring oxidation, the second ring oxidation, respectively. The wave 3 can be ascribed to the amine oxidation. The wave 4 (–0.759 V) is assigned to the first ring reduction.

4. Cartesian coordinates of the M05-2X/cc-pVDZ optimized geometries

H_2FAP

C	-5.565592	1.137171	1.207519
C	-4.894133	0.627246	0.098088
C	-5.669526	0.191384	-0.974532
C	-7.056026	0.254526	-0.947071
C	-7.696092	0.769792	0.172012
C	-6.950437	1.215423	1.254727
C	-3.405775	0.563688	0.063163
C	-2.796469	-0.694761	0.090042
N	-1.459204	-0.934156	0.015000
C	-1.336805	-2.281709	0.041005
C	-2.640280	-2.935280	0.158446
C	-3.553374	-1.941522	0.191443
C	-0.129677	-3.000681	-0.028347
C	-0.204341	-4.488372	-0.055194
C	-0.718854	-5.161575	-1.161617
C	-0.809803	-6.545979	-1.200412
C	-0.369735	-7.289725	-0.113989
C	0.153358	-6.648290	1.000613
C	0.228174	-5.262271	1.019735
C	1.146323	-2.436261	-0.074064
C	2.396402	-3.141112	-0.148398
C	3.398256	-2.214739	-0.142790
C	2.793932	-0.912897	-0.068877
N	1.440682	-1.104618	-0.039409
C	3.455625	0.312356	-0.024785
C	2.842268	1.580918	0.011292
N	1.511313	1.817529	-0.051104
C	1.386249	3.173136	0.000323
C	2.689926	3.819061	0.125201
C	3.602520	2.820865	0.128516
C	0.183206	3.898646	-0.041900
C	0.250210	5.386275	-0.076972
C	0.826910	6.052769	-1.164585
C	0.891661	7.439055	-1.206658
C	0.380795	8.211273	-0.151847
C	-0.196308	7.546506	0.941339
C	-0.260303	6.159513	0.971900
N	0.495847	9.593510	-0.162904

C	4.944770	0.257928	0.000140
C	5.630691	-0.228002	1.111348
C	7.017175	-0.283834	1.150231
C	7.748765	0.160408	0.057572
C	7.093702	0.652679	-1.063299
C	5.706498	0.694139	-1.081950
C	-1.096543	3.322926	-0.056834
N	-1.391701	1.990250	0.032514
C	-2.740065	1.797855	-0.002426
C	-3.346843	3.088124	-0.130765
C	-2.343070	4.018716	-0.171430
F	-0.448302	-8.615558	-0.140071
H	-0.701603	1.250330	0.094461
H	-2.817880	-4.002910	0.222748
H	-4.629783	-2.030886	0.287991
H	-4.412792	3.267164	-0.207031
H	-2.438458	5.091463	-0.287654
F	-5.085376	-0.308150	-2.062133
F	-7.775851	-0.165991	-1.984710
F	-9.022427	0.837049	0.205153
F	-7.564700	1.711299	2.326651
F	-4.875082	1.570642	2.261754
F	-1.146445	-4.473321	-2.218697
F	-1.311403	-7.162060	-2.268279
F	0.570788	-7.365719	2.041345
F	0.737749	-4.675572	2.102576
H	2.861375	4.884795	0.221344
H	4.679341	2.905511	0.225387
H	0.750590	-0.362113	-0.020757
H	4.464447	-2.400617	-0.194809
H	2.498045	-4.218577	-0.203615
F	4.954577	-0.658813	2.175766
F	7.646258	-0.755848	2.224092
F	9.076215	0.114145	0.082765
F	7.800186	1.072297	-2.110607
F	5.106532	1.173821	-2.170132
H	-0.704968	5.661805	1.832982
H	-0.586406	8.126320	1.777533
H	1.342541	7.934903	-2.065852
H	1.222825	5.470335	-1.995827
H	0.582710	10.006508	-1.081130
H	-0.177212	10.082187	0.410798

H_3FAP^+ (amino group protonated)

C	-2.315868	4.023439	-0.158933
C	-1.073556	3.314446	-0.053913
N	-1.380471	1.986493	0.021552
C	-2.733548	1.805439	-0.009677
C	-3.327732	3.102357	-0.126141
C	0.216972	3.862663	-0.044949
C	0.302671	5.348888	-0.081416
C	0.892860	5.995902	-1.177396
C	0.988476	7.382253	-1.224057
C	0.478687	8.106958	-0.154925
C	-0.115807	7.510389	0.946151
C	-0.198558	6.120290	0.973714
N	0.572765	9.587384	-0.197687
C	-3.410923	0.581221	0.059158

C	-2.807972	-0.682861	0.090720
N	-1.473705	-0.928226	0.012199
C	-1.361442	-2.278302	0.043806
C	-2.669163	-2.922825	0.169655
C	-3.574554	-1.923492	0.201714
C	-0.162213	-3.008864	-0.029671
C	1.119753	-2.457854	-0.076992
C	2.360131	-3.178426	-0.164147
C	3.372994	-2.265071	-0.154999
C	2.783286	-0.956930	-0.066085
N	1.429933	-1.129924	-0.031137
C	3.463275	0.261193	-0.017101
C	4.951411	0.188336	0.007410
C	5.628084	-0.325677	1.111918
C	7.013403	-0.403818	1.150637
C	7.752379	0.046481	0.064453
C	7.105762	0.566964	-1.049490
C	5.719675	0.630095	-1.067706
F	4.940904	-0.761139	2.166983
F	7.631850	-0.901193	2.215920
F	9.076051	-0.018368	0.089846
F	7.817158	0.995691	-2.087452
F	5.124604	1.140898	-2.146011
C	-4.898541	0.656022	0.098306
C	-5.562563	1.180963	1.205082
C	-6.946598	1.264575	1.257160
C	-7.697958	0.809145	0.181565
C	-7.064367	0.279236	-0.935404
C	-5.678326	0.210337	-0.967174
F	-4.862455	1.627051	2.249133
F	-5.095796	-0.302878	-2.048930
F	-7.787531	-0.148536	-1.964289
F	-9.020833	0.883309	0.218556
F	-7.552376	1.776884	2.323918
C	-0.252105	-4.495894	-0.059559
C	-0.781726	-5.158496	-1.165000
C	-0.886449	-6.541534	-1.206717
C	-0.446975	-7.291726	-0.123343
C	0.090110	-6.658963	0.990657
C	0.180786	-5.274188	1.011737
F	-1.209714	-4.457810	-2.213940
F	-1.400684	-7.147968	-2.270954
F	-0.539724	-8.613387	-0.151689
F	0.506509	-7.380971	2.025348
F	0.704524	-4.689786	2.089272
C	2.861695	1.532054	0.018740
N	1.531187	1.786114	-0.045079
C	1.421139	3.138672	-0.007950
C	2.733310	3.772990	0.110338
C	3.634492	2.765145	0.126422
H	-0.699306	1.236941	0.074714
H	-2.852549	-3.988792	0.241039
H	-4.650921	-2.004339	0.303805
H	-4.392102	3.291703	-0.198200
H	-2.417570	5.096267	-0.269885
H	2.932978	4.834477	0.201796
H	4.712025	2.837905	0.223428
H	0.748292	-0.380725	0.001444
H	4.436383	-2.463302	-0.216230
H	2.447009	-4.256484	-0.231722

H	-0.647055	5.623196	1.831556
H	-0.501150	8.099386	1.778987
H	1.445374	7.873327	-2.083154
H	1.275875	5.398788	-2.002718
H	0.208136	10.000613	0.666814
H	1.544552	9.902711	-0.302728
H	0.033239	9.980082	-0.978847

H_3FAP^+

C	5.559415	1.403652	-1.034172
C	4.872964	0.651807	-0.080823
C	5.627998	-0.000241	0.893712
C	7.013360	0.078823	0.914409
C	7.669966	0.830077	-0.052963
C	6.943008	1.498228	-1.031334
C	3.387718	0.576992	-0.098912
C	2.775556	-0.656089	-0.287857
N	1.432339	-0.920207	-0.160356
C	1.332659	-2.261384	-0.250646
C	2.629798	-2.886694	-0.525763
C	3.528406	-1.884320	-0.550621
C	0.154243	-3.021533	-0.040078
C	0.253334	-4.505547	-0.023014
C	0.978424	-5.171672	0.964541
C	1.076490	-6.555266	0.988922
C	0.431755	-7.303071	0.010501
C	-0.301531	-6.667564	-0.984218
C	-0.380843	-5.282281	-0.991610
C	-1.102330	-2.471671	0.173588
C	-2.327850	-3.163161	0.489902
C	-3.325418	-2.241809	0.538666
C	-2.757851	-0.945293	0.248475
N	-1.406939	-1.141334	0.079800
C	-3.457303	0.242867	0.102787
C	-2.875323	1.516741	-0.112611
N	-1.570381	1.866206	0.148030
C	-1.382761	3.209333	-0.155341
C	-2.604882	3.684506	-0.693141
C	-3.519360	2.652890	-0.659400
C	-0.191087	3.941560	0.016769
C	-0.271217	5.404015	0.000736
C	-1.265138	6.084201	0.732514
C	-1.345034	7.462272	0.727893
C	-0.437200	8.232103	-0.032070
C	0.555364	7.555638	-0.775414
C	0.637010	6.177959	-0.748799
N	-0.530497	9.584189	-0.066557
C	-4.941214	0.192050	0.102276
C	-5.650600	-0.542649	-0.848807
C	-7.037916	-0.572748	-0.858783
C	-7.744380	0.150414	0.094980
C	-7.065158	0.896096	1.051726
C	-5.678605	0.908745	1.045953
C	1.070386	3.333638	0.185589
N	1.386027	2.019110	-0.084631
C	2.712676	1.801022	0.130367
C	3.273226	3.017737	0.607029
C	2.265073	3.953140	0.650195
F	0.513968	-8.623323	0.027727

H	0.805867	1.330946	-0.544585
H	2.806900	-3.944869	-0.680320
H	4.595210	-1.949458	-0.731594
H	4.304299	3.145901	0.915209
H	2.325553	4.973270	1.010459
F	5.020042	-0.718274	1.835868
F	7.710207	-0.551968	1.850409
F	8.990183	0.910099	-0.042336
F	7.573632	2.214710	-1.953214
F	4.879207	2.051745	-1.980399
F	1.601916	-4.472465	1.911853
F	1.772474	-7.166832	1.938703
F	-0.916850	-7.383532	-1.916508
F	-1.090748	-4.691349	-1.953322
H	-2.745204	4.676062	-1.107728
H	-4.537268	2.663657	-1.031802
H	-0.700552	-0.484549	-0.227366
H	-4.370524	-2.415531	0.767329
H	-2.406067	-4.229267	0.668761
F	-4.995310	-1.233716	-1.780275
F	-7.690293	-1.277182	-1.773360
F	-9.066355	0.130392	0.091998
F	-7.742983	1.582757	1.961823
F	-5.044818	1.626273	1.973387
H	1.394252	5.679743	-1.352413
H	1.250374	8.129013	-1.386976
H	-2.106601	7.963865	1.323082
H	-1.960768	5.514457	1.346964
H	-1.165696	10.063850	0.549764
H	0.192779	10.130823	-0.504249
H	-0.999790	1.379230	0.829375

H_4FAP^{2+}

C	2.282556	3.652246	1.116961
C	1.194771	3.214356	0.334053
N	1.495100	1.934442	-0.099348
C	2.767146	1.604143	0.301315
C	3.257398	2.663087	1.086941
C	0.000018	3.921024	0.000004
C	0.000017	5.351144	-0.000039
C	-1.161427	6.091995	0.365236
C	-1.162999	7.461313	0.380329
C	0.000019	8.188397	-0.000181
C	1.163034	7.461275	-0.380624
C	1.161462	6.091955	-0.365392
N	0.000014	9.524137	-0.000251
C	3.447366	0.394533	-0.061962
C	2.801464	-0.791866	-0.340628
N	1.455818	-1.056818	-0.074441
C	1.196328	-2.386664	-0.310883
C	2.387306	-2.960527	-0.874256
C	3.354631	-2.000663	-0.888947
C	0.000030	-3.050328	-0.000019
C	-1.196321	-2.386626	0.310780
C	-2.387364	-2.960628	0.873947
C	-3.354726	-2.000814	0.888606
C	-2.801490	-0.791929	0.340501
N	-1.455951	-1.056924	0.074308
C	-3.447410	0.394526	0.061999

C	-4.922398	0.442085	0.088646
C	-5.702703	-0.466090	-0.634770
C	-7.087722	-0.402604	-0.624313
C	-7.721278	0.584500	0.124853
C	-6.971648	1.503637	0.854543
C	-5.589237	1.426119	0.827152
C	4.922375	0.442093	-0.088557
C	5.589236	1.426165	-0.826981
C	6.971648	1.503676	-0.854325
C	7.721250	0.584500	-0.124652
C	7.087664	-0.402635	0.624434
C	5.702641	-0.466127	0.634821
C	0.000022	-4.531799	-0.000014
C	0.894412	-5.255132	0.792602
C	0.905758	-6.641547	0.798218
C	0.000056	-7.334051	-0.000064
C	-0.905668	-6.641542	-0.798318
C	-0.894356	-5.255127	-0.792656
C	-2.767184	1.604161	-0.301167
N	-1.495093	1.934428	0.099475
C	-1.194754	3.214336	-0.333988
C	-2.282521	3.652221	-1.116887
C	-3.257390	2.663077	-1.086844
F	0.000068	-8.651040	-0.000068
H	1.046240	1.509678	-0.900970
H	2.463705	-3.979177	-1.238285
H	4.363551	-2.092736	-1.277073
H	4.209032	2.661428	1.607404
H	2.305741	4.578527	1.680514
F	5.115889	-1.407405	1.371989
F	7.802952	-1.266599	1.322992
F	9.035060	0.650077	-0.143233
F	7.579406	2.435195	-1.569479
F	4.884902	2.304672	-1.540877
F	1.764196	-4.602906	1.564697
F	1.763604	-7.303925	1.555418
F	-1.763506	-7.303921	-1.555530
F	-1.764161	-4.602898	-1.564720
H	-2.305692	4.578496	-1.680452
H	-4.209015	2.661415	-1.607320
H	-0.956680	-0.545847	-0.643329
H	-4.363756	-2.092942	1.276432
H	-2.463744	-3.979343	1.237795
F	-5.116001	-1.407299	-1.372033
F	-7.803047	-1.266510	-1.322891
F	-9.035075	0.650062	0.143503
F	-7.579386	2.435101	1.569779
F	-4.884878	2.304577	1.541074
H	2.048159	5.559869	-0.705010
H	2.048628	8.003629	-0.707468
H	-2.048603	8.003699	0.707094
H	-2.048127	5.559940	0.704892
H	-0.824733	10.045715	0.256639
H	0.824756	10.045697	-0.257188
H	-1.046342	1.509873	0.901274
H	0.957389	-0.546586	0.644425

[H_3FAP··O_2]$^+$

N	-1.466541	-0.939619	0.081956
C	-1.380944	-2.279495	0.181711
C	-2.680203	-2.888744	0.484645
C	-3.567148	-1.876415	0.514853
C	-2.805428	-0.658710	0.227189
C	-0.212266	-3.052011	-0.044099
C	-0.323453	-4.534995	-0.048704
C	0.323038	-5.311639	0.911789
C	0.231110	-6.696189	0.915034
C	-0.527997	-7.331434	-0.060173
C	-1.186202	-6.583850	-1.029725
C	-1.074893	-5.201100	-1.016399
F	1.057916	-4.721846	1.855474
F	0.858941	-7.411612	1.839528
F	-0.622586	-8.651019	-0.067123
F	-1.907402	-7.194829	-1.960816
F	-1.711927	-4.502392	-1.955105
C	-3.406611	0.576211	0.026438
C	-4.890966	0.666688	0.020024
C	-5.662655	0.005116	-0.934891
C	-7.047094	0.101545	-0.945374
C	-7.685933	0.879407	0.012770
C	-6.942143	1.557445	0.971469
C	-5.559880	1.445877	0.963916
F	-5.072837	-0.738411	-1.868624
F	-7.759728	-0.538152	-1.863249
F	-9.005098	0.976056	0.011644
F	-7.555561	2.299470	1.884755
F	-4.863392	2.104293	1.890953
C	-2.721839	1.791150	-0.231150
C	-3.274241	2.995391	-0.745897
C	-2.263530	3.928696	-0.800825
C	-1.077466	3.318174	-0.306833
N	-1.397091	2.010335	-0.009287
C	0.186420	3.920164	-0.133542
C	1.370135	3.173575	0.043059
C	2.585536	3.623512	0.614961
C	3.489862	2.582416	0.575154
C	2.843893	1.467379	-0.011189
N	1.553837	1.839726	-0.295107
C	3.414906	0.187454	-0.233381
C	2.706041	-0.993419	-0.377306
N	1.353737	-1.179949	-0.204445
C	1.042583	-2.510102	-0.281272
C	2.262991	-3.211018	-0.600965
C	3.264704	-2.296165	-0.662218
C	0.278413	5.379114	-0.116300
C	-0.651050	6.163863	0.596516
C	-0.559625	7.540366	0.621578
C	0.466137	8.206448	-0.086550
C	1.396230	7.426592	-0.809144
C	1.305324	6.049859	-0.812530
N	0.566552	9.556831	-0.056270
C	4.897964	0.126271	-0.228309
C	5.642164	0.844248	-1.165682
C	7.028594	0.825131	-1.166743
C	7.700865	0.071949	-0.210954
C	6.987619	-0.652035	0.737108
C	5.600473	-0.615525	0.722362
F	5.014793	1.569028	-2.091750

F	7.712882	1.512695	-2.071360
F	9.022796	0.045928	-0.203279
F	7.633645	-1.362954	1.651341
F	4.938797	-1.306706	1.649406
O	0.490972	1.018998	2.436509
O	1.482459	0.378422	2.582079
H	2.334185	-4.279217	-0.770103
H	4.307850	-2.477328	-0.894155
H	4.500163	2.571741	0.967635
H	2.727275	4.604306	1.054244
H	-2.317277	4.938731	-1.189704
H	-4.301064	3.116358	-1.070765
H	-4.631567	-1.927743	0.713594
H	-2.866184	-3.943555	0.651359
H	2.017617	5.472762	-1.400165
H	2.182933	7.920376	-1.377555
H	-1.272051	8.121379	1.205202
H	-1.433083	5.673780	1.174489
H	-0.158658	10.112311	0.366528
H	1.240840	10.030508	-0.634185
H	-0.824606	1.353236	0.504191
H	0.650596	-0.518252	0.101779
H	0.970365	1.356868	-0.967710

[H_4FAP··O_2]$^{2+}$

C	-2.283756	-3.585043	1.025235
C	-1.198537	-3.163998	0.229436
N	-1.493259	-1.888423	-0.216610
C	-2.756139	-1.540848	0.193100
C	-3.250104	-2.587427	0.993171
C	-0.013828	-3.886186	-0.112027
C	-0.033499	-5.315228	-0.119155
C	1.122243	-6.074316	0.227341
C	1.105527	-7.443443	0.232315
C	-0.071691	-8.152006	-0.139627
C	-1.229753	-7.406736	-0.500138
C	-1.209421	-6.037895	-0.475235
N	-0.089521	-9.487437	-0.149809
C	-3.427288	-0.325962	-0.173807
C	-2.769746	0.854535	-0.447086
N	-1.423451	1.103457	-0.166027
C	-1.149091	2.431271	-0.395034
C	-2.326830	3.019341	-0.972064
C	-3.304313	2.069974	-0.999728
C	0.050564	3.079495	-0.066313
C	1.236154	2.399890	0.252605
C	2.432910	2.961247	0.817855
C	3.390833	1.992370	0.830372
C	2.825936	0.789932	0.278938
N	1.482491	1.068135	0.016959
C	3.463325	-0.397700	-0.013118
C	4.937909	-0.457753	0.011492
C	5.725997	0.449477	-0.704394
C	7.110349	0.371638	-0.697499
C	7.735241	-0.629407	0.040345
C	6.977614	-1.548121	0.762199
C	5.596042	-1.456153	0.738356
C	-4.902024	-0.363655	-0.206762

C	-5.571958	-1.348098	-0.942091
C	-6.954657	-1.417392	-0.974771
C	-7.701779	-0.489657	-0.253478
C	-7.065315	0.497901	0.492549
C	-5.680014	0.553282	0.508188
C	0.067450	4.560988	-0.061401
C	-0.824393	5.290813	0.727980
C	-0.822579	6.677261	0.737205
C	0.093805	7.363083	-0.054534
C	0.997120	6.663942	-0.849698
C	0.972675	5.277643	-0.847593
C	2.773289	-1.596927	-0.393018
N	1.499875	-1.920301	0.006368
C	1.187503	-3.190842	-0.444693
C	2.268252	-3.628245	-1.237428
C	3.252041	-2.647958	-1.196500
O	-1.072271	-0.508775	2.596013
O	-0.140106	-1.238246	2.708415
F	0.105964	8.680113	-0.051519
H	-1.036791	-1.465199	-1.014436
H	-2.388026	4.039304	-1.335441
H	-4.307199	2.173664	-1.400430
H	-4.197963	-2.571684	1.520313
H	-2.310785	-4.506884	1.595973
F	-5.091182	1.494833	1.243464
F	-7.778279	1.369733	1.183845
F	-9.015930	-0.547646	-0.276840
F	-7.565179	-2.349416	-1.687095
F	-4.870211	-2.234888	-1.648195
F	-1.705025	4.644845	1.493108
F	-1.678371	7.345965	1.491413
F	1.865063	7.320072	-1.600977
F	1.839955	4.619161	-1.617123
H	2.281196	-4.546351	-1.814627
H	4.201614	-2.646945	-1.720709
H	0.970707	0.555632	-0.690499
H	4.401673	2.074714	1.215681
H	2.519752	3.979238	1.181264
F	5.147497	1.403527	-1.431603
F	7.832973	1.234983	-1.389434
F	9.048407	-0.708829	0.055492
F	7.577264	-2.493071	1.466799
F	4.884011	-2.334677	1.444530
H	-2.092837	-5.491174	-0.799736
H	-2.126437	-7.934958	-0.819772
H	1.987446	-8.000195	0.544459
H	2.019796	-5.556638	0.560487
H	0.731712	-10.022047	0.091203
H	-0.923987	-9.995906	-0.401414
H	1.063680	-1.515950	0.826335
H	-0.956504	0.598648	0.578055

Table S1: Computed absolute Energies (in a.u.) used in Schemes 3 and 4

M05-2X/cc-pVDZ geometries	RI-TRIM-MP2/cc-pVDZ
$[H3FAP...O_2]^+$ triplet	-3598.915479
$[H4FAP…O_2]^{2+}$ triplet	-3599.204071
O_2 triplet	-149.970955
H_3FAP^+	-3448.938524

H_4FAP^{2+}	-3449.225698

	M052X-cc-pVDZ	zero-point energy
H_3FAP^+(ring protonation)	-3457.986627	0.535926
H_3FAP^+(amino group protonation)	-3457.939128	0.53653
H_4FAP^{2+}	-3458.277874	0.549399

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