Supporting Information

Noncovalent Binding between Fullerenes and Protonated Porphyrins in the Gas Phase

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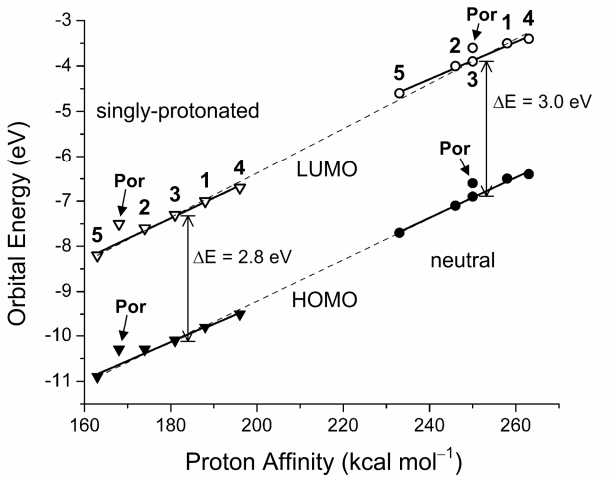

Figure S1. Energy levels of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of porphyrins as a function of proton affinity of porphine nitrogens. Both HOMO and LUMO energies increase linearly with increasing proton affinity: The slopes (in units of eV/eV) of HOMO and LUMO energies are 0.959 and 1.045 for neutral porphyrins, respectively, and

1.053 and 1.139 for singly-protonated porphyrins, respectively. Orbital energies of unsubstituted porphine (**por**) deviate from the linearity established by meso-substituted porphyrins.

Table S1. Total Energy (*E*, in hartree) and Zero-Point Energy (ZPE, in kcal mol^{-1}) of Neutral and Protonated Porphyrins[a,b]

	Neutral (P)		$[P + H]^+$		$[P + 2H]^{2+}$		$[P + 3H]^{3+}$	
	E	ZPE	*E*	ZPE	*E*	ZPE	*E*	ZPE
1	–1890.807687	381.6	–1891.231343	389.6	–1891.542754	396.8		
2	–1954.375780	353.1	–1954.779128	360.6 (**po**^{1})	–1955.067841	367.5 (**po**^{2})	–1955.308219	375.7 (**po**^{2}**py**^{1})
			–1954.763884	361.3 (**py**^{1})	–1955.094348	369.1 (**po**^{1}**py**^{1})	–1955.354893	377.2 (**po**^{1}**py**^{2})
					–1955.105895	370.1 (**py**^{2})	–1955.380586	378.3 (**py**^{3})
3	–2637.089050	417.7	–2637.499431	425.4	–2637.799507	432.5		
4	–3133.031072		–3133.461812		–3133.785433			
5	–3857.085775	282.6	–3857.472015	291.6	–3857.742482	298.6		
Por	–977.745679	183.4	–978.155837	191.0	–978.434007	197.9		

[a] At the Hartree–Fock level with a 3-21G basis set.

[b] Zero-point energies are scaled by a factor of 0.9085.

Table S2. Change of Energy (Δ*E*), Zero-Point Energy (ΔZPE) and Enthalpy (Δ*H*)[a] for the Protonation Reaction (in kcal mol^{-1})

	$P + H^+ \rightarrow [P + H]^+$			$[P + H]^+ \rightarrow [P + 2H]^{2+}$			$[P + 2H]^{2+} \rightarrow [P + 3H]^{3+}$		
	Δ*E*	ΔZPE	Δ*H*	Δ*E*	ΔZPE	Δ*H*	Δ*E*	ΔZPE	Δ*H*
1	–265.8	8.0	–257.8	–195.4	7.2	–188.2			
2	–253.1	7.5	–245.6 (**2** →**po**^{1})	–181.2	6.9	–174.3 (**po**^{1} → **po**^{2})	–150.8	8.2	–142.6 (**po**^{2} → **po**^{2}**py**^{1})
	–243.5	8.2	–235.3 (**2** →**py**^{1})	–197.8	8.5	–189.3 (**po**^{1} → **po**^{1}**py**^{1})	–134.2	6.6	–127.6 (**po**^{1}**py**^{1} → **po**^{2}**py**^{1})
				–207.4	7.8	–199.6 (**py**^{1} → **po**^{1}**py**^{1})	–163.5	8.1	–155.4 (**po**^{1}**py**^{1} → **po**^{1}**py**^{2})
				–214.6	8.8	–205.8 (**py**^{1} → **py**^{2})	–156.2	7.1	–149.1 (**py**^{2} → **po**^{1}**py**^{2})
							–172.4	8.2	–164.2 (**py**^{2} → **py**^{3})
3	–257.5	7.7	–249.8	–188.3	7.1	–181.2			
4	–270.3	7.7[b]	–262.6	–203.1	7.0[b]	–196.1			
5	–242.4	9.0	–233.4	–169.7	7.0	–162.7			
Por	–257.4	7.6	–249.8	–174.6	6.9	–167.7			

[a] $\Delta H = \Delta E + \Delta\text{ZPE}$.

[b] ΔZPE of porphyrin **4** was estimated from the average value of ΔZPE of porphyrins **1**, **2**, **3**, and **por**.

Table S3. Distance (Å) between Protonated Porphyrin and Fullerene, Dihedral Angles of Meso-Substituents, and Out-of-Plane Angle of Porphine Ring

	d (Å)[a]	dihedral angle of substituent (degree)		angle between the opposite pyrrole planes (degree)	
		∠C1–C2–C3–C4	∠C5–C6–C7–C8	$(180 - \theta_a)/2$	$(180 - \theta_b)/2$
[**1** + H]$^+$		117.4	124.9	16.8	15.2
[**1** + H]$^+$·C_{60}	2.79	117.3	124.5	10.5	17.9
[**1** + H]$^+$·C_{70} (end-on)	2.76	118.3	123.5	9.4	19.9
[**1** + H]$^+$·C_{70} (side-on)	2.94	118.5	125.4	9.7	19.9
[**2** + H]$^+$		120.1	127.9	15.7	14.4
[**2** + H]$^+$·C_{60}	2.80	115.4	122.8	9.1	16.9
[**2** + H]$^+$·C_{70} (end-on)	2.76	115.2	122.5	7.6	16.7
[**2** + H]$^+$·C_{70} (side-on)	2.93	115.7	124.6	8.3	18.2
[**3** + H]$^+$		116.1	125.5	17.9	14.9
[**3** + H]$^+$·C_{60}	2.79	115.8	124.2	13.0	16.6
[**3** + H]$^+$·C_{70} (end-on)	2.77	116.4	124.4	11.4	17.0
[**3** + H]$^+$·C_{70} (side-on)	2.93	116.3	124.3	11.3	18.1
[**4** + H]$^+$		119.0	126.2	17.9	16.1
[**4** + H]$^+$·C_{60}	2.77	117.7	123.5	10.0	17.5
[**4** + H]$^+$·C_{70} (end-on)	2.78	120.7	129.6	12.2	20.0
[**4** + H]$^+$·C_{70} (side-on)	2.95	128.0	133.6	15.3	25.1
[**5** + H]$^+$		112.0	117.0	15.4	14.3
[**5** + H]$^+$·C_{60}	2.82	112.2	120.0	12.7	17.5
[**5** + H]$^+$·C_{70} (end-on)	2.81	112.3	119.1	12.8	15.0
[**5** + H]$^+$·C_{70} (side-on)	2.97	114.0	121.6	15.2	19.9
[**2** + 2H]$^{2+}$ (**py**^{2})		89.9	90.2	0.0	0.1
[**2** + 2H]$^{2+}$·C_{60}	2.73	77.8	53.4	0.1	7.4
[**2** + 2H]$^{2+}$·C_{70} (end-on)	2.73	90.6	54.1	6.4	1.4
[**2** + 2H]$^{2+}$·C_{70} (side-on)	2.89	126.3	107.5	10.1	4.6

[a] From the center of four porphine nitrogens to the closest 6:6 C–C bond of fullerene