Electronic Supplementary Information

New Electron Delocalization Tools to Describe the Aromaticity in Porphyrinoids

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Table S6: Aromaticity indices for several pathways of the nine porphyrinoid structures, calculated at the B3LYP, CAM-B3LYP and M06-2X/6-311G(d,p) levels of theory.

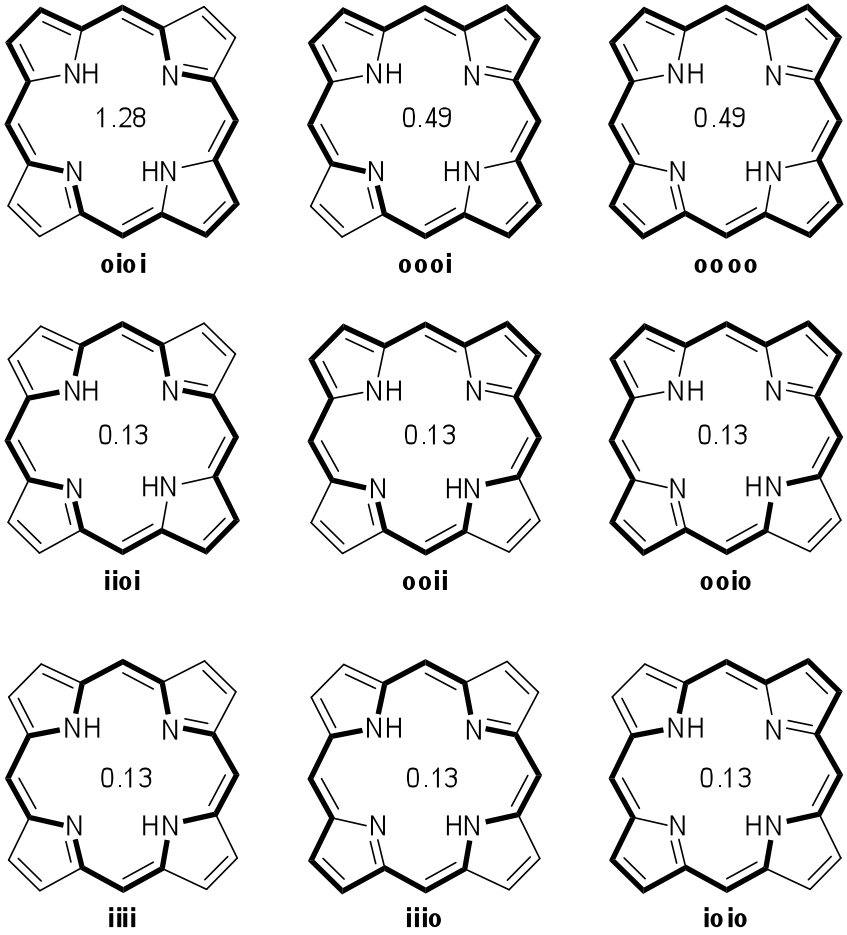

Figure S1. Schematic representation of the different pathways in **18H** and their respective AV1245 values.

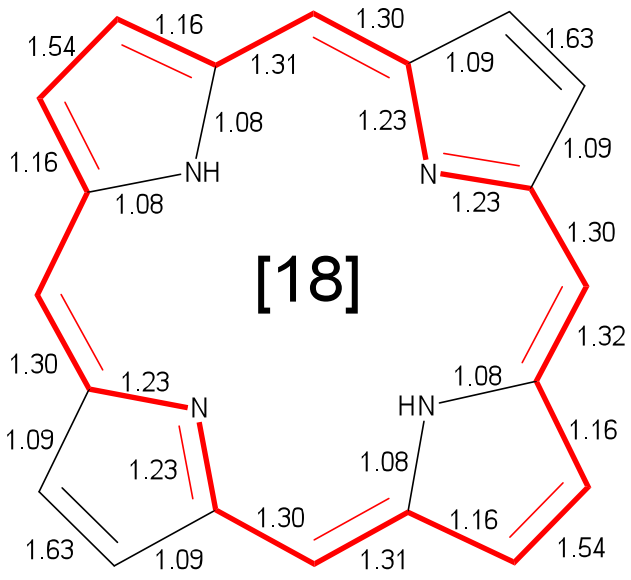

Figure S2. DI values for **18H** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold red bonds.

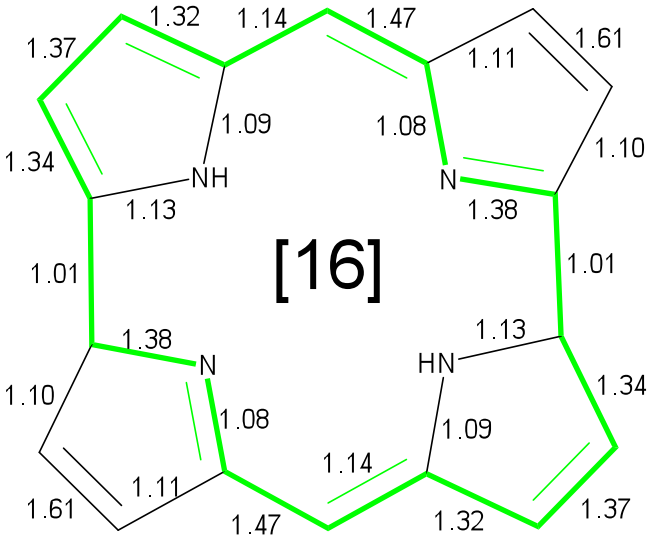

Figure S3. DI values for **16H** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold green bonds.

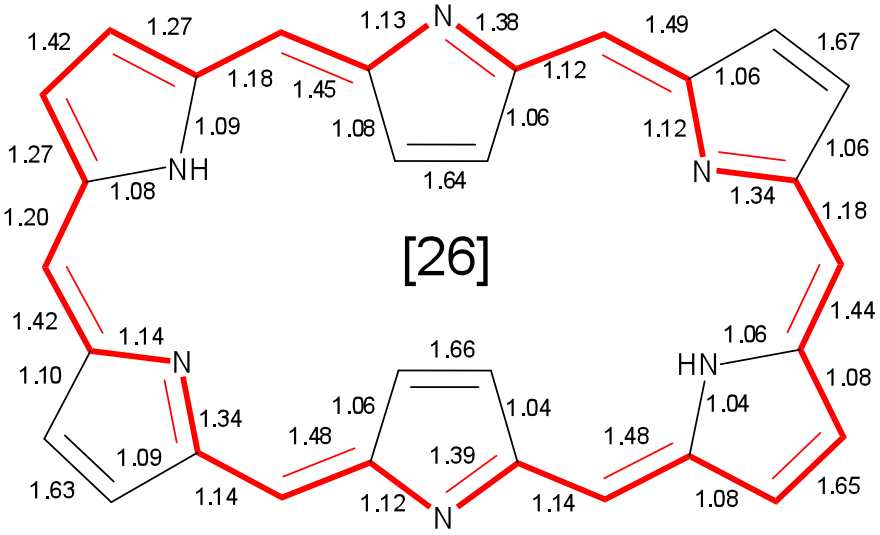

Figure S4. DI values for **26H** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold red bonds.

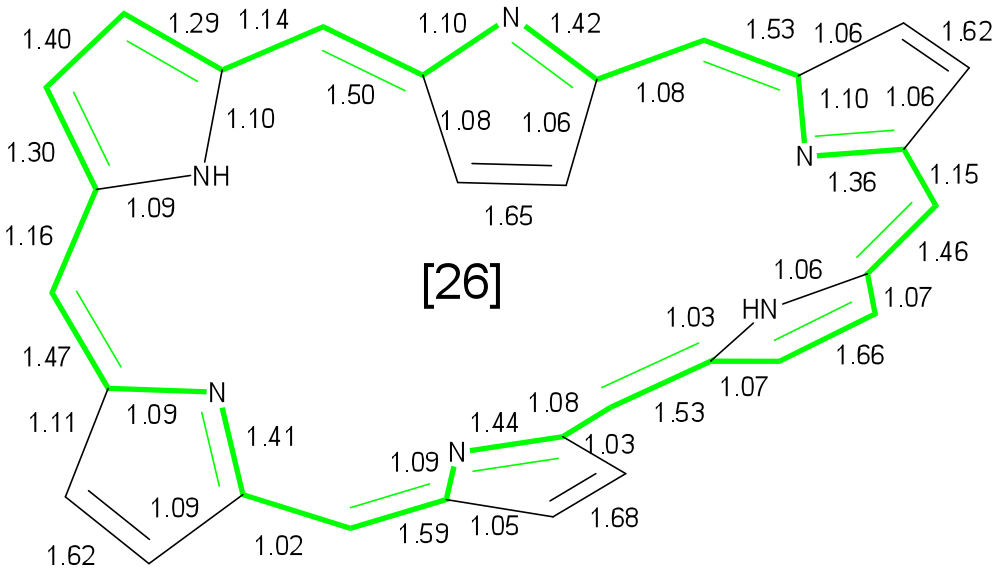

Figure S5. DI values for **26M** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold green bonds.

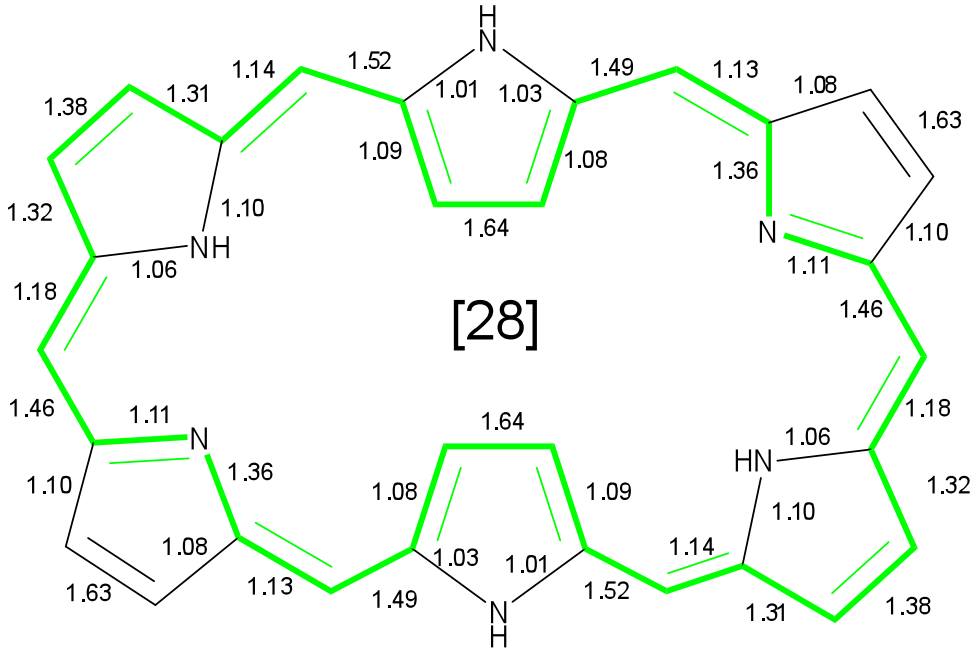

Figure S6. DI values for **28H** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold green bonds.

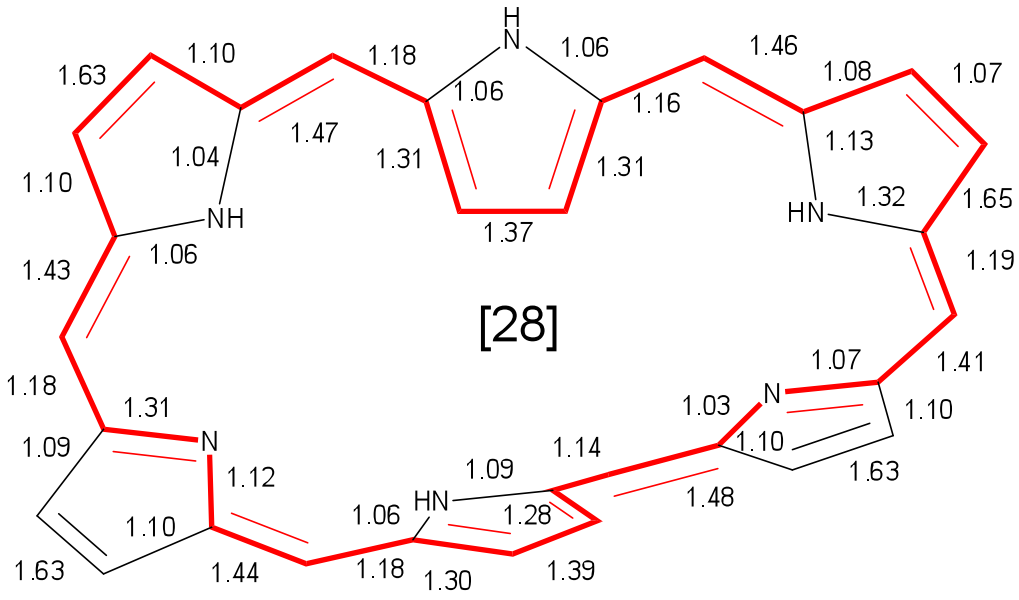

Figure S7. DI values for **28M** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold red bonds.

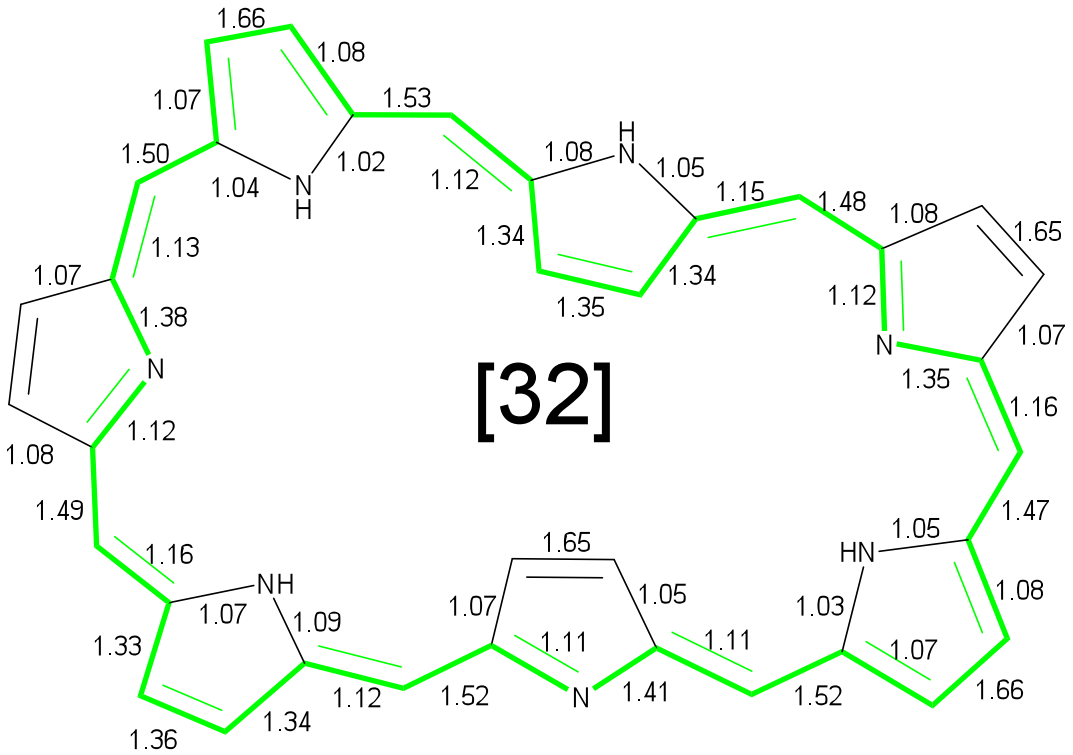

Figure S8. DI values for **32H** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold green bonds.

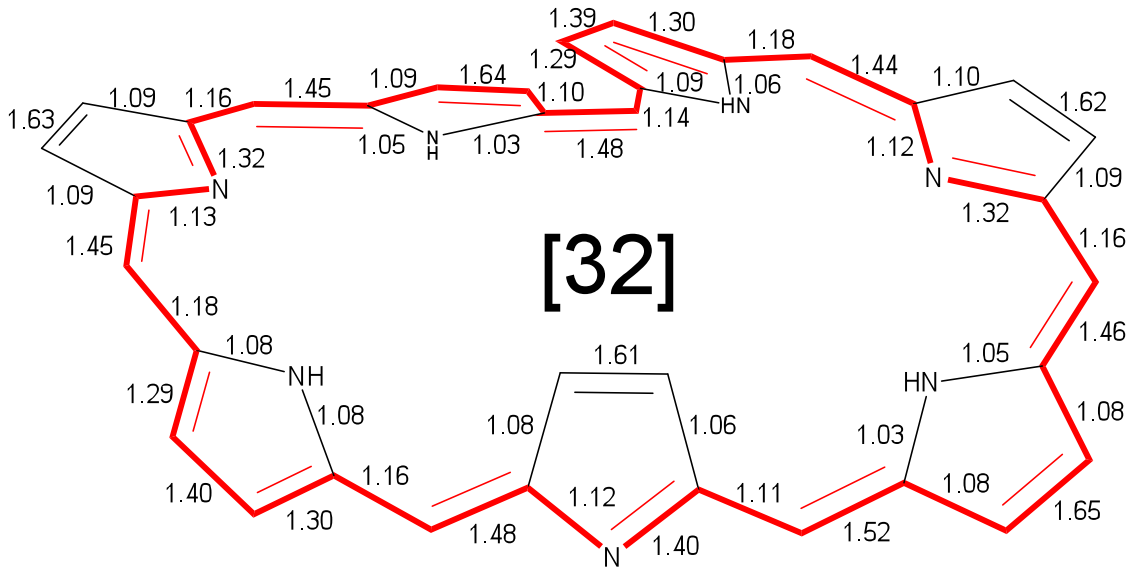

Figure S9. DI values for **32M** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold red bonds.

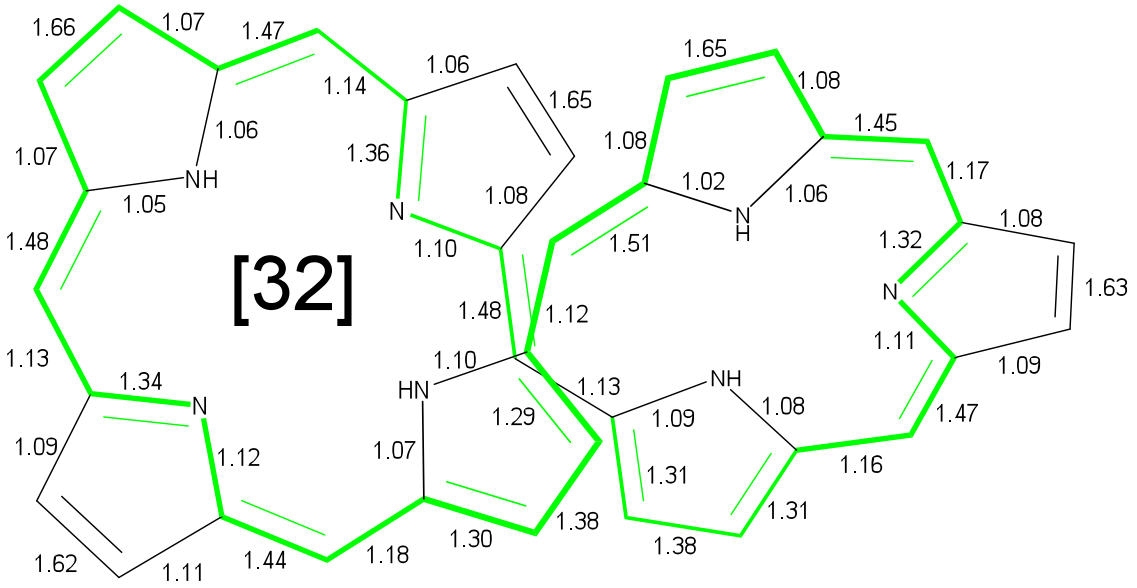

Figure S10. DI values for **32F** calculated at the CAM-B3LYP/6-311G(d,p) level of theory. The annulene-type conjugation pathway is depicted with bold green bonds.

Table S1. Aromaticity indices for the different pathways in **18H** calculated at the B3LYP/6-311G(d,p) level of theory.

Pathway[a)]	FLU	BOA	HOMA	BLA	AV1245	AV_{min}
oioi	0.010	0.000	0.850	0.000	2.19	1.31
oooi (2)	0.016	0.305	0.711	0.289	1.95	0.52
oooo	0.021	0.040	0.585	0.011	1.73	0.52
iioi (2)	0.008	0.362	0.894	0.316	1.59	0.18
ooii (4)	0.014	0.022	0.745	0.006	1.39	0.18
ooio (2)	0.020	0.367	0.611	0.272	1.20	0.18
iiii	0.006	0.000	0.944	0.000	0.93	0.18
iiio (2)	0.013	0.383	0.783	0.309	0.76	0.18
ioio	0.019	0.000	0.640	0.000	0.61	0.18

a) The number in brackets indicates the number of equivalent pathways.

Table S2. Aromaticity indices for the different pathway in **18H** calculated at the M06-2X /6-311G(d,p) level of theory.

Pathway[a)]	FLU	BOA	HOMA	BLA	AV1245	AV_{min}
oioi	0.011	0.000	0.859	0.000	2.13	1.25
oooi (2)	0.017	0.309	0.715	0.288	1.89	0.47
oooo	0.023	0.040	0.584	0.011	1.68	0.47
iioi (2)	0.009	0.366	0.909	0.314	1.55	0.12
ooii (4)	0.016	0.023	0.753	0.006	1.34	0.12
ooio (2)	0.022	0.371	0.614	0.271	1.15	0.12
iiii	0.007	0.000	0.964	0.000	0.90	0.12
iiio (2)	0.014	0.387	0.796	0.308	0.72	0.12
ioio	0.021	0.000	0.647	0.000	0.56	0.12

a) The number in brackets indicates the number of equivalent pathways.

Table S3. MCI values for the imine and pyrrole rings within **18H** at the B3LYP, CAM-B3LYP and M06-2X /6-311G(d,p) levels of theory.

Ring	B3LYP	CAM-B3LYP	M06-2X
Pyrrole	0.023	0.022	0.021
Imine	0.025	0.024	0.023

Table S4. Aromaticity indices for the annulene pathway of the nine porphyrinoid structures, calculated at the B3LYP/6-311G(d,p) level of theory. The numbers in parenthesis are the minimum value for BLA, BOA and FLU, and the maximum value for AV1245, AV_{min} and HOMA among all possible pathways.

Porphyrin	pathway	FLU	BOA	HOMA	BLA	AV1245	AV_{min}
16H	oioi	0.018	0.165 (0.000)	0.549	0.047 (0.000)	1.40 (1.84)	0.17
18H	oioi	0.010 (0.006)	0.000	0.850 (0.944)	0.000	2.19	1.31
26H	oiioii	0.008 (0.006)	0.000	0.887 (0.943)	0.000	2.30	1.25
26M	oiioii	0.020 (0.018)	0.259 (0.016)	0.655 (0.723)	0.063 (0.001)	1.33 (1.39)	0.13
28H	ooiooi	0.016 (0.013)	0.203 (0.000)	0.713 (0.811)	0.047 (0.000)	1.60 (1.70)	0.64
28M	oooioi	0.010 (0.009)	0.039 (0.002)	0.833 (0.886)	0.009 (0.000)	2.07	1.05
32H	ooioioi	0.016 (0.013)	0.219 (0.006)	0.723 (0.821)	0.051 (0.000)	1.56	0.76
32M	iooioio	0.010 (0.008)	0.038 (0.000)	0.849 (0.913)	0.009 (0.000)	2.08	1.14
32F	oioiooi	0.015 (0.011)	0.195 (0.001)	0.721 (0.830)	0.046 (0.001)	1.55 (1.62)	0.72

Table S5. Aromaticity indices for the annulene pathway of the nine porphyrinoid structures, calculated at the M06-2X/6-311G(d,p) level of theory. The numbers in parenthesis are the minimum value for BLA, BOA and FLU, and the maximum value for AV1245, AV_{min} and HOMA among all possible pathways.

Porphyrin	pathway	FLU	BOA	HOMA	BLA	AV1245	AV_{min}
16H	oioi	0.021	0.223 (0.000)	0.517	0.062 (0.000)	1.18 (1.56)	0.14
18H	oioi	0.011 (0.007)	0.000	0.859 (0.964)	0.000	2.13	1.25
26H	oiioii	0.017 (0.014)	0.228 (0.000)	0.743 (0.823)	0.055 (0.001)	1.70	0.66
26M	oiioii	0.027 (0.024)	0.328 (0.009)	0.546 (0.643)	0.080 (0.002)	1.06 (1.13)	0.13
28H	ooiooi	0.021 (0.017)	0.274 (0.000)	0.618 (0.772)	0.064 (0.000)	1.35 (1.48)	0.43
28M	oooioi	0.017 (0.012)	0.219 (0.001)	0.730 (0.841)	0.051 (0.001)	1.58 (1.60)	0.67
32H	ooioioi	0.023 (0.018)	0.308 (0.006)	0.588 (0.732)	0.072 (0.001)	1.19 (1.24)	0.46
32M	iooioio	0.019 (0.014)	0.241 (0.002)	0.678 (0.805)	0.057 (0.000)	1.48 (1.52)	0.58
32F	oioiooi	0.020 (0.015)	0.259 (0.004)	0.631 (0.784)	0.062 (0.000)	1.29 (1.40)	0.49

Table S6. Aromaticity indices for several pathways of the nine porphyrinoid structures, calculated at the B3LYP, CAM-B3LYP and M06-2X/6-311G(d,p) levels of theory.

Porphyrin	Pathway	B3LYP						CAM-B3LYP						M06-2X					
		FLU	BOA	HOMA	BLA	AV1245	AV_{min}	FLU	BOA	HOMA	BLA	AV1245	AV_{min}	FLU	BOA	HOMA	BLA	AV1245	AV_{min}
16H	oioi	0.018	0.165	0.549	0.047	1.40	0.17	0.021	0.227	0.547	0.063	1.19	0.13	0.021	0.223	0.517	0.062	1.18	0.14
	ioio	0.026	0.127	0.342	0.022	1.33	0.04	0.031	0.177	0.293	0.034	1.13	0.05	0.032	0.178	0.241	0.034	1.11	0.04
	iiii	0.021	0.000	0.532	0.000	0.78	0.13	0.025	0.000	0.505	0.000	0.62	0.07	0.026	0.000	0.478	0.000	0.61	0.08
	oooo	0.023	0.000	0.378	0.000	1.84	0.10	0.027	0.000	0.354	0.000	1.58	0.07	0.028	0.000	0.302	0.000	1.56	0.06
26H	oiioii	0.008	0.000	0.887	0.000	2.30	1.25	0.019	0.256	0.716	0.062	1.58	0.61	0.017	0.228	0.743	0.055	1.70	0.66
	iooioo	0.023	0.003	0.494	0.002	0.54	0.06	0.031	0.000	0.374	0.001	0.51	0.02	0.031	0.000	0.363	0.002	0.50	0.02
	iiiiii	0.006	0.001	0.943	0.000	1.59	0.22	0.017	0.002	0.787	0.001	1.06	0.12	0.015	0.001	0.819	0.001	1.15	0.10
	oooooo	0.024	0.000	0.475	0.000	1.21	0.06	0.032	0.055	0.340	0.012	1.02	0.01	0.032	0.049	0.328	0.010	1.04	0.02
	oioooo	0.020	0.225	0.575	0.175	1.49	0.06	0.029	0.215	0.420	0.183	1.14	0.14	0.029	0.216	0.420	0.182	1.19	0.02
	oiiiii	0.007	0.242	0.914	0.207	1.96	0.22	0.016	0.199	0.797	0.225	1.41	0.43	0.014	0.159	0.823	0.226	1.51	0.41
26M	oiioii	0.020	0.259	0.655	0.063	1.33	0.13	0.028	0.340	0.542	0.083	1.02	0.04	0.027	0.328	0.546	0.080	1.06	0.13
	iooioo	0.030	0.016	0.311	0.005	0.60	0.06	0.036	0.011	0.231	0.004	0.56	0.03	0.037	0.009	0.200	0.003	0.55	0.04
	iiiiii	0.019	0.033	0.716	0.008	0.81	0.13	0.026	0.027	0.616	0.007	0.61	0.04	0.025	0.017	0.628	0.005	0.63	0.13
	oooooo	0.031	0.036	0.285	0.008	1.10	0.02	0.037	0.061	0.193	0.013	0.97	0.03	0.038	0.060	0.158	0.013	0.97	0.04
	ooiooo	0.028	0.305	0.374	0.166	1.17	0.08	0.034	0.350	0.281	0.155	1.01	0.03	0.034	0.348	0.254	0.155	1.01	0.05
	iiioii	0.021	0.384	0.646	0.182	1.04	0.13	0.029	0.424	0.522	0.172	0.74	0.04	0.028	0.412	0.529	0.175	0.78	0.13
28H	ooiooi	0.016	0.203	0.713	0.047	1.60	0.64	0.021	0.286	0.617	0.066	1.32	0.42	0.021	0.274	0.618	0.064	1.35	0.43
	iioiio	0.021	0.000	0.626	0.000	0.29	0.05	0.026	0.000	0.599	0.000	0.28	0.03	0.026	0.000	0.560	0.000	0.25	0.00
	iiiiii	0.015	0.055	0.785	0.014	0.09	0.05	0.020	0.075	0.722	0.018	0.07	0.03	0.020	0.072	0.739	0.018	0.06	0.00
	oooooo	0.021	0.000	0.580	0.000	1.70	0.18	0.026	0.000	0.482	0.000	1.46	0.08	0.026	0.000	0.471	0.000	1.48	0.08
	ooooio	0.018	0.391	0.644	0.146	1.66	0.18	0.024	0.191	0.547	0.192	1.39	0.08	0.024	0.193	0.542	0.192	1.42	0.08
	ioiiii	0.016	0.227	0.732	0.221	0.50	0.05	0.022	0.223	0.643	0.221	0.38	0.03	0.022	0.292	0.654	0.204	0.39	0.00

Porphyrin	Pathway	B3LYP						CAM-B3LYP						M06-2X					
		FLU	BOA	HOMA	BLA	AV1245	AV_{min}	FLU	BOA	HOMA	BLA	AV1245	AV_{min}	FLU	BOA	HOMA	BLA	AV1245	AV_{min}
28M	oooioi	0.010	0.039	0.833	0.009	2.07	1.05	0.018	0.250	0.682	0.058	1.48	0.60	0.017	0.219	0.730	0.051	1.58	0.67
	iiioio	0.016	0.004	0.730	0.001	0.18	0.06	0.023	0.005	0.594	0.002	0.21	0.02	0.023	0.005	0.609	0.002	0.18	0.01
	iiiiii	0.009	0.002	0.900	0.001	0.07	0.06	0.016	0.000	0.790	0.000	0.12	0.02	0.015	0.001	0.817	0.001	0.10	0.01
	oooooo	0.017	0.004	0.690	0.002	2.01	0.53	0.024	0.042	0.519	0.008	1.50	0.04	0.024	0.037	0.530	0.006	1.58	0.06
	oooooi	0.014	0.222	0.763	0.184	2.06	0.61	0.021	0.265	0.602	0.173	1.50	0.08	0.020	0.258	0.618	0.175	1.60	0.11
	oiiiii	0.010	0.241	0.874	0.216	0.64	0.07	0.018	0.281	0.721	0.207	0.53	0.02	0.017	0.276	0.749	0.208	0.54	0.01
32H	ooioioi	0.016	0.219	0.723	0.051	1.56	0.76	0.023	0.314	0.594	0.073	1.18	0.45	0.023	0.308	0.588	0.072	1.19	0.46
	iioioio	0.024	0.209	0.525	0.171	0.38	0.04	0.029	0.223	0.439	0.167	0.36	0.06	0.031	0.226	0.416	0.166	0.33	0.06
	iiiiiii	0.015	0.013	0.793	0.003	0.41	0.04	0.022	0.018	0.698	0.004	0.32	0.06	0.022	0.015	0.699	0.003	0.31	0.06
	ooooooo	0.024	0.186	0.491	0.152	1.47	0.10	0.030	0.190	0.373	0.151	1.20	0.02	0.031	0.189	0.347	0.151	1.19	0.01
	oooooioo	0.022	0.024	0.567	0.006	1.53	0.10	0.028	0.033	0.451	0.009	1.24	0.02	0.028	0.031	0.436	0.008	1.24	0.01
32M	iooioio	0.010	0.038	0.849	0.009	2.08	1.14	0.020	0.263	0.666	0.062	1.41	0.55	0.019	0.241	0.678	0.057	1.48	0.58
	oiioioi	0.018	0.207	0.672	0.170	0.38	0.01	0.025	0.211	0.541	0.170	0.42	0.02	0.026	0.209	0.538	0.170	0.40	0.00
	iiiiiii	0.008	0.000	0.913	0.000	0.49	0.01	0.018	0.006	0.767	0.001	0.33	0.02	0.017	0.002	0.787	0.000	0.34	0.00
	ooooooo	0.019	0.191	0.641	0.150	1.81	0.36	0.027	0.198	0.474	0.149	1.42	0.07	0.027	0.198	0.467	0.149	1.46	0.07
	oooooio	0.016	0.010	0.719	0.003	1.98	0.49	0.025	0.043	0.543	0.011	1.48	0.07	0.024	0.043	0.544	0.011	1.52	0.07
	iiiiioi	0.012	0.213	0.812	0.183	0.35	0.01	0.020	0.177	0.675	0.192	0.30	0.02	0.020	0.182	0.686	0.191	0.30	0.00
	oiiiioi	0.015	0.003	0.737	0.001	0.35	0.01	0.023	0.021	0.601	0.006	0.34	0.02	0.023	0.018	0.606	0.005	0.33	0.00
32F	oioiooi	0.015	0.195	0.721	0.046	1.55	0.72	0.021	0.277	0.632	0.065	1.26	0.46	0.020	0.259	0.631	0.062	1.29	0.49
	ioioiio	0.021	0.233	0.589	0.164	0.55	0.01	0.026	0.242	0.526	0.162	0.52	0.03	0.026	0.241	0.518	0.162	0.52	0.01
	iiiiiii	0.013	0.010	0.820	0.002	0.44	0.01	0.017	0.016	0.756	0.004	0.38	0.03	0.017	0.015	0.768	0.003	0.39	0.01
	ooooooo	0.023	0.106	0.526	0.171	1.57	0.06	0.028	0.081	0.439	0.177	1.36	0.00	0.028	0.087	0.421	0.176	1.39	0.01
	ioiiiii	0.016	0.273	0.720	0.169	0.410	0.01	0.021	0.295	0.659	0.163	0.38	0.03	0.021	0.289	0.660	0.164	0.38	0.01
	oiooooo	0.020	0.034	0.602	0.009	1.62	0.12	0.025	0.045	0.512	0.011	1.38	0.03	0.025	0.043	0.502	0.011	1.40	0.02