Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Table SI.1. Metallicity measures of CAM-B3LYP/6-31G(d,p) optimized structures at the bond critical points between the small molecule and the aromatic ring (systems in Figure 1).

	Name	ξ_m	ELF	t_{sb}
a	C_6F_6-LiH	0.779	0.024	0.163
c	C_6F_6-CNH	0.608	0.015	0.132
f	C_6F_6-NH_3	0.623	0.015	0.135
d	C_6F_6-NCH	0.551	0.012	0.121
e	C_6F_6-H_2O	0.538	0.012	0.119
b	C_6F_6-FH	0.369	0.006	0.084

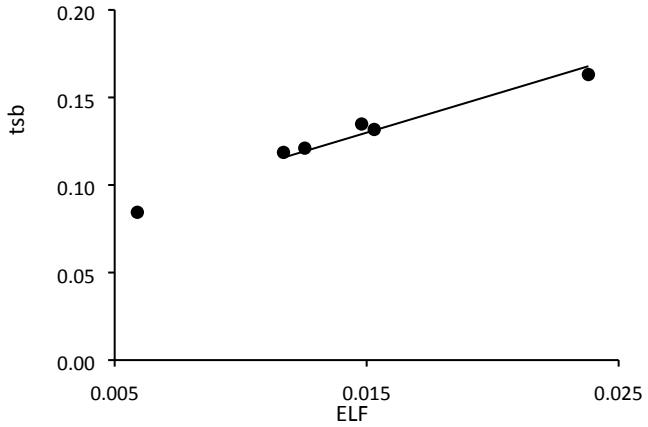

Figure SI.1. Correlation between the localized orbital locator and ELF within gradient expansion approximation.

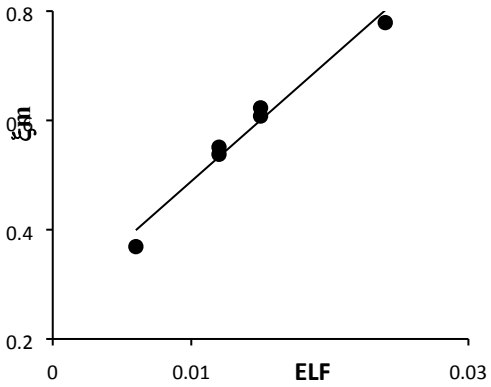

Figure SI.2. Correlation between the bond metallicity and the delocalization within the gradient expansion approximation.

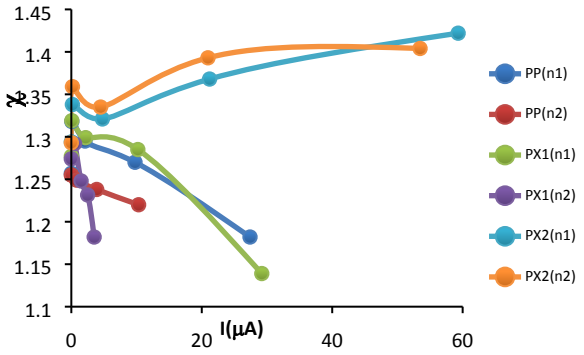

Figure SI.3 Relation of the delocalization index with the induced current.

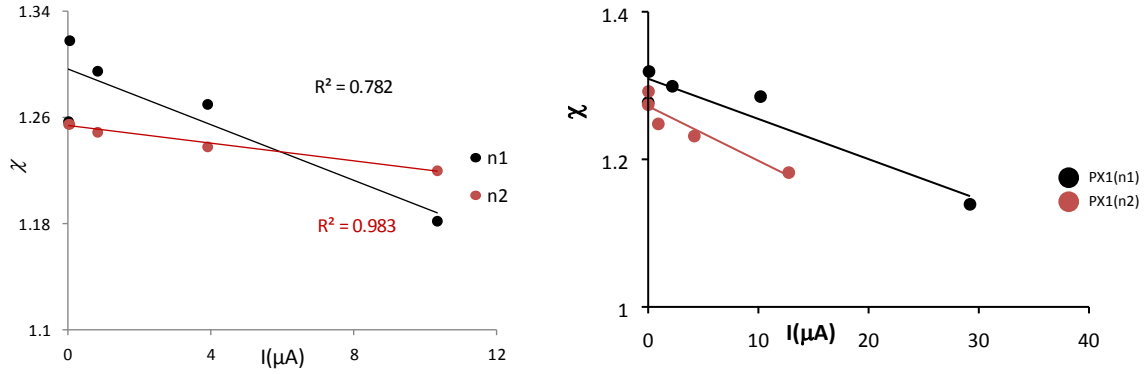

Figure SI.4. Relation of the delocalization indicator with the induced current of PP (left) and PX1 (right)

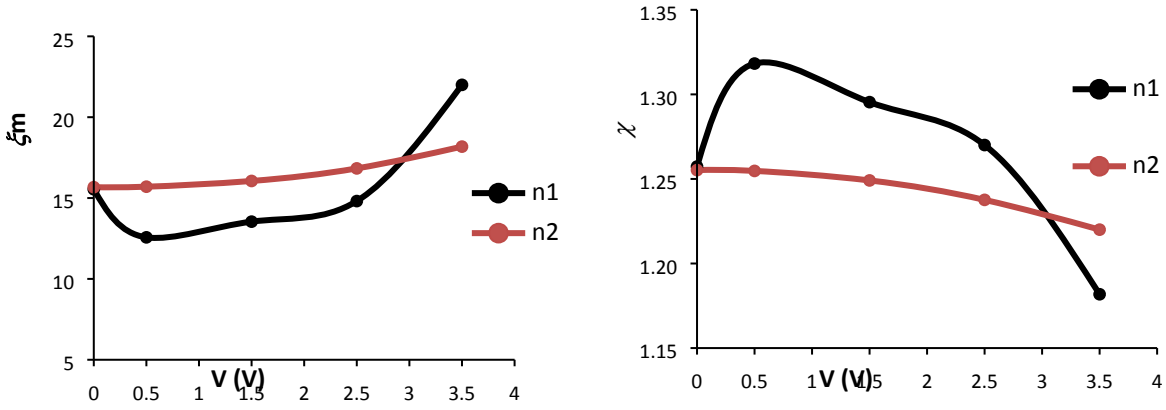

Figure SI.5. Relation of the bond metallicity and the delocalization indicator the applied voltage in *p*-phenylene.

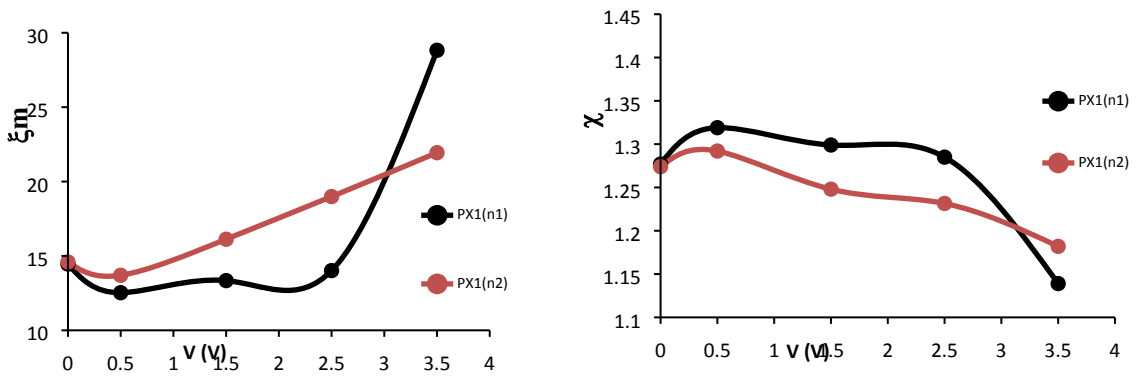

Figure SI.6. Relation of the bond metallicity and the delocalization indicator the applied voltage in *p*-xylylene (PX1)

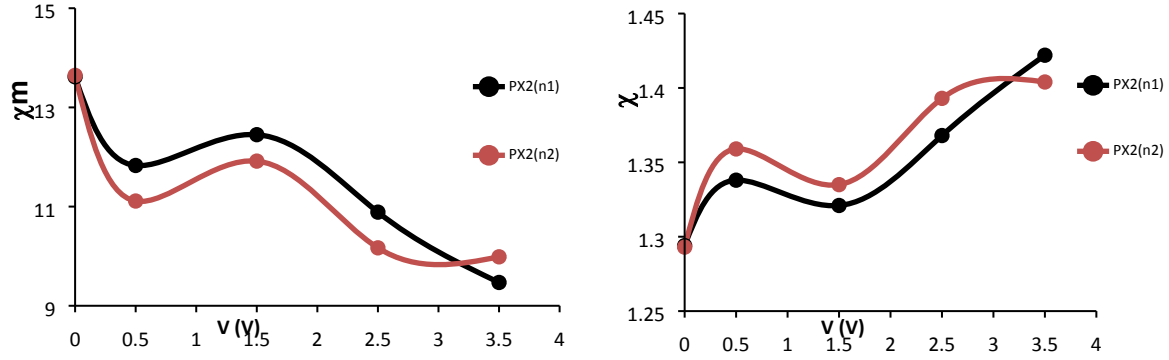

Figure SI.7. Relation of the bond metallicity and the delocalization indicator the applied voltage in *p*-xylylene (PX2).

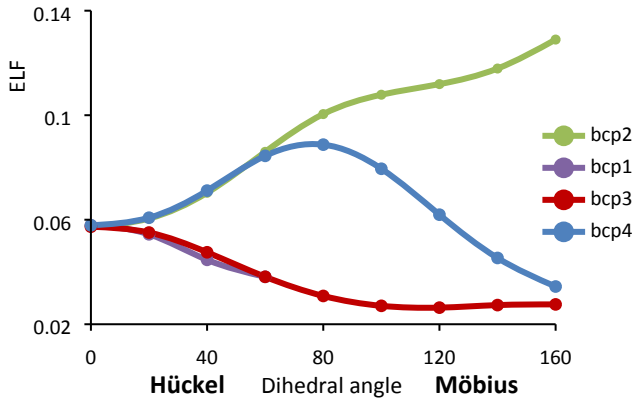

Figure SI.8. Evolution of ELF as function of the amplitude of the dihedral angle.

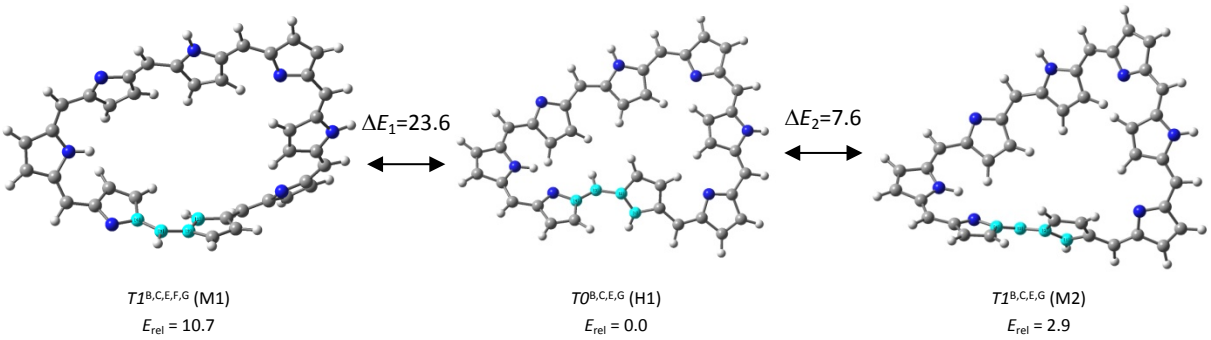

Figure SI.9. Interconversion pathways between the Möbius structures *M1 and M2*.

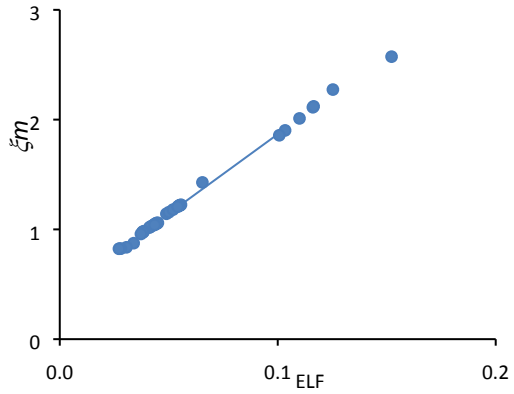

Figure SI.10. (a) Correlation between ξ_m and ELF; (b) Correlation between χ and ELF of the first interconversion in octaphyrins.

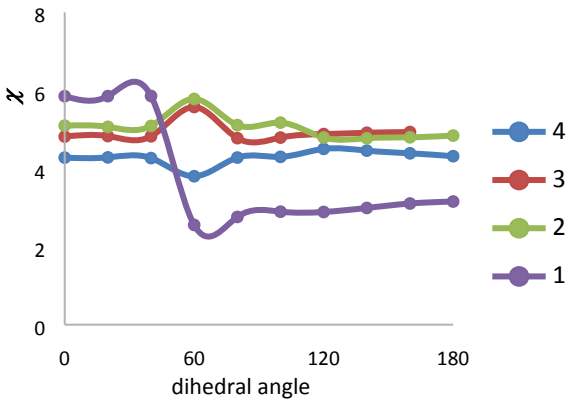

Figure SI.11. Evolution of the delocalization index with the amplitude of the dihedral angle of the interconversion of octaphyrin.

Table.SI.2. Evolution of the delocalization indicator χ and the bond metallicity ξ_m of the different bond critical points with the amplitude of the dihedral angle of the first interconversion of octaphyrin.

Dihedral angle	ξ_m **(1)**	ξ_m **(2)**	ξ_m **(3)**	ξ_m **(4)**	Π	χ **(1)**	χ **(2)**	χ **(3)**	χ **(4)**
0	0.824	0.976	1.048	1.220	-0.370	5.851	5.097	4.817	4.278
20	0.824	0.983	1.044	1.218	-0.304	5.853	5.066	4.831	4.284
40	0.823	0..978	1.046	1.225	-0.223	5.857	5.089	4.825	4.266
60	2.573	0.837	0.874	1.428	0.514	2.554	5.780	5.722	3.801
80	2.273	0.973	1.059	1.219	0.298	2.759	5.112	4.777	4.280
100	2.112	0.958	1.055	1.213	0.013	2.894	5.174	4.792	4.298
120	2.120	1.054	1.030	1.142	-0.237	2.886	4.793	4.873	4.502
140	2.010	1.059	1.021	1.157	-0.366	2.989	4.774	4.918	4.457
160	1.901	1.053	1.017	1.180	-0.427	3.103	4.798	4.934	4.389
180	1.857	1.040	1.008	1.207	-0.435	3.153	4.843	4. 968	4.315

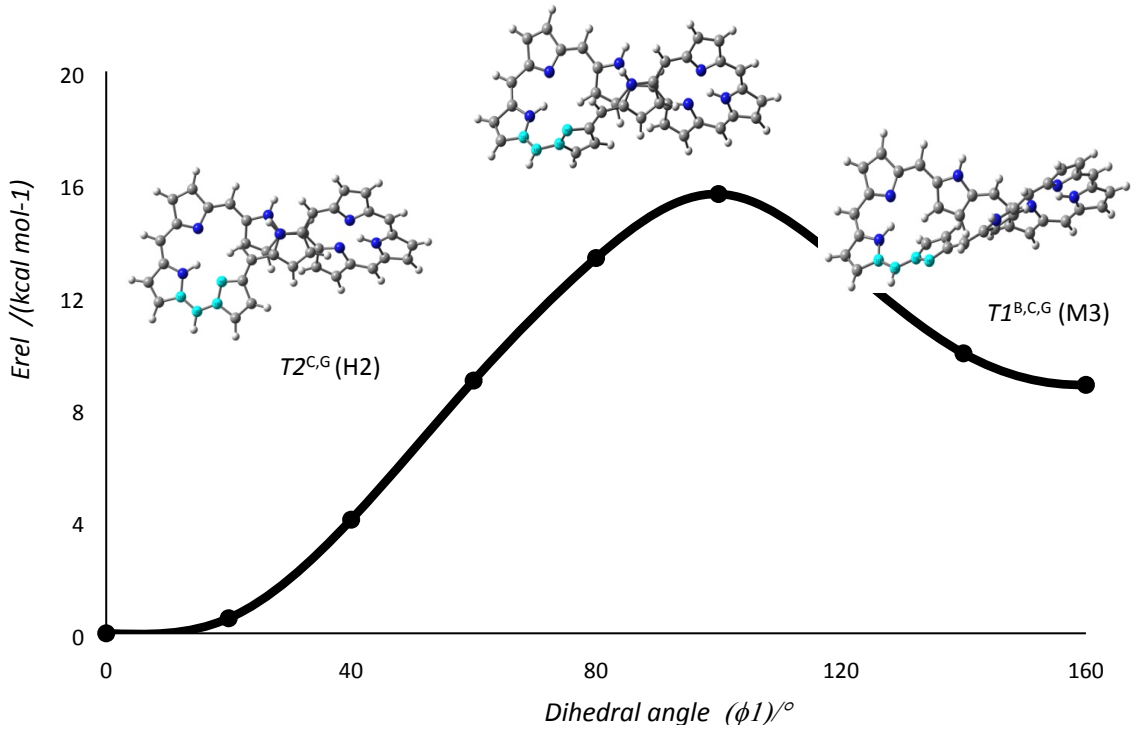

Figure SI.12. Potential energy curve for the topological interconversion between the figure-eight *H2* and the Möbius *M3* conformers.

Table SI.3. Evolution of ξ_m with the amplitude of the dihedral angle 4-5-6-7 (second interconversion of octaphyrins).

Dihedral angle	**bcp2**	**bcp3**	**bcp4**	**bcp5**	**bcp6**	**bcp7**	**bcp8**	**bcp9**
0	0.760	1.007	1.239	1.590	0.796	1.003	1.233	1.112
20	0.845	1.014	1.253	1.603	0.786	1.007	1.253	1.146
40	0.913	1.017	1.231	1.605	0.789	1.016	1.199	1.167
60	0.936	1.017	1.221	1.584	0.806	1.007	1.525	1.156
80	0.893	0.999	1.235	1.604	0.839	1.025	1.621	1.180
100	0.864	0.963	1.206	1.599	0.882	1.021	1.595	1.158
120	0.986	0.963	1.106	1.266	0.924	0.863	1.642	1.164
140	0.992	0.961	1.125	1.167	0.950	0.961	1.738	0.755
160	1.000	0.944	1.164	1.079	0.966	0.944	1.847	0.794

Table SI.4. Evolution of the delocalization indicator χ with the amplitude of the dihedral angle 4-5-6-7 of the second interconversion of octaphyrins.

Dihedral angle	**bcp2**	**bcp3**	**bcp4**	**bcp5**	**bcp6**	**bcp7**	**bcp8**	**Bcp9**	Π
0	6.265	4.971	4.228	3.515	6.026	4.987	4.244	4.597	0.722
20	5.735	4.945	4.192	3.495	6.091	4.971	4.192	4.491	0.724
40	5.381	4.935	4.250	3.492	6.071	4.935	4.336	4.429	0.620
60	5.275	4.934	4.277	3.526	5.963	4.972	3.622	4.460	0.411
80	5.479	5.002	4.240	3.494	5.769	4.904	3.468	4.390	0.138
100	5.629	5.155	4.315	3.501	5.534	4.919	3.508	4.454	-0.126
120	5.056	5.156	4.616	4.159	5.331	5.633	3.435	4.435	-0.329
140	5.031	5.161	4.554	4.429	5.213	5.161	3.301	6.295	-0.485
160	4.999	5.238	4.438	4.706	5.139	5.238	3.166	6.038	-0.575

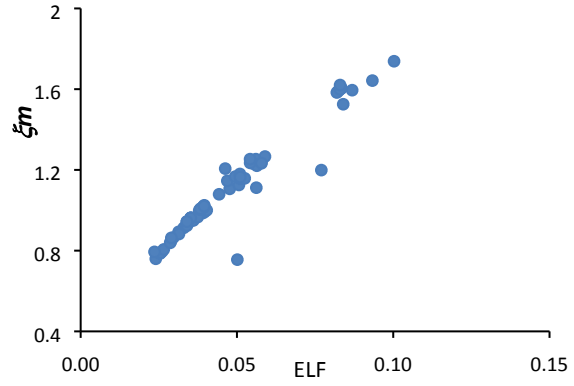

Figure SI.13. Correlation between χ and ELF. (b) Correlation between ξ_m and ELF of the second interconversion of octaphyrins.