Electronic supplementary information (ESI)

Selective resonance Raman enhancement of large amplitude inter-ring vibrations of [3_4](1,2,4,5)cyclophane radical cation; a model of π-stacked dimer radical ions

Hajime Okajima*[a], Teruo Shinmyozu[b] and Akira Sakamoto*[a]

[a] Department of Chemistry and Biological Science, College of Science and Engineering, Aoyamna Gakuin University, 5-10-1 Fuchinobe, Chuo-ku, Sagamihara, Kanagawa 252-5258, Japan.

[b] Institute for Materials Chemistry and Engineering (IMCE), Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.

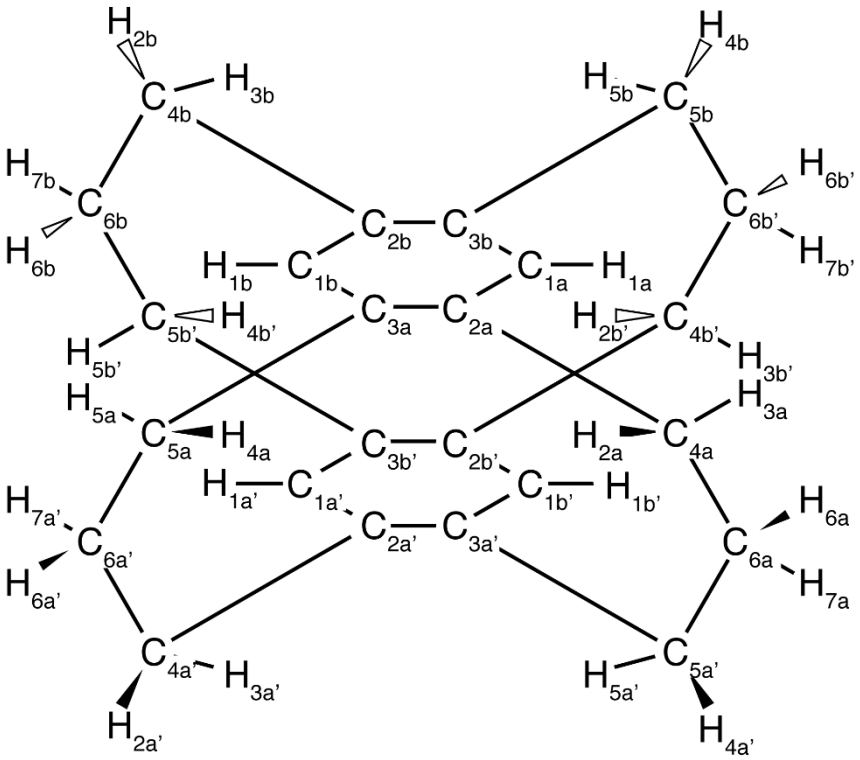

Fig. S1 Numbering of atoms for [3_4](1,2,4,5)cyclophane

Table S1 Structural parameters (bond lengths, angles, and dihedral angles) calculated for the neutral species and the radical cations in the ground S_0 and excited S_2 states of [3$_4$](1,2,4,5)cyclophane. The numbering of atoms is defined in Fig. S1.

Definitions	Bond lengths/Å and angles/deg				
	Neutral	Radical cation			
	S_0 [D_{2h}]	S_0 [D_2] (B)	S_2 [D_2] (C)	B - A	C - B
R($C_{1a}C_{2a}$)	1.398	1.395	1.396	-0.003	0.001
R($C_{1a}C_{3b}$)		1.394	1.395	-0.004	0.001
R($C_{2a}C_{3a}$)	1.408	1.435	1.434	0.027	-0.001
R($C_{2a}C_{4a}$)	1.522	1.511	1.514	-0.010	0.002
R($C_{3a}C_{5a}$)		1.511	1.513	-0.011	0.002
R($C_{4a}C_{6a}$)	1.550	1.550	1.557	0.000	0.007
R($C_{6a}C_{5a'}$)		1.551	1.556	0.001	0.006
R($C_{1a}H_{1a}$)	1.087	1.085	1.086	-0.002	0.000
R($C_{4a}H_{2a}$)	1.091	1.089	1.089	-0.002	0.000
R($C_{5a}H_{4a}$)		1.089	1.089	-0.002	0.000
R($C_{4a}H_{3a}$)	1.097	1.096	1.096	0.000	-0.001
R($C_{5a}H_{5a}$)		1.096	1.095	-0.001	-0.001
R($C_{6a}H_{6a}$)	1.096	1.093	1.094	-0.003	0.000
R($C_{6a}H_{7a}$)	1.094	1.093	1.092	-0.001	-0.001
A($C_{2a}C_{1a}C_{3b}$)	123.696	123.082	122.895	-0.614	-0.187
A($C_{1a}C_{2a}C_{3a}$)	117.856	118.042	118.090	0.186	0.049
A($C_{1a}C_{2a}C_{4a}$)	117.599	118.101	117.951	0.502	-0.150
A($C_{1b}C_{3a}C_{5a}$)		118.069	117.858	0.471	-0.212
A($C_{3a}C_{2a}C_{4a}$)	124.247	123.779	123.620	-0.468	-0.159
A($C_{2a}C_{3a}C_{5a}$)		123.762	123.611	-0.486	-0.151
A($C_{2a}C_{4a}C_{6a}$)	114.678	113.849	114.538	-0.829	0.690
A($C_{3a}C_{5a}C_{6a'}$)		113.939	114.541	-0.739	0.601
A($C_{4a}C_{6a}C_{5a'}$)	117.769	115.919	119.203	-1.850	3.284
A($C_{2a}C_{1a}H_{1a}$)	117.888	118.259	118.317	0.371	0.058
A($C_{3a}C_{1b}H_{1b}$)		118.163	118.151	0.275	-0.012
D($C_{1a}C_{2a}C_{3a}C_{1b}$)	0	0.694	0.833	0.694	0.140
D($C_{4a}C_{2a}C_{3a}C_{5a}$)	0	0.390	0.621	0.390	0.231
D($C_{1a}C_{2a}C_{3a}C_{5a}$)	173.566	177.108	173.793	3.541	-3.315
$-D$($C_{1b}C_{3a}C_{2a}C_{4a}$)		176.024	172.338	2.458	-3.686
D($C_{3b}C_{1a}C_{2a}C_{4a}$)	164.979	166.116	162.455	1.136	-3.661
$-D$($C_{2b}C_{1b}C_{3a}C_{5a}$)		166.536	163.103	1.557	-3.433
D($C_{2a}C_{1a}C_{3b}C_{2b}$)	9.021	10.086	10.267	1.065	0.180
$-D$($C_{3a}C_{1b}C_{2b}C_{3b}$)		10.792	11.109	1.770	0.318
D($C_{2a}C_{3a}C_{1b}H_{1b}$)	179.503	177.448	178.219	-2.056	0.771
$-D$($C_{3a}C_{2a}C_{1a}H_{1a}$)		178.146	179.047	-1.358	0.901

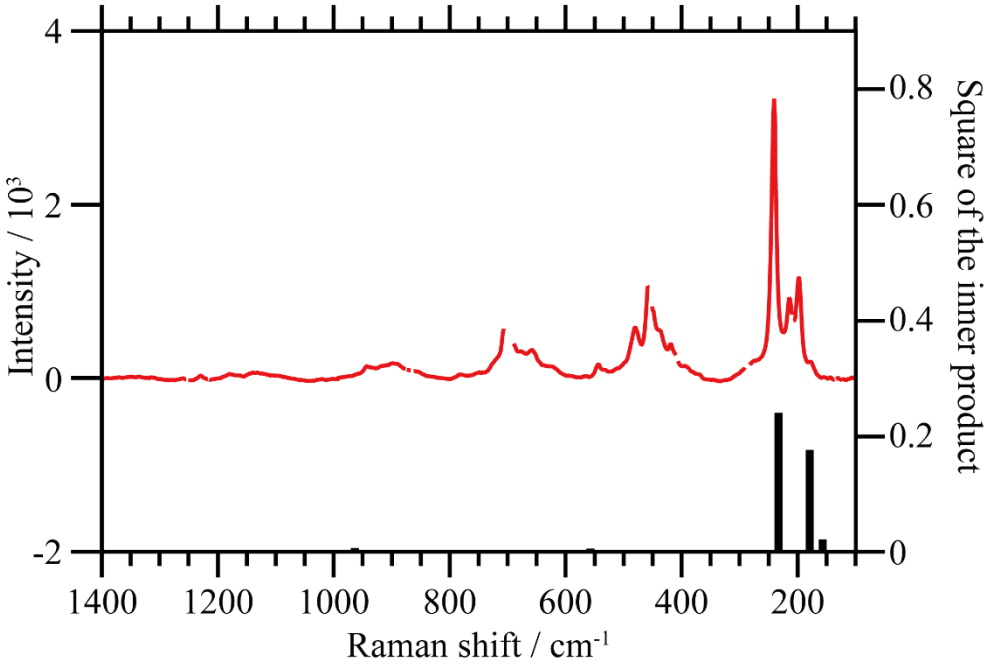

Fig. S2 Resonance Raman spectrum of [3$_4$](1,2,4,5)cyclophane radical cation (red line) and a plot of squares of the inner products of the vibrational corrdinates and the atomic displacements from the S_0 to S_2 states (See the text) calculated for the radical cation (black bars).