Supporting Information for: Assignment of the Raman Spectrum of Benzylic Amide [2]Catenane: Raman Microscopy Experiments and First-Principles Calculations

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Normal mode analysis of benzamide molecule: As mentioned in the main text, we have checked the accuracy of our calculation using a simpler system. We have chosen the benzamide molecule because it is closely related to the structure of the catenane and there are available previous theoretical and experimental results. In particular, ref. 33 of the main text provides a complete description of the normal modes of this molecule (in solution phase) including Raman and infrared data. In table S1 we compare our results with those obtained in the mentioned reference for the 42 modes. In this case, a direct comparison with the discrete peaks of the spectra is possible due to the low number of vibrational modes. As it is seen, the agreement between our results and the experimental ones is remarkable, demonstrating the high accuracy of our calculation method.

Discrete normal modes of the catenane: In Fig. S1 we present a new version of the Fig. 4 of the main text in which the complete discrete set of normal modes with their corresponding intensities has been superimposed (green bars). Notice that these intensities have been rescaled with an arbitrary factor in each case to allow a better visualization.

Animations of the normal modes of the catenane: In addition, a set of files (.xyz) with the coordinates of the normal modes collected in Table 1 of the main text is provided. Each file contains the coordinates of eight snapshots of the vibration motion, Thus, animated visualizations of each normal mode are possible using standard softwares like Jmol, Avogadro, etc. by running a cyclic movie of them with the appropriate speed, leading to the geometrical animation of each mode.

Table S1: Mode list (cm^{-1}) of benzamide molecule, comparing the results of this work with previous calculations and experimental Raman and IR measurements by K. M. Pei et al. *J. Chem. Phys.* **128** (2008) 224310.

Mode	DFT (This work)	DFT	Raman	IR	Descrption
		K. M. Pei et al.			
42	79	59	**	**	Ph–CO–NH_2 torsion
41	123	152	177	**	skeletal mode
40	172	216	245	**	CCN bend
39	228	358	**	**	NH_2 wag
38	374	376	397	**	NH_2 wag
37	402	413	**	415	Ring CCC out of plane bend
36	423	415	**	**	Ring CCC out of plane bend
35	460	503	**	**	CCN bend
34	554	555	**	530	NH_2 twist
33	593	616	**	**	CNH bend, OCN bend
32	610	631	615	615	Ring deformation
31	683	703	**	704	CCH out of plane bend
30	690	726	**	785	CCH out of plane bend
29	741	762	775	771	Ring deformation Ph–CO–NH_2 stretch
28	789	809	**	793	CCH out of plane bend
27	839	863	**	849	CCH out of plane bend
26	920	946	**	918	CCH out of plane bend
25	970	992	**	**	CCH out of plane bend
24	993	1012	**	**	CCH out of plane bend
23	994	1015	1003	1001	Ring trigonal bend
22	1031	1048	1026	1026	Ring deformation
21	1032	1079	**	**	NH_2 rock
20	1091	1112	**	1072	CCH in plane bend, NH_2 rock
19	1115	1142	1124	1122	Ph–CO–NH_2 stretch, NH_2 rock
18	1164	1186	1145	1144	CCH in plane bend
17	1186	1204	1172	1180	CCH in plane bend
16	1304	1338	**	1298	CCH in plane bend, ring stretch
15	1332	1360	**	**	Ring stretch, CCH in plane bend
14	1354	1368	1413	1404	Ph–CO–NH_2 stretch, ring stretch
13	1436	1481	1450	1450	CCH in plane bend
12	1479	1529	1496	1497	Ring stretch, CCH in plane bend
11	1556	1622	1572	1578	NH_2 scissor
10	1579	1628	**	**	Ring stretch
9	1598	1650	1604	1624	Ring stretch
8	1684	1751	1685	1660	C=O stretch
7	3095	3181	3064	3064	Ring CH stretch
6	3106	3189	3064	3064	Ring CH stretch
5	3120	3198	**	**	Ring CH stretch
4	3130	3207	**	**	Ring CH stretch
3	3139	3220	**	**	Ring CH stretch
2	3524	3595	**	**	NH symmetry stretch
1	3653	3729	**	**	NH antisymmetry stretch

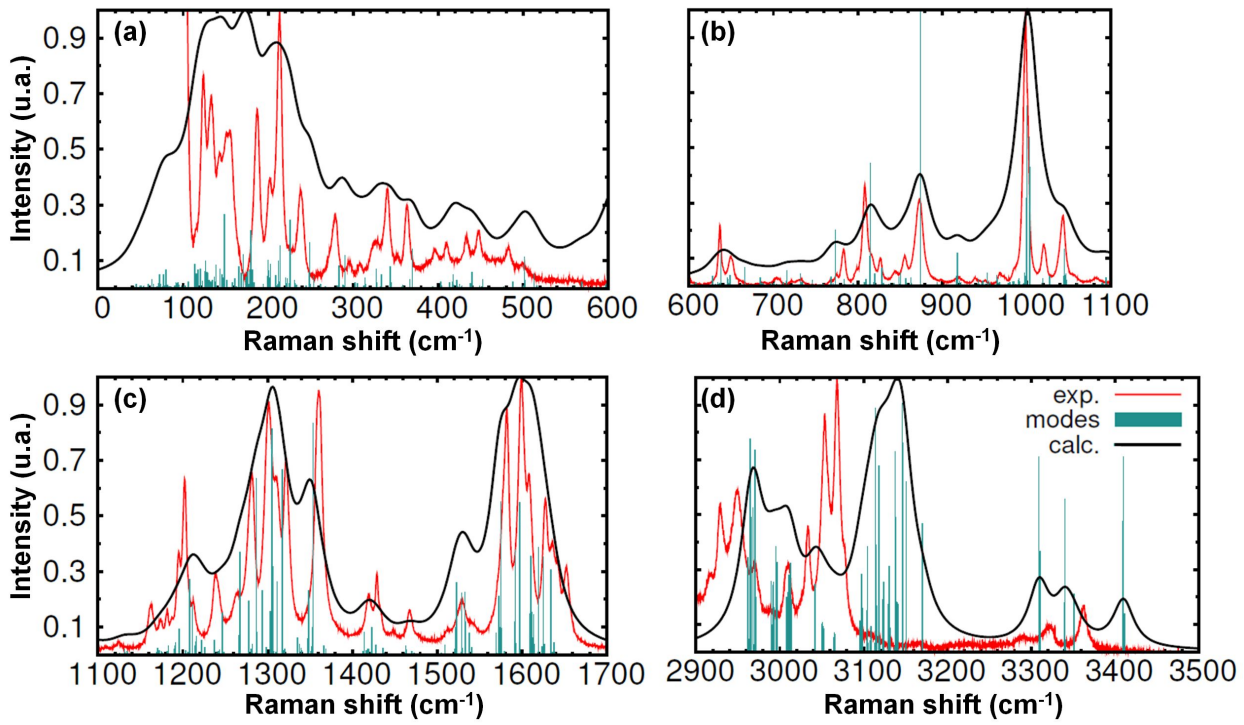

Figure S1: Comparison between the calculated Raman spectrum (black line) and the experimental averaged spectrum (red line) after renormalization in different frequency regions. Unlike Fig. 4 of the main text, the discrete set of normal modes has been superimposed in the graphs (green bars).