

## SUPPLEMENTARY INFORMATION

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## S1. Further experimental details

### S1a Single Shot Steady State Fluorescence

One of the difficulties in obtaining the emission spectrum of  $I_c$  is that it photoconverts during collection. To circumvent this we used a 1 Hz pulsed laser to excite fluorescence in a flow system. Solutions of  $I_c$  in ethanol and ethylene glycol were prepared (at an absorbance of 0.2 at 355 nm). These two isoabsorptive solutions were used to prepare solutions with a range of solvent volume fractions. (100:0, 75:25, 50:50, 25:75 and 0:100 ethanol:ethylene glycol). The absorption spectra of each solution were recorded (specord 600) to confirm the absorbance at 355 nm. The third harmonic of a nanosecond Nd:YAG laser (Innolas spotlight 200) was used for excitation, with fluorescence spectra recorded under conditions where conversion to the metastable form is minimal. The pulse power was kept below 1.0 mJ and the solution was flowed through the beam using a flow cell and a syringe pump to avoid build-up of the metastable isomer during the experiment. The flow rate was sufficient to ensure a fresh solution was present for each pulse (1 Hz). This data is shown in Figures 1 and 4.

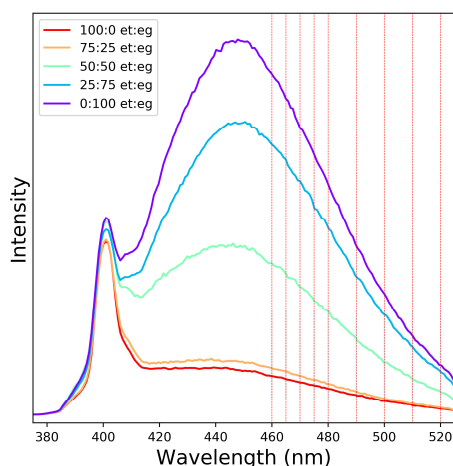


Figure S1. Fluorescence spectra of *cis* motor over a range of volume fractions of ethanol and ethylene glycol. Intensity is corrected for differences in absorbance. Vertical lines correspond to wavelengths where fluorescence upconversion measurements were made (see Figure 2).

### S1b Flow and Conversion Calculations

A second difficulty is ensuring that the solute  $I_c$  is not converted in the beam during the quasi CW up-conversion measurement. It is necessary to ensure that conversion is not so high that the probability of photoproduct absorption (and subsequent emission) becomes significant. Here we calculate the flow rate and conversion rate under our conditions.

Using a graduated cylinder, ethanol and ethylene glycol were pumped through the cell using different speed settings of the pump. The time was measured until 40 mL of solvent was pumped out. The results are given in Figure 1.

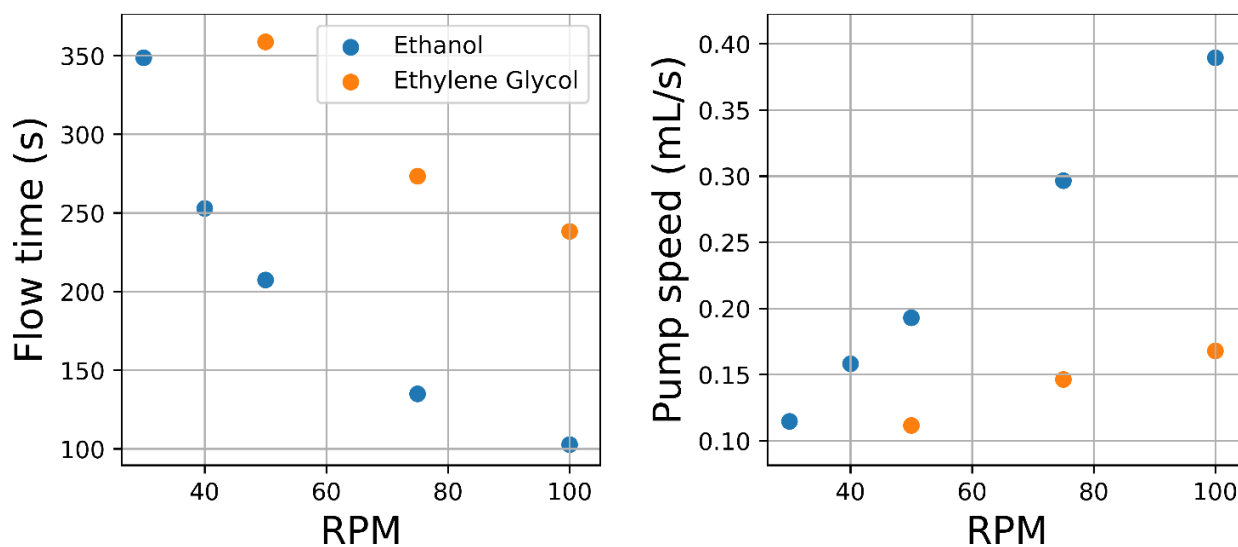


Figure S2: Measured flow times and pump speeds

#### Conversion in the confocal volume

In order to see if we would get significant conversion in the upconversion experiment, the following calculation was done.

A 1 mm pathlength cuvette was used, and assuming the beam is focused to a cylinder of length 1 mm and radius 25  $\mu\text{m}$ , we calculated the focal volume to be:

$$V = \pi r^2 l_{\text{path}} \quad (1)$$

Where  $r$  is the radius of the cylinder and  $l$  the height. We use a concentration such that the absorbance is around 0.5. The molar absorptivity of the  $I_c$  isomer at 400 nm is around  $4000 \text{ M}^{-1} \text{ cm}^{-1}$ . Using the Beer-Lambert law:

$$A = \epsilon c l = -\log(T) \quad (2)$$

Where  $\epsilon$  is the molar absorptivity,  $c$  the concentration of sample and  $l$  the path length of the cell.  $T$  is the percent transmittance. With this equation we can calculate the desired concentration of the sample and also the amount of light that is absorbed by the sample in percentage:

$$T = 10^{-A} \quad (3)$$

We can use equation (4) to get the percentage of light absorbed, which is one minus the percentage of light transmitted:

$$\%A = 1 - T = 1 - 10^{-A} \quad (4)$$

Using the measured flow rate ( $f$ ) of 0.39 mL/s and the estimated size of the confocal volume, we can determine the speed of the molecules through the confocal volume (neglecting diffusion).

$$f = A_{cross}v \quad (5)$$

Where  $A_{cross}$  is the cross section area and  $v$  the speed of the molecules through the confocal volume. In our case  $A_{cross}$  is a rectangle of  $50 \mu\text{m}$  by  $1 \text{mm}$ . Using this speed we can determine the time a molecule would reside in the confocal volume ( $t_R$ ), if it passes through the center then  $l = 50 \mu\text{m}$ ):

$$t = \frac{l}{v} = \frac{lA}{f} = \frac{50 \mu\text{m} * 1 \text{mm} * 50 \mu\text{m}}{0.39 \text{ mL/s}} = 1.67 \times 10^{-5} \text{ s} \quad (6)$$

Furthermore, since we measure the power of the  $400 \text{ nm}$  beam hitting the sample and, using the concentration and volume we can determine the number of molecules in the confocal volume, we can thus determine the number of conversions per second. First, we start by calculating the number of photons hitting the confocal volume per second. Knowing the power of the beam  $P = 5 \text{ mW}$  and the wavelength  $\lambda = 400 \text{ nm}$ , we can calculate the number of photons per second hitting the confocal volume  $R$ :

$$R = \frac{P}{E} = \frac{P\lambda}{hc} \quad (7)$$

From equation (4), we know the percentage of light absorbed. Using this and multiplying by the quantum yield of conversion,  $\phi$  we can calculate the number of molecules converting per second:

$$conv = \phi R \%A = \phi \frac{P\lambda}{hc} (1 - 10^{-A}) \quad (8)$$

Using this initial rate, we can calculate the minimal time it takes to absorb enough photons to convert the entire confocal volume. For this we need the number of molecules in the confocal volume, which is the concentration times the volume, the concentration can be calculated from the absorbance and the volume from equation (1),  $c = A/(\epsilon l_{path})$ :

$$N_{confocal} = c * V * N_A = \frac{A}{\epsilon l_{path}} \pi r^2 l_{path} N_A = \frac{A}{\epsilon} \pi r^2 N_A \quad (9)$$

Since the concentration from the Beer-Lambert law would be in molar units, we need to convert to number of molecules. Therefore, the time it takes to absorb enough photons to convert the entire confocal volume is given by:

$$t_{convert} = \frac{N_{confocal}}{conv} = \frac{\frac{A}{\epsilon} \pi r^2 N_A}{\phi \frac{P\lambda}{hc} (1 - 10^{-A})} = \frac{hc \pi r^2 N_A}{\phi P \lambda \epsilon} \frac{A}{(1 - 10^{-A})} \quad (10)$$

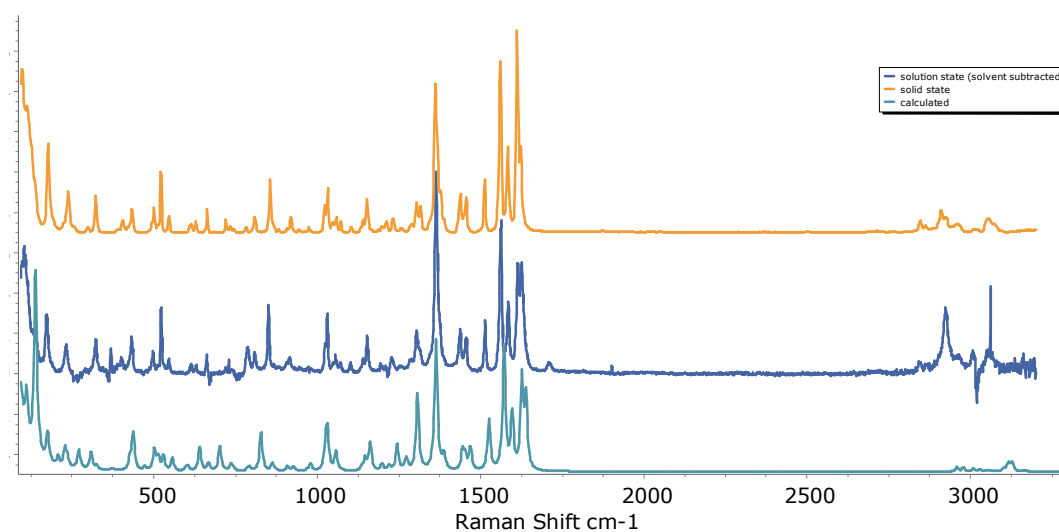
Substituting all the relevant values gives:

$$t_{convert} = 2.5 \times 10^{-4} \text{ s} \quad (11)$$

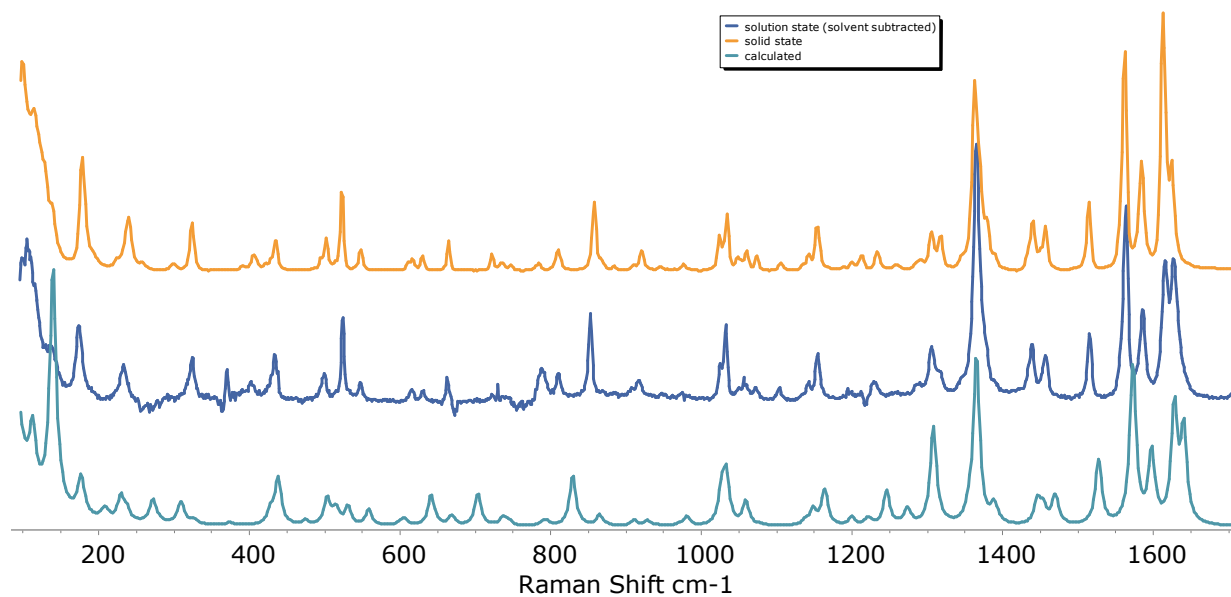
The actual conversion time is longer since the concentration decreases when molecules are converted. The conversion time is longer than the residence time, so conversion should not be an issue on the timescale of the experiment at the powers employed.

## S1c Raman spectroscopy

Raman spectra in the solid state and in solution were obtained using a Raman microscope at 785 nm and macrosampling unit (Perkin Elmer Raman station), respectively. The spectra were compared with the calculated spectrum. Overall there is the expected close correspondence between the spectra, however minor difference in band position are apparent between the solid state and solution spectra. Notably the spectra are similar in the low wavenumber region (90 to 200  $\text{cm}^{-1}$ ) indicating that the bands observed in the solid are not due to phonons. A full list of band positions are given at the end of the SI. The displacements associated with calculated low wavenumber modes are also shown below (Figure S5) and indicate that most of the modes in this region correspond to essentially similar flexing of the entire molecule.



*Figure S3. Raman spectrum at 785 nm of  $I_c$  in the solid state (orange), in  $\text{CHCl}_3$  (blue) Contributions from solvent were subtracted. Negative signals are due to imperfect solvent subtraction. The calculated spectrum (scaling factor of 0.98 applied) in green.*



*Figure S4. Fingerprint region of the Raman spectrum at 785nm of **I<sub>c</sub>** in the solid state (orange), in  $\text{CHCl}_3$  (blue) Contributions from solvent were subtracted. Negative signals are due to imperfect solvent subtraction. The calculated spectrum (scaling factor of 0.98 applied) in green.*

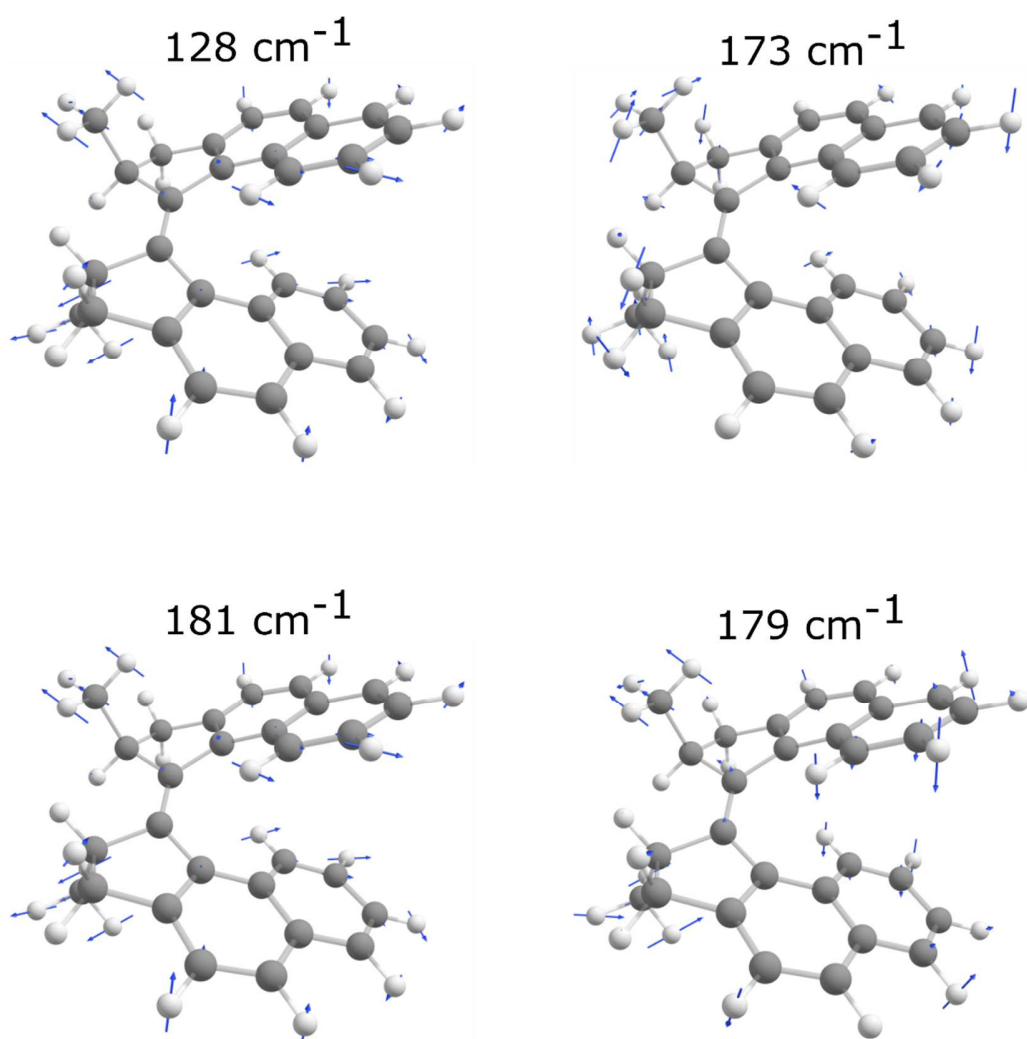


Figure S5 Computed modes at indicated wavenumbers indicating delocalized nature.

## S2 Data Tables

**Table S1** Biexponential fit parameters for  $I_c$  fluorescence decay measured as a function of emission wavelength. Data are fit after the initial 100 fs decay of the FC state has completed.

| Wavelength (nm)             | 460   | 465   | 470  | 475  | 480  | 490  | 500  | 510  | 520  |
|-----------------------------|-------|-------|------|------|------|------|------|------|------|
| $A_1$                       | 0.68  | 0.66  | 0.6  | 0.64 | 0.61 | 0.58 | 0.59 | 0.62 | 0.51 |
| $\tau_1$ (fs)               | 600   | 576   | 752  | 575  | 585  | 687  | 671  | 1043 | 728  |
| $A_2$                       | 0.32  | 0.34  | 0.4  | 0.36 | 0.39 | 0.42 | 0.41 | 0.38 | 0.49 |
| $\tau_2$ (fs)               | 10696 | 10066 | 9575 | 8367 | 7327 | 7051 | 6244 | 7344 | 5446 |
| $\langle \tau \rangle$ (fs) | 9602  | 9130  | 8641 | 7503 | 6588 | 6285 | 5500 | 6150 | 4864 |

The average lifetime was calculated using:

$$\langle \tau \rangle = \frac{A_1 \tau_1^2 + A_2 \tau_2^2}{A_1 \tau_1 + A_2 \tau_2}$$

**Table S2** Biexponential fit parameters at 490 nm for  $I_c$  fluorescence decay as a function of EtOH:EG composition.

| EtOH:EG                     | 100:0 | 75:25 | 50:50 | 25:75 | 0:100 |
|-----------------------------|-------|-------|-------|-------|-------|
| $A_1$                       | 0.58  | 0.6   | 0.48  | 0.56  | 0.18  |
| $\tau_1$ (fs)               | 687   | 1048  | 925   | 3068  | 1616  |
| $A_2$                       | 0.42  | 0.4   | 0.52  | 0.44  | 0.82  |
| $\tau_2$ (fs)               | 7051  | 10682 | 9618  | 22216 | 17267 |
| $\langle \tau \rangle$ (fs) | 6285  | 9430  | 8901  | 19332 | 16957 |

**Table S3** Viscosity data determined using an Ubbelohde viscometer at 293 K

| EtOH:EG | $\rho$ (g L <sup>-1</sup> ) | $\eta$ (mPa s) |
|---------|-----------------------------|----------------|
| 100:0   | 786.638                     | 2.019          |
| 75:25   | 877.165                     | 3.574          |
| 50:50   | 959.746                     | 6.101          |
| 25:75   | 1035.366                    | 10.131         |
| 0:100   | 1108.374                    | 17.238         |



### S3 Computational Details

Calculations were carried out using the electronic structure code Gaussian.<sup>[1]</sup> Geometries were optimized at the B3LYP<sup>[2]</sup>-D3(BJ)<sup>[3]</sup>/def2-TZVP<sup>[4]</sup> level of theory with an ultrafine grid and tight convergence. Raman intensities were also calculated at this level of theory at 298.15 K.

### XYZ Coordinates

|   |              |              |              |   |
|---|--------------|--------------|--------------|---|
| C | 2.662544000  | 2.412818000  | -1.109599000 | $E_{\text{B3LYP-D3(BJ)/def2-TZVP}} =$<br><br>-1081.97391371 |
| C | -0.674342000 | 1.643206000  | 0.019371000  |   |
| C | -1.657374000 | 0.549194000  | 0.025783000  |   |
| C | -2.791950000 | 0.968876000  | 0.704269000  |   |
| C | -2.662543000 | 2.412818000  | 1.109600000  |   |
| C | -1.493538000 | 2.917273000  | 0.225810000  |   |
| C | 0.674342000  | 1.643206000  | -0.019371000 |   |
| C | 1.657374000  | 0.549194000  | -0.025783000 |   |
| C | 2.791951000  | 0.968876000  | -0.704269000 |   |
| C | 1.493538000  | 2.917272000  | -0.225810000 |   |
| C | 3.870803000  | 0.103685000  | -0.934879000 |   |
| C | 1.631810000  | -0.733285000 | 0.592142000  |   |
| C | -1.631810000 | -0.733285000 | -0.592141000 |   |
| H | 3.584859000  | 2.975941000  | -0.952157000 |   |
| H | 2.403945000  | 2.499538000  | -2.170213000 |   |
| C | 2.722539000  | -1.621130000 | 0.330344000  |   |
| C | 3.817153000  | -1.180197000 | -0.452161000 |   |
| C | -3.870803000 | 0.103686000  | 0.934879000  |   |
| C | -3.817153000 | -1.180196000 | 0.452161000  |   |
| C | -2.722539000 | -1.621129000 | -0.330344000 |   |
| C | -2.699060000 | -2.920420000 | -0.890799000 |   |
| C | -0.621327000 | -1.157536000 | -1.484125000 |   |
| C | -1.674950000 | -3.317253000 | -1.709242000 |   |
| C | -0.639120000 | -2.416075000 | -2.026045000 |   |
| C | 2.007898000  | 3.493944000  | 1.097014000  |   |
| C | -2.007898000 | 3.493944000  | -1.097014000 |   |
| H | 4.734795000  | 0.446852000  | -1.490835000 |   |
| H | 4.633227000  | -1.868909000 | -0.634083000 |   |
| H | 0.173622000  | -0.474791000 | -1.738696000 |   |
| H | 0.149393000  | -2.720999000 | -2.701739000 |   |
| H | -1.668934000 | -4.314151000 | -2.130718000 |   |
| H | -3.518106000 | -3.594337000 | -0.669986000 |   |
| H | -4.633227000 | -1.868908000 | 0.634083000  |   |
| H | -4.734794000 | 0.446853000  | 1.490835000  |   |
| H | 2.617829000  | 4.382863000  | 0.921073000  |   |
| H | 1.182170000  | 3.772136000  | 1.753338000  |   |
| H | 2.619614000  | 2.758784000  | 1.623516000  |   |
| H | -2.619614000 | 2.758785000  | -1.623516000 |   |
| H | -1.182169000 | 3.772137000  | -1.753338000 |   |
| H | -2.617829000 | 4.382863000  | -0.921073000 |   |
| H | -2.403944000 | 2.499538000  | 2.170213000  |   |
| H | -3.584858000 | 2.975941000  | 0.952157000  |   |
| H | -0.914379000 | 3.678459000  | 0.746353000  |   |
| H | 0.914379000  | 3.678459000  | -0.746354000 |   |
| C | 2.699060000  | -2.920420000 | 0.890799000  |   |
| C | 0.621327000  | -1.157535000 | 1.484126000  |   |
| C | 0.639120000  | -2.416075000 | 2.026045000  |   |
| C | 1.674949000  | -3.317253000 | 1.709242000  |   |
| H | -0.173622000 | -0.474791000 | 1.738697000  |   |
| H | -0.149393000 | -2.720998000 | 2.701739000  |   |
| H | 1.668933000  | -4.314151000 | 2.130718000  |   |
| H | 3.518105000  | -3.594337000 | 0.669986000  |   |

**Table S4** Peak position and relative intensities for spectra (Figure 3) in solid state, solution and calculated.

| Raman shift [1/cm] | solid state (rel. Intensity) | Raman shift [1/cm] | solution state (rel. Intensity) | Raman shift [1/cm] | calculated (rel. Intensity) |
|--------------------|------------------------------|--------------------|---------------------------------|--------------------|-----------------------------|
| 177.81             | 0.4357                       | 104.2              | 0.6184                          | 35.9242            | 1                           |
| 239.3              | 0.2013                       | 172.97             | 0.2952                          | 43.9189            | 0.82499                     |
| 299.07             | 0.0263                       | 232.76             | 0.1419                          | 55.2154            | 0.110062                    |
| 323.59             | 0.1781                       | 324.38             | 0.1706                          | 81.8538            | 0.051599                    |
| 405.68             | 0.0606                       | 370                | 0.1252                          | 82.5028            | 0.248164                    |
| 435.37             | 0.1133                       | 401.74             | 0.0796                          | 105.6354           | 0.039687                    |
| 501.5              | 0.1177                       | 433.88             | 0.1820                          | 123.7437           | 0.040035                    |
| 523.29             | 0.2906                       | 499.22             | 0.1086                          | 132.7901           | 0.039121                    |
| 547.25             | 0.0749                       | 523.44             | 0.3207                          | 162.968            | 0.059854                    |
| 629.49             | 0.0530                       | 546.8              | 0.0720                          | 173.8385           | 0.036245                    |
| 664.26             | 0.1095                       | 615.52             | 0.0478                          | 178.5872           | 0.007334                    |
| 721.98             | 0.0640                       | 630.28             | 0.0400                          | 222.5964           | 0.03822                     |
| 784.73             | 0.0258                       | 662.64             | 0.0857                          | 233.961            | 0.008573                    |
| 809.46             | 0.0752                       | 729.74             | 0.0620                          | 251.1505           | 0.012972                    |
| 856.14             | 0.2301                       | 788.04             | 0.1313                          | 294.8046           | 0.001755                    |
| 918.91             | 0.0644                       | 809.93             | 0.1090                          | 316.0748           | 0.004551                    |
| 975.88             | 0.0238                       | 852.26             | 0.3383                          | 327.2351           | 0.029057                    |
| 1033.4             | 0.2077                       | 917.34             | 0.0819                          | 393.2534           | 0.001182                    |
| 1059.5             | 0.0734                       | 1031.9             | 0.2964                          | 402.7384           | 0.010633                    |
| 1105.1             | 0.0275                       | 1056.2             | 0.0895                          | 429.8721           | 0.005486                    |
| 1153.1             | 0.1660                       | 1071.9             | 0.0575                          | 434.7406           | 0.00668                     |
| 1212.6             | 0.0567                       | 1103.3             | 0.0540                          | 439.8508           | 0.026862                    |
| 1232.9             | 0.0698                       | 1153.9             | 0.1874                          | 496.8108           | 0.001395                    |
| 1256.4             | 0.0203                       | 1194.2             | 0.0498                          | 504.3255           | 0.007844                    |
| 1305.5             | 0.1457                       | 1229.8             | 0.0760                          | 514.1482           | 0.012584                    |
| 1362.9             | 0.7155                       | 1305.4             | 0.2123                          | 523.8587           | 0.002229                    |
| 1439.4             | 0.1868                       | 1364.8             | 0.9954                          | 533.3569           | 0.04454                     |
| 1513.8             | 0.2589                       | 1438.4             | 0.2232                          | 545.0552           | 0.002086                    |
| 1561.6             | 0.8268                       | 1456.6             | 0.1812                          | 559.0915           | 0.008792                    |
| 1584.1             | 0.4196                       | 1514.9             | 0.2628                          | 628.443            | 0.007451                    |
| 1612.4             | 0.9761                       | 1563               | 0.7580                          | 629.012            | 0.004225                    |
|                    |                              | 1585.4             | 0.3557                          | 648.8838           | 0.005148                    |
|                    |                              | 1615.4             | 0.5463                          | 678.2897           | 0.010422                    |
|                    |                              | 1626.4             | 0.5526                          | 744.6389           | 0.003892                    |
|                    |                              | 1710.4             | 0.0575                          | 748.5332           | 0.001529                    |

|  |  |  |  |          |          |
|--|--|--|--|----------|----------|
|  |  |  |  | 750.11   | 0.001747 |
|  |  |  |  | 756.4224 | 0.002603 |
|  |  |  |  | 797.3976 | 0.003124 |
|  |  |  |  | 802.9735 | 0.001291 |
|  |  |  |  | 820.0367 | 0.012012 |
|  |  |  |  | 860.0513 | 0.009588 |
|  |  |  |  | 864.0958 | 0.043457 |
|  |  |  |  | 887.3937 | 0.001807 |
|  |  |  |  | 899.2811 | 0.001491 |
|  |  |  |  | 920.1665 | 0.001257 |
|  |  |  |  | 929.0738 | 0.00817  |
|  |  |  |  | 930.6405 | 0.00322  |
|  |  |  |  | 990.3265 | 0.007091 |
|  |  |  |  | 1042.655 | 0.036065 |
|  |  |  |  | 1049.962 | 0.00335  |
|  |  |  |  | 1053.289 | 0.028164 |
|  |  |  |  | 1066.648 | 0.004043 |
|  |  |  |  | 1072.498 | 0.007134 |
|  |  |  |  | 1073.185 | 0.017532 |
|  |  |  |  | 1095.222 | 0.001605 |
|  |  |  |  | 1096.306 | 0.003384 |
|  |  |  |  | 1121.364 | 0.007697 |
|  |  |  |  | 1154.999 | 0.003946 |
|  |  |  |  | 1169.59  | 0.004624 |
|  |  |  |  | 1169.753 | 0.00707  |
|  |  |  |  | 1178.318 | 0.018407 |
|  |  |  |  | 1181.679 | 0.001168 |
|  |  |  |  | 1182.146 | 0.015881 |
|  |  |  |  | 1188.461 | 0.00167  |
|  |  |  |  | 1211.608 | 0.001161 |
|  |  |  |  | 1221.241 | 0.007318 |
|  |  |  |  | 1238.728 | 0.001406 |
|  |  |  |  | 1240.087 | 0.013332 |
|  |  |  |  | 1257.006 | 0.018688 |
|  |  |  |  | 1283.767 | 0.006283 |
|  |  |  |  | 1292.704 | 0.001372 |
|  |  |  |  | 1312.144 | 0.019095 |
|  |  |  |  | 1335.806 | 0.00294  |
|  |  |  |  | 1337.029 | 0.056565 |
|  |  |  |  | 1349.424 | 0.001389 |
|  |  |  |  | 1354.665 | 0.013467 |
|  |  |  |  | 1375.151 | 0.003322 |
|  |  |  |  | 1375.594 | 0.006666 |

|  |  |  |  |          |          |
|--|--|--|--|----------|----------|
|  |  |  |  | 1385.753 | 0.128261 |
|  |  |  |  | 1389.144 | 0.035671 |
|  |  |  |  | 1400.617 | 0.038002 |
|  |  |  |  | 1409.194 | 0.003401 |
|  |  |  |  | 1412.841 | 0.013115 |
|  |  |  |  | 1469.417 | 0.017683 |
|  |  |  |  | 1470.253 | 0.008315 |
|  |  |  |  | 1482.5   | 0.007799 |
|  |  |  |  | 1483.612 | 0.013053 |
|  |  |  |  | 1494.443 | 0.023916 |
|  |  |  |  | 1495.059 | 0.001732 |
|  |  |  |  | 1497.686 | 0.003298 |
|  |  |  |  | 1498.106 | 0.001542 |
|  |  |  |  | 1499.498 | 0.006299 |
|  |  |  |  | 1552.834 | 0.058747 |
|  |  |  |  | 1554.622 | 0.010687 |
|  |  |  |  | 1597.3   | 0.17029  |
|  |  |  |  | 1600.89  | 0.03881  |
|  |  |  |  | 1623.659 | 0.093093 |
|  |  |  |  | 1626.644 | 0.021728 |
|  |  |  |  | 1652.772 | 0.177803 |
|  |  |  |  | 1664.334 | 0.102739 |

## References

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