Supporting Information

Fluorescence and absorption of Rhodamine 6G solutions as pressure standards for a diamond-anvil cell

*Ida Moszczyńska, Anna Golczak, Marek Sikorski, Andrzej Katrusiak **

The procedure of obtaining peak centroid position by using OriginPro 8.1 software

Obtained spectra were smoothed with FFT Filter method with a 5-point window. Elimination of the vibrational structure of spectra in the peak centroid method leads to about 2.5 × higher accuracy compared to reading the peak center position directly. To eliminate the vibrational structure, the two Gaussian peaks were fitted by the Multiple Peak Fit function (Figure S1).

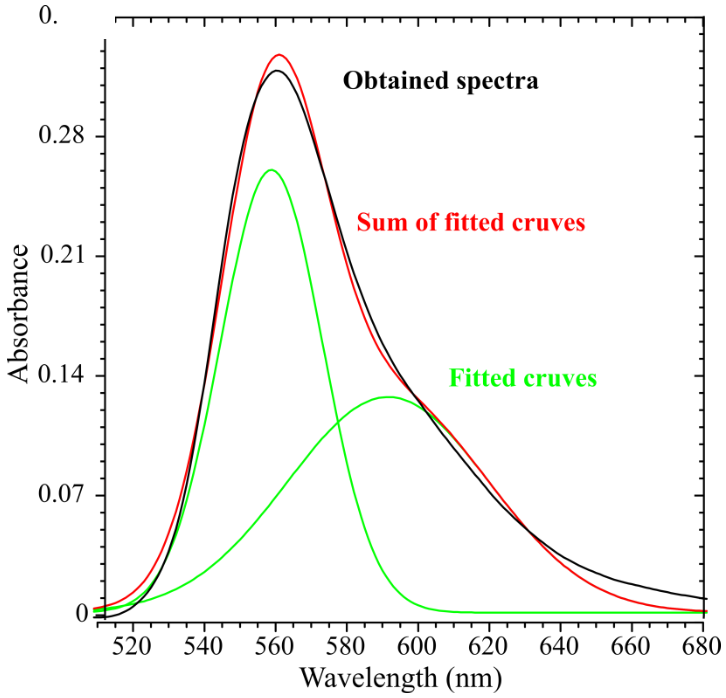

Figure S1. Example of Gaussian peak fitting in a case of absorption spectrum of R6G solution in methanol (1 × 10^{-4} mol/dm^3). Original spectrum fitted Gaussian peaks and sum of fitted Gaussian peaks are shown respectively in black, green and red.

A wide and less intense Gaussian peak was neglected, while the position of the narrow Gaussian centroid contains the information about the pressure (Tables S1, S2 and S3). The peak centroid position was obtained by integration. A similar integration procedure was used for pressure calibration, based on ruby fluorescence.[1]

Table S1. Gaussian peak centroid shift of methanolic R6G solution (concentration 1 × 10^{-4} mol/dm^3) fluorescence spectra dependence on pressure p (GPa). For these data, λ_0 = 558.740 nm.

Pressure (GPa)	Gaussian peak centroid shift $\Delta\lambda=\lambda-\lambda_0$ (nm) $p=0.0218(81)\Delta\lambda+0.0049(4)\Delta\lambda^2$
0.0	0
0.1	2.812
0.2	4.541
0.3	5.911
0.4	7.081
0.5	8.120
0.6	9.063
0.7	9.934
0.8	10.746
0.9	11.510
1.0	12.234
1.1	12.923
1.2	13.583
1.3	14.215
1.4	14.825
1.5	15.413
1.6	15.983
1.7	16.535
1.8	17.071
1.9	17.593
2.0	18.101
2.1	18.597
2.2	19.082
2.3	19.555
2.4	20.019
2.5	20.473
2.6	20.918
2.7	21.355
2.8	21.784
2.9	22.205
3.0	22.619
3.1	23.027
3.2	23.428
3.3	23.822
3.4	24.211

Table S2. Gaussian peak centroid shift of ethanolic R6G solution (concentration 1 × 10^{-4} mol/dm^3) fluorescence spectra dependence on pressure *p* (GPa). For these data, $\lambda_0 = 564.210$ nm.

Pressure (GPa)	Gaussian peak centroid shift $\Delta\lambda=\lambda-\lambda_0$ (nm) $p=(0.1304\pm0.0192)\Delta\lambda+(0.0209\pm0.0035)\Delta\lambda^2$
0.0	0
0.1	0.691
0.2	1.274
0.3	1.789
0.4	2.254
0.5	2.682
0.6	3.081
0.7	3.455
0.8	3.810
0.9	4.147
1.0	4.469
1.1	4.778
1.2	5.075
1.3	5.362
1.4	5.640
1.5	5.909
1.6	6.170
1.7	6.424
1.8	6.672
1.9	6.913

Table S3. Gaussian peak centroid shift of isopropanol R6G solution (concentration 1 × 10^{-4} mol/dm^3) fluorescence spectra dependence on pressure *p* (GPa). For these data, $\lambda_0 = 561.292$ nm.

Pressure (GPa)	Gaussian peak centroid shift $\Delta\lambda=\lambda-\lambda_0$ (nm) $p=(0.0547\pm0.0002)\Delta\lambda+(0.0048\pm0.0001)\Delta\lambda^2$
0.0	0
0.1	1.602
0.2	2.912
0.3	4.047
0.4	5.063
0.5	5.991
0.6	6.851
0.7	7.655
0.8	8.414
0.9	9.134
1.0	9.820
1.1	10.478
1.12	10.606

Table S4. Gaussian peak centroid shift of aqueous R6G solution (concentration 5×10^{-3} mol/dm^3) fluorescence spectra dependence on pressure *p* (GPa). For these data, $\lambda_0 = 558.000$ nm.

Pressure (GPa)	Gaussian peak centroid shift $\Delta\lambda=\lambda-\lambda_0$ (nm) $p=(0.0372\pm0.0126)\Delta\lambda+(0.0026\pm0.0010)\Delta\lambda^2$
0.0	0
0.1	2.314
0.2	4.165
0.3	5.753
0.4	7.165
0.5	8.451
0.6	9.638
0.7	10.747
0.8	11.791
0.9	12.780
0.96	13.351

Table S5. Gaussian peak centroid shift of methanolic R6G solution (concentration 1 × 10^{-4} mol/dm^3) absorbance spectra dependence on pressure *p* (GPa). For these data, λ_0 = 510.070 nm.

Pressure (GPa)	Gaussian peak centroid shift $\Delta\lambda=\lambda-\lambda_0$ (nm) $p=(0.1028\pm0.0066)\Delta\lambda+(0.0091\pm0.0006)\Delta\lambda^2$
0.0	0
0.1	0.901
0.2	1.692
0.3	2.406
0.4	3.061
0.5	3.671
0.6	4.243
0.7	4.784
0.8	5.298
0.9	5.789
1.0	6.259
1.1	6.712
1.2	7.149
1.3	7.571
1.4	7.981
1.5	8.378
1.6	8.764
1.7	9.141
1.8	9.508
1.9	9.866
2.0	10.217
2.1	10.559
2.2	10.894
2.3	11.223
2.4	11.546
2.5	11.862
2.6	12.173
2.7	12.479
2.8	12.780
2.9	13.076
3.0	13.367
3.1	13.654
3.2	13.936
3.3	14.215
3.4	14.489

Table S6. Gaussian peak centroid shift of ethanolic R6G solution (concentration 1 × 10^{-4} mol/dm^3) absorbance spectra dependence on pressure p (GPa). For these data, λ_0 = 530.585 nm.

Pressure (GPa)	Gaussian peak centroid shift $\Delta\lambda=\lambda-\lambda_0$ (nm) $p=(0.1073\pm0.0125)\Delta\lambda+0.0084(0.0016)\Delta\lambda^2$
0.0	0
0.1	0.873
0.2	1.651
0.3	2.360
0.4	3.016
0.5	3.629
0.6	4.206
0.7	4.754
0.8	5.276
0.9	5.776
1.0	6.256
1.1	6.718
1.2	7.165
1.3	7.597
1.4	8.016
1.5	8.424
1.6	8.821
1.7	9.207
1.8	9.584
1.9	9.953

Table S7. Gaussian peak centroid shift of isopropanol R6G solution (concentration 1 × 10^{-4} mol/dm^3) absorbance spectra dependence on pressure p (GPa). For these data, λ_0 = 531.003 nm.

Pressure (GPa)	Gaussian peak centroid shift $\Delta\lambda=\lambda-\lambda_0$ (nm) $p=(0.1032\pm0.0170)\Delta\lambda+(0.0018\pm0.0030)\Delta\lambda^2$
0.0	0
0.1	0.954
0.2	1.877
0.3	2.773
0.4	3.645
0.5	4.493
0.6	5.321
0.7	6.128
0.8	6.918
0.9	7.690
1.0	8.446
1.1	9.187
1.12	9.334

Table S8. Gaussian peak centroid shift of aqueous R6G solution (concentration 1×10^{-4} mol/dm^3) absorbance spectra dependence on pressure *p* (GPa). For these data, $\lambda_0 = 509.604$ nm.

Pressure (GPa)	Gaussian peak centroid shift $\Delta\lambda=\lambda-\lambda_0$ (nm) $p=(0.4259\pm0.0368)\Delta\lambda+(-0.0046\pm0.0152)\Delta\lambda^2$
0.0	0
0.1	0.236
0.2	0.472
0.3	0.710
0.4	0.949
0.5	1.190
0.6	1.431
0.7	1.674
0.8	1.918
0.9	2.164
0.96	2.312

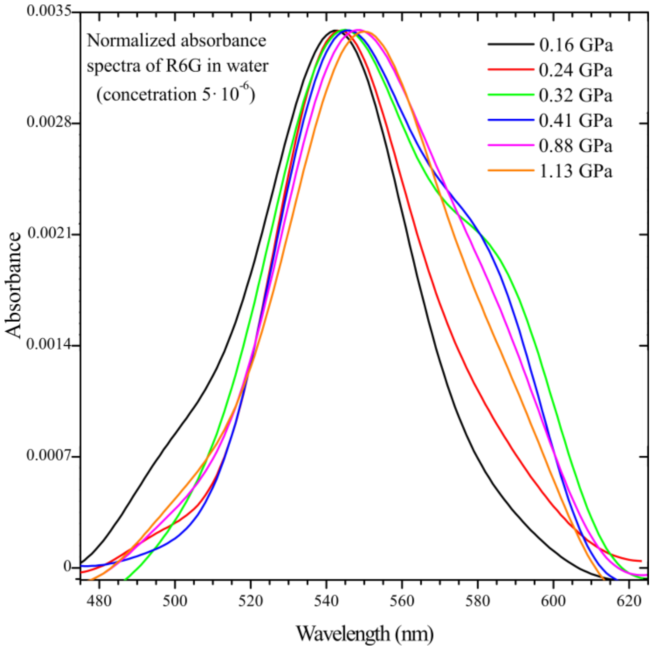

Figure S2. Absorption spectrum of R6G dissolved in water (5×10^{-6} mol/dm^3) at different applied pressure *p* (GPa).

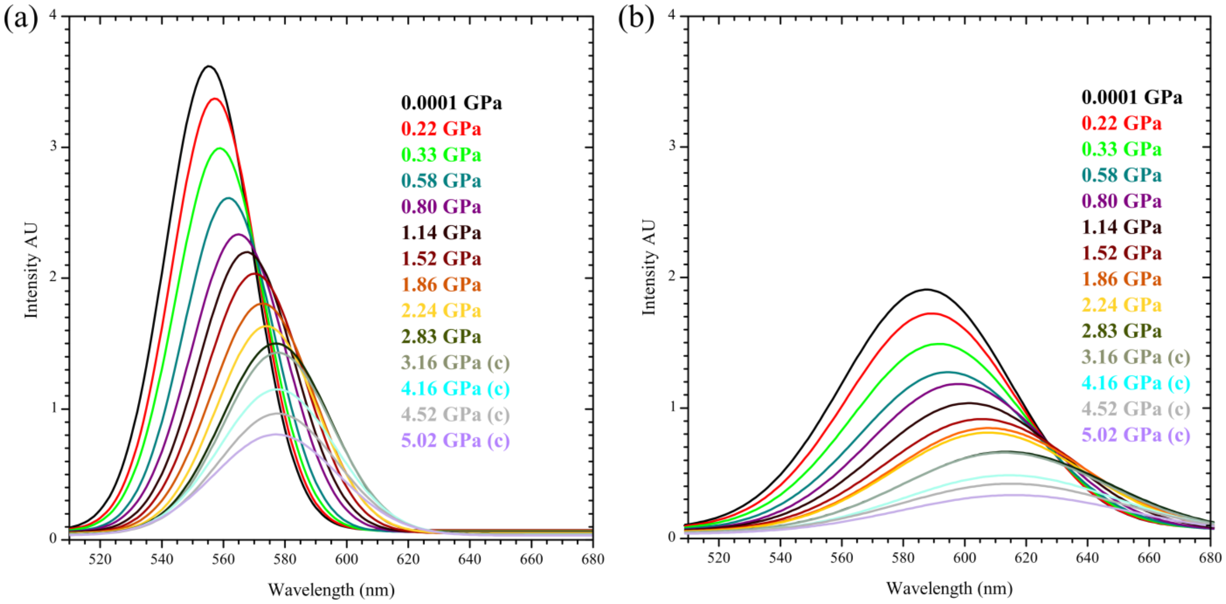

Figure S3. Emission spectra of R6G in methanol at different applied pressure *p* (GPa).. HI (a) and LI (b) peaks are shown as fitted normalized functions. Symbol “c” (crystal) was used to indicated points over hydrostatic limit of methanol.

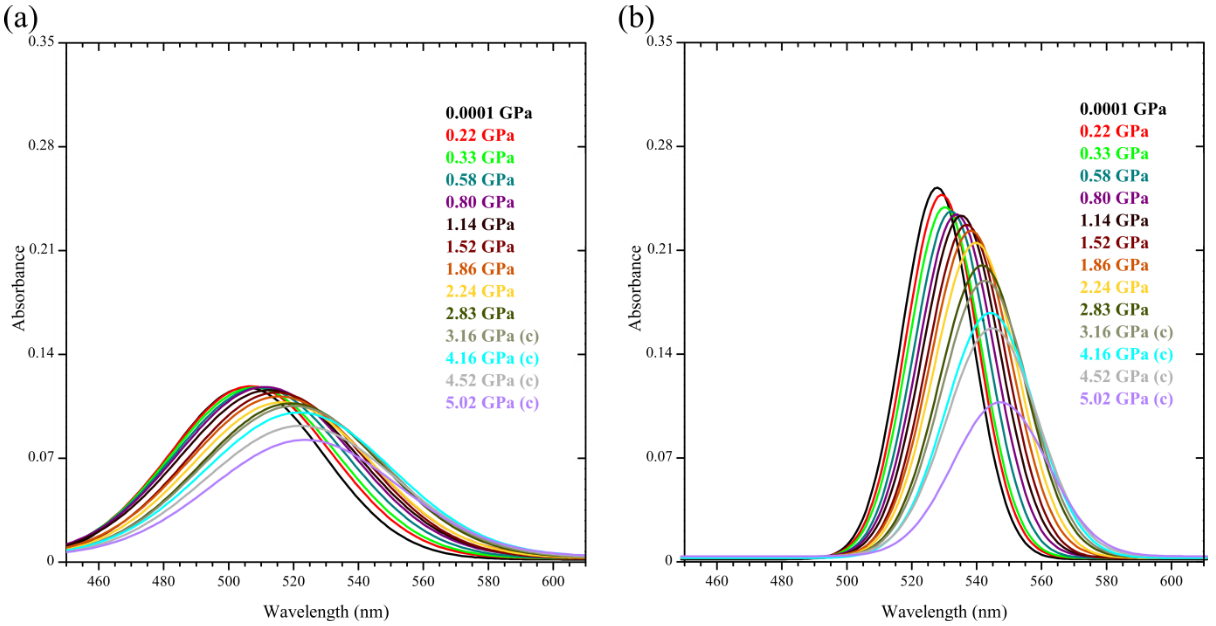

Figure S4. Absorption spectra of R6G in methanol at different applied pressure .*p* (GPa). LI (a) and HI (b) peaks are shown as fitted normalized functions. Symbol “c” (crystal) was used to indicated points over hydrostatic limit of methanol.

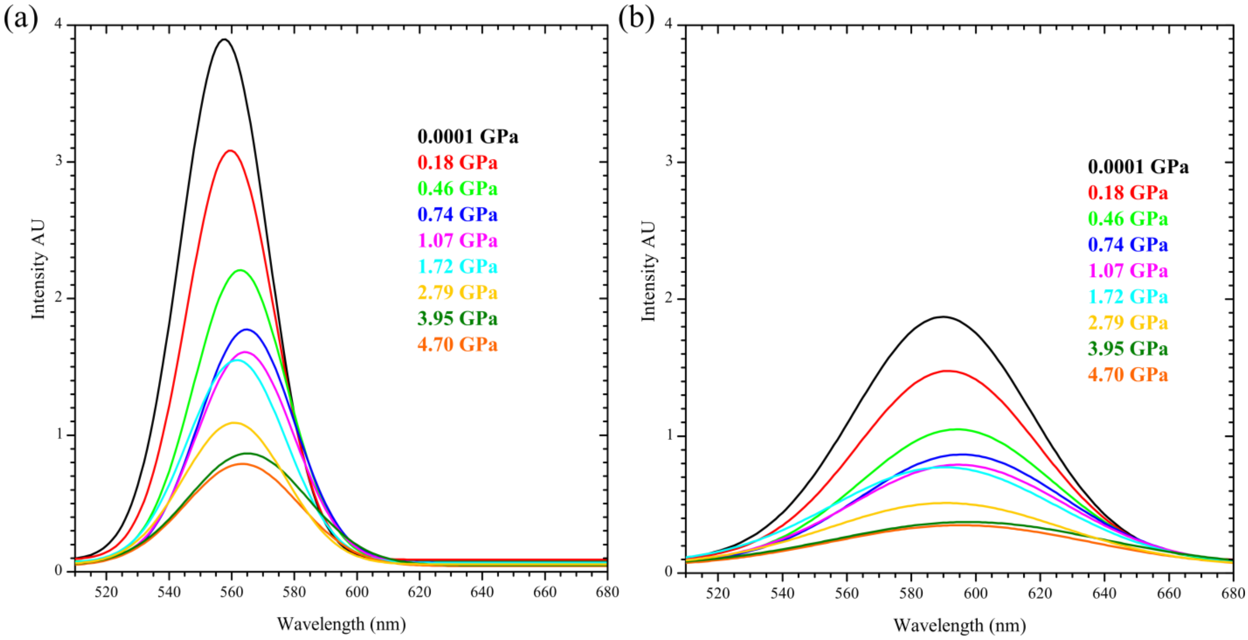

Figure S5. Emission spectra of R6G in 2-propanol at different applied pressure *p* (GPa).. HI (a) and LI (b) peaks are shown as fitted normalized functions.

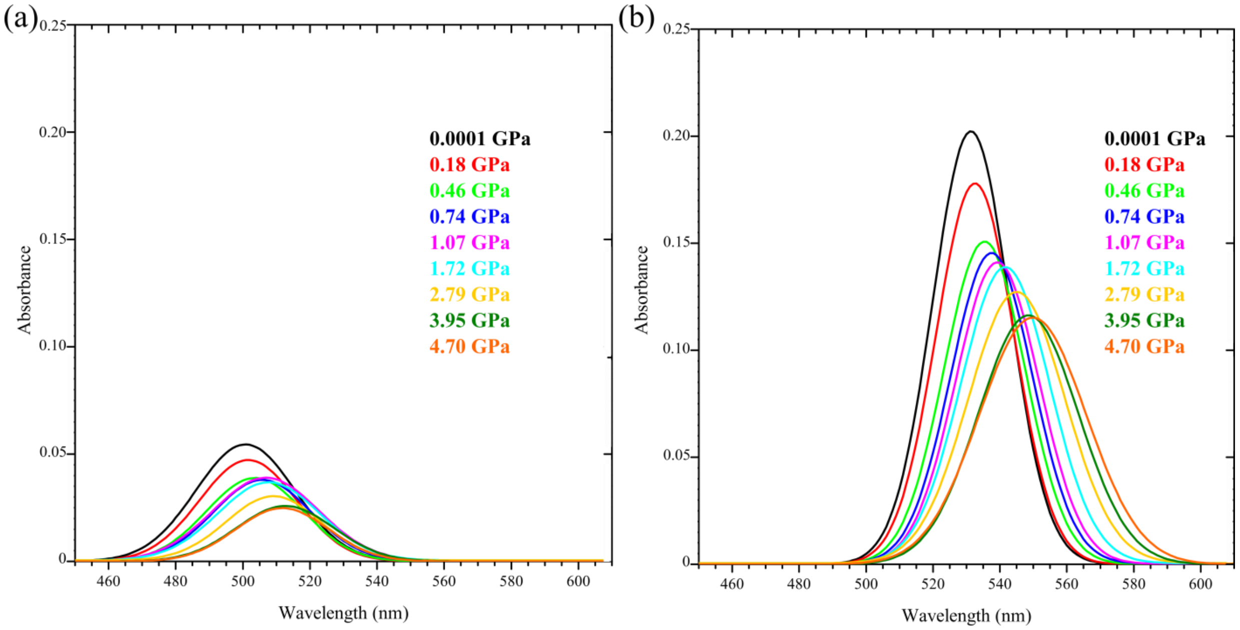

Figure S6. Absorption spectra of R6G in 2-propanol at different applied pressure *p* (GPa).. LI (a) and HI (b) peaks are shown as fitted normalized functions.

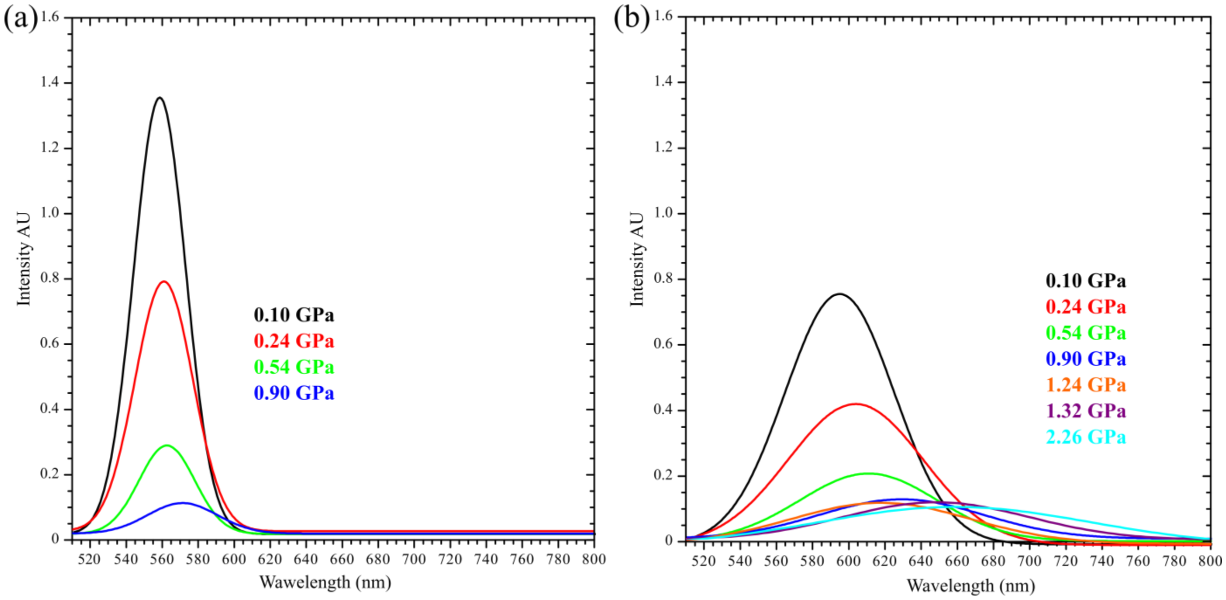

Figure S7. Emission spectra of R6G in water at 5·10^{-3} mol/dm^3 at applied different pressure *p* (GPa).. HI (a) and LI (b) peaks are presented as fitted normalized functions.

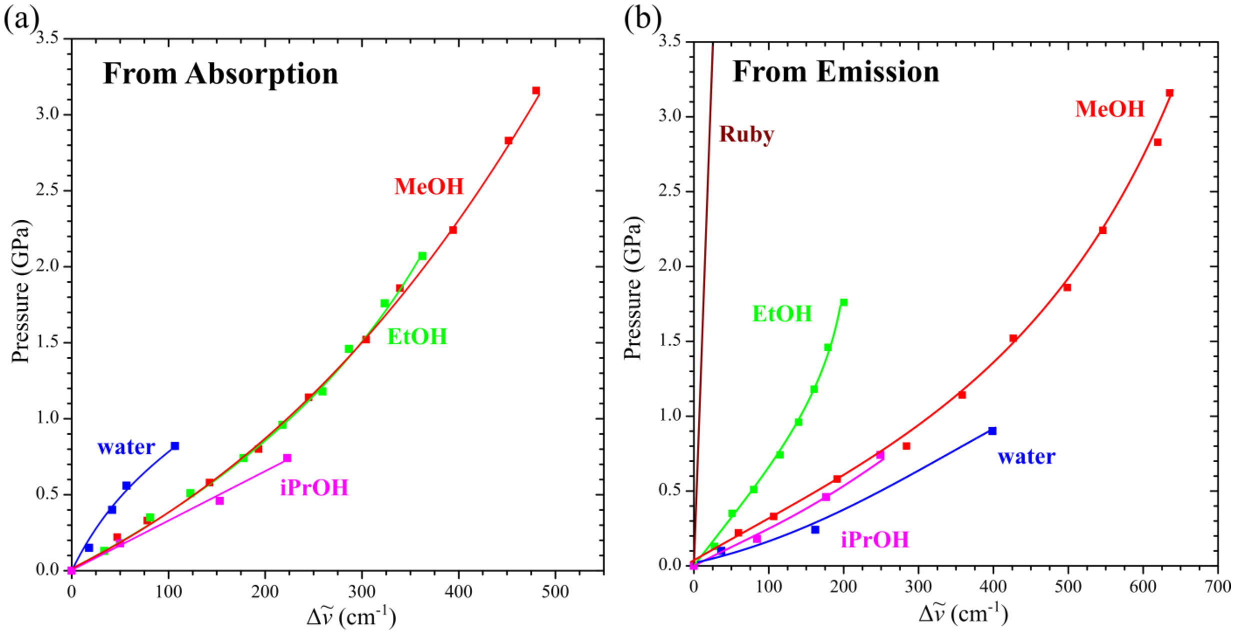

Figure S8. Pressure plotted as a function of HI absorption and emission peak shift. R6G concentrations for alcoholic solutions equals 1 × 10^{-4} mol/dm^3, while for aqueous 5 × 10^{-3} mol/dm^3.

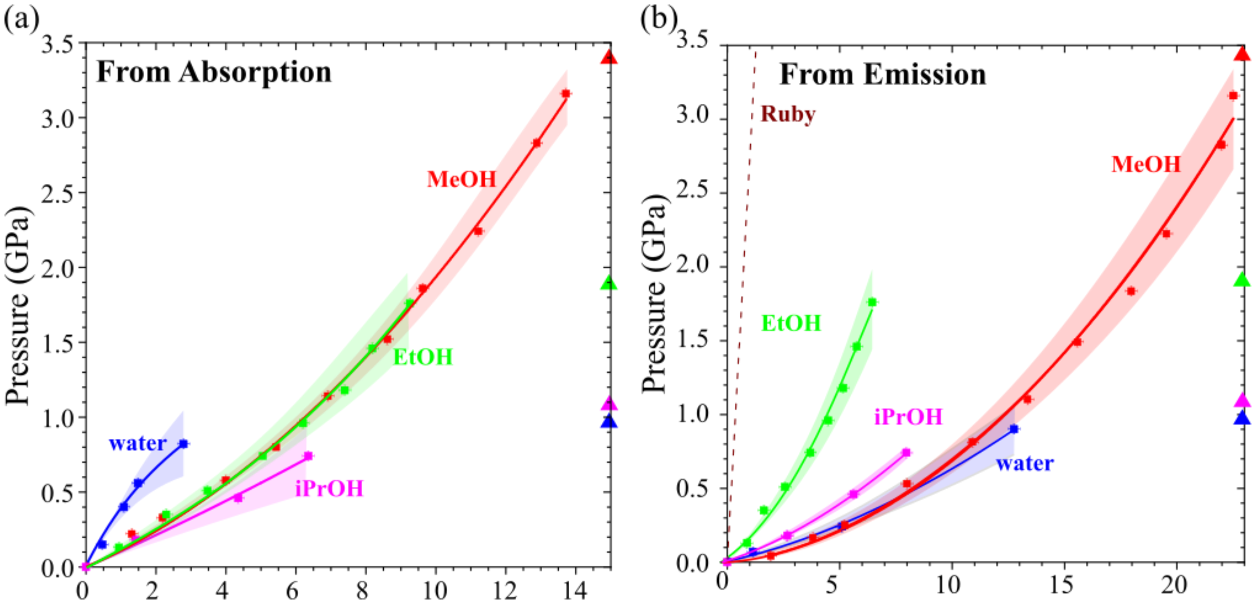

Figure S9. Pressure plotted as a function of HI absorption and emission peak shift. R6G concentrations for alcoholic solutions equals 1 × 10^{-4} mol/dm^3, while for aqueous 5 × 10^{-3} mol/dm^3. Highlights indicate the uncertainty regions of regression-lines, calculated according the equation: $p = (a \pm a_{esd})\Delta\lambda + (b \pm b_{esd})\Delta\lambda^2$, where parameters a, b and their standard deviations a_{esd} and b_{esd} are given in Tables S1-S8.

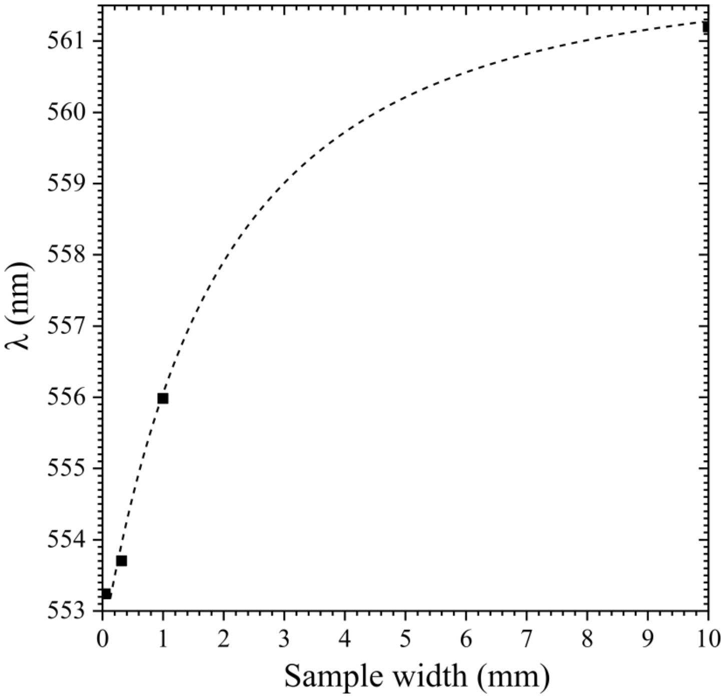

Figure S10. Dependence of sample width on luminescence shift, measured for methanol solution, concentration 1 × 10^{-4} mol/dm^3 at ambient conditions (0.1 MPa, 293 K).

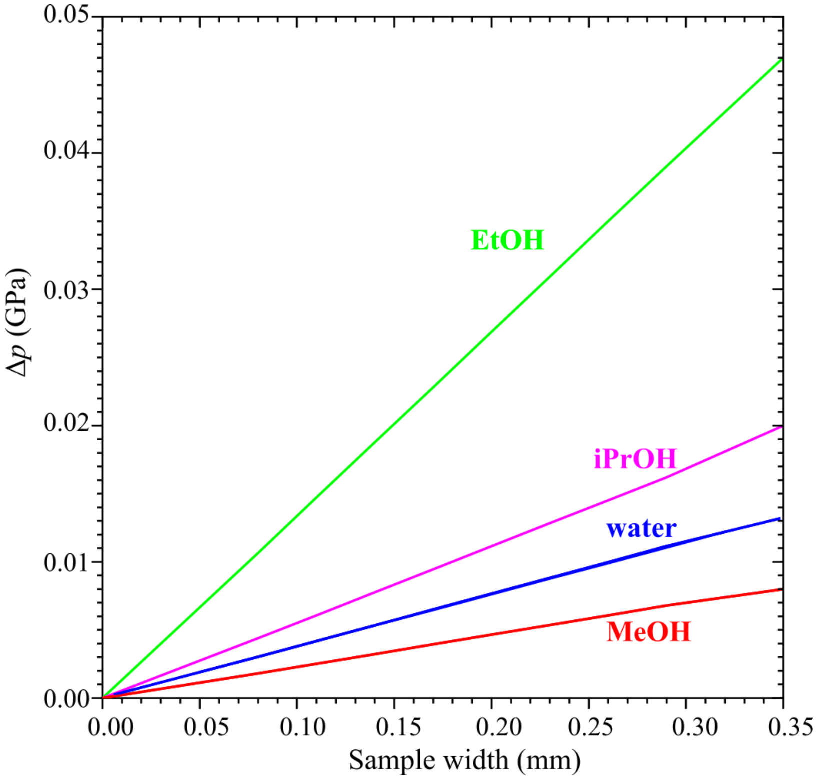

Figure S11. Pressure-calibration shift (error) depending on the Rhodamine 6G solution (concentration 1×10^{-4} mol/dm^3) thickness (sample width) as determined from the measurements of the luminescence of the methanol, ethanol, isopropanol and water solutions at 0.1 MPa and 293 K (*cf. Figure S12 in the Supporting Information*).

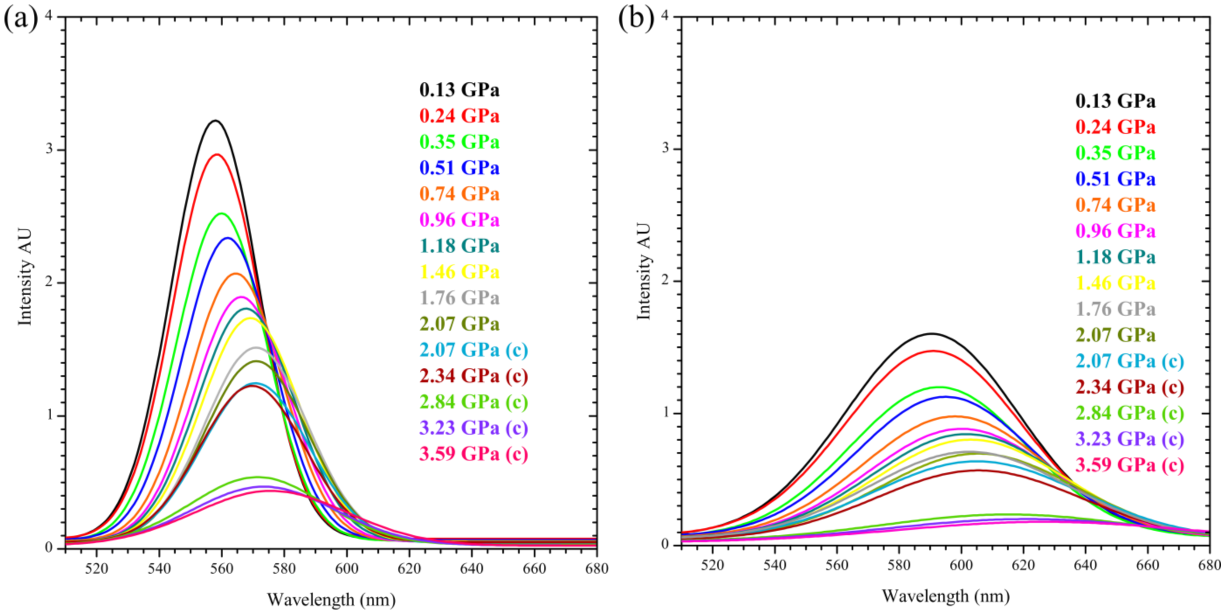

Figure S12. Emission spectra of R6G in ethanol at different applied pressure *p* (GPa).. HI (a) and LI (b) peaks are shown as fitted normalized functions. Symbol "c" (crystal) was used to indicated points over hydrostatic limit of ethanol.

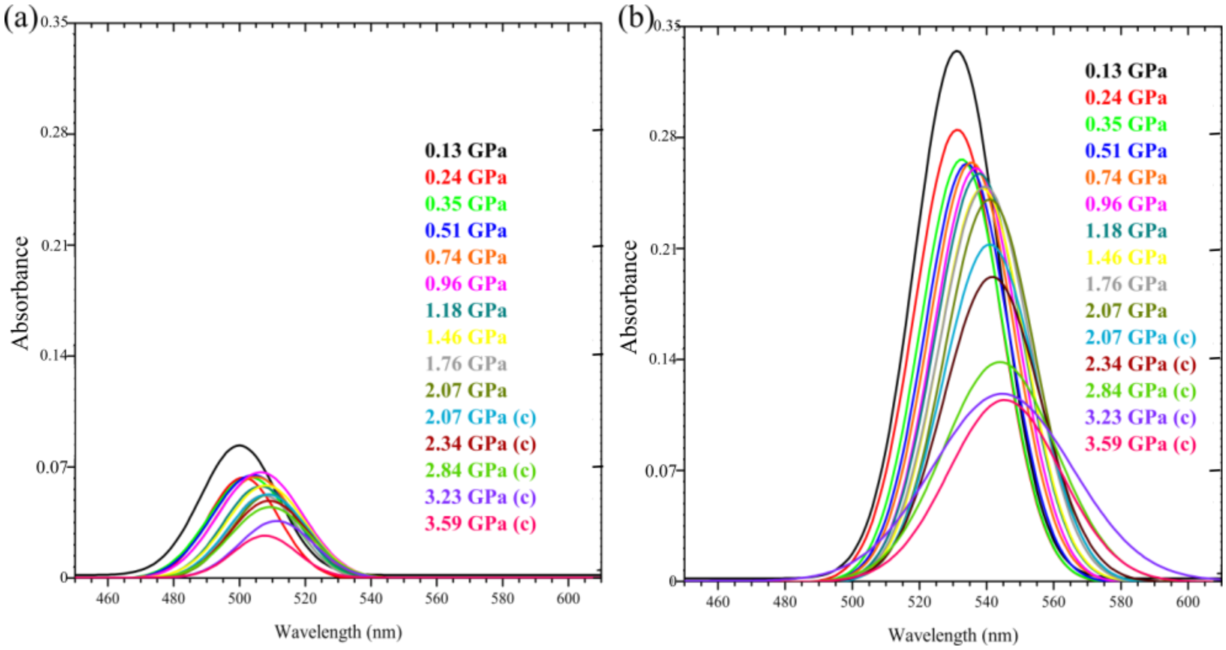

Figure S13. Absorption spectra of R6G in ethanol at different applied pressure *p* (GPa).. LI (a) and HI (b) peaks are shown as fitted normalized functions. Symbol “c” (crystal) was used to indicated points over hydrostatic limit of ethanol.

Protocol for determining pressure from absorption and fluorescence of R6G is solutions

To facilitate the determination of pressure in a DAC we provide a protocol of such calibration.

Manual Instruction for Pressure Calibration by using the R6G method

1. Prepare a pressure calibrating medium by dissolving 4.8 × 10^{-4} g of R6G in 10 cm^3 of solvent (you can use methanol, ethanol or isopropanol) to obtain concentration 1 × 10^{-4} mol/dm^3.

2. Prepare DAC:

- Clean the DAC with acetone
- Drill a hole (4 mm diameter) in a steel plate.
- Center the gasket on diamonds collets (the gasket needs to be preindented).

3. Measure the fluorescence spectrum of the empty DAC with gasket to make sure that your DAC is clean. Fluorolog 3-22 Spex Horiba Jobin-Yvon spectrofluorometer settings:
    - Front Face mode
    - Excitation slit: 5 nm
    - Emission slit: 5 nm
    - Integration time: 0.1 s
    - Excitation wavelength: 490 nm
4. Put the sample together with a pressure calibrating medium (prepared in Step 1) in the DAC.
5. To obtain λ_0, measure the fluorescence spectrum at $p = 0$ in next iteration make measurements of λ_i applying the pressure under study with a Fluorolog 3-22 Spex Horiba Jobin-Yvon spectrofluorometer using the settings specified in Step 3. (*cf.* The photo of experiment shown at the end of this protocol as a Figure S14)
6. Smooth the obtained fluorescence spectra by using OriginPro 8.1 software function FFT filter with 5-point window. (Analysis → Signal Processing → Smooth)
7. Eliminate the vibrational structure of spectrum by fitted of the spectrum to two Gauss peaks by using OriginPro 8.1 software function (Analysis → Peaks and Baseline → Multiple Peak Fit).
8. Integrate obtained Higher Intensity Gauss peak in the limits from 520 to 660 nm. (Gadgets → Integration).
9. Read the peak centroid position.
10. Repeat steps 5-9 with pressure applied to the DAC to obtain λ_i.
11. Go to the SI tables (S1/S2/S3) and directly correlate the observed $\Delta\lambda$ to p, or use the equations presented in Table 1. Please note that we recommend using $p(\Delta\lambda)$ to be applied when $\Delta\lambda = \lambda_i - \lambda_0$, where λ_0 – the maximum of emission at normal pressure, λ_i – is the

pressure under study. The $\Delta\lambda$ has to be expressed in nm, and p will be in GPa. That procedure should avoid any calibration problems of the instruments.

The above protocol can be easily adapted to use absorption spectra and a spectrophotometer instead of emission spectra and a spectrofluorometer, applying respective equation from Table 1.

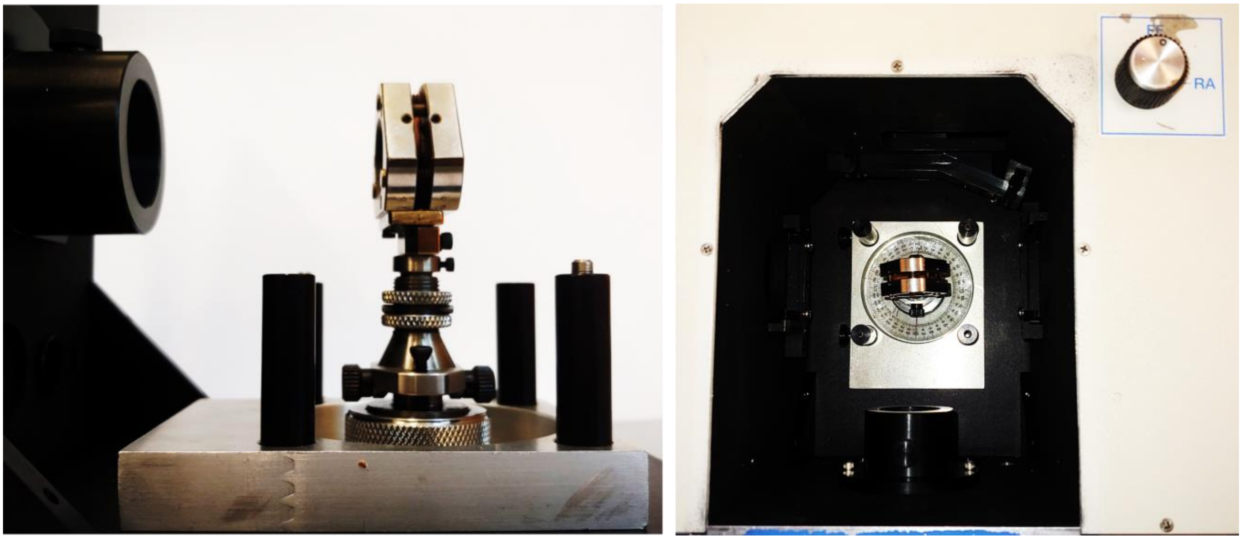

Figure S14. A side (left) and top (right) views of the front-face fluorescence-measurement setup for the diamond-anvil cell mounted in a Fluorolog 3-22 Spex Horiba Jobin Yvon spectrofluorometer.

Reference

[1] G. J. Piermarini, S. Block, J. D. Barnett, R. A. Forman,. *J. Appl. Phys.* **1975**, *46*, 2774–2780. DOI: 10.1063/1.321957.