Imperial College London

Mapping the phase diagram of a three-liquid mixture with the help of a solvatochromic fluorescent dye.

In this experiment you will map the ternary phase diagram of a mixture of three liquids - water, toluene and ethanol - to determine the compositions at which the liquids are, or are not, miscible. You will use fluorimetry and a solvatochromic fluorescent molecule, whose emission wavelength depends on solvent polarity, to help determine the composition of mixtures.

You will encounter relevant concepts on (ternary) phase diagrams in the *Solids, Liquids and Interfaces Module* (Lecture 4), while solvatochromic fluorophores and their applications will be discussed in the *Analysis of Molecules Materials and Mixtures Module* (Lecture 22). Basic notions are also summarized below.

Experimental Objectives

1. Construct the ternary phase diagram of water, ethanol and toluene by locating the boundary (known as the binodal curve) separating the single-phase region from the two-phase region.
2. Trace tie-lines (discussed below) within the two-phase region.

Learning Outcomes

1. Acquire a practical understanding of equilibrium thermodynamic concepts as seen in the *Solids, Liquids and Interfaces Module*, including phase coexistence, phase diagrams, miscible/immiscible fluids and binodal regions.
2. Acquire a practical understanding of the behavior of polarity-sensitive fluorescent dyes as seen in the *Analysis of Molecules Materials and Mixtures Module.*
3. Develop computer-assisted data analysis skills (curve fitting).

1. Background

1.1 Review of ternary phase diagrams

Consider the three liquids A, B and C, where B and C are only sparingly miscible with each other and A is completely miscible with both B and C. Their ternary phase diagram is shown in Fig. 1, and we will now discuss its characteristics while summarizing the notions we will need to understand and use this type of diagram.

In Fig. 1, the three **axes** are labelled with the mass fraction of each component m_i/M, where m_i is the mass of a given fluid ($i = A, B, C$) and M is the total mass of the liquid ($M = m_A + m_B + m_C$).

The **apices** of the plot represent pure systems: the apex labelled as A represents $m_A/M = 1$, the one labelled as B indicates $m_B/M = 1$, and that labeled as C marks $m_C/M = 1$.

The **edges** of the plot represent two-component mixtures. For instance, the edge between apices A and B indicates a two component AB system, with $(m_A + m_B)/M = 1$ and $m_C/M = 0$, and analogously for the BC and AC edges.

Every other point within the triangular plot indicates three-component mixtures. To understand how to identify a point associated to a given composition (and vice versa), see Fig. 2 and caption.

Let's now go back on our edges and the corresponding binary systems. Since A is completely miscible with both B and C, binary systems AB and AC always display a single, homogeneous phase at any point of the corresponding edges.

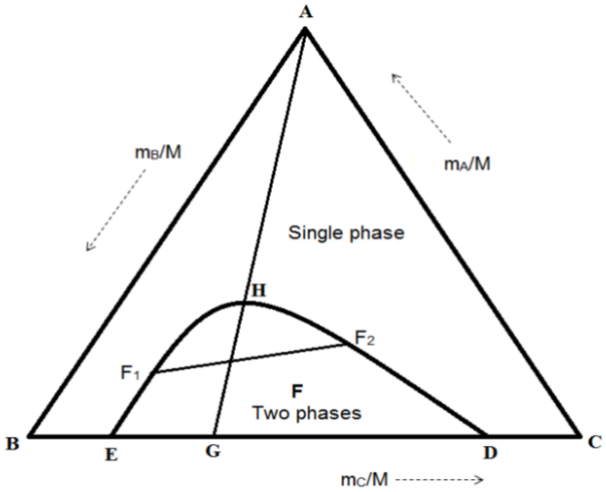

***Figure 1**. The ternary phase diagram for two partially miscible liquids B and C and a fully miscible liquid A.*

B and C, however, are only partially miscible, so we will observe **phase coexistence** in some regions of the BC edge. With reference to Fig. 1, if we start with pure B, we can increase slightly the proportion of C. Initially, C is soluble in B, so the system will still display a single phase. However, by the time we reach point E in the graph, the two liquids are no longer miscible, and we observe **two liquid phases**, a B-rich phase with composition corresponding to point E and C-rich phase with composition corresponding to point D. If we keep increasing the fraction of C, the system will continue to show two phases with these same compositions, but the amount of the B-rich phase will decrease, and that of the C-rich phase will increase. By further increasing the mass fraction of C we will reach point D, above which the B-rich phase of composition E disappears, and only a single C-rich phase is present. At mass ratios between points E and D, liquids B and C are **immiscible**, meaning that a mixture prepared with a mass ratio in this range will de-mix into the two coexisting phases. Points E and D mark the **binodal** of the BC binary system, separating the single-phase from the two-phase regions of the same diagram.

Let us now move away from the BC edge and consider once more the ternary system. Here, as shown in Fig. 1, we find a **binodal curve**, pinned onto the BC edge at points E and D and passing through point H. This curve separates the two-phase region (below the curve), form the single-phase region (above the curve) of the ternary phase diagram. Any ABC sample prepared with a composition that falls above the curve will display a single, uniform phase, while any sample with composition below the binodal will display two coexisting phases: B-rich and C-rich.

The segment connecting points F_1 and F_2 on the binodal curve is a ***tie line,*** representing a path along which we observe two-phase coexistence with compositions F_1 and F_2. If we start at F_1 we find 100% of this mixture, rich in component B. As we move towards F_2 we find that a second liquid phase appears of composition given by the point F_2, *i.e.* rich in C, ending up at point F_2 with 100% of this composition. Our location on the tie line defines the relative amount of these two phases. The tie line is the line along which the chemical potential of each liquid phase is equal.

Figure 3 shows the ternary phase diagram for mixtures of water, ethanol and toluene, which is object of this experiment. Specifically, we will determine the location of the binodal line and of two tie-lines, following the steps described below. Note that ethanol is fully soluble with both water and toluene, while water and toluene are immiscible at any mass ratio. Therefore, in our ternary phase diagram the binodal curve is pinned at the pure-water and pure-toluene apices of the diagram. Hence, if we start from pure-water and we try to move

towards pure-toluene we observe immediately a binary mixture, given that the two liquids are immiscible.

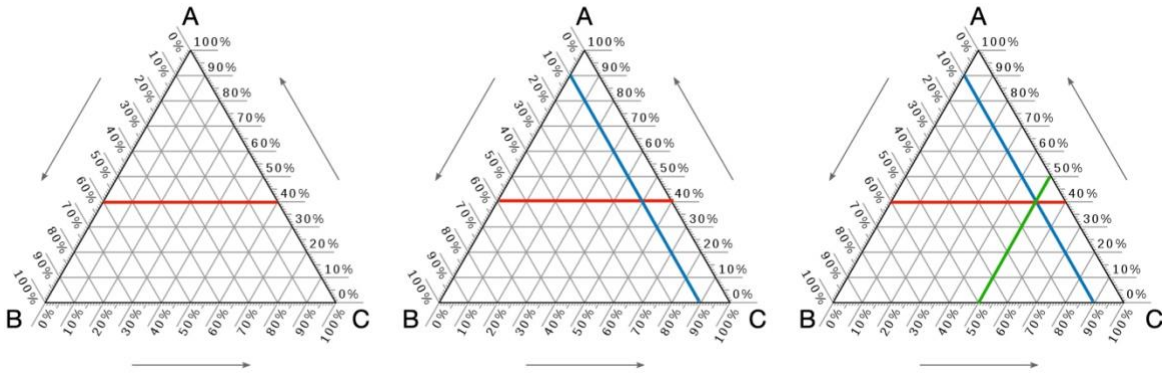

***Figure 2**. **How to locate a point with given composition on a ternary phase diagram.** For each point, the mass fraction of a given component is indicated by the distance from the edge opposite to the apex corresponding to that component. For instance, let us locate the point corresponding to $m_A/M = 0.4$, $m_B/M = 0.1$ and $m_C/M = 0.5$. First, we trace a line perpendicular to the BC edge at 0.4 times the distance from point A (red line). This line represents all the points in the phase diagram with $m_A/M = 0.4$. We then repeat the procedure for the blue line, marking all the points with $m_B/M = 0.1$. Red and blue line intersect in a single point that also belongs to the green line, corresponding (as expected) to $m_C/M = 0.5$. The intersection of the three lines is the location we are looking for.*

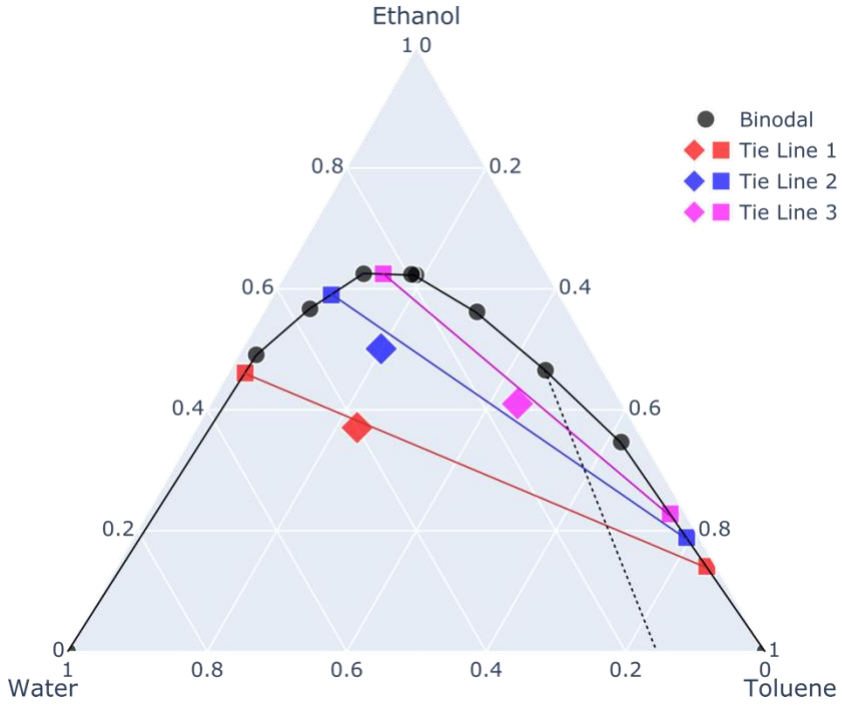

***Figure 3**. **Experimental phase ternary phase diagram for water, ethanol and toluene.** The binodal line (black) is re-constructed from discrete points (black circles) as described in this document. Note that the binodal line is pinned at the pure water and pure toluene apices as a consequence of the fact that the two liquids are immiscible at all mass ratios. The dashed line marks the path from a water-toluene binary mixture (bottom) to a point on the binodal, which one can trace by gradually adding ethanol. You will follow this approach to determine points on the binodal. Colored symbols and lines mark experimental tie-lines. The diamonds indicate the overall composition of the ternary samples (Table 2), while the squares indicate the tie-line endpoints extracted as discussed in section 4.3.*

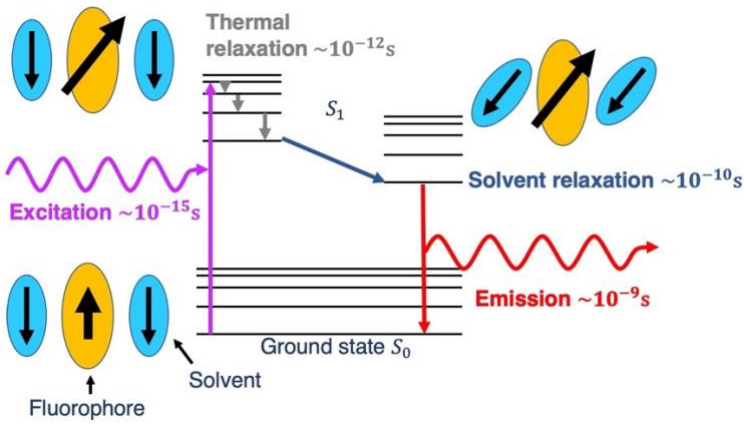

Figure 4. How solvent relaxation leads to solvatochromism in fluorescent molecules. *A fluorophore (orange) is initially in its ground state (S_0), surrounded by solvent molecules (blue). Dipoles in both are oriented to minimze dipole-dipole interaction energy. Upon photon absorption, the fluorophore becomes excited (S_1 state), leading to an increase in the magnitude of the dipole moment and a change in its orientation – dipole-dipole interaction energy with the solvent is no longer minimized. After a (possible) thermal relaxation step, but before photon emission via fluorescence, solvent relaxation occurs, consisting in the re-orientation of the solvent molecules to minimize dipole-dipole interactions once more. Solvent relaxation leads to a decrease in the energy of S_1 compared to S_0, ultimately resulting in a red shift in fluorescence emission. The latter is stronger for solvents with larger polarity, as these produce a larger decrease in S_1 energy upon solvent relaxation.*

1.2 Review of solvatochromic fluorescent molecules

A solvatochromic fluorescent molecule is one in which the wavelength of fluorescent emission depends on the polarity of the solvent. You have studied the mechanism underlying this effect in the Photochemistry Course (*Electronic States and Bonding Module*) and will review it in the *Analysis of Molecules, Materials and Mixtures Module*, so we will only briefly discuss it here with reference to Fig. 4. Consider a fluorescent molecule in its electronic ground state S_0 surrounded by solvent molecules, both with given electric dipole moments. At equilibrium, the dipoles of the solvents and the fluorophores are arranged to minimize dipole-dipole interaction energy. When the fluorescent molecule becomes excited (in its S_1 singlet state) upon absorption of an incident photon, its dipole moment generally changes in both direction and magnitude, typically becoming stronger. Photon absorption, and the subsequent thermal relaxation occur over fast timescales ($\sim 10^{-15}$ and $\sim 10^{-12}$s, respectively). The solvent molecules do not have enough time to respond, so they will suddenly find themselves in an energetically unfavorable configuration. This results in an excess dipole-dipole interaction energy that drives a **solvent relaxation** process, over which the solvent molecules re-arrange around the fluorophore to minimize dipole-dipole interaction energy once more, leading to a decrease in the energy of the excited state compared to the ground state. While slower than photon absorption and thermal relaxation, solvent relaxation occurs over timescales faster than fluorescent radiative decay ($\sim 10^{-10}$s the former and $\sim 10^{-9}$s the latter), therefore the emitted photon will see its energy decreased, and its wavelength red-shifted, due to the solvent relaxation process.

The energy decrease that the S_1 state experiences during solvent relaxation is larger for solvents with stronger dipole moments, hence the red-shift in fluorescence emission wavelength will be stronger for more polar solvents, leading to **solvatochromism.**

A good solvatochromic dye is one in which the dipole moment of the S_1 state is much stronger than that of the S_0 state. A well-known molecule that possesses this feature is **prodan**, the dye we will use in this experiment, whose structure is shown in Fig. 5a. Prodan has an excitation band peaked at ~ 360 nm (roughly independent on the type of solvent), and an emission band that shifts strongly depending on solvent polarity. Figure 5b shows the

emission spectrum of Prodan in the three pure solvents relevant to this experiment. Water, being the most polar solvent, causes the strongest red-shit (emission peak $528\ \mathrm{nm}$) followed by ethanol (emission peak $502\ \mathrm{nm}$) and the least polar toluene (emission peak $428\ \mathrm{nm}$).
The emission wavelength measured in (uniform) mixtures of two solvents is intermediate between those measured in the individual solvents – this property will help us draw the tie-lines in the ternary phase diagrams!

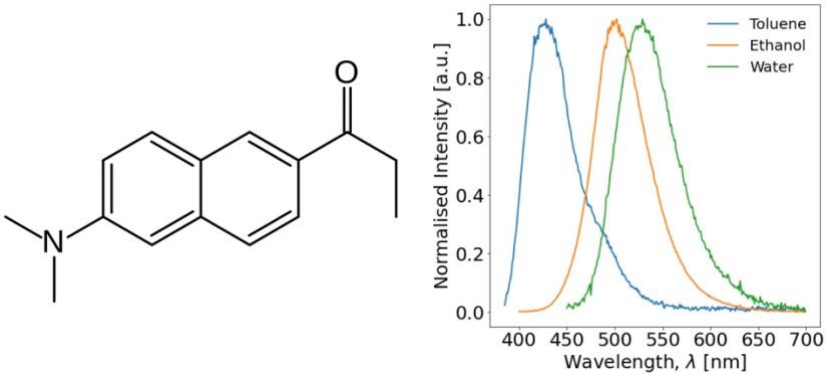

***Figure 5**. **Prodan structure (left) and its emission spectra in relevant solvents (right).** The fluorescence spectra are acquired on the setup you will be using and have been normalized to the peak intensity.*

2. *Experimental Setup and Reagents*

You will be provided with the following equipment:

- A fume cupboard, where all steps except for spectroscopic measurements will be conducted.
- A fluorescence spectrophotometer consisting in a digital spectrometer from Ocean Optics (USB650), fitted with cuvette holder integrated with an LED excitation source, suitable for exciting prodan.
- Black cloth to screen the fluorimeter from ambient light.
- 3x glass cuvettes for your samples with lids
- 2x Separating funnels
- 4x 100 mL conical flasks
- 3x 50 mL burettes for dispensing solvents
- 2-20 µl micropipette + tips
- 100-1000 µl micropipette + tips
- Small beakers for collecting samples, pouring etc.
- Clamp stands + clamps
- Solvent disposal container
- Pipette-tip disposal containers
- Desktop air pump to dry glassware and cuvettes
- Triangular graph paper (also available on blackboard)
- PPE (gloves, googles, lab coat)

And the following reagents

- Prodan solution at $0.9\ mg/ml$ concentration in ethanol
- Distilled water
- Toluene ($\geq 99.5\%$)
- Ethanol (99.8%)

2.1 How to collect prodan emission spectra with the fluorimeter

The instrument is controlled by a tailor made LabView interface – "MS2-2 Spectrometer software" – pre-installed on your computer. A snapshot of the interface is shown in Fig. 6, and the various features on it function as follows:

Integration time - Sets the integration time for a single capture from the spectrometer.

Scans to average - Sets the number of acquisitions from the spectrometer that are averaged to give the spectrum displayed on the screen.

Store background spectrum - Stores the current spectrum as the background and switches to 'Background subtracted' display mode, shown in Fig. 6 (compare top and middle).

Clear background spectrum - Deletes the currently stored background spectrum and stops subtracting it.

Save current spectrum - Saves the live spectrum (as shown on the screen, so background subtracted if that is what is selected) as a CSV file with a header that shows the acquisition parameters.

Show data processing - Shows the window where the data processing happens (*e.g.* background subtraction).

Store spectrum - Stores the current live spectrum and displays is as a static spectrum (shown as a thin grey line) for comparison with the current live spectrum - shown in Fig. 6 (bottom). Note that this is not saved to a file unless you use the next button.

Save stored spectrum - Same function as "save current spectrum" but saves the last spectrum that was stored rather than the live spectrum.

Spectrometer Information - This is information about the currently connected spectrometer.

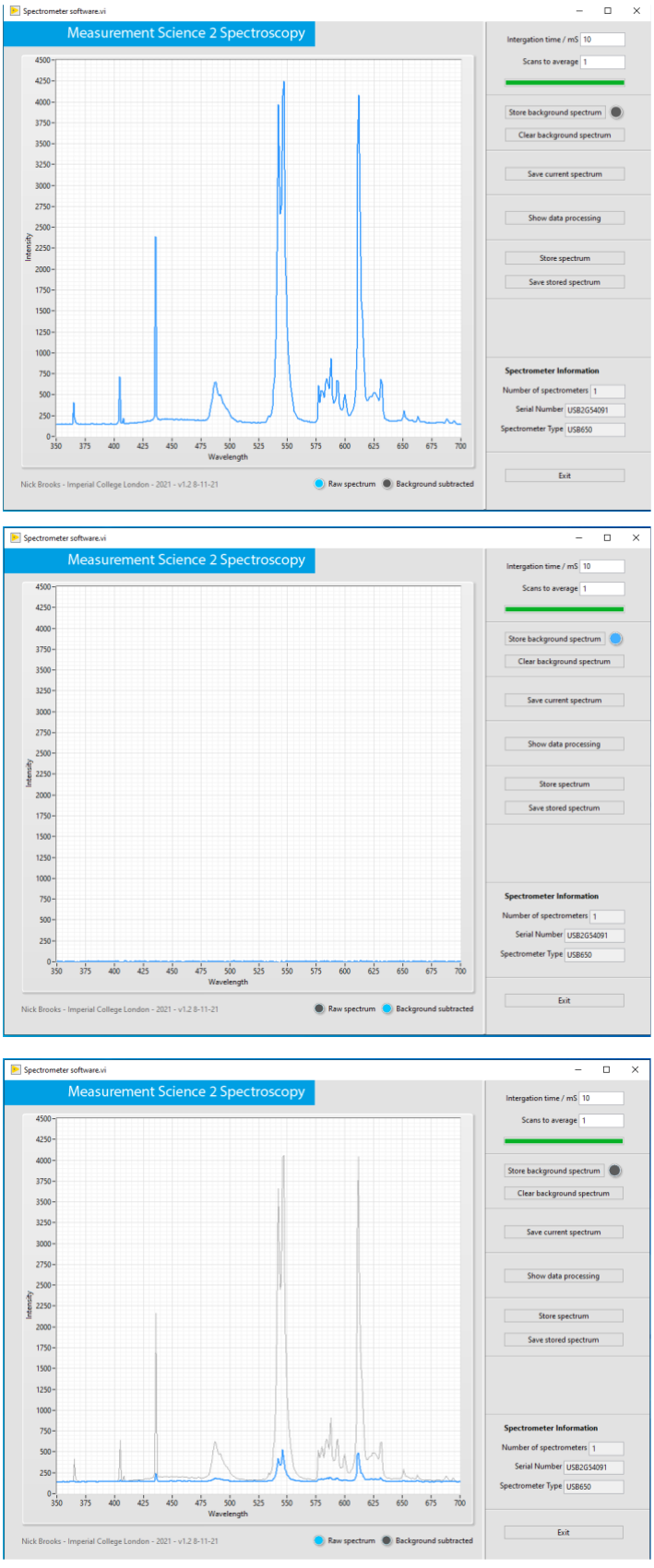

Figure 6. Snapshots from the LabView spectrometer interface. Refer to the text for description of all features and functionalities.

Underneath the spectrum graph there are two buttons:
Raw spectrum - Clicking this will show the live raw spectrum (this will be the only active option if there is no background saved).
Background subtracted - Shows the live spectrum with the stored background spectrum subtracted (this will be automatically selected when you store a background spectrum).

In this experiment you will need to measure the fluorescence emission spectrum of prodan in various solvents or single-phase mixtures of solvents. Every time you need to acquire one such spectra you should follow the steps below:

1) Inject the solvent (water, ethanol, toluene, or uniform mixture of them) into a **clean cuvette** using the large micropipette (remember to use a new tip every time and see note below on correct micropipette use). Aim for a volume close to 2 ml. Close the cuvette with the lid. Note that at this stage there is no prodan in the sample, so no fluorescence emission is expected. This is because we will need to measure the background signal before adding prodan.
2) Load the cuvette into the spectrophotometer, switch on the excitation LED (toggle switch on the cuvette holder), and cover with the black cloth. As the spectrometer measures continuously, you will see a signal appearing on the screen. The spikes and other irregular features are instrumental noise from the sensor, that we will eliminate through background subtraction.
3) Set the **integration time** and **scans to average number**. Note that these values should not be changed between background acquisition (point 4 below) and measurement (point 6 below) but can be changed between measuring one sample and the next, although we recommend sticking to the same value for simplicity. See step 3.1 in the next section for a guide on how to set reasonable values.
4) Acquire and store the background signal by pressing **store background spectrum**. The **background subtracted** button at the bottom of the interface will be automatically selected and the spectral curve shown after this stage should be flat and roughly zero.
5) Using the small micropipette, add ~2-3 µl of prodan solution to your sample, and mix carefully by stirring with the pipette tip. Alternatively to stirring, you can use the large pipette (clean tip) mix the sample by pipetting up and down gently. Your sample is now fluorescent – put the lid back, insert it in the fluorimeter and cover with the cloth. Note that by adding some ethanol, at this stage we have “perturbed” the composition of our mixture. However, since we are adding a very small amount (less than 1% of the total volume), we can neglect the consequent change in solvent polarity and thus emission wavelength.
6) The instrument will now measure the background-subtracted fluorescent spectrum, which should resemble the emission profile of prodan, as shown in Fig. 5. Some sharp spikes may persist in the curve, which are not perfectly eliminated by the background subtraction. These can most often be ignored, but if they are too severe you may want to repeat background collection and measurement with a higher **scan to average** value. If this does not help, seek attention from the demonstrators.
7) Export the data in CSV format by clicking **save current spectrum** or, preferably, first store/visualise the spectrum with **store spectrum** and then save with **save stored spectrum**. You can collect multiple repeats of each

measurement and average them for improved accuracy and to calculate error-bars.

8) You can now remove the cuvette, empty it in the dedicated disposal container and rinse it thoroughly with ethanol by filling it half-way, holding it closed with the lid and your thumb, and shaking gently. Repeat rinsing a few (3-5) times, and then dry the cuvette with the desktop air pump provided. Note that it's very important that the cuvette is clean and does not have prodan or solvent contaminations before moving on to the next sample.

2.2 Micropipette use

Micropipettes are used for precision liquid handling in a variety of lab settings. Please watch this youtube video from Eppendorf to learn about proper micropipette use.

Before starting to use pipettes for sample handling, we recommend that you practice a couple of times by pipetting some liquid (any of the solvents will do) into the solvent waste to gain confidence.

Please pay particular attention to the following:

- **Never use a pipette without a tip on**. Liquid should not touch the opening at the end of the pipette, where the tip locks.
- **Always dispose of the tip immediately after use.** This avoids cross contamination.
- **Never rest a pipette horizontally if it has a tip inserted.** Doing this risks liquid entering the pipette opening.

3. Experiment

Below we describe, step-by-step, the tasks that you should complete in this experiment. Note that you do not necessarily have to carry them out in the order they are listed below. For instance, it may be convenient to first prepare the sample for tie-line determination (section 3.4), as this will need to equilibrate for a long time to allow phase separation to complete.

We therefore invite you to first go through all the tasks listed below, and then make your own plan of action.

Note: all steps involving toluene handling need to be conducted under the fume cupboard. With exception of the spectroscopic measurements which are safe to conduct outside due to the small volumes involved and the use of the cuvette stopper.

3.1 Identify values for integration time and scans to average parameters

The **integration time** should be set to maximize signal without saturating the sensor. However, you do not a priori know the intensity of the fluorescent signal at the time of setting this value, as this needs to be done prior to background collection, and thus before prodan is added. We therefore recommend using test solutions in the pure solvents to determine a reasonable value. Prepare, in the cuvette, samples of toluene, water and ethanol with addition of ~2 µl prodan solution. Then, **without subtracting the background**, change integration time until you see a saturation of the signal. To be on the safe side, a reasonable integration time value should be somewhat smaller than the one leading to saturation (~70%). You may note that the signal from prodan in water is weaker compared to ethanol and toluene (because the quantum yield of the dye depends on polarity too!). Thus, the integration time value determined for water may be unsuitable for toluene-rich or ethanol-rich solutions. Because, in most instances, you will be working with mixtures of the three solvents, a conservative choice could be to use, for the whole experiment, the smallest

integration time identified among the pure solvents. However, we leave this strategic decision to you!
The **scans to average** parameter can be decided more freely. Generally, the more you average the cleaner your data will be, but you may want to consider the trade-off between accuracy and measurement time.

3.2 Acquire prodan emission spectra in the pure solvents
Follow the instructions in section 2.1 to acquire the prodan emission spectra for the three pure solvents: water, ethanol and toluene. You should get curves similar to those shown in Fig. 5. While you do not need to perform curve fitting to identify the emission peak at this stage (see section 4 on data analysis), it is advisable to check that the peak position is roughly in the right place.

3.3 Determine points on the binodal curve
To determine the binodal curve you will start with binary liquid mixtures of toluene and water. As discussed above and shown in Fig. 3, these two liquids are immiscible at all ratios, meaning that the binary samples you will prepare will be within the two-phase region of the ternary phase diagram. You will then gradually add ethanol, thus moving closer and closer to the binodal along the dashed line in Fig. 3. Eventually the samples will display a single, uniform phase, indicating that you have reached the binodal.

One would need to repeat this procedure for roughly 8 points, in addition the pure toluene and pure water apices, to obtain a good approximation of the binodal curve. Due to time constrains, we **only ask you to measure four of these points**, while we will provide the data for the remaining points. Proceed as follows:

1) Start with preparing four toluene/water solutions in the 100 mL conical flasks according to the compositions in Table 1. You can use burettes and/or the 100-1000 µl pipette to measure volumes. For all samples you will notice that the two liquids do not mix and will rather form two phases.

V(water) / cm^3	V(toluene) / cm^3	V(ethanol) / cm^3
4.0	25.4	
10.0	11.5	
10.0	4.9	
16.5	1.0	

***Table 1**. **Composition of samples for binodal-curve identification.** The right-hand-side column should be complete with the ethanol volumes which induce sample mixing, as described in the text. A digital version of this table is available in excel format on blackboard.*

2) Using a burette, gradually and very slowly add a controlled amount of ethanol, until you notice that the two layers have disappeared. Note down the volume of ethanol you added to complete Table 1.
3) Following the steps in section 2.1 acquire the prodan emission spectrum of the uniform sample. You will need the peak emission wavelength for producing your tie-line, as discussed in section 4.

3.4 Determine the location of tie-lines
To determine tie-lines you will have to prepare ternary samples with composition that falls within the binodal region. The samples will separate into two phases, and for each you will

determine the peak wavelength of prodan emission. Using the binodal data you will then be able to trace the tie-lines, as discussed in section 4.

We ask you to determine **two tie-lines** associated to two of the compositions shown in Table 2, but if you have spare time, you can try determining the third too.

V(water) / cm^3	V(toluene) / cm^3	V(ethanol) / cm^3
8.0	5.3	9.4
6.0	4.6	12.7
3.0	10.15	10.4

Table 2. Composition of samples for tie-line identification

Proceed as follows:

1) Prepare your ternary mixtures of choice in the separating funnels. Make sure the funnels are stoppered at all times after preparation, to prevent evaporation.
2) Shake the mixtures for 5 - 10 minutes to thoroughly mix the components.
3) Allow the mixtures to equilibrate and settle into two distinct layers. As equilibration may take some time, while you wait you can complete the tasks described in sections 3.1 and 3.2.
4) Once the two layers have formed and are clearly distinct, extract with the pipette a sample of the toluene-rich top phase, and a sample of the bottom phase using the tap. Beakers can be used to help collecting the samples. You should extract enough of each phase to fill your cuvettes.
5) For both these samples, acquire the prodan fluorescence spectra as discussed in section 2.1.

4. Data analysis

Note: You should start your data analysis during the scheduled post-lab session, from 13:00 to 16:00 on the afternoon of the second lab day. You can either work from home or make use of the workstations allocated in the computer room (see MS2.2 blackboard page). Analysis can be done individually or with your experiment team mates, but the subsequent report writing must be done individually. During the post-lab session, remote support from GTAs will be available on the MS2.2 Teams channel.

4.1 *Constructing the binodal curve*

Table 3 shows the data we provide you to help drawing the binodal curve, specifically the mass ratios of the three liquids for 4 points on the binodal, alongside the prodan peak emission wavelength corresponding to each. These data are also available in excel format on blackboard.

Using the information that you have obtained by following the steps in section 3.1, specifically the volume of ethanol you needed to add to reach the binodal, you will be able to find the mass ratios for the four missing points (marked in yellow). Note that you will need to convert volumes into masses, for which you will need the density of the pure liquids (available from the internet). You can now use the triangular graph paper provided to sketch your binodal. Follow the procedure explained in Fig. 2 to place the 8 points (or 10 including the pure water and toluene), and then connect the neighboring points with straight lines. For your report, you can use Python to plot the phase diagram, following the example in Appendix 1, but this is optional, and you can stick to the manual drawing if preferred.

Ethanol mass fraction	Water mass fraction	Toluene mass fraction	Prodan emission peak (nm)
0	0	1	
0.347	0.033	0.620	490.5
0.562	0.132	0.306	496.9
0.624	0.195	0.181	499.2
0.567	0.369	0.064	503.4
0	1	0	

***Table 3**. **Mass fractions corresponding to points in the binodal and corresponding prodan peak emissions.** Missing data are highlighted in yellow. You will be able to fill these gaps by completing the experiments and analysing the resulting data. A digital version of this table is available in excel format on blackboard.*

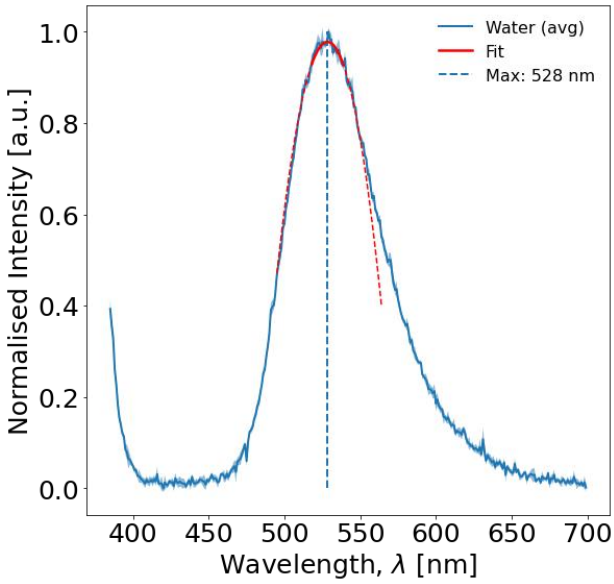

***Figure 7**. **Determination of peak emission wavelength from parabolic fit**. In this example, the prodan emission spectrum recorded in water is fitted with a parabola (red solid line) in the region spanning 20 nm around the (rough) position of the maximum. The red dashed line indicates the same parabola, plotted outside the fitted interval. Note the deviation from the experimental spectrum: the parabolic fit is only valid around the maximum! The vertical dashed line marks the position of the maximum of the parabola which we can use to approximate the peak emission wavelength of prodan in this sample.*

4.2 Determining prodan peak emission wavelength from the spectra

We ask you to determine the wavelength (in nm) of the emission peak of prodan in all the samples you have measured, including the pure solvents (section 3.1). You will need (some of) these data to trace the tie-lines. To determine the peak wavelength you should, **using Python - not Excel**, fit the region of the spectrum close to the peak (approximately 50 nm around the peak position) with a parabola, as shown for example in Fig. 7. The position of

the maximum of the parabolic fit can be then taken as the peak emission wavelength. You can average over repeated spectrum acquisitions to extract your final value, and use the standard deviation to estimate uncertainties. Note however that you will not need to propagate uncertainties to tie-line determination (4.3).
Now you have the peak emission wavelengths for all the points on the binodal. It will be helpful to note this down next to the corresponding points on your graph paper, as well as in Table 3.

4.3 Constructing the tie-line(s)
For each tie-line you have studied in section 3.1 you now have two prodan peak emission wavelengths, one for each of the two liquid phases corresponding to the endpoints of the tie-line. Your task now is to determine the location of these endpoints on the binodal curve. We are going to do so graphically (and approximately) through linear interpolation.
For each endpoint, proceed as follows:

1) Consider the peak wavelength of one endpoint, λ_e, and identify the two points on your binodal dataset with peak wavelengths within which your end-point-wavelength falls: λ_n and λ_{n+1}, with $\lambda_n < \lambda_e, < \lambda_{n+1}$.
2) Calculate the relative position of your tie-line endpoint in the interval defined by the two binodal peak wavelengths as:

$$R = \frac{\lambda_e - \lambda_n}{\lambda_{n+1} - \lambda_n}$$

   For example, if your end-point-wavelength is $\lambda_e = 498.5$ nm, and the two relevant points on the binodal have wavelengths $\lambda_n = 496.9$ nm and $\lambda_{n+1} = 499.2$ nm, then:

$$R = \frac{498.5\ \text{nm} - 496.9\ \text{nm}}{499.2\ \text{nm} - 496.9\ \text{nm}} = 0.7$$

   Meaning that our tie-line end point will be about 70% of the way between the two binodal points, taking the point with lower peak wavelength as reference.
3) Using this information, you can now draw the tie-line end point on the graph. In our example, simply consider the straight segment connecting the two binodal points and place the tie-line endpoint **approximately** 70% of the way from the low-wavelength binodal point with the help of a ruler.
4) Following the procedure detailed in the caption of Fig. 2 you can determine the composition of the liquid corresponding to the tie-line endpoint: extract the mass fractions of water, ethanol, and toluene.
5) Repeat for the second tie-line end point.
6) Connect the two tie-line endpoints with a straight segment on your phase diagram
7) From the volumes of your chosen tie-line sample (Table 2) calculate the mass ratios, then mark the location of this point on your phase diagram. This point should roughly fall on the tie-line, but small deviations are expected in view of the approximate approach we have taken.

Repeat the above steps for all tie-lines you have collected.

5. Report

For your report, please follow the guidelines in the **MS2.2 Report Guidance** document available on blackboard. Pay attention to the **strict 1000-word limit** (excluding captions, tables, references, and equations).

For this experiment we would like you to include in the Results and Discussion section the following elements:

1) A table equivalent to Table 3 in this document but completed with the data you have extracted experimentally. You should also add a row corresponding to the pure ethanol sample for which you have determined the prodan peak emission wavelength, although it is not part of the binodal.
2) An analogous table with the data you extracted for the tie-line, namely the mass fractions of the endpoints, that of the initial (two-phase) sample, and the prodan peak emission wavelengths of the endpoints.
3) Plots of all the prodan emission spectra you have collected, including the pure substances, the binodal samples and the tie-line samples. These should include the parabolic fits you have used to find the location of the peak. You can combine different curves in the same graph, *e.g.* all the pure substances in one graph, all the binodal points in another and all the tie-line points in a third, but you should use the graphical solution that gives the best clarity. You can normalize the curves to the value of their maximum. **Plots should be done in Python, not Excel.**
4) A (good resolution) picture of your hand-drawn ternary phase diagram. Alternatively, and optionally, you can use Python to plot the ternary diagrams as exemplified in Appendix 1.

The deadline for report submission is two weeks after the end of your post-lab data analysis session at 4pm. Refer to the blackboard tables for precise dates/times.

6. References

All necessary background information on (ternary) phase diagrams can be found on Atkins' Physical Chemistry.

1. Atkins' Physical Chemistry. P. W Atkins, Julio De Paula Oxford: Oxford University Press 11th ed.

This practical was inspired by the following work (available on blackboard).

2. K. K. Karukstis *et al.* Spectroscopic Determination of Ternary Phase Diagrams, J. Chem. Ed., 77(6), 701-703, (2000)

Appendix 1: Ternary plots in python

A sample python script for plotting binodal and tie-line points on a ternary phase diagram is supplied on blackboard, alongside a demo dataset in CSV format. You can use this as a starting point for plotting your own dataset. Note that the demo dataset supplied here is relative to a different system. You should replace it with your own!