Investigation of photo-induced ultrafast processes in purely organic molecular crystals by time-resolved photocrystallography

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Abstract

An investigation of the properties of PyDMA18 molecule (and several structurally similar ones) is reported. The methods used for characterisation include single crystal x-ray diffraction and UV-Vis absorption and emission. The crystals for the diffraction experiments were grown using Pyridine as solvent. The data revealed an unreported earlier low temperature phase transition. The work included also analysis of photocrystallographic and time-resolved photoluminescence spectroscopy data.

Contents

1 Introduction

This report is summarizing my summer student project at FS-SCS group, DESY, Hamburg. The members of FS-SCS are focused on investigating structural changes in molecules and energy conversion within them with special stress put on time dependence of these processes.

Photocrystallography is a relatively new and still developing technique. The main aim is the determination of the full three-dimensional structure of a crystal in photoactivated or short-lived high-energy state, using single-crystal X-ray diffraction. The photoactivated state my have significantly different structure comparing to the ground state. The photoactivation is usually achieved by irradiating the crystal with a laser or a set of LED lights in the UV-Vis wavelength range. Photocrystallography has wide applications, particularly in the area of solar energy conversion, optoelectronics and photonics [1]. A part of the project was processing of the photocrystallographic data collected earlier by my supervisor at the Advanced Photon Source, the USA, for a compound PyDMA10.

During this project I focused on study of a molecule: pyrene-CH=CH-N,N'-dimethyl--aniline (PyDMA18) and several compounds that are structurally similar: pyrene-CH2-NO-CO-N,N'-dimethylaniline (PyDMA2), pyrene-CH2-C6H4-CH2-CH2-N,N'-dimethylaniline (PyDMA4), pyrene-CH2-C6H4-CH2-N,N'-dimethylaniline (PyDMA10), pyrene-CH2-C6H4-CH2-CH2-C6H4-CH2-N,N'-dimethylaniline (PyDMA22). These molecules also consist of pyrene(Py) and dimethylaniline(DMA) connected by different bridging groups.

PyDMA18 was chosen for the study because it is exhibiting intramolecular charge transfer, which may be traced with use of the methods of photocrystallography. The compound was recrystallized in order to obtain good quality crystals.

Selected crystals from recrystallized samples were studied with use of single-crystal X-ray diffraction on an in-house diffractometer and at P24 beamline at PETRA III storage ring, DESY, Hamburg. We observed low-temperature phase transition in the temperature range between 195-200K. This convinced us to study this compound in more details and the project will be continued in the future with the intention to publish the results in a journal.

To complement the knowledge about this compound I processed solid-state time-resolved luminescence spectroscopic data collected in advance for crystals of PyDMA18 at P66 beamline at DESY, Hamburg by my supervisor. In order to compare solid-state behavior of the molecules to the molecules in solution we collected a series of UV-Vis absorption and fluorescence spectroscopy data. The data was collected also for four other but chemically similar compounds: PyDMA2, PyDMA4, PyDMA10, PyDMA22.

2 Crystallography and photocrystallography

In this section basic concepts and definitions needed for the project will be introduced.

The main aim of crystallography is a determination of the three-dimensional arrangement of atoms in crystalline materials. This is archived by X-ray diffraction experiments. The wavelength of X-rays is similar to interatomic distances and atoms form in crystalline materials periodic arrays. Crystal serve as diffraction grating for X-rays. The diffraction pattern carries the information about the structure of the gating. From the intensities of reflexions collected in XRD experiments one can determine the crystal structure of studied sample. The solution is involving Fourier transform and retrieval of the information about the phase. There are several methods of solving the phase problem. After that the initial structure is refined by least-square method where the measured intensities are compared to theoretically calculated intensities of the current model. The parameters of the model describing atomic positions in the unit cell are adjusted in order to find the best fitting to experimental data.

Photocrystallography is a technique focused on the determination of the full three-dimensional structure of a crystal in photoactivated or short-lived high-energy state, using single-crystal X-ray diffraction. The photoactivation is usually achieved by irradiating the crystal with a beam of a laser or a set of LED lights in the UV-Vis wavelength range.

The determination of the structure in the excited state may be achieved by a laser pump-probe time-resolved experiments. The studied crystal is irradiated with laser and after given time single diffraction image is collected. The position of crystal is changed according to XRD data collection strategy (scan) and another pump-probe cycle is following. The experiment is repeated with many different time delays in order to find the time delay when the photoexcited state population is the highest. The crucial factor of a successful data collection and the main obstacle is the maximum overlap between the pump and probe on the crystal. Usually the experimental setup is designed in a way, that the laser-pump beam is coming perpendicular to the X-ray probe beam. The laser-pump beam and the X-ray probe beam cross-sections may be different what creates an additional difficulty in interpretation.

3 Experiments

3.1 Crystallization

The most important precondition for X-Ray diffraction studies is that crystals of studied compound are available and are of sufficient quality. In this project we tried several ways to recrystallize PyDMA18.

The simplest method is the direct crystallization from the solvent. Solutions of PyDMA18 with chlorobenzene and pyridine were prepared and left for evaporation in vials. I prepared also three crystallizations with a use of binary mixture method. In this case to the solution of the compound with the primary solvent, a secondary solvent is added. The secondary solvent has lower boiling temperature than the primary solvent and both are miscible with each other. I prepared three binary mixtures with PyDMA18. The details of the prepared samples are presented in the table 1.

Table 1: Crystallizations of PyDMA18 crystals - details

Solvent 1 / volume [ml]	Mass of PyDMA18 [g]	Solvent 2 / volume [ml]
chlorobenzene /1	8.2	
cyclohexane /1	9.1	ethyl acetate/2
dimethyloforamide /1	9.2	acetonitrile/1
pyridine /1	9.0	
dimethylsulfide /1	10.2	acetonitrile/2

After approximately three weeks, crystals in the vials were observed. The crystals from the pyridine vial were of good quality. The crystals were orange and the shape resembled plates. This sample was chosen for the XRD studies.

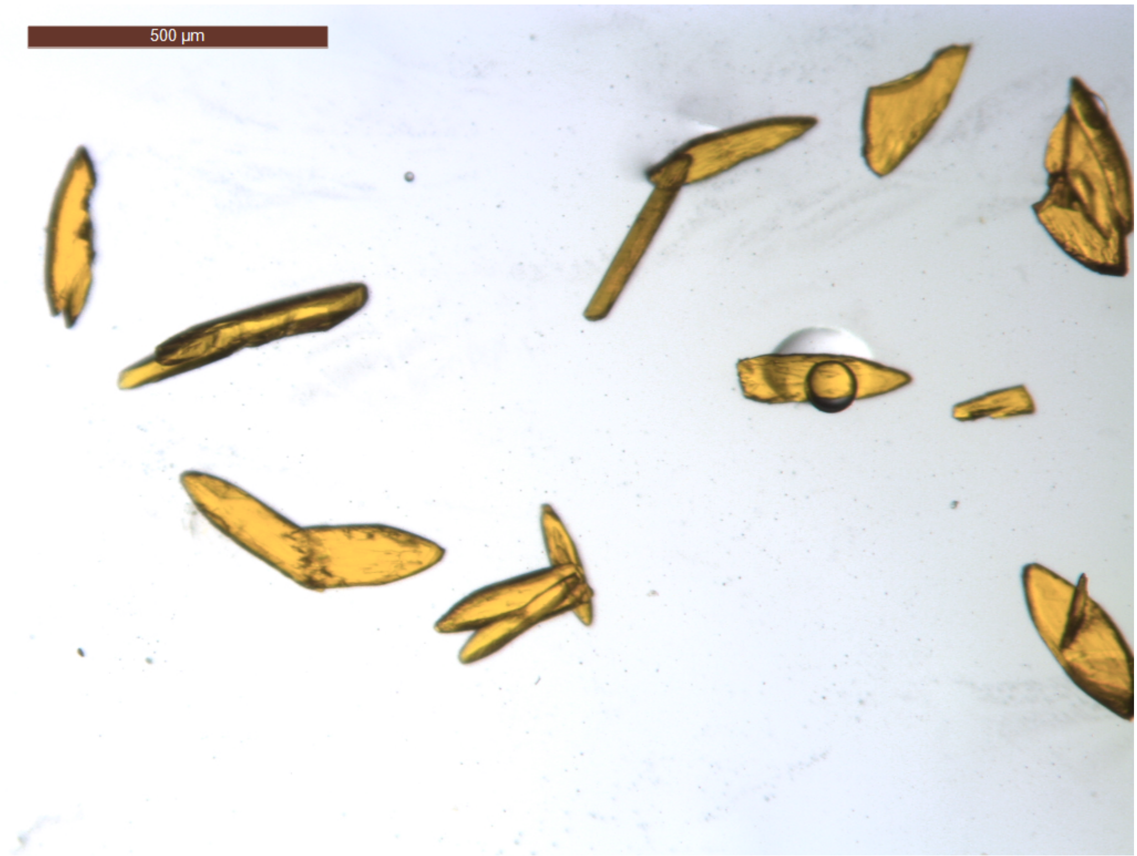

Figure 1: Microphotography of PyDMA18 crystals crystallized with use of pyridine

3.2 XRD experiments

Selected crystals from the PyDMA18 sample crystallized with pyridine were studied using single-crystal X-ray diffraction. The data was collected using in-house diffractometer as well as the kappa diffractometer at P24 beamline (experimental hutch 1), PETRA III storage ring, DESY, Hamburg.

At first we collected single-crystal data with in-house diffractometer with Mo X-ray microsource. The crystal was triclinic. The structure was solved and then refined with a use of SHELXL algorithm [2] algorithm in OLEX2 package [3]. The details of the measurement and data refinement are given in the table 2. Z is the number of molecules in the asymmetric unit, which is 2 in this case. The visualisation of the asymmetric unit of PyDMA18 at room temperature is presented in the figure 2.

Table 2: Details of a room temperature XRD measurement and refinement of the structure of PyDMA18 crystal crystallized with pyridine as solvent

Empirical formula	C26H21N1
Formula weight	347.44
Temperature/K	296.15
Crystal system	triclinic
Space group	P-1
a/Å	10.6407(12)
b/Å	12.0408(15)
c/Å	16.351(2)
α/°	81.993(4)
β/°	89.444(4)
γ/°	64.304(3)
Volume/Å3	1866.3(4)
Z	4
ρ_{calc}/g/cm3	1.229
μ/mm-1	0.071
Radiation	MoKα ($\lambda = 0.71073$)
2θ range for data collection/°	2.52 to 49.644
Reflections collected	12960
Independent reflections	6114 [$R_{\text{int}} = 0.0186$, $R_\sigma = 0.0290$]
Data/restraints/parameters	6114/0/655
Goodness-of-fit on F2	1.034
Final R indexes [I>= σ (I)]	R1 = 0.0503, wR2 = 0.1554
Final R indexes [all data]	R1 = 0.0943, wR2 = 0.1826
Largest diff. peak/hole / e Å-3	0.17/-0.12

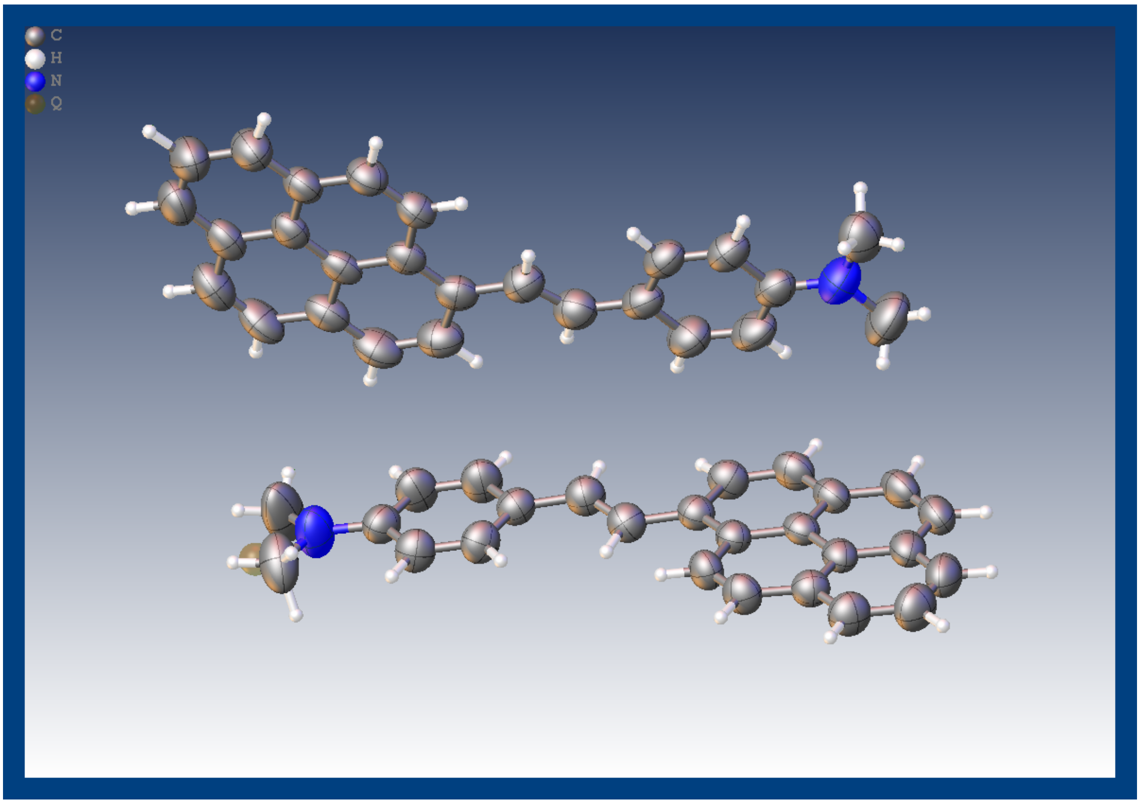

Figure 2: Asymmetric unit of PyDMA18 at room temperature

After obtaining good quality XRD data for the room temperature the aim was to collect the data at the temperature of 100 K. The sufficient quality data collection at 100 K was not possible because of ice crystals forming around the sample during the measurement. The diffraction signal from the ice was increasing during the experiment. We were able to calculate the lattice parameters and we observed a major change in the crystal comparing structure comparing to the room temperature data. This may be considered as a sign of phase transition. We collected short scans in different temperatures and determined unit cell dimensions. The determined volumes are presented in the table 3.

The unit cell volumes determined for all temperatures lower than 195 K were two times larger than the unit cell volume for the structure of PyDMA18 in room temperature. This may suggest that between 195 K and 200 K PyDMA18 has a phase transition.

Table 3: Unit cell volume of PyDMA18 crystals in different temperatures

Temperature[K]	volume [Å^3]
175K	3641
180K	3640
190K	3655
195K	3658
200K	1840

In order to determine the low temperature structure the crystals were measured with use of synchrotron radiation at P24 beamline. The use of synchrotron radiation is making the measurement faster and therefore the problems with ice are not that severe. We collected the extended datasets at the temperatures of 150 K and 195 K. Data collection consisted of two phi scans and 6 omega scans. Additionally phiscans for temperatures of 155 K, 160 K, 165 K, 170 K, 175 K, 180 K, 185 K, 200 K, 300 K. They will allow to trace and to quantify the changes in unit cell dimensions during phase transition. The details of the measurement and data refinement are presented in the table 4. The visualization of the asymmetric unit is presented in the figure 3.

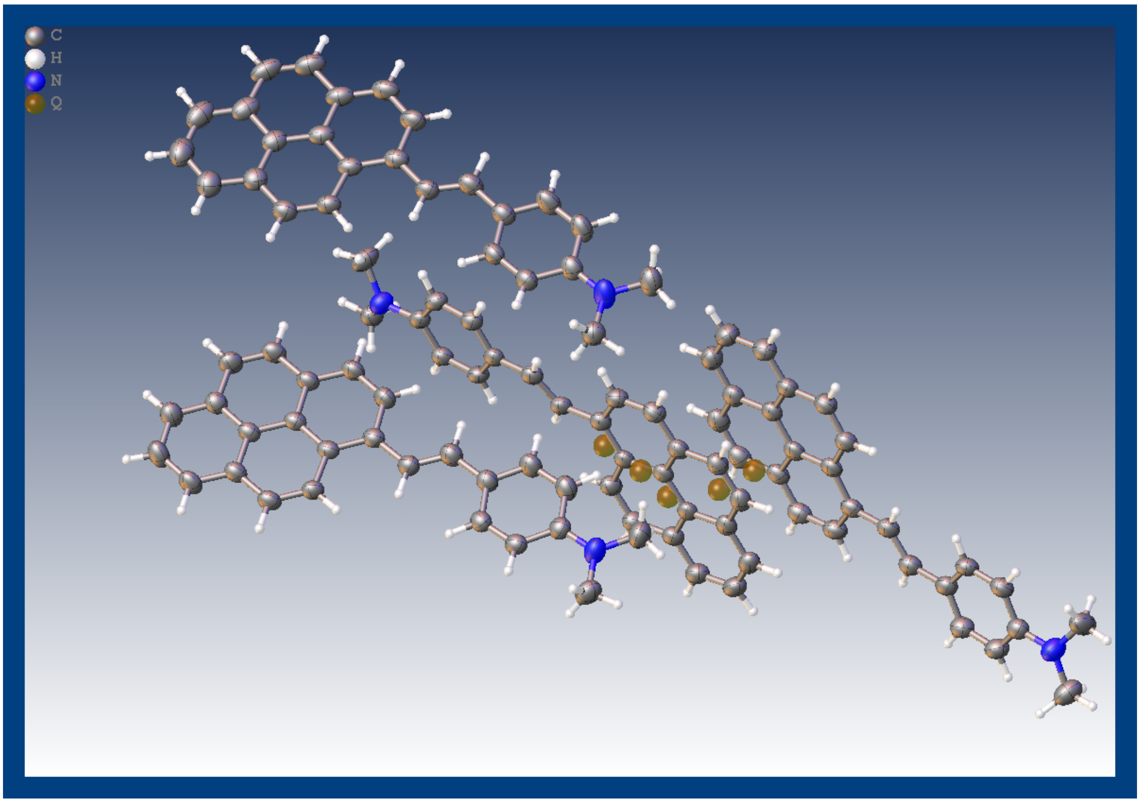

Figure 3: Asymmetric unit of PyDMA18 at 150K

Table 4: Details of the measurement and data refinement collected for crystal of PyDMA18 at 150K

Empirical formula	C26H21N
Formula weight	347.44
Temperature/K	150
Crystal system	triclinic
Space group	P-1
a/Å	10.6705(2)
b/Å	18.8305(5)
c/Å	20.9391(6)
α/°	65.503(3)
β/°	75.305(2)
γ/°	73.913(2)
Volume/Å3	3632.03(18)
Z	8
ρcalcg/cm3	1.271
μ/mm-1	0.076
Radiation	synchrotron (λ = 0.72697)
2θ range for data collection/°	4.116 to 54.044
Reflections collected	41809
Independent reflections	12529 [Rint = 0.0485, Rsigma = 0.0431]
Data/restraints/parameters	12529/0/1306
Goodness-of-fit on F2	1.043
Final R indexes [I¿=2σ (I)]	R1 = 0.0705, wR2 = 0.2033
Final R indexes [all data]	R1 = 0.0899, wR2 = 0.2261
Largest diff. peak/hole / e Å-3	0.32/-0.29

3.3 UV-Vis spectroscopy

Comparing the behavior of studied compounds in solid state and in solution carries often valuable information for understanding the chemical and physical processes that involve these molecules. UV-Vis absorption spectroscopy and fluorescence spectroscopy measurements were performed for PyDMA18 in solution. Also other four chemically similar compounds were measured: PyDMA2, PyDMA4, PyDMA10, PyDMA22.

For each sample a series of solutions was prepared. The series of solutions included:

- 2 mM, 1.5 mM, 1 mM, 0.1 mM, 0.05 mM, 0.01 mM solutions of each compound with acetonitrile

- 2 mM, 1.5 mM, 1 mM, 0.1 mM, 0.05 mM, 0.01 mM solutions of each compound with toluene

- 2 mM, 1.5 mM, 1 mM, 0.1 mM, 0.05 mM, 0.01 mM solutions of each compound with ethyl acetate.

This gives 90 samples that were measured subsequently with UV-Vis absorption spectrometer and fluorescence spectrometer.

Before each measurement approximately 250μl of the solution was poured into a cuvette of 1 mm thickness. After the measurements the cuvette was rinsed with the same solvent.

UV-Vis absorption spectra were collected using a Cary-5E UV-VIS spectrophotometer (Varian Australia) in the range between 200 and 500 nm. The absorption spectra for the compound of interest were corrected using a reference spectrum corresponding to the solvent that is used to dissolve the compound.

Jobin Yvon Horiba Model Fluorolog was used to collect the fluorescence emission spectra. The instrument is equipped with a 450 W Xenon lamp for excitation. While collecting the fluorescence emission spectra, the width of the entrance and exit slit width was 2 nm. The measurements of samples PyDMA2, PyDMA4, PyDMA10, PyDMA22 were excited with wavelangth of 345 nm and the sample PyDMA18 was excited with wavelength 390 nm.

4 Data processing

A relevant part of the project was also processing of the photocrystallographic and time-resolved luminescence spectroscopy data collected in advance by my supervisor at the Advanced Photon Source, US and at P66 beamline at DESY, Hamburg.

4.1 Photocrystallography

Twelve time-resolved pump-probe photocrystallographic datasets were collected for crystals of PyDMA10 at the 14-ID beamline at the BioCARS station at the Advanced Photon Source, US with probe delays of 400 ps, 500 ps, 700 ps, 800 ps, 900 ps, 1 ns (2 datasets), 2 ns, 100 ns, 500 ns, 1 μs and 50 μs. The crystals were irradiated with X-ray pink Laue radiation with maximum intensity at wavelenght of 0.82656 Å.

The data was processed with LAUEUTIL software. [4] [5] In this software the ratio method is implemented. The diffraction images are collected in the same crystal orientation one with laser on and another one with laser off. The integration does not require knowledge of the sample's unit cell dimensions. Miller indices are assigned later using the orientation matrix. After integrating the ratios the dataset was averaged with the SORTAV. [6]

On the basis of merged datasets photodifference maps were prepared. Photodifference maps are revealing if there is any significant structural difference between laser on and laser off data. Unfortunately in the given datasets we do not find any changes induced by laser pump. The explanations may be that either the delay time was not properly adjusted or the overlap of the pump and the probe regions within the crystals was too small.

4.2 Time-resolved luminescence spectroscopy

The solid-state time-resolved spectroscopy datasets were collected for PyDMA18 at temperatures of 13 K, 80 K, 100 K, 130 K, 180K, 220 K, 295 K with excitation wavelenght of 277 nm. Emission decay data were collected for the given temperatures at selected wavelenghts:

- 13 K: 308 nm, 331 nm, 344 nm, 361 nm, 373 nm, 434 nm, 461 nm, 503 nm
- 80 K: 331 nm, 345 nm, 361 nm, 374 nm, 437 nm, 463 nm, 518 nm
- 100 K: 331 nm, 345 nm, 361 nm, 374 nm, 437 nm, 463 nm, 518 nm
- 130 K: 311nm, 331 nm, 345 nm, 362 nm, 374 nm, 437 nm, 466 nm, 494 nm, 510 nm
- 180 K: 332 nm, 345 nm, 360 nm, 373 nm, 434 nm, 465 nm
- 220 K: 332 nm, 346 nm, 362 nm, 467 nm
- 295 K: 334 nm.

The wavelengths where the decay was measured were corresponding to bands observed in the emission spectra.

The emission spectra at given temperatures are presented in the figure 4. In the emission spectra at room temperature only higher energy band at approximately 350 nm was observed. At the temperatures lower than 220 K also a lower energy band was observed at wavelength approximately 460 K. At temperatures 13 K, 80 K and 100 K also band with wavelength approximately 510 K was increasingly visible. These results are with good agreement with the temperature dependent X-ray diffraction data and observed phase transition temperature.

5 Summary and outlook

During the Summer Programme a thorough investigation of the structural properties and phase transition of the PyDMA18 was performed. The activities included a growth of high quality single crystals, measurements of absorption and fluorescence spectra with UV-vis spectroscopy and, most importantly — single crystal x-ray diffraction experiments, both at the laboratory source, as well as P24 beamline at PETRA III light source. The highlight of this project was the observation of phase transition in PyDMA18 crystals. We will continue with processing the XRD data from P24 beamline and UV-Vis spectra that were collected only in the last days of the project. An experiment to study the reversibility of this phase transition with pressure is also planned.

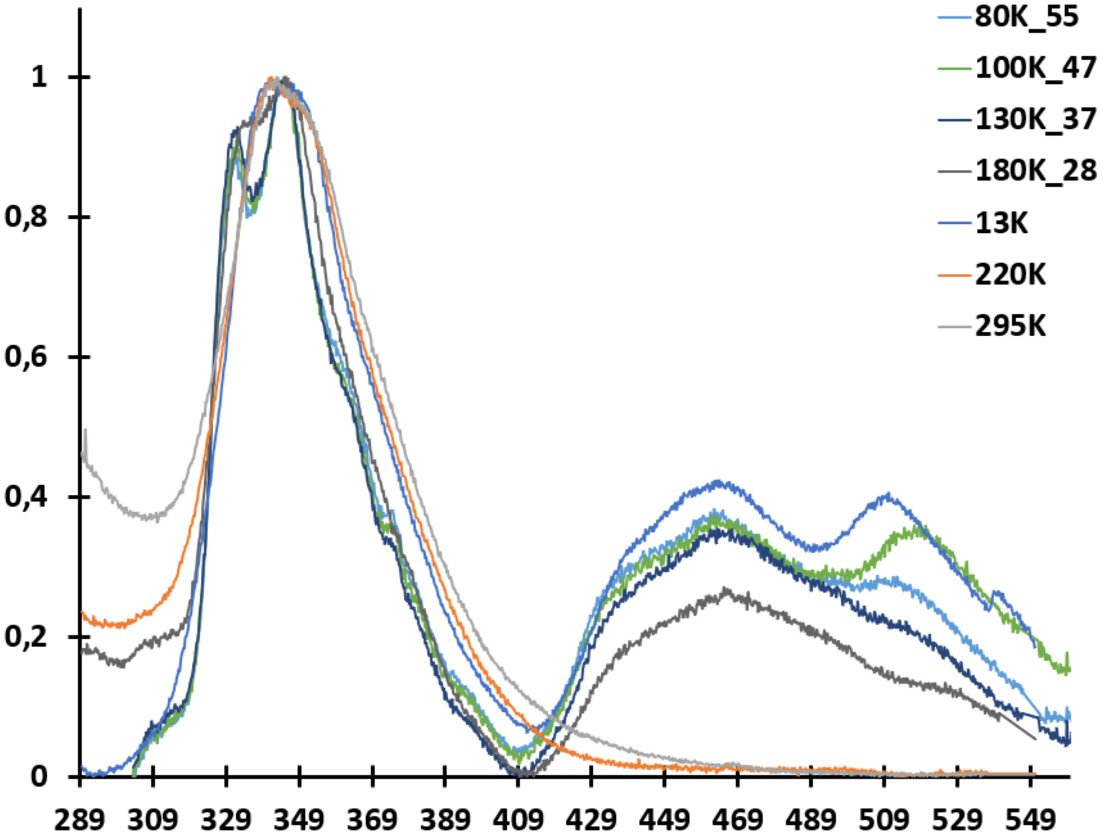

Figure 4: Emission spectra of PyDMA18 at temperatures 13K, 80K, 100K, 130K, 180K, 220K, 295K excited with wavelength of 277 nm

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