

# Exploring the effects of vibrational strong coupling on supramolecular chemistry: perylene crystallization in a Fabry-Perrot cavity

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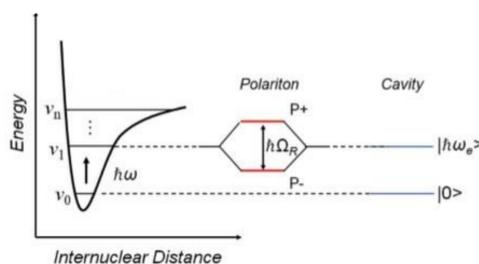
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## Introduction

The coupling of molecular vibrations or electronic transitions to optical cavity vacuum fields was shown to alter molecular and material properties i.e., by modifying the reactivity of organic reactions [1] and enhancing the electrical current in organic semiconductors [2] by an order of magnitude, reflecting an increase of the carrier mobility. The alteration of chemical reactivity has been attributed to a reshaping of the Morse potential of the coupled bond modified by vibrational strong coupling (VSC), predicting a shortening or strengthening of the coupled bond and hence a change of its energy. Therefore, if the energy and the strength of a bond involved in intermolecular interactions would be altered by coupling with the vacuum field, VSC may influence crystal nucleation as well as crystal growth. As first examples, the modification of the supramolecular aggregation of a conjugated polymer [3] and the influence on the pseudo-polymorphism of zeolite imidazolate frameworks [4] are confirming the influence of VSC in supramolecular chemistry.

In a typical setup, molecular vibrations are coupled to an optical mode by placing materials between two metal mirrors in a standard Fabry-Perrot (FP) cavity. When the vibrational modes of molecules are resonant with the optical modes of the cavity, new vibro-polaritonic states ( $P^+$  and  $P^-$ ) are formed, separated by the Rabi-splitting energy ( $\Omega_R$ ).

This work is focused on the crystallization of perylene in a FP cavity, to explore the effect of VSC on crystal growth and polymorphism. Together with the optimization of crystallization parameters, the results of cooperative VSC in a recrystallization experiment of perylene are shown.



Energy level diagram of vibro-polaritonic states  $P^+$  and  $P^-$ , separated by the Rabi splitting energy

## Experimental design

- FP cavity consists of two parallel mirrors separated with a 25- $\mu\text{m}$ -thick spacer. The mirrors were fabricated by depositing ca. 10 nm of Au on  $\text{CaF}_2$  substrates, which were additionally covered with ca. 100 nm of polyvinyl alcohol (PVA) to isolate the metal from solution. All the components were assembled into a microfluidic cell. The non-cavity experiments were performed using the same microfluidic cell, but the  $\text{CaF}_2$  substrates were not covered with Au.

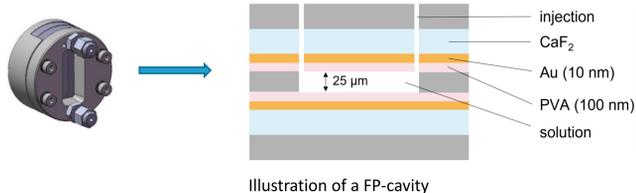
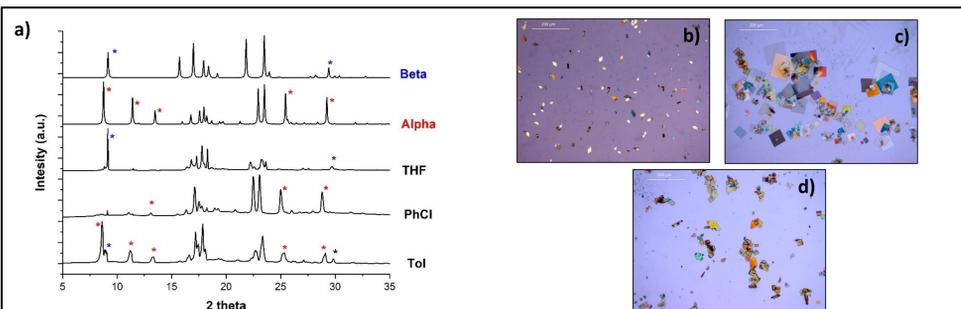


Illustration of a FP-cavity

### Crystallization experiment in a FP-cavity:

Solution and cavity are heated  $\rightarrow$  Solution is injected in the cavity  $\rightarrow$  cooling at RT

- Two crystal forms of perylene (historically named alpha and beta) are reported. Both crystallize in the monoclinic space group  $P2_1/c$ . The two forms are easily distinguishable under an optical microscope since the  $\alpha$  form crystallize in rectangular shaped platelets and the  $\beta$  form in rhomboidal platelets. Crystallization of the  $\alpha$  form has been obtained through solvent evaporation of a solution 20mg/mL in chlorobenzene, while the crystallization of  $\beta$  form was obtained through solvent evaporation of a 4 mg/mL solution in THF. Concomitant crystallization occurs in case of recrystallization in toluene, cooling from 80°C to room temperature a 11 mg/mL solution. XRD confirmed that rectangular platelets are referred to the  $\alpha$  form and rhomboidal platelets to the  $\beta$  form.



a) XRD patterns of perylene crystals. Alpha is  $\alpha$  phase simulated pattern, Beta is the  $\beta$  phase simulated pattern, THF is the powder pattern obtained by solvent evaporation of 4 mg/mL solution in THF at room temperature, PhCl is the powder pattern obtained by solvent evaporation of 20 mg/mL in chlorobenzene at 100 °C, Tol is the powder pattern obtained by cooling a solution 11 mg/mL in toluene from 80 °C to room temperature. Optical micrographs of b) THF, c) PhCl, d) Tol. The scale bar is 200  $\mu\text{m}$ .

## Conclusions and future perspectives

Experimental conditions to obtain crystallization of perylene inside a FP-cavity have been established, showing a concomitant formation of  $\alpha$  and  $\beta$  forms, in recrystallization experiments. Cooperative VSC has been achieved by coupling molecular vibration of the solvent (benzonitrile) with the optical modes of the cavity. The ratio between the two polymorphs has not been significantly altered by VSC.

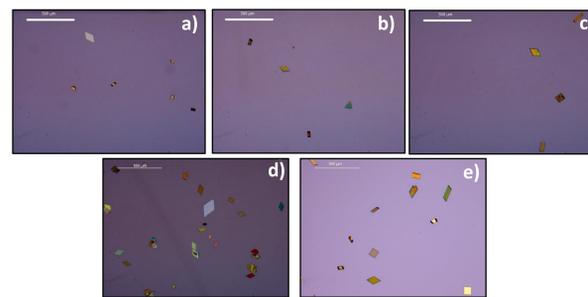
We observed shifts of the cavity optical modes which may be a reason of instability and an issue for reproducibility of crystallization experiments in a FP-cavity.

To avoid these shifts caused by the temperature change of the cavity, crystallization experiments at constant temperature (like antisolvent crystallization) should be performed in future experiments.

## Results

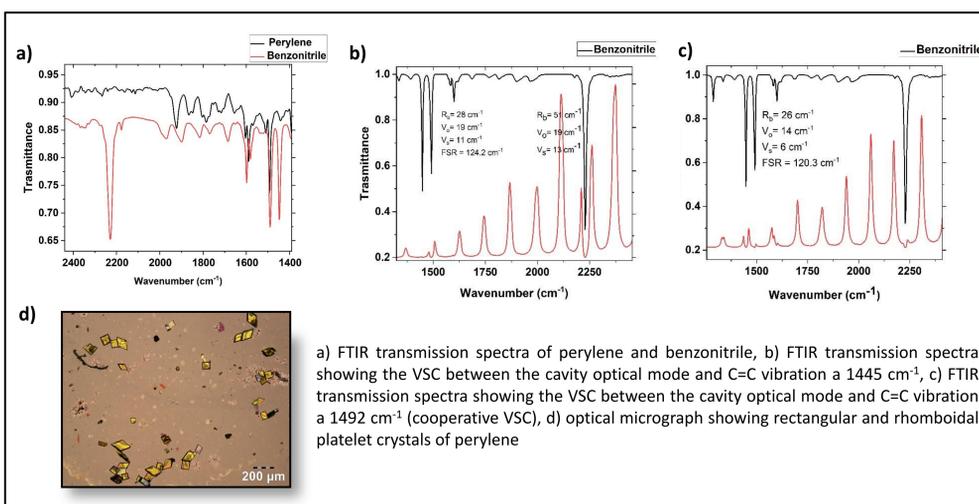
- Solubility of perylene in the different solvents has been studied at room temperature and at the maximum working temperature inside the cell. After optimizing the solutions concentration, the solutions were injected in the cell (non-cavity experiment) one at a time and let it cool at room temperature. In all the cases we found the formation of perylene crystals inside the microcavity, except for toluene solution. Crystals with both rectangular (referred to the  $\alpha$  form) and rhomboidal shapes (referred to the  $\beta$  form) were found in all the crystallization experiments, pointing out the concomitant crystallization of both polymorphic phases in recrystallization experiments.

Solvent	b.p. (°C)	Max T in the cell (°C)	Solubility at RT (mg/mL)	Solubility at Max T in cell (mg/mL)
Toluene	110	40	2	3
p-Xylene (a)	138	60	2	6
Chlorobenzene (b)	132	60	3	8
Mesitylene (c)	164	60	2	7
o-Dichlorobenzene (d)	180	80	4	20
Benzonitrile (e)	191	80	3	20



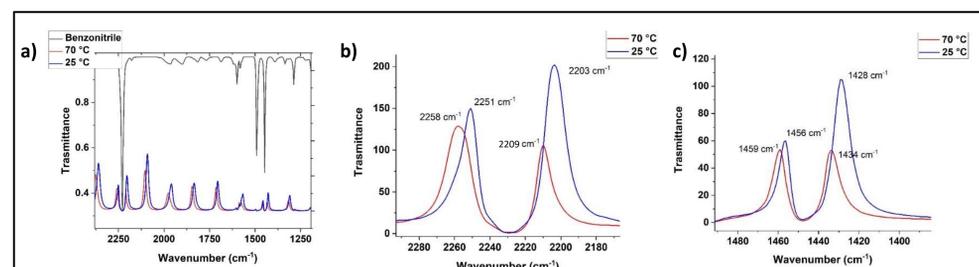
Polarized optical microscope images of perylene crystals inside the cell from perylene solutions of: (a) 7 mg/mL in p-Xylene, (b) 6 mg/mL in chlorobenzene, (c) 8 mg/mL in mesitylene, (d) 20 mg/mL in 1,2-dichlorobenzene, (e) 20 mg/mL in benzonitrile. Scale bar is 500  $\mu\text{m}$ .

- A solution of 10 mg/mL of perylene in benzonitrile was prepared and heated at 70°C. The solution was subsequently injected into the microfluidic cell (preheated at 70 °C). The distance between the mirrors was adjusted to tune the optical mode of the cavity, achieving cooperative VSC between the 12<sup>th</sup> mode of the cavity and the C=C stretching vibration of benzonitrile at 1492  $\text{cm}^{-1}$ . Crystallization of perylene was obtained by cooling the cavity to 25°C with a rate of 1°C/min. Rectangular (referred to  $\alpha$  form) and rhomboidal (referred to the  $\beta$  form) platelet crystals were formed between the mirrors and their ratio was determined by direct observation using optical microscopy. We performed the same experiment in non-cavity condition and by coupling the benzonitrile C=C stretching vibration at 1445  $\text{cm}^{-1}$ , which is not resonant with perylene vibrations (no cooperative VSC). In all the experiments we found ca. 10-20% of rectangular crystals and no significant variation was observed in cooperative VSC regime.



a) FTIR transmission spectra of perylene and benzonitrile, b) FTIR transmission spectra showing the VSC between the cavity optical mode and C=C vibration at 1445  $\text{cm}^{-1}$ , c) FTIR transmission spectra showing the VSC between the cavity optical mode and C=C vibration at 1492  $\text{cm}^{-1}$  (cooperative VSC), d) optical micrograph showing rectangular and rhomboidal platelet crystals of perylene

- Shifts of the cavity optical modes were observed during the experiments. These drifts are related to distance variation between the mirrors caused by the cooling of the cavity and may influence the stability and reproducibility of the experiment.



a) FTIR transmission spectra showing the vibro-polaritonic states formed when the C=C stretching vibration at 1445  $\text{cm}^{-1}$  and the C≡N stretching at 2228  $\text{cm}^{-1}$  are strongly coupled to optical modes. b) and c) enlargement of the spectra which highlights the shift of the polaritonic states during the crystallization.

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## References

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