# Evaluating the Structural and Electronic Properties of Stimuli-responsive Materials

UNIVERSIDAD DE MÁLAGA

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ESAM 1st European School on Advanced Materials

**1st European School on Advanced Materials**
October, 2023
Gandia, Valencia (Spain)

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# Organic Conjugated Materials


**INTRINSIC PROPERTIES OF MOLECULAR SYSTEMS** + **ELECTRICAL AND OPTICAL PROPERTIES OF SEMICONDUCTORS AND METALS**

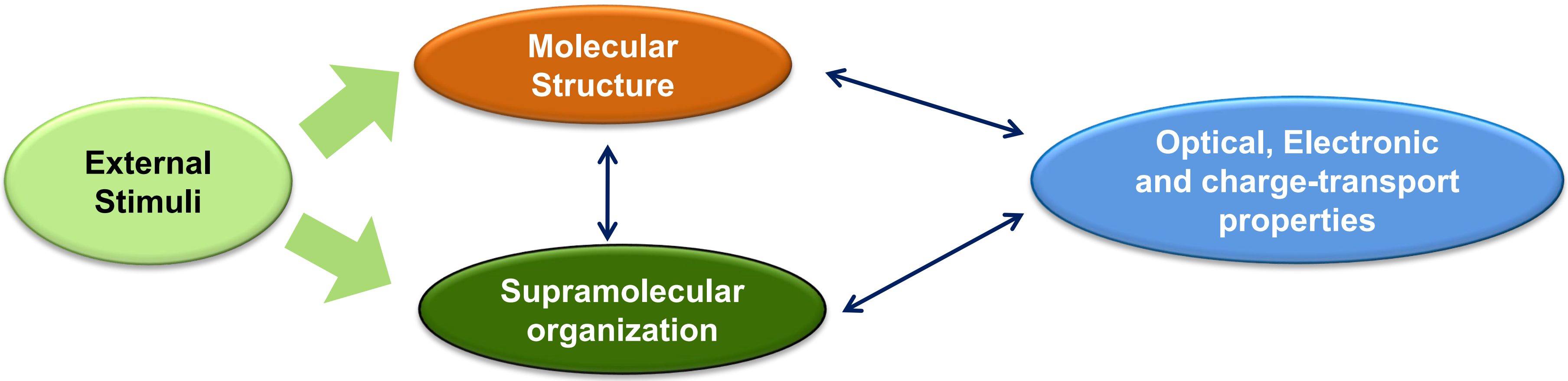
INTRINSIC PROPERTIES OF MOLECULAR SYSTEMS:

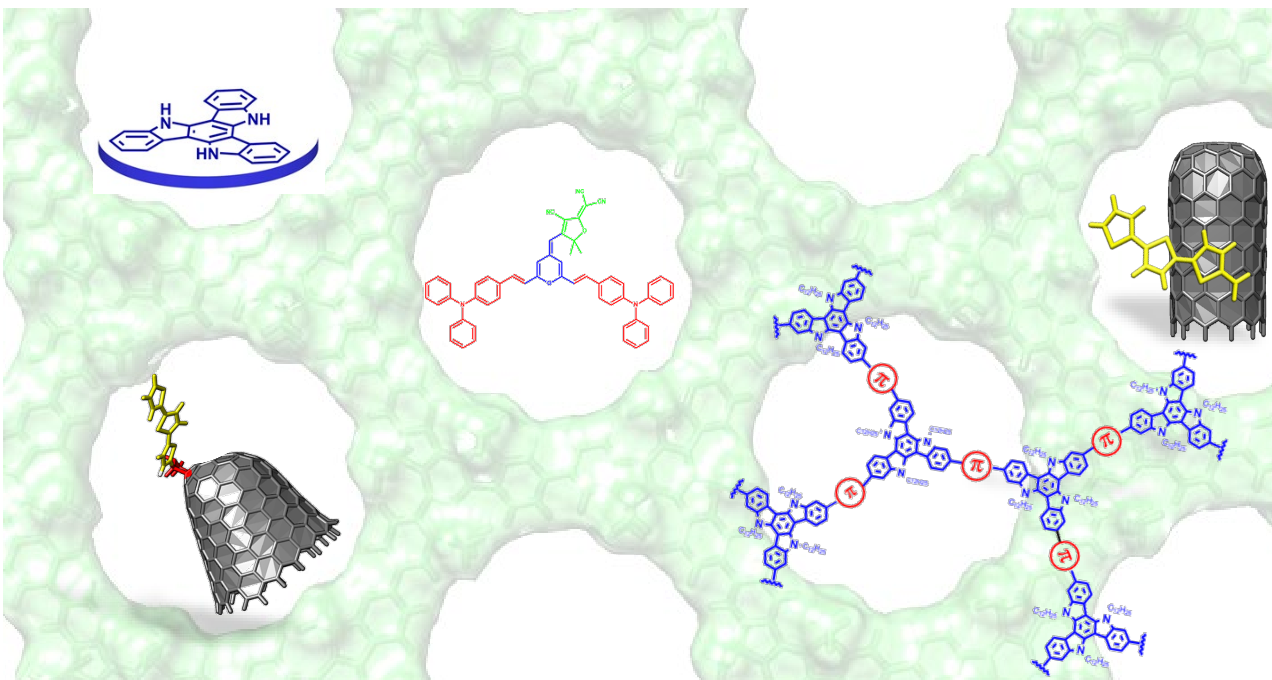
- Synthetic versatility
- Transparency
- Flexibility
- Biocompatibility
- Processability

ELECTRICAL AND OPTICAL PROPERTIES OF SEMICONDUCTORS AND METALS:

- Conductivity, superconductivity
- Elctrochromism
- NonLinear Optics

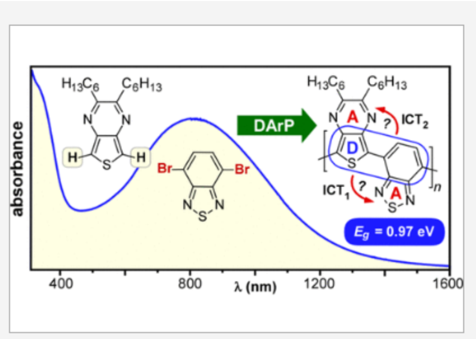
# Research Activity

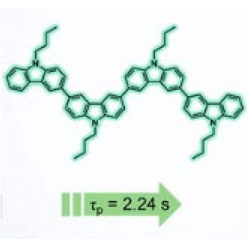


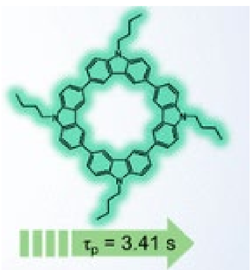



# Research Activity

## Electronic Property Tuning




*J. Am. Chem.Soc.* **2020**, *31*, 6971 – 6978.

*Macromolecules* **2022**, *55*, 3458-3468.

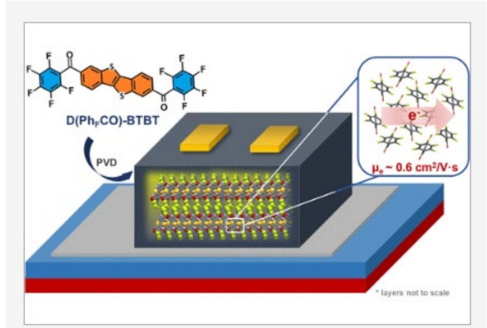
*Adv. Func. Mater.* **2022**, *32*, 2200065.

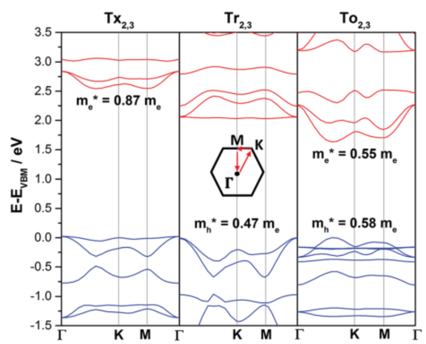
*Chem. Mater.* **2019**, *31*, 5254 – 5263.

*Mater. Adv.* **2021**, *2*, 4255-4263.

*Nanoscale.* **2023**, 15, 12280.

## Understanding Charge-transport




*J. Mater. Chem. C* **2023** ,11, 8027-8036

*J. Mater. Chem. C* **2020,** 8, 15759-15770.

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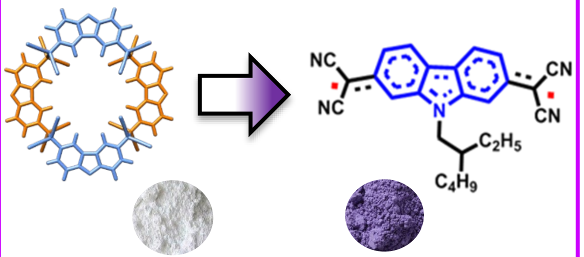
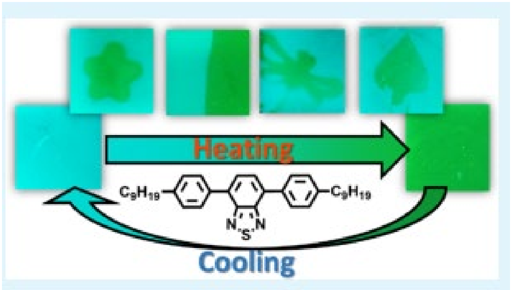
*J. Mater. Chem. C* **2020,** 8, 15416-15425

*Chem. Eur.* **2018**, *24*, 3576 – 3583.

*J. Mol. Liq.* **2023**, 390, 23085.

## Stimuli-responsive Organic Materials



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*Chem. Eur.* **2021**, *27*, 5509 – 5520 (hot paper).

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*Comm.Chem.* **2020**, *3*, 118.

*ACS Appl. Inter.* **2020**, *12*, 10929-10937.

*Int. J. Mol. Sci.* **2023**, 24, 14739.

# Research Activity

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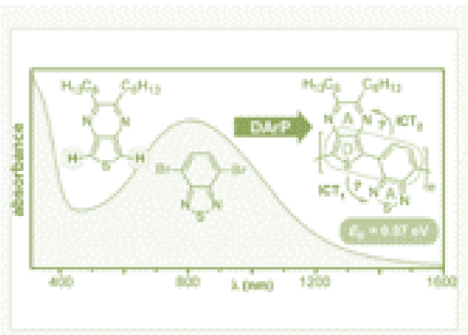

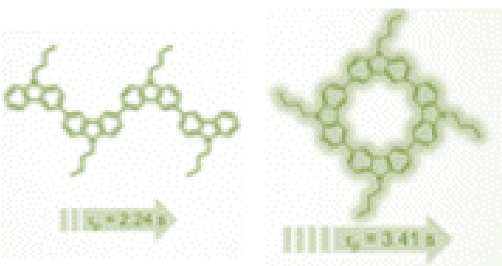

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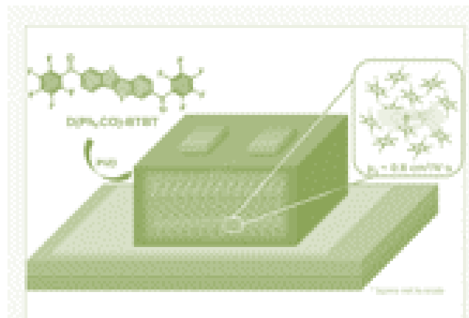

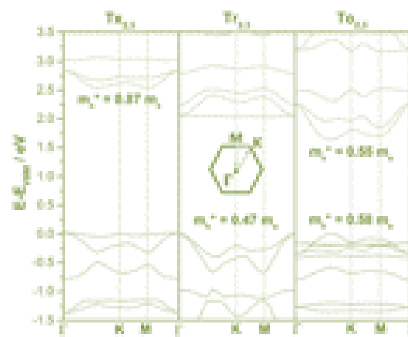

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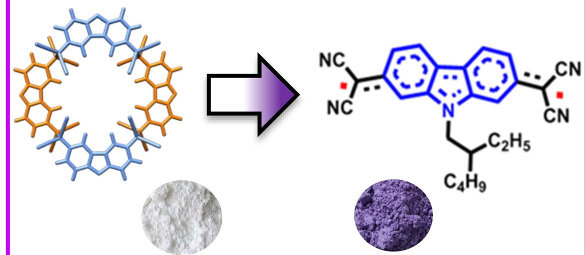
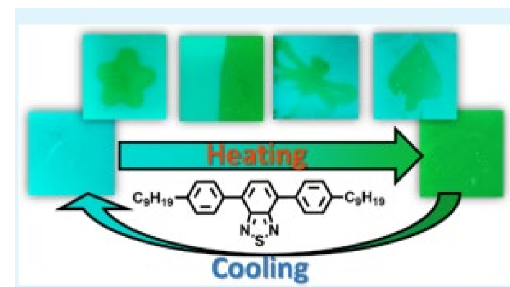
## Stimuli-responsive Organic Materials

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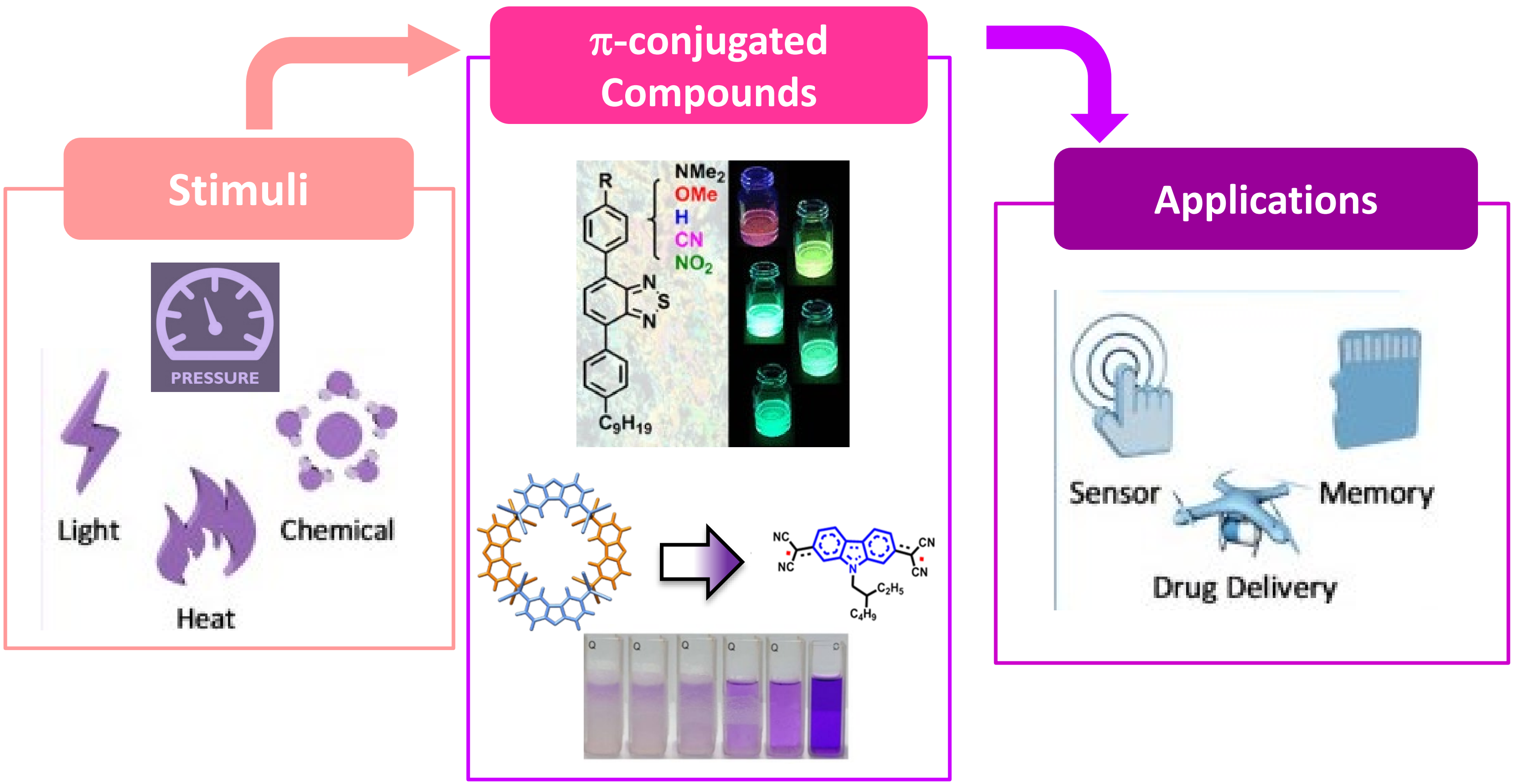

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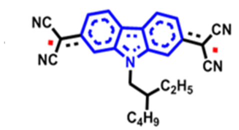
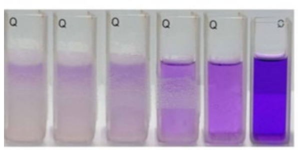
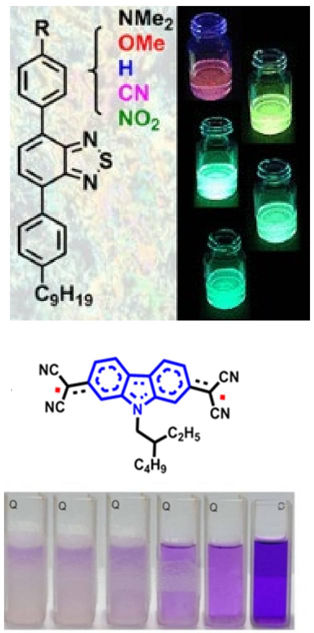


**METHODOLOGY**

| **Theory** | + | **Experiments** |
|---|---|---|
| DFT Calculations | | Raman Spectroscopy |
| | | CV, spectroelectrochemistry, etc |
| | | OFETs fabrication |

# Stimuli-responsive Organic Materials

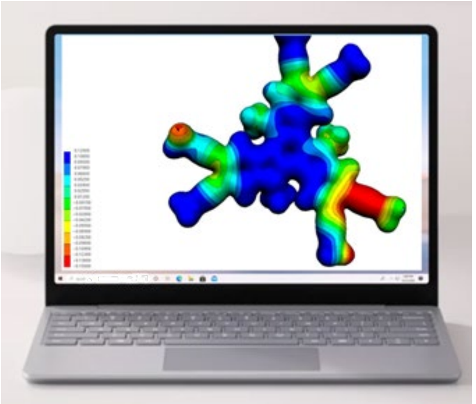


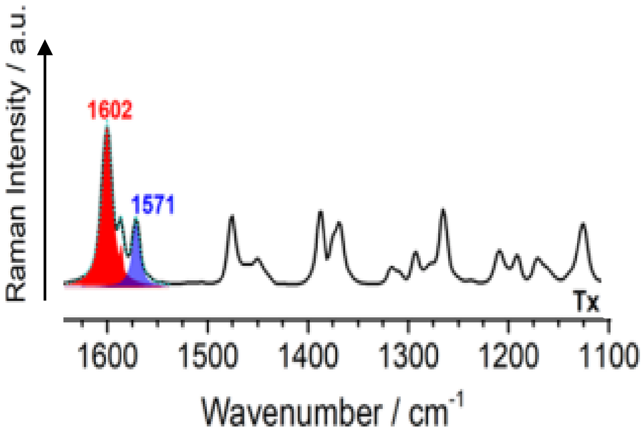

**METHODOLOGY**

**Theory** + **Experiments**

DFT Calculations

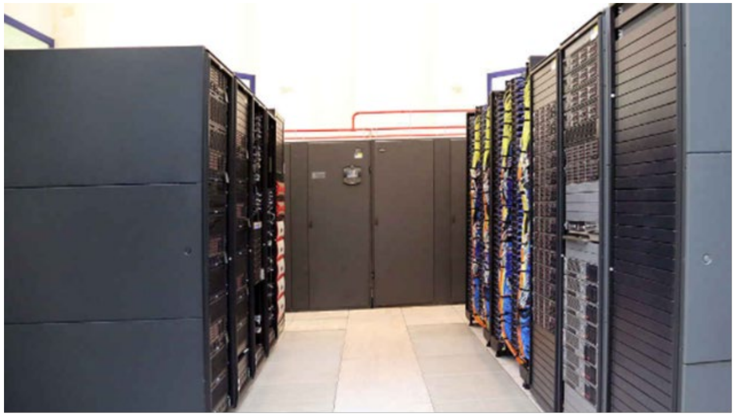
Raman Spectroscopy

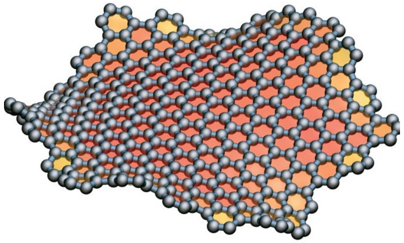


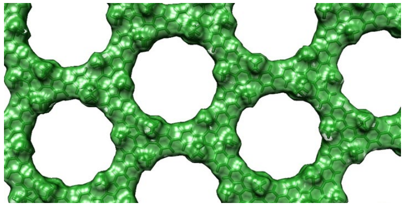


# Stimuli-responsive Organic Materials

## *In Silico* Characterization Methods







Interpretation of experimental results

Safe and environmentally friendly

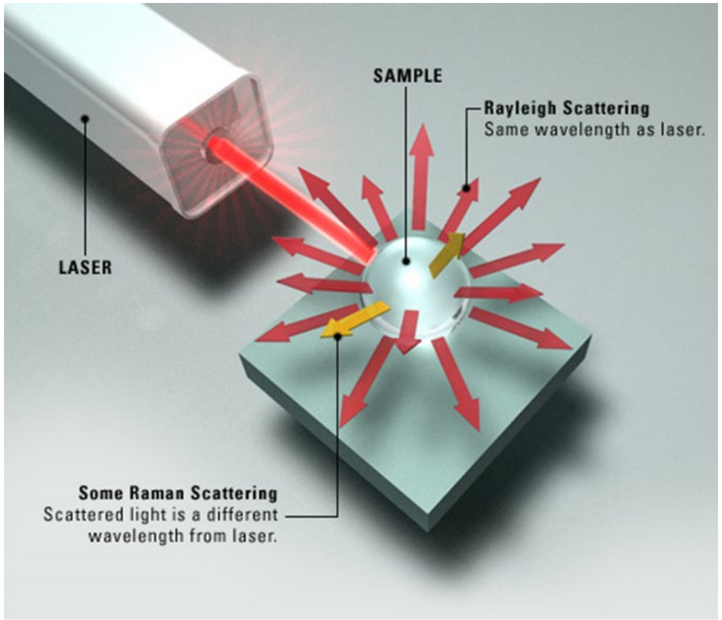
Characterization of materials before synthesizing them

More cost-effective than experiments

**Powerful tool to guide the rational design**

# Stimuli-responsive Organic Materials

**Raman Spectroscopy**




Non-destructive characterization

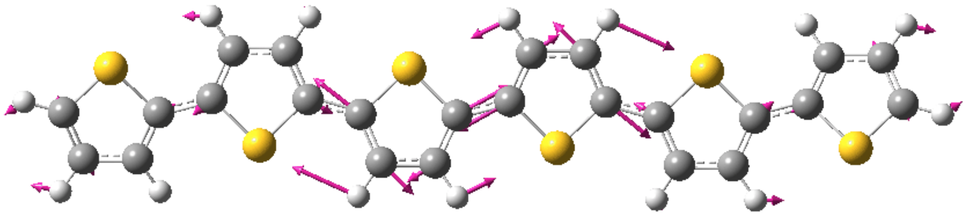
No sample preparation

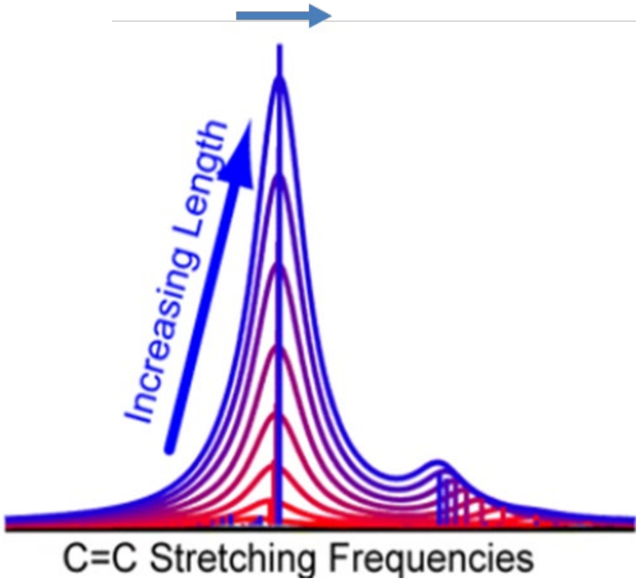
Characterization of $\pi$-conjugated molecules

**Explore the electronic properties of $\pi$- conjugated materials**

# Stimuli-responsive Organic Materials

**Raman Spectroscopy**





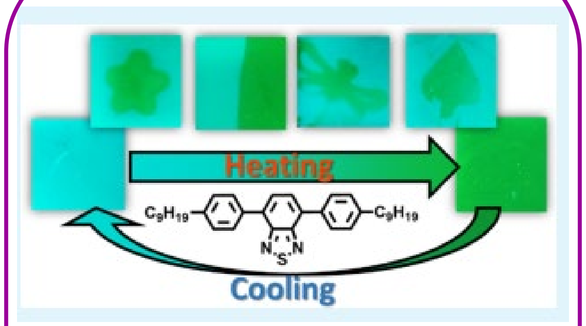

**Intense Raman band = ECC mode**
(*collective CC stretching vibrations*)

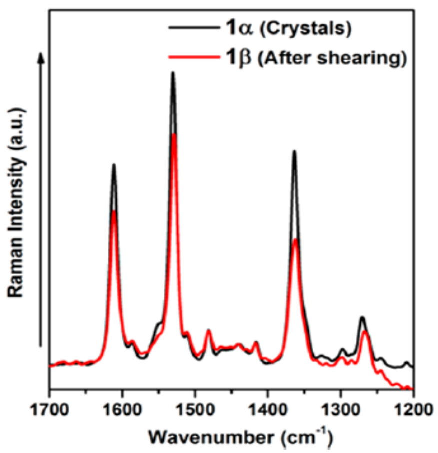
Strong electron-phonon coupling

**Explore the electronic properties of π- conjugated materials**

# Stimuli-responsive Organic Materials

## Benzothiadiazole-based Polymorphs

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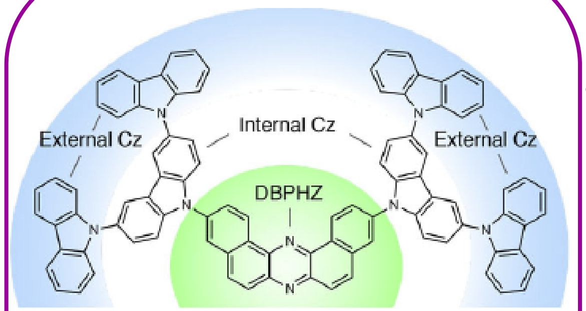
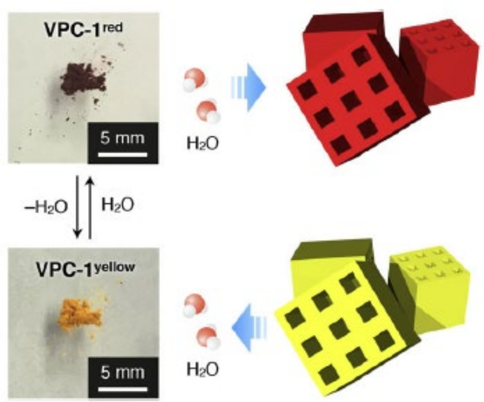
*ACS Appl. Inter.* **2020**, *12*, 10929-10937.

## Carbazole Dendrons (VDW porous crystal)

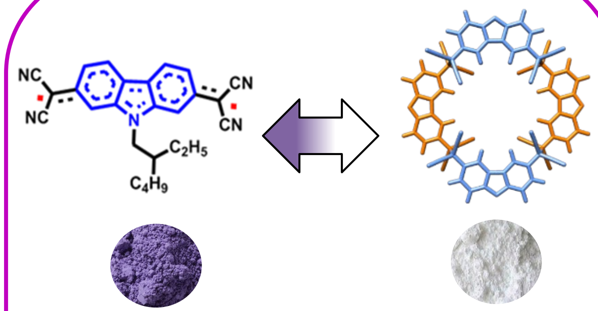


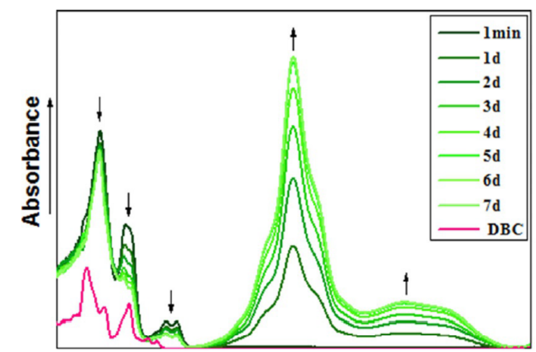




*Comm.Chem.* **2020**, *3*, 118.

*Ruiz Delgado, et al, manuscript submitted*

## Carbazole-based Diradicals



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# Stimuli-responsive Organic Materials

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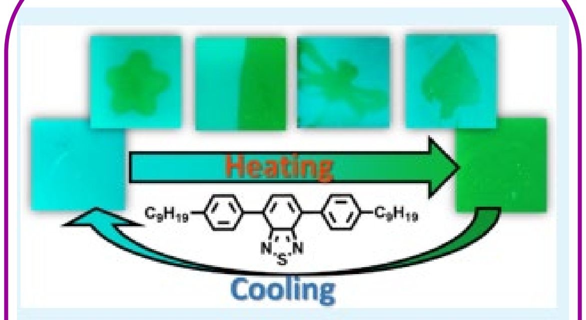


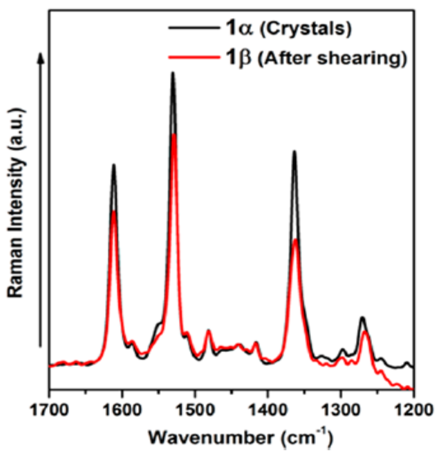


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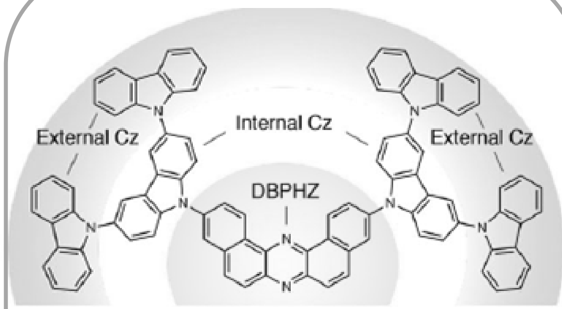


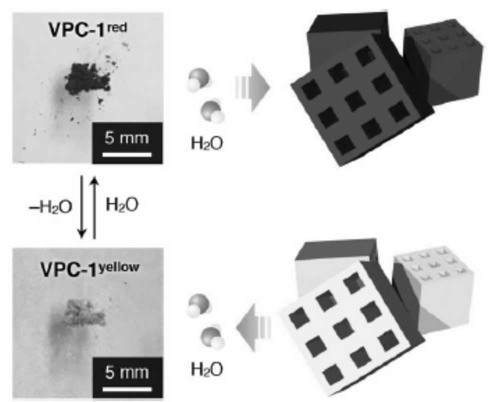


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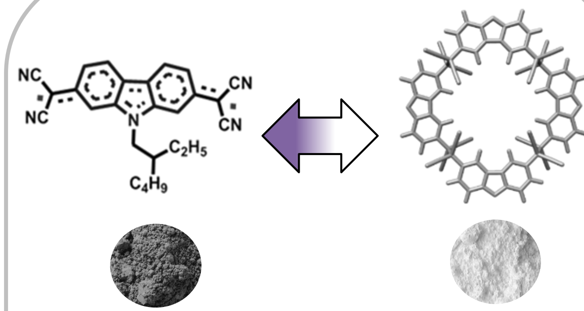


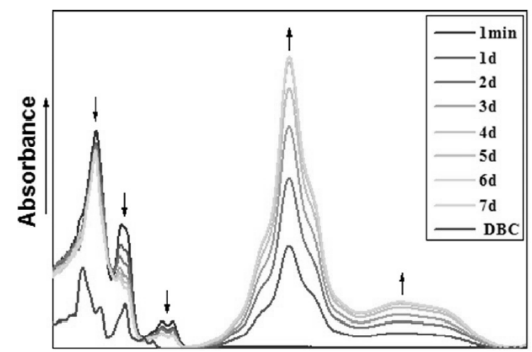


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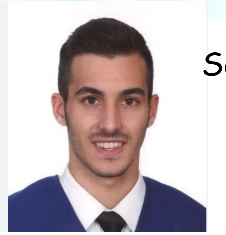
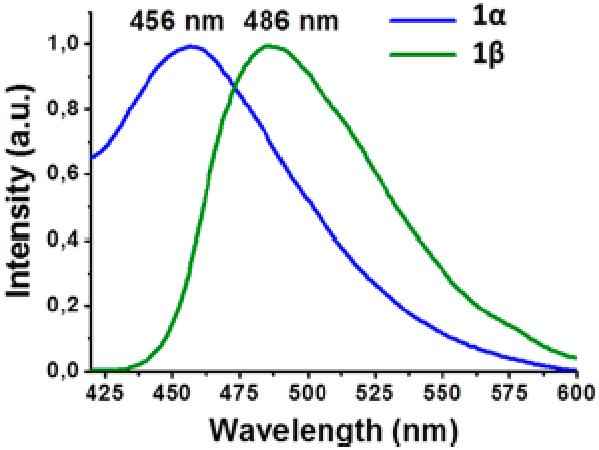


Sergio Gámez-Valenzuela
(UMA)

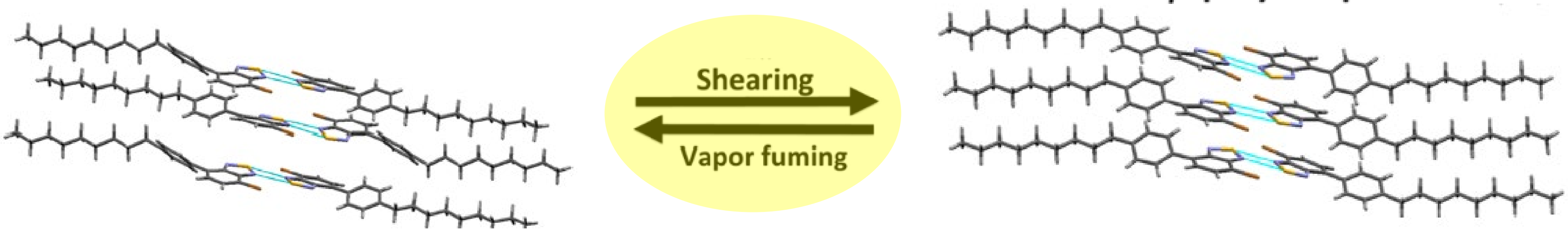
Berta Gómez-Lor (ICMM)



1α-polymorph

1β-polymorph




Interconversion between the two phases can be **reversibly induced by mechanical stress or solvent vapors**

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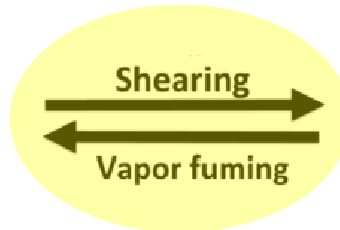
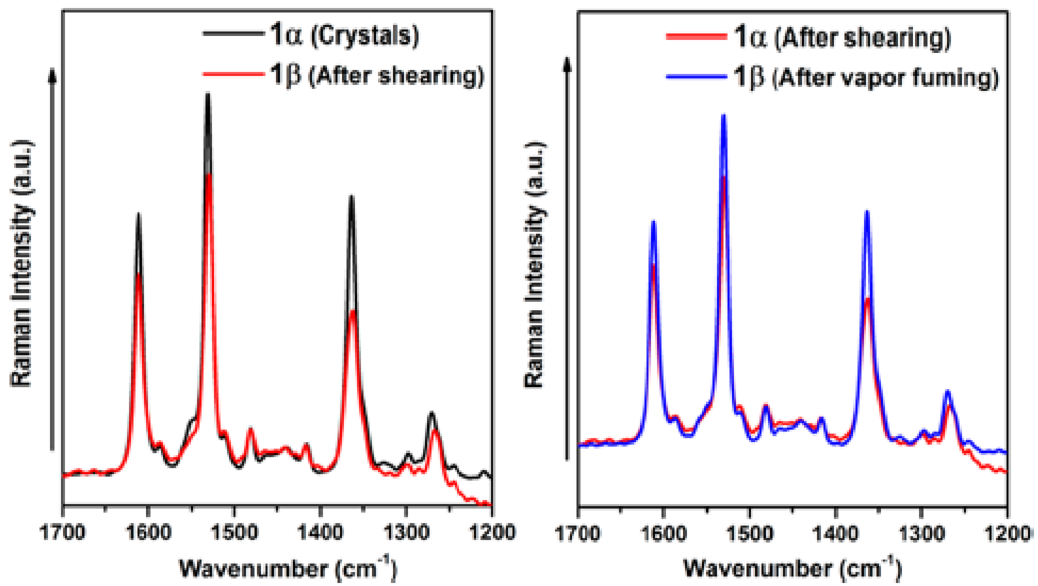
# 1 Benzothiadiazole-based Polymorphs

1α-polymorph


1β-polymorph


**FT-Raman** spectroscopy points to a **supramolecular origin** of the switchable fluorescence

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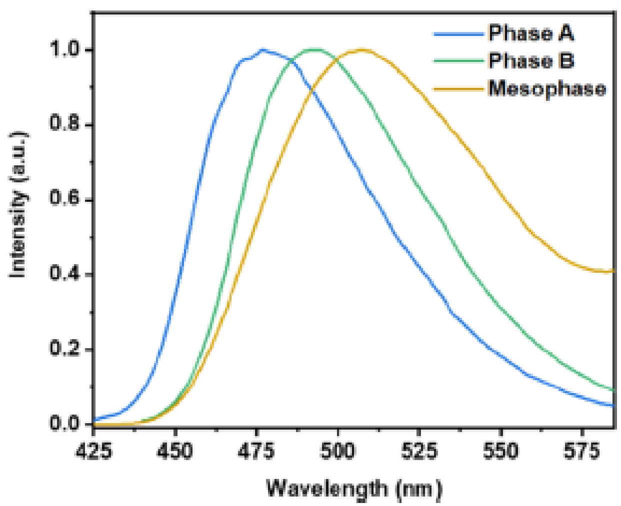
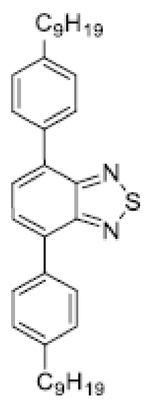
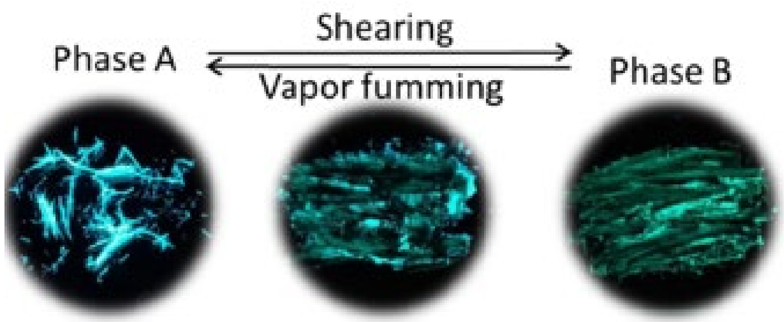
# 1 Benzothiadiazole-based Polymorphs




**Two distinct light-emitting crystalline phases** assembled in layers

*ACS Appl. Inter.* **2020**, *12,* 10929-10937.

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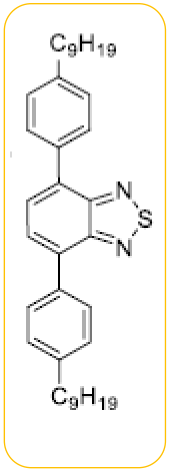


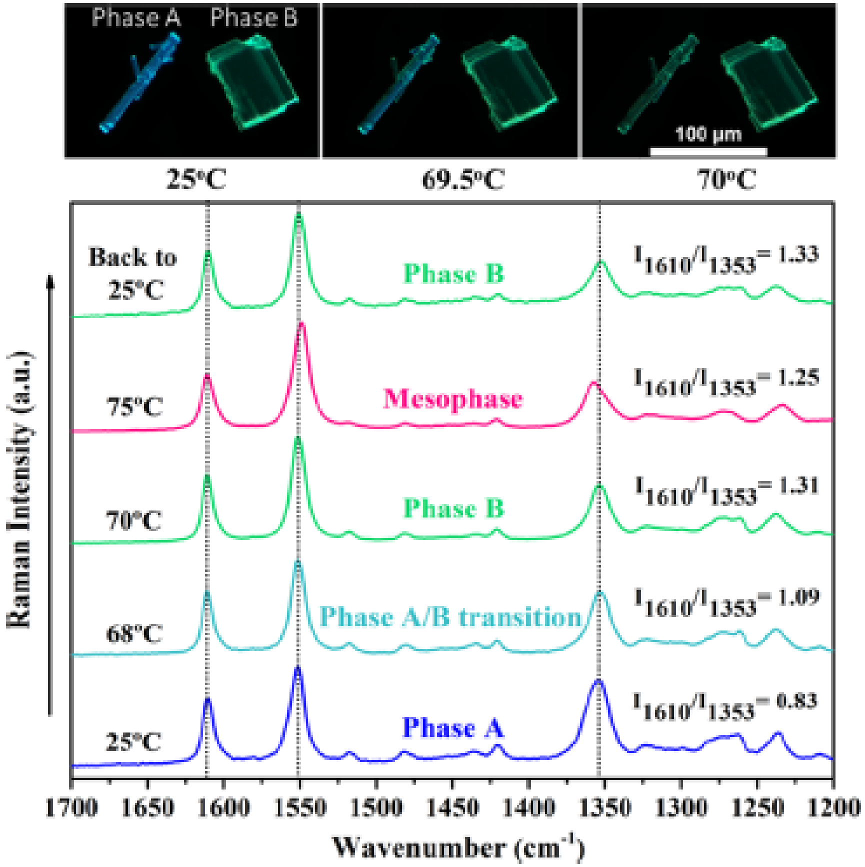


The **$I_{1610}$/$I_{1353}$** intensity ratio difference is ascribed to different **π−π intermolecular arrangements**

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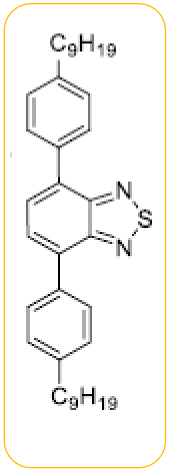


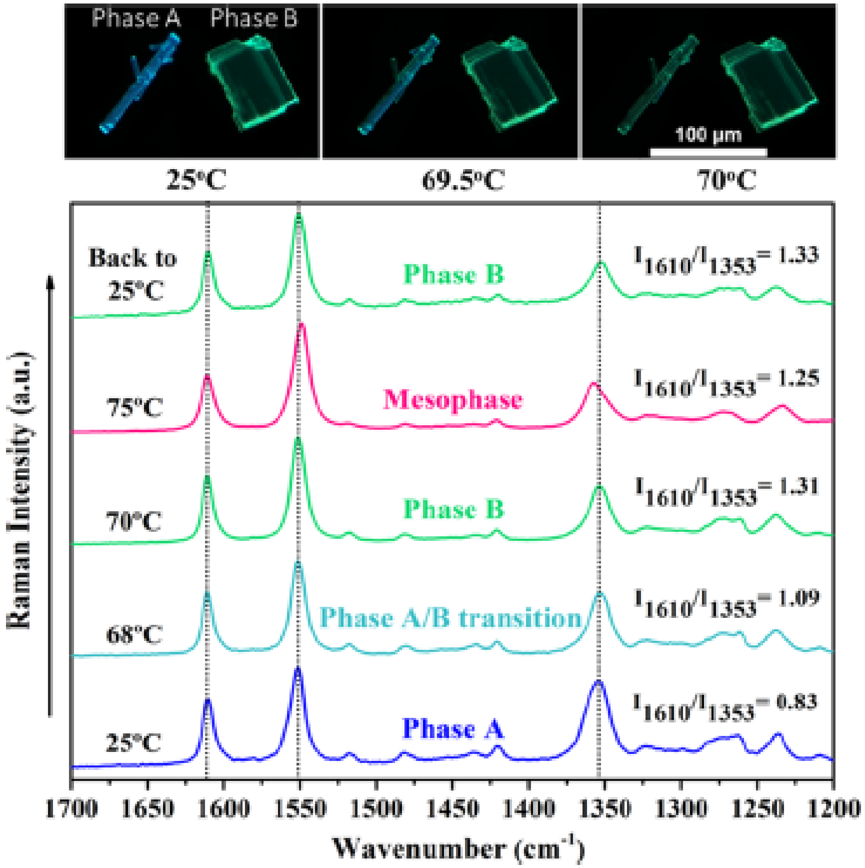


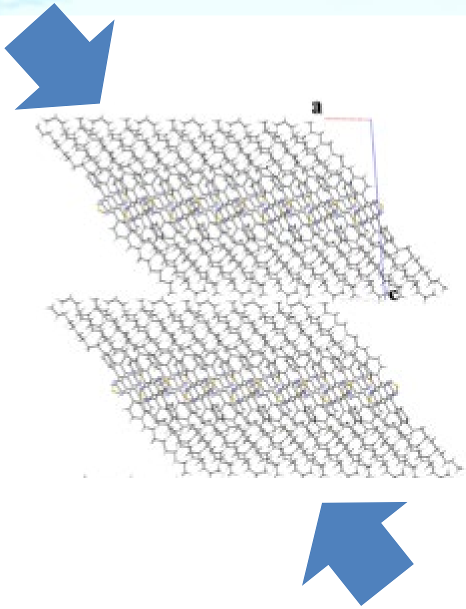

**Sliding of the molecules** along the long molecular axis (**slip planes**)

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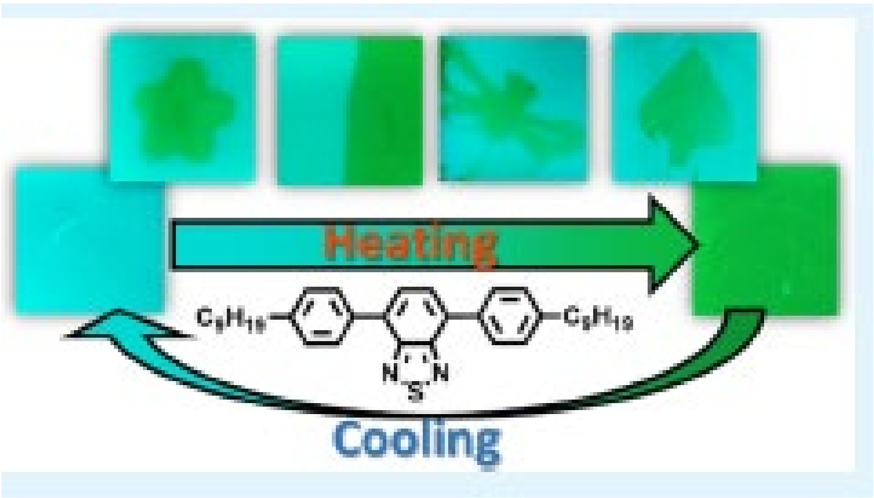


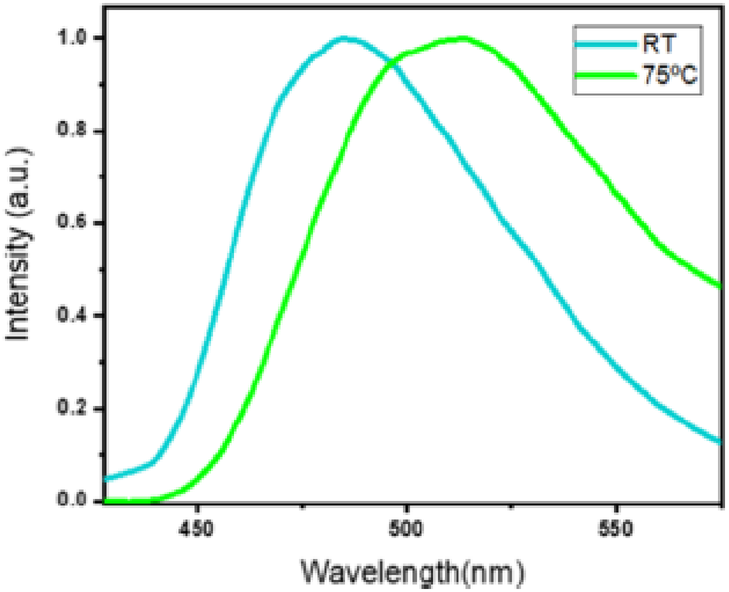


**Blending this molecule with a biodegradable polymer** such as PVA **increase the reversibility** of the thermally activated transformation

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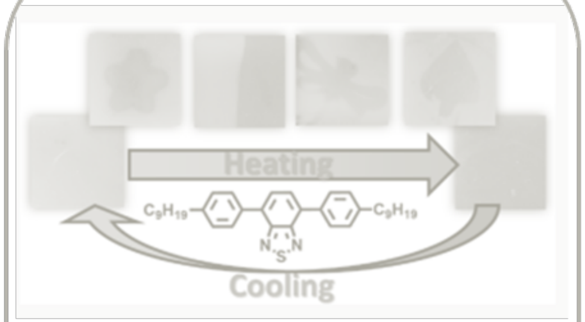
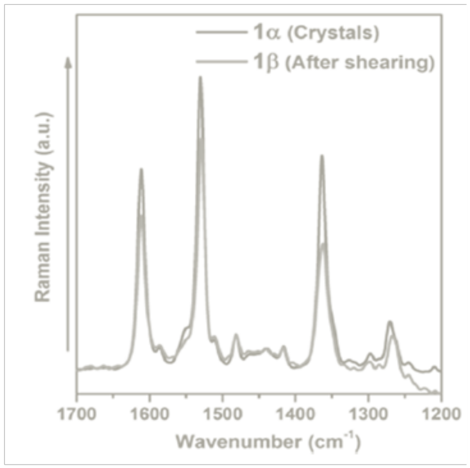
# 2 Carbazole-based Dendrons

## Benzothiadiazole-based Polymorphs

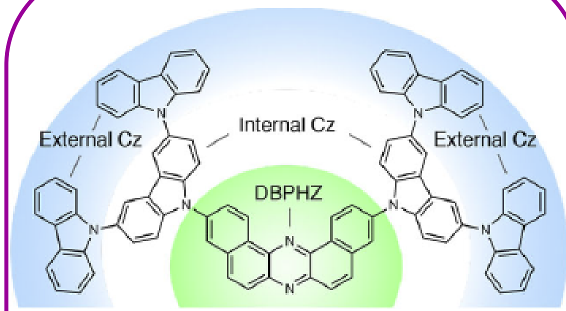


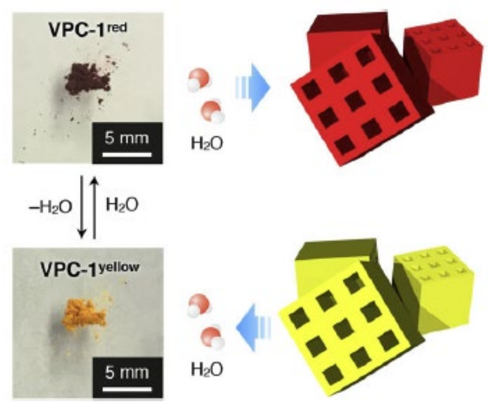




*J. Am. Chem. Soc.* **2020**, *142*, 17147-17155.

*ACS Appl. Inter.* **2020**, *12*, 10929-10937.

## Carbazole Dendrons (VDW porous crystal)

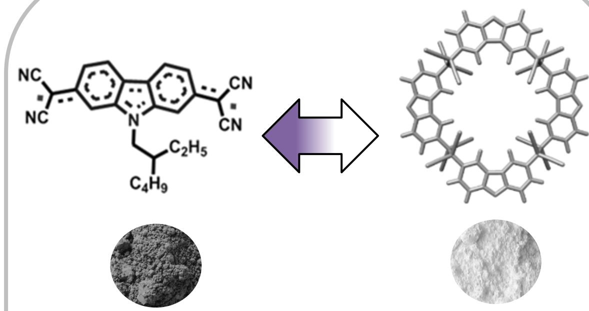


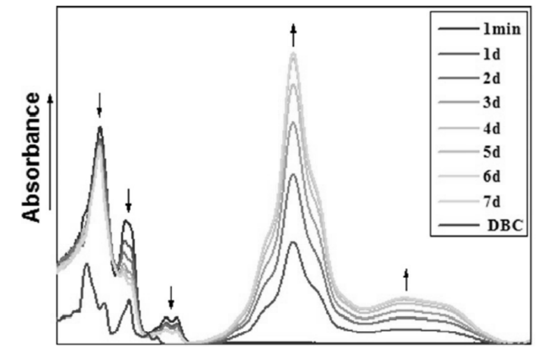




*Comm.Chem.* **2020**, *3*, 118.

*Ruiz Delgado, et al, manuscript submitted*

## Carbazole-based Diradicals





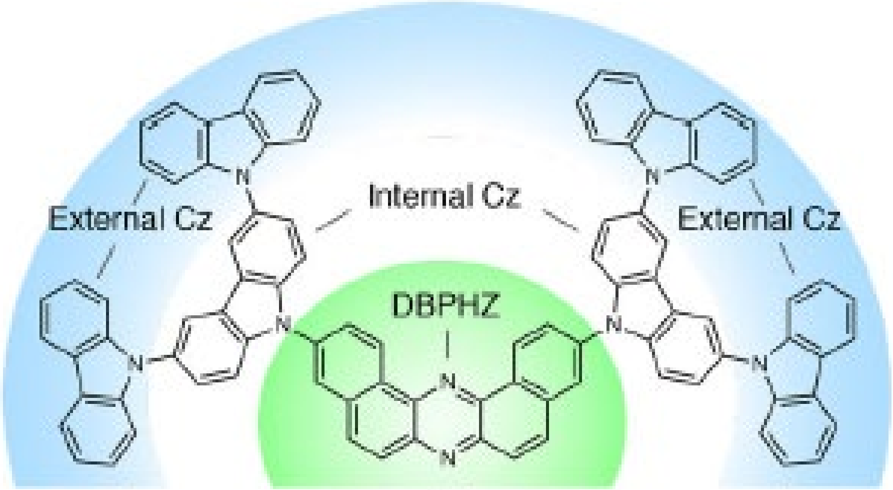

*J. Phys. Chem. Lett.* **2022**, *13*, 6003 – 6010

*Chem. Eur.* **2021**, *27*, 5509 – 5520 (hot paper)

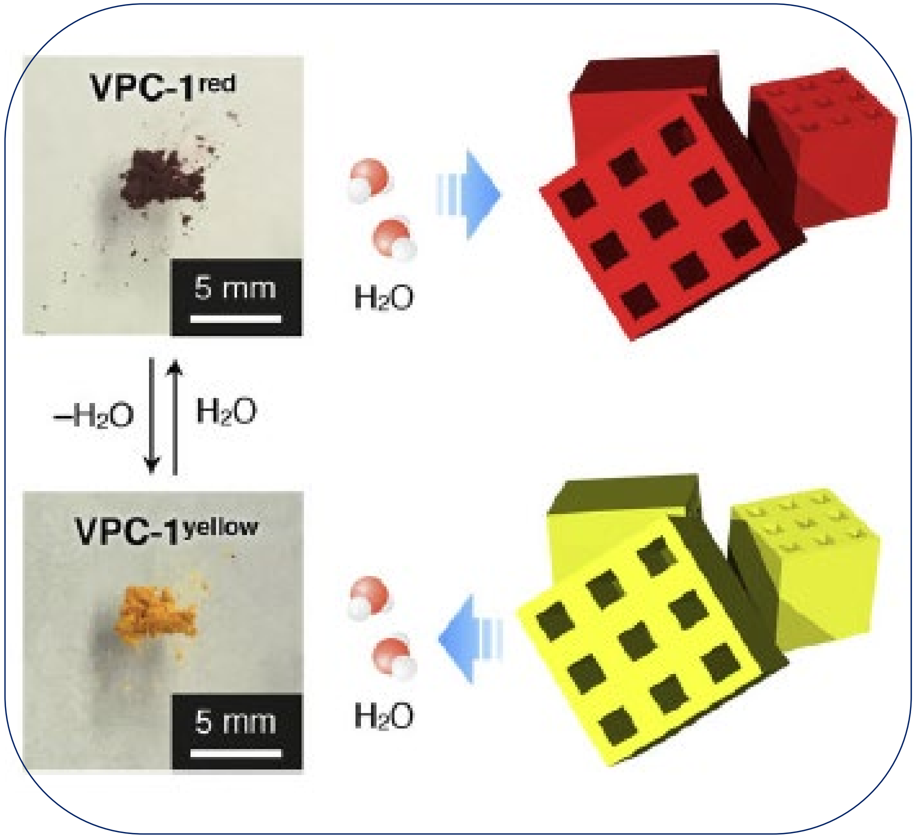
*ACS Omega* **2019**, *4*, 4761 – 4769

*Chem. Eur.* **2017**, *23*, 13776 – 13783

# 2 Carbazole-based Dendrons




**1**

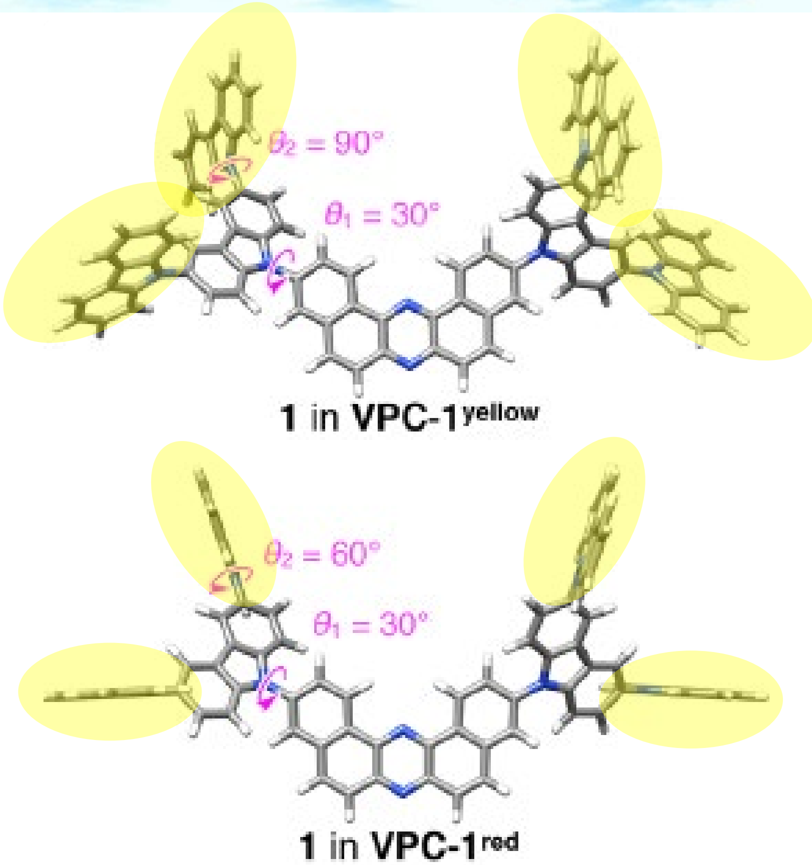


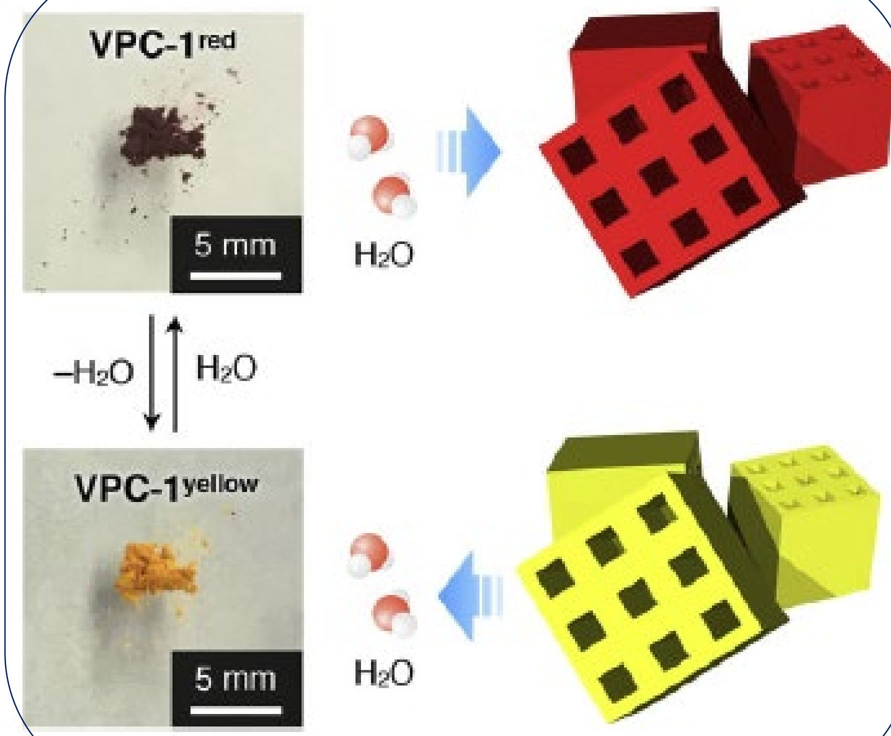

**VPC-1** exhibits reversible colour changes upon uptake/release of $H_2O$ molecules

*Comm.Chem.* **2020**, *3,* 118.

*Ruiz Delgado, et al, manuscript submitted*

# Carbazole-based Dendrons



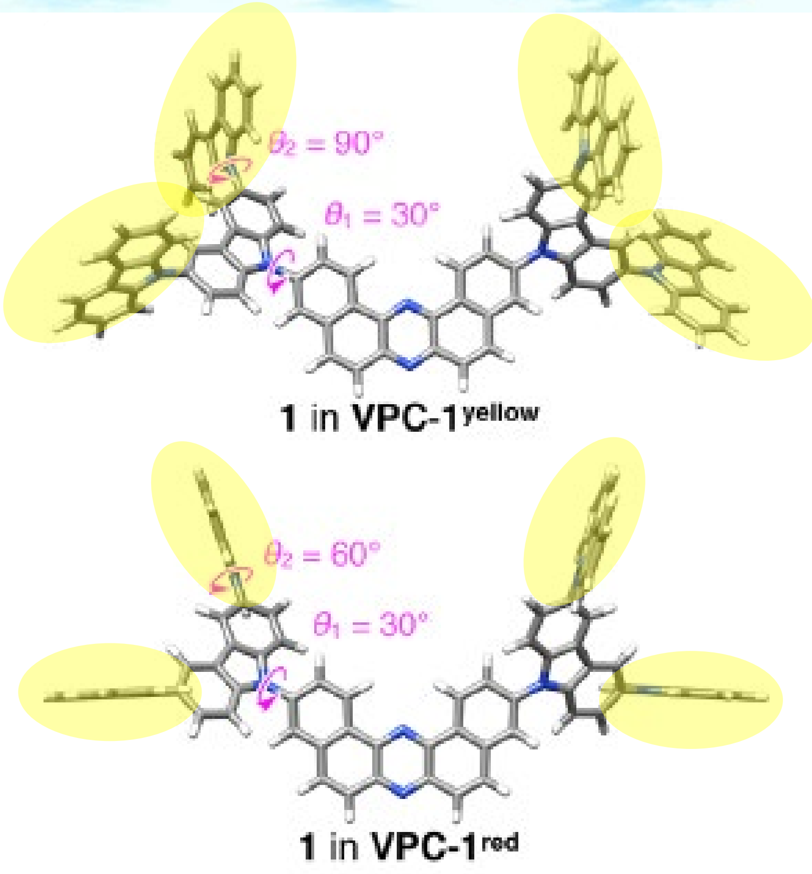



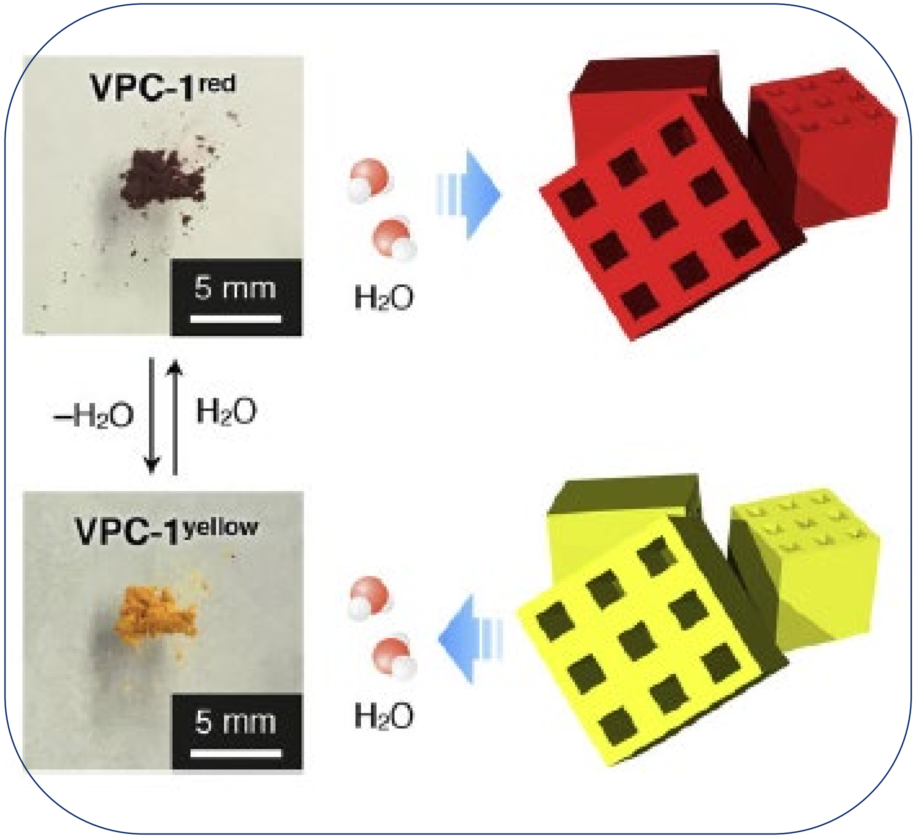

The **outermost carbazole units twist simultaneously** while the **crystal preserve** its lattice structure

*Comm.Chem.* **2020**, *3,* 118.

*Ruiz Delgado, et al, manuscript submitted*

# 2 Carbazole-based Dendrons



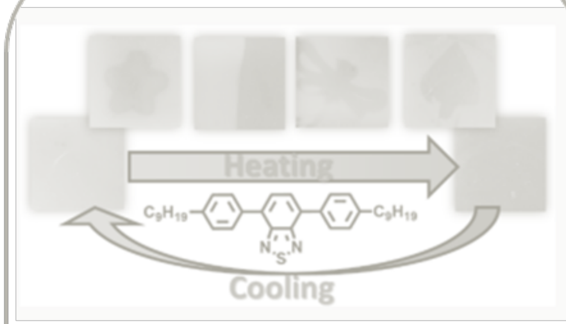

**Attractive** candidates towards high performance **sensors** under water-containing conditions

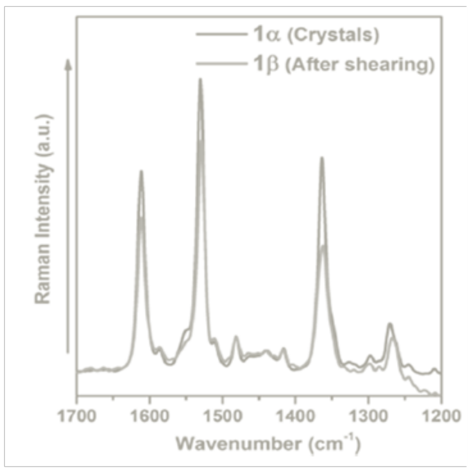
*Comm.Chem.* **2020**, *3,* 118.

*Ruiz Delgado, et al, manuscript submitted*

# 3 Carbazole-based Diradicals

## Benzothiadiazole-based Polymorphs

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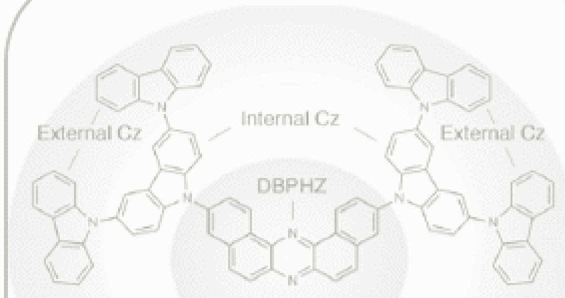
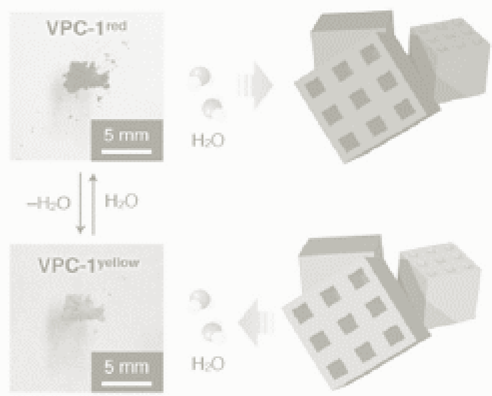
## Carbazole Dendrons (VDW porous crystal)




*Comm.Chem.* **2020**, *3*, 118.

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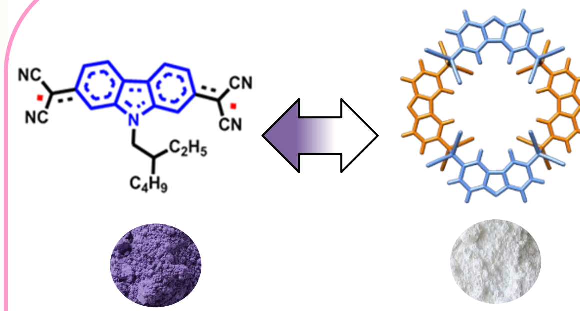
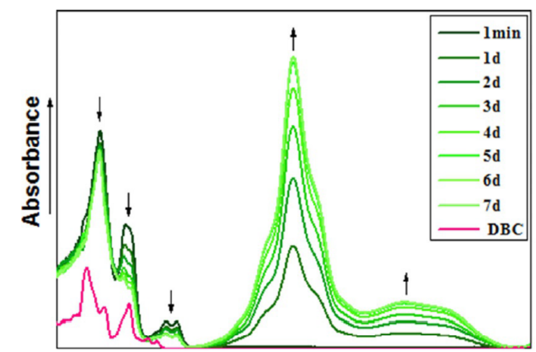
## Carbazole-based Diradicals




*J. Phys. Chem. Lett.* **2022**, *13*, 6003 – 6010

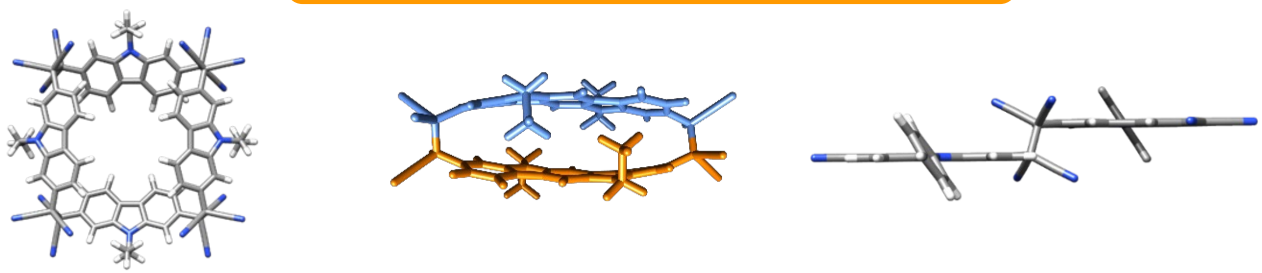
*Chem. Eur.* **2021**, *27*, 5509 – 5520 (hot paper)

*ACS Omega* **2019**, *4*, 4761 – 4769

*Chem. Eur.* **2017**, *23*, 13776 – 13783

# 3 Carbazole-based Diradicals

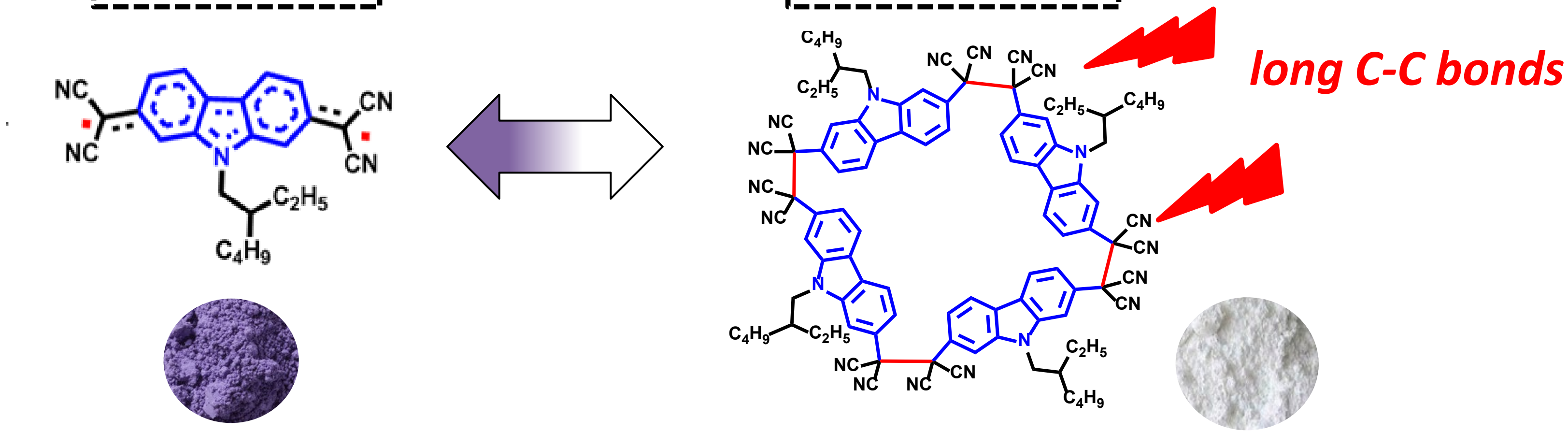
**Dynamic Covalent Chemistry**



Irene Badía-Domínguez
(UMA)

Diradicals

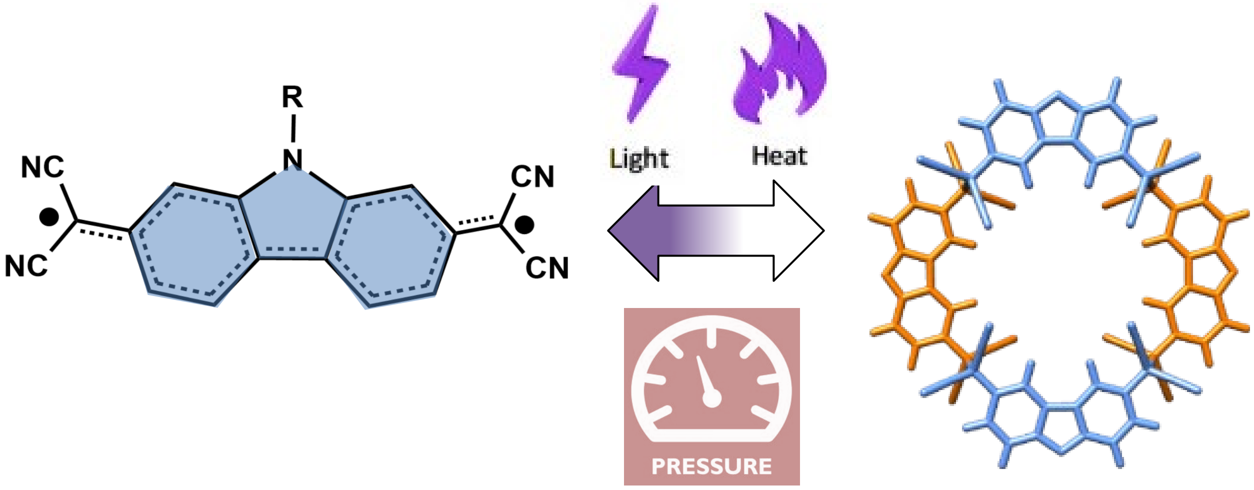
σ-aggregates




Diradical compounds can **selectively construct σ-bonded aggregates** through the **formation of reversible covalent bonds**

1

# Carbazole-based Diradicals




1) Diradical character

2) Cyclophane formation

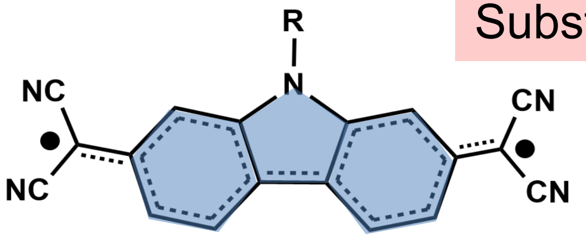
3) Reversibility

1

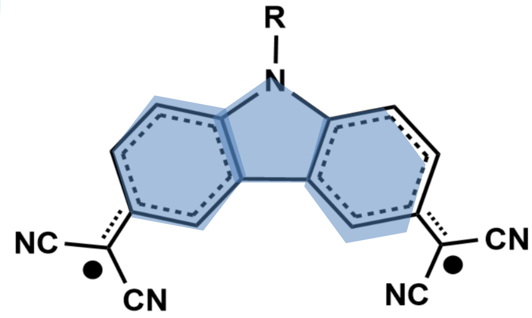
# Stimuli-responsive Organic Materias

## Substitution Pattern

***p*-Cz**

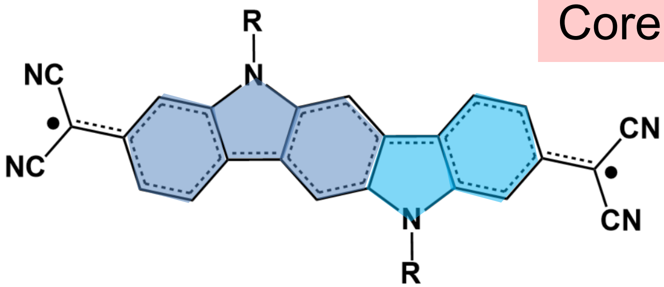


***m*-Cz**

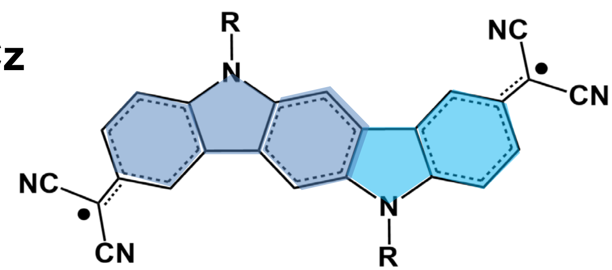


## Core Elongation

***p*-ICz**

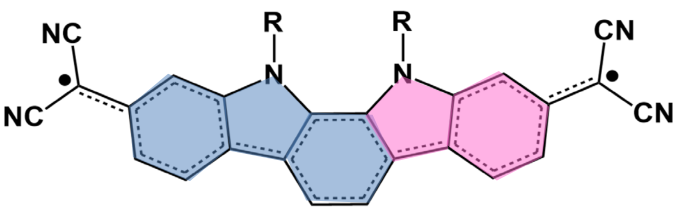


***m*-ICz**

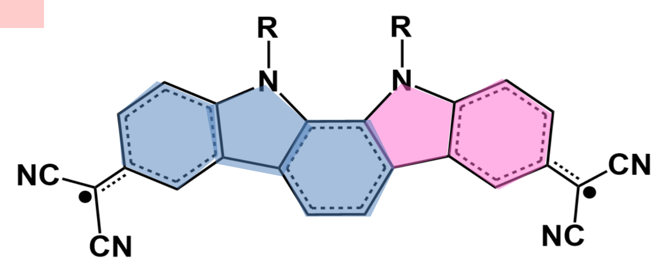


## Structural Isomerism

***p*-ICz-23a**



***m*-ICz-23a**




*J. Phys. Chem. Lett.* **2022**, *13, 6003−6010*

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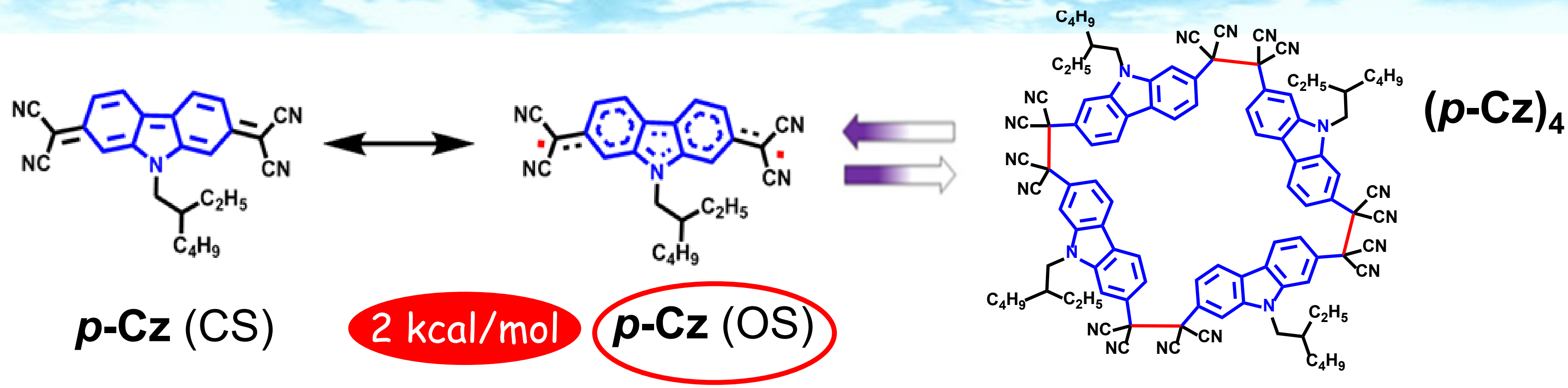
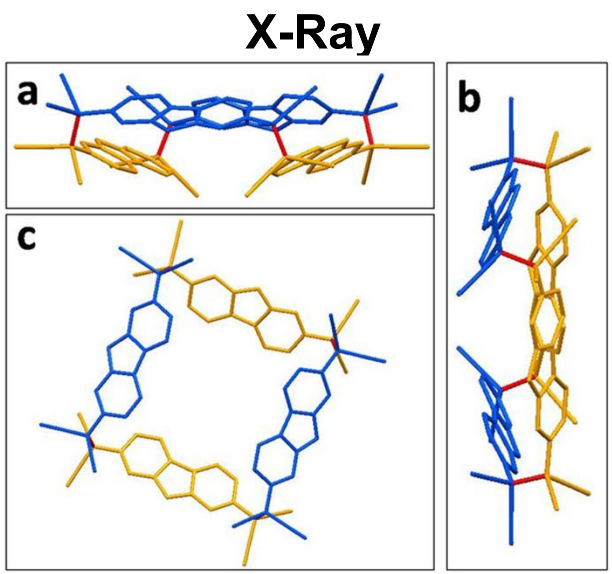
*Chem. Eur. J.* ***2017***, *23, 13776 – 13783*

# Stimuli-responsive Organic Materias




1.63 Å

*Long C-C bonds*

1.53 Å

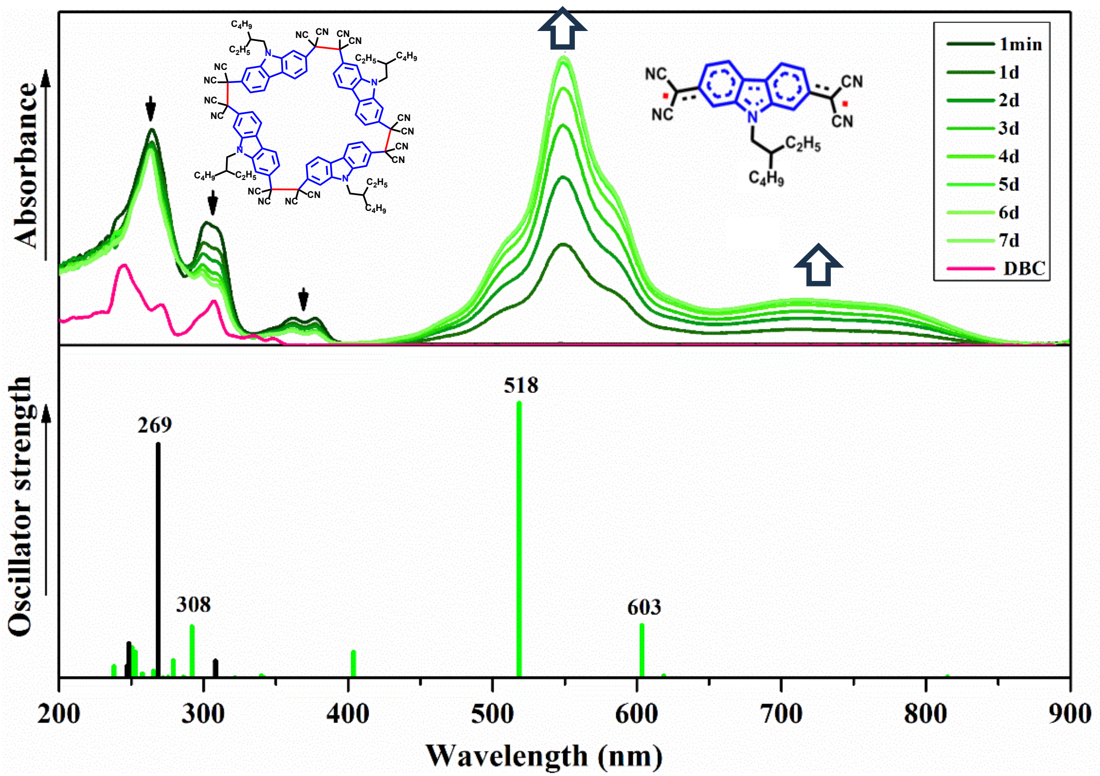
*C(sp$^3$)-C(sp$^3$)*

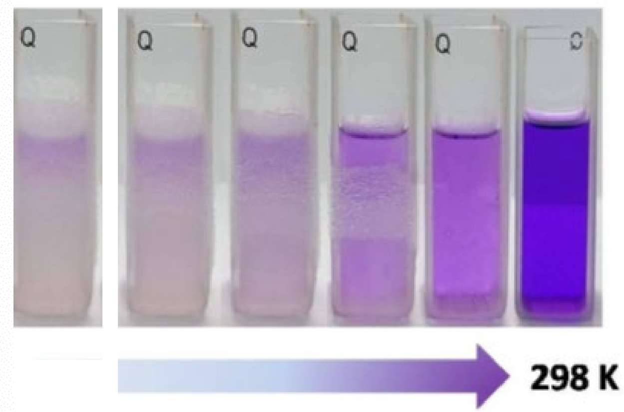
Formation of long sigma-C-C bong of 1.63 angstrom **by coupling of the unpaired electrons of diradicaloid *p*-Cz**

*Chem. Eur. J.* ***2017***, *23, 13776 – 13783*

# Stimuli-responsive Organic Materias

## UV-Vis Spectra

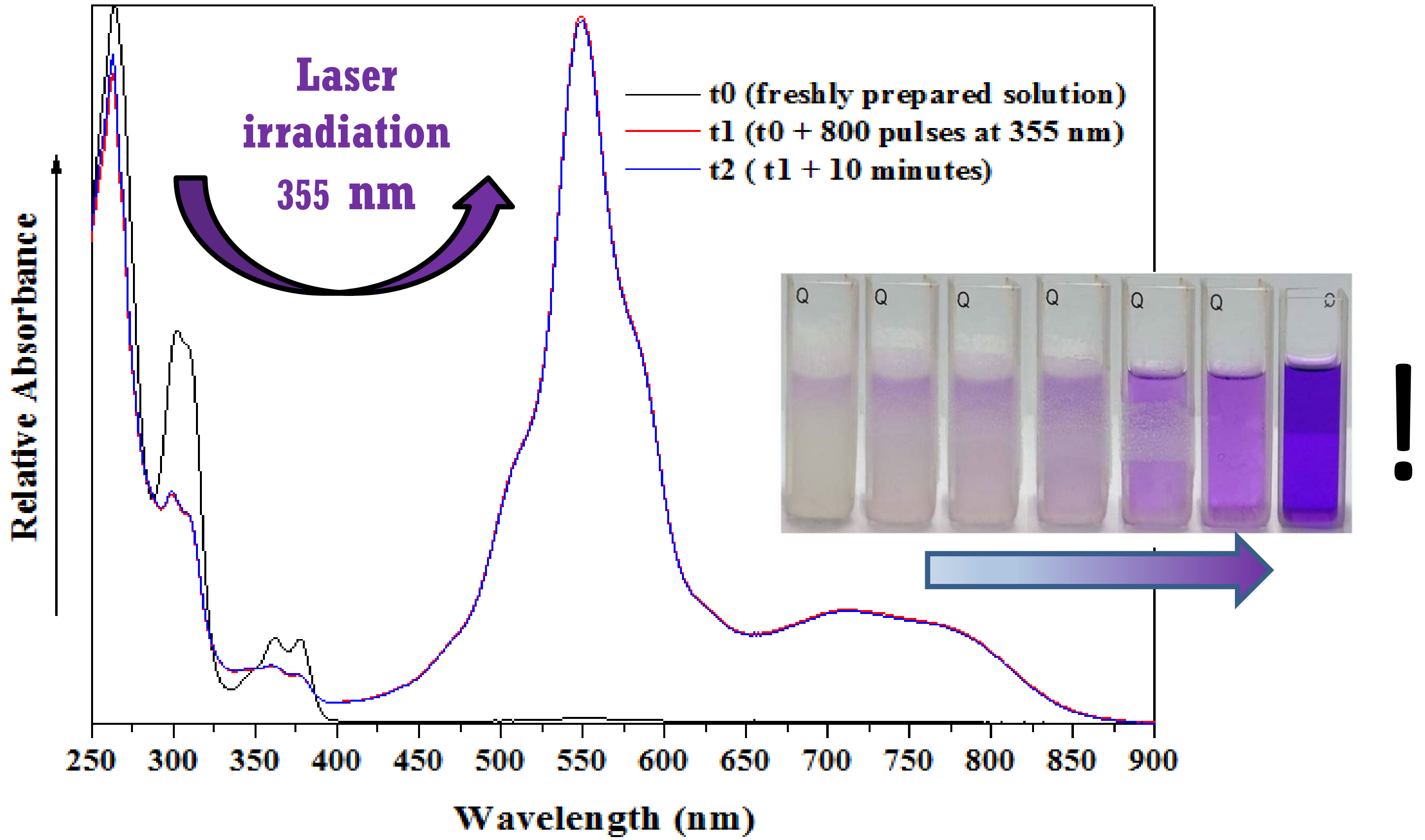



Transformation of a freshly prepared solution of **(*p*-Cz)$_4$** (↓) in $CHCl_3$ to diradicaloid ***p*-Cz** (↑) as a function of time

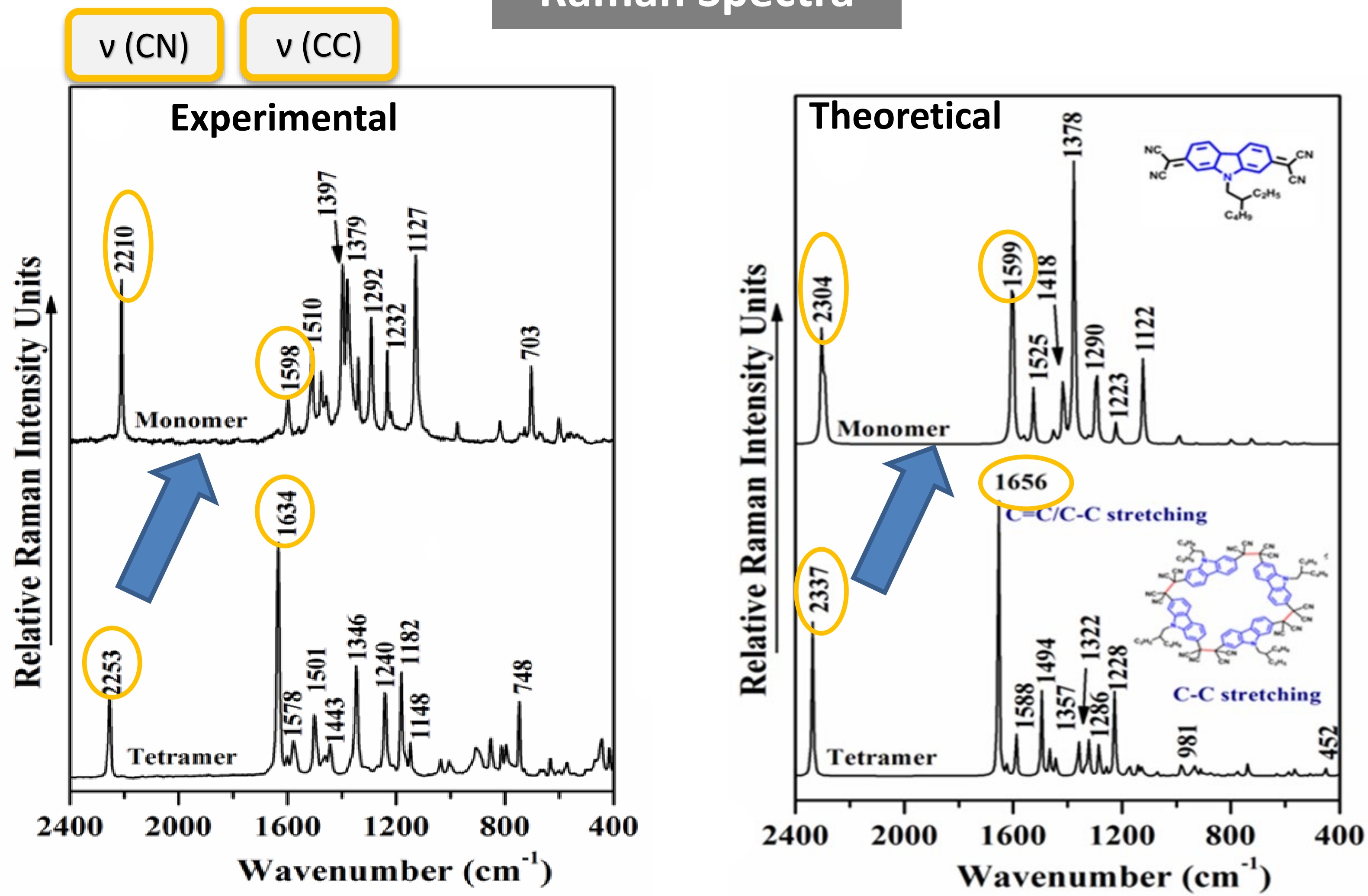
## UV-Vis Spectra

**Reversible photochromic behavior**

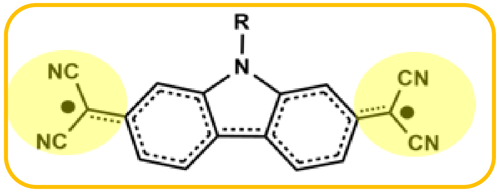



The freshly prepared **solution turns purple** on irradiation with UV light

# Raman Spectra

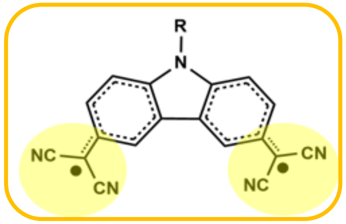


Substitution Pattern




***p*-Cz**

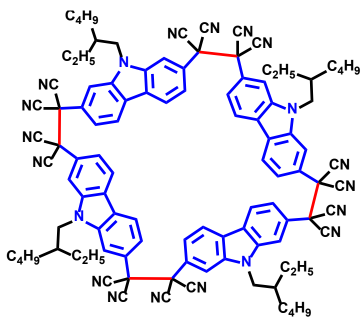
Vs



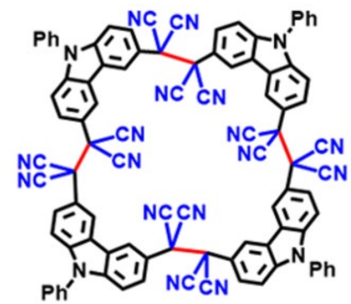

***m*-Cz**

# 1 Stimuli-responsive Organic Materias

Substitution Pattern



($p$-Cz)$_4$ **X-Ray** ✓

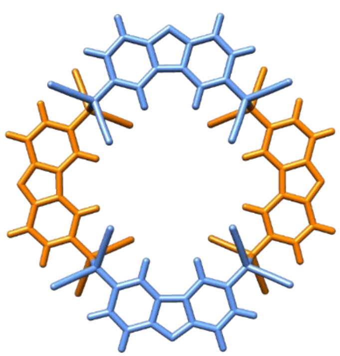


($m$-Cz)$_4$ **X-Ray** ✗

Aggregate Structure?

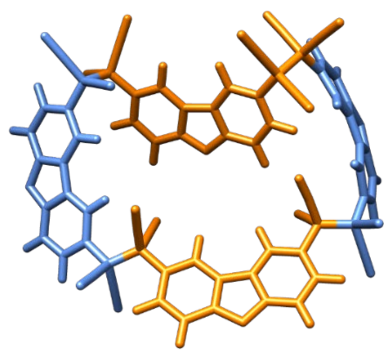
Top view

**Ring-shaped**



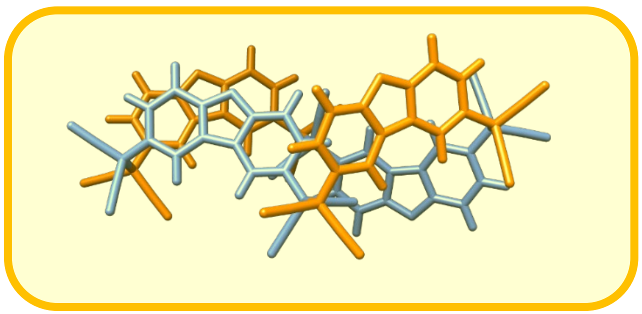
$\Delta G_f^o$= -63.6 Kcal/mol

**Distorted ring-shaped**



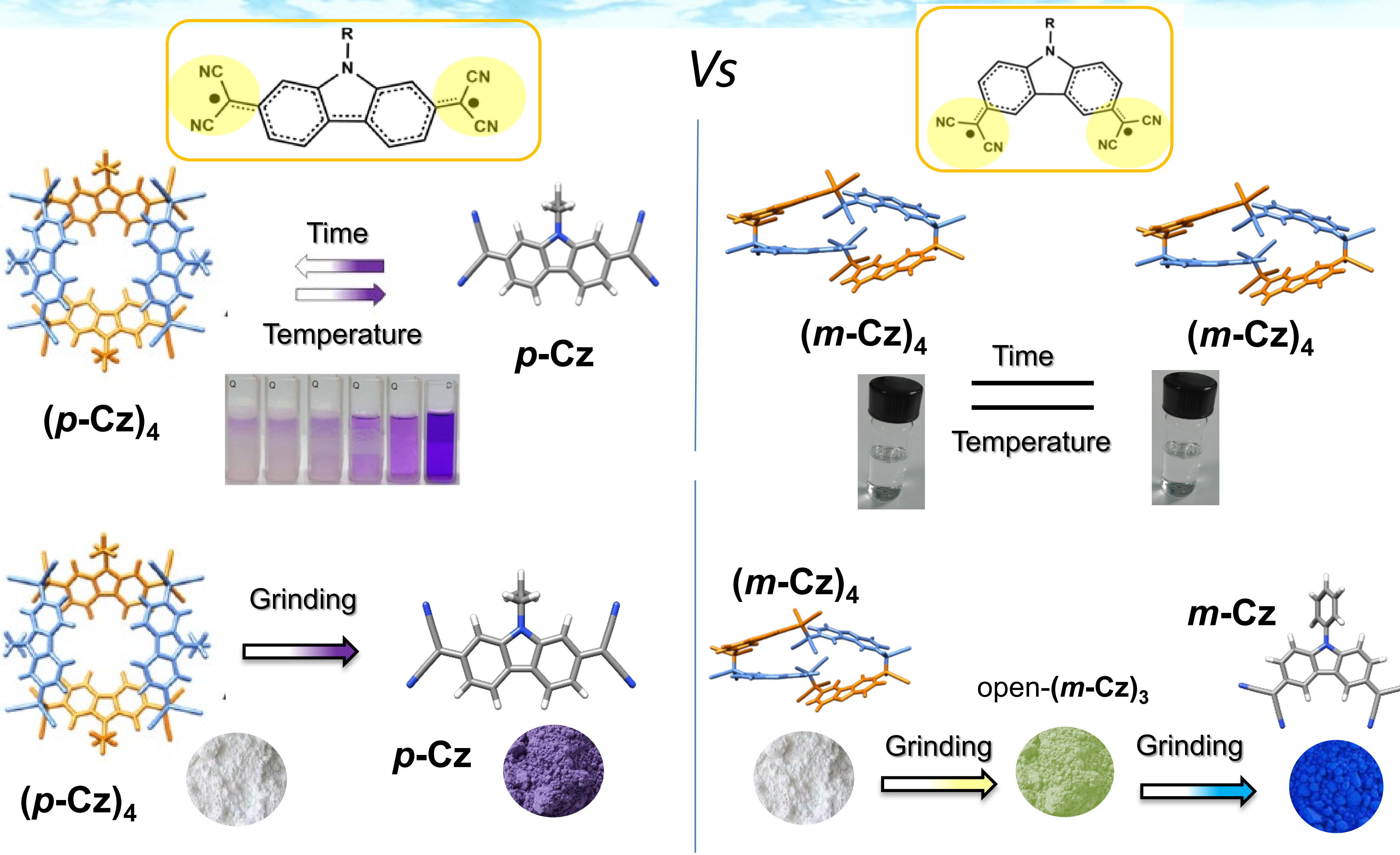
$\Delta G_f^o$= -45.5 Kcal/mol

**Folded structure**



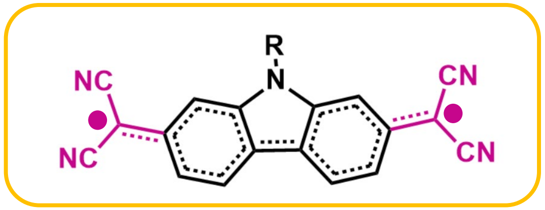
$\Delta G_f^o$= -70.1 Kcal/mol

## 1 Stimuli-responsive Organic Materias



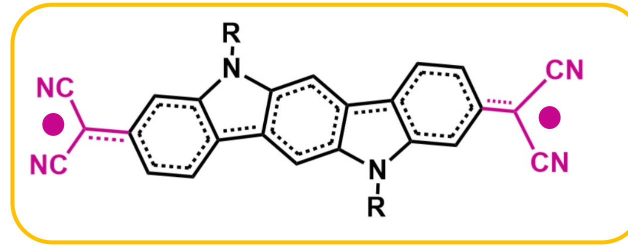

**Dynamic monomer/cyclic oligomer transformation** in solution and solid state

Core Elongation

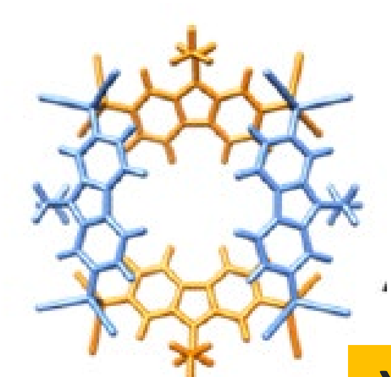



***p*-Cz**

*Vs*

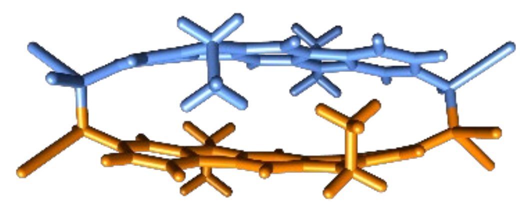



***p*-ICz**



**(*p*-Cz)$_4$**

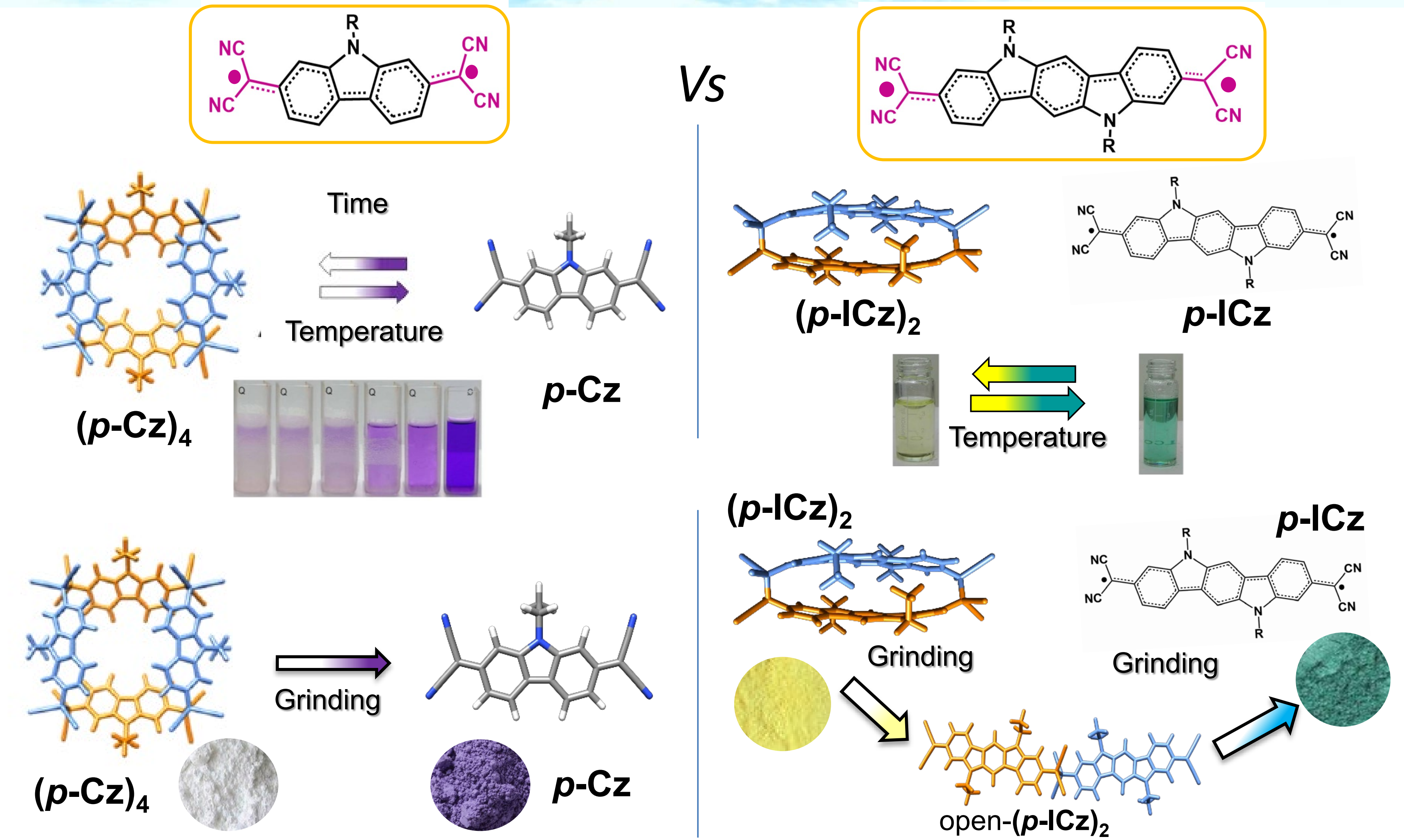
X-Ray



**(*p*-ICz)$_2$**

X-Ray

# 1 Stimuli-responsive Organic Materias



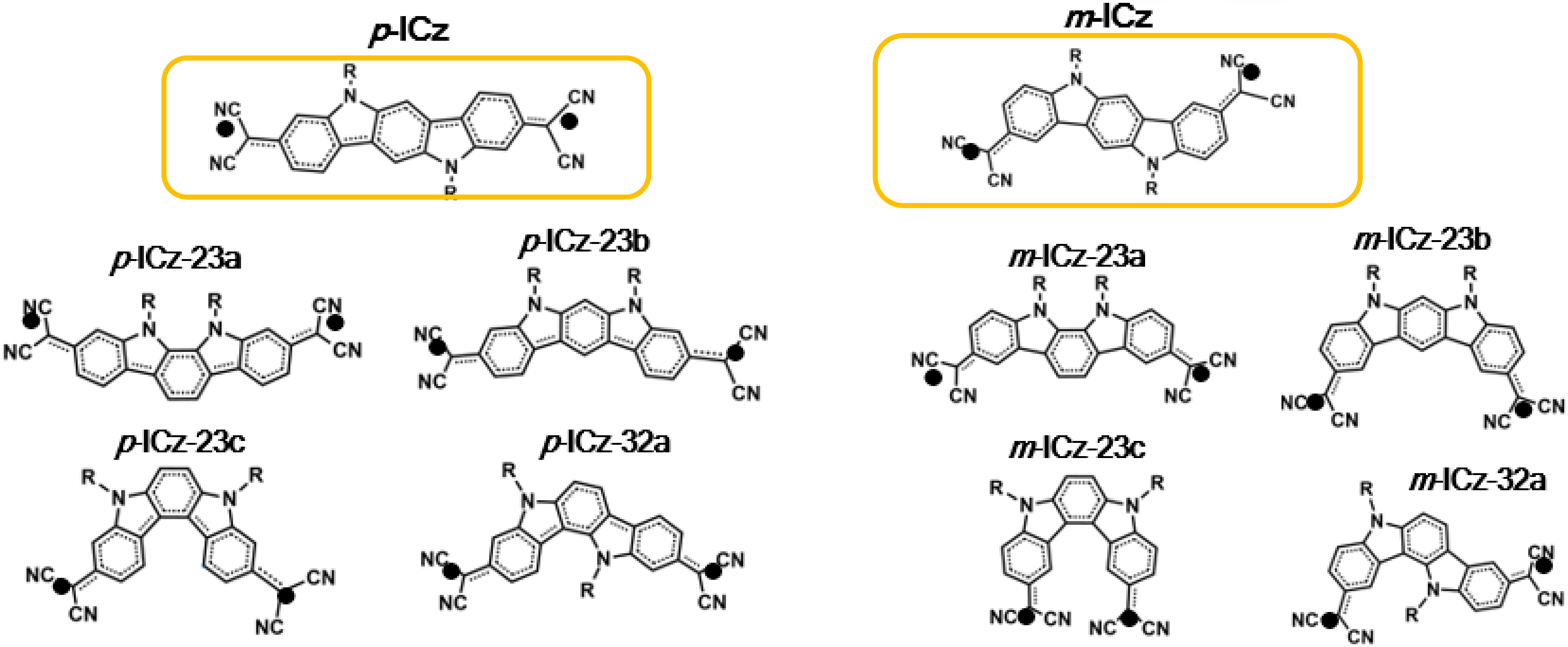

**Dynamic monomer/cyclic oligomer transformation** in solution and solid state

## Structural Isomerism

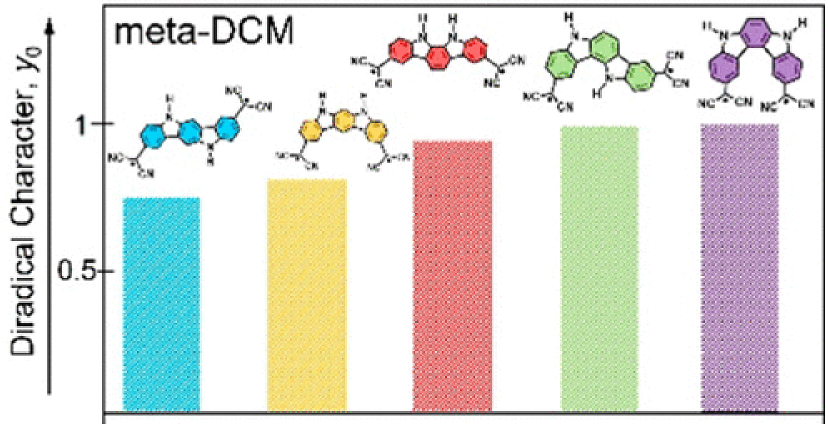
THE JOURNAL OF PHYSICAL CHEMISTRY LETTERS
A JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JPCL Letter

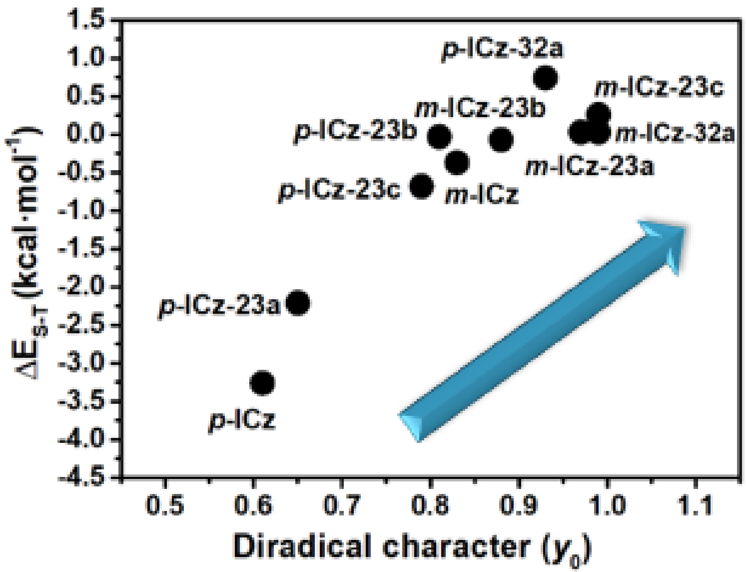
### Tuning the Diradical Character of Indolocarbazoles: Impact of Structural Isomerism and Substitution Position

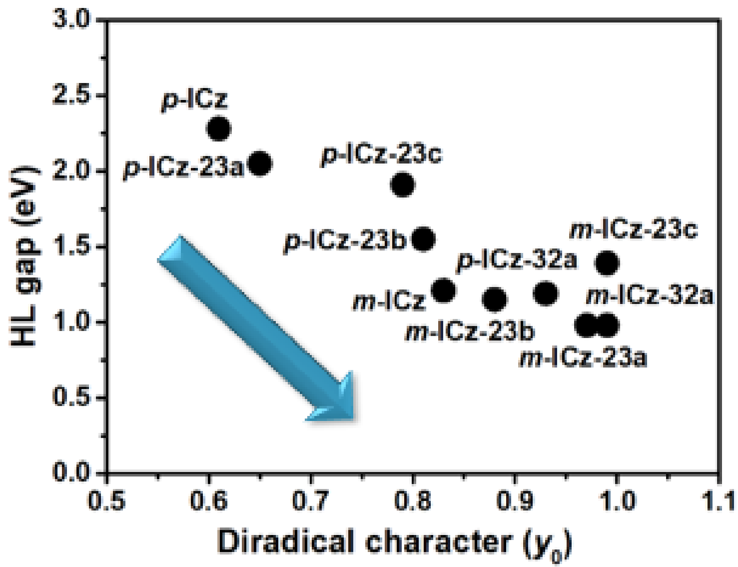
Irene Badía-Domínguez, Sofia Canola, Víctor Hernández Jolín, Juan T. López Navarrete, Juan C. Sancho-García, Fabrizia Negri,* and M. Carmen Ruiz Delgado*



## Structural Isomerism

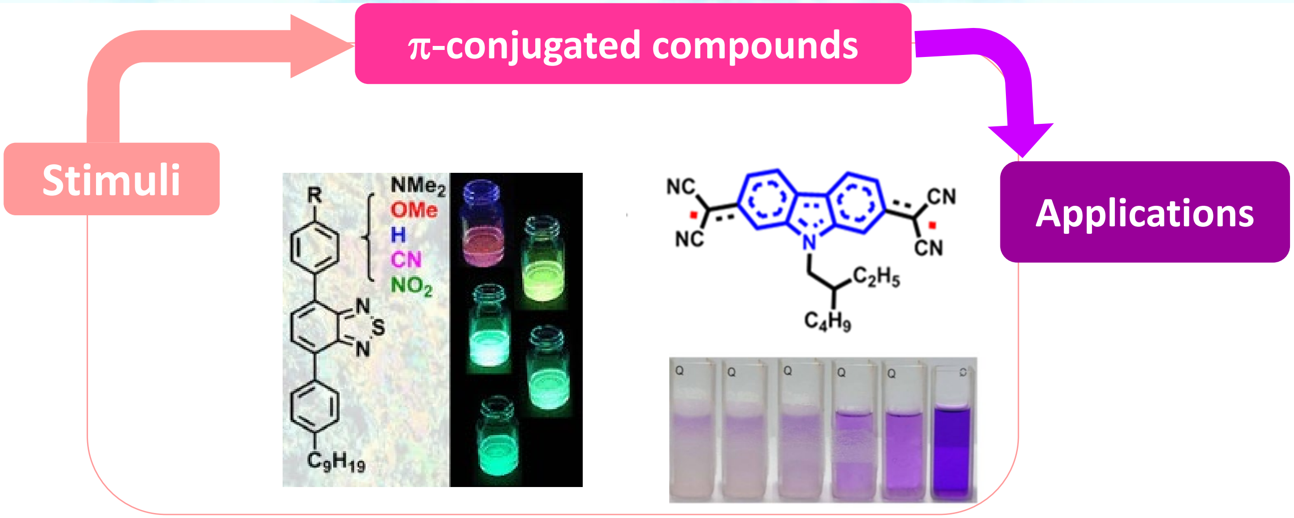



Structural isomerism represent a very effective way to **modulate the diradical properties**

## Conclusions




- **Slip-planes** have been identified as an attractive design principle in search of **mechanochromic** systems

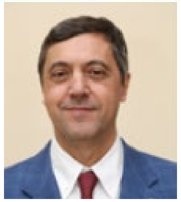
- **VDW porous crystals** can be attractive candidates towards **high performance sensors** under water-containing conditions

- **DCC** is a very good strategy to obtain **new multiresponsive chromic soft materials**

Isolated Monomer ⟷ Cyclophane Aggregates

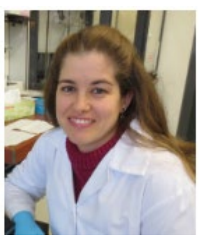
- New **molecular design strategies** toward the development of novel stimuli responsive materials

# Acknowledgments



Prof. Juan T. López Navarrete


Prof. Rocío Ponce Ortiz

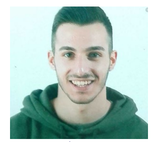

Prof. Víctor Hernández Jolín


Prof. María Moreno Oliva

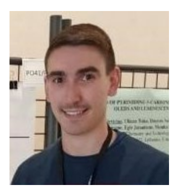
Dra. Alexandra Harbuzaru


Dra Irene Badía-Domínguez


Sergio Gámez-Valenzuela


Sara Fernández Palacios


Raúl González Núñez



<u>Collaborators</u>

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Frantisek Hartl (Reading University)

Sabine Ludwigs (U. Stutgart)

Gjergji Sini (U. Cergy-Pontoise)

Seth Rasmussen (Norht Dakota State U)


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JUNTA DE ANDALUCIA

## Acknowledgments