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# On the Nature of Color Diversity in Phenylenevinylene-based Polymorphs

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KEYWORDS: Luminescence, fluorescence, polymorphism, supramolecular, topology.

ABSTRACT: In this work we present a joint experimental and theoretical study of the light emitting properties of the *E,E-2,5*-dimethoxy-1,4-bis[2-(4-carboxylatestyril)]benzene, a phenylenevinylene (PV, from now on) derivate in solid state. Careful crystal growth under different conditions of this PV luminophore yields three different crystals with dissimilar color emissions with maxima ranging between 504 and 565 nm. Single crystal structure elucidation indicates that they correspond to a DMF solvate denoted **2**·**DMF** (yellow) and two conformational polymorphs named **2** $\alpha$  (yellow) and **2** $\beta$  (orange). Analysis of the close contacts and the framework topologies help us to rationalize the different colors observed, not only on the base of different

intramolecular conformations, but also of the different intermolecular interactions observed. Particularly, the presence of different, C-H··· $\pi$  and  $\pi$ ··· $\pi$  interactions in  $2\alpha$  and in  $2\beta$  polymorphs respectively, give rise to different supramolecular frameworks with **hex** and **bcu** topologies correspondingly. Theoretical studies reinforce the hypothesis that cooperative  $\pi$ ··· $\pi$  interactions in the crystal lattice are responsible for the red shifted color observed in the polymorph  $2\beta$ . In fact, contrary to what it is observed with the polymorph  $2\alpha$ , as we incorporate more monomers in the calculations of the optical properties of polymorph  $2\beta$ , the estimated energy for the vertical excitation from the ground state to the first excited state moves to lower values.

#### 1. INTRODUCTION

Controlling the optical properties of organic molecular aggregates in  $\pi$ -conjugated systems has acquired great relevance during the last few years. Assemblies of  $\pi$ -conjugated units have been found to offer an efficient pathway for excitons, allowing the development of new materials such as molecular crystals, gels, and liquid crystals with stimuli responsible light emitting properties.

Besides, efficient light emitting of  $\pi$ -conjugated organic materials arouse much interest in close relation to the development of novel organic electronic devices such as organic light emitting diodes (OLEDs), or chemical sensors, which take advantage of the interesting optical properties of  $\pi$ -conjugated molecules as active layers.<sup>1</sup> However, although an enormous number of efficient fluorophores with different chemical structures are known and there are well established structure-property relationships to tune their optical properties at the molecular level (mainly by varying the extension of the  $\pi$ -system and the electronic nature of attached functional groups), the knowledge on the factors that control bulk light emitting properties is still very limited.<sup>2</sup> In fact, the design of

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molecules that are highly emissive in solid and crystalline states (states in which these compounds are intended to be used in thin-film devices) has proved challenging since strong intermolecular interaction and close packing usually lead to quenching of emission.

Single crystal analysis provides invaluable information on how each molecule is arranged and how it interacts with the surrounding molecules in the solid-state, and offers an excellent opportunity to investigate the macroscopic properties that depend on the molecular arrangement. In the last few years many efforts have been dedicated to tune the emission color of organic fluorophores through crystal engineering and to establish clear design rules for optimize light emission by analyzing intermolecular interactions in single crystals.<sup>3-4</sup> In this context, lightemitting polymorphs, are of particular interest as they allow correlating the changes in the solidstate luminescent properties, exclusively on the basis of the molecular conformation and packing, without the interference of potential effects exerted by different functional groups. <sup>5-7</sup>

In the search of highly emitting organic materials, PVs occupy a distinctive place. These molecules not only present very efficient light emitting properties in solid state, but also exhibit very high optical and thermal stability and film forming proclivity.<sup>8-12</sup> Due to their favorable properties, these molecules have been incorporated in different optoelectronic devices.<sup>13</sup> Furthermore, their tendency to self-assemble in supramolecular aggregates has been successfully exploited to develop soft materials with tunable light emitting properties through a supramolecular approach. Thereby, understanding the key factors that govern the light emitting properties and therefore broaden their potential applications.<sup>14-17</sup>

Herein we present the solid state light emitting properties of the PV derivative *E*,*E*-2,5-dimethoxy-1,4-bis[2-(4-carboxylatestyril)] benzene (2) which crystallize in two conformational polymorphs (denoted  $2\alpha$  and  $2\beta$ ) and a DMF solvate (named 2·DMF). The three crystals showed different color emissions when excited at 360 nm. Single crystal analysis and computational calculations allow us to correlate the emission colors observed with intramolecular conformational and/or supramolecular differences found in the different crystals.

#### 2. METHODOLOGY

2.1. Experimental Section. Commercially available precursors were used as received without further purification and solvents were dried according to standard procedures. Melting points were determined using a Stuart SMP10 melting point apparatus and the reported values are uncorrected. Infrared spectra were recorded with KBr discs on a Shimadzu IR Prestige-21 FT-IR spectrophotometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken on a Bruker Advance 400 spectrometer using CDCl<sub>3</sub> or DMSO- $d_6$  as solvents, chemical shifts are reported as  $\delta$  values in units of ppm. UV-Vis spectra were measured in a double channel Thermo Scientific Evolution 300 UV-Vis spectrophotometer with xenon lamp based platform. Fluorescence spectra were registered in DMSO solutions on a PTI QuantaMaster 300 spectrofluorometer with xenon lamp.

2.2. Single crystal X-ray structure determination. Single-crystal X-ray data were obtained in a Bruker four circle kappa-diffractometer equipped with a Cu INCOATED microsource, operated at 30 W power (45kV, 0.60mA) to generate Cu K $\alpha$  radiation ( $\lambda = 1.54178$  Å), and a Bruker VANTEC 500 area detector (microgap technology). Single crystal X-Ray diffraction data were collected exploring over a hemisphere of the reciprocal space in a combination of  $\varphi$  and  $\omega$  scans to reach a resolution of 0.86 Å, using a Bruker APEX2<sup>18</sup> software

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suite (each exposure of 40 s covered 1° in  $\omega$ . Unit cell dimensions were determined for leastsquares fit of reflections with I > 20  $\sigma$ . A semi-empirical absorption and scale correction based on equivalent reflection was carried out using SADABS.<sup>19</sup> The space group determination was carried out using XPREP.<sup>20</sup> The structures were solved by direct methods. The final cycles of refinement were carried out by full-matrix least-squares analyses with anisotropic thermal parameters of all non-hydrogen atoms. The hydrogen atoms were fixed at their calculated positions using distances and angle constraints. All calculations were performed using SMART<sup>21</sup> and APEX2<sup>18</sup> software for data collection, SAINT<sup>21</sup> for data reduction, SHELXTL<sup>20</sup> and OLEX2<sup>22</sup> to resolve and refine the structure respectively. CCDC 1895790, CCDC 1895648, CCDC 1895649 and CCDC 1895650 contain the supplementary crystallographic data for **1**, **2** $\alpha$ , **2** $\beta$  and **2**-DMF, respectively.

**2.3. Linear Spectroscopy.** UV-Visible studies were carried out on a PerkinElmer Lambda XLS+ spectrometer. Fluorescence spectra were recorded on an Aminco SLM 8000 spectrophotometer.

**2.4. Theoretical Calculations.** In order to understand the interaction that drives the crystal growth and optical responses of crystals and monomers in solution and solid state, computational calculations using methods based on density functional theory (DFT) and time-dependent DFT were performed. The calculations were carried out on the oligomers (up to 10 monomers) for the different crystal structures.

*DFT and TDDFT calculations*: Electronic structure calculations were carried out at the B3LYP-D3BJ/6-31+G(d) level of theory. This combination of functional and basis set has been proved to provide a proper geometrical description.<sup>23</sup> B3LYP-D3BJ considers the hybrid nonlocal B3LYP density functional<sup>24-25</sup> complemented with empirical dispersion corrections computed as

a sum of two and three-body energies, as defined by Grimme *et al.*<sup>26-27</sup> This correction allows including long-range dispersion contributions to the computed *ab initio* B3LYP energy and gradients. The inclusion of these dispersion terms has been shown to be relevant in determining interaction occurring in crystal structure, which are in some cases the differential interaction.<sup>28</sup> All the electronic structure calculations were performed by using the Gaussian09 software package.<sup>29</sup> TDDFT offers a good solution for the vertical excitation of the system from the ground state to the different excited states which can be related with the absorption peaks in an experimental spectrum.<sup>23, 30-31</sup> For the TDDFT calculations we have computed the first fifteen single excited state for every system.

#### **3. RESULTS AND DISCUSSION**

Considering that the luminescence characteristics of the PV derivatives greatly depend on their configuration/conformation relationships, we have focused in synthetic methodologies that yield pure *trans* configuration, as it promotes the ideal arrangement of  $\pi$  orbitals for an uninterrupted electron flow through the structure. Therefore, the synthesis of **1** was performed using a previously optimized solvothermal Heck reaction, which produces the compound with the desired stereoselectivity in good yield (Scheme 1).<sup>32</sup>





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The catalytic system offered by  $Pd(dba)_2$  and  $P(OPh)_3$  has been found to be ideal for obtaining PV systems with  $2\frac{1}{2}$  electronic conjugation length and *trans-trans* configuration, selectively. This high selectivity can be attributed to the steric hindrance and electronic properties of the phosphite ligand, which results in an enhanced orientation control of the substrates during the C – C coupling step and also in an improvement of the catalytic cycle kinetics. Moreover, the phosphite ligand confers to the Pd in the catalyst high stability, preventing the aggregation and precipitation of Pd(0) black.<sup>33</sup> Spectroscopic characterization confirms the *trans-trans* configuration of this compound (see S. I.). Hydrolysis of 1, under basic conditions result in the obtaining of 2 with excellent yield, without affecting the *trans-trans* configuration according to the spectroscopic characterization (see S. I.).

The UV-Vis absorption and fluorescence spectra of **2** were initially determined in a 10<sup>-5</sup> M DMSO solution. As can be observed in figure 2, compound **2** has two absorption bands at 337 and 408 nm which can attributed to  $\pi \rightarrow \pi^*$  electronic transition and to a  $n \rightarrow \pi^*$  transition respectively. When irradiated at the absorption maximum the solution emits in the blue region (475nm) showing a quantum yield ( $\phi_{FL}$ ) of 0.50 (Figure 1).



Figure 1. Experimental UV-Vis absorption and fluorescence spectra of 2 in DMSO.

#### 3.1. Crystal Growth and Structure Determination by single crystal X-ray Diffraction

With the aim of understanding the origin of the color variations in the solid state, we have attempted to obtain single crystals of sufficient quality for structure determination. Interestingly, by systematically varying the growing conditions we could obtain three different crystals of **2**, showing different colors (Figure 2).



**Figure 2.** Above: crystal morphology for different compounds of 2 (left to right:  $2\alpha$ ,  $2\beta$  polymorphs and **2**·**DMF** solvate). Down: view of the same set of crystals under UV light.

Slow evaporation at room temperature of a DMF solution of **2**, give rise to the DMF solvate (**2**•**DMF**) which grows as elongated plate-like yellow crystals. Conversely, crystallization of **2** from a hot CH<sub>2</sub>Cl<sub>2</sub> solution give rise to a mixture of the two polymorphs  $2\alpha$  and  $2\beta$  as large yellow prismatic crystals and small plate-liquid orange crystal respectively (Figure 2). The three crystalline materials of **2** emit strongly when irradiated with UV light ( $\lambda_{exc}$ : 400nm) showing maxima at 504, 522 and 565 nm for  $2\alpha$  polymorph, **2**•**DMF** solvate and the  $2\beta$  polymorph respectively (Figure 3).



**Figure 3.** Experimental fluorescence spectra for the three derivates of **2** in solid state irradiated at 400 nm.

After a careful crystal growth process, it was possible to obtain selectively the different crystals. Thus, crystals of  $2\alpha$  were obtained exclusively in a mixture of CH<sub>2</sub>Cl<sub>2</sub>/EtOH/DMF 1:1:1.5, heated up to 60°C for 3 days and then cooled down to room temperature. A variation in the solvent mixture (H<sub>2</sub>O/EtOH/DMF 1:1:1) allowed us to obtain exclusively orange crystals of polymorph  $2\beta$ . Interestingly the solubility of the two polymorphs is also very different. Once crystallized, the orange crystals of polymorph  $2\beta$  are practically insoluble while yellow crystals of polymorph  $2\alpha$ are highly soluble in most organic solvents. Furthermore, we were able to recrystallize compound 1, its structure determination and the supramolecular analysis are placed in the SI section 3.

Single crystal structure determination shows that the solvate 2·DMF crystallizes in the monoclinic  $P2_1/n$  space group. Meanwhile, the two conformational polymorphs  $2\alpha$  and  $2\beta$  crystallize in the triclinic *P*-*1* and in the Monoclinic  $P2_1/n$  space group respectively (Table 1).

Compound	1	2α	2β	2·DMF
Formula	$C_{28}H_{26}O_{6}$	$C_{52}H_{44}O_{12}$	$C_{26}H_{22}O_{6}$	$C_{32}H_{36}N_2O_8$
Molecular	158 10	860.87	130 11	576.63
Weight /gmol <sup>-1</sup>	430.49	800.87	430.44	570.05
Temperature/K	296(2)	296(2)	296(2)	296(2)
Wavelength/Á	1.54178	1.54178	1.54178	1.54178
Crystal System	Triclinic	Triclinic	Monoclinic	Monoclinic
Space Group	P-1	P-1	$P2_l/n$	$P2_l/n$
a/Á	6.2418(6)	7.7009(11)	13.1512(11)	11.2332(5)
b/Á	7.6927(7)	11.0569(19)	9.6461(10)	12.0858(5)
c/Á	12.4052(11)	14.529(2)	17.3222(14)	11.3519(5)
$\alpha/^{\circ}$	75.9000(5)	83.033(12)	90	90
β/°	79.585(5)	81.212(12)	101.203(6)	106.384(3)
γ/°	76.023(6)	89.103(11)	90	90
V/Á <sup>3</sup>	555.87(7)	1213.6(3)	2155.6(3)	1478.58(11)
Ζ	1	1	4	2
Dx/ g.cm <sup>-3</sup>	1.370	1.178	1.326	1.259
µ/mm <sup>-1</sup>	0.784	0.688	0.719	0.768
F(000)	242	452	724	596
GOF F <sup>2</sup>	1.198	0.997	0.923	1.075
Final	$D_{1} = 0.077($	D1.01105	D1.00700	D1.00525
R indexes	K1: 0.0776	K1: 0.1185	K1: 0.0700	KI: 0.0525
[I>2σ(I)]	WK2: 0.2227	WK2: 0.2988	WK2: 0.1823	WK2: 0.1413
R indices	R1: 0.0880	R1: 0.2145	R1: 0.1529	R1: 0.0813
(all data)	wR2: 0.2649	wR2: 0.3481	wR2: 0.2520	wR2: 0.1796

**Table 1.** Main crystallographic and refinement data for the different isolated crystals of compounds 1 and 2

At a molecular level, the main structure differences between the three crystalline materials of 2 rely in their torsion angles ( $\omega$ ) and the dihedral angles between the planes of the aromatic rings (Table 2, Figure 4). Among the two polymorphs ( $2\alpha$  and  $2\beta$ ) significant changes between the plane

of the central ring and those of the peripheral rings are appreciated (35.75°, 31.38° for polymorph  $2\alpha$  and 11.97°, 17.02° for polymorph  $2\beta$ ).

Table 2. Experimental angle values for the different arrangements of 2				
	Polymorph	Solvate	Polymorph	
Angle	2α	2·DMF	2β	
<b>(</b> C11, C10, C5, C3)	107.61°	150.54°	146.81°	
<b>\U0111</b> (C31, C30, C25, C23)	120.40°	-	146.35°	
Plane 1	35.75°	12.40°	11.97°	
Plane 2	31.38°	-	17.02°	

The planarity of the molecules will determine the effective  $\pi$ -conjugation length which affects the emission color, and could explain the red-shifting observed in case of polymorph  $2\beta$ , which is planarized when compared to polymorph  $2\alpha$ . However, in case of 2-DMF solvate, the dihedral angle between the ring planes (12.40°) is closer to the values shown by polymorph  $2\beta$  but emits in yellow, and therefore the color of this species cannot be explained solely on the basis of intramolecular conformation. This points to significant contribution of supramolecular interactions in the origin of the red-shifting observed in polymorph  $2\beta$ . Note that the origin of red shift commonly observed in the spectra of aggregated  $\pi$ -conjugated molecules has been attributed to the delocalization of electronic excitation over several molecular units because of the favorable  $\pi$ -overlap between neighboring molecules. <sup>34</sup>

#### 3.2. Supramolecular Analysis

In order to understand the influence of the supramolecular arrangement in the colors observed for the polymorphs, we have studied the interaction network of the crystals and analyzed the nature of the interactions among the neighboring molecular units (see SI section 3 the summary and strength classification of the intermolecular hydrogen bonds and weak interactions).





**Figure 4.** View of the angle between the planes of the aromatic rings for  $2\alpha$ , **2**·**DMF** and **2** $\beta$ . (Drawings and angle measurements performed with Mercury Crystallographic program<sup>35</sup>).

In case of the supramolecular network of **2-DMF**, the following intermolecular hydrogen bonds and other weak interactions are involved (the values presented are *d*, *D* and  $\theta$  respectively): i) synthon by i) O1-H1···O20<sub>DMF</sub> (1.627Å, 2.608Å and 176.78°) and ii) C20-H20···O2 (2.538Å, 3.219Å and 123.06°) growing the framework along *b* axis, iii) C13<sup>ii</sup>-H13C<sup>ii</sup>···π</sup> (3.074Å, 3.961Å and 152.77°), iv) C13<sup>iii</sup>-H13B<sup>iii</sup>···O20<sub>DMF</sub> (2.790Å, 3.371Å and 121.45°) and v)  $\pi$ C8=C9··· $\pi_{ring}$ (3.912Å, off-center parallel stacking (offset 29.35°)) growing the structure along *a* axis, than together with vi) C4<sup>i</sup>-H4<sup>i</sup>···O2 (2.518Å, 3.476Å and 156.77°), vii) C22-H22A<sub>DMF</sub>···O1(2.812Å, 3.453Å and 123.58°) connects the framework along *c* axis giving rise to a 3D supramolecular arrangement. This framework can be described as an 8-connected uninodal net (considering as node the single molecule) with **bcu** (body centered cubic; 8/4/c1; sqc3) topology (Figure 5).



**Figure 5.** Above: Atomic representation of **2**•**DMF** showing its asymmetric unit (drawings performed with Mercury Crystallographic program).<sup>35</sup> enter: view along *c* axis of the supramolecular (left) and an augmentation view of the principal weak interactions between molecules (right). Down: supramolecular packing showing the 8-connected node (central molecule) and the resulting topological **bcu** representation of this connectivity (topology simplification made using TOPOS program).<sup>36</sup>

For both polymorphs of **2**, we found as a common characteristic the presence of a synthon among the terminal carboxylic acid of both independent molecules. For  $2\alpha$ : O21-H21···O2 (1.676Å, 2.630

and 158.67°), and O1-H1···O22 (1.656Å, 2.629Å and 159.76° Å) grows the framework along *a* axis. Meanwhile the synthon in **2** $\beta$ : O21-H21···O2 (1.563Å, 2.623Å and 166.83°), and O1-H1···O22 (1.647Å, 2.633Å and 166.64°) grows the framework parallel and perpendicular to the (011) plane (Figure 6).

In case of  $2\alpha$  supramolecular arrangement, the following additional intermolecular weak interactions are observed (the values presented are *d*, *D* and  $\theta$  respectively): i) C26<sup>iii</sup>-H26<sup>iii</sup>-··O22 (2.666Å, 3.482Å and 146.84°), ii) C27<sup>iii</sup>-H27<sup>iii</sup>-··O1 (2.604Å, 3.405Å and 157.52°), iii) C6-H6···O2<sup>iii</sup> (2.663Å, 3.498Å and 138.12°), iv) C7-H7···O21<sup>iii</sup> (2.679Å, 3.659Å and 132.05°), v) C24-H24<sup>iii</sup>··· $\pi$  (2.966Å, 3.554Å and 122.59°) and vi) C4-H4<sup>iv</sup>··· $\pi$  (2.997Å, 3.676Å and 131.22°) which grow the framework along *c* and *a* axis, building a layered supramolecular structure in the plane (0 2 1). Finally, the presence of the weak interaction vii) C13<sup>ii</sup>-H13<sup>ii</sup>···O23 (2.682Å, 3.421 and 134.08°) grows the crystal along *b* axis, giving rise to its 3D supramolecular framework, that can be described as an 8-connected uninodal net (considering each single molecule as a node) with **hex** (hexagonal primitive 8/3/h4, sqc4) topology (Figure 6).

The **2**β supramolecular framework is formed besides with the synthon growing along *a* by the following intermolecular weak interactions (the values presented are *d*, *D* and  $\theta$  respectively): i) C33<sup>i</sup>-H33B<sup>i</sup>···O22 (2.634Å, 3.312 Å and 128.00°), ii) C31<sup>i</sup>-H31<sup>i</sup>···O22 (2.507Å, 3.405 Å and 162.26°), iii) C13-H13C···O1 (2.895Å, 3.408Å and 114.58°), iv) C33-H33A···O3 (2.811Å, 3.450Å, 124.72°), v) C13-H13B···C1 (2.791Å, 3.357 Å and 118.41°), vi) C3-H3···C8 (2.883Å, D:3.791 Å and 165.71°), vii) C29-H29··· $\pi_{ring}$  (3.224Å, 3.614Å, 107.51°), viii)C8-H8··· $\pi_{ring}$  (3.338Å, 3.385Å and 84.91°) and ix)  $\pi_{C28=C29}$ ··· $\pi_{ring}$  (3.506Å, off-center parallel stacking (offset 10.83°)),which grow the framework along *b* and *c* axis giving rise to a 3D supramolecular framework, that can be



**Figure 6.** Above: an augmented view of the common synthon founded for both polymorphs, followed by the ORTEP <sup>37</sup> representation of the asymmetric unit for each polymorph (Left:  $2\alpha$  and right:  $2\beta$ ). Centre: supramolecular arrangement for each case, showing an augmentation of the weak interactions involved in the process. Below: Supramolecular topology representation of the 8-connected net for each case.

described as an 8-connected uninodal net (considering each single molecule as a node) with **bcu** topology (Figure 6). As we can determine through the topological analysis, all three derivates of **2** can be described as 8-connected nets, using the single molecule as node. After a careful analysis of the supramolecular arrangements for all three crystalline materials of **2**, the increment in the number of interactions involved (hydrogen bonds,  $\pi \cdots \pi$  and CH  $\cdots \pi$  interactions) follows the particular order: **2**·**DMF** <  $2\alpha$  <  $2\beta$ , which can be related to the red-shifting observed in the light emitting properties that together with the planarity behaviour ( $2\alpha$  < 2·**DMF** and  $2\beta$ ) could help us to rationalize the colour variations of these PV derivates.

#### **3.3.** Computational Analysis

By using the experimental crystal structure coordinates of polymorphs  $2\alpha$  and  $2\beta$  and of the DMF solvate denoted **2-DMF**, the packing energies for the different crystal were calculated by subtracting *n* times the energy of a single PV molecule to the energy of the packed PV with *n* molecular units (Figure 7).

The relative packing energies for the packed PV, up to 10 monomers, extracted from the  $2\alpha$  polymorph structure are shown in Figure 8. In this figure we can see how the energy difference resulting from adding a new molecular unity on the crystal remains essentially constant. It is worth noting that for the trimer and pentamers (meaning three and five PV molecular units) of polymorph  $2\alpha$  we calculated two different packing energies (Figure 7).

As shown above, the crystal structure of polymorph  $2\alpha$  is mainly stabilized by CH··· $\pi$  interactions and different PV packing units are linked among them by H-bond interactions. The



Figure 7. Geometrical arrangement for the decamers and packing energies (kcal/mol) exhibiting in  $2\alpha$  (above), solvate 2·DMF (center) and  $2\beta$  (below).

CH… $\pi$  interactions are 3,030 Å between CH<sub>3</sub> group and benzene rings, while ranged among 2,967 and 3,129 Å between the H of the benzene ring and the centroid of the adjacent benzene ring of the closest neighbor PV. Hydrogen bond interactions are among 3,077 and 3,991 Å; both distances are in the range of the experimental reported data.<sup>38-39</sup> Thus, the effect of adding a new PV molecular unit in the crystal generates low cooperativity.

The packing energy of the orange crystal resulting from polymorph  $2\beta$  was calculated in an analogous way (Figure 7). However, in this case the higher symmetry of the crystal structure allows forming a unique PV packed structure. The packing energy, as in the previous case, remains constant and low cooperativity was energetically observed. This crystal structure presents a more regular arrangement, mainly stabilized by  $\pi \cdots \pi$  stacking interactions between the C-C bond and the benzene rings with stacking distances of 3,613 Å, and 3,553 Å from the centroid of the terminal benzene ring and the carboxyl group. These  $\pi \cdots \pi$  stacking interactions generate a more compact structure, and the number of interactions by monomer explains the lower polymerization energy compared with the yellow crystal structure ( $2\alpha$  polymorph).

Table 3	Theoretical I	IV-Vis hic	phest excitation	hand for the ol	ligamers f	formed in	both no	alvmorn	he
I ADIC J.	Theoremean	J V - V 15 III §	gnest excitation		ingointers i	United in	uoun pu	JIYMOIP	115.

2α polymorph		2β polymorph		
Number	Highest Excitation	Number	Highest Excitation	
of Monomers	Band (nm)	of Monomers	Band (nm)	
1	469.8	1	457.8	
2	467.5	2	430.6	
3	423.3	4	441.0	
5r	486.2	6	475.3	
5t	475.4	8	488.0	
8	493.1	10	506.3	
10	492.6			

The influence of the addition of a new molecular PV packing unit on the spectroscopic properties of the two polymorphs has also been calculated, finding two effects as shown in Table 3 and Figure 8. The first effect is the red shifted displacement of the main absorption band when a new molecular unit is added. This is consistent with the experimental evidences of the shift in the maximum of absorption between the solution and crystals spectra (see Figures 1 and 3), assuming that the electronic transitions of PV molecules in solution correspond to independent PV molecular units. On the other hand, as can be appreciate in Table 4 and Figure 8, polymorph  $2\alpha$  has almost

reached its maximum shift with the aggregation of 10 molecular units, while polymorph  $2\beta$  apparently can still be shifted more (Also see, S.I. Section 4).



Figure 8. Vertical excitation spectra from the TDDFT calculations for each molecular PV unit in  $2\alpha$ , solvate 2-DMF and  $2\beta$  where **n** indicates the number of monomers.

The second observed effect corresponds to the number of bands observed in the absorption spectra; for the molecular PV unit it is possible to observe three bands in both cases, while for the packed system the number of bands decreases reaching a single band. This means that the stacking and packing interactions decrease the excitation energy between the ground state surface and the excited potential surfaces (the origin of the luminescent properties).

The inclusion of solvent molecules in the calculations does not modify the observed trends (Figure 7 and 8, crystal **2-DMF**). As in the previous cases, a clear displacement in the wavenumber in the

emission spectra is observed upon the inclusion of monomeric unities. This result indicates that the red shifting observed in the spectrum of this crystallographic form compared to that of polymorph  $2\alpha$ , is due not only to the planarity of the molecule but also depends on the intermolecular interactions. Additional computational data is presented in the S.I, section 4.

#### 4. CONCLUSIONS

The synthesis of the phenylenevinylene derivative **1** was carried out with high stereoselectivity using a two-fold Heck reaction in the key step (*trans – trans* configuration) and its basic hydrolysis yielded PV **2**, which is highly fluorescent in solid state and in solution. Careful crystallization of the phenylenevinylene derivate **2** resulted in three crystalline species (two polymorphs  $2\alpha$ -yellow and  $2\beta$ -orange) and a DMF solvate **2**-DMF with different colors and fluorescence properties in solid state when irradiated at 400 nm.

The differences observed in the color emission have been rationalized on the basis of a careful analysis of the supramolecular interactions as well as of the topology of the crystalline frameworks. Although, the topological analysis is not frequently used in organic materials, by using it in these compounds we show here its utility to explain supramolecular related properties.

In particular the high planarity of the polymorph  $2\beta$  found by crystal structure determination, implies that the  $\pi$  – electronic conjugation and the  $\pi$  –  $\pi$  stacking interactions are much more favorable, resulting in a decreasing in the energy needed for the electrons to delocalize along the structure and causing a red shift in the colour of the polymorph. Both experiments and computational calculations show that the different spectroscopic properties of these polymorphs

 have an important intermolecular contribution as they are strongly influenced by the differences in their packing interactions.

## ASSOCIATED CONTENT

## **Supporting Information**

The Supporting Information is available free of charge on the ACS Publications website at DOI:

10.1021/

- Synthesis and experimental characterization of A, B, 1 and 2.
- Single-crystal XRD crystal data and structure refinement for 1.

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## Notes

 The authors declare no competing financial interest

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## "For Table of Contents Use Only"

## On the Nature of Color Diversity in Phenylenevinylene-based Polymorphs

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**Synopsis**: Experimental and theoretical study of the light emitting properties of a phenylenevinylene derivate in solid state.