



Columnar mesomorphism in molecular alloys based on Halogen-Bridged Pt^{II}/Pt^{IV} mixed valence complexes. The key role of the Pt^{II}/Pt^{IV} ratio

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ABSTRACT

In this paper, we studied the thermotropic behavior and phase diagrams of blends of two platinum-based metallomesogens with different oxidation states and ligands, which are prone to self-association through the formation of a mixed-valence system via Pt^{II}...Cl-Pt^{IV} interactions. The constituent molecules are *cis*-[PtCl₂(CNL)₂] (CNL = 2-(6-(4-isocyanophenoxy)hexyloxy)-3,6,7,10,11-pentakisidodecyloxytriphenylene) and [PtCl₄(Bipy)] (Bipy = didodecyl 2,2'-bipyridyl-4,4'-dicarboxylate), which display an organic/inorganic segregated multi-columnar mesophase and a lamellar mesomorphism, respectively. Firstly, the phase diagram was constructed using polarized optical microscopy, differential scanning calorimetry and X-ray scattering data. The results indicated that compositions exceeding 50 % of [PtCl₂(CNL)₂] led to columnar mesophases very similar to the one of pure [PtCl₂(CNL)₂], where triphenylene cores and platinum moieties are segregated into different columnar units. Then, employing tight-binding quantum chemical methods, we studied the supramolecular organization in the columnar mesophases, as well as the electronic structure properties of mixtures with compositions larger than 50 % of [PtCl₂(CNL)₂]. The results revealed that the formation of the metal-organic columns relies on a fine balance between Pt^{II}...Pt^{II} and Pt^{II}...Cl-Pt^{IV} intermolecular interactions, which strongly depend on the composition of the system. A deep analysis of the density of states showed that lower concentrations of [PtCl₄(Bipy)] result in a hole-doped system, while at higher [PtCl₄(Bipy)] concentrations the intervalence charge transfer between the metal center in different oxidation states significantly changes the electronic structure.

1. Introduction

Metallomesogens constitute a class of functional materials that can be tailored for specific applications in optoelectronics, display technologies, chemo-sensing, bio-related fields or even in catalysis [1–7]. The great versatility of these systems is due to the combination of features arising from the metal-based coordination complex (such as specific metal-based interactions, luminescence, magnetism, catalytic activity, or redox behavior) along with the supramolecular organization and fluidity of the mesophase [1,8,9]. In this sense, a large variety of metals and ligands have been used to prepare metal-containing liquid crystals [10]. Among them, discotic metallomesogens that self-assemble into columnar mesophases are particularly intriguing. The unique properties of these materials, derived from their columnar structure, make them promising materials for applications such as conductive devices, field-effect transistors, or photovoltaic solar cells. These properties are largely determined by the inter-disc separation within the columnar stacking and, consequently, by the intermolecular interactions that hold

the molecules together in the supramolecular structure. Currently, considerable efforts are being made toward the rational design of metallomesogens with enhanced properties for use in optoelectronic devices. Among these, complexes exhibiting square-planar coordination, such as Pt^{II} or Pd^{II}, have attracted great attention as promising functional materials for multiple applications [11–18].

A widely studied family of columnar liquid crystals is based on hexasubstituted triphenylenes, which are classical examples of semi-conducting mesophases. Their properties can be easily modulated through chemical functionalization of the triphenylene system with a wide variety of functional groups, including metal complexes [19–34]. In this sense, functionalizing the triphenylene system at the end of one alkoxy substituent has proven to be an interesting strategy for the formation of hybrid organic/inorganic mesophases with segregated columns of different nature [35–43].

A useful and well-known alternative to chemical functionalization for fine-tuning the properties of liquid crystal materials is doping or mixing two or more species [44–50]. This strategy has already been used

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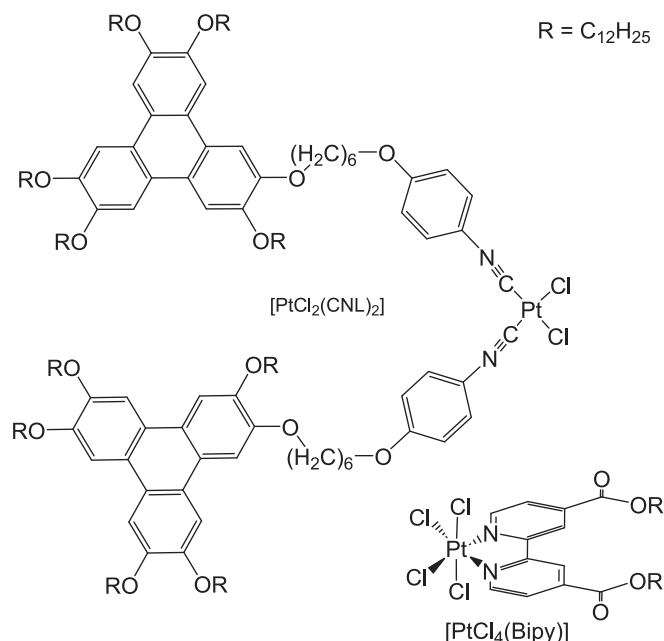
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Scheme 1. Chemical structure of $[\text{PtCl}_2(\text{CNL})_2]$ and $[\text{PtCl}_4(\text{Bipy})]$ molecules forming the liquid crystalline molecular alloys here studied.

Table 1

Optical, Thermal and Thermodynamic Data for mixtures $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ in the whole range of compositions.

<i>m</i> (%mol $[\text{PtCl}_2(\text{CNL})_2]$)	Transition ^a	Temperature ^b (°C)	ΔH ^b (kJ/mol)
0	Cr → Lam	55 ^c	31.0 ^c
	Lam → I	140 ^c	14.7 ^c
10	G _{Lam} → Lam	24	—
	Lam → I	117	1.3
15	G → I	26	—
20	G → I	26	—
30	G → I	23	—
40	G → I	25	—
45	G → I	27	—
50	Cr → Col _{rec}	−23	7.4
	Col _{rec} → I	73	3.6
60	Cr → Col _{rec}	−25	10.7
	Col _{rec} → I	70	5.6
70	Cr → Col _{rec}	−17	16.8
	Col _{rec} → I	81	6.7
80	Cr → Col _{rec}	−14	23.3
	Col _{rec} → I	81	11.7
90	Cr → Col _{rec}	−13	26.5
	Col _{rec} → I	84	10.3
100	Cr → Col _{rec}	−13	26.3
	Col _{rec} → I	83	13.2

^a Cr: crystal phases; G: glassy phases; G_{Lam}: glassy phases with columnar mesophase; Col_{rec}: columnar rectangular mesophase; Lam: lamellar mesophase; I: isotropic liquid. DSC measurements were performed at a scanning rate of 10 °C/min.

^b Data collected from the second heating DSC cycle. The transition temperatures are given as peak onsets.

^c Data collected from the first heating DSC.

to control temperature range, electrical permittivity and viscosity in nematic mesophases, as well as charge mobility in semiconducting columnar mesophases [31–34,51]. In addition, chemical blending is also being explored as an economical and environmentally friendly alternative to chemical synthesis for producing a great variety of new advanced materials such as metal–organic frameworks [52], polymers [53,54], or biocomposites [55]. Surprisingly, reports on liquid crystalline blends involving metallomesogens are limited to a few examples, which can be broadly categorized into two different types. The first type

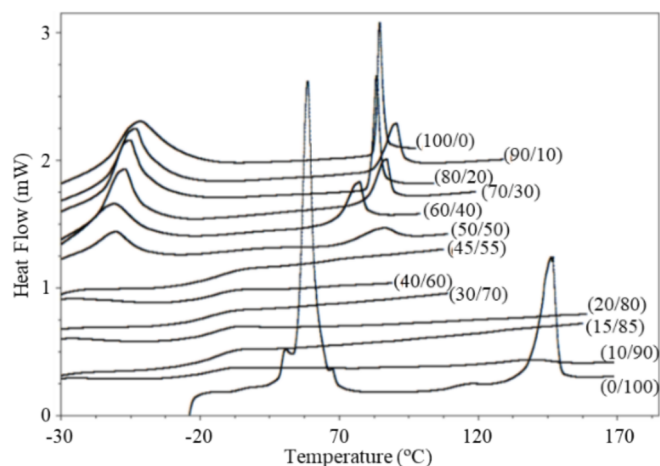


Fig. 1. Heating DSC scans of the $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures. The compositions are given in brackets. All the mesomorphic mixtures display enantiotropic mesomorphism. The DSC scans (first heating, first cooling and second heating) for all studied mixtures are given in the supporting information part (Figs. S1–S13).

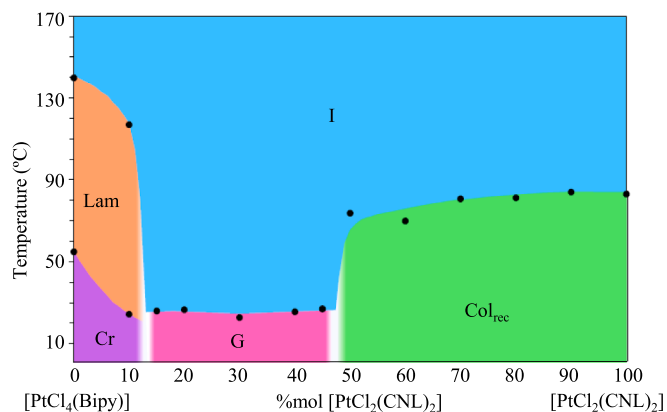


Fig. 2. $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ phase diagram. The boundary of the white region could not be clearly determined.

comprises mixtures of two complexes with the same metal center but different ligands [56–58]. The second class is less common and involves blends based on different metal-containing molecules, so called liquid crystalline molecular alloys [59–61]. In this context, we have recently reported an uncommon modulation of organic/inorganic segregation in columnar mesophases of metal–organic triphenylene liquid crystals, by mixing two structurally dissimilar metallomesogens of Pt^{II} [62].

Moving to more complex systems, here we have turned our attention to mesomorphic blends of two platinum complexes in different oxidation states, prone to generating mixed valence systems (see Scheme 1) [61,63–65]: $\text{cis-}[\text{Pt}^{\text{II}}\text{Cl}_2(\text{CNL})_2]$ (CNL = 2-(6-(4-isocyanophenoxy)hexyloxy)-3,6,7,10,11-pentakis(dodecyloxy)triphenylene), that displays an organic/inorganic segregated columnar mesophase [27], and $[\text{Pt}^{\text{IV}}\text{Cl}_4(\text{Bipy})]$ (Bipy = didodecyl 2,2'-bipyridil-4,4'-dicarboxylate), which exhibits lamellar mesomorphism [61]. Both components were chosen based on their miscibility, absence of ligand scrambling reactions, and aiming to study the effect of metal-based interactions in the mesophase [61,63–65]. For compositions equal to or greater than 50 % of $[\text{PtCl}_2(\text{CNL})_2]$, we found liquid crystalline molecular alloys displaying multicolumnar mesophases supported by synergistic π - π and halogen-bridged $\text{Pt}^{\text{II}}\cdots\text{Cl}\cdots\text{Pt}^{\text{IV}}$ interactions. The effect of the mixture composition on the supramolecular arrangement of the molecules in the columnar mesophase at the molecular level and electronic structure properties of the mesophase have been studied by quantum chemical

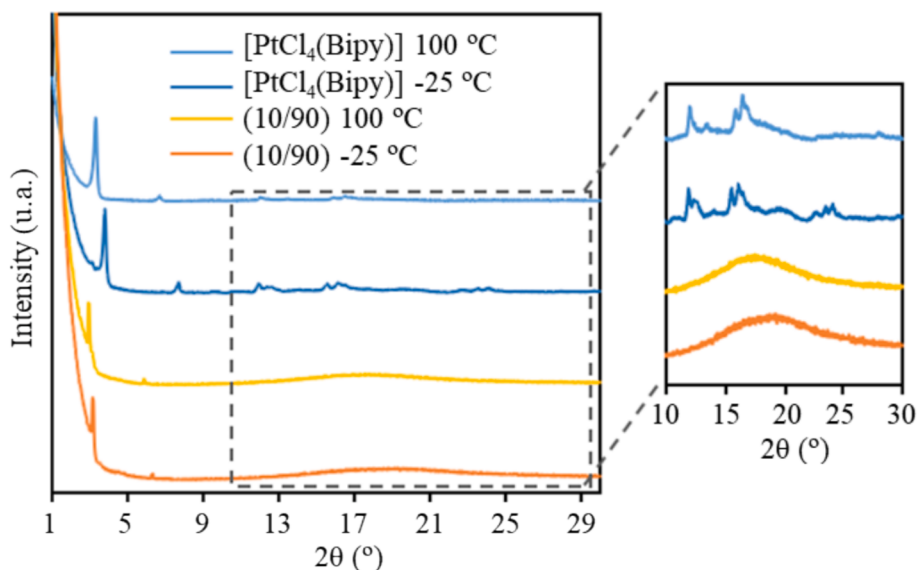


Fig. 3. Diffraction patterns in the mesophase state of pure complex $[\text{PtCl}_4(\text{Bipy})]$, along with the 10 % $[\text{PtCl}_2(\text{CNL})_2]$ /90 % $[\text{PtCl}_4(\text{Bipy})]$ mixture in the Lam mesophase (100 °C).

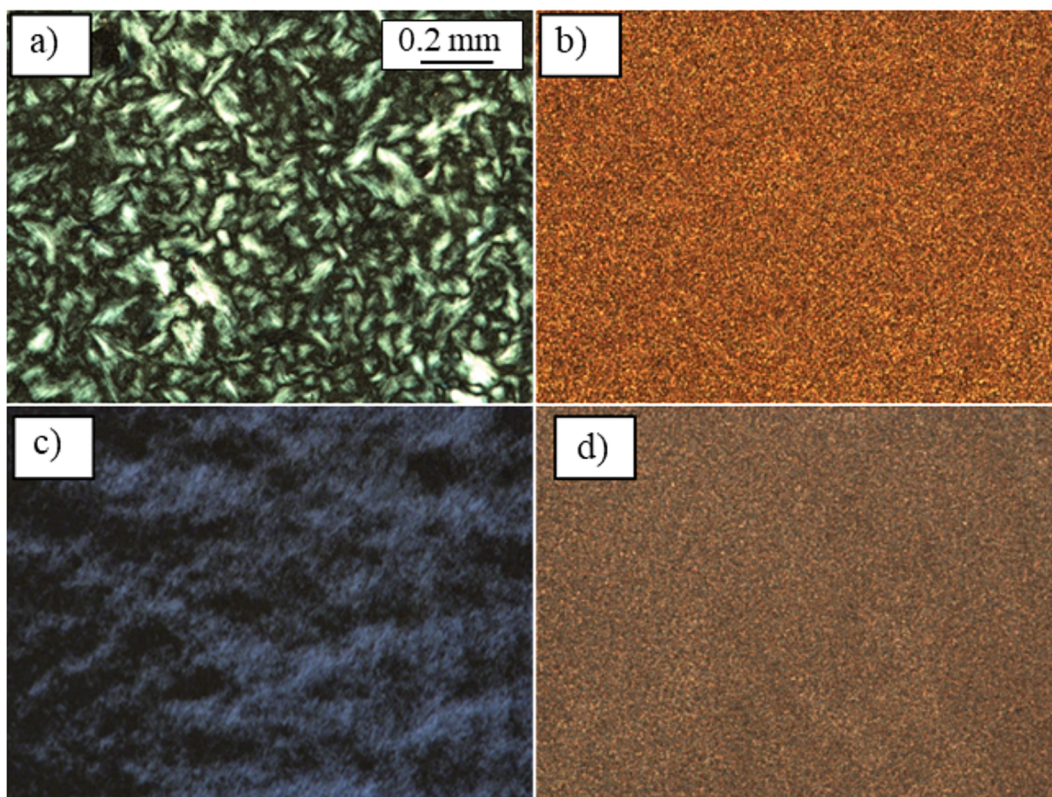


Fig. 4. Optical polarizing microscopy photographs (x100, crossed polarizers) on cooling from the isotropic phase of a) pure $[\text{PtCl}_4(\text{Bipy})_2]$ at 120 °C; b) pure $[\text{PtCl}_2(\text{CNL})_2]$ at 70 °C; c) 90 % $[\text{PtCl}_4(\text{Bipy})]$ /10 % $[\text{PtCl}_2(\text{CNL})_2]$ at 120 °C; d) 30 % $[\text{PtCl}_4(\text{Bipy})]$ /70 % $[\text{PtCl}_2(\text{CNL})_2]$ at 70 °C.

calculations. The size of the studied model systems (up to 3703 atoms) and their complexity, resulting from their metal–organic nature, surpass common theoretical studies on supramolecular systems, including liquid crystals. Specifically, extended tight-binding methods (xTB) [66,67] have been successfully applied to study $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures with composition larger than 50 % of $[\text{PtCl}_2(\text{CNL})_2]$. xTB methods have been specifically designed to accurately describe molecular structure and non-covalent interactions in large systems with a

reduced computational cost compared to other approaches such as Density Functional Theory (DFT) or composite methods.

2. Results and discussion

2.1. Thermal behavior and mesogenic properties

Both $[\text{PtCl}_2(\text{CNL})_2]$ [27] and $[\text{PtCl}_4(\text{Bipy})]$ [61] compounds were

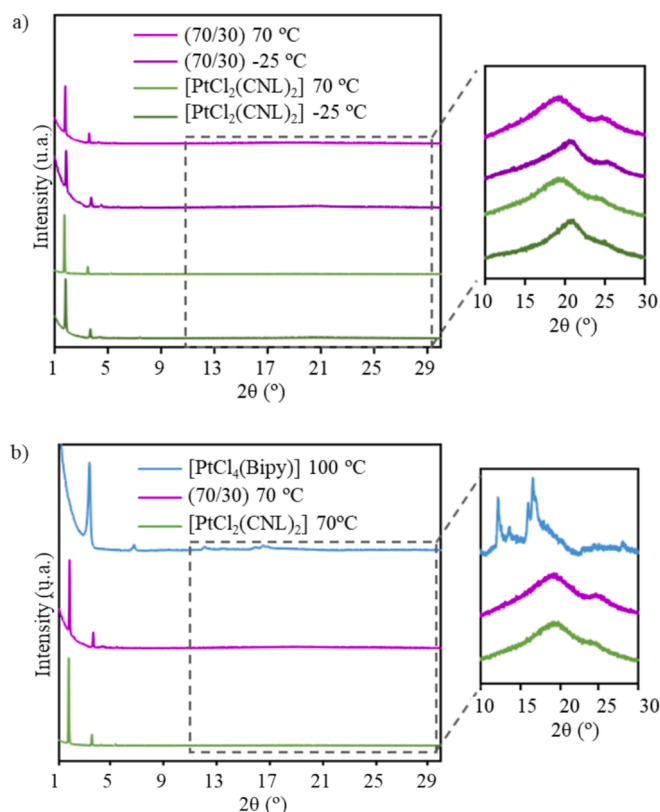


Fig. 5. a) Diffraction patterns in the mesophase state of pure complexes $[\text{PtCl}_2(\text{CNL})_2]$ and $[\text{PtCl}_4(\text{Bipy})]$, along with the 70 % $[\text{PtCl}_2(\text{CNL})_2]$ /30 % $[\text{PtCl}_4(\text{Bipy})]$ mixture in the Col_{rec} mesophase (70 °C) b) Diffraction patterns in the mesophase state of pure complex $[\text{PtCl}_2(\text{CNL})_2]$, along with the 70 % $[\text{PtCl}_2(\text{CNL})_2]$ /30 % $[\text{PtCl}_4(\text{Bipy})]$ mixture in the Lam mesophase (100 °C).

synthesized following procedures described in the literature. The binary mixtures of pure compounds were prepared by dissolving the corresponding weights of the two compounds together in dichloromethane at ambient temperature, followed by solvent removal under vacuum. The choice of this solvent was based on the high solubility of the pure precursors in this medium, its low coordinating ability towards transition metals, and its easy removal in vacuum.

The phase diagram of binary $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ system (where m represents the percentage in %mol of $[\text{PtCl}_2(\text{CNL})_2]$ compound) was established using polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray scattering data. Transition temperatures and thermal data are collected in Table 1 and Fig. 1, while the corresponding phase diagram is shown in Fig. 2.

The enantiotropic mesomorphic behavior of this system is highly dependent on the composition. For concentrations lower than 10 % of $[\text{PtCl}_2(\text{CNL})_2]$, when the samples are heated to the melting temperatures, the system exhibits only a lamellar mesophase (Lam) with similar features to that of the parent precursor $[\text{PtCl}_4(\text{Bipy})]$ (see reference [62] and Figs. 3 and 4). Subsequent heating produces the transition from the mesophase to an isotropic liquid. Both transitions appear in the DSC scans as two endothermic peaks. In contrast to the pure $[\text{PtCl}_4(\text{Bipy})]$ compound, the width of the peaks in the 10 % $[\text{PtCl}_2(\text{CNL})_2]$ /90 % $[\text{PtCl}_4(\text{Bipy})]$ mixture indicates the presence of a quite disordered solid rather than a crystalline phase (Fig. 1 and Fig. S2 in the Supplementary material). For compositions between 15 and 45 %, the solid phases melt directly to an isotropic liquid and these mixtures are not liquid crystals. In this range of compositions, the DSC scans display the characteristic patterns of disordered solid, showing the corresponding glass transition temperatures. When the concentration exceeds 50 %, a rectangular columnar mesophase, analogous to that of the $[\text{PtCl}_2(\text{CNL})_2]$ complex, is

observed (Fig. 4). In this case, both the crystal/mesophase and mesophase/isotropic transitions are observed by DSC as two exothermic peaks similar to those of the pure Pt^{II} complex, whose structure contains simultaneously, π -stacking of the triphenylene discs in columns, and aggregation of the metallic moieties into segregated columnar zones [27]. This suggests that in the mesophase, the Pt^{II} and Pt^{IV} moieties should be arranged within the same columnar region, likely associated through $\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl}\cdots\text{Pt}^{\text{II}}\cdots$ interactions, as has been reported for related systems [61,63–65,68]. These results show at least two notable aspects that deserve further study: i) the columnar mesophase only emerges for compositions greater than 50 % in Pt^{II} ; and ii) the presence of the octahedral complex of Pt^{IV} in the mixture does not produce any significant effect on the columnar mesomorphic behavior of the Pt^{II} square planar complex.

2.2. Supramolecular structure of $[\text{PtCl}_2(\text{CNL})_2]$ and $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures in the columnar phases

To further analyze the supramolecular arrangement of the molecules in the Col_{rec} phase for $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures, we carried out theoretical calculations by using Grimme's extended semiempirical tight-binding method (GFN2-xTB) [66,67,69]. This tight-binding method includes electrostatic and exchange correlation Hamiltonian terms and the D4 dispersion model [70]. The GFN2-xTB was designed to accurately describe molecular structure and non-covalent interactions for large systems like those reported herein with a reduced computational cost [67]. In addition, this method has proven effective to study non-covalent interactions with various contexts, such as biochemical systems [67,71], transition metal complexes [72] and supramolecular materials [73,74], including liquid crystals [62,75,76].

Theoretical calculations were first conducted for the pure compound $[\text{PtCl}_2(\text{CNL})_2]$ and subsequently for $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures with composition greater than 50 % of $[\text{PtCl}_2(\text{CNL})_2]$. Please refer to the “Computational Details” section in the Supplementary information for a more detailed description.

2.2.1. Pure $[\text{PtCl}_2(\text{CNL})_2]$ ($m = 100$)

As previously mentioned, $[\text{PtCl}_2(\text{CNL})_2]$ exhibits a columnar mesophase, which structure is formed by the segregation of organometallic columns (coming from the packing of the metallic fragments at the nodes of a rectangular lattice), which are intercalated by a network of organic columns (resulting from the π -stacking of triphenylene moieties) [27]. Both organometallic and organic columns are surrounded by the aliphatic continuum, making each column electronically independent of the others. Thus, the resulting properties should arise from the interactions between fragments (organometallic or triphenylene) within the same column. The study of such columnar mesophase through quantum chemical methods would require expensive and complex theoretical calculations including several thousand atoms. However, as a first approach, this arrangement can be studied through a minimum energy model of the supramolecular stack of $[\text{PtCl}_2(\text{CNL})_2]$ molecules, where alkoxy side chains have been replaced by methoxy groups for computational economy.

The study of the stacking of two $[\text{PtCl}_2(\text{CNL})_2]$ molecules (please refer to the “Building the supramolecular cluster model of $[\text{PtCl}_2(\text{CNL})_2]$ ” section in the Supplementary information for a more detailed description) shows that the most stable arrangements would be found for cores rotated each other around 135° along the stacking axis (z -axis). The rotation of each monomeric unit around the stacking axis leads to each triphenylene core overlaps through π - π interactions with another triphenylene disc of the next stacking molecule. This supramolecular model produces a columnar organometallic region with the triphenylene fragments distributed in its periphery, where the triphenylene discs should not give rise to a continuous stacking of triphenylene units, but rather organic columnar regions with empty areas between triphenylene groups. The two-dimensional expansion of this supramolecular

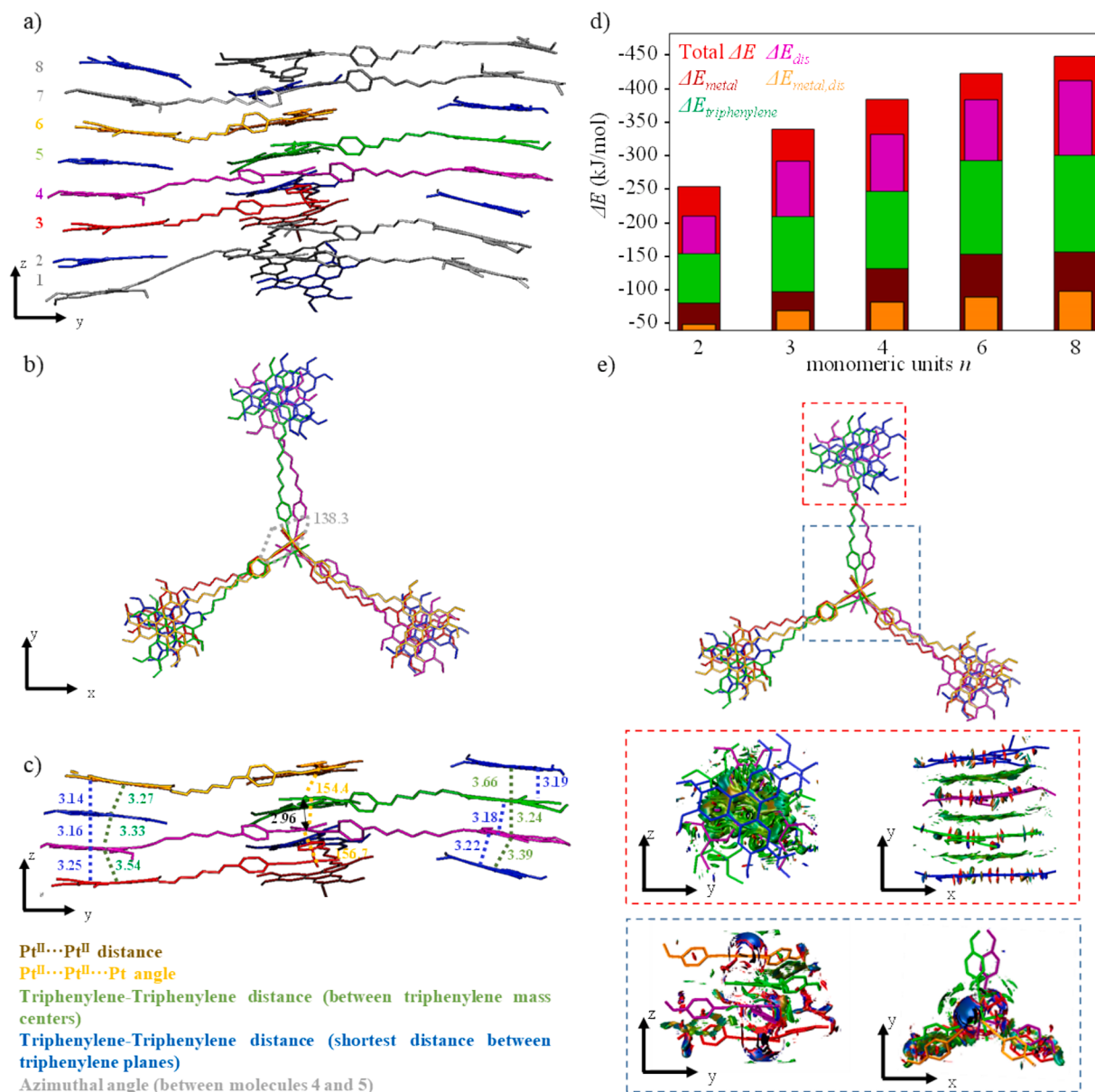


Fig. 6. A) side view of the minimum-energy optimized structure calculated at the GFN2-xTB level for the octamer cluster of $[\text{PtCl}_2(\text{CNL})_2]$; Molecules stacked along z -axis are labelled 1–8. Molecules 3–6 are shown in red, purple, green and orange, respectively; *extra* triphenylene molecules are in blue. Hydrogen atoms are omitted. b) upper and c) side views of four central molecules taken from the central region, along with the main intermolecular structural parameters. Units: intermolecular distances are in Å, angular and azimuthal angles are in degrees. d) Calculated binding Energies (ΔE) for $[\text{PtCl}_2(\text{CNL})_2]$ compound. e) RDG isosurfaces (isovalue = 0.5 a.u.) of $[\text{PtCl}_2(\text{CNL})_2]$ (for the sake of clarity, only molecules 3–7 are represented with special interest on organic and organometallic regions). The color of the RDG isosurfaces is related to the nature of the intermolecular interactions, indicating repulsive or steric (red), van der Waals (green) or strong attractive (blue) interactions.

arrangement, through the complementary interpenetration of the organic regions (triphenylene) from neighboring organometallic columns, leads to the columnar rectangular lattice, in agreement with the reported results [27]. In this simple molecular model, each Pt fragment is surrounded by three triphenylene discs, two of them originate from the same molecule, while the third *extra* disc comes from a neighboring molecule, which metallic fragment would be in a different metallic column.

Fig. 6a–c) displays the optimized structure of an octamer cluster (containing 1752 atoms) describing the columnar phase of $[\text{PtCl}_2(\text{CNL})_2]$. Since the optimized octamer structure exhibits terminal effects, we have focused on the main structural parameters obtained from the central region. The stacking of $[\text{PtCl}_2(\text{CNL})_2]$ molecules shows that the most stable arrangement was found for cores rotated each other

along the stacking axis (z -axis) 138.3° and with an intermolecular $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ distance of 2.96 Å. The mean values for the $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ distances, azimuthal angle along the stacking axis (z -axis) and twisting angle between phenyl ring and Pt^{II} atom are 2.96 Å, 138.3° and 155.6° , respectively. The rotation of each $[\text{PtCl}_2(\text{CNL})_2]$ molecule around the stacking axis results in the sandwiching of each triphenylene core between one triphenylene core coming from the adjacent molecule and an *extra* triphenylene (whose metallic motif would be in a different metallic column). The arrangement between the triphenylene leads to typical π - π stacking distances 3.39 Å / 3.19 Å (measured as the distance between mass centers / as the shortest distance between adjacent triphenylene). It is noteworthy that theoretical π - π stacking distances are consistent with experimental data obtained from SAXS measurements [27].

The interaction energy (ΔE) per $[\text{PtCl}_2(\text{CNL})_2]$ molecule was

Table 2Description of the supramolecular models here used to study $x\text{PtCl}_2(\text{CNL})_2/y[\text{PtCl}_4(\text{Bipy})]$ mixtures with $m > 50$.

Label	m	x^a	y^a	$x + y_a$	Number of atoms ^b	Distribution ^c
i	100	8		8	1752	
ii	94 ^d	16	1	17	3703	:
iii	93 ^d	14	1	15	3265	:
iv	92 ^d	12	1	13	2827	:
v	91	10	1	11	2389	:
vi	89	8	1	9	1951	:
vii	86	6	1	7	1513	:
viii	80	4	1	5	1075	:
ix	75	6	2	8	1712	:
x	73	8	3	11	2349	:
xi.i	67 ^d	8	4	12	2548	:
xi.ii	67	6	3	9	1911	:
xi.iii	67	4	2	6	1274	:
xii	57	4	3	7	1527	:
xiii	55 ^d	6	5	11	2309	:
xiv	53 ^d	8	7	15	3145	:

^a x and y stand for the number of $[\text{PtCl}_2(\text{CNL})_2]$ and $[\text{PtCl}_4(\text{Bipy})]$ molecules in the supramolecular cluster model.^b Total number of atoms in the cluster. Alkoxy side chains were replaced by methoxy groups for computational economy.^c Solid and broken vertical lines stand for $[\text{PtCl}_2(\text{CNL})_2]$ and $[\text{PtCl}_4(\text{Bipy})]$ molecule distributions, respectively, along the columnar structure.^d Due to the large number of atoms, these systems were optimized using a GFN-FF partially polarizable generic force-field, which is adequate for the accurate description of structures and dynamics of large systems (see supporting information for more details) [81].

calculated according to:

$$\Delta E = [E_n - n(E_{[\text{PtCl}_2(\text{CNL})_2]} - E_{\text{extra-triphenylene}})]/n \quad (1)$$

where E_n , $E_{[\text{PtCl}_2(\text{CNL})_2]}$ and $E_{\text{extra-triphenylene}}$ represent the total energy of the cluster, $[\text{PtCl}_2(\text{CNL})_2]$ monomer and *extra* triphenylene molecules, respectively; n corresponds to the number of $[\text{PtCl}_2(\text{CNL})_2]$ monomers in the cluster. Eq. (1) quantifies the change in energy upon the formation of the columnar structure from its constituent molecules. In general, highly negative ΔE values would indicate highly favored process [85]. As shown in Fig. 6d, $|\Delta E|$ exhibits hyperbolic behavior with an asymptotic limit of ~ 460.0 kJ/mol. As our system is comprised of on-chemically interacting columns, ΔE can be expressed as the sum of the binding energy resulting from the interaction between metallic fragments in the inorganic column (ΔE_{metal}) and the staking between the triphenylene units within the organic columns ($\Delta E_{\text{triphenylene}}$): $\Delta E = \Delta E_{\text{metal}} + \Delta E_{\text{triphenylene}}$. See [supplementary materials](#) for a more detailed description about energy decomposition. $|\Delta E_{\text{triphenylene}}|$ reaches an asymptotic value 145.0 kJ/mol, i.e., a contribution of 32 % to the total ΔE . Regarding $|\Delta E_{\text{metal}}|$, it asymptotically approaches a value of ~ 155.0 kJ/mol (34 % contribution to ΔE). It is noteworthy that the dispersion energy contribution to the ΔE_{metal} ($\Delta E_{\text{metal,dis}}$) constitutes ~ 63 % of ΔE_{metal} . The $\Delta E_{\text{metal,dis}}$ originates from the van der Waals interactions between adjacent organometallic regions to the Pt atoms. Therefore, our theoretical calculations suggest that the formation of stable columnar structure is due to dispersion interactions with the organic columns and the interplay between $\text{Pt}^{\text{II}} \cdots \text{Pt}^{\text{II}}$ and van der Waals interaction in the organometallic columns. These results are consistent with previous studies indicating that $\text{Pt}^{\text{II}} \cdots \text{Pt}^{\text{II}}$ and $\pi \cdots \pi$ interactions are the main driving force for the formation of columnar mesophase in Pt metal-omesogens [78–80].

Finally, an analysis of the intermolecular interactions has been carried out considering Reduced Density Gradient (RDG) isosurfaces [77] to illustrate the strength and nature of the intermolecular interactions (Fig. 6e). As previously discussed, the columnar phase of $[\text{PtCl}_2(\text{CNL})_2]$ is mainly supported by a combination of: i) dispersion (or van der Waals) interactions between triphenylene cores that define the organic columns (greenish-surfaces between triphenylene discs); ii) metal–metal and dispersion interactions (blue and green RDG isosurfaces between

adjacent organometallic fragments).

2.2.2. $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures

For $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures with compositions greater than 50 % in the Pt^{II} component, as previously discussed, only a hexagonal columnar structure (Col_{rec}) practically identical to that of pure compound $[\text{PtCl}_2(\text{CNL})_2]$ is observed (Figs. 1, 2, 4 and 5). This finding suggests that the organometallic columns are formed through self-assembly of the metal–organic fragments of Pt^{II} and Pt^{IV} , while organic columns arise from the stacking of triphenylene units.

Starting from the cluster model system for $[\text{PtCl}_2(\text{CNL})_2]$, several supramolecular clusters have been built to study the columnar structure of $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures with $m > 50$, in which $[\text{PtCl}_4(\text{Bipy})]$ molecules have been uniformly distributed along the structure (see Table 2). Hence, each $[\text{PtCl}_4(\text{Bipy})]$ molecule is consistently located between two Pt^{II} fragments, allowing the formation of $\text{Pt}^{\text{II}} \cdots \text{Cl} - \text{Pt}^{\text{IV}} - \text{Cl} \cdots \text{Pt}^{\text{II}}$ interactions [61,63–65,68]. In addition, each platinum unit, whether Pt^{II} or Pt^{IV} , is surrounded by three triphenylene discs in a very similar molecular arrangement to that described in the supramolecular cluster model of $[\text{PtCl}_2(\text{CNL})_2]$. As shown below, our supramolecular model structures for $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures effectively describe the coexistence of segregated columns with different nature. Please refer to the “Building the supramolecular cluster models of $x[\text{PtCl}_2(\text{CNL})_2]/y[\text{PtCl}_4(\text{Bipy})]$ mixtures” section in the [Supplementary information](#) for a more detailed description.

As seen in Table 2, supramolecular structures have been categorized into three groups depending on the composition m (% in Pt^{II}): a) from 80 % to 94 %, b) from 67 % to 75 %; and c) from 53 % to 57 %. In the first case ($m = 80$ –94, structures labelled as ii–viii), mixtures have been studied through large supramolecular clusters with only one $[\text{PtCl}_4(\text{Bipy})]$ molecule. As representative examples, Fig. 7 displays the optimized structure of the clusters for $8[\text{PtCl}_2(\text{CNL})_2]/1[\text{PtCl}_4(\text{Bipy})]$ ($m = 89$) and $4[\text{PtCl}_2(\text{CNL})_2]/1[\text{PtCl}_4(\text{Bipy})]$ ($m = 80$) mixtures. The columns formed by stacking of the triphenylene fragments are practically identical to those previously described for the $[\text{PtCl}_2(\text{CNL})_2]$ compound, displaying π -stacking distances of 3.40 Å, and $\Delta E_{\text{triphenylene}}$ values of around 145 kJ/mol Pt. As for the metal–organic region, the Pt^{II} and Pt^{IV} moieties self-associate by the formation of a mixed-valence system through $\text{Pt}^{\text{II}} \cdots \text{Cl} - \text{Pt}^{\text{IV}}$ interactions with $\text{Pt}^{\text{IV}} - \text{Cl}$ bonds and

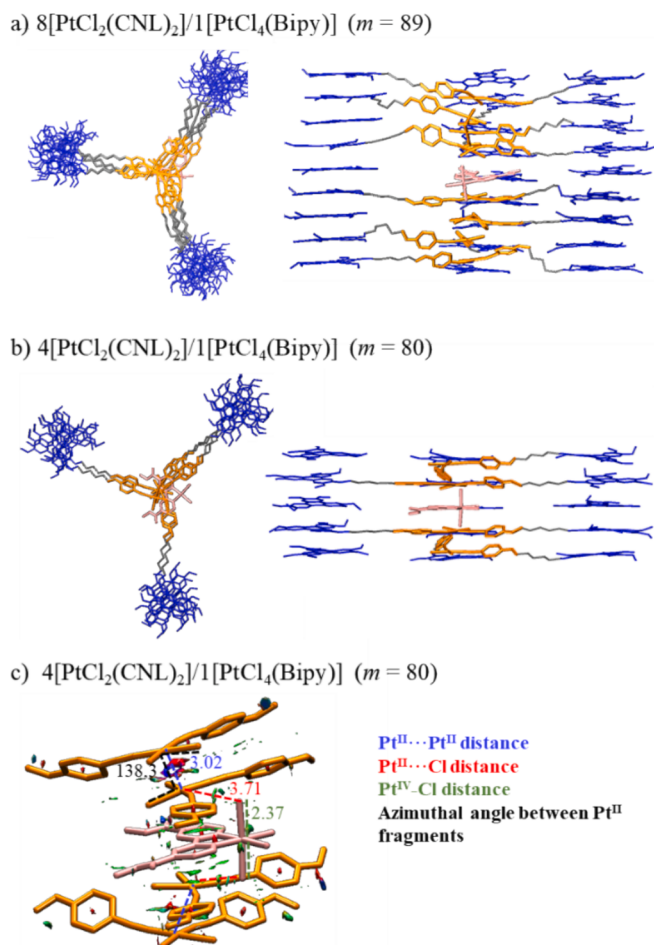


Fig. 7. A) and b) upper and side views of the minimum-energy structure for supramolecular cluster of $8[\text{PtCl}_2(\text{CNL})_2]/1[\text{PtCl}_4(\text{Bipy})]$ ($m = 89$) and $4[\text{PtCl}_2(\text{CNL})_2]/1[\text{PtCl}_4(\text{Bipy})]$ ($m = 80$) mixtures. c) Emphasis on the organometallic region for cluster of $4[\text{PtCl}_2(\text{CNL})_2]/1[\text{PtCl}_4(\text{Bipy})]$ mixture, along with RDG isosurfaces (isovalue = 0.3 a.u.) and main average structural parameters. Pt^{II} and Pt^{IV} fragments are depicted in orange and pink, respectively, while triphenylene fragments and alkyl chains are in blue and grey, respectively. Hydrogen atoms are omitted for clarity. Units: intermolecular distances are in Å and azimuthal angles are in degrees. The color of the RDG isosurfaces is related to the nature of the intermolecular interactions, indicating repulsive or steric (red), van der Waals (green) or strong attractive (blue) interactions.

$\text{Pt}^{\text{II}}\cdots\text{Cl}$ contacts of 2.37 Å and 3.71 Å, respectively (Fig. 7c). Although $\text{Pt}^{\text{II}}\cdots\text{Cl}$ intermolecular distances are larger than the sum of van der Waals radii, the presence of a green RDG isosurfaces between both atoms reveals weak interactions between them. On the other hand, the influence of $[\text{PtCl}_4(\text{Bipy})]$ concentration on the structural properties of neighboring $[\text{PtCl}_2(\text{CNL})_2]$ stacked molecules has been assessed by comparing $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ distances and azimuthal angle with the pure $[\text{PtCl}_2(\text{CNL})_2]$. The mean values are around 3.02 Å and 138.3° , respectively. Thus, low concentrations of $[\text{PtCl}_4(\text{Bipy})]$ do not significantly affect the columnar structure of $[\text{PtCl}_2(\text{CNL})_2]$.

For compositions in the range $m = 67\text{--}75$ (ix–xi), the mixtures have been studied through supramolecular clusters that exhibit an alternation of $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ and $\text{Pt}^{\text{II}}\cdots\text{Cl}\cdots\text{Pt}^{\text{IV}}\cdots\text{Cl}\cdots\text{Pt}^{\text{II}}$ stacks, leading to $\cdots(\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{IV}}\cdots\text{Cl})\cdots$ chains along the metal–organic column (see Table 2). This implies that $y = x/2$ or $x/2-1$ (being x and y the number of $[\text{PtCl}_2(\text{CNL})_2]$ and $[\text{PtCl}_4(\text{Bipy})]$ molecules in the supramolecular cluster model), with the main difference lying in the number of $[\text{PtCl}_2(\text{CNL})_2]$ molecules at the border. Fig. 8 shows the optimized structure of the clusters for $6[\text{PtCl}_2(\text{CNL})_2]/2[\text{PtCl}_4(\text{Bipy})]$ ($m = 75$) and $6[\text{PtCl}_2(\text{CNL})_2]/3[\text{PtCl}_4(\text{Bipy})]$ ($m = 67$) mixtures. Similar structural

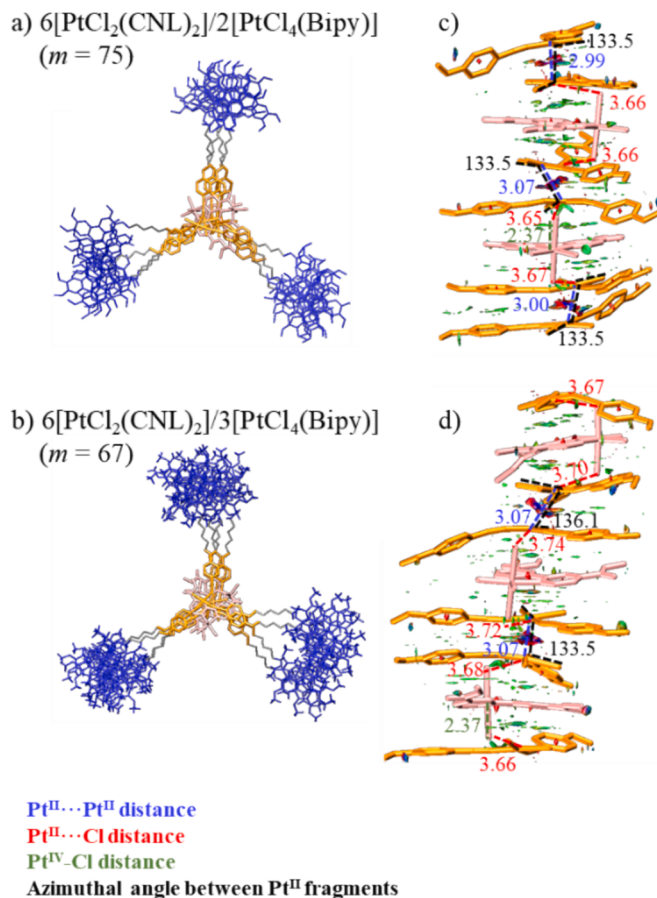


Fig. 8. A), b) upper view of the minimum-energy structure for supramolecular cluster of $6[\text{PtCl}_2(\text{CNL})_2]/2[\text{PtCl}_4(\text{Bipy})]$ ($m = 75$) and $6[\text{PtCl}_2(\text{CNL})_2]/3[\text{PtCl}_4(\text{Bipy})]$ ($m = 67$) mixtures. c), d) Emphasis on the organometallic region, along with RDG isosurfaces (isovalue = 0.3 a.u.) and main average structural parameters. Pt^{II} and Pt^{IV} fragments are depicted in orange and pink, respectively, while triphenylene fragments and alkyl chains are in blue and grey, respectively. Hydrogen atoms are omitted for clarity. Units: intermolecular distances are in Å and azimuthal angles are in degrees. The color of the RDG isosurfaces is related to the nature of the intermolecular interactions, indicating repulsive or steric (red), van der Waals (green) or strong attractive (blue) interactions.

features are noted for $8[\text{PtCl}_2(\text{CNL})_2]/3[\text{PtCl}_4(\text{Bipy})]$ ($m = 73$) and $4[\text{PtCl}_2(\text{CNL})_2]/2[\text{PtCl}_4(\text{Bipy})]$ ($m = 67$) mixtures. As the first case, previously discussed, the $\text{Pt}^{\text{II}}\cdots\text{Cl}$ intermolecular distances (3.68 Å) are larger than the sum of the intermolecular van der Waals radii, but the presence of a green RDG isosurface between both atoms reflects weak $\text{Pt}^{\text{II}}\cdots\text{Cl}$ intermolecular interactions. The $\text{Pt}^{\text{II}}\cdots\text{Cl}$ distances are slightly shorter than those found for mixtures with $80 < m < 90$ (3.71 Å). This slight shortening can be related to the increase of strengthening of $\text{Pt}^{\text{II}}\cdots\text{Cl}$ interactions upon increasing $[\text{PtCl}_4(\text{Bipy})]$ concentrations. The $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ distances and azimuthal angle are 3.07 Å and 134.4° (average values taken from the central region), respectively. Hence, there is a small increase in the $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ distance for $65 < m < 75$.

The last group involves structures with $m = 53\text{--}57$ (xii–xiv), which supramolecular structures are constituted by an alternation of $[\text{PtCl}_2(\text{CNL})_2]$ and $[\text{PtCl}_4(\text{Bipy})]$ molecules. Considering that the percentages slightly higher than 50 % are due to the cluster size considered, the results obtained here also represent the case of a 50 % mixture. Fig. 9 illustrates the optimized structure of the cluster for $4[\text{PtCl}_2(\text{CNL})_2]/3[\text{PtCl}_4(\text{Bipy})]$ ($m = 57$) mixture. Two main differences are observed in comparison with the previous supramolecular structures with $65 > m > 100$. Firstly, due to the alternation between Pt^{II} and Pt^{IV} complexes, the interaction between $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ complexes disappears. Secondly, although

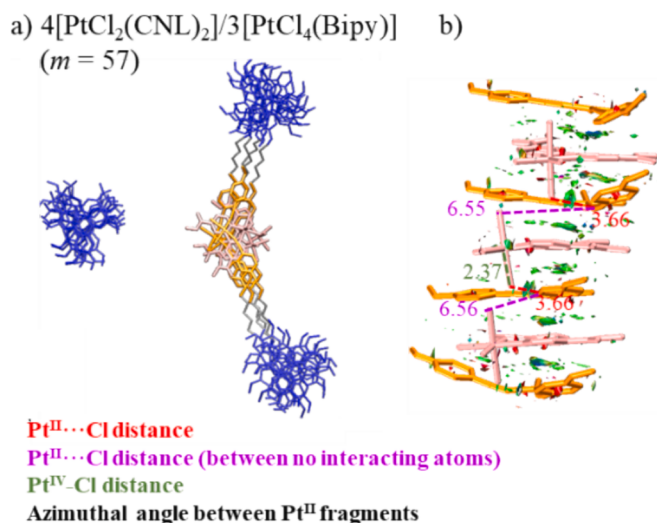


Fig. 9. A) upper view of the minimum-energy structure for supramolecular cluster of $4[\text{PtCl}_2(\text{CNL})_2]/3[\text{PtCl}_4(\text{Bipy})]$ ($m = 57$) mixture. b) Emphasis on the organometallic region, along with RDG isosurfaces (isovalue = 0.3 a.u.) and main average structural parameters. Pt^{II} and Pt^{IV} fragments are depicted in orange and pink, respectively, while triphenylene fragments and alkyl chains are in blue and grey, respectively. Hydrogen atoms are omitted for clarity. Units: intermolecular distances are in Å and azimuthal angles are in degrees. The color of the RDG isosurfaces is related to the nature of the intermolecular interactions, indicating repulsive or steric (red), van der Waals (green) or strong attractive (blue) interactions.

the molecular arrangement is similar to that of the previous cases, each Pt^{II} moiety is not arranged symmetrically with respect to the Pt^{IV} fragment, and two different Pt^{II}...Cl-Pt^{IV} intermolecular distances are found: 3.66 Å and 6.56 Å. The latter being too long to allow any intermolecular interaction, which was confirmed by the absence of green RDG isosurfaces. Consequently, for compositions close to 50 %, the molecular packing of the metal-organic fragments does not form one-dimensional chains Pt^{II}...Cl-Pt^{IV}...Cl...Pt^{II}, and the metal-organic column is better described as a stacking of discrete Pt^{II}...Cl-Pt^{IV}...Cl dimers.

2.3. Binding energies for $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures with $50 < m < 100$

Similarly to pure $[\text{PtCl}_2(\text{CNL})_2]$, the interaction energy (ΔE) for supramolecular structures describing the columnar mesophase of $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures can be expressed as the sum of the binding energy resulting from the interaction between metallic fragments (ΔE_{metal}) and the triphenylene discs in organic columns ($\Delta E_{\text{triphenylene}}$). As stated, $|\Delta E_{\text{triphenylene}}|$ reaches values around 145 kJ/mol Pt for all compositions. Fig. 10a) presents calculated ΔE_{metal} values. For the first set of supramolecular structures with $m = 80-94$, $|\Delta E_{\text{metal}}|$ increases with m , reaching a value close to 175.0 kJ/mol Pt. This value is similar to those calculated for the pure $[\text{PtCl}_2(\text{CNL})_2]$, indicating that for low $[\text{PtCl}_4(\text{Bipy})]$ compositions, the organometallic column is mainly stabilized by interactions between Pt^{II} moieties. For supramolecular structures with m values in the range of 67–75 and 53–57, $|\Delta E_{\text{metal}}|$ falls between 152.5 kJ/mol Pt and 131.4 kJ/mol Pt, respectively. In all cases, the dispersion contribution to ΔE_{metal} ($\Delta E_{\text{metal,dis}}$) accounts for approximately 61 % of ΔE_{metal} .

As seen in Fig. 10a), the variation of ΔE_{metal} with m fits wells to the ΔH data collected from the second DSC cycle for the Col_{rec} → I transition (similar conclusions can be drawn when comparing the total ΔE with ΔH , given that $\Delta E_{\text{triphenylene}}$ yields approximately the same value for all supramolecular structures). The ΔH data collected for the Col_{rec} → I transition represent the energy required to disrupt the supramolecular interactions between molecules within the columnar mesophases,

leading to the isotropic liquid. Meanwhile, the calculated binding energies arise from the supramolecular interactions between molecules that form the columnar mesophase. Thus, both ΔH and binding energies are indicative of the strength of the interaction between molecules in the columnar mesophase.

ΔE_{metal} has been decomposed into contributions from Pt^{II}...Pt^{II} and Pt^{II}...Cl-Pt^{IV}...Cl...Pt^{II} stacks, i.e., $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}}$ and $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}}$, respectively. For each of these energies, the dispersion contribution ($\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}, \text{dis}}$ and $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}, \text{dis}}$, respectively), arising from van der Waals interactions between adjacent organometallic regions to the Pt atoms, has been also obtained (see Fig. 10b). See Supplementary materials for a more detailed description about energy decomposition. According to the binding energies discussed in the previous paragraph, there are three concentration ranges with a distinct balance of Pt^{II}...Pt^{II} and Pt^{II}...Cl-Pt^{IV}...Cl...Pt^{II} interactions contributing to the stabilization of the organometallic columns. Mixtures with m around 50 could be described through structures xii–xiv ($m = 53-57$), implying an alternation between Pt^{II} and Pt^{IV} organometallic centers. In this situation, $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}}$ is the main contribution to ΔE_{metal} , with values around $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}| = 107.5$ kJ/mol Pt (where $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}, \text{dis}}$ constitutes 65 % of $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}$). Because this is the primary contribution, structures xii–xiv ($m = 53-57$) structures yield similar ΔE_{metal} values.

As m increases (structures ix – xi with $m = 67-75$), the supramolecular structures result in the formation of ...Pt^{II}...Pt^{II}...Cl-Pt^{IV}...Cl... chains. Thus, in addition to $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}}$, there is also a contribution from $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}}$. Both $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}|$ and $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}|$ energies average 109.4 kJ/mol Pt and 81.2 kJ/mol Pt, with the dispersion contribution around 71 % and 56 %, respectively. Therefore, for this range of concentrations, there is a small increase of $|\Delta E_{\text{metal}}|$ mainly due to the appearance of interactions between couple of Pt^{II} organometallic fragments located between $[\text{PtCl}_4(\text{Bipy})]$ molecules. In comparison to structures xii–xiv, $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}$ is not considerably affected, while $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}, \text{dis}}$ yields higher values. This is because now both Cl atoms in the axial plane of $[\text{PtCl}_4(\text{Bipy})]$ are forming an intermolecular interaction with adjacent Pt^{II}.

Finally, for higher compositions of Pt^{II} complex (structures ii–viii with $m = 84-90$), wherein one $[\text{PtCl}_4(\text{Bipy})]$ molecule ($y = 1$) is located between large stacks of $[\text{PtCl}_2(\text{CNL})_2]$, three contributions are present. $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}|$ that yields average values of 104.4 kJ/mol Pt (with a 61 % dispersion contribution), and two kinds of Pt^{II}...Pt^{II} contributions: one coming from Pt^{II}...Pt^{II} stacks adjacent to the $[\text{PtCl}_4(\text{Bipy})]$ unit and the interaction energy from the whole stack of $[\text{PtCl}_2(\text{CNL})_2]$ molecules around $[\text{PtCl}_4(\text{Bipy})]$, denoted as $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}}$ and $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}, \text{stack}}$, respectively. $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}|$ falls between 77.5 kJ/mol Pt and 93.3 kJ/mol Pt for $m = 80$ and 93, respectively. Meanwhile $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}, \text{stack}}|$ ranges between 77.5 kJ/mol Pt and 143.8 kJ/mol Pt for $m = 80$ and 91, respectively (dispersion contribution 61 % instead of m). Hence, $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}, \text{stack}}$ reaches similar values than those obtained to the pure $[\text{PtCl}_2(\text{CNL})_2]$ for high m compositions. Thus, at higher m compositions $|\Delta E_{\text{metal}}|$ grows with m mainly due to the increasing contribution of $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}, \text{stack}}$ while $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}}$ and $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}}$ remain slightly less affected.

As seen in Fig. 10, for the transition between structures ix – xi ($m = 67-75$) and ii – viii ($m = 80-94$), there is a diminution of $|\Delta E_{\text{metal}}|$ for $m = 80-86$, which have been analogized to a decrease in ΔH around $m = 80-90$. For $m = 80$ (structure viii), both $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}|$ and $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}|$ contributions are something lower than those calculated for structures ix – xi ($m = 67-75$); meanwhile for compositions something larger than $m = 80$, both diminutions are not compensated for the contribution of $\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}, \text{stack}}$, thus there is a diminution in the $|\Delta E_{\text{metal}}|$ for $m = 80-86$. From this point, the increase of $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}, \text{stack}}|$ contribution (although $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Pt}^{\text{II}}|$ also slightly increases) is enough to compensate the $|\Delta E_{\text{Pt}^{\text{II}} \dots \text{Cl} - \text{Pt}^{\text{IV}} \dots \text{Cl} - \text{Pt}^{\text{II}}|$ diminution, leading to an increase of $|\Delta E_{\text{metal}}|$ and ΔH at high m values up to reaching similar values to the pure $[\text{PtCl}_2(\text{CNL})_2]$ compound.

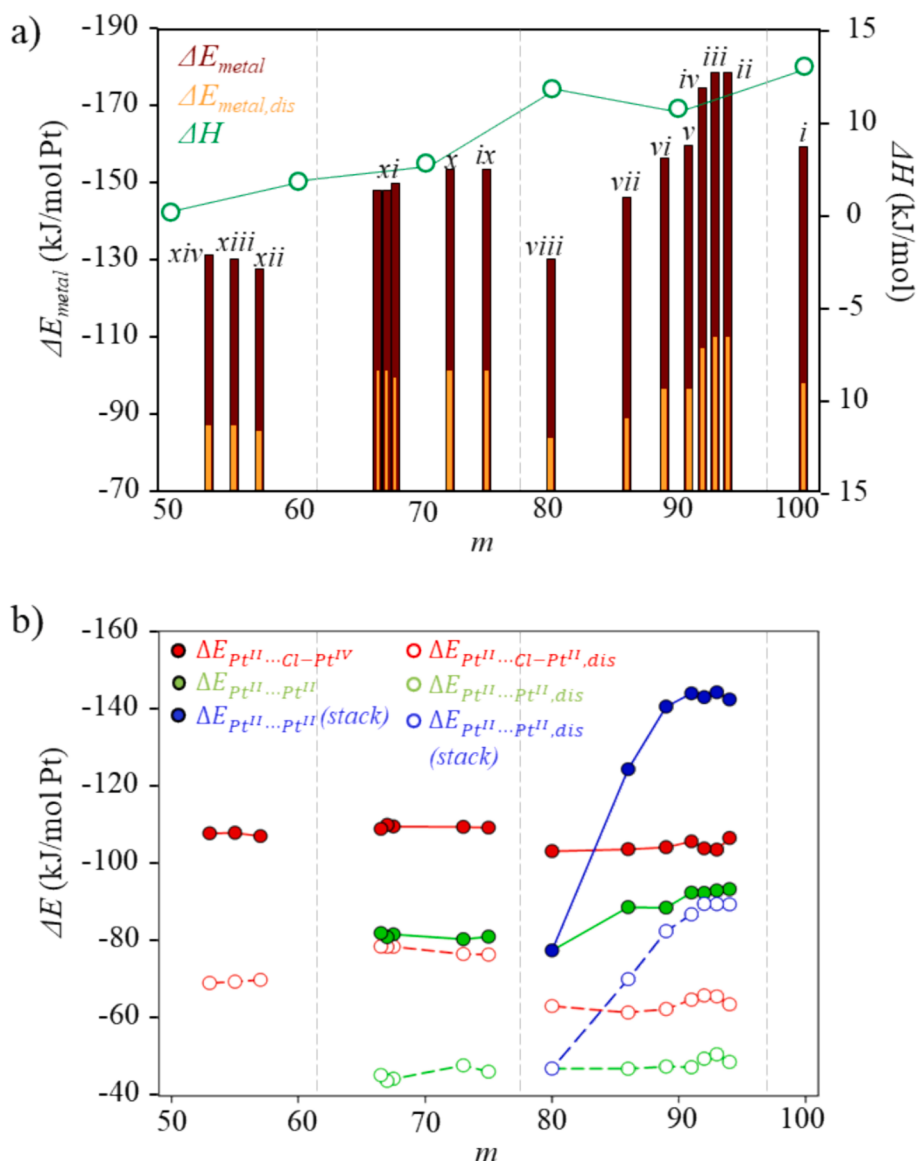


Fig. 10. a) Calculated binding energies of the organometallic collum (ΔE_{metal}) for [PtCl₂(CNL)₂]/[PtCl₄(Bipy)] mixtures along to experimental ΔH data collected from the second heating DSC cycle for Col_{rec} $\rightarrow$ I transition (see Table 1). Data for pure [PtCl₂(CNL)₂] compound are also displayed. b) ΔE_{metal} decomposition in $\Delta E_{Pt^{II}...Pt^{II}}$ and $\Delta E_{Pt^{II}...Pt^{IV}}$ contributions. See Table 2 for labelling i-xiv.

2.4. Electronic structure properties

Halogen bridged Pt^{II}/Pt^{IV} mixed-valence complexes can be considered one-dimensional (1D) electronic systems due to the formation of Cl-Pt^{IV}-Cl...Pt^{II}... interactions. These kind of systems are attracting considerable attention as 1D materials because of their attractive physical properties [65,82–84], such as larger third-order nonlinear optical susceptibilities, luminescence with a significant Stokes shift, long-range migration of spin-solitons and polarons along 1D chain, among others.

Finally, this section explores the electronic structure of [PtCl₂(CNL)₂]/[PtCl₄(Bipy)] mixtures, beyond ...Cl-Pt^{IV}-Cl...Pt^{II}... chains, also including electronic structure properties of ...Pt^{II}...Pt^{II}...Cl-Pt^{IV}-Cl... chains, as well as the presence of small quantities of Pt^{IV} in ...Pt^{II}...Pt^{II}...chains. Fig. 11 illustrates the density of states (DOS) for supramolecular structures of pure [PtCl₂(CNL)₂] and x [PtCl₂(CNL)₂]/ y [PtCl₄(Bipy)] mixtures. The total energy density of states (DOS) has been decomposed as the sum of the partial density of states (PDOS) contributions corresponding to the organic and organometallic columns.

Furthermore, the latter can also be expressed as the sum of the PDOS corresponding to the Pt^{II} and Pt^{IV} fragments.

Despite the composition, column segregation results in an electronic structure characterized by independent contributions from both organic and organometallic columns. The partial density of states contributions from the organic columns remains mainly unaffected by the composition, with an energy difference of approximately 2.4 eV between occupied and unoccupied states. As a result, the analysis of the electronic structure has been focused on the PDOS from the organometallic region. The electronic structure of [PtCl₂(CNL)₂] resembles the DOS reported for a single molecule (see Fig. S18). According to the partial density of states (PDOS), both the valence band maximum (VBM) and conduction band minima (CBM) are largely made up of Pt^{II} (5d) orbitals combined with Cl (3s and 3p) orbitals. Though, there is a slightly larger contribution from Pt^{II} to the VBM.

For x [PtCl₂(CNL)₂]/ y [PtCl₄(Bipy)] mixtures, the increase in [PtCl₄(Bipy)] concentration (i.e., lower m values) can be understood as a p -doping, leading to a hole-doped system derived from the substitution of Pt^{II} organometallic fragments by Pt^{IV} ones. Thus, there is a

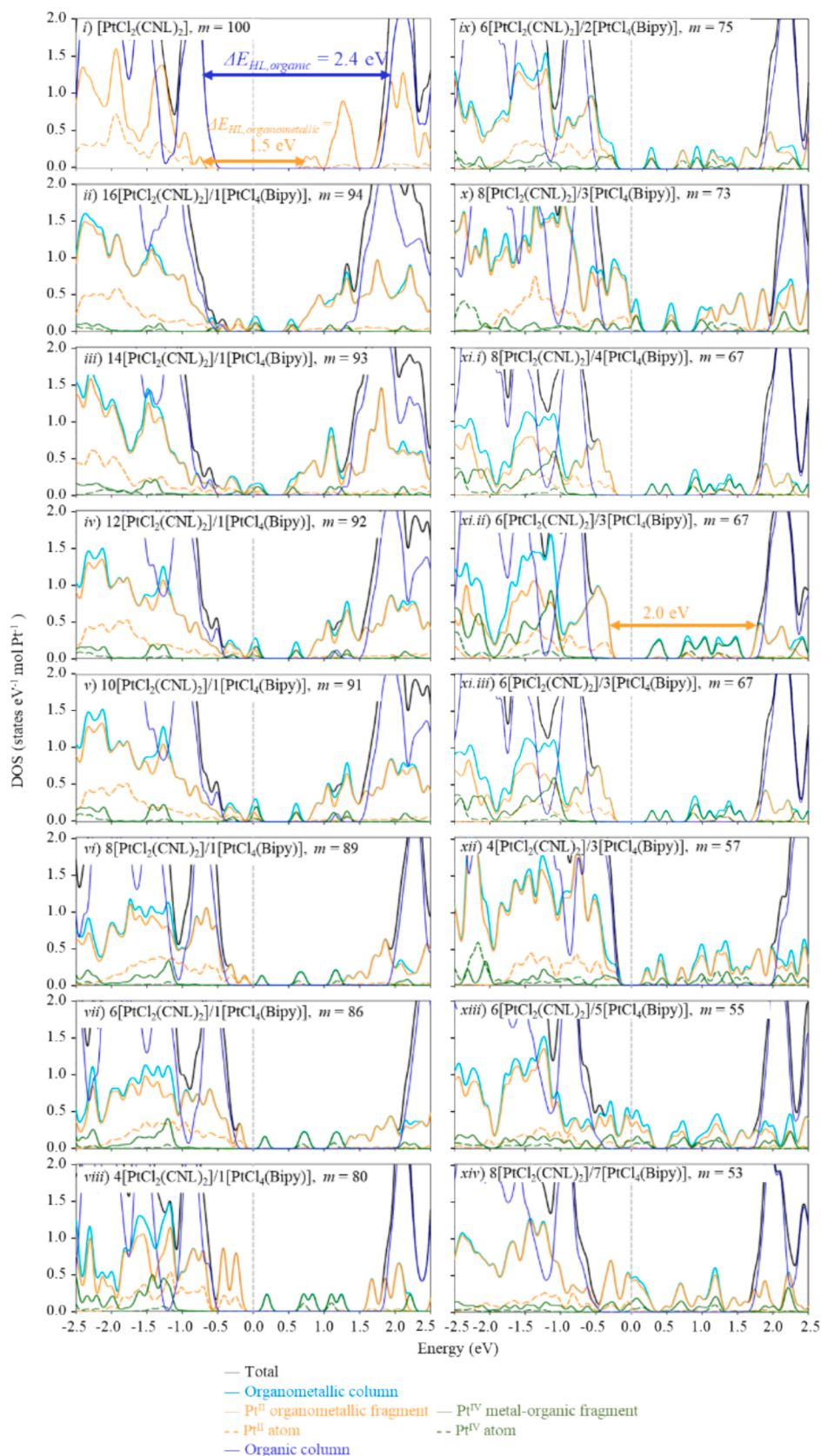


Fig. 11. Density of states (DOS) for [PtCl₂(CNL)₂] and x [PtCl₂(CNL)₂]/ y [PtCl₄(Bipy)] supramolecular structures. Partial density of states (PDOS) contributions from both organic (dark blue) and organometallic (clear blue) columns are also displayed. In addition, for the organometallic column, PDOS corresponding to Pt^{II} and Pt^{IV} organometallic fragments (orange and green solid lines, respectively), as well as from the Pt atoms (Pt^{II} and Pt^{IV}, dotted lines) are shown. The zero of energy was set at the Fermi level energy (vertical dotted line).

considerable shift of the Fermi level deeper into the occupied bands upon increasing $[\text{PtCl}_4(\text{Bipy})]$ concentrations. The Fermi level changes from -8.4 eV / -8.5 eV for $m = 100 / 96$ to -9.8 eV for $m = 53$. The PDOS plots also reveal that both the valence and the conduction bands have been modified, even at low $[\text{PtCl}_4(\text{Bipy})]$ concentrations. Like the binding energy trends with m , three different tendencies can be found as a function of the composition. For structures *ii-viii* ($m = 80-96$), new levels appear between VBM and CBM of $[\text{PtCl}_2(\text{CNL})_2]$ due to Pt^{IV} complex. The appearance of new contributions in both VBM and CBM, mainly originating from Cl ($3s$ and $3p$) orbitals in the axial plane of $[\text{PtCl}_4(\text{Bipy})]$, is attributed to the intermolecular interactions above described between Cl and Pt^{II} atoms. For $m = 96-91$, the Fermi level is situated at the valence band. Moving to $m = 89-80$, the Fermi level continues to shift within the occupied bands, with contributions from Pt^{IV} organometallic moiety becoming dominant in both edge bands.

For structures *ix-xi* ($m = 67-75$), the states initially defined as the VBM for $[\text{PtCl}_2(\text{CNL})_2]$ originating from Pt^{II} orbitals now appear empty. These levels are located above the Fermi level, which continues to move inside the occupied states. This is due to an intervalence charge transfer (IVCT) between Pt centers in different oxidation states [65,82,83]. For $m = 75, 73$ (structures *ix, x*), the state hybridization between Pt^{II} and Cl (coming from Pt^{IV}) orbitals due to the $\text{Pt}^{\text{II}}\cdots\text{Cl}-\text{Pt}^{\text{IV}}$ intermolecular interactions is also observed, now at energies above the Fermi level. For $m = 67$ those levels become mostly attributed to Pt^{IV} ligands. Thus, for this composition, the electronic structure can be described with both valence and conduction bands originating from Pt^{II} moieties, resulting in an energy gap of around of around 2.0 eV . Additionally, there is also an in-gap empty states, mainly attributed to $[\text{PtCl}_4(\text{Bipy})]$, which would lead to a wide intermediate band just below the CBM. This in-gap band results in an energy gap of around 0.5 eV with VBM. For compositions $m = 53-57$ (structures *xii-xiv*), a considerable IVCT occurs, leading to an electronic structure with no gap between empty and filled states.

3. Conclusions

A series of liquid crystalline molecular alloys, based on Pt^{II} and Pt^{IV} organometallic complexes with different ligands, have been studied using a combined experimental and computational approach. The coexistence of Pt atom in two different oxidation states allows the formation of halogen-bridged mixed valence compounds through $\text{Pt}^{\text{II}}\cdots\text{Cl}-\text{Pt}^{\text{IV}}$ interactions. The constituent complexes are an isocyanotriphenylene derivative labeled as $[\text{PtCl}_2(\text{CNL})_2]$, exhibiting an organic/inorganic segregated columnar mesophase, and $[\text{PtCl}_4(\text{Bipy})]$ (Bipy: didodecyl 2,2'-bipyridyl-4,4'-dicarboxylate) displaying a lamellar mesomorphism.

The thermal behavior and mesogenic properties of $[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures across the entire range of concentrations were studied using optical microscopy, differential scanning calorimetry and X-ray scattering. The resulting phase diagram reveals three main regions. Compositions falling between 15 % and 45 % of $[\text{PtCl}_2(\text{CNL})_2]$ do not exhibit liquid crystal behavior. Meanwhile, for compositions exceeding 50 % of $[\text{PtCl}_2(\text{CNL})_2]$, a single mesophase is obtained, closely resembling the columnar structure of $[\text{PtCl}_2(\text{CNL})_2]$, i.e., with a segregation between organic and organometallic columns.

Quantum chemical calculations based on extended tight-binding density functional methods were applied to study the supramolecular self-assembly of molecules within the columnar mesophases at the molecular level. For the pure $[\text{PtCl}_2(\text{CNL})_2]$, theoretical calculations were conducted on a model system composed of eight stacked molecules (containing 1752 atoms). While some approaches were done for computational economy, our model system provided a satisfactory description of the columnar segregation at a molecular level. In addition, the formation of stable columnar structure is due to dispersion interactions in the organic columns and the interplay between $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ and van der Waals interaction in the organometallic columns. For

$[\text{PtCl}_2(\text{CNL})_2]/[\text{PtCl}_4(\text{Bipy})]$ mixtures several supramolecular model systems were built varying the number of $[\text{PtCl}_2(\text{CNL})_2]$ (x) and $[\text{PtCl}_4(\text{Bipy})]$ (y) molecules, with the composition m defined as $x/(x+y)\cdot 100$. The size of the model systems reached up to 3703 atoms. Again, our supramolecular model structures effectively describe the coexistence of segregated columns with different natures, where the properties derived from the organic columns are like those described for the pure compound. Regarding the supramolecular structure within the organometallic column, supramolecular structures were categorized into three groups: 1) model systems leading to $m = 80-94$, composed of one $[\text{PtCl}_4(\text{Bipy})]$ molecule located between large stacks of $[\text{PtCl}_2(\text{CNL})_2]$ molecules; 2) Structures with $m = 67-75$, exhibiting an alternation of $\text{Pt}^{\text{II}}-\text{Pt}^{\text{II}}$ and $\text{Pt}^{\text{II}}\cdots\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl}\cdots\text{Pt}^{\text{II}}$ stacks, leading to $\cdots(\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}\cdots\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl})\cdots$ chains along the organometallic column; 3) Structures with $m = 53-57$ characterized by an alternation of $[\text{PtCl}_2(\text{CNL})_2]$ and $[\text{PtCl}_4(\text{Bipy})]$.

Despite the composition, $\text{Pt}^{\text{II}}\cdots\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl}\cdots\text{Pt}^{\text{II}}$ stacks yielded $\text{Pt}^{\text{II}}\cdots\text{Cl}$ intermolecular contacts of approximately $3.7 \text{ \AA}$. Meanwhile, interactions between neighboring Pt^{II} molecules were not significantly affected. Calculated binding energies nicely describe the tendency of ΔH experimentally measured for the rectangular columnar mesophase $\rightarrow$ isotropic liquid transition. Our findings showed that there is distinct balance of $\text{Pt}^{\text{II}}-\text{Pt}^{\text{II}}$ and $\text{Pt}^{\text{II}}\cdots\text{Cl}-\text{Pt}^{\text{IV}}-\text{Cl}\cdots\text{Pt}^{\text{II}}$ interactions contributing to the stabilization of the organometallic columns as a function of the composition. Mixtures with $m = 53-57$ mainly imply $\text{Pt}^{\text{II}}\cdots\text{Cl}-\text{Pt}^{\text{IV}}$ interactions, while for larger concentrations, there is also a contribution from $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ interactions, being the latter lower for $m = 67-75$. However, for $m > 90$ the strength of $\text{Pt}^{\text{II}}\cdots\text{Pt}^{\text{II}}$ interactions surpasses $\text{Pt}^{\text{II}}\cdots\text{Cl}-\text{Pt}^{\text{IV}}$ ones. Finally, the analysis of the density of states for the studied supramolecular model systems shows that the electronic structure is characterized by independent contributions from both organic and organometallic columns. Additionally, the increase in $[\text{PtCl}_4(\text{Bipy})]$ concentration led to a transition from a hole-doped system at low concentrations of $[\text{PtCl}_4(\text{Bipy})]$ to a system with a significant intervalence charge transfer between Pt centers in different oxidation states for $m = 53-75$, resulting in an electronic structure with no gap between empty and filled states.

CRedit authorship contribution statement

Estela de Domingo: Investigation, Formal analysis, Data curation. **Gregorio García:** Writing – review & editing, Writing – original draft, Visualization, Resources, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Silverio Coco:** Writing – review & editing, Writing – original draft, Visualization, Resources, Methodology, Investigation, Funding acquisition, Data curation, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.molliq.2025.127663>.

Data availability

Data will be made available on request.

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