The Formation of Excimers in IsoquinolinyI Pyrazolate Pt(II) Complexes: Role of Cooperativity Effects

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ABSTRACT. The interplay between non-covalent interactions involving metal complexes may lead to the formation of aggregates (i.e., ground state dimers, trimers, n-mers, etc), and this is often linked to dramatic changes in their physical and chemical properties as compared to the original properties of the isolated units. Dimers and trimers can also be formed in the excited states potential energy surfaces, i.e., excimers. Excimers are short-lived but are also often characterized by different optical properties from those of the isolated units. Understanding the nature of non-covalent interactions and the presence or not of cooperativity effects in both aggregates and excimers is thus extremely important to rationalize these variations. In this study, we present computational investigations on isoquinoliny pyrazolate Pt(II) complexes. Our results highlight that cooperativity effects between non-covalent interactions, which are modulated by steric-demanding substituents and metallophilic Pt···Pt interactions, are present only on certain investigated excimers. We use density functional theory (DFT) calculations to examine the cooperativity effects and the changes in the photophysical properties. Different descriptors of cooperativity effects between non-covalent interactions, including the synergetic, genuine non-additive, and total interaction energies were evaluated for a series of Pt(II) aggregates and excimers. In addition, energy decomposition analysis (EDA) calculations were performed to rationalize the origins of the cooperative effects. The cooperative effects in trimer excimers (in their lowest triplet excited state, i.e., T_1) led to shortened Pt···Pt contacts as compared to the trimer aggregates. Furthermore, this synergy between non-covalent interactions is ultimately responsible for the formation of the excimers and the striking changes in the measured photophysical properties. More in detail, we report a change in the character of the lowest-lying triplet excited state when going from dimer excimers (i.e., of mixed triplet ligand-centered and triplet metal-to-ligand charge transfer ($^3LC/^3MLCT$) character) to trimer excimers (i.e., of triplet metal-metal-to-ligand charge transfer (3MMLCT) character). The EDA reveals that the total interaction energy on trimer excimers is subtly controlled by the electrostatic and dispersion terms.

INTRODUCTION

Non-covalent interactions are crucial in many areas of material science, biology, medicine, and modern chemistry, and especially in the field of supramolecular chemistry where they are responsible of the variations in the chemical and physical properties of single molecules when moving to condensed phases, for example, in liquid and solid states.¹ Molecules are individual building blocks and the way in which they organize has a great impact on their chemical and physical properties. On the basis of the interacting molecules, cation- π interactions,²⁻⁵ anion- π interactions,⁶⁻⁹ lone pair interactions,¹⁰ CH $\cdots\pi$ interactions,¹¹ π - π stacking interactions,^{11,12} and metallophilic interactions,¹³⁻¹⁷ have emerged as driving intermolecular forces in aggregated structures. In other scenarios, non-directional hydrophobic (i.e., dispersion-driven) interactions drive the formation of molecular aggregates.¹⁸ Particularly, the interactions involving aromatic rings are of key relevance in both chemical and biological recognition, i.e., they determine the structures of protein, DNA, and many other materials. In any process of aggregation, a large number of non-covalent interactions of different nature operate simultaneously, i.e., from electrostatic and induction to dispersion interactions. The interplay between non-covalent interactions may lead to synergistic or anti-synergistic effects. Cooperative (synergistic) effects between non-covalent interactions exist when the sum of the co-existing interactions in the supramolecular complex is larger than the simple addition of the individual interactions.

The cooperativity between π - π interactions and other non-covalent interactions (i.e., ion- π , hydrogen bonding, etc) has been the scope of multiple investigations.¹⁹⁻³¹ The cooperative effects might be seen on the bonding distances between the molecular units, usually leading to shorter distances in the supramolecular complexes when synergistic effects arise. Scheme 1 displays e.g., the synergistic effects arising due to the co-existence of ion- π and π - π non-covalent interactions. In the latter case, a theoretical study highlighted that cooperative effects are mainly originated from induction effects,²⁹ in which the ion- π interaction induces a dipole moment at the benzene unit favoring its electrostatic interaction with another benzene unit. The cooperativity is reflected in the shortening of both the ion- π and π - π bond distances in the trimers, i.e., the π - π distance is 3.7Å in the dimer, and it decreases to 3.5Å in the trimer.²⁹ Accordingly, significant non-additivity energies were reported for these systems.^{20, 28} Other scenarios involve the strengthening of hydrogen bonding interactions when co-existing with π - π interactions and vice versa,^{20, 32} but also the interplay between π - π and CH- π interactions.³³⁻

Scheme 1. A representative cooperativity effect between non-covalent interactions reported in the literature.²⁸ The main geometric parameters in Å (MP2/6-31G(d)) for the dimers and trimer along with the cooperative energy (MP2/6-311++G(d,p)//MP2/6-31G(d)) are highlighted.

For Pt(II) complexes, the interplay between non-covalent interactions resulting in cooperative effects were highlighted through several studies.³⁹⁻⁴³ For instance, Tam *et. al.* investigated the gelation properties of Pt(II) terpyridyl complexes. The gelation properties were found to be driven by a subtle interplay between Pt···Pt and π - π interactions in addition to hydrophobic interactions.³⁹ Similarly, Rest *et. al.* reported an oligophenylene ethynylene-based amphiphilic Pt(II) complex that forms supramolecular polymeric structures in aqueous and polar media and which are driven by the interplay between π - π and different weak C-H···Cl or C-H···O interactions.⁴⁰ Furthermore, Suponitsky *et. al.* explored the effect of π ··· π stacking interactions on the hyperpolarizability of supramolecular materials.⁴¹ In most of the examples above, aggregates (i.e., ground state dimers and trimers) are formed. Dimers and trimers can also be formed in the excited state potential energy surfaces, those are known as excimers. Excimers, in contrast with aggregates, are short-lived, but can lead to striking changes in the measured photophysical properties. The formation of aggregates and excimers might be originated on subtle changes in the environment and thus their application in the field of chemosensors, bioprobes, stimuli-responsive nanomaterials, and optoelectronic materials is straightforward.^{17, 39} The formation of excimer species is well described in Pt(II) complexes, but also in e.g., gold and silver complexes.⁴⁴ Generally, these complexes display square planar

molecular geometries originated from their d^8 electronic configuration, and thus favoring the formation of intermolecular metallophilic contacts along the sterically undemanding z-axis via $d-d$ orbital interactions. After light excitation of these complexes, relaxation on their excited state potential energy surfaces generally leads to the population of their lowest triplet excited state (T_1). Specifically for isoquinoliny pyrazolate Pt(II) complexes, the initially populated singlet excited states are mainly of mixed ligand-centered (LC) $\pi-\pi^*$ and metal-to-ligand charge transfer (MLCT) character.⁵⁹ From these metal-based singlet excited states very fast and efficient intersystem crossing (ISC) mechanisms do take place leading to the population of the triplet manifold. Finally, relaxation on the triplet manifold leads to the population of the lowest-lying triplet excited states, which are responsible for the experimentally measured photoluminescent profiles with lifetimes expanding up to the microsecond regime.⁵⁹ This manuscript focuses on these very last steps of the photorelaxation cascade.

In this regard, the formation of excimers is particularly notable for Pt(II) complexes bearing azolate chelates in solid states.⁴⁵⁻⁴⁸ The resulting triplet excimers often possess significant metal-metal-to-ligand charge transfer (³MMLCT) character, in which the electron is excited from a filled $Pt \cdots Pt$ d_z^2 orbital with certain antibonding σ^* character to a vacant π^* orbital of the chelate. The energy of the MMLCT excited states has a strong dependence on the $Pt \cdots Pt$ interaction; i.e. shortened interlayer distances correlate with lower MMLCT energies.⁴⁹ The metallophilic interactions can lead to the formation of dimers, trimers, oligomers or even one-dimensional stacked structures, showing in some cases $Pt \cdots Pt$ separations shorter than the sum of van der Waals radii.^{13, 15, 50, 51} Metallophilic $Pt \cdots Pt$ interactions are known to be comparable to the bond strength of hydrogen bonding, but are much weaker than that of typical covalent and ionic bonding.⁵² This means that these relatively weakened metallophilic interactions can be easily disturbed by both steric effect and other intra- or inter-molecular interactions, such as solvation, $\pi-\pi$ stacking, both hydrogen and halogen bonding interactions, etc;⁵³⁻⁵⁷ but also by the global spin configuration of the molecular assembly (S_0 , T_1). It also indicates that metallophilic interactions often coexist with other intermolecular forces that, in turn, would stabilize or destabilize the interlayer interactions.

For Pt(II) supramolecular structures and despite the growing understanding of their aggregates and excimers, most of the work has been directed towards tuning the $\pi \cdots \pi$ stacking and hydrogen bonding interactions.⁵⁸ In a previous work,⁵⁹ we reported square-planar Pt(II) complexes bearing isoquinoliny pyrazolate with tunable photoluminescent properties (see **Pt1-Pt4** in Scheme 2). The computed results revealed that first there are no short $Pt \cdots Pt$

contacts ($< 3.0 \text{ \AA}$) on the ground state species and second that there is a certain degree of conformational flexibility on the formation of aggregates and excimers. A good correlation between the experimental and computed photophysical properties was reported in our previous publications; see e.g., a summary of the simulated UV-Vis absorption characteristics for **Pt1** in Figure S5, where the red-shifted absorption bands due to singlet MMLCT excitations are only found for one specific trimer aggregate conformation. Concerning emission properties, the interlayer distance is the most important factor controlling the character of the excited states: for instance, only for **Pt1** a trimer excimer of $^3\text{MMLCT}$ character bearing short $\text{Pt}\cdots\text{Pt}$ contacts is formed, while for the trimer excimers of **Pt2-Pt4** their lowest triplet states are of mixed $^3\text{LC}/^3\text{MLCT}$ character. These results led us to explore whether cooperative effects between non-covalent interactions play a role in the formation of these excimers and to understand why dimer excimers of $^3\text{MMLCT}$ character are apparently not formed. Specifically, using a first principles level approach, we first aim to understand the packing interactions in both aggregates and excimers of dimer and trimer species and to evaluate possible cooperativity effects when going from the dimer to the trimer species. The cooperative effects are analyzed in terms of geometric and energetic factors including the synergetic energy and the non-additivity energy. Energy decomposition analysis (EDA) was used to decipher the origins of the synergistic effects between non-covalent interactions.

Scheme 2. Molecular geometries of monomers **Pt1-Pt4** and schematic representation of monomer, dimer, and trimer structures.

COMPUTATIONAL DETAILS

All calculations for **Pt1-Pt4** are based on density functional theory (DFT). The geometries of **Pt1-Pt4** in the singlet ground state (S_0) were optimized using the Becke's three-parameter hybrid exchange functional combined with the Lee-Yang-Parr correlation functional^{60,61} including dispersion correction (B3LYP-D3),⁶² in combination with the 6-31G(d) atomic basis set for all non-metal atoms. Relativistic effects were considered for the metal Pt atoms by using the ECP-60-mwb pseudopotential.⁶³ Geometries optimizations of the lowest triplet (T_1) states of **Pt1-Pt4** were performed using unrestricted B3LYP-D3 (UB3LYP-D3) method using the same basis set as in the S_0 optimizations. All optimized structures were confirmed to be local minima by normal mode analysis with all positive frequencies. All geometry optimizations were performed without symmetry constraints. The interaction energies of dimers and trimers are corrected for the basis set superposition error (BSSE) using the Boys-Bernardi counterpoise technique.⁶⁴ The geometry optimizations of **Pt1-Pt4** were carried out with the Gaussian 16 program package.⁶⁵

To evaluate the cooperativity between non-covalent interactions, the synergetic energies (E_{syn}) of **Pt1-Pt4** were performed by subtracting the binding energy of dimers (E_{dimer}) from the binding energy of the trimers (E_{trimer}) as displayed in Equation (1). Their genuine non-additivity energies ($E - E_A$) were also calculated by deducting all pairwise interaction (three in the case of a ternary complex) from the total interaction energy of trimers as given in Equation (2).

$$E_{syn} = E_{trimer} - 2(E_{dimer}) \quad (1)$$

$$E - E_A = E_{ABC} - (E_{AB} + E_{AC} + E_{BC}) \quad (2)$$

Where E_{ABD} , E_{AB} , E_{AC} , E_{BC} terms correspond to the interaction energies of ABC, AB, AC, and BC, respectively, at the optimized ABC trimer geometries. The ABC species is composed of three layers of the monomer unit, i.e., A, B, and C as displayed in Scheme 2. The AB, AC, and BC species correspond to the respective dimer combinations at the optimized ABC trimer geometries. These expressions have been successfully used in the study of cooperativity effects among a variety of systems such as the interplay between ion- π and π - π interactions or between C-H/ π and π - π interactions.^{20, 28, 31}

We have also performed energy decomposition analysis (EDA) to evaluate the contribution of various factors to the total interaction energies.⁶⁶ The EDA of dimers and trimers **Pt1-Pt4** were performed based on the generalized Kohn-Sham (GKS) scheme, i.e., GKS-EDA, as implemented in the Turbomole package.^{67, 68} This scheme divides the total interaction energy

(ΔE_{TOT}) into electrostatic (ΔE_{ele}), exchange-repulsion (ΔE_{exrep}), polarization (ΔE_{pol}), correlation (ΔE_{corr}), and dispersion (ΔE_{disp}) terms as follows in Equation (3).

$$\Delta E_{TOT} = \Delta E_{ele} + \Delta E_{exrep} + \Delta E_{pol} + \Delta E_{corr} + \Delta E_{disp}, \quad (3)$$

The individual terms are defined in the SI. The EDA calculations were performed with the Turbomole 7.1 program package⁶⁹ using the same version of the B3LYP-D3 functional as implemented in Gaussian 16 and the def2-TZVP basis set.⁷⁰

RESULTS AND DISCUSSION

Optimized Structures. The optimized geometries in the S_0 state of monomers **Pt1-Pt4** are shown in Figure 1 (see Figure S1 in the Supporting Information for the T_1 optimized geometries). The S_0 and T_1 optimized geometries of dimers and trimers of **Pt1** are displayed in Figure 2 (see Figure S2-S4 and Table S1-S2 in the Supporting Information for the rest of complexes). We note that through the analysis of the optimized geometries in the multimers one can already assess whether the formation aggregates (S_0) and of excimers (T_1) is likely.

Let us start with the monomers. All monomer Pt(II) complexes adopt a square-planar coordination of the central Pt(II) atom, with the ligands adopting a trans-configuration. The Pt–N bond lengths are almost the same without obvious variation for all monomers.

Figure 1. Optimized geometries (B3LYP-D3/6-31G(d)) in the S_0 state of monomers of **Pt1-Pt4**.

In the case of dimers and trimers, the geometries of different conformers in the S_0 and T_1 potential energy surfaces were optimized. Figure 2 and Figure S2-S4 in the Supporting

Information collect: i) the geometries of all the optimized conformers (see e.g., **Pt1a-c** in Figure 2), ii) their Pt···Pt distances, and iii) their relative energies; both for dimers and trimers. Several conformers are found to be close-lying both in the S_0 and T_1 potential energy surfaces (e.g., within 0.0-2.0 kcal/mol), and thus, likely to be populated at room temperature if thermal equilibrium is at play. These results highlight that there is some degree of conformational flexibility for dimers and trimers at room temperature. Two main intermolecular forces drive the dimers and trimers assembly: intermolecular π - π stacking interactions and Pt···Pt contacts. The former interaction is predominant in all investigated dimer species, regardless whether we consider the S_0 or the T_1 optimized geometries. The interlayer distances range between 3.3 and 3.6 Å (see Figure 2). For example, the computed interlayer distance for the lowest-energy S_0 dimer of **Pt1** is 3.59 Å (see **Pt1b**). Short Pt···Pt contacts (< 3.0 Å) are only found in the case of selected T_1 optimized conformers; thus, highlighting that the latter interactions might be feasible only in the excimers but not in the aggregates. Furthermore, this is only observed in the trimer excimers but not on the dimer excimers. For example, let us evaluate the case of the excimers of **Pt1**. The lowest-energy T_1 conformer of the dimer of **Pt1** displays an interlayer distance of 3.56 Å (see **Pt1c**). This distance turns significantly shorter in the lowest-energy T_1 conformer of the trimer (see 2.94 Å for **Pt1a**), where the Pt···Pt contacts become more evident. The other T_1 trimer conformers possess significant larger interlayer distances (3.53 and 3.52 Å for **Pt1b** and **Pt1c** respectively) and they are located ca. 5.4 and 4.9 kcal/mol, respectively, above **Pt1a**. Thus, we foresaw that cooperativity between metallophilic interactions might be relevant to rationalize the relevant geometric and energetic differences between the conformers. We recall that these changes are associated to the striking change in their photophysical properties from very diluted solutions to concentrated dilutions or thin films, i.e., yielding red shifted-emission bands and larger photoluminescence quantum yields in the films.⁵⁹

(a) Dimer

(b) Trimer

Figure 2. Optimized conformers (B3LYP-D3/6-31G(d)) in the S_0 and T_1 states of dimers and trimers of **Pt1** along with their relative energies (E_r).

Estimation of Cooperativity between Non-Covalent Interactions. In Table 1 and Table 2, we summarize the binding energies with and without the basis set superposition error (BSSE) correction (E_{BSSE} and E , respectively) and the equilibrium distance (R_e in Å) of dimers **Pt1-Pt4** in their S_0 and T_1 states; and trimers of **Pt1** in their S_0 and T_1 states (see Table S3-S4 in the Supporting Information for the rest of complexes), respectively. The results show that, not surprisingly, the trimer species are more stable than dimer species. For example, the binding energy of **Pt1a** in the S_0 state is increased from -39.0 kcal/mol in the dimer structure to -76.5 kcal/mol in the trimer structure. For dimers, the binding energies of the aggregates (S_0) are on the same order of magnitude as those in the excimers (T_1), see Table 1. However, in the case of trimers, the formation of excimers is clearly more favored than in the case of aggregates (compare in Table 2 E_{BSSE} values ranging between ca. -80/-95 kcal/mol for the T_1 species with respect to ca. -76/-79 kcal/mol for the S_0 species).

To provide an estimation of the extra energetic stabilization or destabilization in trimer species with respect to the dimers, we present the computed values of synergetic (E_{syn}) and genuine non-additivity ($E-E_A$) energies for **Pt1** in Table 2 (see Table S4 in the Supporting Information for trimers **Pt2-Pt4**). These energies are intended to provide an estimation of energetic stabilization or destabilization obtained in trimer species. The E_{syn} is the simplest quantity, which is obtained by subtracting twice the E_{dimer} to the E_{trimer} . Another possibility for evaluating the mutual influence of both interactions in trimer species is $E-E_A$, which is an energy difference between the E of trimer species and all pair of interaction energies in the supramolecular trimers (see SI).

The computed values of E_{syn} and $E-E_A$ of trimers **Pt1** are collected in Table 2 (see Table S4 in the Supporting Information for the rest of complexes). An inspection of the results reveals that the E_{syn} and $E-E_A$ of trimer species are close to zero or slightly negligible in the ground state (values ranging between -3.0 and 0.0 kcal/mol for all possible aggregates), and thus highlighting that cooperative effects are likely not playing a role in the ground state structures. We recall that the computed interlayer distances do not strongly vary when going from dimer to trimer (compare 3.382 vs 3.312 Å in **Pt1a**, see Figure 2-3). However, for the excimers the interlayer distance is strongly shortened when going from dimers to trimers for some of the optimized triplet conformers (see e.g., 2.941 Å in **Pt1a** in Figure 2). Interestingly, this latter conformer displaying unambiguous Pt···Pt contacts, becomes the lowest-lying conformer among all the optimized triplet state structures. Thus, the computed geometric features at the trimer excimers point to strong cooperativity effects when going from dimers to trimers. Indeed, the computed E_{syn} and $E-E_A$ values also highlight the strong cooperative effects in **Pt1a**

(see Table 2). Specifically, while the E_{syn} and $E-E_A$ values for trimer **Pt1a** in S_0 are negligible; they amount up to -16.9 and -8.2 kcal/mol in the T_1 state, respectively. Moreover, for the higher-lying energy conformers in the T_1 state, i.e., **Pt1b-c**, smaller cooperative effects are calculated (E_{syn} values of -15.0 and -1.8 kcal/mol). This is in agreement with the fact that the computed interlayer distances do not strongly vary when going from dimers to trimers for these conformers. In a nutshell, these pieces of evidence indicate a positive synergy between non-covalent interactions for excimers, and especially for the lowest energy conformer of the T_1 state. This trend is not only observed for **Pt1a** but can also be seen in the rest of complexes (see Table S4 in the Supporting Information).

Table 1. Binding energies (B3LYP-D3/def2-TZVP//B3LYP-D3/6-31G(d)) with and without BSSE correction (E_{BSSE} and E in kcal/mol) and Pt···Pt equilibrium distance (R_e in Å) of the dimer conformers of **Pt1** in their S_0 and T_1 states.

Dimer	S_0 state			T_1 state		
	E	E_{BSSE}	R_e	E	E_{BSSE}	R_e
Pt1a	-41.7	-38.9	3.382	-40.5	-39.0	3.331
Pt1b	-42.8	-39.7	3.590	-42.9	-39.3	3.558
Pt1c	-43.0	-40.2	3.590	-42.9	-39.3	3.552

Table 2. Binding energies (B3LYP-D3/def2-TZVP//B3LYP-D3/6-31G(d)) with and without BSSE correction (E_{BSSE} and E), synergetic (E_{syn}), genuine non-additivity ($E-E_A$) energies in kcal/mol and Pt···Pt equilibrium distances (R_{e1} and R_{e2} in Å) of the trimer conformers of **Pt1** in their S_0 and T_1 states.

Trimer	S_0 state						T_1 state					
	E	E_{BSSE}	E_{syn}	$E-E_A$	R_{e1}	R_{e2}	E	E_{BSSE}	E_{syn}	$E-E_A$	R_{e1}	R_{e2}
Pt1a	-81.9	-76.5	1.3	-2.1	3.312	3.312	-100.0	-94.9	-16.9	-8.2	2.941	2.941
Pt1b	-84.8	-79.4	0.0	-2.9	3.516	3.512	-96.9	-93.6	-15.0	-3.1	3.530	3.526
Pt1c	-84.8	-79.5	0.9	-2.2	3.516	3.562	-85.7	-80.4	-1.8	-2.1	3.519	3.552

In Figure 3a are depicted the spin density plots for the dimer and trimer excimers of **Pt1a**. Triplet excited state species dominate the emissive properties of these complexes, as we recently disclosed both experimentally and computationally.⁵⁹ When moving from dimer to trimer excimer the character of T_1 state changes from mixed $^3\text{LC}/^3\text{MLCT}$ character to $^3\text{MMLCT}$. As discussed in our previous report,⁵⁹ this change of character is accompanied by striking changes in the photophysical properties when moving from very diluted solutions to

concentrated dilutions or thin films (i.e., red-shifted emission peaks, higher photoluminescence quantum yields, etc.). Specifically, in our previous report (see a summary of the computed emission energies in Table S5 for all the complexes),⁵⁹ for trimer **Pt1a** (which possesses $^3\text{LC}/^3\text{MMLCT}$ character) an emission band peaking at 842 nm was reported. This band is red-shifted in comparison with the computed energy maxima for trimers **Pt1b** and **Pt1c** which possess mixed $^3\text{LC}/^3\text{MLCT}$ character (i.e., 755 and 788 nm; respectively) but also with respect of dimers **Pt1b** and **Pt1c** (749 nm). In opposition to trimer-emission, dimer-emission resembles more to the monomer emission since their responsible emissive states are also of $^3\text{LC}/^3\text{MLCT}$ character. In Figure 3b are displayed the spin density plots for the the trimer conformers of **Pt1**. In contrast to the trimer of **Pt1a**, both T_1 states of trimers **Pt1b** and **Pt1c** can be better described as having mixed $^3\text{LC}/^3\text{MLCT}$ character. Thus, having in mind that these conformers are energetically close-lying, we can rationalize why e.g., subtle changes in the environment may lead to the formation of aggregates in the excited state potential energy surfaces, as observed experimentally.⁵⁹

Figure 3. (a) Optimized geometries (B3LYP-D3/6-31G(d)) and spin density distributions of dimer and trimer excimers of **Pt1a** and (b) spin density distributions of trimers **Pt1a-c** (Iso-contour value 0.0002: blue for alpha spin and green for beta spin).

Energy Decomposition Analysis. To provide an estimation of the extra energetic stabilization obtained in the excimers of the supramolecular complexes when going from the dimer to the trimer species, and to obtain a rationalization of the origins of this cooperativity, we performed energy decomposition analysis (EDA) calculations as given in Equation (3). The analysis was performed for all dimer conformers of Pt1-Pt4 and for the trimer conformers of Pt1, in both their S_0 and T_1 states. Figure 4 depicts the possible fragmentation schemes that we have used. While the fragmentation of dimers is straightforward (see Figure 4a), several fragmentation schemes are possible for the trimers, especially for the T_1 state. Specifically, for the excimer trimers, layers A, B and C can be spin restricted or spin unrestricted (the total wavefunction is maintained as spin unrestricted). Furthermore, layers A and C also can be treated as the first fragment and the middle (B) layer can be treated as a second fragment where they can be spin restricted or spin unrestricted. This leads to five different possibilities for excimer trimers (Type I-V, see Figure 4b-c), which were all analysed in the EDA calculations for comparative purposes.

Figure 4. Fragmentation schemes used in EDA calculations; (a) dimers **Pt1**, (b) trimers **Pt1** using a three-layer fragmentation, and (c) trimers **Pt1** in which the terminal monomers (AC) is treated as the first fragment and the middle monomer (B) as second fragment.

Firstly, GKS-EDA calculations were done on all optimized conformers in both their S_0 and T_1 states. The results for the dimers and trimers of **Pt1** are listed in Table 3 (see Table S6 in the Supporting Information for the rest of complexes). Secondly, to evaluate how the global EDA total interaction energy (ΔE_{tot}) and its different energetic contributions vary along the Pt···Pt bond distances, potential energy curves were computed for both dimers and trimers of **Pt1** as shown in Figure 5. For the latter studies, the conformer **Pt1a** was selected to evaluate the changes when going from dimer to trimer. In the case of trimers, the two Pt···Pt bond distances were symmetrically distorted to build up the potential energy curves.

Let us start the discussion with the values reported in Table 3. First, the dispersion contribution (ΔE_{disp}) dominates the EDA total interaction energies (ΔE_{tot}) for both dimers and trimers in their S_0 or T_1 electronic configurations. The next terms contributing to binding are the ΔE_{exrep} and ΔE_{corr} terms. The ΔE_{ele} contribution is always repulsive (see positive values in Table 3), which can be understood in terms of the electrostatic repulsion between the Pt(II) units, while the polarization term (ΔE_{pol}) remains negligible in all the situations. Therefore, a first inspection of the results clearly reveals that the binding situation is controlled by the electrostatic and dispersion terms, and modulated by the ΔE_{exrep} and ΔE_{corr} terms. Let us now discuss the results in more details. For instance, for the dimer excimer (T_1) of **Pt1a**, the BSSE-corrected dimer binding energy ($E_{\text{tot(BSSE)}}$ in Table 1) is ca. -39.0 kcal/mol. Values of ca. -39 kcal/mol are obtained for the BSSE-corrected GKS-EDA ΔE_{tot} values ($\Delta E_{\text{tot(BSSE)}}$ in Table 3), both for type I and II fragmentations, so that the results are consistent regardless of the considered fragmentation scheme and we thus use here type I fragmentation for **Pt1b** and **Pt1c**. Note that the $\Delta E_{\text{tot(BSSE)}}$ values for the latter compounds amount up to -39.3 kcal/mol in their T_1 states, values also in agreement with those reported in Table 1.

In the case of the trimer **Pt1a**, the $\Delta E_{\text{tot(BSSE)}}$ values slightly vary between the different fragmentation schemes. For instance, type III and IV provide similar $\Delta E_{\text{tot(BSSE)}}$ values of -94.9 and -94.2 kcal/mol, respectively, whereas type I, II, and V render values of -94.1, -91.4, and -96.4 kcal/mol, respectively. Because the computed binding energy is -94.9 kcal/mol (see Table 2), the analysis here is based on type III and IV fragmentations. For trimers **Pt1b** and **Pt1c** the type III fragmentation leads also to the most similar results with respect to the values

reported in Table 2, and thus this type of fragmentation is chosen for comparative purposes. By comparing the trimers **Pt1a**, **Pt1b** and **Pt1c** in their T_1 states, one can notice that the shortening of the Pt···Pt distance in **Pt1a** has a strong influence on the ΔE_{ele} term, which increases from ca. 169.7 and 170.4 kcal/mol in **Pt1b** and **Pt1c**, respectively, to ca. 179.3 kcal/mol in **Pt1a**. This is as expected due to the increasing electrostatic repulsion with decreasing interlayer distances. Conversely, a more favorable dispersion term (ΔE_{disp}) is obtained for the latter (compare ca. -131.9 kcal/mol for **Pt1a** versus -125.5 and -125.1 kcal/mol for **Pt1b** and **Pt1c**, respectively). Therefore, the subtle variations in the ΔE_{exrep} and ΔE_{corr} terms determine the total binding energies, since the ΔE_{pol} remains in all cases negligible. Particularly, the striking changes in the ΔE_{corr} term within the series of conformers are very relevant to explain the observed trends in the ΔE_{tot} values. Thus, the ΔE_{corr} term is more beneficial in the case of **Pt1a** (-72.6 kcal/mol) than in the case of **Pt1b** and **Pt1c** (-62.6 and -62.2 kcal/mol, respectively). Due to the shortened interlayer distances correlation effects are also more relevant in **Pt1a**, which finally leads to a larger total energy for **Pt1a** as compared to those of **Pt1b** and **Pt1c**. Concerning the ΔE_{exrep} values, they amount up to ca. -75.1, -79.1 and -69.3 kcal/mol for **Pt1b**, **Pt1a** and **Pt1c**, respectively. In a nutshell, while dispersion contributions are mainly responsible for the binding energies, the subtle changes in the ΔE_{disp} , ΔE_{exrep} , ΔE_{corr} and ΔE_{ele} terms need to be concomitantly analyzed in order to understand the trends in the binding energies.

Table 3. Total interaction energies with and without BSSE correction ($\Delta E_{(\text{BSSE})}$ and ΔE), electrostatic (ΔE_{ele}), exchange-repulsion (ΔE_{exrep}), polarization (ΔE_{pol}), correlation (ΔE_{corr}), and dispersion (ΔE_{disp}) energies in kcal/mol of dimer and trimer conformers of **Pt1** in their S_0 and T_1 states computed at B3LYP-D3/def2-TZVP//B3LYP-D3/6-31G(d) level.

Pt1		ΔE_{ele}	ΔE_{exrep}	ΔE_{pol}	ΔE_{corr}	ΔE_{disp}	ΔE_{tot}	$\Delta E_{\text{tot(BSSE)}}$
Dimer		S_0 state						
	Pt1a	85.1	-33.9	0.0	-31.8	-60.6	-41.2	-38.9
	Pt1b	83.5	-34.2	0.0	-31.3	-61.0	-43.0	-39.7
	Pt1c	83.4	-34.2	0.0	-31.3	-61.1	-43.2	-40.2
		T_1 state						
	Pt1a I	89.8	-33.8	0.0	-35.0	-63.6	-42.6	-39.9
	II	90.7	-34.9	0.0	-35.0	-61.5	-40.7	-39.0
	Pt1b I	83.0	-32.7	0.0	-31.9	-61.5	-43.1	-39.3
	Pt1c I	83.0	-32.7	0.0	-31.9	-61.5	-43.1	-39.3

Trimer		S ₀ state						
Pt1a	I	165.4	-64.0	0.0	-61.9	-121.4	-81.9	-76.5
	II	163.4	-66.1	0.0	-60.3	-121.4	-84.4	-76.0
Pt1b	I	169.1	-68.1	0.0	-61.6	-124.3	-84.9	-79.4
Pt1c	I	169.0	-68.0	0.0	-61.6	-124.3	-84.9	-79.5
		T ₁ state						
Pt1a	I	180.8	-75.8	0.0	-72.6	-131.9	-99.5	-94.1
	II	160.3	-52.0	0.0	-73.2	-131.9	-96.8	-91.4
	III	179.3	-75.1	0.0	-72.6	-131.9	-100.3	-94.9
	IV	158.9	-54.8	0.0	-71.8	-131.9	-99.6	-94.2
	V	180.3	-79.0	0.0	-71.2	-131.9	-101.8	-96.4
Pt1b	I	167.8	-79.0	0.0	-62.6	-125.5	-99.3	-93.9
	II	169.8	-67.2	0.0	-62.8	-125.5	-85.7	-80.3
	III	169.7	-79.1	0.0	-62.6	-125.5	-97.5	-96.9
	IV	169.5	-69.2	0.0	-62.3	-125.5	-87.5	-82.1
	V	168.3	-81.9	0.0	-62.1	-125.5	-101.2	-95.8
Pt1c	I	167.5	-81.3	0.0	-62.0	-125.1	-100.9	-95.5
	II	167.6	-81.3	0.0	-63.0	-125.1	-101.8	-96.4
	III	170.4	-69.3	0.0	-62.2	-125.1	-86.2	-85.7
	IV	167.5	-83.2	0.0	-61.6	-125.1	-102.4	-97.0
	V	170.3	-71.2	0.0	-61.8	-125.1	-87.8	-82.4

We now analyze the origins of the extra energetic stabilization when going from dimer to trimer excimers of **Pt1a**. Type I and type III fragmentations of dimer and trimer **Pt1a**, respectively, are used to scan the potential energy curve of trimer **Pt1a** along the varying Pt···Pt bond distances (see below). The curve was built up by simultaneously elongating the two Pt···Pt bond distances from 2.9 to 5.7 Å in both the S₀ and T₁ states. The corresponding EDA ΔE_{tot} curves are illustrated in Figure 5a-b, while the individual energy contributions to ΔE_{tot} are displayed in Figure 5c-f. The first thing to note is that the potential energy profile for the dimer of **Pt1a** is analogous for both the ground (aggregate) and triplet (excimer) states, displaying minima around an interlayer distance of ca. 3.4-3.5 Å (see Figure 4a), which is in very good agreement with the interlayer distances obtained in their optimized geometries (we recall to Figure 2). Furthermore, the contributions to the ΔE_{tot} are quite the same for the S₀ and T₁ states (compare Figure 5c and Figure 5e). Conversely, the S₀ and T₁ potential energy profiles for the **Pt1a** trimer are very different (see Figure 5b). Remarkably, while the S₀ potential energy curve possesses one single minimum, the T₁ potential energy curve is more shallow and its minimum is displaced to smaller interlayer distances, in agreement with the fact that different conformers displaying very different interlayer distances (i.e., **Pt1a** and **Pt1b**) are energetically close-lying.

The EDA reveals that the contributions to the ΔE_{tot} are different for the S_0 and T_1 states (compare Figure 5d and Figure 5f). A simple comparison between the latter two figures reveals that the ΔE_{ele} term sharply increases with decreasing Pt···Pt bond distance(s) in the case of S_0 (Figure 5d) but this increase is not so remarkable for T_1 (Figure 5f). In addition, the ΔE_{exrep} and ΔE_{corr} contributions also differ. One can thus conclude that the decreased electrostatic repulsion in the **Pt1a** excimer leads to the cooperative effects observed when going from dimer to trimer excimers. These changes undoubtedly root on the feasibility of delocalizing the spin density within the three molecular units on the T_1 state of the **Pt1a** trimer through the Pt···Pt contacts (see Figure 3a), something neither observed on the other trimer conformers (**Pt1b** and **Pt1c**) nor on the dimer states. The decreased electrostatic repulsion in the triplet state for the trimer excimer of **Pt1a** (as compared to the trimer aggregate) can clearly be seen in the electrostatic potential maps, which are found in Figure S6.

Figure 5. Potential energy curves B3LYP-D3/def2-TZVP of dimer and trimer aggregates and excimers of **Pt1a** along with their Pt···Pt distances (a) total interaction energies with BSSE correction of dimer conformer of **Pt1a** in S_0 and T_1 states and (b) total interaction energies of trimer conformer of **Pt1a** in S_0 and T_1 states. GKS-EDA results in S_0 state for (c) dimer conformer of **Pt1a** and (d) trimer conformer of **Pt1a**. GKS-EDA results in T_1 state for (e) dimer conformer of **Pt1a** and (f) trimer conformer of **Pt1a**. For trimer aggregates and excimers **Pt1a**, both $Pt_A \cdots Pt_B$ and $Pt_B \cdots Pt_C$ were symmetrically distorted to build up the potential energy curves.

CONCLUSIONS

In summary, in this work we stress the importance of synergistic effects between non-covalent interactions in isoquinoliny pyrazolate Pt(II) complexes. Two main intermolecular forces drive the formation of aggregates and excimers: intermolecular $\pi \cdots \pi$ stacking interactions and Pt···Pt contacts. The cooperativity effects between non-covalent interactions drive the formation of trimer excimers through strengthened metallophilic Pt···Pt contacts; which are otherwise neither present in the dimer excimers nor in any of the ground state aggregates herein investigated. The synergistic effects are associated with a striking change in the photophysical properties when moving from very diluted solutions to concentrated dilutions or thin films, i.e., yielding red shifted-emission bands and larger photoluminescence quantum yields in the films, as we reported experimentally in our previous contribution.⁵⁹ The latter properties are beneficial towards attaining very efficient near infrared organic-light emitting diodes (OLEDs). We have performed DFT calculations in monomers, dimers and trimers aggregates and excimers to rationalize the cooperativity effects and the changes in the photophysical properties. Already the computed geometric features at some of the trimer excimers point to strong cooperativity effects when going from dimers to trimers, i.e., the interlayer distances are shortened by ca. 0.5 Å in some cases. These results agree with the computed synergetic and genuine non-additive energies. In addition, EDA calculations were performed to unravel the origins of the cooperative effects. The EDA analysis reveals that while dispersion contributions are mainly responsible for the binding energies, the subtle changes in the ΔE_{ele} contributions are responsible for the cooperative effects. These changes root on the feasibility of delocalizing the spin density in the trimers through the Pt···Pt contacts. All in all, in this work we provide some fundamental understanding on rationalizing excimer formation in isoquinoliny pyrazolate Pt(II) complexes. Future work should be devoted to study other

square-planar Pt(II) architectures. The formation of these excimers and thereto their photophysical properties can be fine-tuned by the supramolecular arrangement or by subtle changes in the environment. Thus, exerting some control on the metallophilic interactions is highly desired to attain tailored molecular design strategies for optoelectronic materials.

ASSOCIATED CONTENT

Supporting Information. Computational results for the rest of complexes (**Pt2-Pt4**) and cartesian coordinates for all equilibrium geometries of **Pt1-Pt4** (Table S1-S6, Figure S1-S4) (PDF).

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Note

There are no conflicts of interest to declare.

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The cooperative effects led to shortened Pt···Pt contacts in the trimer excimers, which are responsible for the striking changes in the emission properties of these isoquinoliny1 pyrazolate Pt(II) complexes.