

# Perylenecarboxydiimide-Gold(I) Organometallic Dyes. Optical Properties and Langmuir Films

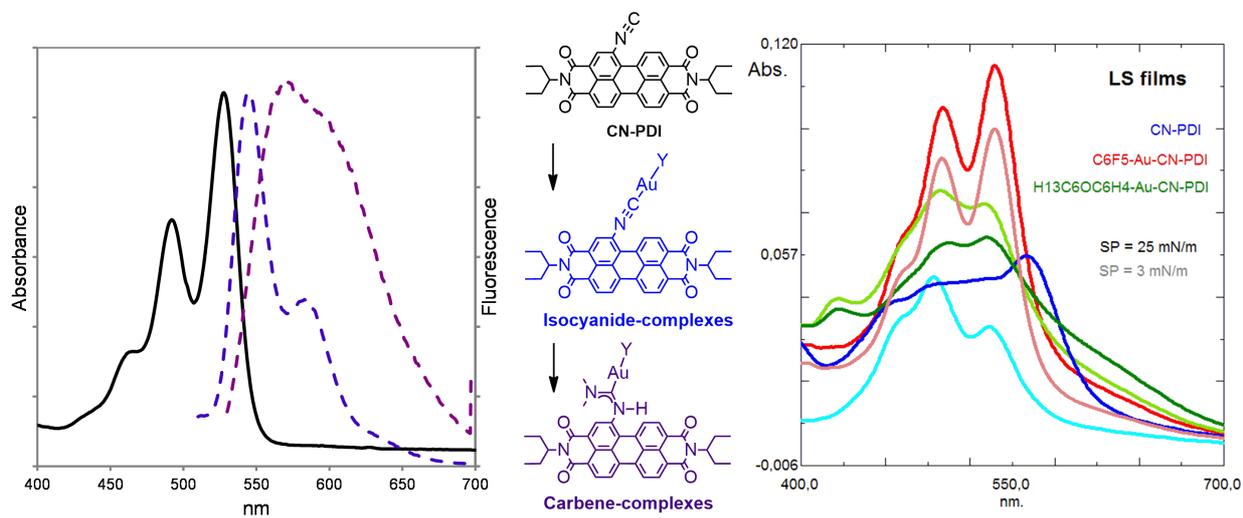
Cristina Domínguez,<sup>a</sup> María Jesús Baena,<sup>a</sup> Silverio Coco,<sup>a,\*</sup> and Pablo Espinet.<sup>a,\*</sup>

<sup>a</sup> IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Castilla y León, Spain.

e-mail addresses: [scoco@qi.uva.es](mailto:scoco@qi.uva.es) (S. Coco), [espinet@qi.uva.es](mailto:espinet@qi.uva.es) (P. Espinet)

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## Graphical abstract



# Perylenecarboxydiimide-Gold(I) Organometallic Dyes. Optical Properties and Langmuir Films

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<sup>a</sup> IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Castilla y León, Spain.

**e-mail addresses:** [scoco@qi.uva.es](mailto:scoco@qi.uva.es) (S. Coco), [espinet@qi.uva.es](mailto:espinet@qi.uva.es) (P. Espinet)

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## Abstract

A new perylenediimide-isocyanide *N,N'*-bis(1-ethylpropyl)-1-isocyanide-perylene-3,4:9,10-bis(dicarboximide) (CN-PDI), as well as the isocyanide [AuY(CN-PDI)] and carbene [Au-Y-{C(NH-PDI)(NMe<sub>2</sub>)}] (Y = Cl, C<sub>6</sub>F<sub>5</sub>, 4-C<sub>6</sub>F<sub>4</sub>OC<sub>6</sub>H<sub>13</sub>, 1/2- $\mu$ -C<sub>6</sub>F<sub>4</sub>C<sub>6</sub>F<sub>4</sub>) gold complexes therefrom, have been synthesized and characterized. All complexes are strongly colored and display fluorescence in solution associated with the perylene fragment. The influence of the metal fragment on these properties is very small in the isocyanide complexes, but more pronounced in the carbene derivatives, revealing a higher electronic connection between the metal and the PDI group in the carbene-complexes. Stable Langmuir films are formed by CN-PDI, [C<sub>6</sub>F<sub>5</sub>-Au-CN-PDI] and [H<sub>13</sub>C<sub>6</sub>OC<sub>6</sub>F<sub>4</sub>-Au-CN-PDI], in which, remarkably, by varying the compression of the films at the air/water interface it is possible to modulate the molecular orientation with respect to the subphase and the molecular arrangement in LS multi-layered films.

## 1. Introduction

Perylene diimides (PDIs) constitute a classical type of organic chromophores with remarkable stability and interesting optical and optoelectronic properties that make them suitable for a wide range of applications [1],[2], including color pigments [3], fluorescent dyes [4], optical power limiters [5], fluorescent solar light collectors [6],[7], xerographic photoreceptors [8], and optical sensors [9],[10]. In addition, the tendency of these dyes to self-assemble into supramolecular architectures [11], has been utilized for the development of functional supramolecular systems, such as liquid crystals [12], highly fluorescent J-aggregates [13], and thin films with a good molecular ordering [14],[15].

A very useful procedure to modify the properties of these dyes is the variation of substituents, especially in the bay positions, which has a pronounced influence on the electronic and optical properties of these systems [1],[16],[17]. There are many reports on the effects of introducing different types of organic substituents in the bay positions in PDIs and the structure/property relationship is relatively well established. However, the number of studies for inorganic substituents is much lower, the majority of them focusing on luminescent properties [11],[18],[19]. For example 1,7-dipalladium PDI complexes in which the two metal centers are directly connected to the perylene core through metal-carbon  $\sigma$ -bonds are highly fluorescent, revealing weak electronic interactions between the palladium centers and the PDI  $\pi$ -system [20]. In contrast, similar alkynyl platinum(II) complexes with the metal center connected to the PDI core through an alkynyl group undergo fluorescence quenching through an intersystem crossing mechanism facilitated by the strong spin-orbit coupling in the Pt-C $\equiv$ C- fragments [21].

A simple strategy to modulate the properties of PDI systems using metallic fragments is the functionalization of the perylene core in the desired position with coordinating donors groups that can act as ligands for metal complex formation. In this regard, isocyanides are versatile

ligands that form stable organometallic complexes with most transition metals. Isocyanide metal complexes are used as polymerization catalysts [22], as molecules for one-dimensional electric conductors [23], and as metallomesogens that behave as liquid crystals [24]. Furthermore, isocyanide metal complexes are precursors of carbene complexes [25], which are also catalytic systems [26], and very useful materials for therapeutic applications [27]. Surprisingly, the great potential of isocyanide derivatives has not been exploited to modulate the properties of PDI systems. Only recently, our group reported luminescent perylene derivatives functionalized with an isocyanide group, namely 3-isocyanoperylene and *N*-(2,5-di-*tert*-butylphenyl)-9-isocyanoperylene-3,4-dicarboximide, their gold(I) complexes [AuX(CNR)] (X = fluoroaryl), and their corresponding carbene derivatives [AuX{C(NEt<sub>2</sub>)(NHR)}] [28].

Related to this, Langmuir films are ideal systems for the study of the arrangement of molecules in two dimensions, the interactions that hold together the molecules in the film, and the collective properties that can appear associated to the supramolecular arrangement [29],[30]. The variety of compounds that can be studied by this technique is huge. Interestingly, in the case of films based on metal complexes, it should be possible to achieve functionalized films with properties associated to the presence of the metal such as catalytic activity [31], electric conductivity [32], magnetic properties, or just structural variations that determine the behavior of the film [33],[34],[35]. In this regard, several studies have been reported on PDIs [36],[37],[38],[39]. However, to the best of our knowledge, Langmuir films based on bay substituted organometallic PDIs, have not been reported.

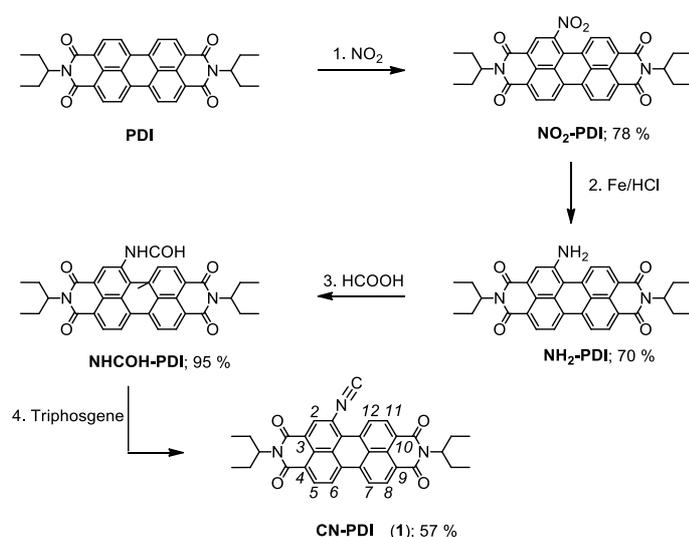
On these grounds, we decided to extend our initial study of perylene isocyanide systems to perylene diimide molecules functionalized with an isocyanide group in a bay position, their gold(I) complexes, and some carbene derivatives, aiming not only at modifying the properties of the system, but also at exploring the applicability of these organometallic systems to self-

assembling in Langmuir films. The techniques and synthetic methods used are given in the Supplementary Information.

## 2. Results and Discussion

### 2.1. Synthesis and Characterization

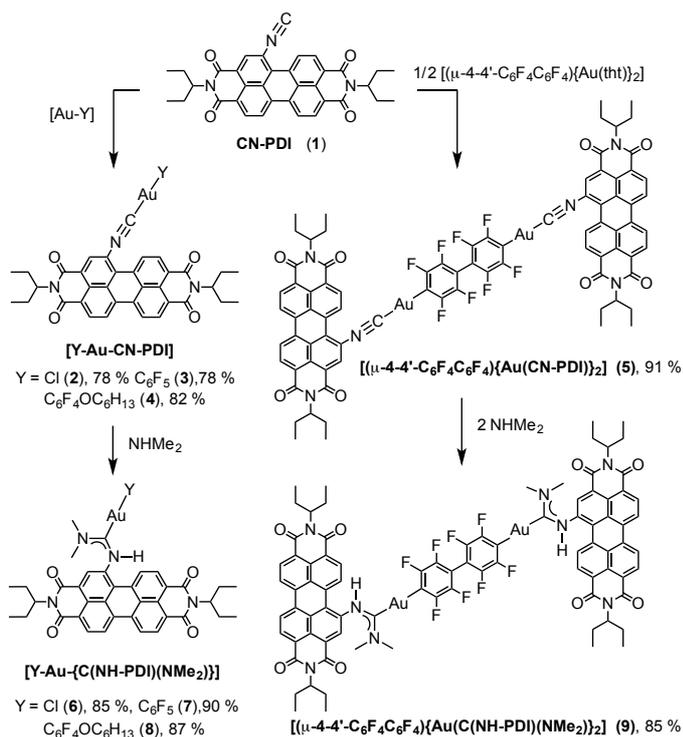
The previously unreported *N,N'*-bis(1-ethylpropyl)-1-isocyano-perylene-3,4:9,10-bis(dicarboximide) (**1**) was synthesized as depicted in Scheme 1: nitration of *N,N'*-bis(1-ethylpropyl)-perylene-3,4:9,10-bis(dicarboximide) with a saturated solution of NO<sub>2</sub>, using methanesulfonic acid as catalyst, afforded the corresponding nitro derivative [40]. The transformation of the nitro compound to the isocyanide required reduction to the corresponding amine by metallic iron in acidic medium, formylation, and finally the dehydration with bis(trichloromethyl)carbonate (triphosgene) and triethylamine [24].



**Scheme 1.** Synthesis of ligand CN-PDI (**1**). Experimental conditions: 1) NO<sub>2</sub> (saturated solution of NO<sub>2</sub> gas in CH<sub>2</sub>Cl<sub>2</sub>, methanesulfonic acid, 30 °C, 3 days. 2) THF, 65 °C, 10 min. 3) acetic anhydride, toluene, ethanol, silicagel, 40 °C, 30 min. 4) NET<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, 30 °C, 30 min.

The  $^1\text{H}$  NMR spectrum of the free ligand **1** shows a pseudodoublet at 9.65 ppm and a complex collection of signals between 8.77 and 8.67 ppm in the aromatic region, as a consequence of the overlapping of the signal of  $\text{H}^2$  and those of the three AB spin subsystems present in the molecule. The N-CH signal appears at 5.05 ppm, and the rest of the alkylic protons are observed in the range 1.94-0.92 ppm. Its FTIR spectrum in KBr shows the characteristic  $\nu(\text{C}\equiv\text{N})$  band of the isocyanide group at  $2102\text{ cm}^{-1}$ , as reported for aryl isocyanides [24].

The isocyanide complexes  $[\text{AuY}(\text{CN-PDI})]$  [ $\text{Y} = \text{Cl}$  (**2**),  $\text{C}_6\text{F}_5$  (**3**),  $\text{C}_6\text{F}_4\text{OC}_6\text{H}_{13}$  (**4**)] and  $[(\mu\text{-C}_6\text{F}_4\text{C}_6\text{F}_4)\{\text{Au}(\text{CN-PDI})\}_2]$  (**5**) were synthesized by direct reaction of **1** with the corresponding gold(I) precursor  $[\text{AuCl}(\text{tht})]$  [41],  $[\text{Au}(\text{C}_6\text{F}_5)(\text{tht})]$  [41], or  $[\text{Au}_2(\mu\text{-C}_6\text{F}_4\text{C}_6\text{F}_4)(\text{tht})_2]$  [42], as depicted in Scheme 2. The IR spectra of the gold complexes exhibit a  $\nu(\text{C}\equiv\text{N})$  absorption for the isocyanide group at higher wavenumbers than for the free ligand, as a consequence of coordination [43]. The  $^1\text{H}$  NMR spectra are all similar to that of the isocyanide ligand discussed above.  $^{19}\text{F}$  NMR spectra of complexes **3–5** show the typical pattern of the perfluorophenyl groups [43]. Complex **3** displays three signals corresponding to the AA'MXX' spin system (-115.8, -156.7 and -162.2 ppm), complex **4** shows two slightly distorted doublets (-118.2 and -157.6 ppm) flanked by two pseudotriplets (AA'XX' spin system with  $J_{\text{AA}'} \approx J_{\text{XX}'}$ ), and the dinuclear complex **5** shows two multiplets (-116.9 and -139.8 ppm) corresponding to  $\text{F}_{\text{ortho}}$  and  $\text{F}_{\text{meta}}$  respectively.

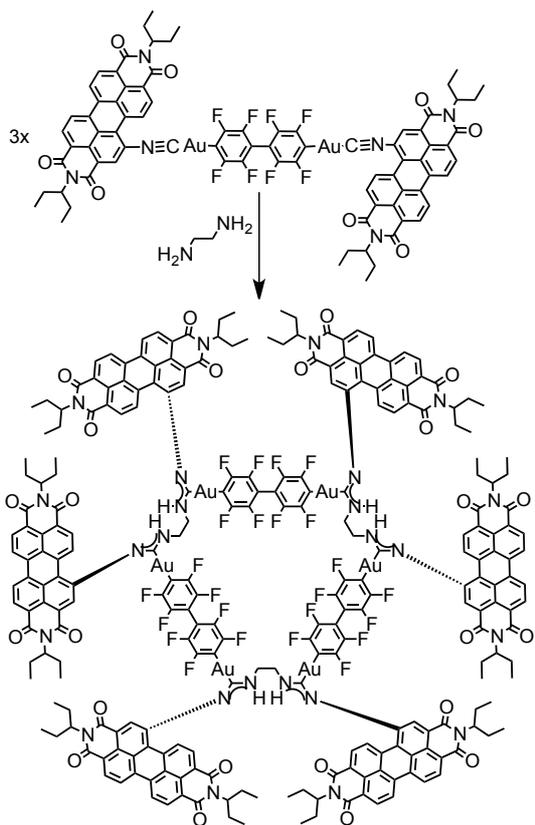


**Scheme 2.** Synthesis of isocyanide complexes **2–5**

The gold carbene complexes **6–9** were prepared, as reported for similar cases [44], by nucleophilic attack with dimethylamine to the coordinated isocyanide group (Scheme 2). Their FTIR spectra showed the disappearance of the  $\nu(C\equiv N)$  band and the appearance of  $\nu(N-H)$  ( $3450\text{--}3250\text{ cm}^{-1}$ ) and  $\nu(C=N)$  ( $1550\text{--}1510\text{ cm}^{-1}$ ) carbene absorptions. The latter absorption appears overlapped with bands of the PDI moiety [45], which prevented unequivocal assignment. <sup>1</sup>H NMR spectra are analogous to those of the isocyanide parents but showing two additional signals characteristic of the carbene fragment: a singlet from the amine proton, in the range 9.27-9.73 ppm, and two singlets (at *c.a.* 3–4 ppm) from the amine methyls. The unequivocal assignment of the amine proton and the perylene proton H<sup>2</sup> (8.75–8.86 ppm) has been done using heteronuclear multiple quantum correlation (HMQC) 2D experiments (see Figure S11 in SI). The <sup>19</sup>F NMR spectra are similar to those of isocyanide precursors. Although two

isomers are possible, depending on the arrangement of the perylene group relative to the gold fragment, only one isomer was observed by  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra at room temperature. Its structure most likely corresponds to the less hindered isomer (depicted in Scheme 2), as found in related systems [46].

In addition to the carbene-complexes described above, we decided to explore the reactivity of the dinuclear derivative **5** towards a diamine in order to obtain a cyclic structure with several metallic centers and PDIs, reminiscent of the macrocycles bearing three or more PDI units found in the literature [47]. The reaction was carried out with **5** and ethylenediamine in 1:1 molar proportion to favor the cyclization (Scheme 3). The formation of the carbene-complex **10** was confirmed by FTIR. Its  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra are similar to those of the dinuclear carbene-complex **9**. Analysis of **10** by mass spectrometry (MALDI-TOF) was not useful due to the fragmentation of the molecule in the conditions of the experiment, but the molecular weight determined by vapor pressure osmometry supported its hexanuclear nature (molecular weight calculated for  $\text{C}_{252}\text{H}_{192}\text{N}_{24}\text{Au}_6\text{F}_{24}\text{O}_{24}$ : 5578.21 g/mol; found: 5470 g/mol). In addition, the presence of a unique product was verified by a diffusion NMR experiment (DOSY) in deuterated THF, where all the signals showed the same diffusion coefficient (Fig. S12 in SI). Furthermore, as discussed later, complex **10** displays a high extinction coefficient (six times higher than **7**), because of its oligomeric structure.



**Scheme 3.** Synthesis of the hexanuclear carbene-complex **10**.

## 2.2. Photophysical studies.

The UV-Vis absorption and fluorescence data for the free isocyanide **1**, the Au<sup>I</sup> complexes **2–5** and the carbene-complexes **6–10**, in dichloromethane or tetrahydrofuran solution, are summarized in Table 1. All the spectra were registered at high dilutions ( $10^{-6}$ – $10^{-7}$  M) to avoid autoabsorption phenomena induced by molecular aggregation [48].

**Table 1.** Electronic Absorption ( $\lambda_{ab}$ ) and Fluorescence Maxima ( $\lambda_{ex}$ ,  $\lambda_{em}$ ), Fluorescence Quantum Yields ( $\Phi_{FI}$ ) and Fluorescence Lifetimes ( $\tau$ ) for **1–5** in CH<sub>2</sub>Cl<sub>2</sub> and for **6–10** in THF solution.

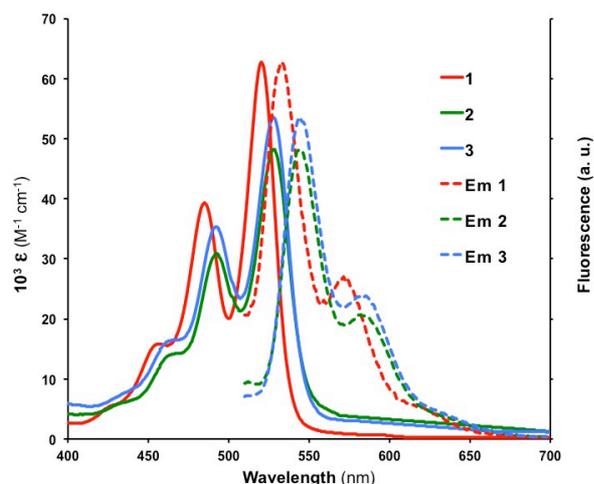
Comp	$\lambda_{ab}/\text{nm}$	$\lambda_{ex}/\text{nm}$	$\lambda_{em}/\text{nm}$	$\Phi_{FI}$	$\tau^c/\text{ns}$
	( $10^3 \text{ } \epsilon/\text{M}^{-1}\text{cm}^{-1}$ )				
<b>1</b>	520 (62.3)	482	530	$0.50 \pm 0.03^a$	4.15 (1.088)

<b>2</b>	527 (48.3)	489	541	$0.51 \pm 0.07^a$	4.59 (1.181)
<b>3</b>	527 (53.6)	489	541	$0.50 \pm 0.04^a$	4.77 (1.118)
<b>4</b>	528 (59.1)	489	539	$0.67 \pm 0.04^a$	4.82 (1.190)
<b>5</b>	528 (91.0)	489	541	$0.50 \pm 0.04^a$	4.84 (1.155)
<b>6</b>	522 (37.0)	487	590	$0.15 \pm 0.0^b$	3.74 (1.117)
<b>7</b>	523 (52.4)	488	569	$0.10 \pm 0.01^b$	3.72 (1.138)
<b>8</b>	521 (50.0)	487	585	$0.11 \pm 0.01^b$	3.59 (1.111)
<b>9</b>	522 (39.0)	504	559	$0.21 \pm 0.02^b$	4.07 (1.212)
<b>10</b>	522 (171.7)	483	575	$0.10 \pm 0.01^b$	4.60 (1.129)

<sup>a</sup> Determined in chloroform relative to *N,N'*-bis(1-hexylheptyl)-3,4:9,10-perylene-bis(dicarboximide) in ethanol ( $\Phi_{\text{Fl}} = 0.99$ ) and using an excitation wavelength of 487 nm. <sup>b</sup> Determined in chloroform relative to Rhodamine B in ethanol ( $\Phi_{\text{Fl}} = 0.70$ ) and using an excitation wavelength of 510 nm. <sup>c</sup>Fluorescence lifetimes; numbers in parentheses indicate the  $\chi^2$  parameter.

The electronic absorption spectra of the free isocyanide and its gold complexes are all very similar, displaying a very structured spectral pattern with absorption bands and extinction coefficients typical of bis(*N*-ethylpropyl)perylene-carboxydiimide [12]. The coordination of the isocyanide ligand to the metal center produces a slight bathochromic shift (7–8 nm), in accordance with the higher electron withdrawing character of the coordinated isocyanide group on the perylene core [1],[14].

The free isocyanide and its gold complexes are luminescent at room temperature in dichloromethane solution. As for their electronic spectra, all the emission spectra are similar, showing a very structured pattern with the maximum appearing in the range 530–541 nm. Their lifetimes and quantum yields, as well as the small Stokes shift, are typical of fluorescent perylene-carboxydiimides (Figure 1).



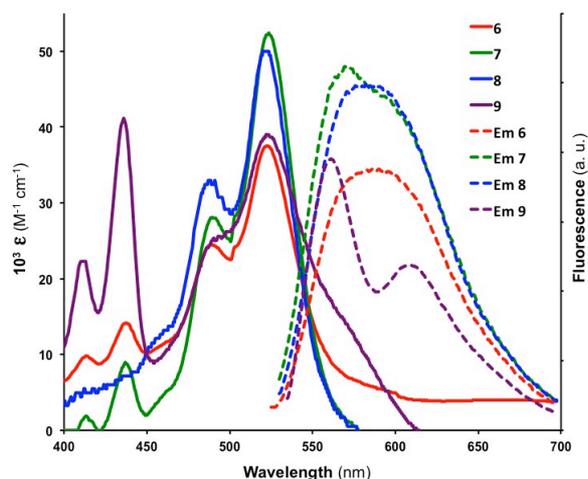
**Figure 1.** UV-vis absorption (solid line) and emission spectra (dashed line) for compounds **1**, **2** and **3** in  $\text{CH}_2\text{Cl}_2$  ( $10^{-6}$  M) as representative examples.

The limited influence of the metal on the emission spectra indicates that the participation of the metallic fragment in the transitions is small, and that the coordination of the metal to the ligand CN-PDI does not significantly distort the planarity and rigidity of the chromophore [49].

The intensity of the emission was almost completely lost in the solid state (KBr dispersion), both at room temperature and at 77 K. Most likely this behavior is due to reabsorption effects, often found in chromophores with a small Stokes shift and high ability for aggregation [49],[50].

Concerning the carbene complexes, the spectroscopic data for compounds **6–10** are collected in Table 1 and in Figure 2. The absorption spectra of the carbene-complexes display  $S_0-S_1$  absorption bands similar to those of their isocyanide precursors, but in this case the bands undergo a broadening and a slight hypsochromic shift (2–4 nm). These differences reveal a lower planarity, and consequently lower molecular symmetry of the perylene core, compared with the corresponding isocyanide complex, caused by the more sterically demanding carbene substituent in a bay position. In accordance with this structural distortion, the carbene complexes display a second absorption band at around 400 nm that is attributed to the transition from the ground state

to a higher excited state ( $S_0$ – $S_2$ ) [51]. These transitions are forbidden for unsubstituted PDIs, but in bay-substituted PDIs with a twisted core it becomes partially allowed and can be observed [52].



**Figure 2.** UV-vis absorption (solid line) ( $10^{-6}$  M solutions in THF) and emission spectra (dashed line) ( $10^{-7}$  M solutions in THF) of carbene complexes **6–9**.

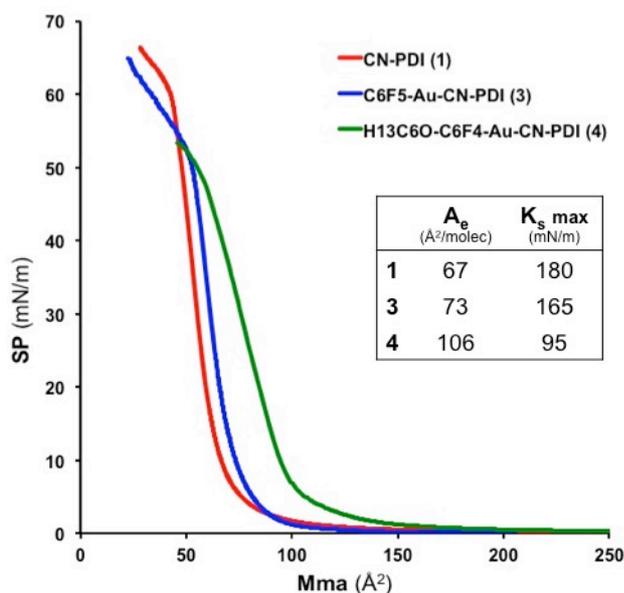
Similar to the isocyanide complexes, the carbene derivatives show an intense fluorescence emission band associated to their  $S_0$ – $S_1$  absorption bands, but in this case the vibronic structure is lost (except for complex **9**) and a marked bathochromic shift is observed. The emission maxima increases in the order  $\mathbf{9} < \mathbf{7} < \mathbf{8} < \mathbf{6}$  in accordance to the electron-withdrawing ability of the metallic fragment [AuX] on the perylene moiety, which varies in the opposite order:  $C_{12}F_8 > C_6F_5 > C_6F_4OC_6H_{13} > Cl$ . The Stokes shifts have values  $\sim 2000\text{ cm}^{-1}$  (except for **9**, which maintains a shift below  $500\text{ cm}^{-1}$ ), much higher than the values of the isocyanide parents ( $455$ – $525\text{ cm}^{-1}$ ). A marked decrease of the quantum yields with respect to those of **1–5** (Table 1) is produced. This behavior is likely due to a photoinduced electron transfer effect (PET) involving

the carbene moiety on the fluorophore [53]. This result evidences a higher electronic influence of the metal-carbene fragment on the electronic density of the PDI group than the metal-isocyanide fragment, thus varying the photophysical properties of the PDI.

Finally, in the solid state, the fluorescent emission results deactivated, even at low temperature (77 K), as above discussed for the isocyanide complexes.

### 2.3. Fabrication of Langmuir and Langmuir-Schaefer thin films.

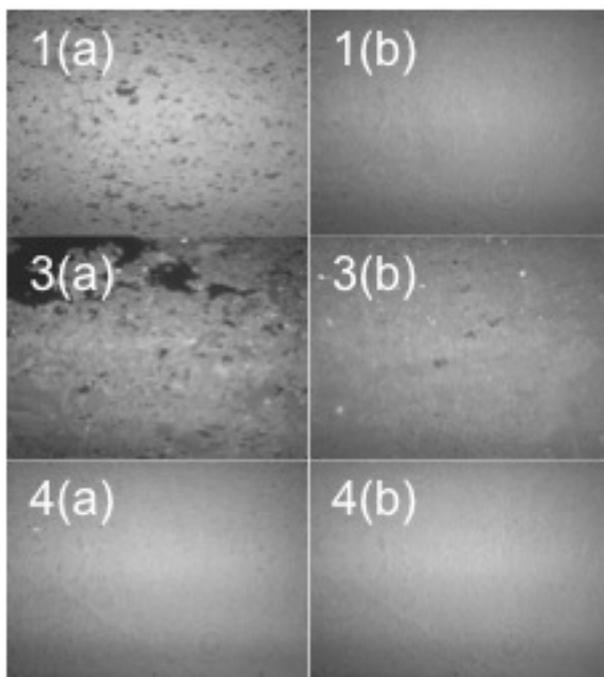
Considering the self-organizing properties of perylene derivatives, we decided to study their ability to form thin films. Compounds **1**, **3** and **4** were chosen for this study in order to compare the behavior of the free isocyanide CN-PDI with that of the Au-perfluorophenyl derivatives. The three compounds form Langmuir films at the air-water interface. The isotherms obtained at  $20 \pm 1$  °C, the molecular areas extrapolated to zero surface pressure ( $A_e$ ), and the maximum value of the Young modulus ( $K_s$ ) are shown in Figure 3.



**Figure 3.** Isotherms of the Langmuir films of compounds **1**, **3** and **4**. Inset: values of the calculated  $A_e$  (molecular area extrapolated to zero) and maximum Young modulus,  $K_s$ .

The three isotherms show collapse pressures around 40–60 mN/m that indicate a good cohesion of the molecules in the film and a good anchorage to the water surface. The Young modulus ( $K_s$ ) increase as the surface pressure increases, reaching their maximum values ( $K_{s\text{ max}} = 180$  mN/m for the free isocyanide **1**, 165 mN/m for **3**, and 95 mN/m for **4**), and then falling to zero once the collapse is produced. These  $K_{s\text{ max}}$  values indicate that the floating films of **1** and **3** are in a liquid condensed phase (LC) while the film of **4** with a clearly lower Young modulus, is in a liquid intermediate phase (I) [54]. This variation reveals that the films of the gold complexes are less rigid than that of the free isocyanide ligand. This is most likely due to higher steric hindrance of the organometallic fragment (especially in the case of compound **4** containing an additional alkoxylic chain), which to some extent hinders self-assembling process in the system and consequently reduces the film cohesion.

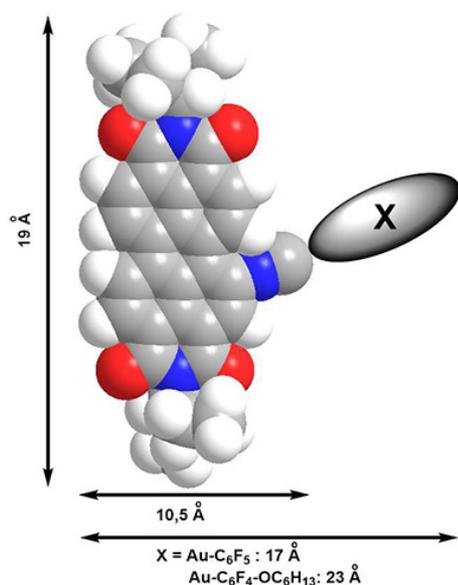
In accordance with these results, **1** and **3** start forming the film at a similar molecular area, much lower than **4** does. In this respect, the Brewster's angle microscopy (BAM) images (Figure S13 in SI) show that at low SP (1–3 mN/m) **1** and **3** exhibit not unified aggregates but, as the compression increases, a homogeneous film is formed until the collapse. In the case of **4**, a continuous and homogeneous monolayer is observed from the initial stages of the film formation (Figure 4). Thus, it seems that the alkoxylic chain prevents the intermolecular interactions in **4** from being as strong as in **1** or **3**, hence the film formed by **4** has the lowest stiffness and is the only one in the series showing reversible isotherms, at least up to a SP = 10 mN/m (Fig S14 in SI).



**Figure 4.** BAM micrographs for compounds **1**, **3** and **4** at (a) SP = 3 mN/m and (b) SP = 30 mN/m.

The studies on Langmuir films at the air-water interface formed by PDIs substituted only in the amide position are coincident in proposing an anchorage to water of the carboxidiimide edge of the substituted perylene, with the molecules self-assembled in the film through  $\pi$ - $\pi$  interactions and the molecular plane making an angle to the perpendicular to the surface [36],[37],[38],[39]. The compounds reported here also fit well in this model (Figure 5) [55]. We have considered a molecular thickness of 3.4 Å for the  $\pi$ - $\pi$  stacking [36]. Moreover, we have chosen as the anchored side of the perylene the half that bears the isocyanide substituent because the electronic influence of the cyanide should somewhat increase the proton acceptor character of that carboxidiimide edge. This effect will be enhanced upon coordination to the metal fragment. Note also that the asymmetry created by the substituent in the perylene bay position allows for different stacking arrangement of the substituent in contiguous perylenes (coincidence in a

eclipsed arrangement, alternation scattering the successive substituents, or random), but our data do not allow to draw conclusions about this.

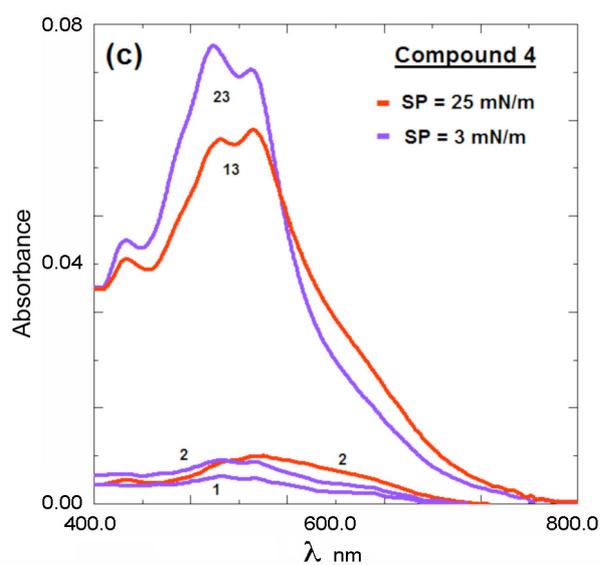
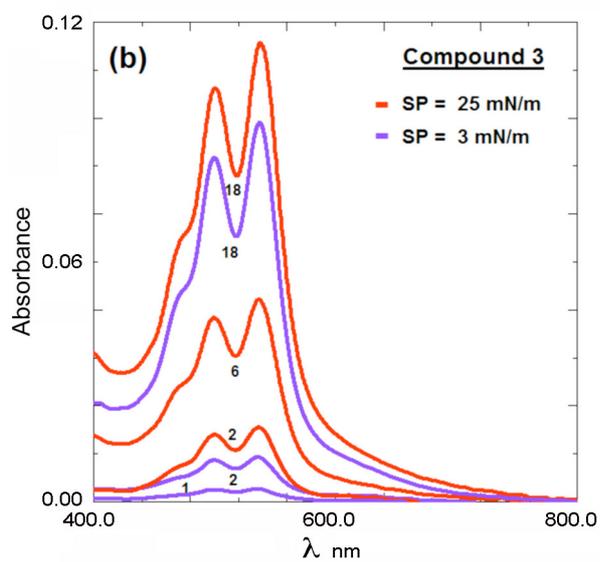
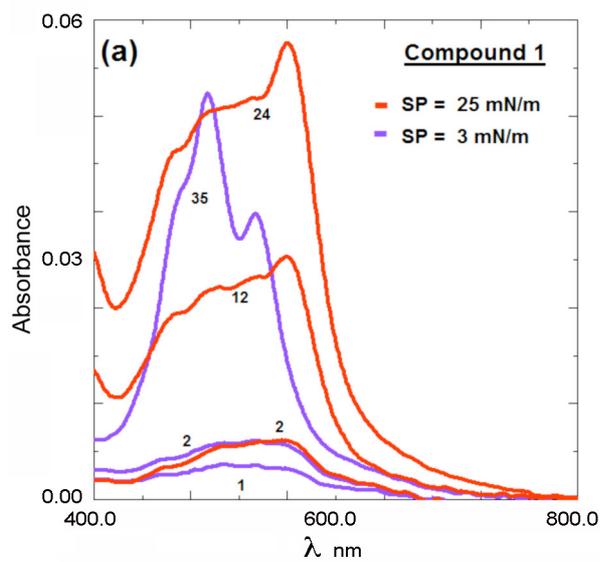


**Figure 5.** Molecular model for compounds **1**, **3** and **4**, and its relevant dimensions. X represents the metal fragment bonded to the isocyanide group, only for **3** and **4**.

The molecular area ( $A_e$ ) found for **1** (substituent X does not exist in this case) is  $\sim 67 \text{ \AA}^2$ , which is smaller than the molecular area ( $199 \text{ \AA}^2$ ) calculated on the basis of the space-filling model depicted in Figure 5. The effective molecular area would be  $\sim 36 \text{ \AA}^2$  ( $10.5 \text{ \AA} \times 3.4 \text{ \AA}$ ) if the molecules were oriented perpendicularly to the water surface. Since the observed area is  $67 \text{ \AA}^2$ , the molecules in a head-on disposition should be tilted over the subphase, by an angle of ca.  $58^\circ$  with respect to the normal to the subphase. Similarly, for compounds **3** and **4**, the molecular areas found ( $73 \text{ \AA}^2$  for **3** and  $106 \text{ \AA}^2$  for **4**) are much smaller than the area occupied by the molecules laying flat on the subphase, but larger than the effective molecular area for a perpendicular disposition ( $58 \text{ \AA}^2$  for **3** and  $80 \text{ \AA}^2$  for **4**). These results suggest that the molecules, anchored head-on, should be tilted by ca.  $38^\circ$  and ca.  $42^\circ$ , respectively, relative to the normal to the subphase. This disposition should give dense films with high cohesion, as observed.

Although often the LB method is the best for one for transferring the floating film to a substrate with a good preservation of the molecular order, in our case it was not efficient and only the first monolayer of **4** could be satisfactorily transferred (transfer ratio TR = 1). Similar to other PDIs [56],[57], the LS horizontal lifting method proved more adequate to form a multilayered film, reaching TRs values in the range 0.7–0.4 for **1**, 0.9–0.7 for **3** and 1–0.9 for **4**, depending on the conditions.

The analysis by electronic spectroscopy of the monolayer transferred to a solid substrate can also give information on the molecular organization, since different types of aggregates lead to different spectral shifts. The absorption spectra corresponding to the LS films of compounds **1**, **3** and **4** obtained by different numbers of depositions (number of liftings) and different grade of film compression (SP = 25 or 3 mN/m) are shown in Figure 6.



**Figure 6.** Absorption spectra of the LS films of a) **1**, b) **3** and c) **4**, deposited at SP = 25 mN/m and SP = 3 mN/m. The numbers close to the curves indicate the number of liftings done to prepare the film.

The absorption spectra of the perylenes in the solid state can be explained by the molecular exciton model [58]. The bathochromic shift with respect to the absorption in solution is due to intermolecular interactions leading to J-type aggregates (in-line aggregation, columnar aggregates with large tilted stacks) while the hypsochromic shift is due to the formation of H-type aggregates (cofacial aggregation, columnar aggregates with a small slippage angle). In both cases, the existence of other intermediate situations causes the observation in the spectrum of, in theory, forbidden bands [59]. The absorption can be also related to the strength of the intermolecular interactions. When the interactions are strong, the absorption band extends from 400 to 700 nm. As the molecular interactions get weaker, the long wavelength component decreases [8].

Taking all this into account, when the deposition of **1** is carried out under a film compression corresponding to a SP = 25 mN/m (Figure 6a), the LS film displays a broad absorption peak in the range 400 nm–650 nm, with the absorption maximum at 575 nm (bathochromic shift = 60 nm) that confers a purple shade to the multilayer film (J-aggregate). In contrast, when the floating film was transferred at a lower grade of compression (SP = 3 mN/m), the absorption maximum shows a clear blue shift (40 nm) revealing the formation of a face-on aggregate (H-aggregate). Therefore, varying the compression of the films at the air/water interface it is possible to modulate the formation of aggregates H or J, and consequently the final properties of the transferred films.

For compound **3** (Figure 6b), the spectral absorption pattern is independent of the compression on the floating film or the number of transferred layers. This band-splitting, compared with the absorption spectra in solution, is typical of systems in which the transition dipoles are oblique and forming such an angle ( $\beta$ ) that two  $S_0-S_1$  transitions are allowed [59]. The different intensity of the two bands depends on the orientation angle  $\beta$  [60]. Here, the intensity ratio is maintained in a value of  $1.11 \pm 0.01$ , thus giving a  $\beta$  angle of *ca.*  $87^\circ$ . Probably this fact is a consequence of preference that gold complexes [AuX(CNR)] (X = halogen, fluoroaryl) show for crossed type arrangement of molecules through intermolecular aurophilic interactions [43],[61].

Concerning the spectra of **4** LS films at two different deposition pressures (Figure 6c), they are less structured but both show two maxima at the same wavelengths, although with changed intensities: more intense the band at lower wavelength for the lower compression, and more intense the band at higher wavelengths for lower compression. These differences are moderate, but sufficient to appreciate a change in the color shade of the multi-layered films. Independently of the compression, the spectra show a hypsochromic shift with respect to the monomer in solution. This supports that H-type aggregates are predominant.

In summary, a color control dependent on the deposition pressure can be clearly achieved for the free CN-PDI ligand, while the CN-PDI complexes have this ability restricted to some extent due to the concurrence of other intermolecular interactions in addition to the  $\pi$ - $\pi$  stacking in the solid state. These results show how the intrinsic aggregation tendency of the perylenediimides can be modulated by the coordination of a metal fragment. Thus, the combination of the deposition pressure with the type of metal fragment present in the perylene system opens the possibility of preparing a rich diversity of nanostructured films.

### **3. Conclusions**

In this work, a new isocyanide ligand, *N,N'*-bis(1-ethylpropyl)-1-isocyanide-perylene-3,4:9,10-bis(dicarboximide) (CN-PDI), in which the rich reactivity of the isocyanide group and the chromonic properties of the PDI are combined, allows its complexation with chloro- and perfluoroaryl-Au<sup>I</sup> fragments, leading to the corresponding isocyanide-complexes that further react with methylamine to afford their carbene-complexes. These molecular structures are unprecedented.

Photophysical studies show that neither the isocyanide group nor the metallic fragment affect the planarity and electronic density of the perylenic moiety, and the visible absorption and the emission of the compounds in solution are almost the same as for the unsubstituted PDI. On the contrary, the carbene-complexes show marked differences in the emission, indicating that both the carbene group and the metallic fragment are interacting electronically with the PDI. All these compounds are highly colored and have intense fluorescent emissions in solution. In the solid state, the emission was lost due to aggregation effects.

Finally, the ability of some of these molecules to form thin films was also evaluated showing that the CN-PDI ligand and the [C<sub>6</sub>F<sub>5</sub>-Au] and [H<sub>13</sub>C<sub>6</sub>O-C<sub>6</sub>F<sub>4</sub>-Au] substituted CN-PDI form stable Langmuir films at the air-water interface. The molecular disposition in the monolayer is tilted head-on. The transfer of these floating monolayers to a solid substrate in order to obtain nanostructured multi-layered films was possible by the Langmuir-Schaefer horizontal deposition method and their electronic absorption spectra reveal that the molecular aggregation in the films could be controlled, to some extent, through the deposition pressure.

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### Supplementary Information

Techniques and synthetic methods. Synthesis and Characterization data for compounds **1** – **10**.

NMR spectra. Additional BAM images. Additional Langmuir isotherms. Absorption spectra of drop-cast films. Fluorescence decays for **1** and **3** and **7**.

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