

Correspondence: Prof. P. Espinet

Synergistic π - π and Pt-Pt interactions in Luminescent Hybrid Inorganic/Organic Dual Columnar Liquid Crystals

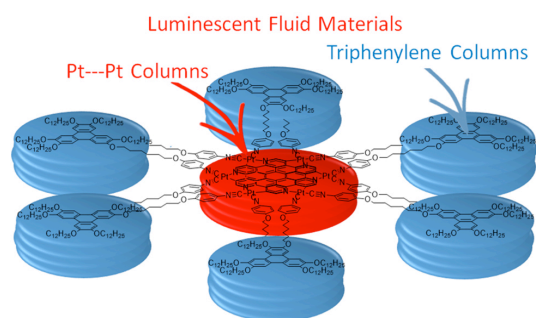
*Emiliano Tritto,^a Rubén Chico,^a Josu Ortega,^b César L. Folcia,^c Jesús Etxebarria,^c Silverio Coco,^{*a} and Pablo Espinet.^{*a}*

^a IU CINQUIMA/Química Inorgánica, Facultad de Ciencias, Universidad de Valladolid, 47071 Valladolid, Castilla y León, Spain. ^b Department of Applied Physics II, ^c Condensed Matter Physics, University of the Basque Country, UPV/EHU, 48080 Bilbao, Spain.

Electronic Supplementary Information (ESI) Available: Materials and methods. Full details of synthetic methods, spectroscopic data and analytical data for the new compounds.

Table of contents

Hybrid Inorganic/Organic dual columnar materials displaying aggregation-induced enhanced phosphorescence based on inter-disk Pt---Pt interactions in a fluid state.



Abstract

A new triphenylene-isocyanide CN-C₆H₄-O-(CH₂)₆-TriPh, non mesogenic, and their *ortho*-metalladated benzoquinolate (bzq) complexes, [M(bzq)X(CN-C₆H₄-O-(CH₂)₆-TriPh)] (M = Pd, Pt; X = Cl, I) and [Pt(bzq(CN-C₆H₄-O-(CH₂)₆-TriPh)₂]A (A = NO₃⁻, BF₄⁻, PF₆⁻), all displaying a columnar mesophase, have been prepared. The structure of the mesophase, determined by X-ray diffraction methods, is uncommon and consists of a central column formed by stacking of the organometallic benzoquinoline-platinum fragments, surrounded by six columns in hexagonal disposition formed by stacking of the triphenylene groups. These materials show aggregation-induced phosphorescence based on inter-disk Pt···Pt interactions.

Introduction

Since the discovery of discotic LCs by Chandrasekhar *et al.* in 1977,¹ the development of these nanostructured materials has been enormous.² They present unique electronic and optoelectronic properties that make them suitable for a wide range of potential applications such as conductive devices,³ field-effect transistors, or photovoltaic solar cells.^{4,5,6,7,8,9} They are also commercially applied as negative birefringence films used to improve the viewing angle of commonly used liquid crystals displays.^{10,11}

The vast majority of discotic liquid crystals display columnar mesophases leading to an effective space fill supported by different non-covalent intermolecular interactions. The challenge to design and prepare, in a rational way, functional structures and materials is to gain control on the physical properties of the supramolecular arrangement. Many systematic studies on the influence of the molecular constitution and stacking on the mesomorphism have been reported for organic liquid crystals.^{5,12,13,14,15} There are also studies on metal-containing liquid crystals (metallomesogens).¹⁶ It is important to note that metallomesogens can display intermolecular interactions additional to those existing in purely organic systems. In this regard, it is well

established that metallophilic interactions play a key role in the crystalline packing of some metal complexes,^{17,18,19,20,21,22,23,24} in their self-assembling in solution,^{25,26,27} and in the formation of liquid crystalline phases.^{28,29,30}

In this respect we are interested in developing columnar materials able to support of metal-containing molecular fragments in the periphery of the organic columns responsible for the basic self-organization.^{31,32} Depending on the type and distribution of the metal fragments, new or modified properties are hoped for the aggregate. For instance metal–metal interactions along the columnar direction might induce luminescence, as reported for platinum complexes,^{28,29} or electric one-dimensional conductivity along the stacked metal fragments. A specially interesting discoid organic system favorable to our purpose is the triphenylene group, which is prone to induce columnar mesophases and can be easily functionalized with donor groups able to coordinate metal-containing fragments to the system.^{4,33} There are already a few reports of liquid crystalline metal-organic triphenylene systems with covalently bonded Hg,³⁴ Cr⁰,³⁵ Zn^{II},³⁶ Cu^{II} and Ni^{II},³⁷ Ag^I,³⁸ or Pt complexes.³⁹

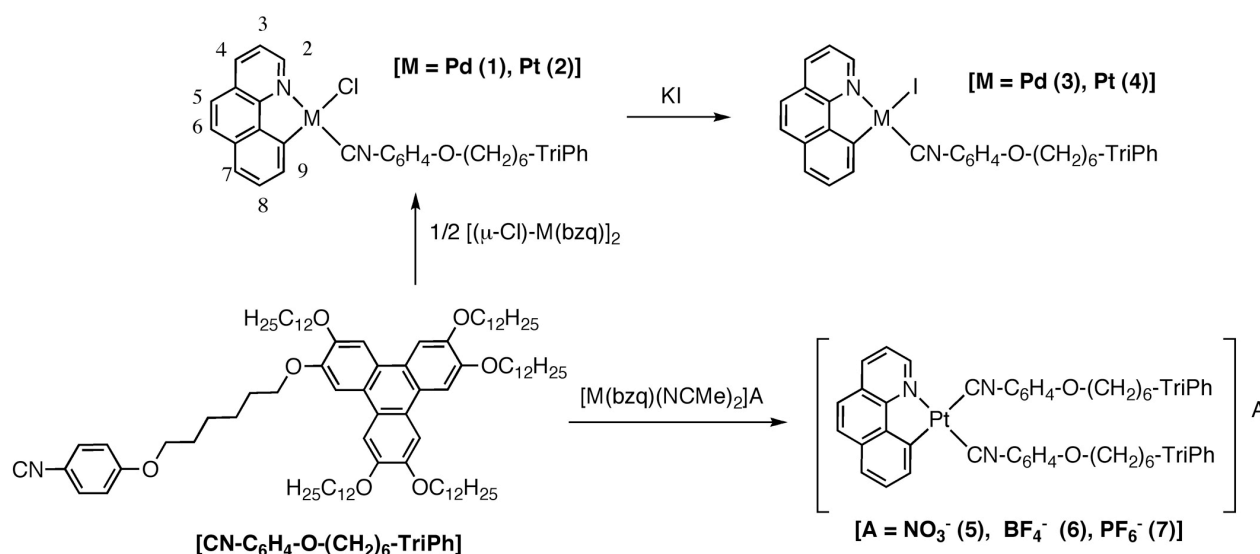
Recently we have reported a family of liquid crystalline mono and dinuclear orthometallated palladium complexes that display very interesting columnar mesophases close to ambient temperature.⁴⁰ Their structures contain columnar packing of triphenylene moieties that support an independent stack of metal fragments. Therefore, an accumulation, in a fluid material, of Pd-containing columnar zones in a sea of fully organic columns has been induced, although the disks of the Pd-containing columns are not associated through metal–metal interactions. In this occasion we use benzoquinolate (bzq) platinum moieties, which are known to pile up in the solid state, as well as their Pd similar complexes, because the Pt complexes are known to display Pt··Pt interactions in the solid state.^{41,42} We were glad to see that the cationic benzoquinolate platinum(II) complexes with 2-(6-(4-isocyanophenoxy)hexyloxy)-3,6,7,10,11-

pentakis(dodecyloxy)triphenylene reported here display luminescence supporting that its columnar arrangement in the mesophase is reinforced by inter-disc Pt···Pt interactions.

Results and Discussion

Synthesis and Characterization

2-(6-(4-isocyanophenoxy)hexyloxy)-3,6,7,10,11-pentakis(dodecyloxy)triphenylene (**CN-C₆H₄-O-(CH₂)₆-TriPh**), which has not been reported yet, was synthesized by conventional methods,^{43,44} starting from the corresponding nitro derivative.⁴⁰ First direct transformation into the N-formamide by reduction with powder tin and formic acid, and subsequent dehydration with triphosgene (“bis(trichloromethyl)-carbonate”) and triethylamine. Details are given in the experimental section.



Scheme 1. Synthesis of palladium and platinum complexes.

The IR spectrum of **(CN-C₆H₄-O-(CH₂)₆-TriPh)** shows a strong $\nu(\text{CN})$ absorption for the isocyanide group at 2122 cm^{-1} , as reported for similar aryl isocyanides.⁴⁵ Its ¹H NMR spectrum shows, as expected, an AA'XX' spin system for the aryl protons of the isocyanide group and a singlet for the triphenylene core. In addition, a multiplet and a triplet are observed in the range

4.2-3.9 ppm, corresponding to the first methylene groups of the alkoxy moieties. The remaining chain hydrogen atoms appear overlapped in the range 1.9-1.3 ppm.

The isocyanide complexes were synthesized as depicted in Scheme 1. Elemental analyses, yields, relevant IR data and ^1H NMR spectra for the complexes are given in the experimental section. The IR spectra of the metal complexes exhibit $\nu(\text{CN})$ absorptions for the isocyanide group at higher wavenumbers than for the free ligand, as a consequence of coordination.⁴⁵ Neutral monoisocyanide complexes **1-4** display one $\nu(\text{CN})$ absorption band,⁴¹ while ionic bisisocyanide derivatives **5-7** show two $\nu(\text{CN})$ absorption bands, as expected for two terminal isocyanide ligands in a *cis* arrangement.⁴² In the IR spectra of **5-7** a strong and broad band appears corresponding to the anions: at 1050 cm^{-1} for BF_4^- , 1350 cm^{-1} for NO_3^- and 840 cm^{-1} for PF_6^- .⁴⁶ The ^1H NMR resonances associated to the triphenylene isocyanide ligand are all similar to those of the free isocyanide ligand discussed above. It is worth noting that coordination of the isocyanide produces only a slight deshielding mainly for aromatic protons in *ortho* positions to the isocyanide group (ca. 0.3 ppm for the neutral complexes and ca. 0.5 ppm for the cationic derivatives). In addition the ^1H NMR spectra exhibit the expected signals for the benzoquinoline group.⁴²

Mesomorphic behavior.

The free isocyanide ligand used and the mono-isocyanide complexes are not mesomorphic, but all the bis-isocyanide cationic derivatives show mesomorphic behavior at room temperature. Optical, thermal and thermodynamic data of the compounds, obtained by polarized optical microscopy (POM), differential scanning calorimetry (DSC), and X-ray scattering, are collected in Table 1.

Table 1. Optical, thermal and thermodynamic data of complexes.

Compound	Transition ^a	Temperature ^b (°C)	ΔH^b (kJmol ⁻¹)
CNR	C→I	49	81.6
[Pd(bzq)Cl(CNR)] (1)	C→I	36	28.9
[Pt(bzq)Cl(CNR)] (2)	C→I	34	13.0
[Pd(bzq)I(CNR)] (3)	C→C'	32	32.4
	C'→I	75	26.0
[Pt(bzq)I(CNR)] (4)	C→C'	34	20.2
	C'→I ^c	66	34.8
[Pt(bzq)(CNR) ₂]NO ₃ (5)	C→Col _h	28	5.8
	Col _h →I ^d	92	1.3
[Pt(bzq)(CNR) ₂]BF ₄ (6)	C→Col _h	-9.3	27.0
	Col _h →I	155	22.7
[Pt(bzq)(CNR) ₂]PF ₆ (7)	C→Col _h	-9.0	18.9
	Col _h →I	143	21.5

^aCol_h columnar hexagonal; I, isotropic liquid; C, C' crystals. ^bData collected from the second heating DSC cycle. The transition temperatures are given as peak onsets. ^cCombined transition. ^dTransition with decomposition.

The cationic compounds display a columnar hexagonal mesophase in a wide range of temperatures. The POM optical texture, when formed on cooling from the isotropic melt, shows a mosaic texture (Figure 1). This suggests a columnar mesophase, later identified as columnar hexagonal.

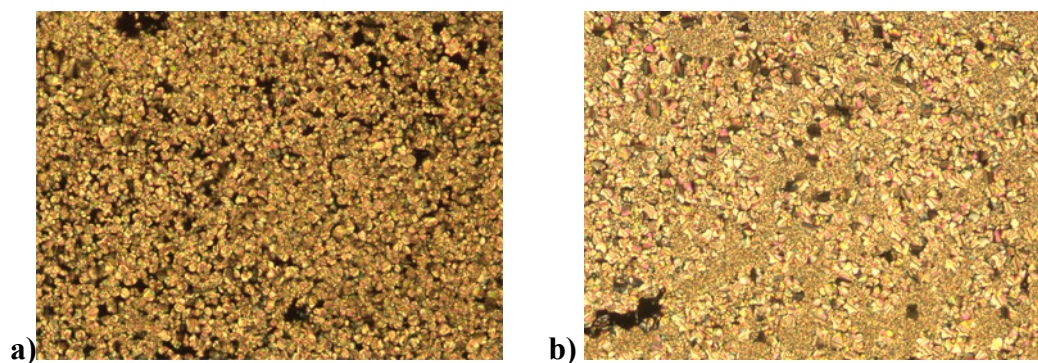


Figure 1. POM textures (x 100) of the mesophases on cooling from the isotropic liquid: a) [Pt(bzq)(CNR)₂]BF₄ **(6)** at 150 °C, b) [Pt(bzq)(CNR)₂]PF₆ **(7)** at 135 °C.

Complexes **6** and **7** display good thermal stability, even in the isotropic state. In contrast, the nitrate derivative **(5)** shows thermal instability and undergoes some decomposition at the clearing transition at relatively low temperature. This behavior is associated to the known thermal

instability of nitrate in the presence of many heavy metal cations.⁴⁷ A similar result has been reported for mesomorphic gold(I) and silver(I) ionic isocyanide complexes.⁴⁶

It is interesting to compare the thermal behavior of the neutral **2-4** complexes, which are not liquid crystals, with that of the mesomorphic cationic derivatives **5-7**. The observed variation in thermal properties is as follows: The melting points decrease in the order neutral complexes > cationic derivatives. On the contrary, the clearing points follow the opposite trend and decrease in the order cationic derivatives > neutral complexes (note that since the neutral complexes melt directly to isotropic liquid their clearing points are not observed, which means that their theoretical clearing points are lower than their melting points).

We can consider the cationic molecules **5-7** as formal derivatives of the neutral complexes obtained by substitution of a halogen ligand by an isocyanide. The process involves doubling the number of alkoxylic chains in the system. Consequently the melting points should decrease, as observed. In the case of clearing temperatures, the additional electrostatic interactions present in the cationic complexes are likely the main factor for producing higher clearing temperatures in the ionic derivatives than in neutral ones.

X-ray diffraction studies in the mesophase

In order to elucidate the structural properties of these mesophases, X-ray diffraction measurements were carried out. In all cases the diffraction diagram is typical of a hexagonal columnar liquid crystal phase. The results are quite similar for the three compounds. Here we show the results for complex **7**.

The diagram presents a diffuse halo at wide angles $2\theta \approx 20^\circ$ (Figure 2a) indicating the fluid character of the mesophase. The distance (4.5 Å) corresponds to the width of the alkyl chains that fill the empty space. At low angles an unusual amount of reflections is observed (see Figure 2b).

Remarkably, all of them can be successfully indexed according to a hexagonal lattice, with cell parameter $a = 71.6 \text{ \AA}$ (Table 2).

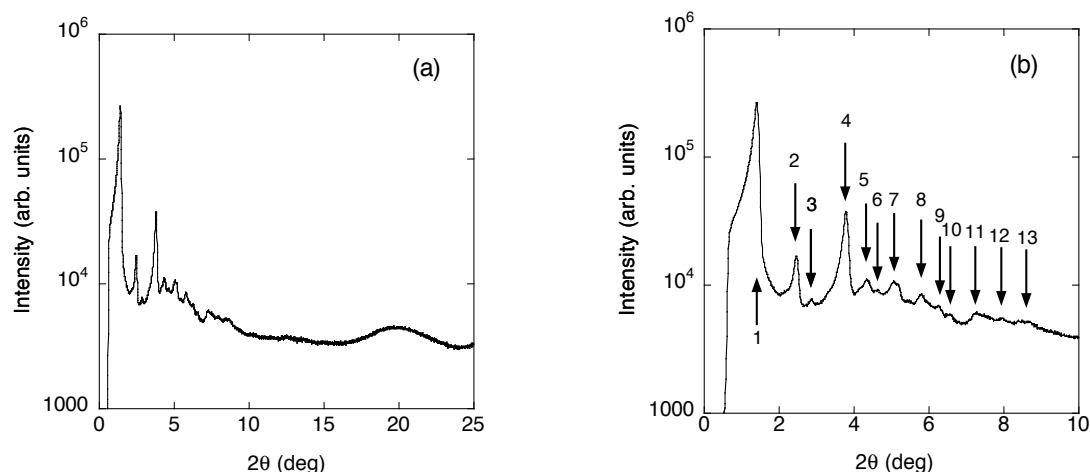


Figure 2 (a) Powder diffraction diagram of compound 7 at room temperature. (b) Identification of the low-angle reflections (see Table 2)

Table 2. X-ray reflections at low angles for compound 7 and their indexation according to a hexagonal lattice with $a = 71.6 \text{ \AA}$. All combinations of signs in the Miller indices are possible and correspond to symmetry equivalent reflections. Each peak in the powder diagram has a multiplicity either of 6 or 12.

Reflection No.	2θ (deg) (experimental)	2θ (deg) (theoretical)	Miller indices (hk)	Ratio of spacings $d(10)/d(hk)$
1	1.42	1.42	$\pm(10) \pm(01) \pm(1-1)$	1
2	2.44	2.45	$\pm(11) \pm(1-2) \pm(2-1)$	$\sqrt{3}$
3	2.83	2.84	$\pm(20) \pm(02) \pm(2-2)$	$\sqrt{4}$
4	3.75	3.75	$\pm(12) \pm(2-3) \pm(3-1)$ $\pm(21) \pm(3-2) \pm(1-3)$	$\sqrt{7}$
5	4.28	4.26	$\pm(30) \pm(03) \pm(3-3)$	$\sqrt{9}$
6	4.64	4.92	$\pm(22) \pm(2-4) \pm(4-2)$	$\sqrt{12}$
7	5.13	5.11	$\pm(13) \pm(4-1) \pm(3-4)$ $\pm(31) \pm(1-4) \pm(4-3)$	$\sqrt{13}$
8	5.73	5.68	$\pm(40) \pm(04) \pm(4-4)$	$\sqrt{16}$
9	6.22	6.18	$\pm(23) \pm(5-2) \pm(3-5)$ $\pm(32) \pm(2-5) \pm(5-3)$	$\sqrt{19}$
10	6.53	6.50	$\pm(14) \pm(5-1) \pm(4-5)$ $\pm(41) \pm(1-5) \pm(5-4)$	$\sqrt{21}$
11	7.45	7.50	$\pm(24) \pm(6-2) \pm(4-6)$ $\pm(42) \pm(2-6) \pm(6-4)$	$\sqrt{28}$
12	7.95	7.89	$\pm(51) \pm(6-5) \pm(1-6)$	$\sqrt{31}$

13	8.63	8.62	$\pm (15) \pm (5-6) \pm (6-1)$	$\sqrt{37}$
			$\pm (34) \pm (7-3) \pm (4-7)$	
			$\pm (43) \pm (3-7) \pm (7-4)$	

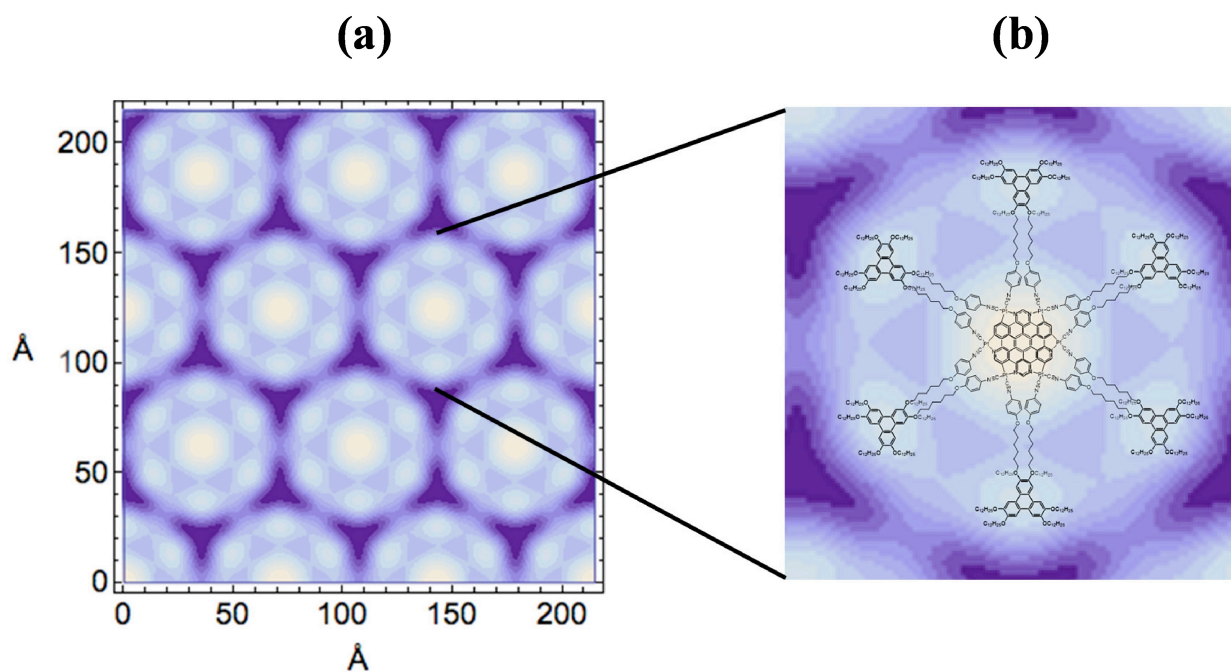
The next step in our X-ray study was to deduce the charge-density maps of the structures. To this aim, the intensity of the different reflections must be considered apart from their peak angular positions. The procedure is based on the inverse Fourier transform of the diffraction diagram, and it can be carried out if the structure factors are real, as is our case according to the symmetry of the materials. In this situation the square root of the intensities are the moduli of the structure factors, and only their signs are to be determined. The correct sign combination is decided by the physical merit of the obtained density map, taking into account the packing conditions, molecular sizes and optimization of the steric interactions. The technical details of the procedure can be found in ref..⁴⁸

Four reflections with the highest intensities (once corrected from Lorentz and polarization factors) were considered (Nos. 1, 2, 4 and 7 in Table 2). The map shown in Figure 3a was chosen out of the set of all possible maps. The brightest areas correspond to the highest electron density. The plane group is $p6mm$, which is the maximal hexagonal plane symmetry. (The other possible hexagonal group, $p6$, is chiral, and seems to be difficult to justify since the constituent molecules are achiral). We interpret the columns as formed by the stacking of 6 molecules arranged as indicated in Figures 3b and 3c. Triphenylene groups (blue in Fig 3c) occupy the peripheral part of the columns and the metallic fragments are within the central part (red in Fig. 3c). The distance triphenylene- metal is about 25 Å, in good accordance with the calculations (ACD Laboratories Chems sketch). Since there are 6 triphenylene blocks per unit cell, and there are 12 triphenylene groups every 6 molecules, we deduce that the triphenylene segments should overlap in pairs with those of the neighboring molecule. We have not been able to observe the triphenylene stacking distance in the X-ray diagram. There is no reason to think that the stacked distance between

triphenylene groups in our complexes should be very different from that found in many structures of organic systems with stacked triphenylene groups, which are found in the range 3.43–3.66 Å (average 3.54 Å).⁴⁹ Assuming this value, this corresponds to a h value about 7 Å for the repeat unit containing two triphenylenes).

Complexes **5** and **6** have similar diagrams. For compound **6** we again obtain $a = 71.6$ Å, with practically the same amount of reflections and similar reflection intensities. Compound **5** has $a = 70.2$ Å and presents fewer reflections. The charge density map is in this case slightly more "blurred". The X-ray patterns for **5** and **6** are shown in the ESI (Figure S1).

The proposed molecular organization within the columns should be considered as ideal. In practice, there must be some disorder and the molecular arrangement can be slightly displaced or rotated at random about the column axis. In this regard, it must also be said that the anions have not been localized in any compound. Overall, the hexagonal symmetry displayed by the columns themselves is noteworthy. This marked symmetry is clearly manifested by the richness of reflections observed in these materials, seldom found in other liquid crystals.



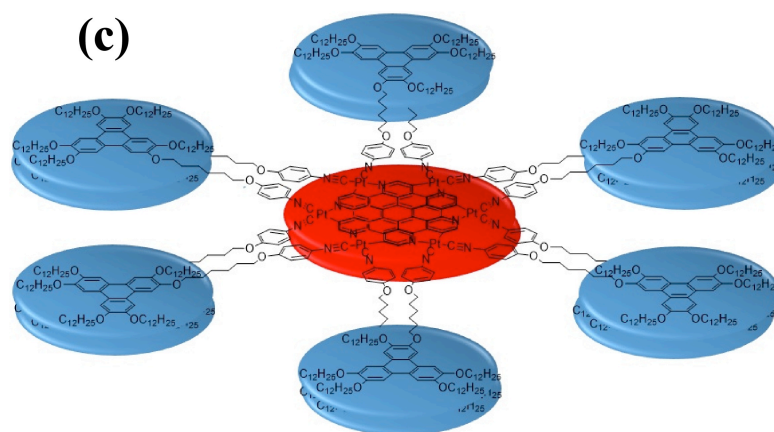


Figure 3. (a) Charge density map deduced from the X-ray measurements of compound **7** (PF_6^-). (b) and Arrangement of molecules giving rise to a disc-like object with a charge density in accordance to (a). This object, formed by six molecules, is the repeating unit whose stacking originates the columns in the columnar mesophase. (c) Schematic diagram showing the internal organization of the columns.

Photophysical studies

The study of luminescent liquid crystal based on metal complexes is a topic of current interest.^{50,51} In the context of this article our specific interest is due to the fact that the study of luminescence is a way to detect the existence of metallophilic interactions in the different states of the materials. Solid materials with aggregation-induced emission or aggregation-induced enhanced emission have been reported.⁵² Among them a particularly interesting case is found in a few organometallic complexes of Re^{I} ,⁵³ Pt^{II} ,^{22,54,55} and Ir^{III} ,⁵⁶ which show aggregation induced phosphorescence based on weak metallophilic interactions in the solid state. Our compounds are hoped to be related to those but are uncommon because this aggregation-induced emission occurs in a fluid mesophase. Detecting luminescence is how we can know, at least for Pt, that we are succeeding to produce structures that pile up metal fragments at distances of interaction, which could not be proved by SAXS studies. In this respect it is pertinent to remark two studies where luminescent behavior and $\text{Pt}\cdots\text{Pt}$ metallophilic interactions are connected.^{28,29}

The UV-Vis absorption and fluorescence spectra of the free isocyanide and the palladium and platinum complexes in dichloromethane solution are summarized in Table 3.

Table 3. UV-Visible and luminescence data for the free isocyanide and the cyclometalated complexes in dichloromethane solution at 298 K (10^{-5} M)

Compound	λ (ϵ)/nm ($\text{mol}^{-1} \text{cm}^{-1}$)	λ_{ex} /nm	λ_{em} /nm	Φ_{f}
CNR	345 (4428), 307 (33011), 279 (149356), 270 (97423), 260 (73671)	324	385	0.17
(1)	346 (7172), 309 (41261), 279 (153746), 270 (107770), 261 (89202)	278	385	0.16
(2)	344 (9051), 308 (45732), 279 (144531), 269 (107375), 260 (91273)	278	385	0.17
(3)	346 (9370), 307 (48359), 279 (160392), 270 (115760), 261 (96416)	275	385	0.15
(4)	345 (10922), 308 (43284), 279 (136527), 270 (97794), 261 (81511)	277	385	0.09
(5)	345 (12557), 307 (77420), 279 (239180), 270 (171549), 261 (139118)	271	385	0.13
(6)	345 (15189), 308 (86389), 279 (268449), 270 (193135), 262 (158221)	285	385	0.17
(7)	346 (15961), 307 (87735), 279 (258187), 270 (187617), 261 (154189)	272	385	0.11

The electronic spectra are all very similar, displaying a very structured spectral pattern with absorption bands and extinction coefficients typical of hexakis(*n*-alkyloxy)triphenylene chromophores (Figure 4), which are assigned to triphenylene π - π^* transitions.^{57,58} In the complexes reported here the isocyanide group is located too far from the triphenylene core, thus significant influence on its electronic transitions is not expected. In fact the free isocyanide and their Pd and Pt complexes display similar electronic spectra. Note also that the characteristic absorptions of benzoquinoline and phenyl isocyanide groups present in the complexes are not observed, probably due to their overlap with the most intense bands of the triphenylene moiety.

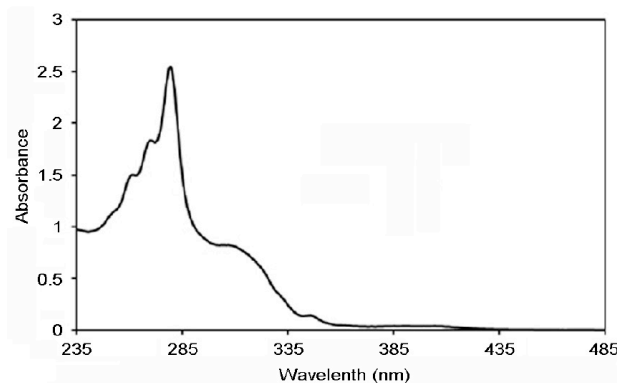


Figure 4. UV-Visible absorption spectrum of $[\text{Pt}(\text{bzq})(\text{CNR})_2]\text{BF}_4$ (**6**), recorded in CH_2Cl_2 solution (10^{-5} M) at room temperature.

The free isocyanide and the Pd and Pt complexes are luminescent at room temperature in dichloromethane solution (Table 3). As for their electronic spectra, all the emission spectra are similar, showing a very structured pattern with the maximum at 385 nm (black curve in Figure 5), typical of fluorescent 2,3,6,7,10,11-hexaalkoxytriphenylenes.⁵⁷ Similarly, the quantum yields for the complexes (Φ) measured in dichloromethane solution at room temperature,⁵⁹ are of the same order of magnitude than for the 2,3,6,7,10,11-hexadodecyloxytriphenylene in the same conditions (0.17).

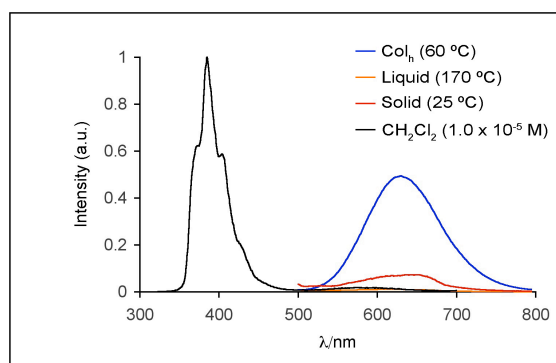


Figure 5. Normalized luminescence emission spectra of **6** in dichloromethane solution, in the solid state, in the isotropic liquid and in the mesophase.

In the solid state, the luminescent emission centered in the triphenylene core of the complexes above discussed is lost but the metal complexes display new emission bands at lower energy than those shown in solution (Table 4).

Table 4. Luminescence for the cyclometalated complexes in solid and liquid crystal phase

Compound	Solid		Mesophase	
	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\lambda_{\text{ex}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$
(1)	463	495, 626		
(2)	470	644		
(3)	465	497, 626		
(4)	469	647		
(5)	470	643	478	646
(6)	470	644	470	639
(7)	471	643	472	633

The emission spectra of palladium complexes **1** and **3** (Figure 6a) show a structured sharp band at ca. 495 nm (vibronic progression of 1300 cm^{-1}) with very short life-time ($\tau/\text{ns} = 2.3$ (**1**), 2.0 (**3**)) corresponding to fluorescence. In addition, a very weak and structureless phosphorescence broad band at 626 nm is hardly observed, with life-time in the range of microseconds ($\tau/\mu\text{s} = 0.2$ (**1**), 0.2 (**3**)). Based on these life-time data the high-energy structured emission band can be assigned as a ligand based intraligand emission. Similarly, the broad emission at 626, which is not observed in solution, is tentatively assigned to an excimeric transition in the molecular aggregated state. Considering that palladium has only very poor tendency to establish metalophilic interactions, this association might suggest π -stacking interactions. In contrast, platinum complexes (**2**, **4-7**) display an intense structureless phosphorescence emission band (Figure 6b) in the range 643-647 nm, with life-times $\tau/\mu\text{s} = 7.5$ (**2**), 6.3 (**5**), 6.2 (**6**), 7.0 (**7**)). This type of emission band, which is not observed in solution, has been reported in the solid state for orthometalated-benzoquinolate chloroisocyanide,⁶⁰ and bisisocyanide Pt complexes (non mesogenic) with almost identical coordination spheres, and has been assigned to excimeric-like $^3\pi\pi^*$ and $^3\text{MMLCT}$ transitions localized on excited states originated by π - π and Pt \cdots Pt interactions generating an emissive state.⁴² The different intensity of the band for the Pd and Pt complexes reflects the different

contributions to intermolecular interactions in the case of Pt (where metallophilia is important and Pd, where metallophilia is modest).

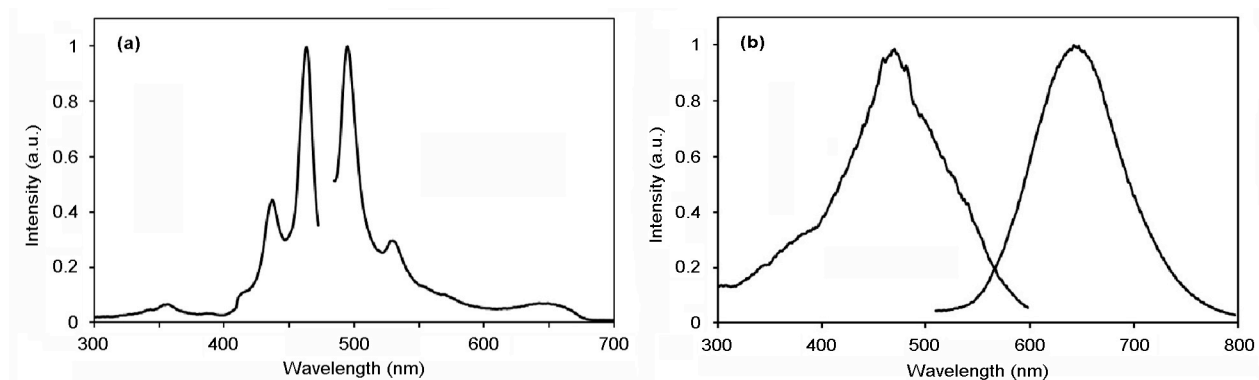


Figure 6. Normalized luminescence excitation and emission spectra in solid state at room temperature of [Pd(bzq)Cl(CNR)] (a) and [Pt(bzq)Cl(CNR)] (b).

The most interesting luminescence behavior in our materials is found for the cationic complexes. Figure 5 shows, as a representative example, the luminescence spectra of the Pt complex **6** recorded in the solid state, in the isotropic liquid and in the mesophase. It can be seen that: a) the structureless band disappears in the isotropic liquid where there is no molecular stacking; and, very interestingly, b) the intensity of the emission band is higher in the mesophase, than in the solid state, strongly suggesting that the intermolecular disk to disk π - π and Pt \cdots Pt interactions are reinforced very efficiently when the disks can self-assemble more efficiently into columns in the fluid mesophase. These interesting results, along with the different behavior observed in the palladium derivatives, strongly support that Pt \cdots Pt interactions are contributing to the stability of the columnar structure in the mesophase. It is well known that metallophilic interactions can have energies in the order of medium H-bond interactions).⁶¹

In conclusion, the metal complexes reported here (M = Pd or Pt) show a number structural features that make them different classes. Only the cationic Pt complexes produce, in the mesophases, a double columnar system stacking, on one hand, metal containing moieties

connected by Pt···Pt metallophilic interactions and, on the other, triphenylene moieties. The later kind of columns is similar to typical examples of organic liquid-crystalline semiconductors. The columnar stacking via metallophilic interactions could produce some kind of conduction along these flexible columns. This possibility is suggested by the existence of crystalline columnar organometallic complexes that show intermolecular metallophilic interactions and display conducting behavior in the rigid solid structure. For example, some Pt^{II} complexes that form 1D micro and nanowires,²³ display semiconducting properties.⁶² Furthermore, some halogen-bridged mixed-valence platinum complexes, display metallic conductivity at room temperature.^{63,64}

Conduction might occur in our materials through three different ways: a) along the stack of the triphenylene organic groups; b) along the columns of the organometallic platinum-benzoquinolate fragments with Pt···Pt interactions, which is our main interest; and c) since it is an ionic system, through ionic conduction. Conductivity studies are under way.

Acknowledgments. This work was sponsored by the Ministerio de Ciencia e Innovación (Project CTQ2014-52796-P), the Junta de Castilla y León (Project VA302U13), MINECO-FEDER of Spain-UE (Project MAT2012-38538-C03-02), and the Basque Country Government (Project GI/IT-449-10). We thank Prof. E. Lalinde (University of La Rioja) for measurement of fluorescence life-time measurements. E. T. thanks the European Commission (Erasmus Mundus) for a grant.

References

- ¹ S. Chandrasekhar and B. K. Sadashiva, K. A. Suresh, *Pramana*, 1977, **9**, 471.
- ² S. Kumar, in *Chemistry of discotic liquid crystals*, ed. V. Perce, CRC Press, Boca Raton, 2011.
- ³ *Liquid Crystalline Semiconductors: Materials, Properties and Applications*, eds. R. J. Bushby, S. M. Kelly and M. O'Neill, Springer, Dordrecht, 2013.
- ⁴ B. R. Kaafarani, *Chem. Mater.*, **2011**, 378-396.
- ⁵ S. Sergeyev, W. Pisula and Y. H. Geerts, *Chem. Soc. Rev.*, 2007, **36**, 1902.
- ⁶ T. Kato, T. Yasuda and Y. Kamikawa, *Chem. Commun.*, 2009, 729.

-
- ⁷ S. Laschat, A. Baro, N. Steinke, F. Giesselmann, C. Hägele, G. Scalia, R. Judele, E. Kapatsina, S. Sauer, A. Schreivogel and M. Tosoni, *Angew. Chem., Int. Ed.*, 2007, **46**, 4832.
- ⁸ A. W. Hains, Z. Liang, M. A. Woodhouse and B. A. Gregg, *Chem. Rev.*, 2010, **110**, 6689.
- ⁹ M. Oukachmih, P. Destruel, L. Seguy, G. Ablart, P. Jolinat, S. Archambeau, M. Mabilia, S. Fouet and H. Bock, *Sol. Energy Mater. Sol. Cells.*, 2005, **85**, 535.
- ¹⁰ H. Mori, Y. Itoh, Y. Nishuira, T. Nakamura and Y. Shinagawa, *Jpn. J. Appl. Phys.*, 1997, **36**, 143.
- ¹¹ K. Kawata, *Chem. Rec.*, 2002, **2**, 59.
- ¹² T. Kato, N. Mizoshita and K. Kishimoto, *Angew. Chem., Int., Ed.* 2005, **45**, 38.
- ¹³ S. Kumar, *Chem. Soc. Rev.*, 2006, **35**, 83.
- ¹⁴ X. Feng, V. Marcon, W. Pisula, M. R. Hansen, J. Kirkpatrick, F. Grozema, D. Andrienko, K. Kremer and K. Müllen, *Nature Materials*, 2009, **8**, 421.
- ¹⁵ I. Tahar-Djebbar, F. Nekelson, B. Heinrich, B. Donnio, D. Guillon, D. Kreher, F. Mathevet and A.-J. Attias, *Chem. Mater.*, 2011, **23**, 4653.
- ¹⁶ For reviews see: (a) B. Donnio, D. Guillon, D. W. Bruce and R. Deschenaux, in *Metallomesogens, Comprehensive Organometallic Chemistry III: From Fundamentals to Applications*, Vol. 12, eds.: R. H. Crabtree and D. M. P. Mingos, Elsevier, Oxford, UK, 2006: *Applications III: Functional Materials, Environmental and Biological Applications*, (ed.: D. O'Hare), ch. 12.05, pp. 195-294. (b) B. Donnio, *Inorg. Chim. Acta*, 2014, **409**, 53.
- ¹⁷ E. J. Fernandez, A. Laguna and J. M. Lopez-de-Luzuriaga, *Dalton Trans.*, 2007, 1969.
- ¹⁸ H. Schmidbaur and A. Schier, *Chem. Soc. Rev.*, 2012, **41**, 370.
- ¹⁹ Y. Kajitani, K. Tsuge, Y. Sasaki and M. Kato, *Chem. Eur. J.*, 2012, **18**, 11196.
- ²⁰ R. N. McDougald, B. Chilukuri, H. Jia, M. R. Perez, H. Rabaâ, X. Wang, V. N. Nesterov, T. R. Cundari, E. Bruce, B. E. Gnade and M. A. Omary, *Inorg. Chem.*, 2014, **53**, 7485.
- ²¹ S.-W. Lai, T.-C. Cheung, M. C. W. Chan, K.-K. Cheung, S.-M. Peng and C.-M. Che, *Inorg. Chem.*, 2000, **39**, 255.
- ²² M.-X. Zhu, W. Lu, N. Zhu and C.-M. Che, *Chem. Eur. J.*, 2008, **14**, 9736.
- ²³ Y. Sun, K. Ye, H. Zhang, J. Zhang, L. Zhao, B. Li, G. Yang, B. Yang, Y. Wang, S.-W. Lai and C.-M. Che, *Angew. Chem. Int. Ed.*, 2006, **45**, 5610.
- ²⁴ V. W.-W. Yam, K. H.-Y. Chan, K. M.-C. Wong, and B. W.-K. Chu, , *Angew. Chem., Int. Ed.*, 2006, **45**, 6169.
- ²⁵ C. Yang, M. Messerschmidt, P. Coppens and M. A. Omary, *Inorg. Chem.*, 2006, **45**, 6592.

-
- ²⁶ S. Y.-L. Leung, A. Y.-Y. Tam, C.-H. Tao, H. S. Chow and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2012, **134**, 1047.
- ²⁷ K. M.-C. Wong and V. W.-W. Yam, *Acc. Chem. Res.*, 2011, **44**, 424.
- ²⁸ V. N. Kozhevnikov, B. Donnio and D. W. Bruce, *Angew. Chem., Int. Ed.*, 2008, **47**, 6286.
- ²⁹ V. N. Kozhevnikov, B. Donnio, B. Heinrich and D. W. Bruce, *Chem. Commun.*, 2014, **50**, 14191.
- ³⁰ K. Fujisawa, Y. Okuda, Y. Izumi, A. Nagamatsu, Y. Rokusha, Y. Sadaike and O. Tsutsumi, *J. Mater. Chem. C*, 2014, **2**, 3549.
- ³¹ S. Coco, C. Cordovilla, C. Domínguez, B. Donnio, P. Espinet and D. Guillon, *Chem. Mater.*, 2009, **21**, 3282.
- ³² C. Domínguez, B. Heinrich, B. Donnio, S. Coco and P. Espinet, *Chem. Eur. J.*, 2013, **19**, 5988.
- ³³ R. J. Bushby, N. Boden, C. A. Kilner, O. R. Lozman, Z. Lu, Q. Liu and M. A. Thornton-Pett, *J. Mater. Chem.*, 2003, **13**, 470.
- ³⁴ S. Kumar and S. K. Varshney, *Liq. Crystals*, 2001, **28**, 161.
- ³⁵ J. L. Schulte, S. Laschat, R. Schulte-Ladbeck, V. von Arnim, A. Schneider and H. Finkelmann, *J. Organomet. Chem.*, 1998, **552**, 171.
- ³⁶ A. N. Cammidge and H. Gopee, *Chem. Commun.*, 2002, 966.
- ³⁷ B. Mohr, G. Wegner and K. Ohta, *Chem. Commun.*, 1995, 995.
- ³⁸ F. Yang, X. Bai, H. Guo and C. Li, *Tetrahedron Lett.*, 2013, **54**, 409.
- ³⁹ J. Shi, Y. Wang, M. Xiao, P. Zhong, Y. Liu, H. Tan, M. Zhu and W. Zhu, *Tetrahedron*, 2015, **71**, 463.
- ⁴⁰ E. Tritto, R. Chico, G. Sanz-Enguita, C. L. Folcia, J. Ortega, S. Coco and P. Espinet, *Inorg. Chem.*, 2014, **53**, 3449.
- ⁴¹ A. Díez, J. Forniés, C. Larráz, E. Lalinde, J. A. López, A. Martín, M. T. Moreno and V. Sicilia, *Inorg. Chem.*, 2010, **49**, 3239.
- ⁴² A. Díez, J. Forniés, S. Fuertes, E. Lalinde, C. Larráz, J. A. López, A. Martín, M. T. Moreno and V. Sicilia, *Organometallics*, 2009, **28**, 1705.
- ⁴³ C. Cordovilla, S. Coco, P. Espinet and B. Donnio, *J. Am. Chem. Soc.*, 2010, **132**, 1424.
- ⁴⁴ S. Kumar and M. Manickam, *Synthesis*, 1998, 1119.
- ⁴⁵ S. Coco, F. Díez-Expósito, P. Espinet, C. Fernández-Mayordomo, J. L. Martín-Álvarez and A. M. Levelut, *Chem. Mater.*, 1998, **10**, 3666.

-
- ⁴⁶ M. Benouazzane, S. Coco, P. Espinet, J. M. Martín-Alvarez and J. Barberá, *J. Mater. Chem.*, 2002, **12**, 691.
- ⁴⁷ K. Jones, in *The Chemistry of Nitrogen, Comprehensive Inorganic Chemistry*, eds. Bailar Jr, J. C., Emeléus; Nyholm, H. J. R.; Trotman-Dickenson and A. F., Pergamon Press, Oxford, 1973, vol. 2, p. 386.
- ⁴⁸ C. L. Folcia, I. Alonso, J. Ortega, J. Etxebarria, I. Pintre and M. B. Ros, *Chem. Mater.*, 2006, **18**, 4617.
- ⁴⁹ M. Ichihara, H. Suzuki, B. Mohr, and K. Ohta, *Liq. Cryst.*, 2007, **34**, 401.
- ⁵⁰ K. Binnemans, *J. Mater. Chem.*, 2009, **19**, 448.
- ⁵¹ For example see: a) C. Cuerva, J. A. Campo, P. Ovejero, M. R. Torres, E. Oliveira, S. M. Santos, C. Lodeiro, and M. Cano, *J. Mater Chem. C* 2014, **43**, 9167; b) E. I. Szerb, D. Pucci, A. Crispini, and M. La Deda, *Mol. Cryst. Liq. Cryst.* 2013, **573**, 34; c) N. M. Selivanova, A. I. Galeeva, A. T. Gubaydullin, V. S. Lobkov, and Y. G. Galyametdinov, *J. Phys. Chem. B*, 2012, **116**, 735; d) M. Spencer, A. Santoro, G. R. Freeman, A. Diez, P. R. Murray, J. Torroba, A. C. Whitwood, L. J. Yellowlees, J. A. G. Williams, and D. W. Bruce, *Dalton Trans.* 2012, 14244.
- ⁵² Y. Hong, J. W. Y. Lam and B. Z. Tang, *Chem. Soc. Rev.*, 2011, **40**, 5361.
- ⁵³ B. Manimaran, P. Thanasekaran, T. Rajendran, R.-J. Lin, I.-J. Chang, G.-H. Lee, S.-M. Peng, S. Rajagopal and K.-L. Lu, *Inorg. Chem.*, 2002, **41**, 5323.
- ⁵⁴ A. Y.-Y. Tam, K. M.-C. Wong and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2009, **131**, 6253.
- ⁵⁵ F. Camerel, R. Ziessel, B. Donnio, C. Bourgogne, D. Guillon, M. Schmutz, C. Iacovita and J.-P. Bucher, *Angew. Chem. Int. Ed.*, 2007, **46**, 2659.
- ⁵⁶ J. S.-Y. Lau, P.-K. Lee, K. H.-K. Tsang, C. H.-C. Ng, Y.-W. Lam, S.-H. Cheng and K. K.-W. Lo, *Inorg. Chem.*, 2009, **48**, 708.
- ⁵⁷ D. Markovitsi, A. Germain, P. Millié, P. Lécuyer, L. K. Gallos, P. Argyrakis, H. Bengs and H. Ringsdorf, *J. Phys. Chem.*, 1995, **99**, 1005.
- ⁵⁸ S. Marguet, D. Markovitsi, P. Millié, H. Sigal and S. Kumar, *J. Phys. Chem. B*, 1998, **102**, 4697.
- ⁵⁹ R. A. Velapoldi and H. H. Tønnesen, *Journal of Fluorescence*, 2004, **14**, 465.
- ⁶⁰ A. Díez, J. Forniés, C. Larraz, E. Lalinde, J. A. López, A. Martín, M. T. Moreno, and V. Sicilia, *Inorg. Chem.* 2010, **49**, 3239-3251.
- ⁶¹ H. Zhang, Y. Wang, in *Aggregation-Induced Emission: Fundamentals*, ed. A. Qin and B. Z. Tang, JohnWiley & Sons, 2013, ch. 10.5.4, p. 225.

⁶² S. Zhao, F. Yu, G. Yang, H. Zhang, Z. Su and Y. Wang, *Dalton Trans.*, 2012, **41**, 7272.

⁶³ K. Otsubo, A. Kobayashi, H. Kitagawa, M. Hedo, Y. Uwatoko, H. Sagayama, Y. Wakabayashi and H. Sawa, *J. Am. Chem. Soc.*, 2006, **128**, 8140.

⁶⁴ A. Guijarro, O. Castillo, L. Welte, A. Calzolari, P. J. S. Miguel, C. J. Gómez-García, D. Olea, R. di-Felice, J. Gómez-Herrero and F. Zamora, *Adv. Funct. Mater.*, 2010, **20**, 1451.