Luminescent Pt–Ag Clusters based in Neutral Benzoquinolate Cyclometalated Platinum Complexes

Antonio Martín,^{*,[a]} Úrsula Belío,^[a] Sara Fuertes^[a] and Violeta Sicilia^[b]

Dedicated to Prof. Juan Forniés on the occasion of his 65th birthday

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Complexes $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}]$ $\{\text{bzq} = 7,8\text{-benzoquinolate}; \text{L} = \text{PPh}_3$ (**2**), pyPh_2 (**3**), tht (**4**), MeCN (**5**) $\}$ are prepared by replacing the acetone ligand in $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{Me}_2\text{CO})]$ (**1**) with the corresponding L. The structures of complexes **2**, **3** and **4** have been established by X-ray diffraction. Despite their neutral nature, complexes **1–5** react with AgClO_4 in 2:1 molar ratio giving the corresponding trinuclear $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}\}_2\text{Ag}]\text{ClO}_4$ $\{\text{L} = \text{Me}_2\text{CO}$ (**6**), PPh_3 (**7**), pyPh_2 (**8**), tht (**9**), MeCN (**10**) $\}$ which contain $\text{Pt} \rightarrow \text{Ag}$ dative bonds. The structures of complexes **7**, **9** and **10** have been established by X-ray diffraction and confirm the existence of the $\text{Pt} \rightarrow \text{Ag}$ bonds (*ca.* 2.8 Å) and short η^1 bonding $\text{Ag} \rightarrow \text{C}$ interactions with the C_{ipso} of the bzq (*ca.* 2.4 Å). Moreover, complexes **3**, **4**, **7**, **9** and **10** show intermolecular $\pi \cdots \pi$ interactions between the aromatic rings of the bzq ligands (separations of *ca.* 3.5 Å). The reactions of **1–5** with $[\text{Ag}(\text{PPh}_3)(\text{OCIO}_3)]$ in 1:1 molar ratio proceed with interchange of ligands between the metals and formation of $[\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)(\text{PPh}_3)\}_2\text{Ag}]\text{ClO}_4$ (**7**) and $[\text{AgL}_2]\text{ClO}_4$ (X-ray). Only in the case of $\text{L} = \text{pyPh}_2$ (**3**), the dinuclear complex $[(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\text{PtAg}(\text{pyPh}_2)]\text{ClO}_4$ (**11**) has been identified

and its structure determined by X-ray diffraction. **11** contains a $\text{Pt} \rightarrow \text{Ag}$ (2.8147(1) Å) and a $\eta^1\text{-Ag} \rightarrow \text{C}_{\text{ipso}}(\text{bzq})$ interaction (2.293(1) Å). The electronic absorption and luminescence behaviours of **1–11** have been investigated. The lower lying absorption bands of the mononuclear complexes are ascribed to ligand-centered [$^1\text{IL}, \pi \rightarrow \pi^*(\text{bzq})$] character mixed with some metal-to-ligand charge transfer [$^1\text{MLCT}$ ($5d(\text{Pt}) \rightarrow \pi^*(\text{bzq})$)]. For the trinuclear complexes are assigned to [$^1\text{ILCT}/^1\text{MM}'\text{LCT}$ [$\pi \rightarrow \pi^*(\text{bzq})$]/($d/s(\text{Pt}, \text{Ag}) \rightarrow \pi^*(\text{bzq})$)] transitions and to mixed [$^1\text{MLCT}/^1\text{L}'\text{LCT}$ [MLCT ($5d(\text{Pt}) \rightarrow \pi^*(\text{bzq})$)/ $[\text{L}'\text{LCT}, \text{Ar}_f \rightarrow \text{bzq}]$] for the dinuclear complex **11**, on the bases of Time-Dependent Density Functional Theory (TD-DFT) calculations carried out on **2**, **4**, **5**, **9**, **10** and **11Me** in CH_2Cl_2 . Only **2** and the heteronuclear compounds are emissive in the solid state at room temperature, however all of them are emissive at 77K (solid and glasses). The main phosphorescent emission seems in each case to be due to a transition similar in character to the lowest energy electronic absorption.

[a] Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC - Universidad de Zaragoza, Departamento de Química Inorgánica, Facultad de Ciencias, 50009 Zaragoza, Spain.

[b] Instituto de Síntesis Química y Catálisis Homogénea (ISQCH), CSIC - Universidad de Zaragoza, Departamento de Química Inorgánica, Escuela de Ingeniería y Arquitectura de Zaragoza, Campus Río Ebro, Edificio Torres Quevedo, 50018, Zaragoza Spain.

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Introduction

Metallophilic interactions between closed or pseudo closed shell transition metals (d^{10} , d^8 , d^{10s^2}) is a field of great interest in Inorganic Chemistry.^[1–12] In this respect, square planar complexes of Pt(II) are a particular well suited system which has allowed to prepare a huge variety of heteropolymetallic complexes involving $\text{Pt(II)}(d^8) \rightarrow \text{M}$ dative bonds,^[5, 13–32] being the acidic M centre Cu(I), Ag(I), Au(I), Cd(II), Hg(II), Tl(I), Sn(II) and Pb(II).

These metal–metal bonds can be used as a tool in molecular or crystal engineering, acting as a sort of link between different subassemblies. Thus, a wide array of interesting structural types,

involving different nuclearities have been reported, from simple linear bimetallic compounds to infinite one-dimensional chains.^[15–19, 22–24, 30, 32–39]

Besides, among other interesting properties, some complexes containing $\text{Pt} \rightarrow \text{Ag}$ bonds have been shown to exhibit interesting photophysical and photochemical properties,^[1–10, 18, 31, 39–53] which in some cases have been exclusively attributed to the presence of metallophilic bonds.

In the course of our current research, we have developed synthetic methods for the preparation of complexes containing $\text{Pt} \rightarrow \text{M}$ bonds, mainly based on the use of perhalophenyl platinate(II) complexes.^[13, 16, 17, 34, 37, 38, 54–57] We expanded this work with the simultaneous use of strong ligand field cyclometalated C^N ligands, such as 7,8-benzoquinolate (bzq).^[16, 17, 39, 53] This strong ligand field causes the d_{z^2} platinum orbital to raises its energy and favours the formation of stronger $\text{Pt} \rightarrow \text{M}$ dative bonds.^[58, 59] Thus, we have reported that the anionic $[\text{Pt}(\text{bzq})(\text{C}_6\text{X}_5)_2]^-$ ($\text{X} = \text{F}, \text{Cl}$) is a suitable starting material for the preparation of complexes with unsupported $\text{Pt} \rightarrow \text{M}$ bonds.^[16, 17, 39] Depending on the reaction conditions, the complexes obtained show different structural features: bimetallic $\text{Pt} \rightarrow \text{M}$ $[\{\text{Pt}(\text{bzq})(\text{C}_6\text{X}_5)_2\}\text{ML}]^{n+}$ ($\text{M} = \text{Cd}, \text{L} = \text{cyclen}, \text{X} = \text{F}, n = 1$;^[16] $\text{M} = \text{Ag}, \text{L} = \text{PPh}_3, \text{X} = \text{F}$ or $\text{Cl}, n = 0$ ^[17, 39]), $\text{M} = \text{Ag}, \text{L} = \text{tetrahydrothiophene (tht)}, \text{X} = \text{F}, n = 0$ ^[17, 39]), trimetallic

“sandwich” Pt–Ag–Pt [$\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}_2\text{Ag}\}^+$,¹⁷ or the polymer metallic chain system $\cdots\text{Pt}-\text{Ag}-\text{Pt}-\text{Ag}-\text{Pt}\cdots$ [$\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}_2\text{Ag}\}_x$.³⁹ All the Pt–Ag complexes, besides the intermetallic bonds, also contain very unusual η^1 bonding interactions between the silver(I) centre and the C_{ipso} of the bzq ligand and are additionally stabilized by short or long-range $\pi\cdots\pi$ stacking interactions between the aromatic rings of the bzq ligands.

All these complexes exhibited interesting photoluminescent properties. For complexes [$\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}_2\text{Ag}(\text{L})$] (and also for [$\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}_2\text{Ag}\}_x$ upon dissolution in donor solvents as acetone or THF) the formation of the Pt–Ag bond produces a significant blue shift of the lowest-lying absorption in relation to the starting material [$\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2$]. This fact has been attributed to the stabilization and modification of the nature of the HOMO, which changes the character of the transition from $^1\text{IL}/^1\text{MLCT}$ in [$\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2$] to admixture $^1\text{L}'\text{LCT}/^1\text{MLCT}$ with a lower weight of the $^1\text{MLCT}$ in the bimetallic fragments. The emission in [$\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}_2\text{Ag}(\text{L})$] is also mainly associated to an admixture of $^3\text{MLCT}/^3\text{L}'\text{LCT}$, only slightly modified by the Ag centre. By contrast, both the experimental data in solid state and the theoretical calculations on “[$\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}_2\text{Ag}\}^+$ ” as the model for [$\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}_2\text{Ag}\}_x$ suggest that excitation of the polymer moves electron density from the platinum fragments, the C_6F_5 rings having a remarkable contribution to an orbital with a strong Pt, Ag metallic character. Absorption and emission of the polymer in the solid state is therefore suggested to be associated with an electronic transition of a mixed [$\text{Pt}(\text{bzq}) \rightarrow \text{Ag}$]/[$\text{Ar} \rightarrow \text{Ag}$] character. For the trimetallic complex [$\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}_2\text{Ag}\}$, two different polymorphs were obtained from acetone/*n*-hexane, exhibiting visibly different luminescences at room temperature. The crystal structures of both of the anions are different, not only in their form, with a different conformation of the platinum planes, but also in terms of packing.

In this paper we continue our study on this kind of complexes exploring the ability of the starting materials [$\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)(\text{L})$] ($\text{L} = \text{Me}_2\text{CO}$, PPh_3 , pyPh_2 , tht , MeCN) to form new complexes of diverse nuclearity containing Pt–Ag bonds. In principle, the neutral [$\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)(\text{L})$] have a drawback with respect to the previously used [$\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2$], since the anionic nature of this later should increase the electron density on the Pt centre and thus favour the $\text{Pt} \rightarrow \text{Ag}$ dative bond.^[13] Nevertheless, there are examples of neutral platinum complexes used as starting materials in the preparation of $\text{Pt} \rightarrow \text{Ag}$ dative bonds with success.^[32, 53] Thus, after the preparation of the corresponding [$\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)(\text{L})$] starting materials, we have achieved the preparation of several trimetallic Pt–Ag–Pt and one bimetallic Pt–Ag complexes, which have been characterised and studied by X-ray crystallography and NMR spectroscopy. Finally, their optical properties have been investigated and time-dependent density functional theory (TD-DFT) calculations have been performed to gain a better insight into the nature of the electronic transitions.

Results and Discussion

Synthesis and characterization of the cyclometalated complexes [$\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}$] ($\text{L} = \text{PPh}_3$ (2), pyPh_2 (3), tht (4), MeCN (5))

Complex [$\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{Me}_2\text{CO})$] (1) is a suitable precursor for the preparation of complexes [$\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}$] because the acetone group is easily replaced by other L ligands.^[60] Thus, the addition of equimolar amounts of PPh_3 , pyPh_2 (2,6-diphenylpyridine) or tht (tetrahydrothiophene, SC_4H_8) to acetone solutions of 1 at 0°C under

protective Ar atmosphere allows to obtain the corresponding complexes [$\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}$] ($\text{L} = \text{PPh}_3$ (2), pyPh_2 (3), tht (4)) as yellow solids which precipitate after partial evaporation of the solvent. Complex [$\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{MeCN})$] (5) is obtained by dissolving 1 in acetonitrile in the same conditions. After two minutes of stirring, the solvent was removed to dryness under vacuum and the resultant yellow solid identified as 5 (See Experimental Section).

The IR spectra of complexes 2–5 confirm the replacement of the acetone in 1, since the ν_{CO} vibration band at 1669 cm^{-1} is absent; and the bands corresponding to the corresponding ligands incorporated to the coordination sphere of the Pt atoms are now present (see Experimental). The ^1H NMR spectra of these complexes also show the signals due to the new ligands, besides the ones attributed to the bzq ligand with the expected relative intensity. The ^{19}F NMR spectra of 2–5 present the same pattern of three signals corresponding to the pentafluorophenyl ligand. The two *ortho*-F cause one downfield signal with platinum satellites. At higher field one signal of the *meta*-F and one of the *para*-F can be observed. For 2 the ^{31}P NMR spectrum shows a singlet signal with platinum satellites attributable to the phosphorus atom of the PPh_3 ligand. All the NMR details are compiled in the Experimental section.

Figure 1. View of the molecular structure of the complex [$\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)$] (2)

Table 1. Selected bond lengths (Å) and angles (°) for [$\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)$]-0.2 Me_2CO (2·0.2 Me_2CO)

Pt(1)–C(1)	2.015(6)	Pt(1)–C(17)	2.041(6)
Pt(1)–N(1)	2.107(5)	Pt(1)–P(1)	2.3224(16)
C(1)–Pt(1)–C(17)	92.5(2)	C(1)–Pt(1)–N(1)	172.7(2)
C(17)–Pt(1)–N(1)	80.6(2)	C(1)–Pt(1)–P(1)	89.36(17)
C(17)–Pt(1)–P(1)	176.16(19)	N(1)–Pt(1)–P(1)	97.70(15)

The structures of complexes 2, 4 and 5 have been established by X-ray diffraction studies. Figures 1–3 show views of the corresponding complexes and Tables 1–3 list a selection of relevant bond distances and angles. In all three cases, they are square planar complexes, with the bzq ligand coplanar to the metal plane. The pentafluorophenyl ligand is in a *trans* position with respect to the nitrogen atom of the bzq ligand. As it has been previously observed in other platinum(II) complexes containing the bzq ligand, the complexes establish a supramolecular arrangement through $\pi\cdots\pi$

interactions of the bzq aromatic ring system of different moieties which stack in a parallel, head to tail fashion. Thus, in **2** four units of the complex $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)]$ are stacked (see Figure S1 in Supplementary information) with interplanar bzq distances of *ca.* 3.4 Å, while in **4** the asymmetric unit contains three stacked units of the complex $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{tht})]$ (see Figure 2b) with interplanar bzq distances of *ca.* 3.3–3.4 Å. No other $\pi\cdots\pi$ interactions are observed among these groups of four or three units and other adjacent ones. On the other hand, in **5** an infinite array of stacked $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{MeCN})]$ units is found with similar interplanar bzq distances (see Figure S2 in Supplementary information). This kind of supramolecular arrangement has been found in other complexes with the bzq ligand^[17, 18, 39, 53, 60, 61] or other cyclometalated planar ligands.^[32, 62] Along with the H bonding, this kind of $\pi\cdots\pi$ stacking is one of the most important secondary interactions^[63–68] in the field of modern supramolecular chemistry,^[69–72] playing an important role in processes such as molecular self-assembly and self-recognition of aromatic entities in the crystal state.

Figure 2. a) View of the molecular structure of the complex $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{tht})]$ (**4**). b) Supramolecular arrangement of the three units showing the $\pi\cdots\pi$ stacking

Table 2. Selected bond lengths (Å) and angles (°) for $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{tht})]\cdot 2/3\text{CH}_2\text{Cl}_2$ (**4**· $2/3\text{CH}_2\text{Cl}_2$)

Pt(1)–C(17)	2.000(7)	Pt(1)–C(1)	2.003(8)
Pt(1)–N(1)	2.078(7)	Pt(1)–S(1)	2.3719(19)
C(17)–Pt(1)–C(1)	91.8(3)	C(17)–Pt(1)–N(1)	82.1(3)
C(1)–Pt(1)–N(1)	173.9(3)	C(17)–Pt(1)–S(1)	176.1(2)
C(1)–Pt(1)–S(1)	92.1(2)	N(1)–Pt(1)–S(1)	93.98(19)

Figure 3. View of the molecular structure of the complex $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{MeCN})]$ (**5**)

Table 3. Selected bond lengths (Å) and angles (°) for $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{MeCN})]$ (**5**)

Pt–C(17)	1.993(7)	Pt–C(1)	2.016(8)
Pt–N(2)	2.070(7)	Pt–N(1)	2.085(7)
C(17)–Pt–C(1)	93.6(3)	C(17)–Pt–N(2)	175.5(3)
C(1)–Pt–N(2)	90.3(3)	C(17)–Pt–N(1)	81.6(3)
C(1)–Pt–N(1)	173.9(3)	N(2)–Pt–N(1)	94.6(3)

Reactivity of **1-5** toward AgClO_4 . Synthesis and characterization of $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\}_2\text{Ag}]\text{ClO}_4$ [**L** = Me_2CO (**6**), PPh_3 (**7**), pyPh_2 (**8**), tht (**9**), MeCN (**10**)]

Complexes **1-5** were reacted toward the silver salt AgClO_4 with the aim to achieve heterometallic complexes containing $\text{Pt}\rightarrow\text{Ag}$ dative bonds. As mentioned above, it has been previously reported that an anionic nature of the $\text{Pt}(\text{II})$ precursor favours the obtaining of such $\text{Pt}\rightarrow\text{M}$ complexes because the additional electron density borne by the platinum centre that can be donated to the acidic centre.^[13] Hence, despite that some neutral $\text{Pt}(\text{II})$ precursors have been used,^[32, 53] most of the success in the preparation of complexes with $\text{Pt}\rightarrow\text{M}$ donor acceptor bonds has been obtained with anionic $\text{Pt}(\text{II})$ complexes as starting materials.

In any case, we have investigated the reactivity of **1-5** toward AgClO_4 in either 1:1 or 2:1 molar ratios. The 1:1 proportion could lead to the preparation of discrete dinuclear $[\text{Pt}\cdots\text{Ag}]^+$ complexes (Scheme 1A), or polymeric infinite $[\cdots\text{Pt}\cdots\text{Ag}\cdots\text{Pt}\cdots\text{Ag}\cdots]^{n+}$ species (Scheme 1B), while the 2:1 molar ratio could lead to the trinuclear $[\text{Pt}\cdots\text{Ag}\cdots\text{Pt}]^+$ “sandwiches” (Scheme 1C).

Thus, the reaction of complexes **1-5** with AgClO_4 in 2:1 molar ratio was carried out in acetone at 0°C under Ar atmosphere and in the absence of light for 30 min. After work up the reaction mixtures, compounds $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\}_2\text{Ag}]\text{ClO}_4$ [**L** = Me_2CO (**6**), PPh_3 (**7**), pyPh_2 (**8**), tht (**9**), MeCN (**10**)] were obtained as yellow solids and identified *via* their analytical and spectroscopic data (see below in Experimental Section) as the corresponding compounds. When the reactions are carried out in the same experimental conditions but in a 1:1 molar ratio, only oily residues could be obtained, which were identified as mixtures of **6-10** and unreacted AgClO_4 .

Scheme 1

These results indicate that only the trinuclear complexes depicted in Scheme 1C can be isolated. The stability of the trinuclear complexes toward the ones that could be obtained as a result of 1:1 reactions can be rationalized in the light of the neutral character of the starting Pt(II) products **1-5**. These complexes would not have enough electron density on their basic metal Pt(II) centre to satisfy the requirements of one acidic silver centre, but two Pt(II) have to cooperate to stabilize the trinuclear complex with the formation of two Pt→Ag bonds with the same Ag(I). It is noteworthy to remember that, as mentioned above, the similar $[(C_6F_5)_2(bzq)PtAg]_x$ complex^[39] to the one that would be the result of the path depicted in Scheme 1B does exist, but that in this case the starting material is an anionic Pt(II) complex $[Pt(C_6F_5)_2(bzq)]^-$, and thus the Pt(II) centre seems to be more able to fulfil the electron necessities of the silver centre.

The IR spectra of complexes **6-10** show the presence of two signals assignable to the ClO_4^- anion, one sharp at 621 cm^{-1} and another broad at 1095 cm^{-1} . Besides, the expected signals caused by the bzq and corresponding ligands L can be found.

The 1H NMR spectra of complexes **6-10** show the signals corresponding to the ligands L, besides the ones attributed to the bzq ligand with the expected relative intensity. The ^{19}F NMR spectra of **6-10** present only one set of signals indicating the equivalence of the pentafluorophenyl groups of the two $Pt(C_6F_5)_2(bzq)L$ subunits. The pattern of the signals is similar to the one described above for complexes **2-5**. Finally, for **7** the ^{31}P NMR spectrum shows a singlet signal with platinum satellites attributable to the phosphorus atom of the PPh_3 ligand. All the details of these NMR data are compiled in the Experimental section.

Crystal structures of the complexes $[Pt(C_6F_5)_2(bzq)L]_2AgClO_4$ [L = PPh_3 (**7**), tht (**9**), MeCN (**10**)]

The structures of complexes **7**, **9** and **10** have been established by X-ray diffraction studies. Figures 4-6 show views of the corresponding complexes and Tables 4-6 list a selection of relevant bond distances and angles.

The determination of the crystal structures confirms that in the solid state these complexes are trinuclear, with a “sandwich” disposition. The two $Pt(C_6F_5)_2(bzq)L$ fragments are linked to the silver centre through Pt→Ag donor acceptor bonds. The Pt–Ag distances are $2.823(1)$ and $2.745(1)\text{ Å}$ for **7**, $2.835(1)$ and $2.841(1)\text{ Å}$ for **9**, and $2.792(1)$ and $2.765(1)\text{ Å}$ in the case of **10**. These distances are in the range found for other complexes containing

Pt→Ag bonds.^[13, 17, 23, 24, 32, 34, 35, 39, 54, 73-79] The structures of **7**, **9** and **10** can be compared with the ones described for the two polymorphs of the analogous complex $(NBu_4)[\{Pt(C_6F_5)_2(bzq)\}_2Ag]$,^[17] also a “sandwich” type complex with a Pt–Ag–Pt bond system similar to the complex described here. As mentioned above, the starting material for $(NBu_4)[\{Pt(C_6F_5)_2(bzq)\}_2Ag]$ is anionic, and the resulting trinuclear complex is also anionic. Thus, stronger Pt–Ag bonds, and hence shorter Pt–Ag distances, could be expected in $(NBu_4)[\{Pt(C_6F_5)_2(bzq)\}_2Ag]$. The two polymorphs of this anionic “sandwich” show Pt–Ag distances of $2.758(1)$, $2.684(1)$, $2.702(1)$ and $2.690(1)\text{ Å}$, in general slightly shorter than the ones found in **7**, **9** and **10**, but a difference that can also be attributed to steric factors caused by the disposition of the ligands in the complexes or to the intermolecular packing forces.^[80]

Figure 4. a) View of the molecular structure of the cation of the complex $[Pt(C_6F_5)_2(bzq)(PPh_3)]_2Ag^+ClO_4^-$. (b) Supramolecular arrangement of the infinite $\pi\cdots\pi$ stacking array.

Besides the Pt–Ag bonds, in complexes **7**, **9** and **10** the silver centre also establishes a short η^1 interaction with the C_{ipso} of the bzq ligands (C(17) and C(36) in Figures 4-6), with Ag–C distances $2.351(4)$ and $2.460(3)\text{ Å}$ for **7**, $2.347(8)$ and $2.339(8)\text{ Å}$ for **9** and $2.425(8)$ y $2.467(8)\text{ Å}$ for **10**. These η^1 -Ag–C contacts have been previously found in other “(bzq)Pt→Ag”^[17, 39] or “(L)Pt→Ag” complexes in which L is another aromatic planar cyclometalated ligand similar to the bzq, such as 2-phenylpyridinate, 2-(2-tienyl)pyridinate^[23] or ethyl 2,6-diphenylisonicotinate.^[32] These η^1 -

Ag–C interactions are important and, along the Pt→Ag bonds, contribute to fulfil the electron density requirements of the acidic silver centre. The affinity of this metal for some π -donor systems is well known,^[33, 69–72, 81–89] being the most usual the η^1 and η^2 coordination modes. Ag–C lines are usually perpendicular to the aromatic planar ring system, which is more or less observed also in **7**, **9** and **10**, given the geometric limitations imposed by the Pt–Ag bonds. Thus, the angles between the Ag–C lines and the perpendicular to the best bzq planes are 15.5(1)° and 20.3(1)° for **7**, 13.6(1)° and 12.1(1)° for **9**, and 14.6(2)° and 18.3(2)° for **10**.

Table 4. Selected bond lengths (Å) and angles (°) for $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\}_2\text{Ag}]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$ (**7**·CH₂Cl₂)

Pt(1)–C(1)	2.028(4)	Pt(1)–C(17)	2.062(4)
Pt(1)–N(1)	2.106(3)	Pt(1)–P(1)	2.3472(10)
Pt(1)–Ag	2.8225(3)	Pt(2)–C(20)	2.024(4)
Pt(2)–C(36)	2.071(4)	Pt(2)–N(2)	2.122(3)
Pt(2)–P(2)	2.3336(10)	Pt(2)–Ag	2.7447(3)
Ag–C(17)	2.351(4)	Ag–C(36)	2.460(3)
C(1)–Pt(1)–C(17)	90.64(15)	C(1)–Pt(1)–N(1)	168.49(13)
C(17)–Pt(1)–N(1)	80.36(14)	C(1)–Pt(1)–P(1)	91.30(10)
C(17)–Pt(1)–P(1)	176.22(10)	N(1)–Pt(1)–P(1)	98.11(9)
C(20)–Pt(2)–C(36)	91.66(15)	C(20)–Pt(2)–N(2)	168.58(13)
C(36)–Pt(2)–N(2)	80.29(13)	C(20)–Pt(2)–P(2)	89.74(11)
C(36)–Pt(2)–P(2)	173.72(10)	N(2)–Pt(2)–P(2)	99.14(9)
C(17)–Ag–C(36)	134.78(13)	Pt(2)–Ag–Pt(1)	161.994(13)

On the other hand, in **7** the silver centre is located relatively close to one of the *ortho* fluorine atom of each pentafluorophenyl group (Ag···F(5) = 2.838(2) Å, Ag···F(6) = 2.691(2) Å), while in **10** only one *o*-F is relatively near the Ag atom (Ag···F(6) = 2.699(10) Å) and in **9**, the separation is longer (Ag···F(5) = 2.914(5) Å, Ag···F(6) = 2.898(4) Å). This short distances are frequently found in pentafluorophenyl complexes and are considered as secondary contacts that also contribute to complete the electron donation the acidic silver and thus to the final stabilization of the complex.^[13]

Figure 5. View of the molecular structure of the cation of the complex $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{tht})\}_2\text{Ag}]\text{ClO}_4$ (**9**)

Table 5. Selected bond lengths (Å) and angles (°) for $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{tht})\}_2\text{Ag}]\text{ClO}_4 \cdot 1.5\text{Me}_2\text{CO}$ (**9**·1.5Me₂CO)

Pt(1)–C(1)	2.001(5)	Pt(1)–C(17)	2.019(5)
Pt(1)–N(1)	2.081(5)	Pt(1)–S(1)	2.3685(14)
Pt(1)–Ag	2.8350(5)	Pt(2)–C(20)	2.002(5)
Pt(2)–C(36)	2.020(5)	Pt(2)–N(2)	2.092(5)
Pt(2)–S(2)	2.3686(14)	Pt(2)–Ag	2.8410(5)
Ag–C(17)	2.347(5)	Ag–C(36)	2.339(6)
C(1)–Pt(1)–C(17)	93.6(2)	C(1)–Pt(1)–N(1)	171.74(19)
C(17)–Pt(1)–N(1)	81.6(2)	C(1)–Pt(1)–S(1)	92.72(14)
C(17)–Pt(1)–S(1)	171.82(16)	N(1)–Pt(1)–S(1)	92.77(13)
C(20)–Pt(2)–C(36)	93.9(2)	C(20)–Pt(2)–N(2)	173.8(2)
C(36)–Pt(2)–N(2)	81.6(2)	C(20)–Pt(2)–S(2)	91.98(15)
C(36)–Pt(2)–S(2)	173.95(18)	N(2)–Pt(2)–S(2)	92.69(13)
C(36)–Ag–C(17)	154.1(2)	Pt(1)–Ag–Pt(2)	149.139(19)

Figure 6. View of the molecular structure of the cation of the complex $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{MeCN})\}_2\text{Ag}]\text{ClO}_4$ (**10**)

Table 6. Selected bond lengths (Å) and angles (°) for $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{NCMe})\}_2\text{Ag}]\text{ClO}_4 \cdot 2.5\text{CH}_2\text{Cl}_2 \cdot 0.5n\text{-C}_6\text{H}_{14}$ (**10**·2.5CH₂Cl₂·0.5n-C₆H₁₄)

Pt(1)–C(17)	1.999(7)	Pt(1)–C(1)	2.029(8)
Pt(1)–N(3)	2.061(9)	Pt(1)–N(1)	2.072(7)
Pt(1)–Ag	2.7924(8)	Pt(2)–C(20)	2.013(10)
Pt(2)–C(36)	2.006(7)	Pt(2)–N(4)	2.063(7)
Pt(2)–N(2)	2.096(7)	Pt(2)–Ag	2.7646(8)
Ag–C(17)	2.425(8)	Ag–C(36)	2.467(8)
C(17)–Pt(1)–C(1)	93.7(3)	C(17)–Pt(1)–N(3)	175.3(3)
C(1)–Pt(1)–N(3)	90.9(3)	C(17)–Pt(1)–N(1)	83.1(3)
C(1)–Pt(1)–N(1)	176.8(3)	N(3)–Pt(1)–N(1)	92.2(3)
C(20)–Pt(2)–C(36)	93.2(3)	C(20)–Pt(2)–N(4)	90.0(3)
C(36)–Pt(2)–N(4)	174.4(3)	C(20)–Pt(2)–N(2)	175.1(3)
C(36)–Pt(2)–N(2)	81.9(2)	N(4)–Pt(2)–N(2)	94.8(3)
C(17)–Ag–C(36)	136.59(19)	Pt(2)–Ag–Pt(1)	147.79(3)

The Pt–Ag–Pt angles are 161.99(1)° in **7**, 149.14(2)° in **9** and 147.79(3)° for **10**. The Pt–Ag lines are not perpendicular to the square planar environments of the Pt atoms, being the angles to the perpendicular to these planes 32.1(1)° for Pt(1) and 24.7(1)° for Pt(2) in **7**, 30.1(1)° for Pt(1) and 34.1(1)° for Pt(2) in **9**, and 32.4(2)° y 32.6(2)°, respectively for **10**. In principle, the best

disposition for an optimal Pt→M occurs when the intermetallic line is perpendicular to the Pt square planar, maximizing the overlapping of the full 5d₂₂ Pt(II) orbital, containing the electron pair donated to form the dative bond, and the empty orbitals of the acidic metal centre. Nevertheless, in this kind of complexes there are some other factors that make the Pt–Ag bond to deviate from this ideal perpendicular disposition. Some of these factors are electronic, such as the η¹–Ag–C interactions or the *o*-F contacts, or steric resulting from the presence of bulky ligands such as C₆F₅ or PPh₃ along other less sterically demanding such as bzq, Me₂CO or MeCN.

In this line, complexes **7**, **9** and **10** show substantial conformational differences in the relative disposition of the two square planar environments of each structure. In principle, two relative dispositions of the Pt planes are possible in these “sandwich” trinuclear complexes (see Scheme 2). In the A disposition, the coordination of the two Pt centres takes place in such a way that the positions of the N and C_{ipso} of each bzq ligand are alternate, and thus, also the relative positions of the L and C₆F₅ ligands of each “Pt(C₆F₅)(bzq)L” fragment. On the other hand, in the B disposition the relative positions of all the analogous atoms bonded to the Pt in each “Pt(C₆F₅)(bzq)L” fragment coincide. The two conformations have been previously found in similar complexes containing the bzq and C₆F₅ ligands.^[17, 39] Moreover, it is necessary to take in consideration the possibility of the “Pt(C₆F₅)(bzq)L” fragments to turn around the Pt–Ag bonds and the variability of the Pt–Ag–Pt angles (see above). For all these reasons, complexes **7**, **9** and **10** (and (NBu₄)[{Pt(C₆F₅)₂(bzq)}₂Ag]^[17]) are very flexible and able to adapt their geometry to the electronic and steric demands mentioned above, as well as the crystal packing effects.

Scheme 2

Thus, in complex **7** the dihedral angle between the best Pt square planes is 25.6(1)°, leaning one over the other in such a way that the bzq ligands of the two subunits are almost eclipsed one over the other (torsion angle N(1)–Pt(1)–Pt(2)–N(2) = 67.4(1)°) with an A conformation (see Scheme 2). This disposition allows the maximum separation between the phenyl groups of the two PPh₃

ligands, the bulkiest in the complex. An A type conformation is also observed in **9**, with a dihedral angle of 24.4(1)° between the two Pt planes, but here the two “Pt(C₆F₅)(bzq)(tht)” fragments are rotated and the torsion angle N(1)–Pt(1)–Pt(2)–N(2) is only 15.4(1)°. On the other hand, complex **10** shows a B type conformation, probably in order to allow the maximum separation of the most sterically demanding ligands of the complex, in this case the pentafluorophenyl groups.

The study of the supramolecular packing of complexes **7**, **9** and **10** has shown an infinite array of cations connected through π···π interactions of the planar aromatic rings of the bzq ligands, in a similar fashion than the one described above for complexes **2**, **4** and **5** and in other complexes previously reported.^[17, 18, 32, 39, 53, 60-62] The interplanar separations are close to 3.4 Å, and as example, Figure 4b shows a fragment of this array as found in complex **7**.

Reactivity of 1-5 toward [Ag(PPh₃)(OCIO₃)].

Since the reaction of complexes **1-5** with AgClO₄ did not result in the syntheses of neither dinuclear discrete complexes nor polymeric infinite species containing Pt–Ag bonds, we tried another silver reagent [Ag(PPh₃)(OCIO₃)]. In this complex, the silver centre coordinates to a strong PPh₃, which blocks one of its possible coordination positions and contributes to fulfil the electronic requirements of the acidic silver. The aim was the preparation of dinuclear complexes [Pt(bzq)(C₆F₅)LAg(PPh₃)]ClO₄, containing a donor acceptor Pt→Ag bond. This synthetic strategy is well known and has used before with positive results.^[13, 17, 54, 79]

Thus, complexes **1-5** with [Ag(PPh₃)(OCIO₃)] were reacted in 1:1 molar ratio in acetone at 0°C and in an Ar atmosphere. After 30 min of stirring, the acetone is completely removed and the oily residues are treated with *n*-hexane, giving rise to yellow solids that are filtered off and dried in air.

The more significant spectroscopic data of these solids is the presence in the ³¹P NMR of a singlet signal with platinum satellites, indicating that all the solids correspond to complexes containing a Pt–PPh₃ bond. These spectroscopic data seem to indicate that, at least for complexes **1**, **3-5**, the PPh₃ ligand migrates from the silver centre to the platinum one. In all cases crystals suitable for their analysis by X-ray diffraction were obtained and identified as the complex [{Pt(bzq)(C₆F₅)(PPh₃)₂Ag]ClO₄ (**7**). In the case that the starting material is [Pt(C₆F₅)(bzq)(PPh₃)] (**2**), a second signal was also observed in the ³¹P NMR spectrum of the resulting material. At room temperature this signal is broad and resolves at -70°C in a doublet of doublets, a pattern typical for a phosphorus atoms bonded to a silver centre (silver has two NMR active isotopes, ¹⁰⁷Ag, 51.8% abundance, and ¹⁰⁹Ag, 48.2% abundance). Crystals obtained from the crude solid could be also studied by X-ray diffraction, being identified as [Ag(PPh₃)₂](ClO₄).

On the other hand, when the starting material is [Pt(C₆F₅)(bzq)(pyPh₂)] (**3**), it is possible to obtain crystals which have been identified through X-ray diffraction as the dinuclear complex [(C₆F₅)(bzq)(PPh₃)PtAg(pyPh₂)]ClO₄ (**11**), which contains a donor-acceptor Pt→Ag (see below).

All these results are summarized in Scheme 3. It seems that the migration of the PPh₃ ligand from Ag to Pt corresponds to a higher lability of the Pt–O bonds (when L = Me₂CO), Pt–N (when L = MeCN or pyPh₂), or Pt–S bonds (when L = tht), than the Pt–P bonds. The final formation of the trinuclear sandwich **7** is probably caused by the final stability of this complex, while the existence of

$[\text{AgL}_2]^+$ has only been confirmed for $\text{L} = \text{PPh}_3$, but given the presence of signals of the rest of corresponding L in the IR and ^1H NMR spectra, it is sensible to assume an overall reaction process as depicted in Scheme 3b.

Scheme 3

However, the identification of $[(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\text{PtAg}(\text{pyPh}_2)]\text{ClO}_4$ (**11**) is interesting. Its existence could indicate that the formation of the trinuclear **7** occurs through a pathway as the one represented in Scheme 3a. For some reason, only in the case of $\text{L} = \text{pyPh}_2$, the intermediate compound **11** could be detected. Apart from the evident electronic reasons, an important difference between the other L ligands used (Me_2CO , MeCN , tht) and pyPh_2 is the size, and thus, the steric hindrance caused by this later. Thus, kinetic reasons could be under the fact that **11** evolves slower enough than the rest of complexes and some crystals could be formed prior to the complete conversion to **7**.

Crystal structure of the complex $[(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\text{PtAg}(\text{pyPh}_2)]\text{ClO}_4$ (**11**)

As mentioned above, the crystal structure of complex **11** has been determined by means of an X-ray diffraction study. Figure 7 shows a view of the complex cation and Table 7 lists a selection of relevant bond distances and angles.

The study confirms the presence of a donor acceptor $\text{Pt} \rightarrow \text{Ag}$ bond in the structure, with an intermetallic distance of $2.8147(1) \text{ \AA}$. This distance is similar to those found in complex $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\}_2\text{Ag}]\text{ClO}_4$ (**7**) (cf. $2.823(1)$ and $2.745(1) \text{ \AA}$), which also contains the “ $\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)$ ” fragment. On the other hand, it is slightly longer than those found in the analogous complexes $[(\text{C}_6\text{X}_5)_2(\text{bzq})\text{PtAg}(\text{PPh}_3)]^-$ ($2.728(1) \text{ \AA}$ for $\text{X} = \text{F}$ and $2.675(3) \text{ \AA}$ for $\text{X} = \text{Cl}$),^[17] perhaps because of the anionic nature of these later compounds in comparison with the neutral nature of **11**. Moreover, in the same way as it has been described for complexes **7**, **9** and **10** (see above) and other similar “ $(\text{bzq})\text{Pt} \rightarrow \text{Ag}$ ” complexes,^[17, 39] the silver centre establishes an interaction $\eta^1\text{-Ag}-\text{C}$ with the *ipso* carbon atom of the *bzq* ligand with a distance $\text{Ag}-\text{C}(17)$ of $2.293(1) \text{ \AA}$. This value is shorter than the one found in **7** (cf. $2.351(4)$ and $2.460(3) \text{ \AA}$), **9** (cf. $2.347(8)$ and $2.339(8) \text{ \AA}$), and **10** (cf. $2.425(8)$ and $2.467(8) \text{ \AA}$), or in complexes $[(\text{C}_6\text{X}_5)_2(\text{bzq})\text{PtAg}(\text{PPh}_3)]^-$ ($2.352(3) \text{ \AA}$ for $\text{X} = \text{F}$ and $2.557(5) \text{ \AA}$ for $\text{X} = \text{Cl}$),^[17] which seems to indicate a stronger interaction. In fact, the silver centre clearly leans toward the position of the C_{ipso} of the *bzq* ligand, being the angle between the $\text{Pt}-\text{Ag}$ line and the perpendicular of the best Pt square plane of $44.6(1)^\circ$, a broad value (compare with the analogous angles in **7**, $32.1(1)^\circ$ y $24.7(1)^\circ$, **9**,

$30.1(1)^\circ$ and $34.1(1)^\circ$, **10**, and $32.4(2)^\circ$ and $32.6(2)^\circ$, $[(\text{C}_6\text{F}_5)_2(\text{bzq})\text{PtAg}(\text{PPh}_3)]^-$,^[17] $34.9(1)^\circ$, or $[(\text{C}_6\text{Cl}_5)_2(\text{bzq})\text{PtAg}(\text{PPh}_3)]^-$,^[17] $27.2(1)^\circ$), and the $\text{Pt}-\text{Ag}-\text{N}(2)$ angle $146.5(1)^\circ$. This disposition “so bent” is probably caused by the steric hindrance caused by two PPh_3 and pyPh_2 bulky ligands present in **11**, which try to separate as much as possible each other. The coordination sphere of the silver centre is completed by the pyPh_2 ligand, with a $\text{Ag}-\text{N}(2)$ distance of $2.190(1) \text{ \AA}$, in the usual range for this kind of bonds.^[90-95]

Figure 7. View of the molecular structure of the cation of the complex $[(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\text{PtAg}(\text{pyPh}_2)]\text{ClO}_4$ (**11**)

Table 7. Selected bond lengths ($\text{\AA}$) and angles ($^\circ$) for $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\}_2\text{Ag}(\text{pyPh}_2)]\text{ClO}_4 \cdot \text{CH}_2\text{Cl}_2$ (**11**· CH_2Cl_2)

Pt–C(1)	2.0140(13)	Pt–C(17)	2.0633(15)
Pt–N(1)	2.1143(11)	Pt–P	2.3286(4)
Pt–Ag	2.8147(1)	Ag–N(2)	2.1898(12)
Ag–C(17)	2.2929(14)		
C(1)–Pt–C(17)	92.64(6)	C(1)–Pt–N(1)	172.95(5)
C(17)–Pt–N(1)	80.42(5)	C(1)–Pt–P	89.90(4)
C(17)–Pt–P	173.14(4)	N(1)–Pt–P	97.13(4)
N(2)–Ag–Pt	146.48(3)		

In this case, complex **11** does not show extended intermolecular interactions through $\pi \cdots \pi$ interactions of the planar aromatic rings of the *bzq* ligand.

Photophysical properties

Absorption Spectra and Theoretical Calculations. UV–vis spectra data of compounds **1–11** in solution are summarized in Table S1. Data of the precursor complex **1** have been also included for comparative purposes. In dichloromethane solution (10^{-4} M), the mononuclear complexes **1–5** exhibit high-energy bands (range 250–380 nm), whose intensity and shapes are typical of ligand-centered transitions (^1IL , C_6F_5 , *bzq*) somewhat perturbed by platinum coordination (see Figure 8 for complex **2**).^[39, 96, 97] In addition, they show a modest shoulder (ϵ : $1.0 - 2.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$) centered at ca. 400 nm generally attributed to $^1\text{MLCT}/^1\text{IL}$

Table 8. Photophysical data for compounds **1-5** in the solid state

Compound		$\lambda_{\text{absorption}}/\text{nm}$	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}$
1	298K	304, 394, 412 (tail to 450)	405	467, 482, 496, 578 _{max}	a
	77K		420	504, 540 _{max} , 583	204 (44%), 21.0(56%), at 504 nm 212.2(40%), 25.6(60%), at 540 nm
2	298K	301, 388, 405 (tail to 450)	390	481 _{max} , 490, 515 _{max} , 554, 599 _{sh}	a
	77K		390	479 _{max} , 490, 515 _{max} , 529 _{sh} , 556, 596 _{sh}	82.0(58%), 221.5(42%), at 479 nm, 42.1(28%), 107.0(72%), at 515 nm
3	298K	302, 408, 427 (tail to 460)	410	497, 590 _{max} , 632	a
	77K		410	515, 529, 555 _{max} , 590 _{sh}	158.4(32 %), 35.8 (68%), at 515 nm 242.7(25%), 40.7(75%), at 555 nm
4	298K	303, 387, 402 (tail to 450)	400	594, 627 _{max}	a
	77K		400	512, 552 _{max} , 596 _{sh}	517.5(26%), 199.3 (74%), at 512 nm 440.1(42%), 147.0(58%), at 552 nm
5	298K	307, 390, 405 (tail to 450)	390	482, 514, 580 _{sh} , 632 _{max}	a
	77K		390	512, 549 _{max}	366.8(39%), 90.7 (61%), at 512 nm 508.7(36%), 84.5(64%), at 549 nm

a) too weak emission to be measured.

Table 9. Photophysical data for compounds **6-11** in the solid state

Compound		$\lambda_{\text{absorption}}/\text{nm}$	$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm} [\Phi]$	$\tau/\mu\text{s}$
6	298K	306, 335, 411 (tail to 550)	415	515 _{sh} , 581 _{max}	8.2(98%), 120.2 (2%), at 515 nm 6.7 (92%), 67.0 (8%), at 581 nm
	77K		415	509, 597 _{max}	18.7 at 509 nm, 16.9 at 597 nm
7	298K	305, 324, 401 (tail to 460)	400	468 _{sh} , 503, 530 _{max} , 565 sh [0.032]	23.8 (86%), 79.1 (14%) at 502 nm 20.1 (40%), 78.2 (60%) at 528 nm
	77K		400	492, 591 _{max}	15.6 at 492 nm 21.7 (65%), 45.5 (35%), at 591 nm
8	298K	303, 342, 409 (tail to 485)	410	540 _{sh} , 584 _{max} , 630 _{sh}	8.7 at 540 nm 3.1 (86%), 11.8(14%) at 584 nm
	77K		410	500, 638 _{max}	12.7 at 500 nm, 14.6 at 638 nm
9	298K	300, 401 (tail to 460)	400	520 _{sh} , 551 _{max} , 575 _{sh}	8.1 at 520 nm, 6.8 at 551 nm, 8.9 at 575 nm
	77K		400	499, 607 _{max}	19.4 at 499 nm, 33.2 at 607 nm
10	298K	300, 336, 394, 408 (tail to 465)	390	514, 562 _{max}	1.5 at 514 nm, 1.9 at 562 nm
	77K		390	500, 540 _{sh} , 601 _{max}	14.2 at 500 nm, 19.5 at 540 nm, 15.8 at 601 nm
11	298K	302, 397 (tail to 500)	370	490, 519 _{max} , 554 [0.15]	17.6 at 490 nm, 17.9 at 519 nm, 18.0 at 554 nm
	77K		370	480, 492 _{sh} , 509 _{sh} , 565 _{max}	21.0 at 480 nm, 21.8 at 492 nm, 27.5 at 509 nm, 26.8 at 565 nm

Table 10. Population analysis (%) of frontier MOs in the ground state for complexes [Pt(C₆F₅)(bzq)L] (L= PPh₃ (**2**), tht (**4**), MeCN (**5**)), [(C₆F₅)(bzq)(PPh₃)PtAg(pyMe₂)]⁺ (**11Me**) and [{Pt(C₆F₅)(bzq)L}₂Ag]⁺ (L = tht (**9**) and MeCN (**10**)).

Comp	HOMO						LUMO					
	eV	Pt (1/2)	Ag	Bzq	C ₆ F ₅	L	eV	Pt (1/2)	Ag	Bzq	C ₆ F ₅	L
2	-5.68	14		84	0	2	-1.84	4		95	0	1
11Me	-8.71	12	0	4	77	6	-4.47	3	9	84	1	3
4	-5.71	20		79	0	1	-1.88	4		96	0	0
9	-8.64	16/16	10	55	2	1	-4.71	1/2	12	83	1	1
5	-5.59	23		75	0	2	-1.86	4		95	0	1
10	-8.58	22/2	6	56	13	1	-4.46	2/4	17	73	2	2

transitions. UV-vis spectra of complexes **1-5** recorded in different solvents showed a modest solvatochromism (see Figure S3 for complex **2**) for the absorption bands, particularly in the lower-energy spectral region, which is characteristic of charge-transfer (CT) transitions.

The absorption spectra of the heteronuclear (**6-11**) complexes, are all of them quite similar to those of their precursor (**1-5**) as much in the solid state as in solution (Tables 8, 9 and S1; Figures 8, S4 and S5 in Supplementary Information). Complexes containing Pt-Ag dative bonds often show a blue shift in the low energy absorption maxima; donation of electron density increases electrophilicity of the Pt centre, lowering the energy of the HOMO, and then raising the energy of the ¹MLCT absorption bands.^[17, 39] In complexes **6-11** little if any shift of the low energy absorption maxima with respect to those of the starting compounds is observed. Similar behavior was previously observed in dichloromethane solution of the trinuclear complex, (NBu₄)[{Pt(bzq)(C₆F₅)₂Ag}],^[17] which was explained by the partially cleavage of the Pt-Ag bond in solution. However, this feature cannot be invoked in the solid state.

Figure 8. Frontier orbitals plots for complexes **2** and **11Me** in CH₂Cl₂ obtained by DFT; calculated electronic transitions (bars) and experimental UV-vis spectrum of **2** and **11** in CH₂Cl₂ (10⁻⁴M)

To better explain the nature of the lower-energy transitions, time-dependent density functional theory (TD-DFT) calculations were carried out using the hybrid density functionals B3LYP for **2**, **4**, **5** and M06 for **9**, **10**, **11Me** (**11Me** is a model complex derived from complex **11** by replacing the Ph groups with Me ones in the

pyPh₂ ligand in order to simplify the calculation process). The geometric parameters of the optimized S₀ structures (Tables S2-S7 in Supplementary Information) agree well with the experimental values. Relevant data about the calculated lower-energy electronic transitions in CH₂Cl₂ and frontier molecular orbital (MOs) involved in them are listed in Tables 10 and 11. In the mononuclear complexes, the highest occupied molecular orbital (HOMO) is mostly constructed from orbitals located on the bzq (75% **5** - 84% **2**) and the platinum center (23% **5** - 14% **2**). The lower unoccupied molecular orbital (LUMO) is well located on the imine ring (~95%). Figure 8 shows that the calculated lowest energy electronic transition in CH₂Cl₂ (bars) for compound **2** fits well, within the accuracy of the method, with the experimental absorptions. Calculations indicate that the major contribution to the lowest lying absorption involves the HOMO→LUMO (94%) transition, indicating a remarkable ligand-centered [¹IL, π-π* (bzq)] mixed with some metal-to-ligand charge transfer [¹MLCT (5d(Pt)→π*(bzq))] character. Contrary to other benzoquinolate Pt(II) complexes described up to now,^[39, 96, 97] no ligand-to-ligand charge transfer [¹L'LCT, Ar₁→bzq or L→bzq] transitions are involved in this absorption. On view of the data showed in Tables 10 and 11 and Figures S4 and S5 the same assignments can be made for the lowest lying absorption of compounds **4** and **5**, but in these cases the transition shows a little higher ¹MLCT character. The blue shift observed in the calculated lowest energy transition of **2** (381 nm) in relation to that of the other mononuclear complexes (382 nm **4**, 386 nm **5**) can be due to the lower level of energy of the d_π(Pt) orbitals because of the electron-withdrawing character of PPh₃ with respect to tht and MeCN ligands,^[98-101] since no significant contribution of the L ligands to the frontier orbitals have been observed.

Table 11. Selected singlet excited states calculated by TD-DFT for complexes **2**, **4**, **5** and **9**, **10** and **11Me** in CH₂Cl₂ solution.

Compound	λ _{exc} (calc.) [nm]	o.s.	Transition (Percentage contribution)
2	381.2	0.0524	HOMO → LUMO (94.4%)
11Me	369.3	0.0695	HOMO → LUMO (94.5%)
4	382.2	0.0610	HOMO → LUMO (94.0%)
9	405.2	0.0516	HOMO → LUMO (94.5%)
5	386.9	0.0577	HOMO → LUMO (94.8%)
10	385.3	0.0342	HOMO → LUMO (85.8%);

Calculations performed on the trinuclear complexes **9** and **10** show that the HOMO is constructed from orbitals located on the bzq (~55%) and the platinum centers (32% **9**, 24% **10**) and with less weight from silver (10% **9**, 6% **10**) and C₆F₅ orbitals (2% **9**, 13% **10**). The LUMO is well located on the imine ring (83% **9**, 73% **10**) and the silver atom (12% **9**, 17% **10**). Therefore, it seems that formation of two Pt-Ag bonds decreases the weight of the bzq and increases the metallic character (Pt/Ag) of the HOMO and LUMO orbitals with respect to those of the starting complexes.

In the dinuclear complex **11Me**, the HOMO is mainly constructed from orbitals located on the C₆F₅ (77%) and the platinum center (12%) with no contribution of the AOs of the silver atom and just a marginal contributions of bzq orbitals (4%). The LUMO is well located on the imine ring (84%) with only a small metallic character (3% Pt, 9% Ag). Therefore, the formation of a Pt-Ag bond in **11Me** changes dramatically the composition of the frontier orbitals, specially that of the HOMO, decreasing the weight of the bzq orbitals and increasing those of the electron-withdrawing C₆F₅ group, as it was observed previously for the

dinuclear complexes $[\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}\text{AgL}]$ ($\text{L} = \text{PPh}_3, \text{tht}$).^[39] Taking into account that the lowest energy electronic absorption of each one of these heteronuclear complexes is associated with a HOMO $\rightarrow$ LUMO transition (Table 11) it could be ascribed to $^1\text{ILCT}/^1\text{MM}^*\text{LCT} [\pi-\pi^*(\text{bzq})]/(d/s(\text{Pt},\text{Ag}) \rightarrow \pi^*(\text{bzq}))$ for **9** and **10** and to mixed $^1\text{MLCT}/^1\text{L}^*\text{LCT}$ [$\text{MLCT} (5d(\text{Pt}) \rightarrow \pi^*(\text{bzq}))/[\text{L}^*\text{LCT}, \text{Ar} \rightarrow \text{bzq}]$] for **11Me**. Therefore, the formation of Pt–Ag bonds lead to the stabilization of the HOMO and LUMO orbitals and to the change of the electronic transitions nature; however, the effect in the transitions energy is small and not always the transitions are shifted to higher energies.

The diffuse reflectance UV-vis spectra of complexes **1–11** in the solid state exhibit a similar profile to those in solution (see Figure S6 for **1–5**). Therefore, the same origin of the absorptions can be presumed. This fact indicate that the $\pi\cdots\pi$ interactions observed in the solid state (Figures 2b, 4b, S1 and S2) have a very small effect, if any, in the lowest energy absorption maxima except for complex **3**, in which such absorption appears red shifted in relation to that of the other mononuclear complexes.

Emission spectra. Complexes **1–5** are scarcely emissive in the solid state at room temperature but becomes brightly emissive at 77 K exhibiting an asymmetric yellow emission whose excitation spectrum resembles the absorption one (see Table 8 and Figure 9 for complex **4**). Emission lifetimes are rather long and always fit to two components, as observed in many benzoquinolate Pt(II) complexes.^[97] Therefore the phosphorescent emission can be ascribed to an admixture of $^3\text{IL}/^3\text{MLCT}$ excited states, probably with a remarkable ^3IL character, especially for complex **2**.

Figure 9. Normalized excitation and emission spectra of **4** in the solid state at 77 K

It is worth to note that at 298 K only compound **2** results moderately emissive (see Figure 10a). The emission (and excitation) profile of **2** is similar to those observed at 77K and arise mainly from excited states originated in the monomer species. However in compounds **1, 3–5** the weak emission seems to come from barely emissive aggregates.^[18, 102] By contrast, the heteronuclear compounds **6–11** are emissive in the solid state at room temperature (see Figure 10b) showing that in a general trend, the presence of Pt–Ag dative bonds in the heteronuclear compounds enhance dramatically the emission intensity when it is compared to that of their Pt(II) starting complexes.

At 298 K the heteronuclear compounds **6–11** (see Table 9 and Figure 10b) exhibit a yellow-green ($\lambda_{\text{max}} = 530 \text{ nm}$ **7**, 519 nm **11**),

yellow ($\lambda_{\text{max}} = 551 \text{ nm}$ **9**, 562 nm **10**), or yellow-orange ($\lambda_{\text{max}} = 581 \text{ nm}$ **6**, 584 nm **8**) phosphorescence which is clearly enhanced upon cooling to 77 K.

Figure 10. a) Unnormalized emission spectra of **1–5** in the solid state at 298 K. b) Unnormalized emission spectra of **6–11** in the solid state at 298 K; insets: compounds **2, 8** and **11** at 298K upon excitation at $\lambda = 365 \text{ nm}$

Compounds **7** and **11**, which contain the fragment “ $\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)(\text{PPh}_3)$ ” show emission spectra very similar one to another at 298K (Figure 10b) and also at 77K (Figure 11). Taking into account the TD-DFT calculations performed for compound **11Me** and the emission behaviour described previously for complex $[\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}\text{Ag}(\text{PPh}_3)]$,^[39] the emission band observed at 298 K can be mainly arise from a mixed $^3\text{MLCT}/^3\text{L}^*\text{LCT}$ excited state. At 77K the emission clearly resolves into two bands: a weaker high energy (HE) emission at $\sim 490 \text{ nm}$, and an intense broad asymmetrical low energy (LE) band ($\lambda_{\text{max}} = 591 \text{ nm}$ **7**, 565 nm **11**) with its maximum clearly red-shifted with respect to that at 298 K. The HE emission which resembles the emission of the corresponding precursor can be tentatively assigned to $^3\text{IL}/^3\text{MLCT}$ excited state.

The emission spectra of the trinuclear compounds **6, 8–10** at 77 K show a similar profile to that of compound **7**, but with their maxima shifted to lower energies ($\lambda_{\text{max}} = 597 \text{ nm}$ **6**, 638 nm **8**, 607 nm **9**, 601 nm **10**) (see figure S7 for complex **10**). TD-DFT calculations performed on complexes **9** and **10** showed an important contribution of the metallic orbitals (Pt/Ag) to the frontier orbitals along with a small one of the C_6F_5 orbitals.

Because of that it seems plausible to assign the more intense LE band observed in the spectra of **8-10** to a $^3\text{MM}^*\text{LCT}/^3\text{ILCT}$ emissive state.

Complexes **1-11** are emissive in rigid matrix of CH_2Cl_2 (10^{-3} M) at 77 K (Table S8 in Supplementary Information). Compounds **1-5** show several emissions upon excitation in the range 350-400 nm. They show low intensity bands between 460-525 nm and a high intensity asymmetric band centered at ca. 600 nm with tail to 700 nm. 2-Me-THF glassy solutions of **1-5** show similar profiles. At low concentration (10^{-5} M), the low energy band shows similar energy and lifetime, but different profile to that in the solid state at 77 K (see figures 9 and 12 for complex **4**), which could be attributed to a bigger deformation of the excited state geometry in CH_2Cl_2 at 77 K. The increasing intensity of the low energy band with respect to the higher energy ones with the concentration (range 10^{-5} M to 10^{-3} M) added to the red shift of its maximum (see Figure 12 for compound **4**), suggest that emissive ground-state aggregates due to close $\pi\cdots\pi$ intermolecular contacts could be not completely excluded at higher concentration. The emission spectra of the heteronuclear compounds in rigid matrix of CH_2Cl_2 (10^{-3} M, 77 K, registered for **7-9**, **11**) showed similar profile to those in the solid state at 77 K; therefore the same origin can be presumed for these bands.

Figure 11. Normalized emission spectra of **2**, **7** and **11** in the solid state at 77 K. Inset: images of the compounds **7** and **11** at 77 K upon excitation at $\lambda = 365$ nm

Figure 12. Emission spectra of **4** in CH_2Cl_2 (77 K) when $\lambda_{\text{exc}} = 400$ nm.

Conclusions

Despite its neutral character, complexes $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}]$ ($\text{L} = \text{Me}_2\text{CO}$, PPh_3 , pyPh_2 , tht , MeCN) have proven to be suitable precursors for the preparation of complexes containing Pt–Ag dative bonds. The bzq ligand seems to play an important role in the stabilization of the heteropolynuclear complexes formed in a twofold way. Firstly, being a strong field ligand raises the energy of the d_{z^2} platinum orbital and favours the formation of stronger Pt→Ag dative bonds. On the other hand, in these complexes the silver centres establishes short η^1 interactions with the C_{ipso} of the bzq ligand which contribute to fulfil the electron density requirements of the acidic silver centre. Nevertheless, only trimetallic “sandwich” complexes $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}\}_2\text{Ag}]^+$ can be prepared, even if other Pt:Ag ratios are used. Therefore, it seems that the silver centre “needs” to be surrounded by two subunits $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}]$, with their corresponding Pt–Ag and Ag– C_{ipso} interactions, which contrasts with the complexes $[\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}\text{Ag}(\text{L})]$ and $[\{\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2\}\text{Ag}]_x$, in which the Pt:Ag ratio is 1:1, obtained with the anionic $[\text{Pt}(\text{bzq})(\text{C}_6\text{F}_5)_2]^-$ in which in principle the Pt has an excess of electron density. Only in one case, a 1:1 product $[(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\text{PtAg}(\text{pyPh}_2)]\text{ClO}_4$ (**11**) have been observed, its relative stability caused by the presence of bulkier ligands that slow down the transformation into $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\}_2\text{Ag}]\text{ClO}_4$ (**7**).

Moreover, complexes $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})\text{L}\}_2\text{Ag}]^+$ have shown to be flexible and able to adapt their geometry (to some extent) to the bulkiness of the ancillary L ligands, preserving at the same time the Pt–Ag and Ag– C_{ipso} interactions.

The photophysical properties of these complexes have been discussed with the aid of TD-DFT calculations on several compounds (**2**, **4**, **5**, **9**, **10**, **11Me** in CH_2Cl_2). While in the mononuclear complexes the lower lying absorption bands are ascribed to mixed $[^1\text{IL}, \pi\cdots\pi^*(\text{bzq})]/[^1\text{MLCT} (5d(\text{Pt})\rightarrow\pi^*(\text{bzq}))]$ transitions in the heteronuclear compounds, the formation of Pt–Ag bonds changes the character of the transition to $^1\text{ILCT}/^1\text{MM}^*\text{LCT} [\pi\cdots\pi^*(\text{bzq})]/(d/s(\text{Pt},\text{Ag})\rightarrow\pi^*(\text{bzq}))]$ for the trinuclear complexes and to mixed $^1\text{MLCT}/^1\text{L}^*\text{LCT} [\text{MLCT} (5d(\text{Pt})\rightarrow\pi^*(\text{bzq}))]/[^1\text{L}^*\text{LCT}, \text{Ar}\rightarrow\text{bzq}]$ for the dinuclear complex **11**. However, although the formation of the Pt–Ag bonds perturbs the frontier orbitals, it does not always shift the HOMO→LUMO transition to higher energies. With the exception of compound **2**, the mononuclear complexes are not emissive in the solid state at room temperature. However the heteronuclear compounds are. All compounds become brightly emissive in the solid state at 77 K. The main phosphorescent emission has been tentatively associated in all the compounds with a transition similar in character to their lowest lying absorption.

Experimental Section

Physical Measurements: C, H and N analyses, conductivity, IR and NMR spectra were performed as described elsewhere.^[16] Diffuse reflectance UV-vis (DRUV) spectra were recorded on a Thermo electron corporation evolution 600 spectrophotometer equipped with a Praying Mantis integrating sphere. The solid samples were homogeneously diluted with silica. The mixtures were placed in a homemade cell equipped with quartz window. Steady-state photoluminescence spectra were recorded on a Jobin-Yvon Horiba Fluorolog FL-3-11 Tau 3 spectrofluorimeter using slit width of 3 nm for both excitation and emission. Phosphorescence lifetimes were recorded with a Fluoromax phosphorimeter accessory containing a UV xenon flash tube with a flash rate between 0.05 and 25 Hz. Phase shift and modulation were recorded over the frequency range of 0.1-100 MHz.

Nanosecond lifetimes were recorded with an IBH 5000F Coaxial nanosecond flashlamp. The lifetime data were fitted using the Jobin-Yvon software package and the Origin Pro 8 program. The quantum efficiency was determined using a Quantaaurus quantum yield equipment from Hamamatsu model C11347-11.

Preparations: Literature methods were used to prepare the starting material [Pt(C₆F₅)(bzq)(Me₂CO)] (1).^[60]

Caution!: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of material should be prepared and these should be handled with great caution.

Preparation of [Pt(C₆F₅)(bzq)L] {L = PPh₃ (2), pyPh₂ (3), tht (4)}. To a solution of [Pt(bzq)(C₆F₅)(Me₂CO)] (1) (0.200 g, 0.335 mmol) in Me₂CO (10 mL) at 0°C and under Ar atmosphere, 0.335 mmol of L (L = PPh₃, 0.0879 g; pyPh₂, 0.0775 g; tht, 30 µL) was added. After 2 min of stirring the solution was concentrated until ca. 2 mL. The yellow precipitate which appeared was filtered off, washed with *n*-hexane (10 mL) and air dried.

[Pt(C₆F₅)(bzq)(PPh₃)] (2). 0.242 g, 90% yield. C₃₇H₂₂F₅NPpt (801.63) calcd.: C 55.37, H 2.89, N 1.75; found: C 55.32, H 2.90, N 1.79. IR (cm⁻¹): 1498 (w), 1458 (w), 1433 (w), 1096 (w, ν_{PPh₃}), 1058 (w), 955 (m), 804 (m, C₆F₅, X-sensitive vibr.),^[103] 693 (w), 529 (m), 509 (m). Λ_M (Me₂CO) = 4.17 Ω⁻¹cm²mol⁻¹. ¹H NMR (Me₂CO-d₆, 295 K). See scheme 4 for the atom numbering scheme of the bzq ligand: δ 8.55 (H4, dd, ³J_{H(4),H(3)} = 8.08 Hz, ⁴J_{H(4),H(2)} = 1.25 Hz), 8.33 (H2, dd, ³J_{H(2),H(3)} = 5.35 Hz, ⁴J_{H(2),H(4)} = 1.07 Hz, ³J_{Pt,H(2)} = 26.85 Hz), 7.93 (H5, d, ³J_{H(5),H(6)} = 8.72 Hz), 7.78 (H6, m, overlapped with 6H-*m*-Ph and H7), 7.78 (H7, m, overlapped with 6H-*m*-Ph and H6), 7.78 (6H-*m*-Ph, m, overlapped with H6 and H7), 7.51 (3H-*p*-Ph, m, ³J_{H_p-H_m} = 7.50, ³J_{H_p-H_o} = 1.60), 7.43 (H8, m, overlapped with 6H-*o*-Ph), 7.43 (6H-*o*-Ph, m, overlapped with H8), 7.23 (H3, dd, ³J_{H(3),H(4)} = 8.06 Hz, ³J_{H(3),H(2)} = 5.37 Hz), 7.00 (H9, dd, ³J_{H(9),H(8)} = 7.26 Hz, ³J_{H(9),H(7)} = 6.22 Hz, ³J_{Pt,H(9)} = 52.01 Hz). ¹⁹F NMR (Me₂CO-d₆, 295 K), δ -118.50 (*o*-F, ³J_{F,Pt} = 508.6 Hz), 167.94 (*m*-F, br m), -168.37 (*p*-F). ³¹P NMR (Me₂CO-d₆, 295 K), δ 28.05 (s, ³J_{P,Pt} = 1982.2 Hz).

Scheme 4

[Pt(C₆F₅)(bzq)(pyPh₂)] (3). 0.220 g, 85% yield. C₃₆H₂₁F₅N₂Pt (771.65) calcd.: C 56.03, H 2.74, N 3.63; found: C 55.88, H 2.86, N 3.52. IR (cm⁻¹): 1497 (w), 1448 (m), 1435 (w), 1056 (w), 951 (m), 793 (m, C₆F₅, X-sensitive vibr.),^[103] 696 (m, ν_{pyPh₂}). Λ_M (Me₂CO) = 5.66 Ω⁻¹cm²mol⁻¹. ¹H NMR (Me₂CO-d₆, 295 K), δ 8.67 (H2, m, ³J_{H(2),H(3)} = 5.30 Hz), 8.64 (H4, d, ³J_{H(4),H(3)} = 8.10 Hz, ⁴J_{H(4),H(2)} = 1.20 Hz), 8.26 (4H-*o*-Ph, m, ³J_{H_o,H_m} = 7.09 Hz, ⁴J_{H_o,H_p} = 1.50 Hz), 7.98-7.86 (m, overlapped signals of 2H-*m*-py and H-*p*-py), 7.85 (H5, d, ³J_{H(5),H(6)} = 8.80 Hz), 7.78 (H6, d, ³J_{H(6),H(5)} = 8.80 Hz), 7.73 (H3, m, overlapped with H2 and H4), 7.56 (H7, d, ³J_{H(7),H(8)} = 7.97 Hz), 7.53 (4H-*m*-Ph, m, ³J_{H_m,H_o} = 7.45 Hz, ³J_{H_m,H_p} = 1.40 Hz), 7.46 (2H-*p*-Ph, tt, ³J_{H_p,H_m} = 7.28 Hz, ⁴J_{H_p,H_o} = 1.30 Hz), 7.25 (H8, dd, ³J_{H(8),H(7)} = 7.66 Hz, ³J_{H(8),H(9)} = 7.35 Hz), 6.89 (H9, dd, ³J_{H(9),H(8)} = 7.35 Hz, ³J_{H(9),Pt} = 74.1 Hz). ¹⁹F NMR (CD₂Cl₂, 295 K), δ -119.04 (*o*-F, ³J_{F,Pt} = 513 Hz), -166.61 (*p*-F, t), 167.75 (*m*-F, br m).

[Pt(C₆F₅)(bzq)(tht)] (4). 0.214 g, 98 % yield. C₂₃H₁₆F₅N₂SPt (628.52) calcd.: C 43.95, H 2.57, N 2.23, S 5.10; found: C 44.08, H 2.32, N 2.33, S 5.10. IR (cm⁻¹): 1501 (m), 1451 (m), 1437 (m), 1267 (w, ν_{SC}), 1255 (w, ν_{SC}), 1061 (m), 951 (s), 798 (m, C₆F₅, X-sensitive vibr.).^[103] Λ_M (Me₂CO) = 0.2

Ω⁻¹cm²mol⁻¹. ¹H NMR (Me₂CO-d₆, 295 K), δ 9.35 (H2, dd, ³J_{H(2),H(3)} = 5.24 Hz, ⁴J_{H(2),H(4)} = 1.31 Hz, ³J_{H(2),Pt} = 23.4 Hz), 8.70 (H4, dd, ³J_{H(4),H(3)} = 8.08 Hz, ⁴J_{H(4),H(2)} = 1.26 Hz), 7.89 (H5, d, ³J_{H(5),H(6)} = 8.76 Hz), 7.84 (H3, dd, ³J_{H(3),H(4)} = 8.08 Hz, ³J_{H(3),H(2)} = 5.26 Hz), 7.80 (H6, d, ³J_{H(6),H(5)} = 8.75 Hz), 7.63 (H7, dd, ³J_{H(7),H(8)} = 7.92 Hz, ⁴J_{H(7),H(9)} = 0.70 Hz), 7.34 (H8, dd, ³J_{H(8),H(9)} = 8.04 Hz, ³J_{H(8),H(7)} = 7.31 Hz), 6.82 (H9, d, ³J_{H(9),H(8)} = 6.76 Hz, ³J_{H(9),Pt} = 62.01 Hz), 3.23 (4H-*m*-tht, m), 1.87 (4H-*o*-tht, m). ¹⁹F NMR (Me₂CO-d₆, 295 K), δ -118.82 (*o*-F, ³J_{F,Pt} = 512.53 Hz), -166.09 (*p*-F), -166.90 (*m*-F, br m).

Preparation of [Pt(C₆F₅)(bzq)(MeCN)] (5). Complex [Pt(bzq)(C₆F₅)(Me₂CO)] (1) (0.200 g, 0.335 mmol) was dissolved in MeCN (10 mL) at 0°C under Ar atmosphere. After 2 min of stirring the solution was evaporated to dryness. The yellow residue was treated with *n*-hexane (10 mL), filtered off and finally air-dried. 0.179 g, 92 % yield. C₂₁H₁₁F₅N₂Pt (581.40) calcd.: C 43.38, H 1.91, N 4.82; found: C 42.99, H 1.79, N 4.71. IR (cm⁻¹): 2154 (vw, ν_{CN}), 1497 (m), 1453 (m), 1062 (m), 953 (vs), 798 (m, C₆F₅, X-sensitive vibr.).^[103] Λ_M (Me₂CO) = 7.01 Ω⁻¹cm²mol⁻¹. ¹H NMR (Me₂CO-d₆, 295 K), δ 9.19 (H2, dd, ³J_{H(2),H(3)} = 5.18 Hz, ⁴J_{H(4),H(2)} = 1.20 Hz, ³J_{H(2),Pt} = 21.78 Hz), 8.65 (H4, dd, ³J_{H(4),H(3)} = 8.06 Hz, ³J_{H(4),H(2)} = 1.20 Hz), 7.85 (H5, d, ³J_{H(5),H(6)} = 8.83 Hz), 7.75 (H6, d, ³J_{H(6),H(5)} = 8.83 Hz), 7.74 (H3, d, ³J_{H(3),H(4)} = 8.46 Hz, ³J_{H(3),H(2)} = 5.00 Hz, overlapped with H6), 7.58 (H7, dd, ³J_{H(7),H(8)} = 7.88 Hz, ⁴J_{H(7),H(9)} = 0.60 Hz), 7.30 (H8, dd, ³J_{H(7),H(8)} = 7.82 Hz, ³J_{H(7),H(9)} = 7.62 Hz), 6.96 (H9, d, ³J_{H(9),H(8)} = 7.62 Hz, ³J_{H(9),Pt} = 58.51 Hz), 2.61 (H_{MeCN}, s). ¹⁹F NMR (Me₂CO-d₆, 295 K), δ -119.08 (*o*-F, ³J_{F,Pt} = 513 Hz), -167.12 (*p*-F), 168.05 (*m*-F, br m).

Preparation of [Pt(C₆F₅)(bzq)L]₂AgClO₄ {L = Me₂CO (6), PPh₃ (7), pyPh₂ (8), tht (9)}. To a solution of [Pt(bzq)(C₆F₅)L] (L = Me₂CO, 0.250 g, 0.418 mmol; L = PPh₃, 0.250 g, 0.187 mmol; L = pyPh₂, 0.200 g, 0.260 mmol; L = tht, 0.200 g, 0.385 mmol) in Me₂CO (20 mL) at 0°C and under Ar atmosphere, AgClO₄ {L = Me₂CO, 0.043 g, 0.209 mmol; L = PPh₃, 0.019 g, 0.093 mmol; L = pyPh₂, 0.0270 g, 0.130 mmol; L = tht, 0.040 g, 0.193 mmol) was added. After 30 min of stirring in absence of light the solution was concentrated until ca. 2 mL. Over the resultant yellow suspension, *n*-hexane (10 mL) was added. The yellow precipitate was filtered off and air dried.

[Pt(C₆F₅)(bzq)(Me₂CO)]₂AgClO₄ (6). 0.154 g, 56 %. C₄₄H₂₈AgClF₁₀N₂O₆Pt₂ (1404.18) calcd.: C 37.64, H 2.01, N 2.00; found: C 37.87, H 2.11, N 1.99. IR (cm⁻¹): 1620 (w), 1503 (w), 1455 (w), 1442 (w), 1096 (m, ν_{ClO₄}), 1059 (m), 953 (m), 801 (m, C₆F₅, X-sensitive vibr.),^[103] 621 (m, ν_{ClO₄}). Λ_M (Me₂CO) = 134.35 Ω⁻¹cm²mol⁻¹. ¹H NMR (Me₂CO-d₆, 295 K), δ 8.70 (H2, dd, ³J_{H(2),H(3)} = 8.11 Hz, ⁴J_{H(2),H(4)} = 1.14 Hz), 8.64 (H4, m, ³J_{H(4),H(3)} = 8.11 Hz), 7.86 (H3, H5 and H6, m), 7.63 (H7, dd, ³J_{H(7),H(8)} = 7.94 Hz, ⁴J_{H(7),H(9)} = 0.52 Hz), 7.19 (H8, dd, ³J_{H(8),H(7)} = 7.47 Hz, ³J_{H(8),H(9)} = 7.58 Hz), 6.90 (H9, d, ³J_{H(9),H(8)} = 7.06 Hz, ³J_{H(9),Pt} = 71.21 Hz), 2.14 (H_{Me₂CO}, s). ¹⁹F NMR (Me₂CO-d₆, 295 K), δ -117.89 (*o*-F, ³J_{F,Pt} = 502.3 Hz), -165.06 (*p*-F), -166.66 (*m*-F, br m).

[Pt(C₆F₅)(bzq)(PPh₃)]₂AgClO₄ (7). 0.132 g, 82 % yield. C₇₄H₄₆AgClF₁₀N₂O₄P₂Pt₂ (1812.60) calcd.: C 49.03, H 2.56, N 1.55; found: C 48.98, H 2.59, N 1.59. IR (cm⁻¹): 1500 (m), 1458 (m), 1435 (m), 1093 (m, ν_{ClO₄}), 1060 (m), 954 (s), 804 (s, C₆F₅, X-sensitive vibr.),^[103] 693 (s), 621 (m, ν_{ClO₄}), 529 (s, ν_{PPh₃}), 509 (s, ν_{PPh₃}). Λ_M (Me₂CO) = 266.06 Ω⁻¹cm²mol⁻¹. ¹H NMR (Me₂CO-d₆, 295 K), δ 8.61 (H4, dd, ³J_{H(4),H(3)} = 8.05 Hz, ⁴J_{H(4),H(2)} = 0.90 Hz), 8.34 (H2, d, ³J_{H(2),H(3)} = 5.35 Hz, ³J_{H(2),Pt} = 25.77), 7.94 (H5, d, ³J_{H(5),H(6)} = 8.72 Hz), 7.82 (H6, d, ³J_{H(6),H(5)} = 8.74 Hz), 7.74 (H7, m, overlapped with 6H-*m*-Ph, m), 7.53 (3H-*p*-Ph, ³J_{H_p,H_m} = 7.46 Hz, ⁴J_{H_p,H_o} = 1.18 Hz), 7.45 (H8 and 6H-*o*-Ph, m), 7.29 (H3, dd, ³J_{H(3),H(4)} = 8.05 Hz, ³J_{H(3),H(2)} = 5.37 Hz), 7.11 (H9, t, ³J_{H(9),H(8)} = 6.22 Hz, ³J_{H(9),Pt} = 49.30 Hz). ¹⁹F NMR (Me₂CO-d₆, 295 K), δ -117.89 (*o*-F, ³J_{F,Pt} = 504.3 Hz), -167.07, -167.54 (*m*-F, *p*-F br m). ³¹P NMR (Me₂CO-d₆, 295 K), δ 27.23 (s, ³J_{P,Pt} = 2081.1 Hz).

[Pt(C₆F₅)(bzq)(pyPh₂)]₂AgClO₄ (8). 0.207 g, 96 % yield. C₇₂H₄₂AgClF₁₀N₄O₄Pt₂ (1750.61) calcd.: C 49.40, H 2.42, N 3.20; found: C 48.97, H 2.52, N 3.34. IR (cm⁻¹): 1501 (w), 1452 (w), 1439 (w), 1093 (w,

$\nu_{\text{ClO}_4^-}$), 1058 (m), 953 (m), 797 (s, C_6F_5 , X-sensitive vibr.),^[103] 622 (w, $\nu_{\text{ClO}_4^-}$), 696 (w). $\Lambda_{\text{M}}(\text{Me}_2\text{CO}) = 241.43 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. ^1H NMR ($\text{Me}_2\text{CO}-d_6$, 295 K), δ 8.70 (H2, dd, $^3J_{\text{H}(2),\text{H}(3)} = 8.12$ Hz, $^4J_{\text{H}(2),\text{H}(4)} = 1.10$ Hz, overlapped with H4), 8.67 (H4, m, overlapped with H2), 8.02 (H-*p*-py, m), 8.15 (4H-*o*-Ph, m), 7.90 (2H-*m*-py, m), 7.88 (H5, d, $^3J_{\text{H}(5),\text{H}(6)} = 8.79$ Hz), 7.84 (H6, d, $^3J_{\text{H}(6),\text{H}(5)} = 8.85$ Hz), 7.63 (H7, dd, $^3J_{\text{H}(7),\text{H}(8)} = 7.97$ Hz, $^4J_{\text{H}(7),\text{H}(9)} = 0.54$ Hz), 7.49 (4H-*m*-Ph and 2H-*p*-Ph, m), 7.24 (H8, dd, $^3J_{\text{H}(8),\text{H}(7)} = 7.62$ Hz, $^3J_{\text{H}(8),\text{H}(9)} = 7.45$ Hz), 6.89 (H9, d, $^3J_{\text{H}(9),\text{H}(8)} = 7.28$ Hz, $^3J_{\text{H}(9),\text{Pt}} = 71.51$ Hz). ^{19}F NMR ($\text{Me}_2\text{CO}-d_6$, 295 K), δ -118.26 (*o*-F, $^3J_{\text{F,Pt}} = 505.91$ Hz), -165.50 (*p*-F), -166.94 (*m*-F, br m).

[[Pt(C₆F₅)(bzq)(tht)]₂Ag]ClO₄ (9). 0.200 g, 71% yield. $\text{C}_{46}\text{H}_{32}\text{AgClF}_{10}\text{N}_2\text{O}_4\text{Pt}_2\text{S}_2$ (1464.37) calcd.: C 37.73, H 2.20, N 1.91, S 4.38; found: C 37.29, H 2.01, N 1.92, S 3.89. IR (cm^{-1}): 1503 (m), 1453 (m), 1439 (m), 1269 (w, ν_{SCl}), 1256 (w, ν_{SCl}), 1086 (m, $\nu_{\text{ClO}_4^-}$), 1061 (s), 952 (s), 801 (m, C_6F_5 , X-sensitive vibr.),^[103] 621 (w, $\nu_{\text{ClO}_4^-}$). $\Lambda_{\text{M}}(\text{Me}_2\text{CO}) = 238.73 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. ^1H NMR (Acetone- d_6 , 295 K), δ 9.26 (H2, dd, $^3J_{\text{H}(2),\text{H}(3)} = 5.24$ Hz, $^4J_{\text{H}(2),\text{H}(4)} = 1.27$ Hz, $^3J_{\text{H}(2),\text{Pt}} = 21.9$ Hz), 8.77 (H4, dd, $^3J_{\text{H}(4),\text{H}(3)} = 8.10$ Hz, $^4J_{\text{H}(4),\text{H}(2)} = 1.21$ Hz), 7.93 (H3, dd, $^3J_{\text{H}(3),\text{H}(4)} = 8.08$ Hz, $^3J_{\text{H}(3),\text{H}(2)} = 5.23$ Hz), 7.91 (H5, d, $^3J_{\text{H}(5),\text{H}(6)} = 8.74$ Hz), 7.86 (H6, d, $^3J_{\text{H}(6),\text{H}(5)} = 8.77$ Hz), 7.73 (H7, dd, $^3J_{\text{H}(7),\text{H}(8)} = 8.00$ Hz, $^4J_{\text{H}(7),\text{H}(9)} = 0.70$ Hz), 7.34 (H8, dd, $^3J_{\text{H}(8),\text{H}(9)} = 7.89$ Hz, $^3J_{\text{H}(8),\text{H}(7)} = 7.20$ Hz), 6.86 (H9, d, $^3J_{\text{H}(9),\text{H}(8)} = 7.03$ Hz, $^3J_{\text{H}(9),\text{Pt}} = 58.53$ Hz), 3.17 (4H-*m*-tht, m), 1.86 (4H-*o*-tht, m). ^{19}F NMR ($\text{Me}_2\text{CO}-d_6$, 295 K), δ -117.47 (*o*-F, $^3J_{\text{F,Pt}} = 506.05$ Hz), -164.62 (*p*-F), -165.86 (*m*-F, br m).

Preparation of [[Pt(C₆F₅)(bzq)(MeCN)]₂Ag]ClO₄ (10). To a solution of [Pt(bzq)(C₆F₅)(MeCN)] (0.200 g, 0.344 mmol) in Me_2CO (20 mL) at 0°C and under Ar atmosphere, AgClO_4 {0.0357 g, 0.172 mmol} was added. After 30 min of stirring in absence of light the solution was evaporated to dryness. The yellow residue was treated with *n*-hexane (10 mL), filtered off and finally air-dried, 0.211 g, 96 % yield. $\text{C}_{42}\text{H}_{22}\text{AgClF}_{10}\text{N}_4\text{O}_4\text{Pt}_2$ (1370.13) calcd.: C 36.82, H 1.62, N 4.09; found: C 37.17, H 2.02, N 3.73. IR (cm^{-1}): 2165 (vw, ν_{CN}), 1504 (m), 1443 (m), 1456 (m), 1060 (s), 1090 (m, $\nu_{\text{ClO}_4^-}$), 953 (s), 804 (m, C_6F_5 , X-sensitive vibr.),^[103] 623 (m, $\nu_{\text{ClO}_4^-}$). $\Lambda_{\text{M}}(\text{Me}_2\text{CO}) = 225.67 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. ^1H NMR ($\text{Me}_2\text{CO}-d_6$, 295 K), δ 9.17 (H2, dd, $^3J_{\text{H}(2),\text{H}(3)} = 5.13$ Hz, $^4J_{\text{H}(2),\text{H}(4)} = 1.06$ Hz, $^3J_{\text{H}(2),\text{Pt}} = 24.70$ Hz), 8.73 (H4, dd, $^3J_{\text{H}(4),\text{H}(3)} = 8.18$ Hz, $^4J_{\text{H}(4),\text{H}(2)} = 1.03$ Hz), 7.89 (H5, d, $^3J_{\text{H}(5),\text{H}(6)} = 8.74$ Hz), 7.87 (H3, m, overlapped with H5 and H6), 7.84 (H6, d, $^3J_{\text{H}(6),\text{H}(5)} = 8.79$ Hz), 7.68 (H7, d, $^3J_{\text{H}(7),\text{H}(8)} = 7.95$ Hz), 7.27 (H8, dd, $^3J_{\text{H}(8),\text{H}(7)} = 7.75$ Hz, $^3J_{\text{H}(8),\text{H}(9)} = 7.69$ Hz), 6.95 (H9, d, $^3J_{\text{H}(9),\text{H}(8)} = 7.69$ Hz, $^3J_{\text{H}(9),\text{Pt}} = 63.0$ Hz), 2.65 (H-MeCN, s). ^{19}F NMR ($\text{Me}_2\text{CO}-d_6$, 295 K), δ -117.87 (*o*-F, $^3J_{\text{F,Pt}} = 492.0$ Hz), -165.81 (*p*-F), -167.14 (*m*-F, br m).

Preparation of [Pt(C₆F₅)(bzq)(PPh₃)Ag(pyPh₂)]ClO₄ (11). To a solution of [Pt(bzq)(C₆F₅)(pyPh₂)] (0.200 g, 0.259 mmol) in Me_2CO (20 mL) at 0°C and under Ar atmosphere, [Ag(OCIO₃)(PPh₃)] (0.121 g, 0.259 mmol) was added. After 30 min of stirring in absence of light the solution was evaporated to dryness. The oily yellow residue was treated with *n*-hexane (10 mL) and allowed to stir for 60 min. After this time, the yellow solid formed is filtered off and finally air-dried, 0.263 g, 88 % yield. $\text{C}_{54}\text{H}_{36}\text{AgClF}_5\text{N}_2\text{O}_4\text{PPt}$ (1241.25) calcd.: C 52.25, H 2.92, N 2.26; found: C 52.02, H 2.81, N 2.24. IR (cm^{-1}): 1501 (w), 1456 (w), 1435 (w), 1092 (m, $\nu_{\text{ClO}_4^-}$), 1059 (w), 957 (w), 803 (w, C_6F_5 , X-sensitive vibr.), 621 (w, $\nu_{\text{ClO}_4^-}$), 693 (w), 531 (w), 512 (w). $\Lambda_{\text{M}}(\text{Me}_2\text{CO}) = 246.87 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$. ^1H NMR ($\text{Me}_2\text{CO}-d_6$, 295 K), δ 8.64 (H4, dd, $^3J_{\text{H}(4),\text{H}(3)} = 8.07$ Hz, $^3J_{\text{H}(4),\text{H}(2)} = 1.0$ Hz), 8.34 (H2, d, $^3J_{\text{H}(2),\text{H}(3)} = 5.36$ Hz, $^3J_{\text{H}(2),\text{Pt}} = 26.36$ Hz), 8.15 (4H-*o*-Ph, m), 8.06 (H-*p*-py, m), 7.99 (H5, d, $^3J_{\text{H}(5),\text{H}(6)} = 8.74$ Hz), 7.91 (2H-*m*-py, m), 7.85 (H6, d, $^3J_{\text{H}(6),\text{H}(5)} = 8.87$ Hz), 7.74 (H7 and H-*m*-Ph (PPh₃), m), 7.55-7.42 (H8 and 3H-*p*-Ph (PPh₃), 6H-*o*-Ph (PPh₃), 4H-*m*-Ph (PPh₂), 2H-*p*-Ph (PPh₂), m), 7.32 (H6, dd, $^3J_{\text{H}(3),\text{H}(4)} = 8.06$ Hz, $^4J_{\text{H}(3),\text{H}(2)} = 5.38$ Hz), 7.13 (H9, t, $^3J_{\text{H}(9),\text{H}(8)} = 6.21$ Hz, $^3J_{\text{H}(2),\text{Pt}} = 47.40$). ^{19}F NMR ($\text{Me}_2\text{CO}-d_6$, 295 K), δ -116.93 (*o*-F, $^3J_{\text{F,Pt}} = 500.65$ Hz), 167.16 (*m*-F, br m), -166.88 (*p*-F). ^{31}P NMR ($\text{Me}_2\text{CO}-d_6$, 295 K), δ 26.59 (s, $J_{\text{P,Pt}} = 2147.8$ Hz).

Table 12. Crystal data and structure refinement for complexes [Pt(C₆F₅)(bzq)(PPh₃)]·0.2Me₂CO (2·0.2Me₂CO), [Pt(C₆F₅)(bzq)(tht)]·2/3CH₂Cl₂ (4·2/3CH₂Cl₂) and [Pt(C₆F₅)(bzq)(MeCN)] (5).

	2·0.2Me ₂ CO	4·2/3CH ₂ Cl ₂	5
Formula	C ₃₇ H ₂₃ F ₅ NPPt	C ₂₃ H ₁₆ F ₅ NPtS	C ₂₁ H ₁₁ F ₅ N ₂ Pt
Formula weight	814.24	685.14	581.41
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group	<i>P</i> -1	<i>Pc</i>	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	14.3213(3)	16.1169(3)	13.851(2)
<i>b</i> [Å]	14.7249(4)	12.4389(2)	7.4016(7)
<i>c</i> [Å]	16.0887(5)	16.4671(3)	17.653(2)
α [°]	80.101(3)	90	90
β [°]	79.902(2)	93.036(2)	108.066(14)
γ [°]	66.437(2)	90	90
<i>V</i> [Å ³]	3042.17(14)	3296.63(10)	12406.2(7)
<i>Z</i>	4	6	4
<i>D_c</i> [g cm ⁻³]	1.778	2.071	2.245
<i>T</i> [K]	100(1)	100(1)	100(1)
μ (Mo- <i>Kα</i>) [mm ⁻¹]	4.726	6.697	8.217
<i>F</i> (000)	1586	1968	1096
θ range [°]	4.2–26.0	4.2–28.9	4.1–25.5
Reflections collected	28562	34078	11311
Independent reflections	11905	14799	3170
<i>R</i> _{int}	0.0292	0.0425	0.0601
<i>R</i> ₁ , <i>wR</i> ₂ ^{<i>a</i>} (<i>I</i> > 2 σ (<i>I</i>))	0.0426, 0.0826	0.0364, 0.0908	0.0416, 0.0988
<i>R</i> ₁ , <i>wR</i> ₂ ^{<i>a</i>} (all data)	0.0536, 0.0849	0.0413, 0.0926	0.0525, 0.1026
GO _F (<i>F</i> ²) ^{<i>b</i>}	1.122	1.030	1.030
Absolute structure par.	-	0.020(5)	-

^{*a*} $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. ^{*b*} Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

X-ray structure determinations. Crystal data and other details of the structure analyses are presented in Tables 12 and 13. Suitable crystals for X-ray diffraction studies were obtained by slow diffusion of *n*-hexane into concentrated solutions of the complexes in 3 mL of CH₂Cl₂ or Me₂CO. Crystals were mounted at the end of quartz fibres. The radiation used in all cases was graphite monochromated MoK α ($\lambda = 0.71073$ Å). X-ray intensity data were collected on an Oxford Diffraction Xcalibur diffractometer. The diffraction frames were integrated and corrected from absorption by using the CrysAlis RED program.^[104] The structures were solved by Patterson and Fourier methods and refined by full-matrix least squares on *F*² with SHELXL-97.^[105] All non-hydrogen atoms were assigned anisotropic displacement parameters and refined without positional constraints, except as noted below. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters equal to 1.2 times the *U*_{ISO} values of their attached parent atoms (1.5 times for the methyl hydrogen atoms). In the structure of 4·2/3CH₂Cl₂, three complete complexes are found in the asymmetric unit. In two of them, the β CH₂ fragments of the tht ligands are disordered over two positions which were refined with partial occupancy 0.60/0.40 and 0.65/0.35. Weak restraints were applied in the interatomic C-C distances and thermal parameters of these fragments. For 10·2.5CH₂Cl₂·0.5*n*-C₆H₁₄, restraints were used in some structural and thermal parameters of the C atoms of the bzq ligands. Very diffuse solvent was found during the refinement stages and was modelled as several dichloromethane moieties, some of them disordered, with a total occupancy of 2.5, and half of a *n*-hexane molecule. Restraints were used in the structural and thermal parameters of these units.

Table 13. Crystal data and structure refinement for complexes $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\}_2\text{Ag}]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ (**7**·CH₂Cl₂), $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{tht})\}_2\text{Ag}]\text{ClO}_4\cdot 1.5\text{Me}_2\text{CO}$ (**9**·1.5Me₂CO), $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{MeCN})\}_2\text{Ag}]\text{ClO}_4\cdot 2.5\text{CH}_2\text{Cl}_2\cdot 0.5n\text{-C}_6\text{H}_{14}$ (**10**·2.5CH₂Cl₂·0.5n-C₆H₁₄), and $[(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)\text{Pt}(\text{pyPh}_2)]\text{ClO}_4\cdot\text{CH}_2\text{Cl}_2$ (**11**·CH₂Cl₂).

	7 ·CH ₂ Cl ₂	9 ·1.5Me ₂ CO	10 ·2.5CH ₂ Cl ₂ ·0.5n-C ₆ H ₁₄	11 ·CH ₂ Cl ₂
Formula	C ₇₄ H ₄₆ AgClF ₁₀ N ₂ O ₄ P ₂ Pt ₂ ·CH ₂ Cl ₂	C ₄₆ H ₃₂ AgClF ₁₀ N ₂ O ₄ Pt ₂ S ₂ ·1.5Me ₂ CO	C ₄₂ H ₂₂ AgClF ₁₀ N ₄ O ₄ Pt ₂ ·2.5CH ₂ Cl ₂ ·0.5n-C ₆ H ₁₄	C ₅₄ H ₃₆ AgClF ₅ N ₂ O ₄ PPt·CH ₂ Cl ₂
<i>M_r</i>	1897.49	1551.47	1625.54	1326.15
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> [Å]	13.1438(2)	13.5673(8)	13.9756(4)	13.4888(2)
<i>b</i> [Å]	35.7903(8)	14.4385(11)	14.3662(3)	13.5126(2)
<i>c</i> [Å]	14.3105(3)	15.3982(8)	16.1823(3)	14.6245(2)
α [°]	90	72.599(6)	79.6218(17)	106.249(1)
β [°]	102.9667(19)	68.987(5)	69.783(2)	107.091(1)
γ [°]	90	64.745(7)	64.539(2)	90.684(1)
<i>V</i> [Å ³]	6560.3(2)	2508.2(3)	2750.84(11)	2433.18(6)
<i>Z</i>	4	2	2	2
<i>D_c</i> [g cm ⁻³]	1.921	2.052	1.963	1.810
<i>T</i> [K]	100(1)	100(1)	100(1)	100(1)
μ [mm ⁻¹]	4.804	6.175	5.796	3.542
<i>F</i> (000)	3672	1485	1548	1300
θ range [°]	4.2–28.9	4.3–28.9	4.1–28.9	4.2–35.3
Reflections collected	57416	49929	58605	91933
Independent reflections	15626	11819	13069	18524
<i>R_{int}</i>	0.0427	0.0600	0.0624	0.0286
<i>R</i> ₁ , <i>wR</i> ₂ ^{<i>a</i>} (<i>I</i> > 2σ(<i>I</i>))	0.0347, 0.0566	0.0395, 0.0997	0.0571, 0.1524	0.0190, 0.0419
<i>R</i> ₁ , <i>wR</i> ₂ ^{<i>a</i>} (all data)	0.0531, 0.0586	0.0569, 0.1070	0.0942, 0.1646	0.0244, 0.0425
GOF (<i>F</i> ²) ^{<i>b</i>}	1.008	1.044	1.030	1.027

^{*a*} $R_1 = \sum(|F_o| - |F_c|) / \sum |F_o|$. $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$. ^{*b*} Goodness-of-fit = $[\sum w(F_o^2 - F_c^2)^2 / (n_{\text{obs}} - n_{\text{param}})]^{1/2}$.

Full-matrix least-squares refinement of these models against *F*² converged to final residual indices given in Tables 12 and 13. CCDC 906692-906698 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methods. Density functional calculations were performed using the hybrid functionals B3LYP^[106, 107] for complexes **2**, **4** and **5** and the M06^[108] for complexes **9–11Me** under the Gaussian09 package.^[109] The SDD pseudopotential and associated basis set^[110] was used for platinum and silver atoms, and the 6-31G(d)^[111, 112] basis set was used for all other atoms. Geometry optimisations were performed under no symmetry restrictions, using initial coordinates derived from X-ray data of the same or comparable complexes. Frequency calculations were used to confirm the stationary points were true minima. The time-dependent density-functional (TD-DFT) calculations were performed using the polarized continuum model approach implemented in the Gaussian 09 software. A Mulliken population analysis was included for interpretation purposes. Molecular orbitals were visualized using the Molekel program package.^[113]

Supporting Information (see footnote on the first page of this article): Absorption data of 10⁻⁴ M solutions of **1–11** at room temperature (Table S1). DFT-Optimized coordinates and selected singlet excited states calculated by TD-DFT for complexes **2**, **4**, **5**, **9**, **10** and **11Me** in CH₂Cl₂ (Tables S2–S7). Emission data of 10⁻³ M solutions of **1–5** at 77K (Table S8). Views of the supramolecular arrangement showing the π – π stacking for complexes **2** and **5** (Figures S1 and S2). Normalized absorption spectra of **2** in solution

of different solvents (10⁻⁴ M) at room temperature (Figure S3). Energy levels and electron-density diagrams of the frontier molecular orbitals involved in the lower energy excited calculated states for **4**, **5**, **9** and **10** (Figures S4 and S5). Normalized DRUV spectra of complexes **1–5** in the solid state (Figure S6). Normalized emission and excitation spectra of **5** and **10** in the solid state (Figure S7).

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Entry for the Table of Contents

((Key Topic))

Trimetallic $[\{Pt(C_6F_5)(bzq)L\}_2Ag]^+$ or bimetallic $[(C_6F_5)(bzq)(PPh_3)Pt-Ag(pyPh_2)]^+$ clusters containing Pt–Ag bonds have been prepared from $[Pt(C_6F_5)(bzq)L]$ ($bzq = 7,8$ -benzoquinolate). All these complexes have luminescent properties which have been studied and interpreted with the help of TD-DFT calculations.

Antonio Martín,* Úrsula Belío, Sara Fuertes and Violeta Sicilia..... Page No. – Page No.

Luminescent Pt–Ag Clusters based in Neutral Benzoquinolate Cyclometalated Platinum Complexes

Keywords: Donor-acceptor systems, heterometallic complexes, Luminescence, metal-metal interactions, pi interactions, X-ray diffraction.

SUPPORTING INFORMATION

Table S1. Absorption data for **1** to **11** in solutions 10^{-4} M at room temperature.

Compound	Solvent	$\lambda_{\text{abs}} / \text{nm} (10^3 \epsilon \text{ M}^{-1} \text{cm}^{-1})$
1	Toluene	288(9.3), 300(8.4), 314(8.2), 338(5.3), 372(2.7), 412(1.5), 432(1.6)
	CH ₂ Cl ₂	300(7.3), 346(2.4), 400(1.4)
2	Toluene	268(12.1), 278(12.6), 306(15.2), 362(3.1), 396(2.1), 412(2.1)
	THF	302(20.5), 356(4.1), 388(2.7), 404(2.8)
	CH ₂ Cl ₂	302(6.9), 352(1.4), 388(0.9), 402(1.0)
	DMF	270(21.7), 288(19.8), 350(3.0), 384(2.0), 398(2.1)
	NCMe	298(15.5), 352(3.0), 382(2.1), 394(2.2)
3	Toluene	288(26.6), 302(24.6), 340(7.8), 370(4.1), 416(2.3), 432(2.3)
	THF	300(18.0), 334(5.1), 370(2.6), 416(1.0), 430(0.6)
	CH ₂ Cl ₂	300(6.2), 334(2.3), 370(1.0), 402(0.7)
	DMF	268(22.0), 296(16.2), 336(7.8), 360(3.8), 412(2.2)
	NCMe	294(16.4), 332(8.0), 358(3.9), 412(2.2)
4	Toluene	288(10.2), 306(9.3), 358(2.3), 398(1.5), 410(1.6)
	THF	278(15.6), 292(14.2), 304(13.4), 352(3.8), 398(2.4)
	CH ₂ Cl ₂	304(7.8), 320(5.3), 354(1.6), 400(1.4)
	DMF	304(8.5), 326(6.3), 362(2.6), 408(1.7)
	NCMe	302(14.4), 320(10.3), 348(3.7), 388(2.5), 400(2.6)
5	Toluene	286(22.0), 306(8.9), 356(3.3), 372 (3.1), 400(1.2)
	2-Me-THF	282(11.0), 304(16.2), 330(8.9), 356(3.8), 392(2.8), 404(3.0)
	CH ₂ Cl ₂	304(11.4), 350(3.0), 394(2.0), 406(2.1)
	DMF	266(12.1), 306(9.9), 334(7.4), 358(3.5), 412(2.1)
	NCMe	302(22.8), 348(3.7), 390(2.5), 400(2.6)
6	CH ₂ Cl ₂	284(4.6), 330(2.1), 390(0.9), 406(0.8)
7	CH ₂ Cl ₂	300(6.9), 356(1.3), 398(1.0)
8	CH ₂ Cl ₂	298(8.6), 332(3.7), 408(1.2)
9	CH ₂ Cl ₂	300(8.0), 326(4.2), 354(1.7), 402(1.4)
10	CH ₂ Cl ₂	298(5.3), 336(2.4), 392(0.9), 406(1.0)
11	CH ₂ Cl ₂	300(5.6), 358(0.7), 400(5.6)

Table S2. DFT-Optimized coordinates of [Pt(C₆F₅)(bzq)(PPh₃)] (2)

Center	Coordinates (Angstroms)		
	X	Y	Z

Pt	0.607532000	-0.394177000	0.019904000
P	-0.807681000	1.549342000	0.037913000
F	-1.257802000	-1.402798000	-2.361714000
F	-3.349378000	-3.103587000	-2.409414000
F	-4.272764001	-4.229008001	-0.092406000
F	-3.068124000	-3.617466000	2.285769000
F	-0.977402000	-1.917538000	2.359719000
N	2.535249000	0.623449000	0.008162000
C	-1.012751000	-1.608530000	-0.001219000
C	-1.667781000	-1.943076000	-1.184726000
C	-2.753789000	-2.813694000	-1.240703000
C	-3.226750000	-3.388206000	-0.063795000
C	-2.608624000	-3.076474000	1.144314000
C	-1.525500000	-2.199492000	1.152124000
C	2.805340000	1.930606000	-0.006108000
C	4.112659000	2.439152000	-0.005248000
C	5.179009001	1.558253000	0.008475000
C	4.932980001	0.171511000	0.014163000
C	5.968267001	-0.823221000	0.018753000
C	5.659475001	-2.152085000	0.011091000
C	4.297819001	-2.611624000	-0.002642000
C	3.951188000	-3.979206000	-0.023720000
C	2.616148000	-4.344142001	-0.045300000
C	1.588159000	-3.376354000	-0.042133000
C	1.870031000	-2.011960000	-0.014343000
C	3.247586000	-1.652717000	0.001516000
C	3.581128000	-0.262087000	0.011100000
C	-0.725406000	2.557522000	1.579626000
C	0.253846000	2.256137000	2.538441000
C	0.335767000	2.992925000	3.722745000
C	-0.561765000	4.033475000	3.963555000
C	-1.552149000	4.330509001	3.022893000
C	-1.638758000	3.594062000	1.841896000
C	-0.360486000	2.682024000	-1.351326000
C	-0.041935000	2.076992000	-2.581305000
C	0.305177000	2.858557000	-3.683807000
C	0.358933000	4.249910001	-3.569107000
C	0.057625000	4.857058001	-2.349018000
C	-0.304462000	4.079730000	-1.245952000
C	-2.625367000	1.293588000	-0.159012000
C	-3.312661000	1.627351000	-1.333150000
C	-4.680713001	1.365699000	-1.448773000
C	-5.374152001	0.769954000	-0.395950000
C	-4.695552001	0.434731000	0.779152000
C	-3.330878000	0.691387000	0.897217000
H	1.958261000	2.604348000	-0.027553000
H	4.263479001	3.513426000	-0.016640000
H	6.203362001	1.922951000	0.010613000
H	7.003851001	-0.493162000	0.025333000
H	6.454003001	-2.894798000	0.012471000

H	4.735318001	-4.732307001	-0.025755000
H	2.348768000	-5.398227001	-0.065011000
H	0.558963000	-3.719472000	-0.063027000
H	0.933972000	1.427525000	2.363432000
H	1.094069000	2.743337000	4.459821001
H	-0.500428000	4.603837001	4.886517001
H	-2.263763000	5.129357001	3.213676000
H	-2.429480000	3.813318000	1.130039000
H	-0.065563000	0.993619000	-2.667442000
H	0.543228000	2.377924000	-4.628754001
H	0.638501000	4.857209001	-4.425810001
H	0.101732000	5.938694001	-2.252239000
H	-0.533437000	4.566672001	-0.303475000
H	-2.787034000	2.090661000	-2.161441000
H	-5.200595001	1.629398000	-2.365833000
H	-6.436982001	0.564169000	-0.489013000
H	-5.227207001	-0.033421000	1.603002000
H	-2.812768000	0.420459000	1.812818000

Table S3. DFT-Optimized coordinates of [Pt(C₆F₅)(bzq)(tht)] (**4**)

Center	Coordinates (Angstroms)		
	X	Y	Z

Pt	-0.358287	0.388816	0.032677
S	0.620091	2.659090	0.104656
F	1.621091	-0.451672	-2.359258
F	4.027442	-1.656122	-2.350300
F	5.228893	-2.339600	0.011223
F	3.973697	-1.786211	2.378698
F	1.570080	-0.575837	2.399174
N	-2.393570	1.105585	0.056206
C	1.472541	-0.482886	0.019428
C	2.159505	-0.782165	-1.157322
C	3.409278	-1.399688	-1.185842
C	4.024853	-1.748726	0.013795
C	3.381687	-1.466122	1.216628
C	2.133178	-0.846118	1.193771
C	-2.847197	2.358243	0.113619
H	-2.097909	3.141369	0.156137
C	-4.216918	2.664480	0.122172
H	-4.529190	3.702365	0.169850
C	-5.140917	1.635120	0.069885
H	-6.207660	1.845146	0.074810
C	-4.693266	0.300172	0.011431
C	-5.561010	-0.842802	-0.043109
H	-6.635505	-0.679489	-0.041853
C	-5.048783	-2.107132	-0.094841
H	-5.719254	-2.962443	-0.135512
C	-3.631766	-2.352618	-0.095839
C	-3.071414	-3.647194	-0.145360
H	-3.724848	-4.514981	-0.186697
C	-1.694881	-3.796392	-0.140049
H	-1.264555	-4.794419	-0.177979
C	-0.830275	-2.680950	-0.086423
H	0.240637	-2.854443	-0.084026
C	-1.329283	-1.381752	-0.037652
C	-2.747177	-1.242582	-0.043616
C	-3.293345	0.076394	0.007927
C	1.711034	2.908859	-1.380730
H	1.826161	1.948634	-1.885523
H	1.207905	3.607933	-2.052908
C	3.038339	3.444250	-0.830241
H	3.839380	3.306080	-1.565089
H	2.954742	4.519739	-0.629310
C	3.320617	2.684401	0.473588
H	3.579669	1.644840	0.247914
H	4.155127	3.124554	1.030975
C	2.036160	2.721579	1.311877
H	1.938492	3.658247	1.867879
H	1.940158	1.881426	2.000182

Table S4. DFT-Optimized coordinates of [Pt(C₆F₅)(bzq)(MeCN)] (**5**)

Center	Coordinates (Angstroms)		
	X	Y	Z
Pt	-0.209590	0.568715	0.000565
F	1.829557	-0.105003	2.379057
F	4.387986	-0.951870	2.365788
F	5.694502	-1.369830	-0.000215
F	4.397808	-0.919962	-2.365817
F	1.839424	-0.072731	-2.378219
N	-2.305334	1.047128	0.001135
N	0.494825	2.554100	0.004441
C	1.720145	-0.066389	0.000322
C	2.426528	-0.299358	1.179623
C	3.749778	-0.738476	1.202281
C	4.418772	-0.952113	-0.000062
C	3.754779	-0.722271	-1.202186
C	2.431431	-0.283492	-1.179038
C	-2.894902	2.242201	0.003174
H	-2.234406	3.102868	0.004321
C	-4.290100	2.392095	0.003784
H	-4.719873	3.388265	0.005460
C	-5.091083	1.261835	0.002211
H	-6.174697	1.350828	0.002645
C	-4.496302	-0.015760	-0.000029
C	-5.225663	-1.252991	-0.001921
H	-6.311899	-1.216357	-0.001482
C	-4.568977	-2.450175	-0.004301
H	-5.135855	-3.378332	-0.005784
C	-3.132742	-2.530765	-0.005007
C	-2.425472	-3.751871	-0.007767
H	-2.972576	-4.691267	-0.009362
C	-1.040437	-3.737867	-0.008538
H	-0.496486	-4.679564	-0.010806
C	-0.311357	-2.528758	-0.006422
H	0.772486	-2.575802	-0.007230
C	-0.956588	-1.293708	-0.003367
C	-2.382787	-1.325109	-0.002921
C	-3.080133	-0.078687	-0.000512
C	0.996772	3.596682	0.006351
C	1.647745	4.901422	0.008623
H	1.305344	5.494189	0.862718
H	1.417362	5.440805	-0.915584
H	2.732275	4.771858	0.080842

Table S5. DFT-Optimized coordinates of $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{tht})\}_2\text{Ag}]^+(\mathbf{9})$

Center	Coordinates (Angstroms)		
	X	Y	Z
Pt	-2.733908	-0.502044	0.393030
Pt	2.733649	-0.502407	-0.393049
Ag	-0.000197	0.151714	-0.000319
S	-4.311316	-0.809305	-1.472865
S	4.310099	-0.809931	1.473732
F	-4.915223	1.009953	1.997873
F	-5.506970	3.607299	2.305979
F	-4.056210	5.509829	1.025999
F	-1.989173	4.774958	-0.578787
F	-1.374684	2.205397	-0.918146
F	1.374641	2.205555	0.916858
F	1.990215	4.774879	0.577668
F	4.058491	5.508925	-1.025854
F	5.509412	3.605802	-2.304813
F	4.916593	1.008679	-1.996881
N	-2.202099	-2.600107	0.497807
N	2.201377	-2.600377	-0.497803
C	-3.127252	1.486121	0.526215
C	-4.166806	1.915816	1.345776
C	-4.498661	3.253596	1.525380
C	-3.758332	4.231996	0.870270
C	-2.701170	3.852966	0.052521
C	-2.416310	2.501021	-0.100233
C	-2.647680	-3.616763	-0.230295
C	-2.239196	-4.938627	-0.007696
C	-1.324865	-5.198800	0.989945
C	-0.816111	-4.139101	1.762515
C	0.153572	-4.302735	2.802408
C	0.603277	-3.232120	3.512223
C	0.121140	-1.907355	3.253163
C	0.554331	-0.778724	3.980663
C	0.041795	0.468669	3.694415
C	-0.910029	0.648889	2.668328
C	-1.360454	-0.428815	1.905797
C	-0.831546	-1.715126	2.228596
C	-1.290308	-2.842614	1.483627
C	3.127901	1.485566	-0.526371
C	2.416878	2.500755	0.099556
C	2.702273	3.852583	-0.053127
C	3.760086	4.231197	-0.870241
C	4.500488	3.252509	-1.524818
C	4.168087	1.914839	-1.345322
C	2.646660	-3.617136	0.230327
C	2.237939	-4.938920	0.007652
C	1.323625	-5.198887	-0.990051
C	0.815187	-4.139071	-1.762679
C	-0.154466	-4.302482	-2.802633
C	-0.603835	-3.231767	-3.512518
C	-0.121311	-1.907137	-3.253512
C	-0.554082	-0.778417	-3.981128

C	-0.041200	0.468837	-3.694909
C	0.910614	0.648830	-2.668765
C	1.360701	-0.428976	-1.906188
C	0.831368	-1.715138	-2.228893
C	1.289689	-2.842704	-1.483780
C	-4.077955	0.592857	-2.659881
C	-5.156163	1.610723	-2.321734
C	-6.404771	0.814868	-1.965665
C	-5.992164	-0.231639	-0.939333
C	4.076959	0.592768	2.660137
C	5.156051	1.609815	2.322343
C	6.404305	0.813063	1.967025
C	5.991452	-0.233311	0.940657
H	-3.355615	-3.375780	-1.022659
H	-2.649175	-5.733896	-0.625043
H	-0.989987	-6.216916	1.191023
H	0.518489	-5.307063	3.017073
H	1.336558	-3.368763	4.307058
H	1.287691	-0.908495	4.776867
H	0.369805	1.334789	4.267486
H	-1.292569	1.652029	2.479668
H	3.354498	-3.376307	1.022823
H	2.647689	-5.734278	0.625036
H	0.988486	-6.216919	-1.191118
H	-0.519632	-5.306720	-3.017295
H	-1.337123	-3.368234	-4.307375
H	-1.287415	-0.908008	-4.777384
H	-0.368906	1.335019	-4.268059
H	1.293452	1.651859	-2.480131
H	-3.051390	0.962697	-2.563571
H	-4.213247	0.176108	-3.665846
H	-4.839116	2.222552	-1.464087
H	-5.326135	2.286601	-3.169246
H	-6.802604	0.321863	-2.864494
H	-7.200718	1.451569	-1.560144
H	-6.651810	-1.104477	-0.914279
H	-5.906398	0.178828	0.071694
H	3.050721	0.963285	2.563013
H	4.211321	0.176276	3.666332
H	4.839864	2.221701	1.464418
H	5.326043	2.285745	3.169807
H	6.801391	0.319926	2.866109
H	7.200859	1.449176	1.561770
H	6.650611	-1.106526	0.915896
H	5.906238	0.177141	-0.070421

Table S6. DFT-Optimized coordinates of $[\{\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{MeCN})\}_2\text{Ag}]^+(\mathbf{10})$

Center	Coordinates (Angstroms)		
	X	Y	Z
Pt	-2.426815	1.263754	0.220613
Pt	2.104053	-1.711161	-0.673664
Ag	0.229068	0.093582	0.366461
F	-3.671777	1.135523	3.136166
F	-4.083746	-0.900438	4.833018
F	-3.393986	-3.429084	4.138599
F	-2.292679	-3.907061	1.693181
F	-1.901591	-1.902486	-0.029242
F	2.442534	-0.585245	2.276598
F	3.906656	1.421654	3.282223
F	5.479236	2.921207	1.658554
F	5.690748	2.293932	-0.975384
F	4.306877	0.238650	-1.995012
C	-2.762224	-0.291879	1.489088
C	-3.329859	-0.094744	2.744227
C	-3.547222	-1.132098	3.644856
C	-3.197404	-2.431111	3.291631
C	-2.637744	-2.670995	2.043610
C	-2.448892	-1.606411	1.171924
N	-1.908194	2.960585	-0.997211
C	-2.490193	3.400866	-2.104384
H	-3.378612	2.861121	-2.428951
C	-1.998619	4.496202	-2.826801
H	-2.518474	4.824837	-3.722716
C	-0.860721	5.136655	-2.381529
H	-0.451106	5.988214	-2.924217
C	-0.222694	4.690975	-1.209181
C	0.962523	5.280131	-0.664137
H	1.418443	6.117591	-1.190470
C	1.502501	4.812361	0.494945
H	2.400974	5.271896	0.907085
C	0.910383	3.720945	1.211221
C	1.428993	3.235425	2.432064
H	2.318823	3.699812	2.857769
C	0.817724	2.180104	3.070085
H	1.218642	1.811958	4.012527
C	-0.312987	1.539341	2.510468
H	-0.768813	0.714104	3.056629
C	-0.870738	1.976922	1.302964
C	-0.235298	3.096511	0.676816
C	-0.795536	3.594304	-0.534619
C	3.287230	-0.236777	0.085232
C	3.247848	0.095813	1.435497
C	3.981149	1.139914	1.985182
C	4.796936	1.901470	1.159685
C	4.894827	1.582741	-0.190219
C	4.159553	0.515656	-0.696123
N	0.679891	-3.113040	-1.460822
C	0.525024	-4.394457	-1.153474
H	1.237595	-4.811802	-0.444678

C	-0.493947	-5.178947	-1.705724
H	-0.578716	-6.224009	-1.421584
C	-1.369723	-4.604785	-2.602777
H	-2.168982	-5.192251	-3.053758
C	-1.234320	-3.246002	-2.936892
C	-2.095887	-2.551505	-3.844928
H	-2.892490	-3.110821	-4.335272
C	-1.907401	-1.229399	-4.108279
H	-2.551344	-0.713734	-4.821936
C	-0.856350	-0.480935	-3.483384
C	-0.629820	0.885236	-3.746193
H	-1.264857	1.405068	-4.464355
C	0.396635	1.547843	-3.109262
H	0.576488	2.601445	-3.321844
C	1.220024	0.892900	-2.170751
H	1.999841	1.470883	-1.674253
C	1.049220	-0.461946	-1.881011
C	0.001680	-1.136559	-2.575840
C	-0.188430	-2.527147	-2.328459
N	-3.968221	0.535868	-1.024089
C	-4.793246	0.031281	-1.657208
C	-5.823240	-0.608223	-2.447680
H	-6.444617	0.143187	-2.946710
H	-6.463265	-1.220742	-1.803168
H	-5.364171	-1.252923	-3.205597
N	3.176856	-3.119098	0.494141
C	3.827320	-3.808852	1.155058
C	4.644172	-4.668420	1.984948
H	4.087436	-4.968571	2.879374
H	5.549150	-4.134698	2.295102
H	4.937024	-5.565695	1.429036

Table S7. DFT-Optimized coordinates of $[(C_6F_5)(bzq)(PPh_3)PtAg(pyMe_2)]^+$ (**11Me**)

Center	Coordinates (Angstroms)		
	X	Y	Z
Pt	-0.204245	-0.537548	-0.655999
Ag	2.291457	0.729911	-0.144665
P	-2.070671	-0.771623	0.796370
F	-0.023262	2.273495	0.908505
F	-0.719967	4.738299	0.171230
F	-1.979432	5.167007	-2.211132
F	-2.494770	3.070154	-3.854342
F	-1.754836	0.581386	-3.155833
N	0.728607	-2.483100	-0.335683
N	3.252873	1.571889	1.626404
C	-0.829858	1.330587	-1.118261
C	-0.615560	2.428930	-0.299210
C	-0.981868	3.722738	-0.644730
C	-1.619846	3.943750	-1.858657
C	-1.877443	2.866546	-2.700603
C	-1.479507	1.590240	-2.318745
C	0.374676	-3.450469	0.504592
C	1.043705	-4.678313	0.573589
C	2.106696	-4.909904	-0.270897
C	2.510740	-3.906738	-1.169863
C	3.590721	-4.064283	-2.095523
C	3.927636	-3.062337	-2.950680
C	3.232619	-1.809663	-2.939678
C	3.567369	-0.748234	-3.809158
C	2.878340	0.442477	-3.754449
C	1.827766	0.628251	-2.828375
C	1.445876	-0.388602	-1.944692
C	2.174479	-1.616008	-2.025335
C	1.799105	-2.688731	-1.158410
C	-3.278552	-2.021034	0.254731
C	-2.990447	-2.819820	-0.855544
C	-3.912576	-3.766153	-1.294610
C	-5.125671	-3.912954	-0.631259
C	-5.426942	-3.108094	0.466284
C	-4.511520	-2.160606	0.905353
C	-1.483498	-1.263711	2.457202
C	-0.377278	-0.574443	2.975444
C	0.148225	-0.923641	4.213815
C	-0.409912	-1.976160	4.936992
C	-1.500695	-2.669612	4.424106
C	-2.041123	-2.313669	3.190407
C	-3.082237	0.723760	1.052016
C	-3.017271	1.488048	2.217150
C	-3.752391	2.667070	2.317848
C	-4.554359	3.083137	1.261360
C	-4.628936	2.317395	0.098652
C	-3.893531	1.145070	-0.009007
C	3.619527	0.728626	2.614318
C	4.114077	1.214409	3.818765
C	4.234525	2.587443	3.996864

C	3.860538	3.441006	2.970248
C	3.363874	2.905870	1.784266
C	3.470835	-0.736977	2.356443
C	2.917621	3.779151	0.658001
H	-0.474182	-3.246465	1.155108
H	0.705669	-5.429189	1.282316
H	2.639379	-5.860309	-0.253629
H	4.129451	-5.010793	-2.107145
H	4.740189	-3.197452	-3.663808
H	4.378101	-0.884994	-4.524057
H	3.140642	1.253060	-4.431915
H	1.284165	1.574976	-2.831471
H	-2.048197	-2.681569	-1.389562
H	-3.686022	-4.378767	-2.164956
H	-5.848675	-4.648513	-0.978653
H	-6.383940	-3.213613	0.973518
H	-4.759140	-1.514843	1.749125
H	0.060854	0.246835	2.402830
H	0.997771	-0.372467	4.616693
H	0.006349	-2.254809	5.903177
H	-1.939641	-3.490963	4.987288
H	-2.893377	-2.864728	2.793350
H	-2.396597	1.167239	3.053191
H	-3.700777	3.257877	3.230295
H	-5.127916	4.004359	1.342526
H	-5.260099	2.637139	-0.728590
H	-3.949464	0.550032	-0.922908
H	4.410499	0.517094	4.599161
H	4.624236	2.988245	4.930504
H	3.947271	4.519951	3.074755
H	2.411784	-1.008095	2.221700
H	3.863484	-1.331726	3.188634
H	4.008908	-1.031850	1.443432
H	3.310234	4.796445	0.760274
H	1.821041	3.846104	0.634311
H	3.253194	3.378386	-0.309328

Table S8. Emission data for compounds **1-5** in solution (10^{-3} M) at 77K

Compound		$\lambda_{\text{exc}}/\text{nm}$	$\lambda_{\text{em}}/\text{nm}$	$\tau/\mu\text{s}$
1	CH ₂ Cl ₂	385	474, 507, 548 _{sh} , 579 _{max} , 610, 667 _{sh}	202.6(58.7%), 51.5(41.3%) (474 nm) 95.8(69.2%), 64.0(30.8%) (579 nm) 323.9(44.0%), 39.6(60.0%) (610 nm)
2	CH ₂ Cl ₂	370	472, 504, 545 _{sh} , 578 _{max} , 607, 665 _{sh}	358.4(70.0%), 1091.1 (30.0%) (472 nm) 725.7(77.0%), 116.0(33.0%) (504 nm) 581.3(33.0%), 922.7(67.0%) (578 nm) 387.4(24.0%), 869.6(76%) (607 nm)
	2-Me-THF	370	466, 476, 498, 510, 539, 578 _{sh} , 608 _{max} , 640 _{sh}	
3	CH ₂ Cl ₂	370	481, 516, 548 _{sh} , 582 _{max} , 620, 664 _{sh}	58.6(68.4%), 268.3(31.6%) (481 nm) 73.4(59.1%), 212.0(48.9%) (516 nm) 178.8(81.6%), 31.9(18.4) (582 nm) 21.1(47.6%), 173.0(52.4) (620 nm)
4	CH ₂ Cl ₂	400	468, 478, 501, 544 _{sh} , 588 _{sh} , 606 _{max}	426.9(41.3%), 86.1(58.7%) (468 nm) 293.4(57.8%), 560.9(42.2%) (478 nm) 559.0(55.4%), 245.7(44.6%) (588 nm) 95.2(33.4%), 458.0(66.6%) (606 nm)
	2-Me-THF	370	464, 475, 496, 510, 537, 573 _{sh} , 600 _{max} , 644	
5	CH ₂ Cl ₂	400	471, 503, 540 _{sh} , 568 _{max} , 601 _{sh}	559.6(65.5%), 97.0(34.5%) (471 nm) 280.6(65.5%), 785.3(11.7%) (503 nm) 473.1(64.2%), 122.1(35.8%) (540 nm) 198.2(53.8), 552.4(46.2%) (568 nm)
	2-Me-THF	380	463, 478, 514, 541, 579 _{sh} , 608 _{max} , 648 _{sh}	
7	CH ₂ Cl ₂	370	479, 500, 580, 617 _{max}	23.3(88.6%), 221.3(11.4%) (479 nm) 24.0(98.9%), 148.4(1.1%) (580 nm) 23.9(97.5%), 20.7(2.5%) (617 nm)
8	CH ₂ Cl ₂	390	489, 526, 592 _{max}	
9	CH ₂ Cl ₂	390	484, 520 _{sh} , 595 _{max}	
11	CH ₂ Cl ₂	386	476, 610 _{max}	33.3(87.3%), 554.5(12.7%) (476 nm) 25.3(98.8%), 298.1 (1.2%) (610 nm)

Figure S1. View of the supramolecular arrangement of the four units of the complex $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{PPh}_3)]$ (**2**) showing the $\pi\cdots\pi$ stacking.

Figure S2. View of the supramolecular arrangement of the infinite array for the complex $[\text{Pt}(\text{C}_6\text{F}_5)(\text{bzq})(\text{MeCN})]$ (**5**) showing the $\pi \cdots \pi$ stacking.

Figure S3. Absorption spectra of **2** in solution of different solvents (10^{-4} M) at room temperature.

Figure S4: Frontier orbitals plots for complexes **4** and **9** in CH_2Cl_2 obtained by DFT; calculated electronic transitions (bars) and experimental UV-vis spectrum of **4** and **9** in CH_2Cl_2 (10^{-4}M).

Figure S5: Frontier orbitals plots for complexes **5** and **10** in CH_2Cl_2 obtained by DFT; calculated electronic transitions (bars) and experimental UV-vis spectrum of **5** and **10** in CH_2Cl_2 (10⁻⁴M).

Figure S6. Normalized DRUV spectra of complexes **1-5** in the solid state. Inset image: compound **2** at 298K.

Figure S7. Normalized emission and excitation spectra of **5** and **10** in the solid state.