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# **Mono- and diplatinum polyynediyl complexes as potential push-pull chromophores: synthesis, characterization, TD-DFT modeling, photophysical and NLO properties**

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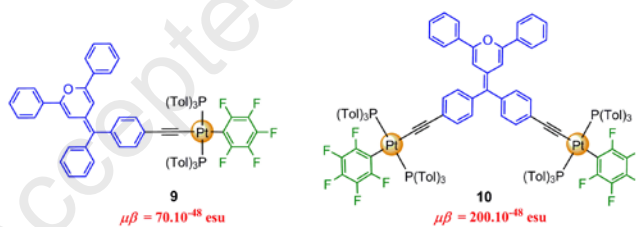
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## Abstract

This paper presents the syntheses, the photophysical and the electrochemical characterizations of four new mono- and diplatinum polyynediyl complex chromophores end-capped with diphenylpyranylidene and pentafluorophenyl moieties. The nonlinear optical properties (NLO) of these compounds is investigated using the Electric-Field-Induced Second Harmonic generation (EFISH) technique and their experimental optical properties are confirmed by Time-Dependent Density Functional Theory (TD-DFT) with a range-separated hybrid. All complexes show positive  $\mu\beta$  values. While the inductive electron-withdrawing pentafluorophenyl ligand, the length of the polyene linkers and the number of platinum centers do not seem to significantly affect the NLO responses of these complexes, their structural configuration plays a significant role, as shown by the V-shaped complex **10** exhibiting the highest  $\mu\beta$  value of the series of complexes, twice as high as that of the linear complex **9**.

## TOC Graphic :



## INTRODUCTION

Considerable research efforts have been recently made to develop organic and organometallic molecular systems exhibiting interesting nonlinear optical (NLO) properties, as they offer potential applications in many fields, including photonics,<sup>1</sup> photodynamic therapy,<sup>2</sup> optical limiting devices,<sup>3</sup> optical data storage<sup>4</sup> and optoelectronics.<sup>5</sup> Among these systems, transition metal complexes are particularly attractive. Unlike pure organic chromophores, they display low-energy, high-intensity metal-ligand charge transfer transitions that make these systems quite flexible. For example, their NLO properties can be modified and easily tuned<sup>6</sup> by changing the nature and/or the oxidation state of the metal center or by varying the type of ligands coordinated to the metal.

Among the above-mentioned organometallic systems, platinum acetylide complexes have been the least investigated, especially compared to their ruthenium counterparts. However, these platinum complexes displayed luminescence and energy photoconversion properties that could make them very attractive candidates in applications such as opto-electronics, photonics and solar cells.<sup>7</sup> A variety of functional materials<sup>8</sup> have resulted from the supramolecular self-assemblies<sup>9</sup> of platinum acetylide complex building blocks. These complexes have also been used as dyes for applications ranging from production of photoinduced energy and hydrogen to electron transfer systems.<sup>10</sup> Recently, Tian et al. reported on several platinum acetylide complexes exhibiting significant photoconversion efficiencies.<sup>11</sup> In addition, in these complexes, large NLO responses can be anticipated due to the conjugated character and the linear structure of the alkynyl unit.<sup>12</sup>

Over the past few years, we have developed an interest in synthesizing and studying the properties of asymmetrical push-pull dialkynyl platinum-based complexes exhibiting a D- $\pi$ -Pt- $\pi$ -A arrangement, with pyranilidene ligands used as pro-aromatic donor groups (D),<sup>13</sup> and various  $\pi$ -linkers coupling on each side the platinum diacetylide unit to the electron-donating (D) and the electron-accepting (A) groups. In our investigations, cyanoacetic groups and diazanyl fragments were used as electron-withdrawing groups (A), and the obtained complexes tested in Dye-Sensitized Solar Cell (DSSC) and NLO devices, respectively. In the first series of complexes containing cyanoacetic groups, all investigated complexes exhibited good photoconversion efficiency (PCE) (up to 4.7%) depending on the lengths and types of

the  $\pi$ -linkers.<sup>14</sup> The second-order NLO characterization of some complexes resulted in positive  $\mu\beta$  values determined by Electric-Field-Induced Second Harmonic (EFISH). These  $\mu\beta$  values dramatically increased (up to  $3600 \cdot 10^{-48}$  esu) upon methylation of the pyrimidinyl groups.<sup>15</sup>

These promising results led us to pursue the studies of these platinum complexes. In particular, we became interested in replacing the diazine fragments, by another electron-withdrawing group: pentafluorophenyl ( $C_6F_5$ ). Fluorine, usually in the form of pentafluorophenyl group, has been widely incorporated into organic molecular NLO systems<sup>16</sup> and organic systems used as dyes in DSSC.<sup>17</sup> The  $\pi$ - $\pi$  stacking ability of the aromatic ring combined with the enhanced electron-withdrawing property of  $C_6F_5$  have made this group an attractive candidate as inductive electron-withdrawing moiety, as both of these characteristics allow to increase the optical transparency and to decrease the optical loss in these compounds.<sup>18</sup> In addition, push-pull structures bearing a pentafluorophenyl group exhibit low molecular dipole moments. This property allows polymers doped with push-pull systems containing pentafluorophenyl groups to show poling with high temporal stability.<sup>16</sup>

Pentafluorophenyl ligands have also been used in mono- and diplatinum complexes.<sup>19</sup> For instance, Gladysz and co-workers have synthesized a wide range of symmetrical and asymmetrical pentafluorophenyl-substituted di- and tetraplatinum polyynediyl complexes comprising extended  $sp$ -hybridized chains.<sup>20</sup> Several, more intricate structures based on these diplatinum polyynediyl complexes were also reported, where double helices of  $sp^3$ -hybridized carbon chains enveloped  $sp$ -hybridized carbon chains,<sup>21</sup> and rotaxane-type assemblies were formed through shielding the  $sp$ -hybridized chains with a macrocycle.<sup>22</sup> These platinum-alkynyl complexes display long-range electronic charge transfer and represent excellent systems for investigating charge delocalization mechanisms over extended distances. This characteristic led to their use as simple electronic components.<sup>23</sup>

We present herein the synthesis of several push-pull dialkynyl mono- and diplatinum-based complexes incorporating pyranilidene ligands as donor groups, and pentafluorophenyl ligand as inductive accepting groups (Chart 1), and the determination of their second-order NonLinear Optical (NLO) properties.

We are particularly interested in investigating the impact of the inductive electron-accepting pentafluorophenyl ligand that differs from mesomeric electron acceptor groups typically used in most of the known organometallic ‘‘push-pull’’ structures. We also investigated the presence of two metal centers connected by  $\pi$ -conjugated bridges, and the length of the *sp*-hybridized carbon chains onto the NLO properties of the systems. In addition to the NLO responses, we also characterized the structures of the synthesized complexes and studied their electrochemical and physical properties.

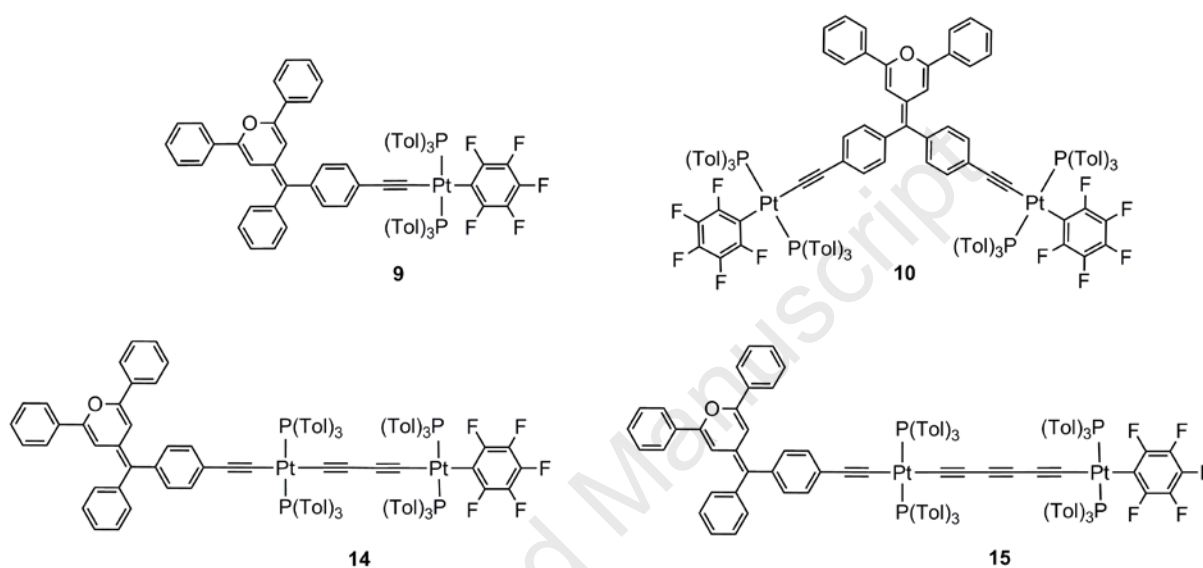
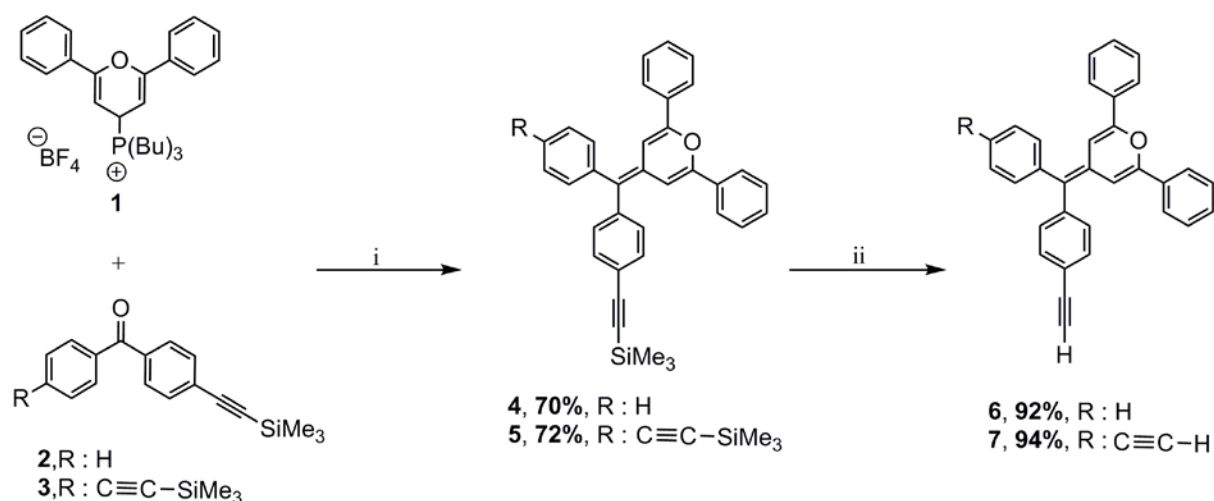


Chart 1: Chemical structures of complexes 9-10 and 14-15.

## RESULTS AND DISCUSSION

**Synthesis and Characterization.** The synthesis of the complexes required 4-[(4-ethynylphenyl)-phenyl-methylene]-2,6-diphenyl-4H-pyran **6**, and 4-(bis(4-ethynylphenyl)methylene)-2,6-diphenyl-4H-pyran **7** as starting materials. Compound **6** was prepared following published procedures,<sup>14</sup> while compound **7** synthesis was a two-step process (Scheme 1). First, a Wittig reaction between tributyl(2,6-diphenyl-4H-pyran-4-yl)-phosphonium tetrafluoroborate **1**<sup>24</sup> and *bis*-(4-(2-trimethylsilylethynyl))benzophenone **3**<sup>25</sup> in presence of *n*-BuLi led to the diphenylpyranilidene unit **5** in good yield. Then, terminal alkyne **7** is obtained through the quantitative desilylation of compound **5** in basic medium.

**Scheme 1: Synthetic routes of ligands 6-7<sup>a</sup>**

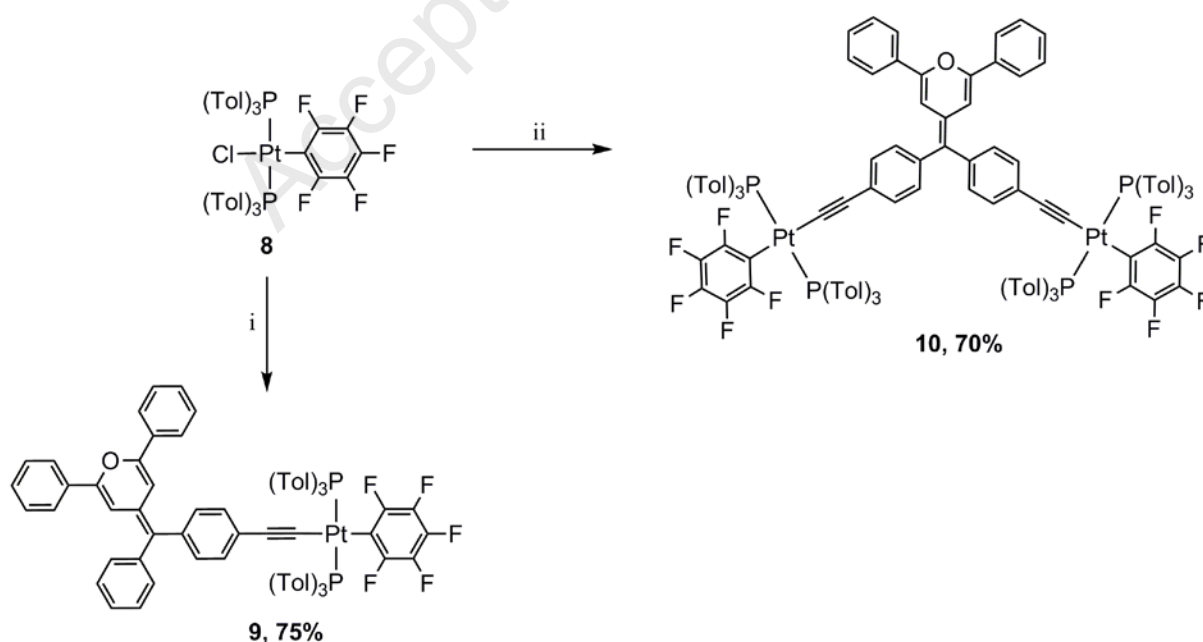


<sup>a</sup>Conditions: (i) *n*-BuLi, THF, -78°C to rt, 3h; (ii) K<sub>2</sub>CO<sub>3</sub>, MeOH/CH<sub>2</sub>Cl<sub>2</sub> 1:2, rt, 12h.

The precursor **8** (*trans*-[(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>PtCl]),<sup>19d</sup> and the complexes **11**<sup>14</sup> (4-[(4-ethynyl-phenyl)-phenyl-methylene]-2,6-diphenyl-4H-pyran-substituted chloride), **12** (*trans*-[(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>Pt(C≡C)<sub>2</sub>H]) and **13** (*trans*-[(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>Pt(C≡C)<sub>3</sub>SiEt<sub>3</sub>]) were synthesized according to previously reported procedures.<sup>20d</sup> The synthetic approach to the asymmetrical platinum complex **9** and the diplatinum complexes **10**, **14**, and **15** (Schemes 2 and 3), was performed using widely reported substitution of platinum chloride complexes by terminal acetylenes.<sup>14,15,19,20,21</sup> All complexes were prepared under similar conditions by conventional cross-coupling reaction catalyzed by copper(I) iodide, in diethylamine and THF. The reactions were conducted overnight under ambient temperature and led to the complexes **9**, **10**, **14**, and **15** in 70 to 82% yields. As shown in Scheme 3, *trans*-[(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>Pt(C≡C)<sub>3</sub>H] was generated *in situ* from *trans*-[(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>Pt(C≡C)<sub>3</sub>SiEt<sub>3</sub>] **13** and *n*Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup>. The progress of the reactions was monitored by <sup>31</sup>P NMR, revealing the concomitant consumption of the starting material and the formation of the products **9**, **10**, **14**, and **15**. The new complexes **9**, **10**, **14**, and **15** were characterized by IR, UV/Vis, NMR (<sup>1</sup>H, <sup>31</sup>P, <sup>19</sup>F and <sup>13</sup>C) and high-resolution mass spectroscopies. These characterizations match up the suggested structures.

The signature  $\nu_{C\equiv C}$  band of the metal-bonded alkynyl group, in the 2228-2103  $\text{cm}^{-1}$  range, is observed on the IR spectra of the complexes **9**, **10**, **14**, and **15**. Characteristic signals of the vinylic H resonance of the methylenepyran (singlet at  $\delta = 6.70$  ppm), of the disubstituted phenyl rings (two doublet signals at  $\delta = 7.50$  and 7.25 ppm;  $^3J_{\text{HH}} = 7.9$  and 8.1 Hz) and of the alkyne protons (singlet at  $\delta = 3.15$  ppm) were observed on the  $^1\text{H}$  NMR spectrum of the symmetrical ligand **7**. In complex **10**, the inductive effect of the platinum coordination resulted in an upfield shift of the hydrogen atoms of the disubstituted phenyl rings ( $\delta = 6.65$  and 6.19 ppm) and of the vinylic protons ( $\delta = 6.49$  ppm) of the methylenepyran. The complexes **9**, **14**, and **15** display similar shifts. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of the complexes **9**, **10**, **14**, and **15** show the expected peaks for the tri(*p*-tolyl)phosphines, the pyranilidene ligand and the  $\pi$ -conjugated linker. The  $^{31}\text{P}$  NMR spectra of the monoplatinum complex **9** and the symmetrically substituted diplatinum **10** display sharp singlets, indicating that the phosphine ligands coordinated to the platinum adopted *trans* geometries (for example  $\delta = 17.61$  ppm,  $^1J_{\text{PtP}} = 2691$  Hz, for **9**). Due to the asymmetrical substitutions of the platinum moieties on butadiynediyl **14** and hexatriynediyl **15** complexes, the  $^{31}\text{P}$  NMR spectra show two phosphorus signals (for example  $\delta = 16.31$  ppm,  $^1J_{\text{PtP}} = 2708$  Hz, 14.69 ppm,  $^1J_{\text{PtP}} = 2627$  Hz, for **14**). Finally,  $^{19}\text{F}$  NMR spectra of the complexes display three multiplet signals that can be attributed to the three different fluorine atoms on the pentafluorophenyl groups.

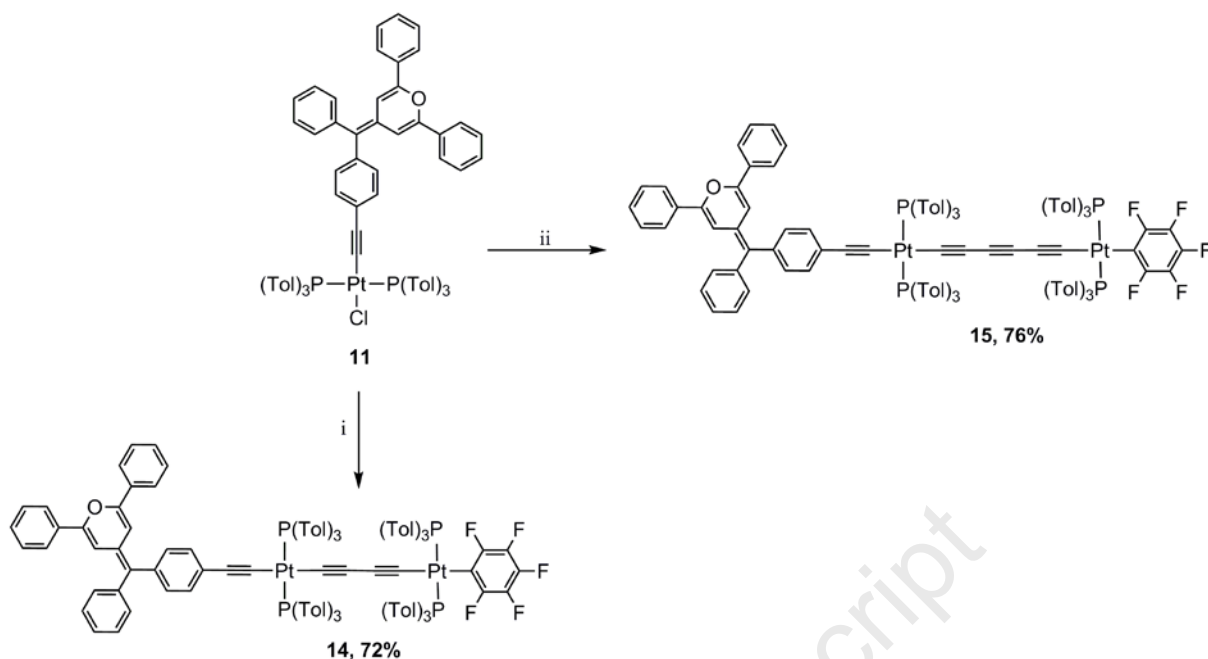
#### Scheme 2: Synthesis of mono- and diplatinum complexes 9-10<sup>a</sup>



<sup>a</sup>Conditions: (i) 1.2 equiv of 4-[(4-ethynyl-phenyl)-phenyl-methylene]-2,6-diphenyl-4H-pyran **6**, CuI, THF/ $\text{Et}_2\text{NH}$  1:2, rt, 12h; (ii) 0.5 equiv of 4-(bis(4-ethynylphenyl)methylene)-2,6-diphenyl-4H-pyran **7**, CuI, THF/ $\text{Et}_2\text{NH}$  1:2, rt, 12h.



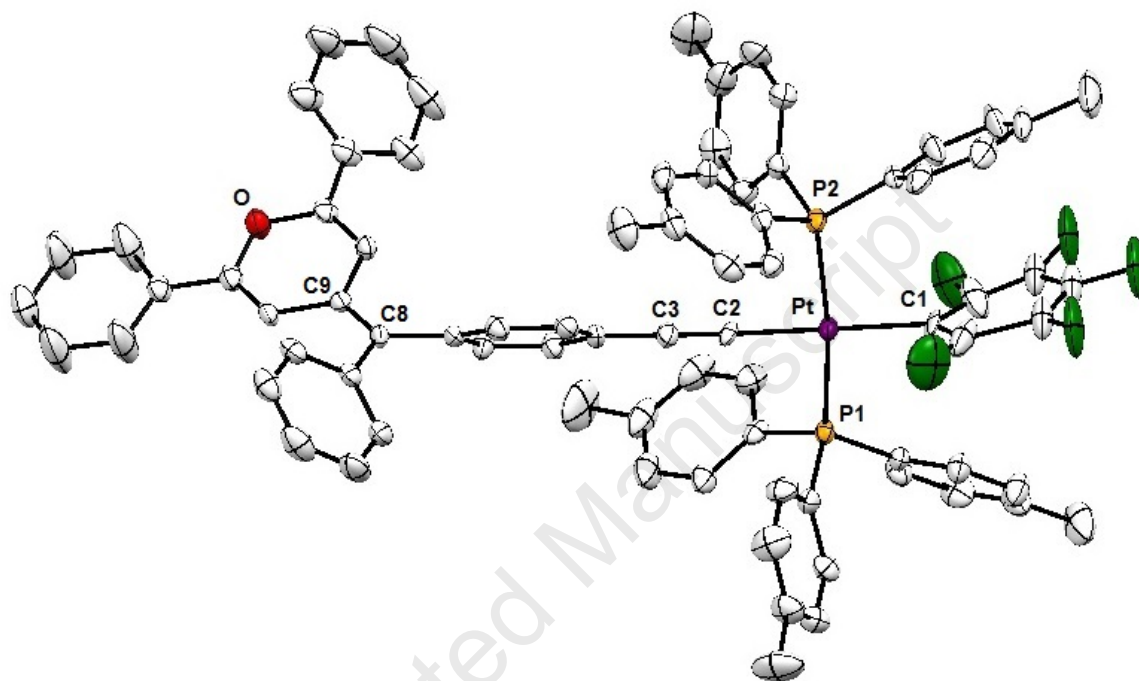
**Scheme 3: Synthesis of diplatinum complexes 14-15<sup>a</sup>**



<sup>a</sup>Conditions: (i) 1 equiv of *trans*-[(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>Pt(C≡C)<sub>2</sub>H] **12**, CuI, THF/Et<sub>2</sub>NH 1:2, rt, 48h; (ii) 1 equiv of *trans*-[(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>Pt(C≡C)<sub>3</sub>SiEt<sub>3</sub>] **13**, *n*Bu<sub>4</sub>N<sup>+</sup>F<sup>-</sup>, THF, 30 min and CuI, Et<sub>2</sub>NH, rt, 48h.

**Structural Description.** For the determination of the crystallographic structures, complexes **9**, and **14** were grown as monocrystals by the slow diffusion of pentane into a concentrated solution of **9** in dichloromethane and of **14** in chloroform. Figures 1 and 2 give the thermal ellipsoid plots obtained from the crystallographic structures. The crystallographic data and structure refinement details are given in Tables S1 and S2 in the Supporting Information (SI).<sup>26</sup> The monoplatinum complex **9** crystallizes in the monoclinic space group, with a slightly distorted square planar geometry around the four-coordinated platinum atom (Figure 1). The molecular structure confirms the *trans* configuration of the pentafluorophenyl group, the pyran-2-ylidene ligand and the two tri(*p*-tolyl)-phosphines around the platinum center. Typical bond lengths and angles around the platinum were determined.<sup>14</sup> The C1–Pt–C2≡C3 group adopt an almost linear structure with Pt–C2≡C3 and C1–Pt–C2 angles of 176.3(6)° and 172.40(3)°, respectively. In contrast, the P1–Pt–P2 angle is slightly more bent at 169.73(6). The Pt–C2 distance of 1.994(6) Å and the C1≡C2 bond length of 1.213(9) Å are consistent with those observed for other platinum coordinated to acetylide ligands.<sup>27</sup> The exocyclic bond C8–C9 of the methylenepyran was found to be 1.357(9) Å long, which is slightly lower than the range of the exocyclic C–C bond lengths (1.39–1.40 Å) generally reported in

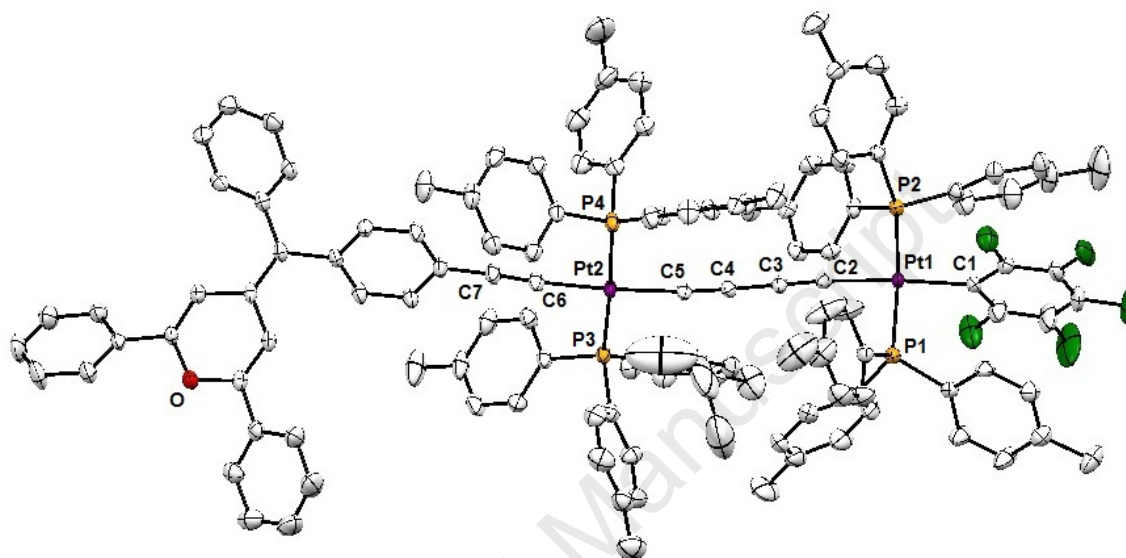
methylenepyran Fischer-type carbene complexes. In these complexes, the electron withdrawing effect of the carbene moiety leads to a ground state structure leaning to the cyanine limit,<sup>28</sup> while the exocyclic bond C8–C9 measured in complex **9** suggests a weak pyrylium character for this complex structure.



**Figure 1.** ORTEP drawing of the monoplatinum complex **9** with thermal ellipsoids at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å), and angles (deg): C1–Pt = 2.069(6), Pt–C2 = 1.994(6), Pt–P2 = 2.2952(17), C2–C3 = 1.213(9), C8–C9 = 1.357(9); C1–Pt–C2 = 172.40(3), P1–Pt–P2 = 169.73(6), Pt–C2–C3 = 176.30(6), P2–Pt–C1 = 92.05(17), P2–Pt–C2 = 85.20(2).

Unlike the monoplatinum complex **9**, the diplatinum complex **14** crystallizes in the triclinic space group (Figure 2). The bond lengths and angles in the tetraphosphine complex **14** with Pt(C≡C)<sub>2</sub>Pt linkage were typical and similar to those reported for the asymmetrically butadiynediyl-substituted diplatinum analogues (Figure 3).<sup>20b</sup> The C2≡C3, C4≡C5 and C6≡C7 bond lengths are within the normal range of 1.210(6), 1.215(6) and 1.202(6) Å, respectively. In addition, the platinum-platinum Pt1•••Pt2 distance (7.798 Å) is slightly below the sum of all the intermediary bond lengths (7.814 Å). The Pt1–C2≡C3–C4≡C5–Pt2 chain is quasilinear,

with angles in the ranges of 173.7(4)-179.60(5)°. The diplatinum complex **14** presents a significant “twist” associated with the square planar end-groups with an angle measured at 8.7°. In this approach, the angle between the planes in the crystal structure were determined by using the P-Pt-P bonds on one segment, and the platinum from the other ([P1Pt1P2]-Pt2 vs. [P3Pt2P4]-Pt1).

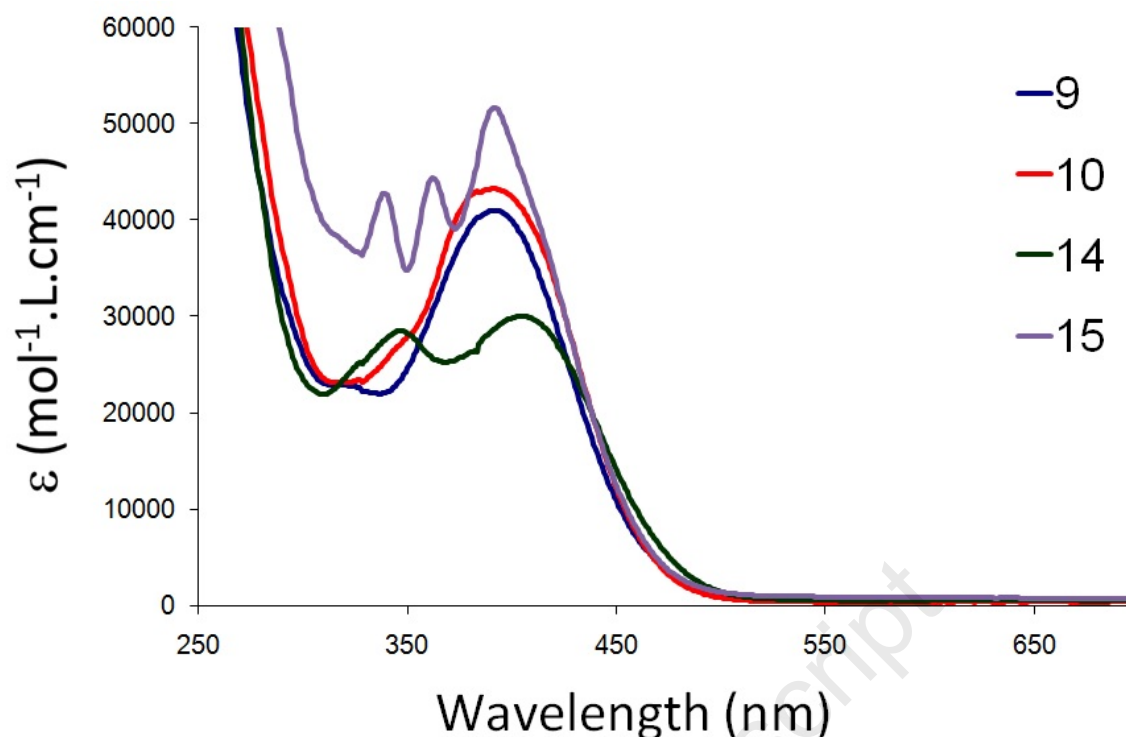


**Figure 2.** ORTEP drawing of the diplatinum complex **14** with thermal ellipsoids at 50% probability level. All hydrogen atoms and solvent molecules are omitted for clarity. Selected bond distances (Å), and angles (deg): C1–Pt1 = 2.058(4), Pt1–C2 = 2.007(4), Pt1–P2 = 2.3037(11), C2–C3 = 1.2010(6), C3–C4 = 1.383(6), C4–C5 = 1.215(6), C5–Pt2 = 1.999(4), Pt2–P4 = 2.3054(11), Pt2–C6 = 1.996(4) C6–C7 = 1.202(6); C1–Pt1–C2 = 175.87(17), P1–Pt1–P2 = 173.98(4), Pt1–C2–C3 = 175.30(4), P1–Pt1–C1 = 92.12(12), P1–Pt1–C2 = 83.76(12), C2–C3–C4 = 179.30(5), C3–C4–C5 = 177.00(5), C5–Pt2–C6 = 176.14(19), P3–Pt2–P4 = 176.62(4), Pt2–C5–C4 = 173.70(4), Pt2–C6–C7 = 175.60(4), P4–Pt2–C5 = 90.42(12), P4–Pt2–C6 = 87.89(13).

**Photophysical Properties.** Complexes **9-10** and **14-15** UV-Vis absorption spectra, recorded in diluted dichloromethane are shown on Figure 3, and the corresponding spectroscopic data are collected in Table 1. Complexes **9** and **10** both exhibit a single major prominent band at 391 nm on their UV-visible spectra, while complexes **14** and **15** display multiples bands in the 330-410 nm range that can therefore be viewed as signature of the multi-ethynyl bridge. Indeed, as observed in the UV-visible spectra of a series of polyynes platinum complexes of increasing conjugated lengths,<sup>29</sup> the complexes **14-15** spectra display more absorption bands of increasing intensities. In most push-pull complexes, the lower-energy absorption bands can be attributed to an intramolecular charge-transfer (ICT) transition between the electron donor and the electron acceptor fragments.<sup>15</sup> In complexes **9-10** and **14-15** the lower-energy absorption bands  $\lambda_{\text{max}}$  in the 330–410 nm range are observed and correlate with intra-ligand charge transfer (ICT) transitions ( $\pi$ - $\pi^*$ ) centered on the pyranilidene moieties (see TD-DFT calculations for additional information). Extinction coefficient of the complex **15** is significantly larger than that of the complex **14** which displays an extinction coefficient of  $3.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 404 nm, while complex **15** extinction coefficient is  $5.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$  at 391 nm. Complex **15** displays a maximum absorption more intense than that of complex **14**. This can be explained by the partial contribution on the ethynyl linkers in the electron delocalization toward the pyranilidene moieties.

**Table 1. Absorption property of the complexes 9-10 and 14-15 recorded in dichloromethane solution ( $2 \times 10^{-5} \text{ M}$ ) at room temperature.**

Complex	$\lambda_{\text{max}}^{\text{abs}}/\text{nm}$ ( $\epsilon \times 10^4 \text{ M}^{-1} \cdot \text{cm}^{-1}$ )
<b>9</b>	391 (4,1)
<b>10</b>	391 (4,3)
<b>14</b>	347 (2,9), 404 (3,0)
<b>15</b>	339 (4,3), 362 (4,4), 391 (5,2)



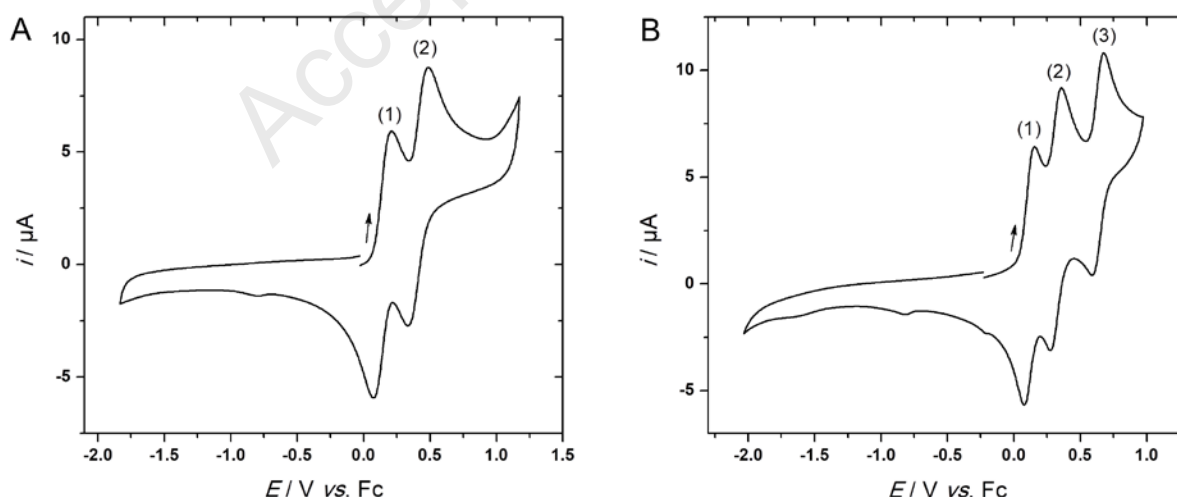
**Figure 3.** UV-Vis absorption spectra of complexes **9-10** and **14-15** in dichloromethane solution ( $2 \times 10^{-5}$  M) at room temperature.

**Electrochemical Properties.** Cyclic voltammetry (CV) studies of complexes **9-10** and **14-15** were recorded in  $\text{CH}_2\text{Cl}_2/\text{NBu}_4\text{PF}_6$  0.1 M by using a platinum working electrode. Table 2 lists the electrochemical data. The mono-Pt complex **9** displays two reversible systems at  $E^{0'}(1) = 0.14$  V and  $E^{0'}(2) = 0.41$  V vs. Fc (Figure 4). Its redox behavior is similar to that obtained for its chloro-pyranilidene analogous complex **11** (0.14 V and 0.37 V, see Table 2). This indicates that the pentafluorophenyl moiety does not substantially participate in the delocalization of the charge upon oxidation. Such result is consistent with the theoretical calculations (*vide infra*, Figure 5). Coulometric analysis of the exhaustive electrolysis of the solution at 0.60 V indicates a global uptake of two electrons, hence suggesting that the processes (1) and (2) are monoelectronic. The insertion of one diacetylene (complex **14**) or one trisacetylene (complex **15**) Pt unit between the pentafluorophenyl group and the first Pt center induces a slight decrease of the formal potential values for both processes (1) and (2) compared to those of complex **9** (Figure 4, and Table 2). Hence, the second Pt acetylene unit stabilizes the pyrylium radical cation likely through charge delocalization. In addition, the CV studies display a third reversible redox reaction at higher potential values for these two complexes ( $E^{0'}(3) = 0.64$  V and 0.73 V for **14** and **15**, respectively). According to previous studies performed on pentafluorophenyl Pt complexes, the system at  $E^{0'}(3)$  can be ascribed to

the oxidation of the bis-platinum core on both compounds.<sup>20b,20d</sup> For instance, the *trans,trans*-(C<sub>6</sub>F<sub>5</sub>)(PTol<sub>3</sub>)<sub>2</sub>Pt(C≡C)<sub>3</sub>Pt(PTol<sub>3</sub>)<sub>2</sub>(Tol) complex which is an analogue of **15** displays an oxidation peak at 0.58 V *vs.* Fc in dichloromethane.<sup>20b</sup> Noteworthy, the complex **10** exhibits rather low potential values upon oxidation ( $E^{0'}(1) = 0.08$  V and  $E^{0'}(2) = 0.31$  V, see Table 2, Figure S22, SI) by comparison to complex **9**. Its redox behavior can be correlated to its specific architecture, since the two pentafluorophenyl Pt units are symmetrically positioned on each side of the pyranilidene. The decrease of the potential (*vs.* complex **9**) can be assigned to the stronger stabilization of the electrochemically generated pyrylium radical cation **10**<sup>+</sup> and dication **10**<sup>2+</sup>. This effect occurs because the charge is likely delocalized over the two phenylacetylene units, instead of one for **9**, **14** and **15**, in agreement with the symmetry of the molecule. This proposition is consistent with the difference of localization of the spin density calculated for the SOMOs of complexes **9**<sup>+</sup> and **10**<sup>+</sup> (Figure S23, SI).

**Table 2. Electrochemical data for complexes 9, 10, 11, 14, and 15 (0.5 mM) at a Pt working electrode in CH<sub>2</sub>Cl<sub>2</sub>/NBu<sub>4</sub>PF<sub>6</sub> 0.1 M ( $E$  / V *vs.* Fc<sup>+</sup>/Fc,  $\nu = 0.1$  V s<sup>-1</sup>).**

Complex	$E_{pa}(1)$	$E^{0'}(1)$	$E_{pa}(2)$	$E^{0'}(2)$	$E_{pa}(3)$	$E^{0'}(3)$
<b>9</b>	0.21	0.14	0.48	0.41		
<b>10</b>	0.12	0.08	0.37	0.31		
<b>11</b>	0.18	0.14	0.41	0.37		
<b>14</b>	0.15	0.12	0.36	0.32	0.68	0.64
<b>15</b>	0.17	0.13	0.40	0.36	0.77	0.73



**Figure 4. Cyclic voltammograms at a Pt working electrode of complexes 9 (panel A) and 14 (panel B) in CH<sub>2</sub>Cl<sub>2</sub>/NBu<sub>4</sub>PF<sub>6</sub> 0.1 M ( $E$  / V *vs.* Fc<sup>+</sup>/Fc,  $\nu = 0.1$  V s<sup>-1</sup>,  $C = 0.5$  mM). The arrows indicate the scanning direction. The numbers (1), (2) and (3) refer to the redox systems, see text for details.**

**Second-Order NLO Measurements.** Complexes **9**, **10**, **14**, and **15** second-order NLO responses were determined by the EFISH method in chloroform with a non-resonant incident wavelength of 1907 nm, following experimental conditions described in the literature.<sup>30</sup> It is worth mentioning that there is not overlap between the second harmonic at a wavelength of 953 nm and any of the absorption bands of the chromophores. As previously reported, the EFISH technique provides information about  $\mu\beta(2\omega)$ , the scalar product of the vector component of the first hyperpolarizability tensor ( $\beta$ ) and the dipole moment vector,  $\mu$ <sup>31</sup> of the chromophores, as shown on Eq. 1. For the studied Complexes **9**, **10**, **14**, and **15**, we assumed that the third-order term ( $\gamma_0(-2\omega, \omega, \omega, 0)$ ) in this equation was negligible.

$$\gamma_{\text{EFISH}} = \mu\beta/5kT + \gamma_0(-2\omega, \omega, \omega, 0) \quad \text{Eq. 1}$$

The EFISH measurements are gathered in Table 3. All complexes exhibited positive  $\mu\beta$  values, indicating that the excited states of the chromophores are more polarized than their ground states. In addition, these results confirm that chromophores ground and excited states are polarized in the same direction. For all four complexes,  $\mu\beta$  values are rather low and the margin of error is probably higher than the  $\pm 10\%$  value generally reported for EFISH measurements. Complexes **9**, **14**, and **15** exhibited similar NLO response. This seems to indicate that an increase in the length of the polyene linker or the addition of a second platinum center have essentially no major impact on the NLO response, which is qualitatively consistent with the theoretical calculations (*vide infra*, Figure 5). On the other hand, the V-shaped complex **10** displays a NLO responses ( $\mu\beta$  value) more than twice higher than that of the linear complex **9**, in part due by the larger dipole moment induced by this specific configuration. These trends are consistent with results previously presented.<sup>32</sup>

**Table 3.** Measured  $\mu\beta$  values, theoretically determined dipole moment  $\mu$  and deduced second-hyperpolarizability  $\beta$  for complexes **9**, **10**, **14**, and **15**.

	<b>9</b>	<b>10</b>	<b>14</b>	<b>15</b>
$\mu\beta$ [ $10^{-48}$ esu] <sup>a</sup>	70	200	110	60
$\mu$ [D]	3.5	6.0	5.1	5.3
$\beta$ [ $10^{-30}$ esu]	20	33	22	11.3

<sup>a</sup>  $\mu\beta(2\omega)$  at 1907 nm in  $\text{CHCl}_3$ . Molecular concentrations used for the measurements were in the range of  $10^{-2}$  to  $10^{-3}$  M.

The low  $\mu\beta_{\text{EFISH}}$  values observed in the present work are consistent with, yet lower than, those obtained in previous studies of similar platinum complexes. For example, P. Nguyen *et al.* described the synthesis and the NLO properties of several asymmetrical platinum bis(phenylacetylide) complexes substituted with various donor-acceptor groups.<sup>33</sup> Their Pt bis(acetylide) complex containing a *p*-methoxyphenyl fragment as donor group and a *p*-nitrophenyl fragment as acceptor group exhibits a moderate  $\mu\beta_{\text{EFISH}}$  value of  $310 \times 10^{-48}$  esu (operating at 1064 nm). We recently reported the second order NLO responses of a series of D- $\pi$ -Pt- $\pi$ -A platinum complexes made of a platinum bis(acetylide) segment separated from electron donor pyranilidene and electron acceptor pyrimidine groups by  $\pi$ -conjugated linkers.<sup>15</sup> These neutral complexes also showed relatively low  $\mu\beta$  values between  $170$  to  $390 \times 10^{-48}$  to esu (operating at 1907 nm). However, unlike these complexes, the complexes presented in this work contained an inductive accepting group with the pentafluorophenyl ligand that would lead to lower  $\mu\beta$  values.

**Theoretical Calculations.** Theoretical calculations (see experimental section for details) were used to confirm the experimental data and obtain a better understanding of the complex properties. For all molecules, TD-DFT shows that the lowest electronic excited state presents a large oscillator strength and is located at ca. 400 nm, which fits experiment. More specifically, the theoretical analyses was able to determine transitions at 396 nm ( $f=1.31$ ), 405 nm ( $f=1.50$ ), 399 nm ( $f=1.58$ ) and 399 nm ( $f=1.62$ ) for **9**, **10**, **14**, and **15**, respectively. In all cases, these transitions can be mainly ascribed to HOMO to LUMO electronic promotions. These orbitals are displayed in Figure 5. For each complex, both orbitals are largely localized on the pyranilidene moieties. Remarkably, the HOMO displays a partial contribution on the ethynyl linkers, but nothing on the two external phenyl rings of the pyranilidene, unlike the LUMO, which shows significant contribution on these two phenyls. There is therefore a significant charge-transfer in these systems, even though the pentafluorophenyl moieties play no role in it. As often in very large compounds, the ICT does not take place from one end of the molecule to the other,<sup>34</sup> but, in contrast, the  $\pi$ -conjugated bridge plays the role of donor. The shapes of the LUMO, that are similar in **9**, **10**, and **15** are also consistent with the fact that these compounds show similar NLO response. The DFT computed  $\beta(-2\omega; \omega, \omega)$  at 1907 nm are  $23$ ,  $39$ ,  $34$  and  $29 \times 10^{-30}$  esu for **9**, **10**, **14**, and **15**, respectively. These values are obviously of the same order of magnitude as the one measured, with the maximal response



obtained for **10**, due to its arrangement allowing for a "double" ICT transition as shown on Figure 5.

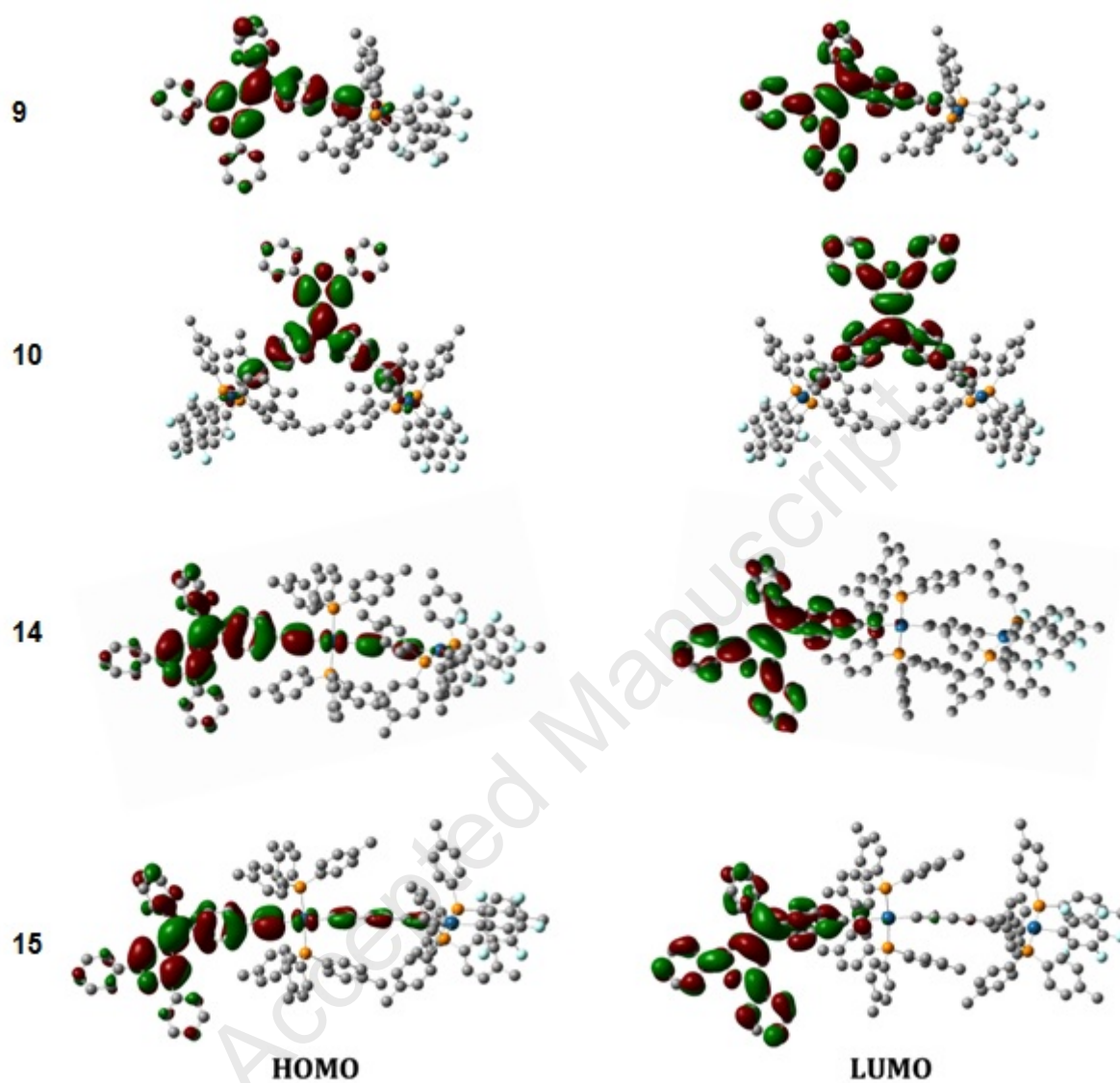


Figure 5: CAM-B3LYP frontier orbitals for the investigated systems. From top to bottom: 9, 10, 14, and 15. Hydrogen atoms omitted for clarity.

## CONCLUSION

We have synthesized a series of new mono- and diplatinum polyynediyl complex chromophores end-capped with diphenylpyranylidene and pentafluorophenyl moieties. The photophysical and electrochemical properties of the complexes substantiated by their theoretical (TD-)DFT studies indicate that they display adequate opto-electronic characteristics and consequently potential as NLO chromophores. Unexpectedly, the inductive electron-withdrawing pentafluorophenyl ligand of these platinum polyynediyl complexes seem to have a much weaker impact on the electronic properties than the mesomeric acceptors in analogous “push-pull” structures, as shown by the relatively low NLO responses and theoretical results. All investigated complexes display a positive  $\mu\beta$ . Similar NLO responses obtained for complexes (**9**, **14** and **15**) with polyene linkers of various lengths show that increasing the length of these linkers does not systematically yield larger NLO responses in such complexes. However, the shape of the complex is important, as shown by the V-shaped complex **10** exhibiting the highest  $\mu\beta$  value of the series of complexes, twice as high as that of the linear complex **9**, due to an adequate arrangement of the individual dipolar contributions. Experiments are currently underway to vary the components of the promising V-shaped complex **10** with different mesomeric acceptor groups (malononitrile, indane-1,3-dione, pyrimidine or pyrimidinium) to enhance the charge transfer in these systems and consequently improve the NLO responses.

## EXPERIMENTAL SECTION

**General Methods.** NMR spectra were acquired at room temperature on a Bruker AC-300 spectrometer ( $^1\text{H}$  at 300 MHz,  $^{13}\text{C}$  at 75 MHz,  $^{31}\text{P}$  at 121 MHz,  $^{19}\text{F}$  at 282 MHz) and referenced as follows:  $^1\text{H}$  NMR, residual  $\text{CHCl}_3$  ( $\delta = 7.26$  ppm);  $^{13}\text{C}\{^1\text{H}\}$  NMR, internal  $\text{CDCl}_3$  ( $\delta = 77.16$  ppm);  $^{31}\text{P}\{^1\text{H}\}$  NMR, external  $\text{H}_3\text{PO}_4$  ( $\delta = 0.00$  ppm). The chemical shifts  $\delta$  are reported in parts per million relative to TMS ( $^1\text{H}$ , 0.0 ppm) and  $\text{CDCl}_3$  ( $^{13}\text{C}$ , 77.16 ppm). The coupling constant  $J$  is given in Hz. In the  $^1\text{H}$  NMR spectra, the following abbreviations are used to describe the peak pattern: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), and m (multiplet). Acidic impurities in  $\text{CDCl}_3$  were removed by treatment with anhydrous  $\text{K}_2\text{CO}_3$ . IR spectra were recorded on a Perkin-Elmer spectrum 100 spectrometer with an ATR sampling accessory. UV-visible spectra were recorded on a Perkin-Elmer Lambda 25 spectrometer using standard 10 mm quartz cells. High resolution mass analyses using a Bruker MicroTOFQ II apparatus and Elemental analyses using a Microanalyseur Flash EA1112 CHNS/O Thermo Electron were performed at the “Centre Régional de Mesures Physiques de l'Ouest” (CRMPO, University of Rennes 1). Column chromatographies were performed using silica gel Acros SI 60 (60–200 mesh ASTM). Thin-layer chromatography (TLC) was carried out on EMD Silica Gel 60 F<sub>254</sub> (Merck) was visualized with 365 nm UV light.

**X-ray Structure Determination.** Diffraction data for complex **9** (CCDC 1831483) were collected at 150(2) K using a Bruker APEX CCD diffractometer with graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å). The crystallographic data for complex **14** (CCDC 1831485) was collected on a Bruker D8 VENTURE CCD diffractometer equipped with a multilayer monochromator device (Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å). Crystal structures were solved by dual-space algorithm using the SHELXT program,<sup>35a</sup> and then refined with full-matrix least-square methods based on  $F^2$  (SHELXL-2014).<sup>35b</sup> All non hydrogen atoms were refined with anisotropic atomic displacement parameters. H atoms were finally included in the structural model in their calculated positions, and constrained to ride on the attached carbon atom. In the case of **9**, the contribution of the disordered solvents to the structure factor factors was calculated by the PLATON/SQUEEZE procedure<sup>35c</sup> and then taken into account in the final SHELXL-2014 least-squares refinement. Relevant collection and refinement data for all compounds are given in the Supporting Information. All data can be obtained from the Cambridge Structural Database via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

**Electrochemical Measurements.** The electrochemical studies were performed in a glovebox (Jacomex) ( $O_2 < 1$  ppm,  $H_2O < 1$  ppm) with a home-made 3-electrode cell (WE: Pt, RE: Ag wire, CE: Pt). Ferrocene was added at the end of each experiment to determine the redox potential values. The standard potential of the  $Fc^+/Fc$  couple in  $CH_2Cl_2/NBu_4PF_6$  was measured experimentally with reference to the standard calomel electrode (SCE):  $E^0(Fc^+/Fc) = 0.47$  V vs. SCE, and recalibrated vs. NHE assuming that  $E^0(SCE) = 0.24$  V vs. NHE. The potential of the cell was controlled by an AUTOLAB PGSTAT 100 (Metrohm) potentiostat monitored by the NOVA<sup>®</sup> software (Metrohm). Dichloromethane was freshly distilled from  $CaH_2$  and kept under Ar in the glovebox. The supporting salt  $NBu_4PF_6$  was synthesized from  $NBu_4OH$  (Fluka) and  $HPF_6$  (Aldrich). It was then purified, dried under vacuum for 48 hours at  $100^\circ C$ , and then kept under  $N_2$  in the glovebox.

**Computational Details.** The ground state geometries of all compounds were optimized at DFT level of theory with the M06<sup>36</sup> functional combined with the LanL2DZ atomic basis set and pseudopotential, completed with additional functions on all non-hydrogen atoms ( $d$  functions of  $\alpha = 0.587, 0.961, 1.577$  and  $0.364$  for C, O, F and P, respectively and  $f$  function of  $\alpha = 0.993$  for Pt.). During our calculations, we imposed a tight convergence threshold of  $1 \times 10^{-10}$  a.u. on the SCF energies and we used the so-called *ultrafine* integration grid [pruned (99590) grid]. TD-DFT calculations and simulation of the non-linear optical properties were performed using the CAM-B3LYP<sup>37</sup> and  $\omega B97X-D$ <sup>38</sup> range-separated hybrid functionals, respectively. These choices are justified because the former functional provides accurate charge-transfer parameters, whereas the latter presents a correct asymptotic behavior, which is needed to obtain accurate NLO properties. The same atomic basis sets as in the optimization step was applied. Bulk solvation effects have been quantified by the Polarizable Continuum Model (PCM),<sup>39</sup> with dichloromethane as solvent for optimization and TD-DFT calculations and chloroform as solvent for the nonlinear optical properties calculations. For the TD-DFT part, we applied the linear response (LR-PCM) model in its *non-equilibrium* limit, which is suited for absorption spectra.<sup>40</sup> All our calculations were carried out with the latest version of the Gaussian 16 program package.<sup>41</sup>

**Materials.** All reactions were conducted under a dry nitrogen atmosphere using Schlenk techniques, but workups were carried out in air. The starting materials were purchased from Sigma-Aldrich, TCI or Alfa-Aesar and were used as received. The solvents were used as received except tetrahydrofuran that was distilled under a dry nitrogen atmosphere over

sodium and benzophenone. Compounds **4**, **6**, **8**, **11**, **12** and **13** were obtained according to reported procedures.<sup>14, 19d, 20d</sup>

**Syntheses. Compound 5.** A Schlenk flask was charged with tributyl(2,6-dithiophen-4H-pyran-4-yl)phosphonium tetrafluoroborate (615 mg, 1.15 mmol), 30 mL of anhydrous THF and *n*-BuLi in hexane solution (0.5 mL, 1.16 mmol) at  $-78^{\circ}\text{C}$  under argon protection. The solution was stirred at  $-78^{\circ}\text{C}$  for 15 min and *bis*-(4-(2-trimethylsilylethynyl))benzophenone (450 mg, 1.15 mmol) dissolved in dry THF (10 mL) was added dropwise. The solution was stirred at  $-78^{\circ}\text{C}$  under argon 30 min and then moved to room temperature and stirred overnight. After the reaction, the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (hexane/dichloromethane = 5/1) to give **5**. Yield: 490 mg (yellow solid), 72%.

IR (ATR,  $\text{cm}^{-1}$ ) 2152 ( $\nu_{\text{C}=\text{C}}$ ), 1660, 1597, 1492 ( $\nu_{\text{C}=\text{C}}$ ), 1250 ( $\nu_{\text{C}-\text{O}}$ ). NMR ( $\delta$  (ppm),  $\text{CDCl}_3$ ):  $^1\text{H}$  (300 MHz): 7.70 – 7.60 (m, 4H), 7.45 (d,  $^3J_{\text{HH}} = 8.2$  Hz, 4H), 7.42 – 7.34 (m, 6H), 7.19 (d,  $^3J_{\text{HH}} = 8.3$  Hz, 4H), 6.68 (s, 2H), 0.28 (s, 18H).  $^{13}\text{C}\{^1\text{H}\}$  (75 MHz): 1512.14, 142.57, 133.43, 132.15, 130.53, 129.31, 128.74, 127.76, 124.81, 124.76, 124.63, 121.16, 105.41, 105.01, 94.79, 0.17. Anal. Calcd for  $\text{C}_{40}\text{H}_{38}\text{OSi}_2$ : C, 81.30; H, 6.48. Found: C, 81.42; H, 6.40. HRMS (ESI):  $m/z$ , calculated for  $\text{M}^{+\bullet}$  ( $\text{C}_{40}\text{H}_{38}\text{OSi}_2$ ): 590.2461, found: 590.2458.

**Compound 7.** In a round bottom flask, to a methanol (10 mL) and dichloromethane (20 mL) solution of compound **5** (507 mg, 1.0 mmol) was added  $\text{K}_2\text{CO}_3$  (550 mg, 4.0 mmol), and the reaction mixture was stirred at room temperature overnight. Deionized water was used to quench the reaction; dichloromethane was added to extract the product. The organic layer as dried over  $\text{MgSO}_4$ , filtered and the solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/dichloromethane = 5/1) to give **7**. Yield: 420 mg (orange solid), 94%.

IR (ATR,  $\text{cm}^{-1}$ ) 3285 ( $\nu_{\text{C}-\text{H}}$ ), 2106 ( $\nu_{\text{C}=\text{C}}$ ), 1653, 1599, 1491 ( $\nu_{\text{C}=\text{C}}$ ), 1237 ( $\nu_{\text{C}-\text{O}}$ ). NMR ( $\delta$  (ppm),  $\text{CDCl}_3$ ):  $^1\text{H}$  (300 MHz): 7.74 – 7.61 (m, 4H), 7.50 (d,  $^3J_{\text{HH}} = 7.9$  Hz, 4H), 7.46 – 7.36 (m, 6H), 7.25 (d,  $^3J_{\text{HH}} = 8.1$  Hz, 4H), 6.70 (s, 2H), 3.15 (s, 2H).  $^{13}\text{C}\{^1\text{H}\}$  (75 MHz): 152.22, 142.82, 133.37, 132.33, 130.58, 129.33, 128.73, 127.87, 124.82, 124.27, 120.17, 104.87, 83.95, 77.67. Anal. Calcd for  $\text{C}_{34}\text{H}_{22}\text{O}$ : C, 91.45; H, 4.97. Found: C, 91.12; H, 4.97. HRMS (ESI):  $m/z$ , calculated for  $\text{M}^{+\bullet}$  ( $\text{C}_{34}\text{H}_{22}\text{O}$ ): 446.1671, found: 446.1679.

**Complex 9.** A 100 ml Schlenk flask, charged with **6** (152 mg, 0.36 mmol), *trans*-(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>PtCl **8** (300 mg, 0.30 mmol), and cuprous iodide (5.7 mg, 10 mol%), was degassed and back-filled with argon three times. Then diethylamine (20 mL) and dried THF (10 mL) were introduced into the reaction flask by syringe. The reaction mixture was stirred under argon protection at room temperature for 12h. The solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/petroleum ether 1/2) and recrystallized by layer–layer diffusion in CH<sub>2</sub>Cl<sub>2</sub>/n-pentane to give **9** as yellow needles. Yield: 315 mg, 75%.

IR (ATR, cm<sup>-1</sup>) 2129 (ν<sub>C=C</sub>), 1656, 1599, 1494, 1450 (ν<sub>C=C</sub>), 1277 (ν<sub>C-O</sub>). NMR (δ (ppm), CDCl<sub>3</sub>): <sup>1</sup>H (300 MHz): 7.72 – 7.53 (m, 16H), 7.45 – 7.27 (m, 8H), 7.24 – 7.15 (m, 3H), 7.11 (d, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 12H), 6.77 (d, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz, 2H), 6.63 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1H), 6.55 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1H), 6.26 (d, <sup>3</sup>J<sub>HH</sub> = 8.2 Hz, 2H), 2.35 (s, 18H). <sup>13</sup>C{<sup>1</sup>H} and JMOD (75 MHz): 151.14 (C), 151.05 (C), 145.92 (dd, <sup>1</sup>J<sub>CF</sub> = 215.5 Hz, <sup>2</sup>J<sub>CF</sub> = 19.1 Hz, *o* to Pt, (C)), 142.63 (C), 140.53 (C), 138.43 (C), 134.57 (virtual t, <sup>2</sup>J<sub>CP</sub> = 6.4 Hz, <sup>42</sup> *o* to P, (CH)), 133.87 (C), 133.81 (C), 130.70 (CH), 130.63 (CH), 129.27 (CH), 128.89 (CH), 128.60 (virtual t, <sup>3</sup>J<sub>CP</sub> = 5.9 Hz, <sup>42</sup> *m* to P, (CH)), 128.43 (C), 128.29 (CH), 128.04 (virtual t, <sup>1</sup>J<sub>CP</sub> = 29.6 Hz, <sup>42</sup> *i* to P, (C)), 127.20 (C), 126.76 (C), 126.48 (CH), 125.66 (C), 124.77 (CH), 124.67 (CH), 114.70 (C), 105.42 (CH), 105.34 (CH), 21.48 (CH<sub>3</sub>). <sup>43</sup> <sup>31</sup>P (121 MHz): 17.61 (s, <sup>1</sup>J<sub>PtP</sub> = 2691 Hz). <sup>44</sup> <sup>19</sup>F{<sup>1</sup>H} (282 MHz): -117.53 (m, <sup>3</sup>J<sub>F,Pt</sub> = 291.3 Hz, 2F, *o* to Pt), -165.66 (m, 2F, *m* to Pt), -166.42 (t, <sup>3</sup>J<sub>F,F</sub> = 19.7 Hz, 1F, *p* to Pt). Anal. Calcd for C<sub>80</sub>H<sub>63</sub>OF<sub>5</sub>P<sub>2</sub>Pt: C, 69.01; H, 4.56. Found: C, 69.17; H, 4.59. HRMS (ESI): m/z, calculated for M<sup>+</sup> (C<sub>80</sub>H<sub>63</sub>OF<sub>5</sub>P<sub>2</sub><sup>195</sup>Pt): 1391.392, found: 1391.390.

**Complex 10.** A 100 ml Schlenk flask, charged with **7** (67 mg, 0.15 mmol), *trans*-(C<sub>6</sub>F<sub>5</sub>)(Tol<sub>3</sub>P)<sub>2</sub>PtCl **8** (300 mg, 0.30 mmol), and cuprous iodide (5.7 mg, 10 mol%), was degassed and back-filled with argon three times. Then diethylamine (20 mL) and dried THF (10 mL) were introduced into the reaction flask by syringe. The reaction mixture was stirred under argon protection at room temperature overnight. The solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/petroleum ether 1/1) and recrystallized by layer–layer diffusion in CH<sub>2</sub>Cl<sub>2</sub>/n-pentane to give **10** as orange needles. Yield: 250 mg, 70%.

IR (ATR,  $\text{cm}^{-1}$ ) 2115 ( $\nu_{\text{C}=\text{C}}$ ), 1661, 1599, 1498, 1449 ( $\nu_{\text{C}=\text{C}}$ ), 1283 ( $\nu_{\text{C}-\text{O}}$ ). NMR ( $\delta$  (ppm),  $\text{CDCl}_3$ ):  $^1\text{H}$  (300 MHz): 7.67 – 7.46 (m, 28H), 7.41 – 7.28 (m, 6H), 7.10 (d,  $^3J_{\text{HH}} = 7.7$  Hz, 24H), 6.65 (d,  $^3J_{\text{HH}} = 8.2$  Hz, 4H), 6.49 (s, 2H), 6.19 (d,  $^3J_{\text{HH}} = 8.3$  Hz, 4H), 2.34 (s, 36H).  $^{13}\text{C}\{^1\text{H}\}$  and JMOD (75 MHz): 150.75 (C), 146.22 (dm,  $^1J_{\text{CF}} = 222.6$  Hz, *o* to Pt, (C)), 140.51 (C), 138.53 (C), 134.58 (virtual t,  $^2J_{\text{CP}} = 6.3$  Hz,  $^{42}$  *o* to P, (CH)), 133.91 (C), 130.48 (CH), 129.38 (CH), 128.60 (virtual t,  $^3J_{\text{CP}} = 5.5$  Hz,  $^{42}$  *m* to P, (CH)), 128.05 (virtual t,  $^1J_{\text{CP}} = 29.6$  Hz,  $^{42}$  *i* to P, (C)), 127.27 (C), 127.09 (C), 125.07 (C), 124.68 (CH), 114.72 (C), 112.22 (C), 105.69 (CH), 21.49 ( $\text{CH}_3$ ). $^{31}\text{P}$  (121 MHz): 17.59 (s,  $^1J_{\text{PtP}} = 2692$  Hz). $^{19}\text{F}\{^1\text{H}\}$  (282 MHz): -117.53 (m,  $^3J_{\text{F,Pt}} = 291.3$  Hz, 2F, *o* to Pt), -165.66 (m, 2F, *m* to Pt), -166.42 (t,  $^3J_{\text{F,F}} = 19.7$  Hz, 1F, *p* to Pt). Anal. Calcd for  $\text{C}_{130}\text{H}_{104}\text{OF}_{10}\text{P}_4\text{Pt}_2$ : C, 65.43; H, 4.39. Found: C, 65.17; H, 4.30. HRMS (ESI): *m/z*, calculated for  $\text{M}^+$  ( $\text{C}_{130}\text{H}_{104}\text{OF}_{10}\text{P}_4^{195}\text{Pt}_2$ ): 2384.617, found: 2384.621.

**Complex 14.** A 100 ml Schlenk flask, charged with chloro complex **11** (360 mg, 0.28 mmol), *trans*-( $\text{C}_6\text{F}_5$ )( $\text{C}_6\text{H}_4$ ) $\text{Pt}(\text{C}\equiv\text{C})_2\text{H}$  **12** (292 mg, 0.28 mmol), and cuprous iodide (5.4 mg, 10 mol%), was degassed and back-filled with argon three times. Then diethylamine (20 mL) and dried THF (10 mL) were introduced into the reaction flask by syringe. The reaction mixture was stirred under argon protection at room temperature for 48h. The solvent was then removed under reduced pressure. The residue was purified by column chromatography on silica gel (dichloromethane/petroleum ether 1/1) and recrystallized by layer–layer diffusion in  $\text{CHCl}_3$ /n-pentane to give **14** as yellow needles. Yield: 450 mg, 72%.

IR (ATR,  $\text{cm}^{-1}$ ) 2118 ( $\nu_{\text{C}=\text{C}}$ ), 1652, 1599, 1498, 1454 ( $\nu_{\text{C}=\text{C}}$ ), 1279 ( $\nu_{\text{C}-\text{O}}$ ). NMR ( $\delta$  (ppm),  $\text{CDCl}_3$ ):  $^1\text{H}$  (300 MHz): 7.70 – 7.58 (m, 5H), 7.57 – 7.42 (m, 24H), 7.41– 7.31 (m, 7H), 7.22 – 7.14 (m, 3H), 6.97 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 12H), 6.91 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 12H), 6.73 (d,  $^3J_{\text{HH}} = 8.3$  Hz, 2H), 6.61 (s, 2H), 5.98 (d,  $^3J_{\text{HH}} = 8.3$  Hz, 2H), 2.28 (s, 18H), 2.25 (s, 18H).  $^{13}\text{C}\{^1\text{H}\}$  and JMOD (75 MHz): 151.04 (C), 150.97 (C), 146.00 (dd,  $^1J_{\text{CF}} = 223.4$  Hz,  $^2J_{\text{CF}} = 22.7$  Hz, *o* to Pt, (C)), 142.49 (C), 140.35 (C), 140.04 (C), 139.66 (C), 138.15 (C), 135.14 (virtual t,  $^2J_{\text{CP}} = 6.2$  Hz,  $^{42}$  *o* to P, (CH)), 134.60 (virtual t,  $^2J_{\text{CP}} = 6.3$  Hz,  $^{42}$  *o* to P', (CH)), 133.80 (C), 133.77 (C), 131.06 (CH), 130.62 (CH), 129.38 (C), 129.09 (CH), 128.98 (C), 128.86 (CH), 128.80 (CH), 128.73 (CH), 128.62 (CH), 128.57 (CH), 128.36 (virtual t,  $^3J_{\text{CP}} = 5.4$  Hz,  $^{42}$  *m* to P; *m* to P' obscured, (CH)), 128.21 (CH), 127.88 (virtual t,  $^1J_{\text{CP}} = 29.3$  Hz,  $^{42}$  *i* to P; *i* to P' obscured, (C)), 126.94 (C), 126.41 (CH), 125.57 (C), 124.66 (CH), 124.63 (CH), 114.88 (C), 111.90 (C), 105.50 (CH), 105.33 (CH), 104.20 (C), 103.16 (C), 93.41 (C), 21.53 ( $\text{CH}_3$ ), 21.37

(CH<sub>3</sub>).<sup>43</sup> <sup>31</sup>P (121 MHz): 16.31 (s, <sup>1</sup>J<sub>PtP</sub> = 2708 Hz), 14.69 (s, <sup>1</sup>J<sub>PtP</sub> = 2627 Hz).<sup>44</sup> <sup>19</sup>F{<sup>1</sup>H} (282 MHz): -117.23 (m, <sup>3</sup>J<sub>F,Pt</sub> = 286.2 Hz, 2F, *o* to Pt), -165.83 (m, 2F, *m* to Pt), -166.94 (t, <sup>3</sup>J<sub>F,F</sub> = 19.7 Hz, 1F, *p* to Pt). Anal. Calcd for C<sub>126</sub>H<sub>105</sub>OF<sub>5</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 67.43; H, 4.72. Found: C, 67.06; H, 4.63. HRMS (ESI): m/z, calculated for M<sup>+</sup> (C<sub>126</sub>H<sub>105</sub>OF<sub>5</sub>P<sub>4</sub><sup>195</sup>Pt<sub>2</sub>): 2242.6326, found: 2242.6356.

**Complex 15.** A 100 ml Schlenk flask charged with *trans*-(C<sub>6</sub>F<sub>5</sub>)(*p*-tol<sub>3</sub>P)<sub>2</sub>Pt(C≡C)<sub>3</sub>SiEt<sub>3</sub> **13** (375 mg, 0.32 mmol) and THF (10 mL), was degassed and back-filled with argon three times. Then wet nBu<sub>4</sub>N<sup>+</sup>F (1.0 M in THF/5 wt% H<sub>2</sub>O, 0.070 mL, 0.070 mmol) was added with stirring. After 0.5 h, chloro complex **11** (400 mg, 0.32 mmol), cuprous iodide (6.1 mg, 10 mol%), and diethylamine (20 mL) were introduced into the reaction flask. The reaction mixture was stirred under argon protection at room temperature for 48h. The solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (hexane/dichloromethane: 1/1) to give **15** as a yellow solid. Yield: 550 mg, 76%.

IR (ATR, cm<sup>-1</sup>) 2103 (ν<sub>C=C</sub>), 1654, 1599, 1498, 1453 (ν<sub>C=C</sub>), 1277 (ν<sub>C-O</sub>). NMR (δ (ppm), CDCl<sub>3</sub>): <sup>1</sup>H (300 MHz): 7.71 – 7.59 (m, 16H), 7.59 – 7.49 (m, 12H), 7.43 – 7.28 (m, 8H), 7.24 – 7.19 (m, 3H), 7.18 – 7.06 (m, 24H), 6.80 (d, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz, 2H), 6.65 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1H), 6.63 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1H), 6.16 (d, <sup>3</sup>J<sub>HH</sub> = 8.3 Hz, 2H), 2.37 (s, 18H), 2.28 (s, 18H). <sup>13</sup>C{<sup>1</sup>H} and JMOD (75 MHz): 151.06 (C), 145.94 (dm, <sup>1</sup>J<sub>CF</sub> = 219.3 Hz, *o* to Pt, (C)), 142.50 (C), 140.52 (CH), 140.33 (C), 138.48 (C), 135.00 (virtual t, <sup>2</sup>J<sub>CP</sub> = 6.2 Hz, <sup>42</sup> *o* to P, (CH)), 134.55 (virtual t, <sup>2</sup>J<sub>CP</sub> = 6.4 Hz, <sup>42</sup> *o* to P', (CH)), 133.79 (C), 130.91 (CH), 130.63 (CH), 129.22 (CH), 128.88 (CH), 128.70 (CH), 128.67 (CH), 128.63 (CH), 128.60 (virtual t, <sup>3</sup>J<sub>CP</sub> = 5.5 Hz, <sup>42</sup> *m* to P'; *m* to P' obscured, (CH)), 128.53 (CH), 128.28 (CH), 128.24 (CH), 127.86 (virtual t, <sup>1</sup>J<sub>CP</sub> = 29.9 Hz, <sup>42</sup> *i* to P; *i* to P' obscured, (C)), 126.95 (C), 126.79 (C), 126.45 (CH), 125.68 (C), 124.70 (CH), 124.65 (CH), 113.31 (C), 110.79 (C), 105.41 (CH), 105.33 (CH), 99.08 (C), 96.73 (C), 21.48 (CH<sub>3</sub>), 21.45 (CH<sub>3</sub>).<sup>43</sup> <sup>31</sup>P (121 MHz): 16.97 (s, <sup>1</sup>J<sub>PtP</sub> = 2668 Hz), 16.70 (s, <sup>1</sup>J<sub>PtP</sub> = 2596 Hz).<sup>44</sup> <sup>19</sup>F{<sup>1</sup>H} (282 MHz): -117.52 (m, <sup>3</sup>J<sub>F,Pt</sub> = 289.6 Hz, 2F, *o* to Pt), -165.65 (m, 2F, *m* to Pt), -166.50 (t, <sup>3</sup>J<sub>F,F</sub> = 19.5 Hz, 1F, *p* to Pt). Anal. Calcd for C<sub>128</sub>H<sub>105</sub>OF<sub>5</sub>P<sub>4</sub>Pt<sub>2</sub>: C, 67.78; H, 4.67. Found: C, 67.34; H, 4.61. HRMS (ESI): m/z, calculated for M<sup>+</sup> (C<sub>128</sub>H<sub>105</sub>OF<sub>5</sub>P<sub>4</sub><sup>195</sup>Pt<sub>2</sub>): 2266.633, found: 2266.615.



## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI:XXX.

X-ray diffraction data for compounds **9** and **14**, graphic stick and ball representation of the molecular structure of complex **10**, list of xyz Cartesian coordinates for **10** (x // **a** cell axis), experimental cyclic voltammograms data for compounds **10** and **15**, the spin density of complexes **9<sup>+</sup>** and **10<sup>+</sup>** and the NMR spectra for all new compounds.

### Accession Codes

CCDC 1831483, 1831485 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif), or by emailing [data\\_request@ccdc.cam.ac.uk](mailto:data_request@ccdc.cam.ac.uk), or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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### Notes

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