# Synthesis and Spectroscopic and Electronic Characterization of New Cis-Configured Di- to Multiplatinum Alkynyls

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Utilization of Sonogashira coupling reactions with *cis*-[Pt(dppe)Cl$_2$] and varying amounts of the alkynyl ligands HC≡CRC≡CH (where R = *p*-C$_6$H$_4$, *p*-C$_6$H$_4$-*p*-C$_6$H$_4$) afford the monoplatinum complexes *cis*-[Pt(dppe)(C≡CRC≡CH)$_2$] (R = *p*-C$_6$H$_4$ (**1a**), *p*-C$_6$H$_4$-*p*-C$_6$H$_4$ (**1b**)), the diplatinum complexes *cis*-[(HC≡CRC≡C)Pt(dppe)(C≡CRC≡C)Pt(dppe)(C≡CRC≡CH)] (R = *p*-C$_6$H$_4$ (**2a**), *p*-C$_6$H$_4$-*p*-C$_6$H$_4$ (**2b**)), the triplatinum complexes *cis*-[(HC≡CRC≡C)Pt(dppe)(C≡CRC≡C)Pt(dppe)(C≡CRC≡C)Pt(dppe)-(C≡CRC≡CH)] (R = *p*-C$_6$H$_4$ (**3a**), *p*-C$_6$H$_4$-*p*-C$_6$H$_4$ (**3b**)), and the respective oligomeric species **4a**,**b**, all in reasonable yields. X-ray diffraction studies of **2a** reveal the presence of two independent diplatinum molecules in the asymmetric unit, each with $C_i$ symmetry. All the complexes have been fully characterized by NMR and mass spectrometry, and GPC analysis of **4a**,**b** indicate their oligomeric nature, with a degree of polymerization of ca. 4. Electronic spectral studies indicate that the optical band gap decreases with increasing chain length but that the intensity of the triplet state emission increases with the number of repeating units. As expected, there is less effective $\pi$-conjugation along the chain in the cis configuration as compared to the analogous trans-oriented species.

## Introduction

The study of transition-metal alkynyl $\sigma$-complexes continues to attract researchers because of the interesting electronic properties that they exhibit: i.e., their potential use as large-area flexible displays in the electronics industry.[1−5] The first reported platinum and palladium acetylides were synthesized by Hagihara et al. in the 1970s,[6] and since then, many new classes of materials have been extensively studied and investigated with the introduction of different group 8,[1,5,7] group 9,[1,8] group 10[1−4,9] and other transition metals.[1,3−5,10] These rigid-rod species possess a range of properties, including nonlinear optical effects, liquid crystallinity, electrical conductivity, and photovoltaic behavior, which differ from those of conventional organic materials.[1−10] The relatively low oxidation states of late transition metals in the $\sigma$-alkynyl complexes are usually stabilized by the presence of auxiliary ligands, and the complexes can exist in either a trans or a cis configuration.[1−5] In group 10 systems, especially with platinum, owing to the thermodynamic stability of the trans isomer, the majority of luminescent investigations have focused on the trans complexes with monodentate auxiliary ligands (L). The $\sigma$-acetylide complexes often exist as the diterminal alkynes *trans*-[PtL$_2$(C≡CR)$_2$] and polyynes *trans*-[−PtL$_2$−C≡CRC≡C−]$_n$ with a wide variety of aromatic ring systems (R).[1−4,6,9,10c,11]

In the study of *cis*-platinum ethynyl materials, the introduction of chelating auxiliary ligands, such as bidentate phosphines (dppe, dppp) or diimine groups ($^t$Bu$_2$bipy),[12,13] helps to overcome the thermodynamic instability of cis isomers, and diimine-

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(1) Long, N. J.; Williams, C. K. *Angew. Chem., Int. Ed.* **2003**, *42*, 2586 and references therein.

(2) (a) Wong, W. Y. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 197 and references therein. (b) Wong, W. Y. *Comments Inorg. Chem.* **2005**, *26*, 39.

(3) Silverman, E. E.; Cardolaccia, T.; Zhao, X.; Kim, K. Y.; Haskins-Glusac, K.; Schanze, K. S. *Coord. Chem. Rev.* **2005**, *249*, 1491 and references therein.

(4) Yam, V. W.-W. *Acc. Chem. Res.* **2002**, *35*, 555 and references therein.

(5) Schwab, P. F. H.; Levin, M. D.; Michl, J. *Chem. Rev.* **1999**, *99*, 1863.

(6) (a) Fujikura, Y.; Sonogashira, K.; Hagihara, N. *Chem. Lett.* **1975**, 1067. (b) Sonogashira, K.; Yatake, T.; Tahoda, Y.; Takashashi, S.; Hagihara, N. *J. Chem. Soc., Chem. Commun.* **1977**, 291. (c) Sonogashira, K.; Takahashi, S.; Hagihara, N. *Macromolecules* **1977**, 879. (d) Sonogashira, K.; Ohga, K.; Hagihara, N. *J. Organomet. Chem.* **1980**, *188*, 237.

(7) (a) Hurst, S. K.; Ren, T. *J. Organomet. Chem.* **2003**, *670*, 188. (b) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 21.

(8) (a) Bruce, M. I.; Zaitseva, N. N.; Skelton, B. W.; Somers, N.; White, A. H. *Aust. J. Chem.* **2003**, *56*, 509. (b) Ara, I.; Berenguer, J. R.; Eguizábal, E.; Forniés, J.; Lalinde, E.; Martín, A.; Martínez, F. *Organometallics* **1998**, *17*, 4578.

(9) (a) D'Amato, R.; Fratoddi, I.; Cappoto, A.; Altamura, P.; Delfini, M.; Bianchetti, C.; Bolasco, A.; Polzonetti, G.; Russo, M. V. *Organometallics* **2004**, *23*, 2860. (b) D'Amato, R.; Furlani, A.; Colapietro, M.; Portalone, G.; Casalboni, M.; Falconieri, M.; Russo, M. V. *J. Organomet. Chem.* **2001**, *627*, 13.

(10) (a) Horn, C. R.; Martín-Alvarez, J. M.; Gladysz, J. A. *Organometallics* **2002**, *21*, 5386. (b) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; Smith, M. E.; White, A. H. *Dalton Trans.* **2002**, 995. (c) Vicente, J.; Chicote, M. T.; Alvarez-Falcón, M. M.; Jones, P. G. *Organometallics* **2005**, *24*, 2764.

(11) (a) Adams, C. J.; Bowen, L. E. *Dalton Trans.* **2005**, 2239. (b) Khan, M. S.; Al-Mandhary, M. R. A.; Al-Suti, M. K.; Hisahm, A. K. Raithby, P. R.; Ahrens, B.; Mahon, M. F.; Male, L.; Marseglia, E. A.; Tedesco, E.; Friend, R. H.; Köhler, A.; Feeder, N.; Teat, S. J. *Dalton Trans.* **2002**, 1358. (c) Khan, M. S.; Kakkar, A. K.; Long, N. J.; Lewis, J.; Raithby, P.; Nguyen, P.; Marder, T. B.; Wittmann, F.; Friend, R. H. *J. Mater. Chem.* **1994**, *4*, 1227. (d) Bruce. M. I.; Davy, J. Hall, B. C.; Jansen van Galen, Y.; Skelton, B. W.; White, A. H. *Appl. Organomet. Chem.* **2002**, *16*, 559. (e) Deeming, A. J.; Hogarth, G.; Lee, M. Y. V.; Saha, M.; Redmond, S. P.; Phetmung, H. T.; Orpen A. G. *Inorg. Chim. Acta* **2000**, *309*, 109. (f) Fratoddi, I.; Battocchio, C.; Furlani, A.; Mataloni, P.; Polzonetti, G.; Russo, M. V. *J. Organomet. Chem.* **2003**, *674*, 10. (g) Vicente, J.; Chicote, M. T.; Alvarez-Falcón, M. M.; Jones, P. G. *Chem. Commun.* **2004**, 2658. (h) Long, N. J.; White, A. J. P.; Williams, D. J.; Younnus, M. *J. Organomet. Chem.* **2002**, *649*, 94.

(12) (a) Bruce, M. I.; Costuas, K.; Halet, J. F.; Hall, P. C.; Low, B. C.; Nicholson, B. L.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2002**, 383. (b) Janka, M.; Anderson, G. K.; Rath, N. P. *Organometallics* **2004**, *23*, 4382. (c) Wong, W. Y.; Lu, G. L.; Choi, K. H. *J. Organomet. Chem.* **2002**, *659*, 107. (d) Bruce, M. I.; Hall, B. C.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1999**, *592*, 74. (e) Yamazaki, S.; Deeming, A. J. *J. Chem. Soc., Dalton Trans.* **1993**, 3051.

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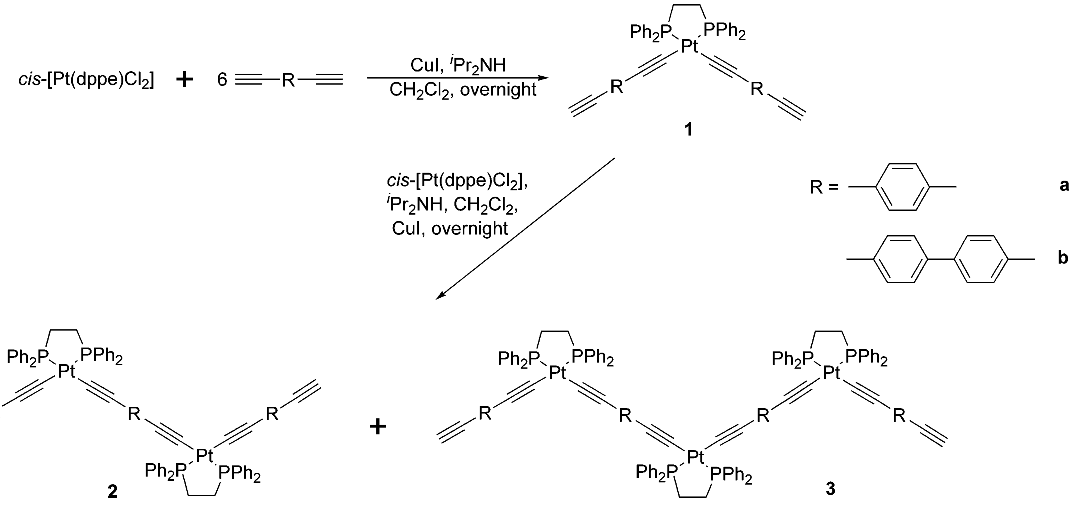
**Scheme 1. General Scheme for the Synthesis of Monomeric Complexes 1a,b and Dimeric Complexes 2a,b and 3a,b**



stabilized platinum acetylenic cis complexes exhibit interesting white[14] and red[15] optoelectronic properties. However, within this area, most of the investigations are limited to monoplatinum dienyl complexes and there are still very few reports on bis(ethynyl) and oligomeric species with phosphine-chelating auxiliary ligands. To address this issue, we report here the synthesis, characterization, and systematic study of the electronic properties of a series of cis-configured monomeric (**1**), dimeric (**2**), trimeric (**3**), and oligomeric (**4**) platinum complexes with the ancillary ligand bis(diphenylphosphino)ethane and diacetylenic ligands 1,4-diethynylbenzene (**a**) and 4,4′-diethynylbiphenyl (**b**). These species represent precursors toward the construction of metal−alkynyl molecular shapes, such as squares, hexagons, and catenanes.

During the course of our research and the preparation of this paper, compounds **1a**,**b** were independently reported by Raithby et al.[16]

## Results and Discussion

**Syntheses and Characterization.** Scheme 1 illustrates the reactions used in the syntheses of the complexes **1a**,**b**−**3a**,**b**. The conventional Sonogashira coupling routes using *cis*-[Pt(dppe)Cl$_2$ and excess $HC\equiv CRC\equiv CH$ (R = *p*-C$_6$H$_4$, *p*-C$_6$H$_4$-*p*-C$_6$H$_4$) in diisopropylamine and dichloromethane with CuI catalyst were employed to afford the monoplatinum complexes *cis*-[Pt(dppe)($C\equiv CRC\equiv CH$)$_2$] (R = *p*-C$_6$H$_4$ (**1a**), *p*-C$_6$H$_4$-*p*-C$_6$H$_4$ (**1b**)), with an average 70% yield as the major product and the diplatinum complexes *cis*-[($HC\equiv CRC\equiv C$)Pt(dppe)($C\equiv CRC\equiv C$)Pt(dppe)($C\equiv CRC\equiv CH$)] (R = *p*-C$_6$H$_4$ (**2a**), *p*-C$_6$H$_4$-*p*-C$_6$H$_4$ (**2b**)) with an average 12% yield as the minor product. However, in the synthesis of the triplatinum derivatives, where excess monoplatinum species were used instead of excess $HC\equiv CRC\equiv CH$, the conventional method mainly resulted in insoluble products with a small amount of isolated soluble products characterized as the diplatinum species, owing to the ligand exchange reaction between triplatinum and monoplatinum complexes. However, an improved synthesis utilizing a high dilution method, diisopropylamine and dichloromethane (1/20), reduced the rate of ligand exchange. The yields of the desired triplatinum complexes *cis*-[($HC\equiv CRC\equiv C$)Pt(dppe)($C\equiv CRC\equiv C$)Pt(dppe)($C\equiv CRC\equiv C$)Pt(dppe)($C\equiv CRC\equiv CH$)] (R = *p*-C$_6$H$_4$ (**3a**), *p*-C$_6$H$_4$-*p*-C$_6$H$_4$ (**3b**)) were thus 27% and 23%, respectively, with the formation of byproduct dimeric complexes **2a**,**b** in yields of 36% and 41%, respectively.

Neutral platinum-containing molecular squares using monoplatinum cis complexes as reactants were first reported by Bruce and co-workers[12a] under methanol and anhydrous sodium acetate reaction conditions. Later, it was discovered that the molecular squares could be also synthesized under CuI-mediated coupling conditions in a solvent mixture of diethylamine with CH$_2$Cl$_2$ or THF, as reported by Lin and co-workers[17] and Anderson and co-workers.[12b] Unfortunately, in our case, the reaction of monomeric complex **1a** and *cis*-[Pt(dppe)Cl$_2$] in refluxing diethylamine/THF only yielded an insoluble yellow precipitate and the same result was obtained in a more polar solvent system: diisopropylamine/CH$_2$Cl$_2$ (3/40, v/v). Coupling reactions were also attempted between $HC\equiv CRC\equiv CH$ (R = *p*-C$_6$H$_4$, *p*-C$_6$H$_4$-*p*-C$_6$H$_4$) and *cis*-[Pt(dppe)Cl$_2$], in a 1/1 ratio with a polar solvent system: diisopropylamine/CH$_2$Cl$_2$ (3/40, v/v). The isolated product remained a yellow insoluble precipitate with $HC\equiv C$-*p*-C$_6$H$_4$$C\equiv CH$, whereas with $HC\equiv C$-*p*-C$_6$H$_4$-*p*-C$_6$H$_4$$C\equiv CH$, the soluble oligomeric species **4b**, along with an insoluble yellow precipitate, were obtained (Scheme 2). The result of the $HC\equiv C$-*p*-C$_6$H$_4$-*p*-C$_6$H$_4$$C\equiv CH$ reaction was the same as that reported in the literature[18] synthesized via a less polar solvent system: refluxing toluene/diethylamine. In addition, utilizing methanol and anhydrous sodium acetate, the reactions between monoplatinum complexes (**1a**,**b**) and *cis*-[Pt-

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(13) (a) Kwok, C. C.; Ngai, H. M. Y.; Chan, S. C.; Sham, I. H. T.; Che, C. M.; Zhu, N. *Inorg. Chem.* **2005**, *44*, 4442. (b) Hissler, M.; Connick, W. B.; Geiger, D. K.; McGarrah, J. E.; Lipa, D.; Lachicotte, R. J.; Eisenberg, R. *Inorg. Chem.* **2000**, *39*, 447. (c) Adams, C. J.; James, S. J.; Liu, X.; Raithby, P. R.; Yellowlees, L. J. *Dalton Trans.* **2000**, 63. (d) James, S. L.; Younus, M.; Raithby, P. R.; Lewis, J. *J. Organomet. Chem.* **1997**, *543*, 233. (e) Chan, C. W.; Cheng, L. K.; Che, C. M. *Coord. Chem. Rev.* **1994**, *132*, 87.

(14) (a) Che, C. M.; Chan, S. C.; Xiang, H. F.; Chan, M. C. W.; Liu, Y.; Wang, Y. *Chem. Commun.* **2004**, 1484. (b) D'Andrade, B. W.; Brooks, J.; Adamovich, V.; Thompson, M. E.; Forrest, S. R. *Adv. Mater.* **2002**, *14*, 1032.

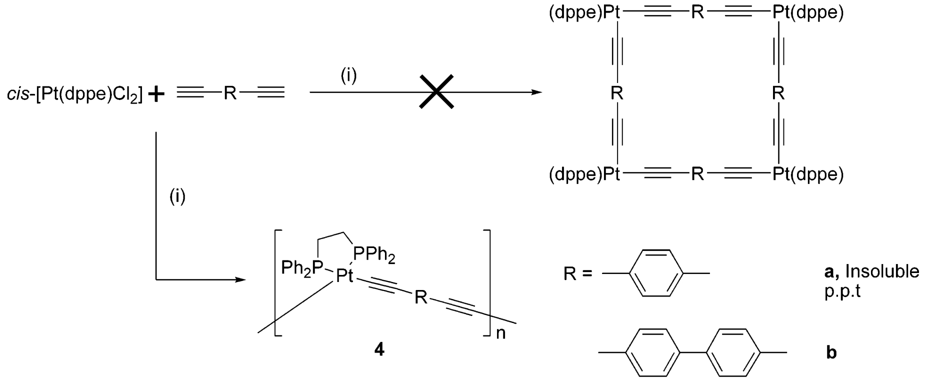
(15) (a) Siemeling, U.; Bausch, K.; Fink, H.; Bruhn, C.; Baldus, M.; Angerstein, B.; Plessow, R.; Brockhinke, A. *Dalton Trans.* **2005**, 2365. (b) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Che, C. M.; Zhu, N.; Lee, S. T. *J. Am. Chem. Soc.* **2004**, *126*, 4958. (c) Lu, W.; Mi, B. X.; Chan, M. C. W.; Hui, Z.; Zhu, N.; Lee, S. T., Che, C. M. *Chem. Commun.* **2002**, 206.

(16) Saha, R.; Abdul Qaium, M.; Debnath, D.; Younus, M.; Chawdury, N.; Sultana, N.; Kociok-Köhn, G. K.; Ooi, L. L.; Raithby, P. R.; Kijima, M. *Dalton Trans.* **2005**, 2760.

(17) (a) Lee, S. J.; Luman, C. R.; Castellano, F. N.; Lin, W. *Chem. Commun.* **2003**, 2124. (b) Lee, S. J.; Hu, A.; Lin, W. *J. Am. Chem. Soc.* **2002**, *124*, 12948.

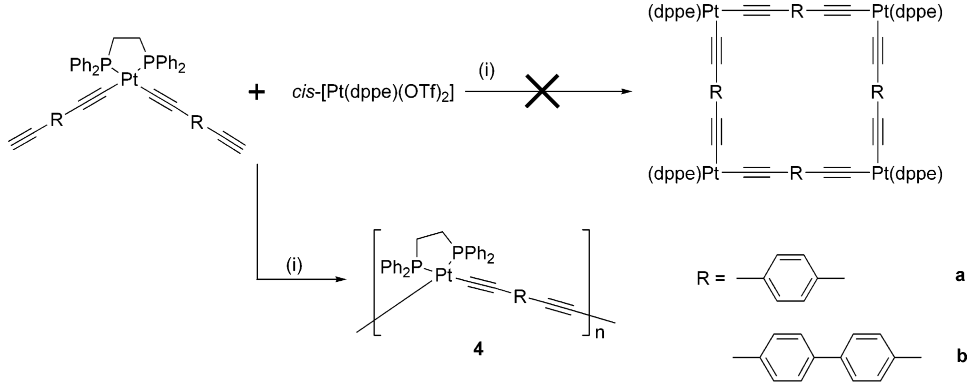
(18) Iucci, G.; Infante, G.; Polzonetti, G. *Polymer* **2002**, *43*, 655.

**Scheme 2. Sonogashira Coupling Synthesis of Oligomeric Species 4a,b**



(i) CuI, $CH_2Cl_2$, $^iPr_2NH$, overnight

**Scheme 3. Another Synthetic Pathway for Oligomeric Species 4a,b**



(i) anhydrous NaOAc, MeOH, $CH_2Cl_2$

(dppe)(OTf)$_2$] gave the oligomeric mixtures **4a**,**b**, respectively, with complex $^{31}P\{^1H\}$ NMR spectral patterns but no insoluble precipitate (Scheme 3). No neutral platinum molecular squares could be isolated from any reaction.

All the complexes and oligomeric species were stable in air and could be stored without any special precautions. However, they did not exhibit good solubility and were only soluble in polar solvents such as dichloromethane and DMF, and this solubility decreased with an increase in the numbers of the repeating unit. The new complexes were fully characterized by IR, $^1H$ and $^{31}P\{^1H\}$ NMR, and elemental analysis. The molecular weights of the monomeric and dimeric complexes were measured by FAB-MS, whereas the trimeric complexes were characterized by MALDI-MS and, furthermore, by MALDI high-resolution mass spectrometry. The molecular weight distribution of the oligomeric species was measured by gel permeation chromatography (GPC) methods. The molecular and crystal structure of the dimeric complex **2a** was determined by single-crystal X-ray crystallography. X-ray analysis of **2a** revealed the presence of two independent diplatinum molecules (A and B) in the asymmetric unit, each with $C_i$ symmetry (molecule A is shown in Figure 1 and molecule B in Figure S1 in the Supporting Information). Though the unique platinum atom in each molecule has a distorted-square-planar coordination

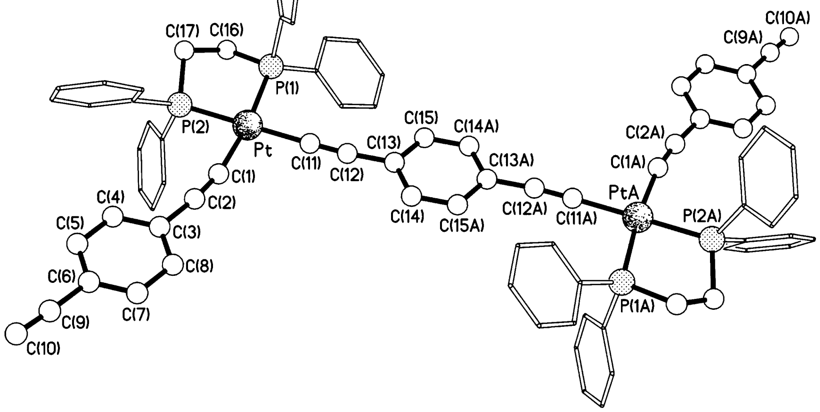


**Figure 1.** Molecular structure of one (A) of the two $C_i$-symmetric independent molecules present in the crystals of **2a**.

**Table 1. Selected Bond Lengths (Å) and Angles (deg) for the Two $C_i$-Symmetric Independent Molecules (A and B) Present in the Crystals of 2a**

| | A | B |
|---|---|---|
| Pt−P(1) | 2.2871(19) | 2.2709(18) |
| Pt−C(1) | 2.019(7) | 2.020(7) |
| C(1)−C(2) | 1.195(10) | 1.202(10) |
| C(11)−C(12) | 1.182(10) | 1.197(9) |
| Pt−P(2) | 2.2723(18) | 2.2701(17) |
| Pt−C(11) | 2.025(7) | 2.005(6) |
| C(9)−C(10) | 1.170(13) | 1.167(14) |
| P(1)−Pt−P(2) | 84.82(7) | 85.80(6) |
| P(1)−Pt−C(11) | 93.8(2) | 88.4(2) |
| P(2)−Pt−C(11) | 177.8(2) | 173.7(2) |
| Pt−C(1)−C(2) | 168.9(6) | 171.0(6) |
| C(6)−C(9)−C(10) | 177.7(11) | 179.0(15) |
| C(11)−C(12)−C(13) | 173.7(10) | 173.1(8) |
| P(1)−Pt−C(1) | 172.1(2) | 176.66(19) |
| P(2)−Pt−C(1) | 89.0(2) | 96.88(18) |
| C(1)−Pt−C(11) | 92.6(3) | 88.8(3) |
| C(1)−C(2)−C(3) | 173.2(8) | 172.8(8) |
| Pt−C(11)−C(12) | 176.8(7) | 170.2(6) |

geometry (cis angles in the range 84.82(7)−93.8(2)° for molecule A and 85.80(6)−96.88(18)° for molecule B; {Pt,P(1),P(2),C(1),C(11)} coplanar to within ca. 0.07 Å for molecule A and to within ca. 0.03 Å for molecule B), the two molecules have noticeably different relative positions for the alkynyl substituents (see Figure S4 in the Supporting Information), the P(2)−Pt−C(1) and P(1)−Pt−C(11) angles varying between the two molecules by ca. 7.9 and 5.4°, respectively (Table 1).

The complexes have both terminal and bridging alkynyl−aryl−alkynyl ligands, and it is the orientation of the terminal ligand that is the main difference between the two independent molecules (see Figure S4). In molecule A the C(3)/C(8) aryl ring is oriented near parallel (ca. 10°) to the platinum coordination plane, while in molecule B this ring is steeply inclined (ca. 82°). In each case the aryl ring of the bridging ligand is almost parallel with the platinum coordination plane, the inclination angles being ca. 8 and 6° in molecules A and B, respectively. It is also noticeable that the two molecules have different bends away from linearity for the alkynyl units. In molecule A the bends at C(1) and C(2) move the C(3)/C(8) aryl ring in the direction of P(2), whereas in molecule B they move the aryl ring away from P(2). For the C(11)≡C(12) unit, the difference is less marked, but Figure S4 clearly shows a greater bend toward P(1) in molecule B with regard to molecule A. However, whereas for the C(1)≡C(2) alkynyl moiety the magnitudes of the departures from linearity were similar for the two molecules (with a maximum difference of ca. 2°), for the C(11)≡C(12) ligand there is a difference of ca. 7° for the angle at C(11). In molecule A the Pt−P bond distances are distinctly asymmetric, with that trans to the terminal alkynyl−aryl−alkynyl ligand (Pt−P(1) = 2.2871(19) Å) being longer than that trans to the bridging ligand (Pt−P(2) = 2.2723(18) Å). In molecule B, in contrast, the two bonds are the same, being 2.2709(18) and 2.2701(17) Å to P(1) and P(2), respectively. In each molecule the Pt−C distances are the same (2.019(7) and 2.025(7) Å in molecule A, 2.020(7) and 2.005(6) Å in molecule B). The closest literature examples[19] have symmetric terminal alkynyl ligands, and in each case the Pt−P distances are essentially the same.

The C(9′)≡C(10′)−H proton from molecule B approaches both the C(1)≡C(2) and C(11)≡C(12) triple bonds in molecule A, forming bifurcated C−H···π hydrogen bonds with H···π distances and C−H···π angles of 2.91 Å and 120° to the C(1)≡C(2) bond and 3.00 Å and 125° to the C(11)≡C(12) bond. The C(9)≡C(10) linkage in molecule A is involved in a π···π interaction with the C(3)/C(8) aryl ring in a centrosymmetrically related counterpart with a centroid···centroid separation of ca. 3.48 Å. The closest approach to the C(1′)≡C(2′) and C(11′)≡C(12′) bonds in molecule B are from ethyl protons on C(16) and C(17), respectively, in molecule A (H···π = 3.06 Å and C−H···π = 106° for the C(1′)≡C(2′) bond, H···π = 2.75 Å and C−H···π = 166° for the C(11′)≡C(12′) bond), and the closest approach to the C(9′)≡C(10′) bond is from the C(9)≡C(10)−H proton in molecule A at H···π = 2.95 Å, C−H···π = 160°.

IR spectroscopy is a useful diagnostic tool for the characterization of C≡C bond units, as most compounds exhibited a single IR $\nu_{C\equiv C}$ stretch at around 2101 cm$^{-1}$. If more than two ligand moieties were present in the complexes, multiple $\nu_{C\equiv C}$ bands might be observed (i.e. in **2a** and **3a**, two $\nu_{C\equiv C}$ stretches were observed at 2104 and 2116 cm$^{-1}$). For the IR $\nu_{C\equiv CH}$ stretching vibration, only a single absorption peak at around 3296−3301 cm$^{-1}$ was observed for all the complexes **1a**,**b**−**3a**,**b** and the oligomeric species **4a**,**b**.

In all cases, $^1H$ NMR signals arising from the protons of the organic fragments were observed and clearly identified in the alkynyl and aromatic regions. The methylenic protons of the dppe group, $P(CH_2)P$, gave the expected peaks at δ 2.3−2.5, and singlet signals were observed at δ 3.05−3.16 due to the presence of C≡C*H*. Between the two series of complexes, the C≡C*H* signals in **1a**−**3a** are shifted more upfield than those in **1b**−**3b**, due to the poor shielding effect in C≡C*H* caused by the presence of an additional phenyl ring in $-C\equiv C$-*p*-$C_6H_4$-*p*-$C_6H_4C\equiv C-$ moieties. The aromatic protons of dppe and the ligand moieties gave complicated multiplets around δ 7.1−8.2. For the complexes **1a**−**3a**, a new singlet at δ 7.04 was observed in **2a** arising from the *p*-$C_6H_4$ moiety in the inner core and the integral signal intensity was doubled in **3a**. This phenomenon implied that the electron densities on the ligand moieties in the inner core increased when the number of repeating units increased. The increased electron density was induced by the presence of cis-configured platinum atoms in complexes **2a** and **3a**.

The $^{31}P\{^1H\}$ NMR signals in the cis complexes were more complicated than those in the relevant trans complexes. In the analogous trans complexes, all $^{31}P\{^1H\}$ signals are singlets with two Pt−P satellite signals. However, in the cis complexes, this pattern was only observed in the monomeric complexes **1a**,**b**. In the dimeric complexes **2a**,**b**, due to the two different chemical environments on the four phosphorus atoms, **2a** showed two doublet signals and **2b** displayed an AA′BB′ pattern—a pseudoquartet with central and satellite $^{31}P\{^1H\}$ signals. In the trimeric complexes **3a**,**b**, the $^{31}P\{^1H\}$ NMR spectra were basically a combination of the spectra of the respective monomeric and dimeric complexes (Figure 2). As a result, in the oligomeric species **4a**,**b**, only complicated multiplet $^{31}P\{^1H\}$ signals were observed but all the Pt−P coupling constants were in the range consistent with reported values.[12a,b,e,16]

Mass spectral data for complexes **1a**,**b**−**2a**,**b** showed intense molecular ion peaks at $m/z$ 844 $[M + H]^+$ for **1a**, $m/z$ 996 $[M]^+$ for **1b**, $m/z$ 1561 $[M]^+$ for **2a**, and $m/z$ 1791 $[M]^+$ for **2b**. The loss of ligand fragments also gave sensible fragmentation patterns. The soft ionization mode MALDI reduces the degree of fragmentation, enhancing the parent ion signals, as compared

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[19] (a) Janka, M.; Anderson, G. K.; Raith, N. P. *Organometallics* **2004**, *23*, 4382; (b) Bruce, M. I.; Costuas, K.; Halet, J.-F.; Hall, B. C.; Low, P. J.; Nicholson, B. K.; Skelton, B. W.; White, A. H. *Dalton Trans.* **2002**, 383. (c) Falvella, L. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Martin, A.; Moreno, M. T.; Sacristán, J. *Chem. Eur. J.* **1999**, *5*, 474.

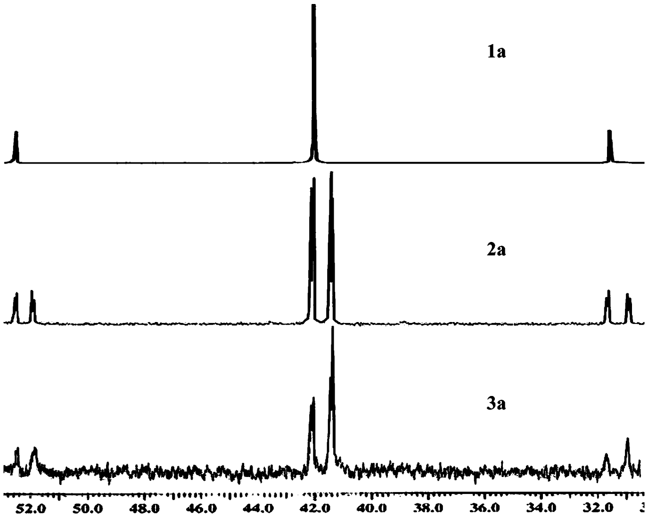

**Figure 2.** $^{31}P\{^1H\}$ NMR spectra for complexes **1a**−**3a**.

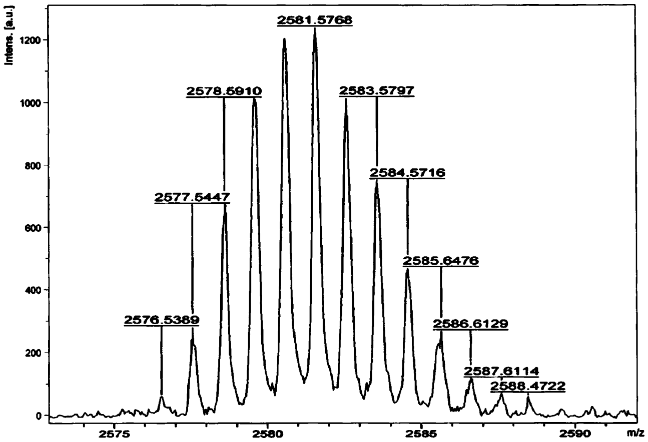

**Figure 3.** MALDI-HRMS and isotopic distribution of the triplatinum complex **3b**.

**Table 2. Structural Properties of the Oligomers**

| oligomer | $M_w$ | $M_n$ | $M_w/M_n$ |
|---|---|---|---|
| **4a** | 2520 | 2070 | 1.2 |
| **4b** | 3540 | 2560 | 1.4 |

**Table 3. Spectral Absorption Data for the Complexes 1a,b−3a,b and Oligomeric Species 4a,b Recorded in CH$_2$Cl$_2$ at Room Temperature**

| complex | $\lambda_{max}$ (nm)[a] | $E_g$ (eV) |
|---|---|---|
| **1a** | 289 (4.05), 298 (3.98), 303 (4.05), 326 (3.71) | 3.28 |
| **2a** | 290 (6.37), 300 (6.28), 326 (5.58), 359 (4.00) | 3.12 |
| **3a** | 292 (6.26), 305 sh (6.08), 327 (5.82), 359 (4.86) | 3.02 |
| **4a** | 218 (15.5), 290 (14.3), 331 (13.5), 359 (11.6) | 2.42 |
| **1b** | 262 sh (4.27), 325 (10.69) | 3.16 |
| **2b** | 262 sh (4.68), 334 (11.72) | 3.08 |
| **3b** | 262 sh (9.69), 344 (24.20) | 2.86 |
| **4b** | 342 (14.4) | 2.50 |

[a] Extinction coefficients are shown in parentheses (×10$^4$).

**Table 4. Photoluminescence (PL) Data for Complexes 1a,b−3a,b Recorded in CH$_2$Cl$_2$ at Room Temperature**

| complex | $\lambda_{em}$ (nm) | Stokes shift ($T_1 \rightarrow S_0$) (eV) | $\Delta E$[a] (eV) | intensity ratio ($T_1 \rightarrow S_0$, $S_1 \rightarrow S_0$)[b] |
|---|---|---|---|---|
| **1a** | 328, 344, 353, 482, 522 | 1.23 | 1.21 | 0.12 |
| **2a** | 355, 370, 382, 505, 535 | 1.00 | 1.04 | 0.68 |
| **3a** | 339, 353, 505, 535 | 1.00 | 1.20 | 0.82 |
| **1b** | 325, 340, 356, 532, 575 | 1.48 | 1.48 | 0.64[c] |
| **2b** | 325, 340, 355, 544, 585 | 1.32 | 1.53 | 2.03[c] |
| **3b** | 337, 353, 369 sh, 546, 584 | 1.35 | 1.41 | 8.16[c] |

[a] Energy difference between singlet emission (S$_1$) and triplet emission (T$_1$). [b] Ratio of the intensities of triplet emission to singlet emission at room temperature. [c] Scale: 1 × 10$^{-2}$.

with other conventional common ionization methods.[20] Therefore, it was selected as an ionization source in the MALDI-MS measurements of the trimeric species **3a**,**b**, showing parent peaks at *m/z* 2279.4 and 2581.6, respectively. In MALDI-HRMS, the spectra also exhibited intense parent ion signals for the cations at *m/z* 2279.4604 and 2581.5768 (Figure 3), respectively, which matched the calculated isotopic distribution patterns. The molecular weight data of the oligomeric species **4a**,**b** determined by GPC in DMF are tabulated in Table 2. The comparatively high retention volumes and low $M_w$ values indicated that the species only contained low-molecular-weight components and the degree of polymerization calculated from $M_n$ was 4 for both **4a** and **4b**, very low compared with other known *trans*-platinum polyynes.[9,11b,c,21] This result could be ascribed to the extremely low solubility of *cis*-platinum compounds and higher molecular weight, more truly polymerized species were too insoluble to analyze. The oligomers could not be purified via column chromatography, due to their adherence to the packing agents. The GPC system used for the work was calibrated with a mixture of narrow-distribution poly(methyl methacrylate) calibrants, and the results were expressed as PMMA equivalent molecular weights. Although there could be considerable differences between PMMA equivalents and actual molecular weights of the samples,[9] the presence of the end group $-C\equiv CH$ signals in NMR and IR data provided evidence that the degree of polymerization was not high in **4a**,**b**.

**Spectroscopic Data.** The electronic spectral data for all the complexes **1a**,**b**−**3a**,**b** and oligomeric species **4a**,**b** are summarized in Tables 3 and 4, primarily characterized by UV−vis and photoluminescent spectroscopy at room temperature in CH$_2$Cl$_2$. All of the compounds exhibited intense absorptions in the near-UV region (ca. 262−359 nm). In every case, the first absorption peak is due to the $\pi - \pi^*$ transition[22] in the organic system with some LMCT character resulting from the possible admixture of a metal d orbital and a ligand $\pi^*$ orbital, which may alter the overall energy of the optical transition.[23] We associate the lowest energy peak with the (0,0) vibronic peak of a $S_0 \rightarrow S_1$ transition from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO), which are mainly delocalized $\pi$ and $\pi^*$ orbitals. In the **a** series of complexes, as compared to the free ligand, a new lowest energy absorption peak with increasing extinction coefficient was observed on going from **1a** to **3a** (Figure 4), which indicated that $\pi$ conjugation is continued through the metals along the chain with an increase of repeating unit. Likewise, in the **b** series (Figure 5), the bathochromic shift in the first absorption transitions from **1b** to **3b** arose from an electron excitation which was also delocalized over more than

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(20) Karas, M.; Krüger, R. *Chem. Rev.* **2003**, *103*, 427.

(21) (a) Wong, W. Y.; Wong, C. K.; Poon, S. Y.; Lee, A. W. M.; Mo, T.; Wei, S. *Macromol. Rapid Commun.* **2005**, *26*, 376. (b) Wong, W. Y.; Wong, C. L.; Lu, G. L.; Lee, A. W. M.; Cheah, K. W.; Shi, J. X. *Macromolecules* **2003**, *36*, 983.

(22) (a) Chawdury, N.; Köhler, A.; Friend, R. H.; Younus, M.; Long, N. J.; Raithby, P. R.; Lewis, J. *Macromolecules* **1998**, *31*, 722. (b) Whittle, C. E.; Weinstein, J. A.; George, M. W.; Schanze, K. S. *Inorg. Chem.* **2001**, *40*, 4053.

(23) Wilson, J. S.; Köhler, A.; Friend, R. H.; Al-Suti, M. K.; Al-Mandhary, M. R. A.; Khan, M. S.; Raithby, P. R. *J. Chem. Phys.* **2000**, *113*, 7627.

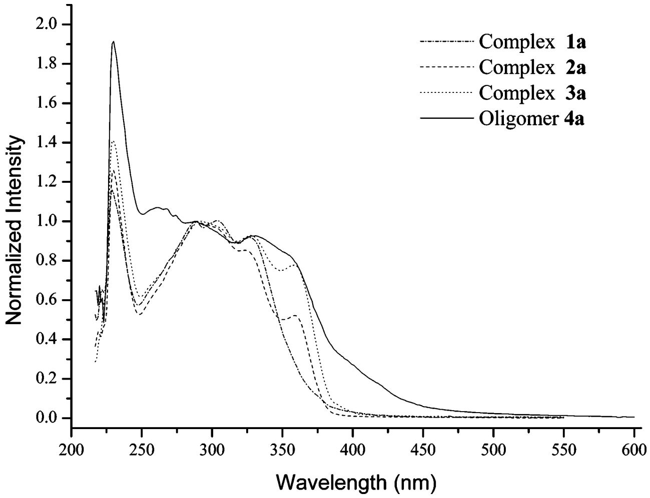

**Figure 4.** Comparison of normalized UV−vis absorption spectra of complexes **1a**−**3a** and oligomeric **4a**.

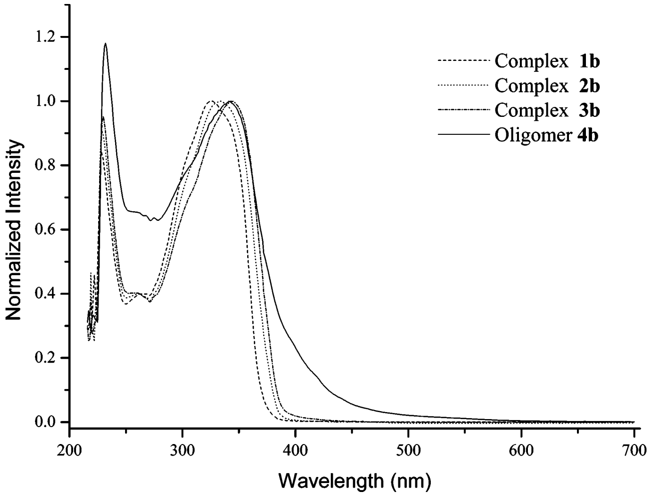

**Figure 5.** Comparison of normalized UV−vis absorption spectra of complexes **1b**−**3b** and oligomeric **4b**.

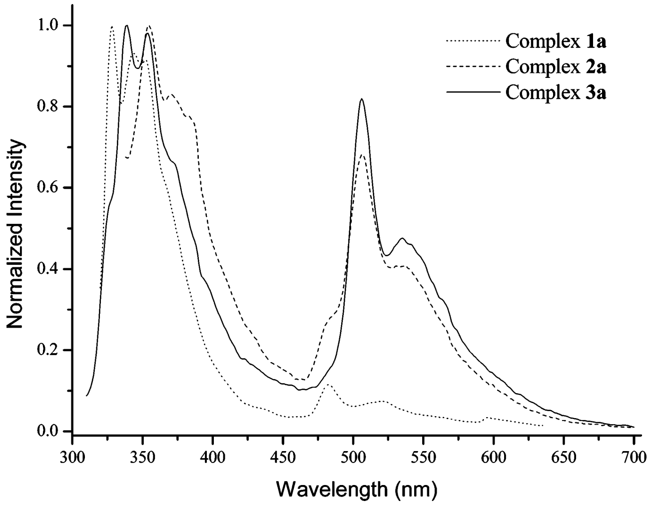

**Figure 6.** Comparison of normalized photoluminescent emission spectra of complexes **1a**−**3a**.

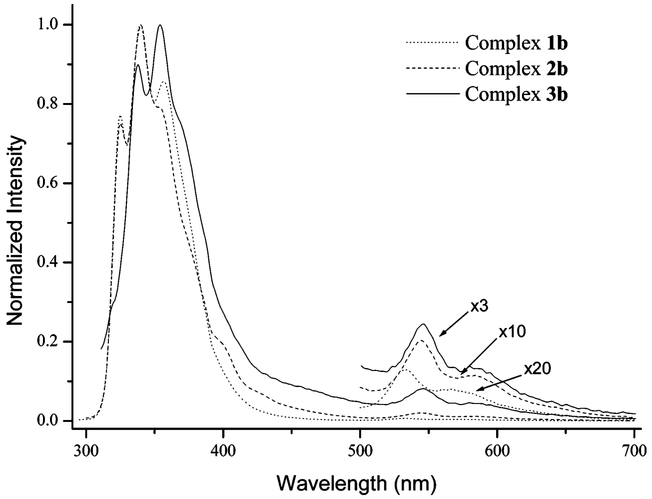

**Figure 7.** Comparison of normalized photoluminescent emission spectra of complexes **1b**−**3b**.

one repeating unit. It should be noted that the $\lambda_{max}$ values of the lowest energy absorptions in **4a**,**b** were not significantly different from those observed from complexes **3a**,**b**, respectively, which indirectly reflects the fact that **4a**,**b** are mainly a mixture of low-molecular-weight oligomeric species. The solution $\lambda_{max}$ values decreased in the order **4a** ≈ **3a** ≈ **2a** > **4b** ≈ **3b** > **2a** > **1a**,**b**. In comparison with the optical results of other relevant *trans*-platinum alkynes with (hetero)aromatic spacers,[21b] the lowest energy absorptions in these *cis*-platinum compounds were generally at higher energies. This confirms that the electronic delocalization in the cis configuration was less effective than that in trans configurations for these platinum systems. The optical band gap $E_g$(HOMO→LUMO), determined from the $\lambda_{0-0}$ band edge, also gradually decreased with increasing chain length in the order **1a** > **1b** > **2a** > **2b** > **3a** > **3b** > **4a** > **4b**. Generally, the values of $E_g$ in the **b** series were smaller than those in the **a** series, because more electronic and vibronic structures were present in the **b** series complexes, although the first absorption transition maxima were at lower energies in the **a** series complexes.

The room-temperature photoluminescence emission spectra of complexes **1a**,**b**−**3a**,**b** in $CH_2Cl_2$ are shown in Figures 6 and 7. All of them exhibited two emission bands in the near-UV region and from yellow-green to yellow-orange visible regions at room temperature. The high-energy emissions showed approximate mirror symmetries with the lowest energy excitations expected as in the Franck−Condon model.[24] The intense high-energy photoluminescence peaks near 330 nm (ca. 3.75 eV) were the fluorescence from the same singlet excited state ($S_1 \rightarrow S_0$) with small Stokes shifts between the excitation and emission spectra.[11] In comparison with the free ligand emissions, HC≡C-*p*-$C_6H_4$C≡CH (328 nm) and HC≡C-*p*-$C_6H_4$-*p*-$C_6H_4$-C≡CH (340 nm), there was no significant difference in the high-energy emissions between the free ligands and complexes **1a**,**b**−**3a**,**b**, indicating that the singlet state emissions were ligand-based emissions without the influence of the intrusion of platinum metals in the complexes.

The lower energy bands with substantial Stokes shifts measured ca. >1.00 eV were the phosphorescence $T_1 \rightarrow S_0$ emissions, which were greatly enhanced by the inclusion of platinum metals. The triplet state emissions have been previously assigned in other related polyynes and diynes on the basis of optical measurements.[11,21,25] It was shown that, for the Pt polyynes with different spacers R, the 0−0 vibrational peak of phosphorescence always occurs 0.7 eV below the 0−0 vibra-

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(24) Parker, C. A. *Photoluminescence in Solutions*, Elsevier: Amsterdam, 1968.

(25) Wilson, J. S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Younus, M.; Khan, M. S.; Raithby, P. R.; Köhler, A.; Friend, R. H. *J. Am. Chem. Soc.* **2001**, *123*, 9412.

tional peak of fluorescence.[11,20,25,26] In our cases, the lower energy ($T_1$) bands were ca. 1.00−1.40 eV below the fluorescence ($S_1$). Generally, the $S_1-T_1$ energy gaps were almost the same for the monomers and dimers as well as the trimers in the two series of complexes. All values were greater than those observed from the other analogous monomeric, dimeric, and trimeric platinum alkynyl trans complexes with different spacers R.[11,21b] This result can be attributed to the less effective $\pi$ conjugation along the chain in the cis configurations, as compared to that in the trans orientations. Thus, each chromophore is localized in the backbone, thus reducing the efficiency of the $S_1-T_1$ intersystem crossing. However, from **1a** to **3a** and from **1b** to **3b**, the peak-height ratio of triplet to singlet emission increased from 0.12 to 0.82 and from $6.4 \times 10^{-3}$ and $8.16 \times 10^{-2}$, respectively. This indicates that although the $S_1-T_1$ intersystem-crossing efficiency was reduced in the cis-configured systems, the possibilities of nonradiative decays, e.g. vibration and electron delocalization, were also decreased in the excited-localized chromophores, which enhanced in a stepwise fashion the intensities of triplet-state emissions with an increase in the number of repeating units.

In addition, all complexes also showed a red shift in the triplet state emissions from 482 nm (2.57 eV) to 505 nm (2.46 eV) in **1a**−**3a** and from 532 nm (2.33 eV) to 546 (2.27 eV) in **1b**−**3b**, respectively, due to an increasing number of repeating units. In **1b**−**3b**, the $\lambda_{max}$ values of $T_1$ emissions were of lower energy than those in **1a**−**3a** due to the higher electron density present in the -*p*-$C_6H_4$-*p*-$C_6H_4$ moieties. This feature not only bathochromatically shifted the emission maxima but also reduced the $S_1-T_1$ intensity ratio in **1b**−**3b**, because of the enhanced nonradiative decay caused by the more vibrational structures present in the -*p*-$C_6H_4$-*p*-$C_6H_4$ series of complexes.

As a result, we conclude that the intensity and the energy of triplet state emissions of platinum alkynyl complexes can be fine-tuned by different aromatic spacers R, the number of repeating units, and the cis and trans configurations of platinum metal centers.

## Experimental Section

**General Comments.** All reactions were carried out under a nitrogen atmosphere using standard Schlenk and vacuum line techniques. Dichloromethane and diisopropylamine were purified by standard methods. Separation and purification of complexes were achieved by column chromatography, packed by 5% deactivated Fischer Scientific aluminum oxide neutral particle size 100−250 mesh. All column chromatography separations were carried out in air using laboratory-grade solvents as eluents. Infrared spectra were measured on a Perkin-Elmer FTIR1720 spectrometer, using $CaF_2$ cells with a 0.5 mm path length for solution-state spectroscopy. $^1H$ and $^{31}P\{^1H\}$ NMR spectra were recorded on a JEOL GS 270 MHz NMR spectrometer, using deuterated solvents. Chemical shifts were reported in $\delta$ units (parts per million) downfield from tetramethylsilane and 85% $H_3PO_4$ with the solvents as the reference signal in $^1H$ and $^{31}P\{^1H\}$ NMR spectra, respectively. FAB mass spectra were recorded on a VG AutoSpec-Q mass spectrometer, operating in the positive ion mode, and MALDI mass spectra were obtained by the EPSRC National Mass Spectrometry Service Centre in the Chemistry Department of the University of Wales Swansea. The high-resolution MALDI mass spectra were obtained by the chemistry department of the Hong Kong Baptist University. The GPC molecular weight measurements were carried out by the RAPRA Technology Co. The UV-absorption spectra and the luminescence spectra were measured on a Nicolet Evolution 100 spectrometer and Varian Cary Eclipse fluorescence spectrometer in $CH_2Cl_2$ solution (concentration, $1 \times 10^{-6}$ M), respectively. Elemental analyses were performed by the Health and Human Science department of London Metropolitan University. *cis*-[Pt(dppe)$Cl_2$],[27] *cis*-[Pt(dppe)(OTf)$_2$],[28] 1,4-diethynylbenzene,[29] and 4,4′-diethynylbiphenyl[30] were prepared according to the literature methods, and during the course of our research and the preparation of this paper, compounds **1a**,**b** were independently reported.[16]

**(A) Preparation of Monoplatinum Complex 1a.** To a stirred mixture of excess 1,4-diethynylbenzene (135.1 mg, 1.07 mmol) and *cis*-[Pt(dppe)$Cl_2$] (115 mg, 0.15 mmol) in $^iPr_2NH$ (20 mL) and $CH_2Cl_2$ (40 mL) was added CuI (3.8 mg). The solution was stirred at room temperature over a period of 15 h, after which all volatile components were removed under vacuum. The crude product was taken up in $CH_2Cl_2$ and purified on alumina column chromatography with *n*-hexane/$CH_2Cl_2$ (1/3, v/v) as eluent. From the second colorless band ($R_f$ = 0.86), **1a** was obtained as a white solid (121.3 mg, 83%). Anal. Calcd for $C_{46}H_{34}P_2Pt$: C, 65.48; H, 4.06. Found: C, 65.29; H, 3.94. FT-IR ($CH_2Cl_2$): $\nu$(C≡C)/cm$^{-1}$ 2101, $\nu$(C≡CH)/cm$^{-1}$ 3300. $^1H$ NMR ($CDCl_3$): $\delta$ 2.39 (t, 2H, $P(CH_2)_2P$, $J_{PH}$ = 10.8 Hz), 2.46 (t, 2H, $P(CH_2)_2P$, $J_{PH}$ = 10.6 Hz), 3.03 (s, 2H, ≡CH), 7.03 (d, 4H, $C_6H_4$, $J_{HH}$ = 8.2 Hz), 7.20 (d, 4H, $C_6H_4$, $J_{HH}$ = 8.4 Hz), 7.28−7.42 (m, 12H, $C_6H_5$ in dppe), 7.84−8.02 (m, 8H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 42.02 (s, $J_{Pt-P}$ = 2282 Hz). FAB MS: *m/z* $M^+$, 844.

**(B) Preparation of Monoplatinum Complex 1b.** A mixture of *cis*-[Pt(dppe)$Cl_2$] (98.5 mg, 0.15 mmol) and excess 4,4′-diethynylbiphenyl (300 mg, 1.5 mmol) in $^iPr_2NH$ (20 mL) and $CH_2Cl_2$ (40 mL) with a catalytic amount of CuI (1.1 mg) was stirred for 17 h at room temperature. The crude product was dried in vacuo and was taken up in $CH_2Cl_2$ to undergo alumina column chromatography purification with *n*-hexane/$CH_2Cl_2$ (1/1, v/v) as eluent. **1b** (85.1 mg, 58%) was collected as a very pale yellow solid from the second band ($R_f$ = 0.55). Anal. Calcd for $C_{58}H_{42}P_2Pt$: C, 69.94; H, 4.25. Found: C, 69.99; H, 4.14. FT-IR ($CH_2Cl_2$): $\nu$(C≡C)/cm$^{-1}$ 2101, $\nu$(C≡CH)/cm$^{-1}$ 3301. $^1H$ NMR ($CDCl_3$): $\delta$ 2.39 (t, 2H, $P(CH_2)_2P$, $J_{PH}$ = 10.4 Hz), 2.46 (t, 2H, $P(CH_2)_2P$, $J_{PH}$ = 10.4 Hz), 3.09 (s, 2H, ≡CH), 7.21 (d, 4H, biphenyl, $J_{HH}$ = 8.4 Hz), 7.34 (d, 4H, biphenyl, $J_{HH}$ = 8.4 Hz), 7.30−7.45 (m, 12H, $C_6H_5$ in dppe), 7.49 (s, 8H, biphenyl), 7.87−8.08 (m, 8H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 41.90 (s, $J_{Pt-P}$ = 2280 Hz). FAB MS: *m/z* $M^+$, 996.

**(C) Preparation of Diplatinum Complex 2a. (i) From the Synthesis of Complex 1a.** After the purification of the second band, **1a**, via alumina column chromatography, *n*-hexane/$CH_2Cl_2$ (1/3, v/v) was used as eluent to continue the purification. From the third band ($R_f$ = 0.44), **2a** was isolated as a colorless solid (20.8 mg, 15%).

**(ii) From the Synthesis of Complex 3a.** To a stirred 4/1 molar ratio mixture of **1a** (103.8 mg, 0.12 mmol) and *cis*-[Pt(dppe)$Cl_2$] (20.4 mg, 0.3 mmol) in $^iPr_2NH$ (3.5 mL) and $CH_2Cl_2$ (50 mL) was added CuI (1.2 mg). The solution was stirred at room temperature over a period of 18 h, after which all volatile components were removed under vacuum. The crude product was taken up in $CH_2Cl_2$ and purified by alumina column chromatography with *n*-hexane/$CH_2Cl_2$ (1/3, v/v) as eluent. From the second colorless band ($R_f$ = 0.44), the diplatinum complex **2a** was obtained as a white solid (17.2 mg, 36%).

Anal. Calcd for $C_{82}H_{62}P_4Pt_2$: C, 63.08; H, 4.00. Found: C, 63.08; H, 4.05. FT-IR ($CH_2Cl_2$): $\nu$(C≡C)/cm$^{-1}$ 2104, 2116, $\nu$(C≡CH)/cm$^{-1}$ 3296. $^1H$ NMR ($CDCl_3$): $\delta$ 2.38 (t, 4H, $P(CH_2)_2P$, $J_{PH}$ = 10.6 Hz), 2.45 (t, 4H, $P(CH_2)_2P$, $J_{PH}$ = 10.8 Hz), 3.02 (s, 2H, ≡

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(26) Manna, J.; John, K. D.; Hopkins, M. D. *Adv. Organomet. Chem.* **1995**, *38*, 79.

(27) (a) McDermott, J. X.; White, J. F.; Whitesides, G. M. *J. Am. Chem. Soc.* **1976**, *98*, 6521. (b) Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 1449.

(28) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273.

(29) Grouhi, H.; Nast, R. *J. Organomet. Chem.* **1979**, *182*, 197.

(30) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara *Synthesis* **1980**, 627.

CH), 6.87 (s, 4H, $C_6H_4$), 7.04 (d, 4H, $C_6H_4$, $J_{HH} = 8.4$ Hz), 7.20 (d, 4H, $C_6H_4$, $J_{HH} = 8.1$ Hz), 7.27−7.51 (m, 24H, $C_6H_5$ in dppe), 7.82−7.98 (m, 16H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 41.33 (d, $J_{P-P} = 6.7$ Hz, $J_{Pt-P} = 2284$ Hz), 41.00 (d, $J_{P-P} = 6.7$ Hz, $J_{Pt-P} = 2270$ Hz). FAB MS: *m*/*z* $M^+$, 1561.

**(D) Preparation of Diplatinum Complex 2b. (i) From the Synthesis of Complex 1b.** Similarly to the synthesis of **2a**, diplatinum complex **2b** was also obtained from the alumina column chromatography purification of the monoplatinum complex **1b**, using *n*-hexane/$CH_2Cl_2$ (1/3, v/v) as eluent. From the third colorless band ($R_f = 0.54$), the colorless solid diplatinum complex **2b** (12.3 mg, 9%) was collected.

**(ii) From the Synthesis of Complex 3b.** A mixture of *cis*-[Pt(dppe)$Cl_2$] (9.6 mg, 0.01 mmol) and monoplatinum complex **1b** (43.1 mg, 0.04 mmol) in the molar ratio 1/4 was stirred in $^iPr_2NH$ (3.5 mL) and $CH_2Cl_2$ (50 mL) with a catalytic amount of CuI (1.1 mg) for 17 h at room temperature. The crude yellow product was dried in vacuo and then taken up in $CH_2Cl_2$ to be purified via alumina column chromatography, using *n*-hexane/$CH_2Cl_2$ (1/3, v/v) as eluent. The second colorless band ($R_f = 0.54$) was collected as the very pale yellow solid **2b** (10.7 mg, 41%).

Anal. Calcd for $C_{100}H_{74}P_4Pt_2$: C, 67.11; H, 4.14. Found: C, 66.98; H, 4.28. FT-IR ($CH_2Cl_2$): $\nu(C{\equiv}C)/cm^{-1}$ 2113, $\nu(C{\equiv}CH)/cm^{-1}$ 3299. $^1H$ NMR ($CDCl_3$): $\delta$ 2.38 (t, 8H, $P(CH_2)_2P$, $J_{PH} = 10.8$ Hz), 2.46 (t, 8H, $P(CH_2)_2P$, $J_{PH} = 10.2$ Hz), 3.09 (s, 2H, $\equiv$CH), 7.09 (d, 4H, biphenyl, $J_{HH} = 8.2$ Hz), 7.15 (d, 4H, biphenyl, $J_{HH} = 8.2$ Hz), 7.28 (d, 4H, biphenyl, $J_{HH} = 8.4$ Hz), 7.34 (d, 4H, biphenyl, $J_{HH} = 8.4$ Hz), 7.37−7.46 (m, 24H, $C_6H_5$ in dppe), 7.47 (s, 8H, biphenyl), 7.88−7.98 (m, 16H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 41.76 (d, $J_{P-P} = 8.1$ Hz, $J_{Pt-P} = 2268$ Hz), 41.84 (d, $J_{P-P} = 8.0$ Hz, $J_{Pt-P} = 2267$ Hz). FAB MS: *m*/*z* $M^+$, 1791.

**(E) Preparation of Triplatinum Complex 3a.** The synthetic procedure was the same as for the synthesis of diplatinum complex **2a**. After the separation of **2a** by alumina column chromatography, an *n*-hexane/$CH_2Cl_2$ (1/10, v/v) solvent mixture was used as eluent to continue the column chromatography purification. The third isolated band ($R_f = 0.89$) was a white solid and was characterized as the triplatinum complex **3a** (18.9 mg, 27%). MALDI MS: *m*/*z* $M^+$, 2279.4. HRMS in MALDI mode: calcd for $C_{118}H_{90}P_6Pt_3$, 2279.4509; found, 2279.4604 [M + $H^+$]. FT-IR ($CH_2Cl_2$): $\nu(C{\equiv}C)/cm^{-1}$ 2104, 2115, $\nu(C{\equiv}CH)/cm^{-1}$ 3296. $^1H$ NMR ($CDCl_3$): $\delta$ 2.22−2.54 (m, 12H, $P(CH_2)_2P$), 3.02 (s, 2H, $\equiv$CH), 6.85 (s, 8H, $C_6H_4$), 7.05 (d, 4H, $C_6H_4$, $J_{HH} = 8.2$ Hz), 7.20 (d, 4H, $C_6H_4$, $J_{HH} = 8.4$ Hz), 7.32−7.58 (m, 36H, $C_6H_5$ in dppe), 7.88−8.07 (m, 24H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 41.27 (s, $J_{Pt-P} = 2272$ Hz), 41.31 (d, $J_{P-P} = 8.0$ Hz, $J_{Pt-P} = 2280$ Hz), 41.98 (d, $J_{P-P} = 8.0$ Hz, $J_{Pt-P} = 2270$ Hz).

**(F) Preparation of Triplatinum Complex 3b.** Similar procedures were also applied for the purification of complex **3b**. After the separation of **2b** via alumina column chromatography, a $CH_2Cl_2$/acetone (40/1, v/v) solvent mixture was used as eluent to continue the column chromatography purification. The third isolated band ($R_f = 0.60$) was a white solid and was characterized as the triplatinum complex **3b** (8.8 mg, 23%). MALDI MS: *m*/*z* $M^+$, 2581.6. HRMS in MALDI mode: calcd for $C_{142}H_{106}P_6Pt_3$, 2581.5608; found, 2581.5768. FT-IR ($CH_2Cl_2$): $\nu(C{\equiv}C)/cm^{-1}$ 2113, $\nu(C{\equiv}CH)/cm^{-1}$ 3299. $^1H$ NMR ($CD_2Cl_2$): $\delta$ 2.42 (t, 6H, $P(CH_2)_2P$, $J_{PH} = 10.4$ Hz), 2.49 (t, 6H, $P(CH_2)_2P$, $J_{PH} = 10.1$ Hz), 3.16 (s, 2H, $\equiv$CH), 7.07−7.22 (m, 12H, biphenyl), 7.07−7.29 (m, 12H, biphenyl), 7.29−7.50 (m, 36H, $C_6H_5$ in dppe), 7.51 (s, 8H, biphenyl), 7.85−8.04 (m, 24H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CD_2Cl_3$): $\delta$ 42.06 (s, $J_{Pt-P} = 2272$ Hz), 42.08 (d, $J_{P-P} = 5.4$ Hz, $J_{Pt-P} = 2271$ Hz), 42.19 (d, $J_{P-P} = 5.1$ Hz, $J_{Pt-P} = 2270$ Hz).

**(G) Preparation of Polymeric Species 4a. (i) CuI-Catalyzed Reaction.** Polymerization was carried out by mixing 1,4-diethynylbenzene (19.4 mg, 0.15 mmol), *cis*-[Pt(dppe)$Cl_2$] (102.1 mg, 0.15 mmol), and CuI (1.3 mg) in $^iPr_2NH/CH_2Cl_2$ (63 mL, 1/20, v/v). After stirring at room temperature for 18 h, only an insoluble yellow precipitate was isolated.

**(ii) AgOTf-Catalyzed Reaction.** A solution of anhydrous sodium acetate (8.7 mg, 0.11 mmol) in MeOH (10 mL) was added to **1a** (22.3 mg, 0.03 mmol) in $CH_2Cl_2$ (40 mL). *cis*-[Pt(dppe)$(OTf)_2$] (23.6 mg, 0.03 mmol) in $CH_2Cl_2$ (20 mL) was added to this mixture via a pressure-equalizing dropping funnel over a period of 2 h, during which time the initial pale yellow solution turned to brown. Removal of solvent after 4 h of reaction, extraction with $CH_2Cl_2$, and filtration into *n*-hexane gave the brown precipitate **4a** (32.4 mg, 42%, 4 repeating units). Anal. Calcd for $(C_{36}H_{28}P_2Pt)_n$: C, 60.25; H, 3.93. Found: C, 60.09; H, 3.95. FT-IR ($CH_2Cl_2$): $\nu(C{\equiv}C)/cm^{-1}$ 2115, $\nu(C{\equiv}CH)/cm^{-1}$ 3298. $^1H$ NMR ($CDCl_3$): $\delta$ 2.24−2.64 (m, 4H, $P(CH_2)_2P$), 3.03 (s, 0.12H, $\equiv$CH), 6.68−6.86 (m, 2H, *p*-$C_6H_4$), 6.92−7.64 (m, 14H, *p*-$C_6H_4$ and $C_6H_5$ in dppe), 7.80−8.18 (m, 8H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 40.62−42.55 (m, $J_{Pt-P} = 2316$ Hz).

**(H) Preparation of Polymeric Species 4b. (i) CuI-Catalyzed Reaction.** CuI (1.0 mg) was added to a mixture of 4,4′-diethynylbiphenyl (18.9 mg, 0.09 mmol) and *cis*-[Pt(dppe)$Cl_2$] (62.3 mg, 0.09 mmol) in $^iPr_2NH/CH_2Cl_2$ (63 mL, 1/20, v/v). The yellow solution was stirred at room temperature over a period of 18 h, after which time the solvents were evaporated off. The residue was redissolved in $CH_2Cl_2$ and filtered through a short layer of deactivated alumina to remove impurities and any insoluble precipitate. After removal of the solvent, a yellow solid was obtained, which was then washed with *n*-hexane to leave polymer **4b** in 44% yield (43.0 mg, 5 repeating units). Anal. Calcd for $(C_{42}H_{32}P_2Pt)_n$: C, 63.55; H, 4.06. Found: C, 63.66; H, 3.95. FT-IR ($CH_2Cl_2$): $\nu(C{\equiv}C)/cm^{-1}$ 2114. $^1H$ NMR ($CDCl_3$): $\delta$ 2.26−2.59 (m, 4H, $P(CH_2)_2P$), 7.00−7.72 (m, 20H, *p*-$C_6H_4$-*p*-$C_6H_4$ and $C_6H_5$ in dppe), 7.75−8.09 (m, 8H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 41.14−42.30 (m, $J_{Pt-P} = 2283$ Hz).

**(ii) AgOTf-Catalyzed Reaction.** To a solution containing anhydrous sodium acetate (10.1 mg, 0.12 mmol) and complex **1b** (30.7 mg, 0.03 mmol) in MeOH (10 mL) and $CH_2Cl_2$ (40 mL) was added *cis*-[Pt(dppe)$(OTf)_2$] (27.5 mg, 0.03 mmol) in $CH_2Cl_2$ (20 mL) dropwise over a period of 2 h at room temperature with the exclusion of light. After 4 h of reaction, the solvent was removed in vacuo and the crude solid extracted with $CH_2Cl_2$. The extract was then evaporated to dryness and washed with *n*-hexane to give the brown precipitate **4b** (48 mg, 44%, 4 repeating units). Anal. Calcd for $(C_{42}H_{32}P_2Pt)_n$: C, 63.55; H, 4.06. Found: C, 62.66; H, 3.92. FT-IR ($CH_2Cl_2$): $\nu(C{\equiv}C)/cm^{-1}$ 2113, $\nu(C{\equiv}CH)/cm^{-1}$ 3299. $^1H$ NMR ($CDCl_3$): $\delta$ 2.20−2.67 (m, 4H, $P(CH_2)_2P$), 3.08 (s, 0.45H, $\equiv$CH), 6.44−7.72 (m, 20H, *p*-$C_6H_4$-*p*-$C_6H_4$ and $C_6H_5$ in dppe), 7.78−8.19 (m, 8H, $C_6H_5$ in dppe). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta$ 40.80−42.27 (m, $J_{Pt-P} = 2279$ Hz).

**Crystal data for 2a**: $C_{82}H_{62}P_4Pt_2{\cdot}C_6H_{14}$, $M_r = 1647.55$, triclinic, $P\bar{1}$ (No. 2), $a = 13.0775(4)$ Å, $b = 13.4008(5)$ Å, $c = 22.5520(7)$ Å, $\alpha = 75.072(3)°$, $\beta = 79.571(3)°$, $\gamma = 88.599(3)°$, $V = 3754.7(2)$ Å$^3$, $Z = 2$ (two independent $C_i$-symmetric molecules), $D_c = 1.457$ g cm$^{-3}$, $\mu$(Mo K$\alpha$) = 3.851 mm$^{-1}$, $T = 173$ K, pale yellow plates, Oxford Diffraction Xcalibur 3 diffractometer; 24 804 independent measured reflections, $F^2$ refinement, R1 = 0.084, wR2 = 0.182, 20 867 independent observed absorption-corrected reflections ($|F_o| > 4\sigma(|F_o|)$, $2\theta_{max} = 65°$), 874 parameters. CCDC 290794.

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**Supporting Information Available:** Text, tables, and figures giving additional details of the crystal structure determination for **2a**; crystal data are also given as a CIF file. This material is available free of charge via the Internet at http://pubs.acs.org.

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