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Synthesis and Characterization of Electron Donor–Acceptor Platinum(II) Complexes Composed of *N*,*N*-Diphenylpyridineamine and Triphenylamine Ligands

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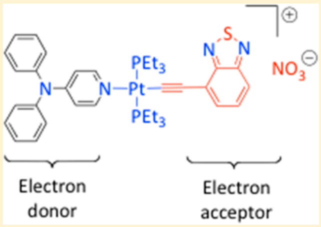
Supporting Information



ABSTRACT: The synthesis and electronic properties of a series of platinum(II) complexes composed of electron-donor and electron-acceptor components as potential photovoltaic materials is reported. The complexes are composed of triphenylamines (TPA) and pyridine-derivatized TPAs as the electron-donating components, and alkynyl derivatives of 2,1,3-benzothiadiazole and cyclopentadithiophenone as the electron acceptors. The complexes containing the pyridine-derivatized ligands were prepared to examine the effect that direct coordination of a heteroatom-modified TPA may have on the electronic properties of donor–acceptor (D–A) complexes. Four complexes composed of *meta*- and *para*- pyridine-derivatized TPAs were prepared, and their electronic properties were compared with three structurally similar complexes composed of TPA, as well as with purely organic D–A compounds. Data collected from UV–vis and cyclic voltammetry show minor differences on the properties of the complexes containing the pyridine-derivatized ligands when compared to the TPA analogs, exhibiting similar highest occupied molecular orbital–lowest unoccupied molecular orbital bandgaps ranging from 2.156 to 2.705 eV for the pyridine-derivatized complexes (**6a**,**b** and **7a**,**b**), 2.038–2.320 eV for the TPA complexes (**8a**,**b** and **9a**), 2.301 eV for organic molecule **10a**, and 1.997 eV for **10b**. All compounds are stable, exhibiting no decomposition in the solid indefinitely, and only minor decomposition in solution. All compounds were characterized by ^{1}H and ^{13}C nuclear magnetic resonance, infrared spectroscopy, and electrospray mass spectrometry. All complexes were also characterized by ^{31}P nuclear magnetic resonance and elemental analysis of CHN; determination of Ag content for **6a**,**b** and **7a**,**b** (carried through the synthetic steps) was determined by inductively coupled plasma optical emission spectrometry. The *para*-pyridine-derivatized complex of 2,1,3-benzothiadiazole (**6a**) was further characterized by X-ray crystallography as a AgNO$_3$ clathrate. X-ray quality crystals were grown from a solution of hexanes/CH$_2$Cl$_2$ and from diffusion of hexanes into a CH$_2$Cl$_2$ solution of the complex, providing a solvent-free crystal and a solvate of CH$_2$Cl$_2$, respectively.

■ INTRODUCTION

Platinum(II) complexes have been investigated for a variety of applications, including the study of solid-state molecular dynamics,[1] photo- and electroluminescence,[2] and charge-transfer (CT) polymers,[3] particularly dialkynyl complexes of Pt(II), the photoactive properties of which can be tuned by structural modifications of the ligands.[4] Triphenylamine (TPA) derivatives such as **1**–**3**, Figure 1, have also been studied in the area of photovoltaic materials and have demonstrated efficient electron-transfer properties within polymers, dendrimers, and metallic assemblies such as **4** and **5**.[3−6] Although TPA analogs have been extensively studied as potential components in electron-transfer materials,[7] pyridine derivatives of TPA, capable of functioning as coordination ligands, as well as electron-transfer components, are unknown. The ability to control the relative orientation of the electron donor and acceptor through self-assembly into well-defined structures is expected to lead to improved electron-transfer efficiencies.[8] For this work, platinum acetylide complexes were chosen as initial models due to their stability, as well as for additional photophysical properties, such as phosphorescent excited states, and efficient electron transfer, which provide them with potential applications in diverse areas as multifunctional materials.[2] The model compounds reported in this work will serve as small molecule references for extended, polypyridyl metallic structures.

In this Article we report the synthesis and characterization of cationic complexes **6a**,**b** and **7a**,**b** composed of *meta*- and *para*-pyridine-derivatized TPAs, Figure 2, neutral alkynyl-TPA complexes **8a**,**b**, and TPA complex **9a** (complex **9b** could not be synthesized following known conditions), as well as purely organic compounds **10a**,**b**, and report the photophysical properties as determined by UV–vis and emission experiments, as well as by cyclic voltammetry, from which their electronic highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) bandgaps were determined. The measured bandgaps range from 2.156 to 2.705 eV for pyridine-derivatized TPA complexes **6a**,**b** and **7a**,**b** and from 2.038 to 2.320 eV for TPA complexes **8a**,**b** and **9a**. The measured bandgap for organic compound **10a** is 2.301; it is 1.997 eV for **10b**. All of these compounds were prepared to

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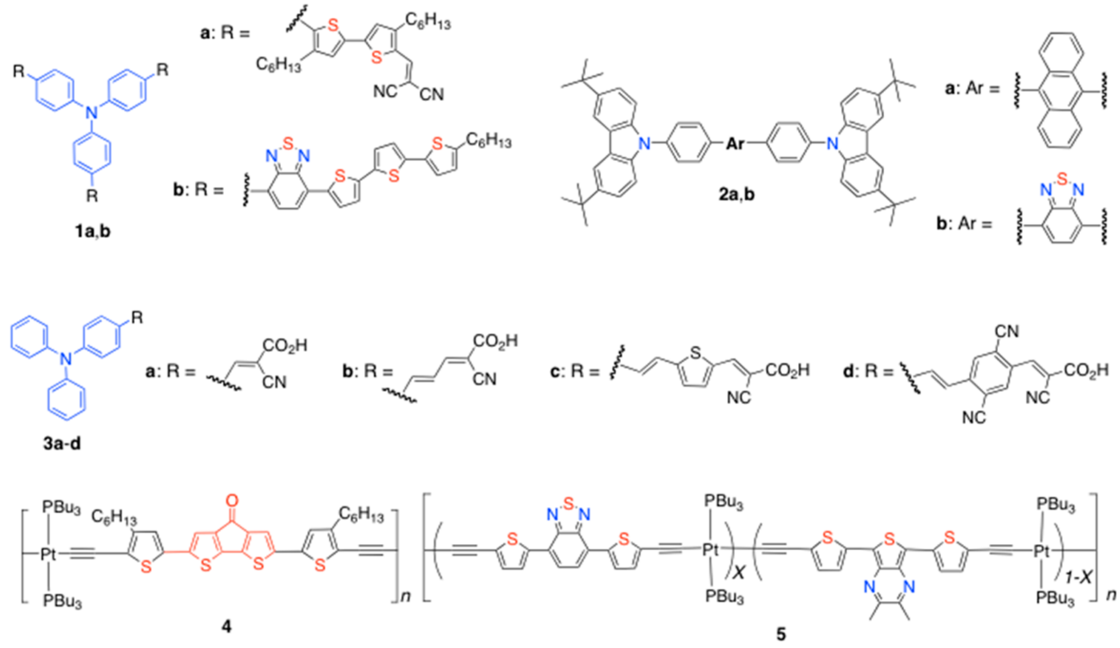


Figure 1. Triphenylamine polymers, dendrimers, and dialkynyl platinum(II) polymers.[2−6]

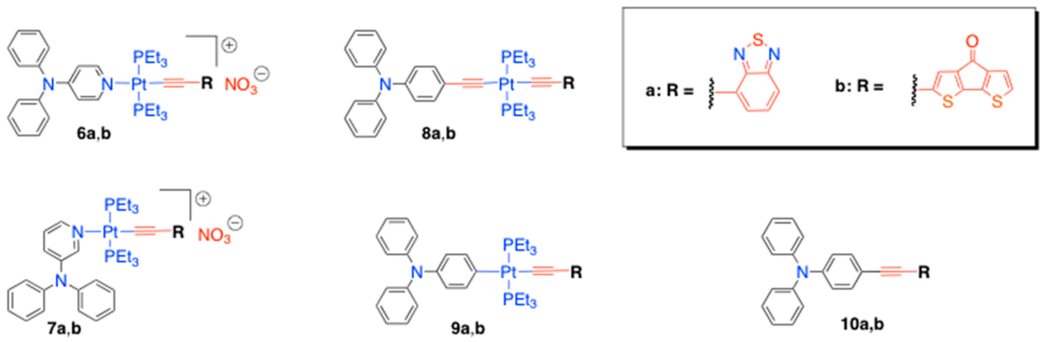


Figure 2. Pyridine-derivatized TPA complexes, neutral TPA complexes, and organic analogues.

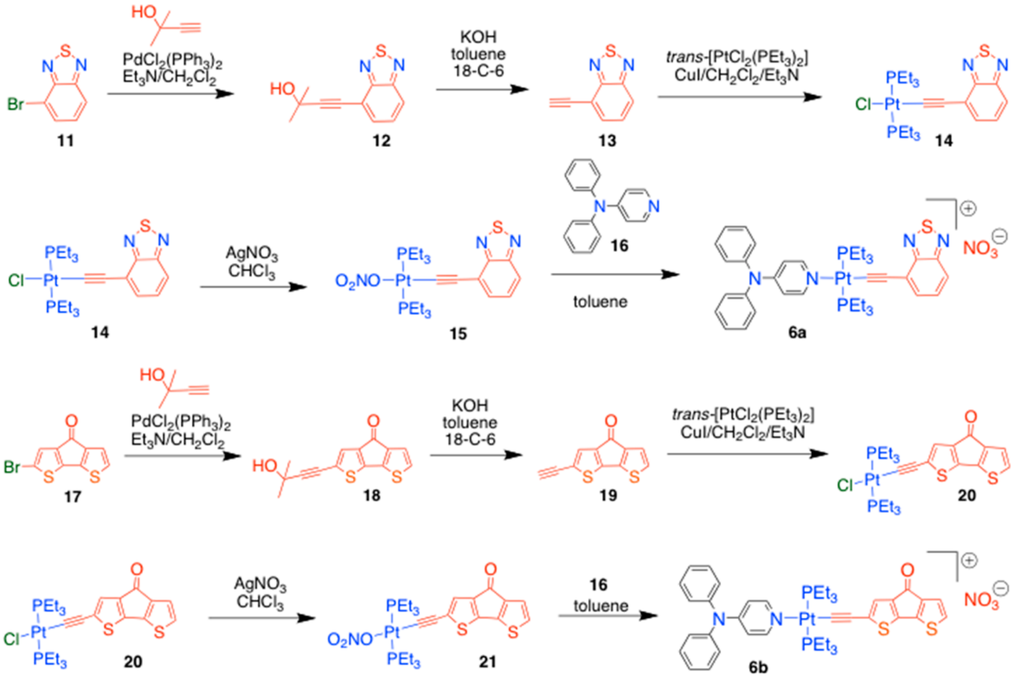
investigate the potential effect that the pyridine-derivatized TPA ligands in complexes **6** and **7** may have on the photophysical properties. Determination of equal, or improved, photophysical properties of pyridine-derivatized TPAs, when compared to the more typically used TPA donors, may lead to extended structures with enhanced electron-donating and -accepting capabilities. We anticipate that electron-donating pyridine derivatives, such as those presented in this work, will serve as useful building blocks for the formation of well-defined metallic assemblies in which the relative position of electron donors and acceptors can be controlled through the formation of extended structures. All complexes were characterized by ^{1}H, ^{13}C, and ^{31}P nuclear magnetic resonance, infrared spectroscopy, electrospray mass spectrometry, and elemental analysis of CHN. Determination of Ag content for **6a,b** and **7a,b** (carried through the synthetic steps) was determined by inductively coupled plama optical emission spectrometry (ICP-OES). Two crystal structures of complex **6a** were characterized by X-ray crystallography, as described in the Results and Discussion section as well as in the Supporting Information; one as a solvent-free structure formed from a solution of hexanes and CH_2Cl_2 and the other as a CH_2Cl_2 solvate from diffusion of hexanes into a CH_2Cl_2 solution of the complex.

■ RESULTS AND DISCUSSION

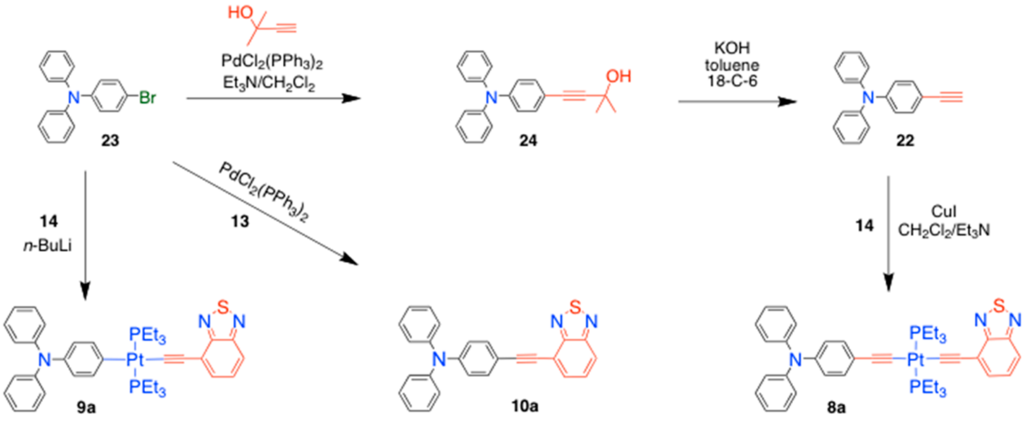
Synthesis of 2,1,3-Benzothiadiazole Derivatives. 2,1,3-Benzothiadiazole derivatives of compounds **6a**−**10a** were prepared by initial bromination of commercially available 2,1,3-benzothiadiazole to provide monobromo product **11**, Scheme 1, under reported conditions using hydrobromic acid and Br_2, followed by a Pd-catalyzed Sonogashira coupling reaction of **11** with commercially available 2-methyl-3-butyn-2-ol to give compound **12** in 65% yield.[4,9] Deprotection of **12** under basic conditions gave alkynyl **13**,[9e,10] which was coupled with *trans*-[$PtCl_2(PEt_3)_2$] under copper-catalyzed conditions, as reported for improved coupling reactions of terminal acetylenes with platinum chloride,[8a] to give chloro complex **14** in 35% yield, which was then converted to nitrato complex **15** by reaction with silver nitrate.[8b−e] Substitution reaction of nitrato **15** with the corresponding *meta*- or *para*-pyridine-derivatized TPA gave the target complexes in 90% yields,[8] as depicted in Scheme 1 for *para*-ligand **16**. The *meta*- and *para*-pyridine-derivatized TPA ligands were synthesized as reported in the literature.[11]

Synthesis of Cyclopentadithiophenone Derivatives. Cyclopentadithiophenone derivatives for complexes **6b**−**8b** and **10b** were prepared following reported conditions for the synthesis of monobromo cyclopentadithiophenone **17**, starting

Scheme 1. Synthesis of Pyridine-Derivatized TPA Complexes



Scheme 2. Synthesis of TPA Species



from commercially available 3-bromothiophene, Scheme 1.[12] Compound **17** was functionalized through a Sonogashira coupling reaction with 2-methyl-3-butyn-2-ol to give **18** in 25% yield.[9c,d,10] Deprotection of **18** under basic conditions gave terminal alkyne **19**, which was then coupled with *trans*-[$PtCl_2(PEt_3)_2$] to give chloro complex **20** in 33% yield, which was converted to nitrato complex **21** by reaction with silver nitrate.[8] Substitution reaction of nitrato **21** with the corresponding *meta*- or *para*-*N*,*N*-diphenylpyridineamine gave the target complexes (**6b** and **7b**) in 90% yields,[8] as depicted in Scheme 1 for substitution using ligand **16**.

Complexes **6a**,**b** and **7a**,**b** contained residual Ag^+ carried through the reaction sequence (from the reaction with $AgNO_3$), ranging from 0.4 to 7.1%, as described in the Experimental Section, and could not be completely removed. However, on the basis of the similarity of the photophysical data collected for all compounds in solution, it is presumed that the presence of the Ag ion does not affect the photophysical properties of these complexes in solution. This is also supported by the weak interactions observed for Ag^+ in the crystal structure of **6a**, described below, as well as in the Supporting Information.

Synthesis of TPA Species 8a,b, 9a, and 10a,b. Complex **8a** was prepared through a coupling reaction of known alkyne **22** under palladium-catalyzed coupling conditions with complex **14** to give **8a** in 58% yield, Scheme 2.[9c,d,10] Alkynyl TPA **22** was prepared by an initial coupling reaction of known bromo-TPA **23** with 2-methyl-3-butyn-2-ol to give alcohol **24** in 65% yield, followed by a base-catalyzed deprotection reaction to give **22** in 46% yield.[9f,13] Complex **8b** was synthesized under similar conditions, by coupling **22** with chloro complex **20** to give **8b** in 42% yield. Compound **9a** was prepared by initial lithiation of monobromo TPA **23**,[13] followed by addition of complex **14** to yield **9a** in 23% yield.[14] Complex **9b** could not be prepared following reported conditions for similar complexes. Bromo-TPA derivative **23** was also subjected to a palladium-catalyzed reaction with alkyne **13**, to produce **10a** in 41% yield. Analogue **10b** was prepared in 26% yield through a similar Pd-catalyzed coupling reaction of **23** with alkynyl cyclopentadithiophenone **19**.

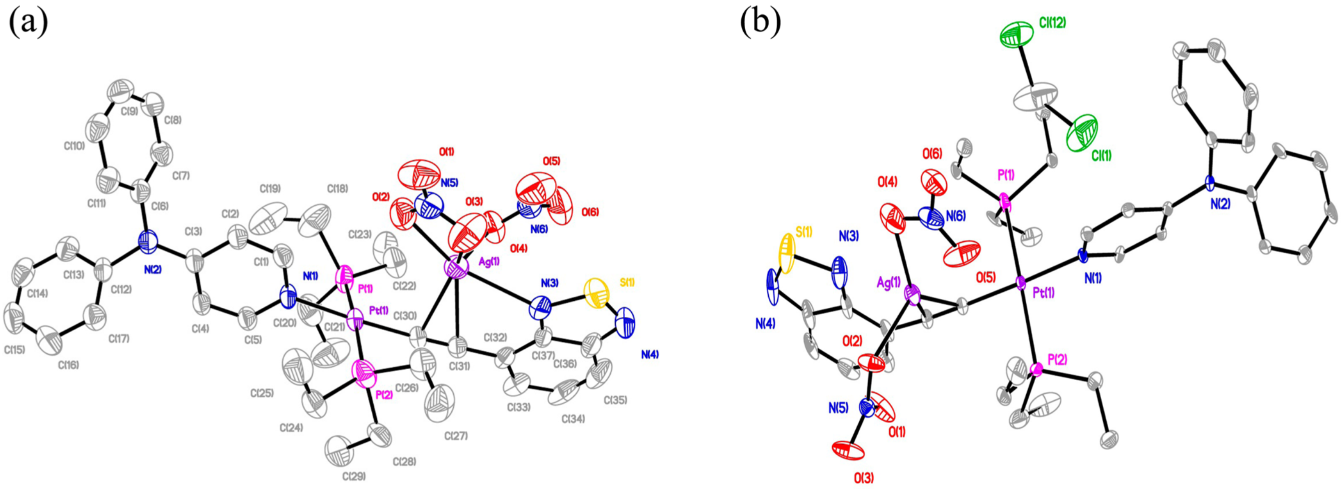


Figure 3. Crystal structures of (a) solvent-free **6a** and (b) CH_2Cl_2 clathrate of **6a**.

X-ray Crystallography. *Solvent-Free Crystal Structure of 6a.* The geometry at the Pt center in this complex displays the expected square planar coordination sphere, with the two phosphine ligands in a trans orientation, with the ethyl groups in a staggered conformation, and exhibiting typical Pt−P bond lengths (2.32 Å), Figure 3, and Table S3 in the Supporting Information. The *N*-pyridyl group is not coplanar with the alkynyl benzothiadiazole group but is tilted by 17°, presumably due to the steric effects caused by the coordination of the alkyne to the Ag cation. The use of the benzothiadiazole in the alkyne ligand makes easier the fixation by coordination of the Ag cation to the alkyne. The coordination observed between the Ag cation and the alkyne is well-known to occur in which a longer distance is observed between the carbon α to the aromatic ring than to the β (average distances are 2.429 and 2.798 Å, respectively);[15] behaving more as an η^1 than as an η^2. In the case of complex **6a**, the observed distances vary slightly, showing distances of 2.477(6) and 2.636(7) Å, with a close contact to Pt of 3.206(3) Å. The Ag cation also coordinates to both nitrate counterions in a bidentate and monodentate fashion. There is a close contact to the Pt of 3.206(3) Å, but as we discuss below it seems to be only that, a close contact (steric interaction) without any bonding interaction.

Dichloromethane Clathrate of 6a. The presence of the CH_2Cl_2 of solvation in the crystal clathrate of **6a** affects the binding of the benzothiadiazole to the Ag cation through an induced rotation along the triple bond, thus exhibiting a greater tilt with respect to the *N*-pyridyl group of 32.2°, as compared to the solvent-free structure, Figure 3. The coordination distances from Ag to the alkyne are more symmetrical, displaying a more η^2 coordination mode than the solvent-free structure, with Ag-alkyne distances of 2.398(11) and 2.472(12) Å. This change in the coordination of Ag to the alkyne is a consequence of the absent interactions between Ag with benzothiadiazole and the Pt center. In this structure, there is no change between the coordination of the Ag cation with the nitrates, as compared to the solvent-free structure. However, the Ag−Pt distance is longer (3.3827(6) Å), and there are no differences on the bond lengths of the ligands coordinated to Pt, suggesting a very weak interaction of the Ag ion on the solvent-free structure.

Electronic Properties. *UV−vis Absorption.* The UV−vis absorption in various organic solvents was measured at 25 °C. These values are presented in Table 1, and representative spectra for pyridine-derivatized TPA complexes **6a** and **6b** are presented in Figure 4. Both *para-* and *meta-*ligands exhibit absorption signals at λ_{max} = 300 nm (not shown), which are assigned to $\pi-\pi^*$ transitions, with no other feature in their spectra.[16] Absorption bands in the near-UV region (~375 nm) are assigned to metal-to-ligand charge transfer transitions (MLCT), as reported for related complexes.[16d,f] This assignment is also consistent with the lack of solvent sensitivity observed for these complexes, as well as with the blue-shifted absorptions observed for the pyridine-derivatized TPA complexes when compared to the Pt−Cl precursors.[16b,d,17]

Table 1. UV−vis at 10^{-5} M and Extinction Coefficients, λ_{abs} in nm (log ε)

compound	CH_2Cl_2	toluene	THF
13	231 (4.34), 309 (4.06) 316 (4.27), 341 (3.77)	317 (4.07), 342 (3.79)	316 (3.80), 341 (3.77)
14	249 (4.34), 283 (4.12) 312 (4.17), 413 (4.00)	312 (4.12), 320 (4.13) 418 (3.95)	311 (4.15), 319 (4.17) 417 (3.98)
19	488 (4.56), 489 (3.41)	289 (4.46), 487 (3.42)	296 (4.28), 487 (3.41)
20	291 (4.17), 352 (4.14) 564 (3.34)	292 (4.28), 346 (4.21) 559 (3.41)	291 (4.30), 347 (4.23) 563 (3.38)
6a	306 (4.43), 387 (3.92)	305 (4.50), 403 (3.96)	298 (4.47), 402 (3.94)
6b	288 (4.44), 545 (3.32)	300 (4.37), 550 (3.36)	299 (4.42), 551 (3.40)
7a	305 (4.47), 388 (4.00)	299 (4.47), 403 (3.97)	298 (4.55), 403 (4.05)
7b	287 (4.53), 545 (3.32)	299 (4.46), 552 (3.38)	294 (4.53), 551 (3.38)
8a	346 (4.48), 423 (4.10)	320 (4.43), 426 (4.04)	319 (4.40), 425 (4.01)
8b	302 (4.37), 367 (4.52), 569 (3.31)	363 (4.44), 561 (3.32)	362 (4.47), 565 (3.31)
9a	306 (4.37), 422 (4.04)	306 (4.55), 423 (3.96)	305 (4.60), 424 (4.01)
10a	312 (4.29), 422 (4.13)	318 (4.41), 423 (4.09)	317 (4.40), 418 (4.10)
10b	297(4.54), 364(4.63), 531(3.66)	362 (4.49), 526 (3.60)	361 (4.55), 525 (3.63)

Benzothiadiazole complexes **6a**−**9a**: transitions in the range of 283−388 nm were also observed for compounds **6a**−**9a** and chloro complex **14**, ascribed to $\pi-\pi^*$ transitions;[16,17] however, complex **14** displays a signal at 413 nm, characteristic of MLCT

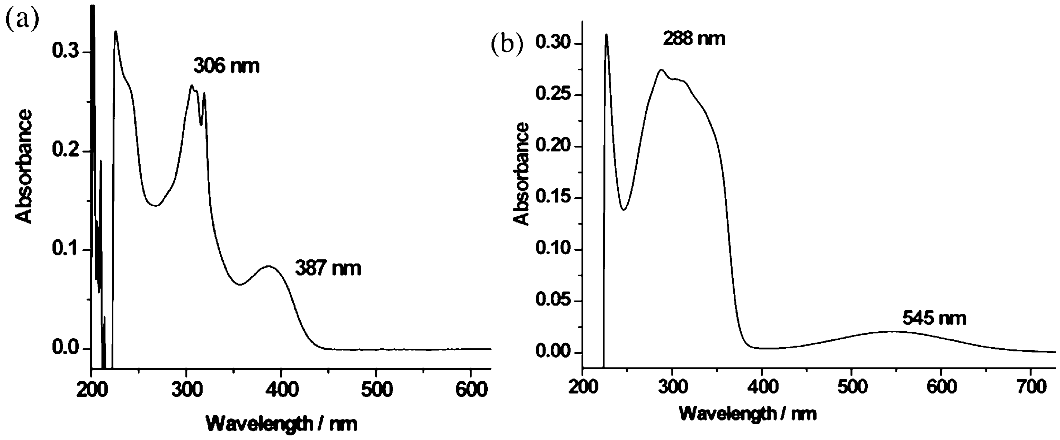


Figure 4. UV−vis spectra of pyridine-derivatized TPA complexes **6a** (a) and **6b** (b).

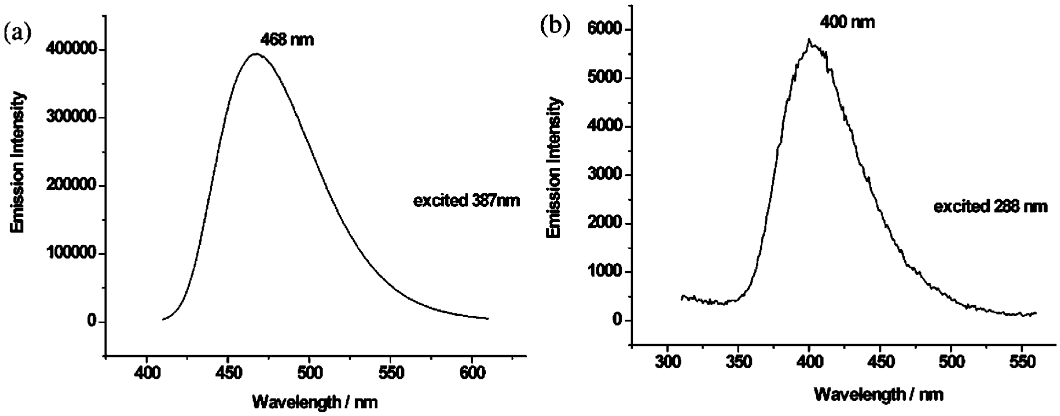


Figure 5. Emission spectra of pyridine-derivatized TPA complexes **6a** (a) and **6b** (b).

transitions for complexes of Pt−Cl, as reported by Mdleleni et al.[16d] Complexes **6a**−**7a** also exhibit a signal in the range of 387−422 nm (blue-shifted relative to **14**), which we interpret as an effect of the electron-withdrawing nature of the pyridine ligand on Pt, presumably lowering the HOMO level of the Pt, thus increasing the HOMO−LUMO gap for MLCT.[5,16,17] On the other hand, complexes **8a** and **9a** exhibit red-shifted signals (423 nm), consistent with complexes containing an extended conjugation.

Cyclopentadithiophenone complexes **6b**−**8b**: transitions in the range of 288−367 nm were observed for compounds **6b**−**8b**, as well as for chloro complex **20**, consistent with reported π−π^* transitions;[16] complex **20** also displays a signal at 564 nm, assigned to MLCT transitions, as reported for complexes of alkynyl cyclopentadithiophenones.[12] Similar to the benzothiadiazole analogs, cyclopentadithiophenone complexes **6b** and **7b** also exhibit blue-shifted signals (545 nm) relative to chloro precursor **20** (564 nm) presumably due to the electron-withdrawing effect of the pyridine-derivatized ligand on Pt, causing an increase in the HOMO−LUMO gap of the MLCT in these complexes.[5,12b,16,17] As expected, complex **8b** exhibits a red-shifted signal (569 nm) that is consistent with its extended conjugation.

No absorption differences were observed between the *meta*- and *para*-analogues of the benzothiadiazole complexes (**6a** and **7a**) or between those of cyclopentadithiophenone (**6b** and **7b**). Organic compounds **10a** and **10b** exhibit π−π^* transitions, along with signals at 422 nm for **10a** and 531 nm for **10b**, which are consistent with absorptions of reported compounds containing extended structures of benzothiadiazole[5,16,17] as well as for those of alkynyl cyclopentadithiophenone.[12b]

Emission Spectra. Emission experiments were performed in CH_2Cl_2, at 10^{-5} M (Figure 5). All complexes of cyclopentadithiophenone (**6b**−**8b**) were blue emitters, with emission maxima ranging from 400 to 403 nm, when excited at their highest energy absorption bands (287−302 nm), as described for similar Pt complexes.[16d,e] Benzothiadiazole complexes containing the pyridine-derivatized TPAs (**6a** and **7a**) emitted in the range of 466−468 nm when excited at their lowest energy absorption band (388 nm); however, benzothiadiazole complexes of TPA (**8a** and **9a**) emitted at 438 and 402 nm, respectively, when excited at their highest energy absorption bands (346 nm for **8a** and 306 nm for **9a**). Contrary to the metallic analogues, organic compounds **10a** and **10b** demonstrated a dependence on the nature of the electron-acceptor, in which **10a** exhibited an emission band at 612 nm when excited at its lowest energy absorption (422 nm), whereas excitation of **10b** at its highest energy absorption (364 nm) induced emission at 413 nm.

Cyclic Voltammetry. The cyclic voltammetry of all compounds was performed in *ortho*-dichlorobenzene solutions (0.05 M n-Bu_4NPF_6) with ferrocene as the internal potential standard. The measured bandgaps for the compounds are listed in Table 2, and their corresponding voltammograms are shown in the Supporting Information. Oxidation presumably occurs from the one-electron oxidation of the tertiary amine center at

Table 2. Bandgaps Measured from the Onset of Oxidation and Reduction Potentials

compounds	band gap (eV)[19]	compounds	band gap (eV)[19]
6a	2.705	**6b**	2.264
7a	2.644	**7b**	2.156
8a	2.320	**8b**	2.038
9a	2.180		
10a	2.301	**10b**	1.997

the pyridine-derivatized TPA ligands in complexes **6a**,**b** and **7a**,**b** and from the TPA ligands in compounds **8a**−**10a**, **8b**, and **10b**, as reported for D−A compounds containing a TPA electron donor.[3−6] Pyridine-derivatized complexes **6a**,**b** and **7a**,**b** undergo oxidation at a higher potential than the other compounds, ranging from 0.707 to 1.141 V, whereas complexes **8a**,**b** and **9a** range from 0.181 to 0.376 V, and organic compounds **10a**,**b** range from 0.493 to 0.593 V. The higher potential for electron removal of complexes **6** and **7** is interpreted to be a consequence of the electron-withdrawing effect of the pyridine substituent on the pyridine-derivatized TPA ligands, making electron removal at the tertiary amine center less efficient when compared with the TPA analogs. Minor differences were observed between the measured bandgaps of *meta*- and *para*-pyridine-derivatized TPA complexes of benzothiadiazole (**6a** and **7a**; Δ = 0.061 eV) as well as for those of cyclopentadithiophenone (**6b** and **7b**; Δ = 0.108 eV). The measured bangaps also show little dependence on the nature of the electron acceptor, with bandgaps differing by 0.441 eV for complexes **6a** versus **6b** and by 0.488 eV for complexes **7a** versus **7b**.

■ CONCLUSIONS

A series of compounds composed of pyridine-derivatized TPAs as electron-donating components and either 2,1,3-benzothiadiazole or cyclopentadithiophenone as the electron acceptors (**6a**,**b** and **7a**,**b**) were synthesized, and their photophysical properties were determined by UV−vis and emission experiments, as well as by cyclic voltammetry, from which their electronic HOMO−LUMO bandagaps were determined. These compounds were prepared to test the potential effect that a pyridine-derivatized TPA functioning as an electron donor may have on the photophysical properties of the complexes. To test the potential effects, analogous TPA complexes **8a**,**b**, and **9a** were prepared and similarly studied. All complexes exhibited comparable HOMO−LUMO bandgaps (2.156−2.705 eV for **6a**,**b** and **7a**,**b** and 2.038−2.320 eV for **8a**,**b** and **9a**), thus indicating no major effect on the properties of the complexes when a pyridine-derivatized electron donor is incorporated in the D−A complexes. This study suggests that electron donor−acceptor complexes composed of extended pyridine-derivatized TPA ligands as the electron-donating components hold promise as potentially useful photovoltaic materials. Photophysical studies on extended structures will be reported soon.

■ EXPERIMENTAL SECTION

General Experimental. All materials were used as received, unless specified. [4-amino pyridine, 18-crown-6 (Sigma-Aldrich), bromobenzene, copper iodide (Alfa Aesar), 4-amino pyridine (TCI America), hexanes (Macron Chemicals), diethyl ether, acetone, potassium carbonate (BDH), dichloromethane, tetrahydrofuran (THF) (EMD)]. Reaction solvents were dried over 4 Å molecular sieves (EMD) at least 24 h before use, or collected from a solvent purification system (MBRAUN). Reactions were monitored by silica gel thin layer chromatography using silica gel plates 60 F_{254} (EMD) and visualized under UV light (254 nm). Compound purifications were performed using 63−200 mesh 60 Å silica gel (EMD). Moisture-sensitive reactions were carried out in oven-dried glassware under a dinitrogen atmosphere, using standard Schlenk techniques. THF was distilled from sodium (Sigma-Aldrich), and Et_2NH (Sigma-Aldrich) was dried from potassium hydroxide (Sigma-Aldrich); both solvents were degassed under N_2 for 30 min before use. ^{1}H, ^{13}C, and ^{31}P NMR spectra were obtained with a JEOL 600 MHz spectrometer. The ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals, and ^{31}P NMR resonances are referenced to an internal standard sample of 85% H_3PO_4 (δ = 0.0). Fourier transform infrared (FTIR) spectra were obtained with a PerkinElmer FT-IR spectrum-100 spectrometer (equipped with ATR accessory) as neat solids or oils. Melting points were measured on a Mel-Temp melting point apparatus (1002D) and are uncorrected. High-resolution mass spectra (HRMS) were acquired by electrospray ionization (ESI) measured on a Jeol AccuTOF JMS-T100LC ESI-MS spectrometer calibrated with PEG-600. UV−vis spectra were recorded on a Cary 50Bio UV−vis spectrophotometer.

Synthesis of Alkynyl Alcohol 2,1,3-Benzothiadiazole 12. Under a dinitrogen atmosphere, a solution of compound **11** (930 mg, 4.44 mmol), 2-methyl-3-butyn-2-ol (756 mg, 9.00 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 0.03 mmol), copper iodide (20 mg, 0.105 mmol), and triphenylphosphine (50 mg, 0.191 mmol) were added to a triethylamine/dichloromethane solution (10 mL/10 mL), and the resulting suspension was stirred at 70 °C for 12 h. The solvent was evaporated, and the crude was purified by column chromatography using 1:2 v/v Et_2O/hexanes, affording 63 mg of **12** in 65% yield as a brown oil. ^{1}H NMR (600 MHz, $CDCl_3$, trimethylsilane (TMS)): δ 1.51 (s, 1H, −OH), 1.69 (s, 6H, CH_3), 7.46 (t, J = 9.0 Hz, 1H, Ar−H), 7.61 (d, J = 7.2 Hz, 1H, Ar−H), 7.89 (d, J = 7.2 Hz, 1H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$): δ 31.49, 65.63, 77.34, 100.90, 116.77, 121.61, 129.38, 132.72, 154.59. FTIR (oil): 3387, 3058, 2980, 2932, 1538, 1488, 1361. HRMS calcd for $C_{11}H_{10}N_2OS$ (M^+) 218.0514; found (ESI): 219.0534 ($M+H^+$).

Synthesis of Compound 13. Under a dinitrogen atmosphere, powdered potassium carbonate (925 mg, 6.70 mmol) and 18-crown-6 (100 mg, 0.38 mmol) were added to a solution of compound **12** (0.63 g, 2.89 mmol) in dry toluene (20 mL). The reaction mixture was heated to reflux for 1 h. After it was cooled to room temperature, the mixture was poured into water (50 mL) and extracted with dichloromethane (2 × 15 mL). The solvent was evaporated, and the crude product was purified using column chromatography with 1:10 v/v Et_2O/hexane to give **13** in 46% yield as a light yellow solid. This compound matched reported characterization.[9e]

Synthesis of Compound 14. Under a dinitrogen atmosphere, alkynyl benzothiadiazole **13** (53 mg, 0.33 mmol) and *trans*-$[PtCl_2(PEt_3)_2]$ (331 mg, 0.66 mmol) were added to a mixture of triethylamine/dichloromethane (10 mL/10 mL) in the presence of a catalytic amount of CuI (20 mg, 0.105 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was then removed under reduced pressure to obtain the crude product. The mixture was purified by chromatography using 1:8 (v/v) Et_2O/hexane as the eluent to produce 73 mg of **14** in 35% yield as a yellow solid, mp 88−90 °C (dec). ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 1.19−1.23 (m, 18H, CH_3), 2.14−2.15 (m, 12H, CH_2), 7.40−7.43 (m, 2H, Ar−H), 7.77−7.79 (m, 1H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 7.93, 14.67, 93.04, 98.23, 118.39, 122.54, 129.68, 130.08, 155.15, 156.29. ^{31}P NMR ($CDCl_3$, 243 MHz): δ 15.86 (s, J_{Pt-P} = 1177.51 Hz). IR (solid): 2958, 2925, 2854, 2109,1730, 1526, 1455. HRMS calcd for $C_{20}H_{33}ClN_2P_2PtS$ (M^+) 625.1176; found (ESI): 625.1192 (M^+).

Synthesis of Nitrato Complex 15. Under a dinitrogen atmosphere, compound **14** (20 mg, 0.032 mmol) and silver nitrate (21 mg, 0.120 mmol) were added to chloroform (10 mL) in the dark. The reaction mixture was stirred at room temperature overnight. The solid was filtered off. The solvent was then removed under reduced pressure to obtain 21 mg of **15** in essentially quantitative yield as a yellow solid.

Synthesis of Compound 6a. Under a dinitrogen atmosphere, compound **15** (20 mg, 0.032 mmol) and *para*-pyridine-derivatized TPA **16** (7.9 mg, 0.032 mmol) were added to dry toluene (10 mL). The reaction was stirred for 12 h. The solvent was removed under reduced pressure. The residue was redissolved in dichloromethane (0.5 mL) and washed with 0.5 mL H_2O. The solvent was then evaporated under a flow of nitrogen, and the residue was washed with 20 mL of diethyl ether to give 24 mg of **6a** in 90% yield as a yellow solid, mp 150−152 °C (dec). ^{1}H NMR (600 MHz, CD_3COCD_3) δ 1.18−1.21 (m, 18H, CH_3), 2.03−2.04 (m, 12H, CH_2), 6.86 (d, J = 6.0 Hz, 2H, Ar−H), 7.36−7.41 (m, 6H, Ar−H), 7.50−7.53 (m, 4H, Ar−H), 7.61 (t, J = 9.0 Hz, 1H, Ar−H), 7.65 (d, J = 8.8 Hz, 1H, Ar−H), 7.65 (d, J = 9.0 Hz, 1H, Ar−H), 8.38 (d, J = 6.0 Hz, 2H, Ar−H). ^{13}C NMR (150 MHz, CD_3COCD_3) δ 7.97, 14.62, 82.54, 102.93, 113.15, 119.53, 120.24, 127.02, 127.22, 127.85, 129.74, 130.60, 131.19, 142.84, 151.24, 154.62, 155.69. ^{31}P NMR (CD_3COCD_3, 243 MHz): δ 16.68 (s, J_{Pt-P} = 1157.80 Hz). IR (solid): 3059, 2960, 2924, 2853, 2118, 1731, 1620, 1590, 1489. HRMS calcd for $C_{37}H_{47}N_4P_2PtS$ (M^+) 836.2639; found (ESI): 836.2648 (M^+). Elemental analysis found: C, 43.32; H, 4.74; N7.89; Ag, 6.40. Calcd for $C_{37}H_{47}AgN_6O_6P_2PtS$: C, 41.58; H, 4.43; N, 7.86; Ag, 10.09%.

Synthesis of Compound 7a. Under a dinitrogen atmosphere, compound **15** (20 mg, 0.032 mmol) and *meta*-pyridine-derivatized TPA (7.9 mg, 0.032 mmol) were dissolved in dry toluene (10 mL). The reaction was stirred for 12 h. The solvent was removed under reduced pressure. The residue was dissolved in 0.5 mL of dichloromethane and washed with 0.5 mL of H_2O. Then the solvent was removed under a flow of nitrogen, and the residue was washed with 20 mL diethyl ether to produce 24 mg of **7a** in 90% yield as a yellow solid, mp 156−158 °C (dec). ^{1}H NMR (600 MHz, CD_3COCD_3) δ 1.13−1.16 (m, 18H, CH_3), 2.02−2.03 (m, 12H, CH_2), 7.27−7.29 (m, 6H, Ar−H), 7.44−7.47 (m, 4H, Ar−H), 7.57−7.67 (m, 4H, Ar−H), 7.85−7.87 (m, 1H, Ar−H), 8.10−8.13 (m, 1H, Ar−H), 8.42−8.43 (m, 1H, Ar−H). ^{13}C NMR (150 MHz, CD_3COCD_3) δ 7.37, 14.10, 84.50, 102.37, 119.56, 120.81, 126.09, 128.10, 129.32, 129.82, 130.28, 130.39, 131.03, 143.24, 144.44, 148.01, 154.93, 155.95. ^{31}P NMR (CD_3COCD_3, 243 MHz): δ 17.03 (s, J_{Pt-P} = 1157.77 Hz). IR (solid): 3059, 2960, 2925, 2853, 2121, 1733, 1587, 1566, 1484, 1333. HRMS calcd for $C_{37}H_{47}N_4P_2PtS$ (M^+) 836.2639; found (ESI): 836.2654 (M^+). Elemental analysis found: C, 42.81; H, 4.67; N, 7.93; Ag, 7.10. Calcd for $C_{37}H_{47}AgN_6O_6P_2PtS$: C, 41.58; H, 4.43; N, 7.86; Ag, 10.09%.

Synthesis of Compound 9a. Under a dinitrogen atmosphere, compound **23** (100 mg, 0.310 mmol) was added to dry ether (10 mL). A 2.5 M solution of *n*-BuLi in hexane (0.4 mL, 1 mmol) was added dropwise at −15 °C. The resulting mixture was stirred for 1 h at −15 °C. Compound **14** (100 mg, 0.160 mmol) in 5 mL of dry ether was added to the solution dropwise. The mixture was allowed to warm to room temperature and then stirred for 1.5 h. The reaction solution was washed with water (50 mL). The combined organic layers were dried over $MgSO_4$. After removal of the solvent under reduced pressure, the residue was purified by column chromatography on silica gel with 1:8 (v/v) Et_2O/hexane as the eluent to give 31 mg of **9a** in 23% yield as a yellow solid, mp: 96−98 °C (dec). ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 1.09−1.14 (m, 18H, CH_3), 1.89−1.91 (m, 12H, CH_2), 6.83 (d, J = 8.4 Hz, 2H, Ar−H), 6.89 (t, J = 7.5 Hz, 2H, Ar−H), 7.00−7.04 (m, 4H, Ar−H), 7.16−7.19 (m, 4H, Ar−H), 7.29 (d, J = 8.4 Hz, 2H, Ar−H), 7.41−7.45 (m, 2H, Ar−H), 7.73−7.76 (m, 1H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 8.24, 15.45, 106.47, 117.65, 121.11, 122.48, 126.15, 128.89, 129.71, 129.91, 139.60, 141.43, 148.55, 151.62, 155,24, 156.53. ^{31}P NMR ($CDCl_3$, 243 MHz): δ 10.88 (s, J_{Pt-P} = 1309.07 Hz). IR (solid): 3037, 2962, 2925, 2872, 2086, 1733, 1587, 1480. HRMS calcd for $C_{38}H_{47}N_3P_2PtS$ (M^+) 834.2614; found (ESI): 834.2622 (M^+). Elemental analysis found: C, 59.18; H, 7.37; N, 3.93. Calcd for $C_{38}H_{47}N_3P_2PtS$: C, 54.67; H, 5.67; N, 5.03%.

Synthesis of Complex 8a. Under a dinitrogen atmosphere, a mixture of alkynyl TPA **22** (24 mg, 0.09 mmol), chloro complex **14** (30 mg, 0.045 mmol), and copper iodide (5 mg, 0.026 mmol) were added to a triethylamine/dichloromethane solution (10 mL/10 mL), and the resulting suspension was stirred at 70 °C for 12 h. The solvent was evaporated, and the crude product chromatographed using 1:2 (v/v) diethyl ether/hexane as the eluent, giving 22 mg of **8a** in 58% yield as a yellow solid, mp 114−116 °C (dec). ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 1.23−1.26 (m, 18H, CH_3), 2.27−2.28 (m, 12H, CH_2), 6.93 (d, J = 8.4 Hz, 2H, Ar−H), 6.98 (t, J = 6.8 Hz, 2H, Ar−H), 7.08 (d, J = 7.5 Hz, 4H, Ar−H), 7.18 (d, J = 7.5 Hz, 2H, Ar−H), 7.22 (t, J = 7.5 Hz, 2H, Ar−H), 7.41−7.45 (m, 2H, Ar−H), 7.76−7.77 (m, 1H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 8.53, 16.55, 105.71, 106.41, 109.79, 118.08, 122.57, 124.06, 129.21, 129.81, 129.97, 131.84, 145.05, 147.85, 155.18, 156.38. ^{31}P NMR ($CDCl_3$, 243 MHz): δ 12.02 (s, J_{Pt-P} = 1177.51 Hz). IR (solid): 3022, 2965, 2927, 2876, 2852, 2094, 1733, 1587, 1489. HRMS calcd for $C_{40}H_{47}N_3P_2PtS$ (M^+) 858.2614; found (ESI): 858.2621 (M^+). Elemental analysis found: C, 55.21; H, 5.87; N, 4.46. Calcd for $C_{40}H_{47}N_3P_2PtS$: C, 55.93; H, 5.51; N, 4.89%.

Synthesis of Compound 10a. Under a dinitrogen atmosphere, alkynyl benzothiadiazole **13** (53 mg, 0.33 mmol) and bromo TPA **23** (225 mg, 0.69 mmol) were added to a solution of triethylamine/dichloromethane (10 mL/10 mL), $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), triphenylphosphine (15 mg, 0.06 mmol), and copper iodide (20 mg, 0.105 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was then removed under reduced pressure. The crude was purified by column chromatography using 1:10 (v/v) Et_2O/hexane to produce 54 mg of **10a** in 41% yield as a yellow solid, mp 66−68 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 7.03 (d, J = 8.4 Hz, 2H, Ar−H), 7.07 (t, J = 7.6 Hz, 2H, Ar−H), 7.14 (d, J = 7.5 Hz, 4H, Ar−H), 7.28 (t, J = 7.5 Hz, 4H, Ar−H), 7.51 (d, J = 9.5 Hz, 2H, Ar−H), 7.54−7.56 (m, 1H, Ar−H), 7.75 (d, J = 6.8 Hz, 1H, Ar−H), 7.95 (d, J = 8.9 Hz, 1H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 84.63, 96.57, 115.26, 117.70, 121.39, 122.02, 123.87, 125.28, 129.39, 129.56, 132.27, 133.08, 147.16, 148. 60, 154.71, 154.76. IR (solid): 3036, 2201, 1724, 1585, 1537, 1487. HRMS calcd for $C_{26}H_{17}N_3S$ (M^+) 403.1143; found (ESI): 404.1156 ($M+H^+$).

Synthesis of Compound 10b. Under a dinitrogen atmosphere, compound **19** (55 mg, 0.20 mmol) and compound **23** (100 mg, 0.37 mmol) were added to a mixture of triethylamine/dichloromethane (10 mL/5 mL) in the presence of $Pd(OAc)_2$ (15 mg, 0.07 mmol), CuI (12 mg, 0.60 mmol), and triphenylphosphine (15 mg, 0.06 mmol). The reaction mixture was refluxed overnight. The solvent was then removed under reduced pressure to obtain the crude product. The crude was purified by column chromatography using 1:10 (v/v) Et_2O/hexane to produce 24 mg of **10b** in 26% yield as a purple solid, mp 122−124 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS) δ 6.97−6.99 (m, 3H, Ar−H), 7.05−7.08 (m, 4H, Ar−H), 7.11−7.12 (m, 4H, Ar−H), 7.25−7.39 (m, 4H, Ar−H), 7.32−7.34 (m, 2H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$, TMS) δ 81.54, 95.81, 114.78, 121.94, 123.93, 125.30, 126.37, 128.03, 129.57, 132.49, 141.61, 142.99, 147.07, 148.50, 148.71, 149.55, 182.33. IR (solid): 3083, 3036, 2192, 1704, 1585, 1511, 1485, 1261. HRMS calcd for $C_{29}H_{17}NOS_2$ (M^+) 459.0752; found (ESI): 459.0739 (M^+).

Synthesis of Compound 18. Under a dinitrogen atmosphere, bromocyclopentadithiophenone **17** (385 mg, 1.39 mmol), 2-methyl-3-butyn-2-ol (378 mg, 4.50 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 0.03 mmol), copper iodide (20 mg, 0.11 mmol), and triphenylphosphine (50 mg, 0.191 mmol) were added to a solution of triethylamine/dichloromethane (10 mL/10 mL), and the resulting suspension was stirred at 70 °C for 12 h. The solvent was evaporated, and the crude product was chromatographed using 1:2 (v/v) Et_2O/hexanes, giving 95 mg of **18** in 25% yield as a dark-red solid, mp 60−62 °C. ^{1}H NMR (600 MHz, $CDCl_3$, TMS): δ 1.58 (s, 6H, CH_3), 7.92−6.93 (m, 2H, Ar−H), 7.02 (d, J = 4.8 Hz, 1H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 31.39, 65.74, 75.04, 99.85, 121.88, 125.19, 125.91, 128.30, 141.23, 142.95, 149.14, 149.20, 182.26. IR (solid): 3382, 3089, 2978, 2929, 2210, 1701, 1433, 1380, 1359. HRMS calcd for $C_{14}H_{10}O_2S_2$ (M^+) 274.0122; found (ESI): 275.0137 ($M+H^+$).

Synthesis of Alkynyl Cyclopentadithiophenone 19. Under a dinitrogen atmosphere, powdered potassium hydroxide (39 mg, 0.7 mmol) and 18-crown-6 (30 mg, 0.114 mmol) were added to a solution of **18** (95 mg, 0.348 mmol) in dry toluene (10 mL). The reaction mixture was heated to reflux for 4 h. After it was cooled to room temperature, the mixture was poured into water (50 mL) and extracted with CH_2Cl_2 (2 × 15 mL). The organic solvent was evaporated, and the crude product was purified using column chromatography with Et_2O/hexane 1:10 (v/v) to give 25 mg of **19** in 33% yield as a red solid, mp 210−212 °C. ^1H NMR (600 MHz, $CDCl_3$, TMS) δ 3.45 (s, 1H, ≡CH), 6.98 (d, J = 4.8 Hz, 1H, Ar−H), 7.08−7.09 (m, 2H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 76.47, 83.51, 121.95, 124.26, 127.04, 128.54, 141.15, 143.34, 148.91, 149.66, 181.91. IR (solid): 3305, 3278, 3231, 3081, 2167, 1703. HRMS calcd for $C_{11}H_4OS_2$ (M^+) 215.9704; found (ESI): 216.9725. ($M+H^+$).

Synthesis of Complex 20. Under a dinitrogen atmosphere, **19** (25 mg, 0.116 mmol) and *trans*-$[PtCl_2(PEt_3)_2]$ (115 mg, 0.23 mmol) were added to a solution of triethylamine/dichloromethane (10 mL/10 mL) in the presence of copper iodide (10 mg, 0.053 mmol). The reaction mixture was stirred at room temperature overnight. The solvent was then removed under reduced pressure to obtain the crude product. The mixture was purified by chromatography over a silica column using 1:8 (v/v) Et_2O/hexane to produce 26 mg of **20** in 33% yield as a red solid, mp 128−130 °C (dec). ^1H NMR (600 MHz, $CDCl_3$, TMS) δ 1.15−1.18 (m, 18H, CH_3), 2.00−2.02 (m, 12H, CH_2), 6.68 (s, 1H, Ar−H), 6.92 (d, J = 4.8 Hz, 1H, Ar−H), 6.95 (d, J = 4.8 Hz, 1H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 8.12, 14.68, 93.58, 94.18, 121.60, 121.73, 126.57, 132.54, 141.43, 142.19, 144.59, 150.78, 183.33. ^{31}P NMR ($CDCl_3$, 243 MHz): δ 15.78 (s, J_{Pt-P} = 1170.94 Hz). IR (solid): 3090, 2964, 2931, 2876, 2105, 1746, 1709, 1453. HRMS calcd for $C_{23}H_{33}ClOP_2PtS_2$ (M^+) 681.0784; found (ESI): 681.0796 (M^+).

Synthesis of Complex 21. Under a dinitrogen atmosphere, compound **20** (26 mg, 0.038 mmol) and silver nitrate (21 mg, 0.12 mmol) were added to chloroform (10 mL) in the dark. The reaction mixture was stirred at room temperature overnight. The solid was filtered off. The solvent was then removed under reduced pressure to obtain 27 mg of **21** in essentially quantitative yield as a red solid.

Synthesis of Complex 6b. Under a dinitrogen atmosphere, compound **21** (26 mg, 0.038 mmol) and *para*-pyridine-derivatized TPA **16** (9.4 mg, 0.038 mmol) were added to dry toluene (10 mL). The reaction was stirred for 12 h. The solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 (0.5 mL) and washed with 0.5 mL of deionized H_2O. The solvent was then removed under a flow of nitrogen, and the residue was washed with 20 mL of diethyl ether to produce 31 mg of **6b** in 89% yield as a red solid, mp 192−194 °C (dec). ^1H NMR (600 MHz, CD_3COCD_3) δ 1.17−1.20 (m, 18H, CH_3), 1.91−1.94 (m, 12H, CH_2), 6.80 (s, 1H, Ar−H), 6.83 (d, J = 7.2 Hz, 2H, Ar−H), 6.97 (d, J = 4.8 Hz, 1H, Ar−H), 7.33 (d, J = 4.8 Hz, 1H, Ar−H), 7.37−7.40 (m, 6H, Ar−H), 7.50−7.52 (m, 4H, Ar−H), 8.33 (d, J = 7.2 Hz, 2H, Ar−H). ^{13}C NMR (150 MHz, CD_3COCD_3) δ 7.37, 14.26, 14.37, 87.95, 98.22, 113.01, 121.13, 121.99, 127.47, 127.63, 128.77, 130.49, 131.12, 141.18, 142.30, 143,43, 145.83, 150.04, 151.84, 154.76, 182.07. ^{31}P NMR (CD_3COCD_3, 243 MHz): δ 17.08 (s, J_{Pt-P} = 1164.36 Hz). IR (solid): 3063, 2966, 2930, 2875, 2106, 1699, 1620, 1590, 1489, 1334. HRMS calcd for $C_{40}H_{47}N_2OP_2PtS_2$ (M^+) 892.2247; found (ESI): 892.2254 (M^+). Elemental analysis found: C, 49.66; H, 5.34; N, 4.41. Calcd for $C_{40}H_{47}N_3O_4P_2PtS_2$: C, 50.31; H, 4.96; N, 4.40%. Only traces of Ag (0.4%) were detected by ICP-OES.

Synthesis of Complex 7b. Under a dinitrogen atmosphere, compound **21** (26 mg, 0.04 mmol) and *meta*-pyridine-derivatized TPA (9.4 mg, 0.04 mmol) were added to dry toluene (10 mL). The reaction was stirred for 12 h. The solvent was removed under reduced pressure. The residue was dissolved in CH_2Cl_2 (0.5 mL) and washed with 0.5 mL of deionized H_2O. The solvent was then removed under a flow of nitrogen, and the residue was washed with 20 mL of diethyl ether to produce 30 mg of **7b** in 88% yield as a red solid, mp 165−167 °C (dec). ^1H NMR (600 MHz, CD_3COCD_3) δ 1.10−1.13 (m, 18H, CH_3), 1.89−1.92 (m, 12H, CH_2), 6.80 (s, 1H, Ar−H), 6.98 (d, J = 4.8 Hz, 1H, Ar−H), 7.26−7.28 (m, 6H, Ar−H), 7.33 (d, J = 4.8 Hz, 1H, Ar−H), 7.43−7.46 (m, 4H, Ar−H), 7.62−7.64 (m, 2H, Ar−H), 8.07−8.08 (m, 1H, Ar−H), 8.41−8.42 (m, 1H, Ar−H). ^{13}C NMR (151 MHz, CD_3COCD_3) δ 7.35, 14.10, 85.52, 98.39, 121.15, 122.26, 123.90, 124.48, 126.07, 128.23, 128.93, 129.46, 129.75, 130.41, 141.17, 142.37, 143.17, 144.57, 145.21, 146.14, 147.98, 149.97, 182.04. ^{31}P NMR (CD_3COCD_3, 243 MHz): δ 16.27 (s, J_{Pt-P} = 1151.21 Hz). IR (solid): 3067, 2965, 2930, 2876, 2108, 1700, 1588, 1566, 1485, 1331. HRMS calcd for $C_{40}H_{47}N_2OP_2PtS_2$ (M^+) 892.2247; found (ESI): 892.2265 (M^+). Elemental analysis found: C, 50.35; H, 5.41; N, 4.25. Calcd for $C_{40}H_{47}N_3O_4P_2PtS_2$: C, 50.31; H, 4.96; N, 4.40%. Only traces of Ag were detected by ICP-OES.

Synthesis of Complex 8b. Under a dinitrogen atmosphere, a mixture of compound **20** (24 mg, 0.04 mmol), alkynyl TPA **22** (31 mg, 0.12 mmol), and copper iodide (5 mg, 0.03 mmol) were added to a triethylamine/dichloromethane solution (10 mL/10 mL), and the resulting suspension was stirred at 70 °C for 12 h. The solvent was evaporated, and the crude product was chromatographed using 1:2 (v/v) Et_2O/hexane as the eluent, giving 17 mg of **8b** in 42% yield as a yellow solid, mp 158−160 °C (dec). ^1H NMR (600 MHz, $CDCl_3$, TMS) δ 1.20−1.22 (m, 18H, CH_3), 2.14−2.15 (m, 12H, CH_2), 6.72 (s, 1H, Ar−H), 6.92−6.94 (m, 4H, Ar−H), 6.98 (t, J = 6.9 Hz, 2H, Ar−H), 7.06 (d, J = 7.5 Hz, 4H, Ar−H), 7.14 (d, J = 6.9 Hz, 2H, Ar−H), 7.22 (t, J = 7.5 Hz, 2H, Ar−H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 8.44, 16.64, 101.69, 105.52, 109.71, 121.33, 121.71, 122.64, 123.98, 124.14, 126.23, 129.22, 131.78, 141.62, 142.21, 144.23, 145.18, 147.82, 150.98, 183.36. ^{31}P NMR ($CDCl_3$, 243 MHz): δ 11.83 (s, $J_{Pt\text{-}P}$ = 1177.50 Hz). IR (solid): 3082, 3059, 3033, 2962, 2926, 2853, 2872, 2085, 1706, 1588, 1491. HRMS calcd for $C_{43}H_{47}NOP_2PtS_2$ (M^+) 914.2222; found (ESI): 914.2234 (M^+). Elemental analysis found: C, 57.76; H, 5.96; N, 1.38. Calcd for $C_{43}H_{47}NOP_2PtS_2$: C, 56.44; H, 5.18; N, 1.53%.

X-ray Diffraction. A specimen of each compound was mounted on a glass fiber, and the X-ray intensity data were measured on a Bruker SMART APEX CCD system equipped with a graphite monochromator and a Mo Kα fine-focus tube (λ = 0.710 73 Å). The frames were integrated using a narrow-frame algorithm, and the structure was solved and refined using the Bruker APEX2 Software Package.[18] The total exposure time was 4.00 h.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Nuclear magnetic resonance (NMR) (^1H, ^{13}C, and ^{31}P), infrared spectra, and mass spectra of all new compounds, UV/vis spectra, emission spectra, cyclic voltammograms, as well as additional crystallographic parameters for both crystal structures of **6a** are available free of charge via the Internet at http://pubs.acs.org. Crystallographic data for solvent-free **6a** and CH_2Cl_2 solvated **6a** were deposited with the Cambridge Crystallographic Data Centre as supplementary publication Nos. 983929 and 984051, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Notes

The authors declare no competing financial interest.

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