

Synthesis of Monodisperse Platinum Acetylide Oligomers End-Capped with Naphthalene Diimide Units

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We report the synthesis and structural characterization of a series of monodisperse platinum acetylide oligomers with the general structure NDI-[Ph-C=C-Pt(PBu₃)₂-C=C-]_n-Ph-NDI, where n = 2, 3, 6, or 10, Ph = 1,4-phenylene, NDI is a substituted 1,4,5,8-naphthalene diimide, and the geometry at the Pt centers is trans. The oligomers were synthesized via an iterative-convergent approach utilizing organometallic synthons that feature orthogonally protected terminal acetylene units. The ³¹P NMR spectra of the oligomers are especially revealing as to their structure, due to a difference in chemical shift for the internal and terminal Pt(PBu₃)₂ units. The oligomers were also characterized by electrochemistry, UV-visible absorption, and photoluminescence spectroscopy. The emission spectroscopy reveals that the triplet exciton is efficiently quenched in the NDI end-capped oligomers, and the quenching is thought to arise due to photoinduced charge separation.

Introduction

Conjugated oligomers and polymers have been the focus of a large body of research directed toward the development of new advanced materials for optical and electronic applications, as well as for addressing fundamental scientific questions.¹⁻⁵ While most work in this field has focused on organic conjugated materials, there has recently been increasing interest in the study of conjugated materials with heavy metal centers incorporated into the conjugated network.⁶⁻⁹ Interest in these materials is driven both by the need to understand fundamental aspects of how the

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metals influence the properties of the conjugated systems and by their possible application in areas such as optoelectronic devices and nonlinear absorption.¹⁰⁻¹⁵

We have been investigating the properties of platinum (Pt) acetylide oligomers and polymers of the type $[-Pt(PR_3)_2 -$ C = C - Ar - C = C -], where Ar is an organic arene and the stereochemistry at the square-planar Pt(II) center is *trans*.^{16–19} These materials provide considerable insight into the influence of the platinum center on a π -conjugated electronic system. In addition, platinum acetylides are useful for application in organic solar cells and as nonlinear absorption materials.^{11–15,20} The most significant effect of the platinum in these conjugated systems is that it introduces strong spinorbit coupling, effectively mixing the singlet and triplet excited states, resulting in efficient production of long-lived triplet excitons.²¹⁻²³

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Article

In several recent publications we described the results of spectroscopic studies that have characterized properties of triplet excitons in platinum acetylide oligomers and polymers.^{16–18} In addition, we have also carried out pulse radiolysis²⁴ investigations to characterize the spectroscopy and spatial extent of negative ion-radicals (polarons) produced by reduction of the platinum acetylide chains.²⁵ Taken together, the spectroscopic and pulse radiolysis studies reveal that triplet excitons and negative polarons are spatially confined on the platinum acetylide chain, being delocalized over a segment corresponding to approximately a single repeat unit, e.g., $[-Pt-C \equiv C-Ph-C \equiv C-Pt-]$, where Ph = 1,4-phenylene.^{18,25} As a continuation of that work, we are interested in developing long platinum acetylide oligomers that are end-capped with molecular units that can act as "traps" for triplet excitons or negative polarons produced on the chains. Time-resolved spectroscopic studies of such endcapped oligomers carried out using laser flash photolysis and pulse radiolysis will provide considerable insight concerning the dynamics of triplet exciton and negative polaron diffusion along the π -conjugated chain.

In this paper we describe synthetic work carried out toward the objective of synthesizing a series of monodisperse platinum acetylide oligomers that are end-capped with naphthalene diimide units, Pt_nNDI_2 , Chart 1. The objective of the synthetic efforts was to prepare relatively long oligomers, in order to enhance the opportunity to measure the dynamics of exciton and polaron hopping along the chains.^{26–30}

The synthetic method that was used to prepare these oligomers is based on an iterative-convergent approach, which was implemented via application of an organometallic synthon that features orthogonally protected terminal acetylenes. While there has been considerable research carried out concerning the synthesis of monodisperse, organic π -conjugated oligomers,^{2,31–37} fewer studies have described the

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Chart 1



Pt_nNDI₂ (n = 2, 3, 6, 10)



Pt-2

preparation of oligomers that contain metal centers in the π -conjugated sequence.^{9,16,38–51} This work is significant, as the protecting group approach that is developed is general and could be used toward the synthesis of a variety of platinum acetylide based oligomers and dendrimers.

Results and Discussion

Molecular and Synthetic Design. The structures of the Pt_nNDI_2 oligomers (n = 2, 3, 6, and 10) synthesized in the course of this work are shown in Chart 1. Each of these oligomers features a platinum acetylide chain with the repeat unit structure $[-Pt(PBu_3)_2-C\equiv C-Ph-C\equiv C-]$ (Ph = 1,4-phenylene) end-capped with 1,4,5,8-naphthalenediimide (NDI) units. The NDI unit is used as the end-cap, as this moiety is reduced at a relatively low potential, making it a good electron acceptor for trapping negative polarons or triplet excitation, respectively.^{52,53} The previously synthesized dimeric complex Pt-2^{16,25} was used as a reference compound for photophysical characterization of the series.

Preparation of the longer oligomers (i.e., n = 6 and 10) presented an interesting synthetic challenge. Consideration of the problem suggested three basic synthetic strategies that could be used. The simplest approach would be a fractionation method.² Here, a short-lived AA/BB type polymerization reaction of Pt(PBu₃)₂Cl₂ and 1,4-diethynylbenzene

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^{*a*}(a) Tetrabutylammonium fluoride (TBAF), THF, rt, 1 h; (b) MnO₂, KOH, ether, rt, 5 h; (c) *cis*-Pt(PBu₃)₂Cl₂, Et₂NH, reflux, 12 h; (d) *cis*-Pt(PBu₃)₂Cl₂, cat. CuI, THF/Et₂NH, rt, 2 h; (e) **2b**, cat. CuI, Et₂NH, rt, 12 h.

Scheme 2^{*a*}

PBu₃ PBu CI - Pt -≡ PBu₃ Pt-CI PBu₃ PBu₂ (10)b, 69% Ρ́Bu₃ . Bua 11 8 48% Pt C 49% PBu₃ 9 12

^a (a) cis-Pt(PBu₃)₂Cl₂, iPr₂NH/MeCN, reflux, 12 h; (b) cat. CuI, THF/Et₂NH, rt, 3 h; (c) **5**, cat. CuI, THF/Et₂NH, rt, 3 h.

could be carried out, followed by quenching the reaction early with the appropriate end-cap. The pitfall in this approach would be that the reaction would be uncontrolled, resulting in a complex mixture of oligomers with different chain lengths that would need to be separated. A stepwise, totally directed approach² would involve a completely linear synthesis with group protection/deprotection needed at each step in the sequence. While product isolation via this route would be much less difficult, the synthesis would require many steps, compromising the overall yields of the target oligomers.³⁸

Although we have previously developed an iterative method for preparation of monodisperse platinum acetylide oligomers,^{16–18,25} because of the need for longer chain lengths in the present study we decided that an iterativeconvergent approach is best suited for the task.^{2,54,55} This route involves the use of orthogonal protecting groups to construct a protected and unsymmetric platinum acetylide oligomer segment as a primary synthon (structure **7**, Scheme 1). Building out from the center of the oligomer ultimately reduced the number of overall synthetic steps involved in assembly of the longer oligomers.

Synthesis. The route used to access the primary synthon 7 is outlined in Scheme 1. First, the monomeric complex 3 was prepared in a sequence beginning with selective deprotection of the hydroxymethyl (HOM) group of known compound $1^{16,32}$ to afford an unsymmetrically protected 1,4-diethynylbenzene (2a) in which one of the ethynyl groups is free and

the other is protected with the triisopropylsilyl (TIPS) unit. Hagihara coupling^{56,57} of this compound with *cis*-Pt-(PBu₃)₂Cl₂ in refluxing diethylamine afforded 3 in a 58% overall yield from 1. Complex 3 was then subjected to Hagihara coupling with compound 2b, which contains a free ethynyl group and one protected with the HOM group. This reaction affords the orthogonally protected complex 6a in 60% yield. This organometallic intermediate is a key building block toward the synthesis of the longer oligomers. First, either of the acetylene protecting groups (HOM or TIPS) can be selectively removed. Moreover, the complex is very soluble in nonpolar solvents, and it can be easily separated by silica chromatography from less polar impurities because the polar HOM unit causes the complex to adsorb more strongly to the support, increasing its retention time on a column. Finally, removal of the HOM protecting group from 6a produces 6b, which was coupled with *cis*-Pt(PBu₃)₂Cl₂ to afford the TIPSprotected synthon 7 in an 89% yield.

Synthesis of the shorter oligomers **11** and **12** was relatively straightforward and consequently did not require synthon **7** (Scheme 2). The end-capped dimer Pt_2NDI_2 (**11** in Scheme 2) was prepared by the copper(I)-catalyzed Hagihara coupling of known compounds **8**⁵⁸ and **10**.²⁵ The end-capped trimer Pt_3NDI_2 (**12** in Scheme 2) was prepared by coupling known complex **5**¹⁶ with the end-cap synthon **9**. The latter was prepared by Hagihara coupling of *cis*-Pt(PBu₃)₂Cl₂ with **8**.

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Scheme 3^a



^a (a) 7, THF/Et₂NH, cat. CuI, rt, 4 h; (b) TBAF, THF, rt, 1 h; (c) 9, THF/Et₂NH, cat. CuI, rt, 3 h.

As outlined in Scheme 3, synthons 7 and 9 were used to allow rapid construction of the longer end-capped oligomers Pt_6NDI_2 and $Pt_{10}NDI_2$ (15 and 17 in Scheme 3). Both endcapped oligomers were synthesized via tetramer 14a, which was produced in high yield by coupling 2 equiv of synthon 7 with diethynylbenzene. Removal of the TIPS protecting groups in 14a using TBAF followed by coupling of the resulting deprotected tetramer 14b with NDI end-cap 9 afforded Pt_6NDI_2 . Finally, the end-capped decamer $Pt_{10}NDI_2$ was synthesized in a sequence beginning with copper(I)-catalyzed coupling of 14b with synthon 7 to yield octamer 16a. The TIPS protecting groups were then removed from 16a with TBAF, and the resulting deprotected octamer (16b) was coupled with NDI end-cap 9 to afford the decamer $Pt_{10}NDI_2$.

³¹P NMR Characterization. The structures of the oligomers were confirmed by ¹H NMR, ³¹P NMR, and elemental analysis (see Experimental Section for details). The ³¹P NMR spectra of the oligomers are especially revealing as to their structures (Figure 1). For each oligomer, the ³¹P spectra appear as a pattern of three resonances centered at $\delta \approx 4$ ppm; a weak "doublet" with $J \approx 2350$ Hz that arises from ¹⁹⁵Pt-³¹P coupling, and a central resonance that is due to PtP₂ units with NMR-silent Pt isotopes (for the trimer, hexamer, and decamer each of the three individual resonance peaks is split as discussed below). The magnitude of the ¹⁹⁵Pt-³¹P coupling constant confirms the *trans* stereochemistry of the PtP₂ units.⁵⁹

Now, to discuss the pattern of splitting that results from the oligomer structures, we focus attention on the central resonance ($\delta \approx 4$ ppm), which is shown expanded in the insets in Figure 1. First, as shown in Figure 1a, for Pt₂NDI₂ the central resonance is a singlet, consistent with the fact that the two PtP₂ centers are equivalent in the dimer. By contrast, for the trimer, Pt₃NDI₂ (Figure 1b), the center resonance appears as two closely spaced singlets with the downfield: upfield ratio of 2:1. The splitting results from the fact that there are two chemically inequivalent sets of phosphines in the oligomer, those on the terminal PtP₂ units and those on the central PtP₂ unit. On the basis of the ratios, we conclude that the resonance for the terminal PtP₂ units is downfield by ca. 0.2 ppm relative to that for the central PtP_2 . The downfield shift for the terminal PtP₂ units may arise due to the electron-withdrawing effect of the NDI unit, which is a relatively strong π -acceptor. Interestingly, for the hexamer, Pt₆NDI₂ (Figure 1c), the center resonance also appears as two closely spaced singlets, but in this case the downfield: upfield ratio is 1:2, which is opposite from that for the trimer. This spectrum is entirely consistent with the structure of the hexamer, which features two terminal PtP2 units and four central PtP₂ units: on the basis of the structure we would predict the ratio of the terminal and central resonance peaks to be 1:2. Finally, a similar pattern is observed in the spectrum of the decamer, $Pt_{10}NDI_2$, where the downfield peak due to the terminal PtP₂ units is considerably weaker compared to the upfield signal due to the central PtPt₂ units. While we are unable to report the numerical integration values for the two signals, inspection of the expanded spectrum in Figure 1d indicates that the downfield:upfield peak ratio is in qualitative agreement with the 1:4 ratio expected on the basis of the oligomer's structure.

Electrochemistry. The objective of the synthesis of the NDI end-capped platinum acetylide oligomers is to use them to investigate charge and exciton transport in π -conjugated organometallic systems. In order to understand the properties of the excited and charged states of these systems, it is essential to have information concerning the accessible redox states. Thus, to obtain information regarding the redox states, cyclic voltammetry was carried out on the simplest member of the series, Pt₂NDI₂. As shown in Figure 2, the cyclic voltammagram of Pt2NDI2 features two quasi-reversible cathodic waves with $E_{1/2} = -0.65 \text{ V} (\Delta E_p = 92 \text{ mV})$ and $-1.05 \text{ V} (\Delta E_p = 46 \text{ mV})$, along with a single quasi-reversible anodic wave at $E_{1/2} = 0.89$ V ($\Delta E_p = 126$ mV) (potentials vs SCE). The cathodic waves are due to sequential one-electron reduction of the two NDI end-groups. Note that each cathodic wave likely corresponds to simultaneous one-electron reduction of both of the NDI units, for example for the first wave at $E_{1/2} = -0.65$ V: NDI-Pt₂-NDI + 2e⁻ \rightarrow (NDI^{-•}- Pt_2 -NDI^{-•})²⁻. This assignment is supported by a number of previous studies of the NDI unit (including a study of a

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Figure 1. ³¹P NMR spectra for the Pt_nNDI_2 series: (a) n = 2;

(b) n = 3; (c) n = 6; (d) n = 10.

platinum acetylide complex that contains NDI units), which demonstrate that the NDI electrophore is reduced in two sequential one-electron processes at potentials in the range -0.6 and -0.8 V vs SCE.^{52,53,58} The anodic wave observed for Pt₂NDI₂ is assigned to one-electron oxidation of an electrophore consisting of the platinum acetylide unit, [-Pt-(PBu₃)₂-C=C-Ph-C=C-Pt(PBu₃)₂-]. This assignment is supported by our recent work on the electrochemical properties of the model complex Pt-2 and a series of platinum acetylide oligomers with a repeat unit structure [-Pt-(PBu₃)₂-C=C-Ph-C=C-]_n.²⁵ This study showed that Pt-2 exhibits a one-electron oxidation at $E_{1/2} = 0.89$ V, while the longer oligomers display similar waves at slightly less anodic potentials.

Absorption and Photoluminescence Spectroscopy. The UV-visible absorption spectra of the series of Pt_nNDI_2 oligomers were recorded in THF, and the spectra are illustrated in the left panel of Figure 3. Each of the complexes absorbs strongly in the near-UV region, with the molar absorptivity increasing with chain length to a maximum of nearly 800 000 M^{-1} cm⁻¹ for the decamer. The near-UV absorption arises from π,π^* transitions localized on the platinum acetylide chain and on the NDI end-groups (both chromophores absorb in the 340-370 nm region). Close inspection of the spectra shows that the shape of the near-UV absorption varies with chain length. In particular, for the dimer and trimer, there are two well-defined absorption band maxima at ca. 360 and 375 nm; however, for the hexamer and decamer the band sharpens and only a single band maximum is seen at 370 nm. This variation arises because the relative contribution of the platinum acetylide chain and NDI chromophores varies across the series. In particular, for the shorter oligomers, the absorption is



Figure 2. Cyclic voltammagram of Pt_2NDI_2 in methylene chloride with 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) as electrolyte, vs SCE.

dominated by π,π^* transitions localized on the NDI endgroup chromophore. The absorption of the NDI chromophore features a pronounced vibronic progression with maxima at 360 and 380 nm,⁵² and these bands are clearly resolved in the Pt₂NDI₂ spectrum. As the length of the platinum acetylide chain increases, the near-UV absorption is increasingly dominated by the long-axis polarized π,π^* transition localized on the organometallic conjugated segment. For the decamer, the near-UV absorption consists of ca. 85% absorption on the platinum acetylide chain, with 15% or less of the oscillator strength on the NDI end-groups. Note that there is a series of weaker, transitions at higher energy that become more prominent in the longer oligomers; these transitions have been previously assigned as arising from short-axis polarized π,π^* transitions on the platinum acetylide chain.^{16,60}

Considerable insight into the excited-state dynamics of the NDI end-capped oligomers comes from photoluminescence spectroscopy. The right panel of Figure 3 compares the emission of the Pt_nNDI_2 series with the emission of the model complex, Pt-2. The spectra were obtained for degassed solutions, and the intensities are normalized to reflect the relative emission quantum yields. First, for Pt-2 the emission is dominated by a structured band with $\lambda_{max} = 519$ nm with a vibronic shoulder at lower energy. This emission is observed for all platinum acetylide oligomers with the repeat unit structure $[-Pt(PBu_3)_2-C \equiv C-Ph-C \equiv C-]$ and its phosphorescence arising from the triplet excited state (exciton). In previous studies we have shown that the phosphorescence energy is invariant with oligomer chain length, a fact that suggests that for longer oligomers the triplet exciton is spatially confined to a relatively short chain segment.^{16,18} The remarkable feature is that the phosphorescence is hardly observed for any of the Pt_nNDI₂ oligomers, a result that clearly indicates that there is a nonradiative pathway available that very effectively quenches the triplet exciton before it is able to phosphorescence. Emission quantum yield studies show that the quenching of the platinum acetylide phosphorescence is nearly quantitative, with the quantum yields for the NDI end-capped oligomers in the range $\Phi_{\rm P} \approx 0.1 - 0.2\%$ compared to the yield of Pt-2, which has $\Phi_P \approx 5\%$.¹⁶

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Figure 3. UV-visible absorption (left) and steady-state emission (right) spectra of Pt_nNDI_2 series in degassed THF at 298 K. The legend is shown in the left panel.

The electrochemical studies on Pt_2NDI_2 provide insight concerning the mechanism for the triplet exciton quenching. In particular, on the basis of the cyclic voltammetry studies we conclude that a charge-separated state in which one NDI acceptor is reduced and the platinum acetylide chain is oxidized, e.g., NDI-[-(Pt(PBu_3)_2-C=C-Ph-C=C-)^{+•}]-NDI^{-•}, lies at ca. 1.55 eV relative to the ground state. (The charge transfer state energy is estimated by taking the difference in the oxidation and reduction potentials of Pt_2NDI_2 .)⁶¹ This charge transfer state lies well below the energy of the triplet exciton state, which lies at ca. 2.4 eV, as estimated from the band maximum of the phosphorescence. Thus, we conclude that the triplet quenching arises from rapid intramolecular photoinduced electron transfer,

$$NDI - [-^{3}(Pt(PBu_{3})_{2} - CC - Ph - CC -)^{*}] - NDI \rightarrow \\NDI - [-(Pt(PBu_{3})_{2} - CC - Ph - CC - -^{+\bullet})]NDI^{-\bullet}$$

which is much faster compared to radiative decay of the triplet exciton. In a forthcoming article we will provide details of picosecond transient absorption spectroscopy experiments that confirm that this process occurs and that also provide significant insight concerning the dynamics of triplet exciton diffusion within the longer platinum acetylide oligomers.

Summary and Conclusions

We have successfully developed an iterative-convergent synthetic method to prepare a series of monodisperse platinum acetylide oligomers that contain as many as 10 repeat units. The oligomers are end-functionalized with naphthalene diimide electron acceptors for use in studies of exciton and electron transport. The iterative-convergent synthetic approach uses organometallic synthons that feature either (or both) HOM or TIPS as protecting groups for the terminal acetylene moieties. These protecting groups are orthogonal: they are removed under different conditions in high synthetic yields, affording monofunctional synthons that can be used in subsequent iterative react-deprotect sequences to construct the longer oligomers. In addition to serving as a protecting group, the polar nature of the HOM unit also has the benefit of facilitating the chromatographic separations. In particular, oligomers that are end-functionalized with the HOM group elute more slowly on silica gel columns compared to the (less polar) reaction byproduct and oligomers that contain only the TIPS protecting groups.

Precedence for the use of the HOM and TIPS as orthogonal protecting groups in synthesis of oligomers comes from the work of Godt et al.;³² this group demonstrated the strategy in the synthesis of phenylene ethynylene oligomers with nine repeat units. There have been many reports involving the synthesis of monodisperse Pt-acetylide materials, some including use of a silyl-protected Pt-acetylides.^{41,42,44,49,62–73} Takahashi et al.³⁸ used a TIPS-protected terminal acetylene organometallic intermediate in a platinum acetylide dendrimer synthesis that was carried out through four generations. However, prior to the present report we are unaware of the incorporation of both of these orthogonal acetylene protecting groups in organometallic intermediates toward the synthesis of organometallic oligomers.

In ongoing physical experiments we are exploring the dynamics of triplet exciton and negative polaron diffusion along the NDI end-capped platinum acetylide oligomers using time-resolved laser photolysis and pulse radiolysis methods. Preliminary analysis of the results of these studies indicate that transport along the platinum acetylide chains occurs via a hopping mechanism, consistent with diffusion of spatially confined exciton and polaron states. The results of this work will be reported in a forthcoming paper.

Experimental Section

Materials and Instruments. All solvents and chemicals used for synthesis of the platinum acetylide oligomers were reagent grade and used without purification unless noted. Silica gel

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(Silicycle Inc., 230–400 mesh, 40–63 μ m, 60 Å) was used for all flash chromatography. All silyl-acetylene starting materials were purchased from GFS Chemical; potassium tetrachloroplatinate and palladium-bis(triphenylphosphyl) dichloride were purchased from Strem Chemicals; all other chemicals were purchased from Sigma-Aldrich. ¹H and ³¹P NMR spectra were obtained on a Varian 300 MHz spectrometer using deuterated chloroform (CDCl₃) as the solvent and tetramethylsilane (TMS) as the internal reference. Elemental analysis was performed at Robertson Microlit Laboratories for all of the final oligomers. Decomposition temperatures were also estimated for all oligomers synthesized using a standard Melt-temp apparatus. All newly synthesized intermediates were characterized by TOF-MS and elemental analysis.

Cyclic voltammetry experiments were performed in dry methylene chloride (CH₂Cl₂) solution containing 0.1 M tetra*n*-butylammonimum hexafluorophosphate (TBAH) as the supporting electrolyte. The three-electrode setup consisted of a platinum microdisc (2 mm^2) working electrode, a platinum wire auxiliary electrode, and a silver wire reference electrode. Solutions were degassed with argon flow prior to measurements, maintaining positive argon pressure during the measurements. The concentrations of oligomers in the solutions were 1 mM. A scan rate of 100 mV/s was used. All potentials were internally calibrated against the ferrocene/ferricinium couple (E = 0.43 V vs SCE in CH₂Cl₂) and potentials plotted vs SCE.

Steady-state absorption spectra were recorded on a Varian Cary 100 dual-beam spectrophotometer. Corrected steady-state emission measurements were conducted on a SPEX F-112 fluorescence spectrometer. Samples were degassed by argon purging for 30 min, and concentrations were adjusted to produce "optically dilute" solutions (i.e., $A_{max} < 0.20$) in THF. Quantum yields were calculated using Ru(byp)₃Cl₂ as a known reference.⁷⁴

Synthesis. Pt₂NDI₂ (11). To a 50 mL flask with stir bar were added 8 (60 mg, 0.13 mmol), 10 (80 mg, 0.06 mmol), THF (3.5 mL), and diethylamine (2 mL). The solution was stirred and degassed with argon for 30 min, followed by the addition of CuI (3 mg) under argon flow. The reaction was stirred at room temperature for 1.5 h. The orange-brown reaction mixture was diluted with CH₂Cl₂, then washed with deionized water and brine, and dried over NaSO₄(s). Evaporation of the organic solvent gave a crude dark green solid. The product was purified by flash chromatography (silica gel, 1:1 hexane/CH₂Cl₂, then 5:2:1 CH₂Cl₂/CHCl₃/hexane) to elute the product as the second fraction. Solvent was evaporated to give the product as a dark green solid. Residual acetone proved difficult to remove. Yield = 90 mg (69.4%). Decomposition temperature: 197–199 °C. ¹H NMR (300 MHz, CDCl₃): δ 0.90 (m, 42H), 1.20-1.80 (br m, 72H), 2.15 (br m, 24H), 4.20 (t, 4H), 7.15 (d, 8H), 7.42 (d, 4H), 8.80 (s, 8H). ³¹P NMR (CDCl₃): δ 4.27 (J_{Pt-P} =2354.33 Hz). MS (MALDI-TOF): calcd for C₁₁₈H₁₂₆N₄O₈P₄Pt₂ [M⁺] 2278.07, found [M⁺] 2278.06. Anal. Calcd for C₁₁₈H₁₂₆N₄O₈P₄Pt₂: C, 62.20; H, 7.17; N, 2.46. Found: C, 62.40; H, 7.22; N, 2.27.

Pt₃NDI₂ (12). To a 50 mL round-bottom flask equipped with a stir bar were added **5** (76 mg, 89.9 μ mol), **9** (220 mg, 0.20 mmol), HNEt₂ (5 mL), and THF (3 mL). The solution was degassed under argon for 10 min, followed by the addition of CuI (~1 mg) to the solution. The reaction was stirred under argon for 2 h. In this time, the mixture turned from a light orange color to a dark orange-brown color. TLC (silica, 1:1 hexane/CH₂Cl₂) revealed a complete consumption of the starting materials. The solution was diluted with CH₂Cl₂ and washed with both deionized water and brine. The organic layer was

dried over NaSO₄(s), and the solvent was removed to give a dark green solid, which was purified by flash chromatography (silica gel, 1:1:0 to 1:1:(1%) hexane/CH₂Cl₂/(acetone)). Fraction 2 moved as a dark orange band down the column; solvent was removed to afford a green solid product. Yield: 290 mg (49%). Decomposition temp: 216–217 °C. ¹H NMR (300 MHz, CDCl₃): δ 0.8–1.1 (br m, 62H), 1.1–1.8 (br m, 96H), 2.08 (br m, 36H), 4.20 (t, 4H), 7.1 (br m, 12H), 7.41 (d, 4H), 8.80 (s, 8H). ³¹P NMR (CDCl₃): δ 4.2 (*J*_{Pt-P} = 2355.49 Hz), 4.0 (*J*_{Pt-P} = 2363.43 Hz). Anal. Calcd for C₁₅₂H₂₂₀N₄O₈P₆Pt₃: C, 60.81; H, 7.39; N, 1.87. Found: C, 60.62; H, 7.40; N, 1.78.

Pt₆NDI₂ (15). To a 50 mL round-bottom flask with a stir bar were added 9 (163 mg, 146 µmol), 14b (200 mg, 66 µmol), THF (5 mL), and HNEt₂ (5 mL). The solution was degassed with argon for 5 min, followed by the addition of CuI (2 mg). Within 2 min the reaction turned a dark orange color and became somewhat opaque with salt formation. After 3 h, the reaction was quenched with deionized H_2O , diluted with CH₂Cl₂, and washed twice with brine. The organic layer was dried over NaSO₄(s) and then the solvent removed to give a crude green-brown solid. The product was purified by flash chromatography (silica gel, 2:1 CHCl₃/hexane), eluting the product as a red band down the column. Solvent was removed from this fraction to afford a dark green solid product, although some residual hexane proved difficult to remove. Yield: 170 mg (50.1%). Decomposition temp $> 400 \,^{\circ}\text{C}$. ¹H NMR (300 MHz, CDCl₃): $\delta 0.90 \,(\text{m}, 114\text{H}) \, 1.2 -$ 1.7 (br m, 158H), 2.15 (br m, 72H), 4.20 (t, 4H), 7.0-7.2 (m, 24H), 7.42 (d, 4H), 8.8 (s, 8H). ³¹P NMR (CDCl₃): δ 4.04 $(J_{Pt-P} = 2365.3 \text{ Hz}), 4.28 (J_{Pt-P} = 2356.1 \text{ Hz}).$ Anal. Calcd for C₂₅₄H₃₉₄N₄O₈P₁₂Pt₆: C, 58.96; H, 7.68; N, 1.08. Found: C, 58.78; H, 8.00; N, 0.98.

Pt10NDI2 (17). To a 25 mL round-bottom flask with a stir bar were added **16b** (400 mg, 65.9 µmol), **9** (161 mg, 145.2 µmol), HNEt₂ (8 mL), and THF (8 mL). The solution was degassed under argon for 10 min, followed by the addition of CuI $(\sim 1 \text{ mg})$. The reaction was stirred at room temperature under argon for 4 h. After this time, the solution was diluted with CH₂Cl₂ and washed with both deionized water and brine. The organic layer was dried over $NaSO_4(s)$, and then the solvent was evaporated to give a dark green crude solid. The product mixture was purified by flash chromatography (silica gel, 2:1:(1%) to 3:1:(1%) to 5:1:(1%) CH₂Cl₂/hexane/ (MeOH)). Fractions 1 and 2 (both yellow color) were degraded starting materials. Fraction 3 (dark orange band) was eluted, samples were collected, and solvent was evaporated to afford a dark green solid as product. Yield: 240 mg (45.0%). Decomposition temp > 400 °C. ¹H NMR (300 MHz, CDCl₃): δ 0.95 (m, 186H), 1.1–1.9 (br m, 264H), 2.15 (br s, 120H), 4.20 (br t, 4H), 7.13 (br m, 40H), 7.45 (br d, 4H), 8.80 (s, 8H). ³¹P NMR (CDCl₃): δ 4.0 (J_{Pt-P} = 2365.26 Hz), 4.2 (J_{Pt-P} = 2365 Hz). Anal. Calcd for C₃₉₀H₆₂₆N₄O₈P₂₀Pt₁₀: C, 58.05; H, 7.82; N, 0.69. Found: C, 57.98; H 7.68; N, 0.72.

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Supporting Information Available: The synthesis and characterization of intermediate compounds 1-10, 13, 14, 16a, and 16b, as well as a CV scan of a Pt_2NDI_2 /ferrocene mixture, is provided. This material is available free of charge via the Internet at http://pubs.acs.org.

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