Self-assembly of alkynylplatinum(II) terpyridine amphiphiles into nanostructures via steric control and metal–metal interactions

Sammual Yu-Lut Leung*, Keith Man-Chung Wong*1, and Vivian Wing-Wah Yam*2

*Institute of Molecular Functional Materials (Areas of Excellence Scheme, University Grants Committee, Hong Kong) and Department of Chemistry, The University of Hong Kong, Hong Kong, People’s Republic of China

Contributed by Vivian Wing-Wah Yam, February 2, 2016 (sent for review December 31, 2015; reviewed by Harry B. Gray and Peter J. Stang)

A series of mono- and dinuclear alkynylplatinum(II) terpyridine complexes containing the hydrophilic oligo(para-phenylene ethynylene) with two 3,6,9-trioxadec-1-yloxy chains was designed and synthesized. The mononuclear alkynylplatinum(II) terpyridine complex was found to display a very strong tendency toward the formation of supramolecular structures. Interestingly, additional end-capping with another platinum(II) terpyridine moiety of various steric bulk at the terminal alkyne would lead to the formation of nanotubes or helical ribbons. These desirable nanostructures were found to be governed by the steric bulk on the platinum(II) terpyridine moieties, which modulates the directional metal–metal interactions and controls the formation of nanotubes or helical ribbons. Detailed analysis of temperature-dependent UV-visible absorption spectra of the nanostructured tubular aggregates also provided insights into the assembly mechanism and showed the role of metal–metal interactions in the cooperative supramolecular polymerization of the amphiphilic platinum(II) complexes.

noncovalent interactions | platinum complex | nanoaggregates

Square-planar $d^8$ platinum(II) poly(pyridine) complexes have long been known to exhibit intriguing spectroscopic and luminescence properties (1–54) as well as interesting solid-state polymorphism associated with metal–metal and π–π stacking interactions (1–14, 25). Earlier work by our group showed the first example, to our knowledge, of an alkynylplatinum(II) terpyridine system $[\text{Pt} (\text{tpy})(\text{C} \equiv \text{CR})(\text{C})]_n$ that incorporates π-donating and solubilizing alkynyl ligands together with the formation of Pt···Pt interactions to exhibit notable color changes and luminescence enhancements on solvent composition change (25) and polyelectrolyte addition (26). This approach has provided access to the alkynylplatinum(II) terpyridine and other related cyclometalated platinum(II) complexes, with functionalities that can self-assemble into metalloogs (27–31), liquid crystals (32, 33), and other different molecular architectures, such as hairpin conformation (34), helices (35–38), nanostructures (39–45), and molecular tweezers (46, 47), as well as having a wide range of applications in molecular recognition (48–52), biomolecular labeling (48–52), and materials science (53, 54). Recently, metal-containing amphiphiles have also emerged as a building block for supramolecular architectures (42–44, 55–59). Their self-assembly has always been found to yield different molecular architectures with unprecedented complexity through the multiple noncovalent interactions on the introduction of external stimuli (42–44, 55–59). Helical architecture is one of the most exciting self-assembled morphologies because of the uniqueness for the functional and topological properties (60–69). Helical ribbons composed of amphiphiles, such as diacetylenic lipids, glutamates, and peptide-based amphiphiles, are often precursors for the growth of tubular structures on an increase in the width or the merging of the edges of ribbons (64, 65). Recently, the optimization of nanotube formation vs. helical nanostructures has aroused considerable interests and can be achieved through a fine interplay of the influence on the amphiphilic property of molecules (66), choice of counteranions (67, 68), or pH values of the media (69), which would govern the self-assembly of molecules into desirable aggregates of helical ribbons or nanotube scaffolds. However, a precise control of supramolecular morphology between helical ribbons and nanotubes remains challenging, particularly for the polycyclic aromatics in the field of molecular assembly (64–69). Oligo(para-phenylene ethynylene)s (OPEs) with solely π–π stacking interactions are well-recognized to self-assemble into supramolecular system of various nanostructures but rarely result in the formation of tubular scaffolds (70–73). In view of the rich photophysical properties of square-planar $d^8$ platinum(II) systems and their propensity toward formation of directional Pt···Pt interactions in distinctive morphologies (27–31, 39–45), it is anticipated that such directional and noncovalent metal–metal interactions might be capable of directing or dictating molecular ordering and alignment to give desirable nanostructures of helical ribbons or nanotubes in a precise and controllable manner.

Herein, we report the design and synthesis of mono- and dinuclear alkynylplatinum(II) terpyridine complexes containing hydrophilic OPEs with two 3,6,9-trioxadec-1-yloxy chains. The mononuclear alkynylplatinum(II) terpyridine complex with

Author contributions: V.W.-W.Y. designed research; S.Y.-L.L. performed research; S.Y.-L.L., K.M.-C.W., and V.W.-W.Y. analyzed data; and S.Y.-L.L., K.M.-C.W., and V.W.-W.Y. wrote the paper.

Reviewers: H.B.G., California Institute of Technology; and P.J.S., University of Utah. The authors declare no conflict of interest.

Data deposition: The atomic coordinates and structure factors have been deposited in the Cambridge Structural Database, Cambridge Crystallographic Data Centre (https://summary.ccdc.cam.ac.uk/structure-summary-form; CSD reference no. CCDC 1948820).

*Present address: Department of Chemistry, South University of Science and Technology of China, Shenzhen 518055, People’s Republic of China.

*To whom correspondence should be addressed. Email: wyyam@hku.hk.

This article contains supporting information online at www.pnas.org/lookup/suppl/doi:10.1073/pnas.1601673113/-/DCSupplemental.
amphiphilic property is found to show a strong tendency toward the formation of supramolecular structures on diffusion of diethyl ether in dichloromethane or dimethyl sulfoxide (DMSO) solution. Interestingly, additional end-capping with another platinum(II) terpyridine moiety of various steric bulk at the terminal alkyne would result in nanotubes or helical ribbons in the self-assembly process. To the best of our knowledge, this finding represents the first example of the steric bulk of the moieties, which modulates the formation of directional metal–metal interactions to precisely control the formation of nanotubes or helical ribbons in the self-assembly process. Application of the nucleation–elongation model into this assembly process by UV-visible (UV-vis) absorption spectroscopic studies has elucidated the nature of the molecular self-assembly, and more importantly, it has revealed the role of metal–metal interactions in the formation of these two types of nanostructures.

Results and Discussion

The mono- and dinuclear alkynylplatinum(II) terpyridine complexes were synthesized by reacting OPE-derived alkynes, prepared by Sonogashira coupling reactions (SI Materials and Methods), with the corresponding platinum(II) precursor complexes in 1:1 and 1:2 ratios, respectively, in degassed dimethylformamide (DMF) containing triethylamine in the presence of a catalytic amount of copper(I) iodide at room temperature. Purification by column chromatography on silica gel using dichloromethane:acetone mixture (10:1 vol/vol) as eluent gave complexes 1–5 (Fig. 1). Diffusion of diethyl ether vapor into dichloromethane solutions of the respective complexes gave clear red gels for complex 1 and dark red powders to yellow crystalline solids for 2–5. All complexes have been well-characterized by the $^1$H and $^{13}$C($^1$H) nuclear magnetic resonance (NMR) and infrared (IR) spectroscopy, electrospray ionization mass spectrometry (ESI-MS), and elemental analyses. The crystal structure of 4 has been determined by X-ray crystallography.

In the 1D 1H NMR experiment at 298 K, mononuclear complex 1 gives almost featureless NMR spectrum in DMSO-$d_6$, whereas dinuclear complexes 2 and 3 show poorly resolved signals under the same conditions (Fig. S1 A–C). After the temperature is increased to 350 K, both signals become dramatically sharpened and well-resolved, with signals corresponding to protons on the terpyridine and OPE moieties shifted back to their typical downfield region (Fig. S1 A–C). The upfield shift and broadening of the proton resonances at room temperature are ascribed to the intermolecular self-assembly through π–π stacking interactions from terpyridines and conjugated OPE units. The completely featureless NMR pattern of 1 in the aromatic region at 298 K compared with those poorly resolved signals of dinuclear complexes 2 and 3 is suggestive of the presence of a higher degree of aggregation for 1 in DMSO-$d_6$. The NMR spectra suggest that the amphiphilic alkynylplatinum(II) terpyridine complexes (1–3) bearing two long hydrophobic alkox (C$_{3}$H$_{6}$O$_{2}$–) and two 3,6,9-trioxadec-1-ylxoy chains would undergo intermolecular aggregation through π–π stacking interactions, in which complex 1 aggregates to a greater extent in DMSO. In sharp contrast, 4 and 5 end-capped with symmetric terpyridine ligands of tert-buty group show well-defined signals at room temperature (Fig. S1D) and have a negligible effect on the spectral patterns on an increase in temperature. The sharp NMR signals suggest that the sterically bulky tert-buty groups at both ends can effectively suppress π–π stacking interactions for this kind of rod-shaped alkynylplatinum(II) terpyridine complex, minimizing molecular aggregation.

The effect of bulky tert-buty groups on π–π stacking interactions can further be supported by X-ray crystallography. Fig. 2A depicts the perspective view of the complex cation of 4. The two platinum(II) terpyridine termini are essentially coplanar and slightly twisted with respect to the OPE moiety, with interplanar angles of 9.41°. Selected bond lengths and bond angles of 4 are collected in Table S1. Interestingly, the planarity of the system between the platinum(II) terpyridine termini and the OPE moiety has manifested the structural feature of the extended π-conjugation as a rigid rod-like complex in the crystal state. In addition, no significant Pt–Pt and π–π stacking interactions are observed from the crystal packing (Fig. 2B), because the interplanar distance between the dimeric structures is found to be 3.81 Å. The interplanar distance suggests that the presence of the sterically bulky tert-buty groups on the terpyridine ligands at both termini effectively hinders the two complex cations from coming into close proximity in the crystal state.

As revealed from the NMR experiments, incorporation of the second platinum(II) terpyridine moiety on the other terminus of the alkyne as well as introduction of substituents on the terpyridine ligands would lead to different degrees of aggregation. To gain a deeper insight into the assembly of amphiphiles (1–3), the self-assembled structures are examined by using EMs. Samples of the clean red gels of complex 1 prepared from slow
diffusion of diethyl ether into dichloromethane solution (Fig. S2A) exhibit an irregular network of molecular tapes characteristic of platinum(II)-containing metallogels (28–31), with widths ranging from ∼50 to 100 nm in the transmission EM (TEM) and SEM images (Fig. S2 B and C). The DMSO solution of this complex would also show an opaque red gel (Fig. S2D), in which a network of fibrous structures with widths in the range of ∼15–30 nm is observed (Fig. S2 E and F). Examination by powder X-ray diffraction (XRD) analysis on I shows the characteristic lamellar packing of the individual molecules in the self-assembled structure with d spacings of 3.60, 1.78, and 0.91 nm in a ratio of ∼4:2:1 (Fig. S2G). These supramolecular structures might be constructed from the multiple layers of complex 1 in a lamellar fashion, leading to these largely random networks of aggregates. In addition, it is worthwhile to note that the peak at 2θ = 25.80° (d spacing = 0.34 nm) is attributed to intermolecular π−π and Pt⋯Pt stacking interactions between the adjacent Pt(II) complexes in the aggregate species (74, 75).

Notably, in sharp contrast, such a largely random network of aggregates could not be found in the dinuclear complexes 2 and 3, which have nanoaggregates in deep red and yellow DMSO solutions, respectively (Fig. 3A). The nanoaggregates of 2 encaped with the unsubstituted terpyridine ligand in DMSO solution have been studied on different surfaces. Interestingly, straight and monodispersed nanotubes with a very uniform diameter of ∼13.0 nm are observed on both carbon-coated copper grids (Fig. 3B) and lacy-carbon-coated grids (Fig. 3C) in TEM images. The tubular architecture can be clearly observed to be of a lower contrast in the interior region and a higher one in the wall region with micrometers in length. The wall is estimated to be ∼4.0-nm thick and results in an internal tube diameter of ∼5.0 nm. Other representative TEM images of the monodispersed nanotubes are provided in SI Materials and Methods (Fig. S3 A and B). The presence of cylindrical and straight nanotubes on the copper grid has been further confirmed by SEM, with nanotubes clearly displaying a uniform diameter of ∼13.0 nm and lengths of 2.0–5.5 μm, respectively, in the SEM images (Fig. 3D). Similar nanotube architecture could also be evidenced by atomic force micrograph (AFM) study on silica wafers (Fig. 3E and Fig. S3 C and D). The height of the tubular nanostructure is found to be only ∼4.0 nm in AFM study, with a width of ∼100 nm (Fig. 3E and Fig. S3 C and D, Lower), indicating a flattened structure on the silica wafers. An independent SEM study of the nanostructures on silica wafers also showed a flattened structure, possibly caused by the interaction between the soft materials and the surfaces.] Dynamic light scattering (DLS) measurements on 2 have also been made to confirm the presence of discrete nanostructures with hydrodynamic diameters of ∼1.19 μm in the DMSO media (Fig. S4). Examinations by small- and wide-angle XRD with synchrotron radiation source have been performed on 2. In the small-angle XRD (Fig. 4A), there is a strong scattering signal at q = 0.63 nm⁻¹, which corresponds to a d spacing of 9.94 nm (76). The molecular length of complex 2 with aliphatic tails in an all-trans configuration is estimated to be ∼6.33 nm. The first d spacing (9.94 nm) is found to satisfy l < d < 2l, where l is the fully extended length of the complex (∼6.33 nm). Thus, it indicates the formation of a partially interdigitated structure in the molecular packing. In addition, the d spacings of 9.94, 5.02, and 2.49 nm in a ratio of ∼4:2:1 are observed in the XRD patterns (Fig. 4 A and B), characteristic of the formation of lamellar packing for the partially interdigitated structures. It is also worthwhile to note that the peak at 2θ = 26.10° (d spacing = 0.34 nm) (Fig. 4B) is indicative of the presence of periodical π−π and Pt⋯Pt stacking interactions in the solid state of the self-assembled materials. Therefore, it is believed that the wall of the nanotubes is constructed from complexes with partially interdigitated hydrocarbon chains. They would adopt a lamellar packing with formation of π−π and Pt⋯Pt stacking interactions, leading to long and straight tubular architectures, which is schematically depicted in Fig. 4C.

In stark contrast to 2, the TEM images of 3 with bulky substituents on one of the terminal terpyridines show helical ribbons with a very uniform diameter of ∼9.5 nm self-assembled into lengths of 0.7–2.1 μm (Fig. 5). It is also found that the single ribbons with the same diameter would entangle to form a double strand of ribbons at different magnifications on the carbon-coated copper grids (Fig. 5 B and C). Other representative TEM images for these two types of helical ribbons

---

**Fig. 3.** (A) Photograph of 2 ([Pt] = 256 μM) and 3 ([Pt] = 280 μM) in DMSO at room temperature. TEM images of 2 at 256 μM prepared from DMSO solution on (B) carbon-coated copper grids and (C) lacy carbon-coated grids. (D) SEM image of 2 at 864 μM prepared from DMSO solution on copper grid. (E, Upper) Tapping mode AFM image of 2 showing straight and monodispersed aggregates on the silica wafers. (E, Lower) Height profile obtained along the red line.

**Fig. 4.** (A) Small- and (B) wide-angle XRD patterns by the synchrotron radiation source on the bulk sample of 2. Numerical values indicate d spacings (nanometers). (C) Schematic representation of the self-assembled complex 2 to form the wall of the nanotubes.

---

Leung et al.
are provided in SI Materials and Methods (Fig. S5 A and B). Subsequent AFM study on 3 has also been used to confirm the presence of well-defined helical ribbons with heights of ~4.0–9.5 nm as shown in Fig. S5C. DLS measurements on 3 have also revealed the presence of discrete aggregates with hydrodynamic diameters of ~0.93 μm, comparable with those of the nanotubes in DMSO media (Fig. S4B). The observed diameter of the helical ribbons in the TEM image (~9.5 nm) is much longer than the estimated molecular length of 3 with fully extended aliphatic tails in an all-trans configuration (~6.5 nm). Therefore, it is likely that the nanostructures are associated with two complexes forming an interdigitated morphology, in line with the strong hydrophobic–hydrophobic interactions between aliphatic tails in DMSO medium.

The distinctive morphologies of 1–3 have prompted us to study their self-assembly behavior using UV-vis absorption spectroscopy. At 326 K, the UV-vis absorption spectrum of 1 in DMSO solution ([Pt] = 843 μM) shows intense intraligand π→π* transitions of the terpyridine and alkynyl ligands at ~332–387 nm together with a low-energy absorption at ~479 nm, which is assigned as metal-to-ligand charge transfer [dn(Pt)→π*(tpy)] transition mixed with alkynyl-terpyridine ligand-to-ligand charge transfer [π(C≡CR)→π*(tpy)] character (Fig. S6A) (21–26). On decreasing the temperature, emergence of a low-energy absorption tail at 525 nm, typical of the metal-metal–ligand charge transfer (MMLCT) absorption band, is observed with depletion of the metal-to-ligand charge transfer ligand-to-ligand charge transfer band at 479 nm (Fig. S6A). The plot of the absorbance at 525 nm is found to show a small deviation from the linear relationship of Beer’s law (Fig. S6B), supportive of the participation of Pt←Pt interactions in the self-assembly process. Interestingly, complex 2 end-capped with the unsubstituted terpyridine ligand would experience stronger metal–metal interactions, which was reflected in the more significant growth and red shift of the MMLCT absorption band (550 nm) on decreasing temperature (Fig. 6A) together with the significant deviation of the MMLCT absorption band from the linear relationship of Beer’s law at various concentrations (Fig. S6 C and D). In sharp contrast, the temperature does not impose a significant effect on the low-energy absorption band of 3 (Fig. 5 A and B), and the UV-vis absorption spectra show a good agreement with Beer’s law at various concentrations (Fig. S7 C and D), suggestive of the lack of metal–metal interactions in the self-assembly process because of the presence of the sterically bulky tert-butyl groups. Interestingly, the cooling curve of 2 obtained by plotting the fraction of aggregated species (fagg) against temperature at 532 nm is found to be clearly nonsigmoidal (Fig. 6B), indicative of a cooperative supramolecular polymerization mechanism (77). Therefore, the nucleation–elongation model has been used to further understand the details of the self-assembly process of 2 into nanotubes. The thermodynamic parameters for the supramolecular polymerization of 2 have been obtained (details are in SI Materials and Methods). At the given concentration of 354 μM, the enthalpy released during the self-assembly for elongation (ΔHagg) and the elongation temperature (Tagg) are determined to be about ~63.2 kJ mol⁻¹ and 341 K, respectively. Moreover, the low value for the equilibrium constant of the nucleation step (Kagg), which is found to be 0.00068, is suggestive of the highly unfavorable nucleation process. The nucleus size, <Nagg(Tagg)>, has been found to be around 11 molecules before the elongation process. At room temperature, the number-averaged degree of polymerization is determined to be around 500 molecules. Therefore, it is plausible to suggest that among 11 molecules would first self-assemble into the initial critical-sized nuclei through the hydrophobic–hydrophobic interactions from the long alkoxy chains in DMSO as reflected by the fact that the MMLCT absorption band is less obvious and to a lesser extent at this temperature. After below the elongation temperature and beyond, the nuclei would cooperatively elongate themselves into a larger aggregate, which is further assisted by the directional Pt←Pt and π–π stacking interactions from the platinum terpyridine moiety that favor parallel stacking in the self-assembly process. The formation of parallel stacking would ultimately lead to the construction of tubular architectures with the monolayer configuration through noncovalent Pt←Pt and π–π stacking interactions as depicted schematically in Fig. 7. Unlike complex 2, the aggregation of 3 would be altered by the presence of sterically bulky tert-butyl groups at one of the termini as well as the hindrance of the formation of directional metal–metal interactions. Thus, the bulky tert-butyl groups would destabilize the eclipsed stacking of 3 in the formation of aggregates, and the complexes would alternatively adopt an interdigitated morphology arising from the strong hydrophobic–hydrophobic interactions between aliphatic tails in DMSO. The steric bulk introduced by the substituents would also discourage edge-to-face interactions and favor π–π stacking interactions in a staggered manner. Thus, together with the stabilization by π–π stacking interactions of the terpyridine and OPE moieties, complex 3 would self-assemble into helical ribbons (Fig. S8), distinctive from the straight nanotubes of complex 2 with the presence of directional metal–metal interactions. It is also important to note that not only does the additional platinum(II) terpyridine moiety of various bulkiness dictate the molecular ordering and alignment to give desirable nanostructures of helical ribbons or nanotubes but also, it suppresses the formation of multiple layers, leading to the self-assembly of well-defined nanostructures.

Fig. 5. TEM images of 3 self-assembled into (A) helical ribbons and (B and C) a double strand of ribbons in DMSO solution at different magnifications.

Fig. 6. (A) UV-vis absorption spectral traces of 2 in DMSO ([Pt] = 354 μM) on decreasing temperature. (B) Plot of fraction of aggregation at 532 nm vs. temperature from 359 to 297 K. The apparent absorbance values have been obtained by correcting to a 1-cm path length equivalence.
Summary and Prospects

To conclude, amphiphilic alkylnylplatinum(II) terpyridine complexes with scaffolds of OPEs would undergo interesting supramolecular self-assembly. The mononuclear complex would preferentially adopt lamellar packing into supramolecular structures, whereas self-assembly of the dinuclear complexes would form well-defined nanostructures, ranging from metal–metal interactions. Their morphologies have also been characterized by XRD, and the supramolecular self-assembly of mono- and dinuclear alkylnylplatinum(II) terpyridine complexes has been examined by NMR and temperature-dependent UV–vis experiments. It is envisaged that such directional interactions would emerge as a prime driving force for providing precise tuning of the self-assembly of metallosupramolecular n-conjugated amphiphiles into helical ribbons or nanotubes with their topological uniqueness and may find interesting functional properties.

Materials and Methods

Materials and Reagents. Dichloro(1,5-cyclooctadiene)platinum(II) (Strem Chemicals Co. Ltd.), 3-bromooiodobenzene (Apollo Scientific Ltd.), 1,3-diiodobenzene (Alfa Aesar Chemical Co. Ltd.), tetra-n-butylammonium fluoride (1.0 M; Sigma-Aldrich Co. Ltd.), trimethylsilylacetylene (GFS Chemical Co. Ltd.), 3-bromoiodobenzene (Apollo Scientific Ltd.), 1,3-diiodobenzene (Camb), triisopropylacetylene (GFS Chemical Co. Ltd.), and triethylamine (Apollo Scientific Ltd.) were purchased from the corresponding chemical companies. DMSO (ACS spectrophotometric grade; Sigma-Aldrich Co. Ltd.) was used for spectroscopic studies without additional purification.

Synthetic Details. The mono- and dinuclear alkylnylplatinum(II) terpyridine complexes were synthesized by reacting the OPE-derived alkenes, prepared by Sonogashira coupling (K. Zhu, S. N., S. N., unpublished results), with the corresponding platinum(II) precursor complexes with 1:1 and 1:2 ratios, respectively, in degassed DMF containing triethylamine in the presence of a catalytic amount of copper(I) iodide at room temperature. The details of the synthesis and characterization are given in SI Materials and Methods and Scheme S1.

Physical Measurements and Instrumentation. Bruker AVANCE 400 or 500 (400 and 500 MHz) on a Fourier-transform NMR spectrometer was used to record 1H and 13C NMR spectra with chemical shifts relative to that of tetramethylsilane ([CD3]2Si). The Thermo Scientific DFS High-Resolution Magnetic Sector Mass Spectrometer was used to record positive-ion ESI mass spectra. IR spectra were obtained from the preparation of KBr disk on a Bio-Rad FTS-7 Fourier-Transform IR Spectrophotometer (4,000-400 cm⁻¹). Elemental analyses of the complexes were sent to the Institute of Chemistry, Chinese Academy of Sciences for analysis by the Flash EA 1112 Elemental Analyzer. Varian Cary 50 UV-Vis Spectrophotometer was used to record UV-vis spectra at various temperatures monitored by the Varian Cary Single-Cell Peltier Thermostat. TEM experiments were performed in the Philips Tecnai G2 20 S-TWIN with an accelerating voltage of 200 kV. The TEM images were taken by Gatan MultiScan, model 794. SEM experiments were performed on the Hitachi S4800 FEG operating at 4.0–6.0 kV. Step-scanned powder X-ray diffraction (PXRD) data were collected by the Bruker AXS D8 ADVANCE (Philips PW1830 Powder X-Ray Diffractometer in Bragg-Brentano θ/2θ reflection mode with a graphite monochromatized Cu-Kα, radiation (λ = 1.540562 Å) and nickel filter. Topographical images and phase images of AFMs were collected on an Asylum MFP3D Atomic Force Microscope with an ARIZ Scanning Tool under constant temperature and atmospheric pressure.

ACKNOWLEDGMENTS. We thank Mr. Frankie Yu-Fee Chan at the Electron Microscope Unit of The University of Hong Kong for helpful technical assistance. We also thank Dr. Lap Szeto for technical assistance. We thank Mr. Frankie Yu-Fee Chan at the Electron Microscope Unit of The University of Hong Kong for helpful technical assistance. We also thank Dr. Lap Szeto for technical assistance. We also thank Dr. Lap Szeto for technical assistance. We also thank Dr. Lap Szeto for technical assistance.


Synthesis and Characterization the Oligo(para-phenylene ethynylene)-Derived Alkynyl Ligands. The synthetic route for rod-shaped ligands of oligo(para-phenylene ethynylene) (OPE) is shown in Scheme S1L4.

Synthesis of L1. To a 100-mL two-necked, round-bottomed flask fitted with a magnetic stirrer, we added 1,4-diiodo-2,5-bis(n-butyloxy)benzene (500 mg, 1.05 mmol), tris(dibenzylideneacetone)dipalladium(0) (48 mg, 0.05 mmol), and copper(I) iodide (10 mg, 0.05 mmol). Dry tetrahydrofuran (THF) (50 mL) and triethylamine (20 mL) were then transferred to the mixture; 1-ethyl-4-trisopropylsilylethylenebenzene (896 mg, 3.15 mmol) was added. The reaction mixture was heated to reflux for 72 h. After the residue was purified by column chromatography (70–230 mesh) using hexane:ethyl acetate (1:1 vol/vol) mixture as eluent to give L1 as a pale yellow solid. Yield: 719 mg (98%).1H NMR (400 MHz, CDCl3, 298 K, relative to MeSi): δ = 1.14 [d, 36H, –Si(CH(CH3)2)3], 1.26 [multiplet (m), 6H, –Si(CH(CH3)2)3], 1.54, 1.84, 4.03 (12H, –C6H12), 7.04 (s, 2H, –C6H12), 7.45 (s, 8H, –C6H4–); 13C (1H) NMR (125.8 MHz, CDCl3, 298 K, relative to MeSi): δ = 11.3, 37.1 [C on –trisopropylsilyl (TIPS)], 69.2, 36.5, 18.8, 13.6 (C on –C6H12), 76.5, 79.0, 83.3, 87.8 (C ≡ C), 114.3, 117.4, 122.1, 123.8, 131.4, 132.0 (C on phenyl rings); IR (KBr): 2,140 cm–1 ν(C ≡ C); positive ESI MS: ion clusters at m/z 794.64 [M]+; and elemental analyses calculated (percentage) for C56H52O2Si12: C, 79.74 and H, 9.01; found: C, 79.47 and H, 9.21.

**Scheme S1.** Synthetic routes for (A) rod-shaped ligands of OPE and (B) the unsymmetrical alkynylplatinum(II) terpyridine complexes with the OPE derivatives.

Synthesis of L2. The titled compound was prepared according to the procedure similar to that described for the preparation of L1, except that 1,4-diiodo-2,5-bis(3,6,9-trioxadec-1-yloxy)benzene (687 mg, 1.05 mmol) was used in place of 1,4-diiodo-2,5-bis(n-butyloxy)benzene to give L2 as a pale yellow solid. Yield: 758 mg (79%).1H NMR (400 MHz, CDCl3, 298 K, relative to MeSi): δ = 1.14 [d, 36H, –Si(CH(CH3)2)3], 1.26 [m, 6H, –Si(CH(CH3)2)3], 3.35 (s, 6H, –OCH3), 3.50, 3.62, 3.66, 3.80, 3.92, 4.20 (m, J = 4.7 Hz, 24H, –OCH2–); 7.04 (s, 2H, –C6H4–), 7.45 (s, 8H, –C6H4–); 13C (1H) NMR (125.8 MHz, CDCl3, 298 K, relative to MeSi): δ = 11.3, 37.1 (C on –TIPS), 69.6, 69.9, 69.7, 70.5, 70.6, 70.7, 71.9 [C on –3,6,9-trioxadec-1-yloxy (TEG)], 76.5, 79.0, 83.3, 87.8 (C ≡ C), 114.3, 117.4, 122.1, 123.8, 131.4, 132.0 (C on phenyl rings); IR (KBr): 2,134 cm–1 ν(C ≡ C); positive ESI MS: ion clusters at m/z 694.23 [M]+; and elemental analyses calculated (percentage) for C56H52O2Si12: C, 72.31 and H, 8.58; found: C, 72.18 and H, 8.61.

**Synthesis of L3.** To a solution of L1 (300 mg, 0.38 mmol) in tetrahydrofuran (200 mL), a solution of tetra-n-butylammonium fluoride (TBAF) (0.1 M) in tetrahydrofuran (1 mL) was added. The solution was stirred for 15 min, and the solvent was removed. After that, the residue was purified by column chromatography (70–230 mesh) using chloroform or dichloromethane as eluent to give L3 as a pale yellow solid. Yield: 178 mg (99%).1H NMR (400 MHz, CDCl3, 298 K, relative to MeSi): δ = 0.88 (s, 6H, –C6H4), 1.54, 1.84, 4.03 (m, 12H, –C6H12), 3.18 (s, 2H, –C ≡ C), 7.03 (s, 2H, –C6H4–), 7.45 (s, 8H, –C6H4–); 13C (1H) NMR (125.8 MHz, CDCl3, 298 K, relative to MeSi): δ = 69.2, 36.5, 18.8, 13.6 (C on –C6H4), 77.5, 79.0, 83.3, 87.8 (C ≡ C), 114.2, 117.4, 122.0, 123.8, 131.4, 132.1 (C on phenyl rings); IR (KBr): 2,112 cm–1 ν(C ≡ C); positive ESI MS: ion clusters at m/z 471.09 [M]+; and elemental analyses calculated (percentage) for C40H58O2Si6: C, 86.77 and H, 6.43; found: C, 86.60 and H, 6.15.

**Synthesis of L4.** The titled compound was prepared according to the procedure similar to that described for the preparation of L3, except that L2 (300 mg, 0.31 mmol) was used in place of L1 to give L4 as a pale yellow solid. Yield: 200 mg (99%).1H NMR (400 MHz, CDCl3, 298 K, relative to MeSi): δ = 3.18 (s, 2H, –C ≡ C), 3.35 (s, 6H, –OCH3), 3.50, 3.62, 3.66, 3.80, 3.92, 4.20 (m, J = 4.7 Hz, 24H, –OCH2–); 7.03 (s, 2H, –C6H4–), 7.45 (s, 8H, –C6H4–); 13C (1H) NMR (125.8 MHz, CDCl3, 298 K, relative to MeSi): δ = 69.6, 69.9, 69.7, 70.5, 70.6, 70.7, 71.9 [C on –TEG], 77.5, 79.0, 83.3, 87.8 (C ≡ C), 114.2, 117.4, 122.0, 123.8, 131.4, 132.1 (C on phenyl rings); IR (KBr): 2,122 cm–1 ν(C ≡ C); positive ESI MS: ion clusters at m/z 651.56 [M]+; and elemental analyses calculated (percentage) for C40H52O2Si6: C, 73.83 and H, 6.51; found: C, 73.60 and H, 6.44.

Synthesis and Characterization the Unsymmetrical Alkynylplatinum(II) Terpyridine Complexes with the OPE Derivatives. The synthetic route for unsymmetrical alkynylplatinum(II) terpyridine complexes with the OPE derivatives is shown in Scheme S1B.

**Synthesis of 1.** To a solution of L4 (500 mg, 0.76 mmol) and [Pt(R–tpy)Cl]OTf, where R–tpy = 4-‘(3,5-bis(1-octadecyloxy)phenyl)-2,2′:6′,2″-terpyridine (943 mg, 0.76 mmol) in degassed N,N-dimethylformamide (DMF) (30 mL) containing triethylamine (5 mL), a catalytic amount of CuI was added. The solution was stirred overnight at room temperature. After removing the solvent, the reaction mixture was purified by column chromatography on silica gel using the chloroform:acetonitrile (10:1 vol/vol) mixture as eluent followed by the diffusion of diethyl ether vapor into an acetonitrile solution of the complex to give 1 as a dark red solid.

Leung et al. 10.1073/pnas.1601673113

**Supporting Information**
Synthesis and Characterization of the Symmetrical Alkynylplatinum(II) Terpyridine Complexes with the OPE Derivatives.

Synthesis of 4. The titled complex was prepared according to the procedure similar to that described for the preparation of I, except that [L3] (60 mg, 0.13 mmol) and ([Bu(tpy)PtCl][OTf]) (249 mg, 0.32 mmol) were used in place of L4 to give 4 as a yellow solid. Yield: 153 mg (60%). 1H NMR (400 MHz, CDCl3, 298 K, relative to MeSi): δ = 1.03 (t, J = 7.4 Hz, 6H, -Bu), 1.52 (s, 36H, -Bu), 1.63 (s, 18H, -Bu), 1.84 (m, 4H, -Bu), 2.83 (m, 4H, -Bu), 4.07 (t, J = 7.4 Hz, 4H, -Bu), 7.04 (s, 2H, pPE), 7.49 (s, 8H, pPE), 7.65 (dd, J = 6.0 Hz, J = 1.6 Hz, 4H, tpy), 8.40 (d, J = 1.6 Hz, 4H, tpy), 8.47 (s, 4H, tpy), 9.17 (d with Pt satellites, J = 6.0 Hz, 4H, tpy); 13C (1 H) NMR (125.8 MHz, CDCl3, 298 K, relative to MeSi): δ = 30.2, 36.5 (C on -Bu), 68.9, 69.9, 70.1, 70.4, 70.7, 71.5 (C on -PE), 70.5 (Pt-C = C), 114.8, 117.8, 120.9, 122.0, 122.4, 125.3, 126.7, 128.1, 128.4 (C on phenyl rings), 131.4, 131.9, 132.7, 134.1, 141.4, 151.3, 153.6, 153.7, 153.9, 158.8, 160.8 (C on terpyridine); IR (KBr): 2,134 cm⁻¹ ν(C = C); positive FAB MS: ion clusters at m/z [M-2OTf⁺] 830.8; and elemental analyses calculated (percentage) for C54H38Pt2O2N4P2S2•CH2Cl2: C, 53.45; H, 4.93; and N, 4.11; found: C, 53.51; H, 4.92; and N, 4.18.

Synthesis of 5. The titled complex was prepared according to the procedure similar to that described for the preparation of 4, except that L4 (83 mg, 0.13 mmol) was used in place of L3. Yield: 209 mg (75%). 1H NMR (400 MHz, CDCl3, 298 K, relative to MeSi): δ = 1.52 (s, 36H, -Bu), 1.63 (s, 18H, -Bu), 3.36 (s, 6H, -OCH3), 3.53, 3.62, 3.66, 3.82, 3.94, 4.22 (t, J = 4.7 Hz, 2H, tpy), 6.77 (s, 1H, tpy), 7.20 (s, 2H, pPE), 7.28 (s, 2H, tpy), 7.52 (s, 8H, pPE), 7.94 (m, 4H, tpy), 8.62 (m, 11H, tpy), 8.89 (d, J = 6.0 Hz, 2H, tpy), 8.94 (s, 2H, tpy), 9.24 (d with Pt satellites, 4H, tpy); 13C (1 H) NMR (159.0 MHz, CDCl3, 298 K, relative to MeSi): δ = 13.5, 21.7, 28.6, 35.9 (C on -C6H5), 68.6, 69.9, 70.1, 70.4, 70.7, 71.8 (C on -TEG), 70.5 (Pt-C = C), 114.1, 117.8, 120.9, 122.0, 124.6, 124.8, 124.9, 126.2, 126.3, 126.4, 127.5 (C on phenyl rings), 129.6, 130.1, 131.5, 132.4, 142.4, 142.6, 143.1, 146.1, 151.8, 153.7, 154.5, 154.7, 154.9, 162.1 (C on terpyridine); IR (KBr): 2,111 cm⁻¹ ν(C = C); positive FAB MS: ion clusters at m/z [M-2OTf⁺] 920.8; and elemental analyses calculated (percentage) for C54H10F6O2N4O2Pt2S2•CH2Cl2: C, 50.95; H, 4.97; and N, 3.63; found: C, 50.74; H, 5.00; and N, 3.75.

X-Ray Crystallography. A single crystal of 4 suitable for X-ray crystallographic studies was obtained by the diffusion of diethyl ether vapor into a concentrated dichloromethane solution of the complex. Selected bond lengths and bond angles of 4 are collected in Table S1. The crystal was mounted in a glass capillary, and the intensity data were collected on a Bruker SMART 1000 CCD Diffractometer using graphite-monochromated MoKα radiation (λ = 0.71073 Å). Raw frame data were integrated using the SAINT program (78). Semiepipirical absorption corrections with SADABS (79) were applied. The structures were solved by direct methods using the SHELXL-97 program (80) and refined by full-matrix least-squares on F² using the SHELXL-97 program (80). In the final stage of least-squares refinement, nonhydrogen atoms of the solvent molecules were refined isotropically; other nonhydrogen atoms were refined anisotropically. Hydrogen atoms were generated by the program SHIELXL-97 (80). The positions of hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times that of the associated C atoms and participated in the calculation of final R indices.

The crystal data for 4•2CH2Cl2 are discussed here. An orange plate crystal of [C54H38Pt2O2N4P2S2•CH2Cl2] having approximate dimensions of 0.06 × 0.14 × 0.32 mm was mounted in a glass capillary. All measurements were made on a Bruker SMART 1000 CCD Detector with graphite monochromated Mo-Kα radiation. The crystal-to-detector distance was 50.00 mm. Indexing was performed from 60 images that were exposed for 10 s for a preliminary unit cell determination; 109 of a total of...
141 reflections were successfully indexed. The crystal-to-detector
distance was 50.00 mm. Cell constants and an orientation matrix
for data collection corresponded to a C-centered monoclinic cell
with dimensions $a = 26.537$ (3) Å, $b = 9.2986$ (12) Å, $c = 19.391$ (2)
Å, $V = 4,714.9$ (10) Å$^3$, and $\beta = 99.811^\circ$ (2$^\circ$). For $Z = 2$ and formula
weight (F.W.) = 2,129.96, the calculated density is 1.500 g/cm$^3$.

Of 25,600 reflections that were collected, 8,258 reflections were unique
($R_{int} = 0.0500$); equivalent reflections were merged. Selected bond
distances and angles are summarized in Table S1.

**Nucleation–Elongation Model Studies.** The solution of 2 in DMSO
was slowly cooled from 359 to 297 K at a rate of 0.5 K min$^{-1}$ to
ensure that self-assembly would take place under thermodynamic
control (77). Based on the UV-vis absorption spectral change at
532 nm on cooling (Fig. 6B, Inset), the value of $\alpha_{agg}$ can be
obtained by applying Eq. S1 (77), where $A_A$ and $A_m$ are the
absorbance for pure monomeric and pure aggregate species,
respectively, and $A(T)$ is the apparent absorption coefficient at
the given temperature:

$$\alpha_{agg}(T) = \frac{A(T) - A_m}{A_A - A_m} \quad \text{[S1]}$$

The plot of the $\alpha_{agg}$ value vs. temperature from the range of 359–
297 K (Fig. 6B, Inset) can be applied to the nucleation–elongation
model developed by Meijer and coworkers (77). The fraction
of aggregate species ($\alpha_{agg}$) in the elongation regime can be
defined by Eq. S2 (77), in which $\Delta H_e$ is the enthalpy correspond-
ing to the aggregation (elongation) process, $T$ is the absolute
temperature, $T_e$ is the elongation temperature, $R$ is the ideal
gas constant, and $\alpha_{SAT}$ is a parameter to ensure that $\alpha_{agg}/\alpha_{SAT}$
would not exceed unity (77):

$$\alpha_{agg}(T) = \alpha_{SAT} \left(1 - \exp \left[\frac{-\Delta H_e}{RT_e^2} (T - T_e)\right]\right) \quad \text{[S2]}$$

The enthalpy release during the self-assembly of 2 in the elongation
process ($\Delta H_e$), the elongation temperature ($T_e$), and $\alpha_{SAT}$ are
determined to be $-63.2$ kJ mol$^{-1}$, 341 K, and 1.082, respectively.

However, in the nucleation regime, the fraction of aggregate
species ($\alpha_{agg}$) can be defined by Eq. S3 (77), in which $K_a$ is the
dimensionless equilibrium constant of the activation step at the
elongation temperature. By applying Eq. S3 to the nucleation
regime, $K_a$ has been determined to be 0.00068. The low value of
this dimensionless constant is suggestive of a highly unfavorable
nucleation process:

$$\alpha_{agg}(T) = \frac{1}{\alpha_{SAT} K_a} \left(1 - \exp \left[\frac{2}{3} - 1 \cdot \frac{\Delta H_e}{RT_e^2} (T - T_e)\right]\right) \quad \text{[S3]}$$

The average length of the stack $<N_n(T_e)>$ averaged over the nu-
cleated species at $T_e$ is the number of aggregated molecules in the
nucleus size at the elongation temperature given by Eq. S4 (77).
The number of aggregated molecules in the nucleus was calcu-
lated to be around 11, which indicates that a critical-sized large
nucleus has to be formed before the highly favorable elongation
process:

$$<N_n(T_e)> = \frac{1}{K_a^{3/4}} \quad \text{[S4]}$$

Moreover, the number-averaged degree of polymerization,
$<N_n>$, which can be described by Eq. S5 (77), can be estimated
to be about 500 molecules at room temperature:

$$<N_n> = \frac{1}{\sqrt{K_a}} \frac{\alpha_{agg}}{\alpha_{SAT} - \alpha_{agg}} \quad \text{[S5]}$$
Fig. S1. Partial $^1$H NMR spectra of (A) 1, (B) 2, and (C) 3 in DMSO-$d_6$ on increasing the temperature. Proton signals correspond to the terpyridine ligands (▼) and OPE moieties (●). (D) Partial $^1$H NMR spectra of 4 and 5 in DMSO at room temperature.
Fig. S2.  (A) Photograph of the clear red gels for complex 1 prepared from the diffusion of diethyl ether into dichloromethane solution. (B) TEM and (C) SEM images for the clear red gels of complex 1. (D) Photograph of the opaque red gel for complex 1 prepared in DMSO solution. (E) TEM and (F) SEM images for the opaque red gel of complex 1. (G) Powder XRD pattern on the bulk sample of 1. Numerical values indicate d spacings (in nanometers).
Fig. S3. Representative TEM images of the monodispersed nanotubes on (A) carbon-coated copper and (B) lacey carbon-coated grids. (C, Upper and D, Upper) Representative tapping mode AFM images of 2 at different magnifications showing straight and monodispersed aggregates on the silica wafers. (C, Lower and D, Lower) Height profiles obtained along the red lines.

Fig. S4. Dynamic light scattering (DLS) measurements for (A) 2 and (B) 3 in DMSO media.
Fig. S5. Representative TEM images of 3 self-assembled into (A) helical ribbons and (B) double strands of ribbons in DMSO solution. (C, Upper) Tapping mode AFM image of 3 showing double strands of ribbons on silica wafers. (C, Lower) Height profile obtained along the red line.

Fig. S6. (A) UV-vis absorption spectral traces of 1 in DMSO ([Pt] = 843 μM) on increasing temperature. (B) UV-vis absorption spectral changes of 1 in DMSO as the concentration is increased from 69 to 1,005 μM. (Inset) A plot of the apparent absorbance at 525 nm as a function of concentration. (C) UV-vis absorption spectral changes of 2 in DMSO as the concentration is increased from 17 to 1,442 μM. (D) A plot of the apparent absorbance at 550 nm as a function of concentration. The apparent absorbance values have been obtained by correcting to a 1-cm path length equivalence.
Fig. S7.  
(A) UV-vis absorption spectral traces of 3 in DMSO ([Pt] = 360 μM) on decreasing temperature and (B) plot of absorbance at 463 nm vs. temperature from 353 to 297 K. (C) UV-vis absorption spectral changes of 3 in DMSO as the concentration is increased from 28 to 510 μM. (D) A plot of the apparent absorbance at 530 nm as a function of concentration. The apparent absorbance values have been obtained by correcting to a 1-cm path length equivalence.

Fig. S8.  
Schematic representation of helical ribbons in 3 with the interdigitated morphology of aliphatic tails.
Table S1. Selected bond distances and angles with estimated SDs in parentheses for 4

<table>
<thead>
<tr>
<th>Bond</th>
<th>Distances and angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bond distances (Å)</td>
<td></td>
</tr>
<tr>
<td>Pt(1)−N(1)</td>
<td>1.988 (8)</td>
</tr>
<tr>
<td>Pt(1)−N(2)</td>
<td>1.958 (6)</td>
</tr>
<tr>
<td>Pt(1)−N(3)</td>
<td>1.995 (8)</td>
</tr>
<tr>
<td>Pt(1)−C(28)</td>
<td>1.954 (8)</td>
</tr>
<tr>
<td>C(28)−C(29)</td>
<td>1.222 (11)</td>
</tr>
<tr>
<td>Bond angles (°)</td>
<td></td>
</tr>
<tr>
<td>N(3)−Pt(1)−N(1)</td>
<td>160.6 (3)</td>
</tr>
<tr>
<td>N(3)−Pt(1)−N(2)</td>
<td>80.2 (3)</td>
</tr>
<tr>
<td>N(1)−Pt(1)−N(2)</td>
<td>80.4 (3)</td>
</tr>
<tr>
<td>N(1)−Pt(1)−C(28)</td>
<td>98.2 (3)</td>
</tr>
<tr>
<td>N(3)−Pt(1)−C(28)</td>
<td>101.2 (3)</td>
</tr>
<tr>
<td>N(2)−Pt(1)−C(28)</td>
<td>177.6 (3)</td>
</tr>
<tr>
<td>Pt(1)−C(28)−C(29)</td>
<td>173.7 (8)</td>
</tr>
</tbody>
</table>

The number in parentheses refers to estimated SDs.