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Platinum Acetylide Complexes Containing Iptycene as Cores: A New Family of Unexpected Efficient Organometallic Gelators

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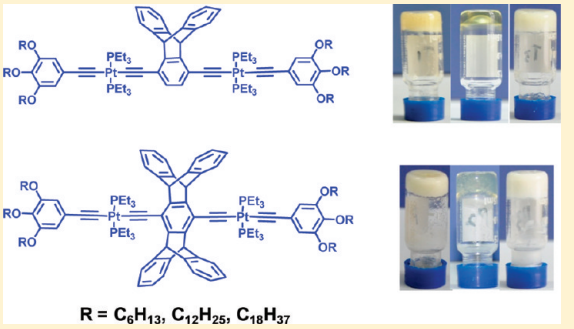
Supporting Information

ABSTRACT: A new family of platinum acetylide derivatives containing iptycene building blocks end-capped with 3,4,5-tris(alkoxy)phenyl substituents has been successfully synthesized. The structure of the newly designed complexes was characterized by multinuclear NMR (^{1}H, ^{31}P, and ^{13}C) and mass spectroscopy and elemental analysis. Unexpectedly, all compounds presented good gel formation properties in some common organic solvents. The morphology of the xerogels was investigated by scanning electron microscopy (SEM). An investigation using electronic absorption and emission spectra was carried out to study the spectroscopic properties of all organometallic complexes in both solution and gel states.



A gel is a solid, jellylike material, which has a continuous structure with macroscopic dimensions that are permanent on the time scale of an analytical experiment.[1] Usually, gels are formed by warming a small amount of gelator in an appropriate solvent until the solid is dissolved. When the solution is cooled to below T_{gel} (temperature of gelation), the entire volume of the solvent is immobilized and can support its own weight without collapsing. In the most cases, it is believed that the phenomenon of gelation arises from fibers becoming entangled and trapping solvent via surface tension. The physical characteristics of gels can range from those of surfactants in solution to those of polymers.[2]

Recently, organogels prepared via a "bottom-up" strategy from small- or medium-sized molecules have evolved to be one of the most attractive subjects within supramolecular chemistry, due to their potential applications in materials and biological fields.[3] In the process of organogelation, self-assembly has been proven to play an essential role. Driven by noncovalent interactions, such as hydrogen bonding, solvophobic interactions, $\pi-\pi$ stacking, electrostatic interactions, and van der Waals forces, the organic gelator molecules self-assemble to form nanometer-scale fibrous structures, which sequentially build up a micrometer-scale interwoven three-dimensional network entrapping solvent molecules.[4] This process is spontaneous and can be easily controlled without using technologically advanced techniques. By a small modification of the structure of the gelator subunit or by changing the experimental conditions, such as the polarity of the solvents, the morphologies and the properties of the resulted organogels could be finely tuned. This provides a simple, yet highly efficient approach to the preparation of functional soft materials from small building blocks.[5]

Supramolecular gels containing metal-organic subunits have currently attracted great interest. Conceptually, in comparison to conventional organic gelators, there is no obvious difference of a gelator containing a strongly bound metal ion within the molecule. However, the introduction of a metal center, especially a transition-metal center, into the skeletons of gelator molecules can affect self-aggregation modes and allow additional scope for tuning gel properties.[6] For example, Adia and co-workers have successfully synthesized an interesting class of trinuclear Au(I) pyrazolate metallacyclic gels. Upon doping or dedoping of Ag(I) ions, the gel−sol phase transition showed a reversible switching of red−green−blue luminescence.[6i] In addition, a new family of organometallic gelators comprised of platinum(II) terpyridyl alkynyl species has been reported by Yam's group, which shows drastic color and emission changes during sol−gel transitions.[6j] However, in comparison to the considerable work on supramolecular organogels, relatively few studies have explored the synthesis and properties of supramolecular gels consisting of metal-organic subunits. Particularly, the construction of functionalized organometallic gels is still challenging.

In the past decades, iptycene units have been extensively explored in supramolecular chemistry and material sciences because of not only their three-dimensional, noncompliant structures but also their wide applications in the areas of electro-and

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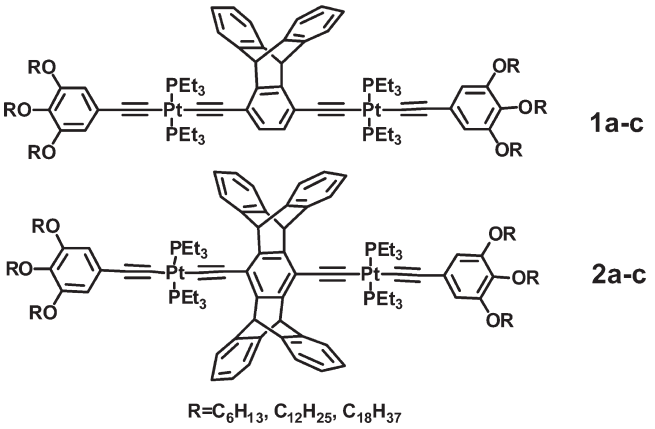


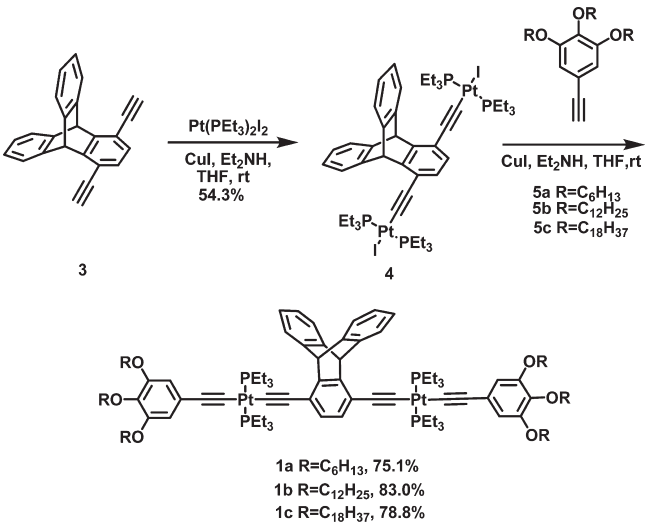
Figure 1. Chemical structures of the iptycene-containing platinum acetylide organogelators **1a**−**c** and **2a**−**c**.

photochemistry, sensors, and molecular devices.[7] Surprisingly, until now, there has been no report on organometallic gelators containing iptycene moieties, to the best of our knowledge. This might be caused by the fact that iptycene groups usually prevent effective packing during the formation of regular aggregates. On the basis of our previous research[8] on the synthesis and utilization of platinum acetylide building blocks, we designed and synthesized a new family of platinum complexes, in which the iptycene groups were introduced into the platinum acetylide frameworks, followed by the decoration of long alkyl chains on two sides of the molecules (Figure 1). Unexpectedly, all newly designed complexes featured efficient gel formation properties in most nonpolar alkyl solvents and some polar solvents. Obviously, this surprising result provides an opportunity to construct new iptycene-containing organometallic gels.

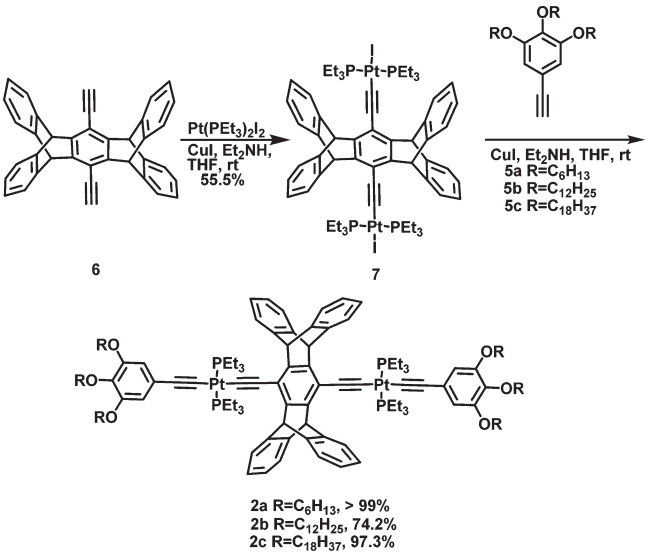
Results and Discussion. The target molecules **1a**−**c** and **2a**−**c** were synthesized by two steps of cross-coupling reactions, starting with the triptycene diacetylene and pentiptycene diacetylene, respectively (Schemes 1 and 2). The molecular structures of compounds **1a**−**c** and **2a**−**c** were characterized with multinuclear NMR (^{1}H, ^{31}P, and ^{13}C) and mass spectroscopy and elemental analysis. The multinuclear NMR analyses of **1a**−**c** and **2a**−**c** exhibited very similar characteristics, which all suggested the formation of discrete, highly symmetric platinum acetylide conjugates with triptycene or pentiptycene as cores. For instance, the ^{31}P{^{1}H} NMR spectra of **1a**−**c** displayed a sharp singlet (ca. 12.1 ppm) shifted downfield from that of the starting platinum compound **4** by approximately 2.7 ppm due to electron withdrawal by the large π-conjugated bridges. Similar results were also observed in the case of **2a**−**c**. In addition, the ^{1}H NMR spectra of all complexes showed characteristic proton resonances of 1,4-bis-substituted triptycene or pentiptycene in the bridgehead area, one singlet at 6.01 ppm for **1a**−**c**, and one singlet at 5.93 ppm for **2a**−**c**, respectively.

Unfortunately, all attempts to grow X-ray-quality single crystals of the compounds **1a**−**c** and **2a**−**c** have proven unsuccessful. However, single crystals of the precursors **4** and **7**, suitable for X-ray diffraction studies, were grown by slow vapor evaporation of a solution of a solvent mixture (dichloromethane/methanol 1/1) at ambient temperature for 5−7 days. ORTEP representations of the structures of **4** and **7** are shown in Figure 2. The platinum atoms in both complexes were found to adopt a slightly distorted trans-square-planar geometry with C−Pt−P and

Scheme 1. Synthesis of Platinum Acetylide Derivatives Containing Triptycene Building Blocks End-Capped with 3,4,5-Tris(alkoxy)phenyl Substituents 1a−c



Scheme 2. Synthesis of Platinum Acetylide Derivatives Containing Pentiptycene Building Blocks End-Capped with 3,4,5-Tris(alkoxy)phenyl Substituents 2a−c



P−Pt−I angles in the ranges 84.9 and 95.6°, which might be caused by the steric demand of the bulky triethylphosphine ligands (Table 1). The C1−C2 bond was shorter than the C≡C bond in the compound end-capped with an acetylenylbenzene group (the bond length is 1.221 Å).[9] This difference may be dictated by the acetylenylbenzene group, which makes the C1−C2 bond more electron rich. A view of the unit cell packing diagrams for **4** and **7** viewed along the *a* axis are also shown in Figure 2. It is quite evident from the diagram that, due to the large steric constraint imposed by the PEt_3 groups and the iptycene units, the distances between the nearest two platinum atoms in the adjacent molecules are approximately 7.37 Å for **4** and 15.20 Å for **7**, which exceed the distance for the existence of a

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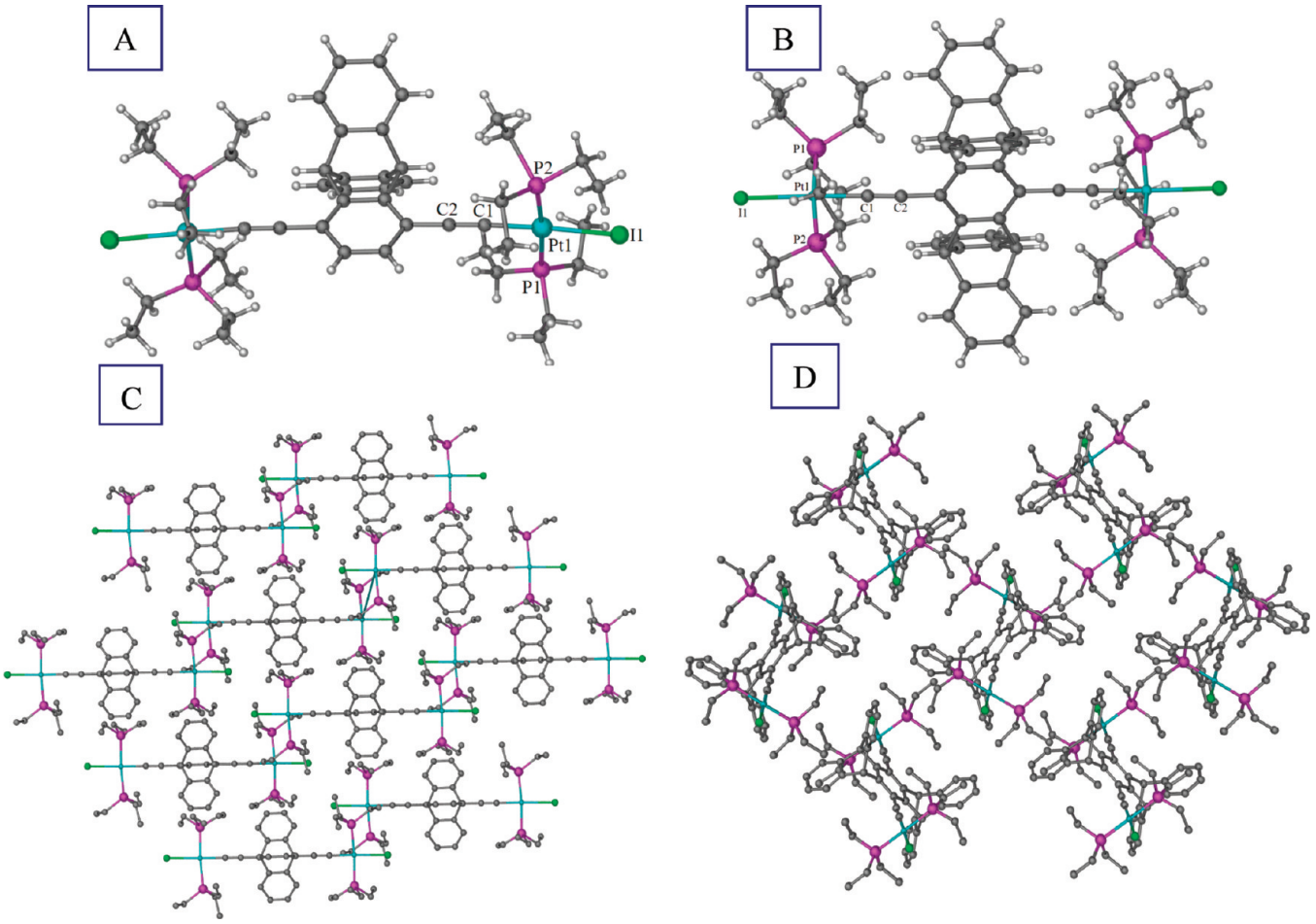

Figure 2. Crystal structures of precursors **4** (A) and **7** (B) and packing diagrams for **4** (C) and **7** (D) viewed along the *a* axis.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4 and 7

Compound **4**			
Pt(1)−C(1)	1.944(6)	Pt(1)−P(1)	2.298(2)
Pt(1)−P(2)	2.302(2)	Pt(1)−I(1)	2.6367(5)
C(1)−C(2)	1.204(9)	C(2)−C(3)	1.436(8)
C(1)−Pt(1)−I(1)	176.7(2)	P(2)−Pt(1)−P(1)	174.76(9)
P(2)−Pt(1)−I(1)	95.01(6)	P(1)−Pt(1)−I(1)	90.16(7)
C(1)−Pt(1)−P(2)	85.8(2)	C(1)−Pt(1)−P(1)	88.9(2)
C(1)−C(2)−C(3)	179.4(7)		
Compound **7**			
Pt(1)−C(1)	1.961(5)	Pt(1)−P(1)	2.3081(16)
Pt(1)−P(2)	2.3076(15)	Pt(1)−I(1)	2.6427(4)
C(1)−C(2)	1.208(7)	C(2)−C(3)	1.425(7)
C(1)−Pt(1)−I(1)	177.05(17)	P(2)−Pt(1)−P(1)	174.06(5)
P(2)−Pt(1)−I(1)	95.60(4)	P(1)−Pt(1)−I(1)	90.17(4)
C(1)−Pt(1)−P(2)	84.90(15)	C(1)−Pt(1)−P(1)	89.41(15)
C(1)−C(2)−C(3)	175.4(6)		

Pt−Pt interaction. Thus, the Pt−acetylide chains are well separated in the crystal. It was expected that the optical properties of the molecules in the gel state should be very similar to those of the isolated molecules in solution.

The gelation properties of compounds **1a**−**c** and **2a**−**c** were evaluated in various aromatic, nonaromatic, polar, and nonpolar solvents. A weighed sample (2.0 μmol) was mixed with a solvent (50 μL) in a capped vial. The mixture was then heated until the solid was completely dissolved. Subsequently the clear solution was cooled to 298 K (for **1b**, 275 K) to form a gel. Surprisingly, it was found that all compounds except **1a** exhibited good gel formation properties in the most nonpolar solvents such as *n*-hexane, *n*-pentane, *n*-octane, etc. and some polar solvents such as *n*-propanol. The organometallic gels melt to a clear nonviscous solution that could be reversibly turned back to the gel state upon cooling. Photographs of selected organometallic gels and their corresponding solutions are shown in Figure 3.

The critical gelator concentrations (CGCs) of complexes **1a**−**c** and **2a**−**c** were determined by measuring the minimum amount of compound required for the formation of a gel. In comparison to the lowest molecular weight organic gelator molecules, the CGCs of **1a**−**c** and **2a**−**c** were slightly higher. For instance, the CGC of **1c** in ethyl acetate is 24 mg/mL, indicating that one molecule of **1c** could entrap approximately 0.8×10^3 solvent molecules. Considering the large molecular weight of these compounds, for example, 2976 Da for **1c**, the CGCs obtained were still acceptable. It was obvious that the compounds containing triptycene as cores can form gels more

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easily than those containing pentiptycene as the building block, presumably due to the static hindrance. It is worth noting that compounds **1b** and **2b**, due to their C12 alkoxy chain, could generate transparent gels in a nonpolar solvent, which was quite different from the case for other compounds. All the above results demonstrate that the structural factors, including the shape of the gelator molecules, have a dramatic influence on the formation of the supramolecualr gels. The gelation properties of all six compounds **1a**−**c** and **2a**−**c** are summarized in Table 2.

The aggregation structures of the xerogels (air-dried gels) were investigated by scanning electron microscopy (SEM) (Figure 4). The typical fibrous networks were observed in the electron micrographs of xerogels **1c** and **2c** in hexane. For instance, in the case of **1c**, a three-dimensional (3D) network comprised of entangled fibers with diameter of 260−900 nm was found. Similarly, the xerogels of **2c** from hexane exhibited a dense network consisting of larger fibers with diameters of 570−1550 nm. Interestingly, the morphologies of the xerogels **1c** were strongly dependent on the polarity of the tested solvents. For example, in *n*-propanol, a globular morphology with a mean diameter of 4.6 μm was obtained, which was quite different from its morphology in nonpolar solvent (Figure 4D). This outcome again proved that by changing experimental conditions, such as the polarity of solvents, the morphology of the resulted organometallic gel could be tuned.

The electronic absorption spectra of compounds **1a**−**c** and **2a**−**c** in dilute dichloromethane solutions at 298 K exhibited similar characteristics (Figure S14, Supporting Information). The absorption spectra were dominated by a strong and relatively broad band in the near-UV region (330−350 nm) with weaker transitions at higher energy. The dominant absorption band was assigned as the long-axis-polarized π,π^* transition of the Pt−acetylide chromophore. In comparison to **1a**−**c**, the absorption spectra of complexes **2a**−**c** presented a small bathochromic shift (ca. 20 nm) of the main absorption band peaks. In addition, the emission spectra of compounds **1a**−**c** featured a moderately intense emission band with a maximum at ∼510 nm. In the case of **2a**−**c**, the predominant band was similar to those of **1a**−**c** but exhibited a blue shift about 20 nm. Interestingly, in

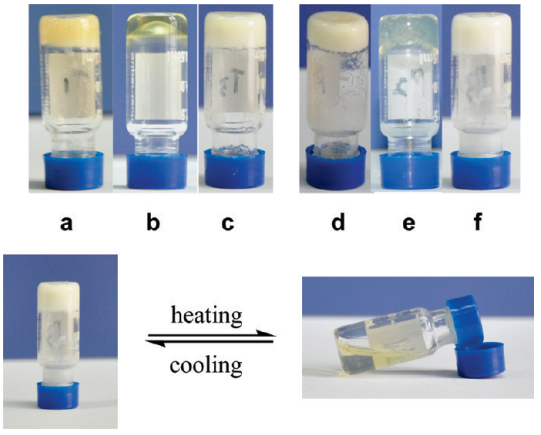

Figure 3. (Top) Photographs of the gel forms of **1a**−**c** (a−c) and **2a**−**c** (d−f) in hexane. (Bottom) Photographs of the gel (left) and sol (right) forms of **2c** in hexane.

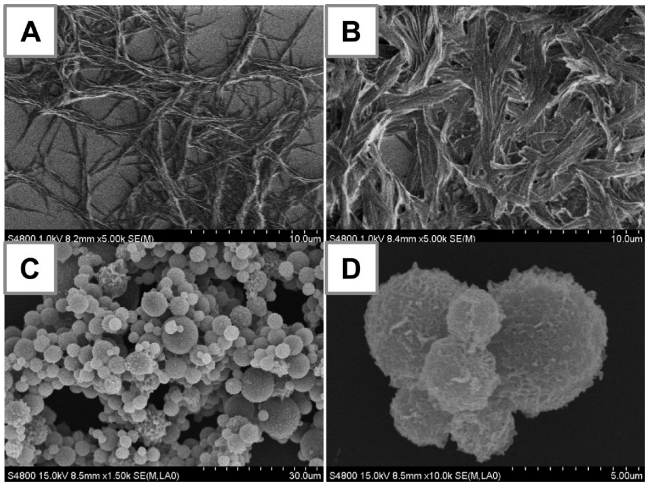

Figure 4. SEM images of the xerogels of **1c** in hexane (A), **2c** in hexane (B), **1c** in *n*-propanol (C), and **1c** in *n*-propanol at higher magnification (D).

Table 2. Summary of Gelation Properties[a]

solvent	1a	1b	1c[c]	2a	2b	2c[c]
cyclohexane	G (39.3)[b]	S	S	S	S	P
n-hexane	G (19.7)[b]	G (65.3)[b]	G (60.0)	G (32.0)	G (24.0)[b]	G(63.0)
n-heptane	G (29.5)[b]	G (65.3)[b]	G (60.0)	P	G (24.0)[b]	G(63.0)
n-octane	G (39.3)	G (65.3)[b]	G (60.0)	P	G (24.0)[b]	G(63.0)
n-decane	G (39.3)	G (65.3)[b]	G (60.0)	P	G (21.2)[b]	G(63.0)
dodecane	PG	G (37.7)[b]	G (60.0)	I	G (14.3)[b]	G(63.0)
toluene	S	S	S	S	S	S
xylenes	S	S	S	S	S	P
ethyl acetate	S	S	G (24.0)	S	P	P
tetrahydrofuran	S	S	S	S	S	S
dioxane	S	S	G (60.0)	S	S	P
acetone	S	P	P	S	G (40.8)	I
n-propanol	G (29.5)	G (8.4)	G (60.0)	I	G (40.8)	I
2-propanol	G (19.7)	G (25.8)	P	I	I	I

[a] Legend: G, opaque stable gel; PG, partial gel; S, soluble; I, insoluble; P, precipitation. Values in parentheses are the critical gelator concentrations (CGCs) in mg/mL. All gels are light yellow unless otherwise noted. [b] The gel is transparent or translucent. [c] The gel is white.

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comparison to the corresponding emission band in the dilute solution, the emission bands of **1a**−**c** in the gel state were observed at ca. 506−507 nm, blue-shifted about 6 nm. Additionally, the dominant emission bands in the gel state of **2a**−**c** were almost identical with those in the dilute solution, which might be caused by the efficiency of pentiptycene in preventing interchain aggregation being higher than that of triptycene.[10] The photophysical data of **1a**−**c** and **2a**−**c** are summarized in Table S1 (Supporting Information).

An investigation of concentration- and temperature-variation spectra was carried out in both solution and gel state. No significant changes were observed in variable-concentration absorption and emission spectra of **1a**−**c** and **2a**−**c** (Figures S15 and S16, Supporting Information). However, it was found that the organometallic gels **1a**−**c** showed temperature-dependent emission properties (Figure S17, Supporting Information). For instance, the spectra of gel **1a** exhibited a small red shift upon increasing the temperature from 298 to 338 K. Similar results were found in the investigation of the temperature-dependent emission spectra of **1b**,**c**. In contrast, **2a**−**c** showed no significant shifts in the temperature-variation emission spectra. This was conceivable because the interchain aggregation effect became weak by introducing the iptycene moiety into the skeletons. Moreover, the crystal-packing patterns of the precursor **4** and **7** provide further support for the obtained results.

Although several models have been developed to indicate the transition from a simple organic molecule to a gel,[3] it is still challenging to illustrate the exact mechanisms of such processes. On the basis of all the above experimental facts, a possible procedure for the formation of obtained organometallic gels is proposed. At the beginning, the primary ordered strands are formed from simple building blocks mostly driven by solvophobic interactions and other weaker bonds such as van der Waals interactions. Subsequently, these strands evolve to be secondary structures of fibrils or bunches of fibrils (fibers). Finally, the three-dimensional network is obtained from the mutual entanglement of linear fibers or the cross-linking of branching fibers. It is noted that the spectroscopic investigations did not provide obvious proof for the existence of Pt−Pt interactions in the aggregate structures in this study. In previous reports on supramolecular assemblies consisting of platinum terpyridine chromophores, it has been well illustrated that the Pt−Pt interactions play an important role in the formation of supramolecular aggregates.[4a,6j] The lack of significant Pt−Pt interactions in our systems might be caused by the fact that the platinum centers are sterically congested by iptycene units.

Conclusion. In summary, we have successfully synthesized a new series of platinum(II) acetylide complexes **1a**−**c** and **2a**−**c** containing iptycene as cores. The structures of all compounds were characterized by multinuclear NMR (^{1}H, ^{31}P, and ^{13}C) and mass spectroscopy and elemental analysis. Unexpectedly, all compounds give rise to gels in some common organic solvents, which provides a simple yet highly efficient approach to the preparation of iptycene-containeing soft materials from medium-sized building blocks. It was found that the compounds containing the triptycene moiety can form gels more easily than those containing a pentiptycene subunit. By a change in the polarity of the solvents, the morphology of the resulting organogels of **1c** could be tuned. This is the first report on the synthesis and study of the properties of organometallic gels containing an iptycene building block, which obviously enriches the library of organometallic gels. Continued research to better understand the properties and utilization of this new family of organometallic gels is being carried out.

EXPERIMENTAL SECTION

1. General Experimental Procedures. Triptycene diacetylene and penptycene diacetylene were synthesized according to the literature procedures.[10] Tetrahydrofuran (THF) was distilled from sodium/benzophenone. Diethylamine (Et_2NH) was dried from potassium hydroxide. Both of THF and Et_2NH were degassed by nitrogen (N_2) for 30 minutes before use. All reactions were performed in standard glassware under an inert N_2 atmosphere. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on Bruker 300 MHz spectrometer (^{1}H: 300 MHz; ^{13}C: 75 MHz; ^{31}P: 121.4 MHz) at 298 K. 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). Coupling constants (J) are denoted in Hz and chemical shifts (δ) in ppm. Multiplicities are denoted as follows: s = singlet, d = doublet, m = multiplet, t = triplet.

UV-Vis spectra were recorded with a Cary 50Bio UV-vis spectrophotometer. Emission spectra were measured on a Cary eclipse luminescence spectrometer. Samples for absorption and emission measurements were contained in 1 cm or 0.2 cm quartz cuvettes. SEM images of xerogels were obtained by using a S-4800 (Hitachi Ltd.) with an accelerating voltage of 1.0 kV. Samples were prepared by dropping dilute gels onto a silicon wafer.

2. Synthetic procedures. *Synthesis of* ***4***. To a solution of CuI (24.6 mg, 0.129 mmol) and $Pt(PEt_3)_2I_2$ (2.53 g, 3.687 mmol) in a mixed solvent of 113 mL THF and 44 mL Et2NH was added dropwise a solution of compound **3** (278.7 mg, 0.922 mmol) in THF (30 mL) under an atmosphere of nitrogen. The mixture was then stirred at room temperature for 3 hours. The solvent was removed in vacuo and the residue was purified via column chromatography with dichloromethane as eluent afforded the light yellow solid of **4** with a yield of 54.3%: R*f* = 0.47 (dichloromethane/petroleum ether 3:2). Mp: 256 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30 (dd, *J* = 3.3 and 5.4 Hz, 4H), 6.98 (dd, *J* = 3.3 and 5.4 Hz, 4H), 6.84 (s, 2H), 5.98 (s, 2H), 2.31-2.21 (m, 24H), 1.28-1.17 (m, 36H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.56, 144.47, 127.04, 124.89, 123.39, 120.86, 98.25, 93.18, 51.97, 16.53, 8.32.^{31}P NMR ($CDCl_3$, 121.4 Hz): δ 9.42 (s, $^1J_{Pt\text{-}P}$ = 2323.6 Hz).

Synthesis of ***1a-c***. Under an atmosphere of nitrogen, a mixed solvent of 7.0 mL THF and 7.0 mL Et_2NH was added to a mixture of compound **4** (180 mg, 0.127 mmol), compound **5a** (204.6 mg, 0.508 mmol), and CuI (3.9 mg, 0.018 mmol). The mixture was stirred at room temperature for 2 hours. The solvent was removed in vacuo and the residue was purified via column chromatography with dichloromethane as eluent afforded the light yellow solid of **1a**. The similar procedure was employed for the preparation of compounds **1b** and **1c**.

Compound ***1a***. Yield, 75.1%, R*f* = 0.50 (acetone/petroleum ether 1:5). Mp: 106 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30 (dd, *J* = 3.3 and 5.4 Hz, 4H), 6.97-6.94 (m, 4H), 6.82 (s, 2H), 6.52 (s, 4H), 6.01 (s, 2H), 3.98-3.90 (m, 12H), 2.25-2.18 (m, 24H), 1.81-1.71 (m, 12H), 1.47-1.25 (m, 72H), 0.91 (t, *J* = 6.6 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.57, 145.76, 144.38, 137.11, 127.18, 124.73, 123.36, 120.98, 110.54, 109.77, 107.22, 105.59, 73.33, 68.99, 52.02, 31.67, 31.48, 30.16, 29.29, 25.67, 22.57, 22.52, 16.42, 13.97, 13.92, 8.40. ^{31}P NMR ($CDCl_3$, 121.4 Hz): δ 12.10 (s, $^1J_{Pt\text{-}P}$ = 2367 .4 Hz). Anal. Calcd for $C_{100}H_{154}O_6P_4Pt_2 \cdot CH_2Cl_2$: C, 59.14; H, 7.67. Found: C, 59.31; H, 7.68. MALDI

HRMS: m/z calced for $C_{100}H_{155}O_6P_4Pt_2$, ($[M + H]^+$) 1966.00, found 1966.0.

Compound ***1b***. Yield, 83%; R*f* = 0.58 (acetone/petroleum ether 1:7). Mp: 78 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.30 (dd, J = 3.3 and 5.4 Hz, 4H), 6.97-6.94 (m, 4H), 6.82 (s, 2H), 6.52 (s, 4H), 6.01 (s, 2H), 3.97-3.89 (m, 12H), 2.25-2.20 (m, 24H), 1.83-1.67 (m, 12H), 1.46-1.22 (m, 144H), 0.88 (t, J = 6.9 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.54, 145.83, 144.31, 136.91, 127.16, 124.70, 123.56, 123.36, 120.99, 110.97, 109.69, 107.20, 105.53, 73.34, 68.92, 52.02, 31.85, 30.24, 29.67, 29.65, 29.62, 29.59, 29.36, 29.31, 29.30, 26.06, 22.61, 16.35, 14.03, 8.39. ^{31}P NMR ($CDCl_3$, 121.4 Hz): δ 11.87 (s, $^1J_{Pt\text{-}P}$ = 2379.4 Hz). Anal. Calcd for $C_{136}H_{226}O_6P_4Pt_2$: C, 66.10; H, 9.22. Found: C, 65.68; H, 9.63. MALDI HRMS: m/z calced for $C_{136}H_{227}O_6P_4Pt_2$, ($[M + H]^+$) 2470.56, found 2470.7.

Compound ***1c***. Yield, 78.8%; R*f* = 0.60 (acetone/petroleum ether 1:12). Mp: 67 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.29-7.28 (m, 4H), 6.97-6.96 (m, 4H), 6.82 (s, 2H), 6.52 (s, 4H), 6.01 (s, 2H), 3.98-3.90 (m, 12H), 2.25-2.20 (m, 24H), 1.81-1.71 (m, 12H), 1.46-1.23 (m, 216H), 0.88 (t, J = 6.9 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.61, 145.92, 144.35, 137.04, 127.22, 124.74. 123.63, 123.43, 121.07, 111.02, 109.85, 109.64, 107.27, 105.62, 73.42, 69.04, 52.10, 31.91, 30.31, 29.71, 29.66, 29.44, 29.35, 26.13, 22.67, 16.43, 14.08, 8.45.^{31}P NMR ($CDCl_3$, 121.4 Hz): δ 12.12 (s, $^1J_{Pt\text{-}P}$ = 2377.0 Hz).

Synthesis of ***7***. To a solution of CuI (6 mg, 0.029 mmol) and $Pt(PEt_3)_2I_2$ (573 mg, 0.836 mmol) in 25 mL THF and 10 mL Et_2NH was added dropwise a solution of compound **6** (100 mg, 0.209 mmol) in THF (10 mL) under an atmosphere of nitrogen. Then the mixture was stirred at room temperature for 1.5 hours. The solvent was removed in vacuo and the residue was purified via column chromatography with dichloromethane/petroleum ether (1:1) as eluent afforded the light yellow solid of **7** with a yield of 55.5%: R*f* = 0.48 (dichloromethane /petroleum ether 1:1). Mp: >300 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (dd, J = 3.3 and 5.4 Hz, 8H), 6.91 (dd, J = 3.3 and 5.4 Hz, 8H), 5.91 (s, 4H), 2.31-2.25 (m, 24H), 1.35-1.25 (m, 36H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 145.92, 141.53, 124.78, 123.24, 116.96, 95.86, 95.66, 52.09, 16.62, 8.69, 8.38. ^{31}P NMR ($CDCl_3$, 121.4 Hz): δ 9.59 (s, $^1J_{Pt\text{-}P}$ = 2318.8 Hz).

Synthesis of ***2a-c.*** Under an atmosphere of nitrogen, a mixed solvent of 6.0 mL THF and 6.0 mL Et_2NH was added to a mixture of compound **7** (180 mg, 0.113 mmol), compound **5a** (181.9 mg, 0.452 mmol) and CuI (3.0 mg, 0.016 mmol). The mixture was then stirred at room temperature for 2 hours. The solvent was removed in vacuo and the residue was purified via column chromatography with dichloromethane as eluent afforded the light yellow solid of **2a.** The similar procedure was employed for the preparation of compounds **2b** and **2c.**

Compound ***2a.*** Yield >99%: R*f* = 0.40 (dichloromethane). Mp: 266 °C dec. ^{1}H NMR (CDCl3, 300 MHz): δ 7.22 (dd, J = 3.3 and 5.1 Hz, 8H), 6.89 (dd, J = 3.3 and 5.4 Hz, 8H), 6.57 (s, 4H), 5.93 (s, 4H), 4.00-3.92 (m, 12H), 2.27-2.23 (m, 24H), 1.86-1.70 (m, 12H), 1.49-1.30 (m, 72H), 0.92 (t, J = 6.9 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 152.55, 146.19, 141.20, 136.94, 124.52, 123.59, 123.15, 117.09, 113.63, 109.78, 105.54, 104.43, 73.32, 68.93, 52.11, 31.69, 31.50, 30.17, 29.29, 25.69, 22.59, 22.54, 16.40, 14.00, 13.95, 8.54. ^{31}P NMR ($CDCl_3$, 121.4 Hz): δ 12.22 (s, $^1J_{Pt\text{-}P}$ = 2372.2 Hz). Anal. Calcd for $C_{114}H_{162}O_6P_4Pt_2$: C, 63.91; H, 7.62. Found: C, 63.77; H, 7.91. MALDI HRMS: m/z calced for $C_{114}H_{163}O_6P_4Pt_2$, ($[M + H]^+$) 2142.06, found 2142.1.

Compound ***2b***. Yield, 74.2%: R*f* = 0.60 (dichloromethane / petroleum ether 6:1). Mp: 188 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.23 (dd, J = 3.3 and 5.1 Hz, 8H), 6.90-6.88 (m, 8H), 6.57 (s, 4H), 5.93 (s, 4H), 4.00-3.92 (m, 12H), 2.27-2.23 (m, 24H), 1.83-1.73 (m, 12H), 1.41-1.27 (m, 144H), 0.87 (t, J = 6.6 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): 8 152.60, 146.24, 141.25, 136.94, 124.59, 123.61, 123.23, 117.17, 113.68, 109.77, 105.58, 104.49, 73.42, 68.99, 52.15, 31.91, 30.30, 29.73, 29.65, 29.42, 29.36, 26.12, 22.67, 16.44, 14.11, 8.62. ^{31}P NMR ($CDCl_3$, 121.4 Hz): δ 12.23 (s, $^1J_{Pt\text{-}P}$ = 2372.2 Hz). MALDI HRMS: m/z calced for $C_{150}H_{235}O_6P_4Pt_2$, ($[M + H]^+$) 2646.63, found 2646.9.

Compound ***2c***. Yield, 97.3%: R*f* = 0.60 (dichloromethane / petroleum ether 4:1). Mp: 140 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.22 (dd, J = 3.0 and 4.8 Hz, 8H), 6.90-6.87 (m, 8H), 6.57 (s, 4H), 5.93 (s, 4H), 4.00-3.91 (m, 12H), 2.27-2.23 (m, 24H), 1.83-1.72 (m, 12H), 1.48-1.26 (m, 216H), 0.88 (t, J = 4.5 Hz, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): 8 152.63, 146.27, 141.29, 136.98, 124.62, 123.64, 123.26, 117.20, 113.72, 109.82, 105.62, 104.52, 73.47, 69.05, 52.18, 31.92, 29.73, 29.47, 29.37, 26.16, 22.69, 16.47, 14.13, 8.66. ^{31}P NMR ($CDCl_3$, 121.4 Hz): δ 12.26 (s, $^1J_{Pt\text{-}P}$ = 2372.2 Hz). Anal. Calcd for $C_{186}H_{306}O_6P_4Pt_2$: C, 70.86; H, 9.78. Found: C, 70.56; H, 10.17. MALDI HRMS: m/z calced for $C_{186}H_{307}O_6P_4Pt_2$, ($[M + H]^+$) 3151.19, found 3151.4.

■ ASSOCIATED CONTENT

Supporting Information. Figures and text giving details of the syntheses and ^{1}H, ^{31}P, and ^{13}C NMR spectra of **4**, **1a**−**c**, **7**, and **2a**−**c**, high-resolution MALDI mass spectra of **1a**,**b** and **2a**−**c**, electronic absorption spectra of **1a**−**c** and **2a**−**c** in dilute solution and gel states, concentration-variation electronic absorption spectra, concentration-variation emission spectra, and temperature-dependent emission spectra of gels. This material is available free of charge via the Internet at http://pubs.acs.org.

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