ORGANOMETALLICS

Synthesis of Platinum Acetylide Derivatives with Different Shapes and Their Gel Formation Behavior

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S Supporting Information

ABSTRACT: The synthesis of a series of platinum acetylide derivatives, featuring linear, triangular, and rectangular shapes, respectively, is described. The structures of these complexes were characterized by multinuclear NMR (¹H, ¹³C, and ³¹P), CSI-TOF mass spectrometry, and elemental analysis. It was found that these complexes exhibited unexpectedly different gel formation properties in the most common organic solvents. Moreover, the organometallic gels of C1 and C2 exhibited concentration- and temperature-dependent emission properties.



Supramolecular gels, as a family of classical soft materials, have received a great deal of attention due to their wide applications in material sciences and biological fields. In particular, the smart organogelators have been extensively explored in the areas of organic light emission diodes (OLEDs), photovoltaic cells, drug delivery, and light harvesting systems.¹ Given the scientific importance of understanding gel-phase behavior, there has been considerable focus on the design and synthesis of artificial architectures that can be employed to underpin nanostructured gels. So far, a variety of organogelators based on hydrogen bonding, $\pi - \pi$ stacking, solvophobic interaction, and van der Waals interactions have been reported.²

Recently there has been growing interest in the investigation of organometallic gels, because the presence of metal centers allows for the additional scope for tuning gel properties such as catalytic activity, magnetism, and photo- and electrochemistry.³ For instance, a trinuclear Au(I) pyrazolate complex, which can form red-luminescent organometallic gels via Au(I)–Au(I) metallophilic interaction, has been reported by Aida's group.^{3g} In addition, Yam and co-workers have reported a new family of alkynylplatinum(II) bzimpy complexes, which exhibited unusual luminescence enhancement during the gel-to-sol phase transition at elevated temperature.^{3h}

Previously we have reported the construction of nanoscale functionalized polygons and polyhedra via coordination-driven self-assembly from platinum building blocks.⁴ Recently, our research interests have turned to the fabrication of large-scale supramolecular microstructures, such as organometallic gels, via noncovalent interaction from small- or medium-sized molecules. With the aim to gain further insight into the structural requirements for organometallic gelators, a series of platinum acetylide derivatives with different shapes (Scheme 1) have been designed and synthesized. Moreover, the structural effects on their gelation properties have been investigated.

RESULTS AND DISCUSSION

All platinum acetylide derivatives consist of a π -conjugated, rigid core moiety with different shapes and peripheral alkyl chain groups. The π -conjugated core skeleton was synthesized by using multistep synthetic strategies, including palladiumcatalyzed cross-coupling reactions, in accordance with similar procedures reported in the literature.^{36,5} Subsequent coupling reactions with the corresponding alkynes resulted in the final target compounds in high yield. An exact description of the synthesis and characterization of linear complexes A1 and A2, triangular complexes B1 and B2, and rectangular complexes C1 and C2 can be found in the Supporting Information.

The presence of a π -conjugated aromatic core and peripheral alkyl chains on the newly designed complexes stimulated us to investigate their gelation abilities in various organic solvents by the "stable to inversion in a test tube" method. Surprisingly, linear molecules **A1** and **A2** could not form gels even at high concentration at room temperature. Only unstable turbid gels were

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Scheme 1. Chemical Structures of Target Molecules A-C





Figure 1. (A) Photograph of C1 gel formation in various organic solvents at their CGCs (from left to right): (a) cyclohexane; (b) *n*-hexane; (c) *n*-heptane; (d) *n*-propyl alcohol; (e) isopropyl alcohol; (f) *n*-dodecane; (g) *n*-octane; (h) *n*-decane. (B) Photograph of C2 gel formation in various organic solvents at their CGCs (from left to right): (a) *n*-hexane; (b) *n*-heptane; (c) *n*-dodecane; (d) *n*-octane; (e) *n*-decane.

obtained from A2 in some nonpolar solvents under extremely high concentrations (25-50 mg/mL) at low temperatures (0 °C). This observation is obviously different from that previously reported, in which the gel formation of similar but shorter platinum acetylide complexes was observed.^{3f} This result demonstrates that a small modification of the gelator structure may lead to a complete loss of gelation ability. Meanwhile, triangular complexes **B1** and **B2** exhibited high solubility in the most tested solvents and could not form gels. However, rectangular complexes **C1** and **C2** displayed unexpectedly strong gelation ability in the most nonpolar solvents and a few polar solvents (Figure 1). For example, the critical gelator concentrations (CGCs) of **C1** in isopropyl alcohol and **C2** in *n*-dodecane were 2.0 and 5.8 mg/mL, indicating that one rectangular C1 and C2 molecule could entrap approximately 2.42×10^4 and 0.35×10^4 solvent molecules, respectively. The organometallic gels obtained from C1 and C2 are very stable and do not show any significant change after several weeks. Upon heating, the organometallic gels melt to a clear nonviscous solution that could reversibly turn back to the gel state upon cooling. The gel-to-solution phase-transition temperature (T_{gel}) values of the complexes C1 and C2 in several different solvent systems were determined at CGCs given in Table S2 (Supporting Information). It was found that the gel formed by C2 turned into a viscous fluid more readily than that formed by C1, suggesting that C1 has a better thermal stability of gel.



Figure 2. SEM images of the xerogels of C1 in isopropyl alcohol (a, scale bar 5 μ m, 2.0 mg/mL) and C2 in *n*-octane (b, scale bar 5 μ m, 5.8 mg/mL) and TEM image of the xerogels of C2 in hexane (c, scale bar 0.2 μ m, 5.8 mg/mL).



Figure 3. (a) Normalized emission spectra of C1 in hexane solution at different concentrations at 298 K. (b) Normalized emission spectra of C1 at different temperatures at 5.5×10^{-4} M concentration. Arrows indicates changes in spectra with increasing temperature from 298.2 to 323.2 K. The excitation wavelength is 345 nm.

In order to investigate the morphologies of this family of organometallic gels, scanning electron microscopy (SEM) was performed with the corresponding xerogels (air-dried gels). The typical fiberlike or ribbonlike morphologies for C1 and C2 in different solvents were observed (Figure 2 and Figures S15 and S16, Supporting Information). For example, the xerogels of C1 in isopropyl alcohol showed a three-dimensional (3D) network comprised of entangled fibers with diameter of 100–200 nm. The 3D network consisting of interwoven fibers was further confirmed by the transmission electron microscopy (TEM) investigation of xerogels C2.

The absorption and emission properties of this series of platinum acetylide derivatives were studied extensively (see the Supporting Information). The electronic absorption spectra of A-C in dilute dichloromethane solution (ca. 10^{-5} M) showed similar absorption patterns. The absorption spectra were dominated by a strong and relatively broad band in the near-UV region (ca. 345 nm) with weaker transitions at higher energy. The dominant absorption band was described as an admixture of $\pi - \pi^*$ and Pt- π^* transitions according to similar previous reports.^{3f,h-j,6} Each of the complexes exhibited a weak fluorescence band that is Stokes-shifted from the low-energy absorption. Upon being excited at 344 nm, A and B feature a band with maximum at 464 nm in dilute dichloromethane solution (ca. 10^{-5} M). Notably, with an exitation wavelength of 345 nm, C1 and C2 showed an emission band at 511 nm in dilute dichloromethane solution and gave a blue shift (39 nm) compared to that in the gel state in hexane (ca. 472 nm). The photophysical data are summarized in Table S3 (Supporting Information).

Detailed concentration-dependent and variable-temperature UV-vis and emission spectroscopy of C1 and C2 was performed in hexane solutions. Fluorescence spectra are frequently sensitive to the microenvironment around the fluorescent probe, thus providing important information on the molecular organization of chromophores. Although no significant changes were observed in UV-vis absorption spectra, C1 and C2 both exhibited concentration- and temperature-dependent emission properties in hexane solution. As shown in Figure 3a, in very dilute solutions $(5.5 \times 10^{-6} \text{ and } 1.1 \times 10^{-5} \text{ M})$, the spectrum of C1 showed an emission band at 511 nm, similar to that observed in dilute dichloromethane solutions. As concentrations increased from 1.1×10^{-5} to 5.5×10^{-4} M at 298 K, the low-energy emission band at 511 nm was found to drop in intensity with a concomitant growth of a new emission band at 472 nm. It is also significant that there is an isoemissive point maintained during the concentration altering, suggesting that the spectra are dominated by two principal forms of the species. Meanwhile, as shown in Figure 3b, upon warming a gelled solution of C1 $(5.5 \times 10^{-4} \text{ M})$, the high-energy broad emission band at 472 nm decreased in intensity while the low-energy band at 511 nm increased, with a well-defined isoemissive point at 495 nm. Over the same temperature range the sample undergoes a gel-sol transition; therefore, the thermally induced red shift in the emission spectra is clearly associated with the phase transition. It is well-known that an increase in concentration or a decrease in temperature would favor aggregate formation.⁷ We attribute the "blue" emission band (λ_{max} 472 nm) to the C1 aggregate state present in the gel and the "red" emission band (λ_{max} 511 nm) to

the monomeric form in the molecularly dissolved state. Similar concentration- and temperature-dependent behavior was also observed in the emission spectrum of C2 in hexane (Figures S24 and S25, Supporting Information).

CONCLUSION

In summary, a series of platinum acetylide derivatives featuring linear, triangular, and rectangular shapes have been successfully synthesized. It was found that they displayed unexpectedly different gelation behavior. For example, linear molecules A and triangular molecules B formed gels only with difficulty, while rectangular molecules C1 and C2 exhibited very high gel formation efficiency in most organic solvents, even at concentrations as low as 2.0 and 5.8 mg/mL, respectively. Again, all these results indicate that the structural factors, including the shape of the gelator molecules and the number of the side alkyl chains, play an essential role during the formation of the supramolecualr gels, although it has not been well understood up to date. In conclusion, we have reported the synthesis of a series of platinum acetylide derivatives, which presented different gel formation properties. This research obviously enriches the library of organometallic gels and might be helpful in gaining further insight into the structural requirements for organometallic gelators.

EXPERIMENTAL SECTION

The target molecules C1 and C2 were prepared by a six-step synthetic scheme as shown in Scheme S3 (see Supporting Information). Compounds 10-14 and 6 were prepared according to previously reported synthetic procedures^{36,Sc-5e,8} and showed spectroscopic properties identical with those reported therein.

Synthesis of Compound 15. A solution of *trans*-diiodobis-(triethylphosphine)platinum (1.32 g, 1.93 mmol) and cuprous iodide (14.7 mg, 8 mol %) in a THF/Et₂NH mixture (20 mL/10 mL) was stirred at room temperature, and 14 (72.0 mg, 0.24 mmol) dissolved in THF (10 mL) was added dropwise for 0.5 h. After another 1 h a small amount of diethylammonium iodide started precipitating out of solution. The solvent was removed in vacuo. The yellow-red residue was separated by column chromatography on silica gel (dichloromethane/ petroleum ether 3/2) to give the desired product **15** as a wheat-colored solid. Yield: 390 mg, 64%. Mp: 222 °C. ¹H NMR (300 MHz, CDCl₃): δ 1.11–1.22 (m, 72H), 2.19–2.23 (m, 48H), 7.17 (s, 2H), 7.21 (s, 4H). ¹³C NMR (75 MHz, CDCl₃): δ 8.10, 8.24, 8.39, 16.12, 16.34, 16.57, 16.81, 17.03, 73.42, 81.44, 91.14, 91.33, 91.52, 98.95, 121.36, 128.47, 128.71, 128.93, 131.38, 133.72. ³¹P NMR (121 MHz, CDCl₃): δ 9.10 (J_{Pt-P} = 2309.9 Hz). Anal. Calcd for C₇₂H₁₂₆I₄P₈Pt₄: C, 34.21; H, 5.02. Found: C, 34.60; H, 5.12.

Synthesis of Compound C1. A 100 mL Schlenk flask was charged with 15 (100.0 mg, 0.04 mmol), 6a (125.7 mg, 0.32 mmol), and cuprous iodide (3.0 mg, 10 mol %), degassed, and back-filled three times with N₂. Et₂NH (4 mL) and dried THF (4 mL) were introduced into the reaction flask by syringe. The reaction mixture was stirred under an inert atmosphere at room temperature for about 4 h. The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (acetone/petroleum ether 1/7) to give C1 (124.2 mg, 86.6%) as a wheat-colored solid. Mp: 110 $^\circ$ C. 1 H NMR (CDCl₃, 400 MHz): δ 0.89 (br, 36H), 1.17–1.28 (m, 72H), 1.32 (br, 48H), 1.45 (br, 24H), 1.70-1.79 (m, 24H), 2.15-2.17 (m, 48H), 3.90 - 3.95 (m, 24H), 6.48 (s, 8H), 7.18 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 8.35, 14.00, 16.13, 16.30, 16.48, 22.59, 29.32, 30.19, 31.55, 31.73, 69.00, 73.42, 105.38, 108.20, 109.66, 121.06, 123.48, 128.74, 131.38, 134.31, 136.99, 152.59. ³¹P NMR (CDCl₃, 161.9 MHz): δ 11.64 $(J_{Pt-P} = 2365.4 \text{ Hz})$. HR CSI-TOF-MS of C1: m/z 1814.0 $[M + 2H]^{2+}$.

Anal. Calcd for $C_{176}H_{290}O_{12}P_8Pt_4{:}$ C, 58.29; H, 8.06. Found: C, 58.30; H, 8.05.

Synthesis of Compound C2. Following the procedure for C1, 15 (100.0 mg, 0.04 mmol), **6b** (203.2 mg, 0.32 mmol), cuprous iodide (3.0 mg, 10 mol %), Et₂NH (4 mL), and dried THF (4 mL) yielded **C2** as a wheat-colored solid (180 mg, 98.4%) after purification by column chromatography on silica gel (acetone/petroleum ether 1/7). Mp: 117 °C. ¹H NMR (CDCl₃, 400 MHz): δ 0.88 (t, 36H, *J* = 6.4 Hz), 1.17–1.37 (m, 264H), 1.43–1.44 (m, 24H), 1.70–1.79 (m, 24H), 2.15–2.16 (m, 48H), 3.90 – 3.94 (m, 24H), 6.47 (s, 8H), 7.17 (s, 6H). ¹³C NMR (CDCl₃, 100 MHz): δ 8.35, 14.10, 16.10, 16.27, 16.45, 22.67, 26.10, 29.35, 29.37, 29.37, 29.42, 29.64, 29.68, 29.71, 29.73, 30.27, 31.90, 69.01, 73.45, 105.28, 105.43, 105.59, 108.24, 108.67, 108.83, 108.98, 109.68, 121.03, 123.48, 131.39, 136.96, 152.57. ³¹P NMR (CDCl₃, 161.9 MHz): δ 11.61 (J_{Pt-P} = 2365.4 Hz). HR CSI-TOF-MS of **C2**: m/z 2319.1 [M + 2H]²⁺. Anal. Calcd for C₂₄₈H₄₃₄O₁₂P₈Pt₄: C, 64.25; H, 9.44. Found: C, 64.53; H, 9.34.

ASSOCIATED CONTENT

Supporting Information. Text, tables, and figures giving details of synthesis and characterization of the compounds and supplementary experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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