Electronic Supplementary Information (ESI) For

A series of new star-shaped or branched platinum acetylide derivatives: synthesis, characterization, and their self-assembly behavior†

Bo Jiangab†, Li-Jun Chena†, Lin Xua, Shun-Ying Liub, Hai-Bo Yanga

a Shanghai Key Laboratory of Green Chemistry and Chemical Processes, Department of Chemistry, East China Normal University, 3663 N. Zhongshan Road Shanghai, 200062, P.R. China.

b Shanghai Engineering Research Center for Molecular Therapeutics and New Drug Discovery and Development, East China Normal University, 3663 N. Zhongshan Road Shanghai, 200062, P.R. China.

Table of Contents:

1. General Information.................................................................................................................................................S3

2. Synthetic Experimental Details of New Platinum-Acetylide Complexes 1a–b and 2a–b.................................S4

3. Characterization of Complexes 1a–b and 2a–b........................................................................................................S9

4. UV-vis and Fluorescence Spectra of 1a–b and 2a–b.................................................................................................S11

5. Additional SEM Images of Complexes 1a and 2a at Different Scales.................................................................S13

6. Concentration-Dependent and Temperature-Dependent 1H NMR Spectra of Complexes 1a and 2a. ..............................................................................................................................................................S14

7. Gelation Tests. ...............................................................................................................................................................S18

8. Multiple Nuclear NMR (1H, 31P, and 13C NMR) Spectra and MALDI-TOF MS of New Compounds. ..................................................................................................................................................................S20

9. References..................................................................................................................................................................S34
1. General Information.

$^1$H NMR, $^{13}$C NMR and $^{31}$P NMR spectra were recorded on 400 MHz Spectrometer ($^1$H: 400 MHz; $^{13}$C: 100 MHz; $^{31}$P: 161.9 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 a internal standard sample of 85% H$_3$PO$_4$ (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, br = broad. UV-Vis spectra were recorded on a Cary 50Bio UV-Visible spectrophotometer. Fluorescence spectra were measured on a Cary Eclipse fluorescence spectrophotometer. Samples for absorption and emission measurements were contained in 1 cm × 1 cm or 1 cm × 0.2 cm quartz cuvettes. SEM images were obtained using an S-4800 (Hitachi Ltd.) with an accelerating voltage of 10.0 kV. Samples were prepared by evaporating a solution of molecules 1a–b and 2a–b onto a SiO$_2$/Si substrate (1×1 cm$^2$).
2. Synthetic Experimental Details of New Platinum-Acetylide Complexes 1a–b and 2a–b.

**Materials and Reagents.** All solvents were dried according to standard procedures and all of them were degassed under N₂ for 30 minutes before use. Reagents were used as purchased. All reactions were performed in standard glassware under an inert N₂ atmosphere. Compounds 3¹, 5⁵, 7³, and 8⁴ were prepared as previous report.

**Scheme S1.** Synthesis route of the precursors 4 and 6.

**Synthesis of compound 4.** A solution of trans-diiodobis (triethyl-phosphine) platinum (530 mg, 0.78 mmol) and cuprous iodide (26 mg, 13.7 mol %) in a THF/Et₂NH mixture (60 mL/50 mL) was stirred at room temperature, and 3 (300 mg, 0.39 mmol) dissolved in THF (30 mL) was added dropwise for 1.5 h. The solvent was removed in vacuo. The residue was separated by column chromatography on silica gel (petroleum ether/ethyl acetate 10:1) to give the desired product 4 (300 mg, 53%) as a wheat-colored solid. Rf = 0.4 (petroleum ether/ethyl acetate 10:1). M.p. 46 °C. IR (neat): v/cm⁻¹ 3259, 3106, 3019, 2920, 2851, 2189, 2123, 2047, 1900, 1845, 1640, 1579, 1524, 1505, 1468, 1426, 1401, 1336, 1292, 1236, 1215, 1114, 1034, 1005, 951, 859, 836, 764, 729, 668, 642. ¹H NMR (400 MHz; CDCl₃): δ 7.63 (s, 1H), 7.50 (d, 2H, J = 8.4 Hz), 7.28 (d, 2H, J = 8.4 Hz), 7.03 (s, 2H), 3.99-4.049 (m, 6H), 2.21-2.25 (m, 12H), 1.73-1.82 (m, 6H), 1.26 (m, 72H), 0.86 (m, 9H); ³¹P NMR (161.9 MHz; CDCl₃): δ 8.63 (JPt,p = 2323.3 Hz); ¹³C NMR (CDCl₃; 100 MHz): δ 165.4, 153.2, 141.4, 135.4, 131.2, 129.9, 119.9, 105.7, 73.5, 69.4, 31.9, 30.3, 29.7, 29.6, 29.4,
29.3, 26.0, 22.7, 16.7, 16.6, 16.4, 14.1, 8.3.

**Synthesis of compound 6.** Following the procedure for the preparation of 4. Compound 5 (260 mg, 0.4 mmol), trans-diiodobis (triethyl-phosphine) platinum (545 mg, 0.8 mmol), cuprous iodide (27 mg, 14 mol %), Et₂NH (45 mL) and dried THF (80 mL) yielded 6 as a wheat-colored solid (366 mg, 76%) after purification by column chromatography (dichloromethane/petroleum ether 1:1). Rf = 0.6 (dichloromethane/petroleum ether 1:1). M.p. 42 ºC. IR (neat): v/cm⁻¹ 3013, 2920, 2851, 2104, 1772, 1654, 1586, 1499, 1466, 1413, 1379, 1333, 1225, 1170, 1114, 1035, 1011, 980, 825, 769, 728, 665, 631. ¹H NMR (400 MHz; CDCl₃): δ 6.47 (s, 2H), 3.89-3.95 (m, 6H), 2.21-2.23 (m, 12H), 1.75 (m, 6H), 1.26 (m, 72H), 0.86 (m, 9H); ³¹P NMR (161.9 MHz; CDCl₃): δ 8.66 (J₉₈₋₆₂ = 2326.5 Hz); ¹³C NMR (CDCl₃, 100 MHz): δ 152.7, 137.3, 123.2, 109.5, 73.4, 69.1, 31.9, 30.3, 29.7, 29.6, 29.4, 26.1, 22.7, 16.8, 16.6, 16.4, 14.1, 8.4, 8.3.

**Scheme S2.** Synthesis route of target molecules 1a-b.

**Synthesis of compound 1a.** A 50 mL Schlenk flask was charged with 7 (25 mg, 0.03 mmol), 4 (485 mg, 0.36 mmol), and cuprous iodide (8.0 mg, 5 mol %), degassed, and back-filled three times with N₂. Et₂NH (3 mL) and dried THF (7 mL) were introduced into the reaction flask by syringe. The reaction mixture was stirred under an inert atmosphere at room temperature for about 17 h.
The solvent was removed by evaporation on a rotary evaporator. The residue was purified by column chromatography on silica gel (dichloromethane/acetone 50:1) to give 1a (70 mg, 28.9%) as an orange red solid. Rf = 0.8 (dichloromethane/acetone 50:1). IR (neat): ν/cm⁻¹ 3734, 2961, 2922, 2851, 2200, 2099, 1583, 1504, 1466, 1335, 1276, 1261, 1105, 1034, 821, 803, 764, 751, 647, 635, 621, 609. ¹H NMR (400 MHz; CD₂Cl₂): δ 7.73 (s, 6H), 7.48-7.54 (m, 24H), 7.25-7.31 (m, 24H), 7.03 (s, 12H), 3.97-4.05 (m, 36H), 2.20 (m, 72H), 1.71-1.84 (m, 36H), 1.27 (s, 396H), 0.88 (m, 54H); ³¹P NMR (161.9 MHz; CD₂Cl₂): δ 11.96 (Jₚₚ = 2358.9 Hz); ¹³C NMR (CD₂Cl₂, 100 MHz): δ 165.5, 153.6, 141.6, 131.9, 131.7, 131.4, 130.4, 120.2, 114.8, 105.8, 73.9, 69.7, 32.4, 30.7, 30.1, 29.8, 26.5, 23.1, 17.0, 16.8, 16.6, 14.3, 8.6. MALDI-TOF MS of 1a: m/z calcd for C₄₄H₆₉₆N₆O₂₃P₁₂Pt₆ ([M+H]+) 8038.82, found 8038.76.

**Synthesis of compound 1b.** Following the procedure for the preparation of 1a, 6 (440 mg, 0.36 mmol), 7 (30 mg, 0.036 mmol), cuprous iodide (10 mg, 0.05 mol %), Et₂NH (3 mL) and dried THF (7 mL) yielded 1b as an orange red solid (85 mg, 32.2%) after purification by column chromatography (dichloromethane/acetone 50:1). Rf = 0.5 (dichloromethane/acetone 50:1). M.p. 74 ºC. IR (neat): ν/cm⁻¹ 2959, 2922, 2852, 2200, 2098, 1742, 1591, 1568, 1499, 1466, 1414, 1378, 1332, 1262, 1228, 1170, 1113, 1035, 832, 768, 732, 631. ¹H NMR (400 MHz; CD₂Cl₂): δ 7.52 (d, J = 6.8 Hz, 12H), 7.30 (d, J = 7.6 Hz, 12H), 6.45 (s, 12H), 3.85-3.94 (m, 36H), 2.18 (m, 72H), 1.54 (m, 36H), 1.27 (s, 396H), 0.88 (m, 54H); ³¹P NMR (161.9 MHz; CD₂Cl₂): δ 11.64 (Jₚₚ = 2357.3 Hz); ¹³C NMR (CD₂Cl₂, 100 MHz): δ 153.1, 137.0, 131.9, 131.3, 130.4, 127.3, 124.0, 119.4, 109.4, 100.4, 88.4, 73.8, 69.3, 32.4, 30.2, 30.1, 29.9, 29.8, 29.8, 26.6, 23.1, 16.9, 16.8, 16.6, 14.3, 8.6. MALDI-TOF MS of 1b: m/z calcd for C₄₄H₆₆₆N₆O₂₂P₁₂Pt₆ ([M+H]+) 7324.59, found 7323.24.
Scheme S3. Synthesis route of target molecules 2a-b.

Synthesis of compound 9. Following the procedure for the preparation of 1a. 8 (60 mg, 0.12 mmol), trans-diiodobis (triethyl-phosphine) platinum (945 mg, 1.4 mmol), cuprous iodide (10.5 mg, 5.5 mol%), Et$_3$NH (10 mL) and dried THF (20 mL) yielded 9 as a yellow solid (150 mg, 33.8%) after purification by column chromatography (dichloromethane:). $R_f = 0.8$ (dichloromethane). M.p. 168 °C. IR (neat): $\tilde{v}$/cm$^{-1}$ 3738, 3670, 3658, 2988, 2968, 2927, 2903, 2882, 2731, 2356, 2114, 1772, 1748, 1568, 1453, 1408, 1378, 1254, 1199, 1155, 1049, 1034, 975, 868, 764, 742, 729, 682, 627. $^1$H NMR (400 MHz; CDCl$_3$): $\delta$ 7.63 (s, 3H), 7.21 (d, $J = 1.2$ Hz, 6H), 7.18 (s, 3H), 2.21-2.25 (m, 72H), 1.13-1.21 (m, 108H); $^{31}$P NMR (161.9 MHz; CDCl$_3$): $\delta$ 8.74 ($J_{P-P} = 2318.4$ Hz); $^{13}$C NMR (CDCl$_3$; 100 MHz): $\delta$ 134.0, 133.3, 130.6, 128.7, 124.0, 122.4, 99.2, 91.2, 91.0, 90.9, 90.4, 87.3, 29.7, 16.7, 16.6, 16.4, 8.3.

Synthesis of compound 2a. Following the procedure for the preparation of 1a. 9 (150 mg, 0.039 mmol), 3 (360.5 mg, 0.466 mmol), cuprous iodide (10 mg, 5 mol %), Et$_3$NH (3.5 mL) and dried
THF (7 mL) yielded 2a as a gray solid (131 mg, 43.8%) after purification by column chromatography (dichloromethane). Rf = 0.5 (dichloromethane). M.p. 108 °C. IR (neat): ν/cm\(^{-1}\) 2963, 2921, 2851, 2099, 1644, 1581, 1465, 1402, 1335, 1261, 1092, 798, 766, 684. \(^1\)H NMR (400 MHz; CD\(_2\)Cl\(_2\)): δ 7.80 (s, 6H), 7.67 (s, 3H), 7.50 (d, J = 8 Hz, 12H), 7.26 (d, J = 8 Hz, 12H), 7.21 (s, 6H), 7.17 (s, 3H), 7.03 (s, 12H), 3.96-4.02 (m, 36H), 2.19 (m, 72H), 1.70-1.84 (m, 36H), 1.22-1.48 (m, 396H), 0.88 (m, 54H). \(^{31}\)P NMR (161.9 MHz, CD\(_2\)Cl\(_2\)): δ 11.95 (J\(_{Pt-P}\) = 2362.1 Hz); \(^{13}\)C NMR (CD\(_2\)Cl\(_2\); 100 MHz): δ 164.6, 152.7, 140.7, 130.7, 129.4, 124.3, 119.3, 104.9, 72.9, 68.8, 31.4, 29.8, 29.1, 28.9, 25.6, 22.1, 16.1, 15.9, 15.7, 13.3, 7.6. MALDI-TOF MS of 2a: m/z calcd for C\(_{420}\)H\(_{884}\)N\(_6\)O\(_{24}\)P\(_{12}\)Pt\(_6\) ([M+H]+) 7738.72, found 7738.60.

**Synthesis of compound 2b.** Following the procedure for the preparation of 1a. 9 (92 mg, 0.024 mmol), 5 (188 mg, 0.29 mmol), cuprous iodide (6 mg, 3 mol %), Et\(_2\)NH (2.5 mL) and dried THF (4.5 mL) yielded 2b as a gray solid (75 mg, 44.5%) after purification by column chromatography (dichloromethane). Rf = 0.4 (dichloromethane). M.p. 70 °C. IR (neat): ν/cm\(^{-1}\) 2922, 2852, 2096, 1567, 1497, 1467, 1413, 1379, 1332, 1227, 1115, 1035, 868, 828, 767, 733, 683, 631. \(^1\)H NMR (400 MHz; CD\(_2\)Cl\(_2\)): δ 7.65 (s, 3H), 7.19 (s, 6H), 7.16 (s, 3H), 6.44 (s, 12H), 3.85-3.95 (m, 36H), 2.15-2.19 (m, 72H), 1.77 (m, 36H), 1.21-1.27 (s, 396H), 0.88 (m, 54H). \(^{31}\)P NMR (161.9 MHz, CD\(_2\)Cl\(_2\)): δ 11.94 (J\(_{Pt-P}\) = 2362.1 Hz); \(^{13}\)C NMR (CD\(_2\)Cl\(_2\); 100 MHz): δ 153.2, 137.2, 134.3, 134.2, 130.8, 129.5, 124.6, 124.2, 122.6, 110.0, 109.6, 108.6, 91.1, 87.4, 73.8, 69.4, 32.4, 30.8, 30.2, 30.1, 29.9, 29.8, 26.6, 23.1, 17.0, 16.9, 16.7, 14.3, 8.6. MALDI-TOF MS of 2b: m/z calcd for C\(_{378}\)H\(_{654}\)O\(_{20}\)P\(_{12}\)Pt\(_6\) ([M+H]+) 7024.5, found 7024.1.
3. Characterization of Complexes 1a–b and 2a–b.

Fig. S1 $^{31}$P NMR spectra (CD$_2$Cl$_2$, 298 K) of (A) star-shaped complex 1a, (B) platinum-acetylide precursor 4.

Fig. S2 $^{31}$P NMR spectra (CD$_2$Cl$_2$, 298 K) of (A) star-shaped complex 1b, (B) platinum-acetylide precursor 6.
Fig. S3 $^{31}$P NMR spectra (CD$_2$Cl$_2$, 298 K) of (A) branched complex 2a, (B) branched complex 2b, (C) branched hexakisplatinum precursor 9.
4. UV-vis and Fluorescence Spectra of 1a-b and 2a-b.

Table S1. Photophysical data for compounds 1a, 1b, 2a and 2b.

<table>
<thead>
<tr>
<th>Compound (concentration/M)</th>
<th>solvent(298K)</th>
<th>λ&lt;sub&gt;abs&lt;/sub&gt; (nm)</th>
<th>ε (M&lt;sup&gt;-1&lt;/sup&gt;cm&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>λ&lt;sub&gt;ε&lt;/sub&gt; (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a (4.0 × 10&lt;sup&gt;-6&lt;/sup&gt;)</td>
<td>Methylene chloride</td>
<td>260.9</td>
<td>133250</td>
<td>491.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>301.9</td>
<td>184500</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>341.0</td>
<td>243250</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>410.0</td>
<td>264500</td>
<td></td>
</tr>
<tr>
<td>1b (4.0 × 10&lt;sup&gt;-6&lt;/sup&gt;)</td>
<td>Methylene chloride</td>
<td>267.1</td>
<td>150250</td>
<td>492.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td>334.9</td>
<td>180500</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>409.0</td>
<td>224750</td>
<td></td>
</tr>
<tr>
<td>2a (3.0 × 10&lt;sup&gt;-6&lt;/sup&gt;)</td>
<td>Methylene chloride</td>
<td>297.1</td>
<td>177229</td>
<td>398.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td>350.0</td>
<td>208228</td>
<td></td>
</tr>
<tr>
<td>2b (3.0 × 10&lt;sup&gt;-6&lt;/sup&gt;)</td>
<td>Methylene chloride</td>
<td>270.1</td>
<td>200596</td>
<td>396.96</td>
</tr>
<tr>
<td></td>
<td></td>
<td>292.9</td>
<td>232906</td>
<td>479.85</td>
</tr>
<tr>
<td></td>
<td></td>
<td>339.0</td>
<td>236263</td>
<td></td>
</tr>
</tbody>
</table>

Fig. S4 (A) UV-vis absorption spectrum and (B) emission spectrum of complex 1a in CH<sub>2</sub>Cl<sub>2</sub> (concentration = 4.0 × 10<sup>-6</sup> M).
Fig. S5 (A) UV-vis absorption spectrum and (B) emission spectrum of complex 1b in CH₂Cl₂ (concentration = 4.0 × 10⁻⁶ M).

Fig. S6 (A) UV-vis absorption spectrum and (B) emission spectrum of complex 2a in CH₂Cl₂ (concentration = 3.0 × 10⁻⁶ M).

Fig. S7 (A) UV-vis absorption spectrum and (B) emission spectrum of complex 2b in CH₂Cl₂ (concentration = 3.0 × 10⁻⁶ M).

Fig. S8 Concentration dependent emission spectra of 1a (A) and 1b (B) in CH₂Cl₂/Acetone = 1:1.
5. Additional SEM Images of Complexes 1a and 2a at Different Scales.

Fig. S9 SEM images of star-shaped complex 1a prepared in CH$_2$Cl$_2$/Acetone = 3:1 at different scales.

Fig. S10 SEM images of star-shaped complex 1a prepared in CH$_2$Cl$_2$/Acetone = 1:1 at different scales.

Fig. S11 SEM images of branched complex 2a prepared in CH$_2$Cl$_2$/Acetone = 3:1 at different scales.
6. Concentration-Dependent and Temperature-Dependent $^1$H NMR Spectra of Complexes 1a and 2a.

Fig. S12 Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$) of star-shaped complex 1a at different concentrations at 25 °C showing the aromatic region (using TMS as internal standard).
Fig. S13 Partial $^1$H NMR spectra (400 MHz, CD$_2$Cl$_2$) of branched complex 2a at different concentrations at 25 °C showing the aromatic region (using TMS as internal standard).
Fig. S14 Partial $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 25 mg/mL) of 1a at variable temperature (using TMS as internal standard).
Fig. S15 Partial $^1$H NMR spectra (500 MHz, CD$_2$Cl$_2$, 25 mg/mL) of 2a at variable temperature (using TMS as internal standard).

A weighed sample of gelator was mixed with a solvent (0.05 mL) in a septum-capped vial and heated. If the compound was unable to dissolve, it was noted as insoluble (I). If a clear solution was obtained, the hot resulting solution was left for 24 h at room temperature. The aggregation state was then assessed. If no flow was observed when inverting the vial, a stable gel was formed and noted as gelation (G). If precipitation occurred, P was noted. If the clear solution (>100 mg/mL) was retained, it was marked as soluble (S). Repeated heating and cooling confirmed the thermo-reversibility of the gelation process. The critical gelator concentration (CGCs) of the organogelator was determined by measuring the minimum amount of gelator required for the formation of a stable gel at 25 °C. The SEM Samples were prepared by spinning the gels on a silicon substrate, dried under air.

Table S2. Gelation properties and critical gelator concentrations (CGCs) of complexes in various organic solvents at 25°C.²

<table>
<thead>
<tr>
<th>solvent</th>
<th>2a</th>
<th>2b</th>
<th>1a</th>
<th>1b</th>
</tr>
</thead>
<tbody>
<tr>
<td>cyclohexane</td>
<td>G(11.5)</td>
<td>S</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>n-hexane</td>
<td>G(19.5)</td>
<td>S</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>n-heptane</td>
<td>G(19.5)</td>
<td>S</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>acetone</td>
<td>P</td>
<td>I</td>
<td>I</td>
<td>P</td>
</tr>
<tr>
<td>tetrahydrofuran</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>ethyl acetate</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>n-propanol</td>
<td>I</td>
<td>I</td>
<td>I</td>
<td>I</td>
</tr>
<tr>
<td>toluene</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
<tr>
<td>n-dodecane</td>
<td>I</td>
<td>S</td>
<td>P</td>
<td>S</td>
</tr>
<tr>
<td>n-octane</td>
<td>G(15.6)</td>
<td>S</td>
<td>PG</td>
<td>S</td>
</tr>
<tr>
<td>n-decane</td>
<td>G(19.5)</td>
<td>S</td>
<td>PG</td>
<td>S</td>
</tr>
<tr>
<td>dioxane</td>
<td>S</td>
<td>S</td>
<td>S</td>
<td>S</td>
</tr>
</tbody>
</table>
The value given in parentheses is the CGC in mg/mL.

Table S3. The gel-sol phase-transition temperature ($T_{gel}$) of branched complex 2a.

<table>
<thead>
<tr>
<th>solvent</th>
<th>cyclohexane</th>
<th>n-hexane</th>
<th>n-heptane</th>
<th>n-octane</th>
<th>n-decane</th>
</tr>
</thead>
<tbody>
<tr>
<td>2a</td>
<td>46-48°C</td>
<td>52-54°C</td>
<td>45-47°C</td>
<td>51-53°C</td>
<td>43-45°C</td>
</tr>
</tbody>
</table>

Fig. S16 SEM images of the xerogels of branched complex 2a prepared in different solvents: (a) cyclohexane; (b) n-hexane; (c) n-heptane; (d) n-octane; (e) n-decane. Scale bar is 5.0 µm. Samples were prepared by spinning the gels on a silicon substrate, dried under air.
8. Multiple Nuclear NMR ($^1$H, $^{31}$P, and $^{13}$C NMR) Spectra and MALDI-TOF MS of New Compounds.

Fig. S17 (A) $^1$H NMR, (B) $^{31}$P NMR and (C) $^{13}$C NMR spectra of platinum-acetylide precursor 4 in CDCl$_3$.
Fig. S18 (A) $^1$H NMR, (B) $^{31}$P NMR and (C) $^{13}$C NMR spectra of platinum-acetylide precursor 6 in CDCl$_3$. 
Fig. S19 (A) $^1$H NMR, (B) $^{31}$P NMR and (C) $^{13}$C NMR spectra of branched hexakisplatinum precursor 9 in CDCl$_3$. 
Fig. S20 (A) $^1$H NMR, (B) $^{31}$P NMR, (C) $^{13}$C NMR spectra and (D) MALDI-TOF MS of star-shaped complex 1a in CD$_2$Cl$_2$. 
Fig. S21 (A) $^1$H NMR, (B) $^{31}$P NMR, (C) $^{13}$C NMR spectra and (D) MALDI-TOF MS of star-shaped complex 1b in CD$_2$Cl$_2$. 

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013
Fig. S22 (A) $^1$H NMR, (B) $^{31}$P NMR, (C) $^{13}$C NMR spectra and (D) MALDI-TOF MS of branched complex 2a in CD$_2$Cl$_2$.
Fig. S23 (A) $^1$H NMR, (B) $^{31}$P NMR, (C) $^{13}$C NMR spectra and (D) MALDI-TOF MS of branched complex 2b in CD$_2$Cl$_2$.  

Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2013
9. References


