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Electronic Supplementary Information for

# Engineering Orthogonality in the Construction of Alternating Rhomboidal Copolymer with High Fidelity via Integrative Self-Sorting

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#### 1. Measurements

Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded with a Bruker Avance DMX 400 and 500 spectrophotometer with use of the deuterated solvent as the lock and the residual solvent or TMS as the internal reference. <sup>1</sup>H and <sup>13</sup>C NMR chemical shifts are reported relative to residual solvent signals, and <sup>31</sup>P{<sup>1</sup>H} NMR chemical shifts are referenced to an external unlocked sample of 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0.0). The correlated spectroscopy (COSY) and two-dimensional diffusion-ordered (2D DOSY) NMR spectra were recorded on a Bruker DRX500 spectrometer. DOSY experiments were performed using a modified version of the Bruker sequence ledbpgp2s. The experiments were processed with standard Bruker 1D and 2D DOSY software. The diffusion coefficients were determined by fitting the intensity decays to the equation below:

## $I = I_0 \exp[-D\gamma^2 g^2 \delta^2 (\Delta - \delta/3)]$

where I and  $I_0$  represent the signal intensities in presence and absence of gradient pulses respectively, D is the diffusion coefficient,  $\gamma$  is the <sup>1</sup>H gyromagnetic ratio,  $\delta$  is duration of the gradient pulse,  $\Delta$  is the total diffusion time and g is the applied gradient strenght. The diffusion coefficient values were determined using the decay of the intensity of selected proton signals and the T1/T2 processing tool of the Bruker software Topspin 1.3. The diffusion time was  $\Delta = 100$  ms and the duration of the pulse gradient was  $\delta = 2$  ms. Dynamic light scattering (DLS) was carried out Malvern ZS90 zeta-sizer instrument at room temperature. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. Transmission electron microscope (TEM) image was obtained using JEOL JEM 2100 high resolution transmission electron microscope.

2. <sup>1</sup>H NMR and <sup>31</sup>P{<sup>1</sup>H} NMR spectra of 60° organoplatinum(II) acceptor **1**, and <sup>1</sup>H NMR spectrum of 120°B21C7-functionalized ligand **2** 



*Fig. S2.* <sup>31</sup>P $\{^{1}H\}$  NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, room temperature, 161.8 MHz) of 1.



*Fig. S3.* <sup>1</sup>H NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, room temperature, 400 MHz) of **2**.

3. <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra of precursor S5







Fig. S5. <sup>13</sup>C NMR spectrum (CDCl<sub>3</sub>, room temperature, 125 MHz) of S5.







4. <sup>1</sup>H NMR, <sup>13</sup>C NMR and mass spectra of 120°BPP34C10-functionalized ligand 3





Fig. S9. Electrospray ionization mass spectrum of 3.







Fig. S11. <sup>1</sup>C NMR spectrum (CD<sub>3</sub>CN, room temperature, 100 MHz) of 4.

### Spectrum 1A Plot - 2012-6-12 18:58



Fig. S12. Electrospray ionization mass spectrum of 4.



Fig. S14.  ${}^{31}P{}^{1}H$  NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, room temperature, 161.8 MHz) of 5.



Fig. S15. Experimental (red) and calculated (blue) electrospray ionization mass spectra of 5.



*Fig. S17.* <sup>31</sup>P{ $^{1}$ H} NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>, room temperature, 161.8 MHz) of **6**.



Fig. S18. Experimental (red) and calculated (blue) electrospray ionization mass spectra of 6.





*Fig. S19.* The <sup>1</sup>H NMR NMR spectra (400 MHz, CD<sub>3</sub>CN, room temperature) of (a) B21C7 7, (b) an equimolar solution of 7 and 10, (c) 10, (d) 8, (e) an equimolar solution of 8 and 9, and (f) BPP34C10 9. c = 5.00 mM.



*Fig. S20.* The <sup>1</sup>H NMR NMR spectra (400 MHz, CD<sub>3</sub>CN, room temperature) of (a) B21C7 7, (b) an equimolar solution of 7, 8, 9 and 10, (c) 8, (d) 10, (e) an equimolar solution of 7, 8, 9 and 10, and (f) BPP34C10 9. c = 5.00 mM.

9. <sup>31</sup>P{<sup>1</sup>H} NMR spectra of self-sorting metallacyclic assemblies



*Fig. S21.* <sup>31</sup>P{<sup>1</sup>H} NMR spectra (CD<sub>2</sub>Cl<sub>2</sub>, room temperature, 161.8 MHz) of the individual metallacycles **5** (a), **6** (c) and the self-sorting assemblies (b).

10. Partial COSY NMR spectrum of the alternating metallacyclic copolymer



*Fig. S22.* Partial COSY NMR (500 MHz,  $CD_2Cl_2/CD_3CN$  1:1 v/v, 293 K) spectrum of the alternating metallacyclic copolymer at a concentration of 6.00 mM.

11. DOSY NMR experiments of the alternating metallacyclic copolymer at different concentrations



*Fig. S23.* DOSY NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>CN 1:1 v/v, room temperature, 500 MHz) of the alternating metallacyclic copolymer at 120 mM.



*Fig. S24.* DOSY NMR spectrum ( $CD_2Cl_2/CD_3CN$  1:1 v/v, room temperature, 500 MHz) of the alternating metallacyclic copolymer at 96.0 mM.



*Fig. S25.* DOSY NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>CN 1:1 v/v, room temperature, 500 MHz) of the alternating metallacyclic copolymer at 60.0 mM.



*Fig. S26.* DOSY NMR spectrum ( $CD_2Cl_2/CD_3CN$  1:1 v/v, room temperature, 500 MHz) of the alternating metallacyclic copolymer at 35.0 mM.



*Fig. S27.* DOSY NMR spectrum (CD<sub>2</sub>Cl<sub>2</sub>/CD<sub>3</sub>CN 1:1 v/v, room temperature, 500 MHz) of the alternating metallacyclic copolymer at 13.0 mM.

### 12. Estimation of the molecular weight of the ARC

The estimation of the molecular weight of the formed supramolecular polymer employs the following methods: Firstly, the extent of reaction *p* can be estimated by calculating the integration ratio of linear species and cyclic species signals in <sup>1</sup>H NMR. Secondly, the degree of polymerization could be calculated by adopting Carothers equation that n = 1/(1-p). Finally, the product of *n* and molecular weight of repeating units can lead to the molecular weight of the copolymer. For example, When the crown unit concentration is 26 mM, the integration ratio of linear species and cyclic species signals is 0.72. Based on the Carothers equation, the degree of polymerization *n* has been calculated with the value about 3.57. After knowing that the molecular weight of one repeating unit is 8696.95, the molecular weight could be calculated by the following equation: 8696.95 × 3.57 ≈ 31 kDa, corresponding to about 7 repeated rhomboidal units.