Supporting Information

## Controlling the supramolecular polymerization of dinuclear isocyanide gold(I) arylethynylene complexes through tuning the central $\pi$ -conjugated moiety

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## Curve-fitting for solvent-dependent self-assembly

The normalized degree of aggregation ( $\alpha_{agg}$ ) was deduced from the absorbance change in UV-vis spectra upon increasing the volume fraction (*f*) of good solvents, according to Eq. (1):

$$\alpha_{agg} = \frac{A(f) - A(f=0)}{A(f=1) - A(f=0)}$$
(1)

Where A(f) is the absorbance at a given volume fraction of good solvents.

The nucleation-elongation model for solvent-dependent self-assembly was reported by Meijer and coworkers,<sup>1,2</sup> as described by Eq. (2) and (3). The simulation and curve-fittings with the equilibrium model were performed using MATLAB R2018.

$$\Delta G_f = \Delta G_f + m_{\times} f_{(2)}$$
$$K_e = exp^{(0)} (-\Delta G_f / RT)_{(3)}$$

 $\Delta G_f$  represents the Gibbs free energy gain upon addition of monomer in poor solvent. *R* is the gas constant, and *T* is the temperature. The dependence of  $\Delta G_f$  on *f* is described by the m-value.

The cooperativity factor  $\sigma$  is given by Eq. (4):

$$\sigma = \frac{K_n}{K_e}$$
(4)

Where  $K_n$  and  $K_e$  are the binding constants for the nucleation and elongation steps, respectively.

## Procedures for self-assembly experiments

Compound 1-3 was suspended in hydrocarbon-based solvents such as *n*-hexanes, heptane, and MCH at a concentration of 0.5 mg mL<sup>-1</sup>, gently heated to ensure complete dissolution, then allowed to cool to ambient temperature over 24 h. A drop of each solution was dropcast onto carbon-coated copper grids for analysis by TEM. Atomic force microscopy (AFM) images were collected by dropcasting from solution (0.5 mg mL<sup>-1</sup>) onto carbon coated mica.



Figure S1. MALDI-TOF mass spectra of 1.



Figure S2. MALDI-TOF mass spectra of 2.



Figure S3. MALDI-TOF mass spectra of 3.



Figure S4. <sup>1</sup>H NMR spectrum of 1 in CDCl<sub>3</sub>.



Figure S5<sup>13</sup>C NMR spectrum of 1 in CDCl<sub>3</sub>.



Figure S6. <sup>1</sup>H NMR spectrum of 2 in CDCl<sub>3</sub>.



Figure S7. <sup>13</sup>C NMR spectrum of 2 in CDCl<sub>3</sub>.



Figure S8. <sup>1</sup>H NMR spectrum of 3 in CDCl<sub>3</sub>.



Figure S9. <sup>13</sup>C NMR spectrum of 3 in CDCl<sub>3</sub>.



Figure S10. IR spectra of the isocyanide ligand and complexes 1-3.



Figure S11. Thermogravimetric analysis (TGA) for 1-3.



**Figure S12**. (a) TEM images of a) seed micelles of 1. (b-e) TEM images of fibre-like micelles after addition of (b) 0.25, (c) 0.5, (d) 1, (e) 2 eq. of 1 unimer to seed micelles. (f) Linear dependence of average contour length ( $L_n$ ) on the monomer to seed molar ratio for the seeded growth of 1.



Figure S13. Histogram plots of micelle contour length after addition of 1 unimer to seed micelles.



Figure S14. H NMR spectra of 3 in CDCl<sub>3</sub> (top) and d12-cyclohexane/ CDCl<sub>3</sub> (10 : 1, v/v) (bottom).



**Figure S15**. Pt(II) complex with bulky phosphine ligand reported by Wang and coworker.<sup>3</sup> The critical gelation concentration is reported to be 10 mM (*ca.* 20 mg/mL), which is much higher than complex **3** (critical gelation concentration: 10 mg/mL). The result confirms that less-bulky isocyanide ligand allows closer packing of molecules.



Figure S16. XRD spectra of 1 and 3 in the solid and xerogel states.



**Figure S17**. (a) UV-vis spectra changes of **1** ( $c = 1 \times 10^{-5}$  M) upon Ag<sup>+</sup> titration in EtOH/CHCl<sub>3</sub> (1 : 1, v/v). (b and c) Emission spectra changes of **1** ( $c = 1 \times 10^{-5}$  M) upon Ag<sup>+</sup> titration in EtOH/CHCl<sub>3</sub> (1 : 1, v/v).

## References

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