Electronic Supplementary Information

Seeded-growth self-assembled polymerization of a ferrocene-bearing palladium(II)-terpyridyl bimetallic complex

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1. General Information

All reactions were carried out under an inert atmosphere. All chemicals and solvents were commercially available and purchased from Acros Organics. They were used as received unless otherwise stated. ¹H and ¹³C NMR spectra were measured on a Bruker Avance-III 400 MHz FT-NMR Spectrometer at ambient temperature, with reference to the NMR solvent residual resonances. Mass spectrometry experiments for ligand Py-PEG₁₆ and 2 were performed on an Agilent 6540 Liquid Chromatography -Electrospray Ionization Quadrupole-TOF Mass Spectrometer. For 3, the experiments were performed on a Bruker UltrafleXtreme MALDI-TOF Mass Spectrometer. Samples were prepared by mixing trans-2-[3-(4-tert-butylphenyl)-2-methyl-2propenylidene]malonitrile matrix (10 mg/mL in 1,4-dioxane) with a solution of target compounds (1 mg/mL in 1,4-dioxane) in a 1:9 (v/v) ratio. 0.5 μ L of the mixed solution was drop-cast onto the MALDI-TOF stainless steel sample plate and allowed to dry in air. The single crystals of 2 were prepared by diffusing diethyl ether (Et_2O) into its acetonitrile (ACN) solution at 2 °C, and the structure was characterized on a Bruker D8 Venture single crystal X-Ray diffractometer at room temperature.¹

UV-vis Absorption Spectroscopy. UV-vis absorption spectra were measured on a Varian Cary 4000 UV-visible Spectrometer employing standard quartz cells (1 cm) from 200 to 800 nm. Kinetic studies of the living crystallization-driven supramolecular polymerization were performed using the same equipment. The detection wavelength was set at 600 nm with the signal averaging time at 0.1 s. UV-vis analysis in solution avoids the potential drying of solvents and aggregation effects that may confuse the TEM analysis on the kinetic growth.

Computational Details. Energy calculations of **2** based on its single crystal structure were carried out using B3LYP/GENECP functional in which the 6-311G(d) basis set for main group atoms and LanL2DZ for Fe and Pd atoms were used. For TD-DFT calculations, the PBE1PBE/GENECP functional was used for optimization of the structure with the 6-311G(d) basis set for main group atoms and LANL2DZ for Fe and Pd atoms, as well as the polarizable continuum model in which acetonitrile was considered as the solvent.

Sonication. Seeds for crystallization-driven supramolecular polymerization were prepared by a mild sonication on self-assembled nanostructures at 0 °C in a Crest P500D-45 ultrasonic cleaner for 2 h.

TEM. TEM micrographs for the nanoribbons and platelets were acquired on a JEOL JEM-2100F Field Emission STEM equipped with an Olympus SIS digital camera which was operated at 200 kV. The sample was prepared by drop-casting 10 μ L of the solution from crystallization-driven supramolecular polymerization experiments onto a copper grid with carbon membrane support. No staining was required. Nanoribbons and platelets were statistically analyzed using the ImageJ software developed by National Institutes of Health in the US.

AFM. AFM characterizations were performed on the Bruker MultiMode 8 Scanning Probe Microscope. The sample was prepared by spin-coating 10 μ L of solution from crystallization-driven supramolecular polymerization experiments on a silica wafer. The image was characterized on a 2 μ m × 2 μ m area. **DLS.** DLS experiments were performed on the Zetasizer Nano-ZS Dynamic Light Scattering System.

XRD. The XRD experiments were performed on a Rigaku Smartlab 9 kW X-ray Diffractometer in parallel beam (PB) mode. The sample was drop-cast onto a silicon wafer for the measurement.

2. General Procedures for the Synthesis of Ligand and Complexes

Synthesis of Py-PEG₁₆. The ancillary ligand was synthesized according to a reported literature method.² Ts-PEG₁₆-Me (3.00 g, 3.37 mmol, 1.0 equiv), 4-hydroxypyridine (320 mg, 3.37 mmol, 1.0 equiv) and K₂CO₃ (512 mg, 3.70 mmol, 1.1 equiv) were dissolved in ACN (100 mL) and the mixture was refluxed for 1 day. After filtration to remove the solid, ACN was evaporated under vacuum. The crude product was washed with H₂O (50 mL) and brine (50 mL), and it was extracted into DCM and dried over MgSO₄. The product was obtained after silica gel chromatography (DCM:MeOH = 8:1, v/v) as a light-yellow oil (yield = 55%). ¹H NMR (400 MHz, Chloroform-*d*): δ 7.41–7.31 (m, 2H), 6.33–6.20 (m, 2H), 3.88 (t, *J* = 4.9 Hz, 2H), 3.66 (t, *J* = 4.9 Hz, 2H), 3.59–3.40 (m, 54H), 3.32 (s, 2H), 3.27 (s, 3H). HRMS (ESI): [C₃₈H₇₂NO₁₇]⁺ = 814.4837 [calcd: 813.4722].

Synthesis of 2. The complex 2 was synthesized based on a reported literature method with some slight modifications.¹ 4'-(Ferrocenyl)-[2,2':6',2'']terpyridine (389 mg, 0.5 mmol, 1 equiv) was dissolved in 15 mL ACN, and Pd(OAc)₂ (112 mg, 0.5 mmol, 1 equiv) was added into the solution. After 1 h of stirring, a dark blue slurry was observed. HBF₄·Et₂O (0.27 mL, 1.0 mmol, 2.0 equiv) was added dropwise into the slurry to exchange the acetate ligand by the MeCN ligand. The mixture was stirred for another 30 min, and it was dropped into 50 mL of diethyl ether (Et₂O) for precipitation. The precipitate was centrifuged at 6000 rpm to afford a black solid. The crude product was recrystallized from ACN/Et₂O to afford black crystals (yield = 90%). ¹H NMR

(400 MHz, Acetonitrile-*d*₃): δ 8.56 (d, *J* = 5.6 Hz, 2H), 8.45 (d, *J* = 4.3 Hz, 4H), 8.12 (s, 2H), 7.83 (t, *J* = 5.2 Hz, 2H), 5.25 (s, 2H), 4.89 (s, 2H), 4.22 (s, 5H), 1.96 (s, 3H).
¹³C NMR (100 MHz, CD₃CN): δ 161.53, 158.94, 155.90, 153.85, 144.27, 129.89, 126.37, 120.80, 78.21, 75.07, 72.19, 69.97. HRMS (ESI): [C₂₇H₂₁FeN₄Pd]⁺ = 563.0163 [calcd: 564.0229].

Synthesis of 3. To a solution of **2** (369 mg, 0.5 mmol, 1.0 equiv) in ACN (15 mL) Py-PEG₁₆ (407 mg, 0.5 mmol, 1.0 equiv) was dissolved in 5 mL ACN and the solution was added via syringe. The solution was stirred at reflux temperature vigorously for 24 h. After cooling to room temperature, the solution was added dropwise into 100 mL of Et₂O to precipitate a purple solid. The mixture was washed with Et₂O and centrifuged at 6000 rpm to afford a black gum (yield = 82%). ¹H NMR (400 MHz, Chloroform-*d*): δ 8.49 (s, 2H), 8.16 (s, 2H), 8.10 (s, 2H), 7.98 (s, 2H), 7.87 (s, 2H), 7.63 (s, 2H), 7.31 (s, 2H), 5.21 (s, 2H), 4.55 (s, 2H), 4.33 (s, 2H), 4.03 (s, 5H), 3.87 (s, 2H), 3.62 (s, 59H), 3.37 (s, 4H). ¹³C NMR (100 MHz, CDCl₃): δ 179.04, 160.30, 157.28, 154.06, 150.47, 144.34, 143.06, 129.01, 126.28, 119.19, 118.08, 74.34, 72.04, 71.35, 70.65, 69.59, 69.27, 59.15. HRMS (MALDI-TOF): [C₆₃H₈₉FeN₄O₁₇Pd]⁺ = 1335.369 [calcd: 1336.469].

3. NMR and Mass Spectra



Fig. S1. ¹H NMR spectrum of 2 in acetonitrile- d_3 .



Fig. S2. ¹³C NMR spectrum of 2 in acetonitrile- d_3 .



Fig. S3. ¹H NMR spectrum of Py-PEG₁₆ in CDCl₃.



Fig. S4. ¹H NMR spectrum of 3 in CDCl₃.



Fig. S5. ¹³C NMR spectrum of 3 in CDCl₃.



Fig. S6. ESI-mass spectrum of Py-PEG₁₆.



Fig. S7. ESI-mass spectrum of 2.



Fig. S8. MALDI-TOF mass spectrum of 3.

4. X-Ray Crystallographic Details

A single crystal was selected and mounted at room temperature.¹ Intensity data were collected on a Bruker D8 Venture system using fine-focus sealed tube Mo-Kα radiation. Unit cell determination, data collection strategy and integration were carried out with the Bruker APEX2 suite of programs. Multi-scan absorption correction was applied.³ The structure was solved with XS⁴ and refined by full-matrix least-squares methods based on F² with SHELXL-2013⁵. The crystallographic data of complex **2** have been deposited on the Cambridge Crystallographic Data Centre with the CCDC number of 1530670.¹

Empirical formula	$C_{29}H_{25}B_2F_8FeN_5Pd$	
Formula weight	779.41	
Temperature	173	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	<i>P</i> -1	
Unit cell dimensions	a = 11.2240(10) Å	$\alpha = 90.56(2)^{\circ}$
	b = 11.5166(10) Å	$\beta = 112.57(2)^{\circ}$
	c = 13.5262(10) Å	$\gamma = 109.78(2)^{\circ}$
Volume	1499.5(4) Å ³	
Z	2	
Density (calculated)	1.726 g cm ⁻³	
Absorption coefficient	1.163 mm ⁻¹	
F(000)	776	
Crystal size	0.50 x 0.30 x 0.30 mm ³	
Theta range for data collection	2.71 to 30.97°	
Index ranges	-16<=h<=16, -16<=k<=12, -19<=l<=19	
Reflections collected	15868	
Independent reflections	9012 [R(int) = 0.0176]	
Completeness to $\theta = 30.97^{\circ}$	94.5%	
Absorption correction	Multi-scan	
Max. and min. transmission	0.746 and 0.627	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	9012 / 15 / 430	

Goodness-of-fit on F ²	1.127
Final R indices [I>2sigma(I)]	R1 = 0.0461, wR2 = 0.1101
R indices (all data)	R1 = 0.0582, wR2 = 0.1211
Largest diff. peak and hole	1.641 and -0.775 e.Å ⁻³



Fig. S9. (a) Vertical view and (b) front view of 2. Hydrogen atoms are neglected for clarity.



Fig. S10. C–H··· π interactions in 2.



Fig. S11. $H \cdots F$ hydrogen bonding in **2**.



5. Optical and Electrochemical Data

Fig. S12. (a) UV–vis absorption spectra of 2 in experiment at 2×10^{-5} M (blue), in simulation (green), 3 at 2×10^{-5} M (black) and the oscillation strength of the simulated peaks (olive bar). (b) CV spectra of 2 (blue) and 3 (black) measured in ACN. (c) HOMO and LUMO structures of 2 from DFT calculations.

	HOMO ^a	LUMO ^b	$E_{\rm g}^{{\rm opt}b}$	HOMO ^c	LUMO ^c	E_{g}^{c}
	(eV)	(eV)	(eV)	(eV)	(eV)	(eV)
2	-4.94	-3.27	1.67	-10.50	-8.55	1.95
3	-4.90	-3.20	1.70			

Table S1. Electrochemical Properties of Complexes 2 and 3

^{*a*}For both complexes HOMO = $-[E_{onset} + 4.8]$ eV, $E_{ox(ferrocene)} = 0.45$ eV vs Ag/AgCl, in which E_{onset} is the onset value of oxidation potentials. ^{*b*}LUMO = HOMO + E_{g}^{opt} , in which E_{g}^{opt} represents the optical bandgap estimated from the UV–vis absorption edge. ^{*c*}Obtained from DFT energy calculations, where LUMO = HOMO + E_{g} .



Fig. S13. UV-vis absorption spectra of 2 obtained from TD-DFT calculations.

Table S2. Selected parameters for the UV-vis absorption of 2 calculated by TD-DFT,

	Electronic transition ^a	Excitation energy	\mathbf{F}^{b}	Composition ^c	\mathbf{CI}^d
Absorption	$S_0 \rightarrow S_1$	2.15 eV (576 nm)	0.0004	H−1→L	0.53460
				$H-1\rightarrow L+4$	0.11954
	$S_0 \rightarrow S_2$	2.22 eV (558 nm)	0.0424	H→L	0.51626
				$H\rightarrow L+4$	0.10490
	$S_0 \rightarrow S_{13}$	3.53 eV (351 nm)	0.2303	H−3→L	0.65624
				H−2→L	-0.12872

based on the optimized ground state geometries.

^{*a*}Only selected excited states were considered. The numbers in parentheses are the excitation energy in wavelength. ^{*b*}Oscillator strength. ^{*c*}H represents HOMO and L represents LUMO. Only the main configurations are presented. ^{*d*}Coefficient of the wavefunction for each excitation. The CI coefficients are in absolute values.



Fig. S14. The UV–vis absorption spectra of 3 in ACN/CHCl₃ solvent mixture at 2×10^{-5} M at ambient temperature. (a) in full ratio; (b) in 100%, 30% and 10%. The percentage represents the ACN portion in ACN/CHCl₃.

6. TEM Images and XRD Data



Fig. S15 TEM image of self-assembled 3 in (a) $ACN/CHCl_3$ (3:7, v/v) and (b) pure

 $CHCl_3$ at the concentration of $2\times 10^{\text{--}4}$ M.





Fig. S16 TEM images of seed-growth self-assembled **3** in different unimer/seed ratio: (a – b) 1:1, (c – d) 2:1, (e – f) 3:1, (g – h) 4:1 and (i – j) 5:1. The solvent ratio is kept at 3:7 of ACN/CHCl₃. The images on the left column show the structures at 8 h, and those on the right column show the structures at 24 h.



Fig. S17 TEM images of seed-growth self-assembled 3 after aging for 7 days.



Fig. S18 (a) Experimental XRD pattern of self-assembled **3** (blue line) and simulated XRD pattern of the model complex **2** (black line). (b) The TEM image showing crystal lattice of nanostructure and (c) the zoomed-in TEM image for fast Fourier transformation (FFT) pattern. (d) FFT pattern of the crystal lattice. (e) The profiles of the crystal lattices showing the d-spacing values.

7. AFM Images

AFM experiments on the self-assembled nanoribbons were performed. The average height of the nanoribbons is 3.9 nm. It is quite close to 10 times of the π - π distance (3.44 Å) in the single crystal model, from which we can predict that 10 unimers aggregate along the direction of π - π aggregation. Due to the equipment limitations, the resolution of the AFM graph is low.

However, it is very difficult to judge the packing in the direction of long and wide axis, since the PEG unit is a flexible chain.



Fig. S19 AFM image of 3 after supramolecular polymerization and its height configuration.

8. DLS Data

DLS experiments of different unimer concentrations were performed. The intensity data are plotted and listed below. All samples were characterized three times and the average was taken.



Fig. S20 DLS spectra of different samples at different molar ratio

Sample	PDI	Peak 1 Mean	Peak 2 Mean	Peak 1 Area	Peak 2 Area
		Diameter	Diameter	Intensity	Intensity
		(nm)	(nm)	(%)	(%)
U/S = 1	0.337	242.0	40.35	91.80	8.20
U/S = 2	0.342	265.4	32.38	95.27	4.73
U/S = 3	0.374	285.1	51.83	92.30	7.70
U/S = 4	0.375	297.8	54.68	91.73	8.27
U/S = 5	0.410	305.2	57.75	91.63	8.37

Table S3 DLS data of the self-assembled structures at 24 h

U/S = unimer/seed molar ratio

These two peaks represent the existence of rod-like or ribbon-like nanostructures, where the peak with higher intensity represents the translational motion of the structures, and the peak with smaller intensity represents the rotational motion of the structures.⁶ As the ratio increases, the average length also increases in the direction of translational motion.

9. Statistical Calculation Details

The images were analyzed using the ImageJ software package developed by the US National Institute of Health.

Number-average length (L_n) and weight-average length (L_w) were calculated as shown below:

$$L_{n} = \frac{\sum_{i=1}^{n} N_{i}L_{i}}{\sum_{n}^{i=1} N_{i}} \qquad L_{w} = \frac{\sum_{i=1}^{n} N_{i}L_{i}^{2}}{\sum_{n}^{i=1} N_{i}L_{i}}$$

Number-average width (W_n) and weight-average width (W_w) are calculated in the same formula.

The standard deviations (σ) of the measured lengths (widths) are related to (L_w/L_n) assuming a Gaussian distribution:

$$\frac{L_w}{L_n} - 1 = \left(\frac{\sigma}{L_n}\right)^2 \qquad \frac{W_w}{W_n} - 1 = \left(\frac{\sigma}{W_n}\right)^2$$

The data are listed below.

Table S4 Length of the self-assembled structures

Sample	Average	$L_{n}(\mu m)$	$L_{w}(\mu m)$	L_w/L_n	σ
	Length (µm)				
U/S = 1	1.111	1.018	1.079	1.059	0.248
U/S = 2	2.307	2.274	2.342	1.030	0.392
U/S = 3	3.068	3.076	3.091	1.005	0.217
U/S = 4	3.989	3.998	4.017	1.005	0.274
U/S = 5	5.003	5.081	5.320	1.047	1.101

U/S = unimer/seed molar ratio

Table S5 Width of the self-assembled structures

Sample	Average	$W_{n}(nm)$	$W_{w}(nm)$	W _w /W _n	σ
	Width (nm)				
U/S = 1	86.75	77.47	87.42	1.128	0.028
U/S = 2	72.79	74.96	79.14	1.056	0.018

U/S = 3	71.92	69.91	73.76	1.055	0.016
U/S = 4	80.33	83.29	84.65	1.016	0.011
U/S = 5	70.75	74.66	79.12	1.060	0.018

U/S = unimer/seed molar ratio

The width of the self-assembled structures is kept the same at around 76.5 nm, and

the length of the structures is proportional to the U/S ratio.



Fig. S21 Linear relationship of the ratio of unimer to seed and the L_n

10. References

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