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Electronic Supplementary Information

Coordination-driven micellelization of block copolymers with gold(I) complexes induces remarkable phosphorescence enhancements with reversible mechanochromism

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Materials and instruments: [Au(THT)Cl] and [Au(C_6F_5)THT] were prepared according to literature methods.[4] Block copolymers of polystyrene-*block*-poly(4-vinylpyridine) (S_n-*b*-V_m, *n = 106*, *m = 38*, *PDI* = 1.09; *n = 576*, *m = 38*, *PDI* = 1.10; *n = 1114*, *m* = 38, *PDI* = 1.07, Table S1) were commercially available from *Polymer Source Inc.* and used without additional purification. The numbers in subscript denoted the degrees of polymerization of the block copolymers. They were synthesized by using alkyllithium-initiated living anionic polymerization. The detailed procedures were addressed in the previously published papers.[S1,S2]

S1 S. K. Varshney, X. F. Zhong and A. Eisenberg, *Macromolecules*, 1993, **26**, 701.

S2 Z. Gao, S. K. Varshney, S. Wong and A. Eisenberg, *Macromolecules*, 1994, **27**, 7923.

Table S1 Molecular Characterization of polystyrene-*block*-poly(4-vinylpyridine) Diblock Copolymers.

Samples	M_n, polystyrene (kg/mol)	M_n, poly(4-vinylpyridine) (kg/mol)	*PDI*
S_{106}-*b*-V_{38}	11	4.0	1.09
S_{576}-*b*-V_{38}	60	4.0	1.10
S_{1114}-*b*-V_{38}	116	4.0	1.07

^{1}H NMR spectra were performed with a *JNM-ESC400* spectrometer. The metallopolymers were dissolved in *d*-chloroform ($CDCl_3$), in which tetramethylsilane was added as an internal standard for the measurements. Fourier transform infrared (FT-IR) were performed with a Nicolet NEXUS 670 spectrometer. Elemental analyses were performed with an Elementar VarioELcube. UV−vis absorption spectra were recorded by using a SHIMADZU UV-2550 spectrophotometer. Luminescence measurements were made on a Hitachi-7000 spectrofluorometer with a xenon lamp as the excitation source (150 W). Dynamic light scattering (DLS) measurements were performed on a Brookhaven BI-200SM spectrometer. Transmission electron microscopy (TEM) images were performed with an FEI Tecnai F30 operating at 300 kV or a JEM-2100 operating at 200 kV.

Preparation and Characterization:

SVAu-1: To a stirring solution of S_{106}-*b*-V_{38} (50.0 mg, 0.127 mmol 4-vinylpyridine) in dichloromethane (DCM, 20 mL) was added [Au(C_6F_5)THT] (57.3 mg, 0.127 mmol). The resulting reaction mixture was further stirred for 1 h and evaporated to dryness under vacuum. The residue was dissolved in a minimal amount of DCM and precipitated from diethylether. The white product was dried overnight in vacuo. Yield = 53.9 mg (56 %).

SVAu-2: This metallopolymer was synthesized according to the same procedure used to prepare **SVAu-1**, except that S_{576}-*b*-V_{38} (50.0 mg, 0.029 mmol) and [Au(C_6F_5)THT] (13.4 mg, 0.029 mmol) were used as starting materials. Yield = 42.1 mg (71 %).

SVAu-3: This metallopolymer was synthesized according to the same procedure used to prepare **SVAu-1**, except that S_{1115}-*b*-V_{38} (50.0 mg, 0.016 mmol) and [Au(C_6F_5)THT] (7.167 mg, 0.016 mmol) were used as starting materials. Yield = 45.0 mg (80 %).

SVAu-4: To a stirring solution of S_{106}-*b*-V_{38} (50.0 mg, 0.127 mmol 4-vinylpyridine) in dichloromethane (DCM, 20 mL) was added [AuCl(THT)] (40.6 mg, 0.127 mmol). The resulting reaction mixture was further stirred for 1 h and evaporated to dryness under vacuum. The residue was dissolved in a minimal amount of DCM and precipitated from diethylether. The white product was dried overnight in vacuo. Yield = 40.6 mg (51 %).

SVAu-5: This metallopolymer was synthesized according to the same procedure used to prepare **SVAu-4**, except that S_{576}-*b*-V_{38} (50.0 mg, 0.029 mmol) and [AuCl(THT)] (9.5 mg, 0.029 mmol) were used as starting materials. Yield = 40.0 mg (72 %).

SVAu-6: This metallopolymer was synthesized according to the same procedure used to prepare **SVAu-4**, except that S_{1114}-*b*-V_{38} (50.0 mg, 0.016 mmol) and [AuCl(THT)] (5.1 mg, 0.016 mmol) were used as starting materials. Yield = 44.4 mg (82 %).

Table S2. Elemental Analyses Established Compositions of gold(I)-containing metallopolymers.

Sample, Chemical formula	Calculated				Found			
	C	H	N	Au	C	H	N	Au
SVAu-1, $(C_8H_8)_{106}(C_7H_7N)_{38}(AuC_6F_5)_{19}$	67.19	5.12	2.24	17.05	68.85	4.88	1.33	16.82
SVAu-2, $(C_8H_8)_{576}(C_7H_7N)_{38}(AuC_6F_5)_{32}$	80.45	6.50	0.70	8.33	81.08	6.08	0.84	8.10
SVAu-3, $(C_8H_8)_{1114}(C_7H_7N)_{38}(AuC_6F_5)_{35}$	84.93	6.97	0.40	5.19	85.22	6.03	0.68	5.26
SVAu-4, $(C_8H_8)_{106}(C_7H_7N)_{38}(AuCl)_{17}$	70.47	5.91	2.80	17.64	71.51	5.78	1.54	17.94
SVAu-5, $(C_8H_8)_{576}(C_7H_7N)_{38}(AuCl)_{25}$	83.87	7.04	0.76	7.06	83.82	6.77	0.77	7.32
SVAu-6, $(C_8H_8)_{1114}(C_7H_7N)_{38}(AuCl)_{38}$	85.55	7.18	0.41	5.81	85.39	7.01	0.65	5.89

Table S3. Photophysical Data for the Solid Metallopolymers of SVAu-1, SVAu-2, and SVAu-3. Their emission lifetimes were fitted by using triple-exponential methods. Relative weighting (RW) of components were also listed in this Table.

Sample	Emission, λ_{max} / nm	τ_1 / ns	RW$_1$ / %	τ_2 / ns	RW$_2$ / %	τ_3 / ns	RW$_3$ / %	Φ_{em} / %
SVAu-1	530	85.52	9.37	331.91	47.01	653.96	43.61	5.2
SVAu-2	528	136.35	7.32	490.41	77.87	1008.61	14.80	17
SVAu-3	519	113.30	5.29	406.28	55.64	732.18	39.07	16

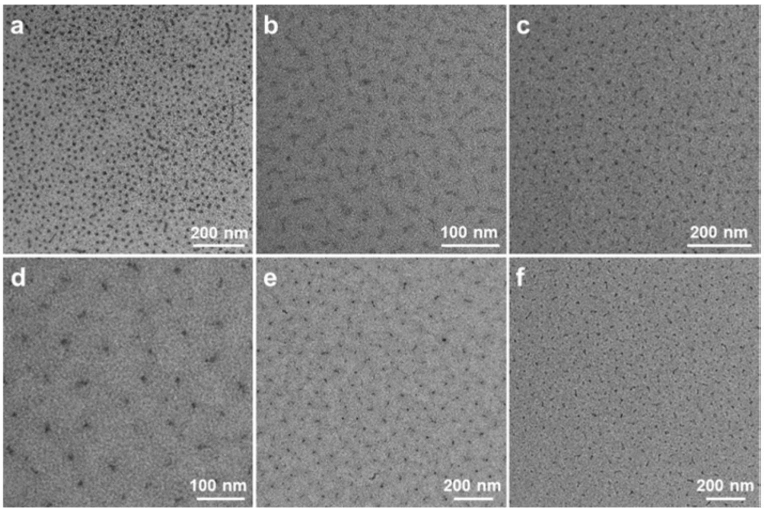

Fig. S1 TEM images of SVAu-1 (a), SVAu-2 (b), SVAu-3 (c), SVAu-4 (d), SVAu-5 (e), and SVAu-6 (f). The solutions with concentrations of 0.4 mmol/L for the 4-vinylpyridine unit were cast onto carbon-coated copper grids.

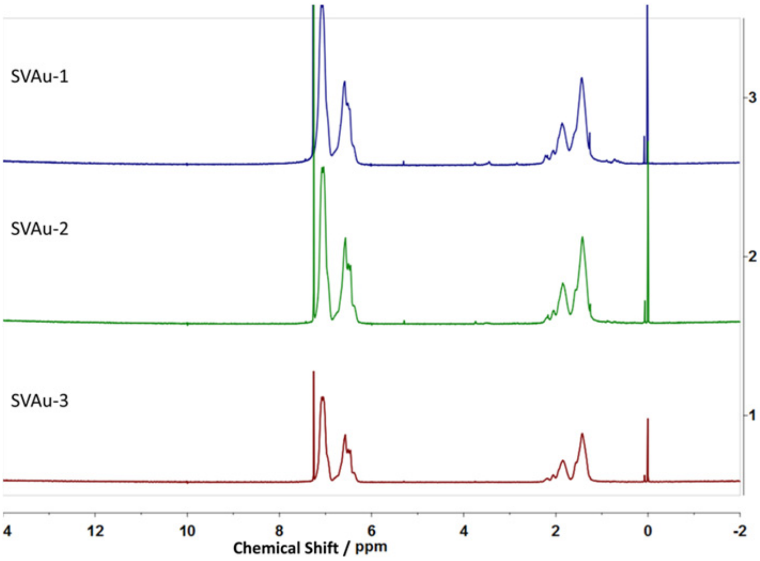

Fig. S2 ^{1}H NMR spectra of SVAu-1, SVAu-2, and SVAu-3.

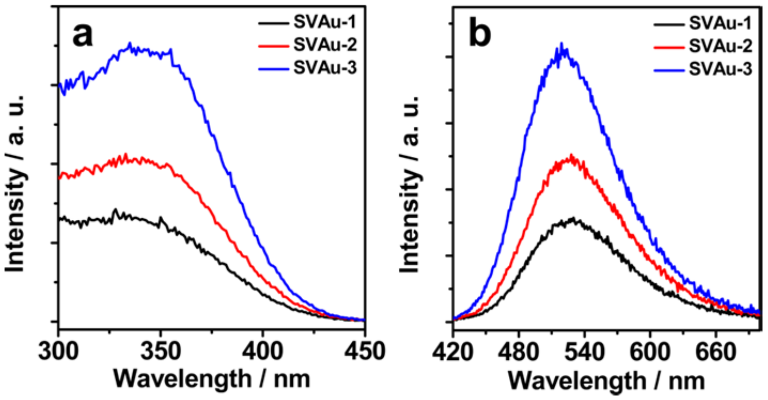

Fig. S3 Excitation (a) and emission spectra (b) of SVAu-1, SVAu-2, and SVAu-3 in their solid states.

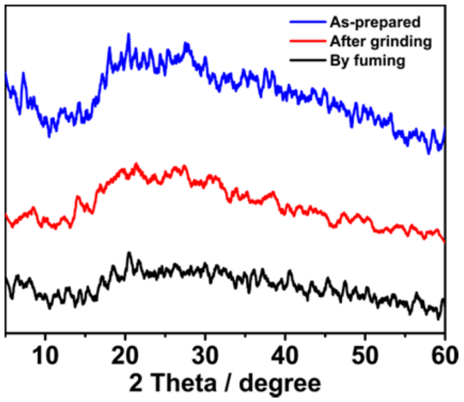

Fig. S4 Powder X-ray diffraction patterns of the as-prepared, after-grinding, and by-fuming samples.

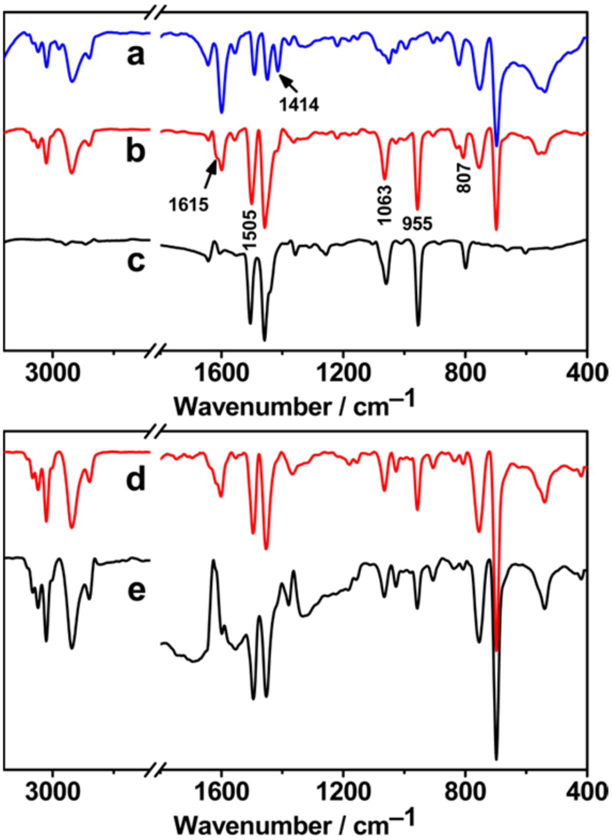

Fig. S5 FT-IR spectra of S_{106}-*b*-V_{38} (a), SVAu-1 (b), [Au(C_6F_5)THT] (c), SVAu-2 (d), and SVAu-3 (e).

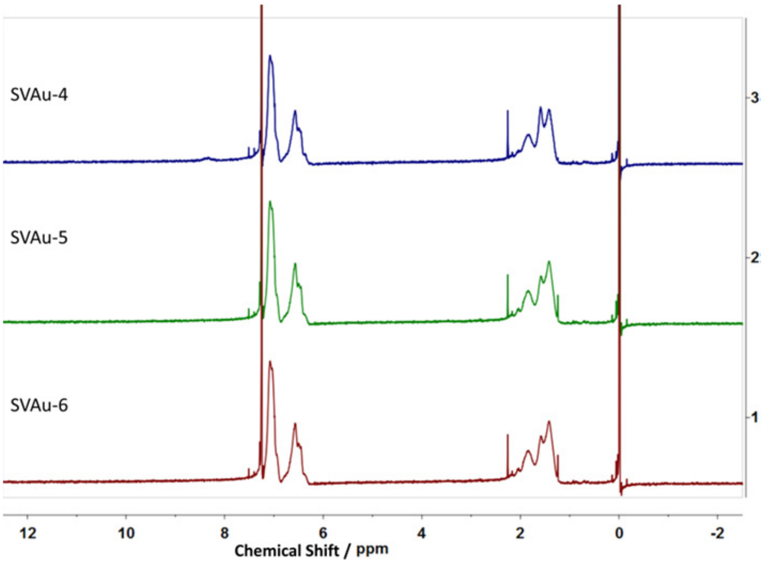

Fig. S6 ^{1}H NMR spectra of SVAu-4, SVAu-5, and SVAu-6.

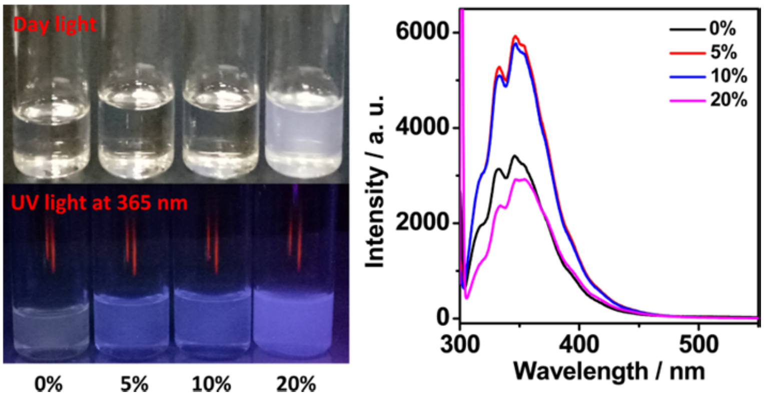

Fig. S7 Photographs of SVAu-3 in the THF/water solvents under the day light and UV light at 365 nm and their corresponding emission spectra. The solution concentrations were 0.4 mmol/L for the 4-vinylpyridine unit. SVAu-3 was first dissolved in tetrahydrofuran, to which water was added with a volume ratio of 5%, 10%, and 20%. Further increase in the water content leads to the formation of precipitates at the bottom of the bottle. Upon excitation at 300 nm, however, structured emission bands were clearly observed at 316, 332, 347, 354, and 396 nm, probably attributed to a metal-perturbed intraligand emission. The intense green emission associated with aurophilic Au(I)···Au(I) interactions was totally invisible at 512 nm. The increase in the water content did not induce an AIE feature of the emission. This further supported the different luminescence enhancement mechanism of the gold(I)-containing metallopolymers.