Supporting Information

Synthesis and characterization of a luminescence metallosupramolecular hyperbranched polymer

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General Considerations. All reaction operations were performed under an anhydrous Ar atmosphere. Anhydrous toluene and tetrahydrofuran (THF) were distilled over Na and benzophenone. Dichloromethane was dried over CaH_2. All chemicals were used as received without any further treatment. ^{1}H NMR and ^{13}C NMR spectra were recorded on Varian 600 NMR or Bruker 400 NMR spectrometers with tetramethylsilane (TMS) as an internal standard. High resolution ESI-MS were obtained on a Bruker APEX II FT-MS mass spectrometer. DLS measurements were performed on a Brookhaven BI-200SM spectrometer. TEM images were performed with a FEI Tecnai F30 operating at 300 kV. UV-vis Absorption spectra were recorded by using a Shimadzu 2550 spectrophotometer. Luminescence measurements were made on a Hitachi F-7000 spectrofluorimeter with a xenon lamp as the excitation source.

4: 255 mg (0.50 mmol) of **3**[1] was dissolved in acetone of 20 mL. 217 mg (0.50 mmol) cis-$[Pt(DMSO)_2Cl_2]$[2] was added to the solution and the mixture was stirred in dark for 12 h at 20 °C. Evaporation of the yellow solution gave the pale yellow microcrystalline precipitate. After filtration, 0.25 g of yellow crystal was obtained by washing with acetone, ether and then drying in the air atmosphere at 20 °C. Yield: 72%. ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si) δ 3.54 (s, 8H), 3.87 (t, J_{HH} = 4.4 Hz, 4H), 3.98 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 4.12 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 4.59 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 6.84-6.88 (m, 4H), 7.71 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 5.2Hz, 2H,), 8.89 (dd, $^3J_{HH}$ = 8.4 Hz, $^5J_{HH}$ = 0.8 Hz, 2H) 9.40 (d, $^3J_{HH}$ = 5.2 Hz, 2H). Anal. Calcd for $C_{30}H_{34}Cl_2N_2O_8Pt$: C 44.13; H 4.20; N 3.43. Found: C 44.55; H 4.31; N 3.73. ESI-MS calcd for

$[C_{30}H_{34}ClN_2O_8Pt]^+$ 780.1651, found 780.1646.

5: A Schlenk tube was charged with **4** (0.100 g, 0.12 mmol), 4-ethynylbenzaldehyde[3] (39 mg, 0.30 mmol), CuI (6 mg), and 10 mL of a solvent mixture of CH_2Cl_2/NEt_3 (9:1 v/v). The resultant heterogeneous solution was allowed to stir for 24 h at 40 °C, The solvent was removed under a reduced pressure. The crude product was recrystallized from dichloromethane and methanol. **5** was isolated as a brown solid (109 mg, 90% yield). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si), δ 3.75 (s, 8H), 3.84 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 3.96 (t, $^3J_{HH}$ = 4.0 Hz, 4H), 4.10 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 4.54 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 6.85 (m, 4H), 7.70 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.79 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.85 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.8 Hz, 2H), 8.96 (dd, $^3J_{HH}$ = 8.4 Hz, $^5J_{HH}$ = 1.2 Hz, 2H), 9.70 (d, $^3J_{HH}$ = 4.8 Hz, 2H) 9.96 (s, 2H). Anal. Calcd for $C_{48}H_{44}N_2O_{10}Pt{\cdot}0.5CH_2Cl_2$: C, 55.67; H, 4.33; N, 2.68. Found: C, 55.43; H, 4.10; N, 2.18. ESI-MS calcd for $[C_{48}H_{44}N_2O_{10}Pt+Na]^+$ 1026.2541, found 1026.2571.

6: A Schlenk tube was charged with **5** (0.05 g, 0.050 mmol), $ZnCl_2$ (10 mg), benzylamine (0.22 g, 2.0 mmol) and 20 mL of CH_2Cl_2/MeOH (9:1 v/v) and the resultant solution was allowed to stir for 40 h at room temperature. The product was isolated on a medium-porosity glass frit; washed with small amounts of methanol, ethanol, and diethyl ether; recrystallized from a methanol/CH_2Cl_2 mixture; washed with methanol and diethyl ether; and dried under vacuum. **6** was isolated as a brown solid (48 mg, 82% yield). ^1H NMR (400 MHz, $CDCl_3$, Me_4Si), δ 3.75 (s, 8H), 3.84 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 3.96 (m, 4H), 4.10 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 4.54 (m, 4H), 4.83 (s, 4H), 6.85 (m, 4H), 7.35 (m, 10H), 7.60 (d, $^3J_{HH}$ = 8.4 Hz, 4H), 7.70 (d, $^3J_{HH}$ = 8.0 Hz, 4H), 7.80 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 4.4 Hz, 2H), 8.37 (s, 2H), 8.92 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 9.78 (d, $^3J_{HH}$ = 4.0 Hz, 2H). Anal. Calcd for $C_{62}H_{58}N_4O_8Pt{\cdot}CH_2Cl_2$: C, 59.71; H, 4.77; N, 4.42. Found: C, 59.34; H, 4.49; N, 4.69. ESI-MS calcd for $[C_{62}H_{58}N_4O_8Pt+H]^+$ 1182.3981, found 1182.3973.

1: A Schlenk tube was charged with **6** (0.05 g, 0.042 mmol), sodium triacetoxyborohydride (65 mg, 0.30 mmol), and 20 mL of dichloromethane. The resultant solution was stirred for 48 h. The solution was then poured over water and extracted with dichloromethane, dried with $MgSO_4$, filtered, and evaporated to dryness to give the desired product. The crude product was recrystallized from dichloromethane and methanol. **1** was isolated as a brown solid (34 mg, 70% yield). ^{1}H NMR (400 MHz, CD_2Cl_2, Me_4Si), δ 3.65 (m, 8H), 3.84 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 3.76 (s, 4H), 3.77 (s, 4H), 3.88 (m, 4H), 4.01 (t, $^3J_{HH}$ = 4.8 Hz, 4H), 4.54 (m, 4H), 4.49 (s, 4H), 6.80 (m, 4H), 7.20-7.45 (m, 10H), 7.81 (m, 2H), 7.92 (d, $^3J_{HH}$ = 8.4 Hz, 2H), 9.75 (m, 2H). Anal. Calcd for $C_{62}H_{62}N_4O_8Pt{\cdot}CH_2Cl_2$: C, 59.50; H, 5.07; N, 4.41. Found: C, 59.36; H, 4.48; N, 4.74. ESI-MS calcd for $[C_{62}H_{62}N_4O_8Pt+Na]^+$ 1209.2514, found 1209.2558.

2: A Schlenk tube was charged with **4** (0.100 g, 0.12 mmol), ethynylbenzene (31 mg, 0.30 mmol), CuI (6 mg), and 10 mL of a solvent mixture of CH_2Cl_2/NEt_3 (9:1 v/v). The resultant heterogeneous solution was allowed to stir for 24 h at 40 °C, The solvent was removed under a reduced pressure. The crude product was recrystallized from dichloromethane and methanol. **2** was isolated as a brown solid (97 mg, 85% yield). ^{1}H NMR (400 MHz, $CDCl_3$, Me_4Si), δ 3.75 (s, 8H), 3.86 (t, $^3J_{HH}$ = 4.0 Hz, 4H), 3.93 (m, 4H), 4.10 (t, $^3J_{HH}$ = 4.4 Hz, 4H), 4.53 (m, 4H), 6.86 (m, 4H), 7.2-7.4 (m, 10H), 7.59 (d, $^3J_{HH}$ = 8.0 Hz, 2H), 7.78 (m, 2H), 8.89 (d, $^3J_{HH}$ = 8.4 Hz, 2H). Anal. Calcd for $C_{46}H_{44}N_2O_8Pt{\cdot}0.8CH_2Cl_2$: C, 55.33; H, 4.52; N, 2.76. Found: C, 55.58; H, 4.05; N, 2.46. ESI-MS calcd for $[C_{48}H_{44}N_2O_{10}Pt+2Na]^{2+}$ 496.6267, found 496.6275.

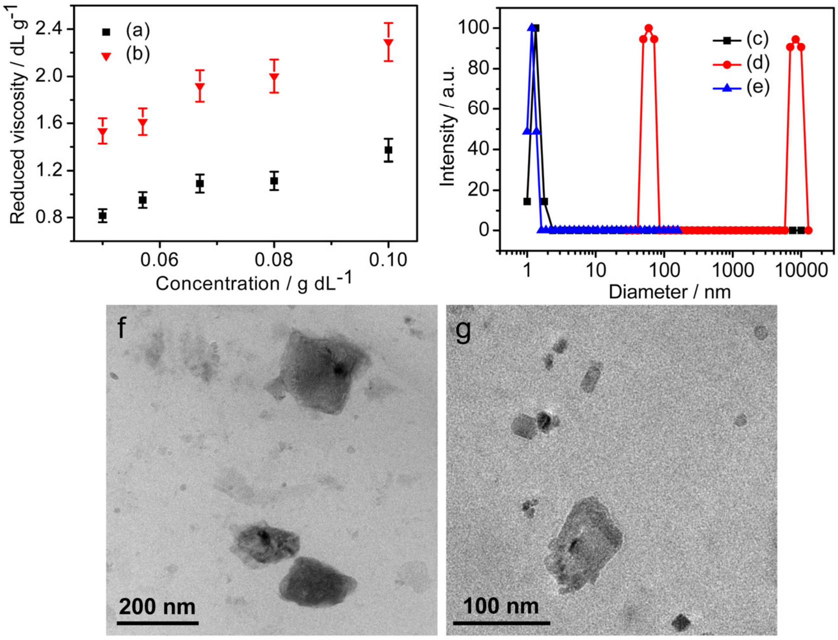

Fig. S1 Reduced viscosity as a concentration function of **1** (a) and TFA-**1** (b) in their dichloromethane solutions at 18 °C. DLS plots of **1** (in CH_2Cl_2, 1.0×10^{-3} molL^{-1}, c), TFA-**1** produced by adding 2.2 equiv of TFA into the solution of **1** (d), **1** obtained by treating 2.4 equiv of P_1-*t*-Bu to TFA-**1** (e). TEM images of TFA-**1** as drop cast onto carbon-coated copper grids at the concentrations of 1×10^{-3} (f) and 5×10^{-5} mol/L (g).

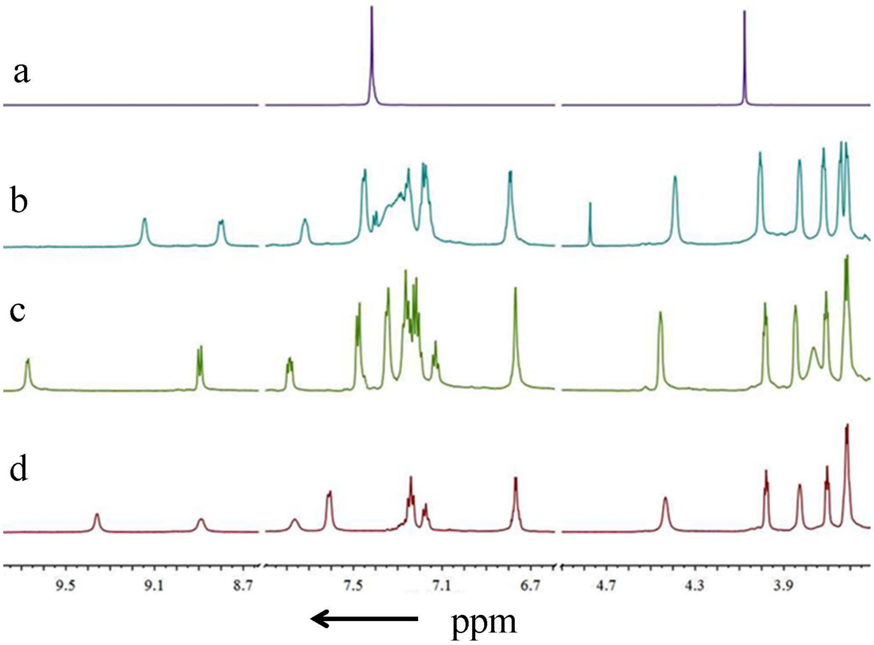

Fig. S2 ^{1}H NMR spectra (600 MHz CD_2Cl_2) of the mixture of **2** and **7** with a molar ratio of 1:1 at a concentration of 1×10^{-3} mol/L (b), after addition of 1.1 equiv of P_1-*t*-Bu (c), the original spectrum of **7** in CD_3CN (a), and the original spectrum of **2** in CD_2Cl_2 (d).

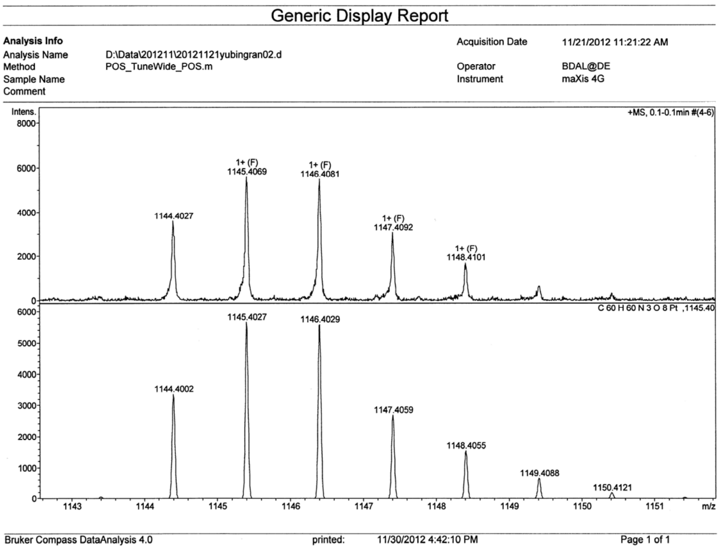

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Fig. S3 The experimental (a) and theoretical (b) ESI-MS spectra of [**2•7**]$^+$.

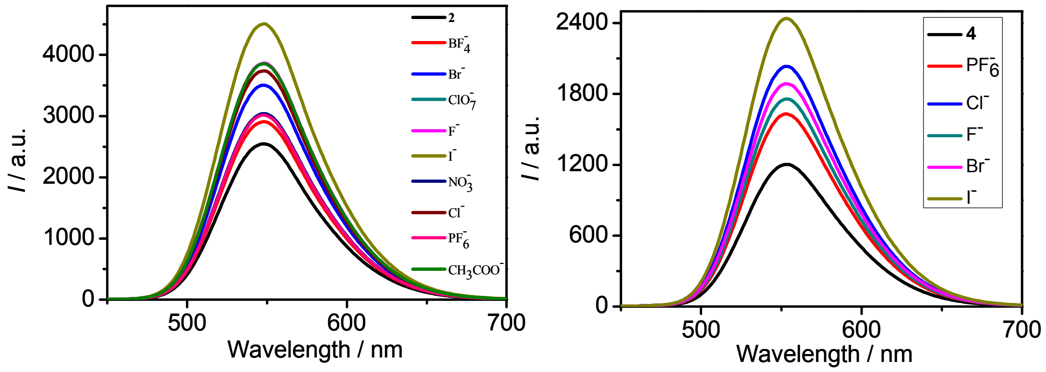

Fig. S4 Fluorescence spectral changes of **1** (a) and **2** (b) upon addition with tetrabutylammonium (TBA) salts in dichloromethane.

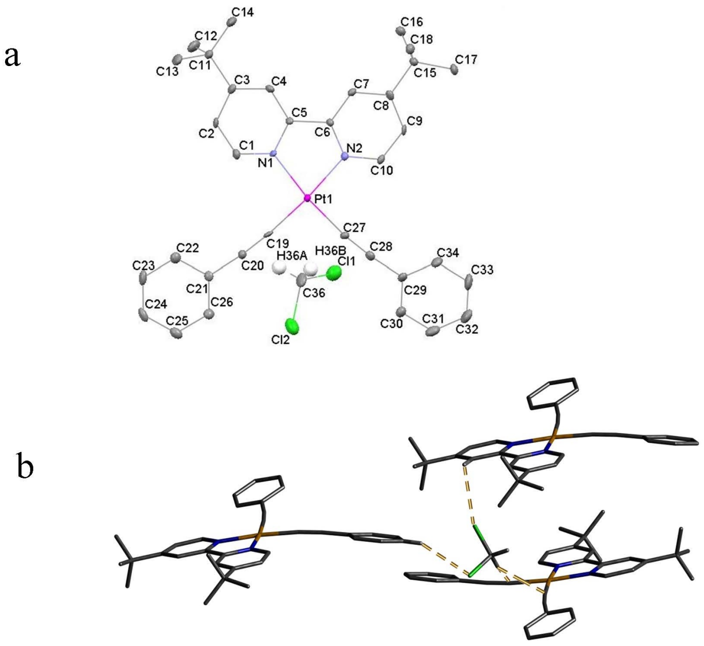

Fig. S5 (a) Perspective view of **8**•CH_2Cl_2 (50% probability ellipsoids). (b) The weak C−H···π(C≡C) interactions occurred between the two acidic protons of the CH_2Cl_2 molecule and the bis(acetylide).

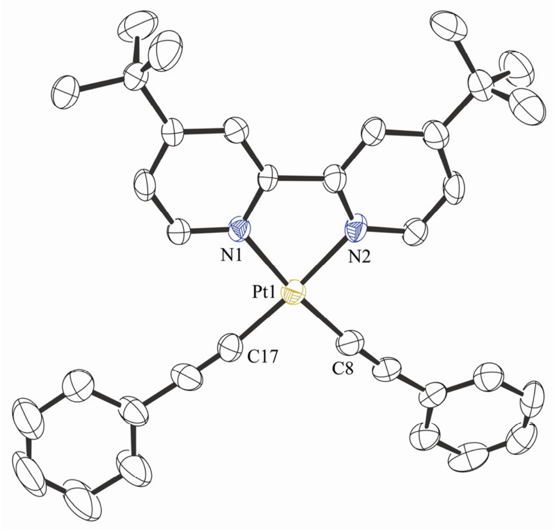

Fig. S6 Perspective view of **8** (50% probability ellipsoids).

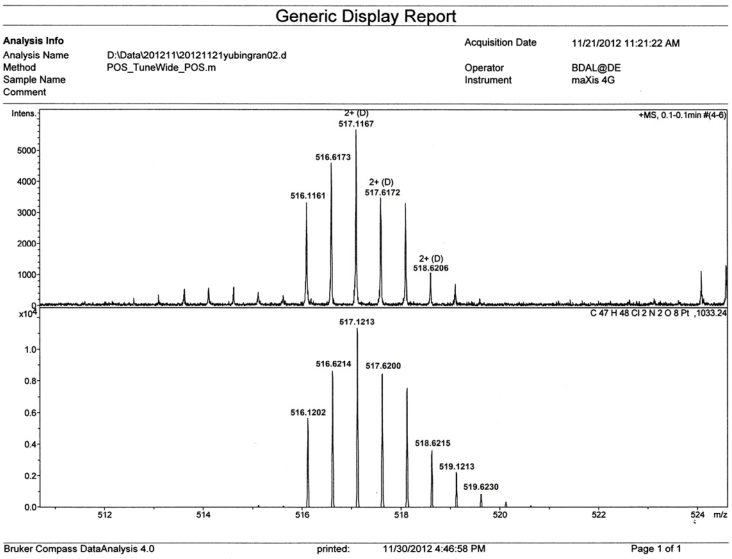

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Fig. S7 The experimental (a) and theoretical (b) ESI-MS spectra of [**2•CH$_2$Cl$_2$•2H**]$^{2+}$.

Table S1. X-ray crystallographic data for **8**•$CH_2Cl_2$and **8**.

	8•CH_2Cl_2	**8**
formula	$C_{35}H_{36}Cl_2N_2$ Pt	$C_{34}H_{34}N_2Pt$
fw	750.65	665.72
temp	100(10)	292 (10)
crystal system	triclinic	triclinic
space group	P-1	P-1
a, Å	10.3930(4)	10.5062(8)
b, Å	10.4002(4)	10.8025(5)
c, Å	15.2797(7)	14.7466(7)
α,°	109.735(4)	78.098(4)
β,°	90.674(3)	79.170(5)
γ,°	97.278(3)	82.432(5)
V, $Å^3$	1539.41(11)	1600.95(17)
Z	2	2
density(calcd) g·cm^{-3}	1.619	1.381
Absorb .coeff. mm^{-1}	4.758	4.404
F(000)	744	660
θ range	3.02-25.68	3.14-28.50
	-7<H<12	-31<h<28
index ranges	-12<k<12	-15<k<13
	-18< l< 18	-32<l<38
data/restr./param	5842/0/ 367	6055/0 /340
GOF	1.028	0.976
final *R* indices	0.0643	0.0802
$[I > 2\sigma(I)]$	0.1376	0.1936
CCDC number	923693	923694

References

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3 X. Wang, V. Ervithayasuporn, Y. Zhang and Y. Kawakami, *Chem. Commun.* 2011, **47**, 1282-1284.