

Organogel of an 8-quinolinol platinum(II) chelate derivative and its efficient phosphorescence emission effected by inhibition of dioxygen quenching.

Michihiro Shirakawa,^a Norifumi Fujita,^a Takahiro Tani,^a Kenji Kaneko^b and Seiji Shinkai*^a

^a Department of Chemistry and Biochemistry, Graduate School of Engineering, Kyushu University, 6-10-1 Hakozaki, Higashi-ku, Fukuoka 812-8581, Japan.; Fax: (+81) 92-642-3611; Tel: (+81) 92-642-3583; E-mail: seijitcm@mbox.nc.kyushu-u.ac.jp

^b HVEM Laboratory, Kyushu University, Fukuoka 812-8581, Japan

General. All starting materials and solvents were purchased from Tokyo Kasei Organic Chemicals, Wako Organic Chemicals, or Aldrich and used as received. The ¹H NMR spectra were recorded on a Bruker AC 250 (250 MHz) spectrometer or on a Bruker DRX 600 (600 MHz) spectrometer. Chemical shifts are reported in ppm downfield from tetramethylsilane as the internal standard. Mass spectral data were obtained using a Perseptive Voyager RP matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometer. UV-vis spectra were recorded with a Shimadzu UV-2500 PC spectrophotometer. Luminescence spectral measurements were performed using a Perkin Elmer LS 55 luminescence spectrometer.

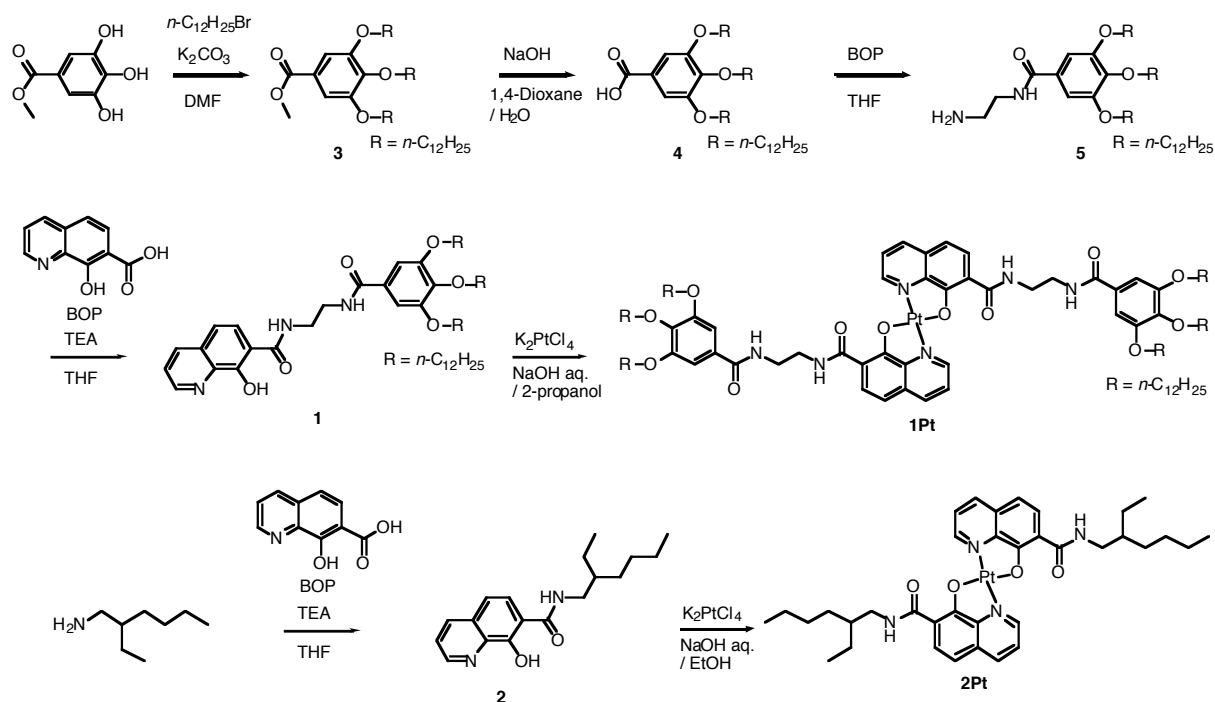
Gelation Tests. The gelator and the solvent were put in a septum-capped test tube and the mixture were heated until the solid was dissolved. The sample vial was cooled in air to 25 °C, and then left for 1 h at this temperature. The state of the materials was evaluated by the “stable-to-inversion of a test tube” method.

SEM. A piece of the gel was placed on a carbon-coated copper grid and removed after 10 seconds, leaving some small patches of the gel on the grid. The sample thus obtained was shielded by Pt and examined with a Hitachi S-5500 scanning electron microscope. The accelerating voltage was 25 kV.

TEM. A carbon-coated copper grid was immersed in the gel and dried for 12 h under reduced pressure. The grid was examined with a Hitachi H-600 or a FEI TECNAI-20 transmission electron microscopes.

CLSM. The **1Pt** + *p*-xylene gel was placed on a glass plate and observed with a BIO-RAD Radiance 2000 AGR3 microscope. The excitation wavelength was 514 nm (argon laser with reflector turret).

Scheme S1 Synthetic scheme of **1Pt** and **2Pt**.



Synthesis. Compounds **1Pt** and **2Pt** were synthesized according to Scheme S1 and identified by ^1H NMR, MALDI-TOF mass measurements, and/or elemental analysis. Compound **4** was prepared as described earlier. 3,4,5-trihydroxybenzoic acid methyl ester was converted into its ether (**3**) by the reaction with 1-bromododecane. Subsequent hydrolysis of the ester groups with NaOH yielded **4**.

Synthesis of 5. compound **4** (2.8 g, 4.1 mmol) was dissolved in THF (100 ml). BOP reagent (2.8 g, 6.2 mmol) and ethylenediamine (5.0 g, 83 mmol) were added to the solution and refluxed for 3h. After cooling the mixture to room temperature, the solution was concentrated under reduced pressure. The resultant residue was purified was dissolved in CHCl_3 and washed with brine three times. The organic layer was dried over anhydrous Na_2CO_3 and concentrated under reduced pressure. The resultant residue was subjected to column chromatography [silica gel, $\text{CHCl}_3/\text{MeOH} = 5:1$ (v/v)] to give **5** in 90% (2.7 g) yield as white solid. ^1H NMR (600 MHz, CDCl_3 , TMS, rt) δ 0.84-0.88 (m, 9H), 1.26-1.33 (m, 48H), 1.45-1.49 (m, 6H), 1.72-1.75 (m, 2H), 1.78-1.81 (m, 4H), 2.95 (t, $J = 5.9$, 2H), 3.49 (q, $J = 5.8$, 2H), 4.00 (m, 6H), 6.61 (t, $J = 5.0$, 1H), 6.99 (s, 2H); MALDI-TOF-MS [alpha-cyano-4-hydroxy cinnamic acid] m/z: calcd for M^+ ; 716.64, found 717.7; Elemental analysis calcd for $\text{C}_{45}\text{H}_{84}\text{N}_2\text{O}_4 \cdot 0.25 \text{H}_2\text{O}$; C 73.52, H 11.79, N 3.81, found; C 73.43, H 11.71, N 3.97.

Synthesis of 1. compound **5** (2.0 g, 4.1 mmol) was dissolved in THF (30 ml). BOP reagent (1.9 g, 4.2 mmol), triethylamine (430 mg, 4.2 mmol) and 8-hydroxyquinoline-7-carboxylic acid (790 mg, 4.2 mmol) were added to the solution and refluxed for 3h. After cooling the mixture to room temperature, the solution was concentrated under reduced pressure. The resultant residue was purified was dissolved in CHCl_3 and washed with brine three times. The organic layer was dried over anhydrous Na_2CO_3 and concentrated under reduced pressure. The resultant residue was subjected to column chromatography [silica gel, $\text{CHCl}_3/\text{MeOH} = 20:1$ (v/v)] to give **1** in 84% (2.1 g) yield as white solid. ^1H NMR (250 MHz, CDCl_3 , TMS, rt) δ 0.84-0.88 (m, 9H), 1.20-1.60 (m,

54H), 1.67-1.88 (m, 6H), 3.67-3.79 (m, 2H), 3.79-3.91 (m, 2H), 3.97 (t, $J = 6.5$, 2H), 4.04 (t, $J = 6.5$, 4H), 7.07 (s, 2H), 7.37 (d, $J = 8.7$, 1H), 7.50-7.60 (m, 2H), 8.14 (d, $J = 9.0$, 1H), 8.18 (m, 1H), 8.42-8.48 (m, 1H), 8.86 (m, 1H): MALDI-TOF-MS [dithranol] m/z calcd for $M+H^+$; 888.68, found; 888.61: Elemental analysis calcd for $C_{55}H_{89}N_3O_6$; C 74.36, H 10.10, N 4.73, found; C 74.26, H 10.06, N 4.73.

Synthesis of 1Pt. A solution of K_2PtCl_4 (23 mg, 55 μ mol) in aqueous NaOH (pH 10, 1 ml) was added to a suspension of compound **1** (100 mg, 0.11 mmol) in 2-propanol (30 ml). The reaction mixture was refluxed for 20 h. After cooling the mixture to room temperature, the solution was concentrated under reduced pressure. The resultant residue was subjected to column chromatography [silica gel, $CHCl_3/MeOH = 20:1$ (v/v)] to give **1Pt** in 40% (44 mg) yield as orange solid. 1H NMR (250 MHz, $CDCl_3$, TMS, rt) δ 0.84-0.90 (m, 18H), 1.20-1.60 (m, 108H), 1.60-1.81 (m, 12H), 3.72-3.82 (m, 4H), 3.79-3.91 (m, 8H), 3.98 (t, $J = 6.5$, 8H), 6.94 (d, $J = 8.7$, 2H), 7.09 (s, 4H), 7.42 (m, 2H), 7.60 (m, 2H), 8.1-8.2 (m, 4H), 8.47-8.55 (m, 2H), 9.38-9.48 (m, 2H): MALDI-TOF-MS [dithranol] m/z calcd for $M+H^+$; 1969.30, found; 1969.54: Elemental analysis calcd for $C_{110}H_{176}N_6O_{12}Pt \cdot 0.50 H_2O$; C 66.77, H 9.02, N 4.25, found; C 66.70, H 8.96, N 4.25.

Synthesis of 2. 2-Ethylhexylamine (360 g, 2.8 mmol) was dissolved in THF (30 ml). BOP reagent (1.9 g, 4.2 mmol), triethylamine (420 mg, 4.2 mmol) and 8-hydroxyquinoline-7-carboxylic acid (790 mg, 4.2 mmol) were added to the solution and refluxed for 3h. After cooling the mixture to room temperature, the solution was concentrated under reduced pressure. The resultant residue was dissolved in $CHCl_3$ and washed with brine three times. The organic layer was dried over anhydrous Na_2CO_3 and concentrated under reduced pressure. The resultant residue was subjected to column chromatography [silica gel, $CHCl_3/MeOH = 10:1$ (v/v)] to give **2** in 80% (670 mg) yield as white solid. 1H NMR (250 MHz, $CDCl_3$, TMS, rt) δ 0.87-0.98 (m, 6H), 1.20-1.50 (m, 8H), 1.60-1.70 (m, 1H), 3.50 (t, $J = 5.3$, 2H), 7.34 (d, $J = 8.9$, 1H), 7.48 (dd, $J = 8.2, 4.2$, 1H), 7.99 (br, 1H), 8.13-8.18 (m, 2H), 8.83 (d, $J = 3.3$, 1H): MALDI-TOF-MS [dithranol] m/z calcd for $M+H^+$; 301.18, found; 303.84.

Synthesis of 2Pt. A solution of K_2PtCl_4 (140 mg, 0.33 mmol) in aqueous NaOH (pH 10, 1 ml) was added to a suspension of compound **2** (200 mg, 0.67 mmol) in ethanol (20 ml). The reaction mixture was refluxed for 20 h. After cooling the mixture to room temperature, the solution was concentrated under reduced pressure. The resultant residue was subjected to column chromatography [silica gel, $CHCl_3$] to give **2Pt** in 4% (10 mg) yield as orange solid. 1H NMR (250 MHz, $CDCl_3$, TMS, rt) δ 0.87 (t, $J = 6.8$, 6H), 0.97 (t, $J = 7.3$, 6H), 1.20-1.80 (m, 18H), 3.50 (m, 4H), 7.07 (d, $J = 8.6$, 2H), 7.28 (m, 2H), 8.19 (d, $J = 4.2$, 2H), 8.27 (d, $J = 8.6$, 2H), 8.33 (d, $J = 8.1$, 2H), 8.71 (br, 2H): MALDI-TOF-MS [dithranol] m/z calcd for $M+H^+$; 794.32, found; 793.30. Elemental analysis calcd for $C_{36}H_{46}N_4O_4Pt$; C 54.47, H 5.84, N 7.06, found; C 54.29, H 5.84, N 7.06.

Gelation properties of **1Pt** in organic solvents

Table S1 Gelation properties of **1Pt** in organic solvents

Solvent	Phase ^a	CGC ^b / mg•ml ⁻¹ (mM)
Methanol	P	-
Ethanol	P	-
2-Propanol	G	10 (5.0)
1-Butanol	G	0.50 (0.25)
Benzene	G	0.50 (0.25)
Toluene	G	0.20 (0.10)
Pyridine	S	-
<i>p</i> -Xylene	G	0.10 (0.050)
Anisole	G	1.0 (0.50)
Hexane	G	0.20 (0.10)
Cyclohexane	G	0.10 (0.050)
Methylcyclohexane	G	0.10 (0.050)
Octane	G	0.10 (0.050)
Decane	G	0.10 (0.050)
Decalin	G	0.20 (0.10)
Dichloromethane	G	10 (5.0)
Chloroform	S	-
1,1,2,2-Tetrachloroethane	S	-
Acetone	G	1.0 (0.50)
Tetrahydrofuran	G	5.0 (1.0)
Ethyl acetate	G	1.0 (0.50)
Acetonitrile	P	-
1,4-Dioxane	G	0.50 (0.25)
<i>N,N'</i> -Dimethylformamide	G	5.0 (1.0)
Dimethylsulfoxide	P	-

^a The solution was warmed until **1Pt** (10 mg•ml⁻¹) was dissolved and then cooled to 25 °C: G = gel, S = solution, P = precipitate.

^b Critical gelation concentration (CGC): this denotes the minimum concentration necessary for gelation of solvents.