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Synthesis and characterization of bioorganometallic conjugates composed of NCN-pincer platinum(II) complexes and uracil derivatives

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ABSTRACT

The conjugation of the NCN-pincer platinum(II) complexes as an oraganometallic compound and the uracil derivatives as a nucleobase was demonstrated to give the corresponding bioorganometallics. The NCN-pincer ligands bearing the 6-ethynyl-1-octyluracil, 5-ethynyl-1-octyluracil, and the furanopyrimidine moiety were synthesized. In a crystal state, the NCN-pincer ligand bearing the 6-ethynyl-1-octyluracil moiety was found to form a hydrogen-bonded dimer through intermolecular hydrogen bonds between the uracil moieties, which was connected through π–π interaction between the uracil and benzene moieties of the NCN-pincer ligand. The reaction of the NCN-pincer ligand bearing the 6-ethynyl-1-octyluracil moiety with $[Pt(tolyl\text{-}4)_2(SEt_2)]_2$ led to the formation of the NCN-pincer platinum(II) complex bearing the 6-ethynyl-1-octyluracil moiety. The NCN-pincer platinum(II) complex bearing the furanopyrimidine moiety was obtained by the reaction of the NCN-pincer ligand bearing the furanopyrimidine moiety with $[Pt(tolyl\text{-}4)_2(SEt_2)]_2$. The single-crystal X-ray structure determination of the NCN-pincer platinum(II) complex bearing the furanopyrimidine moiety revealed the formation of the furanopyrimidine ring and the π stack dimer between the furanopyrimidine and benzene moieties of the NCN-pincer ligand in the crystal packing. The NCN-pincer platinum(II) complexes bearing the 6-ethynyl-1-octyluracil moiety or the furanopyrimidine moiety exhibited emission in both solution and solid states.

1. Introduction

Highly-ordered molecular assemblies are constructed in biosystems to fulfill unique functions. The double helical DNA is created by A-T and G-C base pairs, which are controlled mainly by complementary hydrogen bonding, π-stacking interaction, and hydrophobic interaction [1]. Architectural control of molecular self-organization is of importance for the development of functional materials [2]. Regulation of hydrogen bonding [3] is a key factor in the design of various molecular assemblies by virtue of its directionality and specificity [4]. The reversibility and tuneability of hydrogen bonding is also of fundamental importance in the chemical and/or physical properties of molecular assemblies. Nucleobases are known to have a specific ability to form directionally controlled multiple and complementary hydrogen bonding. The utilization of self-assembling properties of nucleobases is considered to be a relevant strategy to design well-defined molecular assemblies [5]. On the other hand, the research field of bioorganometallic chemistry, which is a hybrid area between biology and organometallic chemistry, has received extensive interest, and considerable efforts have been devoted to conjugate organometallic compounds with biomolecules such as DNA, amino acids, and peptides [6]. The transition metal complexes composed of pincer ligands, which contain a stable metal-carbon σ bond, have been extensively investigated and utilized as a variety of materials and catalysts [6k,7]. A combination of pincer complexes with nucleobases is allowed to design novel bioconjugates depending on both properties. We herein report the characterization of bioorganometallic conjugates composed of the NCN-pincer platinum (II) complexes and the uracil derivatives.

2. Results and discussion

The synthesis of the NCN-pincer ligands **4**–**5** bearing the uracil moiety and **6** bearing the furanopyrimidine moiety is outlined in Scheme 1. Regioselective iodination of 1-octyluracil, which was prepared by the alkylation of uracil with 1-iodooctane in the presence of K_2CO_3, was performed as reported to afford 6-iodo-1-octyluracil and 5-iodo-1-octyluracil [8], respectively. The Sonogashira coupling reaction of 6-iodo-1-octyluracil or 5-iodo-1-octyluracil with trimethylsilylacetylene in the presence of a catalytic amount of $PdCl_2(PPh_3)_2$ and CuI, followed by removal of the TMS protecting group with KOH in methanol gave 6-ethynyl-1-octyluracil (**1**) or

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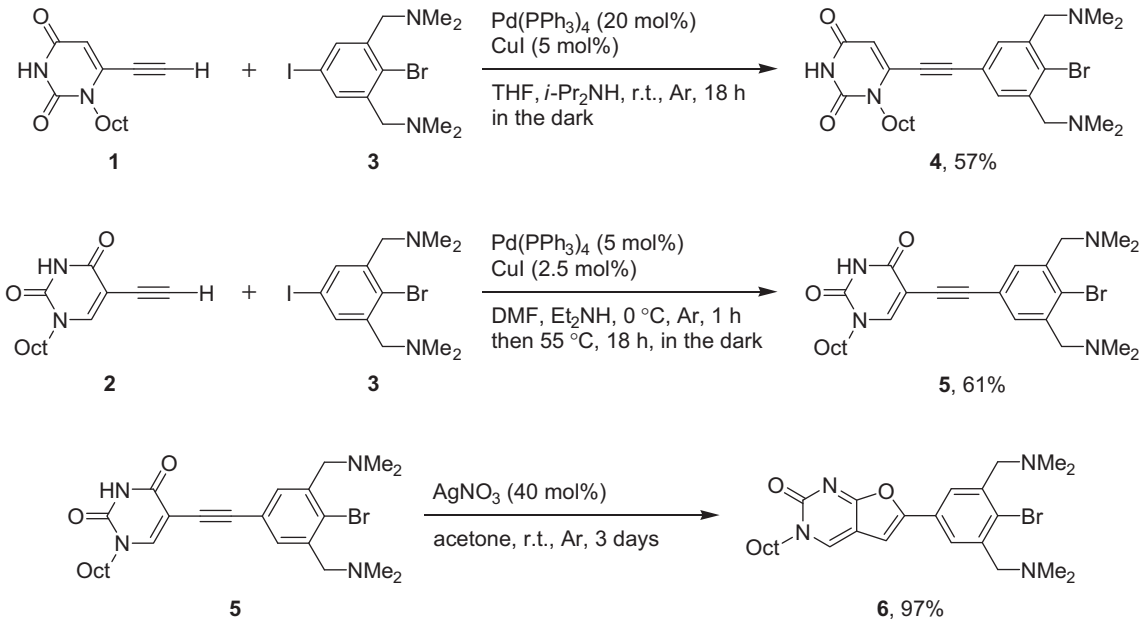


Scheme 1. Synthesis of the NCN-pincer ligands **4**–**6**.

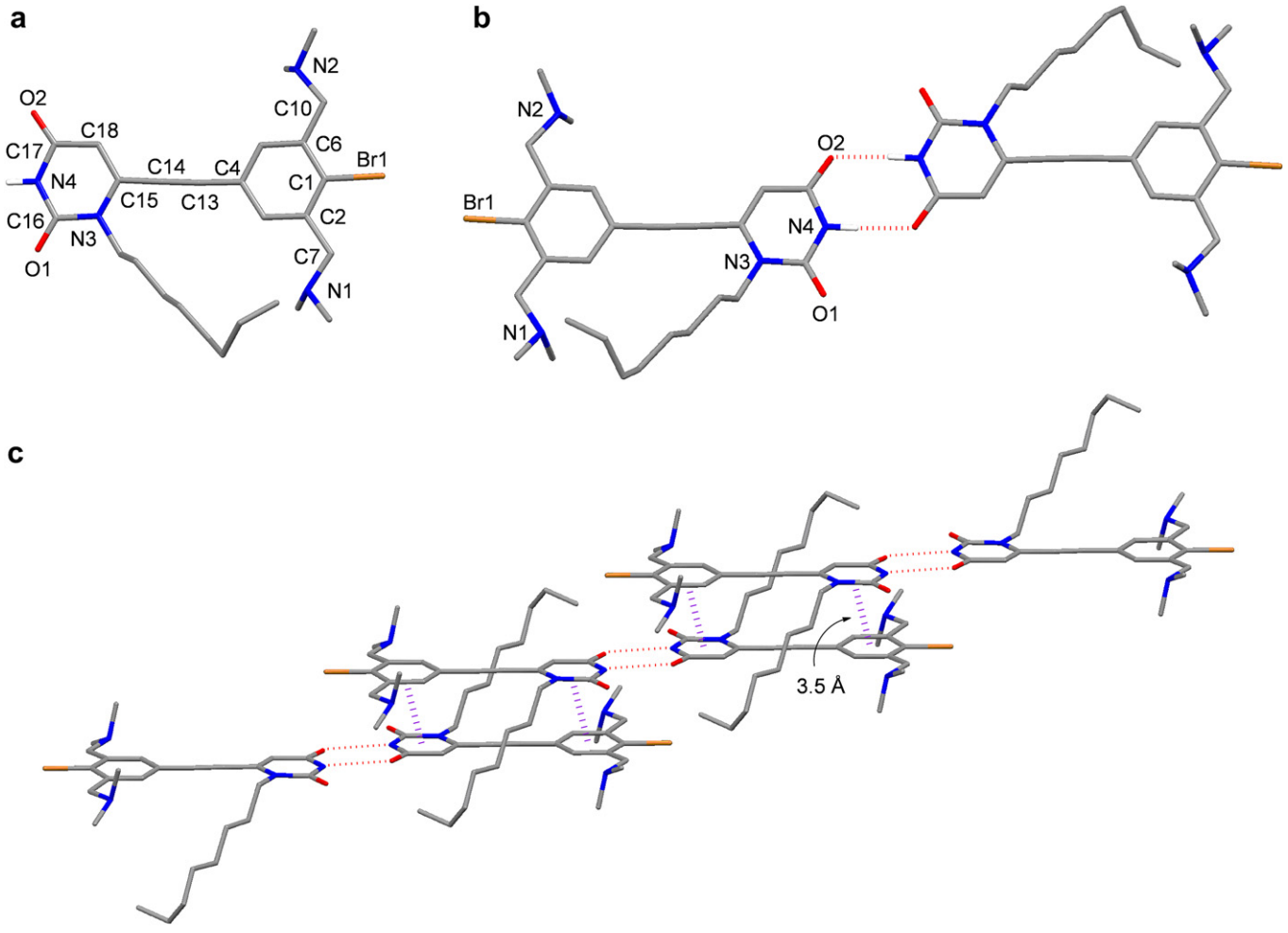


Fig. 1. (a) Molecular structure of **4**, (b) a hydrogen-bonded dimer through intermolecular hydrogen bonds between the uracil moieties, and (c) a portion of a layer containing the molecular assembly through π–π interaction between the uracil and benzene moieties of the NCN-pincer ligand in a crystal packing of **4**.

Table 1.
Crystallographic data for **4** and **9**.

	4	**9**
Empirical formula	$C_{26}H_{37}N_4O_2Br_1$	$C_{26}H_{37}N_4O_2Br_1Pt_1$
Formula weight	517.51	712.60
Crystal system	Triclinic	Monoclinic
Space group	*P*-1 (No. 2)	$P2_1/a$ (No. 14)
a (Å)	8.67021(16)	16.9880(16)
b (Å)	12.2101(2)	9.0621(9)
c (Å)	13.1104(2)	17.5430(19)
α (°)	91.8970(7)	
β (°)	100.4125(7)	91.325(3)
γ (°)	106.8234(7)	
V (Å3)	1301.26(4)	2700.0(5)
Z	2	4
*D*calcd (g cm^{-3})	1.321	1.753
μ(Cu Kα) (cm^{-1})	23.783	
μ(Mo Kα) (cm^{-1})		66.898
T (°C)	−150	−150
λ(Cu Kα) (Å)	1.54187	
λ(Mo Kα) (Å)		0.71075
*R*1 [a]	0.058	0.084
*wR*2 [b]	0.157	0.230

[a] $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.
[b] $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

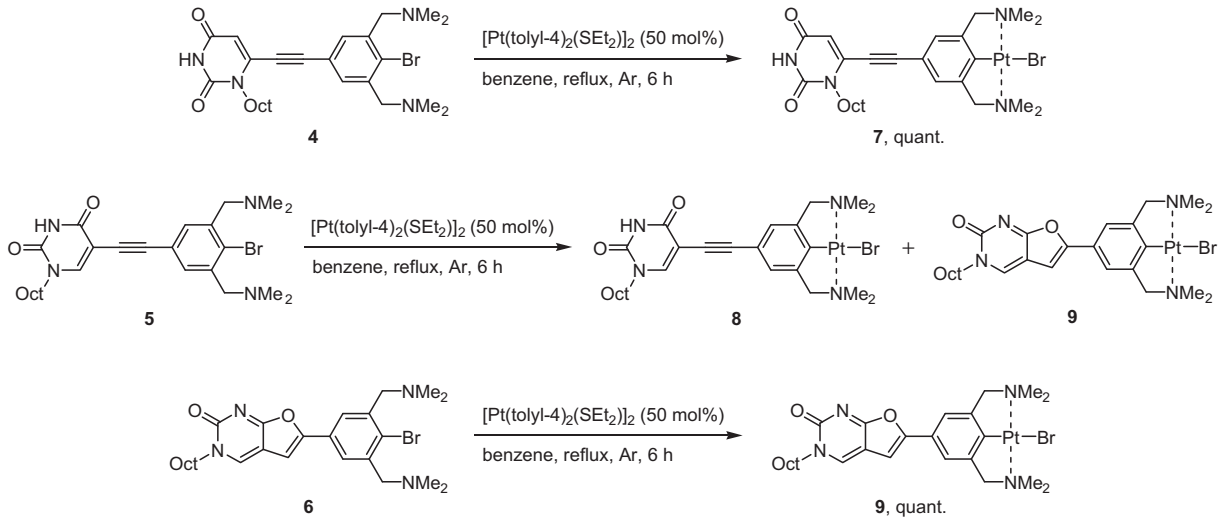
5-ethynyl-1-octyluracil (**2**), respectively. The Pd-catalyzed coupling reaction of **1** or **2** with 4-bromo-3,5-bis(dimethylaminomethyl) iodobenzene (**3**), which was prepared according to the literature method [9], afforded the desired NCN-pincer ligands **4** or **5** bearing the uracil moiety in 61 or 57% yields, respectively. The NCN-pincer ligand **6** bearing the furanopyrimidine moiety was obtained quantitatively by treatment with a catalytic amount of $AgNO_3$.

The single-crystal X-ray structure determination of the NCN-pincer ligand **4** revealed that the benzene moiety of the NCN-pincer ligand is nearly parallel to the uracil moiety probably due to the π-conjugation; the dihedral angle between the least squares planes of the benzene moiety of the NCN-pincer ligand and the uracil moiety is 2.3(1)° (Fig. 1a and Table 1). Selected bond distances and angles are listed in Table 2. The NCN-pincer ligand **4** was found to form a hydrogen-bonded dimer through intermolecular hydrogen bonds between the uracil moieties (N(4)···O(2), 2.818(4) Å; N(4)-H···O(2), 176(2)°) (Fig. 1b). Furthermore, each hydrogen-bonded dimer was connected through π-π interaction between the benzene moiety of the NCN-pincer ligand and the uracil moiety in a crystal packing as shown in Fig. 1c. This π−π interaction might require the orientation of the benzene moiety of the NCN-pincer ligand within a limited range of location parallel to the uracil moiety.

The NCN-pincer platinum(II) complex **7** bearing the uracil moiety was obtained quantitatively by the reaction of the NCN-pincer ligand **4** with $[Pt(tolyl\text{-}4)_2(SEt_2)]_2$ (Scheme 2). On the contrary, the reaction of the NCN-pincer ligand **5** with 50 mol% amount of $[Pt(tolyl\text{-}4)_2(SEt_2)]_2$ resulted in the complex mixture with the NCN-pincer platinum(II) complexes **8** and **9** bearing the uracil and the furanopyrimidine moiety, respectively. Deprotonation of the uracil moiety is assumed to result in cyclization of the oxy anion of the uracil moiety onto the triple bond, followed by protonation to afford the furanopyrimidine moiety. An alternative mechanism might be that the coordination of the triple bond **5** to $[Pt(tolyl\text{-}4)_2(SEt_2)]_2$ enhances the electrophilicity of the triple bond, wherein the subsequent nucleophilic attack of the carbonyl oxygen on the electron deficient triple bond to form the furanopyrimidine ring. The separation of these platinum(II) complexes was unsuccessful at this stage. The NCN-pincer platinum(II) complex **9** bearing the furanopyrimidine moiety could be obtained quantitatively by the reaction of the NCN-pincer ligand **6** with $[Pt(tolyl\text{-}4)_2(SEt_2)]_2$. The single-crystal X-ray structure determination of **9** revealed the formation of the furanopyrimidine ring, which is nearly parallel to the benzene moiety of the NCN-pincer ligand with the dihedral angle between the two planes of 8.0(4)° (Fig. 2a). In a crystal packing, a π stack dimer between the furanopyrimidine and benzene moieties of the NCN-pincer ligand was observed as shown in Fig. 2b.

Table 2
Selected bond distances (Å) and angles (°) for **4** and **9**

	4	**9**		**4**	**9**
Bond distances (Å)					
C(1)–Br(1)	1.895(4)		C(15)–C(18)	1.361(5)	1.415(15)
Pt(1)–Br(1)		2.6241(13)	C(17)–C(18)	1.439(5)	
C(1)–C(2)	1.402(4)	1.494(16)	O(2)–C(13)		1.416(12)
C(1)–C(6)	1.401(5)	1.407(15)	O(2)–C(18)		1.344(12)
C(2)–C(7)	1.527(5)	1.470(16)	N(3)–C(15)	1.380(4)	
C(6)–C(10)	1.533(4)	1.494(16)	N(3)–C(16)	1.395(5)	1.362(14)
N(1)–C(7)	1.460(4)	1.528(13)	N(3)–C(17)		1.396(15)
N(2)–C(10)	1.445(5)	1.511(14)	N(4)–C(16)	1.379(5)	
Pt(1)–N(1)		2.077(8)	N(4)–C(17)	1.382(4)	1.385(15)
Pt(1)–N(2)		2.083(9)	N(4)–C(18)		1.290(14)
C(4)–C(13)	1.431(5)	1.450(14)	O(1)–C(16)	1.207(4)	
C(13)–C(14)	1.209(5)	1.335(14)	O(1)–C(17)		1.202(15)
C(14)–C(15)	1.426(5)	1.452(14)	O(2)–C(17)	1.234(4)	
C(15)–C(16)		1.352(14)			
Bond angles (°)					
C(1)–C(2)–C(7)	120.5(3)	113.7(10)	C(16)–N(4)–C(17)	127.7(3)	
C(1)–C(6)–C(10)	121.7(3)	110.8(9)	N(4)–C(17)–C(18)	114.6(3)	
C(2)–C(7)–N(1)	113.9(3)	108.9(9)	C(15)–C(18)–C(17)	119.9(3)	
C(6)–C(10)–N(2)	112.7(3)	110.1(9)	N(3)–C(15)–C(18)	121.6(3)	
Pt(1)–C(1)–C(2)		117.5(7)	C(13)–C(14)–C(15)	178.6(3)	106.6(9)
Pt(1)–C(1)–C(6)		123.3(8)	C(14)–C(15)–C(18)	121.4(3)	106.1(8)
C(1)–Pt(1)–N(1)		83.6(4)	C(15)–C(18)–O(2)		109.1(9)
C(1)–Pt(1)–N(2)		80.4(4)	C(18)–O(2)–C(13)		107.6(7)
Pt(1)–N(1)–C(7)		110.4(6)	O(2)–C(13)–C(14)		110.5(8)
Pt(1)–N(2)–C(10)		110.2(6)	C(15)–C(16)–N(3)		118.6(10)
C(1)–Pt(1)–Br(1)		176.9(3)	C(16)–N(3)–C(17)		123.8(9)
N(1)–Pt(1)–Br(1)		98.2(2)	N(3)–C(17)–N(4)		117.4(10)
N(2)–Pt(1)–Br(1)		97.8(2)	C(17)–N(4)–C(18)		116.4(10)
C(15)–N(3)–C(16)	122.0(3)		N(4)–C(18)–C(15)		128.4(10)
N(3)–C(16)–N(4)	114.2(3)		C(16)–C(15)–C(18)		115.0(9)



Scheme 2. Synthesis of the NCN-pincer platinum(II) complexes **7-9**.

The UV/Vis spectrum of a solution of the platinum(II) complex **7** in dichloromethane showed a broad absorption at around 370 nm, assignable to an intramolecular charge transfer band, wherein the NCN-PtBr moiety behaves as a donor (Fig. 3a). The platinum(II) complex **7** in dichloromethane exhibited an emission at around 450 nm (Fig. 3b). It should be noted that the emission at around 550 nm probably due to the aggregation based on π–π interaction was observed in a solid state together with an emission at around 450 nm as shown in Fig. 3b. The platinum(II) complex **9** in dichloromethane also showed a broad absorption assignable to an intramolecular charge transfer band at around 380 nm in the UV/Vis spectrum (Fig. 3c) and an emission at around 450 nm in the emission spectrum (Fig. 3d). In the solid state spectrum of **9**, the emission probably due to the aggregation based on π–π interaction was observed at around 600 nm together with an emission at around 450 nm as shown in Fig. 3d. This result is consistent with the formation of the π stack dimer in a crystal packing (Fig. 2).

3. Conclusion

The bioorganometallic conjugates composed of the NCN-pincer platinum(II) complexes as an oraganometallic compound and the uracil derivatives as a nucleobase were designed. The NCN-pincer ligand bearing the uracil moiety was demonstrated to form a hydrogen-bonded dimer through intermolecular hydrogen bonds between the uracil moieties. Furthermore, each hydrogen-bonded dimer was connected through π–π interaction in a crystal packing. The NCN-pincer platinum(II) complexes bearing the uracil or the furanopyrimidine moiety, respectively, were found to exhibit emission in both solution and solid states. The NCN-pincer palladium(II) complexes have been demonstrated to serve as homogeneous catalysts [6k,7]. The NCN-pincer platinum(II) complexes bearing the uracil or the furanopyrimidine moiety are envisioned to exhibit catalytic activities by the formation of the corresponding cationic complexes. Such application and dynamic control of aggregated platinum(II) complexes as a catalyst are now in progress.

4. Experimental

4.1. General materials and experimental procedures

All reagents and solvents were purchased from commercial sources and were further purified by the standard methods, if necessary. 1-Octyluracil [8], 5-ethynyl-1-octyluracil (**2**) [8], 4-bromo-3,5-bis(dimethylaminomethyl)iodobenzene (**3**) [9], and [Pt(tolyl-4)$_2$(SEt$_2$)]$_2$ [10] were prepared by the literature methods. Melting points were determined on a Yanagimoto Micromelting Point Apparatus and were uncorrected. Infrared spectra were

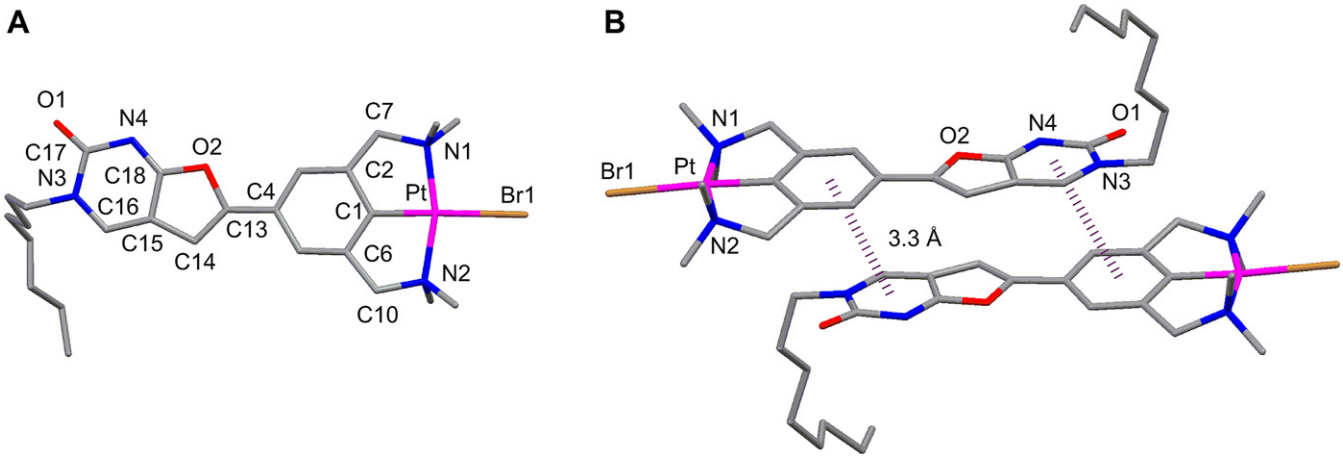


Fig. 2. (a) Molecular structure of **9** and (b) a π stack dimer between the furanopyrimidine and benzene moieties of the NCN-pincer ligand in a crystal packing of **9**.

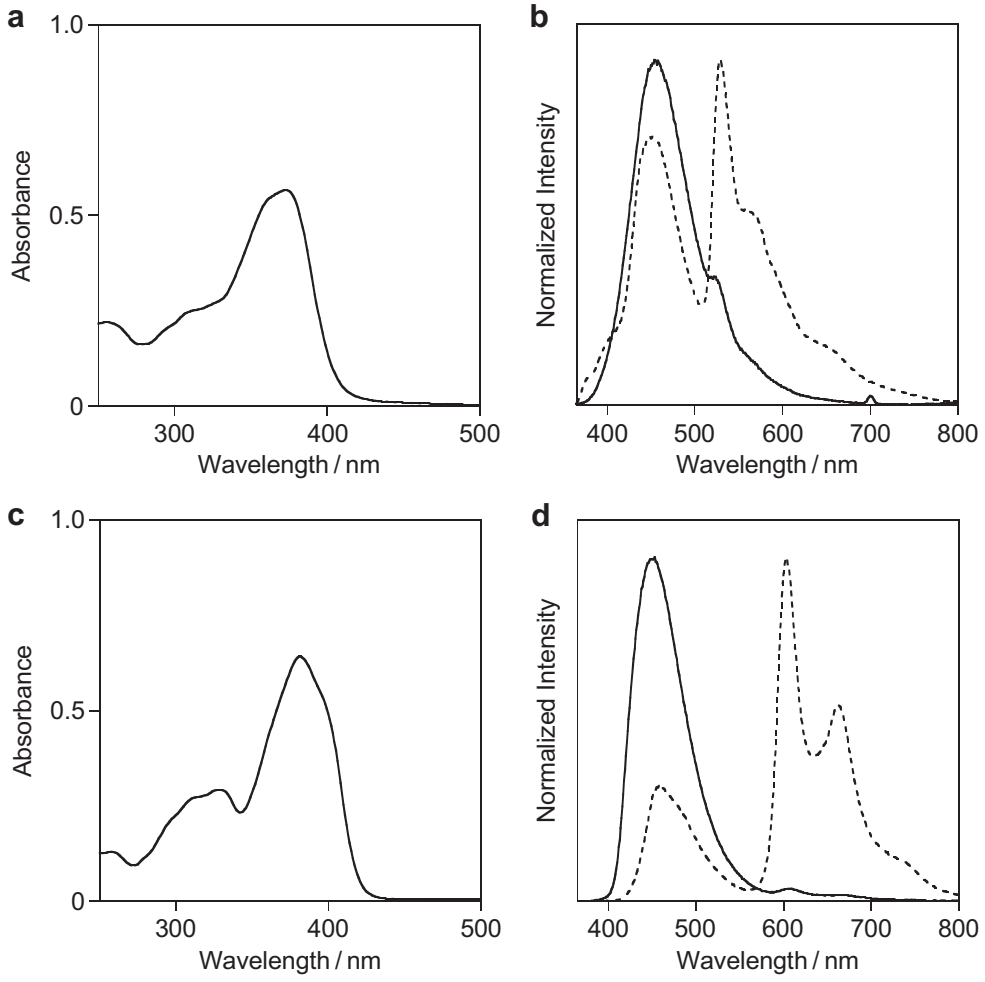


Fig. 3. (a) Electronic spectrum of **7** in dichloromethane (2.0×10^{-4} M), (b) emission spectra of **7** in dichloromethane (- (a long solid line) 2.0×10^{-4} M, $\lambda_{ex} = 350$ nm) and a solid state (···, $\lambda_{ex} = 350$ nm), (c) Electronic spectrum of **9** in dichloromethane (2.0×10^{-4} M), and (d) emission spectra of 9 in dichloromethane (- (a long solid line), 2.0×10^{-4} M, $\lambda_{ex} = 350$ nm) and a solid state (···, $\lambda_{ex} = 350$ nm).

obtained with a JASCO FT/IR-480 Plus spectrometer. ^{1}H NMR spectra were recorded on a JNM-ECS 400 (400 MHz) spectrometer with tetramethylsilane as an internal standard. Mass spectra were run on a JEOL JMS-700 mass spectrometer.

4.1.1. Synthesis of 6-iodo-1-octyluracil

To a THF solution (25 mL) of diisopropylamine (2.8 mL, 20 mmol) was added BuLi (1.66 M hexane solution, 18 mL, 30 mmol) dropwise at −78 °C, and the resulting solution was stirred under Ar at −78 °C for 10 min and 0 °C for 10 min. To the resulting solution, was added a THF solution (20 mL) of 1-octyluracil (1.8 g, 8.0 mmol) dropwise at −78 °C, and the resulting solution was stirred under Ar at −78 °C for 1.5 h. A THF (10 mL) solution of I_2 (4.1 g, 16 mmol) was added dropwise to the resulting solution and the reaction mixture was stirred under Ar at −78 °C for 2 h. The resulting solution was then treated with glacial acetic acid (5 mL) and the resulting solution was stirred at room temperature for 10 h. The resulting mixture was diluted with dichloromethane, washed with saturated $Na_2S_2O_3$ aqueous solution, saturated $NaHCO_3$ aqueous solution, brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and purification of the crude product by silica-gel column chromatography (from $CHCl_3$ to 4/1 $CHCl_3$/EtOAc) gave 6-iodo-1-octyluracil (1.7 g, 61%) as a white solid.

6-Iodo-1-octyluracil: mp 127–128 °C (uncorrected); IR (KBr) 3148, 3016, 2952, 2920, 1690, 1562, 1444, 1406, 1173, 1070 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$, TMS, 1.0×10^{-2} M) δ 8.34 (br s, 1H), 6.41 (s, 1H), 4.05 (t, 2H, $J = 8.1$ Hz), 1.64–1.72 (m, 2H), 1.26–1.37 (m, 10H), 0.89 (t, 3H, $J = 7.0$ Hz); HRMS (FAB) m/z calcd for $C_{12}H_{19}N_2O_2I$ (([M]$^+$)), 350.0486; found, 350.0493.

*4.1.2. Synthesis of 6-ethynyl-1-octyluracil **(1)***

To a toluene (30 mL) solution of 6-iodo-1-octyluracil (0.70 g, 2.0 mmol), $PdCl_2(PPh_3)_2$ (70.2 mg, 0.10 mmol), CuI (9.5 mg, 0.050 mmol), and triethylamine (3.0 mL, 22 mmol) was added trimethysilylacetylene (1.7 mL, 12 mmol) dropwise at room temperature. The resulting mixture was stirred under Ar at room temperature for 12 h and the solvent was evaporated. The residue was poured into water and extracted with dichloromethane. The dichloromethane solution was washed with brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and purification of the crude product by silica-gel column chromatography (from $CHCl_3$ to 4/1 $CHCl_3$/EtOAc) yielded 1-octyl-6-[(trimethysilyl) ethynyl]uracil (0.47 g, 73%) as a white solid. The mixture of 1-octyl-6-[(trimethysilyl)ethynyl]uracil (100 mg, 0.31 mmol) and KOH (26 mg, 0.46 mmol) in methanol (5 mL) was stirred under Ar at room temperature for 2 h. Water was added, and the organic phase was extracted with dichloromethane. The dichloromethane solution was washed with brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and purification of the crude product by silica-gel column chromatography (from $CHCl_3$ to 4/1

$CHCl_3$/EtOAc) afforded 6-ethynyl-1-octyluracil (**1**) quantitatively as a white solid.

1: mp 142–143 °C (uncorrected); IR (KBr) 3195, 3040, 2919, 2852, 2107, 1722, 1690, 1590, 1453, 1414, 1178 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$, TMS, 1.0×10^{-2} M) δ 8.25 (br s, 1H), 5.99 (s, 1H), 3.97 (t, 2H, $J = 7.7$ Hz), 3.66 (s, 1H), 1.66–1.74 (m, 2H), 1.25–1.40 (m, 10H), 0.88 (t, 3H, $J = 7.1$ Hz); HRMS (FAB) *m/z* calcd for $C_{14}H_{20}N_2O_2$ (($[M]^+$)), 248.1519; found, 248.1526.

*4.1.3. Synthesis of the NCN-pincer ligand **4***

A mixture of 6-ethynyl-1-octyluracil (**1**, 410 mg, 1.65 mmol), 4-bromo-3,5-bis(dimethylaminomethyl)iodobenzene (**3**, 600 mg, 1.51 mmol), $Pd(PPh_3)_4$ (300 mg, 0.26 mmol), CuI (14 mg, 0.074 mmol), and diisopropylamine (24 mL, 171 mmol) was stirred under Ar at room temperature for 18 h and the solvent was evaporated. Water was added, and the organic phase was extracted with dichloromethane. The dichloromethane solution was washed with brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and purification of the crude product by silica-gel column chromatography (AcOEt) gave the NCN-pincer ligand **4** (447 mg, 57%) as a white solid.

4: mp 166–168 °C (uncorrected); IR (KBr) 3148, 3025, 2928, 2857, 2821, 2773, 2214, 1711, 1671, 1575, 1464, 1352, 1017 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0×10^{-2} M) δ 8.54 (br s, 1H), 7.57 (s, 2H), 5.96 (s, 1H), 4.03 (t, 2H, $J = 7.8$ Hz), 3.54 (s, 4H), 2.30 (s, 12H), 1.73–1.80 (m, 2H), 1.21–1.42 (m, 10H), 0.85 (t, 3H, $J = 6.9$ Hz); HRMS (FAB) *m/z* calcd for $C_{26}H_{37}N_4O_2Br$ ($[M + H]^+$), 517.2173; found, 517.2153.

*4.1.4. Synthesis of the NCN-pincer ligand **5***

To a mixture of 4-bromo-3,5-bis(dimethylaminomethyl)iodobenzene (**3**, 200 mg, 0.50 mmol), $Pd(PPh_3)_4$ (29 mg, 0.025 mmol), CuI (2.3 mg, 0.012 mmol), and diethylamine (6 mL, 58 mmol) was added the DMF (6 mL) solution of 5-ethynyl-1-octyluracil (**2**, 137 mg, 0.55 mmol) dropwise at 0 °C. The resulting mixture was stirred under Ar at 55 °C for 18 h and the solvent was evaporated. Water was added and the organic phase was extracted with dichloromethane. The dichloromethane solution was washed with brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and purification of the crude product by silica-gel column chromatography (from dichloromethane to 93/7 dichloromethane/methanol) yielded the NCN-pincer ligand **5** (0.16 g, 62%) as a white solid.

5: mp 173–174 °C (uncorrected); IR (KBr) 3164, 3053, 2949, 2925, 2855, 2772, 2219, 1691, 1627, 1427, 1354, 1175, 1026 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0×10^{-2} M) δ 8.49 (br s, 1H), 7.56 (s, 1H), 7.48 (s, 2H), 3.74 (t, 2H, $J = 7.5$ Hz), 3.51 (s, 4H), 2.28 (s, 12H), 1.67–1.74 (m, 2H), 1.26–1.36 (m, 10H), 0.88 (t, 3H, $J = 6.8$ Hz); HRMS (FAB) *m/z* calcd for $C_{26}H_{37}N_4O_2Br$ ($[M + H]^+$), 517.2173; found, 517.2165.

*4.1.5. Synthesis of the NCN-pincer ligand **6***

A mixture of the NCN-pincer ligand **5** (30 mg, 0.058 mmol) and $AgNO_3$ (4.0 mg, 0.024 mmol) was stirred in acetone (2.5 mL) under Ar at room temperature for 3 days and the solvent was evaporated. Water was added and the organic phase was extracted with dichloromethane. The dichloromethane solution was washed with brine, and then dried over Na_2SO_4. The solvent was evaporated in vacuo and purification of the crude product by alumina column chromatography afforded the NCN-pincer ligand **6** (29 mg, 97%) as a white solid.

6: mp 191–193 °C (uncorrected); IR (KBr) 3104, 3016, 2925, 2854, 2815, 2766, 1667, 1604, 1572, 1453, 1379, 1260, 1171, 1130, 1019 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0×10^{-2} M) δ 7.90 (s, 1H), 7.77 (s, 2H), 6.83 (s, 1H), 3.98 (t, 2H, $J = 7.5$ Hz), 3.58 (s, 4H), 2.31 (s, 12H), 1.76–1.83 (m, 2H), 1.25–1.39 (m, 10H), 0.88 (t, 3H, $J = 7.0$ Hz); HRMS (FAB) *m/z* calcd for $C_{26}H_{37}N_4O_2Br$ ($[M + H]^+$), 517.2173; found, 517.2159.

*4.1.6. Synthesis of the NCN-pincer platinum(II) complex **7***

A mixture of the NCN-pincer ligand **4** (35 mg, 0.068 mmol) and $[Pt(tolyl\text{-}4)_2(SEt_2)]_2$ (32 mg, 0.034 mmol) was stirred in benzene (2.0 mL) under Ar at reflux temperature for 6 h. After evaporation of the solution, the NCN-pincer platinum(II) complex **7** was isolated quantitatively as a yellow solid by reprecipitation from dichloromethane and diethyl ether.

7: mp 238–242 °C (decomp.); IR (KBr) 3152, 3005, 2925, 2857, 2199, 1706, 1675, 1573, 1466, 1447, 1399, 1217, 1081, 1017 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0×10^{-2} M) δ 8.49 (br s, 1H), 7.00 (s, 2H), 5.90 (s, 1H), 3.99–4.08 (m, 6H), 3.09 (s, 12H), 1.71–1.79 (m, 2H), 1.21–1.41 (m, 10H), 0.87 (t, 3H, $J = 7.0$ Hz); HRMS (FAB) *m/z* calcd for $C_{26}H_{37}N_4O_2Br^{194}Pt$ ($[M]^+$), 710.1721; found, 710.1722.

*4.1.7. Synthesis of the NCN-pincer platinum(II) complex **9***

A mixture of the NCN-pincer ligand **6** (30 mg, 0.058 mmol) and $[Pt(tolyl\text{-}4)_2(SEt_2)]_2$ (30 mg, 0.032 mmol) was stirred in benzene (2.0 mL) under Ar at reflux temperature for 6 h. After evaporation of the solution, the NCN-pincer platinum(II) complex **9** was isolated quantitatively as a yellow solid by reprecipitation from dichloromethane and diethyl ether.

9: mp 229–233 °C (decomp.); IR (KBr) 3080, 3008, 2924, 2854, 1668, 1598, 1574, 1450, 1412, 1375, 1163, 1126 cm^{-1}; ^1H NMR (400 MHz, CD_2Cl_2, 1.0×10^{-2} M) δ 7.85 (s, 1H), 7.25 (s, 2H), 6.64 (s, 1H), 4.07 (s, 4H), 3.96 (t, 2H, $J = 7.3$ Hz), 3.10 (s, 12H), 1.75–1.82 (m, 2H), 1.25–1.38 (m, 10H), 0.88 (t, 3H, $J = 7.0$ Hz); HRMS (FAB) *m/z* calcd for $C_{26}H_{37}N_4O_2Br^{194}Pt$ ($[M]^+$), 710.1721; found, 710.1745.

4.2. General procedure of UV/Vis measurement

UV/Vis spectra were obtained using a Hitachi U-3500 spectrophotometer in a dichloromethane solution with the concentration 2.0×10^{-4} M for the platinum(II) complexes **7** and **9** under Ar at 298 K. UV/Vis spectra were measured using 1-mm pathlength quartz cuvettes.

4.3. General procedure of emission measurement

Emission spectra were measured using a Shimadzu RF-5300PC spectrofluorophotometer in a dichloromethane solution with the concentration 2.0×10^{-4} M for the platinum(II) complexes **7** and **9** under Ar at 298 K. Emission spectra were measured using 1-mm pathlength quartz cuvettes.

4.4. X-ray structure analysis

All measurements for **4** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Cu Kα radiation. All measurements for **9** were made on a Rigaku RAXIS-RAPID Imaging Plate diffractometer with graphite monochromated Mo Kα radiation. The structures of **4** and **9** were solved by direct methods and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. The H atoms involved in hydrogen bonding were located in electron density maps. The remainder of the H atoms were placed in idealized positions and allowed to ride with the C atoms to which each was bonded. Crystallographic details are given in Table 1.

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Appendix A. Supplementary material

CCDC 790374 and 790375 contain the supplementary crystallographic data (excluding structure factors) for compounds **4** and **9** for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

References

[1] (a) W. Saenger, Principles of Nucleic Acid Structure. Springer-Verlag, New York, 1984;
(b) V.A. Bloomfield, D.M. Crothers, I. Tinoco Jr., Nucleic Acids: Structures, Properties, and Functions. University Science Books, Sausalito, CA, 2000.
[2] (a) D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375–1406;
(b) V. Balzani, A. Credi, F.M. Raymo, J.F. Stoddart, Angew. Chem. Int. Ed. 39 (2000) 3348–3391;
(c) G.F. Swiegers, T.J. Malefetse, Chem. Rev. 100 (2000) 3483–3538.
[3] G.A. Jeffrey, An Introduction to Hydrogen Bonding, first ed. Oxford University Press, New York, 1997.
[4] (a) M.M. Conn, J. Rebek Jr., Chem. Rev. 97 (1997) 1647–1668;
(b) E.A. Archer, H. Gong, M.J. Krische, Tetrahedron 57 (2001) 1139–1159;
(c) L.J. Prins, D.N. Reinhoudt, P. Timmerman, Angew. Chem. Int. Ed. 40 (2001) 2382–2426.
[5] For recent reviews, see: (a) S. Sivakova, S.J. Rowan, Chem. Soc. Rev. 34 (2005) 9–21;
(b) J.T. Davis, G.P. Spada, Chem. Soc. Rev. 36 (2007) 296–313;
(c) J.L. Sessler, C.M. Lawrence, J. Jayawickramarajah, Chem. Soc. Rev. 36 (2007) 314–325;
(d) K. Tanaka, M. Shionoya, Coord. Chem. Rev. 251 (2007) 2732–2742;
(e) J. Müller, Eur. J. Inorg. Chem. (2008) 3749–3763;
(f) S. Lena, S. Masiero, S. Pieraccini, G.P. Spada, Chem. Eur. J. 15 (2009) 7792–7806;
(g) G.H. Clever, M. Shionoya, Coord. Chem. Rev. 254 (2010) 2391–2402.
[6] (a) G. Jaouen, A. Vessiéres, I.S. Butler, Acc. Chem. Res. 26 (1993) 361–369;
(b) R. Severin, R. Bergs, W. Beck, Angew. Chem. Int. Ed. 37 (1998) 1634–1654;
(c) R.H. Fish, G. Jaouen, Organometallics 22 (2003) 2166–2177;
(d) T. Moriuchi, T. Hirao, Chem. Soc. Rev. 33 (2004) 294–301;
(e) D.R. van Staveren, N. Metzler-Nolte, Chem. Rev. 104 (2004) 5931–5986;
(f) C. Baldoli, P. Cerea, C. Giannini, E. Licandro, C. Rigamonti, S. Maiorana, Synlett (2005) 1984–1994;
(g) G. Jaouen (Ed.), Bioorganometallics; Biomolecules, Labeling, Medicine, Wiley-VCH, Weinheim, 2006 (and references therein);
(h) R. Alberto, J. Organomet. Chem. 692 (2007) 1179–1186;
(i) G. Erker, J. Organomet. Chem. 692 (2007) 1187–1197;
(j) C.G. Hartinger, P.J. Dyson, Chem. Soc. Rev. 38 (2009) 391–401;
(k) B. Wieczorek, H.P. Dijkstra, M.R. Egmond, R.J.M. Klein Gebbink, G. van Koten, J. Organomet. Chem. 694 (2009) 812–822;
(l) W. Beck, Z. Naturforsch. B. 64 (2009) 1221–1245;
(m) A. Lataifeh, S. Beheshti, H.-B. Kraatz, Eur. J. Inorg. Chem. (2009) 3205–3218;
(n) T. Moriuchi, T. Hirao, Acc. Chem. Res. 43 (2010) 1040–1051.
[7] M. Albrecht, G. van Koten, Angew. Chem. Int. Ed. 40 (2001) 3750–3781.
[8] M. Takase, M. Inoueye, J. Org. Chem. 68 (2003) 1134–1137.
[9] G. Rodríguez, M. Albrecht, J. Schoenmaker, A. Ford, M. Lutz, A.L. Spek, G. van Koten, J. Am. Chem. Soc. 124 (2002) 5127–5138.
[10] B.R. Steele, K. Vrieze, Transit. Met. Chem. 2 (1977) 140–144.