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PAPER

A novel amphiphilic pincer palladium complex: design, preparation and self-assembling behavior†

Go Hamasaka,[a] Tsubasa Muto[a,b] and Yasuhiro Uozumi*[a,b,c]

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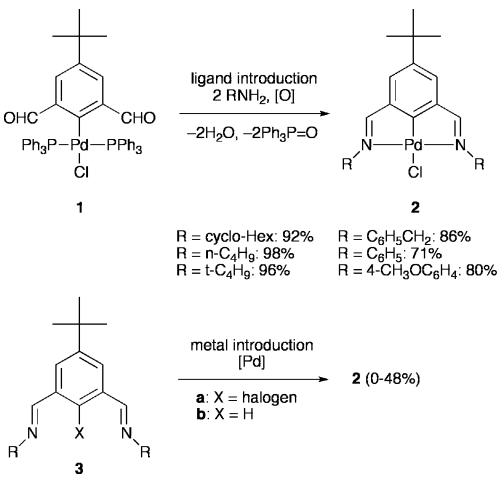
Amphiphilic pincer palladium complexes bearing hydrophilic and hydrophobic side chains on the planar NCN palladium pincer backbone were designed and prepared *via* the ligand introduction route. The complexes self-assembled under aqueous conditions to form vesicles with bilayer membranes containing palladium species. The catalytic activity of the vesicles in the Miyaura–Michael reaction in water was investigated.

Introduction

Palladium complexes containing monoanionic terdentate ligands, so-called pincer complexes, have received much attention as catalysts in synthetic organic chemistry[1] and also as organometallic compounds in the field of materials science.[2] Recently, we developed a new strategy for the synthesis of pincer palladium complexes, *the ligand introduction route*, in which the metal is introduced onto the aromatic ring prior to the construction of the ligand units.[3,4] This strategy enabled us to prepare a novel class of pincer palladium complexes having sterically demanding and/or chemically unstable functional groups. Representative examples are shown in Scheme 1. In this manner, NCN palladium pincer complexes **2** bearing a planar pincer core moiety and imine ligand units (-CH═NR) were prepared from the 2,6-dialdehyde precursor **1** *via* dehydrative condensation with primary amines under mild oxidative conditions (Scheme 1).[3] In contrast, metallation of the pincer ligands **3** *via* oxidative addition [from **3a** (X = halogen)] or CH-metallation [from **3b** (X = H)] resulted in poor yields of the desired pincer complexes **2** because of the steric bulkiness and/or the chemical reactivity of the imine units.

The self-assembling construction of potentially functionalized, highly-ordered molecular architectures *via* non-covalent interactions among the monomer units is rapidly generating interest from a wide range of chemists.[5] In particular, it has been reported that organic molecules having rigid planar backbones with both hydrophobic and hydrophilic side chains often form bilayer assemblages.[6] If hydrophobic and hydrophilic side chains are incorporated onto the planar NCN palladium pincer backbone, the resulting amphiphilic palladium pincer complexes would adopt a self-assembled architecture having catalytic activity.[7,8] We report here the design, preparation, and self-assembling vesicle formation of amphiphilic palladium pincer complexes and their application to the Miyaura–Michael reaction[9] in water.



Scheme 1 Preparation of NCN Pincer Palladium Complexes *via* the Ligand Introduction Route.

Results and Discussion

The pincer palladium complexes **4** and **5** having pairs of hydrophobic dodecyl chains and hydrophilic tri(ethylene glycol) (TEG) chains, located opposite to one another on the rigid planar backbone, were designed and prepared for use in the formation of self-assembled molecular architectures (Fig. 1 and 2).

Preparation of Pincer Complexes 4 and 5

The amphiphilic NCN pincer palladium complexes **4** and **5** could ideally be obtained by dehydrative condensation of their 2,6-dialdehyde precursors **6** and **7** and primary amines **8** and **9**, respectively, *via* the ligand introduction route (Scheme 2).

[a]*Institute for Molecular Science, Myodaiji, Okazaki, 444-8787, Japan. E-mail: uo@ims.ac.jp; Fax: (+81)564-59-5574*
[b]*The Graduate School for Advanced Studies, Myoudaiji, Okazaki, 444-8787, Japan*
[c]*Riken, Hirosawa, Wako, 351-0198, Japan. E-mail: uo@riken.jp*
† Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of all new compounds. See DOI: 10.1039/c1dt10556f

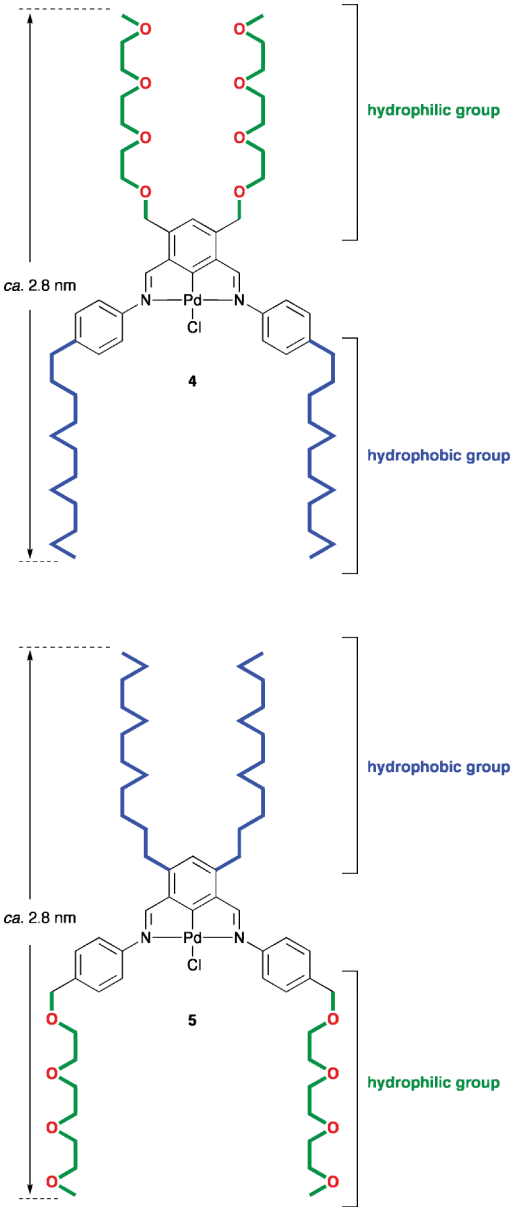


Fig. 1 Design of Amphiphilic Pincer Palladium Complexes.

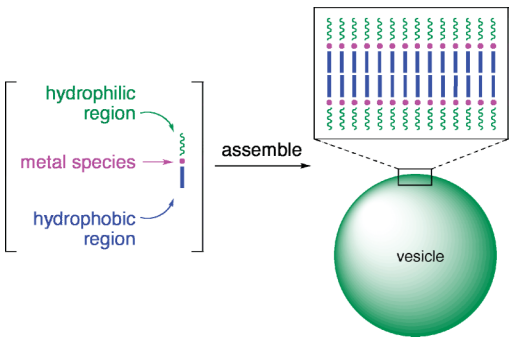
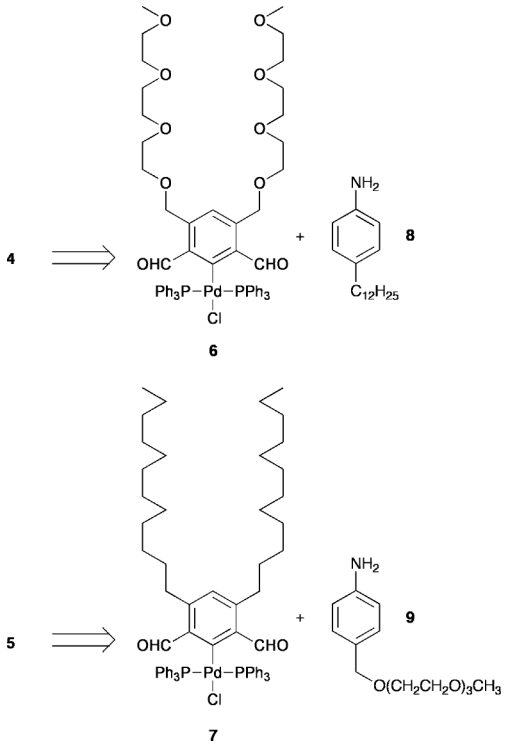
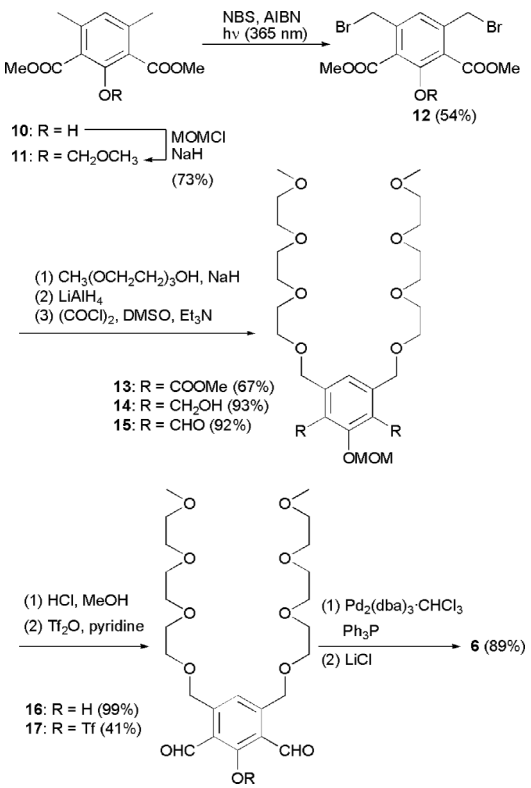


Fig. 2 Concept of Vesicle Formation *via* Self-Assembly of Amphiphilic Pincer Complexes.



Scheme 2 Synthetic Precursors of Pincer Complexes **4** and **5**.



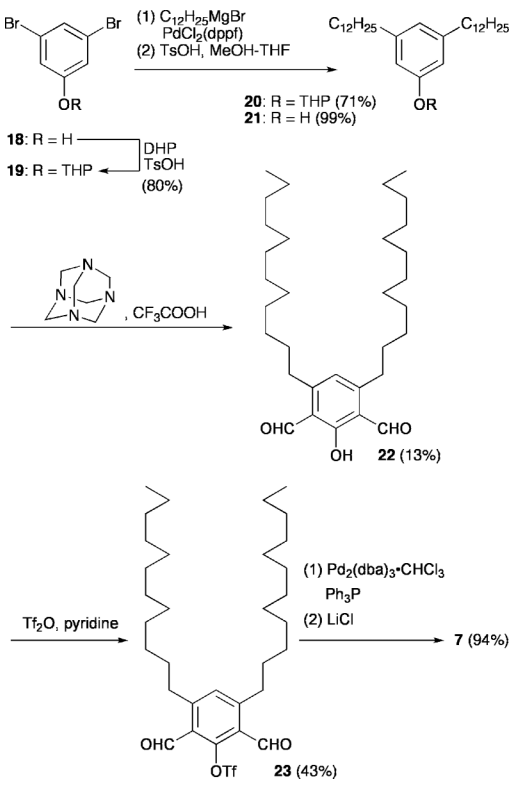
Scheme 3 Preparation of Precursor **6**.

The precursor **6** was prepared from the phenol **10** in nine steps (Scheme 3). Thus, phenol **10** was protected with a methoxymethyl (MOM) group (73%) and the resulting MOM ether **11** was treated with *N*-bromosuccinimide under radical conditions to give 1,5-bis(bromomethyl)arene **12** in 54% yield. The hydrophilic methoxy[tri(ethylene glycol)] [$CH_3(OCH_2CH_2)_3OH$;

MeOTEGOH] units were incorporated at the benzylic positions to give the 1,5-bis(MeOTEGOCH$_2$)arene **13** in 67% yield.

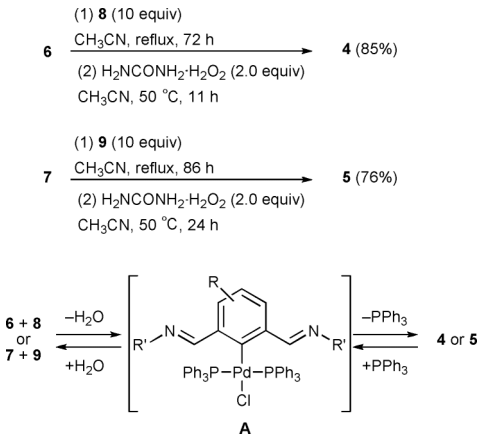
The methoxycarbonyl groups of **13** were converted to CHO groups (compound **15**) *via* $LiAlH_4$ reduction to **14** (93%) and subsequent Swern oxidation (92%). After removal of the *O*-MOM group, the resulting phenol **16** was treated with triflic anhydride to give the *O*-Tf ester **17**. Complexation of the triflate **17** was carried out with dipalladiumtris(dibenzylideneacetone) [$Pd_2(dba)_3$] in the presence of triphenylphosphine to afford an arylpalladium[bis(triphenylphosphine)] complex, which was subsequently treated with lithium chloride to provide the desired arylpalladium chloride bis(triphenylphosphine) complex **6** bearing formyl groups at both *ortho* positions.

We prepared precursor **7** with hydrophilic and hydrophobic groups in the opposite orientation to those of precursor **6** from 3,5-dibromophenol (**18**) in seven steps (Scheme 4). The hydrophobic dodecyl groups were introduced at the 3,5-positions of compound **19**, which was readily obtained from **18** by treatment with dihydropyran, through palladium-catalyzed Grignard cross-coupling with dodecylmagnesium bromide, to afford 3,5-bis(dodecyl)phenol (**20**) in 71% yield. After removal of the *O*-THP moiety, formyl groups were introduced at the 2,6-positions of the phenol with hexamethylenetetramine to give the diformylated phenol **22** in 13% yield. The phenol was treated with triflic anhydride and the resulting triflate **23** (43%) underwent complexation with $Pd_2(dba)_3/PPh_3$ followed by treatment with LiCl to give the desired precursor **7** in 94% yield.



Scheme 4 Preparation of Precursor **7**.

Pincer complexation of **6** and **7** was achieved by ligand introduction with the hydrophobic aniline **8** and the hydrophilic aniline **9**, respectively (Scheme 5). Thus, the hydrophilic precursor



Scheme 5 Preparation of Pincer Complexes **4** and **5**.

6 reacted with 10 equiv of the aniline **8** bearing a hydrophobic 4-alkyl substituent in refluxing acetonitrile for 72 h followed by treatment with urea-hydroperoxide at 50 °C to give an 85% yield of the amphiphilic pincer palladium complex **4** as an amorphous material. The hydrophobic precursor **7** underwent a similar ligand introduction protocol with the hydrophilic aniline **9** to afford the amphiphilic pincer palladium complex **5** having the opposite orientation of the hydrophilic and hydrophobic side chains, also as an amorphous material in 76% isolated yield. The pincer complexes **4** and **5** were formed through condensation of the 2,6-formyl groups of **6** and **7** with primary amines **8** and **9** affording the corresponding intermediates **A**, and subsequent ligand exchange by the resulting imine functionalities constructing the Pd–N bonds. Irreversible trapping of PPh_3 ligands liberated from a possible intermediate **A** by oxidation with urea-hydrogenperoxide is essential to promote this pincer complexation process.[3]

Self-Assembly of Pincer Complexes 4 and 5

With the amphiphilic pincer palladium complexes **4** and **5** in hand, we next turned our attention to demonstrating their self-assembling potential. After thorough screening, we were pleased to find that both complexes **4** and **5** exhibited good assembling potential under aqueous conditions. Thus, to an acetonitrile solution of **4** was added water (H_2O/CH_3CN = 9/1) and the resulting aqueous mixture was concentrated at 80 °C for 6 h, during which time acetonitrile was slowly vaporized, to afford a pale yellow aqueous suspension.[10] The resulting suspension was cooled and centrifuged (4000 rpm, 15 min) to give nano-precipitates. The precipitate was diluted with water and studied by dynamic light scattering (DLS) to demonstrate the formation of the vesicle $\mathbf{4}_{vscl}$ (average diameter = 463 nm) [Fig. 3(a)]. The amphiphilic pincer complex **5** was treated in water at 60 °C for

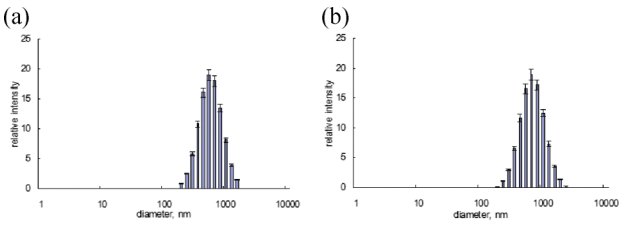


Fig. 3 Histograms of the Size Distributions of (a) **4** and (b) **5**.

4 h, and the resulting aqueous mixture was cooled to ambient temperature and vortexed to afford an aqueous slurry of $\mathbf{5}_{vscl}$.[10] A dynamic light scattering (DLS) study of the slurry demonstrated that the vesicle $\mathbf{5}_{vscl}$ having an average diameter of 550 nm was formed [Fig. 3(b)].

In order to determine the morphologies of bilayer vesicles of $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$, we performed atomic force microscopy (AFM), transmission electron microscopy (TEM) and scanning electron microscopy (SEM) analyses. The samples for AFM, TEM and SEM studies were prepared by dropping the suspensions of $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ in water onto a freshly cleaved mica surface and a copper grid covered with a carbon membrane and a silicon wafer, respectively, followed by drying under ambient conditions. The spherical morphologies of $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ were confirmed by AFM and SEM images [Fig. 4(a) and (b) and Fig. 6(a) and (b), respectively]. TEM observation of vesicular composites $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ showed that these composites were hollow structures and the thicknesses of both the vesicle membranes were observed to be *ca.* 6–7 nm [Fig. 5(a) and (b)]. These data are consistent with those of the bilayer membranous structures of **4** and **5** each having both monomer lengths of *ca.* 2.8 nm in their structures.[11]

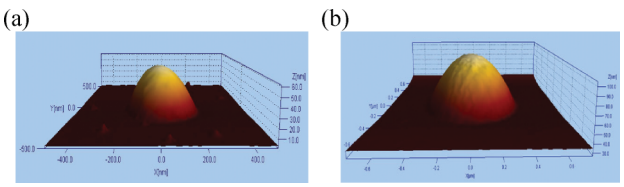


Fig. 4 AFM Images of (a) **4** and (b) **5**.

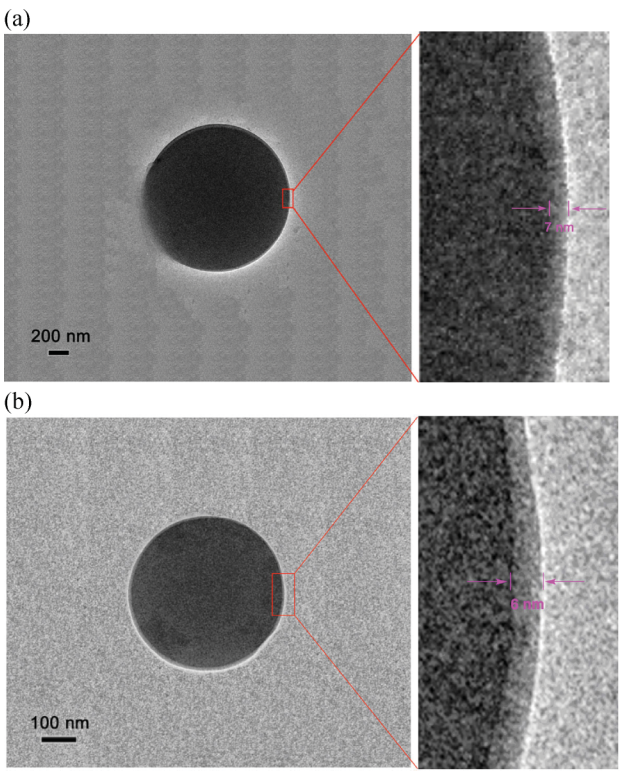


Fig. 5 TEM Images of (a) **4** and (b) **5**.

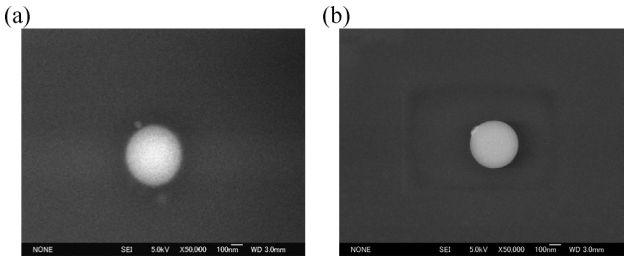


Fig. 6 SEM Images of (a) **4** and (b) **5**.

The incorporation of the fluorescent reagent, fluorescein, into $\mathbf{4}_{vscl}$ revealed a hollow structure with an inner hydrophobic region in the exterior membrane.[10b] Thus, when the isolated $\mathbf{4}_{vscl}$ was exposed to fluorescein under aqueous conditions, the fluorescent vesicles, $\mathbf{4}_{vscl}$/fluorescein, were obtained [Fig. 7(a) and 8(a)]. A similar hollow structure of $\mathbf{5}_{vscl}$ was also observed microscopically with the same fluorescence reagent [Fig. 7(b) and 8(b)].

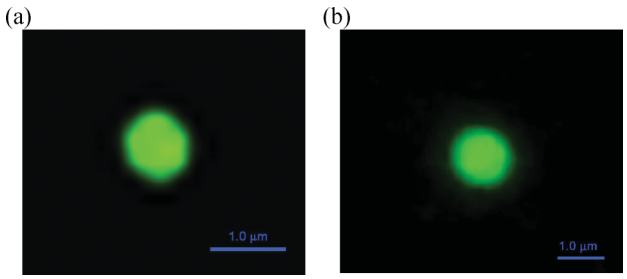


Fig. 7 Fluorescence microscopic images of (a) **4**/Fluorescein and (b) **5**/.

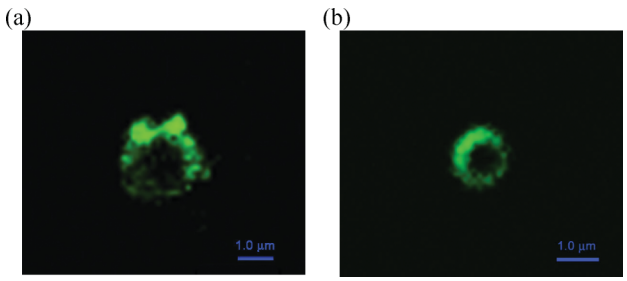


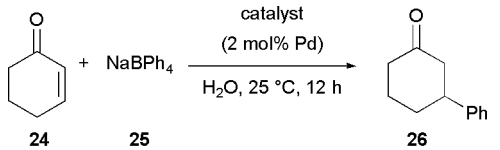
Fig. 8 CLSM images of (a) **4**/Fluorescein and (b) **5**/Fluorescein.

These experiments demonstrated that the structure of the vesicle $\mathbf{4}_{vscl}$ was similar to that of $\mathbf{5}_{vscl}$. Therefore, the inversion of the positions of hydrophobic and hydrophilic groups on the pincer backbone did not strongly influence vesicle formation *via* self-assembly of **4** and **5**.

Miyaura–Michael Reaction in Water

With the desired vesicles $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ in hand, we next explored their catalytic potential for the Miyaura–Michael reaction[9] of 2-cyclohexene-1-one (**24**) with sodium tetraphenylborate (**25**; Table 1). The vesicle $\mathbf{4}_{vscl}$ (2 mol% Pd) promoted the Miyaura–Michael reaction of **24** with **25** (1.5 equiv) in water to give the desired arylated product **26** in 19% yield in 12 h with >99% reaction selectivity (entry 1), whereas monomer **4** afforded only a 5% yield of **26** with much lower selectivity (entry 2). Thus, only a slight promotion of the Miyaura–Michael reaction in water was

Table 1 Miyaura–Michael Reaction of 2-Cyclohexene-1-one (**24**) with Sodium Tetraphenyl borate (**25**)



entry	catalyst	conv.,%[a]	yield,%[a]	selectivity,%[a]
1	$\mathbf{4}_{vscl}$	19	19	>99
2	**4**	21	5	24
3	$\mathbf{5}_{vscl}$	85	83	98
4	**5**	23	7	30

[a] Determined by ^{1}H NMR analysis using an internal standard ($Cl_2CHCHCl_2$).

observed by the self-assembling of **4**. The reaction of **24** with **25** proceeded in the presence of vesicle $\mathbf{5}_{vscl}$ to provide **26** in 83% yield with 98% reaction selectivity (entry 3). In contrast, only a 7% yield of the arylated product **26** was obtained when monomer **5** was used as the catalyst (entry 4). Significant acceleration of the Miyaura–Michael reaction in water was observed by the formation of vesicles. Therefore, the construction of self-assembled vesicles is required for the efficient catalysis of the Miyaura–Michael reaction in water. In addition, the catalytic activity of the vesicle $\mathbf{5}_{vscl}$ bearing hydrophilic tri(ethylene glycol) chains close to the palladium center is higher than that of the vesicle $\mathbf{4}_{vscl}$ bearing hydrophobic dodecyl chains close to the palladium center (entries 1 and 3).

Conclusions

Two amphiphilic pincer palladium complexes bearing hydrophobic or hydrophilic side chains, which self-assembled in aqueous media to provide bilayer vesicles, were designed and prepared. The catalytic performances of the obtained vesicles $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ are superior to that of the monomeric complexes **4** and **5** for the Miyaura–Michael reaction in water. In this reaction, the position of hydrophilic and hydrophobic groups on the pincer backbone is critical. Detailed catalytic abilities of the vesicles $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$, in particular in an aqueous reaction medium, are being examined for various palladium catalyses in our laboratory and will be reported in due course.

Experimental section

General

When manipulations were performed under a nitrogen atmosphere, nitrogen gas was dried by passage through P_2O_5. Commercially available chemicals (purchased from Aldrich, TCI, Kanto, Wako, Nacalai and AlfaAesar) are used without further purification unless otherwise noted. NMR spectra were recorded on a JEOL JNM-A500 spectrometer (500 MHz for ^{1}H, 125 MHz for ^{13}C, 202 MHz for ^{31}P). Chemical shifts are reported in δ (ppm) referenced to an internal tetramethylsilane standard for ^{1}H NMR. Chemical shifts of ^{13}C NMR are given related to $CDCl_3$ as an internal standard (δ 77.0). The ^{31}P NMR data are reported relative to external 85% H_3PO_4. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded in $CDCl_3$ at 25 °C. EI-TOF-MS analysis was carried out in a JEOL JMS-T100GC. ESI mass spectra were recorded on a JEOL JMS-T100LC spectrometer. FAB mass spectra were recorded on a JEOL JMS-777V spectrometer; *meta*-nitrobenzyl alcohol was used as a matrix. MALDI mass spectra were recorded on an Applied Biosystems Voyager DE-STR spectrometer; dithranol was used as a matrix. Elemental analyses were performed on Yanaco CHN Corder MT-6. Melting points were determined using a Yanaco micro melting point apparatus MP-J3 and are uncorrected. IR spectra were obtained using a JASCO FT/IR-460plus spectrometer in ATR mode. Dynamic light scatterings (DLS) were observed on an Ohtsuka electronics Co. DLS-6100P system using a He–Ne 10 mW 632.8 nm laser. Transmission electron microscopy (TEM) images were obtained using JEOL JEM-2100F. Scanning electron microscopy (SEM) images were obtained using JEOL JSM-6700F. Atomic force microscopy (AFM) observations were performed using Agilent Technologies Pico-Scan2500 in conventional tapping mode under air. Fluorescence microscopy images were obtained using a Keyence BZ-8000 with a ×60 oil immersion objective lens. Confocal laser scanning microscopy (CLSM) images were obtained using a Nikon A1R with a ×100 oil immersion objective lens. Millipore water was obtained from a Millipore Milli-Q Academic A10 purification unit. $Pd_2(dba)_3{\cdot}CHCl_3$,[12] 1,3-benzenedicarboxylic acid-2-hydroxy-4,6-dimethyl-1,3-dimethyl ester (**10**)[13] and [2-[2-(2-methoxyethoxy)ethoxy]ethoxy] *p*-toluenesulfonate[14] were prepared by literature methods. A theoretical calculation was carried out using the Gaussian 03 program[15] with RHF method. The geometry of the pincer complexes **4** and **5** were optimized by using a STO-3G basis set.

Preparations

4,6-Dimethyl-2-methoxymethoxyisophthalic acid dimethyl ester (11). Under a nitrogen atmosphere, sodium hydride (5.0 g, 125 mmol, 60% in oil) was slowly added to a solution of 1,3-benzenedicarboxylic acid-2-hydroxy-4,6-dimethyl-1,3-dimethyl ester (**10**) (20.0 g, 83.9 mmol) in anhydrous tetrahydrofuran (600 mL) at 0 °C. After stirring at 0 °C for 0.5 h, chloromethyl methyl ether (12.8 mL, 169 mmol) was added to the resulting mixture, and then the reaction mixture was allowed to warm to 25 °C. The reaction mixture was stirred at 25 °C for 3 h, and quenched with saturated ammonium chloride aqueous solution (200 mL) at 0 °C. The resulting mixture was exctracted with ethyl acetate (200 mL, 3 times). The combined organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The crude product was chromatographed on silica gel (eluent: 10–30% AcOEt/n-hexane) to give **11** (17.3 g, 61.3 mmol, 73% yield) as white powder. Mp: 57.5–58.0 °C; ^{1}H NMR ($CDCl_3$, 500 MHz) δ 6.86 (s, 1H, Ar*H*), 4.99 (s, 2H, -OCH_2OCH_3), 3.90 (s, 6H, -CO_2CH_3), 3.47 (s, 3H, -OCH$_2$OCH_3), 2.29 (s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 167.6 (-*C*O_2CH$_3$), 151.9 (Ar*C* attached to OCH$_2$OCH$_3$), 138.2 (Ar*C* attached to CH_3), 127.9 (Ar*C* attached to H), 126.5 (Ar*C* attached to CO_2CH_3), 101.2 (-O*C*H$_2$OCH$_3$), 57.3 (-OCH$_2$O*C*H$_3$), 52.0 (-CO_2*C*H$_3$), 19.5 (*C*H$_3$ attached to Ar); IR (ATR) 3853, 3734, 3649, 3628, 3432, 2994, 2964, 2929, 2831, 2070, 1908, 1721 (C=O), 1685, 1635, 1606, 1561, 1475, 1438, 1391, 1380, 1289, 1257, 1201, 1159, 1110, 1092, 1030, 972, 960, 926, 901, 874, 862, 809, 797, 770, 760, 656, 637, 629, 569 cm^{-1};

EI-TOF-MS *m/z* 282 ([M]$^+$), 251 ([M–OMe]$^+$), 206 ([M–OMe–MOM]$^+$), 191 ([M–OMe–MOM–Me]$^+$), 175 ([M–2OMe–MOM]$^+$), 148 ([M–2OOMe–MOM]$^+$); Anal. Calcd for $C_{14}H_{18}O_6$: C, 59.57: H, 6.43%. Found: C, 59.23: H, 6.34%.

4,6-Bis(bromomethyl)-2-methoxymethoxy isophthalic acid dimethyl ester (12). Under a nitrogen atmosphere, a mixture of **11** (7.0 g, 24.8 mmol), *N*-bromosccinimide (9.7 g, 54.6 mmol) and AIBN (0.41 g, 2.5 mmol) in anhydrous dichloromethane (250 mL) was irradiated with a 100 W high pressure Hg lamp (λ = 365 nm, Riko-kagaku Co., Lid., UVL-100HA 300P) at 25 °C for 1 h to give a yellow solution. The resulting solution was washed with water (250 mL, 3 times). The combined organic layer was dried over Na_2SO_4 and concentrated in *vacuo* to give a yellow solid. The resulting solid was recrystallized from ethyl acetate (200 mL) to afforded **12** (5.9 g, 13.4 mmol, 54% yield) as white needles. Mp: 141.0–141.5 °C; ^{1}H NMR (CD_2Cl_2, 500 MHz, ref. 5. 30 ppm for CH_2Cl_2 in CD_2Cl_2) δ 7.27 (s, 1H, Ar*H*), 4.96 (s, 2H, -OCH_2OCH$_3$), 4.49 (s, 4H, -CH_2Br), 3.93 (s, 6H, -CO$_2$CH_3), 3.43 (s, 3H, -OCH$_2$OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.0 (-*C*O$_2$CH$_3$), 153.3 (Ar*C* attached to OCH$_2$OCH$_3$), 138.8 (Ar*C* attached to CH$_2$Br), 129.0 (Ar*C* attached to H), 127.8 (Ar*C* attached to CO$_2$CH$_3$), 101.6 (-O*C*H$_2$OCH$_3$), 57.6 (-OCH$_2$OCH$_3$), 52.8 (-CO$_2$*C*H$_3$), 28.9 (-*C*H$_2$Br); IR (ATR) 3034, 3011, 2956, 2884, 2832, 1721 (C═O), 1602, 1567, 1476, 1452, 1434, 1421, 1389, 1308, 1264, 1212, 1201, 1153, 1116, 1041, 1015, 971, 953, 902, 871, 860, 802, 786, 735, 685, 650, 618, 578 cm^{-1}; ESI-TOF-MS *m/z* 463 ([M+Na]$^+$); Anal. Calcd for $C_{14}H_{16}Br_2O_6$: C, 38.21: H, 3.66%. Found: C, 38.47: H, 3.69%.

2-Methoxymethoxy-4,6-bis(2,5,8,11-tetraoxadodecyl)isophthalic acid dimethyl ester (13). Under a nitrogen atmosphere, sodium hydride (0.87 g, 21.6 mmol, 60% in oil) was added to a solution of triehyleneglycohol monomethyl ether (3.5 g, 21.6 mmol) in anhydrous THF (108 mL). After being stirred at 0 °C for 30 min, **12** (4.8 g, 10.8 mmol) was slowly added. The reaction mixture was stirred at 0 °C for 3 h, and quenched with water (5 mL). The resulting mixture was extracted with ethyl acetate (50 mL, 3 times). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was chromatographed on silica gel (eluent: 0–10% MeOH/AcOEt) to give **13** (4.4 g, 7.2 mmol, 67% yield) as colorless oil. ^{1}H NMR (CD_2Cl_2, 500 MHz, ref. 5. 30 ppm for CH_2Cl_2 in CD_2Cl_2) δ 7.25 (s, 1H, Ar*H*), 4.95 (s, 2H, -OCH_2OCH$_3$), 4.55 (s, 4H, ArCH_2O-), 3.85 (s, 6H, -CO$_2$CH_3), 3.58–3.53 (m, 20H, -OC$_2H_4$-), 3.48–3.46 (m, 4H, -OC$_2H_4$-), 3.42 (s, 3H, -OCH$_2$OCH_3), 3.31 (s, 6H, -CH$_2$(OC$_2$H$_4$)$_3$OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 166.8 (-*C*O$_2$CH$_3$), 152.5 (Ar*C* attached to OCH$_2$OCH$_3$), 139.4 (Ar*C* attached to CH$_2$(OC$_2$H$_4$)$_3$OCH$_3$), 127.2 (Ar*C* attached to H), 123.6 (Ar*C* attached to CO$_2$CH$_3$), 101.5 (-O*C*H$_2$OCH$_3$), 71.8 (*C*H$_2$ attached to Ar), 70.7 (-O*C*$_2$H$_4$-), 70.54 (-O*C*$_2$H$_4$-), 70.52 (-O*C*$_2$H$_4$-), 70.44 (-O*C*$_2$H$_4$-), 70.35 (-O*C*$_2$H$_4$-), 69.8 (-O*C*$_2$H$_4$-), 58.9 (-CH$_2$(OC$_2$H$_4$)$_3$O*C*H$_3$), 57.4 (-OCH$_2$O*C*H$_3$), 52.3 (-CO$_2$*C*H$_3$); IR (ATR) 3007, 2873, 1731 (C═O), 1607, 1569, 1541, 1507, 1456, 1430, 1351, 1298, 1246, 1199, 1099 (C–O–C), 1030, 988, 951, 914, 854, 808, 748, 666 cm^{-1}; ESI-TOF-MS *m/z* 629 ([M+Na]$^+$); Anal. Calcd for $C_{28}H_{46}O_{14}\cdot 0.5H_2O$: C, 54.62: H, 7.69%. Found: C, 54.59: H, 7.61%.

2,6-Dihydroxymethyl-3,5-bis(2,5,8,11-tetraoxadodecyl)phenyl methoxymethyl ether (14). Under a nitrogen atmosphere, lithium aluminum hydride (0.69 g, 18.1 mmol) was added to a solution of **13** (4.4 g, 7.3 mmol) in anhydrous THF (300 mL) at 0 °C. The reaction mixture was stirred at 25 °C for 14 h and then cooled to 0 °C. After carefully quenching with water (2.8 mL) and 15% NaOH aqueous solution (0.7 mL), the resulting mixture was filtered through Celite and eluted with ethyl acetate. The filtrate was dried over Na_2SO_4. The obtained solution was concentrated under reduced pressure to give **14** (3.7 g, 6.7 mmol, 93% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.13 (s, 1H, Ar*H*), 5.24 (s, 2H, -OCH_2OCH$_3$), 4.68 (s, 2H, -CH_2OH), 4.67 (s, 2H, -CH_2OH), 4.66 (s, 4H, ArCH_2O-), 3.67–3.62 (m, 23H, -OC$_2H_4$- and -OCH$_2$OCH_3), 3.57–3.52 (m, 4H, -OC$_2H_4$-), 3.36 (s, 6H, -CH$_2$(OC$_2$H$_4$)$_3$OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 156.7 (Ar*C* attached to OCH$_2$OCH$_3$), 137.6 (Ar*C* attached to CH$_2$(OC$_2$H$_4$)$_3$OCH$_3$), 134.3 (Ar*C* attached to CH$_2$OH), 127.0 (Ar*C* attached to H), 101.4 (-O*C*H$_2$OCH$_3$), 72.0 (-*C*H$_2$(OC$_2$H$_4$)$_3$OCH$_3$), 71.8 (-O*C*$_2$H$_4$-), 70.47 (-O*C*$_2$H$_4$-), 70.42 (-O*C*$_2$H$_4$-), 70.3 (-O*C*$_2$H$_4$-), 69.3 (-O*C*$_2$H$_4$-), 58.9 (-CH$_2$(OC$_2$H$_4$)$_3$O*C*H$_3$), 57.5 (-OCH$_2$O*C*H$_3$), 56.4 (-*C*H$_2$OH) (One of the CH$_2$ signals of ethylene glycol group might be overlapped with the other peaks of carbon); IR (ATR) 3484 (O–H), 2917, 1469, 1383, 1351, 1286, 1236, 1200, 1090 (C–O–C), 1017, 889, 630 cm^{-1}; ESI-TOF-MS *m/z* 573 ([M+Na]$^+$); Anal. Calcd for $C_{26}H_{46}O_{12}\cdot 0.67H_2O$: C, 55.50: H, 8.48%. Found: C, 55.28: H, 8.56%.

2,6-Diformyl-3,5-bis(2,5,8,11-tetraoxadodecyl)phenyl methoxymethyl ether (15). Under a nitrogen atmosphere, oxalyl chloride (2.8 mL, 32.6 mmol) was added to a solution of anhydrous DMSO (4.7 mL, 66.2 mmol) in anhydrous dichloromethane (100 mL) at −78 °C. After being stirred at −78 °C for 5 min, a solution of **14** (3.6 g, 6.5 mmol) in anhydrous dichloromethane (100 mL) was added, and the reaction mixture was stirred for 30 min at −78 °C. Then, triethylamine (13.5 mL, 97.4 mmol) was added, and allowing the solution to warm 25 °C. After being stirred at 25 °C for 30 min, the reaction mixture was quenched with water (200 mL). The resulting mixture was extracted with CH_2Cl_2 (50 mL, 3 times). The combined organic layer was dried over Na_2SO_4 and concentrated in *vacuo*. The crude product was chromatographed on silica gel (eluent: 3% MeOH/AcOEt) to give **15** (3.3 g, 6.0 mmol, 92% yield) as yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.46 (s, 2H, C*H*O), 7.94 (s, 1H, Ar*H*), 5.16 (s, 2H, -OCH_2OCH$_3$), 4.96 (s, 4H, ArCH_2O-), 3.74–3.54 (m, 27H, -C$_2H_4$O- and -OCH$_2$OCH_3), 3.37 (s, 6H, -CH$_2$O(C$_2$H$_4$O)$_3$CH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 191.0 (-*C*HO), 164.4 (Ar*C* attached to OCH$_2$OCH$_3$), 148.3 (Ar*C* attached to CH$_2$(OC$_2$H$_4$)$_3$OCH$_3$), 125.9 (Ar*C* attached to CHO), 122.2 (Ar*C* attached to H), 103.4 (-O*C*H$_2$OCH$_3$), 71.9 (*C*H$_2$O attached to Ar), 70.7 (-O*C*$_2$H$_4$-), 70.62 (-O*C*$_2$H$_4$-), 70.58 (-O*C*$_2$H$_4$-), 70.47 (-O*C*$_2$H$_4$-), 70.43 (-O*C*$_2$H$_4$-), 58.9 (-CH$_2$(OC$_2$H$_4$)$_3$O*C*H$_3$), 58.3 (-OCH$_2$O*C*H$_3$), (One of the CH$_2$ signals of ethylene glycol group might be overlapped with the other peaks of carbon); IR (ATR) 2873, 1730, 1683 (C═O), 1595, 1555, 1457, 1370, 1350, 1287, 1248, 1224, 1201, 1095 (O–C–O), 1029, 981, 898, 850, 794, 665 cm^{-1}; ESI-TOF-MS *m/z* 569 ([M+Na]$^+$); Anal. Calcd for $C_{26}H_{42}O_{12}\cdot 1.5H_2O$: C, 54.44: H, 7.91%. Found: C, 54.32: H, 7.55%.

2,6-Diformyl-3,5-bis(2,5,8,11-tetraoxadodecyl)phenol (16). Under a nitrogen atmosphere, a solution of hydrogen chloride

in methanol (10% HCl, 3 mL) was added to a solution of **15** (3.3 g, 6.0 mmol) in methanol (10 mL) at 25 °C. After being stirred at 25 °C for 2 h, the solvent was removed under reduced pressure to give **16** (3.0 g, 6.0 mmol, 99% yield) as yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 12.82 (s, 1H, -O*H*), 10.52 (s, 2H, -C*H*O), 7.37 (s, 1H, Ar*H*), 4.91 (s, 4H, ArCH_2O-), 3.73–3.64 (m, 20H, -C_2H_4O-), 3.56–3.54 (m, 4H, -C_2H_4O-), 3.37 (s, 6H, -OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) 193.4 (-*C*HO), 166.8 (Ar*C* attached to OH), 149.5 (Ar*C* attached to $CH_2(OC_2H_4)_3OCH_3$), 119.0 (Ar*C* attached to CHO), 118.6 (Ar*C* attached to H), 71.9 (-*C*H_2O-), 71.0 (-C_2H_4O-), 70.67 (-C_2H_4O-), 70.63 (-C_2H_4O-), 70.55 (-C_2H_4O-), 70.47 (-C_2H_4O-), 70.3 (-C_2H_4O-), 59.0 (-O*C*H_3); IR (ATR) 2872, 1682 (CHO), 1641, 1619, 1558, 1489, 1455, 1415, 1387, 1349, 1321, 1288, 1228, 1200, 1098 (O–C–O), 1031, 941, 889, 850, 804, 718, 671, 638, 598 cm^{-1}; ESI-TOF-MS *m*/*z* 525 ([M+Na]$^+$); Anal. Calcd for $C_{24}H_{38}O_{11}\cdot H_2O$: C, 55.37: H, 7.74%. Found: C, 55.53: H, 7.47%.

2,6-Diformyl-3,5-bis(2,5,8,11-tetraoxadodecyl)phenyl trifluoromethanesulfonate (17). Undrer a nitrogen atmosphere, to a solution of **16** (60 mg, 0.12 mmol) in pyridine (1 mL) and dichloromethane (2 mL) was added trifluoromethanesulfonic anhydride (0.20 mL, 1.2 mmol) dropwise at −10 °C for 3 min. After being stirred for 1 h at −10 °C, the reaction mixture was quenched with 10% hydrochloric acid (1 mL) and the resulting mixture was extracted with dichloromethane (5 mL, 3 times). The combined organic layer was dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was chromatographed on silica gel (eluent: 0–3% MeOH/AcOEt) to give **17** (41 mg, 0.050 mmol, 41% yield) as colorless oil. ^{1}H NMR ($CDCl_3$, 500 MHz) δ 10.39 (s, 2H, C*H*O), 8.20 (s, 1H, Ar*H*), 4.98 (s, 4H, ArCH_2O-), 3.76–3.64 (m, 20H, -OC$_2H_4$-), 3.55–3.53 (m, 4H, -OC$_2H_4$-), 3.37 (s, 6H, -OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.4 (*C*HO), 150.4 (Ar*C* attached to OTf), 148.6 (Ar*C* attached to $CH_2(OC_2H_4)_3OCH_3$), 126.8 (Ar*C* attached to CHO), 125.8 (Ar*C* attached to H), 118.5 (q, J_{C-F} = 320 Hz, SO_2CF_3), 71.9 (-*C*$H_2(OC_2H_4)_3OCH_3$), 70.68 (-C_2H_4O-), 70.62 (-C_2H_4O-), 70.60 (-C_2H_4O-), 70.53 (-C_2H_4O-), 70.46 (-C_2H_4O-), 70.43 (-C_2H_4O-), 59.0 (O*C*H_3); IR (ATR) 2874, 1698 (C═O), 1607, 1547, 1467, 1431, 1404, 1371, 1350 (S═O), 1294, 1209 (CF_3), 1101 (S═O), 1028, 994, 950, 906, 880, 850, 808, 763, 643, 602, 577 cm^{-1}; ESI-TOF-MS *m*/*z* 657 ([M+Na]$^+$); Anal. Calcd for $C_{25}H_{37}F_3O_{13}S\cdot 0.5H_2O$: C, 46.65: H, 5.95%. Found: C, 46.76: H, 5.89%.

***trans*-[2,6-Diformyl-3,5-bis(2,5,8,11-tetraoxadodecyl)phenyl]-chloro bis(triphenylphosphine)palladium (6). 17** (0.18 g, 0.29 mmol), $Pd_2(dba)_3\cdot CHCl_3$ (0.15 g, 0.15 mmol) and triphenylphosphine (0.15 g, 0.58 mmol) were dissolved in 2 mL of anhydrous dichloromethane under a nitrogen atmosphere, and the solution was stirred at 25 °C for 20 h. After removal of the solvent, the residue and lithium chloride (0.12 g, 2.9 mmol) were dissolved in a mixture of acetone (1.8 mL) and water (0.2 mL). The reaction mixture was stirred at 25 °C for 20 h and then concentrated under reduced pressure. The residue was dissolved in chloroform (10 mL), which was washed with water (5 mL, 2 times), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was chromatographed on silica gel (eluent: 0–5% MeOH/AcOEt) to give **10** (0.30 g, 0.26 mmol, 89% yield) as yellow oil. ^{1}H NMR (CD_2Cl_2, 500 MHz, ref. 5. 30 ppm for CH_2Cl_2 in CD_2Cl_2) δ 10.96 (s, 2H, C*H*O), 7.46–7.49 (m, 12H, *o*-Ph*H* of PPh_3), 7.35 (t, 6H, *J* = 7.3 Hz, *p*-Ph*H* of PPh_3), 7.26 (t, 12H, *J* = 7.3 Hz, *m*-Ph*H* of PPh_3), 7.07 (s, 1H, Ar*H*), 4.30 (s, 4H, ArCH_2O-), 3.59–3.55 (m, 16H, -OC$_2H_4$-), 3.50–3.46 (m, 8H, -OC$_2H_4$-), 3.30 (s, 6H, -OCH_3); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 195.8 (*C*HO), 181.4 (Ar*C* attached to Pd), 146.5 (Ar*C* attached to $CH_2(OC_2H_4)_3OCH_3$), 136.2 (Ar*C* attached to CHO), 134.1 (virtual t, *J* = 6.2 Hz, *m*-Ph*C* of PPh_3), 130.3 (*p*-Ph*C* of PPh_3), 129.7 (virtual t, *J* = 23.6 Hz, *ipso*-Ph*C* of PPh_3), 128.1 (virtual t, *J* = 5.2 Hz, *o*-PhC of PPh_3), 122.0 (Ar*C* attached to H), 71.9 (-*C*$H_2(OC_2H_4)_3OCH_3$), 71.0 (-C_2H_4O-), 70.6 (-C_2H_4O-), 70.5 (-C_2H_4O-), 70.4 (-C_2H_4O-), 70.2 (-C_2H_4O-), 58.9 (O*C*H_3), (One of the CH_2 signals of ethylene glycol group might be overlapped with the other peaks of carbon); ^{31}P NMR ($CDCl_3$, 202 MHz) δ 22.2; IR (ATR) 3055, 2872, 2706, 1969, 1828, 1675 (C═O), 1570, 1534, 1481, 1435, 1378, 1345, 1273, 1248, 1195, 1093 (O–C–O), 1028, 998, 940, 883, 849, 791, 745, 721, 692, 636, 618 cm^{-1}; ESI-TOF-MS *m*/*z* 1175 ([M+Na]$^+$), 1115 ([M–Cl]$^+$), 913 ([M–PPh_3+Na]$^+$), 853 [M–Cl–PPh_3]$^+$), 651 ([M–2PPh_3+Na]$^+$), 591 ([M–Cl–2PPh_3]$^+$); Anal. Calcd for $C_{60}H_{67}ClO_{10}P_2Pd$: C, 62.56: H, 5.86%. Found: C, 62.33: H, 5.87%.

3,5-Dibromo-(tetrahydro-2*H*-pyran-2-yloxy)benzene (19). *p*-Toluenesulfonic acid (240 mg, 1.3 mmol) was added to a solution of 3,5-dibromobenzene (**18**) (10.4 g, 41.3 mmol) and 3,4-dihydro-(2*H*)-pyran (18.7 mL, 206 mmol) in anhydrous dichloromethane (100 mL) at 0 °C. The solution was stirred for 3 h at 0 °C and subsequently for 30 min at 25 °C. The reaction mixture was poured into saturated aqueous sodium bicarbonate (50 mL). The organic layer was separated, washed with saturated aqueous sodium bicarbonate (50 mL, 2 times), water (50 mL) and brine (50 mL), and then dried over $MgSO_4$. After removal of the solvent, the resulting mixture was silica gel (eluent: 5% AcOEt/n-hexane) to give (33.1 mmol, 80%). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.27 (t, *J* = 1.8 Hz, 1H, Ar*H*), 7.16 (d, *J* = 1.8 Hz, 2H, Ar*H*), 5.38 (t, *J* = 3.0 Hz, 1H, -OC*H*O-), 3.82 (td, *J* = 3.0, 10.9 Hz, 1H, CH_2), 3.60–3.64 (m, 1H, CH_2), 1.91–1.97 (m, 1H, CH_2), 1.82–1.85 (m, 2H, CH_2), 1.57–1.74 (m, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.2 (Ar*C* attached to O), 127.1 (Ar*C*), 122.8 (Ar*C* attached to Br), 118.7 (Ar*C*), 96.5 (*C*H), 61.9 (*C*H_2 attached to O), 30.0 (*C*H_2), 24.9 (*C*H_2), 18.3 (*C*H_2); IR (ATR) 2942, 1582, 1556, 1433, 1420, 1389, 1373, 1355, 1292, 1248 (C–O–C), 1228 (C–O–C), 1200 (C–O–C), 1183, 1118 (C–O–C), 1104 (C–O–C), 1073, 1050, 1036 (C–O–C), 1021 (C–O–C), 988, 955, 921, 893, 872, 833, 817, 744, 692, 668, 629, 571 cm^{-1}; FAB-MS *m*/*z* 336 ([M]$^+$); Anal. Calcd for $C_{11}H_{12}Br_2O_2$: C, 39.32: H, 3.60%. Found: C, 39.20: H, 3.62%.

3,5-Didodecyl(tetrahydro-2*H*-pyran-2-yloxy)benzene (20). To a solution of **19** (6.0 g, 17.8 mmol) and dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) (726 mg, 0.90 mmol) in 40 mL of anhydrous THF was added dodecylmagnesium bromide (2 M in diethyl ether, 36 mL, 72 mmol) under a nitrogen atmosphere. The reaction mixture was refluxed at 75 °C for 72 h and then cooled to 25 °C. After quenching with a small amount of methanol, the resulting mixture was filtrated through Celite and eluted with n-hexane and *tert*-butyl methyl ether. Upon removal of the solvent, the resulting mixture was chromatographed on silica gel (eluent: 1–5% AcOEt/n-hexane) to give **20** (6.51 g, 12.6 mmol, 71%) as colorless oil. ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.69 (br s, 2H, Ar*H*),

6.62 (br s, 1H, Ar*H*), 5.40 (t, *J* = 3.0 Hz, 1H, -OC*H*O-), 3.91–3.96 (m, 1H, CH_2), 3.58–3.62 (m, 1H, CH_2), 2.53 (t, *J* = 7.9 Hz, 4H, -CH_2(CH$_2$)$_{10}$CH$_3$), 1.96–2.03 (m, 1H, CH_2), 1.82–1.87 (m, 2H, CH_2), 1.62–1.71 (m, 2H, CH_2), 1.55–1.59 (m, 4H, CH$_2$), 1.25–1.29 (m, 36H, -CH$_2$(CH_2)$_{10}$CH$_3$), 0.88 (t, *J* = 7.0 Hz, 6H, -CH$_2$(CH$_2$)$_{10}$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$) δ 157.0 (Ar*C* attached to O), 144.1 (Ar*C* attached to C$_{12}$H$_{25}$), 122.0 (Ar*C*), 113.7 (Ar*C*), 96.3 (*C*H), 62.0 (*C*H$_2$ attached to O), 36.0 (*C*H$_2$ attached to Ar), 31.9 (*C*H$_2$), 31.4 (*C*H$_2$), 30.5 (*C*H$_2$), 29.68 (*C*H$_2$), 29.66 (*C*H$_2$), 29.62 (*C*H$_2$), 29.5 (*C*H$_2$), 29.4 (*C*H$_2$), 29.3 (*C*H$_2$), 25.3 (*C*H$_2$), 22.7 (*C*H$_2$), 18.8 (*C*H$_2$), 14.1 (*C*H$_3$) (One of the CH$_2$ signals of dodecyl group might be overlapped with the other peaks of carbon.); IR (ATR) 2921, 2852, 1455, 1284, 1202 (C–O–C), 1152, 1125 (C–O–C), 1106 (C–O–C), 1078, 1038 (C–O–C), 1021 (C–O–C), 990, 954, 906, 871, 855, 720, 700 cm^{-1}; FAB-MS *m*/*z* 514 ([M]$^+$); Anal. Calcd for C$_{35}$H$_{62}$O$_2$: C, 81.65: H, 12.14%. Found: C, 81.46: H, 12.15%.

3,5-Didodecylphenol (21). *p*-Toluenesulfonic acid (190 mg, 1.0 mmol) was added to a solution of **20** (10.59 g, 20.6 mmol) in THF (20 mL) and methanol (20 mL) at 25 °C and the reaction mixture was stirred for 1 h at 25 °C, quenched with water and extracted with *tert*-butyl methyl ether (20 mL, 3 times). The organic layer was washed with water (20 mL) and brine (20 mL), and dried over Na$_2$SO$_4$. The organic layer was concentrated under reduced pressure to give **21** (8.84 g, 20.5 mmol, 99%) as colorless powder. Mp. 33–34 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 6.57 (br s, 1H, Ar*H*), 6.46 (br s, 2H, Ar*H*), 4.48 (br s, 1H, O*H*), 2.51 (t, *J* = 7.9 Hz, 4H, -CH_2(CH$_2$)$_{10}$CH$_3$), 1.56–1.59 (m, 4H, CH_2), 1.25–1.29 (m, 36H, -CH$_2$(CH_2)$_{10}$CH$_3$), 0.88 (t, *J* = 7.0 Hz, 6H, -CH$_2$(CH$_2$)$_{10}$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$) δ 155.3 (Ar*C* attached to O), 144.6 (Ar*C* attached to C$_{12}$H$_{25}$), 121.2 (Ar*C*), 112.4 (Ar*C*), 35.8 (*C*H$_2$ attached to Ar), 31.9 (*C*H$_2$), 31.3 (*C*H$_2$), 29.68 (*C*H$_2$), 29.64 (*C*H$_2$), 29.60 (*C*H$_2$), 29.5 (*C*H$_2$), 29.3 (*C*H$_2$), 22.6 (*C*H$_2$), 14.1 (*C*H$_3$) (Two of the CH$_2$ signals of dodecyl group might be overlapped with the other peaks of carbon.); IR (ATR) 3271 (O–H), 2952, 2913, 2848, 1595, 1469, 1450, 1305, 1291, 1277, 1254, 1149 (C–O), 1122, 1022, 991, 959, 854, 718, 696, 642 cm^{-1}; FAB-MS *m*/*z* 431 ([M+1]$^+$); Anal. Calcd for C$_{30}$H$_{54}$O: C, 83.65: H, 12.64%. Found: C, 83.43: H, 12.59%.

3,5-Didodecyl-2,6-diformylphenol (22). **21** (4.30 g, 10.0 mmol) and hexamethylenetetramine (2.80 g, 20 mmol) were dissolved in anhydrous trifluoroacetic acid (20 mL) under a nitrogen atmosphere, and the resulting solution was refluxed at 100 °C for 24 h. To the reaction mixture was added 4 N HCl (20 mL) and the mixture was stirred for 24 h at 100 °C. After being cooled to 25 °C, the mixture was extracted with CH$_2$Cl$_2$ (30 mL, 3 times). The combined organic layer was dried over MgSO$_4$, and concentrated in *vacuo*. The resulting crude mixture was chromatographed on silica gel (eluent: 30–50% CHCl$_3$/n-hexane) to give **22** (648 mg, 1.3 mmol, 13%) as yellow powder. Mp. 30.5–31.0 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 12.82 (s, 1H, -O*H*), 10.43 (br s, 2H, -C*H*O), 6.60 (s, 1H, Ar*H*), 2.93 (t, *J* = 7.9 Hz, 4H, -CH_2(CH$_2$)$_{10}$CH$_3$), 1.56–1.62 (m, 4H, CH_2), 1.25–1.39 (m, 36H, -CH$_2$(CH_2)$_{10}$CH$_3$), 0.88 (t, *J* = 6.7 Hz, 6H, -CH$_2$(CH$_2$)$_{10}$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$) δ 192.2 (br, *C*HO), 167.6 (br, Ar*C* attached to C$_{12}$H$_{25}$), 154.6 (Ar*C* attached to O), 124.0 (Ar*C*), 118.4 (br, Ar*C* attached to CHO), 33.3 (*C*H$_2$ attached to Ar), 31.89 (*C*H$_2$), 31.84 (*C*H$_2$), 29.68 (*C*H$_2$), 29.63 (*C*H$_2$), 29.61 (*C*H$_2$), 29.39 (*C*H$_2$), 29.32 (*C*H$_2$), 22.6 (*C*H$_2$), 14.0 (*C*H$_3$) (Two of the CH$_2$ carbons of dodecyl group might be overlapped with the other peaks of carbon.); IR (ATR) 2921, 2852, 1687 (CHO), 1638 (CHO), 1615, 1552, 1487, 1465, 1420, 1385, 1348, 1296, 1233, 1179, 1115, 1085 cm^{-1}; FAB-MS *m*/*z* 487 ([M+1]$^+$); Anal. Calcd for C$_{32}$H$_{54}$O$_3$: C, 78.96: H, 11.18%. Found: C, 78.62: H, 11.18%.

3,5-Didodecyl-2,6-diformylphenyl trifluoromethanesulfonate (23). To a solution of **22** (105 mg, 0.215 mmol) in pyridine (2 mL) and anhydrous dichloromethane (2 mL) under a nitrogen atmosphere was added trifluoromethanesulfonic anhydride (0.36 mL, 2.15 mmol) dropwise at −10 °C for 3 min, and the resulting mixture was stirred for 1.5 h at −10 to 0 °C. The reaction mixture was quenched with 1.5 N HCl (10 mL) and extracted with dichloromethane (20 mL, 3 times). The combined organic layer was dried over Na$_2$SO$_4$. After removal of the solvent, the resulting mixture was chromatographed on silica gel (eluent: 30–50% CHCl$_3$/n-hexane) to give **23** (56.8 mg, 0.092 mmol, 43%) as pale yellow oil. ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.39 (s, 2H, C*H*O), 7.22 (s, 1H, Ar*H*), 3.00 (t, *J* = 7.6 Hz, 4H, -CH_2(CH$_2$)$_{10}$CH$_3$), 1.55–1.61 (m, 4H, CH_2), 1.26–1.38 (m, 36H, -CH$_2$(CH_2)$_{10}$CH$_3$), 0.88 (t, *J* = 6.7 Hz, 6H, -CH$_2$(CH$_2$)$_{10}$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$) δ 187.4 (*C*HO), 152.4 (Ar*C* attached to C$_{12}$H$_{25}$), 151.6 (Ar*C* attached to CHO), 133.9 (Ar*C*), 125.9 (Ar*C* attached to CHO), 118.5 (q, J_{C-F} = 320.6 Hz, SO$_2$*C*F$_3$), 33.8 (*C*H$_2$ attached to Ar), 31.9 (*C*H$_2$), 31.5 (*C*H$_2$), 29.68 (*C*H$_2$), 29.66 (*C*H$_2$), 29.64 (*C*H$_2$), 29.61 (*C*H$_2$), 29.5 (*C*H$_2$), 29.3 (*C*H$_2$), 22.7 (*C*H$_2$), 14.1 (*C*H$_3$) (One of the CH$_2$ signals of dodecyl group might be overlapped with the other peaks of carbon.); IR (ATR) 2922, 2853, 1701 (CHO), 1604, 1539, 1465, 1431, 1406, 1375, 1213 (S═O), 1134 (S═O),1070, 964, 891, 810, 761, 722, 673, 601 cm^{-1}; ESI-MS *m*/*z* 619 ([M+1]$^+$); Anal. Calcd for C$_{33}$H$_{53}$F$_3$O$_5$S: C, 64.05: H, 8.63: S, 5.18%. Found: C, 64.09: H, 8.69: S, 5.24%.

***trans*-(3,5-Didodecyl-2,6-diformylphenyl)chlorobis(triphenylphosphine)palladium (7).** **22** (747 mg, 1.21 mmol), Pd$_2$(dba)$_3$·CHCl$_3$ (620 mg, 0.60 mmol), and triphenylphosphine (635 mg, 2.42 mmol) were dissolved in 15 mL of anhydrous dichloromethane under a nitrogen atmosphere, and the solution was stirred at 25 °C for 39 h. After removal of the solvent, the residue and lithium chloride (513 mg, 12.1 mmol) were suspended in a mixture of acetone (13.5 mL) and water (1.5 mL). The reaction mixture was stirred at room temperature for 24 h and then extracted with chloroform (30 mL, 3 times). The organic layer was dried over Na$_2$SO$_4$ and concentrated in *vacuo*. The residual material was chromatographed on silica gel (eluent: CHCl$_3$) to give **7** (1292 mg, 1.14 mmol, 94%) as yellow powder. Mp. 76–78 °C; ^{1}H NMR (500 MHz, CDCl$_3$) δ 10.91 (s, 2H, C*H*O), 7.47–7.51 (m, 12H, *o*-Ph*H* of PPh$_3$), 7.32 (t, *J* = 7.3 Hz, 6H, *p*-Ph*H* of PPh$_3$), 7.23 (t, *J* = 7.3 Hz, 12H, *m*-Ph*H* of PPh$_3$), 6.21 (s, 1H, Ar*H*), 2.33 (t, *J* = 7.9 Hz, 4H, -CH_2(CH$_2$)$_{10}$CH$_3$), 1.23–1.31 (m, 36H, -CH$_2$(CH_2)$_{10}$CH$_3$), 1.11 (br s, 4H, CH_2), 0.88 (t, *J* = 7.0 Hz, 6H, -CH$_2$(CH$_2$)$_{10}$CH_3); ^{13}C NMR (125 MHz, CDCl$_3$) δ 195.0 (*C*HO), 180.3 (t, J_{C-P} = 4.1 Hz, Ar*C* attached to Pd), 150.6 (Ar*C*), 136.9 (Ar*C* attached to CHO), 135.0 (t, J_{C-P} = 6.2 Hz, *p*-Ph*C* of PPh$_3$), 134.3 (t, J_{C-P} = 6.2 Hz, *m*-Ph*C* of PPh$_3$), 130.14 (t, J_{C-P} = 22.8 Hz, *ipso*-Ph*C* of PPh$_3$), 130.12 (Ar*C* attached to C$_{12}$H$_{25}$), 128.0 (virtual t, J_{C-P} = 5.2 Hz, *o*-Ph*C* of PPh$_3$), 33.7 (*C*H$_2$ attached to Ar), 31.9 (*C*H$_2$), 31.6 (*C*H$_2$), 29.9 (*C*H$_2$), 29.69 (*C*H$_2$), 29.67 (*C*H$_2$), 29.65 (*C*H$_2$), 29.4 (*C*H$_2$), 29.3 (*C*H$_2$), 22.7 (*C*H$_2$), 14.1 (*C*H$_3$) (One of

the CH_2 signals of dodecyl group might be overlapped with the other peaks of carbon.); ^{31}P NMR (202 MHz, $CDCl_3$) δ 22.0; IR (ATR) 2922, 2851, 1681 (CHO), 1567, 1519, 1481, 1465, 1434, 1414, 1186, 1094, 1072, 998, 742, 721, 692 cm^{-1}; ESI-TOF-MS *m/z* 1099 ([M–Cl]$^+$); Anal. Calcd for $C_{68}H_{83}ClO_2P_2Pd$: C, 71.88: H, 7.36%. Found: C, 71.64: H, 7.35%.

4-(2,5,8,11-tetraoxadodecyl)aniline (9). 4-Aminobenzylalcohol (2.0 g, 16.2 mmol) and sodium hydride (972 mg, 60% in oil, 24.3 mmol) were suspended in anhydrous THF (30 mL) under a nitrogen atmosphere. After the suspension was stirred at 25 °C for 1.5 h, a anhydrous THF solution (5 mL) of [2-[2-(2-methoxyethoxy)ethoxy]ethoxy] *p*-toluenesulfonate (6.2 g, 19.5 mmol) was added at 25 °C, and the resulting mixture was refluxed for 24 h. After the mixture was cooled to 25 °C, a small amount of water was added to the reaction mixture, which was extracted with dichloromethane (30 mL, 3 times). The combined organic layer was dried over $MgSO_4$ and concentrated in *vacuo*. The resulting residue was chromatographed on silica gel (eluent: 70–90% AcOEt/n-hexane) to give **9** (2.34 g, 8.74 mmol, 54%) as pale yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 7.13 (d, J = 8.54 Hz, 2H, Ar*H*), 6.65 (d, J = 8.54 Hz, 2H, Ar*H*), 4.43 (s, 2H, -C*H*$_2$O(C$_2$H$_4$O)$_3$CH$_3$), 3.37–3.69 (m, 12H, -CH$_2$O(C$_2$*H*$_4$O)$_3$CH$_3$), 3.37 (s, 3H, -CH$_2$O(C$_2$H$_4$O)$_3$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0 (Ar*C* attached to CH_2), 129.4 (Ar*C*), 128.0 (Ar*C* attached to NH_2), 114.8 (Ar*C*), 73.1 (*C*H$_2$ attached to C$_6$H$_4$), 71.9 (OC$_2$H$_4$O), 70.65 (OC$_2$H$_4$O), 70.60 (OC$_2$H$_4$O), 70.55 (OC$_2$H$_4$O), 70.50 (OC$_2$H$_4$O), 68.8 (OC$_2$H$_4$O), 59.0 (OCH$_3$); IR (ATR) 3445 (NH_2), 3358 (NH_2), 3235, 2867, 1777, 1626, 1613, 1518, 1453, 1348, 1286, 1249, 1175, 1085 (C–O), 1024, 941, 822, 559 cm^{-1}; ESI-TOF-MS *m/z* 292 ([M+Na]$^+$); Anal. Calcd for $C_{14}H_{23}NO_4 \cdot 0.25H_2O$: C, 61.40: H, 8.65: N, 5.11%. Found: C, 61.10: H 8.54: N, 4.99%.

[3,5c-Bis(2,5,8,11-tetraoxadodecyl)-2,6-bis(*N*-4-dodecylphenylimino)phenyl]chloropalladium (4). Under a nitrogen atmosphere, **6** (0.40 g, 0.35 mmol) and 4-dodecyl aniline (**8**) (0.90 g, 3.5 mmol) were dissolved in anhydrous MeCN (4 mL). The solution was refluxed under a nitrogen atmosphere for 72 h to give a yellow solution. After the solution cooled to 25 °C, urea hydrogen peroxide (68 mg, 0.72 mmol) was added and the reaction mixture was stirred at 50 °C for 11 h. After removal of the solvent, the residue was chromatographed on silicagel (eluent: 0–5% MeOH/AcOEt) followed by gel permeation chromatography (eluent: $CHCl_3$) to afford the pincer complex **4** (0.33 g, 0.29 mmol, 85% yield) as yellow solids. Mp. 56.5–57.0 °C; ^1H NMR ($CDCl_3$, 500 MHz) δ 8.57 (s, 2H, C*H*=N), 7.45 (d, 4H, J = 8.5 Hz, Ar*H*), 7.17 (d, 4H, J = 8.0 Hz, Ar*H*), 6.93 (s, 1H, Ar*H*), 4.71 (s, 4H, ArC*H*$_2$O-), 3.67 (s, 8H, -OC$_2$*H*$_4$-), 3.60–3.49 (m, 16H, -OC$_2$*H*$_4$-), 3.35 (s, 6H, -OC*H*$_3$), 2.60 (t, 4H, J = 7.0 Hz, C*H*$_2$C$_{10}$H$_{20}$CH$_3$), 1.62–1.57 (m, 4H, C*H*$_2$), 1.31–1.26 (m, 36H, CH$_2$C$_{10}$*H*$_{20}$CH$_3$), 0.88 (t, 6H, J = 7.0 Hz, -CH$_2$(CH$_2$)$_{10}$C*H*$_3$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ 187.4 (Ar*C* attached to Pd), 172.7 (H*C*=N), 146.8 (Ar*C*), 143.0 (Ar*C* attached to HC=N), 141.3 (Ar*C* attached to CH$_2$(OC$_2$H$_4$)$_3$OCH$_3$), 139.8 (Ar*C*), 128.3 (Ar*C*), 123.6 (Ar*C*), 123.1 (Ar*C* attached to H), 71.8 (CH$_2$O attached to Ar), 71.5 (-C$_2$H$_4$O-), 70.50 (-C$_2$H$_4$O-), 70.49 (-C$_2$H$_4$O-), 70.46 (-C$_2$H$_4$O-), 70.44 (-C$_2$H$_4$O-), 69.8 (-C$_2$H$_4$O-), 59.0 (OCH$_3$), 35.6 (*C*H$_2$ attached to Ar), 31.9 (*C*H$_2$), 31.3 (*C*H$_2$), 29.65 (*C*H$_2$), 29.63 (*C*H$_2$), 29.60 (*C*H$_2$), 29.57 (*C*H$_2$), 29.48 (*C*H$_2$), 29.40 (*C*H$_2$), 29.31 (*C*H$_2$), 22.6 (*C*H$_2$), 14.1 (*C*H$_3$); IR (ATR) 2922, 2852, 1599 1579 (C=N), 1531, 1504, 1465, 1420, 1345, 1308, 1290, 1253, 1201, 1189, 1092 (O–C–O), 1034, 980, 940, 885, 860, 835, 767, 723, 676, 632, 616, 559 cm^{-1}; MALDI-TOF-MS Calcd. for C60H95N2O8Pd ([M–Cl]$^+$): *m/z* = 1077.61, found 1077.67; Anal. Calcd for $C_{60}H_{95}ClN_2O_8Pd$: C, 64.67: H, 8.59: N, 2.51%. Found: C, 64,79: H, 8.54: N, 2.57%.

[3,5-Didodecyl-2,6-bis{*N*-4-(2,5,8,11-tetraoxadodecyl)phenylimino}phenyl]chloropalladium (5). Under a nitrogen atmosphere, **7** (280 mg, 0.25 mmol) and **9** (730 mg, 2.5 mmol) were dissolved in anhydrous MeCN (5 mL). The solution was refluxed under a nitrogen atmosphere for 86 h to give a yellow solution. After the solution was cooled to 25 °C, urea hydrogen peroxide (46 mg, 0.50 mmol) was added and the resulting mixture was stirred at 50 °C for 24 h. After removal of the solvent, the residue was chromatographed on silica gel (eluent: 1–2% MeOH/$CHCl_3$) followed by gel permeation chromatography (eluent: $CHCl_3$) to afford the pincer complex **5** (208.6 mg, 0.187 mmol, 76%) as yellow oil. ^1H NMR (500 MHz, $CDCl_3$) δ 8.23 (s, 2H, C*H*=N), 7.47 (d, J = 7.9 Hz, 4H, Ar*H*), 7.36 (d, J = 8.5 Hz, 4H, Ar*H*), 6.72 (s, 1H, Ar*H*), 4.57 (s, 4H, -OC*H*$_2$C$_6$H$_4$N=), 3.63–3.69 (m, 20H, -O(C$_2$*H*$_4$O)$_3$CH$_3$), 3.54–3.56 (m, 4H, -O(C$_2$*H*$_4$O)$_3$CH$_3$), 3.37 (s, 6H, -O(C$_2$H$_4$O)$_3$C*H*$_3$), 2.76 (t, J = 7.6 Hz, 4H, -C*H*$_2$(CH$_2$)$_{10}$CH$_3$), 1.61–1.66 (m, 4H, C*H*$_2$), 1.25–1.38 (m, 36H, -CH$_2$(C*H*$_2$)$_{10}$CH$_3$), 0.87 (t, J = 6.7 Hz, 6H, -CH$_2$(CH$_2$)$_{10}$C*H*$_3$); ^{13}C NMR (125 MHz, $CDCl_3$) δ 187.5 (Ar*C* attached to Pd), 171.9 (*C*H=N), 148.4 (Ar*C*), 146.3 (Ar*C*), 139.8 (Ar*C*), 138.3 (Ar*C*), 127.8 (Ar*C*), 125.6 (Ar*C*), 123.7 (Ar*C*), 72.7 (*C*H$_2$ attached to C$_6$H$_4$), 71.9 (OC$_2$H$_4$O), 70.6 (OC$_2$H$_4$O), 70.5 (OC$_2$H$_4$O), 70.3 (OC$_2$H$_4$O), 69.5 (OC$_2$H$_4$O), 59.0 (OCH$_3$), 34.1 (*C*H$_2$ attached to Ar), 31.9 (*C*H$_2$), 31.7 (*C*H$_2$), 29.66 (*C*H$_2$), 29.63 (*C*H$_2$), 29.5 (*C*H$_2$), 29.4 (*C*H$_2$), 29.39 (*C*H$_2$), 29.34 (*C*H$_2$), 22.6 (*C*H$_2$), 14.1 (*C*H$_3$) (One of the CH_2 signals of dodecyl group and one of the CH_2 signals of triethyleneglycol group might be overlapped with the other peaks of carbon.); IR (ATR) 2921, 2852, 1574, 1526, 1505, 1464, 1348, 1199, 1097 (C–O), 1017, 943, 827 cm^{-1}; MALDI-TOF-MS Calcd. for $C_{60}H_{95}N_2O_8Pd$ [M–Cl]$^+$: *m/z* = 1077.61; Found 1077.62; Anal. Calcd for $C_{60}H_{95}ClN_2O_8Pd$: C, 64.67: H, 8.59: N, 2.51%. Found: C, 64.45: H, 8.52: N, 2.61%.

Formation of vesicles

4$_{vscl}$: Ten mg of **4** was placed in a 30 mL sample tube and dissolved with 1 mL of CH_3CN to give a pale yellow solution. Then, 9 mL of Millipore water was added to the solution, which was slowly concentrated at 80 °C for 6 h without stirring to generate a pale yellow suspension of **4**$_{vscl}$. The obtaining yellow suspension of **4**$_{vscl}$ was centrifuged (4000 rpm, 15 min) to give a precipitate and a supernatant. The supernatant was removed by decantation to afford the vesicle **4**$_{vscl}$. The resulting aqueous suspension was diluted with 1 mL of Millipore water. The suspension was characterized by DLS (vide infra) and microscopic analyses (vide infra).

5$_{vscl}$: A chloroform solution of **5** (0.1 mL, 10 mg mL^{-1}) was charged in a 4 mL vial. After evaporation of the chloroform, a thin film of **5** was formed on the inner glass surface of the vial. Then, 2 mL of Millipore water was added to the vial followed by heating the resulting mixture at 60 °C for 4 h without stirring. After standing at 25 °C for overnight, the sample was vortexed for 5 min to generate a pale yellow suspension of **5**$_{vscl}$. The suspension was characterized by DLS (vide infra) and microscopic analyses (vide infra).

Dynamic light scattering (DLS) analysis

The vesicle suspensions of $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ were placed in a glass tube. The DLS measurement was performed with 200 times repetition of signal scans. Particle sizes are estimated using the Cumulant method of data analysis.

Transmission electron microscopy (TEM) analysis

Samples for TEM analysis were prepared by the following method: suspensions of the vesicle $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ were dropped onto a copper grid covered with a carbon membrane and then air-dried. The obtained samples were measured by TEM.

Scanning electron microscopy (SEM) analysis

Samples for SEM analysis were prepared by the following method: a suspension of the vesicle $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ were dropped onto a silicon wafer (Nilaco, P, Low, <0.02 Ωcm) and then air-dried. The obtained samples were measured by SEM.

Atomic force microscopy (AFM) analysis

Samples for AFM analysis were prepared by the following method: a suspension of the vesicle $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ were dropped onto freshly cleaved mica then air-dried. AFM analyses were performed under air in a conventional tapping mode.

Fluorescence microscopy and confocal laser scanning microscopy (CLSM) analyses

Samples for fluorescence microscopy and CLSM were prepared by the following method: to suspensions of $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ in water (0.1 mg/1 mL) were added 1 μL of an EtOH solution of fluoresceine (0.45 mM) to give stained $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$, respectively. The stained $\mathbf{4}_{vscl}$ and $\mathbf{5}_{vscl}$ were cast (1 drop) onto slide glasses. The resulting slide glasses were subjected to fluorescence microscopy and CLSM.

Miyaura–Michael reaction (general procedure)

To a vial 1 mL aqueous suspension of $\mathbf{4}_{vscl}$ (2.6 mg, 2.4×10^{-3} mmol), 2-cyclohexene-1-one (**24**, 11.5 mg, 0.12 mmol) and sodium tetraphenylborate (**25**, 61.6 mg, 0.18 mmol) were added. The reaction mixture was agitated with shaking at 25 °C for 12 h. The reaction mixture was quenched with sodium chloride, and then extracted with MTBE (1.5 mL x 4 times). The combined extract was dried over Na_2SO_4, and then filtered through silica gel using MTBE as an eluent. After removal of the solvent, the product was dissolved by a $CDCl_3$ solution of 1,1,2,2-tetrachloroethane an internal standard. The chemical yield was determined by ^{1}H NMR measurement.

3-Phenylcyclohexanone (26). [CAS: 20795-53-3]. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31–7.34 (m, 2H, Ph*H*), 7.21–7.25 (m, 3H, Ph*H*), 2.98–3.04 (m, 1H, C*H* attached to Ph), 2.57–2.62 (m, 1H, CH_2), 2.50–2.55 (m, 1H, CH_2), 2.43–2.48 (m, 1H, CH_2), 2.34–2.41 (m, 1H, CH_2), 2.12–2.17 (m, 1H, CH_2), 2.06–2.10 (m, 1H, CH_2), 1.73–1.89 (m, 2H, CH_2); ^{13}C NMR (125 MHz, $CDCl_3$) δ 210.9 (*C*=O), 144.3 (Ph*C* attached to cyclohexanone), 128.6 (Ph*C*), 126.6 (Ph*C*), 126.5 (Ph*C*), 48.9 (*C*H attached to Ph), 44.7 (*C*H_2), 41.1 (*C*H_2), 32.7 (*C*H_2), 25.5 (*C*H_2); MS *m*/*z* 174 (M^+).

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Notes and references

1 For a recent review, see: N. Selander and K. J. Szabó, *Chem. Rev.*, 2011, **111**, 2048; and references therein.
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