Supporting Information of


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Experimental Section

General.

4,5-Diiododibenzo[24]crown-8 (DB24C8-I$_2$),
4,4’,5,5’-tetradiododibenzo[24]crown-8 (DB24C8-I$_4$),
[FeCH$_2$NH$_2$CH$_2$C$_6$H$_4$-4-OCH$_2$CH$_2$CH=CH$_2$]PF$_6$ (3) (Fc = Fe(C$_5$H$_4$)(C$_5$H$_5$)),
IC$_6$H$_4$-4-OCH$_2$(CH$_2$OCH$_2$)$_3$CH$_2$OC$_6$H$_4$-4-I and tetra(ethyleneglycol) diacrylate were prepared by literature methods. Other chemicals were commercially available. NMR spectra ($^1$H, $^{13}$C{$^1$H}) were recorded on Varian MERCURY300 or JEOL EX-400 spectrometers. IR absorption spectra were recorded on Shimadzu FT/IR-8100 spectrometers. Fast atom bombardment mass spectra (FABMS) were obtained from a JEOL JMS-700 (matrix, 2-nitrophenyl n-octyl ether (NPOE)) spectrometer. ESI-TOF-MS were obtained from a micrOTOF II (Bruker) spectrometer. Elemental analyses were carried out with a Yanaco MT-5 CHN autorecorder. Thermogravimetric analysis (TGA) was recorded on a Seiko TG/DTA6200R. Differential scanning calorimetry (DSC) was recorded on a Seiko DSC6200S. Gel permeation chromatography was performed by using an LC-908 recycling preparative
HPLC (Japan Analytical Industry Co., Ltd.) with two columns for the separation of low-molecular-weight organic compounds: JAIGEL-1H and JAIGEL-2H (styrene polymer gels).

![Scheme S1  Synthesis of 1 and 2]

**4,5-di(pyridinylethynyl)benzo[24]crown-8 (2)**

A THF solution (24 mL) of 4,5-diiododibenzo[24]crown-8 (DB24C8-I₂) (1.40 g, 2.00 mmol), CuI (15 mg, 0.040 mmol), PdCl₂(PPh₃)₂ (28 mg, 0.020 mmol), 2-ethynlypyridine (0.50 mL, 4.8 mmol), 0.5 M aqueous ammonia (16 mL, 8.0 mmol) was stirred for 8 h at room temperature. The organic product was extracted with CH₂Cl₂ and the solution was dried over MgSO₄. Evaporation of the solvent gave a crude product which was washed with hexane to yield 4,5-di(pyridinylethynyl)benzo[24]crown-8 (2) as a gray solid (1.23 g, 1.9 mmol, 95%).

\(^1\)H NMR (400 MHz, CDCl₃, r.t.): \(\delta\) 3.84 (br, 8H, CH₂), 3.91-3.94 (m, 8H, CH₂), 4.14-4.17 (m, 8H, CH₂), 6.87 (m, 4H, C₆H₄), 7.09 (s, 2H, C₆H₂), 7.23 (ddd, 2H, H₅-pyridyl, \(J = 6, 5, 2\) Hz), 7.64-7.66 (4H, H₃ and H₄-pyridyl), 8.62 (dd, 2H, H₆-pyridyl, \(J = 5, 1\) Hz); \(^{13}\)C\(^{\{1\}}\)H NMR (100 MHz, CDCl₃, r.t.): \(\delta\) 69.4 (2C, CH₂), 69.6 (CH₂), 67.0 (CH₂), 71.3 (CH₂), 71.5 (CH₂), 88.0 (C=C), 91.7 (C=C), 114.0, (C₆H₄), 116.0 (C₆H₂), 118.5, 121.3 (C₃H₄), 122.6 (C₅-pyridyl), 127.2, (C₃ or C₄-pyridyl), 136.0 (C₃ or C₄-pyridyl), 143.5, 148.8, 149.2 (C₆-pyridyl), 149.9; Anal. Calcd. for C₃₈H₃₈N₂O₈(H₂O)₀.₅: C, 69.18; H, 5.96; N, 4.25. Found: C, 69.32; H, 5.77; N, 4.61.
(4,5-dipyridinylethynylbenzo[24]crown-8)PdCl₂ (1)

A DMSO solution (3.0 mL) of 2 (330 mg, 0.50 mmol) and PdCl₂(cod) (95 mg, 0.30 mmol) was stirred for 30 min at 50 °C. The resulting solid was collected by filtration, washed with methanol and diethyl ether, and dried in vacuo to form 1 as yellow solid (230 mg, 0.28 mmol, 92%).

1H NMR (300 MHz, CDCl₃, r.t.): δ 3.86 (br, 8H, CH₂), 3.92-3.98 (m, 8H, CH₂), 4.15-4.18 (m, 4H, CH₂), 4.23-4.26 (m, 4H, CH₂), 6.88 (m, 4H, C₆H₄), 7.15 (s, 2H, C₆H₂), 7.31 (m, 2H, H₅-pyridyl), 7.60 (d, 2H, H₃-pyridyl, J = 8 Hz), 7.73 (m, 2H, H₄-pyridyl), 8.86 (d, 2H, H₆-pyridyl, J = 6 Hz);

13C{¹H} NMR (100 MHz, CDCl₃, r. t.): δ 69.3 (CH₂), 69.5 (CH₂), 69.6 (CH₂), 69.9 (CH₂), 71.3 (CH₂), 71.5 (CH₂), 90.1 (C≡C), 96.3 (C≡C), 113.9 (C₆H₄), 116.0 (C₆H₂), 118.6, 121.3 (C₆H₄), 123.7 (C₅-pyridyl), 128.8 (C₃ or C₄-pyridyl), 137.6 (C₃ or C₄-pyridyl), 145.1, 148.7, 150.0, 153.0 (C₆-pyridyl); IR (KBr disk, r.t.) ν 2919, 2812, 2213, 1592, 1514, 1256 cm⁻¹; m.p.: ca. 240 °C (by DSC. decomp.); 5% weight loss temperature: 238 °C (by TGA. scan rate = 5 °C/min); Anal. Calcd. for C₃₈H₃₈N₂O₈Pd(H₂O)₃: C, 51.74; H, 5.03; N, 3.18; Found: C, 51.76; H, 4.67; N, 3.22. ESI-TOF-MS (eluent: MeCN): Calcd. for C₃₈H₃₈N₂O₈Na: 851.1. Found: m/z = 851.1 ([M + Na]⁺).

[(FeCH₂NH₂CH₂CH₂C₆H₄-4-OCH₂CH₂CH₂CH=CHCH₂CH₂OC₆H₄-4-CH₂NH₂CH₂Fe)(3)₂](PF₆)₂ (4) (Fc = Fe(C₅H₄)(C₅H₅))

1 (331 mg, 0.40 mmol) and 3 (172 mg, 0.33 mmol) was dissolved in CH₂Cl₂ (3.0 mL), followed by addition of a Ru–carbene complex, (H₂IMes)(PCy₃)Cl₂Ru=CHPh, (14 mg, 0.017 mmol). The mixture was refluxed for 15 h. The resulting solid was collected by filtration, washed with dichloromethane, and dried in vacuo to form 4 as yellow solid (241 mg, 0.10 mmol, 62%).

1H NMR (300 MHz, dmso-d₆, r.t.): δ 2.25 (m, 4H, CH₂), 3.68-4.23 (66H, CH₂-crown, C₅H₄, C₅H₅), 4.38 (s, 4H, NCH₂), 4.43 (s, 4H, NCH₂), 5.38 (2H, CH₂=CH), 6.59 (d, 4H, C₆H₄-axle, J
= 9 Hz), 6.88 (m, 4H, C\textsubscript{6}H\textsubscript{4}-crown), 6.93 (m, 4H, C\textsubscript{6}H\textsubscript{4}-crown), 7.04 (brs, 2H, NH\textsubscript{2}), 7.15 (d, 4H, C\textsubscript{6}H-axle, J = 9 Hz), 7.41 (s, 4H, C\textsubscript{6}H\textsubscript{4}), 7.55 (m, 4H, H\textsubscript{5}-pyridyl), 7.77 (d, 4H, H\textsubscript{3}-pyridyl, J = 8 Hz), 8.01 (dd, 4H, H\textsubscript{6}-pyridyl), 8.89 (d, 4H, H\textsubscript{6}-pyridyl, J = 6 Hz); \textsuperscript{13}C{\textsuperscript{1}H} NMR (100 MHz, dmso-\textsubscript{d}\textsubscript{6}, r.t.): δ 31.9 (OCH\textsubscript{2}CH\textsubscript{2}), 47.9 (NCH\textsubscript{2}), 51.1 (NCH\textsubscript{2}), 67.0 (OCH\textsubscript{2}CH\textsubscript{2}), 67.6 (CH\textsubscript{2}-crown), 68.7 (C\textsubscript{3}H\textsubscript{5} and C\textsubscript{3}H\textsubscript{4}), 68.8 (CH\textsubscript{2}-crown), 68.9 (C\textsubscript{3}H\textsubscript{5} or C\textsubscript{3}H\textsubscript{4}), 69.2 (CH\textsubscript{2}-crown), 69.6 (C\textsubscript{3}H\textsubscript{5} or C\textsubscript{3}H\textsubscript{4}), 69.9 (CH\textsubscript{2}-crown), 70.2 (CH\textsubscript{2}-crown), 70.4 (CH\textsubscript{2}-crown), 76.4, 90.2, (C=O), 94.8 (C=O), 112.4 (C\textsubscript{6}H\textsubscript{4}-crown), 114.0 (C\textsubscript{6}H\textsubscript{4}-axle), 115.9 (C\textsubscript{6}H\textsubscript{2}), 117.6, 121.0 (C\textsubscript{6}H\textsubscript{4}-crown), 123.5, 124.8 (C\textsubscript{5}-pyridyl), 128.1 (C\textsubscript{3}-pyridyl), 128.7 (CH\textsubscript{2}=CH), 130.4 (C\textsubscript{6}H\textsubscript{4}-axle), 140.0 143.7, 147.1, 148.9, (C\textsubscript{4}-pyridyl), 152.8 (C\textsubscript{6}-pyridyl), 158.6; IR (KBr disk, r.t.) ν 2211, 1592, 1514, 1252, 1105, 843 (PF\textsubscript{6}), 558 (PF\textsubscript{6}) cm\textsuperscript{-1}; m.p.: ca. 200 °C (by DSC, decomp.); 5% weight loss temperature: 235 °C (by TGA, scan rate = 5 °C/min); Anal. Calcd. for C\textsubscript{118}H\textsubscript{124}Cl\textsubscript{12}FeN\textsubscript{6}O\textsubscript{18}P\textsubscript{2}Pd\textsubscript{2}(H\textsubscript{2}O)\textsubscript{3}: C, 52.02; H, 4.81; N, 3.08. Found: C, 51.91; H, 4.81; N, 3.03; ESI-TOF-MS (eluent: MeCN): Calcd. for C\textsubscript{118}H\textsubscript{124}Cl\textsubscript{12}FeN\textsubscript{6}O\textsubscript{18}P\textsubscript{2}Pd\textsubscript{2}: 1190.2 (dication), Found: m/z = 1190.2 ([M – (PF\textsubscript{6})\textsubscript{2}]\textsuperscript{2+}) The assignments of the NMR signals were supported by \textsuperscript{1}H-\textsuperscript{1}H COSY, \textsuperscript{13}C{\textsuperscript{1}H}\textsuperscript{-1}H COSY and DEPT135 spectroscopy.

Typical procedure for the Mizoroki-Heck reaction of methyl acrylate and iodobenzene. (Table 1, run 1)

A DMF solution (8.0 mL) of methyl acrylate (0.090 mL, 1.0 mmol) and triethylamine (0.56 mL, 4.0 mmol) was stirred for 10 min at room temperature, followed by addition of iodobenzene (0.11 mL, 1.0 mmol) and Pd catalyst 1 (1.7 mg, 0.02 mmol). The solution was stirred at 100 °C for 1 h and the resulting solid was removed by filtration. The solvent was removed by evaporation to give a crude product, which is dissolved in CH\textsubscript{2}Cl\textsubscript{2} and partitioned by addition of water. The separated organic phase was dried over MgSO\textsubscript{4}, filtered and evaporated. The obtained crude dried in vacuo to give methyl cinnamate, PhCH=CHCOOMe, in quantitative yield.
The product was determined by $^1$H NMR spectroscopy.

**O(CH$_2$CH$_2$OC$_6$H$_4$-4-I)$_2$ (5a)**

A mixture of IC$_6$H$_4$-4-OH (2.75 g, 12.5 mmol) and K$_2$CO$_3$ (1.80 g, 13 mmol) in MeCN (12 mL) was stirred for 30 min at 90 °C, followed by addition of di(ethylene glycol) di-p-tosylate (2.48 g, 6.0 mmol) in MeCN (18 mL). The mixture was stirred for another 24 h at 90 °C, before being cooled to r.t.. The product was extracted with CH$_2$Cl$_2$, and the organic extract was washed with water, dried over MgSO$_4$, filtered and concentrated under reduced pressure to yield a crude product, which was purified by SiO$_2$ column chromatography (CH$_2$Cl$_2$, R$_f$ = 0.8) to yield O(CH$_2$CH$_2$OC$_6$H$_4$-4-I)$_2$ (5a) as a white powder (1.65 g, 3.22 mmol, 54%). $^1$H NMR (300 MHz, CDCl$_3$, r.t.): δ 3.90 (t, 4H, CH$_2$, $J = 5$ Hz), 4.11 (t, 4H, CH$_2$, $J = 5$ Hz), 6.69 (d, 4H, C$_6$H$_4$, $J = 9$ Hz), 7.54 (d, 4H, C$_6$H$_4$, $J = 9$ Hz); $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$, r.t.): δ 67.6 (CH$_2$), 69.8 (CH$_2$), 83.0 (C$_6$H$_4$), 117.1 (C$_6$H$_4$), 138.2 (C$_6$H$_4$), 158.6 (C$_6$H$_4$); Anal. Calcd. for C$_{16}$H$_{16}$I$_2$O$_3$: C, 37.67; H, 3.16. Found: C, 37.27; H, 2.99; m.p.: 123 °C (by DSC).

**Typical procedure of the Mizoroki-Heck reaction of 5b and 6b. (Table 2, run 3)**

5b used for the following reaction was purified by SiO$_2$ column chromatography to remove stabilizer. A DMF solution (100 mL) of 6b (151 mg, 0.50 mmol), triethylamine (0.28 mL, 2.0 mmol), 5b (299 mg, 0.50 mmol) and Pd catalyst 4 (13 mg, 5.0 × 10$^{-4}$ mmol) was stirred at 100 °C. After 2 h, 10 ml of the solution was sampled and then extracted with CH$_2$Cl$_2$, washed with water, dried over MgSO$_4$, evaporated and dried in vacuo. The obtained solid was analyzed by $^1$H NMR spectroscopy (in CDCl$_3$) and GPC (eluent: THF) to find the formation of 7b and 8b. The yields of the compounds, 7b and 8b, were calculated based on the comparison of the integration of the $^1$H NMR signal with that of the internal standard, 1,3,5-triphenylbenzene, added to the CDCl$_3$ solution. Similar samplings were also
conducted after 4, 8, 12, 24, 48 and 90 h.

Data of 7b: $^1$H NMR (300 MHz, CDCl$_3$, r.t.): $\delta$ 3.70 (m, 16H, OCH$_2$), 3.78 (m, 4H, OCH$_2$), 4.02 (m, 4H, OCH$_2$), 4.36 (m, 4H, OCH$_2$), 6.29 (d, 2H, CH, $J = 16$ Hz) 6.84 (d, 4H, C$_6$H$_4$, $J = 9$ Hz), 7.40 (d, 4H, C$_6$H$_4$, $J = 9$ Hz), 7.74 (d, 2H, CH, $J = 16$ Hz); $^{13}$C NMR (100 MHz, CDCl$_3$, r.t.): $\delta$ 63.6 (OCH$_2$), 67.6 (OCH$_2$), 69.3(OCH$_2$), 69.5 (OCH$_2$), 70.6 (OCH$_2$), 70.8 (OCH$_2$), 70.8 (OCH$_2$), 70.8 (OCH$_2$), 114.8 (C$_6$H$_4$), 115.3 (CH), 127.1, 130.0 (C$_6$H$_4$), 144.4 (CH), 160.4, 167.0; IR (KBr disk, r.t.) ν 2919, 2815, 1707 (C=O), 1636, 1609, 1179 cm$^{-1}$; Anal. Calcd. for C$_{34}$H$_{44}$O$_{12}$(H$_2$O)$_{0.5}$: C, 62.47; H, 6.94. C, 62.76; H, 6.67; m.p.: 95 °C (by DSC. decomp.); 5% weight loss temperature: 362 °C (by TGA. scan rate = 5 °C/min); FABMS: Calcd. for C$_{34}$H$_{44}$O$_{12}$(H$_2$O)$_{0.5}$: 645. Found: m/z = 645 ([M + H]$^+$) (Matrix = NPOE).

Data of 7a: $^1$H NMR (300 MHz, CDCl$_3$, r.t.): $\delta$ 3.77-3.80 (m, 4H, CH$_2$), 3.86-3.89 (m, 4H, CH$_2$), 4.15-4.18 (m, 4H, CH$_2$), 4.38-4.40 (m, 4H, CH$_2$), 6.23 (d, 2H, CH=CH, $J = 16$ Hz), 6.63 (d, 4H, C$_6$H$_4$, $J = 9$ Hz), 7.17 (d, 4H, C$_6$H$_4$, $J = 9$ Hz), 7.60 (d, 2H, CH=CH, $J = 16$ Hz); FABMS: Calcd. for C$_{26}$H$_{29}$O$_8$: 469. Found: m/z = 469 ([M + H]$^+$) (Matrix = NPOE); Anal. Calcd. for C$_{26}$H$_{28}$O$_8$(H$_2$O)$_{0.5}$: C, 65.40; H, 6.12. Found: C, 65.73; H, 6.01; m.p.: 141 °C (by DSC.)

**X-ray structure analyses of 1**

Crystals of 1 suitable for X-ray diffraction study were obtained by recrystallization from NMP/AcOEt. All measurements were made on Rigaku AFC-10R Saturn CCD diffractometer with graphite monochromated Mo-K$\alpha$ radiation. Calculations were carried out by using a program package Crystal Structure™ for Windows.$^6$ All hydrogen atoms were included at the calculated positions with fixed thermal parameters.
References

$^1$H NMR spectrum of 1 (CDCl$_3$, 400 MHz, r.t.)

$^{13}$C($^1$H) NMR spectrum of 1 (CDCl$_3$, 100 MHz, r.t.)
$^1$H NMR spectrum of 2 (CDCl$_3$, 400 MHz, r.t.)

$^{13}$C($^1$H) NMR spectrum of 2 (CDCl$_3$, 100 MHz, r.t.)
$^1$H NMR spectrum of 4 (dmso-$d_6$, 300 MHz, r.t.)

$^{13}$C$\{^1$H$\}$ NMR spectrum of 4 (dmso-$d_6$, 100 MHz, r.t.)
$^1$H NMR spectrum of 7b (CDCl$_3$, 300 MHz, r.t.)

$^{13}$C($^1$H) NMR spectrum of 7b (CDCl$_3$, 77.5 MHz, r.t.)