Supporting Information

Consecutive Modular Ligation as an Access Route to Palladium Containing Polymers

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Experimental Data

Materials

Acetonitrile (VWR, p.a.), chloroform (VWR, p.a.), diethyl ether (VWR, p.a.), diethylamine (Acros Organics, 99%), dimethyl acteamide (DMAc, VWR, p.a.), dimethylformamide (DMF, Fisher Chemical, p.a.), *n*-hexane (VWR, p.a.), methanol (VWR, p.a.), tetrahydrofurane (THF, VWR, p.a.), copper(I) iodide (Sigma Aldrich, 98%), copper(II) sulfate (Sigma Aldrich, 98%), 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU, Fluka. 99%), N, N, N', N'', N''-pentamethyl diethylene triamine (PMDETA, Acros Organics, 99%), sodium ascorbate (SA, Sigma Aldrich, 98%), potassium hydroxide (Roth, 85%), sodium hydroxide (Roth, 99%), sodium sulfate (Na₂SO₄, Roth, 99%), trans-dichlorobis-(triphenylphosphine) palladium(II) (ABCR, 99%), benzyl chloride (ABCR, 99%), 1-bromooctane (Alfa Aesar, 98%), 1-bromoundecane (Fluka, 97%), 2,7-dibromo fluorene (Acros Organics, 99%), 2,6-dibromopyridine (Acros Organics, 98%), 1.8-dibromooctane (Sigma Aldrich, 98%), a,a'-dibromo-p-xylene (Fluka, 98%), propargyl bromide (Acros Organics, 80% in toluene), sodium azide (Sigma Aldrich, 99%), tert-butyllithium (Acros, 1.9 M in pentane), tetrabutylammonium iodide (Acros, 98%), (trimethylsilyl)acetylene (ABCR, 97%), 1-(trimethylsilyl) imidazole (Alfa Aesar, 97%), [Pd(COD)Cl]₂ (Alfa Aesar), were used as received. Copper(I) bromide (Sigma Aldrich, 98%) was purified by sequential washing with sulphurous acid, acetic acid and ethanol, followed by pressure, 1,3-bis(diisopropyl phenyl) imidazoline-2-ylidene drying under reduced (IPr-NHC),¹ p-tosylazide,² 1-iodo-4-methylbenzene,³ and p-tolyl azide³ were synthesized according to literature.

Characterization

Nuclear magnetic resonance (NMR) spectra were recorded in $DMSO-d_6$ or $CDCl_3$ on a Bruker Avance II NMR spectrometer. ¹H NMR spectra were recorded at 400 MHz. Chemical shifts are referenced to internal solvent resonances and are reported relative to tetramethylsilane.

Elemental analyses (EA) were carried out with an Elementar Vario EL or Micro cube instrument.

Molecular weight distributions were measured by size exclusion chromatography (SEC) on a Polymer Laboratories/Varian PL-GPC 50 Plus system comprising a Polymer Laboratories 5.0 μ m bead-size guard column (50 × 7.5 mm²), followed by three PL columns and a differential refractive index detector. The eluent was tetrahydrofurane (THF) at 35 °C with a flow rate of 1 mL·min⁻¹. The SEC system was calibrated using linear polystyrene standards ranging from 2000 g·mol⁻¹ to 2·10⁶ g·mol⁻¹ and the Mark-Houwink relationship for polystyrene ($K = 14.1 \cdot 10^{-5} dL \cdot g^{-1}$, $\alpha = 0.7$).⁴

Static light scattering (SLS) measurements were performed using a MALLS-detector (multiangle laser light scattering detector) SLD 7000 from Polymer Standard Services (PSS), Mainz, Germany. Five concentrations of the polymer were employed ranging from 0.5 g·L⁻¹ to 4.0 g·L⁻¹ to determine the weight-averaged molar mass (M_w^{SLS}) and the second virial coefficient (A_2) . The solutions were prepared by dissolving the polymer in dimethyl acetamide (DMAc). After a stabilizing period of approx. 60 h, the solutions were filtered over 0.2 µL filters and analysed by SLS. The required dn/dc values were measured employing the same solutions with a refractometer dn/dc2010 from PSS, Mainz, Germany.

Synthesis of monomers

1,3-Dipropargylimidazoliumbromide (1)

A solution of 4.0 g 1-(trimethylsilyl) imidazole (28.5 mmol) and 7 mL propargyl bromide (80% in toluene, 65.0 mmol) in 100 mL acetonitrile was heated under reflux for 2 d. Upon cooling the reaction mixture to -20 °C, a white solid precipitated. The precipitate was filtered and dried *in vacuo* to yield 4.0 g (62%) of the pure product.

¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 9.46 (s, 1H, N-CH-N), 7.90 (s, 2H, N-CH-CH-N), 5.28 (d, 4H, CH₂), 3.87 (t, 2H, CH). ¹³C{¹H} NMR (100 MHz, DMSO-d₆, δ , ppm): 136.2 (N-CH-N), 122.7 (N-CH-CH-N), 79.1 (C_q), 76.0 (CH), 40.2 and 38.8 (CH₂).

2,6-Diethynylpyridine (2)

To a 50 mL Schlenk type flask, charged with 35 mL of freshly distilled diethylamine, 2,6-dibromopyridine (3.2 g, 13.3 mmol), (trimethylsilyl)acetylene (3.9 mL, 2.7 g, 27.8 mmol), *trans*-dichlorobis-(triphenylphosphine)palladium(II) (200 mg), and a catalytic amount of copper(I) iodide (20 mg), were added in that order under an argon atmosphere. The mixture was allowed to stir for 12 h, after which the diethylamine was removed *in vacuo*. The residue was extracted with diethyl ether, filtered and the solvent was evaporated. The crude product was purified by column chromatography (hexane / diethyl ether 3:1, $R_f = 0.72$) to yield 3.5 g (98%) of the protected product.⁵

¹H NMR (250 MHz, CDCl₃, δ , ppm): 7.58 (dd, 1H, Py-H₄), 7.37 (d, 2H, Py-H₃,H₅), 0.24 (s, 18H, Si-(CH₃)₃).

For deprotection, 2,6-bis[(trimethylsilyl)ethynyl]pyridine (3.5 g, 12.9 mmol) was dissolved in 70 mL methanol, and 19 mL of a 1 M aqueous solution of potassium hydroxide was added. The solution mixture was allowed to stir for 2 h. The solvent was removed *in vacuo*, and the residue was extracted with diethyl ether. The product was washed several times with water and brine. Purification by column chromatography (hexane / diethyl ether 1:1, $R_f = 0.48$) and recrystallization from hexane yielded 0.5 g (28%) of the pure product as off-white needles.⁵

¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.64 (t, 1H, Py-H₄), 7.44 (d, 2H, Py-H₃,H₅), 3.15 (s, 2H, CH). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 142.8 (Py(C₂,C₆)), 136.7 (Py(C₄)), 127.2 (Py(C₃,C₅)), 82.2 (C_q), 77.9 (CH).

1-Azidoundecane (a)

Sodium azide (NaN₃, 2.8 g, 43.1 mmol) was added to a solution of 1-bromoundecane (4.75 g, 20.2 mmol) in DMF (75.0 mL). The mixture was stirred at 60°C for 10 h, at which point water (80.0 mL) was added and the product was extracted with diethyl ether (3×25 mL). The

organic layer was washed with water $(3 \times 50 \text{ mL})$, dried (Na_2SO_4) and the solvent was evaporated to yield 3.9 g (98%) of a colorless oil.⁶

¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.25 (t, 2H, CH₂-N₃), 1.60 (q, 2H, CH₂-CH₂N₃), 1.45-1.18 (m, 16H, (CH₂)₈), 0.88 (t, 3H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 51.7 (C₁), 32.1 (C₂), 29.7 (C₃), 29.7 (C₄), 29.6 (C₅), 29.5 (C₆), 29.3 (C₇), 29.0 (C₈), 26.9 (C₉), 22.8 (C₁₀), 14.3 (C₁₁).

Benzylazide (b)

Sodium azide (NaN₃, 5.1 g, 78.3 mmol) was added to a solution of benzylchloride (5.5 g 43.45 mmol) in DMF (75.0 mL). The mixture was stirred at 60°C for 10h, at which point water (80.0 mL) was added and the product was extracted with diethyl ether (3×10 mL). The organic layer was washed with water (3×50 mL), dried (Na₂SO₄) and the solvent was evaporated to yield 2.3 g (39%) of a colorless oil.⁶

¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.45-7.29 (m, 5H, Ph-H), 4.35 (s, 2H, CH₂-N₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 135.5 (Ph(C_q)), 129.0 (Ph(C₃,C₅)), 128.5 (Ph(C₂,C₆)), 128.4 (Ph(C₄)), 54.9 (CH₂).

1,8-Diazidooctane (c)

Sodium azide (NaN₃, 3.0 g, 46.1 mmol) was added to a solution of 1,8-dibromooctane (2.0 g 7.3 mmol) in DMF (40.0 mL). The mixture was stirred at 60°C for 10h, at which point water (200.0 mL) was added and the product was extracted with ether (3×25 mL). The organic layer was washed three times with water (3×25 mL), the solvent was evaporated, and the compound was purified by chromatography on silica gel (hexane as eluent solvent) to give 1.42 g (99 %) of a colorless oil.⁶

¹H NMR (400 MHz, CDCl₃, δ , ppm): 3.26 (t, 4H, CH₂-N₃), 1.60 (quin, 4H, CH₂-CH₂N₃), 1.49-1.22 (m, 8H, (CH₂)₄). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 51.6 (C₁,C₈), 29.1 (C₂,C₇), 28.9 (C₃,C₆), 26.7 (C₄,C₅).

α, α '-Diazido-*p*-xylene (d)

Sodium azide (NaN₃, 1.63 g, 25.0 mmol) was added to a solution of α, α '-dibromo-*p*-xylene (2.64 g 10.0 mmol) in DMF (15.0 mL). The mixture was stirred at 60°C for 10h, at which point water (100.0 mL) was added and the product was extracted with ether (3 × 10 mL). The organic layer was washed three times with water (3 × 10 mL), the solvent was evaporated, and the compound was purified by chromatography on silica gel (hexane as eluent solvent) to give 1.83 g (97 %) of white crystals.⁶

¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.35 (s, 4H, Ph-H), 4.36 (s, 4H, CH₂). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 135.7 (Ph(C_q)), 128.8 (Ph(CH)), 54.5 (CH₂).

2,7-Dibromo-9,9-dioctyl fluorene

A mixture of 3.0 g 2,7-dibromo fluorene (8.98 mmol), 334 mg tetrabutylammonium iodide (0.90 mmol) and 30 g aqueous sodium hydroxide (50%) in a three necked flask and 17.5 g of

1-bromooctane (90.6 mmol) in a second flask were freed from oxygen *via* three consecutive freeze/pump/thaw cycles. The deoxygenized 1-bromooctane was added to the first mixture under an argon atmosphere and the reaction mixture was heated to 70 °C for 2 h under reflux and violent stirring. After cooling to ambient temperature, the aqueous phase was extracted with 75 mL chloroform and washed with water (3 × 50 mL). The excess of 1-bromooctane was removed by vacuum distillation and the product was purified *via* column chromatography (hexane / chloroform 9:1, $R_{\rm f} = 0.88$), yielding 5.07 g (99%) of slightly yellow white crystals.^{7,8}

¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.52 (d, 2H, fluorene-H₃,H₆), 7.45 (d, 4H, fluorene-H₁,H₄,H₅,H₈), 1.99 – 1.84 (m, 4H, fluorene-CH₂), 1.26 – 1.00 (m, 20H, (CH₂)₅), 0.83 (t, 6H, CH₃), 0.65 – 0.50 (m, 2H, CH₂-CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 152.7 (fluorene(C_{9a},C_{8a})), 139.2 (fluorene(C_{4a},C_{4b})), 130.3 (fluorene(C₁,C₈)), 126.3 (fluorene(C₄,C₅)), 121.6 (fluorene(C₃,C₆)), 121.3 (fluorene(C₂,C₇)), 55.8 (fluorene(C₉)), 40.3 (octyl(C₁)), 31.9 (octyl(C₆)), 30.0 (octyl(C₃)), 29.3 (d, octyl(C₄,C₅)), 23.8 (octyl(C₂)), 22.7 (octyl(C₇)), 14.2 (octyl(C₈)).

2,7-Diazido-9,9-dioctyl fluorene (e)

40 mL anhydrous tetrahydrofurane (THF) was cooled to -83°C in a flame dried three necked flask when 14.8 mL *tert*-butyllithium (1.9 M in pentane, 28.1 mmol) was added drop wise. After stirring for 15 minutes, 3.6 g 2,7-dibromo-9,9-dioctyl fluorene (6.6 mmol) in 8 mL anhydrous THF were added drop wise. After an additional 15 min of stirring, 4.4 mL *p*-tosylazide (28.5 mmol) in 3 mL anhydrous THF were slowly added. The reaction mixture was allowed to stir for 8 h at -83°C; subsequently, 5 mL of a saturated aqueous solution of ammonium chloride was added and the mixture was allowed to warm to ambient temperature overnight. The solvent was removed under reduced pressure, the mixture was extracted with diethyl ether (200 mL) and filtered, washed with brine (3 × 70 mL), dried (Na₂SO₄) and separated from the solvent under reduced pressure. The product was purified *via* column chromatography (hexane, $R_f = 0.54$) and recrystallization out of hexane, yielding 1.9 g (60%) of a yellow crystalline product.^{7,8}

¹H NMR (400 MHz, CDCl₃, δ , ppm): 7.60 (d, 2H, fluorene-H₃,H₆), 7.04 – 6.97 (m, 2H, fluorene-H₁,H₈), 6.95 (s, 2H, fluorene-H₄,H₅), 1.98 – 1.86 (m, 4H, fluorene-CH₂), 1.24 – 1.01 (m, 20H, (CH₂)₅), 0.83 (t, 6H, CH₃), 0.64 – 0.51 (m, 4H, CH₂-CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 152.7 (fluorene(C_{9a},C_{8a})), 138.9 (fluorene(C_{4a},C_{4b})), 137.8 (fluorene(C₁,C₈)), 120.7 (fluorene(C₄,C₅)), 118.0 (fluorene(C₃,C₆)), 113.7 (fluorene(C₂,C₇)), 55.6 (fluorene(C₉)), 40.5 (octyl(C₁)), 31.9 (octyl(C₆)), 30.0 (octyl(C₃)), 29.3 (octyl(C₄,C₅)), 23.8 (octyl(C₂)), 22.7 (octyl(C₇)), 14.2 (octyl(C₈)).

General Procedure for Screening Reactions

Except the reactions with copper(II) sulfate as the catalyst, all reactions were conducted under an inert atmosphere. All solutions were degassed by percolating with argon. A solution of $0.2 \text{ mol} \cdot \text{L}^{-1}$ dialkyne and $0.4 \text{ mol} \cdot \text{L}^{-1}$ monoazide, 0.2 eq of the copper salt and the ligand or base, respectively, in DMF or THF was stirred at ambient temperature for 24 h. Subsequently, aqueous ammonium hydroxide was added to stop the reaction and the reaction mixture was passed over a small column equipped with neutral alumina to remove the copper catalyst. The solvent was removed under reduced pressure and conversion was determined *via* ¹H NMR spectroscopy in DMSO-d₆ or CDCl₃. NMR data for complete clicked products:

1a: ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 9.49 (s, 1H, N-CH-N), 8.31 (s, 2H, triazole-H), 7.87 (s, 2H, N-CH-CH-N), 5.59 (s, 4H, triazole-CH₂-imidazole), 4.36 (t, 4H, undecane(H₁)), 1.86-1.70 (m, 4H, undecane(H₂)), 1.22 (s, 32H, undecane(H₃-H₁₀)), 0.84 (t, 6H, undecane(H11)). ¹³C{¹H} NMR (100 MHz, DMSO-d₆, δ , ppm): 140.8 (N-CH-N), 125.3 (triazole(C_q)), 123.4 (triazole(CH), N-CH-CH-N), 54.3 (undecane(C₁)), 50.5 (triazole-CH₂-imidazole), 31.9 (undecane(C₂)), 30.2 (undecane(C₃)), 29.6 – 29.2 (m, undecane(C₄-C₈)), 28.9 (undecane(C₉)), 22.7 (undecane (C₁₀)), 14.6 (undecane(C₁₁)).

1b: ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 9.36 (s, 1H, N-CH-N), 8.30 (s, 2H, triazole-H), 7.77 (s, 2H, N-CH-CH-N), 7.39-7.31 (m, 10H, Ph-H), 5.63 (s, 4H, Ph-CH₂), 5.53 (s, 4H, triazole-CH₂-imidazole). ¹³C{¹H} NMR (100 MHz, DMSO-d₆, δ , ppm): 140.6 (N-CH-N), 135.7 (Ph(C_q)), 128.8 (triazole(C_q)), 128.3 (Ph(C₃,C₅)), 128.1 (Ph(C₂,C₆)), 124.7 (s, Ph(C₄)), 122.8 (triazole(CH), N-CH-CH-N).

2a: ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.19 (s, 2H, triazole-H), 8.08 (s, 2H, Py(H₃,H₅)), 7.85 (s, 1H, Py(H₄)), 4.37 (t, 4H, CH₂-triazole), 1.91 (s, 4H, CH₂-CH₂-triazole), 1.32-1.19 (m, 32H, (CH₂)₈), 0.85 (t, 6H, CH₃). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 150.2 (Py(C_q)), 148.4 (Py(C₄)), 137.8 (triazole(C_q)), 122.0 (triazole(CH)), 119.3 (Py(C₃,C₅)), 50.6 (undecane(C₁)), 32.0 (undecane(C₂)), 30.4 (undecane(C₃)), 29.6 (undecane(C₄)), 29.6 (undecane(C₅)), 29.5 (undecane(C₆)), 29.4 (undecane(C₇)), 29.1 (undecane(C₈)), 26.6 (undecane(C₉)), 22.7 (undecane(C₁₀)), 14.18 (undecane(C₁₁)).⁹

2b: ¹H NMR (400 MHz, DMSO-d₆, δ , ppm): 8.70 (s, 2H, triazole-H), 8.03 (s, 3H, Py-H), 7.42-7.32 (m, 10H, Ph-H), 5.71 (s, CH₂). ¹³C{¹H} NMR (100 MHz, DMSO-d₆, δ , ppm): 149.8 (Py(C_q)), 147.4 (Py(C₄)), 138.2 (Ph(C_q)), 135.9 (triazole(C_q)), 128.8 (Ph(C₂,C₆)), 128.2 (Ph(C₄)), 127.9 (Ph(C₃,C₅)), 123.7 (triazole-CH), 118.5 (Py(C₃,C₅)), 53.1 (CH₂).¹⁰

General Procedure for Polymerization Reactions

Except the reactions with copper(II) sulfate as the catalyst, all reactions were conducted under an inert atmosphere with previously degassed solutions. A solution of 0.2 mol·L⁻¹ dialkyne and diazide, 0.2 eq of the copper salt and the ligand or base, respectively, in DMF or THF was stirred at ambient temperature for 100 h. Subsequently, aqueous ammonium hydroxide was added to stop the reaction and the reaction mixture was passed over a small column equipped with neutral alumina to remove the copper catalyst. The solvent was removed under reduced pressure and the resulting polymers were analyzed *via* SEC, ¹H NMR, EA and SLS.

P2e: ¹H NMR (400 MHz, CDCl₃, δ , ppm): 8.82 (s, 2H, triazole-H), 8.25 (d, 2H, Py-H₃,H₅), 8.05 – 7.70 (m, 8H, Py-H₄, fluorene-H), 2.06 (s, 4H, octyl(H₁)), 1.15 – 1.02 (m, 20H, octyl(H₂-H₆)), 0.79 – 0.65 (m, 10H, octyl(H₇,H₈)). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ , ppm): 153.2 (fluorene(C_{9a},C_{8a})), 150.0 (Py(C₂,C₆)), 149.0 (Py(C₄)), 140.5 (fluorene(C_{4a},C_{4b})), 138.2 (triazole(C_q)), 136.6 (fluorene(C₁,C₈)), 121.3 (Py(C₃,C₅)), 120.2 (d, triazole(CH), fluorene(C₄,C₅)), 119.5 (fluorene(C₃,C₆)), 115.5 (fluorene(C₂,C₇)), 56.4 (fluorene(C₉)), 40.4 $(octyl(C_1))$, 31.8 $(octyl(C_6))$, 30.0 $(octyl(C_3))$, 29.3 (d, $octyl(C_4,C_5))$, 24.0 $(octyl(C_2))$, 22.6 $(octyl(C_7))$, 14.1 $(octyl(C_8))$. Elemental analysis: found C, 74.28; H, 7.50; N, 15.71%, $C_{38}H_{45}N_7$ requires C, 76.09, H, 7.56; N, 16.35%.

Synthesis of 2,6-bis(1-(*p*-tolyl)-1*H*-1,2,3-triazol-4-yl)pyridine (3).

A mixture of *p*-tolyl azide (0.100 g, 0.751 mmol) and 2,6-diethynylpyridine (0.047 g, 0.375 mmol) was dissolved in 5 ml DMF. CuSO₄·5H₂O (0.037 g, 0.150 mmol) and sodium ascorbate (0.030 g, 0.150 mmol) were added and the solution was stirred at ambient temperature for 48 h. The reaction mixture was poured into water (100 mLl) and extracted three times with CH₂Cl₂ (60 mL). The combined organic phases were washed with water and dried (Na₂SO₄). The solvent was removed to afford 0.117 g of **3** (97%) as a colorless solid. Single crystals suitable for X-ray structure determination were grown from a saturated dichloromethane solution.

¹H NMR (DMSO-d₆, δ , ppm): 9.33 (s, 2H, triazole-H), 8.08 (s, 3H, pyridine-H), 7.89 (d, 4H, Ph-H), 7.48 (d, 4H, Ph-H), 2.42 (s, 6H, CH₃). ¹³C{¹H} NMR (DMSO-d₆, δ , ppm): 149.5, 148.2, 138.7, 138.6, 134.3, 130.3, 121.7, 120.2, 118.8, 20.6. Elemental analysis: C₂₃H₁₉N₇ requires C, 70.21, H, 4.87; N, 24.92%, found C, 70.18; H, 4.88; N, 24.60%. MS: found 393.407, C₂₃H₁₉N₇ requires 393.170.

Synthesis of 4 and 4'.

Under an argon atmosphere, **3** (0.081 g, 0.206 mmol) and $[Pd(cod)Cl_2)]$ (0.130 g, 0.454 mmol) in 10 mL CH₂Cl₂ were stirred at ambient temperature for 24 h. A brown precipitate was formed and collected by filtration. After washing with CH₂Cl₂ and *n*-pentane, the compound was dried *in vacuo* to yield 0.098 g of **4** (84%). Single crystals suitable for X-ray structure determination were grown from a saturated dimethylsulfoxide solution.

¹H NMR (DMSO-d₆, δ , ppm): 9.94 (s, 2H, triazole-H), 8.61 (t, 1H, pyridine-H(4)), 8.21 (d, 2H, pyridine-H(3,5)), 7.83 (d, 4H, Ph-H), 7.56 (d, 4H, Ph-H) 2.45 (s, 6H, CH₃). ¹³C{¹H} NMR (DMSO-d₆, δ , ppm): 150.8, 147.4, 141.5, 133.7, 131.0, 125.7, 121.9, 121.2, 120.5, 21.2. Elemental analysis: C₄₆H₃₈Cl₆N₁₄Pd₃ requires C, 41.89, H, 2.90; N, 14.87%, found C, 41.54; H, 3.23; N, 14.38%. ESI: found 534.0218, C₂₃H₁₉Cl₁N₇Pd⁺ requires 534.0306.

X-Ray Crystallographic Studies on 3 and 4

Suitable crystals for single crystal diffraction were grown from CH_2Cl_2 (**3**) and DMSO (**4**), covered in mineral oil (Aldrich) and mounted on a glass fiber. Data were collected on a diffractometer equipped with a STOE imaging plate detector system IPDS2 using MoK α radiation with graphite monochromatization ($\lambda = 0.71073$ Å) at 200 K. Subsequent computations were carried out on an Intel Core2Quad. Structure solution was performed by direct methods full matrix least squares refinement against F^2 using SHELXS-97 and SHELXL-97 software.¹¹

Crystal data for **3**: C₂₃H₁₉N₇, M = 393.45, tetragonal, a = 6.1133(9) Å, b = 6.1133(9) Å, c = 52.627(11) Å, V = 1966.8(3) Å³, T = 200(2) K, space group $P4_32_12$, Z = 8, μ (MoK α) = 0.084 mm⁻¹, 10517 reflections measured, 3579 independent reflections ($R_{int} = 0.0418$). The final R_I values were 0.0375 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.0742 (all data). The goodness of fit on F^2 was 0.90.

Crystal data for **4**: C₂₃H₁₉ClN₇Pd, C₂H₆Cl₃OPdS·2C₂H₆OS, *M* = 982.47, triclinic, a = 8.6458(17) Å, b = 13.837(3) Å, c = 17.394(4) Å, $a = 109.67(3)^{\circ}$, $\beta = 102.90(3)^{\circ}$, $\gamma = 95.46(3)^{\circ}$, V = 1876.9(7) Å³, T = 150(2) K, space group *P*-1, Z = 2, μ (MoK α) = 1.451 mm⁻¹, 11365 reflections measured, 6552 independent reflections ($R_{int} = 0.1020$). The final R_I values were 0.0797 ($I > 2\sigma(I)$). The final $wR(F^2)$ values were 0.2102 (all data). The goodness of fit on F^2 was 0.952.

Positional parameters, hydrogen atom parameters, thermal parameters, bond distances and angles have been deposited as supporting information. Crystallographic data (excluding structure factors) for the structures reported in the current study have been deposited with the Cambridge Cambridge Crystallographic Data Centre as supplementary publications no. CCDC 939314 (**3**) and 939315 (**4**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: +44 1223-336-033, email: deposit@ccdc.cam.ac.uk).

Procedure for Loading the Polymer P2e with [Pd(cod)Cl₂]

Under a nitrogen atmosphere a mixture of the polymer (**P2e**) and $[Pd(cod)Cl_2]$ (2.2 eq.) in CH_2Cl_2 was stirred at ambient temperature for 24 h. The formed precipitate was collected by filtration, washed with CH_2Cl_2 and dried *in vacuo*.

P2e_Pd: ¹H NMR (DMSO-d₆, δ , ppm): 10.08 (s, 2H, triazole-H), 9.52 (s, 1H, Py-H₄), 8.70 (d, 2H, Py-H₃,H₅), 8.23-8.07 (m, 6H, fluorene-H), 1.05 (s, 24H, fluorene-(CH₂)₆), 0.75 (s, 10H, fluorene-(CH₂)₆-CH₂-CH₃). Elemental analysis: found C, 53.53; H, 5.47; N, 11.33%, C₇₆H₉₀Cl₆N₁₄Pd₃ requires C, 52.72, H, 5.24; N, 11.32%.

NMR spectra of the screening experiments



Figure S1. ¹H NMR spectra (recorded in DMSO-d₆) of the screening reaction product **1a** employing the different catalytic systems CuSO₄ / SA, CuBr / PMDETA, or CuI / DBU in DMF, and the monomeric mixture (blind) composed of 1,3-dipropargyl imidazolium bromide (**1**) and two equivalents of 1-azidoundecane (**a**). Conversion was determined by comparing the integrals of the highlighted resonances.



Figure S2. ¹H NMR spectra (recorded in DMSO-d₆) of the screening reaction product **1b** employing the different catalytic systems CuSO₄ / SA, CuBr / PMDETA, or CuI / DBU in DMF, and the monomeric mixture (blind) composed of 1,3-dipropargyl imidazolium bromide (**1**) and two equivalents of benzyl azide (**b**). Conversion was determined by comparing the integrals of the highlighted signals.



Figure S3. ¹H NMR spectra (recorded in CDCl₃) of the screening reaction product **2a** employing the different catalytic systems CuBr / PMDETA, CuI / DBU, or CuI / IPr-NHC in THF, and the monomeric mixture (blind) composed of 2,6-diethynyl pyridine (**2**) and two equivalents of 1-azidoundecane (**a**). Conversion was determined by comparing the integrals of the highlighted signals.



Figure S4. ¹H NMR spectra (recorded in DMSO-d₆) of the screening reaction product **2b** employing the different catalytic systems CuBr / PMDETA, CuI / DBU, or CuI / IPr-NHC in THF, and the monomeric mixture (blind) composed of 2,6-diethynyl pyridine (**2**) and two equivalents of benzyl azide (**b**). Conversion was determined by comparing the integrals of the highlighted signals.





Figure S5. SEC traces of polymer **P2e** synthesized either with CuBr / PMDETA (a), CuI / DBU (b), or CuI / IPr-NHC. SEC system was calibrated using linear polystyrene standards in THF. Obtained molar masses and polydispersities are depicted within the diagrams.



¹H NMR spectra of the model compounds 3 and 4

Figure S6. Aromatic proton signals in the ¹H NMR spectra (recorded in DMSO-d₆) of the low molecular model ligand **3** and the subsequent palladium complex **4** after reaction with Pd(cod)Cl₂.

Elemental Analysis

		С	Н	Ν	Σ(CHN)	$Pd_3Cl_6^{\ a}$	\mathbf{Pd}^{b}
3 C ₂₃ H ₁₉ N ₇ 393.44 g⋅mol ⁻¹	cal.	70.21	4.87	24.92	100.00	-	-
	exp.	70.18	4.88	24.60	99.66	-	-
4 C ₄₆ H ₃₈ Cl ₆ N ₁₄ Pd ₃ 1318.87 g⋅mol ⁻¹	cal.	41.89	2.90	14.87	59.67	40.33	24.21
	exp.	41.54	3.23	14.38	59.15	40.85	24.51
P2e C ₃₈ H ₄₅ N ₇ 599.81 g⋅mol ⁻¹	cal.	76.09	7.56	16.35	100.00	-	-
	exp.	74.28	7.50	15.71	97.49	-	-
P2e_Pd $C_{76}H_{90}Cl_6N_{14}Pd_3$ 1731.60 g·mol ⁻¹	cal.	52.72	5.24	11.32	69.21	30.79	18.44
	exp.	53.53	5.469	11.33	70.33	29.7	17.81

Table S1. Comparison of the theoretically expected and experimental determined mass fractions in the model compounds 3 and 4 as well as the polymers P2e and P2e_Pd. The structures are depicted under the table.

^{*a*} difference to 100 %. ^{*b*} mass fraction of Pd assuming 0.5 (PdCl₄²⁻) as the counter ion per complex.









P2e_Pd

Static Light Scattering (SLS) Measurements

SLS provides information on the time-averaged properties of the system. The apparent weight-averaged molar mass (M_m) can be obtained by the Debye relationship:

$$\frac{K \cdot c}{I_r} = \frac{1}{M_m} \cdot \left(1 + \frac{R_g^2 \cdot q^2}{3}\right) + 2 \cdot A_2 \cdot c$$
 Eq. S1

where c is the concentration (in g·L⁻¹), I_r is the relative excess scattering intensity, K gathered optical parameters, R_g is the radius of gyration, q is the scattering wave vector, and A_2 is the second virial coefficient. The absolute weight-averaged molar mass, M_m , was obtained by extrapolating $\frac{K \cdot c}{I_r}$ values to q = 0 and c = 0 according to **Eq. S1** (see **Figures S6** for the Zimm-Plot of polymers **P2e** in dimethyl acetamide). SLS obtained molar weights are collected in **Table 2**.



Figure S6. Zimm-plot obtained by SLS measurement for polymer P2e dissolved in DMAc for 5 concentrations ranging from 0.5 to 4 $g \cdot L^{-1}$.

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