Instrumentation and materials

All manipulations were carried out using Schlenk techniques under an atmosphere of argon. 2,4-pentandione (99%), 4,4-diaminodiphenylmethane (97%), acetophenone, 4,4'-[(9-Fluorenylidene)dianiline, ethanol (90%) was obtained from ABCR. Hydrogen chloride 1.25 M in ethanol was purchased by Acros. Cyclohexene oxide was obtained from ABCR 98% and was distilled over CaH₂ prior to use. Toluene was obtained from the solvent purification system MBraun (typ: MB SPS).

NMR-spectra were recorded on a Bruker ARX-300 spectrometer. All spectra were referenced to TMS or deuterated solvent as an internal standard.

GPC was performed with a PolymerLaboratoriesGPC-50 Plus chromatograph running with HPLC-grade in THF at a flow rate of 1 mL/min and PLgel-Mixed-C as the Column Set (by Varian, Inc. Company). Polystyrene standards were used for calibration.

In-situ IR-measurements were carried out on Mettler-Toledo system under argon atmosphere.

Zn(N(SiMe₃)₂)₂ and complex 1 and 3 were prepared according to the literature procedure.

Ligand and complex synthesis

(2Z,2'Z,4E,4'E)-4,4'-(((9H-Fluorene-9,9-diyl)bis(4,1-phenylene))bis(azanylylidene))bis(pent-2-en-2-ol)

4,4'-[(9-Fluorenylidene)dianiline (2.50 g, 7.17 mmol, 1.0 eq.) and acetylacetone (1.47 ml, 14.35 mmol, 2.0 eq.) were dissolved in toluene (30 ml). p-Toluenesulfonic acid was added and the resulting reaction mixture was heated to 115 °C with a DeanStark trap for three hours. The reaction mixture was washed with saturated NaHCO₃-solution and the solvent was removed under reduced pressure. The product was obtained as a yellow solid and used without further purification (3.52 g, 96%).

¹H NMR (300 MHz, CDCl₃, 292 K): δ [ppm] = 12.37 (s, 2H), 7.00 (m, 8H), 5.13 (s, 2H), 2.04 (s, 3H), 1.91 (s, 3H).

¹³C NMR (75.5 MHz, CDCl₃, 292 K): δ [ppm] = 196.2, 160.1, 150.7, 142.8, 140.1, 137.4, 128.8, 127.9, 127.7, 126.0, 124.2, 120.4, 97.8, 64.6, 29.2, 20.0.

Bd(fluorenyl):H₂

Bd(fluorenyl)₂H₂/2 (1.00 g, 1.71 mmol, 1.0 eq.) and 4,4’-[(9H-fluoren-9,9-diyl)dibenzenammonium chloride (0.72 g, 1.71 mmol, 1.0 eq.) were dissolved in hexafluoro-2-propanol (8.0 ml). Subsequent the reaction mixture was heated to 60 °C over night. The solvent is removed under reduced pressure. The residual solid was dissolved in methylene chloride and washed with saturated NaHCO₃-solution. The solvent is removed under reduced pressure to yield a yellow solid. After adding a small amount of methylene chloride (5 ml) the product precipitated and was finally recrystallized from toluene (0.30 g, 17%).

¹H NMR (300 MHz, THF 292 K): δ [ppm] = 12.37 (s, 2H), 7.00 (m, 8H), 5.13 (s, 2H), 2.04 (s, 3H), 1.91 (s, 3H).

¹³C NMR (75.5 MHz, THF 292 K): δ [ppm] = solubility not sufficient enough

EA (für C₆₀H₄₈N₄ + 2 toluene):
calculated [%]: C 87.74, H 6.15, N 6.11
found [%]: C 87.35 , H 5.86 , N 6.79
Bd(fluorenyl)H₂ (0.23 g, 0.23 mmol, 1.0 eq.) was dissolved in toluene (20 ml) and bis[bis(trimethylsilyl)amido]zinc (0.18 ml, 0.46 mmol, 2.0 eq.) was added at RT. The yellow suspension was heated to 90 °C for 24 hours. The solvent was removed in vacuo. The residue was washed with diethylether (20 ml) and the product is obtained as a yellow powder. (0.11 g, 35%) 

**¹H NMR (300 MHz, CDCl₃, 292 K):** δ[ppm] = 7.80 (m, 8H), 7.42 (m, 8H), 7.14 (m, 8H), 6.62 (m, 8H), 4.93 (s, 2H), 1.88 (s, 12H), -0.17 (s, 36H).

**EA (für C₄₈H₃₆F₆N₄):**

- **calculated [%]:** C 67.85, H 6.48, N 6.59
- **found [%]:** C 66.27 H 6.53, N 5.98

Diisopropylamine (0.06 ml, 0.41 mmol, 2.5 eq.) was dissolved in THF at 0°C. n-BuLi (0.25 mL, 0.41 mmol, 2.5 eq.) was dropwise added and the reaction mixture was stirred for two hours at ambient temperature. Subsequently, the addition of BdmH₂ (0.10 g, 0.16 mmol, 1.0 eq.) took place. After two more hours p-toluenesulfonyl chloride (0.08 g, 0.41 mmol, 2.5 eq.) was added and stirred for 24 hours at room temperature. The reaction mixture was dissolved in methylene chloride. After washing with saturated NaCl-solution, the solid was recrystallized from toluene (0.06 g, 61%).

**¹H-NMR (300 MHz, CDCl₃, 295 K):** δ[ppm] = 13.20 (s, 2H, NH), 7.02 (d, ³J = 8.1 Hz, 8H, C₆H), 6.67 (d, ³J = 8.1 Hz, 8H, C₆H), 3.77 (s, 4H, CH₂), 2.24 (s, 12H, CH₃).

**¹³C-NMR (75.5 MHz, CDCl₃, 294 K):** δ[ppm] = 158.2, 142.2, 138.1, 128.4, 123.6, 103.9, 41.6, 18.9.

**EA (für C₄₅H₄₂N₆ mit Toluol):**

- **calculated [%]:** C 72.84, H 5.77, N 9.44
- **found [%]:** C 72.76, H 5.86, N 9.38
Bdm(Cl)_2H_2 (0.10 g 0.15 mmol, 1.0 eq.) was suspended in toluene (20 ml) and bis[bi(trimethylsilyl)amido]zinc (0.12 ml, 0.30 mmol, 2.0 eq.) was added at RT. The yellow suspension was heated to 90 °C for 24 hours. The solvent was removed in vacuo. The residue was washed with diethylether (20 ml) and the product is obtained as yellow powder. (0.08 g, 0.08 mmol, 51%)

^1H-NMR (300 MHz, CDCl_3, 295 K): δ [ppm] = 7.01 (s br, 16, C_arH), 3.76 (s, 4H, CH_2), 2.32 (s, 12H, CH_3), -0.31 (s br, 36H)
EA (für C_45H_42N_6 mit Toluol): calculated [%]: C 55.27, H 6.57, N 8.06
found [%]: C 54.30, H 6.66, N 7.87

Diisopropylamine (0.28 ml, 2.03 mmol, 2.5 eq.) was dissolved in THF (20 ml) at room temperature. n-BuLi (0.81 mL, 2.03 mmol, 2.5 eq.) was dropwise added and the reaction mixture was stirred for two hours. Subsequently, the addition of BdmH_2 (0.50 g, 0.81 mmol, 1.0 eq.) took place. After two more hours p-toluenesulfonyl chloride (0.37 g, 2.03 mmol, 2.5 eq.) was added and stirred for 24 hours at room temperature. The orange solid was filtered and dissolved in methylene chloride. After washing with saturated NaHCO_3-solution, the solid was recrystallized from toluene (0.76 g, 65%).

^1H-NMR (300 MHz, CDCl_3, 297 K): δ [ppm] = 14.94 (s, 2H, N-H), 7.13 – 7.08 (d, ^3J = 8.35 Hz, 8H, C-H), 6.76 – 6.81 (d, ^3J = 8.35 Hz, 8H, C-H), 3.85 (s, 4H, CH_2), 2.33 (s, 12H, CH_3).

^13C-NMR (75.5 MHz, CDCl_3, 294 K): δ [ppm] = 164.6, 140.6, 140.0, 129.2, 128.4, 123.9, 122.0, 81.0, 41.7, 19.0.
EA (für C_58H_68F_6N_6Si_4Zn_2): calculated [%]: C 82.29, H 6.64, N 11.07
found [%]: C 81.36, H 6.71, N 10.94

Bdm(CN)_2H_2 (0.09 g, 0.15 mmol, 1.0 eq.) was suspended in toluene (20.0 mL) and bis[bi(trimethyl-silyl)amide]zinc (0.12 ml, 0.30 mmol, 2.0 eq.) was added. The yellow suspension was heated to 90 °C for 24 hours. The suspension was separated into a solid and a solution which is dried under reduced pressure. Both fractions were washed with diethylether and dried. Both samples were analytically identical. Due to low solubility NMR spectroscopy was not possible.

EA (für C_58H_68Fe_6Si_6Zn_2): calculated [%]: C 58.63, H 6.69, N 10.94
found [%]: C 59.58, H 6.72, N 10.58
(N,N')-4,4'-Methylene-bis(N-(1-phenylethylidin)anilin) (6)

4,4-Diaminodiphenylmethane (5.00 g, 25.22 mmol, 1.0 eq.) was dissolved in methylene chloride (100 mL) and molecular sieve (3 Å) is added, following the addition of acetophenone (5.91 mL, 50.44 mmol, 2.0 eq.). The reaction was stored at room temperature for two days. After filtration and removal of the solvents under reduced pressure, recrystallization in ethanol led to the final product (5.94 g, 58%).

1H-NMR (300 MHz, CDCl3, 297 K): δ [ppm] = 7.93-8.01 (m, 4H), 7.48-7.38 (m, 6H), 7.18 (d, 3J=8.4 Hz, 4H), 6.74 (d, 3J=8.4 Hz, 4H), 3.97 (s, 2H), 2.25 (s, 6H).

13C-NMR (75.5 MHz, CDCl3, 294 K): δ [ppm] = 165.9, 149.6, 139.62 (s), 136.5, 133.3, 130.7, 129.7, 128.6, 127.4, 119.8, 115.6, 41.0, 17.7.

EA (für C36H33Cl2N2): calculated [%]: C 86.53, H 6.51, N 6.96
found [%]: C 86.14, H 6.61, N 7.04

n',n''-(4,4'-Methylene-bis(4,1-phenylene))bis(2,2,2-trifluoroacetimidoyl chloride) (7)

Triphenylphosphine (34.60 g, 131.92 mmol, 4.8 eq), triethylamine (7.40 mL, 54.97 mmol, 2.0 eq) were dissolved in tetrachloromethane (150 mL). Trifluoroacetic acid (3.27 mL, 43.97 mmol, 1.6 eq.) is dropwise added at 0 °C and stirred for 20 min. Afterwards, 4,4-diaminodiphenylmethane (5.45 g, 37.48 mmol, 1.0 eq.) was added and the reaction mixture was stirred overnight at 85 °C. After removing the solvents under reduced pressure, the reaction mixture was filtrated and washed several times with hexane. The solvent were removed and the raw product was distilled (1·10⁻¹ mmbar, 190 °C) to receive a clear solution (3.12 g, 29%).

1H-NMR (300 MHz, CDCl3, 297 K): δ [ppm] = 7.33-7.24 (m, 2H), 7.16-7.08 (m, 2H), 4.06 (s, 1H).

13C-NMR (75.5 MHz, CDCl3, 294 K): δ [ppm] = 141.7, 140.4, 131.4 (q, 3J = 43.0 Hz), 129.8, 121.6, 117.1 (q, 1J = 277.0 Hz), 41.2.

EA (für C36H33Cl2N2): calculated [%]: C 47.80, H 2.36, N 6.56
found [%]: C 47.71, H 2.28, N 6.41

n-BuLi (11.9 mL, 29.88 mmol, 4.0 eq.) was mixed with diisopropylamine (4.20 mL, 29.88 mmol, 4.0 eq.) in THF (100 mL) at -78 °C. After two hours 4,4'-methen-bis-(N-(phenyl-2-ylidin)aniline) (3.02 g, 7.45 mmol, 1.0 eq.) was added and the reaction mixture is stirred for 16 hours at room temperature before the addition N',N''-(4,4'-methylen-bis-(4,1-phenylene))bis(2,2,2-trifluoroacetimidoylchlorid) (3.00 g, 7.45 mmol, 1 eq.) was conducted. After two more hours the reaction was stopped via addition of saturated NH4Cl-solution. The organic phase was separated, dried over magnesium sulfate and filtered. The organic solvent was removed under reduced pressure, following a recrystallization in acetone and finally in acetonitrile (0.18 g, 3%).

1H-NMR (300 MHz, CDCl3, 297 K): δ [ppm] = 12.76 (s, 2H), 7.44-7.50 (m, 4H), 7.30-7.40 (m, 6H), 7.15 (d, 1J = 8.3 Hz, 4H), 6.84-6.78 (m, 8H), 6.52 (d, 3J = 8.3 Hz, 4H), 5.58 (s, 2H), 3.83 (s, 2H), 3.62 (s, 2H).

13C-NMR (75.5 MHz, CDCl3, 294 K): δ [ppm] = 158.7, 149.9, 149.5, 144.4, 139.4, 138.8, 138.4, 135.8, 129.9, 129.3, 128.8, 128.5, 123.5, 122.0, 94.2, 41.9, 41.0.

EA (für C36H33FeNa): calculated [%]: C 73.01, H 4.53, N 7.40
found [%]: C 72.60, H 4.46, N 7.63
Bdm(CF₃)₂(Ph)₂(Zn(N(TMS))₂)₂ (9)

Bdm(CF₃)₂(Ph)₂H₂ (0.25 g, 0.33 mmol, 1.0 eq.) was dissolved in toluene (50.0 ml) and bis[bis(trimethylsilyl)amido]zinc (0.26 mL, 0.67 mmol, 2.0 eq.) was added at RT. The yellow solution was heated to 90 °C for 24 hours. The solvent was removed in vacuo. The residue was washed with pentane (10 ml) and the product is obtained as a orange powder (0.30 g, 31%).

¹H-NMR (300 MHz, CDCl₃, 295 K): δ [ppm] = 7.43-7.46 (m, 4H), 7.38 – 7.21 (m, 6H), 7.03 (s, 4H), 6.81 (m, 8H), 6.57 (m, 4H), 5.70 (s, 2H), 3.80 (s, 2H), 3.54 (s, 2H). -0.27 (s br., 36H)

¹³C-NMR (75.5 MHz, CDCl₃, 294 K): δ [ppm] = 169.7, 145.7, 144.6, 139.5, 138.7, 138.3, 130.5, 130.0, 129.2, 128.9, 128.4, 124.9, 123.6, 41.8, 4.86

EA (für C₈₆H₆₈F₆N₆Si₄Zn₂):

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Copolymerization with in situ IR
Catalyst was dissolved in cyclohexene oxide (5.0 mL, 49.4 mmol, 1.0 eq.) and toluene (5 – 7.5 mL). The reaction mixture was put in the preheated autoclave and pressurized with carbon dioxide (1, 10, 30, 40 bar). The reaction was terminated after the appropriate reaction time by releasing the gaseous CO\textsubscript{2} and addition of methanol (1.0 mL) and methylene chloride (10 mL). The organic phase was washed with HCl (1 M) and dried with Na\textsubscript{2}SO\textsubscript{4}. After evaporation of the solvent the poly(carbonate) is dissolved in a small amount of methylene chloride and precipitated via addition of methanol. Finally, the poly(carbonate) is dried in an oven to constant weight.

Poly(cyclohexene carbonate)
\[^{1}\text{H}-\text{NMR} (300\text{MHz, CDCl}_3, 292K): \delta [\text{ppm}] = 4.58 (s, 2 H), 1.30 - 2.04 (m, 8 H).\]

Poly(cyclohexene oxide)
\[^{1}\text{H}-\text{NMR} (300\text{MHz, CDCl}_3, 292K): \delta [\text{ppm}] c = 3.50 (s, br. s, 2 H);\]

Copolymerization at one atmosphere CO\textsubscript{2}
Catalyst was dissolved in cyclohexene oxide (2.5 mL, 24.7 mmol, 1.0 eq.) and put into a pressure flask. Afterwards, CO\textsubscript{2} is bubbled through the reaction mixture for 4 min, before the pressure of 1 bar CO\textsubscript{2} is adjusted. After a reaction time of 1 h at 100°C, the reaction was terminated by adding methanol (1.0 mL) and methylene chloride (10 mL). The organic phase was washed with HCl (1 M) and dried with Na\textsubscript{2}SO\textsubscript{4}. After evaporation of the solvent the poly(carbonate) is dissolved in a small amount of methylene chloride and precipitated via addition of methanol. Finally, the poly(carbonate) is dried in an oven to constant weight.

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[a] Copolymerizations were conducted in a preheated schlenk flask for 60 minutes at a catalyst loading of catalyst/epoxide of 1/4000 in neat cyclohexene oxide at one atmosphere CO\textsubscript{2} pressure and 100°C (1 bar CO\textsubscript{2}) [b] The turnover number (TON) is calculated by the number of moles of consumed epoxide divided by the moles of catalyst. [c] TOF = TON/time

Homopolymerization of cyclohexene oxide
Catalyst was dissolved in cyclohexene oxide (2.5 mL, 24.7 mmol, 1.0 eq.) and put into a pressure flask. After a reaction time of 1 h at 100°C, the reaction was terminated by adding methanol (1.0 mL) and methylene chloride (10 mL). The organic phase was washed with HCl (1 M) and dried with Na\textsubscript{2}SO\textsubscript{4}. After evaporation of the solvent the poly(carbonate) is dissolved in a small amount of methylene chloride and precipitated via addition of methanol. Finally, the poly(carbonate) is dried in an oven to constant weight.

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[a] Copolymerizations were conducted in a preheated schlenk flask for 60 minutes at a catalyst loading of catalyst/epoxide of 1/4000 in neat cyclohexene oxide at 100°C [b] The turnover number (TON) is calculated by the number of moles of consumed epoxide divided by the moles of catalyst. [c] TOF = TON/time
GPC-Reports (of table 1)

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Concentration: mg/ml
Column Set: PLgel-Mixed-C

Analysis Using Method: RI-Auswertung
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Calibration Used: 22.03.2013 13:51:19
Calibration Type: Narrow Standard
Curve Fit Used: 3
Calibration Curve: y = 11.880254 - 0.627940x + 0.009126x^2 - 0.000197x^3

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![Graph and Table Data]

Entry 11:

![Graph and Table Data]