

## Supporting Information

# Reactivity Enhancement of Single Component Nickel-Salicylaldiminato-Polymerization Catalysts in Homogeneous Aqueous SDS-Solution

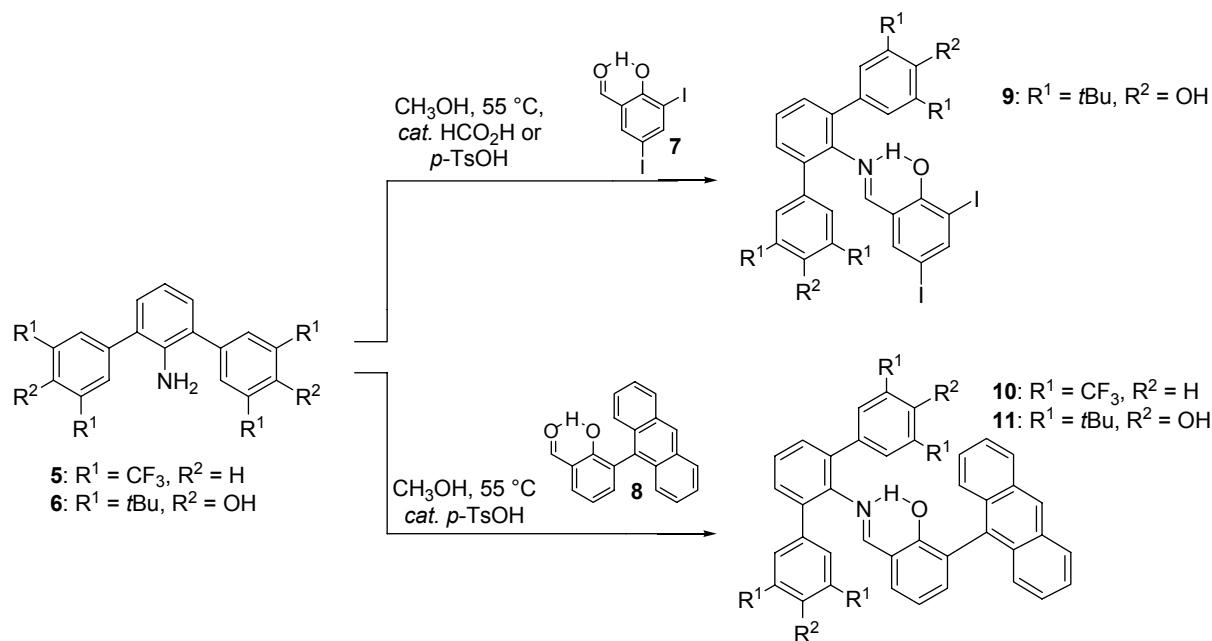
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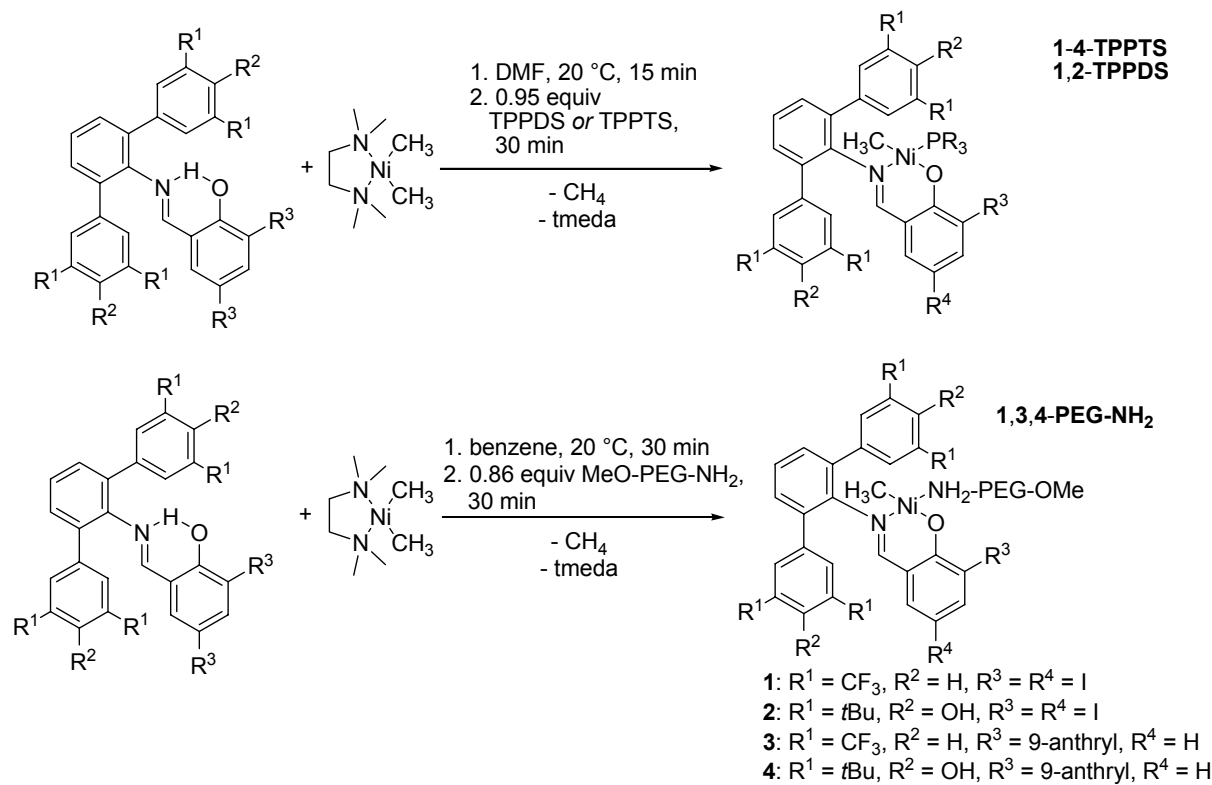
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Scheme S1. Synthesis of ligands 9–11

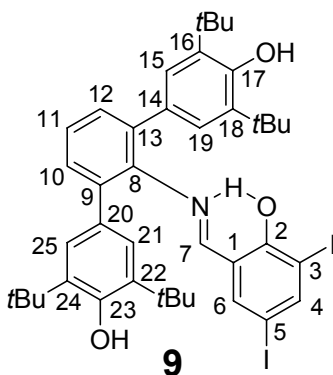
Scheme S2. Synthesis of complexes 1–4-TPPTS and 1,2-TPPDS and complexes 1,3,4-H<sub>2</sub>N-PEG

**General Experimental Considerations and Materials.** All manipulations were carried out using standard Schlenk, vacuum, and glovebox techniques under argon or nitrogen. DMF, methanol- $d_4$ , dms $o$ - $d_6$  were thoroughly degassed by several freeze-pump-thaw cycles and stored in a nitrogen atmosphere glovebox. Benzene and benzene- $d_6$ , were dried over sodium, vacuum transferred, and stored in a nitrogen atmosphere glovebox. Diethyl ether was distilled from purple sodium benzophenone ketyl under argon prior to use. Water was thoroughly freed from oxygen by distillation under a constant stream of nitrogen. Toluene was refluxed under argon and distilled from sodium prior to use. (tmeda)NiMe $_2$  was purchased from M $Ca$ t and used as received. TPPTS was purchased from Aldrich and used as received. MeO-PEG-NH $_2$  was purchased from Fluka and used as received ( $M_n$  = ca 2320 g mol $^{-1}$  was determined by  $^1\text{H}$  NMR experiments with a relaxation delay of 15 s based on the integration of the methyl vs. all methylene signals). Salicylaldimines **9–11** and complex **1-pyr** were synthesized in analogy to known procedures.<sup>1</sup> NMR Spectra were recorded on a Varian Inova 400 or a Bruker Avance DRX 600 instrument.  $^1\text{H}$  chemical shifts were referenced to residual protiated solvent.  $^{31}\text{P}$  chemical shifts were referenced to an external 85% H $_3\text{PO}_4$  standard. The assignment of chemical shifts for new complexes is based on  $^1\text{H}$ -,  $^1\text{H}, ^1\text{H}$ -gCOSY,  $\{^1\text{H}\}^{13}\text{C}$ -, DEPT135,  $^1\text{H}, ^{13}\text{C}$ -gHMQC,  $^1\text{H}, ^{13}\text{C}$ -gHMBC, and if applicable  $\{^1\text{H}\}^{31}\text{P}$  NMR experiments. Elemental analyses were carried out at the Department of Chemistry at the University of Konstanz. Ethylene of 3.5 grade supplied by Gerling Holz + Co was used without further purification. Sodium dodecyl sulfate (SDS) was purchased from Fluka and used without purification. Molecular weights of obtained

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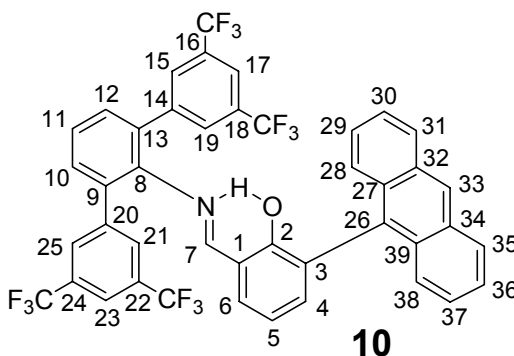
(1) Zuideveld, M.; Wehrmann, P.; Röhr, C.; Mecking, S. *Angew. Chem. Int. Ed.* **2004**, *43*, 869–873.

polyethylenes were determined by HT-GPC vs. linear polyethylene standards on a PL220 instrument equipped with mixed B columns using trichlorobenzene/0.0125% BHT at 160 °C. Differential scanning calorimetry (DSC) of precipitated polymers was measured on a Netzsch DSC 204 F1 with a heating/cooling rate of 10 °C min<sup>-1</sup>. DSC data are reported as second heats. Dynamic light scattering (DLS) on diluted polyethylene dispersions was performed on a Malvern Nano-ZS ZEN 3600 particle sizer (173° back scattering). Repeated measurements after up to 12 months exhibit volume average size deviations in the range of 1-2 nm with respect to the original value. <sup>1</sup>H and <sup>13</sup>C NMR analyses of obtained polyethylenes were conducted in tetrachloethane-*d*<sub>2</sub> at 130 °C in presence of 0.5 w% Cr(acac)<sub>3</sub> as relaxation aid.



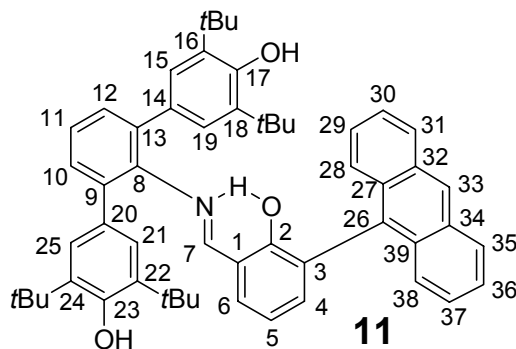
**Salicylaldimine 9.** To a solid mixture of 2,6-bis[4-hydroxy-3,5-di(*tert*-butyl)phenyl]aniline (**6**) (1 mmol, 502 mg) and 2-hydroxy-3,5-diiodobenzaldehyde (**7**) (1.02 mmol, 381 mg) was added methanol (6 ml) and formic acid (5 mg) in a 50 mL flask. The mixture was heated to 55 °C while all material dissolved and stirred for 16 h at 55 °C. After removal of the solvent under reduced pressure an orange oil resulted which solidified upon standing. The orange solid was transferred to a cooled glass-frit (-20 °C), washed with cold methanol (4 × 2 ml, -20 °C), and dried under high vacuum (10<sup>-3</sup> mbar) to leave 713 mg (0.83 mmol, 83 % based on aniline **6**) of analytically pure salicylaldimine **9**. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, 25 °C): δ 13.99 (s br, 1H, 2-OH), 7.97 (d,

$^4J_{\text{HH}} = 1.9$  Hz, 1H, 4-H), 7.70 (s, 1H, 7-H), 7.44 (d,  $^3J_{\text{HH}} = 7.8$  Hz, 2H, 10- and 12-H), 7.36 (t,  $^3J_{\text{HH}} = 7.8$  Hz, 1H, 11-H), 7.13 (s, 4H, 15-, 19-, 21-, and 25-H), 6.96 (d,  $^4J_{\text{HH}} = 1.9$  Hz, 1H, 6-H), 5.21 (s, 2H, 17- and 23-OH), 1.36 (s, 36H, 4 × *t*Bu).  $^{13}\text{C}\{^1\text{H}\}$  NMR (150 MHz,  $\text{CDCl}_3$ , 25 °C):  $\delta$  166.3 ( $\text{C}_q$ , C7), 159.9 ( $\text{C}_q$ , C2), 152.9 ( $\text{C}_q$ , C17 and C23), 148.6 (CH, C4), 143.7 ( $\text{C}_q$ , C8), 139.6 (CH, C6), 135.8 ( $\text{C}_q$ , C16, C18, C22, and C24), 135.7 and 129.9 ( $\text{C}_q$  each, C9, C13, C14, and C20), 129.4 (CH, C10 and C12), 126.8 (CH, C15, C19, C21, and C25), 126.4 (CH, C11), 120.4 ( $\text{C}_q$ , C1), 86.8 ( $\text{C}_q$ , C5), 79.2 ( $\text{C}_q$ , C3), 34.3 ( $\text{C}_q$ , 4 × *t*Bu), 30.2 ( $\text{CH}_3$ , 4 × *t*Bu). Elemental analysis calcd for  $\text{C}_{41}\text{H}_{49}\text{NO}_3\text{I}_2$  (857.7 g mol $^{-1}$ ): C: 57.42, H: 5.76, N: 1.63. Found C: 57.61, H: 5.90, N: 1.55.



**Salicylaldimine 10.** To a solid mixture of 2,6-bis[3,5-di-(trifluoromethyl)-phenyl]aniline (**5**) (1 mmol, 517 mg) and 2-hydroxy-3-(9-anthryl)benzaldehyde (**8**) (284 mg, 0.95 mmol) was added methanol (6 ml) and *p*-toluenesulfonic acid hydrate (3 mg) in a 8 mL screw-cap vial. The mixture was heated to 55 °C while nearly all material dissolved and stirred for 16 h at 55 °C. The resulting mixture was cooled to 0 °C and the pale yellow precipitate was collected by filtration, washed with cold methanol (3 × 3 mL, -20 °C), and dried under high vacuum (10 $^{-3}$  mbar, 4 h) to give 694 mg (0.87 mmol, 92 % based on aldehyde **8**) of analytically pure salicylaldimine **10**.  $^1\text{H}$  NMR (399.8 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  11.86 (s, 1H, OH), 8.16 (s, 1H, 33-H), 7.79 (vd,  $J_{\text{HH}} = 8.8$  Hz, 4H, 28-, 31-, 35-

and 38-H), 7.57 (s, 2H, 17- and 23-H), 7.54 (s, 4H, 15-, 19-, 21- and 25-H), 7.43 and 7.29 (vt each,  $J_{\text{HH}} = 8.8$  Hz, 2:2H, 29-, 30-, 36- and 37-H), 7.06 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 2.0$  Hz, 1H, 4-H), 7.03 (s, 1H, 7-H), 6.87 (m, 3H, 10-12-H), 6.53 (vt,  $J_{\text{HH}} = 7.6$  Hz, 1H, 5-H), 6.50 (dd,  $^3J_{\text{HH}} = 7.6$  Hz,  $^4J_{\text{HH}} = 2.0$  Hz, 1H, 6-H).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{C}_6\text{D}_6$ , 25 °C):  $\delta$  171.2 (CH, C7), 160.1 ( $\text{C}_q$ , C2), 145.8 ( $\text{C}_q$ , C8), 141.0 and 131.6 ( $\text{C}_q$  each, C9, C13, C14 and C20), 138.1 (CH, C4), 132.4 ( $\text{C}_q$ , C26), 132.2 (CH, C6), 132.0 and 131.0 ( $\text{C}_q$  each, C27, C32, C34 and C39), 131.8 ( $\text{C}_q$ , q,  $^2J_{\text{CF}} = 33$  Hz, C16, C18, C22 and C24), 131.0 (CH, C10 and C12), 130.3 (CH, C15, C19, C21 and C25), 128.9 and 126.8 (CH each, C28, C31, C35 and C38), 127.9 ( $\text{C}_q$ , C3), 127.6 (CH, C33), 126.4 (CH, C11), 125.6 and 125.3 (CH each, C29, C30, C36 and C37), 123.7 ( $\text{C}_q$ , q,  $^1J_{\text{CF}} = 273$  Hz, 4  $\times$   $\text{CF}_3$ ), 120.9 (CH, m, C17 and C23), 119.3 (CH, C5), 118.0 ( $\text{C}_q$ , C1). Elemental analysis calcd for  $\text{C}_{43}\text{H}_{23}\text{NOF}_{12}$  (797.6 g mol $^{-1}$ ): C: 64.75, H: 2.91, N: 1.76. Found C: 64.92, H: 3.00, N: 1.50.



**Salicylaldimine 11.** To a solid mixture of 2,6-bis[4-hydroxy-3,5-di(*tert.*-butyl)phenyl]aniline (**6**) (1 mmol, 502 mg) and 2-hydroxy-3(9-anthryl)benzaldehyde (**8**) (284 mg, 0.95 mmol) was added methanol (6 ml) and *p*-toluene sulfonic acid hydrate (3 mg) in a 8 mL screw-cap vial. The mixture was heated to 55 °C while nearly all material

dissolved and stirred for 16 h at 55 °C. The resulting mixture was cooled to 0 °C and the pale yellow precipitate was collected by filtration, washed with cold methanol (3 × 3 mL, -20 °C), and dried under high vacuum (10<sup>-3</sup> mbar, 4 h) to give 686 mg (0.88 mmol, 92 % based on aldehyde **8**) of analytically pure salicylaldimine **11**. <sup>1</sup>H NMR (399.8 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 13.12 (s, 1H, 2-OH), 8.24 (s, 1H, 33-H), 7.87 and 7.79 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.86 (s, 1H, 7-H), 7.48 (d, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 2H, 10- and 12-H), 7.38 (s, 4H, 15-, 19-, 21-, and 25-H), 7.29 (m, 4H, 29-, 30-, 36-, and 37-H), 7.17 (t, <sup>3</sup>J<sub>HH</sub> = 7.7 Hz, 1H, 11-H), 7.03 (dd, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz and <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1H, 4-H), 6.57 (dd, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz and <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1H, 6-H), 6.52 (t, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz, 1H, 5-H), 4.87 (s, 2H, 17- and 23-OH), 1.26 (s, 36H, 4 × *t*Bu). <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, C<sub>6</sub>D<sub>6</sub>, 25 °C): δ 169.4 (CH, C7), 159.9 (C<sub>q</sub>, C2), 153.2 (C<sub>q</sub>, C17 and C23), 145.8 (C<sub>q</sub>, C8), 136.4 and 131.1 (C<sub>q</sub> each, C9, C13, C14, and C20), 136.3 (CH, C4), 136.0 (C<sub>q</sub>, C16, C18, C22, and C24); 133.4, 131.3, and 131.1 (C<sub>q</sub> each, C26, C27, C32, C34, and C39), 132.0 (CH, C6), 129.9 (CH, C10 and C12), 128.8 and 127.5 (CH each, C28, C31, C35, and C38), 127.2 (CH, C15, C19, C21, C25, and C33), 127.0 (C<sub>q</sub>, C3), 126.3 (CH, C11), 125.4 and 125.1 (CH each, C29, C30, C36, and C37), 119.6 (C<sub>q</sub>, C1), 118.5 (CH, C5), 34.4 (C<sub>q</sub>, 4 × *t*Bu), 30.3 (CH<sub>3</sub>, 4 × *t*Bu). Elemental analysis calcd for C<sub>55</sub>H<sub>59</sub>NO<sub>3</sub> (782.1 g mol<sup>-1</sup>): C: 84.47, H: 7.60, N: 1.79. Found C: 84.80, H: 7.90, N: 1.52.

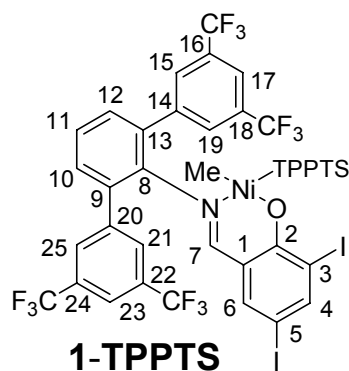
**General Procedure for the Synthesis of Water-soluble ( $\kappa^2$ -N,O) Salicylaldiminato Nickel Methyl Phosphine Complexes 1–4-TPPTS and 1,2-TPPDS.**

To a mixture of (tmeda)NiMe<sub>2</sub> (20.4 mg, 100 μmol) and 105 μmol of the respective salicylaldimine in a septum capped Schlenk tube was added DMF (2.0 mL) via syringe at 20 °C with stirring under nitrogen. Rapid reaction was evident by fast evolution of methane which ceased within 5 min. The resulting orange to red solution was stirred for

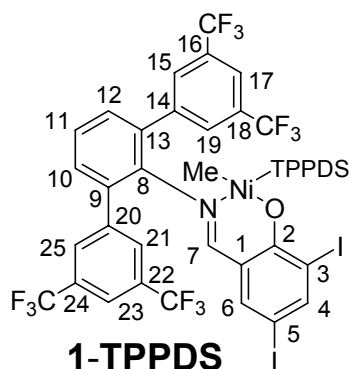


10 min at 20 °C, TPPTS or TPPDS (95  $\mu\text{mol}$ ) and DMF (1 ml) was added and the mixture was stirred for additional 30 min. The solvent was carefully removed under vacuum ( $10^{-3}$  mbar), the residue suspended in diethyl ether (5 mL) and transferred to a gas tight centrifugation vial. The suspension was repeatedly centrifuged, the supernatant removed and the orange solid redispersed with 5 mL portions diethyl ether until the supernatant remained colorless. Analytically pure samples of complexes **1–4** were obtained after removal of the residual solvent under high vacuum ( $10^{-3}$  mbar). Complexes **2–4-TPPTS** were obtained as DMF adducts. Dependent on the solvent used all TPPTS- and TPPDS-complexes dissociate to variable degrees in solution. Except for **4-TPPTS** which in  $\text{dms-}d_6$  is nearly completely dissociated, NMR data is given for undissociated phosphine complexes in  $\text{CD}_3\text{OD}$ .

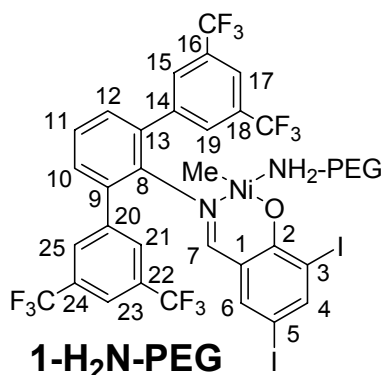
**General Procedure for the Synthesis of Water-soluble ( $\kappa^2\text{-N,O}$ ) Salicylaldiminato Nickel Methyl  $\text{H}_2\text{N-PEG}$  Complexes **1,3,4- $\text{H}_2\text{N-PEG}$** . To a mixture of  $(\text{tmeda})\text{NiMe}_2$  (20.4 mg, 100  $\mu\text{mol}$ ) and 105  $\mu\text{mol}$  of the respective salicylaldimine in a septum capped Schlenk tube was added benzene (4 mL) via syringe at 20 °C under nitrogen. Rapid reaction was evident by fast evolution of methane which ceased within 5 min. The resulting orange to red solution was stirred for 10 min at 20 °C, then a solution of  $\text{MeO-PEG-NH}_2$  ( $M_n = \text{ca } 2320 \text{ g mol}^{-1}$ , 200 mg, ca. 86  $\mu\text{mol}$ ) in benzene (4 mL) was added by syringe and the mixture was stirred for additional 30 min. After sublimation of the frozen solvent ( $-5^\circ\text{C}$ ) the residue was dispersed in diethyl ether (8 mL), the solid collected by filtration and carefully washed with diethyl ether ( $3 \times 5 \text{ ml}$ ). After removal of residual solvent under high vacuum ( $10^{-3}$  mbar) analytically pure samples of complexes **1,3,4- $\text{H}_2\text{N-PEG}$**  were obtained.**



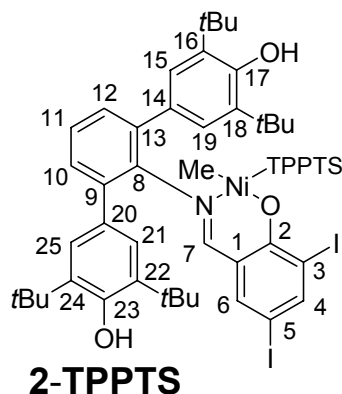
**1-TPPTS.** Following the general procedure for phosphine complexes 133 mg (88  $\mu\text{mol}$ , 93 % based on TPPTS) of compound **1-TPPTS** were obtained as orange powder.  $^1\text{H}$  NMR (399.8 MHz,  $\text{CD}_3\text{OD}$ , 298K):  $\delta$  8.18 (d,  $^4J_{\text{PH}} = 7.7$  Hz, 1H, 7-H), 8.13 (s, 4H, 15-, 19-, 21-, and 25-H), 8.08 (s, 2H, 17- and 23-H), 7.89 (m, 6H, TPPTS), 7.74 (vd,  $J = 8.0$  Hz, 3H, TPPTS), 7.71 (d,  $^4J_{\text{HH}} = 1.9$  Hz, 1H, 4-H), 7.57 (m, 3H, 10–12-H), 7.42 (vt,  $J = 7.9$  Hz, 3H, TPPTS), 7.22 (d,  $^4J_{\text{HH}} = 1.9$  Hz, 6-H), -1.50 (d,  $^3J_{\text{PH}} = 8.0$  Hz, Ni- $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{CD}_3\text{OD}$ , 298 K):  $\delta$  170.2 (CH, C7), 164.1 ( $\text{C}_q$ , C2), 151.2 (CH, C4), 150.5 ( $\text{C}_q$ , C8), 146.3 ( $\text{C}_q$  br., TPPTS), 143.2 (CH, C6), 143.1 ( $\text{C}_q$ , C9 and C13), 139.4 (CH, d,  $J_{\text{PC}} = 19.7$  Hz, TPPTS), 134.8 ( $\text{C}_q$ , C14 and C20), 132.8 ( $\text{C}_q$ , q,  $^2J_{\text{CF}} = 33.2$  Hz, C16, C18, C22, and C24), 132.3 (CH, C10 and C12), 132.0 (CH, C15, C19, C21, and C25), 131.4 (CH, TPPTS), 129.3 (CH, TPPTS), 129.2 (CH, TPPTS), 128.4 (CH, C11), 124.8 ( $\text{C}_q$ , q,  $^1J_{\text{CF}} = 271$  Hz, 4  $\times$   $\text{CF}_3$ ), 122.4 (CH, m, C17 and C23), 120.6 ( $\text{C}_q$ , C1), 96.9 ( $\text{C}_q$ , C5), 73.4 ( $\text{C}_q$ , C3), -7.78 ( $\text{CH}_3$ , d,  $^2J_{\text{PC}} = 37$  Hz, Ni- $\text{CH}_3$ ), *ipso*-C TPPTS not detected.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.8 MHz,  $\text{CD}_3\text{OD}$ , 298K):  $\delta$  32.3. Elemental analysis calcd for  $\text{C}_{48}\text{H}_{27}\text{NO}_{10}\text{S}_3\text{Na}_3\text{PNi}$  (1514.4 g  $\text{mol}^{-1}$ ): C: 38.07, H: 1.80, N: 0.92. Found C: 37.67, H: 2.11, N: 0.83.



**1-TPPDS.** Following the general procedure for phosphine complexes 119 mg (0.84  $\mu\text{mol}$ , 87 % based on TPPDS) of compound **1-TPPDS** were obtained as orange powder.  $^1\text{H}$  NMR (399.8 MHz,  $\text{CD}_3\text{OD}$ , 298K):  $\delta$  8.11 (d,  $^4J_{\text{PH}} = 8.0$  Hz, 1H, 7-H), 8.07 (s, 4H, 15-, 19-, 21-, and 25-H), 8.00 (s, 2H, 17- and 23-H), 7.72 (m, 4H, TPPDS), 7.66 (d,  $^4J_{\text{HH}} = 2.0$  Hz, 4-H), 7.48 (m, 9H, 10–12-H and TPPDS), 7.27 (m, 3H, TPPDS), 7.15 (d,  $^4J_{\text{HH}} = 2.0$  Hz, 6-H), -1.58 (d,  $^3J_{\text{PH}} = 8.0$  Hz, 3H, Ni- $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{CD}_3\text{OD}$ , 298K):  $\delta$  170.2 (CH, C7), 164.0 ( $\text{C}_q$ , C2), 151.2 (CH, C4), 150.5 ( $\text{C}_q$ , C8), 148.8 ( $\text{C}_q$  br., TPPDS), 143.3 (CH, C6), 143.0 ( $\text{C}_q$ , C9 and C13), 136.0 (CH, TPPDS), 135.9 (CH, TPPDS), 135.8 (CH, TPPDS), 135.7 (CH, TPPDS), 134.7 (CH, TPPDS), 134.5 ( $\text{C}_q$ , C14 and C20), 133.7 ( $\text{C}_q$ ,  $^2J_{\text{CF}} = 33$  Hz, C16, C18, C22, and C24), 132.2 (CH, C10 and C12), 131.9 (CH, C15, C19, C21, and C25), 129.2 (CH, TPPDS), 128.3 (CH, C11), 126.6 (CH, TPPDS), 124.8 ( $\text{C}_q$ , q,  $^1J_{\text{CF}} = 273$  Hz, 4  $\times$   $\text{CF}_3$ ), 122.4 (CH, C17 and C23), 120.7 ( $\text{C}_q$ , C1), 96.4 ( $\text{C}_q$ , C5), 73.3 ( $\text{C}_q$ , C3), -7.9 ( $\text{CH}_3$ , d,  $^2J_{\text{PC}} = 35$  Hz, Ni- $\text{CH}_3$ ), 2  $\times$  *ipso*-C TPPDS not detected.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.8 MHz,  $\text{CD}_3\text{OD}$ , 298K):  $\delta$  30.0. Elemental analysis calcd for  $\text{C}_{48}\text{H}_{28}\text{NO}_7\text{S}_2\text{F}_{12}\text{I}_2\text{Na}_2\text{PNi}$  (1412.31  $\text{g mol}^{-1}$ ): C: 40.82, H: 2.00, N: 0.99. Found C: 40.47, H: 1.88, N: 0.74.

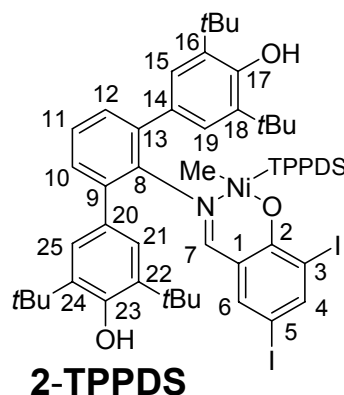


**1-H<sub>2</sub>N-PEG.** Following the general procedure for PEG-complexes 246 mg (ca 81  $\mu\text{mol}$ , ca 94 % based on PEG with  $M_n = \text{ca } 2320 \text{ g mol}^{-1}$ ) of compound **1-H<sub>2</sub>N-PEG** were obtained as red powder.  $^1\text{H NMR}$  (399.8 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta$  8.04 (s, 4H, 15-, 19-, 21, and 25-H), 7.90 (d,  $^4J_{\text{HH}} = 2.0 \text{ Hz}$ , 1H, 4-H), 7.77 (s, 2H, 17- and 23-H), 6.97 (m, 1H, 11-H), 6.87 (m, 2H, 10- and 12-H), 6.72 (d,  $^4J_{\text{HH}} = 2.0 \text{ Hz}$ , 1H, 6-H), 6.48 (s, 1H, 7-H), 3.6–3.2 (s br., 214H, PEG), 3.13 (s, 3H,  $\text{OCH}_3$ ), 3.06 (t,  $^3J_{\text{HH}} = 6.8 \text{ Hz}$ , 2H, PEG), 2.44 (t,  $^3J_{\text{HH}} = 6.8 \text{ Hz}$ , 2H,  $\text{OCH}_2\text{CH}_2\text{NH}_2$ ), 1.00 (t,  $^3J_{\text{HH}} = 6.8 \text{ Hz}$ , 2H,  $\text{OCH}_2\text{CH}_2\text{NH}_2$ ), -1.23 (s, 3H, Ni- $\text{CH}_3$ ),  $\text{NH}_2$  not detected.  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{C}_6\text{D}_6$ , 298 K):  $\delta$  167.0 (CH, C7), 162.9 ( $\text{C}_q$ , C2), 150.0 ( $\text{C}_q$ , C8), 149.8 (CH, C4), 141.8 (CH, C6), 141.4 ( $\text{C}_q$ , C9 and C13), 133.0 ( $\text{C}_q$ , C14 and C20), 131.8 ( $\text{C}_q$ , q,  $^2J_{\text{CF}} = 34 \text{ Hz}$ , C16, C18, C22, and C24), 130.6 (CH, C15, C19, C21, and C25), 123.9 ( $\text{C}_q$ ,  $^1J_{\text{CF}} = 273 \text{ Hz}$ , 4  $\times$   $\text{CF}_3$ ), 121.4 (CH, C17 and C23), 119.8 ( $\text{C}_q$ , C1), 96.9 ( $\text{C}_q$ , C5), 73.0 ( $\text{C}_q$ , C3), 70.8 ( $\text{CH}_2$ , PEG), 58.6 ( $\text{CH}_3$ , PEG- $\text{OCH}_3$ ), 43.0 ( $\text{CH}_2$ ,  $\text{CH}_2\text{NH}_2$ ), -13.0 ( $\text{CH}_3$ , Ni- $\text{CH}_3$ ). Elemental analysis calcd for  $\text{C}_{135}\text{H}_{228}\text{N}_2\text{O}_{53}\text{F}_{12}\text{I}_2\text{Ni}$  ( $3268 \text{ g mol}^{-1}$ ): C: 49.62, H: 7.03, N: 0.86. Found C: 50.00, H: 7.10, N: 0.80.



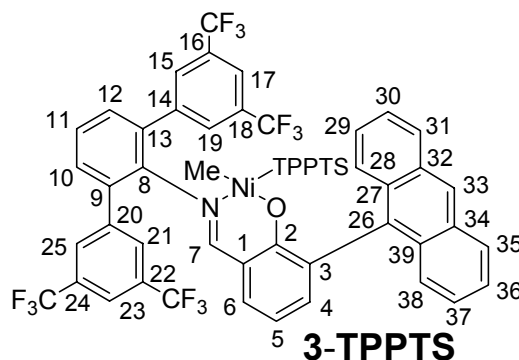
**2-TPPTS • 2 DMF.** Following the general procedure for phosphine complexes 147 mg (89  $\mu\text{mol}$ , 89 % based on TPPTS) of compound **2-TPPTS • 2 DMF** were obtained as pale orange powder. Solvent dependent dissociation of TPPTS is observed for this complex: In *dms**o*-*d*<sub>6</sub> **2-TPPTS • 2 DMF** exhibits two <sup>31</sup>P NMR resonances at 31.4 and -3.9 in a 1:7 ratio, while an inverted ratio of nickel bound phosphine bound to free phosphine of 8:1 is evident in CD<sub>3</sub>OD. Similarly, two sets of signals were observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. NMR data is given for the nickel bound complex **2-TPPTS**. <sup>1</sup>H NMR (399.8 MHz, CD<sub>3</sub>OD, 298K):  $\delta$  7.93 (s br., 2H, 2  $\times$  DMF) 7.86 (m, 4H, 7-H and TPPTS), 7.84 (m, 3H, TPPTS), 7.67 (m, 3H, TPPTS), 7.57 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1H, 4-H), 7.35 (m, 3H, TPPTS), 7.26 (m, 7H, 10–12-H, 15-, 19-, 21-, and 25-H), 7.00 (d, <sup>4</sup>J<sub>HH</sub> = 2.0 Hz, 1H, 6-H), 2.96 and 2.83 (s each, 6H each, 2  $\times$  DMF), 1.23 (s, 36H, 4  $\times$  tBu), -1.44 (d, <sup>3</sup>J<sub>PH</sub> = 8.0 Hz, Ni-CH<sub>3</sub>), 2  $\times$  OH not detected. <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CD<sub>3</sub>OD, 298K):  $\delta$  168.9 (CH, C7), 165.1 (s br. DMF), 163.9 (C<sub>q</sub>, C2), 151.7 (C<sub>q</sub>, C17 and 23), 150.4 (CH, C4), 150.0 (C<sub>q</sub>, C8), 146.1 (C<sub>q</sub> br., TPPTS), 143.1 (CH, C6), 140.3 and 132.3 (C<sub>q</sub> each, C9, C13, C14, and C20), 139.8 (CH, d, J<sub>PC</sub> = 20 Hz, TPPTS), 138.2 (C<sub>q</sub>, C16, C18, C22, and C24), 131.2 (CH, TPPTS), 130.7 (CH, C10 and C12), 129.3 (CH, d, J<sub>PC</sub> = 13 Hz, TPPTS), 128.8 (CH, TPPTS), 127.0 (CH, C11), 126.1 (CH, C15, C19, C21, and C25), 121.9 (C<sub>q</sub>, C1), 96.9 (C<sub>q</sub>, C5), 72.3 (C<sub>q</sub>, C3), 36.9 and 31.6 (CH<sub>3</sub> each, DMF),

35.9 (C<sub>q</sub>, 4 × *t*Bu), 31.1 (CH<sub>3</sub>, 4 × *t*Bu), -7.9 (d, <sup>2</sup>J<sub>PC</sub> = 35 Hz, Ni-CH<sub>3</sub>), *ipso*-C TPPDS not detected. <sup>31</sup>P{<sup>1</sup>H} NMR (161.8 MHz, CD<sub>3</sub>OD, 298K): δ 32.5. Elemental analysis calcd for C<sub>66</sub>H<sub>85</sub>N<sub>3</sub>O<sub>14</sub>S<sub>3</sub>I<sub>2</sub>Na<sub>3</sub>PNi (1653.04 g mol<sup>-1</sup>): C: 47.96, H: 5.18, N: 2.54. Found C: 48.00, H: 5.11, N: 2.47.



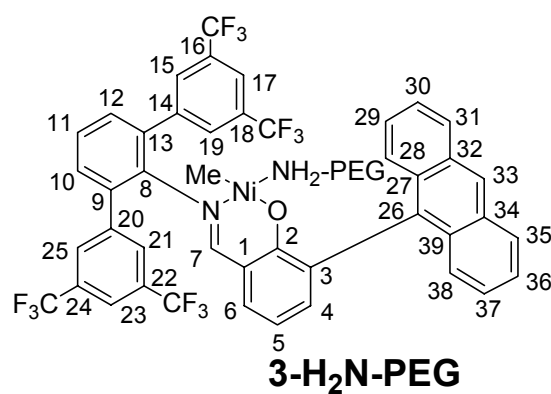
**2-TPPDS.** Following the general procedure for phosphine complexes 118 mg (84 μmol, 88 % based on TPPDS) of compound **2-TPPDS** were obtained as orange powder. <sup>1</sup>H NMR (399.8 MHz, CD<sub>3</sub>OD, 298K): δ 7.76 (vd, J<sub>PH</sub> = 7.6 Hz, 4H, TPPDS), 7.72 (d, <sup>4</sup>J<sub>PH</sub> = 7.6 Hz, 1H, 7-H), 7.64 (d, <sup>4</sup>J<sub>HH</sub> = 2.3 Hz, 1H, 4-H), 7.57 (vt, J<sub>PH</sub> = 9.2 Hz, 4H, TPPDS), 7.49 (m, 2H, TPPDS), 7.36 (m, 1H, TPPDS), 7.30 (m, 2H, TPPDS), 7.26 (m, 3H, 10–12-H), 6.94 d, <sup>4</sup>J<sub>HH</sub> = 2.3 Hz, 6-H), 1.34 (s, 36H, 4 × *t*Bu), -1.42 (d, <sup>3</sup>J<sub>PH</sub> = 7.6 Hz, Ni-CH<sub>3</sub>), 2 × *OH* not detected. <sup>13</sup>C{<sup>1</sup>H} NMR (100.5 MHz, CD<sub>3</sub>OD, 298K): δ 168.5 (CH, C7), 164.1 (C<sub>q</sub>, C2), 154.6 (C<sub>q</sub>, C17 and C23), 150.3 (CH, C4), 149.7 (C<sub>q</sub>, C8), 148.1 (C<sub>q</sub> br., TPPDS), 143.1 (CH, C6), 138.4 (C<sub>q</sub>, C16, C18, C22, and C24), 138.2 and 132.1 (C<sub>q</sub> each, C9, C13, C14, and C20), 135.7 (CH, d, J<sub>PC</sub> = 10.6 Hz, TPPDS), 135.6 (CH, d, J<sub>PC</sub> = 10.6 Hz, TPPDS), 131.2 (CH, TPPDS), 130.1 (CH, C10 and C12), 129.4 (CH, d, J<sub>PC</sub> = 10.6 Hz, TPPDS), 128.3 (CH, C15, C19, C21, and C25), 127.0 (CH, C11), 126.7 (CH, d, J<sub>PC</sub> = 10.0 Hz, TPPDS), 122.4 (C<sub>q</sub>, C1), 96.5 (C<sub>q</sub>, C5), 72.2 (C<sub>q</sub>, C3), 35.7 (C<sub>q</sub>, 4 × *t*Bu), 31.1 (CH<sub>3</sub>, 4 × *t*Bu), -8.5 (CH<sub>3</sub>, d, <sup>2</sup>J<sub>PC</sub> = 36.0 Hz, Ni-CH<sub>3</sub>), 2 × C<sub>q</sub> TPPDS

not detected.  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.8 MHz,  $\text{CD}_3\text{OD}$ , 298K):  $\delta$  29.8. Elemental analysis calcd for  $\text{C}_{60}\text{H}_{72}\text{NO}_9\text{S}_2\text{I}_2\text{Na}_2\text{PNi}$  (1404.8  $\text{g mol}^{-1}$ ): C: 51.30, H: 5.17, N: 1.00. Found C: 51.60, H: 5.45, N: 0.84.



**3-TPPTS • 2 DMF.** Following the general procedure for phosphine complexes 123 mg (78  $\mu\text{mol}$ , 82 % based on TPPTS) of compound **3-TPPTS • 2 DMF** were obtained as orange powder.  $^1\text{H}$  NMR (399.8 MHz,  $\text{CD}_3\text{OD}$ , 298K):  $\delta$  8.37 (d,  $^4J_{\text{PH}} = 8.8$  Hz, 1H, 7-H), 8.24 (s, 4H, 15-, 19-, 21-, and 25-H), 8.03 (s, 2H, 17- and 23-H), 7.97 (s, 1H, 33-H), 7.93 (s br. 2H, 2  $\times$  DMF) 7.74 and 7.31 (m each, 2H each, 28-, 31-, 35-, and 38-H), 7.58 (d,  $^3J_{\text{HH}} = 7.9$  Hz, 2H, 10- and 12-H), 7.52 (m, 3H, TPPTS), 7.25–7.08 (m, 11H, 4-, 29-, 30-, 36-, 37-H, and TPPTS), 6.97 (d,  $^3J_{\text{HH}} = 7.2$  Hz, 1H, 6-H), 6.76 (m, 3H, TPPTS), 6.57 (t,  $^3J_{\text{HH}} = 7.2$  Hz, 5-H), 2.96 and 2.83 (s each, 6H each, 2  $\times$  DMF), -1.72 (d br.,  $^3J_{\text{PH}} = 8.2$  Hz, 3H, Ni- $\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz,  $\text{CD}_3\text{OD}$ , 298K):  $\delta$  170.9 (CH, C7), 166.7 ( $\text{C}_q$ , C2), 165.1 ( $\text{C}_q$  br. DMF), 151.1 ( $\text{C}_q$ , C8), 145.1 ( $\text{C}_q$ , TPPTS), 143.2 and 134.7 ( $\text{C}_q$  each, C9, C13, C14, and C20), 139.0 (CH, C6), 137.9 ( $\text{C}_q$ , d,  $J_{\text{PC}} = 20$  Hz, TPPTS), 135.9 and 128.9 ( $\text{C}_q$  each, C3 and C26), 135.6 (CH, C4), 132.8 and 131.3 ( $\text{C}_q$  each, C27, C32, C34, and C39), 132.3 ( $\text{C}_q$ ,  $^2J_{\text{CF}} = 33$  Hz, C16, C18, C22, and C24), 132.3 (CH, C10 and C12), 132.1 (CH, TPPTS), 131.9 (CH, C15, C19, C21, and C25), 129.9 and 127.8 (CH each, C28, C31, C35, and C38), 128.9 (CH, TPPTS), 128.2 ( $\text{C}_q$ ,

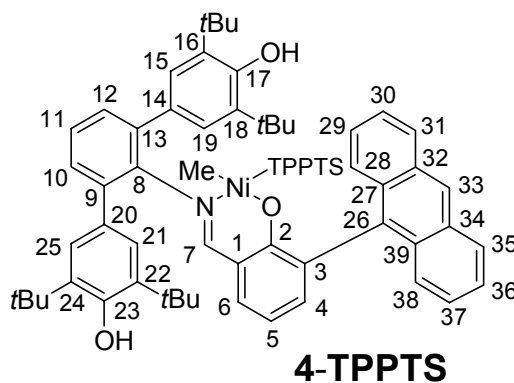
C3), 127.8 (CH, TPPTS), 127.4 (CH, C33), 126.0 (CH, C11), 125.5 and 125.1 (CH each, C29, C30, C36, and C37), 124.8 ( $C_q$ ,  $^1J_{CF} = 273$  Hz,  $4 \times CF_3$ ), 122.0 (CH, C17 and C23), 119.9 ( $C_q$ , C1), 114.8 (CH, C5), 36.9 and 31.6 ( $CH_3$  each, DMF), -12.4 (d,  $^2J_{PC} = 35$  Hz,  $CH_3$ , Ni- $CH_3$ ).  $^{31}P\{^1H\}$  NMR (161.8 MHz,  $CD_3OD$ , 298K):  $\delta$  29.7. Elemental analysis calcd for  $C_{68}H_{51}N_3O_{12}S_3PF_{12}Na_3Ni$  (1585.0 g mol $^{-1}$ ): C: 51.53, H: 3.24, N: 2.65. Found C: 52.02, H: 2.81, N: 2.34.



**3-H<sub>2</sub>N-PEG** (9:1 mixture of isomers, main isomer). Following the general procedure for PEG-complexes 243 mg (ca 76  $\mu$ mol, ca 89 % based on PEG with  $M_n =$  ca 2320 g mol $^{-1}$ ) of compound **3-H<sub>2</sub>N-PEG** were obtained as red powder.  $^1H$  NMR (399.8 MHz,  $C_6D_6$ , 298K):  $\delta$  8.20 (s, 4H, 15-, 19-, 21-, and 25-H), 7.90 and 7.85 (vd each,  $J = 8.6$  Hz each, 2:2H, 28-, 31-, 35-, and 38-H), 7.79 (s, 2H, 17- and 23-H), 7.54 (s, 1H, 33-H), 7.36 and 7.26 (vt each,  $J = 8.6$  Hz each, 2:2H, 29-, 30-, 36-, and 37-H), 7.13 (d,  $^3J_{HH} = 8.0$  Hz, 1H, 4-H), 6.91 (m, 4H, 10–12-H and 1-H), 6.64 (d,  $^3J_{HH} = 8.0$  Hz, 1H, 6-H), 6.38 (t,  $^3J_{HH} = 8.0$  Hz, 1H, 5-H), 3.8–3.2 (m, 210H, PEG), 3.13 (s, 3H, PEG- $OCH_3$ ), 3.07 and 2.85 (t each,  $^3J_{HH} = 5.2$  Hz, 2:2H,  $OCH_2CH_2OCH_3$ ), 2.09 (t,  $^3J_{HH} = 4.4$  Hz, 2H,  $H_2NCH_2CH_2$ ), 1.45 (m, 2H,  $H_2NCH_2CH_2$ ), -0.14 (t,  $^3J_{HH} = 5.0$  Hz, 2H,  $NH_2$ ), -1.50 (s, 3H, Ni- $CH_3$ ).  $^{13}C\{^1H\}$  NMR (100.5 MHz,  $C_6D_6$ , 298 K):  $\delta$  168.0 (CH, C7), 165.3 ( $C_q$ , C2),

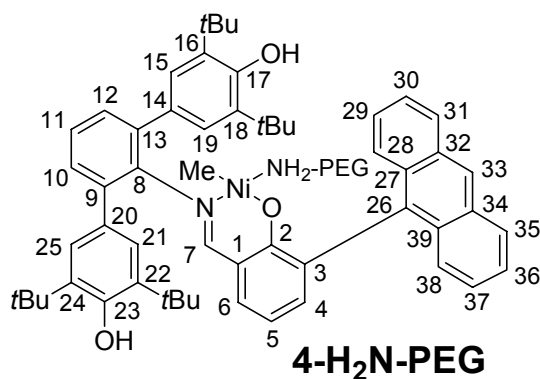


150.8 (C<sub>q</sub>, C8), 141.7 and 133.2 (C<sub>q</sub> each, C13, C14, C19, and C20), 137.5 (CH, C4), 136.3 (C<sub>q</sub>, C26), 133.4 (CH, C6), 132.0 and 131.0 (C<sub>q</sub> each, C27, C32, C34, and C39), 131.6 (C<sub>q</sub>, q, <sup>2</sup>J<sub>CF</sub> = 33 Hz, C16, C18, C22, and C24), 130.8 (CH, C10, C12, C15, C19, C21, and C25), 128.8 and 127.8 (CH each, C28, C31, C35, and C38), 126.6 (CH, C11), 125.9 (CH, C33), 125.4 and 125.1 (CH each, C29, C30, C36, and C37), 124.0 (C<sub>q</sub>, <sup>1</sup>J<sub>CF</sub> = 273 Hz, 4 × CF<sub>3</sub>), 121.1 (CH br., C17 and C23), 119.6 (C<sub>q</sub>, C1), 114.2 (CH, C5); 72.8, 71.6, 71.0, 70.4, and 69.8 (CH<sub>2</sub> each, PEG), 58.7 (OCH<sub>3</sub>), 41.8 (NCH<sub>2</sub>), -13.9 (Ni-CH<sub>3</sub>); C3 not detected. Elemental analysis calcd for C<sub>149</sub>H<sub>238</sub>N<sub>2</sub>O<sub>53</sub>F<sub>12</sub>I<sub>2</sub>Ni (3192 g mol<sup>-1</sup>): C: 56.06, H: 7.51, N: 0.88. Found C: 56.28, H: 7.80, N: 0.81.

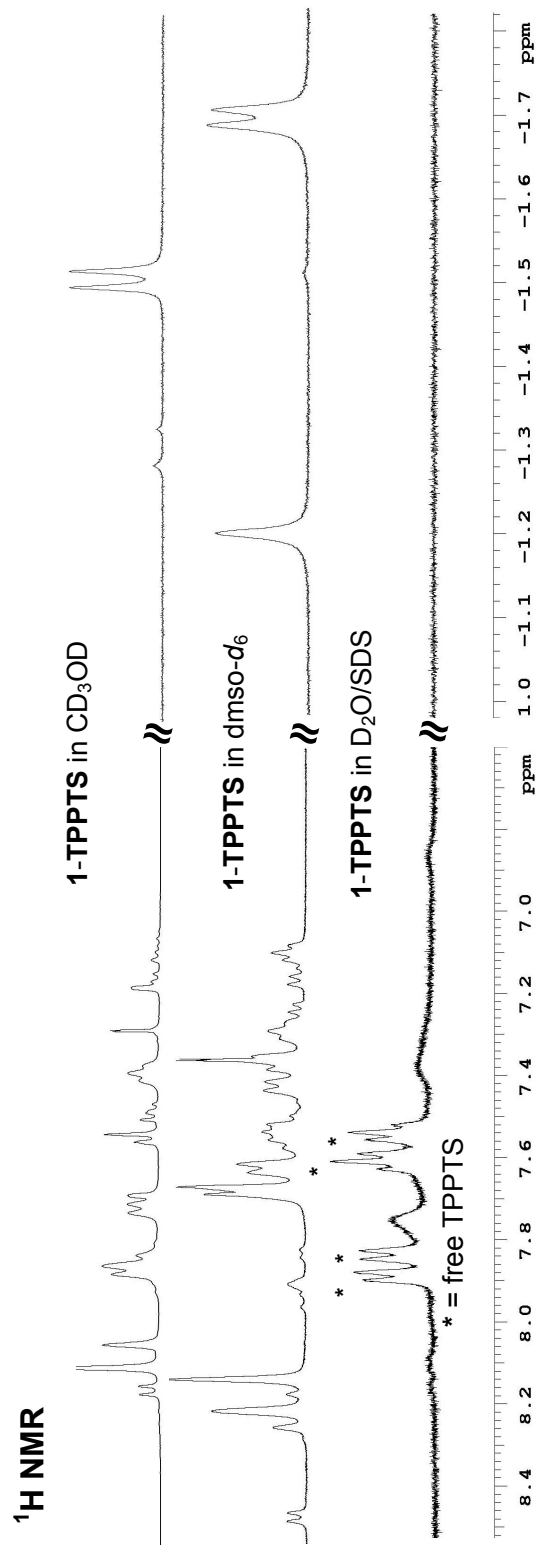


**4-TPPTS • 2 DMF.** Following the general procedure for phosphine complexes 130 mg (83 μmol, 87 % based on TPPTS) of compound **4-TPPTS • 2 DMF** were obtained as orange powder. Solvent dependent dissociation of TPPTS is observed for this complex: In *dms**o*-d<sub>6</sub> **4-TPPTS • 2 DMF** exhibits two <sup>31</sup>P NMR resonances at 26.8 and -3.9 in a 1:9 ratio, while an inverted ratio of nickel bound phosphine bound to free phosphine of ca 2:1 is evident in CD<sub>3</sub>OD. Similarly, two sets of signals were observed in the <sup>1</sup>H and <sup>13</sup>C NMR spectra. NMR data is given for the nickel bound complex **4-TPPTS**. <sup>1</sup>H NMR (399.8 MHz, *dms**o*-d<sub>6</sub>, 298K): δ 8.53 (s, 1H, 33-H), 8.05 and 7.51 (d each, J<sub>HH</sub> = 8.8 Hz each, 2:2H, 28-, 31-, 35-, and 38-H), 7.95 (s, 2H, 2 × DMF), 7.93 (s, 1H, 7-H),

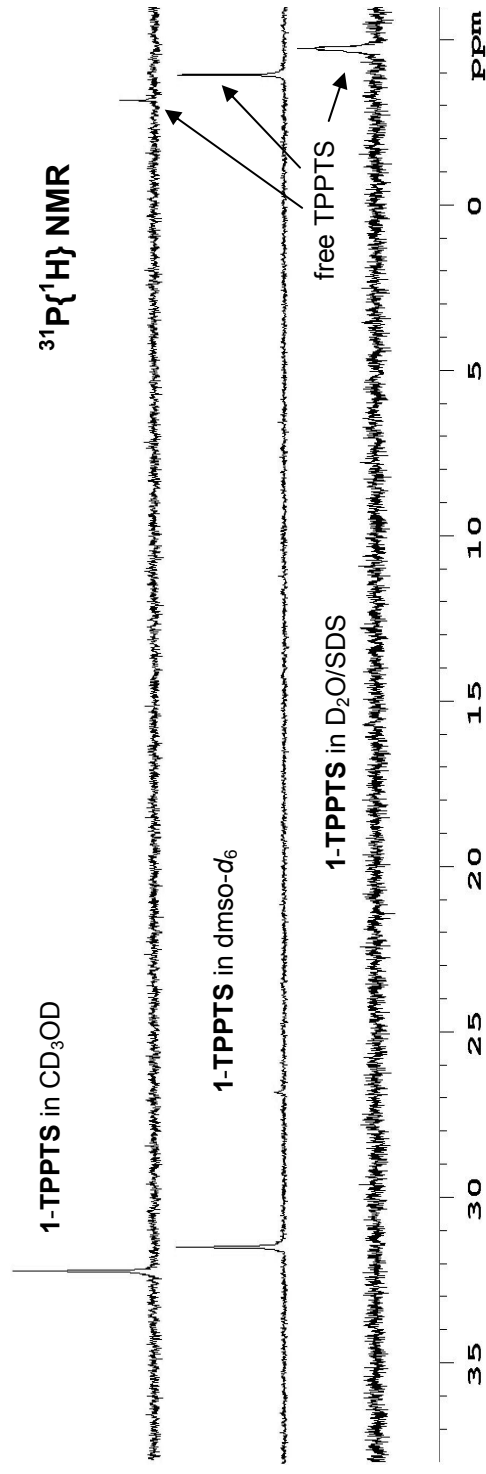
7.64 (vd,  $J_{\text{PH}} = 8.0$  Hz, 6 H, TPPTS), 7.47 and 7.33 (vt each,  $J_{\text{HH}} = 7.7$  Hz each, 2:2H, 29-, 30-, 36-, and 37-H), 7.57 (m, 3H, TPPTS), 7.30 (s, 3H, 10–12-H), 7.25 (s, 4H, 15-, 19-, 21-, and 25-H), 7.13 and 7.06 (d each,  $J_{\text{HH}} = 6.8$  Hz each, 1:1H, 4- and 6-H), 6.94 (s br., 2H, 17- and 23-OH), 6.55 (t,  $J_{\text{HH}} = 6.8$  Hz, 1H, 5-H), 2.84 and 2.72 (s each, 6H each, 2 × DMF), 1.37 (s, 36H, 4 × *t*Bu), -1.23 (s br., 3H, Ni-CH<sub>3</sub>).  $^{13}\text{C}\{^1\text{H}\}$  NMR (100.5 MHz, dms $o$ - $d_6$ , 298 K):  $\delta$  168.8 (CH, C7), 163.1 (C<sub>q</sub>, C2), 162.7 (CH, 2 × DMF), 152.9 (C<sub>q</sub>, C17 and C23), 148.6 (C<sub>q</sub>, C8), 148.3 (C<sub>q</sub>, d,  $J_{\text{PC}} = 8$  Hz, TPPTS), 138.5 (C<sub>q</sub>, C16, C18, C22, and C24), 136.2 and 130.0 (C<sub>q</sub> each, C9, C13, C14, and C20), 136.0 and 134.4 (CH each, C4 and C6), 135.7 (C<sub>q</sub>, d,  $J_{\text{PC}} = 12$  Hz, TPPTS), 135.5 and 128.6 (C<sub>q</sub> each, C3 and C26), 133.0 (CH, d,  $J_{\text{PC}} = 15$  Hz, TPPTS), 130.8 and 129.7 (C<sub>q</sub> each, C27, C32, C34, and C39), 130.4 (CH, d,  $J_{\text{PC}} = 25$  Hz, TPPTS), 128.5 (CH, C10 and C12), 128.3 (CH, d,  $J_{\text{PC}} = 5$  Hz, TPPTS), 128.1 and 126.7 (CH each, C28, C31, C35, and C38), 126.8 (CH, C15, C19, C21, and C25), 126.3 (CH, TPPTS), 126.1 (CH, C11), 125.5 (CH, C33), 125.2 and 125.1 (CH each, C29, C30, C36, and C37), 119.7 (C<sub>q</sub>, C1), 113.3 (CH, C5), 35.7 and 30.7 (CH<sub>3</sub> each, 2 × DMF), 34.6 (C<sub>q</sub>, 4 × *t*Bu), 30.4 (CH<sub>3</sub>, 4 × *t*Bu), -6.4 (CH<sub>3</sub>, Ni-CH<sub>3</sub>).  $^{31}\text{P}\{^1\text{H}\}$  NMR (161.8 MHz, dms $o$ - $d_6$ , 298K):  $\delta$  -3.9. Elemental analysis calcd for C<sub>80</sub>H<sub>87</sub>N<sub>3</sub>O<sub>14</sub>S<sub>3</sub>Na<sub>3</sub>PNi (1569.4 g mol<sup>-1</sup>): C: 61.23, H: 5.59, N: 2.68. Found C: 61.47, H: 5.20, N: 2.40.



**4-H<sub>2</sub>N-PEG** (95:5 mixture of isomers, main isomer). Following the general procedure for PEG-complexes 236 mg (ca 74  $\mu\text{mol}$ , ca 86 % based on PEG with  $M_n = \text{ca } 2320 \text{ g mol}^{-1}$ ) of compound **4-H<sub>2</sub>N-PEG** were obtained as red-orange powder.  $^1\text{H}$  NMR (399.8 MHz,  $\text{C}_6\text{D}_6$ , 298K):  $\delta$  8.23 (s, 1H, 33-H), 8.09 and 7.87 (m each, 2:2H, 28-, 31-, 35-, and 38-H), 7.68 (s, 4H, 15-, 19-, 21-, and 25-H), 7.42 (d,  $^3J_{\text{HH}} = 7.6 \text{ Hz}$ , 2H 10- and 12-H), 7.30 (m, 4H, 29-, 30-, 36-, and 37-H), 7.24 (s, 1H, 7-H), 7.19 (dd,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ ,  $^4J_{\text{HH}} = 1.8 \text{ Hz}$ , 1H, 4-H), 7.14 (t,  $^3J_{\text{HH}} = 7.6 \text{ Hz}$ , 1H, 11-H), 6.61 (dd,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ ,  $^4J_{\text{HH}} = 1.8 \text{ Hz}$ , 1H 6-H), 6.37 (t,  $^3J_{\text{HH}} = 7.8 \text{ Hz}$ , 5-H), 5.09 (s, 2H, 2  $\times$  OH), 3.7–3.2 (m, 225H, PEG), 3.11 and 2.86 (t br. each,  $^3J_{\text{HH}} = 4.0 \text{ Hz}$  each, 2:2H  $\text{CH}_3\text{OCH}_2\text{CH}_2$ ), 3.11 (s, 3H,  $\text{CH}_3\text{O-PEG}$ ), 2.15 (t br,  $^3J_{\text{HH}} = 4.0 \text{ Hz}$ , 2H,  $\text{CH}_2\text{CH}_2\text{NH}_2$ ), 1.53 (m br., 2H,  $\text{CH}_2\text{-NH}_2$ ), 1.47 (s, 36H, 4  $\times$  *t*Bu), -0.01 (t,  $^3J_{\text{HH}} = 7.2 \text{ Hz}$ ,  $\text{NH}_2$ ), -1.27 (s, 3H, Ni- $\text{CH}_3$ ).  $\{^1\text{H}\}^{13}\text{C}$  NMR (100.5 MHz,  $\text{CD}_3\text{OD}$ , 298 K):  $\delta$  168.4 (CH, C7), 164.6 ( $\text{C}_q$ , C2), 153.2 ( $\text{C}_q$ , C17 and C23), 150.2 ( $\text{C}_q$ , C8), 137.2 and 129.7 ( $\text{C}_q$  each, C3 and C26), 136.9 and 131.7 ( $\text{C}_q$  each, C9, C13, C14, and C20), 136.4 (CH, C4), 136.1 ( $\text{C}_q$ , C16, C18, C22, and C24), 133.4 (CH, C6), 132.2 and 131.0 ( $\text{C}_q$  each C27, C32, C34, and C39), 129.1 (CH, C10 and C12), 128.7 and 128.5 (CH each, C28, C31, C35, and C38), 128.1 (CH, C15, C19, C21, and C25), 126.3 (CH, C11), 125.6 (CH, C33), 125.1 and 124.7 (CH each, C29, C30, C36, and C37), 122.0 ( $\text{C}_q$ , C1), 113.0 (CH, C5); 73.3, 71.0, 70.5, 70.1, and 69.9 ( $\text{CH}_2$  each, PEG), 58.6 ( $\text{OCH}_3$ ), 41.7 ( $\text{NCH}_2$ ), 34.8 ( $\text{C}_q$ , 4  $\times$  *t*Bu), 30.7 ( $\text{CH}_3$ , 4  $\times$  *t*Bu), -14.3 (Ni- $\text{CH}_3$ ). Elemental analysis calcd for  $\text{C}_{161}\text{H}_{274}\text{N}_2\text{O}_{55}\text{Ni}$  (3177  $\text{g mol}^{-1}$ ): C: 60.88, H: 8.69, N: 0.88. Found C: 61.52, H: 9.00, N: 1.01. The elemental analysis is not within the error limits; we have therefore added the  $^1\text{H}$  NMR spectrum of **4-H<sub>2</sub>N-PEG** on page S22.



**Figure S1.**  $^1\text{H}$  NMR spectra of complex 1-TPPTS in  $\text{CD}_3\text{OD}$ ,  $\text{dmsO-d}_6$ , and  $\text{D}_2\text{O/SDS}$  solution



**Figure S2.**  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra of complex 1-TPPTS in  $\text{CD}_3\text{OD}$ ,  $\text{dmsO-d}_6$ , and  $\text{D}_2\text{O/SDS}$  solution

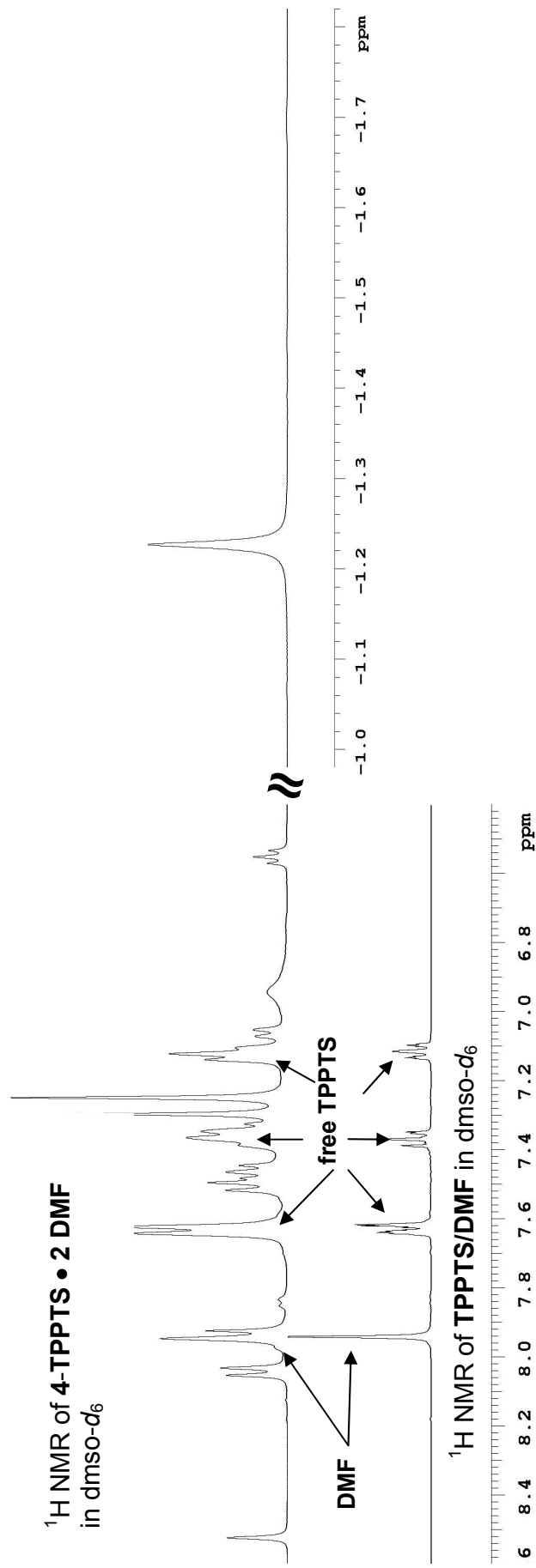


Figure S3.  $^1\text{H}$  NMR spectra of complex 4-TPPTS • 2 DMF and of TPPTS/DMF in  $\text{dmso-}d_6$

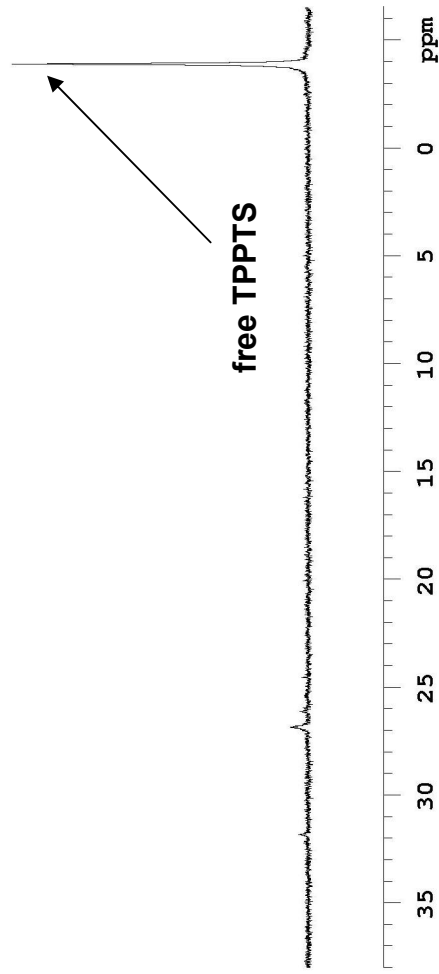


Figure S4.  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of complex 4-TPPTS • 2 DMF in  $\text{dmso-}d_6$

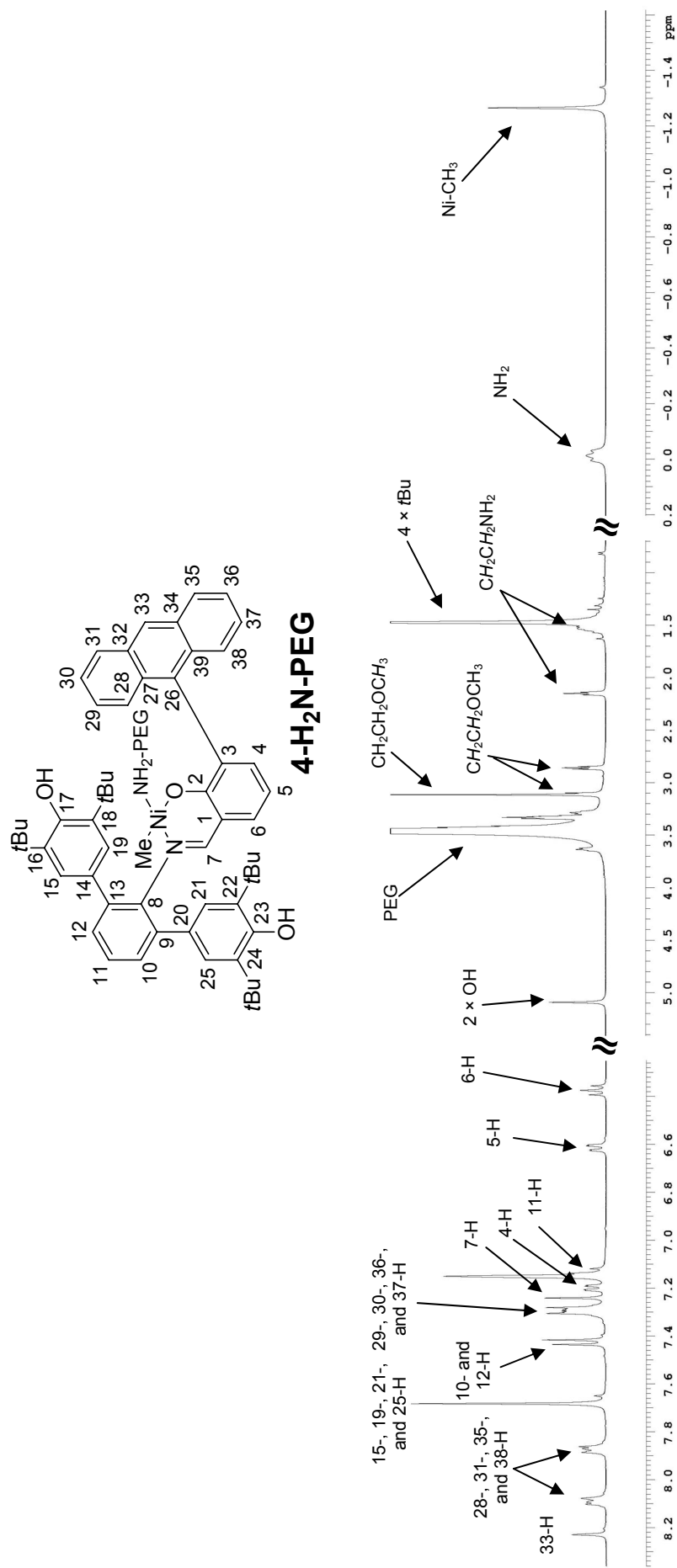


Figure S5. <sup>1</sup>H NMR spectrum of complex **4-H<sub>2</sub>N-PEG** in benzene-d<sub>6</sub>

**General Procedure for the Polymerization of Ethylene in Aqueous SDS**

**Solution.** To a mixture of 750mg SDS and 10  $\mu\text{mol}$  of the respective Ni-methyl complex in a 150 ml Schlenk-flask was added 100 ml distilled and degassed water at room temperature by a teflon cannula. The mixture was stirred for 2 min until a homogeneous solution resulted. The solution was then cannula-transferred to an argon flushed reactor cooled to 12 °C, the reactor valve was closed and the solution stirred until the temperature of the solution reached 13 °C. The reactor was pressurized to 41 bar with constant ethylene feeding while the temperature rose to 15–16 °C within 1 min and the cooling bath was adjusted to 15 °C. The final pressure was obtained within less than 3min in each experiment. After 30 min reaction time ethylene feeding was interrupted, the reactor was carefully depressurized, and the obtained latex was filtrated through a plug of glass-wool. 30 g aliquots of each latex were taken and poured into 150 ml MeOH under vigorous stirring which caused the precipitation of the polymer. The precipitated polymer was filtrated through a teflon-membrane, washed with 2  $\times$  20 mL MeOH, 2  $\times$  20 mL H<sub>2</sub>O, 20 mL acetone, and finally dried at 50 °C to constant weight under reduced pressure (20 mbar).

**General Procedure for the Polymerization of Ethylene in Toluene.** To 10  $\mu\text{mol}$  of the respective TPPDS-, PEG-, or pyridine complex in a 150 ml septum-capped Schlenk-tube under argon was added 100 ml of toluene by Teflon cannula at 20 °C. The mixture was stirred for 5 min, homogenized by sonification, and cannula-transferred to the argon-flushed reactor thermostated 8 °C below the desired reaction temperature. The reactor valve was closed, and the reactor was pressurized to 41 bar with constant ethylene feeding while the temperature rose up to 5 °C above the desired reaction temperature within 2-5 min. The temperature of the cooling/heating bath was adjusted to the desired temperature and the reaction was allowed to proceed. After a total of 30 min reaction time ethylene feeding was interrupted, the

reactor was carefully depressurized, and the content of the reactor was poured into 250 mL of methanol under vigorous stirring. The resulting mixture was stirred for 1 h at 20 °C, the polymer collected by filtration, washed with 2 × 50 mL methanol and 50 mL of acetone and dried to constant weight under vacuum (50 °C, 20 mbar).

**Estimation of the  $N_{\text{part}}/N_{\text{Ni}}$ ,  $N_{\text{chains}}/N_{\text{Ni}}$ ,  $N_{\text{chains}}/N_{\text{part}}$ , and additional comment on the number of active sites.**

The number of particles generated per nickel ( $N_{\text{part}}/N_{\text{Ni}}$ ) is estimated by

$$N_{\text{part}}/N_{\text{Ni}} = \text{yield}[\text{PE}] \times \rho[\text{PE}]^{-1} \times V_{\text{part}}^{-1} \times 6.022 \times 10^{23} \text{ mol}^{-1} \times 10^{-5} \text{ mol}[\text{Ni}],$$

with the obtained yield of polyethylene,  $\text{yield}[\text{PE}]$ , the density of obtained polyethylenes,  $\rho[\text{PE}] = 970 \text{ kg m}^{-3}$ , the average volume of a (spherical) particle,  $V_{\text{part}} = 4/3 \times \pi \times (\varnothing/2)^3$ , where  $\varnothing$  was obtained by DLS measurement, and 10  $\mu\text{mol}$  ( $10^{-5}$  mol) Ni-complex used in each experiment. The error of this estimate might be large due to the error of  $V_{\text{part}}$ , that is the error of the DLS method.

The number of chains per nickel ( $N_{\text{chains}}/N_{\text{Ni}}$ ) is given by

$$N_{\text{chains}}/N_{\text{Ni}} = \text{TON} \times M[\text{C}_2\text{H}_4] \times M_n^{-1}$$

The error of  $N_{\text{chains}}/N_{\text{Ni}}$  will be relatively small (as compared to the error of  $N_{\text{part}}/N_{\text{Ni}}$ ) based on the inaccuracy of the GPC measurement (ca 10%).

The number of chains per particle ( $N_{\text{chains}}/N_{\text{part}}$ ) is given by

$$N_{\text{chains}}/N_{\text{part}} = (N_{\text{chains}}/N_{\text{Ni}}) \times (N_{\text{part}}/N_{\text{Ni}})^{-1}$$

The error of this estimate might be large due to the error of  $N_{\text{part}}/N_{\text{Ni}}$  (vide supra).

Since the observed PDI's (ca 2) indicate that chain transfer is operative, the average  $N_{\text{chains}}/N_{\text{Ni}} = 0.8\text{-}3.8$  (entries 2-5, 9,12, 15, 17 in Table S1), indicate that not every nickel center generates an active site.



no.	cat.	solvent	T [°C]	yield [g]	TON <sup>e</sup> [10 <sup>3</sup> ]	M <sub>n</sub> <sup>f</sup> [10 <sup>5</sup> g mol <sup>-1</sup> ]	M <sub>w</sub> <sup>f</sup> [10 <sup>5</sup> g mol <sup>-1</sup> ]	PDI	branching <sup>h</sup>	T <sub>m</sub> <sup>i</sup> [°C]	particle $\phi$ [nm]	chains per Ni <sup>k</sup>	particles per Ni <sup>l</sup>	chains per particle <sup>m</sup>
1	1-TPPTS	H <sub>2</sub> O <sup>a</sup>	50	0.61 <sup>c</sup>	2.18	0.44	1.1	2.5	12	121	12	1.4	0.1	12.0
2	1-TPPTS	H <sub>2</sub> O <sup>a</sup>	15	1.82 <sup>c</sup>	6.48	0.95	1.8	1.9	5	134	4	1.9	9.3	0.2
3	2-TPPTS	H <sub>2</sub> O <sup>a</sup>	15	1.80 <sup>c</sup>	6.40	0.47	0.9	1.9	18	107	5	3.8	4.7	0.8
4	3-TPPTS	H <sub>2</sub> O <sup>a</sup>	15	1.26 <sup>c</sup>	4.50	0.75	1.5	2.0	5	126	4	1.7	6.4	0.3
5	4-TPPTS	H <sub>2</sub> O <sup>a</sup>	15	1.35 <sup>c</sup>	4.80	1.75	3.5	2.0	15	118	4	0.8	6.9	0.1
6	1-TPPDS	H <sub>2</sub> O <sup>a</sup>	15	2.34 <sup>c</sup>	8.36	0.09	0.6	7.0 <sup>g</sup>	n.d.	129	4	27.3	12.0	2.3
7	1-TPPDS	toluene <sup>b</sup>	15	0.37	1.31	1.48	3.7	2.5 <sup>g</sup>	n.d.	133	n/a	0.3	n/a	n/a
8	1-TPPDS	toluene <sup>b</sup>	50	8.55	30.5	0.31	0.6	2.0	n.d.	120	n/a	28.5	n/a	n/a
9	1-TPPDS	H <sub>2</sub> O <sup>a</sup>	50	1.01 <sup>c</sup>	3.60	0.27	0.6	2.2	n.d.	119	5	3.7	2.6	1.4
10	2-TPPDS	H <sub>2</sub> O <sup>a</sup>	15	2.22 <sup>c</sup>	7.93	0.25	1.5	6.0 <sup>g</sup>	n.d.	104	6	8.9	3.4	2.6
11	2-TPPDS	toluene <sup>b</sup>	15	0.22	0.79	0.65	2.1	3.2 <sup>g</sup>	n.d.	105	n/a	0.3	n/a	n/a
12	1-H <sub>2</sub> N-PEG	H <sub>2</sub> O <sup>a</sup>	15	1.75 <sup>c</sup>	6.25	0.57	1.2	2.1	n.d.	134	15	3.1	0.2	18.1
13	1-H <sub>2</sub> N-PEG	toluene <sup>b</sup>	15	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	n/a	n/a	n/a	n/a	n/a	n/a
14	1-H <sub>2</sub> N-PEG	toluene <sup>b</sup>	50	0.37	1.33	0.28	0.7	2.5	n.d.	121	n/a	1.3	n/a	n/a
15	3-H <sub>2</sub> N-PEG	H <sub>2</sub> O <sup>a</sup>	15	1.78 <sup>c</sup>	6.36	0.84	2.1	2.5	n.d.	136	15	2.1	0.2	12.3
16	3-H <sub>2</sub> N-PEG	toluene <sup>b</sup>	15	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	n/a	n/a	n/a	n/a	n/a	n/a
17	4-H <sub>2</sub> N-PEG	H <sub>2</sub> O <sup>a</sup>	15	2.33 <sup>c</sup>	8.32	3.09	5.9	1.9	n.d.	120	8	0.8	1.5	0.5
18	4-H <sub>2</sub> N-PEG	toluene <sup>b</sup>	15	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	-- <sup>d</sup>	n/a	n/a	n/a	n/a	n/a	n/a
19	1-pyr	toluene <sup>b</sup>	15	0.09	0.32	0.38	0.8	2.1	n.d.	133	n/a	0.2	n/a	n/a
20	1-pyr	toluene <sup>b</sup>	50	5.66	20.2	0.21	1.0	5.0 <sup>g</sup>	n.d.	123	n/a	28.3	n/a	n/a

<sup>a</sup>: polymerization conditions: 10  $\mu$ mol precatalyst, 100 mL H<sub>2</sub>O, 750 mg SDS, 40 bar C<sub>2</sub>H<sub>4</sub>, 30 min, polymer obtained as dispersion. <sup>b</sup>: polymerization conditions: 10  $\mu$ mol precatalyst, 100 mL toluene, 40 bar C<sub>2</sub>H<sub>4</sub>, 30 min. <sup>c</sup>: extrapolated value based on a ca 30.0 g aliquot of PE-latex. <sup>d</sup>: no polymer obtained. <sup>e</sup>: mol [C<sub>2</sub>H<sub>4</sub>]  $\times$  mol<sup>-1</sup> [Ni]. <sup>f</sup>: from GPC vs. linear polyethylene standards at 160 °C. <sup>g</sup>: bimodal distribution. The reason for bimodal molecular weight distributions at 15 °C is not clear so far. In contrast to polymerizations at 15 °C, complex 1-TPPDS exhibits single site behavior at 50 °C in water and toluene as apparent from the observed polydispersities (entries 8 and 9). <sup>h</sup>: methyl branches/1000 carbon atoms determined by inverse gated decoupled <sup>13</sup>C NMR experiments in 1,1,2,2-tetrachloroethane-d<sub>2</sub>/0.5 w% Cr(acac)<sub>3</sub> at 130 °C. <sup>i</sup>: determined by differential scanning calorimetry. <sup>j</sup>: volume average size (diameter) determined by DLS assuming a spherical particle shape. <sup>k</sup>: chains per nickel (N<sub>chains</sub>/N<sub>Ni</sub>) = TON  $\times$  M[C<sub>2</sub>H<sub>4</sub>]  $\times$  M<sub>n</sub><sup>-1</sup>; N<sub>chains</sub> = TON  $\times$  M[C<sub>2</sub>H<sub>4</sub>]  $\times$  M<sub>n</sub><sup>-1</sup>  $\times$  6.022  $\times$  10<sup>23</sup> mol<sup>-1</sup>  $\times$  10<sup>-5</sup> mol [Ni], with the density of obtained polyethylenes  $\rho$ [PE] = 970 Kg m<sup>-3</sup>, the particle volume V<sub>part</sub> = (4/3  $\times$   $\pi$   $\times$  ( $\phi$ /2)<sup>3</sup>), and the average (spherical) particle diameter  $\phi$  obtained by DLS. <sup>m</sup>: chains per particle (N<sub>chains</sub>/N<sub>part</sub>) = (N<sub>chains</sub>/N<sub>Ni</sub>)  $\times$  (N<sub>part</sub>/N<sub>Ni</sub>)<sup>-1</sup>.

**Table S1.** Additional analysis of obtained polyethylenes and polyethylene dispersions

## MW Averages

Mp: 314113

Mn: 25035

Mv: 123009

Mw: 149935

Mz: 383552

Mz+1: 676190

PD: 5.9890

## Distribution Plots

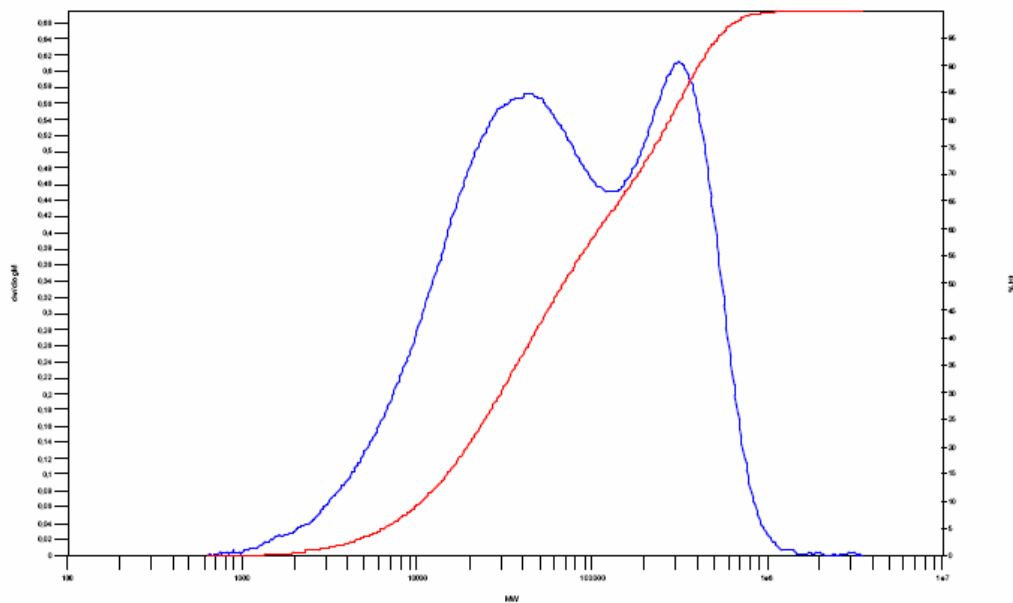


Figure S6. GPC trace of polyethylene obtained with **2-TPPDS** in aqueous solution at 15 °C

## MW Averages

Mp: 250619

Mn: 190569

Mv: 337319

Mw: 373379

Mz: 769398

Mz+1: 1790457

PD: 1.9593

## Distribution Plots

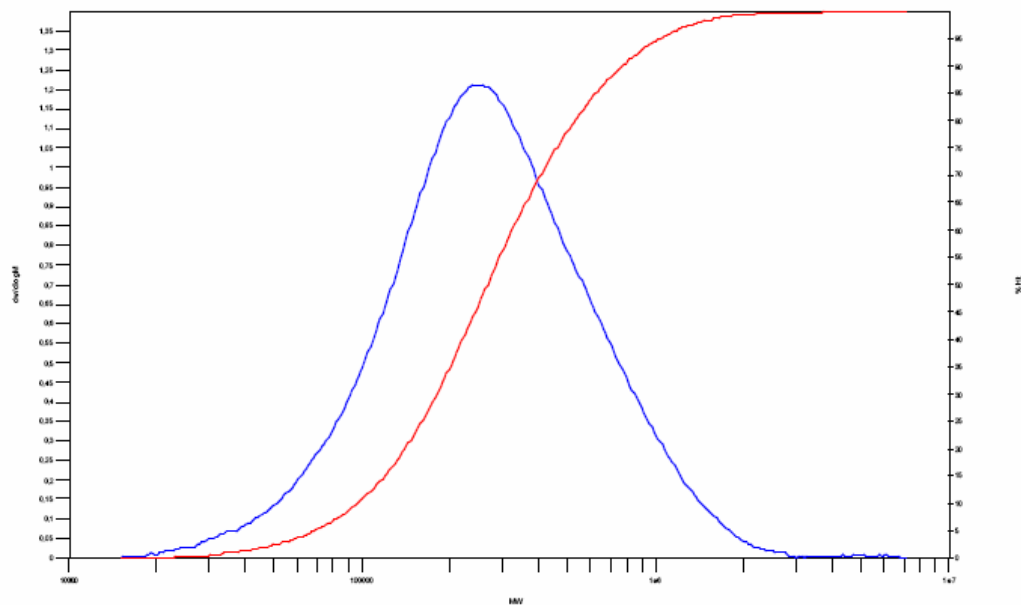
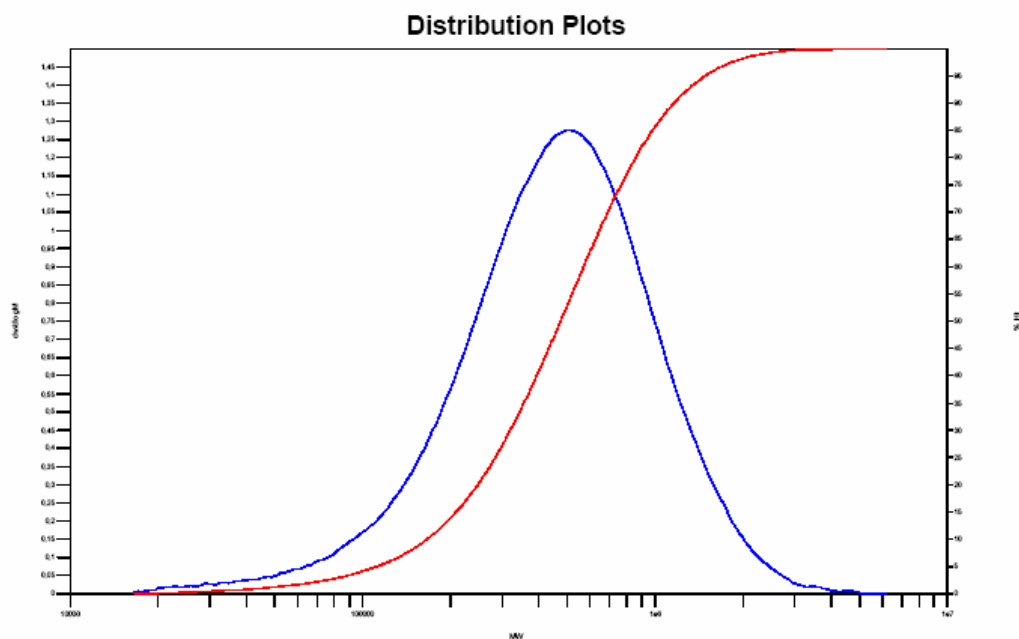


Figure S7. GPC trace of polyethylene obtained with **4-TPPTS** in aqueous solution at 15 °C

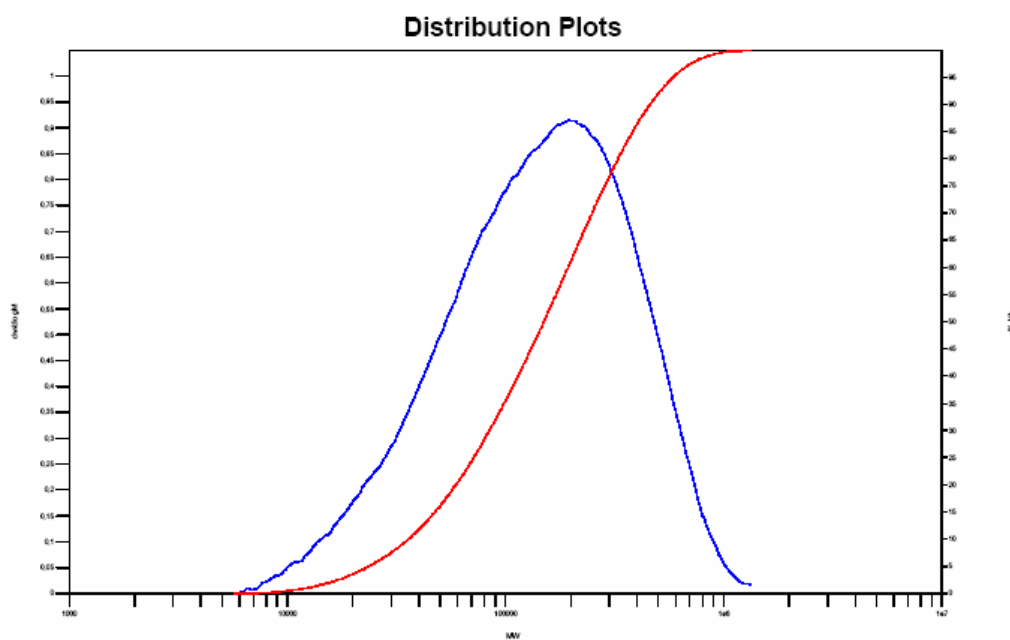
Mp: 503891 Mn: 308672 Mv: 545706 Mw: 590095  
Mz: 953921 Mz+1: 1438128 PD: 1.9117



**Figure S8.** GPC trace of polyethylene obtained with **4-H<sub>2</sub>N-PEG** in aqueous solution at 15 °C

**MW Averages**

Mp: 195733 Mn: 81654 Mv: 183898 Mw: 205236  
Mz: 370884 Mz+1: 529199 PD: 2.5135



**Figure S9.** GPC trace of polyethylene obtained from **3-H<sub>2</sub>N-PEG** in aqueous solution at 15 °C

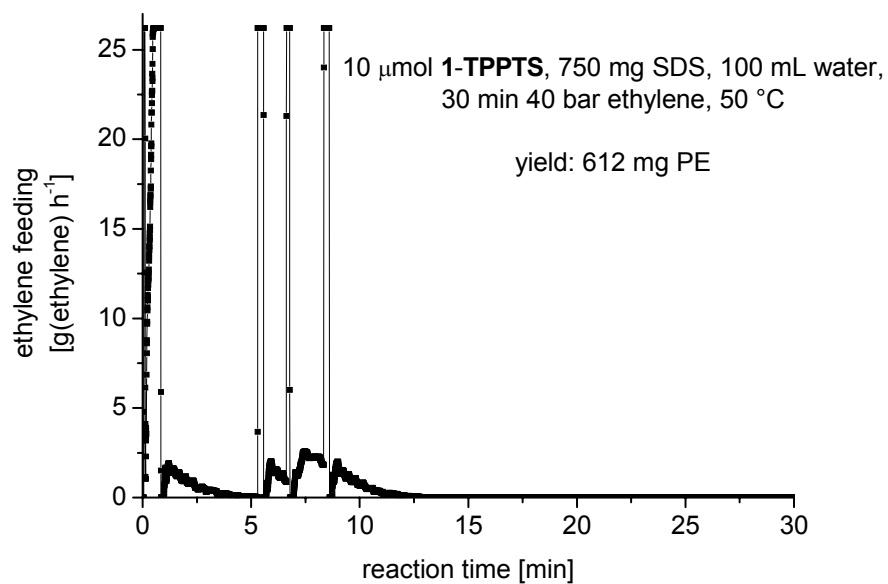


Figure S10. Mass-flow traces for the polymerization of ethylene with 1-TPPTS in water at 50 °C

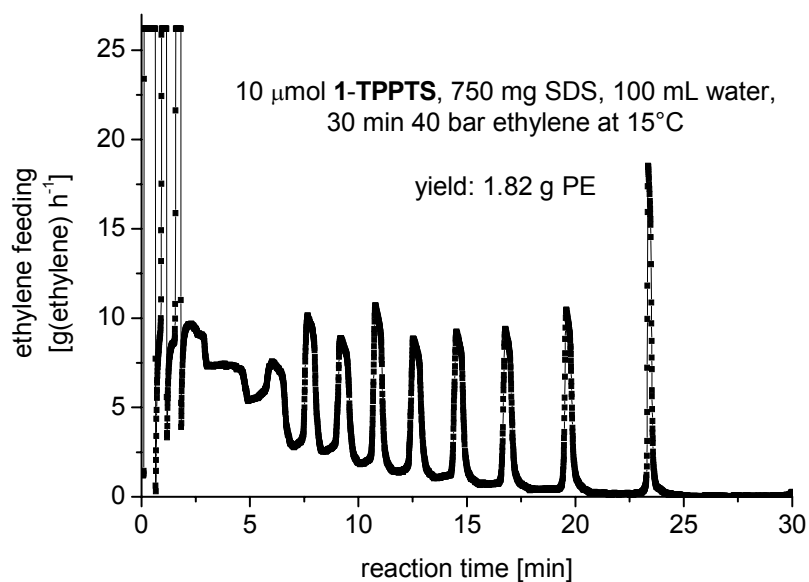
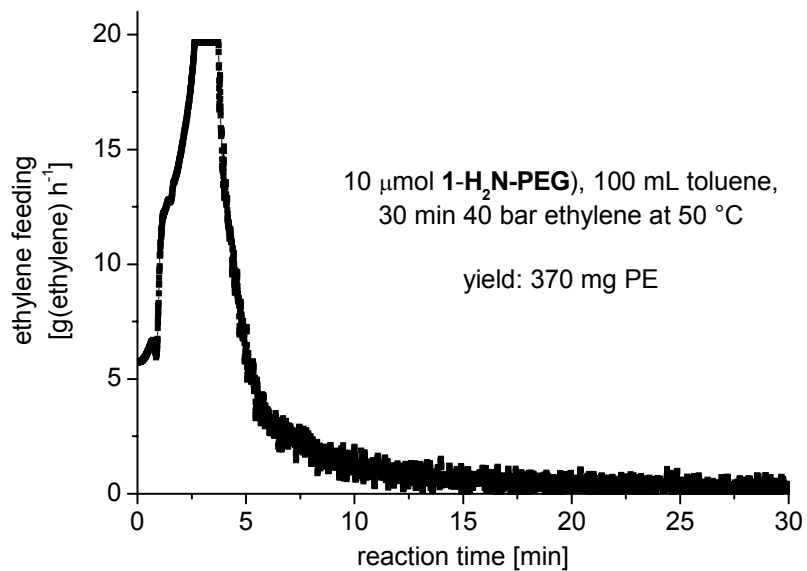
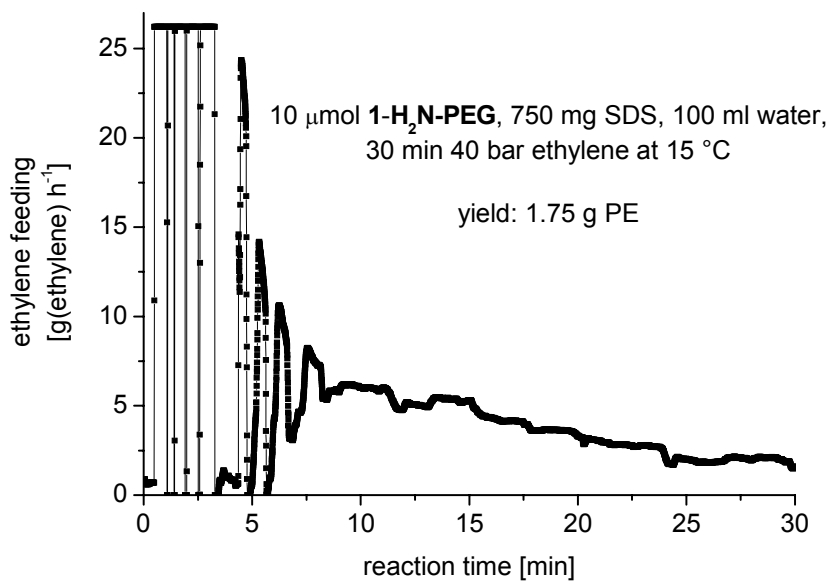


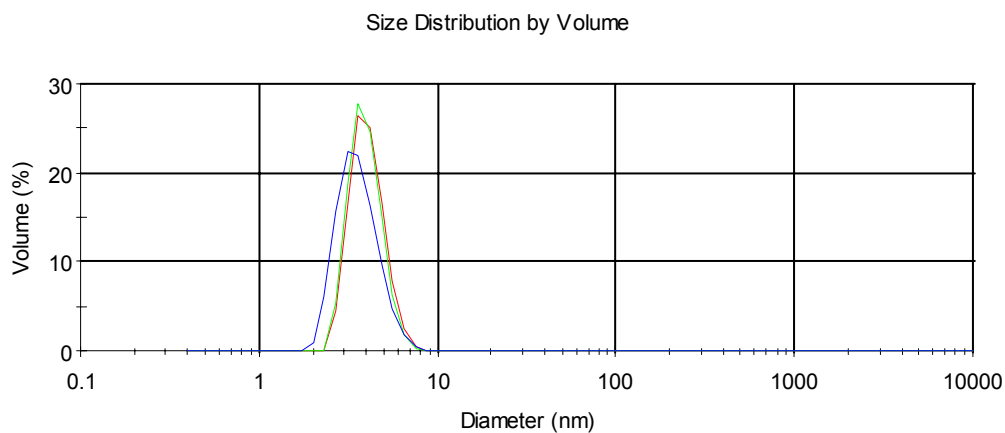
Figure S11. Mass-flow traces for the polymerization of ethylene with 1-TPPTS in water at 15 °C



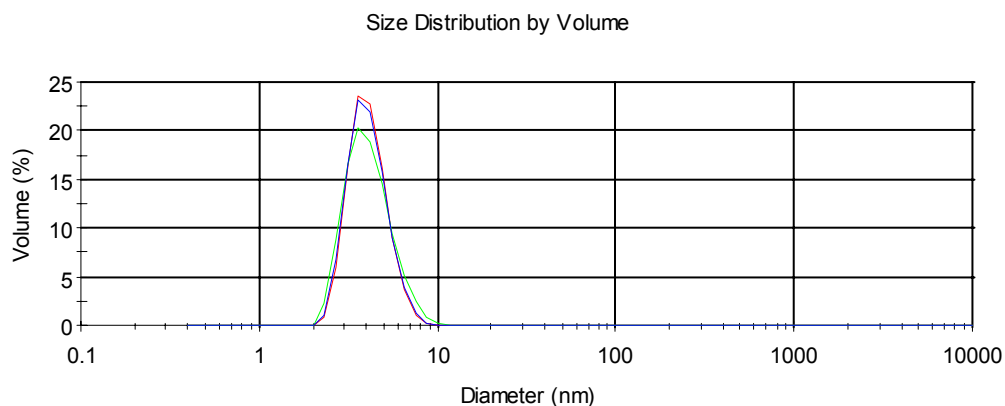
**Figure S12.** Mass-flow traces for the polymerization of ethylene with 1-H<sub>2</sub>N-PEG in toluene at 50 °C



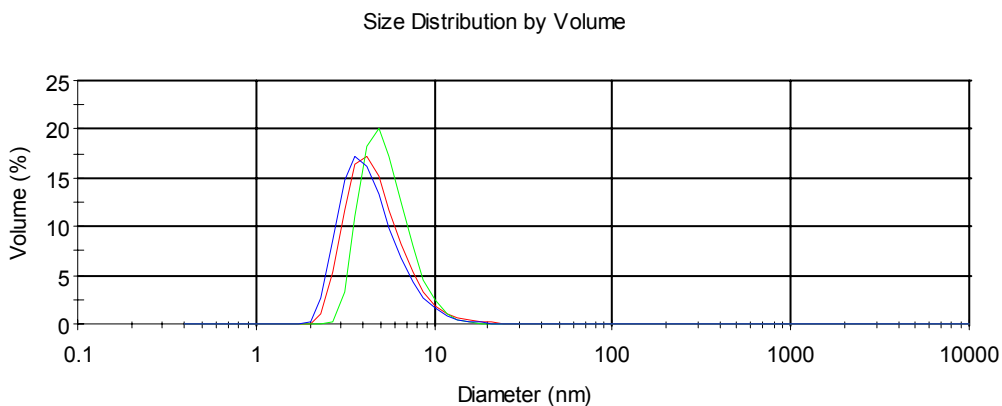
**Figure S13.** Mass-flow traces for the polymerization of ethylene with 1-H<sub>2</sub>N-PEG in water at 15 °C



**Figure S14.** DLS graph of polyethylene-dispersion obtained from 10  $\mu\text{mol}$  **1-TPPTS**, 750 mg SDS, 15  $^{\circ}\text{C}$  after 30 min under 40 bar ethylene: volume average particle diameter (average of 3 runs) = 3.9 nm



**Figure S15.** DLS graph of polyethylene-dispersion obtained from 10  $\mu\text{mol}$  **2-TPPTS**, 750 mg SDS, 15  $^{\circ}\text{C}$  after 30 min under 40 bar ethylene: volume average particle diameter (average of 3 runs) = 4.7 nm



**Figure S16.** DLS graph of polyethylene-dispersion obtained from 10  $\mu\text{mol}$  **2-TPPDS**, 750 mg SDS, 15  $^{\circ}\text{C}$  after 30 min under 40 bar ethylene: volume average particle diameter (average of 3 runs) = 5.8 nm