## Supporting Information

# The Ligand Redox Behavior and Role in 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene) Nickel/TMA (MAO) System for Ethylene Polymerization

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## **General Methods and Materials.**

All manipulations involving air and moisture-sensitive compounds were carried out under an atmosphere of dried and purified nitrogen using standard Schlenk or dry box techniques. Toluene and hexane were dried over sodium/benzophenone and distilled under nitrogen prior to use. Polymerization grade ethylene was further purified by passage through columns of 5 Å molecular sieves and MnO. NMR spectra were recorded on a Varian Mercury-300 MHz at room temperature in CDCl<sub>3</sub>. The elemental analysis was performed on an Elementar model Vario EL cube analyzer. UV-vis spectrum was recorded on Varian Cary 50 UV-vis analyzer; The ESR spectrum was recorded on a JES-FA 200 ESR spectrometer. The molecular weights (MWs) and dispersity (D) of the polymer samples were determined at 150 °C by a PL-GPC 220 type high-temperature gel permeation chromatography. 1,2,4-Trichlorobenzene was employed as the solvent at a flow rate of 1.0 ml/min. The calibration was made by polystyrene standard Easi-Cal PS-1 (PL Ltd.). The differential scanning calorimetry (DSC) measurements were performed on a Netzsch DSC 204 instrument under N<sub>2</sub> atmosphere. The samples were heated at a rate of 10 °C/min and cooled at a rate of 10 °C/min. dipp-BIANNiBr<sub>2</sub> was prepared according to the literature procedure (L. K. Johnson, C. M. Killian, M. Brookhart, *J. Am. Chem. Soc.* **1995**, *117*, 6414-6415). MAO (10% in toluene) was purchased from Sigma-Aldrich and use as received.

Synthesis of  $[dipp-BIANNi]_2(\mu-Cl)_2$  (2) A toluene solution of dipp-BIANNa (0.52 g, 1.0 mmol) was added dropwise to a toluene (20 ml) suspension of NiCl<sub>2</sub>(DME)<sub>2</sub> (0.22 g, 1.0 mmol) at room temperature and the mixture was stirred for 30 minutes. The reaction mixture was filtrated and the solvent was removed under reduce pressure. The residue was washed with hexane and dried in vacuum. The product was obtained as blue powder. Yield: 0.40 g, (67%) Crystals of 2 suitable for X-ray structural determination was grown in toluene/hexane mixed solvent. Anal.Calcd for C<sub>73</sub>H<sub>83</sub>Cl<sub>2</sub>N<sub>4</sub>Ni<sub>2</sub> (%): C, 72.78; H, 6.94; N, 4.65. Found (%): C, 72.84; H, 6.81; N, 4.59.

**Synthesis of [dipp-BIAN]NiCl(Ph<sub>3</sub>P) (3)** A toluene solution of dipp-BIANNa (0.52 g, 1.0 mmol) was added dropwise to a toluene (20 ml) suspension of NiCl<sub>2</sub>(Ph<sub>3</sub>P)<sub>2</sub> (0.65 g, 1.0 mmol) at room temperature and the mixture was stirred for 30 minutes. The reaction mixture was filtrated and the solvent was removed under reduce pressure. The residue was washed with hexane and dried in vacuum. The product was obtained as blue powder. Yield: 0.53 g, (62%) Crystals of **3** suitable for X-ray structural determination was grown in toluene/hexane mixed solvent. Anal.Calcd for  $C_{54}H_{55}ClN_2NiP$  (%): C, 75.67; H, 6.47; N, 3.27. Found (%): C, 75.96; H, 7.19; N, 2.87.

#### Synthesis of [dipp-BIAN]Ni(µ-Cl)<sub>2</sub> AlMe<sub>2</sub> (4)

A toluene solution of AlMe<sub>3</sub> (2.09 mL, 2.1mmol) was added dropwise to a toluene (20 ml) solution of dipp-BIANNiBr<sub>2</sub> (0.30 g, 0.42 mmol) at  $-78^{\circ}$ C. The reaction mixture was stirred overnight. The solvent was removed under reduce pressure and the residue was washed with hexane. The product was obtained as purple powder. Yield: 0.26 g, (79%) Crystals of **4** suitable for X-ray structural determination was grown in toluene/hexane mixed solvent. Anal. Calcd for C<sub>38</sub>H<sub>46</sub>AlBr<sub>2</sub>N<sub>2</sub>Ni: C, 58.79; H, 5.97; N, 3.61. Found: C, 59.41; H, 5.88; N, 3.52.

# General polymerization conditions.

The ethylene polymerization experiments were carried out as follows: A dry 250 mL steel autoclave with a magnetic stirrer was charged with 50 mL of toluene, thermostated at the desired temperature and saturated with ethylene (1.0 atm). The polymerization reaction was started by addition of a mixture of the catalyst and co-activator in toluene (5 mL). The vessel was pressurized to 5 atm with ethylene immediately and the pressure was maintained by continuous feeding of ethylene. The reaction mixture was stirred at the desired temperature for 15min. The polymerization was then quenched by injecting acidified ethanol containing HCl (3 M). The polymer

was collected by filtration, washed with water and ethanol, and dried to a constant weight under vacuum.

# **Crystal Structure Determination.**

The crystals were mounted on a glass fiber using the oil drop. Data obtained with the  $\omega$ -2 $\theta$  scan mode were collected on a Bruker SMART 1000 CCD diffractometer with graphite-monochromated Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The structures were solved using direct methods, and further refinements with full-matrix least squares on  $F^2$  were obtained with the SHELXTL program package. Details of the crystal data, data collections, and structure refinements are summarized in STable 1. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were introduced in calculated positions with the displacement factors of the host carbon atoms. All calculations were performed using the SHELXTL crystallographic software packages. The crystal data in CIF format was deposited to the CCDC (1044662 (2); 1044664 (3); 1044664 (4))

	2	3	4	
Formula	$C_{72}H_{80}CI_2N_4Ni_2$	$C_{64.50}H_{63}CIN_2NiP$	C <sub>38</sub> H <sub>46</sub> AlBr <sub>2</sub> N <sub>2</sub> Ni	
F <sub>w</sub>	1189.72	991.30	776.28	
cryst syst	Monoclinic	Triclinic	Orthorhombic	
space group	P2(1)/n	P-1	Pbcn	
a (Å)	16.1963(11)	11.2339(15)	13.7598(11)	
b (Å)	12.2535(8)	13.5323(18)	18.9444(15)	
c (Å)	16.3252(11)	19.012(3)	14.2281(11)	
α (deg)	90	72.179(2)	90	
β (deg)	94.6890(10)	88.564(2)	90	
γ (deg)	90	84.990(2)	90	
v (ų)	3229.1(4)	2741.0(6)	3708.9(5)	
Ζ	2	2	4	
D <sub>calcd</sub> (gcm <sup>-3</sup> )	1.224	1.201	1.390	
µ (mm⁻¹)	0.709	0.473	2.729	
<i>F</i> (000)	1260	1048	1596	
$\theta_{\max}(\deg)$	26.04	25.10	26.04	
collected refins	20255	13430	22125	
Uniq reflns	6341	9520	3661	
R <sub>int</sub>	0.0406	0.0323	0.0475	
GOF	1.012	1.010	1.015	
R <sub>1</sub> [I>2sigma(I)]	0.0423	0.0763	0.0343	
wR <sub>2</sub> [l>2sigma(l)]	0.0930	0.1714	0.0823	
Largest diff peak, hole (e A^-3)	0.446, -0.267	0.950, -0.691	0.651, -0.301	

STable 1. Summary of crystallographic data for complexes 2, 3, and 4.

				(×10-4)			
1	2	AlMe <sub>3</sub> (200)	2720	5.07	2.8	32.32	109.7
2	2	AlEt <sub>3</sub> (200)	288	1.80	4.0	n.d.	115.2
3	2	Al <sup>i</sup> Bu <sub>3</sub> (200)	576	2.03	4.0	n.d.	114.6
4	3	AlMe <sub>3</sub> (200)	1424	3.44	3.5	n.d.	96.5.
5	3 <sup>f</sup>	AlMe <sub>3</sub> (200)	904	4.50	3.1	24.62	112.7
6	1	AlMe <sub>3</sub> (200)	2808	5.00	2.8	22.66	110.2
7	4	AlMe <sub>3</sub> (200)	2904	4.89	2.8	29.60	116.0
8	1	MAO(500)	3640	5.75	3.3	34.23	110.3
9	2	MAO(500)	3608	5.40	3.4	39.13	112.5
10	4	MAO(500)	3504	5.32	3.3	38.06	108.3
11	$2^g$	AlMe <sub>3</sub> (200)	_	_	-	_	-
12	$2^h$	AlMe <sub>3</sub> (200)	3128	13.68	3.0	27.61	118.9
13	4	AlEt <sub>2</sub> Cl(200)	3464	5.13	2.6	64.52	64.4

<sup>*a*</sup>Polymerization conditions: 5  $\mu$ mol catalyst based on nickel, 60 mL of toluene, 5 bar of ethylene, 20 °C, 15 min. <sup>*b*</sup>Activity in unit of Kg of PE·mol(Ni)<sup>-1</sup>·h<sup>-1</sup>. <sup>*c*</sup>Mw and D (dispersity) were determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C using a lights scattering detector. <sup>*d*</sup>Branches per 1000 carbons determined by <sup>13</sup>C NMR spectroscopy at 130 °C. <sup>*e*</sup>Determined by DSC. <sup>*f*</sup>Polymerization time 60 min. <sup>*g*</sup>One equiv of [Ph<sub>3</sub>C][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was added. <sup>*h*</sup>One equiv of B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> was added.



SFigure 1. The enlarged ESR spectrum of 1/TMA.



SFigure 2. The <sup>13</sup>C NMR of polyethylene produced in run 1.



SFigure 3. The <sup>13</sup>C NMR of polyethylene produced in run 5.



SFigure 4. The <sup>13</sup>C NMR of polyethylene produced in run 6.







SFigure 6. The <sup>13</sup>C NMR of polyethylene produced in run 8.

![](_page_4_Figure_4.jpeg)

SFigure 7. The <sup>13</sup>C NMR of polyethylene produced in run 9.

![](_page_5_Figure_0.jpeg)

SFigure 8. The <sup>13</sup>C NMR of polyethylene produced in run 10.

![](_page_5_Figure_2.jpeg)

SFigure 9. The <sup>13</sup>C NMR of polyethylene produced in run 12.

![](_page_5_Figure_4.jpeg)

SFigure 10. The <sup>13</sup>C NMR of polyethylene produced in run 13.

![](_page_6_Figure_0.jpeg)

SFigure 11. The GPC curve of the polyethylene produced in run 1.

![](_page_6_Figure_2.jpeg)

SFigure 12. The GPC curve of the polyethylene produced in run 2.

![](_page_6_Figure_4.jpeg)

SFigure 13. The GPC curve of the polyethylene produced in run 3.

![](_page_6_Figure_6.jpeg)

SFigure 14. The GPC curve of the polyethylene produced in run 4.

![](_page_7_Figure_0.jpeg)

SFigure 15. The GPC curve of the polyethylene produced in run 5.

![](_page_7_Figure_2.jpeg)

SFigure 16. The GPC curve of the polyethylene produced in run 6.

![](_page_7_Figure_4.jpeg)

SFigure 17. The GPC curve of the polyethylene produced in run 7.

![](_page_7_Figure_6.jpeg)

SFigure 18. The GPC curve of the polyethylene produced in run 8.

![](_page_8_Figure_0.jpeg)

SFigure 19. The GPC curve of the polyethylene produced in run 9.

![](_page_8_Figure_2.jpeg)

SFigure 20. The GPC curve of the polyethylene produced in run 10.

![](_page_8_Figure_4.jpeg)

SFigure 22. The GPC curve of the polyethylene produced in run 12.

![](_page_8_Figure_6.jpeg)

SFigure 23. The GPC curve of the polyethylene produced in run 13.