Plastomeric-like polyethylenes achievable using thermally robust *N,N'*-nickel catalysts appended with electron withdrawing difluorobenzhydryl and nitro groups

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A new set of five unsymmetrical *N,N'*-diiminoacenaphthenes, 1-[2,6-((4-FC₆H₄)₂CH)₂-4-NO₂C₆H₄N]-2-(ArN)C₂C₁₀H₆ (Ar = 2,6-Me₂C₆H₃ **L1**, 2,6-Et₂C₆H₃ **L2**, 2,6-ⁱPr₂C₆H₃ **L3**, 2,4,6-Me₃C₆H₂ **L4**, 2,6-Et₂-4-MeC₆H₂ **L5**), have been synthesized and used to prepare their corresponding nickel(II) halide complexes, LNiBr₂ (**Ni1** – **Ni5**) and LNiCl₂ (**Ni6** – **Ni10**). The molecular structures of **Ni3**(OH₂) and **Ni4** reveal distorted square pyramidal and tetrahedral geometries, respectively, while the ¹H NMR spectra of all the nickel(II) (*S* = 1) complexes show broad paramagnetically shifted peaks. Upon activation with either methylaluminoxane (MAO) or ethylaluminum sesquichloride (Et₃Al₂Cl₂, EASC), **Ni1** – **Ni10** displayed very high activities for ethylene polymerization with the optimal performance being observed using 2,6-dimethyl-containing **Ni1** in combination with EASC (1.66 × 10⁷ g PE mol⁻¹ (Ni) h⁻¹ at 50 °C) which produced high molecular weight plastomeric polyethylene (*M_w* = 3.93 × 10⁵ g mol⁻¹, *T_m* = 70.6 °C) with narrow dispersity (*M_w*/*M_n* = 2.97). Moreover, **Ni1**/EASC showed good thermal stability by operating effectively at an industrially relevant 80 °C with a level of activity (6.01 × 10⁶ g of PE mol⁻¹ (Ni) h⁻¹) that exceeds previously disclosed *N,N'*-nickel catalysts under comparable reaction conditions. This improved thermal stability and activity has been ascribed to the combined effects imparted by the *para*-nitro and fluoride-substituted benzhydryl *ortho*-substituents.

Introduction

The application of α-diimine-containing nickel complexes as catalysts in ethylene polymerization continues to be a topic of considerable interest to both the academic and industrial communities.¹ Among the many types of precatalysts to be explored, 1,2-diiminoacenaphthene-nickel(II) halides² (**A**, Chart 1) have attracted particular attention due, in some measure, to their capacity to produce polyethylenes with elastomeric-type properties.³ Moreover such catalysts can deliver high activities and can show some tolerance towards the incorporation of polar co-monomers. Nevertheless, despite these promising performance characteristics, these catalysts generally exhibit poor thermal stability at temperatures that are required for industrially employed gas-phase polymerizations (70 – 110 °C).⁴ To overcome this drawback, various efforts have been directed towards improving their

thermal stability including through variations to the substituents on the imino-aryl groups and to the ligand backbone itself.

With particular regard to the *N*-aryl group substitution pattern, the introduction of benzhydryl groups to the 2,6-positions in 1,2-bis(arylimino)acenaphthenes,⁵ 2-(aryliminomethyl)pyridines⁶ and 2,3-bis(arylimino)butane derivatives has proved a viable method of enhancing thermal stability.^{4a,7} Furthermore, additional modulation of the performance of these classes of catalyst can be achieved through variations to the *para*-positions of the *N*-aryl group. For example, the unsymmetrical **B**-type precatalysts (Chart 1),^{5a,5c,8} incorporating electron-withdrawing *para*-chloride (**B_{Cl}**)^{5c} or -fluoride (**B_F**)⁸ groups exhibit higher activity, longer lifetimes and afford polyethylenes with significantly higher molecular weights than the electron-donating methyl comparator (**B_{Me}**).^{5a} By comparison the introduction of an electron-withdrawing *para*-nitro substituent (**C**, Chart 1) greatly increases the molecular weight though at the expense of catalytic activity.⁹ Indeed, some support for these observed electronic effects is provided by computational studies regarding correlations between catalytic activity and the core-metal charge.¹⁰

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Electronic Supplementary Information (ESI) available: CCDC 1877303-1877305 contains the supplementary crystallographic data for compounds **L3**, **Ni3** and **Ni4**.

Chart 1 Symmetrical and unsymmetrical *N,N'*-diiminoacenaphthene-nickel(II) halide precatalysts

In recent work, we have found that modifications to the benzhydryl groups themselves provide an additional means of influencing not only the thermal stability and catalytic activity but also the microstructures and properties of the resulting polyethylenes. For example, difluorobenzhydryl-containing **D** (Chart 1),¹¹ shows higher activity, differing levels of branching and enhanced thermal stability when compared to **B** and **C** (Chart 1). With a view to improving the thermal properties and activity further, we now report complexes of type **E** (Chart 1) in which a 2,6-bis(bis-(4-fluorophenyl)methyl)-4-nitrophenyl group provides one N-aryl group while the other can be readily modified in terms of its steric and electronic properties. The catalytic performance of these nickel complexes as precatalysts for ethylene polymerization will be thoroughly investigated and the effect of co-catalyst, temperature and time will be systematically investigated and correlated with the structure of the resulting polyethylene. Comparisons with unsymmetrical **B** – **D** as well as symmetrically substituted **A**_{2,6-iPr2Ph} (Ar = 2,6-*i*Pr₂Ph,^{2c} Chart 1) under comparable reaction conditions will also be discussed. Full synthetic and characterization details will also be presented for the new ligands and complexes.

Results and discussion

Synthesis and characterization of **L1** – **L5** and **Ni1** – **Ni10**

The *N,N'*-diiminoacenaphthenes, 1-[2,6-((4-FC₆H₄)₂CH)₂-4-NO₂C₆H₄N]-2-(ArN)₂C₁₀H₆ (Ar = 2,6-Me₂C₆H₃ **L1**, 2,6-Et₂C₆H₃ **L2**, 2,6-*i*Pr₂C₆H₃ **L3**, 2,4,6-Me₃C₆H₂ **L4**, 2,6-Et₂-4-MeC₆H₂ **L5**), have been prepared in three steps (Scheme 1). Firstly, 2,6-bis(bis(4-fluorophenyl)methyl)-4-nitrobenzamine, has been synthesized by a zinc(II) chloride catalyzed Friedel-Crafts alkylation of 4-nitroaniline.¹² Secondly, this novel aniline can be condensed with acenaphthylene-1,2-dione to form the mono-ketone, 2-(2,6-bis(bis(4-fluorophenyl)methyl)-4-nitrophenylimino)acenaphthylene-1-one, which can then be used in a second condensation reaction with the corresponding Ar-NH₂ to form **L1** – **L5**; similar routes to unsymmetrical α -diimines have been reported elsewhere.^{5a-c,8,13} The five diiminoacenaphthenes have been characterized by FT-IR, ¹H/¹³C NMR spectroscopy and elemental analysis. Additionally, a single crystal of **L3** has been used for an X-ray diffraction study.

Bromide complexes **Ni1** – **Ni5** have been generated in good yield by treatment of **L1** – **L5** with (DME)NiBr₂ (DME = 1,2-dimethoxyethane) in dichloromethane at room temperature (Scheme 1). On the other hand, chloride complexes **Ni6** – **Ni10** have been synthesized by the reaction of **L1** – **L5** with NiCl₂·6H₂O in a mixture of dichloromethane and ethanol. All ten complexes have been characterized by elemental analysis as well as by IR and NMR (¹H and ¹⁹F) spectroscopy. In addition, **Ni4** and the aqua adduct **Ni3(OH₂)** have been the subject of single crystal X-ray diffraction studies.

Single crystals of **Ni3(OH₂)** and **Ni4** suitable for the X-ray determinations were grown by slow diffusion of hexane into a dichloromethane solution of the corresponding complex. Perspective views of **Ni3(OH₂)** and **Ni4** are shown in Figures 2 and 3 along with uncomplexed **L3** in Figure 1; selected bond lengths and angles for all three structures are listed in Table 1. The structures of **Ni3(OH₂)** and **Ni4** show some similarity in that each nickel center is surrounded by two bromide ligands and two nitrogen atoms belonging to the chelating diaryliminoacenaphthene ligand (aryl = 2,6-diisopropylphenyl **Ni3(OH₂)**, 2,4,6-trimethylphenyl **Ni4**). However, they differ in that **Ni3(OH₂)** additionally contains a coordinated water molecule leading to a 5-coordinate geometry as opposed to 4-coordinate for **Ni4**. Indeed, **Ni3(OH₂)** can be best described as distorted square pyramidal with N1, N2, O3 and Br1 forming the basal plane and Br2 the apex (with nickel sitting 0.393 Å

Scheme 1 Synthesis of **L1** – **L5** and their complexes **Ni1** – **Ni10**

Figure 1 ORTEP representation of **L3** with the thermal ellipsoids shown at the 50% probability level; all hydrogen atoms have been omitted for clarity.

Figure 2 ORTEP representation of **Ni3** with the thermal ellipsoids shown at the 50% probability level; all hydrogen atoms have been omitted for clarity.

Figure 3 ORTEP representation of **Ni4** with the thermal ellipsoids shown at the 50% probability level; all hydrogen atoms have been omitted for clarity.

above the square base),¹⁴ while **Ni4** as distorted tetrahedral. Similar 4-coordinate geometries are well known for unsymmetrical 1,2-diiminoacenaphthene derivatives,^{5a-d,9,11,13} while structurally characterized aqua adducts like **Ni3(OH₂)** are more scarce.¹⁵ The variations in the geometries have some noticeable effects on key bond angles. For example, the N(1)–Ni(1)–N(2) bite angle in **Ni3(OH₂)** [79.17(11)°] is smaller than that for **Ni4** [82.85(14)°] as is the Br(1)–Ni(1)–Br(2) angle [100.72(2)° **Ni3(OH₂)** vs. 124.52(3)° **Ni4**]. For both structures there is some modest asymmetry in the binding of the *N,N*-ligand with the difluorobenzhydryl-substituted *N*-aryl group showing the longest distance [Ni(1)–N(2) 2.120(3) **Ni3(OH₂)**, 2.051(4) Å **Ni4** vs. Ni(1)–N(1) 2.111(3) **Ni3(OH₂)**, 2.014(4) Å **Ni4**], which may in part be due to the more sterically hindered *ortho*-substituents. The N1–C1 and N2–C12 bond distances [1.265(4), 1.288(4) Å **Ni3(OH₂)**; 1.279(6), 1.296(5) Å (**Ni4**)] are consistent with C=N double-bond character and indeed reveal little difference to the corresponding distances seen in **L3** [1.273(2), 1.280(2) Å]. In **Ni3(OH₂)** both *N*-aryl groups are inclined almost perpendicularly to the coordination plane with the dihedral angles of 87.70° and 86.39°, while in **Ni4** there is

some variation (88.67° and 75.20°); by comparison the corresponding angles in free **L3** are 84.97° and 80.72°. In addition, the presence of the coordinated water ligand in **Ni3(OH₂)** has the effect that two neighboring molecules assemble through hydrogen bonding interactions (Figures S1). In particular, O(3) undergoes both OH...Br(1) and OH...Br(2) intermolecular interactions (Br(1)...O(3) 3.281 Å; Br(2)...O(3) 3.358 Å).

Table 1 Selected bond lengths (Å) and angles (°) for **L3**, **Ni3** and **Ni4**

	L3	Ni3	Ni4
Bond lengths (Å)			
Ni(1)–Br(1)		2.4297(6)	2.3205(8)
Ni(1)–Br(2)		2.4067(6)	2.3406(8)
Ni(1)–N(1)		2.111(3)	2.014(4)
Ni(1)–N(2)		2.120(3)	2.051(4)
N(1)–C(1)	1.273(2)	1.265(4)	1.279(6)
N(1)–C(45)	1.430(2)	1.456(4)	1.449(5)
N(2)–C(12)	1.280(2)	1.288(4)	1.296(5)
N(2)–C(13)	1.411(2)	1.434(4)	1.428(5)
Bond angles (°)			
N(1)–Ni(1)–N(2)		79.17(11)	82.85(14)
Br(1)–Ni(1)–Br(2)		100.72(2)	124.52(3)
N(1)–Ni(1)–Br(1)		97.14(8)	115.21(10)
N(2)–Ni(1)–Br(1)		158.83(8)	108.24(10)
N(1)–Ni(1)–Br(2)		103.12(8)	104.15(10)
N(2)–Ni(1)–Br(2)		100.41(7)	114.25(10)

All ten complexes are paramagnetic as evidenced by their ¹H NMR spectra, recorded in deuterated dichloromethane, which show broad paramagnetically shifted peaks characteristic of nickel(II) *S* = 1 complexes.¹⁶ In general, the spectra for the nickel bromide complexes (**Ni1** – **Ni5**) proved amenable to assignment which was not the case for chlorides (**Ni6** – **Ni10**) which showed poorly defined and overlapping signals; the origin of these dissimilarities remains unclear. Some differences were also evident in their ¹⁹F{¹H} NMR spectra, with four distinct fluoride resonances for **Ni1** – **Ni3**, one broad resonance for **Ni4** and **Ni5** while chloride-containing **Ni6** – **Ni10**, showed two fluoride resonances. In their FT-IR spectra, two distinct imine stretching frequencies are a feature of all the nickel complexes which fall in the range 1657 – 1643 cm^{−1} which is noticeably lower in wavenumber when compared to that seen in the free ligands (1676 – 1657 cm^{−1}).^{5a-c,8,13}

Catalytic evaluation for ethylene polymerization

(a) Co-catalyst screening.

Complex **Ni1** was selected as the test precatalyst and explored with various alkylaluminum reagents in order to ascertain the most suitable co-catalyst (Table 2). Typically, the tests were performed at 30 °C in toluene under 10 atm C₂H₄ with a run time of 30 minutes. Specifically, four co-catalysts were evaluated namely methylaluminoxane (MAO), modified methylaluminoxane (MMAO), ethylaluminum sesquichloride (EASC) and diethylaluminum chloride (Et₂AlCl). In each case very high activities for ethylene polymerization were observed with their relative values falling in the order: MAO > EASC > Et₂AlCl > MMAO. Common to all the co-catalysts screened, the resultant polyethylenes possessed molecular weights in the

10^5 g mol^{-1} range and exhibited narrow dispersity. On the basis of the higher activities achieved using EASC and MAO, these two co-catalysts were chosen for the further investigations.

Table 2 Screening of four alkylaluminum co-catalysts using **Ni1**^a

Entry	Co-cat	Al:Ni	Mass of PE (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	MAO	2000	7.64	7.64	5.18	1.91	102.3
2	MMAO	2000	5.16	5.16	4.34	2.78	103.9
3	EASC	300	7.03	7.03	1.14	2.72	112.7
4	Et ₂ AlCl	300	5.47	5.47	1.93	2.65	107.9

^a Conditions: 2.0 μmol of **Ni1**; 100 mL of toluene for 10 atm C₂H₄, 30 °C, 0.5 h; ^b Values in units of $10^6 \text{ g (PE) mol}^{-1} (\text{Ni}) \text{ h}^{-1}$; ^c M_w : $\times 10^5 \text{ g mol}^{-1}$; M_w and M_w/M_n determined by GPC; ^d Determined by DSC.

(b) Optimization and catalytic evaluation of **Ni1**/EASC.

With the aim to optimize the reaction parameters of the polymerization (*i.e.*, Al:Ni molar ratio, temperature, reaction duration and pressure), **Ni1** was again used as the test precatalyst, this time using exclusively EASC as the co-catalyst; the results are collected in Table 3.

With the temperature fixed at 30 °C, the Al:Ni molar ratio was increased from 300 to 600 (entries 1 – 4, Table 3) leading to a maximum in activity of $1.12 \times 10^7 \text{ g of PE (mol of Ni)}^{-1} \text{ h}^{-1}$ at an Al:Ni ratio of 600 (entry 4, Table 3). In comparison with benzhydryl-containing **B** and **C** (Chart 1),^{9,11a,13b,17} **Ni1**/EASC under similar conditions showed higher activity and what is more with the advantage of consuming less EASC. With regard to the molecular weight of the polyethylene, a maximum value of $8.10 \times 10^5 \text{ g mol}^{-1}$ was reached when the Al:Ni ratio was 300 (entry 1, Table 3), while at 800 the molecular weight dropped to its lowest level of $1.14 \times 10^5 \text{ g mol}^{-1}$ (entry 6, Table 3). This would suggest that with higher molar ratios of Al:Ni, the rate of chain termination (*e.g.*, chain transfer to aluminum) exceeds

the rate of chain propagation forming polyethylenes with lower molecular weights, which is consistent with previous findings (Figure S2).^{8,11a,13a}

Secondly, in order to shed some light as to the thermostability of **Ni1**/EASC, the reaction temperature of the polymerization was varied with the Al:Ni ratio fixed at 600 (entries 4, 7 – 11, Table 3). The highest activity was observed at 50 °C above which it steadily decreased, an observation that can be accredited to the partial deactivation of the active species and the lower solubility of ethylene in toluene at elevated temperatures;^{9,13a} similar results have been seen with related precatalysts.^{5a-d,11,13} It is worthy of note that this activity at 50 °C surpasses that observed with **B** – **D** (Chart 1) and indeed at 80 °C the polymerization still maintained good activity [$6.01 \times 10^6 \text{ g of PE (mol of Ni)}^{-1} \text{ h}^{-1}$] (for comparison, $1.72 \times 10^6 \text{ g of PE (mol of Ni)}^{-1} \text{ h}^{-1}$ at 50 °C for **C**/EASC, $4.87 \times 10^6 \text{ g of PE (mol of Ni)}^{-1} \text{ h}^{-1}$ at 80 °C for **D_{Me}**/AlEt₂Cl and $0.24 \times 10^6 \text{ g of PE (mol of Ni)}^{-1} \text{ h}^{-1}$ at 80 °C for **D_F**/EASC). As for the molecular weight of the polyethylenes, these was found to decrease as the reaction temperature was raised from 20 to 80 °C (Figure S3), in agreement with more facile chain transfer and termination. Similarly, the T_m values of the polyethylenes also decreased as the temperature was raised with the lowest temperature run (*i.e.* 20 °C) affording polymers displaying the highest T_m 's, characteristic of more linear polymers (see later).

Thirdly, to explore the lifetime of the active species, the polymerization runs using **Ni1**/EASC were evaluated over different reaction times, namely 5, 15, 30 and 60 minutes (entries 9 and 12 – 14, Table 3). The data reveal that the highest activity of $24.90 \times 10^6 \text{ g of PE (mol of Ni)}^{-1} \text{ h}^{-1}$ was observed after 5 minutes and then slowly lowered due to the partial deactivation of the active species.^{5a-c,8,13,18} By contrast, the molecular weights of the polyethylenes gradually increased over time, indicating that at

Table 3 Ethylene polymerization using **Ni1**/EASC^a

Entry	Al:Ni	t (min)	T (°C)	Mass of PE (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	300	30	30	7.03	7.03	8.10	2.77	117.5
2	400	30	30	7.75	7.75	7.86	2.85	117.4
3	500	30	30	11.05	11.05	7.01	2.62	117.0
4	600	30	30	11.25	11.25	6.74	2.91	117.6
5	700	30	30	9.64	9.64	6.63	2.61	116.3
6	800	30	30	8.29	8.29	1.14	2.72	112.7
7	600	30	20	7.89	7.89	7.00	2.90	120.3
8	600	30	40	14.69	14.69	5.89	2.81	92.9
9	600	30	50	16.56	16.56	3.93	2.87	70.6
10	600	30	60	10.84	10.84	3.42	2.58	66.2
11	600	30	80	6.01	6.01	2.91	2.41	– ^g
12	600	5	50	4.15	24.90	3.09	2.54	88.4
13	600	15	50	8.89	17.78	3.19	2.86	85.0
14	600	45	50	18.97	12.64	4.24	2.64	69.1
15	600	60	50	20.39	10.20	5.74	2.32	62.5
16 ^e	600	30	50	3.47	3.47	4.54	2.27	109.5
17 ^f	600	30	50	0.81	0.81	1.86	2.59	108.3

^a Conditions: 2.0 μmol of **Ni1**, 100 mL of toluene, 10 atm C₂H₄; ^b Values in units of $10^6 \text{ g (PE) mol}^{-1} (\text{Ni}) \text{ h}^{-1}$; ^c M_w : $\times 10^5 \text{ g mol}^{-1}$, M_w and M_w/M_n determined by GPC; ^d Determined by DSC; ^e 5 atm C₂H₄; ^f 1 atm C₂H₄; ^g Broad and weak endotherms, amorphous-like polymers.

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longer run times there were still sufficient catalytic species to maintain good activity (Figure S4).^{11b,6e-f,19} As a general feature of all the runs, the polymers showed narrow dispersities (M_w/M_n range: 2.32 – 2.90) in accord with a single site active species. Variations in the ethylene pressure, also had a marked effect on the catalytic activity and the molecular weight of the polymer. On lowering the ethylene pressure from 10 atm to firstly 5 atm and then 1 atm (entries 9, 16, 17, Table 3) saw the activity drop which was accompanied by a lowering in the molecular weight of the polymer; this observation can be attributed to mass transport limitations of the monomer at this low ethylene concentration.^{9,11b}

Overall, it would appear that the introduction of *para*-fluorides to the phenyl groups of the *N*-2,6-benzhydrylphenyl units in **Ni1** has had a positive effect on the catalytic activity, while at the same maintaining high molecular weight. For example, for precatalysts bearing one 2,6-bis(benzhydryl)-4-nitrophenyl group (**C**, Chart 1),⁹ the highest activity reported, under comparable conditions, is 4.61×10^6 g of PE (mol of Ni)⁻¹ h⁻¹ which compares with 16.56×10^6 g of PE (mol of Ni)⁻¹ h⁻¹ for **Ni1**/EASC. Moreover, **Ni1**/EASC exhibited significantly better thermal stability.

Table 4 Ethylene polymerization using **Ni1**/MAO^a

Entry	Precat.	Al:Ni	t (min)	T (°C)	Mass of PE (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	Ni1	1000	30	30	2.64	2.64	7.61	2.55	119.7
2	Ni1	1500	30	30	3.41	3.41	5.59	3.00	119.8
3	Ni1	2000	30	30	7.73	7.73	5.18	1.91	119.4
4	Ni1	2500	30	30	7.64	7.64	1.32	2.34	101.4
5	Ni1	3000	30	30	7.47	7.47	0.79	2.54	106.6
6	Ni1	2000	30	20	5.99	5.99	5.66	2.81	123.6
7	Ni1	2000	30	40	5.04	5.04	0.56	2.25	84.1
8	Ni1	2000	30	50	3.63	3.63	0.35	2.92	71.7
9	Ni1	2000	30	60	2.04	2.04	0.19	2.91	66.3
10	Ni1	2000	5	30	1.98	11.88	3.64	2.48	100.7
11	Ni1	2000	15	30	4.23	8.46	4.54	2.37	105.5
12	Ni1	2000	45	30	8.98	5.99	6.30	2.68	100.8
13	Ni1	2000	60	30	10.01	5.01	8.18	2.87	107.5
14 ^e	Ni1	2000	30	30	2.01	2.01	3.91	2.82	108.8
15 ^f	Ni1	2000	30	30	0.57	0.57	5.64	2.69	112.1
16	A _{2,6} -iPr ₂ Ph	2000	30	20	3.84	3.84	2.72	2.34	107.7

^a Conditions: 2.0 μmol of nickel precatalyst, 100 mL of toluene, 10 atm C₂H₄; ^b Values in units of 10⁶ g (PE) mol⁻¹ (Ni) h⁻¹; ^c M_w : $\times 10^5$ g mol⁻¹, M_w and M_w/M_n determined by GPC; ^d Determined by DSC; ^e 5 atm C₂H₄; ^f 1 atm C₂H₄.

(c) Optimization and catalytic evaluation of Ni1/MAO. Precatalyst **Ni1** was again employed to optimize the reaction parameters this time using MAO as the co-catalyst. Once more the polymerizations were conducted at 10 atm C₂H₄ and the Al:Ni molar ratio, reaction time and temperature systematically varied; the results are collected in Table 4.

On varying the Al:Ni molar ratio from 1000 to 3000, the activity of **Ni1**/MAO at 30 °C reached a peak of 7.73×10^6 g PE mol⁻¹ (Ni) h⁻¹ at 2000 and then steadily decreased (entries 1 – 5, Table 4). Notably, the higher molar ratios gave lower molecular weights for the polyethylenes with modest changes in dispersity; their GPC curves are shown in Figure S5. With regard to the effect of temperature, the polymerizations were

conducted between 20 and 60 °C (entries 3, 6 – 9, Table 4) with the highest activity being observed at 30 °C (which compares with 50 °C for **Ni1**/EASC). Nonetheless, even at 60 °C **Ni1**/MAO retained high activity (2.04×10^6 g PE (mol Ni)⁻¹ h⁻¹) (entry 9, Table 4). On the other hand, the molecular weights of the polyethylenes gradually decreased with increasing polymerization temperature while the dispersity remained generally narrow (M_w/M_n range: 1.70 – 2.91) in support of single-site type catalysts (Figure S6).

As seen with **Ni1**/EASC, the highest catalytic activity using **Ni1**/MAO (entry 10, Table 4) was achieved after 5 minutes [11.88×10^6 g PE mol⁻¹ (Ni) h⁻¹ vs. 24.90×10^6 g PE mol⁻¹ (Ni) h⁻¹ (**Ni1**/EASC)] and then gradually reduced reaching a minimum level of 5.01×10^6 g PE mol⁻¹ (Ni) h⁻¹ after 60 minutes (entry 13, Table 4). Meanwhile the molecular weights of the polyethylenes steadily increased with longer reaction times (Figure S7).

(d) Screening of **Ni1** – **Ni10** with either EASC or MAO.

In order to explore the effect imposed by the *N*-aryl group substitution pattern and halide ligand type on performance, **Ni2** – **Ni10** were additionally screened using the optimized reaction conditions established independently for **Ni1**/EASC and **Ni1**/MAO (see Tables 5 and 6).

Firstly with EASC as co-catalyst, bromide-containing **Ni1** – **Ni5** were initially investigated with the temperature set at 50 °C and the Al:Ni molar ratio at 600 (entries 1 – 5 in Table 5). All five precatalysts displayed high activities [range: 2.97 – 16.56×10^6 g PE mol⁻¹ (Ni) h⁻¹] with their relative values falling in the order: **Ni1** [2,6-di(Me)] > **Ni3** [2,6-di(*i*Pr)] > **Ni2** [2,6-di(Et)] > **Ni4** [2,4,6-tri(Me)] > **Ni5** [2,6-di(Et)-4Me]. Evidently, both electronic and steric effects imparted by the second *N*-aryl group are influential but the trends are, however, far from clear.⁹ Notably, the least sterically hindered system **Ni1** is the most active while the presence of the *para*-methyl groups in **Ni4** and **Ni5** appears to have a negative effect; similar observations have been reported by Wang *et al.*^{13a} In terms of molecular weight, **Ni2** yielded polyethylene with the highest molecular weight of 7.28×10^5 g mol⁻¹ while **Ni3** the lowest at 3.99×10^5 g mol⁻¹. In comparison, the nickel chlorides (**Ni6** – **Ni10**) generally exhibited lower activities [range: 3.68 – 15.53×10^6 g PE mol⁻¹ (Ni) h⁻¹] with: **Ni8** [2,6-di(*i*Pr)] > **Ni6** [2,6-di(Me)] > **Ni7** [2,6-di(Et)] > **Ni9** [2,4,6-tri(Me)] > **Ni10** [2,6-di(Et)-4-Me] (entries 6 – 10, Table 4). It is unclear as to the origin of these variations in catalytic performances between the chlorides and bromides, but is likely due to subtle variations occurring during the activation process and the differences in the counterion type, similar trends have been noted elsewhere.^{9,11b,16}

Secondly, with MAO as the co-catalyst, the nickel bromides **Ni1** – **Ni5** were screened at 30 °C with an Al:Ni molar ratio of 2000. As a general observation, the activities [range: 3.24 – 7.73×10^6 g PE mol⁻¹ (Ni) h⁻¹] were lower (entries 1 – 5, Table 6) than that observed with **Ni1** – **Ni5**/EASC. However, the trends in activity reveal some differences as do the range in molecular weights of the polyethylenes. In this case the relative activity values relate more closely to the steric properties of the precatalyst: **Ni1** [2,6-di(Me)] > **Ni4** [2,4,6-tri(Me)] > **Ni5** [2,6-di(Et)-4-Me] > **Ni2** [2,6-di(Et)] > **Ni3** [2,6-

di(*i*Pr)], with the least bulky system once again the most active and the most bulky now the least active; these observations can be explained in terms of the relative access of the ethylene monomer to the active metal center.^{19,20} By contrast, the increased steric properties retard chain transfer leading to an increase in the molecular weight of the polymer. For example, 2,6-diethyl **Ni3** and 2,6-diisopropyl **Ni5** generate polyethylene with the highest molecular weight with M_w values up to 10.4×10^5 g mol⁻¹ (entries 3 and 5, Table 6). On the other hand, the activities of the chlorides **Ni6** – **Ni10** [range: 2.05 – 6.13×10^6 g

Table 5 Ethylene polymerization using **Ni1** – **Ni10**/EASC under optimized conditions^a

Entry	Precat.	Mass of PE (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	Ni1	16.56	16.56	4.24	2.64	70.6
2	Ni2	4.93	4.93	7.28	2.50	98.3
3	Ni3	12.32	12.32	3.99	2.81	46.9
4	Ni4	4.69	4.69	4.14	2.90	102.6
5	Ni5	2.97	2.97	4.49	2.88	88.9
6	Ni6	9.71	9.71	4.98	2.66	103.3
7	Ni7	6.17	6.17	4.44	2.68	67.5
8	Ni8	15.53	15.53	3.23	2.77	37.8
9	Ni9	4.79	4.79	2.89	2.81	57.8
10	Ni10	3.68	3.68	3.53	2.78	61.4

^a Conditions: 2.0 μmol of precatalyst, 100 mL of toluene, 10 atm C₂H₄, 30 min, 50 °C and Al:Ni molar ratio of 600; ^b Values in units of 10^6 g (PE) mol⁻¹ (Ni) h⁻¹; ^c M_w : $\times 10^5$ g mol⁻¹; M_w and M_w/M_n determined by GPC; ^d Determined by DSC.

Table 6 Ethylene polymerization using **Ni1** – **Ni10**/MAO under optimized conditions^a

Entry	Precat.	Mass of PE (g)	Activity ^b	M_w^c	M_w/M_n^c	T_m^d (°C)
1	Ni1	7.73	7.73	5.18	1.91	119.4
2	Ni2	3.44	3.44	8.21	2.61	95.6
3	Ni3	3.24	3.24	10.39	2.74	72.7
4	Ni4	5.12	5.12	8.21	2.96	100.2
5	Ni5	4.03	4.03	9.35	2.51	98.2
6	Ni6	5.27	5.27	8.21	2.90	106.0
7	Ni7	4.89	4.89	10.59	2.77	107.0
8	Ni8	2.05	2.05	7.93	2.82	86.3
9	Ni9	6.13	6.13	6.12	2.92	101.1
10	Ni10	5.92	5.92	5.06	2.75	101.9

^a Conditions: 2.0 μmol of precatalyst, 100 mL of toluene, 10 atm C₂H₄, 30 min, 30 °C and an Al:Ni molar ratio of 2000; ^b Values in units of 10^6 g (PE) mol⁻¹ (Ni) h⁻¹; ^c M_w : $\times 10^5$ g mol⁻¹; M_w and M_w/M_n determined by GPC; ^d Determined by DSC.

PE mol⁻¹ (Ni) h⁻¹] are again lower than with the bromides albeit less dramatically: **Ni9** [2,4,6-tri(Me)] > **Ni10** [2,6-di(Et)-4-Me] > **Ni6** [2,6-di(Me)] > **Ni7** [2,6-di(Et)] > **Ni8** [2,6-di(ⁱPr)]. As with their bromide counterparts, the polyethylene generated using **Ni6** – **Ni10** displayed high molecular weight in the range 5.1 – 10.6 × 10⁵ g mol⁻¹.

To allow a comparison of the performance of **Ni3**/MAO with a structurally related catalyst, we have also re-tested symmetrical **A**_{2,6-iPr2Ph} (Chart 1)^{2c} with MAO as the co-catalyst (entry 16, Table 4). Under identical conditions (20 °C, 10 atm C₂H₄, Al:Co 2000), **A**_{2,6-iPr2Ph}/MAO showed an activity of 3.84 × 10⁶ g of PE mol⁻¹ (Ni) h⁻¹, which compares favorably with 3.24 × 10⁶ g of PE mol⁻¹ (Ni) h⁻¹ for **Ni3**/MAO (entry 16, Table 4 vs. entry 3, Table 5). Conversely, the molecular weight of the polyethylene produced by **Ni3** was almost four times that observed using **A**_{2,6-iPr2Ph} (*M*_w = 10.39 × 10⁵ g mol⁻¹ vs. 2.72 × 10⁵ g mol⁻¹).

In common to all the polyethylenes obtained using **Ni1** – **Ni10** with either EASC or MAO, narrow dispersities are a feature (*M*_w/*M*_n range: 1.9 – 2.9), indicative of single site-like behavior. Furthermore, the activities using EASC are generally higher than with MAO while the molecular weight of the polyethylene using MAO is greater; in the case of the polymers generated using **Ni3** and **Ni7**, the *M*_w values notably enter the ultra-high molecular weight window (*i.e.*, >1 × 10⁶ g mol⁻¹).

Figure 4 Comparison of the catalytic performance of **Ni4** with previously reported comparators **C**_{2,6-Me2Ph}, **D**_{Me/2,4,6-Me3Ph} and **D**_{F/2,4,6-Me3Ph}.

To enable a comparison to be made with previously reported unsymmetrical bis(arylimino)acenaphthene-nickel catalysts,^{9,11} the molecular weight and activity data for the precatalysts **C**_{2,6-Me2Ph}, **D**_{Me/2,4,6-Me3Ph} and **D**_{F/2,4,6-Me3Ph} (Chart 1) are displayed alongside that for **Ni4** in Figure 4 (Table S1 displays the numerical values); all precatalysts have been screened under optimized conditions with MAO as the co-catalyst at 10 atm C₂H₄. Inspection of the data reveals that the incorporation of a *para*-nitro group in **Ni4** has a positive effect on the molecular weight of the resulting polyethylene in a manner similar to that noted previously.⁹ For instance, for **D**_{Me/2,4,6-Me3Ph}, bearing a 2,6-bis(bis-(4-fluorophenyl)methyl)-4-methylphenyl group (Chart 1),^{11a} the molecular weight of the polymer (4.33 × 10⁵ g mol⁻¹) is almost half that obtained using **Ni4** (8.21 × 10⁵ g mol⁻¹, entry 7, Table 6). In the same way, related observations

can be noted when comparing the polymers generated using **D**_{F/2,4,6-Me3Ph},^{11b} which displays a *M*_w of 4.81 × 10⁵ g mol⁻¹. Moreover, when compared with nitro-containing **C**_{2,6-Me2Ph},⁹ **Ni4** showed higher activity and thermal stability (6.01 × 10⁶ g PE mol⁻¹ (Ni) h⁻¹ at 80 °C, entry 11, Table 3), though the molecular weight of the resulting polyethylene is lower.

Structural properties of the polyethylenes

As can be seen from Tables 2 – 6, the *T*_m values of the polymers obtained in the runs performed at 30 °C or below gave *T*_m's greater than 100 °C suggesting more linear and crystalline structures. Conversely, higher temperature runs led to polymers displaying *T*_m's of less than 100 °C in agreement with more branched and hence less crystalline structures. To confirm this, high temperature ¹³C NMR spectroscopy was performed on four polyethylene samples namely, PE-50_{E/Ni1} [prepared using **Ni1**/EASC at 50 °C (entry 9, Table 3)], PE-20_{E/Ni1} [prepared using **Ni1**/EASC at 20 °C (entry 7, Table 3)], PE-30_{M/Ni1} [prepared using **Ni1**/MAO at 30 °C (entry 3, Table 4) and PE-60_{M/Ni1} [prepared using **Ni1**/MAO at 60 °C (entry 9, Table 4)]; the ¹³C NMR spectra for each sample are shown in Figures 5 – 6 and S8 – S9 with assignments and branching content determinations made using reported approaches.²¹

With regard to the samples prepared at lower temperature, PE-20_{E/Ni1} contained 26 branches/1000 carbons, including isolated methyl (92.5%) and 1,4-paired methyl branches (7.49%) (Figure 5), while PE-30_{M/Ni1} showed 34 branches/1000 carbons, which included methyl (76.4%), ethyl (2.2%), longer chain branches (9.7%), 1,4-paired methyl branches (2.9%) and 1,6-paired methyl branches (8.7%) (Figure 6). This low level of branching present in these two samples is also consistent with their comparable *T*_m values (119.4 vs. 120.3 °C, respectively). By contrast, PE-50_{E/Ni1} and PE-60_{M/Ni1}, prepared at higher temperature, showed a significantly higher branching content of 93 and 111 branches/1000 carbons, respectively. For PE-50_{E/Ni1}, this was composed of methyl (50.7%), ethyl (4.7%), propyl (4.0%), butyl (8.8%), amyl (3.6%), longer chain branches (12.3%), 1,4-paired methyl branches (7.6%) and 1,6-paired methyl branches (8.3%), while for PE-60_{M/Ni1}, this comprised 1,4-paired methyl branches (10.0%) and longer chain branches (19.4%). In comparison with PE-20_{E/Ni1}, the content of methyl-type branches in PE-50_{E/Ni1} decreases from 93 to 51% while the percentage of other types of branches increases. Clearly an increase in the branching content of the polymer results as the temperature of the run is increased with the result that the polymer become less crystalline and more amorphous.^{1e} It is worthy of note that the polymers obtained using **Ni1**, regardless of temperature, are in general more linear with relatively high *T*_m values as well as lower branching contents when compared with those generated using related reported precatalysts.^{8,11,13,22}

Mechanical properties of the polyethylenes

To investigate the mechanical properties of the polymeric materials, samples PE-20_{E/Ni1} (entry 7, Table 3) and PE-60_{E/Ni1} (entry 10, Table 3) were initially studied by stress-strain measurements; the resulting data are presented in Table 7

while stress–strain curves are illustrated in Figure 7.^{6,23} Each mechanical test was performed with five specimens in order to achieve consistent results. Notably, the lowest ultimate tensile stress (5.78 MPa) coupled with the highest strain at break ($\epsilon_b = 363\%$) was observed for PE-60_E/Ni1, a finding that can be attributed to the material being almost amorphous at the measurement temperature. It was apparent that the poor elasticity was caused by poor crystallinity, which can be related to the relatively high branching content.^{5e} As the crystallinity improved in PE-20_E/Ni1 to 38.1%, the ultimate tensile stress increased to 26.05 MPa while the elongation at break reduced to 292.0%, respectively. The observation indicates that the tensile properties of the polyethylene samples were significantly influenced by the branching architectures as well as the crystallinity.^{5e,13a}

Figure 5 ^{13}C NMR spectrum of PE-20_E/Ni1 obtained using Ni1/EASC at 20 °C (entry 9, Table 3).

Figure 6 ^{13}C NMR spectrum of PE-30_M/Ni1 obtained using Ni1/MAO at 30 °C (entry 3, Table 4).

Secondly, the corresponding series of polyethylene samples made with MAO as co-catalyst namely, PE-20_M/Ni1 and PE-60_M/Ni1 (entries 6 and 9 in Table 4), were also tested for stress–strain measurements; the resulting data are given in Table 8 while stress–strain curves are shown in Figure 16. As with PE-20_E/Ni1 and PE-60_E/Ni1, the properties of the polymers are dependent on the branching architectures and crystallinity with PE-60_M/Ni1 showing the lowest ultimate tensile stress (8.86 MPa) and the highest strain at break ($\epsilon_b = 495\%$). It is apparent that the presence of such low elasticity was caused by poor crystallinity, which in-turn relates to the high branching content. Notably, when compared with the elastomeric-type materials generated with previously reported *N,N'*-nickel catalysts,^{5e,9,13a} the ultimate tensile stress of the

current samples are higher and the highest elongation at break lower.

The stress–strain recovery tests, recorded at –10 and 30 °C, were performed on all four samples using dynamic mechanical analysis (DMA) (Figure 8). Typically, these tests were performed at –10 and 30 °C and each cycle repeated up to ten times. Samples PE-20_E/Ni1 and PE-20_M/Ni1 were found too stiff, with the result that the measurements fell outside the stretch limit of the instrument.^{1e} Nonetheless, these findings provide support that these particular polymers are more linear hence display a higher crystalline content. By contrast, samples PE-60_E/Ni1 and PE-60_M/Ni1 behaved satisfactorily in the test and the samples could maintain elasticity even after 10 cycles. As the temperature was increased from –10 to 30 °C the elastic recovery of PE-60_E/Ni1 increased from 48 to 65%. Similarly, the elastic recovery of PE-60_M/Ni1 increased from 26 to 56%. At the same time, the value of the Young's modulus of PE-60_E/Ni1 decreased significantly from 16.3 to 9.3 MPa, while for PE-60_M/Ni1 it decreased from 34.6 to 23.8 MPa. It is worthy of note that the latter values were higher than seen for previously reported comparators,^{5e,9,13a} showing that these samples were less likely to deform. Indeed their properties can be best described as intermediate between that of an elastomer and a LLDPE-like material,²⁵ and hence characteristic of plastomeric-like polymers.²⁶ For example, typical elastomers^{5e,9,13a,27} exhibit low modulus, high elongation at break and good elastic recovery, while the current materials display relatively higher modulus, lower elongation at break and lower elastic recovery properties.

Figure 7 Stress–strain curves for PE-20_E/Ni1, PE-60_E/Ni1, PE-20_M/Ni1 and PE-60_M/Ni1; the vertical line represents the breakage point.

Table 7 Selected properties of PE-20_E/Ni1 and PE-60_E/Ni1 along with PE-20_M/Ni1 and PE-60_M/Ni1.

Sample	<i>T</i> (°C)	<i>T</i> _m ^a (°C)	<i>M</i> _w ^b	Branches/100 C's ^c	<i>X</i> _c ^a (%)	Stress ^d (MPa)	Strain ^d (%)
PE-20 _E /Ni1	20	120.3	7.00	26	38.1	26.05	292.0
PE-60 _E /Ni1	60	66.2	3.42	102	19.9	5.78	363.9
PE-20 _M /Ni1	20	123.6	5.66	30	44.6	39.14	257.2
PE-60 _M /Ni1	60	66.3	0.19	111	25.5	8.86	495.0

^a Determined by DSC; $X_c = \Delta H_f(T_m)/\Delta H_f(T_m^0)$; $\Delta H_f(T_m^0) = 248.3 \text{ J g}^{-1}$; ^b Determined by GPC; ^c Determined by FT-IR spectroscopy;²⁴ ^d Determined using

a universal tester.

Figure 8 Stress-strain recovery tests for PE-60_{E/Ni1} and PE-60_{M/Ni1} at -10 and 30 °C.

Conclusions

The 1-(arylimino)-2-[2,6-bis(bis(4-fluorophenyl)methyl)-4-nitrophenylimino]acenaphthene-nickel(II) halides, **Ni1** – **Ni10**, have been successfully synthesized and fully characterized, including by ^1H and ^{19}F NMR spectroscopy and in two cases by single crystal X-ray diffraction. On activation with MAO or EASC, all the title nickel complexes showed high activities as catalysts for ethylene polymerization with polymer dispersities characteristic of single-site active species. In comparison with previously reported fluoride-free N,N' -nickel catalysts,⁹ these nickel systems exhibit higher activities and better thermal stability operating effectively even at 80 °C with EASC as co-catalyst (6.01×10^6 g of PE (mol of Ni) $^{-1}$ h $^{-1}$), while at the same time maintaining a high molecular weight (as high as 10.6×10^5 g mol $^{-1}$). The feature has been credited to the electron withdrawing properties of the *para*-fluorides along with the *para*-nitro group and their effect on the net charge of the active catalyst. In general, activation with EASC gave more productive catalysts while with MAO the molecular weights of the polymers were higher. Moreover, the branching content of the polymers could be influenced by the temperature of the polymerization run with more branched materials accessible at higher temperatures. The mechanical and elasticity properties of the polymers have been thoroughly investigated and reveal features characteristic of plastomers, materials that can be used in a variety of applications including high-speed, form-fill seal products, display films and fresh produce bags.

Experimental

General considerations

All manipulations of air- and/or moisture-sensitive compounds were carried out under a nitrogen atmosphere using standard

Schlenk techniques. Toluene was refluxed over sodium benzophenone and distilled under nitrogen prior to use. Methylaluminoxane (MAO, 1.46 M solution in toluene) and modified methylaluminoxane (MMAO, 2.0 M in heptane, 3A) were purchased from Akzo Nobel Corp. Diethylaluminum chloride (Et_2AlCl , 1.17 M in toluene) and ethylaluminum sesquichloride ($\text{Et}_3\text{Al}_2\text{Cl}_3$, EASC, 0.87 M in toluene) were purchased from Acros Chemicals. High purity ethylene was purchased from Beijing Yansan Petrochemical Co. and used as received. Other reagents including bis(4-fluorophenyl)methanol were purchased from Aldrich, Acros or local suppliers. ^1H and ^{13}C NMR spectroscopy for the organic compounds, as well as the nickel complexes (^1H NMR and ^{19}F NMR), were performed on Bruker DMX 400 and 600 MHz instruments at room temperature using TMS as an internal standard; δ values are given in ppm. IR spectra were recorded on a PerkinElmer System 2000 FT-IR spectrometer. Elemental analysis was carried out using a Flash EA 1112 microanalyzer. Molecular weights and molecular weight distributions (M_w/M_n) of the polyethylene were determined using a PL-GPC220 instrument at 150 °C with 1,2,4-trichlorobenzene as the solvent. Melting points of the polyethylenes (T_m) were measured from the second scanning run on a PerkinElmer DSC-7 differential scanning calorimeter (DSC) under a nitrogen atmosphere; in the procedure, a sample of about 5.0 mg was heated to 150 °C at a rate of 10 °C min $^{-1}$ and kept for 5 min at 150 °C to remove the thermal history and then cooled at a rate of 10 °C min $^{-1}$ to -20 °C. For the ^{13}C NMR spectra of the polyethylenes, a weighed amount of polyethylene (80 – 100 mg) was combined with 1,1,2,2-tetrachloroethane- d_2 (2 mL) with TMS as an internal standard. Inverse gated ^{13}C spectra recorded on a Bruker DMX 300 spectrometer at 75.47 MHz in 5 mm standard glass tubes at 100 °C with the number of scans between 3000 and 4000. Operating conditions used: spectral width 17.9856 kHz; acquisition time 1.8219 s; relaxation delay 2 s. An estimation of the branching content was made by integration of the corresponding peaks in the ^{13}C NMR spectra using approaches described in the literature.²⁸ The stress-strain curves were obtained using a universal tester (Instron 1122, UK). The stress-strain recovery tests at different temperatures were carried out using a dynamic mechanical analyzer (DMA800, TA) under controlled force mode.

Synthesis of 2,6-bis(bis(4-fluorophenyl)methyl)-4-nitroaniline

A 250 mL round-bottomed flask containing bis(4-fluorophenyl)methanol (21.78 g, 99.0 mmol) and 4-nitroaniline (6.21 g, 45.0 mmol) was stirred and heated to 160 °C for 30 min resulting in the formation of a homogeneous brown melt. A solution of ZnCl_2 (2.00 g, 14.67 mmol) in 12 M HCl (5 mL) was then added dropwise leading to the formation of white fumes in the headspace of the flask. The reaction mixture was stirred and heated to 160 °C for a further 5 h and then allowed to cool to room temperature. The resulting solid was dissolved in CH_2Cl_2 (300 mL), washed with a saturated aqueous solution of NH_4Cl (200 mL) and then twice with brine (200 mL). The resulting brown solution was dried over anhydrous MgSO_4 and concentrated under reduced pressure. The residue was

purified by column chromatography on alumina with petroleum ether/CH₂Cl₂ (10/1 v/v) as the eluent. Following removal of the solvent under reduced pressure, the product was isolated as white powder (8.08 g, 34%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.52 (s, 2H), 7.04 (s, 8H), 7.03 (s, 8H), 5.33 (s, 2H), 4.14 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 163.3, 160.8, 147.8, 138.9, 136.3, 136.3, 130.7, 130.6, 128.0, 124.8, 116.20, 116.0, 50.8. ¹⁹F NMR (565 MHz, CDCl₃): δ -114.4 (s). Anal. calcd for C₃₂H₂₂F₄N₂O₂ (542.53): C, 70.84; H, 4.09; N, 5.16. Found: C, 70.77; H, 4.15; N, 5.09%.

Synthesis of 2-(2,6-bis(bis(4-fluorophenyl)methyl)-4-nitrophenylimino)acenaphthylene-1-one

To a suspension of 2,6-bis(bis(4-fluorophenyl)methyl)-4-nitroaniline (5.42 g, 10.0 mmol) and acenaphthylene-1,2-dione (1.82 g, 10.0 mmol) in toluene (100 mL) was added a catalytic amount of *p*-toluenesulfonic acid (20 mol%). The reaction mixture was stirred and heated to reflux for 6 h. On cooling to room temperature, the mixture was filtered and the volatiles removed under reduced pressure. The residue was recrystallized from dichloromethane and ethanol to afford the product as an orange powder (5.05 g, 72%). ¹H NMR (400 MHz, CDCl₃, TMS): δ 8.16 (s, 2H), 7.79 (t, *J* = 8.4 Hz, 6H), 6.89 (s, 16H), 5.38 (s, 2H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 201.1, 171.3, 152.1, 143.1, 130.9, 130.8, 130.0, 128.2, 127.1, 123.3, 115.5, 115.3, 115.2, 53.40, 50.78. ¹⁹F NMR (565 MHz, CDCl₃): δ -115.5 (s). Anal. calcd for C₄₄H₂₆F₄N₂O₃ (706.70): C, 74.78; H, 3.71; N, 3.96. Found: C, 74.42; H, 3.70; N, 3.93%.

Synthesis of 1-[2,6-{(4-FC₆H₄)₂CH}₂-4-NO₂C₆H₄N]-2-(ArN)C₂C₁₀H₆

(a) Ar = 2,6-Me₂C₆H₃ (**L1**). To a mixture of 2-(2,6-bis(bis(4-fluorophenyl)methyl)-4-nitrophenylimino)acenaphthylene-1-one (1.06 g, 1.50 mmol) and a catalytic amount of *p*-toluenesulfonic acid (20 mol%) in dry toluene (50 mL) was added dropwise 2,6-dimethylaniline (0.22 g, 1.80 mmol). The solution mixture was stirred and heated to reflux for 12 h using a Dean–Stark trap. On completion of the reaction (checked by TLC), the reaction mixture was cooled to room temperature and the volatiles removed under reduced pressure. The crude product was purified by column chromatography on alumina with petroleum ether/ethyl acetate (v/v = 50:3) as the eluent to afford **L1** as a bright yellow powder (0.33 g, 27%). FT-IR (KBr, cm⁻¹): 3045 (w), 1670 (ν_{C=N}, m), 1647 (ν_{C=N}, w), 1588 (m), 1505 (vs), 1470 (w), 1432 (w), 1336 (s), 1278 (w), 1223 (vs), 1158 (m), 1100 (m), 1079 (w), 920 (m), 830.8 (s), 780 (m), 745 (w). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.88 (s, 2H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 1H), 7.34 (t, *J* = 7.2 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 6.8 Hz, 1H), 7.08–6.96 (m, 9H), 6.90–6.86 (m, 4H), 6.61 (d, *J* = 8.0 Hz, 1H), 6.34 (t, *J* = 9.6 Hz, 4H), 6.00 (d, *J* = 8.0 Hz, 1H), 5.62 (s, 2H), 2.20 (s, 6H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 160.2, 160.8, 154.4, 148.2, 141.1, 136.9, 136.0, 134.1, 131.1, 131.0, 130.8, 130.7, 129.7, 129.5, 128.6, 128.3, 124.4, 123.5, 122.6, 115.7, 115.5, 115.3, 115.1, 50.8, 18.1. ¹⁹F NMR (565 MHz, CDCl₃): δ -115.5, -115.7. Anal. calcd for C₅₂H₃₅F₄N₃O₂ (809.27): C, 77.12; H, 4.36; N, 5.19. Found: C, 77.31; H, 4.80; N, 4.84%.

(b) Ar = 2,6-Et₂C₆H₃ (**L2**). Using a similar procedure and molar ratios to that described for **L1**, **L2** was isolated as a bright

yellow powder (0.20 g, 10%). FT-IR (KBr, cm⁻¹): 3066 (w), 2966 (w), 2875 (w), 1657 (ν_{C=N}, w), 1636 (w), 1597 (m), 1506 (vs), 1465 (w), 1434 (w), 1336 (s), 1277 (w), 1224 (vs), 1159 (m), 1100 (w), 1078 (w), 922 (w), 827 (s), 781 (w), 754 (w). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.89 (s, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.73 (d, *J* = 8.0 Hz, 1H), 7.37 (t, *J* = 8.0 Hz, 1H), 7.26 (m, 3H), 7.02–6.96 (m, 9H), 6.90–6.85 (m, 4H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.31 (t, *J* = 8.0 Hz, 4H), 5.80 (d, *J* = 9.6 Hz, 1H), 5.64 (s, 2H), 2.70–2.60 (m, 2H), 2.57–2.47 (m, 2H), 1.17 (t, *J* = 10.0 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 161.7, 158.4, 150.8, 148.1, 140.1, 139.3, 138.2, 137.4, 136.1, 134.1, 131.1, 130.8, 130.7, 126.5, 123.4, 122.0, 115.7, 115.5, 115.3, 115.1, 110.5, 50.7, 27.0, 24.6, 14.39. ¹⁹F NMR (565 MHz, CDCl₃): δ -115.5, -115.7. Anal. calcd for C₅₄H₃₉F₄N₃O₂ (837.90): C, 77.41; H, 4.69; N, 5.01. Found: C, 77.69; H, 4.70; N, 4.89%.

(c) Ar = 2,6-ⁱPr₂C₆H₃ (**L3**). Using a similar procedure and molar ratios to that described for **L1**, **L3** was isolated as a bright yellow powder (0.25 g, 12%). FT-IR (KBr, cm⁻¹): 2960 (w), 2930 (w), 2869 (w), 1662 (ν_{C=N}, w), 1643 (ν_{C=N}, w), 1597 (m), 1506 (vs), 1464 (w), 1333 (s), 1276 (w), 1223 (vs), 1157 (m), 1099 (w), 1044 (w), 921 (w), 829 (s), 781 (m), 752 (w). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.89 (s, 2H), 7.81 (d, *J* = 8.0 Hz, 1H), 7.32 (t, *J* = 8.0 Hz, 3H), 7.26 (m, 3H), 7.05–6.93 (m, 8H), 6.88–6.84 (m, 5H), 6.50 (d, *J* = 7.8 Hz, 1H), 6.28 (t, *J* = 8.0 Hz, 4H), 5.78 (d, *J* = 8.0 Hz, 1H), 5.64 (s, 2H), 2.24–2.20 (m, 1H), 2.02–1.99 (m, 1H), 1.31–1.23 (m, 12H). ¹³C NMR (100 MHz, CDCl₃, TMS): δ 163.1, 162.2, 159.7, 154.8, 146.5, 144.4, 139.8, 137.2, 135.9, 135.3, 134.2, 131.1, 131.0, 130.8, 130.7, 129.9, 129.4, 129.4, 127.9, 126.6, 125.2, 123.8, 123.9, 123.6, 121.2, 115.7, 115.5, 115.4, 115.2, 50.7, 28.8, 24.1, 23.6. ¹⁹F NMR (565 MHz, CDCl₃): δ -115.5, -115.7. Anal. calcd for C₅₆H₄₃F₄N₃O₂ (865.95): C, 77.67; H, 5.01; N, 4.85. Found: C, 77.64; H, 5.16; N, 4.67%.

(d) Ar = 2,4,6-Me₃C₆H₂ (**L4**). Using a similar procedure and molar ratios to that described for **L1**, **L4** was isolated as a bright orange powder (0.13 g, 11%). FT-IR (KBr, cm⁻¹): 2909 (w), 2857 (w), 1666 (ν_{C=N}, w), 1644 (ν_{C=N}, w), 1599 (m), 1505 (vs), 1429 (w), 1334 (s), 1275 (w), 1223 (vs), 1156 (m), 1094 (w), 1041 (w), 919 (w), 832 (s), 779 (m), 734 (w). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.87 (s, 2H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.78 (d, *J* = 8.0 Hz, 1H), 7.38 (t, *J* = 7.8 Hz, 1H), 7.08–6.96 (m, 11H), 6.89–6.86 (m, 4H), 6.68 (d, *J* = 8.0 Hz, 1H), 6.33 (t, *J* = 8.0 Hz, 4H), 5.99 (d, *J* = 7.8 Hz, 1H), 5.62 (s, 2H), 2.40 (s, 3H), 2.16 (s, 6H). ¹³C NMR (100 MHz, CDCl₃): δ 163.5, 162.1, 159.7, 156.0, 154.7, 146.1, 144.3, 143.9, 139.9, 137.9, 136.9, 136.1, 134.1, 133.7, 132.7, 131.1, 131.0, 130.8, 130.7, 130.1, 129.7, 129.3, 128.3, 127.7, 126.6, 124.2, 123.6, 123.5, 122.6, 121.1, 115.7, 115.5, 115.3, 115.1, 50.8, 20.9, 18.1. ¹⁹F NMR (565 MHz, CDCl₃): δ -115.5, -115.8. Anal. calcd for C₅₃H₃₇F₄N₃O₂ (823.87): C, 77.27; H, 4.53; N, 5.10. Found: C, 76.87; H, 4.50; N, 5.12%.

(e) Ar = 2,6-Et₂-4-MeC₆H₂ (**L5**). Using a similar procedure and molar ratios to that described for **L1**, **L5** was isolated as a bright orange powder (0.51 g, 24%). FT-IR (KBr, cm⁻¹): 2965 (w), 2927 (w), 1676 (ν_{C=N}, w), 1648 (ν_{C=N}, w), 1584 (m), 1505 (vs), 1459 (w), 1332 (s), 1226 (vs), 1157 (m), 1097 (w), 1039 (w), 1015 (w), 914 (w), 882 (w), 836 (s), 787 (m), 761 (w). ¹H NMR (400 MHz, CDCl₃, TMS): δ 7.87 (s, 2H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.74 (d, *J* = 8.0 Hz, 1H), 7.36 (t, *J* = 7.8 Hz, 1H), 7.06–6.96

(m, 11H), 6.88–6.85 (m, 4H), 6.66 (d, $J = 8.0$ Hz, 1H), 6.30 (t, $J = 8.0$ Hz, 4H), 5.87 (d, $J = 8.0$ Hz, 1H), 5.62 (s, 2H), 2.64–2.56 (m, 2H), 2.52–2.48 (m, 2H), 1.15 (t, $J = 7.8$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3): δ 163.0, 160.6, 154.7, 145.1, 144.1, 137.0, 135.9, 134.1, 133.9, 131.1, 131.0, 130.8, 130.7, 130.1, 129.9, 129.4, 129.2, 128.2, 128.0, 127.3, 126.6, 123.7, 123.5, 123.1, 115.7, 115.5, 115.3, 115.1, 50.7, 26.9, 24.5, 21.2, 14.52. ^{19}F NMR (565 MHz, CDCl_3): δ -115.5, -115.8. Anal. calcd for $\text{C}_{53}\text{H}_{37}\text{F}_4\text{N}_3\text{NiO}_2$ (851.93): C, 77.54; H, 4.85; N, 4.93. Found: C, 77.56; H, 5.25; N, 4.64%.

Synthesis of [1-[2,6-((4- FC_6H_4) $_2\text{CH}$) $_2$ -4- $\text{NO}_2\text{C}_6\text{H}_4\text{N}$]-2-(ArN) $\text{C}_2\text{C}_{10}\text{H}_6$] NiBr_2

(a) $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**Ni1**). Under a nitrogen atmosphere, a mixture of **L1** (0.20 g, 0.25 mmol) and $(\text{DME})\text{NiBr}_2$ (0.08 g, 0.25 mmol) in dichloromethane (10 mL) and ethanol (5 mL) was stirred at room temperature for 20 h. On completion of the reaction all volatiles were removed under reduced pressure to give a concentrated solution. An excess of diethyl ether was added to induce precipitation. The precipitate was filtered, washed with diethyl ether (3×10 mL) and dried under reduced pressure to give **Ni1** as an orange powder (0.16 g, 62%). FT-IR (KBr cm^{-1}): 2972 (w), 2858 (w), 1654 ($\nu_{\text{C=N}}$, w), 1624 ($\nu_{\text{C=N}}$, w), 1599 (m), 1527 (w), 1504 (vs), 1437 (w), 1341 (m), 1290 (w), 1221 (s), 1157 (m), 1105 (w), 954 (w), 881 (w), 830 (s), 774 (s). ^{19}F NMR (565 MHz, CD_2Cl_2): δ -116.2, -116.3, -116.34, -116.6. ^1H NMR (600 MHz, CD_2Cl_2 , TMS): δ 24.23 (2H, Ar-H_m), 23.75 (1H, An-H), 22.92 (2H, Ar-H_m), 15.56 (1H, An-H), 15.06 (1H, An-H), 14.62 (1H, An-H), 12.45 (0.3H, -CHPh $_2$), 7.81 (3H, Ar-H), 7.60 (4H, Ar-H), 7.18 (2H, Ar-H), 6.43 (3H, Ar-H), 5.72 (4H, Ar-H), 5.57 (1H, Ar-H), 5.15 (1H, An-H), -12.92 (0.41H, Ar-H_p). Anal. calcd for $\text{C}_{52}\text{H}_{35}\text{Br}_2\text{F}_4\text{N}_3\text{NiO}_2$ (1028.35): C, 60.73; H, 3.43; N, 4.09. Found: C, 59.07; H, 3.51; N, 3.89%.

(b) $\text{Ar} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$ (**Ni2**). Using a similar procedure and molar ratios to that described **Ni1**, **Ni2** was isolated as a dark red powder (0.09 g, 71%). FT-IR (KBr cm^{-1}): 2970 (w), 2876 (w), 1644 ($\nu_{\text{C=N}}$, w), 1600 ($\nu_{\text{C=N}}$, w), 1579 (w), 1527 (w), 1504 (vs), 1439 (w), 1344 (m), 1295 (w), 1223 (s), 1158 (m), 1133 (w), 1053 (w), 1015 (w), 957 (w), 881 (w), 836 (s), 772 (m). ^{19}F NMR (565 MHz, CD_2Cl_2): δ -116.2, -116.3, -116.4, -116.6. ^1H NMR (600 MHz, CD_2Cl_2 , TMS): δ 24.14 (1H, An-H), 22.77 (2H, Ar-H_m), 20.33 (2H, Ar-H_m), 15.68 (1H, An-H), 15.05 (1H, An-H), 14.70 (1H, An-H), 11.79 (0.6H, -CHPh $_2$), 7.83 (4H, Ar-H), 7.66 (5H, Ar-H), 7.23 (1H, Ar-H), 5.73 (5H, Ar-H), 5.58 (1H, Ar-H), 1.24 (6H, -CH $_2\text{CH}_3$), -12.55 (1H, Ar-H_p). Anal. calcd for $\text{C}_{54}\text{H}_{39}\text{Br}_2\text{F}_4\text{N}_3\text{NiO}_2$ (1056.40): C, 61.40; H, 3.72; N, 3.98. Found: C, 60.69; H, 3.57; N, 3.92%.

(c) $\text{Ar} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ (**Ni3**). Using a similar procedure and molar ratios to that described **Ni1**, **Ni3** was isolated as an orange powder (0.13 g, 80%). FT-IR (KBr cm^{-1}): 3075 (w), 2968 (w), 2866 (w), 1654 ($\nu_{\text{C=N}}$, w), 1625 ($\nu_{\text{C=N}}$, m), 1601 (w), 1505 (vs), 1465 (w), 1437 (w), 1343 (s), 1287 (w), 1222 (s), 1156 (m), 1103 (w), 1015 (w), 954 (w), 831 (s), 799 (m). ^{19}F NMR (565 MHz, CD_2Cl_2): δ -116.1, -116.3, -116.3, -116.5. ^1H NMR (600 MHz, CD_2Cl_2 , TMS): δ 26.26 (1H, An-H), 24.66 (2H, Ar-H_m), 23.10 (2H, Ar-H_m), 17.32 (2H, An-H), 16.01 (1H, An-H), 12.45

(0.6H, -CHPh $_2$), 8.35 (4H, Ar-H), 7.05 (8H, Ar-H), 6.84 (1H, An-H), 5.64 (4H, Ar-H), 5.03 (1H, An-H), 1.33 (12H, -CH(CH $_3$) $_2$), -15.08 (1H, Ar-H_p). Anal. calcd for $\text{C}_{56}\text{H}_{43}\text{Br}_2\text{F}_4\text{N}_3\text{NiO}_2$ (1084.45): C, 62.02; H, 4.00; N, 3.87. Found: C, 61.88; H, 4.43; N, 3.48%.

(d) $\text{Ar} = 2,4,6\text{-Me}_3\text{C}_6\text{H}_2$ (**Ni4**). Using a similar procedure and molar ratios to that described **Ni1**, **Ni4** was isolated as a dark red powder (0.10 g, 80%). FT-IR (KBr cm^{-1}): 2972 (w), 2865 (w), 1647 ($\nu_{\text{C=N}}$, w), 1621 ($\nu_{\text{C=N}}$, w), 1602 (w), 1534 (w), 1505 (s), 1427 (w), 1342 (m), 1296 (w), 1228 (s), 1158 (m), 1098 (w), 835 (s), 795 (w). ^{19}F NMR (565 MHz, CD_2Cl_2): δ -116.3. ^1H NMR (600 MHz, CD_2Cl_2 , TMS): δ 33.15 (3H, Ar- p -CH $_3$), 28.19 (6H, -CH $_3$), 25.89 (1H, An-H), 24.74 (2H, Ar-H_m), 22.30 (2H, Ar-H_m), 16.53 (1H, An-H), 16.23 (1H, An-H), 15.62 (1H, An-H), 11.20 (0.4H, -CHPh $_2$), 8.35 (4H, Ar-H), 7.12 (8H, Ar-H), 6.73 (1H, An-H), 5.47 (4H, Ar-H), 4.99 (1H, An-H). Anal. calcd for $\text{C}_{53}\text{H}_{37}\text{Br}_2\text{F}_4\text{N}_3\text{NiO}_2$ (1042.37): C, 61.07; H, 3.58; N, 4.03. Found: C, 61.30; H, 3.51; N, 4.02%.

(e) $\text{Ar} = 2,6\text{-Et}_2\text{-4-MeC}_6\text{H}_2$ (**Ni5**). Using a similar procedure and molar ratios to that described **Ni1**, **Ni5** was isolated as a dark red powder (0.17 g, 64%). FT-IR (KBr cm^{-1}): 2988 (w), 2871 (w), 1645 ($\nu_{\text{C=N}}$, w), 1617 ($\nu_{\text{C=N}}$, w), 1599 (w), 1578 (w), 1532 (w), 1505 (vs), 1463 (w), 1339 (m), 1292 (w), 1225 (s), 1157 (s), 1098 (w), 848 (w), 837 (s), 799 (w). ^{19}F NMR (565 MHz, CD_2Cl_2): δ -116.3. ^1H NMR (600 MHz, CD_2Cl_2 , TMS): δ 33.18 (3H, Ar- p -CH $_3$), 26.24 (1H, An-H), 24.53 (2H, Ar-H_m), 22.40 (2H, Ar-H_m), 16.62 (1H, An-H), 16.30 (1H, An-H), 15.73 (1H, An-H), 10.94 (0.4H, -CHPh $_2$), 8.41 (4H, Ar-H), 7.17 (4H, Ar-H), 7.23 (3H, Ar-H), 6.78 (1H, An-H), 5.57 (5H, Ar-H), 5.04 (1H, Ar-H), 1.29 (6H, -CH $_2\text{CH}_3$). Anal. calcd for $\text{C}_{55}\text{H}_{41}\text{Br}_2\text{F}_4\text{N}_3\text{NiO}_2$ (1070.43): C, 61.71; H, 3.86; N, 3.93. Found: C, 61.64; H, 3.84; N, 3.90%.

Synthesis of [1-[2,6-((4- FC_6H_4) $_2\text{CH}$) $_2$ -4- $\text{NO}_2\text{C}_6\text{H}_4\text{N}$]-2-(ArN) $\text{C}_2\text{C}_{10}\text{H}_6$] NiCl_2

(a) $\text{Ar} = 2,6\text{-Me}_2\text{C}_6\text{H}_3$ (**Ni6**). $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.08 g, 0.25 mmol) was added to a solution of **L1** (0.20 g 0.25 mmol) in mixture of dichloromethane and ethanol (5/5 mL) under a nitrogen atmosphere and the mixture stirred for 24 h at ambient temperature. An excess of diethyl ether was added to induce precipitation and the precipitate filtered, washed with diethyl ether (3×10 mL) and then dried under reduced pressure to afford **Ni6** as a brown powder (0.22 g, 94%). FT-IR (KBr cm^{-1}): 3072 (w), 2972 (w), 2857 (w), 1656 ($\nu_{\text{C=N}}$, w), 1628 ($\nu_{\text{C=N}}$, w), 1599 (m), 1529 (w), 1505 (vs), 1438 (w), 1341 (m), 1290 (w), 1220 (s), 1158 (m), 1106 (w), 1013 (w), 954 (w), 882 (w), 831 (m), 775 (m). ^{19}F NMR (565 MHz, CD_2Cl_2): δ -116.3, -116.6. Anal. calcd for $\text{C}_{52}\text{H}_{35}\text{Cl}_2\text{F}_4\text{N}_3\text{NiO}_2$ (939.45): C, 66.48; H, 3.76; N, 4.47. Found: C, 66.03; H, 3.84; N, 4.25%.

(b) $\text{Ar} = 2,6\text{-Et}_2\text{C}_6\text{H}_3$ (**Ni7**). Using a similar procedure and molar ratios to that described for **Ni6**, **Ni7** was isolated as a brown powder (0.11 g, 95%). FT-IR (KBr cm^{-1}): 3076 (w), 2969 (w), 2876 (w), 1658 ($\nu_{\text{C=N}}$, w), 1627 ($\nu_{\text{C=N}}$, w), 1581 (w), 1599 (w), 1506 (vs), 1436 (w), 1338 (m), 1288 (w), 1222 (s), 1157 (m), 1093 (w), 1046 (w), 1014 (w), 948 (w), 879 (w), 830 (s), 772 (m). ^{19}F NMR (565 MHz, CD_2Cl_2): δ -116.3, -116.6. Anal. calcd for $\text{C}_{54}\text{H}_{39}\text{Cl}_2\text{F}_4\text{N}_3\text{NiO}_2$ (967.50): C, 67.04; H, 4.06; N, 4.34. Found: C, 66.81; H, 4.25; N, 4.16%.

(c) Ar = 2,6-*i*-Pr₂C₆H₃ (**Ni8**). Using a similar procedure and molar ratios to that described for **Ni6**, **Ni8** was isolated as a brown powder (0.09 g, 60%). FT-IR (KBr cm⁻¹): 3069 (w), 2968 (w), 2866 (w), 1652 ($\nu_{C=N}$, w), 1625 ($\nu_{C=N}$, w), 1600 (w), 1506 (vs), 1465 (w), 1437 (w), 1343 (m), 1288 (w), 1222 (s), 1157 (m), 1103 (w), 1015 (w), 954 (w), 832 (s), 798 (w), 779 (w). ¹⁹F NMR (565 MHz, CD₂Cl₂): δ -116.3, -116.6. Anal. calcd for C₅₆H₄₃Cl₂F₄N₃NiO₂ (967.50): C, 67.56; H, 4.35; N, 4.22. Found: C, 67.73; H, 4.48; N, 4.01%.

(d) Ar = 2,4,6-Me₃C₆H₂ (**Ni9**). Using a similar procedure and molar ratios to that described for **Ni6**, **Ni9** was isolated as a brown powder (0.14 g, 74%). FT-IR (KBr cm⁻¹): 3067 (w), 2954 (w), 2902 (w), 1655 ($\nu_{C=N}$, w), 1626 ($\nu_{C=N}$, w), 1603 (w), 1588 (w), 1578 (w), 1505 (vs), 1420 (w), 1341 (m), 1290 (w), 1221 (s), 1159 (m), 1099 (w), 1018 (w), 958 (w), 882 (w), 829 (w), 775 (m). ¹⁹F NMR (565 MHz, CD₂Cl₂): δ -116.3, -116.6. Anal. calcd for C₅₃H₃₇Cl₂F₄N₃NiO₂ (953.47): C, 66.76; H, 3.91; N, 4.41. Found: C, 66.34; H, 3.95; N, 4.35%.

(e) Ar = 2,6-Et₂-4-MeC₆H₂ (**Ni10**). Using a similar procedure and molar ratios to that described for **Ni6**, **Ni10** was isolated as a brown powder (0.12 g, 61%). FT-IR (KBr cm⁻¹): 3074 (w), 2968 (w), 2878 (w), 1653 ($\nu_{C=N}$, w), 1625 ($\nu_{C=N}$, w), 1601 (w), 1582 (w), 1506 (vs), 1459 (w), 1434 (w), 1340 (m), 1290 (w), 1226 (s), 1157 (s), 1096 (w), 1047 (w), 955 (w), 832 (s), 778 (m). ¹⁹F NMR (565 MHz, CD₂Cl₂): δ -116.3, -116.6. Anal. calcd for C₅₅H₄₁Cl₂F₄N₃NiO₂ (981.53): C, 67.30; H, 4.21; N, 4.28. Found: C, 67.76; H, 4.14; N, 4.20%.

X-ray crystallographic studies

Single crystals of **L3**, **Ni3** and **Ni4** suitable for the X-ray determinations were grown by laying diethyl ether onto a dichloromethane solution of the corresponding compound at room temperature. With graphite monochromated Mo-K α radiation (λ = 0.71073 Å) at 173(2) K, cell parameters were obtained by global refinement of the positions of all collected reflections. Intensities were corrected for Lorentz and

polarization effects and empirical absorption. The structures were solved by direct methods and refined by full-matrix least squares on F^2 . All hydrogen atoms were placed in calculated positions. Structure solution and refinement were performed by using the Olex2 1.2 package and SHELXT (Sheldrick During the structural refinement, the solvent was squeezed (**Ni3** and **Ni4**) with PLATON software²⁹. Details of the X-ray structure determinations and refinements are provided in Table S2.

Polymerization studies

(a) Ethylene polymerization at 1 atm C₂H₄.

Complex **Ni1** was added to a Schlenk vessel followed by toluene (30 mL) and then the required amount of co-catalyst (EASC, MAO) introduced by syringe. The solution was then stirred at either 50 °C or 30 °C under 1 atm of ethylene C₂H₄. After 30 min, the pressure was vented and the solution quenched with 10% hydrochloric acid in ethanol. The polymer was washed with ethanol, dried under reduced pressure at 40 °C and then weighed.

(b) Ethylene polymerization at 5/10 atm C₂H₄.

The polymerization at high ethylene pressure was carried out in a stainless-steel autoclave (0.25 L) equipped with an ethylene pressure control system, a mechanical stirrer and a temperature controller. At the required reaction temperature the precatalyst (2.0 μ mol) dissolved in toluene (50 mL) was injected into the autoclave, followed by freshly distilled toluene (25 mL). The required amount of co-catalyst (MAO, MMAO, Et₂AlCl, EASC) and more toluene (25 mL) were then injected successively to complete the addition. The autoclave was immediately pressurized to the designated ethylene pressure and the stirring commenced. After the required reaction time, the ethylene pressure was vented and the reaction quenched with 10% hydrochloric acid in ethanol. The polymer was collected and washed with ethanol and dried under reduced pressure at 50 °C and weighed.

Conflicts of interest

There are no conflicts to declare.

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Notes and References

- (a) S. D. Ittel, L. K. Johnson, M. Brookhart, *Chem. Rev.*, 2000, **100**, 1169–1203; (b) V. C. Gibson, C. Redshaw and G. A. Solan, *Chem. Rev.*, 2007, **107**, 1745–1776; (c) C. Bianchini, G. Giambastiani, L. Luconi and A. Meli, *Coord. Chem. Rev.*, 2010, **254**, 431–455; (d) W.-H. Sun, S. Zhang and W. Zuo, *C. R. Chim.*, 2008, **11**, 307–316; (e) H. Suo, I. V. Oleynik, C. Huang, I. Oleynik, G. A. Solan, Y. Ma, T. Liang and W.-H. Sun, *Dalton Trans.*, 2017, **46**, 15684–15697; (f) Z. Wang, G. A. Solan, Q. Mahmood, Q. Liu, Y. Ma, X. Hao and W.-H. Sun, *Organometallics*, 2018, **37**, 380–389; (g) Z. Wang, Q. Liu, G. A. Solan and W.-H. Sun, *Coord. Chem. Rev.*, 2017, **350**, 68–83; (h) Z. Wang, G. A. Solan, W. Zhang and W.-H. Sun, *Coord. Chem. Rev.*, 2018, **363**, 92–108. (i) L. Guo, S. Dai, X. Sui and C. Chen, *ACS Catal.*, 2016, **6**, 428–441; (j) L. Guo, W. Liu and C. Chen, *Mater. Chem. Front.*, 2017, **1**, 2487–2494; (k) C. Chen, *Nat. Rev. Chem.*, 2018, **2**, 6–14; (l) C. Chen, *ACS Catal.*, 2018, **8**, 5506–5514.
- (a) L. K. Johnson, C. M. Killian and M. Brookhart, *J. Am. Chem. Soc.*, 1995, **117**, 6414–6415; (b) C. M. Killian, D. J. Tempel, L. K. Johnson and M. Brookhart, *J. Am. Chem. Soc.*, 1996, **118**, 11664–11615; (c) S. Kong, K. Song, T. Liang, C.-Y. Guo, W.-H. Sun and C. Redshaw, *Dalton Trans.*, 2013, **42**, 9176–9187.
- (a) D. H. Camacho, E. V. Salo, J. W. Ziller and Z. Guan, *Angew Chem Int Ed Engl.*, 2004, **43**, 1821–5; (b) F.-S. Liu, H.-B. Hu, Y. Xu, L.-H. Guo, S.-B. Zai, K.-M. Song, H.-Y. Gao, L. Zhang, F.-M. Zhu and Q. Wu, *Macromolecules*, 2009, **42**, 7789–7796; (c) Q. Mahmood and W.-H. Sun, *Roy. Soc. Open Sci.*, 2018, **5**, 180367.

- 4 (a) J. L. Rhinehart, L. A. Brown, B. K. Long, *J. Am. Chem. Soc.*, 2013, **135**, 16316-9; (b) D. P. Gates, S. A. Svejda, E. Oñate, C. M. Killian, L. K. Johnson, P. S. White and M. Brookhart, *Macromolecules*, 2000, **33**, 2320-2334.
- 5 (a) H. Liu, W. Zhao, X. Hao, C. Redshaw, W. Huang and W.-H. Sun, *Organometallics*, 2011, **30**, 2418-2424; (b) H. Liu, W. Zhao, J. Yu, W. Yang, X. Hao, C. Redshaw, L. Chen and W.-H. Sun, *Catal. Sci. Technol.*, 2012, **2**, 415-422; (c) S. Kong, C.-Y. Guo, W. Yang, L. Wang, W.-H. Sun and R. Glaser, *J. Organomet. Chem.*, 2013, **725**, 37-45; (d) C. Wen, S. Yuan, Q. Shi, E. Yue, D. Liu and W.-H. Sun, *Organometallics*, 2014, **33**, 7223-7231; (e) Z. He, Y. Liang, W. Yang, H. Uchino, J. Yu, W.-H. Sun and C. C. Han, *Polymer*, 2015, **56**, 119.
- 6 (a) W.-H. Sun, S. Song, B. Li, C. Redshaw, X. Hao, Y. S. Li and F. Wang, *Dalton Trans.*, 2012, **41**, 11999-2010; (b) J. Lai, X. Hou, Y. Liu, C. Redshaw and W.-H. Sun, *J. Organomet. Chem.*, 2012, **702**, 52-58; (c) X. Hou, Z. Cai, X. Chen, L. Wang, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2012, **41**, 1617-23; (d) X. Hou, T. Liang, W.-H. Sun, C. Redshaw and X. Chen, *J. Organomet. Chem.*, 2012, **708-709**, 98-105; (e) E. Yue, L. Zhang, Q. Xing, X. P. Cao, X. Hao, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2014, **43**, 423-31; (f) E. Yue, Q. Xing, L. Zhang, Q. Shi, X. P. Cao, L. Wang, C. Redshaw and W.-H. Sun, *Dalton Trans.*, 2014, **43**, 3339-46; (g) J. L. Rhinehart, N. E. Mitchell and B. K. Long, *ACS Catal.*, 2014, **4**, 2501-2504.
- 7 (a) D. Jia, W. Zhang, W. Liu, L. Wang, C. Redshaw and W.-H. Sun, *Catal. Sci. Technol.*, 2013, **3**, 2737; (b) Q. Liu, W. Zhang, D. Jia, X. Hao, C. Redshaw and W.-H. Sun, *Applied Catal. A: Gen.*, 2014, **475**, 195-202.
- 8 L. Fan, S. Du, C. Y. Guo, X. Hao and W.-H. Sun, *J. Polym. Sci., Part A: Polym. Chem.*, 2015, **53**, 1369-1378.
- 9 Q. Mahmood, Y. Zeng, X. Wang, Y. Sun and W.-H. Sun, *Dalton Trans.*, 2017, **46**, 6934-6947.
- 10 (a) T. Zhang, D. Guo, S. Jie, W.-H. Sun, T. Li and X. Yang, *J. Polym. Sci., Part A: Polym. Chem.*, 2004, **42**, 4765-4774; (b) W. Yang, J. Yi and W.-H. Sun, *Macromol. Chem. Phys.*, 2015, **216**, 1125-1133.
- 11 (a) S. Du, S. Kong, Q. Shi, J. Mao, C. Guo, J. Yi, T. Liang and W.-H. Sun, *Organometallics*, 2015, **34**, 582-590; (b) X. Wang, L. Fan, Y. Yuan, S. Du, Y. Sun, G. A. Solan, C. Y. Guo and W. H. Sun, *Dalton Trans.*, 2016, **45**, 18313-18323.
- 12 (a) T. E. Müller, K. C. Hultsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.*, 2008, **108**, 3795-3892; (b) S. Meiries, K. Speck, D. B. Cordes, A. M. Z. Slawin and S. P. Nolan, *Organometallics*, 2012, **32**, 330-339.
- 13 (a) X. Wang, L. Fan, Y. Ma, C.-Y. Guo, G. A. Solan, Y. Sun and W.-H. Sun, *Polym. Chem.*, 2017, **8**, 2785-2795; (b) L. Fan, E. Yue, S. Du, C. Y. Guo, X. Hao and W.-H. Sun, *RSC Adv.*, 2015, **5**, 93274-93282.
- 14 (a) F. Huang, W. Zhang, E. Yue, T. Liang, X. Hu and W.-H. Sun, *Dalton Trans.*, 2016, **45**, 657-666; (b) F. Huang, Q. Xing, T. Liang, Z. Flisak, B. Ye, X. Hu, W. Yang and W.-H. Sun, *Dalton Trans.*, 2014, **43**, 16818-29.
- 15 (a) Z. Wang, Y. Zhang, Y. Ma, X. Hu, G. A. Solan, Y. Sun and W.-H. Sun, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 3494-3505; (b) Z. Sun, E. Yue, M. Qu, I. V. Oleynik, I. I. Oleynik, K. Li, T. Liang, W. Zhang and W.-H. Sun, *Inorg. Chem. Front.*, 2015, **2**, 223.
- 16 B. R. McGarvey, *Inorg. Chem.*, 1995, **34**, 6000.
- 17 Q. Mahmood, Y. Zeng, E. Yue, G. A. Solan, T. Liang and W.-H. Sun, *Polym. Chem.*, 2017, **8**, 6416-6430.
- 18 Z. Sun, F. Huang, M. Qu, E. Yue, I. V. Oleynik, I. I. Oleynik, Y. Zeng, T. Liang, K. Li, W. Zhang and W.-H. Sun, *RSC Adv.*, 2015, **5**, 77913.
- 19 F. Huang, Z. Sun, S. Du, E. Yue, J. Ba, X. Hu, T. Liang, G. B. Galland and W.-H. Sun, *Dalton Trans.*, 2015, **44**, 14281.
- 20 (a) R. Zhang, Z. Wang, Z. Flisak, X. Hao, Q. Liu and W.-H. Sun, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 2601-2610; (b) B. K. Long, J. M. Eagan, M. Mulzer and G. W. Coates, *Angew. Chem. Int. Ed.*, 2016, **55**, 7106-7110; (c) L. Zhong, G. Li, G. Liang, H. Gao and Q. Wu, *Macromolecules*, 2017, **50**, 2675-2682; (d) C. Zou, S. Dai and C. Chen, *Macromolecules*, 2018, **51**, 49-56; (e) S. Dai and C. Chen, *Macromolecules*, 2018, **51**, 6818-6824; (f) G. Song, W. Pang, W. Li, M. Chen and C. Chen, *Polym. Chem.*, 2017, **8**, 7400-7405.
- 21 G. B. Galland, R. F. De Souza, R. S. Mauler and F. F. Nunes, *Macromolecules*, 1999, **32**, 1620.
- 22 (a) S. Yuan, E. Yue, C. Wen and W.-H. Sun, *RSC Adv.*, 2016, **6**, 7431-7438; (b) Y. Chen, S. Du, C. Huang, G. A. Solan, X. Hao and W.-H. Sun, *J. Polym. Sci., Part A: Polym. Chem.*, 2017, **55**, 1971-1983.
- 23 B. Gabrielle, L. Guy, P.-A. Albouy, L. C. Vanel, D. R. Long and P. Sotta, *Macromolecules*, 2011, **44**, 7006-7015.
- 24 T. Usami and S. Takayama, *Polym. J.*, 1984, **16**, 731.
- 25 (a) H. P. Wang, D. U. Khariwala, W. Cheung, S. P. Chum, A. Hiltner and E. Baer, *Macromolecules*, 2007, **40**, 2852-2862; (b) S. Bensason, J. Minick, A. Moet, S. Chum, A. Hiltner and E. Baer, *J. Polym. Sci., Part B: Polym. Phys.*, 1996, **34**, 1301-1315.
- 26 Pierro, G. Zanchin, E. Parisini, J. Martí-Rujas, M. Canetti, G. Ricci, F. Bertini and G. Leone, *Macromolecules*, 2018, **51**, 801-814.
- 27 (a) Y. Na, D. Zhang and C. Chen, *Polym. Chem.*, 2017, **8**, 2405-2409; (b) K. Lian, Y. Zhu, W. Li, S. Dai and C. Chen, *Macromolecules*, 2017, **50**, 6074-6080.
- 28 G. B. Galland, R. Quijada, R. Rojas, G. Bazan and Z. J. A. Komon, *Macromolecules*, 2002, **35**, 339-345.
- 29 (a) G. M. Sheldrick, *Acta Crystallogr.*, 2015, **A71**, 3-8; (b) G. M. Sheldrick, *Acta Crystallogr.*, 2015, **C71**, 3-8.