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PAPER

Double stranded polymeric ladderphanes with 16-π-electron antiaromatic metallocycle linkers†‡

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Three double stranded polymeric ladderphanes with 16-π-electron antiaromatic metallocycle linkers are synthesised by ring opening metathesis polymerisation of the corresponding bisnorbornene monomers. Scanning tunnelling microscopic (STM) images indicate that these polymers can assemble nicely on a graphite surface to form a highly ordered pattern which has been observed in other ladderphanes with different kinds of aromatic linkers. Little change in ^{1}H NMR, absorption spectra and electrochemical oxidation potential between these polymers and the corresponding monomers suggest that there would be no interactions between adjacent antiaromatic linkers in these polymeric ladderphanes. Presumably, the distance between two antiaromatic rings in these ladderphanes (5–6 Å) is far too long in comparison with that between two rings in methylene-bridged antiaromatic superphanes (2.5 Å<), where stabilisation is predicted by theoretical calculations.

Introduction

Cofacial long-range π-stacking towards highly ordered layer arrangement of aromatic rings can result in strong electronic coupling between these π-conjugated systems leading to charge delocalisation.[1] This strategy has offered tremendous opportunities for optoelectronic applications. However, large area processing with such cofacial alignment for device applications is not trivial. It is envisioned that supramolecular architectures may offer a feasibility to align these planar π-systems cofacially. A DNA molecule is a representative supramolecule where all base pairs are cofacially arranged and the spacing between these layers is 3.4 Å. Interactions between cofacially aligned metallocycles in a DNA system are well documented.[2] In order to mimic DNA chemistry, we recently reported a series of polynorbornene-based double stranded ladderphanes **1** with a range of aromatic linkers.[4–6] Similar ladderphanes with disulfide backbones have recently been disclosed.[3] It is noteworthy that **1** can assemble nicely on a graphite surface to form a two-dimensional array.[4–6] These polymers tend to form aggregate along the longitudinal axis of the polymer, presumably by π–π interactions between the styrene and vinyl end groups. Side-by-side van der Waals interactions between the polymer chains may lead to aggregation in the second dimension. Interactions between the aromatic chromophores in **1** are recognised by fluorescence quenching,[6] excimer formation,[6a] Soret band splitting or broadening,[6a,d] and pairing of unpaired electrons.[5c] It is noteworthy that each of the monomeric units in **1** spans about 5–6 Å.[4–6] The presence of the flexible ester linkage in **1** could bring adjacent aromatic chromophores to a more proximal distance so that interactions between these conjugated moieties would be facilitated. For example, the insertion of bidentate DABCO§ ligand into **1** with zinc-porphyrins as part of the linkers further suggests the flexibility of these species connecting two polynorbornene strands.[6d] To the best of our knowledge, no experimental evidence on the interactions between stacking antiaromatic systems is known. Theoretical modeling on stacking of antiaromatic rings in superphane structures with multiple methylene linkers shows that their antiaromaticity can be stabilised by three-dimensional delocalisation which may lead to aromaticity.[7] However, the spacing separated the two antiaromatic rings in these superphanes should be smaller than 2.5 Å in order to gain stabilisation. This distance is also found in theoretical calculations on the transition state of *syn* dimerisation of cyclobutadiene,[8] but far too short for the ordinary π–π stacking between two conjugated systems.[1] Another possible reason for the lack of experimental knowledge of such interactions may be due to the

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‡ Electronic supplementary information (ESI) available: ^{1}H and ^{13}C NMR spectra of **5–7** and polymers **3**, GPC profiles of **3** and voltammograms of **3** and **7**. See DOI: 10.1039/c2ob25114k

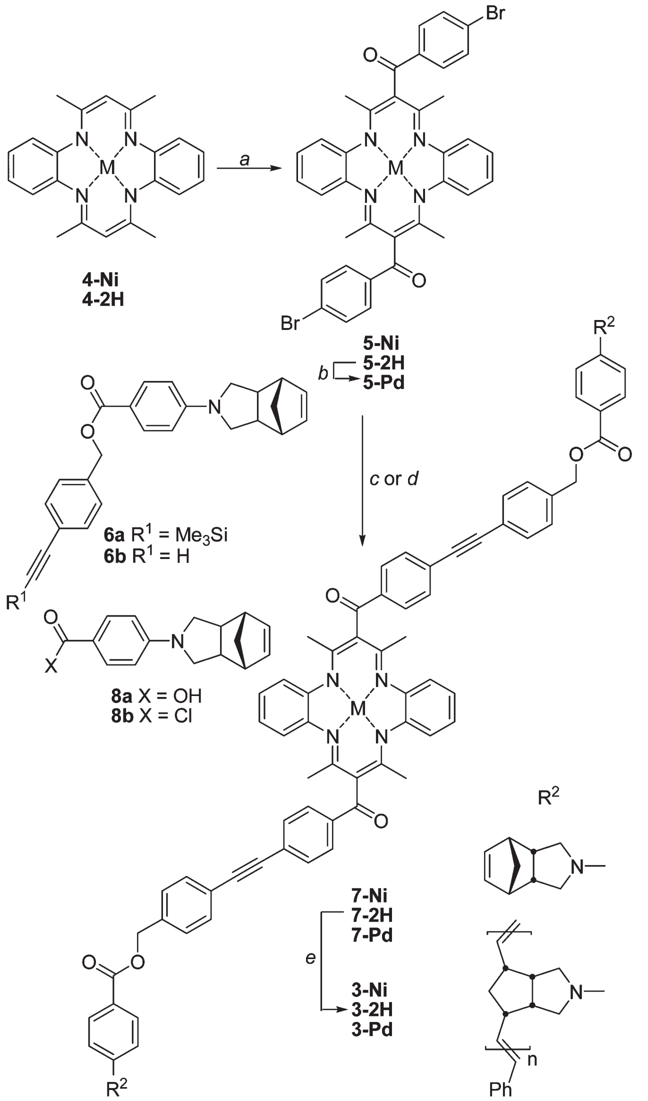
§ 1,4-Diazabicyclo[2.2.2]octane.

relative instability of these antiaromatic species. To illustrate, cyclobutadiene is stable only at very low temperature in argon matrix.[9] The eight-membered cyclooctatetraene, however, is a non-planar cyclic polyene.[10,11] Metal complexes of tetraaza[14]-annulene **2** are known to be stable 16-π-electron antiaromatic systems.[12] It is envisaged that metallocycle **2** would be a suitable linker for a double stranded ladderphane **1** which could serve as a model for studying interactions between antiaromatic rings. We now wish to report the first synthesis and properties of polymeric ladderphanes **3** with such antiaromatic linkers.

Results and discussion

Synthesis

Polymers **3** were designed in a similar manner as those with aromatic linkers described previously.[4–6] The incorporation of benzylic ester moieties in **3** would lead to more flexible linkers to enable possible interactions between chromophores. The syntheses of **3** are outlined in Scheme 1 and the details are described in the Experimental section. Nickelocycle **4-Ni** was treated with 2 equiv of 4-bromobenzoyl chloride in the presence of Et_3N to afford **5-Ni** in 54% yield.[13] Sonogashira reaction of **5-Ni** with **6b** gave 65% yield of the corresponding monomer **7-Ni**. In a similar manner, **4-2H**[14] was converted into **7-2H** in 40% overall yield. Palladium complex **7-Pd** was obtained in 26% overall yield from the reaction of **5-2H** with $PdCl_2$ in the presence of K_2CO_3, followed by Sonogashira coupling. Polymerisation of **7** with the first generation of the Grubbs catalyst (G-I) furnished the corresponding polymers **3**.



Scheme 1 Synthesis of **3**. Conditions: (a) 4-BrC_6H_4COCl, Et_3N,**5-Ni**, 54%, **5-2H**, 66%; (b) $PdCl_2$, K_2CO_3, DMF, 40%; (c) **6b**, $Pd(PPh_3)_4$, CuI, piperidine, **7-Ni** 65%; (d) **6b**, $Pd(PPh_3)_2Cl_2$, piperidine, **7-2H** 61%, **7-Pd** 64%; (e) $(Cy_3)_2Cl_2Ru{=}CHPh$, **3-Ni** 90%, **3-2H** 87%, **3-Pd**, 89%.

Scanning tunnelling microscopic (STM) image

Fig. 1 shows that **3-Ni** formed highly ordered assembled pattern on the graphite surface (HOPG, highly oriented pyrolytic graphite). Aggregation along the longitudinal axis of the polymer by π–π interactions between end groups of **3** and van der Waals interactions between polymer chains would be responsible for this morphology. This kind of morphological images appears to be general for polynorbornene based double and triple stranded ladderphanes **1**,[4–6]

Physical properties of 3

Unlike ladderphanes with aromatic linkers, the chemical shifts of aromatic protons on the core macrocycle linkers in **3** are similar to those in **7**. It is particularly noteworthy that the N–H protons in the macrocycles of both **7-2H** and **3-2H** appear at δ 14.30 and 14.15, respectively, indicating that the antiaromatic paratropic ring currently remains unchanged from the monomer **7-2H** to the corresponding ladderphanes **3-2H**.

The absorption spectra of **7** and **3** in CH_2Cl_2 are shown in Fig. 2 and the λ_{max}'s are tabulated in Table 1. The absorption band around 320 nm would be attributed to the absorption of the 4-aminobenzoate moiety and the aromatic linkers in these molecules. Like related polymers,[4–6] these absorption bands slightly shifted to shorter wavelengths in **3**. The metal to ligand charge transfer (MLCT) band appears at 392 nm for the nickel complexes, while that for palladium complexes at 414 nm.

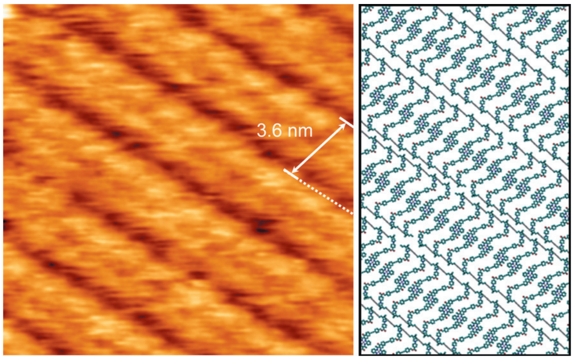


Fig. 1 An STM image and a proposed model of polymer **3-Ni**. The spacing between the double-stranded features is about 3.6 nm. Image size: 15 × 15 nm. Substrate, HOPG; E_{bias}, 0.40 V; $i_{tunneling}$, 43 pA. Solvent: phenyloctane.

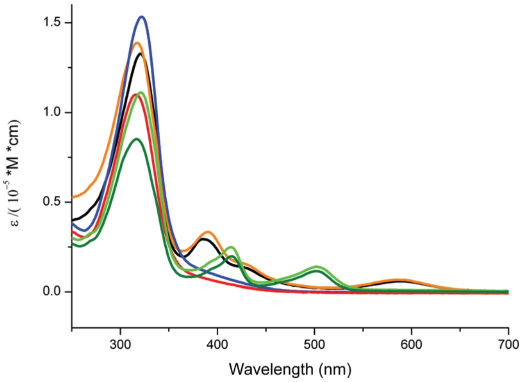


Fig. 2 Absorption spectra of **3-Ni** (black), **7-Ni** (orange), **3-2H** (red), **7-2H** (blue), **3-Pd** (olive), **7-Pd** (green) in CH_2Cl_2.

Table 1 Selected properties of **3** and **8**

Substrate	M_n (PDI)	λ_{max} (nm)[a]	E_{ox} (volt)[b]
7-Ni	—	588, 392, 321	0.24
3-Ni	9500 (1.25)	588, 392, 317	0.24
7-2H	—	321	0.48
3-2H	9700 (1.23)	315	0.48
7-Pd	—	501, 414, 321	0.21
3-Pd	14 000 (1.22)	501, 414, 315	0.21

[a] In CH_2Cl_2. [b] Against ferrocene–ferrocenium couple using differential pulse voltammetry.

The bands at longer wavelengths (588 nm for nickel complexes and 500 nm for palladium complexes) are assigned as ligand to metal charge transfer bands (LMCT). As shown in Fig. 2, the both MLCT and LMCT bands of **3** are essentially same as those of the corresponding monomers **7**. It is noteworthy that strong interactions between linkers were found in ladderphanes with aromatic connectors as revealed by Soret band splitting or broadening in the absorption spectra (porphyrin linkers),[6a,d] excimer formation (oligophenylene–ethynylene linker),[6a] or fluorescence quenching (oligoaryl linkers).[6] Apparently, the behaviour of 16-π-electron antiaromatic linkers in **3** is very different from those of aromatic linkers. The first oxidation potentials for **7** and **3** were measured by cyclic voltammetry and differential pulse voltammetry and the results are also outlined in Table 1. It is interesting to note that both metal-containing monomers (**7-Ni** and **7-Pd**) and polymers (**3-Ni** and **3-Pd**) exhibit reversible first redox processes with same oxidation potentials. The metal free 14-membered heterocycles in both **3-2H** and **7-2H**, however, show irreversible redox reaction, and their oxidation potentials are again same. These results indicate that there would be no changes in frontier orbital energies between monomers **7** and the corresponding polymers **3**. It seems unlikely that interactions between the adjacent antiaromatic 16-π-electron chromophores in **3** would take place leading to some kind of stabilisation in these polymeric ladderphanes.

Conclusions

As mentioned earlier, the spacings separated the adjacent linkers in **2** and **3** are around 5–6 Å. The ester linkers in these polymers would, however, be somewhat flexible and could therefore bring two adjacent chromophores to more proximal positions. As such, evidence for interactions between aromatic linkers is provided by changes in their spectroscopic properties.[4–6] Polymers **3** with antiaromatic 16-π-electron linkers, on the other hand, exhibit completely different behaviour, little interaction between adjacent linker chromophores being observed. As noted in their theoretical predictions, the criterion for the strong interactions between two antiaromatic rings in superphanes leading to aromatic characters is 2.5 Å separation or less between these two rings.[7] The spacing between two antiaromatic rings in **3** is far too long in comparison with those suitable for interactions between two rings in methylene-bridged superphanes.[7] It seems unlikely that the linkers in **3** would move to closer proximity to gain stabilisation, if any, at the expense of other strain that may arise. Although little interaction between adjacent antiaromatic rings was observed in **3**, our results cannot completely rule out the possible stabilisation due to such interactions, provided that the distance between the adjacent two rings could be brought closer. However, the 2.5 Å spacing would be difficult to achieve in the ground state under ordinary conditions because this distance would be the one for the transition state of a σ-bond formation between two π-systems,[8] unless a specially designed substrates such as methylene-bridge superphanes.[7]

Experimental section

General

Melting points were uncorrected. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian 400 Unit plus spectrometer (400 MHz and 100.6 MHz for ^1H and ^{13}C respectively). All ^1H NMR spectra were reported in parts per million (ppm) downfield from TMS using δ 7.26 ppm for $CHCl_3$ as the reference and ^{13}C NMR spectra using δ 77.00 ppm for $CDCl_3$ as the reference. High-resolution mass spectrometric measurements were obtained from a Jeol-JMS-700 mass spectrometer using FAB method in a 3-nitrobenzyl alcohol matrix. Absorption spectra were measured on a Hitachi U-3310 spectrophotometer and emission spectra on a Hitachi F-4500 fluorescence spectrophotometer. Gel permeation chromatography (GPC) was performed on a Waters GPC machine with an isocratic HPLC pump (1515) and a refractive index detector (2414). THF was used as the eluent (flow rate = 1.0 mL min^{-1}). Waters Styragel HR2, HR3, and HR4 columns (7.8 × 300 mm) were employed for the determination of relative molecular weight using polystyrene as standard (M_n values ranged from 375 to 3.5×10^6).

Synthesis of 6a. Under nitrogen, a CH_2Cl_2 (10 mL) solution of **8b**, freshly prepared from **8a** (4.7 g, 18.0 mmol) and oxalyl chloride (3.86 mL, $d = 1.4785$ g mL^{-1}) was added dropwise to a CH_2Cl_2 (30 mL) solution of 4-(2-trimethylsilyl)ethynylbenzyl alcohol[15] (3.5 g, 17.2 mmol) and Et_3N (10 mL) cooled to 0 °C. The mixture was allowed to warm to rt and stirred overnight, then quenched with $NaHCO_3$ solution (5%). The mixture was extracted with CH_2Cl_2. The organic solution was dried ($MgSO_4$) and the solvent was removed *in vacuo* to give the residue which was chromatographed on silica gel (hexane–CH_2Cl_2 = 1 : 1) to give **6a** as a white powder (5.8 g, 76%): mp 198–200 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 0.28 (s, 1H), 1.53 (d, J = 8.2 Hz, 2 H), 1.63 (d, J = 8.2 Hz, 2 H), 2.95–3.00 (m, 4 H), 3,08–3.11 (m, 2 H), 3.28–3.32 (m, 2 H), 5.29 (s, 2H), 6.16 (t, J = 1.8 Hz, 2 H), 6.39 (d, J = 8.0 Hz, 2 H), 7.34 (d, J = 8.0 Hz, 2 H), 7.45 (d, J = 8.0 Hz, 2 H), 7.89 (d, J = 8.0 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.1, 45.5, 46.7, 50.5, 52.1, 65.3, 94.3, 104.8, 110.8, 115.8, 122.5, 127.4, 131.3, 131.9, 135.6, 137.2, 150.3, 166.5; HRMS (FAB) calcd for $C_{28}H_{31}O_2NSi$: 441.2124; found: 441.2121.

Synthesis of 6b. A mixture of **6a** (2.5 g, 5.67 mmol) and K_2CO_3 (1.96 g, 14.2 mmol) in MeOH (250 mL) and THF (20 mL) was heated under reflux for 4 h. After filtration, the solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2. The organic solution was washed with brine and dried ($MgSO_4$). The solvent was removed *in vacuo* to give the residue which was chromatographed on silica gel (hexane–CH_2Cl_2 = 1 : 3) to give **6b** (1.72 g, 82%): mp 200–202 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (d, J = 8.4 Hz,1 H), 1.60 (d, J = 8.4 Hz,1 H), 2.96–3.00 (m, 4 H), 3,08–3.11 (m, 2 H), 3.28–3.31 (m, 2 H), 5.30 (s, 2 H), 6.16 (t, J = 1.8 Hz, 2 H), 6.39 (d, J = 8.8 Hz, 2 H), 7.37 (d, J = 8.2 Hz, 2 H), 7.49 (d, J = 8.2 Hz, 2 H), 7.89 (d, J = 8.8 Hz, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 45.4, 46.7, 50.5, 52.1, 65.2, 83.4, 110.8, 115.8, 121.4, 127.5, 131.3, 132.1, 135.6, 137.6, 150.3, 166.5; HRMS (FAB) calcd for $C_{25}H_{23}O_2N$: 369.1729; found: 369.1727.

Synthesis of 5-Ni. Oxalyl chloride (2.3 mL, 27.0 mmol) was added dropwise to a solution of 4-bromobenzoic acid (2.73 g, 13.5 mmol) in CH_2Cl_2 (30 mL) at 0 °C. After warming to rt, the reaction mixture was stirred for 1 h. The solvent was removed *in vacuo* to give the crude acid chloride which was taken up in benzene (30 mL) and added dropwise at 0 °C to a benzene solution (20 mL) of **4-Ni** (1.02 g, 2.54 mmol) and Et_3N (5.6 mL, 40 mmol). The mixture was refluxed for 5 h and then left to stand at rt for 18 h. After filtration, the filtrate was evaporated *in vacuo* to give the residue which was chromatographed on silica gel (hexane–CH_2Cl_2 = 1 : 3) to afford the **5-Ni** as a green solid (1.05 g, 54%); mp > 300 °C; ^{1}H NMR (400 MHz, $CDCL_3$): δ 11.91 (s, 12 H), 6.59–6.67 (m, 8 H), 7.72 (d, J = 8.2 Hz, 4 H), 8.10 (d, J = 8.2 Hz, 4 H); ^{13}C NMR (75 MHz, $CDCL_3$): δ 20.6, 120.5, 121.7, 122.8, 128.7, 131.1, 132.2, 137.8, 147.0, 153.6, 198.9; HRMS (FAB) *m*/*z* calcd for $C_{36}H_{28}{}^{79}Br_2N_4{}^{58}NiO_2$: 763.9932; found: 763.9940.

Synthesis of 5-2H. In a manner similar to that described above, a mixture of 4-bromoobenzoic acid (2.0 g, 10.0 mmol) **4-2H** (860 mg, 2.50 mmol) was transformed into **5-2H** (1.17 g, 66%): mp 270–271 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.98 (s, 12 H), 7.01–7.11 (m, 8 H), 7.66 (d, J = 8.0 Hz, 4 H), 7.90 (d, J = 8.0 Hz, 4 H), 14.30 (s, 2 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 108.5, 124.3, 124.4, 127.8, 130.8, 132.0, 137.4, 139.7, 160.8, 197.4; HRMS (FAB) calcd for $C_{36}H_{30}{}^{79}Br_2N_4O_2$: 708.0735, found: 708.0729.

Synthesis of 5-Pd. A mixture of **5-2H** (60 mg, 0.08 mmol), $PdCl_2$ (9.13 mg, 0.16 mmol) and K_2CO_3 (86.9 mg, 0.63 mmol) in DMF (8 mL) was refluxed for 1 h. The mixture was cooled to 70 °C and filtered. The solvent was removed *in vacuo* to give the residue which was chromatographed on silica gel (hexane–CH_2Cl_2 = 1 : 1) to afford **5-Pd** as a brown solid (25.6 mg, 40%): mp 274 °C (dec); ^{1}H NMR (400 MHz, $CDCL_3$) δ 1.99 (s, 12 H), 6.62–6.64 (m, 4 H), 6.76–6.79 (m, 4 H),7.69 (d, J = 8.4 Hz, 4 H), 8.09 (d, J = 8.4 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 119.7, 122.1, 123.3, 128.7, 131.1, 132.2, 137.6, 147.2, 152.4, 199.2; HRMS (FAB) calcd for $C_{36}H_{28}{}^{79}Br_2N_4O_2{}^{106}Pd$: 811.9609, found: 811.9614.

Synthesis of 7-Ni. Under nitrogen, $Pd(PPh_3)_4$ (70 mg, 0.1 mmol), CuI (19 mg,0.1 mmol), and **6b** (0.40 g, 0.11 mmol) were added to a solution of **5-Ni** (38.2 mg, 0.05 mmol) in piperidine (2 mL) and toluene (2 mL). After refluxing for 24 h and cooling to rt, the mixture was filtered through Celite. The filtrate was evaporated *in vacuo* and the residue was triturated with CH_2Cl_2. The organic solution was washed with brine, dried ($MgSO_4$) and evaporated *in vacuo* to give the residue which was chromatographed on silica gel (hexane–CH_2Cl_2 = 1 : 4) to afford the **7-Ni** as a green solid (43.6 mg, 65%): mp > 300 °C; ^{1}H NMR (400 MHz, $CDCL_3$) δ 1.53 (d, J = 8.4 Hz, 2 H), 1.63 (d, J = 8.4 Hz, 2 H), 1.94 (s, 12 H), 2.96–2.99 (m, 8 H), 3.10–3.11 (m, 4 H), 3.29–3.33 (m, 4 H), 5.34 (s, 4 H), 6.16 (s, 4 H), 6.40 (d, J = 8.8 Hz, 4 H), 6.59–6.68 (m, 8 H), 7.44 (d, J = 8.4 Hz, 4 H), 7.58 (d, J = 8.0 Hz, 4 H), 7.72 (d, J = 8.4 Hz, 4 H), 7.91 (d, J = 8.8 Hz, 4 H), 8.23 (d, J = 8.0 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 20.6, 45.5, 46.7, 50.5, 52.1, 65.2, 88.9, 92.8, 110.8, 115.7, 120.8, 121.8, 122.0, 122.7, 127.7, 128.4, 129.5, 131.3, 131.7, 132.01, 135.6, 137.7, 138.2, 147.1, 150.3, 153.6, 166.5, 199.2; HMRS(FAB) calcd $C_{86}H_{76}N_6{}^{58}NiO_6$: 1342.4867; found: 1342.4873.

Synthesis of 7-2H. In a manner similar to that described above, a mixture of **5-2H** (50.0 mg, 0.07 mmol), **6b** (103 mg, 0.28 mmol) and $Pd(PPh_3)_2Cl_2$ (2.0 mg, 0.0028 mmol) in piperidine (4 mL) was refluxed for 24 h. After cooing to rt, the mixture was filtered through Celite. The filtrate was evaporated *in vacuo* and the residue was triturated with CH_2Cl_2. The organic solution was washed with brine, dried ($MgSO_4$) and evaporated *in vacuo* to give the residue which was chromatographed on silica gel (hexane–CH_2Cl_2 = 1 : 3) to afford **7-2H** as a yellow solid (55 mg, 61%): mp 283 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.53 (d, J = 8.4 Hz, 2 H), 1.63 (d, J = 8.4 Hz, 2 H), 2.01 (s, 12 H), 2.96–3.00 (m, 8 H), 3.10–3.11 (m, 4 H), 3.29–3.33 (m, 4 H), 5.33 (s, 4 H), 6.17 (s, 4 H), 6.40 (d, J = 8.8 Hz, 4 H), 7.02–7.11 (m, 8 H), 7.43 (d, J = 8.0 Hz, 4 H), 7.56 (d, J = 8.0 Hz, 4 H), 7.67 (d, J = 8.2 Hz, 4 H), 7.91 (d, J = 8.8 Hz, 4 H), 8.02 (d, J = 8.2 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.5, 29.8, 45.5, 46.7, 50.5, 52.2, 65.3, 89.0, 92.4, 108.8, 110.9, 115.8, 122.1, 124.3, 124.4, 127.7, 129.3, 131.3, 131.7, 131.9, 135.6, 137.5, 137.6, 140.2, 150.4, 161.0, 166.5, 197.6; HRMS (FAB) calcd for $C_{86}H_{75}N_6O_6$: 1287.5763, found: 1287.5748.

Synthesis of 7-Pd. In a manner similar to that described above, a mixture of **5-Pd** (50.0 mg, 0.07 mmol), **6b** (103 mg, 0.28 mmol) and $Pd(PPh_3)_2Cl_2$ (2.0 mg, 0.0028 mmol) in piperidine (4 mL) was transformed into **7-2Pd** as a yellow solid (62 mg, 64%): mp 203 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.53 (d, J = 8.6 Hz, 2 H), 1.63 (d, J = 8.6 Hz, 2 H), 2.03 (s, 12 H), 2.96–3.00 (m, 8 H), 3.10–3.11 (m, 4 H), 3.29–3.31 (m, 4 H), 5.34 (s, 4 H), 6.16 (t, J = 1.8 Hz, 4 H), 6.40 (d, J = 8.6 Hz, 4 H), 6.62–6.64 (m, 4 H), 6.78–6.80 (m, 4 H), 7.43 (d, J = 8.2 Hz, 4 H), 7.57 (d, J = 8.2 Hz, 4 H), 7.69 (d, J = 8.4 Hz, 4 H), 7.91 (d, J = 8.6 Hz, 4 H), 8.21 (d, J = 8.4 Hz, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 45.4, 46.6, 50.5, 52.1, 65.2, 88.9, 92.9, 110.9, 114.4, 115.9, 120.2, 122.3, 123.3, 127.8, 128.6, 129.7, 131.4, 131.9, 132.2, 135.8, 137.9, 138.1, 147.4, 150.6, 152.7, 166.8, 199.8; HRMS (FAB) calcd for $C_{86}H_{72}N_6O_6{}^{106}Pd$: 1390.4556, found: 1390.4548.

Synthesis of 3-Ni. Under nitrogen atmosphere, a solution of $(Cy_3P)_2Cl_2Ru{=}CHPh$ (3.2 mg, 0.0037 mmol) in CH_2Cl_2 (1 mL) was added to **7-Ni** (50 mg, 0.037 mmol) in CH_2Cl_2 (10 mL) and the mixture was stirred at rt for 2 h, quenched with ethyl vinyl ether (2 mL) and concentrated *in vacuo* to about 1 mL. MeOH (20 mL) was added and the precipitate was collected. The solid was taken into CH_2Cl_2 and the solution was added slowly to ether (20 mL) to give the solid which was washed with EtOAc until the solution was colourless. The solid was collected as **3-Ni** (70 mg, 90%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27–1.45 (br, 4 H), 1.95 (br, 12 H), 2.94–3.27 (br, 16 H), 4.97–5.34 (br, 8 H), 6.17–7.00 (br, 12 H), 7.33 (br, 4 H), 7.41 (br, 4 H), 7.55 (br, 4 H), 7.75 (br, 4 H), 7.92 (br, 4 H), 8.34 (br, 4 H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 20.9, 44.6, 46.4, 49.5, 65.2, 65.9, 89.1, 92.8, 96.1, 111.5, 116.7, 116.9, 120.9, 121.8, 122.2, 122.8, 126.1, 127.8, 128.0, 128.5, 129.8, 131.5, 131.9, 132.2, 137.8, 138.3, 147.3, 151.0, 153.7, 166.6, 199.3; M_n = 9500, PDI = 1.25.

Synthesis of 3-2H. In a manner similar to that described above, **7-2H** (50 mg, 0.037 mmol) was converted into **3-2H** (41 mg, 87%): ^{1}H NMR (400 MHZ, $CDCl_3$) δ 1.27–1.58 (br, 4 H), 1.87 (br, 12 H), 2.76–3.27 (br, 16 H), 5.30 (br, 8H), 6.51 (br, 4 H), 7.09 (br, 8 H), 7.38 (br, 4 H), 7.52 (br, 4 H), 7.66 (br, 4 H), 7.95 (br, 8 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 19.5, 44.7, 47.0, 49.5, 65.3, 89.0, 92.5, 108.4, 108.8, 111.4, 116.7, 122.1, 124.8, 125.9, 127.6, 128.4, 128.4, 128.7, 129.2, 131.4, 131.7, 132.0, 137.1, 137.5, 138.1, 139.5, 150.8, 160.9, 166.3, 185.5, 197.7; M_n = 9700, PDI = 1.23.

Synthesis of 3-Pd. In a manner similar to that described above, **7-2H** (50 mg, 0.037 mmol) was converted into **3-Pd** (46 mg, 89%): ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.43–1.61 (br, 4 H), 2.0 (br, 12 H), 2.77–3.28 (br, 12 H), 5.34 (br, 8 H), 6.61–6.78 (br, 12 H), 7.42 (br, 4 H), 7.55 (br, 4 H), 7.70 (br, 4 H), 7.94 (br, 4 H), 8.27 (br, 4 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.1, 44.7, 46.7, 49.6, 65.3, 90.0, 92.8, 111.5, 116.7, 120.1, 122.1, 123.3, 125.9, 127.8, 128.4, 128.7, 129.5, 131.4, 131.8, 132.0, 137.6, 138.0, 147.3, 150.8, 152.3, 166.3, 199.1; M_n = 14 000, PDI = 1.22.

STM imaging of 3-Ni. An aliquot of **3** (10-μL) in 1-phenyloctane was placed on a graphite surface (Advanced Ceramics, ZYH grade). The excess solvent was removed by positioning a piece of Kim Wipes at the edge of the graphite.[5d] The polymers were shear-aligned by the flow of the solvent. STM imaging was carried out with a PicoScan controller (Model 4500, Agilent Technologies) at ambient conditions. STM probes were commercially available Pt–Ir tips (PT, Nanotips, Veeco Metrology Group/Digital Instruments, USA). Typical imaging conditions of bias voltage and tunnelling current ranged from 0.30 V to 0.6 V and from 30 pA to 100 pA, respectively. The STM image presented in the paper was not subjected to any data processing.

Voltametric studies of 3 and 7

An ECO Chemie μAutolab III potentiastat–galvanostat was used for cyclic voltammetry and differential pulse voltammetry experiments to determine oxidation potentials. Pt working (surface area: 0.0707 cm^2), Pt wire counter electrode, and Ag–AgCl reference electrodes were employed using 0.1 M Bu_4NPF_6 as electrolyte in CH_2Cl_2 solution. Monomer **7** or polymer **3** was dissolved in the above solution (10^{-3} M) and the aliquot (5 mL) was purged with argon for 10 min and subjected to electrochemical measurements under argon. The voltammograms are shown in the ESI.‡

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