

Mesogenic Dipyrrins – Building Blocks for the Fabrication of Fluorescent and Metal-containing Materials

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Electronic Supporting Information

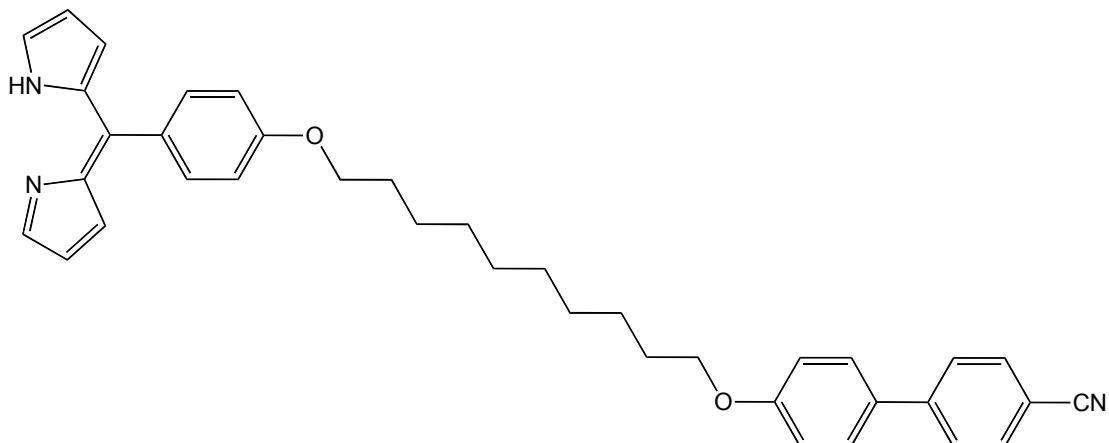
Materials

All materials were used as purchased unless mentioned otherwise. Silica gel 60 (Merck) was used for column chromatography. TLC was performed on Silica gel plates (Merck, Silicagel F254).

Instrumentation

Nuclear magnetic resonance (NMR) spectra were recorded on a Jeol JNM-ECP 400 M Hz FT-NMR spectrometer. Chemical shifts are reported in ppm relative to TMS. Thermal properties were investigated using a Mettler Toledo differential calorimeter (DSC 822e) in nitrogen against an indium standard. Transition temperatures were determined as the onset of the maximum in the endotherm or exotherm. The mesophases were studied on an Olympus BH-2 optical polarising microscope, equipped with a Mettler FP82 HT hot stage and a Mettler FP90 central processor. Pictures of the mesophases were taken using a JVC digital video camera connected to a PC. Software Studio Capture, supplied by Studio86Designs was used for image capturing. XRD studies were performed on a MAR345 diffractometer, equipped with 2D detector, CuK α radiation source, graphite monochromator, $\lambda = 1.541 \text{ \AA}$. FIT2D and Origin software packages were used for XRD data analysis. Purity was determined using Viscotek Detection GPC system comprising of - 270 Dual detector with Viscometry VE3580 RI detector, VE1122 solvent pump, column oven and solvent degasser. Viscotek Omnisec 4.0 software Set of 2 columns plus guard - TSKgel GMHHR-L(<10k mw) 5Im mixed bed 300 x 7.8mm. TSKgel is a porous, highly crosslinked spherical polystyrene divinylbenzene resin. Conventional Calibration - used with RI detector only - calibrated with 10 polystyrene narrow standards to give polystyrene equivalent molecular weight values. Fluorescence spectra were recorded using an AMINCO-Bowman Series 2 (AB2) Spectrofluorometer. Fluorescence microscopy was carried out using a Leica DM IRB equipped with objective L40x/0.55 N PLAN CORR LMC $\infty/0.2$ and fitted with a fluorescence block (excitation 488, dichroic 505nm. 535nm band pass emission filter with 50nm half band width.

4'-(10-(4-Phenoxy-dipyrromethene)decyloxy)biphenyl-4-carbonitrile



5-(4-Hydroxyphenyl)dipyrromethene (500mg, 2.11mmol) was dissolved in butanone (50mL), potassium carbonate (5g 36mmol) and KI (100mg 0.6mmol) were added and the solution was stirred under a dry atmosphere protected from light for 30 minutes. 1.1 eq 4'-(11-Bromodecyloxy)biphenyl-4-carbonitrile was added in one portion and the reaction allowed to proceed for 2 weeks at room temperature. The solvent was removed and the residue re-dissolved in dichloromethane (300mL) and washed with water (2x200mL) and brine (1x200mL). The organic layer was collected and dried over anhydrous magnesium sulphate, following filtration the solvent was removed and the residue passed through a short silica column (SiO_2 1st DCM 2nd DCM:EtOAc 10:1). The relevant fractions were collected and the solvent removed to yield a brown crystalline material. (600mg, 49%);

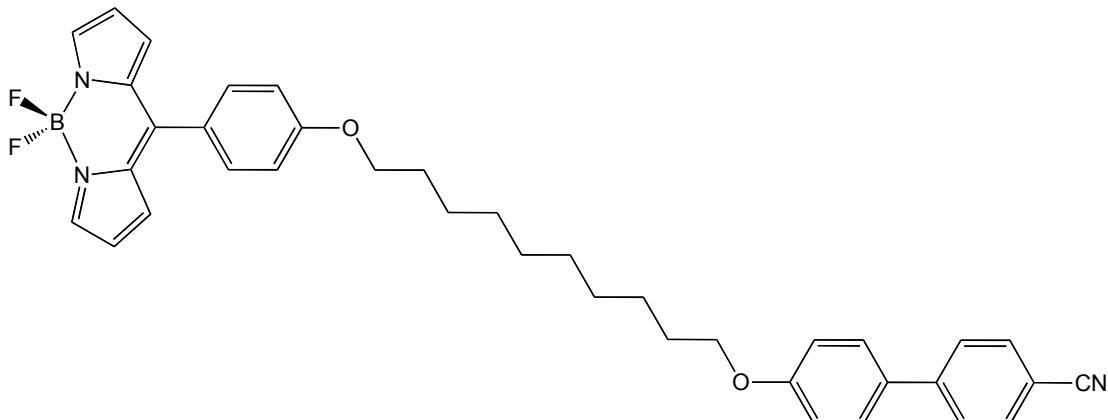
¹H NMR [400 MHz, CDCl_3] δ 1.37 (8H, m, CH_2), 1.50 (4H, m, CH_2), 1.83 (4H, m, $J = 6.60\text{Hz}$, CH_2), 4.00 (2H, t, $J = 6.60\text{Hz}$, OCH_2), 4.04 (2H, t, $J = 6.60\text{Hz}$, OCH_2), 6.40 (2H, d, $J = 3.85\text{Hz}$, pyrrole 3 position), 6.57 (2H, d, $J = 3.85$, pyrrole 2 position), 6.95 (2H, d, $J = 8.43$, 3,5 positions 5-phenyl dipyrromethene), 6.99 (2H, d, $J = 8.61$, 3',5' positions), 7.43 (2H, d, $J = 8.43$, 2,6 positions 5-phenyl dipyrromethene), 7.52 (2H, d, $J = 8.61$ 2'6' positions), 7.63 (2H, bs, pyrrole 1 position) 7.64 (2H, d, 3,5 positons), 7.68 (2H, d, $J = 8.25\text{Hz}$, 2,6 positions);

¹³C NMR [100 MHz, CDCl_3] δ 26.02, 26.04, 29.19, 29.23, 29.34, 29.48, 68.08, 68.13, 76.69, 77.00, 77.32, 109.99, 113.55, 115.05, 117.36, 119.12, 127.05, 128.31, 128.76, 129.45, 131.24, 132.43, 132.54, 140.95, 143.22, 145.26, 15977, 160.00;

MS (MALDI) = 583.8 (M+);

GPC Retention Volume = 22.9ml.

4'-(11-(4,4-Difluoro-8-(4-hydroxyphenyl)-4-bora-3a,4a-diazaindacene)decyloxy)biphenyl-4-carbonitrile



4,4-Difluoro-8-(4-hydroxyphenyl)-4-bora-3a,4a-diazas-indacene (500mg, 1.8mmol) was dissolved in butanone (50mL), potassium carbonate (5g 36mmol) and KI (100mg 0.6mmol) were added and the solution was stirred under a dry atmosphere protected from light for 30 minutes. 1.1 eq 4'-(10-Bromodecyloxy)biphenyl-4-carbonitrile was added in one portion and the reaction allowed to proceed for 2 weeks at room temperature. The solvent was removed and the residue re-dissolved in dichloromethane (300mL) and washed with water (2x200mL) and brine (1x200mL). The organic layer was collected and dried over anhydrous magnesium sulphate, following filtration the solvent was removed and the residue passed through a short silica column (SiO_2 DCM:EtOAc 10:1). The relevant fractions were collected and the solvent removed to yield a bright orange microcrystalline solid, the solid was re dissolved and purified by gravity percolation chromatography (SiO_2 DCM:EtOAc 19:1). A single orange band was obtained (652mg, 59%):

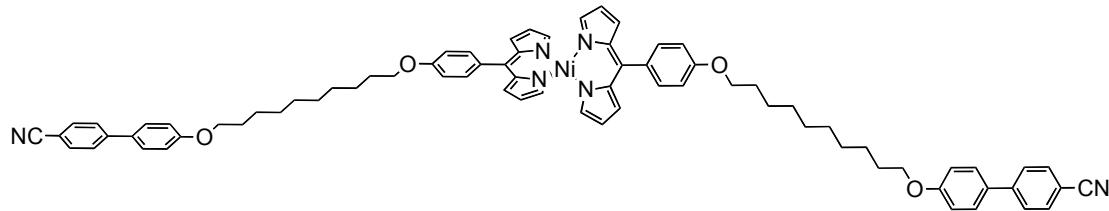
^1H NMR [400 MHz, CDCl_3] δ 1.47 (8H, m, CH_2), 1.75 (4H, m, CH_2), 4.01 (2H, t, $J = 6.42\text{Hz}$ OCH_2), 4.06 (2H, t $J = 6.60\text{Hz}$ OCH_2), 6.55 (2H, dd, $J = 4.03\text{Hz}$, $J = 1.65\text{Hz}$, pyrrole 3 position), 6.97 (2H, m, pyrrole 2 position), 6.99 (2H, d, $J = 8.80\text{Hz}$, 3',5' positions), 7.03 (2H, d, $J = 8.61\text{Hz}$, 3,5 positions 5-phenyl dipyrromethene), 7.53 (2H, d, $J = 8.80\text{Hz}$, 2'6' positions), 7.54 (2H, d, $J = 8.80\text{Hz}$, 2,6 positions 5-phenyl dipyrromethene), 7.64 (2H, d, $J = 8.60\text{Hz}$, 3,5 positons), 7.69 (2H, d, $J = 8.60\text{Hz}$, 2,6 positions), 7.92 (2H, bs, pyrrole 1 position);

^{13}C NMR [100 MHz, CDCl_3] δ 161.712, 159.757, 147.488, 145.242, 143.317, 134.799, 132.561, 132.446, 131.323, 131.270, 128.313, 127.053, 126.083, 119.108, 118.245, 115.044, 114.891, 114.494, 110.025, 77.321, 77.206, 77.000, 76.687, 68.306, 68.131, 29.484, 29.361, 29.338, 29.208, 29.132, 26.015;

HRMS (FAB) = calc. 617.3020, found. 617.3022;

GPC Retention Volume = 22.6mL.

Bis(5-(4-(10-(4'-cyanobiphenyl-4-decyloxy)phenyl)dipyrromethene)nickel



4'-(10-(4-Phenoxy-dipyrromethene)decyloxy)biphenyl-4-carbonitrile (500mg 0.85mmol) was dissolved in dichloromethane (20mL) and heated to reflux, to this solution was added 20 eq. of nickel (II) acetate in a solution of methanol (5mL), the solution was then refluxed for 1 hour and allowed to stir at room temperature overnight. The solvent was removed and the residue re-dissolved in dichloromethane (50mL) and washed with water (3x 200mL) and brine (100mL). Finally, the organic layer was dried over anhydrous magnesium sulphate, filtered, and the solvent removed to yield a brown sticky oil. The residue was passed through a short silica column (SiO_2 DCM). A single bright yellow band was observed and collected, yielding a yellow/green solid after concentration. The solid was redissolved in DCM and further purified by size exclusion chromatography (Sephadex LH20; eluent DCM), the relevant high molecular weight yellow fraction was collected and concentrated to yield a yellow green microcrystalline solid (495mg, 90%):

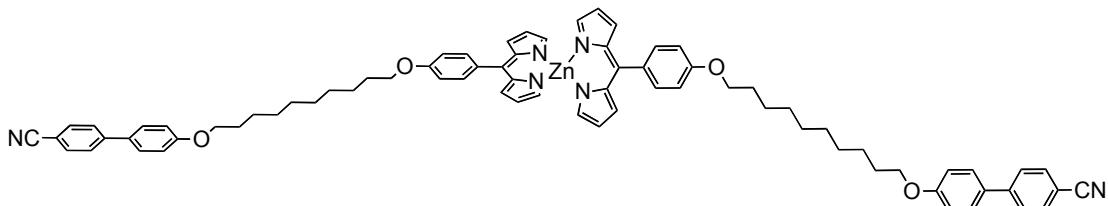
^1H NMR [400 MHz, CDCl_3] δ 1.37 (16H, m, CH_2), 1.50 (8H, m, CH_2), 1.82 (8H, m, $J = 6.60\text{Hz}$, CH_2), 4.00 (4H, t, $J = 6.60\text{Hz}$, OCH_2), 4.04 (4H, t, $J = 6.60\text{Hz}$, OCH_2), 6.79 (4H, dd, $J = 4.03$, pyrrole 3 position), 6.93 (4H, d, $J = 8.60\text{Hz}$, positions 5-phenyl dipyrromethene), 6.99 (4H, d, $J = 8.80\text{Hz}$, 3',5' positions), 7.07 (4H, dd, $J = 4.03\text{Hz}$, pyrrole 2 position), 7.38 (4H, d, $J = 8.80\text{Hz}$, 2,6 positions 5-phenyl dipyrromethene), 7.53 (4H, d, $J = 8.80\text{Hz}$ Ar- CH_2' 6' positions), 7.64 (4H, d, $J = 8.61\text{Hz}$, 3,5 positons), 7.69 (4H, d, $J = 8.61\text{Hz}$, 2,6 positions), 8.55 (4H, bs, pyrrole 1 position);

^{13}C NMR [100MHz, CDCl_3] δ 26.02, 26.04, 29.20, 29.22, 29.35, 29.47, 68.08, 68.14, 110.00, 113.42, 115.05, 119.16, 126.34, 127.06, 128.31, 129.32, 131.25, 132.56, 132.67, 137.72, 139.40, 144.29, 145.26, 159.77, 160.30, 162.35;

HRMS (FAB) = calc. 1222.5515 found. 1222.5531 (M^+);

GPC Retention Volume = 17.9ml.

Bis(5-(4-(10-(4'-cyanobiphenyl-4-decyloxy)phenyl)dipyrromethene)zinc



4'-(10-(4-Phenoxy-dipyrromethene)decyloxy)biphenyl-4-carbonitrile (500mg 0.85 mmol) was dissolved in dichloromethane (20mL) and heated to reflux, to this solution was added 20 eq. of zinc (II) acetate in a solution of methanol (5mL) the solution was refluxed for 1 hour and allowed to stir at room temperature overnight. The solvent was removed and the residue re-dissolved in dichloromethane (50mL) and washed with water (3x 200mL) and brine (100mL), the organic layer was dried over anhydrous magnesium sulphate filtered and the solvent removed to yield a brown sticky oil. The residue was passed through a short silica column (SiO_2 ; DCM). A single bright yellow band was observed and collected, yielding a yellow/green solid after concentration. The solid was redissolved in DCM and further purified by size exclusion chromatography (Sephadex LH20 eluent DCM), the relevant high molecular weight yellow fraction was collected and concentrated to yield a yellow green microcrystalline solid (515mg, 90%):

^1H NMR [400 MHz, CDCl_3] δ 1.38 (12H, m, CH_2), 1.52 (12H, m, CH_2), 1.84 (8H, m, $J_1 = 6.42\text{Hz}$ $J_2 = 6.60\text{Hz}$, CH_2), 4.01 (4H, t, $J = 6.42\text{Hz}$, OCH_2), 4.06 (4H, t, $J = 6.60\text{Hz}$, OCH_2), 6.46 (4H, dd, $J_1 = 4.03$ $J_2 = 1.10$, pyrrole 3 position), 6.77 (4H, dd, $J_1 = 4.03$, $J_2 = 1.10\text{Hz}$, pyrrole 2 position), 6.97 (4H, d, $J = 8.61\text{Hz}$, 3,5 positions 5-phenyl dipyrromethene), 7.00 (4H, d, $J = 8.80\text{Hz}$, 3',5' positions), 7.49 (4H, d, $J = 8.61$, , 2,6 positions 5-phenyl dipyrromethene), 7.51 (4H, d, $J_1 = 1.2\text{Hz}$ pyrrole 1 position) 7.53 (4H, d, $J = 8.80$, 2'6' positions), 7.64, (4H, d, $J = 8.61\text{Hz}$ 3,5 positons), 7.69 (4H, d, $J = 8.61\text{Hz}$, 2,6 positions);

^{13}C NMR [100MHz, CDCl_3] δ 26.03, 26.08, 29.22, 29.29, 29.37, 29.50, 68.09, 68.15, 100.00, 113.08, 115.06, 116.82, 119.13, 127.06, 128.13, 131.25, 131.27, 132.25, 132.56, 132.86, 140.79, 145.27, 148.98, 149.37, 159.64, 159.78;

HRMS (FAB)=calc. 1200.5214, found. 1200.5220;

GPC Retention Volume = 17.84ml.

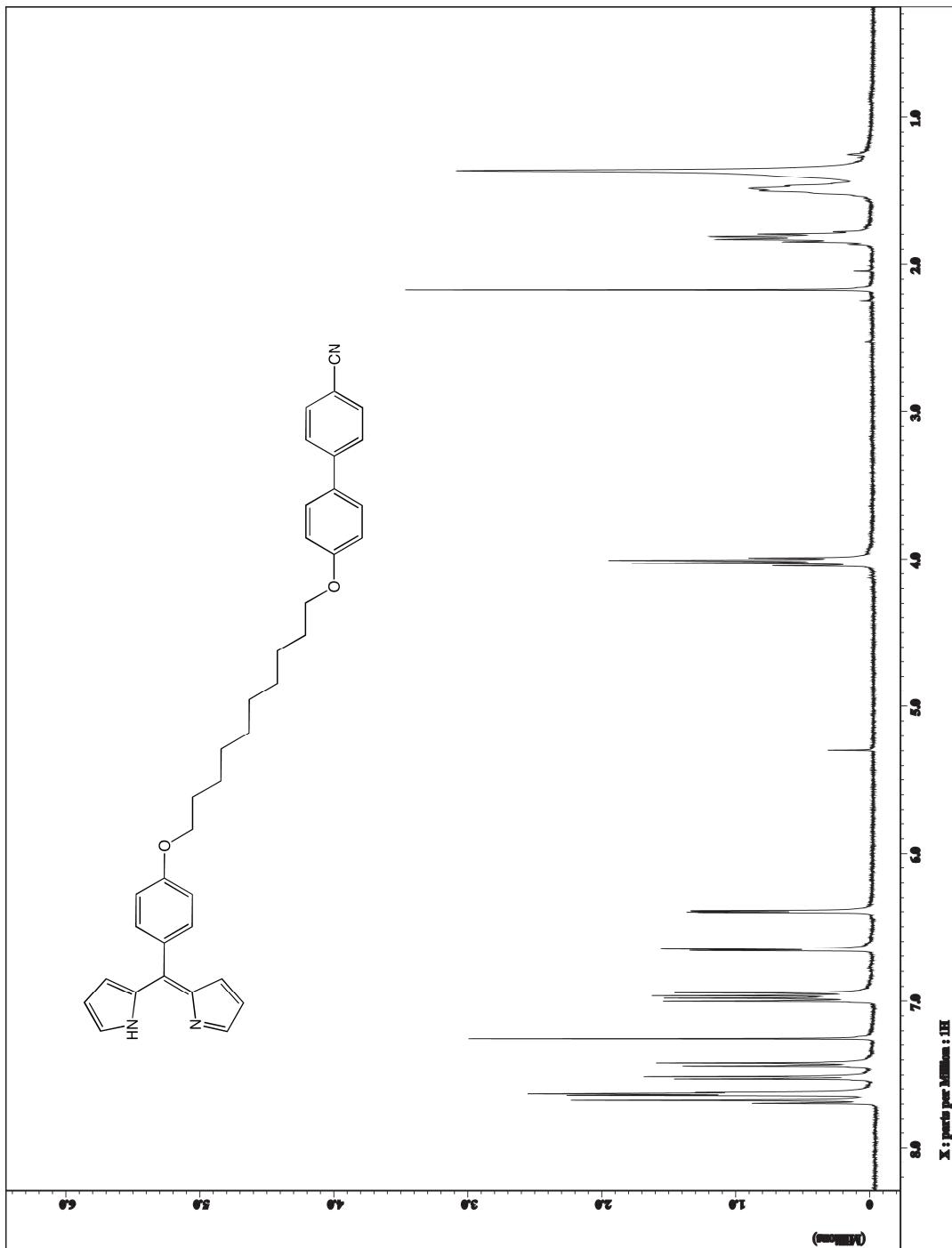


Figure 1. NMR spectra for 4-(10-(4-Phenoxy-dipyrromethene)decyloxy)biphenyl-4-carbonitrile

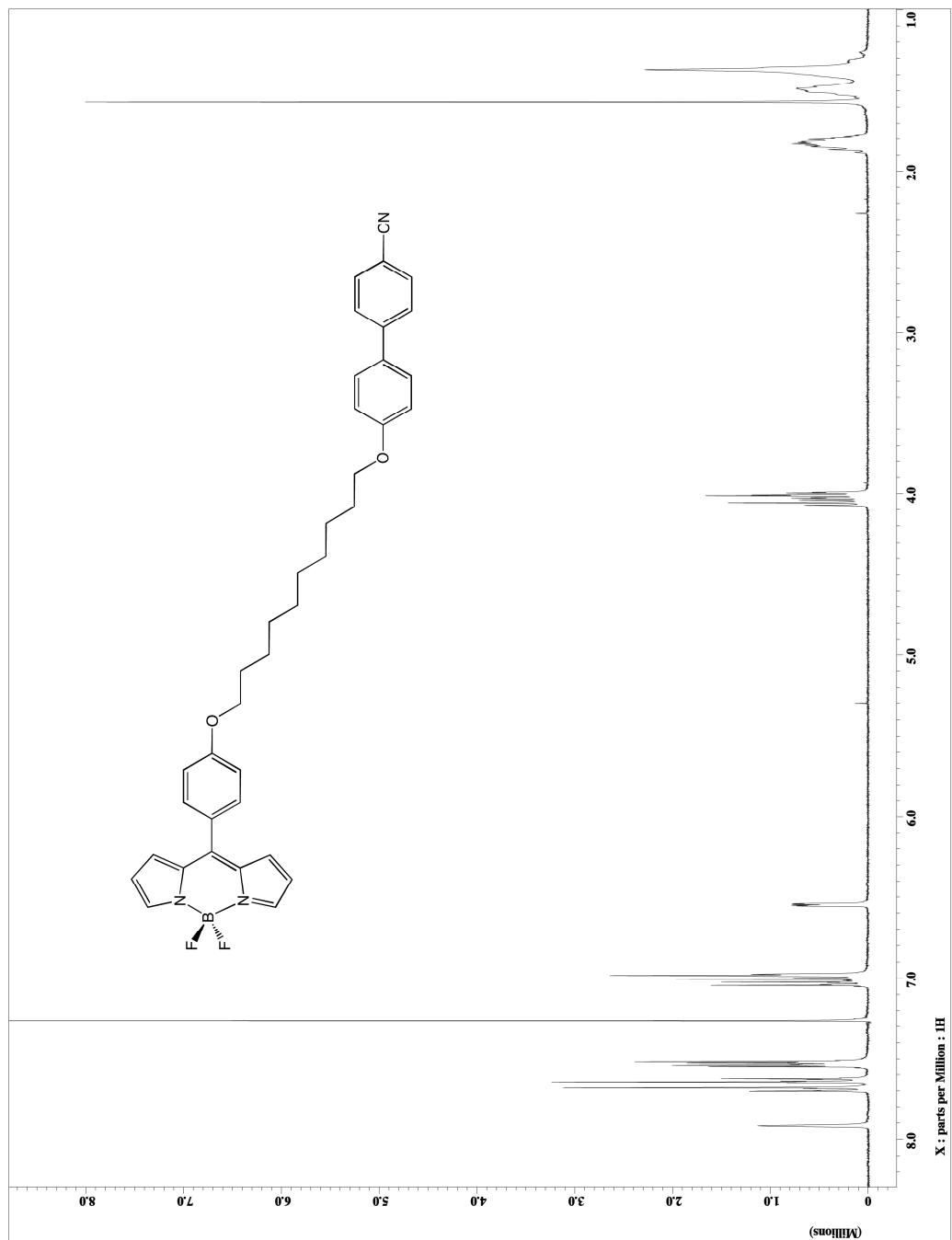


Figure 2. NMR spectra for 4'-(11-(4,4-Difluoro-8-(4-hydroxyphenyl)-4-bora-3a,4a-diazaindacene)decyloxy)biphenyl-4-carbonitrile

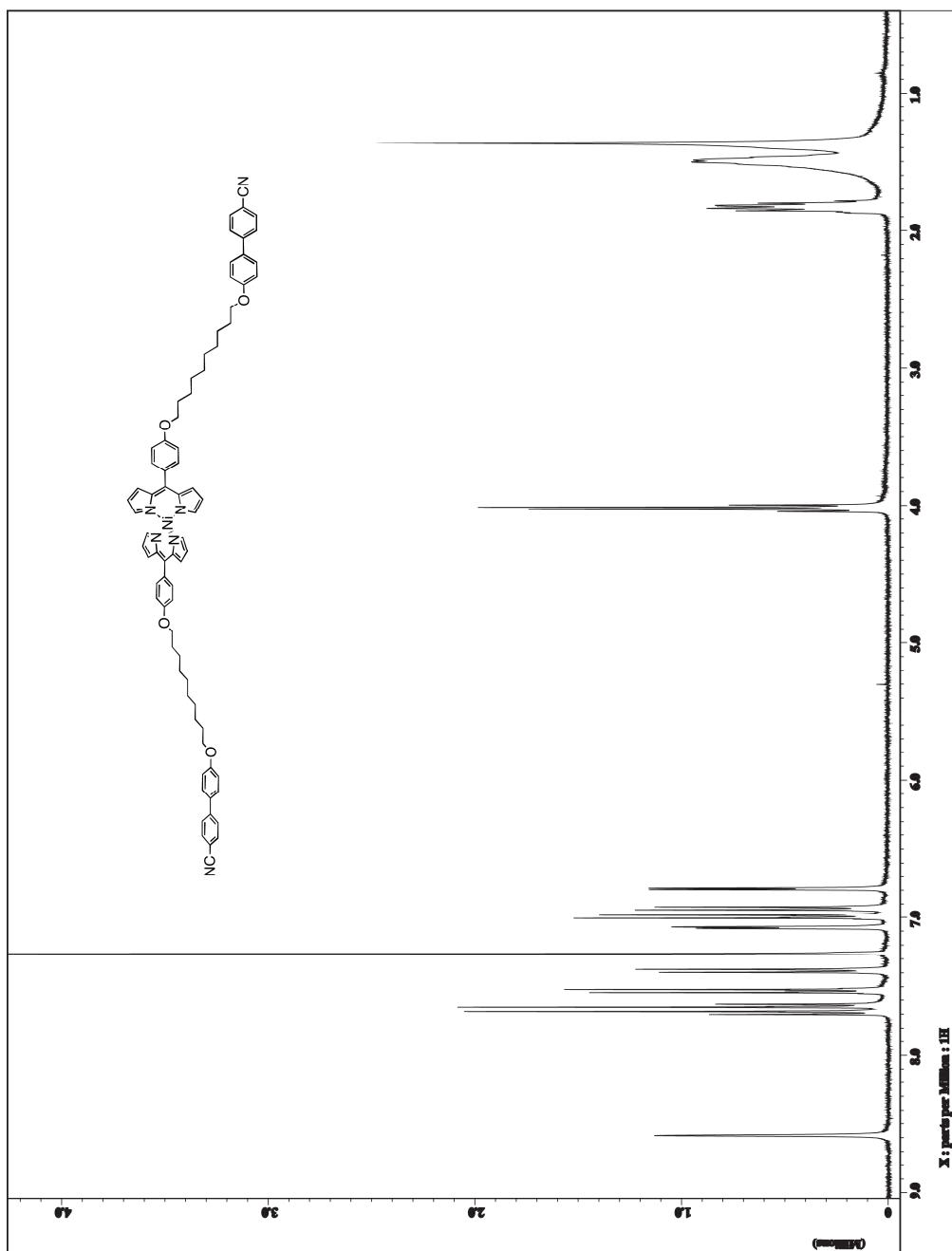


Figure 3. NMR spectra for Bis(5-(4-(10-(4'-cyanobiphenyl-4-decyloxy)phenyl)diphenylmethene)nickel

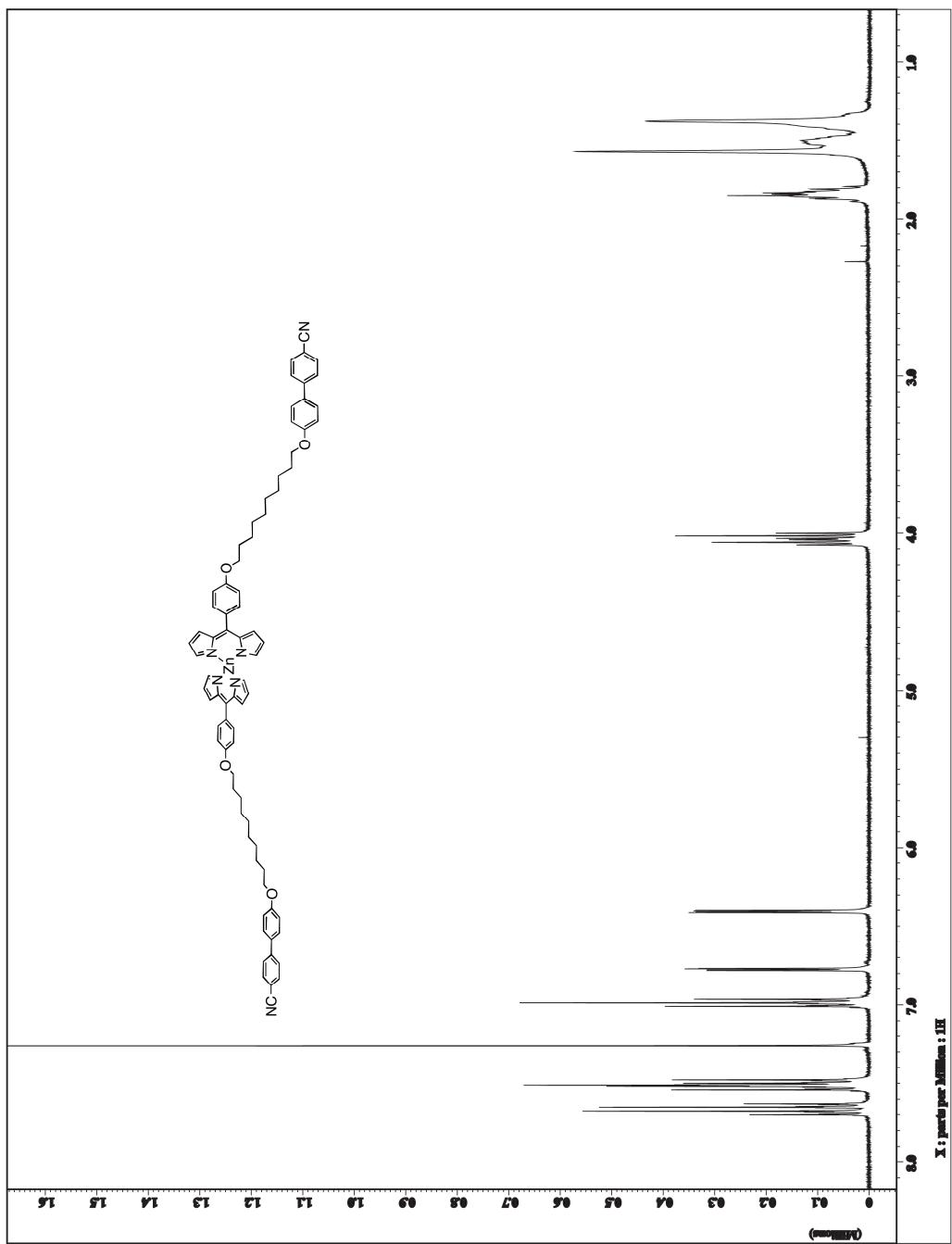


Figure 4. NMR spectra for Bis(5-(4-(10-(4'-cyanobiphenyl-4-decyloxy)phenyl)diphenylmethene)zinc

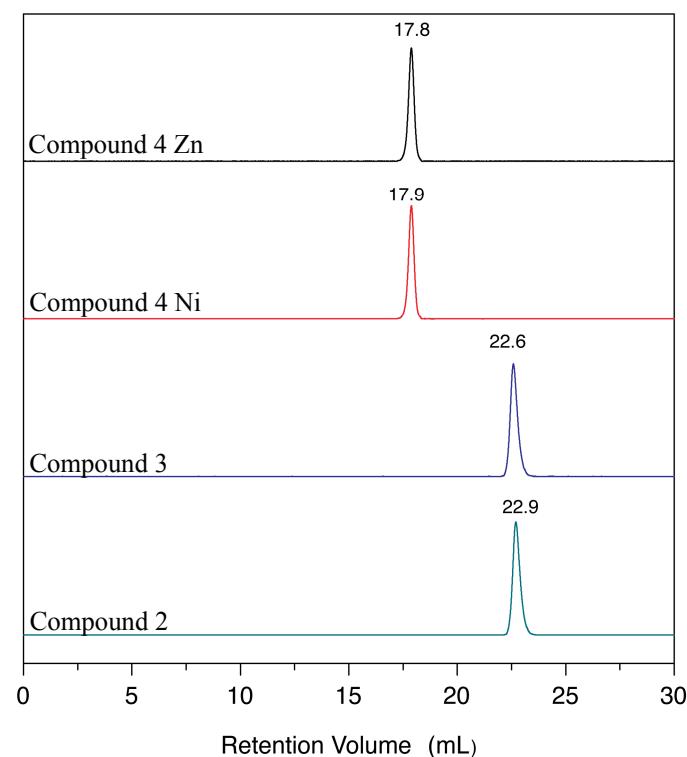


Figure 5. GPC traces of compounds

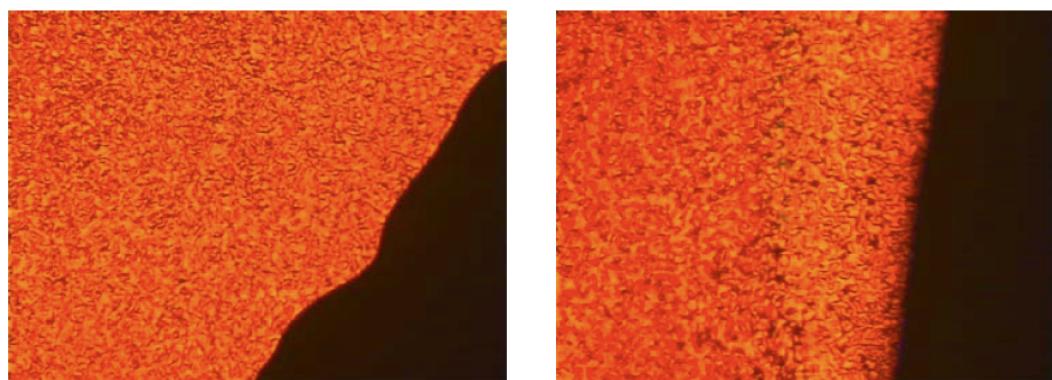


Figure 6. OPM images for compound 2 at 25°C

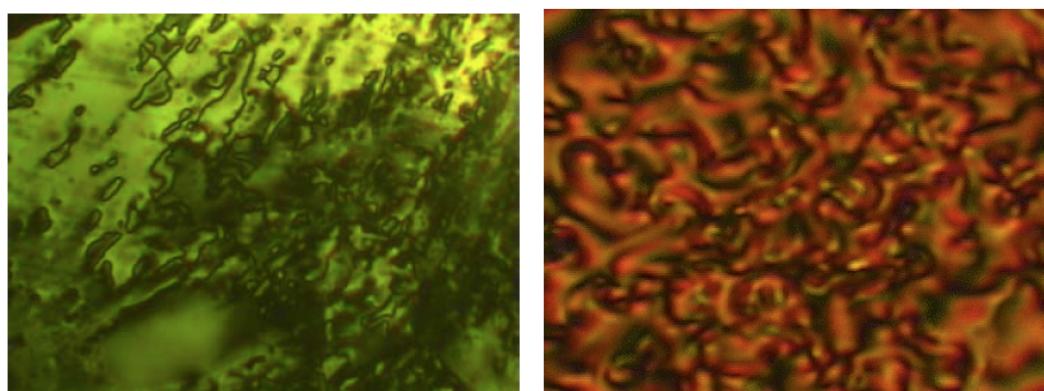


Figure 7. OPM images for compound 3 at 25°C

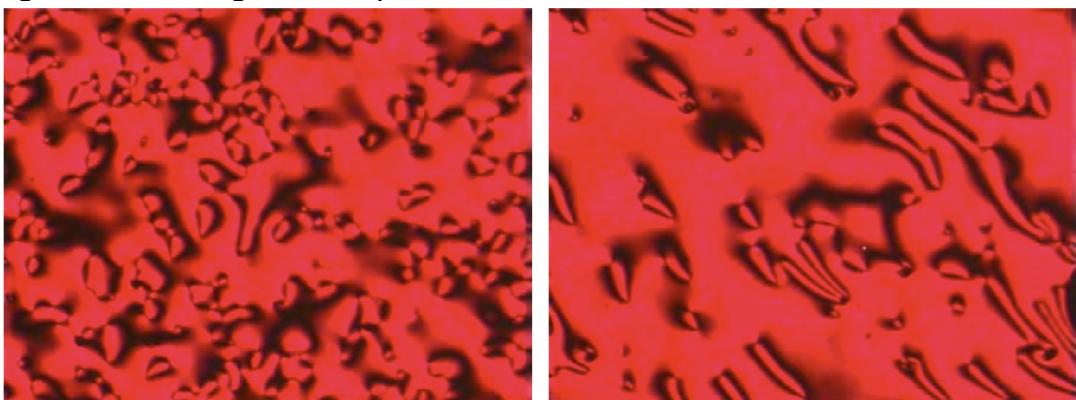


Figure 8. OPM images for compound 4Ni at 133°C

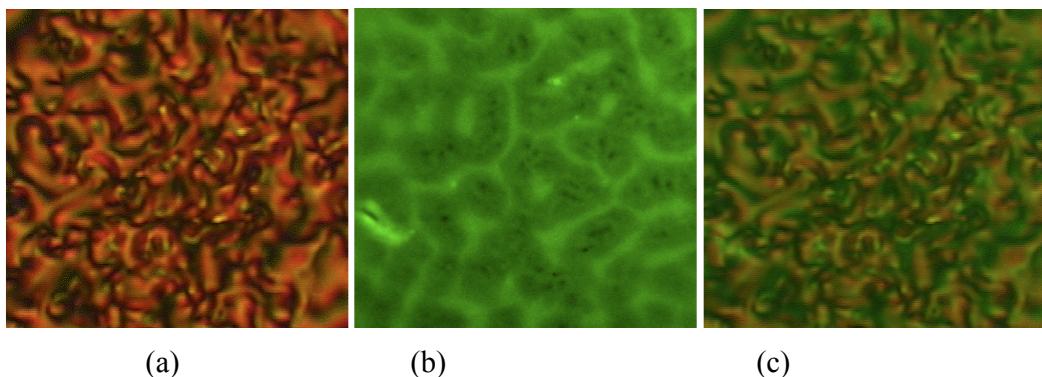


Figure 9. 4 OPM (a), fluorescence (b) ($\lambda_{\text{ex}} = 488 \text{ nm}$; $\lambda_{\text{emm}} > 505 \text{ nm}$) and overlay (c) images for 3;

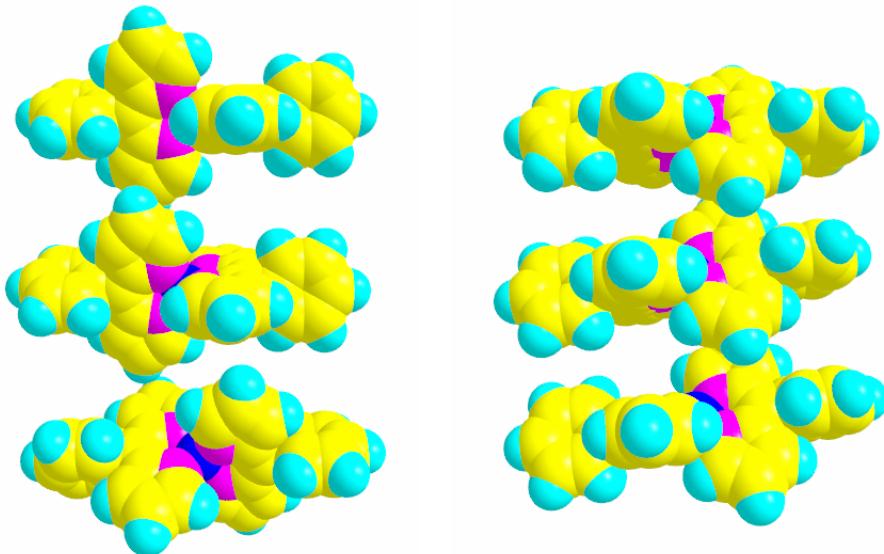


Figure 10. Schematic packing models for Zn dipyrrin and Ni Dipyrrin geometries calculated using PCGAMESS at the DFT (B3LYP) level using 6-311G basis set.^{1,2}

References

- 1 A.A. Granovsky, PC GAMESS version 7.1,
<http://classic.chem.msu.su/gran/gamess/index.html>.
- 2 J.B. Prieto, F.L. Arbeloa, V.M. Martinez, T. A. Lopez, I. L. Arbeloa, *Phys. Chem. Chem. Phys.* 2004, **6**, 4247.