Supporting Information for

Poly(*meta*-phenylene oxides) for the design of a tunable, efficient, and reusable catalytic platform

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[d] Institute for Molecular Science, Okazaki, Aichi 444-8787, Japan

Reagents:

Resorcinol (Aldrich, 99%)
4,6-dicholoropyrimidine (Aldrich, 97%)
DMSO (Wako)
K_2CO_3 (TCI, 99%)
Acetone (Wako)
Orcinol (Aldrich, 97%)
4-(4,6-Dichloro-2-pyrimidyl)morpholine (TCI, 98%)
4,6-Dichloro-5-(2-methoxyphenoxy)-2,2'-bipyrimidine (TCI, 98%)
4,7-dichloro-1,10-phenanthroline (Enovation)
Olivetol (Aldrich, 99%)
$(NH_4)_2PdCl_4$ (Aldrich, 99.995% trace metal basis)
Chloroform (Wako)
Tetrabutylammonium Bromide (TCI, 99%)
K_3PO_4 (Aldrich, 97%)
4-Chlorotoluene (TCI, 98%)
4-Chlorobenzonitrile (TCI, 98%)
4-Chlorophenol (TCI, 98%)
4-Chloroanisole (TCI, 98%)
4-Chloroaniline (TCI, 99%)
trans-2-Phenylvinylboronic acid (Aldrich, 97%)
Chlorobenzene (Aldrich, 99.8%)
Phenylboronic acid (TCI)
Bromobenzene (TCI, 99%)
4-Methylphenylboronic acid (TCI)
4,6-dimethoxypyrimidine (TCI, 98%)
Iodobenzene (Aldrich, 98%)
4-iodotoluene (TCI, 99%)
Butyl acrylate (Aldrich, 99%)
Styrene (TCI, 99%)

Instrumentation:

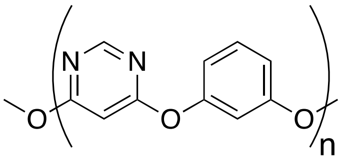
The TEM used for imaging was a JEM-2010F (HR7). Reaction progress and yields were monitored with an Agilent Technologies 6850 series II Network GC System, fitted with a flame ionization detector (GC FID). The SEM used for imaging and elemental mapping was a Hitachi High-Technologies, Miniscope TM3030 Plus fitted with a Bruker, QUANTAX 70 EDS. Palladium was quantified with a Perkin Elmer, NexION 300D ICP-MS. GPC analyses in THF were performed with a WGE GPC running on ParSEC Chromatography V. 5.67. GPC analyses in $CHCl_3$ were performed with a Japan Analytical Industries GPC with one JAIGEL-2.5H and one JAIGEL-3H column in series.

Synthesis of Poly(*m*PO)s:

Poly(*m*PO) 1b, 1c, 1d:

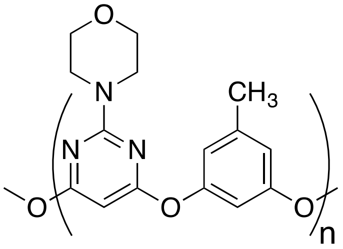
These polymers were synthesized as previously reported.[1]

Poly(*m*PO) 1a:



Under an inert atmosphere, resorcinol (13.5 mmol), 4,6-dicholoropyrimidine (13.5 mmol) and anhydrous DMSO (20 mL) were combined. Upon reaching solution homogeneity, anhydrous K_2CO_3 (20 grams) was added, and the reaction was immediately placed in an aluminum heating block at 100˚C and stirred vigorously for 40 minutes. The reaction was quenched by diluting with DMSO (80 mL) and precipitated in 1 L of distilled water. After stirring to break up large particles, the precipitate was filtered, rinsed with water (300 mL), and acetone (100 mL), and dried under vacuum. ^{1}H NMR (500 MHz, DMSO-D6): δ 8.48-8.42 (1H), 7.55-7.48 (1H), 7.24-7.12 (3H), 6.67-6.61 (1H). ^{13}C NMR (126 MHz, DMSO-D6): δ: 171.4, 158.6, 153.4, 130.9, 119.1, 115.4, 93.5.

Poly(*m*PO) 1e:



Under an inert atmosphere, orcinol (2.14 mmol, 265 mg), 4-(4,6-Dichloro-2-pyrimidyl)morpholine (2.14 mmol, 0.5 g) and anhydrous DMSO (4 mL) were combined. Upon reaching solution homogeneity, anhydrous K_2CO_3 (4 grams) was added, and the reaction was immediately placed in an aluminum heating block at 100˚C and stirred vigorously for 40 minutes. The reaction was quenched by diluting with DMSO (10 mL) and precipitated in 300 mL of distilled water. After stirring to break up large particles, the precipitate was filtered, rinsed with water (100 mL), and acetone (100 mL), and dried under vacuum. ^{1}H NMR (500 MHz, CDCl3): δ 6.92-6.72 (3H), 5.51-5.37 (1H), 3.66-3.57 (4H), 2.42-2.31 (3H).

Poly(*m*PO) 1f:

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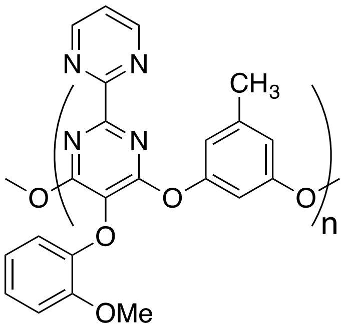
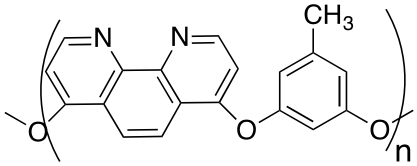
[1] *Macromolecules*, **2009**, *42* (21), 8181–8186



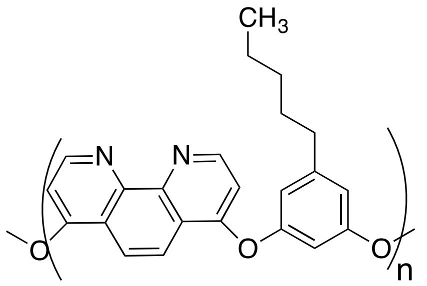
Under an inert atmosphere, orcinol (2.86 mmol, 355.8 mg), 4,6-Dichloro-5-(2-methoxyphenoxy)-2,2'-bipyrimidine (2.866 mmol, 1.0 gram) and anhydrous DMSO (4.25 mL) were combined. Upon reaching solution homogeneity, anhydrous K_2CO_3 (4.25 grams) was added, and the reaction was immediately placed in an aluminum heating block at 100˚C and stirred vigorously for 40 minutes. The reaction was quenched by diluting with DMSO (80 mL) and precipitated in 1 L of distilled water. After stirring to break up large particles, the precipitate was filtered, rinsed with water (300 mL), and acetone (100 mL), and dried under vacuum. ^{1}H NMR (500 MHz, CDCl3): δ 9.04-8.92 (2H), 7.56-7.49 (1H), 3.66-3.57 (4H), 6.99-6.71 (7H), 3.79-3.71 (3H) 2.29-2.19 (3H).

Poly(*m*PO) 1g:



Under an inert atmosphere, orcinol (1 mmol, 124 mg), 4,7-dichloro-1,10-phenanthroline (1 mmol) and anhydrous DMSO (2 mL) were combined. Upon reaching solution homogeneity, anhydrous K_2CO_3 (1.5 grams) was added, and the reaction was immediately placed in an aluminum heating block at 150˚C and stirred vigorously for 40 minutes. The reaction was quenched by diluting with DMSO (10 mL) and precipitated in 1 L of distilled water. After stirring to break up large particles, the precipitate was filtered, rinsed with water (100 mL), and acetone (100 mL), and dried under vacuum. ^{1}H NMR (500 MHz, DMSO-D6): δ 8.99-8.89 (2H), 8.39-8.29 (2H), 7.22-7.14 (2H), 6.59-6.44 (3H), 2.28-2.25 (3H).

Poly(*m*PO) **1h**



Under an inert atmosphere, olivetol (2 mmol, 360 mg), 4,7-dichloro-1,10-phenanthroline (2 mmol, 496 mg) and anhydrous DMSO (4 mL) were combined. Upon reaching solution homogeneity, anhydrous K_2CO_3 (3 grams) was added, and the reaction was immediately placed in an aluminum heating block at 150˚C and stirred vigorously for 40 minutes. The reaction was quenched by diluting with DMSO (20 mL) and precipitated in 1 L of distilled water. After stirring to break up large particles, the precipitate was filtered, rinsed with water (100 mL), and acetone (100 mL), and dried under vacuum. ^{1}H NMR (500 MHz, DMSO-D6): δ 9.01-8.82 (2H), 8.37-8.17 (2H), 7.30-7.03 (5H), 2.76-2.62 (2), 1.72-1.59 (2H), 1.40-1.21 (4H), 0.91-0.81 (3H).

Synthesis of Pd@Poly(*m*PO)s:

Pd@Poly(*m*PO) 1a:

To a 10 mL round bottom, screw-top vial with a stir bar was added **Poly(*m*PO) 1a** (1 mmol of repeat unit, 186 mg) and $CHCl_3$ (2 mL). The mixture was stirred at 60˚C until reaching solution homogeneity, at which point a solution of $(NH_4)_2PdCl_4$ (0.15 mmol, 42 mg) in water (2 mL) was added. The solution was left to stir at 60˚C for another 3 hours, then cooled to room temperature, diluted with acetone (4 mL), washed with H_2O (20 mL), acetone (20 mL), and chloroform (20 mL), and dried under vacuum.

Pd@Poly(*m*PO) 1b:

To a 10 mL round bottom, screw-top vial with a stir bar was added **Poly(*m*PO) 1b** (1 mmol of repeat unit, 200 mg) and $CHCl_3$ (2 mL). The mixture was stirred at 60˚C until reaching solution homogeneity, at which point a solution of $(NH_4)_2PdCl_4$ (0.15 mmol, 42 mg) in water (2 mL) was added. The solution was left to stir at 60˚C for another 3 hours, then cooled to room temperature, diluted with acetone (4 mL), washed with H_2O (20 mL), acetone (20 mL), and chloroform (20 mL), and dried under vacuum.

Pd@Poly(*m*PO) 1c:

To a 10 mL round bottom, screw-top vial with a stir bar was added **Poly(*m*PO) 1b** (1 mmol of repeat unit, 256 mg) and $CHCl_3$ (2 mL). The mixture was stirred at 60˚C until reaching solution homogeneity, at which point a solution of $(NH_4)_2PdCl_4$ (0.15 mmol, 42 mg) in water (2 mL) was added. The solution was left to stir at 60˚C for another 3 hours, then cooled to room temperature, diluted with acetone (4 mL), washed with H_2O (20 mL), acetone (20 mL), and chloroform (20 mL), and dried under vacuum.

Pd@Poly(*m*PO) 1d:

To a 10 mL round bottom, screw-top vial with a stir bar was added **Poly(*m*PO) 1d** (1 mmol of repeat unit, 276.1 mg) and $CHCl_3$ (2 mL). The mixture was stirred at 60˚C until reaching solution homogeneity, at which point a solution of $(NH_4)_2PdCl_4$ (0.15 mmol, 42 mg) in water (2 mL) was added. The solution was left to stir at 60˚C for another 3 hours, then cooled to room temperature, diluted with acetone (4 mL), washed with H_2O (20 mL), acetone (20 mL), and chloroform (20 mL), and dried under vacuum.

Pd@Poly(*m*PO) 1e:

To a 10 mL round bottom, screw-top vial with a stir bar was added **Poly(*m*PO) 1e** (0.3 mmol of repeat unit, 85.5 mg) and $CHCl_3$ (2 mL). The mixture was stirred at 60˚C until reaching solution homogeneity, at which point a solution of $(NH_4)_2PdCl_4$ (0.045 mmol, 12.78 mg) in water (2 mL) was added. The solution was left to stir at 60˚C for another 3 hours, then cooled to room temperature, diluted with acetone (4 mL), washed with H_2O (20 mL), acetone (20 mL), and chloroform (20 mL), and dried under vacuum.

Pd@Poly(*m*PO) 1f:

To a 10 mL round bottom, screw-top vial with a stir bar was added **Poly(*m*PO) 1f** (1 mmol of repeat unit, 384.13 mg) and $CHCl_3$ (2 mL). The mixture was stirred at 60˚C until reaching solution homogeneity, at which point a solution of $(NH_4)_2PdCl_4$ (0.15 mmol, 42.6 mg) in water (2 mL) was added. The solution was left to stir at 60˚C for another 3 hours, then cooled to room temperature, diluted with acetone (4 mL), washed with H_2O (20 mL), acetone (20 mL), and chloroform (20 mL), and dried under vacuum.

Pd@Poly(*m*PO) 1g:

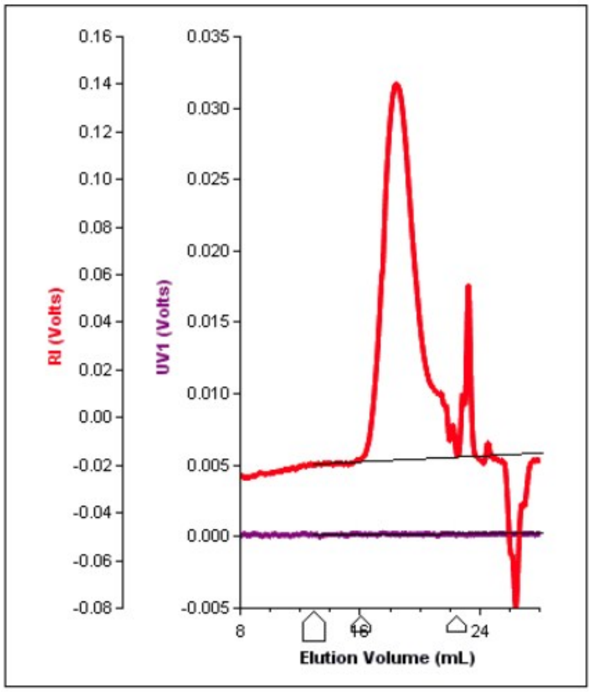
To a 10 mL round bottom, screw-top vial with a stir bar was added **Poly(*m*PO) 1g** (1 mmol of repeat unit, 281.3 mg) and $CHCl_3$ (2 mL). The mixture was stirred at 60˚C until reaching solution homogeneity, at which point a solution of $(NH_4)_2PdCl_4$ (0.15 mmol, 42.6 mg) in water (2 mL) was added. The solution was left to stir at 60˚C for another 3 hours, then cooled to room temperature, diluted with acetone (4 mL), washed with H_2O (20 mL), acetone (20 mL), and chloroform (20 mL), and dried under vacuum.

Pd@Poly(*m*PO) 1h:

To a 10 mL round bottom, screw-top vial with a stir bar was added **Poly(*m*PO) 1h** (1 mmol of repeat unit, 372 mg) and $CHCl_3$ (2 mL). The mixture was stirred at 60˚C until reaching solution homogeneity, at which point a solution of $(NH_4)_2PdCl_4$ (0.15 mmol, 42 mg) in water (2 mL) was added. The solution was left to stir at 60˚C for another 3 hours, then cooled to room temperature, diluted with acetone (4 mL), washed with H_2O (20 mL), acetone (20 mL), and chloroform (20 mL), and dried under vacuum.

GPC traces of Poly(*m*PO)s

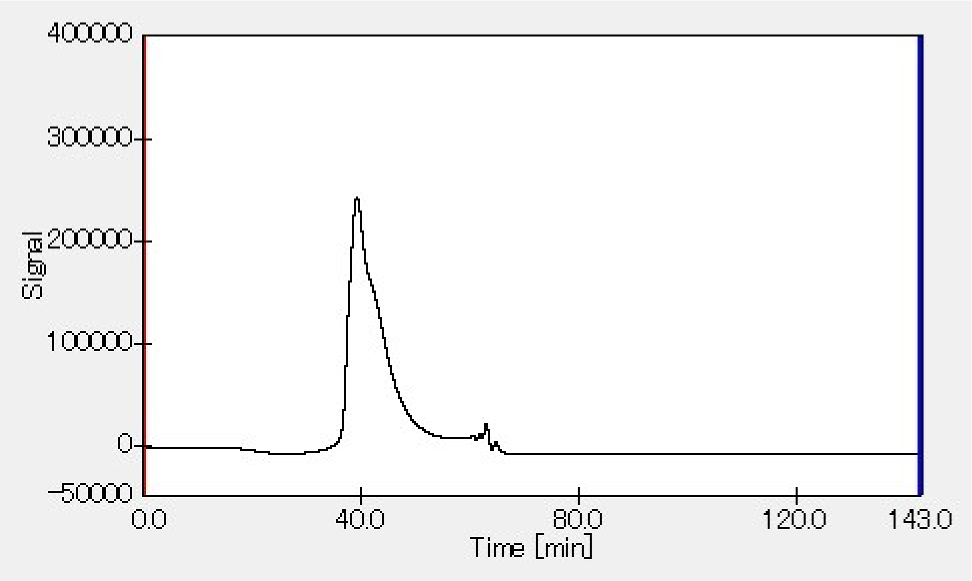
Poly(*m*PO) 1h



Elution solvent: THF
Calibration Standard: Polystyrene
Temperature: 30˚C
Instrument: WGE GPC running on ParSEC Chromatography V. 5.67
Flow rate: 1 mL/min

Mn: 7707 Mw: 20850 Mz: 35260 PDI: 2.7

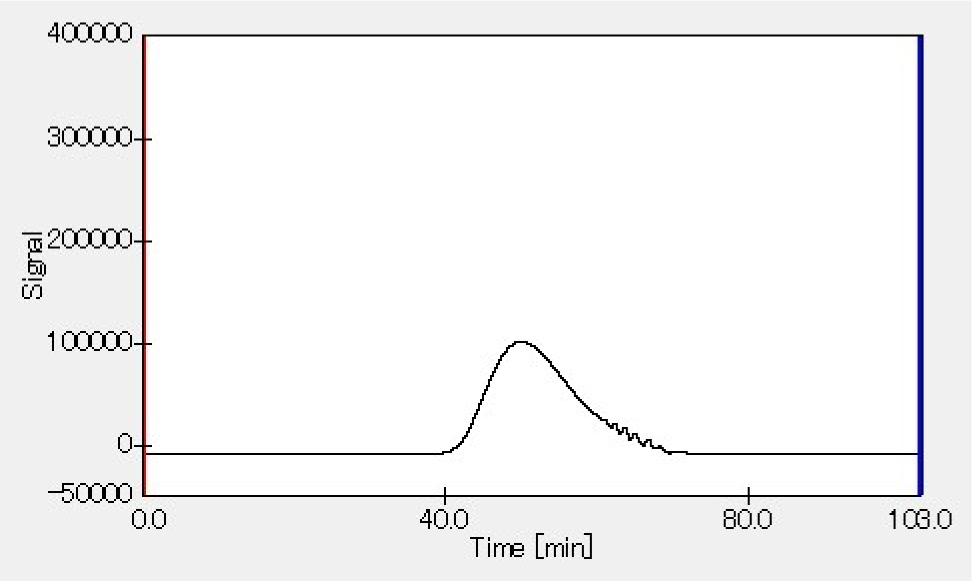
Poly(*m*PO) **1f**



Elution solvent: $CHCl_3$
Calibration Standard: Polystyrene
Temperature: 25˚C
Instrument: Japan Analytical Industries GPC with one JAIGEL-2.5H and one JAIGEL-3H column in series.
Flow rate: 1 mL/min

Mn: 12360 Mw: 48615 Mz: 48615 PDI: 3.9

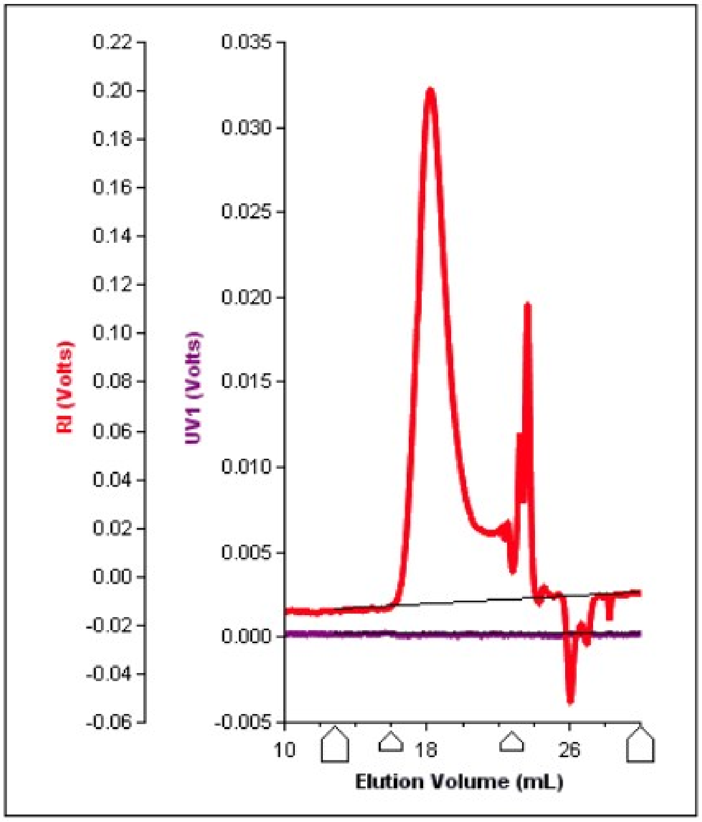
Poly(*m*PO) **1a**



Elution solvent: $CHCl_3$
Calibration Standard: Polystyrene
Temperature: 25˚C
Instrument: Japan Analytical Industries GPC with one JAIGEL-2.5H and one JAIGEL-3H column in series.
Flow rate: 1 mL/min

Mn: 2337 Mw: 10620 Mz: 15821 PDI: 4.5

Poly(*m*PO) **1g**



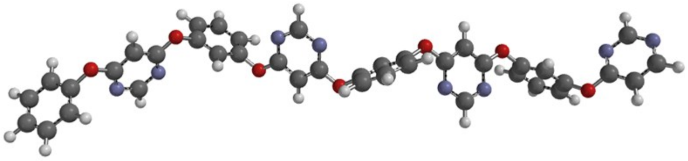
Elution solvent: THF
Calibration Standard: Polystyrene
Temperature: 25˚C
Instrument: WGE GPC running on ParSEC Chromatography V. 5.67
Flow rate: 1 mL/min

Mn: 5634 Mw: 22550 Mz: 37070 PDI: 4.0

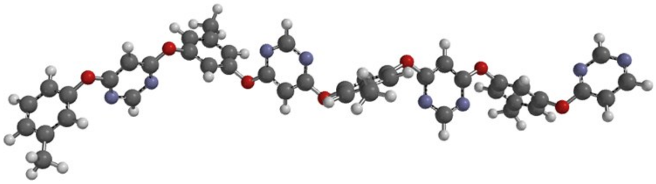
LogP Calculations:

Estimates of polymer logP values were calculated using Spartan ’14. Representative octamers were geometry optimized using PM3 semiempirical methods. End groups were simplified to H-atoms; analogous structures with –OH and/or –Cl end groups showed little difference in final geometries or LogP values. Optimized LogP values and final geometries for **1a-c** are shown below.

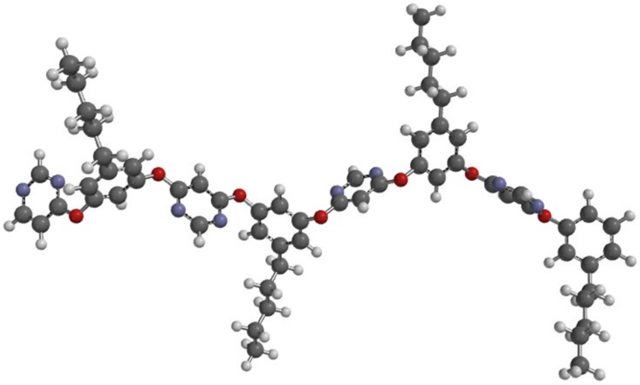
1a: (LogP = 6.68)

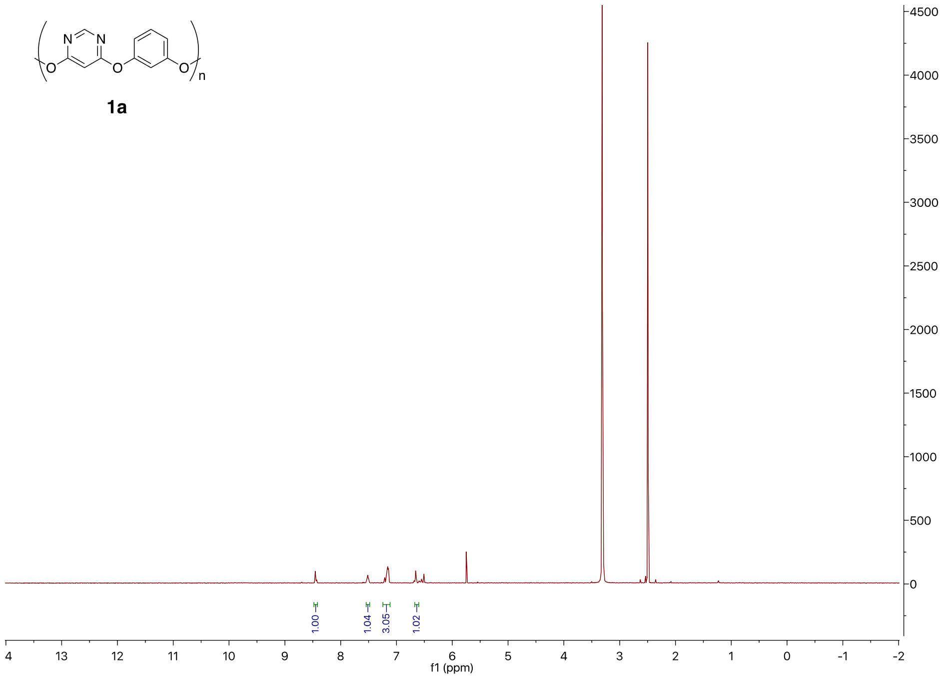


1b: (LogP = 8.63)



1c: (LogP = 15.31)

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1.04
3.05
1.02
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)
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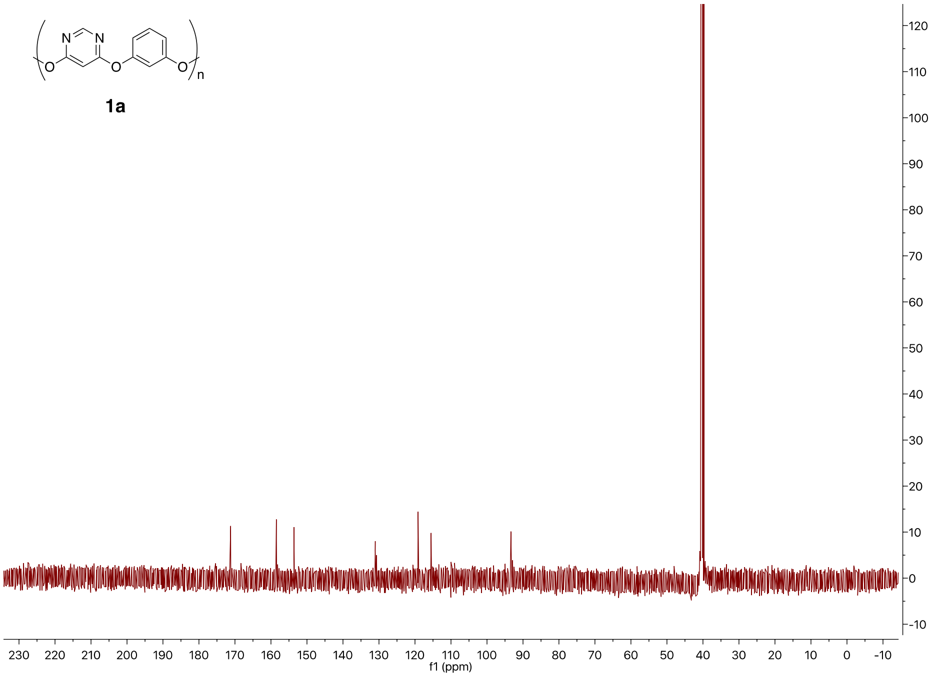
3500
3000
2500
2000
1500
1000
500
0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180
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140
130
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50
40
30
20
10
0
-10
f1 (ppm)
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60
50
40
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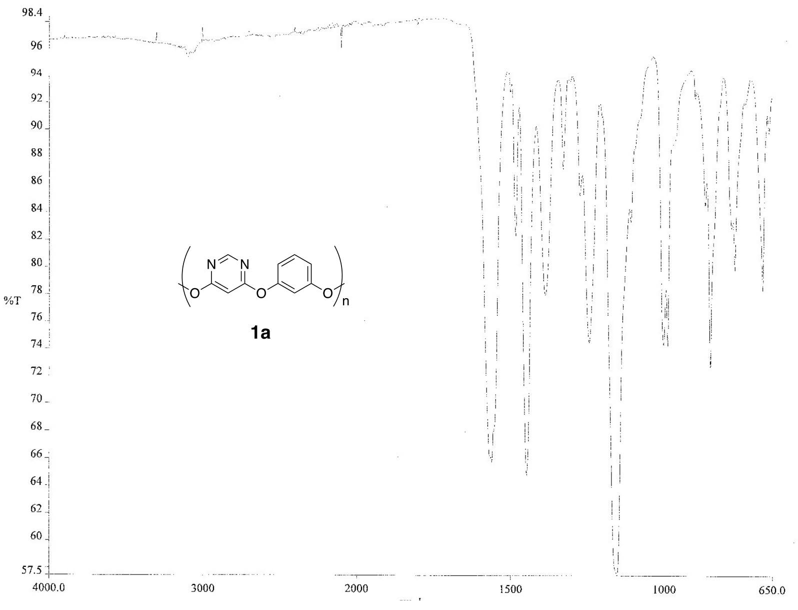
0
-10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86
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%T
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1000
650.0
N
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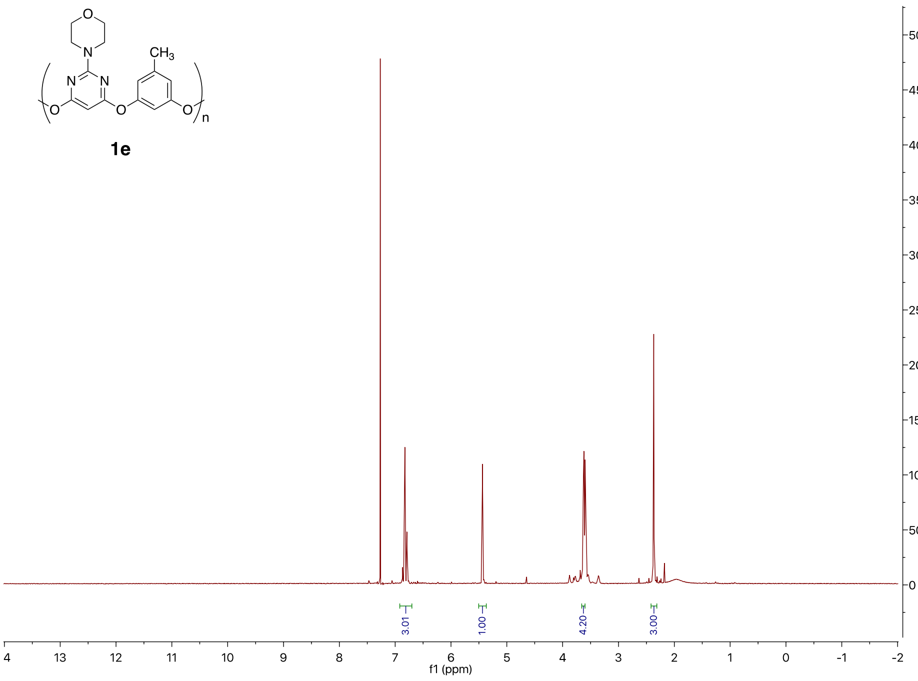
O
O
O
n
1a



CH3
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N
N
O
O
O
O
n
1e
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4500
4000
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3000
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1500
1000
500
0
3.01
1.00
4.20
3.00
4
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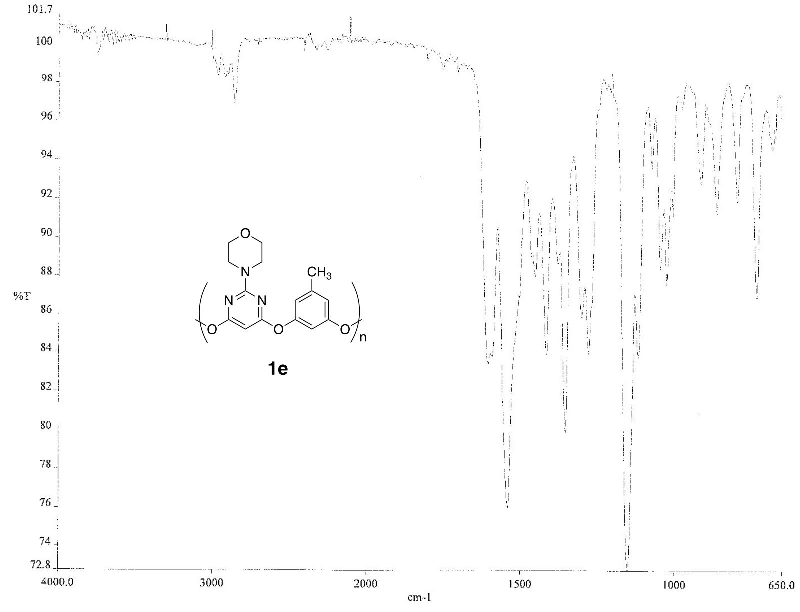
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)



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94
92
90
88
%T
86
84
82
80
78
76
74
72.8
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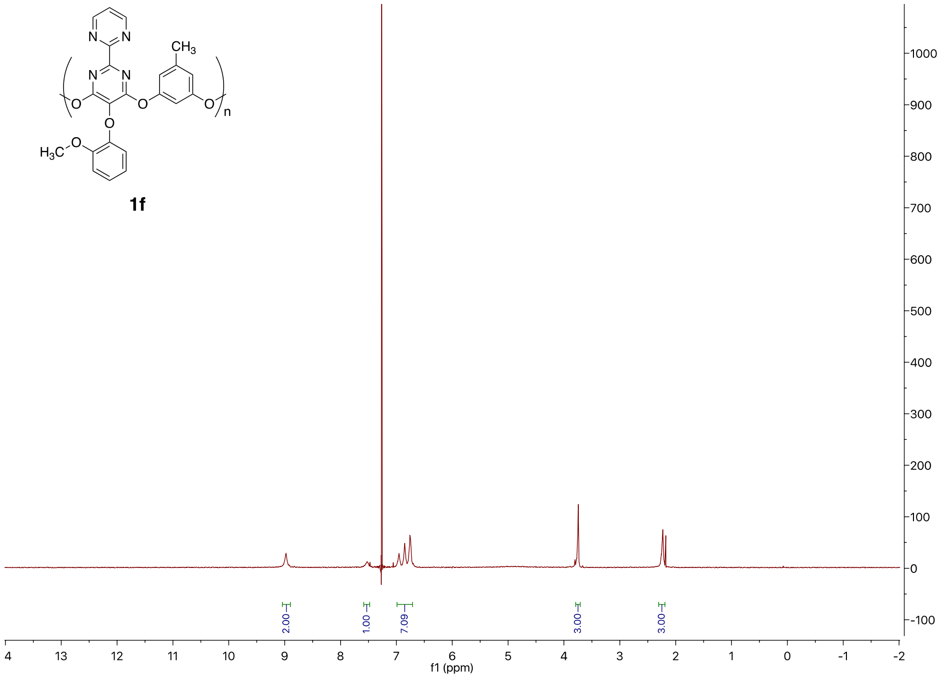
3000
2000
1500
1000
650.0
cm-1
CH3
N
N
N
O
O
O
O
n
1e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N
N
O
O
O
n
O
H3C
O
1f
1000
900
800
700
600
500
400
300
200
100
0
-100
2.00
1.00
7.09
3.00
3.00
4
13
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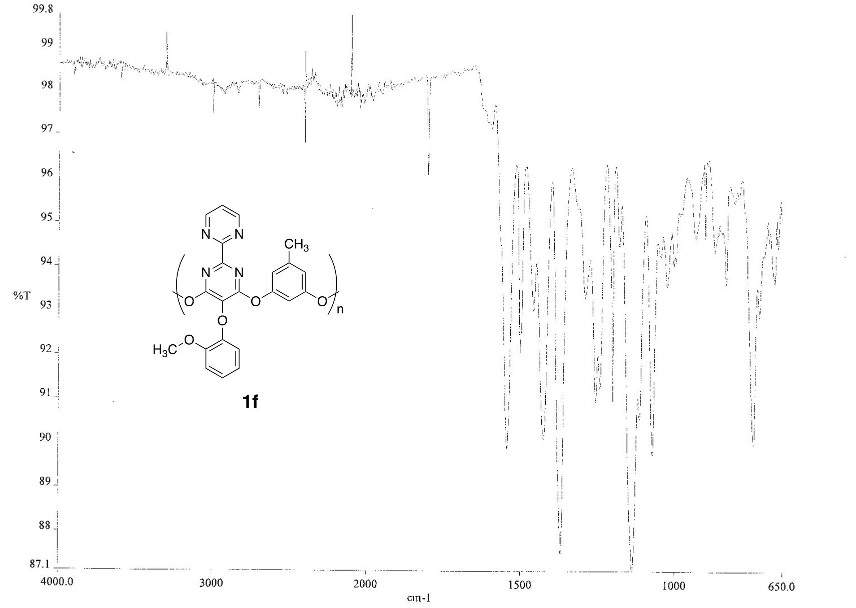
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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97
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95
94
%T
93
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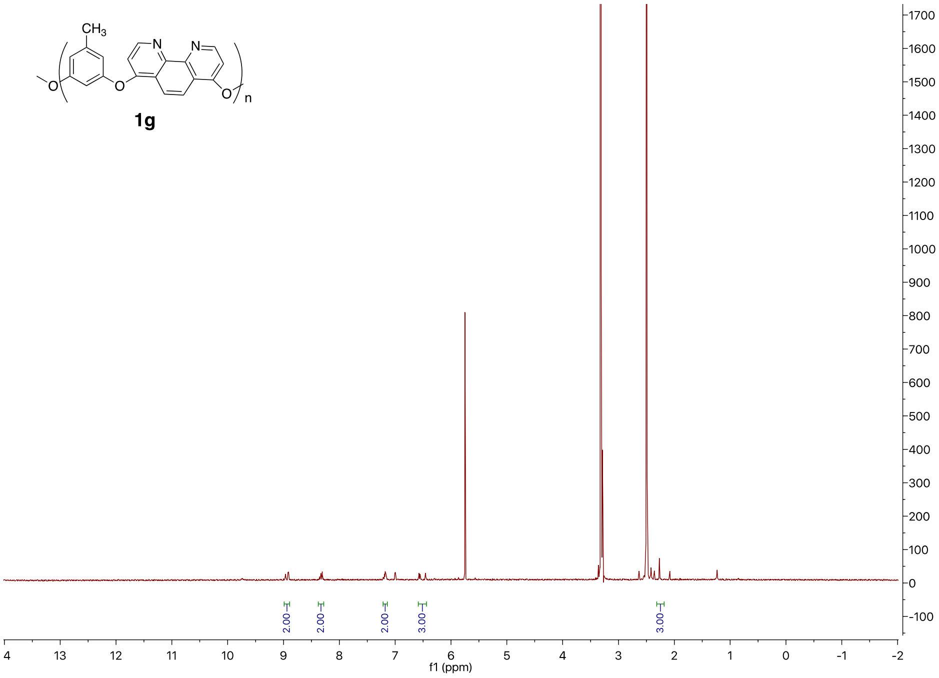
91
90
89
88
87.1
CH3
N
N
N
N
O
O
O
n
O
H3C
O
1f
4000.0
3000
2000
1500
1000
650.0
cm-1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N
O
O
n
1g
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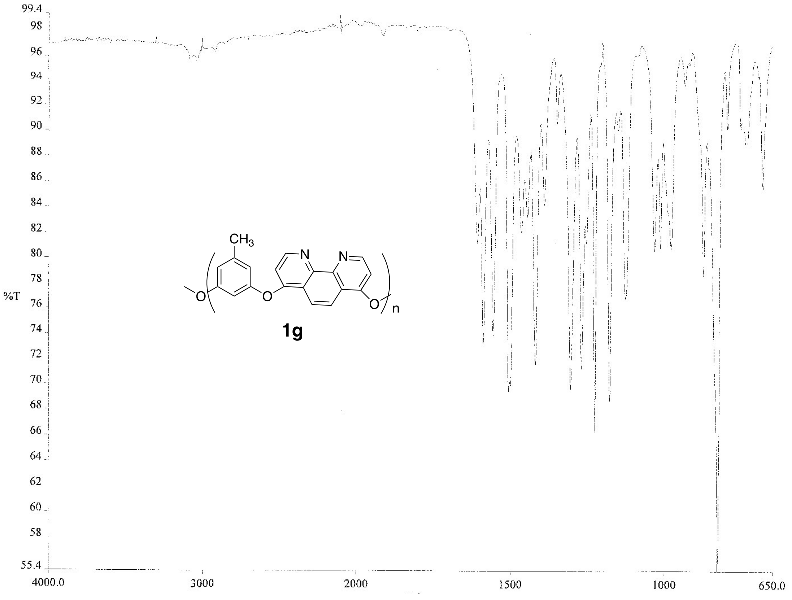
1600
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
2.00
2.00
2.00
3.00
3.00
4
13
12
11
10
9
8
7
6
5
4
3
2
1
0
-1
-2
f1 (ppm)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92
90
88
86
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82
80
78
%T
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74
72
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68
66
64
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60
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55.4
CH3
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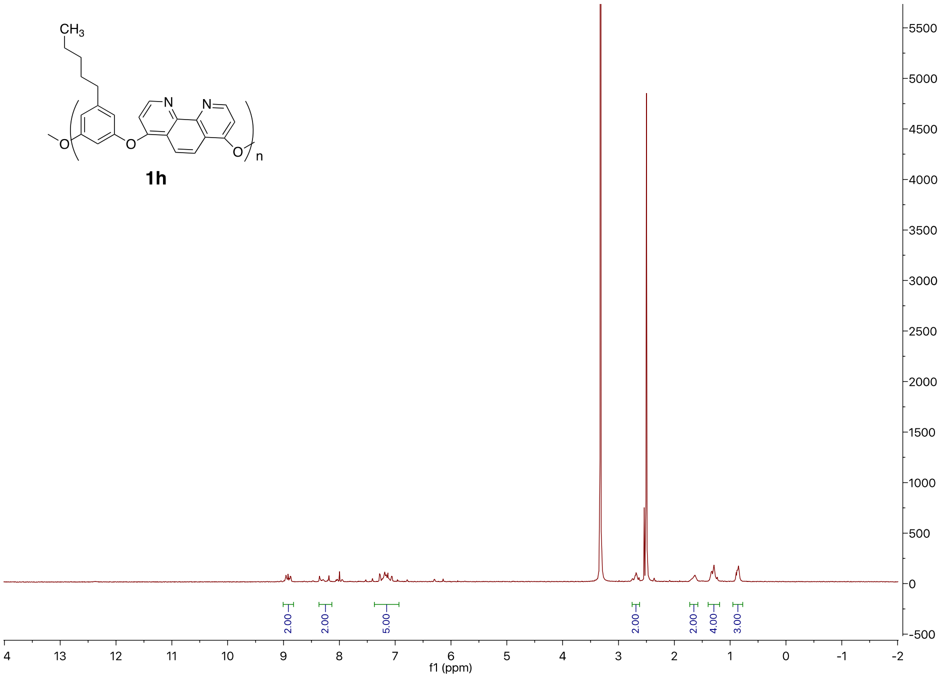
N
O
O
n
1g
4000.0
3000
2000
1500
1000
650.0


CH3
N
N
O
O
O
n
1h
2.00
2.00
5.00
2.00
2.00
4.00
3.00
5500
5000
4500
4000
3500
3000
2500
2000
1500
1000
500
0
-500
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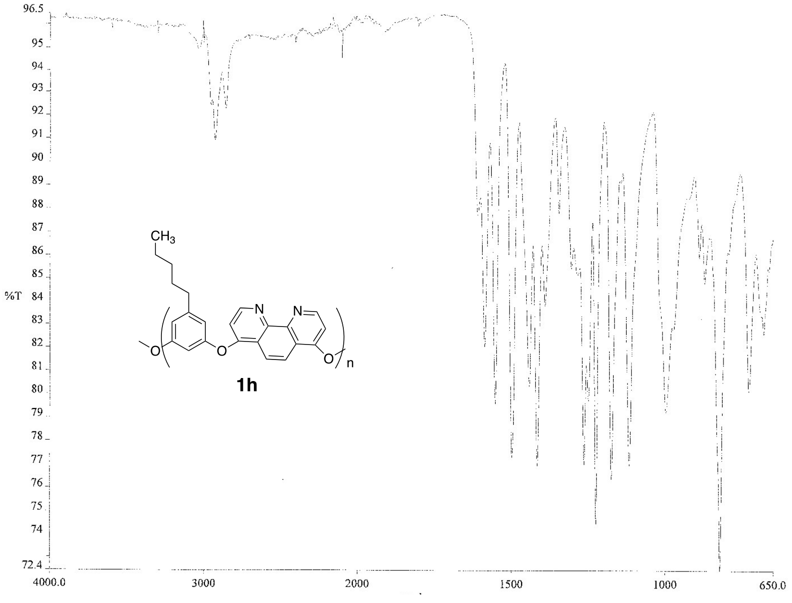
2
1
0
-1
-2
f1 (ppm)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94
93
92
91
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89
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82
81
80
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75
74
72.4
%T
CH3
N
N
O
O
O
n
1h
4000.0
3000
2000
1500
1000
650.0