Experimental

Synthetic Procedure

Synthesis of 1 and 2 via Condensation of p-Terephthalaldehyde with Alcoxyphenyl acetonitrile

\[
\begin{align*}
\text{A} & \quad \text{NaOH} \quad \text{EtOH} \\
\text{B} & \quad \text{NaOH} \quad \text{EtOH}
\end{align*}
\]

To a mixture of alcoxyphenylacetonitrile (245 mg, 1.0 mmol) and p-terephthalaldehyde (77 mg, 0.50 mmol) in ethanol (5 mL), sodium methoxide in methanol (1.0 M, 5 mL) was added and stirred for 10 min at room temperature under air. The reaction mixture was diluted with a large amount of methanol (100 mL), and then filtered to remove solid. The solid was washed with an ethanol (10 mL), and dried under vacuum to give as a powder.

Yellow-colored solid 1: Yield: Quant. (293 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.95 (Ar-\(H\), s, 4H), 7.62 (Ar-\(H\), d, \(J = 9.2\), 4H), 7.42 (Vinylene-\(H\), s, 2H), 6.96 (Ar-\(H\), d, \(J = 8.8\), 4H), 4.00 (O-CH\(_2\)-CH\(_2\)-CH\(_2\)-[CH\(_3\)]\(_4\)-CH\(_3\), t, \(J = 6.4\), 4H), 1.82 (O-CH\(_2\)-CH\(_2\)-CH\(_2\)-[CH\(_3\)]\(_4\)-CH\(_3\), m, 4H), 1.78 (O-CH\(_2\)-CH\(_2\)-CH\(_2\)-[CH\(_3\)]\(_4\)-CH\(_3\), m, 4H), 1.3 (O-CH\(_2\)-CH\(_2\)-CH\(_2\)-[CH\(_3\)]\(_4\)-CH\(_3\), m, 8H), 0.88 (O-CH\(_2\)-CH\(_2\)-CH\(_2\)-[CH\(_3\)]\(_4\)-CH\(_3\), t, \(J = 7.2\), 6H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.5, 138.5, 135.6, 129.6, 127.6, 126.6, 118.1, 115.2, 112.5, 68.4, 32.0, 29.5, 29.4, 29.3, 26.1, 22.8, 14.2. HRMS (ESI) m/z: calcd for C\(_{40}\)H\(_{48}\)N\(_2\)O\(_2\) [M]\(^+\), 588.3710; found, 588.3698.

Yellow-colored solid 2: Yield: Quant. (295 mg). \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 7.95 (Ar-\(H\), s, 4H), 7.62 (Ar-\(H\), d, \(J = 8.8\), 4H), 7.42 (Vinylene-\(H\), s, 2H), 6.97 (Ar-\(H\), d, \(J = 9.2\), 4H), 3.89 (O-CH\(_2\)-CH[CH\(_2\)-CH\(_3\)]-CH\(_2\)-[CH\(_3\)]\(_2\)-CH\(_3\), d, \(J = 3.2\), 4H), 1.76 (O-CH\(_2\)-CH[CH\(_2\)-CH\(_3\)]-CH\(_2\)-[CH\(_3\)]\(_2\)-CH\(_3\), m, 2H), 1.75 (O-CH\(_2\)-CH[CH\(_2\)-CH\(_3\)]-CH\(_2\)-[CH\(_3\)]\(_2\)-CH\(_3\), m, 8H), 1.40 (O-CH\(_2\)-CH[CH\(_2\)-CH\(_3\)]-CH\(_2\)-[CH\(_3\)]\(_2\)-CH\(_3\), m, 10H), 0.88 (O-CH\(_2\)-CH[CH\(_2\)-CH\(_3\)]-CH\(_2\)-[CH\(_3\)]\(_2\)-CH\(_3\), m, 12H). \(^13\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 160.7, 160.5, 138.5, 138.4, 135.6, 129.6, 127.6, 126.6, 126.5, 118.1, 115.2, 112.5, 112.4, 70.9, 68.4, 39.5, 31.9, 30.6, 29.5, 29.4, 29.3, 29.2, 26.1, 24.0, 23.2, 22.8, 14.2, 14.2, 11.2. HRMS (ESI) m/z: calcd for C\(_{40}\)H\(_{48}\)N\(_2\)O\(_2\) [M]\(^+\), 588.3710; found, 588.3718.

Synthesis of E

\[
\begin{align*}
\text{A} & \quad \text{NaOH} \quad \text{HCl aq.} \\
\text{D} & \quad \text{MeOH} \quad \text{CHCl}_3
\end{align*}
\]

To a mixture of 4-octyoxyphenylacetonitrile (2.45 g, 10 mmol) and terephthalaldehyde mono(diethyl acetal) (2.08 g, 10 mmol) in methanol (10 mL), sodium methoxide in methanol (1 M, 10 mL) was added and stirred for 10 min at room temperature under air. The reaction mixture was diluted with methanol (30 mL), and then
filtered to remove yellow solid. The filtrate was poured into a large amount of water (100 mL). The solid was collected by filtration, and then washed with a small amount of methanol (5 mL). The solid was dissolved in chloroform (30 mL). To the solution, concentrated HCl solution (10 mL) was added and stirred by reflux conditions. Chloroform phase was extracted, evaporated, and dried under vacuum to give as a powder.

Yellow-colored solid E: Yield: 93% (3.36 g). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 10.04 (Aldehyde, s, 1H), 7.97 (Ar-$H$, dd, $J = 4.8, J = 4.8, 4H$), 7.62 (Ar-$H$, d, $J = 9.2, 2H$), 7.42 (Vinylene-$H$, s, 1H), 6.96 (Ar-$H$, d, $J = 8.8, 4H$), 4.00 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$, t, $J = 6.4, 4H$), 1.82 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$, m, 4H), 1.78 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$, m, 4H), 1.3 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$, m, 8H), 0.88 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$, t, $J = 7.2, 6H$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 191.4, 160.8, 139.7, 137.8, 136.8, 130.2, 129.6, 127.7, 126.2, 117.7, 115.2, 114.5, 68.4, 32.0, 29.4, 29.3, 29.2, 26.1, 22.8, 14.2. HRMS (ESI) m/z: calcd for C$_{24}$H$_{27}$NO$_2$ [M]$^+$, 361.2040; found, 361.2036.

**Synthesis of 3**

To a mixture of E (361 mg, 1.0 mmol) and B (245 mg, 1.0 mmol) in ethanol (10 mL), sodium methoxide in methanol (1 M, 5 mL) was added and stirred for 10 min at room temperature under air. The reaction mixture was diluted with ethanol (10 mL), and then filtered to remove solid. The solid was washed with an ethanol (10 mL) and a large amount of methanol (100 mL), and dried under vacuum to give as a powder.

Yellow-colored solid 3: Yield: Quant. (588 mg). $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.95 (Ar-$H$, s, 4H), 7.62 (Ar-$H$, d, $J = 8.2, 4H$), 7.42 (Vinylene-$H$, s, 2H), 6.96 (Ar-$H$, d, $J = 3.2, 2H$), 6.96 (Ar-$H$, d, $J = 2.8, 2H$), 4.00 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$, t, $J = 6.8, 2H$), 3.89 (O-$CH_2$-$CH[CH_2$-$CH_3]$-$CH_2$-$[CH_2]_2$-$CH_3$, d, $J = 5.6, 2H$), 1.81 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$ and O-$CH_2$-$CH[CH_2$-$CH_3]$-$CH_2$-$[CH_2]_2$-$CH_3$, m, 3H), 1.78 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$ and O-$CH_2$-$CH[CH_2$-$CH_3]$-$CH_2$-$[CH_2]_2$-$CH_3$ m, 6H), 1.35 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$ and O-$CH_2$-$CH[CH_2$-$CH_3]$-$CH_2$-$[CH_2]_2$-$CH_3$ m, 10H), 0.88 (O-$CH_2$-$CH_2$-$CH_2$-$[CH_2]_4$-$CH_3$ and O-$CH_2$-$CH[CH_2$-$CH_3]$-$CH_2$-$[CH_2]_2$-$CH_3$ t, $J = 7.2, 9H$). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 160.7, 138.4, 135.5, 129.6, 127.5, 126.6, 118.1, 115.2, 112.5, 112.5, 70.9, 39.5, 30.6, 29.2, 24.0, 23.2, 14.2, 11.2. HRMS (ESI) m/z: calcd for C$_{40}$H$_{46}$N$_2$O$_2$ [M]$^+$, 588.3710; found, 588.3707.
**Display Report**

**Analysis Info**
- Analysis Name: D:\Data\Members\hayashi\1\RH9.d
- Method: aPCI_pos_wide.m
- Sample Name: micrOTOF
- Operator: bruker
- Instrument / Ser#: microTOF 10387

**Acquisition Info**
- Acquisition Date: 4/27/2018 2:18:49 PM
- Acquisition Parameter:
  - Source Type: APCI
  - Ion Polarity: Positive
  - Focus: Active
  - Scan Begin: 50 m/z
  - Scan End: 3000 m/z
  - Set Capillary: 4000 V
  - Set End Plate Offset: -500 V
  - Set Dry Gas: 3.0 l/min
  - Set Dry Heater: 200 °C
  - Set Divert Valve: Waste
  - Set Divert Valve: Waste
  - Set Capillary: 4000 V
  - Set End Plate Offset: -500 V
  - Set Dry Gas: 3.0 l/min
  - Set Dry Heater: 200 °C
  - Set Divert Valve: Waste

**Intensities**

1. **Intensities x10^7**
   - Intensities at various m/z values.
   - Key m/z values include 587.3620, 588.3698, 589.3739, 590.3793, 591.3839, 592.3859, 593.3869, 594.3889, 595.3899, 596.3909, 597.3919, 598.3929, 599.3939, 600.3949.

2. **Intensities x10^6**
   - Intensities at various m/z values.
   - Key m/z values include 587.3620, 588.3698, 589.3739, 590.3793, 591.3839, 592.3859, 593.3869, 594.3889, 595.3899, 596.3909, 597.3919, 598.3929, 599.3939, 600.3949.

3. **Intensities x10^5**
   - Intensities at various m/z values.
   - Key m/z values include 587.3620, 588.3698, 589.3739, 590.3793, 591.3839, 592.3859, 593.3869, 594.3889, 595.3899, 596.3909, 597.3919, 598.3929, 599.3939, 600.3949.

**Comment**

Bruker Compass DataAnalysis 4.0

Printed: 4/27/2018 3:33:39 PM  Page 1 of 1
Current Data Parameters
NAME     HAY hayashi_c 1H
EXPNO                10
PROCNO                1
F2 - Acquisition Parameters
Date_          20210123
Time               4.33
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PROBHD   5 mm PABBO BB-
PULPROG            zg30
TD                65536
SOLVENT           CDCl3
NS                    8
DS                    2
FIDRES         0.125483 Hz
AQ            3.9846387 sec
RG               31.29
DW               60.000 usec
TE                299.8 K
D1          1.00000000 sec
======== CHANNEL f1 ========
NUC1                 1H
P1                15.00 usec
PLW1         8.39999962 W
SFO1        400.1324710 MHz
F2 - Processing parameters
SI                65536
SF          400.1300098 MHz
WDW                  EM
SSB      0
LB                 0.30 Hz
PC                 1.00

Current Data Parameters
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EXPNO                10
PROCNO                1
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Time               5.36
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PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 1024
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG               194.19
DW               20.000 usec
TE                299.8 K
D1           2.00000000 sec
D11          0.03000000 sec
======== CHANNEL f1 ========
NUC1                13C
P1                10.00 usec
PLW1        82.00000000 W
SFO1        100.6228293 MHz
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             80.00 usec
PLW2         8.39999962 W
PLW12        0.29530999 W
PLW13        0.29530999 W
SFO2        100.6127563 MHz
F2 - Processing parameters
SI                32768
SF          100.6127563 MHz
WDW                  EM
SSB      0
LB                 1.00 Hz
PC                 1.40
Display Report

Analysis Info
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Method: apci_pos_wide.m
Sample Name: 
Comment: 

Acquisition Date: 4/27/2018 3:46:09 PM
Operator: bruker
Instrument / Ser#: micrOTOF 10387

Acquisition Parameter

Source Type  | APCI | Ion Polarity | Positive | Set Nebulizer | 1.6 Bar |
Focus         | Active | Set Capillary | 4000 V | Set Dry Heater | 200 °C |
Scan Begin    | 50 m/z | Set End Plate Offset | -500 V | Set Dry Gas | 3.0 l/min |
Scan End      | 3000 m/z |  |  | Set Divert Valve | Waste |

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Analysis Info
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Sample Name: micrOTOF
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Acquisition Parameter
Source Type: APCI
Ion Polarity: Positive
Focus: Active
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Scan End: 3000 m/z
Scan Begin: 50 m/z
Scan End: 3000 m/z
Set Capillary: 4000 V
Set End Plate Offset: -500 V
Set Nebulizer: 1.6 Bar
Set Dry Heater: 200 °C
Set Dry Gas: 3.0 l/min
Set Divert Valve: Waste
Waste

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printed: 4/27/2018 3:35:40 PM
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