Interplay between Diamine Structure and Absolute Helicity in Ni-salen Metallofoldamers

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Supporting Information

General Considerations  All reactions were carried out in round bottomed flasks that were flame-dried under vacuum and cooled under nitrogen. Chromatography was performed on silica gel (ICN SiliTech 32-62D, 60Å). For $^{13}$C NMR, multiplicities were distinguished using an APT pulse sequence: typical methylene and quaternary carbons appear 'up' (u); methine and methyl carbons 'down' (dn). FT-IR spectra were collected on a Thermo Electron Co. IR100 spectrometer using a Performer Attenuated Total Reflectance (ATR) probe with a ZnSe plate. X-ray quality crystals of 5 were grown from toluene/CH$_2$Cl$_2$. Circular Dichroism spectra were collected on a JASCO J-810 spectropolarimeter. Wavelength scans were recorded using a 2 nm date pitch and a 50 nm/min scan speed, and spectra were collected in 0.1 cm quartz cells. The spectra of the solutions of 4 ($6.8 \times 10^{-4}$ M in CH$_2$Cl$_2$) and 5 ($4.0 \times 10^{-4}$ M in CH$_2$Cl$_2$) were collected at 20 °C.
A solution of (1R,2R)-cyclopentane-1,2-diamine (0.002 g, 0.020 mmol) in EtOH (1.5 mL) was combined with aldehyde 3¹ (0.021 g, 0.040 mmol) and heated to reflux for 4 h. The reaction mixture was cooled to rt and Ni(OAc)₂·4H₂O (7.5 mg, 0.030 mmol) was added. The mixture was then heated to reflux for another 4 h, and a dark orange precipitate was observed. The precipitate was filtered, washed with cold ethanol, and dried under vacuum to give the title product as a dark orange solid. The yield was 0.012 g (55%). The purity was measured to be ≥ 95% by ¹H NMR. mp: 162-170°C; [α]¹D₂₅ –50º (c 0.012, CH₂Cl₂); ¹H NMR (400MHz, CDCl₃, δ): 10.74 (s, 2H), 10.67 (s, 2H), 8.42 (d, J = 6.8 Hz, 2H), 8.23 (s, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.49 (dd, J = 7.6, 1.2 Hz, 2H), 7.34 (app t, J = 6.8 Hz, 2H), 7.18 (d, J =6.8 Hz, 2H), 6.97 (app t, J = 6.8 Hz, 2H), 6.85 (app t, J = 8.0 Hz, 2H), 6.75-6.69 (m, 4H), 6.62 (d, J = 8.0 Hz, 2H), 4.18 (t, J = 6.8 Hz, 4H), 3.23 (s, 6H), 2.95 (m, 2H), 2.09 (m, 2H), 1.72-1.65 (m, 6H), 1.41-1.25 (m, 12H), 1.17-1.12 (m, 2H), 0.88 (t, J = 6.8 Hz, 6H); ¹³C NMR (100MHz, CDCl₃, δ): 165.2 (u), 162.4 (u), 162.0 (u), 160.9 (u), 157.5 (dn), 157.0 (u), 137.4
(dn), 135.6 (dn), 133.9 (u), 132.6 (dn), 130.7 (dn), 127.8 (u), 126.0 (dn), 124.2 (dn), 123.7 (u), 123.6 (u), 123.3 (dn), 122.6 (u), 120.1 (u), 119.3 (dn), 114.6 (dn), 110.2 (dn), 74.1 (dn), 63.8 (u), 53.9 (dn), 30.5 (u), 27.5 (u), 24.7 (u), 22.0 (u), 21.5 (u), 18.2 (u), 13.0 (dn); IR (cm⁻¹): 2900, 1718, 1708, 1656, 1597, 1527, 1492, 1460, 1431, 1388, 1293, 1253, 1179, 1131, 1080, 1022, 893, 675; UV-vis (6.8 × 10⁻⁶ M in CH₂Cl₂) λmax: 238, 262, 310, 418; HRMS (ESI+) m/z: [M+Na], calcd for C₆₃H₆₆N₆NiO₁₂: 1179.3990, found: 1179.3997.

**Ni Salen 5**

(1S,2S)-(-)-1,2-diphenylethylenediamine (41 mg, 0.19 mmol) was dissolved in EtOH (10 mL), and 1.0 mL (4.1 mg of the diamine, 0.019 mmol) of this solution was combined with compound 3 (20 mg, 0.039 mmol) in EtOH (2 mL). The resulting solution was heated to reflux for 4 h. The reaction mixture was cooled and Ni(OAc)₂·4H₂O was added and heated for 4 h. Water (5 mL) was added to the crude mixture which was then allowed to stand for 16 h at rt. The precipitates were filtered through glass wool, washed with ethanol and water, and
dried under vacuum to give the title compound as a dark orange solid. The yield was 21 mg (84%). The purity was measured to be 94% by $^1$H NMR. mp: 135-140°C; [$\alpha$]$^\circ_{D}$ +550° (c 0.011, CH$_2$Cl$_2$); $^1$H NMR (400MHz, CDCl$_3$, δ): 10.86 (s, 2H), 10.78 (s, 2H), 8.47-8.43 (m, 4H), 7.57 (d, J = 8.0Hz, 2H), 7.55-7.52 (m, 4H), 7.24-7.32 (m, 6H), 7.28-7.20 (m, 2H), 6.98 (d, J = 7.6Hz, 2H), 6.90-6.86 (m, 6H), 6.70-6.67 (m, 6H), 4.20-4.15 (m, 4H), 4.10 (s, 2H), 3.26 (s, 6H), 1.73-1.66 (m, 4H), 1.42-1.26 (m, 12H), 0.89 (t, J = 7.4Hz, 6H); $^{13}$C NMR (100MHz, CDCl$_3$, δ): 165.2 (u), 162.3 (u), 161.2 (u), 160.5 (dn), 159.8 (u), 157.2 (u), 138.1 (dn), 136.1 (dn), 133.8 (u), 133.1 (dn), 132.8 (u), 130.7 (dn), 128.6 (3C, dn), 128.0 (u), 127.8 (2C, dn), 126.5 (dn), 124.1 (dn), 123.9 (2C, u), 123.4 (dn), 122.5 (u), 120.1(u), 119.1 (dn), 114.6 (dn), 110.4 (dn), 76.6 (dn), 63.8 (u), 54.0 (dn), 30.5 (u), 27.5 (u), 24.7 (u), 21.5 (u), 13.0 (dn); IR (cm$^{-1}$): 3001, 2919, 2865, 1713, 1660, 1614, 1537, 1504, 1451, 1291, 1238, 1178, 1134, 1085, 1013, 751, 631; UV-vis (4.0 x 10$^{-6}$ M in CH$_2$Cl$_2$) $\lambda_{max}$: 232, 260, 328, 416; HRMS (ESI+) m/z: [M+Na], calcd for C$_{72}$H$_{70}$N$_6$NiO$_{12}$: 1291.4303, found: 1291.4307.
Ni-salen 6

(11R, 12R)-9,10-dihydro-9,10-ethanoanthracene-11,12-diamine (9.1 mg, 0.038 mmol) was dissolved in EtOH (1 mL). This solution was combined with compound 3 (40 mg, 0.077 mmol) in EtOH (2 mL). The resulting solution was heated to reflux for 4 h. The reaction mixture was cooled and Ni(OAc)$_2$·4H$_2$O (15.0 mg, 0.060 mmol) was added and heated for 4 h. Water (5 mL) was added to the crude mixture which was then allowed to stand for 16 h at rt. The precipitates were filtered through glass wool, washed with ethanol and water, and S-3 dried under vacuum to give the title compound as a dark orange solid. The yield was 0.028 g (57%). mp: 232-238°C; [α]$^{23}_{D}$ –114° (c 0.011, CH$_2$Cl$_2$) $^1$H NMR (400 MHz, CD$_2$Cl$_2$, δ): 10.79-10.46 (m, 4H), 8.26 (dd, J= 7.6, 1.6 Hz, 2H), 7.92-7.81 (m, 2H), 7.41-7.39 (m, 4H), 7.24-7.23 (m, 6H), 7.18-7.17 (m, 4H), 6.98 (s, 2H), 6.79 (app t, J= 8.0 Hz, 2H), 6.68 (app t, J= 7.6 Hz, 2H), 6.51-6.15 (m, 6H), 4.28 (s, 2H), 4.10 (s, 4H), 3.10 (s, 6H), 2.96 (s, 2H), 1.61-1.54 (m, 4H), 1.30-1.19 (m, 12H), 0.78 (t, J= 6.4 Hz, 6H); $^{13}$C NMR (100 MHz, CD$_2$Cl$_2$, δ: peaks were assigned using HMBC and HSQC): 166.4 (u), 163.5 (u), 166.3 (u), 162.0 (u), 158.2 (u), 155.0 (dn), 145.8 (u), 137.8 (dn), 136.8 (dn), 136.2 (u), 135.2 (u), 133.1 (dn), 132.4 (dn), 128.6 (u), 127.1 (dn), 127.0 (dn), 126.8 (dn), 126.3 (u), 125.1 (u), 125.0 (dn), 124.6 (u), 124.2 (dn), 123.3 (u), 122.3 (dn), 121.0 (dn), 120.3 (dn), 115.6 (dn), 111.5 (dn), 75.1 (dn), 65.1 (u), 54.7 (dn), 42.7 (dn), 31.6 (u), 28.6 (u), 25.8 (u), 22.6 (u), 14.0 (dn); IR (cm$^{-1}$): 3655, 2920, 1712, 1659,
1633, 1553, 1536, 1503, 1481, 1461, 1433, 1293, 1135, 752; UV-vis (6.2×10^{-6} M in CHCl_2) \lambda_{\text{max}}: 236, 260, 316, 416; HRMS (ESI+) m/z: [M+Na], calcd for C_{74}H_{70}N_{6}NiO_{12}: 1315.4303, found: 1315.4294.
The label of $H$ is the same as the $C$ attached.
HSQC spectrum of A (400MHz, CDCl₃)

(The label of H is the same as the C attached.)
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HMBG spectrum of 4 (400MHz, CDCl3)

(The label of H is the same as the C attached.)
Variable temperature

$^1$H NMR spectrum of 4 (400MHz, CDCl$_3$)
$^1$H NMR spectrum of 5 (400MHz, CDCl$_3$)

$^{13}$C NMR APT spectrum of 5 (100MHz, CDCl$_3$)
COSY spectrum of 5 (400MHz, CDCl₃)

(The label of H is the same as the C attached.)
HSQC spectrum of 5 (400MHz, CDCl3)

(The label of H is the same as the C attached.)
HMBC spectrum of 5 (400MHz, CDCl₃)

(The label of H is the same as the C attached.)
NOESY spectrum of 5 (400MHz, CDCl$_3$)

(The label of H is the same as the C attached.)
Variable temperature

$^1$H NMR spectrum of 5 (400MHz, CDCl$_3$)

213 K
233 K
253 K
273 K
293 K
$^1$H NMR spectrum of 6 (400MHz, CD$_2$Cl$_2$)

$^{13}$C NMR APT spectrum of 6 (100MHz, CD$_2$Cl$_2$)
COSY spectrum of 6 (400MHz, CDCl₃)

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(The label of H is the same as the C attached.)
The label of H is the same as the C attached.
The label of H is the same as the C attached.
HMBC spectrum of 6 (400 MHz, CDCl₃)
Variable temperature

$^1$H NMR spectrum of 6 (400 MHz, CD$_2$Cl$_2$)

233 K

253 K

273 K

293 K