

Supporting Information

Alternating ring-opening copolymerization of styrene oxide and maleic anhydride using asymmetrical bis-Schiff-base metal(III) catalysts

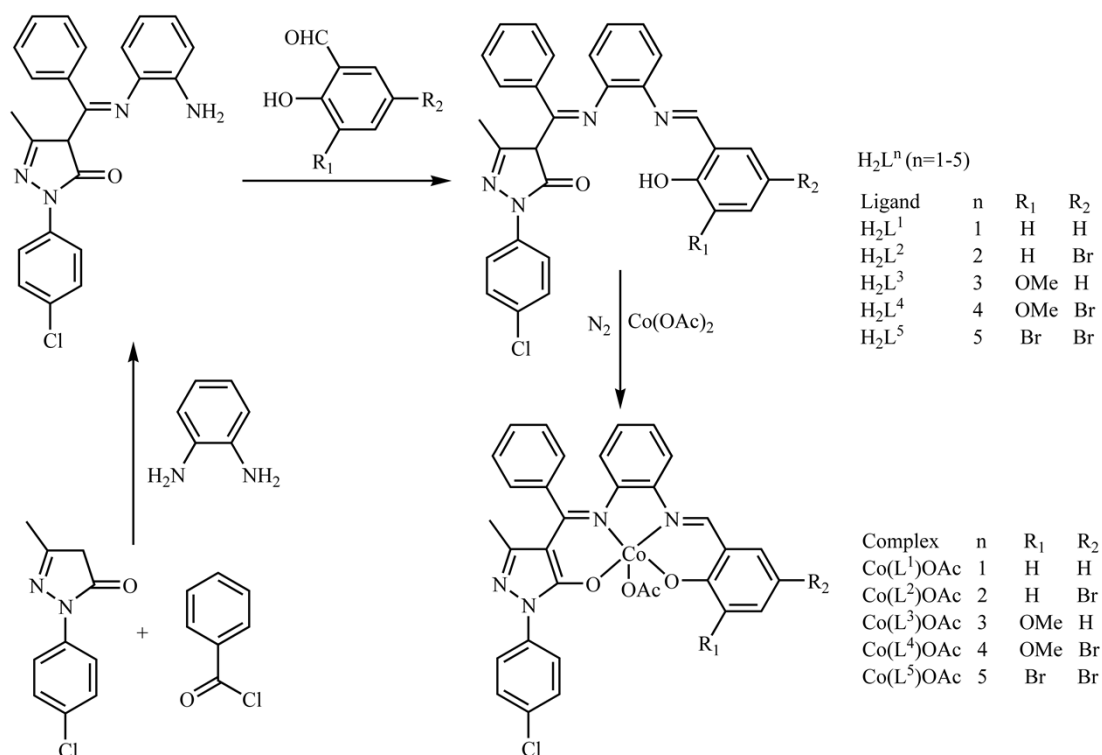
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General procedure for the preparation of the corresponding Co(III)-bis-Schiff-base complexes

$[\text{Co}(\text{L}^n)(\text{OAc})](n=1-5, \mathbf{1-5})$



Scheme S1. synthetic routes of complexes **1-5**

For $[\text{Co}(\text{L}^1)(\text{OAc})]$ (**1**): solid H_2L^1 (152.1 mg, 0.3 mmol) and anhydride $\text{Co}(\text{OAc})_2$ (74.7 mg, 0.3 mmol) were added to a flame dried Schlenk flask charged with a Teflon-coated stir bar.

Under an atmosphere of dry N_2 , absolute CH_2Cl_2 (5 ml) and EtOH (5 ml) were injected and the resultant mixture was stirred at ambient temperature for 5 h. The stopper of the flask was removed, and the resultant reddish brown solution was stirred at room temperature for 2 h while exposed to dry air. The final solution was filtered and the clear filtrate was left to stand at room temperature for several days to give the dark brown polycrystalline solid product of **1**.

Yield: 156.0 mg (84%). Anal. calcd for $\text{C}_{32}\text{H}_{24}\text{CoClN}_4\text{O}_4$: C, 61.64; H, 3.85; N, 8.99. Found:

C, 61.57; H, 3.92; N, 8.94. FT-IR (KBr, cm^{-1}): 3445 (b), 1628 (vs), 1601 (s), 1560 (s), 1524

(m), 1497 (m), 1466 (s), 1433 (m), 1389 (m), 1360 (w), 1339 (w), 1312 (w), 1271 (w), 1240 (w), 1217 (w), 1117 (m), 1092 (m), 1063 (w), 1013 (w), 928 (w), 833 (w), 750 (w), 723 (w), 619 (w), 598 (m), 538 (m), 517 (m). ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 8.32 (s, 1H, -C=N), 8.23 (s, 2H, ArH), 8.03 (d, 1H, $J = 8.0$ Hz, ArH), 7.59 (d, 3H, $J = 6.8$ Hz, ArH), 7.51 (t, 4H, $J = 8.0$ Hz, ArH), 7.36 (d, 1H, $J = 8.0$ Hz, ArH), 7.27-7.26 (m, 2H, ArH), 6.99 (t, 1H, $J = 6.0$ Hz, ArH), 6.66 (t, 1H, $J = 4.8$ Hz, ArH), 6.57 (t, 1H, $J = 3.6$ Hz, ArH), 6.37 (d, 1H, $J = 7.6$ Hz, ArH), 1.32 (s, 3H, -CH₃), 1.06 (s, 3H, -OAc). ESI-MS (in THF): m/z 623.95 [M-H]⁺.

For [Co(L²)(OAc)] (**2**): Dark brown polycrystalline product of complex **2** was prepared in the same way as complex **1** except that **H₂L²** (175.8 g, 0.3 mmol) was used instead of **H₂L¹** (152.1 mg, 0.3 mmol). Yield: 102.0 mg (48%). Anal. calcd for C₃₂H₂₃BrCoClN₄O₄: C, 54.71; H, 3.18; N, 7.98. Found: C, 54.47; H, 3.26; N, 7.89. FT-IR (KBr, cm⁻¹): 3443 (b), 1634 (vs), 1557 (s), 1499 (w), 1464 (w), 1404 (w), 1362 (w), 1339 (w), 1209 (w), 1119 (m), 1034 (w), 993 (w), 928 (w), 831 (w), 781 (w), 723 (w), 617 (w), 540 (m). ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 8.31 (s, 1H, -C=N), 8.28 (s, 2H, ArH), 8.00 (d, 1H, $J = 1.6$ Hz, ArH), 7.73 (s, 1H, ArH), 7.57-7.61 (m, 5H, ArH), 7.32-7.36 (m, 3H, ArH), 7.22 (d, 1H, $J = 8.0$ Hz, ArH), 7.01 (t, 1H, $J = 1.6$ Hz, ArH), 6.70 (t, 1H, $J = 2.0$ Hz, ArH), 6.39 (d, 1H, $J = 1.2$ Hz, ArH), 1.29 (s, 3H, -CH₃), 1.06 (s, 3H, -OAc). ESI-MS (in THF): m/z 702.84 [M-H]⁺.

For [Co(L³)(OAc)] (**3**): Dark brown polycrystalline product of complex **3** was prepared in the same way as complex **1** except that **H₂L³** (161.1 mg, 0.3 mmol) was used instead of **H₂L¹** (152.1 mg, 0.3 mmol). Yield: 145.0 mg (74%). Anal. calcd for C₃₃H₂₆CoClN₄O₅: C, 60.65; H, 3.98; N, 8.58. Found: C, 60.60; H, 4.07; N, 8.51. FT-IR (KBr, cm⁻¹): 3453 (b), 1630 (vs), 1560 (s), 1526 (m), 1506 (w), 1472 (s), 1435 (s), 1402 (m), 1387 (m), 1360 (m), 1312

(m), 1240 (m), 1219 (m), 1182 (m), 1107 (m), 1086 (m), 1011 (w), 984 (w), 922 (w), 843 (w), 781 (w), 758 (m), 723 (m), 700 (w), 600 (m), 546 (m), 511 (w), 492 (w). ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 8.41 (s, 1H, -C=N), 8.40 (s, 1H, ArH), 8.23 (s, 1H, ArH), 8.03 (d, 1H, J = 8.0 Hz, ArH), 7.56 (t, 5H, J = 10.0 Hz, ArH), 7.45 (s, 1H, ArH), 7.36 (d, 1H, J = 1.6 Hz, ArH), 7.17 (d, 1H, J = 7.2 Hz, ArH), 6.98 (s, 1H, ArH), 6.87 (t, 1H, J = 4.0 Hz, ArH), 6.66 (t, 1H, J = 8.0 Hz, ArH), 6.49 (t, 1H, J = 7.2 Hz, ArH), 6.35 (d, 1H, J = 7.2 Hz, ArH), 3.94 (s, 3H, -OCH₃), 1.28 (s, 3H, -CH₃), 1.06 (s, 3H, -OAc). ESI-MS (in THF): m/z 654.01 [M-H]⁺.

For [Co(L⁴)(OAc)] (**4**): Dark brown polycrystalline product of complex **4** was prepared in the same way as complex **1** except that **H₂L⁴** (184.8 mg, 0.3 mmol) was used instead of **H₂L¹** (152.1 mg, 0.3 mmol). Yield: 123.0 mg (56%). Anal. calcd for C₃₃H₂₅BrCoClN₄O₅: C, 54.11; H, 3.42; N, 7.65. Found: C, 54.04; H, 3.51; N, 7.58. FT-IR (KBr, cm⁻¹): 3441 (b), 2974 (m), 2932 (m), 1626 (vs), 1608 (s), 1585 (m), 1568 (s), 1533 (m), 1530 (m), 1499 (m), 1468 (s), 1437 (s), 1385 (m), 1354 (m), 1327 (m), 1312 (m), 1238 (m), 1217 (m), 1178 (m), 1121 (w), 1090 (m), 1063 (m), 1015 (m), 984 (m), 937 (w), 891 (w), 858 (w), 831 (w), 800 (w), 762 (w), 748 (m), 727 (m), 687 (w), 602 (m), 573 (w), 550 (m), 517 (m), 494 (w), 451 (w). ^1H NMR (400 MHz, DMSO- d_6 , ppm): δ 8.39 (s, 1H, -C=N), 8.37 (s, 1H, ArH), 8.25 (s, 1H, ArH), 7.99 (d, 1H, J = 8.0 Hz, ArH), 7.56 (t, 5H, J = 12.8 Hz, ArH), 7.47-7.43 (m, 1H, ArH), 7.34 (t, 2H, J = 12.0 Hz, ArH), 7.00 (t, 1H, J = 6.8 Hz, ArH), 6.93 (s, 1H, ArH), 6.67 (t, 1H, J = 8.0 Hz, ArH), 6.35 (d, 1H, J = 8.0 Hz, ArH), 3.93 (s, 3H, -OCH₃), 1.28 (s, 3H, -CH₃), 1.07 (s, 3H, -OAc). ESI-MS (in THF): m/z 732.9 [M-H]⁺.

For [Co(L⁵)(OAc)] (**5**): Dark brown polycrystalline product of complex **5** was prepared in the same way as complex **1** except that **H₂L⁵** (199.4 mg, 0.3 mmol) was used instead of

H₂L¹ (152.1 mg, 0.3 mmol) . Yield: 96.0 mg (41%). Anal. calcd for C₃₂H₂₂Br₂CoClN₄O₄: C, 49.18; H, 2.82; N, 7.17. Found: C, 49.12; H, 2.93; N, 7.15. FT-IR (KBr, cm⁻¹): 3449 (b), 1634 (vs), 1603 (s), 1588 (s), 1570 (s), 1530 (m), 1497 (m), 1468 (s), 1435 (m), 1391 (m), 1362 (m), 1313 (w), 1215 (w), 1155 (m), 1092 (m), 1065 (w), 1032 (w), 1013 (w), 989 (w), 924 (w), 858 (w), 843 (w), 795 (w), 746 (w), 716 (w), 602 (m), 573 (w), 552 (m), 519 (m), 494 (w). ¹H NMR (400 MHz, DMSO-*d*₆, ppm): δ 8.58 (s, 1H, -C=N), 8.53 (s, 1H, ArH), 8.08 (d, 1H, *J* = 0.8 Hz, ArH), 8.04 (d, 1H, *J* = 1.2 Hz, ArH), 7.87 (s, 2H, ArH), 7.64 (s, 3H, ArH), 7.57 (d, 2H, *J* = 8.0 Hz, ArH), 7.43 (d, 1H, *J* = 5.6 Hz, ArH), 7.23 (t, 1H, *J* = 7.2 Hz, ArH), 7.06 (t, 1H, *J* = 0.8 Hz, ArH), 6.76 (t, 1H, *J* = 8.0 Hz, ArH), 6.50 (d, 1H, *J* = 8.4 Hz, ArH), 1.32 (s, 3H, -CH₃), 1.06 (s, 3H, -OAc). ESI-MS (in THF): *m/z* 781.74 [M-H]⁺.

$^1\text{H NMR}$ (400 MHz, CDCl_3): 7.72-7.35 (m, 5H, -Ph-), 6.33-6.16 (m, 3H, -Ch-, -CH-), 4.50-4.37 (m, 2H, $-\text{CH}_2-$), 3.49 (s, relative to ether content).

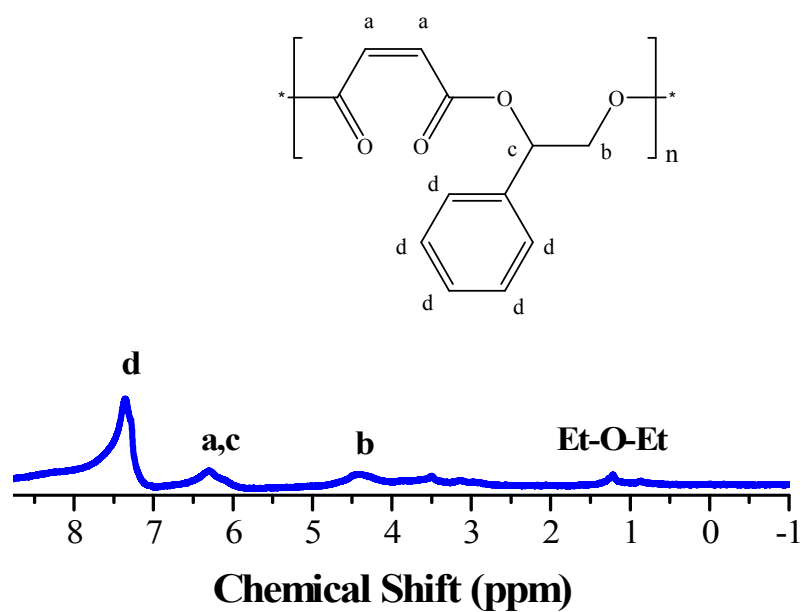


Figure S1. Representative $^1\text{H NMR}$ Spectrum of SO-MA copolymer, Table 3, entry 5.

Copolymer (SO-MA): FT-IR (KBr, cm^{-1}): 3062 (w), 2955 (w), 1735 (vs), 1649 (m), 1573 (w), 1505 (w), 1450 (w), 1400 (m), 1353 (w), 1209 (s), 1158 (s), 1080 (w), 1020 (m), 1000 (m), 867 (w), 815 (w), 758 (m), 701 (m), 639 (w), 520 (w).

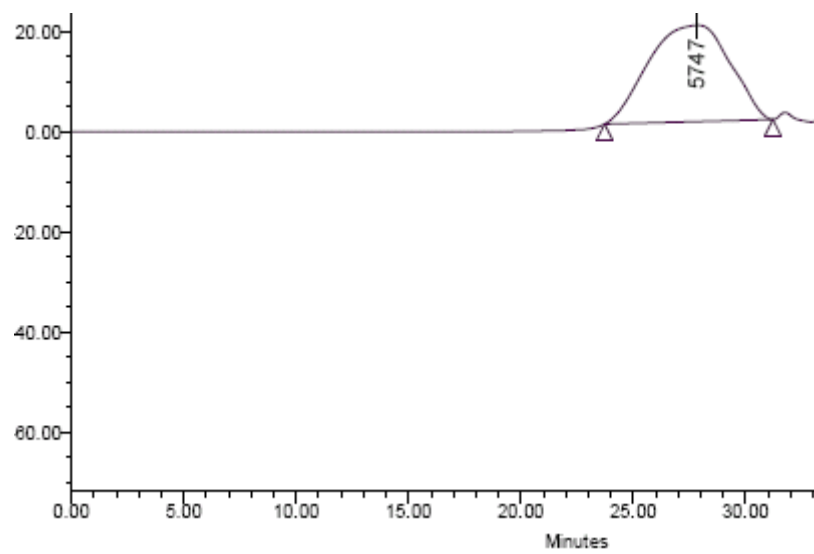


Figure S2. Representative GPC graph of alternating copolymers from SO and MA, Table 4, entry 1.