Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Manganese(II) Schiff-base-mediated reversible deactivation controlled radical polymerization of vinyl acetate

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Experimental

*General Procedure for the Preparation of Schiff-Base Ligands (**1a** = cyclopentyl, **1b** = cyclohexyl and **1a** = cycloheptyl)*

To prepare the Schiff-base ligands **1a-1c**, a solution of salicylaldehyde (4 mmol; 0.49 g) in methanol (20 mL) was slowly added over a solution of the appropriate amine (4 mmol; 0.34, 0.39 and 0.45 g for cyclopentylamine, cyclohexylamine and cycloheptylamine, respectively) in the same solvent (20 mL). The mixture was stirred at room temperature for 16 h and the product was obtained as a yellowish orange oil.

Ligand (*E*)-2-((cyclopentylimino)methyl)phenol: Yield: 88%; Refractive index 1.5626; (a) UV–Vis: $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M^{-1} cm^{-1}]: $\lambda_{max(1)}$ (317), $\varepsilon_{max(1)}$ [5320]; (b) IR (KBr, cm^{-1}): νC=N (1626), νC–O (1277); (c) ^{1}H NMR: ($CDCl_3$, 400 MHz): 13.68 (s, 1H, OH), 8.34 (s, 1H, CH=N), 7.28 (ddd, $^{3}J_{b,a} = {}^{3}J_{b,c}$ = 7.5 Hz, $^{4}J_{b,d}$ = 1.9 Hz, 1H, salicyl-ring), 7.23 (dd, $^{3}J_{d,c}$ = 7.5 Hz, $^{4}J_{d,b}$ = 1.9 Hz, 1H, salicyl-ring), 6.94 (dd, $^{3}J_{a,b}$ = 7.5 Hz, $^{4}J_{a,c}$ = 1.1 Hz, 1H, salicyl-ring), 6.86 (ddd, $^{3}J_{c,d} = {}^{3}J_{c,b}$ = 7.5 Hz, $^{4}J_{c,a}$ = 1.1 Hz, 1H, salicyl-ring), 3.75-3.82 (m, 1H, CH^{Pentyl}), 1.95-1.81 (m, 4H, CH_2^{Pentyl}), 1.65-1.76 (m, 4H, CH_2^{Pentyl}). ^{13}C NMR ($CDCl_3$) δ 162.3, 161.3, 131.8, 130.9, 118.4, 116.9, 70, 34.7, 24.5.

Ligand (E)-2-((cyclohexylimino)methyl)phenol: Yield: 94%; Refractive index 1.5678; (a) UV–Vis: $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M^{-1} cm^{-1}]: $\lambda_{max(1)}$ (316,8), $\varepsilon_{max(1)}$ [7770]; (b) IR (KBr, cm^{-1}): νC=N (1629), νC–O (1274), (c) ^{1}H NMR ($CDCl_3$, 400 MHz): 13.82 (s, 1H, OH), 8.36 (s, 1H, CH=N), 7.28 (ddd, $^{3}J_{b,c}$ = 7.5 Hz, $^{3}J_{b,a}$ = 7.2 Hz, $^{4}J_{b,d}$ = 1.9 Hz, 1H, salicyl-ring), 7.23 (dd, $^{3}J_{d,c}$ = 7.5 Hz, $^{4}J_{d,b}$ = 1.9 Hz, 1H, salicyl-ring), 6.94 (dd, $^{3}J_{a,b}$ = 7.2 Hz, $^{4}J_{a,c}$ = 1.1 Hz, 1H, salicyl-ring), 6.86 (ddd, $^{3}J_{c,b} = {}^{3}J_{c,d}$ = 7.5 Hz, $^{4}J_{c,a}$ = 1.1 Hz, 1H, salicyl-ring), 3.20-3.27 (m, 1H, CH^{Hexyl}), 1.78-1.86 (m, 4H, CH_2^{Hexyl}), 1.50-1.68 (m, 3H, CH_2^{Hexyl}), 1.43-1.25 (m, 3H, CH_2^{Hexyl}). ^{13}C NMR ($CDCl_3$) δ 162.1, 161.4, 131.9, 131.1, 118.9, 118.3, 117.04, 77.3, 77.02, 76.7, 67.4, 25.5, 24.3.

Ligand (E)-2-((cycloheptylimino)methyl)phenol: Yield: 91%; Refractive index 1.5652; (a) UV–Vis: $\lambda_{max(n)}$ (nm), $\varepsilon_{max(n)}$ [M^{-1} cm^{-1}]: $\lambda_{max(1)}$ (316.2), $\varepsilon_{max(1)}$ [10000]; (b) IR (KBr, cm^{-1}): νC=N (1630), νC–O (1270); (c) ^{1}H NMR ($CDCl_3$, 400 MHz): 13.82 (s, 1H, OH), 8.36 (s, 1H, CH=N), 7.28 (ddd, $^{3}J_{b,c}$ = 7.5 Hz, $^{3}J_{b,a}$ = 7.2 Hz, $^{4}J_{b,d}$ = 1.9 Hz, 1H,

salicyl-ring), 7.23 (dd, $^{3}J_{d,c}$ = 7.5 Hz, $^{4}J_{d,b}$ = 1.9 Hz, 1H, salicyl-ring), 6.94 (dd, $^{3}J_{a,b}$ = 7.5 Hz, $^{4}J_{a,c}$ = 1.1 Hz, 1H, salicyl-ring), 6.86 (ddd, $^{3}J_{c,b}$ = $^{3}J_{c,d}$ = 7.5 Hz, $^{4}J_{c,a}$ = 1.1 Hz, 1H, salicyl-ring), 3.37-3.46 (m, 1H, CH^{Heptyl}), 1.74-1.85 (m, 4H, CH_2^{Heptyl}), 1.50-1.68 (m, 8H, CH_2^{Heptyl}). ^{13}C NMR ($CDCl_3$) δ 161.66, 161.39, 131.92, 131.02, 118.91, 118.29, 116.99, 77.34, 77.08, 76.83, 70.12, 36.40, 28.54, 24.24.

Characterization

The bidentate Schiff-bases were prepared from condensation of salicylaldehyde with three different cycloalkylamines in methanol. The ^{1}H NMR spectrum showed two important observations: the completion of the condensation observed by the appearance of a singlet peak at 8.3 ppm belonging to the imine proton (HC=N) and the complete loss of the peak around 5 ppm corresponding to the amine protons. The other peaks observed in the ^{1}H NMR spectrum are as follows: the singlet in the down-filled, at 13.8 ppm, observed in the spectra of **1a-1c,** is assignable to the hydrogen of the OH. Also, for all ligands, the peak group assigned to the CH from salicylaldehyde is in the range of δ 6.8–7.3 ppm. In the higher field, the peaks relative to parts of the ligands of the *N*-cycloalkyl group are observed from 3.2 to 3.8 ppm for CH-N and from 1.4 to 1.9 ppm for CH_2.

Figure S1 Absorption spectra of the manganese(II) complexes in degassed CH_2Cl_2 solution at room temperature ([complex] = 0.2 mM).

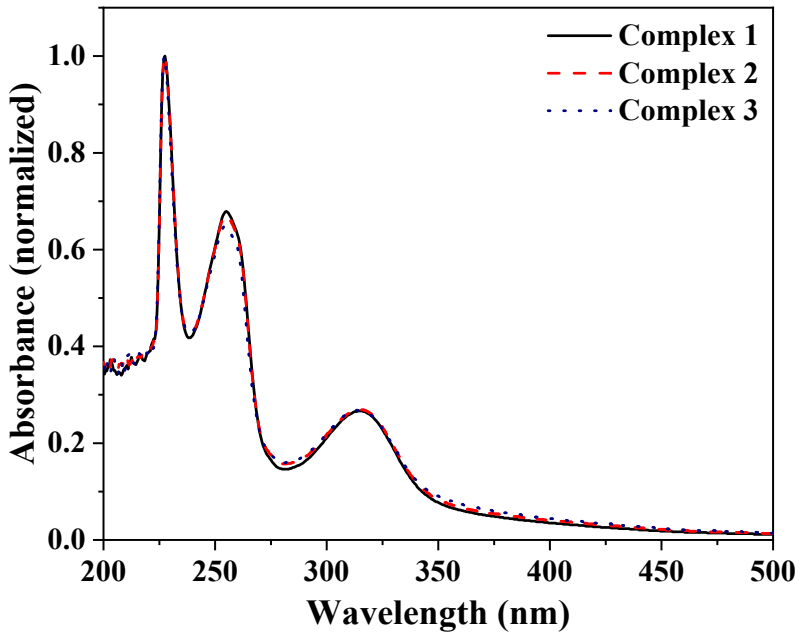

Table S1 Cyclic voltammetry results for complexes **1-3**

Complex	Scan rate (mV s^{-1})	E_{pa} (V)	E_{pc} (V)	ΔE_p[a] (V)	I_{pa}/I_{pc}
1	100	-0.326	-0.741	0.415	1.481
	200	-0.200	-0.755	0.555	1.818
	300	-0.108	-0.762	0.654	1.843
2	100	-0.226	-0.762	0.536	1.430
	200	-0.123	-0.805	0.682	1.861
	300	-0.083	-0.868	0.785	1.957

[a] $\Delta E_p = E_{pa} - E_{pc}$.

Figure S2 GPC traces as a function of time for OMRP of VAc mediated by complexes **1-3**; [VAc]/[AIBN]/[Mn] = 542/3.25/1 with complex in bulk at 55 ºC.