Electronic Supplementary Material (ESI) for New Journal of Chemistry

Supporting Information

Formation of Chiral Heterometallic Oligomers by Combination of Inert Ru(III) Tectons and Labile Ni(II) Connectors

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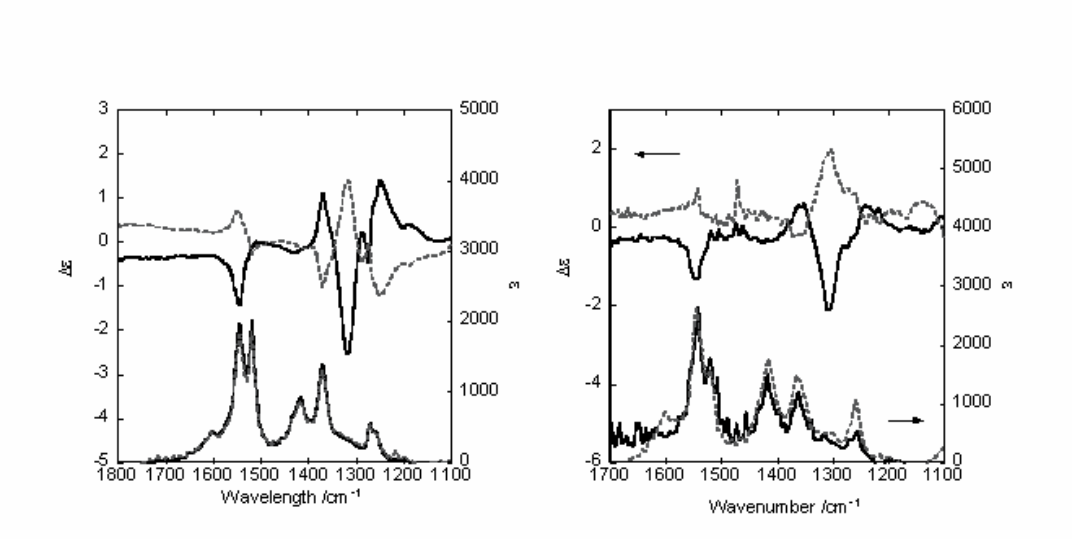


Figure S1. The vibrational circular dichroism spectra of chiral one-handed tecton, [Ru(III)(acac)$_2$(taetH)] (left), and chiral two-handed tecton, [Ru(III)(acac)(taetH)$_2$] (right). The solvent was $CDCl_3$. Dotted and solid curves denote the spectra of Λ- and Δ-enantiomers, respectively.

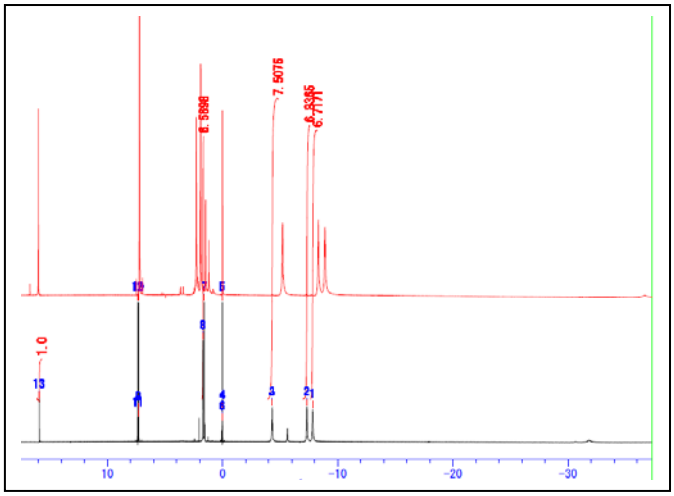


Figure S2. The ^{1}HNMR spectra of one-handed tecton (lower) and two-handed tecton (upper): one-handed tecton: [Ru(III)(acac)$_2$(taetH)], ($CDCl_3$) δ=-31.44 (2H, CH), -7.64(6H, CH_3), -7.24(6H, CH_3), -4.27(6H, CH_3), 1.73(6H, CH_3),15.90(H, OH); two-handed tecton, [Ru(III)(acac)(taetH)$_2$], ($CDCl_3$) δ=-36.74 (H, CH), -8.88 (6H, CH_3), -8.27 (6H, CH_3), 5.16 (6H, CH_3), 1.96 (6H, CH_3), 2.34 (6H, CH_3), 16.06 (2H, OH).

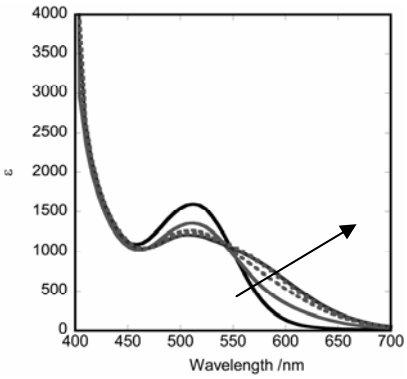


Figure S3. The UV-vis spectrum of a methanol solution of racemic [Ru(III)(acac)$_2$(taetH)], when the various amounts of $Ni(ClO_4)_2$ were added in the presence of ten times excess of tmen.

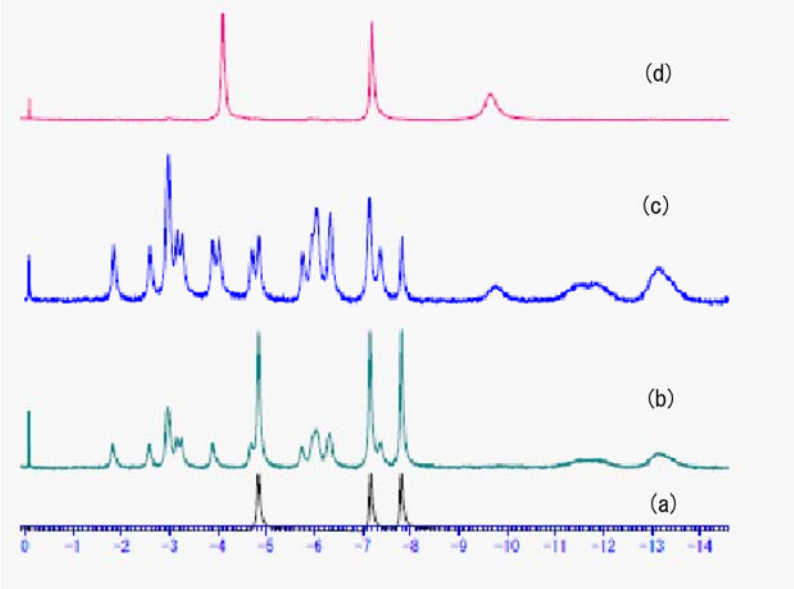


Figure S4. The ^{1}HNMR spectra of a 4:1 (v/v) $CDCl_3/CD_3OD$ solution containing one-handed tecton at a various amount of Ni(II) ion and the excess amount of tmen. The ratio of Ni/Ru was (a) 0, (b) 0.2, (c) 0.5 and (d) 1.2, respectively. The spectra contains the chemical shift region corresponding to the methyl protons of the Ru(III) complex and the methyl and methylene protons in the coordinated tmen.

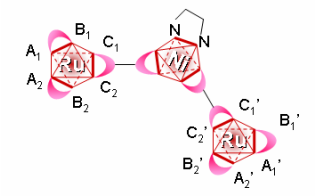
Table S1. Interpretation of the splitting of ^{1}HNMR peaks due to the CH_3 protons in a trinuclear Ru-Ni-Ru complex, [{Ru(III)(acac)$_2$(taet)}$_2$Ni(II)(tmen)].

Racemic case

diastereomers	Relative abundance of diastereomeric species (no stereoselectivity assumed)	Number of split peaks × number of methyl protons	Classification of methyl protons in a trimer as shown in the figure below
Δ–Λ–Δ	1	4×4	$A_1=A_1'$, $A_2=A_2'$,$B_1=B_1'$, $B_2=B_2'$
Λ–Δ–Λ	1		
Δ–Δ–Δ	1	4×4	$A_1^2=A_1'^2$, $A_2^2=A_2'^2$, $B_1^2=B_1'^2$, $B_2^2=B_2'^2$
Λ–Λ–Λ	1		
Δ–Δ–Λ	2	8×4	A_1^3 ,$A_1'^3$, A_2^3 ,$A_2'^3$, B_1^2, $B_1'^2$, B_2^2, $B_2'^2$
Λ–Λ–Δ	2		
Sum		16×4	

Enantiomeric case (Δ-case)

diastereomers	Relative abundance of diastereomeric species (no stereoselectivity assumed)	Number of split peaks × number of methyl protons	Classification of methyl protons in a trimer as shown in the figure below
Δ–Λ–Δ	1	4×2	$A_1=A_1'$, $A_2=A_2'$,$B_1=B_1'$, $B_2=B_2'$
Δ–Δ–Δ	1	4×2	$A_1=A_1'$, $A_2=A_2'$,$B_1=B_1'$, $B_2=B_2'$
Sum		8×2	



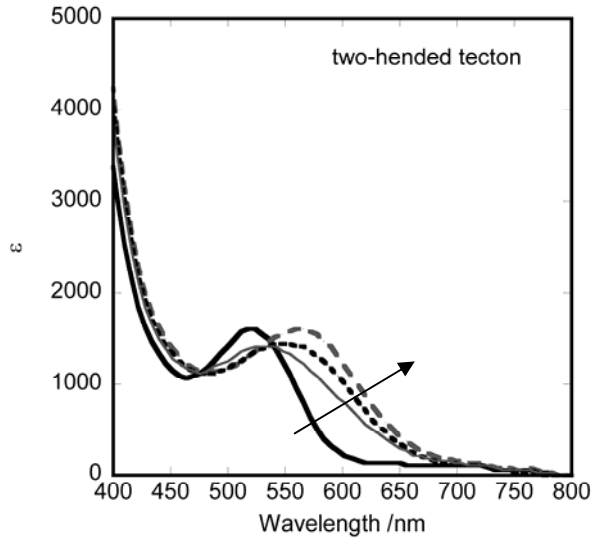


Figure S5. The UV-vis spectra of a methanol/chloroform solution of racemic two-handed tecton, [Ru(III)(acac)(taetH)$_2$], when the various amounts of Ni(ClO_4)$_2$ were added in the presence of ten times excess of tmen.

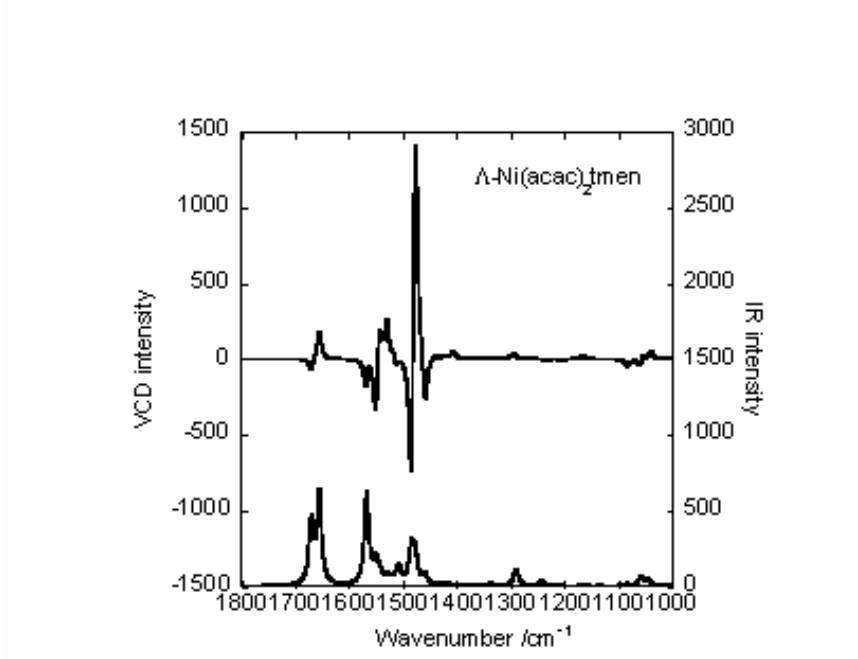


Figure S6. The calculated VCD and IR spectra of Λ-[Ni(acac)$_2$(tmen)]. The details in calculation are described in the text.