Supporting Information.

EXPERIMENTAL

General Information

All experiments, compound manipulations and spectroscopic measurements were performed under an inert atmosphere using nitrogen filled glove-boxes and standard Schlenk line techniques. Solvents were distilled over the appropriate drying agent and stored over molecular sieves. Due to its instability, $[W_2(TiPB)_2(Azu\text{-}2)]^-[CoCp_2]^+$ was synthesised *in situ* by reaction of $W_2(TiPB)_2(Azu\text{-}2)$ with 1 equivalent of $CoCp^*_2$ in THF prior to spectroscopic measurements.

Electronic absorption spectra were recorded on a PerkinElmer Lambda 900 UV/vis/NIR spectrometer, with nitrogen purging. IR quartz cells with 1.00 mm path lengths were employed with sample concentrations of $\sim 10^{-4}$ M. ^{1}H NMR spectra were recorded on a 400 MHz Bruker DPX Avance spectrometer and referenced to residual protio signals of d_8-THF at δ 3.58 and 1.73 ppm. Electrochemical measurements were performed using a Princeton Applied Research (PAR) 173A potentiostat-galvanostat equipped with a PAR 176 current-to-voltage converter using 0.1 M solutions of $^nBu_4NPF_6$ in THF. The voltammetric cell was equipped with a platinum working electrode, a platinum wire auxiliary electrode, and a pseudo-reference electrode consisting of a silver wire in 0.1 M $^nBu_4NPF_6$/THF separated from the bulk solution by a Vycor tip. The potentials are referenced internally to the $FeCp_2^{0/+}$ couple by addition of a small amount of $FeCp_2$ to the solutions. Microanalysis was performed by H. Kolbe Microanalytical Laboratory. X-band EPR spectra were recorded using a Bruker ESP300 Electron Spin Resonance spectrometer. Temperature regulation was achieved by employing a Bruker Variable Temperature unit. Matrix-assisted laser desorption ionization (MALDI) mass spectrum was recorded using a Bruker Reflex III MALDI-TOF mass spectrometer. Dithrinol was used as the matrix, to aid the flight of the molecule.

$W_2(O_2C\text{-}C_6H_2\text{-}2,4,6\text{-}\{^iPr\}_3)_2(2\text{-}O_2C\text{-}6\text{-}EtO_2C\text{-}C_{10}H_6)_2$ $[W_2(TiPB)_2(Azu\text{-}2)_2]$

A solution of $W_2(TiPB)_4$ (0.123 g, 0.09 mmol) and azulene-6-carboethoxy-2-carboxylic acid (0.044 g, 0.18 mmol) was stirred in toluene (10 mL) for 3 days, during which time the product precipitates as a green solid. The precipitate was isolated by centrifugation, and washed with one aliquot (5 mL) of toluene and one aliquot (5 mL) of hexane before drying *in vacuo*. Yield: 0.088 g (72 %). Crystals suitable for X-ray diffraction were grown by carefully layering a THF solution of $W_2(TiPB)_2(Azu\text{-}2)_2$ with hexanes, and allowing the solvents to diffuse slowly at -15°C. NMR (THF-d_8) : ^{1}H (400 MHz) 0.9 (d, 24H), 1.2 (d, 6H), 1.4 (t, 6H), 2.8 (m, 4H), 3.5 (m, 2H), 4.4 (q, 4H), 6.9 (s, 4H), 7.8 (s, 4H), 7.9 (d, 4H), 8.1 (d, 4H). Microanalysis found: C 53.10; H 5.22%, requires: C 53.35; H 5.22%. MALDI-MS 1350.0 (100%, M^+).

Electronic Structure Calculations.

The geometries of the model compounds *trans*-$W_2(O_2CH)_2(2\text{-}O_2C\text{-}6\text{-}MeO_2C\text{-}C_{10}H_6)_2$, $W_2(O_2CH)_2(Azu\text{-}2')_2$, *trans*-$W_2(O_2CH)_2(6\text{-}O_2C\text{-}2\text{-}MeO_2C\text{-}C_{10}H_6)_2$, $W_2(O_2CH)_2(Azu\text{-}6')_2$, were optimized in the gas-phase using density functional theory with the aid of the Gaussian03 suite of programs. The B3LYP functional was used along with the SDD energy consistent pseudopotentials for molybdenum and tungsten and the 6-31G* basis set for all remaining atoms. Optimizations were performed in C_{2v} symmetry and confirmed to be minima on the potential energy surface using harmonic vibrational frequency analysis.

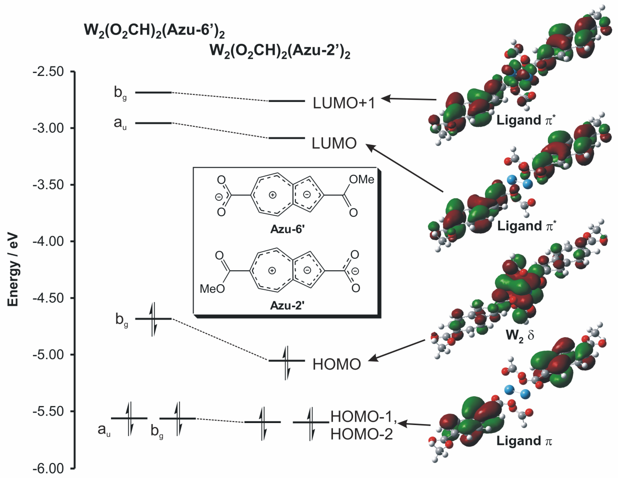

Fig. S1.