Electronic Supplementary Information for Dalton Transactions

Supporting Information

Heterogeneous Fullerene-Supported Osmium Tetroxide Catalyst for the *cis*-Dihydroxylation of Olefins

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Materials and Methods.

Fullerene-C_{60} (99.5%), cyclohexene (99%), 1-hexene (≥99.8%), styrene (99.9%), α-methylstyrene (99%); and GC standards: *cis*-1, 2-cyclohexanediol (99%), 1,2-hexanediol (98%), 1-phenyl-1, 2-ethanediol (97%), 2-phenyl-1,2-propanediol (97%), and dodecane (≥99.8%) were purchased from Sigma-Aldrich and used without further purification. Osmium tetroxide (Pressure Chemical Co. (Pittsburgh, PA)), multi-walled carbon nanotubes (<95%; Cheaptubes.com (Brattleboro, VT)), and pyridine (≥99%; Alfa Aesar), were also used as received. Single-walled carbon nanotubes (HiPCO) were donated by Dr. Mark Thompson (University of Southern California) and purified via a standard acid purification and annealing procedure.[1]

EDX data were collected using a JEOL JSM-6610 scanning electron microscope operating at 20 kV and equipped with an EDAX Apollo silicon drift detector. XPS spectra were measured on a M-Probe Surface Spectrometer by Surface Science (ESCA2703, Al monochromator with charging compensation). FT-IR (KBr) spectra were collected on a Perkin Elmer Spectrum 2000 FT-IR spectrometer. GC data were collected using a 7890A GC System (Agilent Technologies) outfitted with an HP-5 column (J&W Scientific). Dodecane was used as an internal standard and all samples were run in dichloromethane (40 °C for 2 min then ramp to 200 °C at 40 °C/min, hold 2 min). BET surface area was measured with a NOVA2200e Surface Area and Pore Size Analyzer (Quantachrome Instruments). UV-vis spectra were collected with a Shimadzhu UV spectrophotometer (UV-1800).

Osmylation of C_{60}.

(**WARNING**: Osmium tetroxide is extremely toxic and should only be handled in the fume hood using appropriate safety precautions). The 1:2 adduct, $C_{60}(OsO_4)_2 \cdot 4$pyridine, was prepared according to a literature procedure.[2] Briefly, C_{60} (100 mg, 0.14 mmol) was dissolved in toluene (60 mL) by brief sonication and vigorous stirring to give a bright purple solution. A solution of OsO_4 (71 mg, 0.28 mmol) and pyridine (55 μL, 0.70 mmol) in approximately 5 mL of toluene was then added drop-wise to the C_{60} solution, which immediately turned brick-red and opaque. The reaction suspension was stirred at 25 °C for 24 h and the resulting solid was separated by centrifugation and washed several times with toluene.

IR (KBr): cm^{-1} 1608 (m), 1481 (w), 1450 (s), 1213 (w), 1069 (w), 971 (m), 876 (w), 836 (s), 762 (m), 691 (m), 618 (m), 526 (w).

Osmylation of Single- and Multi-walled Carbon Nanotubes.

Both single and multi-walled carbon nanotubes were osmylated according to a literature procedure[3] with slight modifications made. First, pyridine (2.2 mmol per mmol of Os used) was added to the reaction mixture in a 250 mL quartz flask prior to irradiation in the photoreactor (λ = 254 nm, Luzchem Model: LZC-ICH2). Secondly, a range of wt% loadings of Os was evaluated (5-1000 wt%) giving an expected linear increase in the amount of Os detected by XPS in the osmylated tubes.

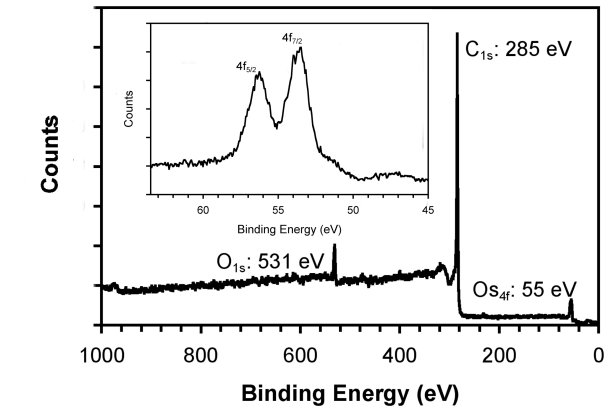

Fig. S1 XPS spectrum of CNT-Os(VI) pre-catalyst; Inset: hi-res scan of Os_{4f} doublet.

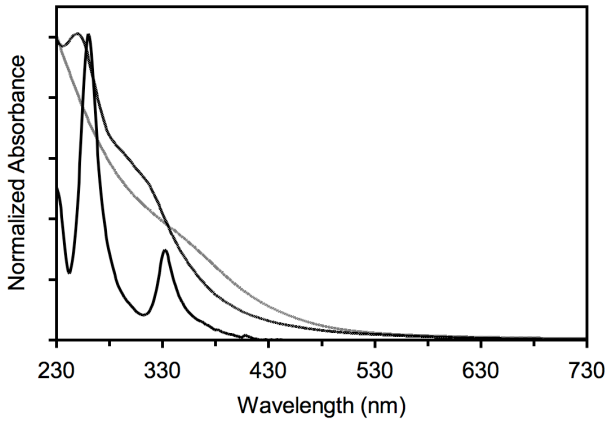

Fig. S2 UV-vis spectra of C_{60} (black) and $C_{60}(OsO_4)_2$·4pyridine pre-catalyst (dark gray), both in DCM. After several catalytic runs, the spectrum of the recovered catalyst (light gray) was taken in DI water due to solubility issues.

(1) J. L. Bahr and J. M. Tour, *Chem. Mater.*, 2001, **13**, 3823.
(2) J. M. Hawkins, A. Meyer, T. A. Lewis, S. Loren and F. J. Hollander, *Science,* 1991, **252**, 312.
(3) S. Banerjee and S. S. Wong, *J. Am. Chem. Soc.*, 2004, **126**, 2073.