REVISED

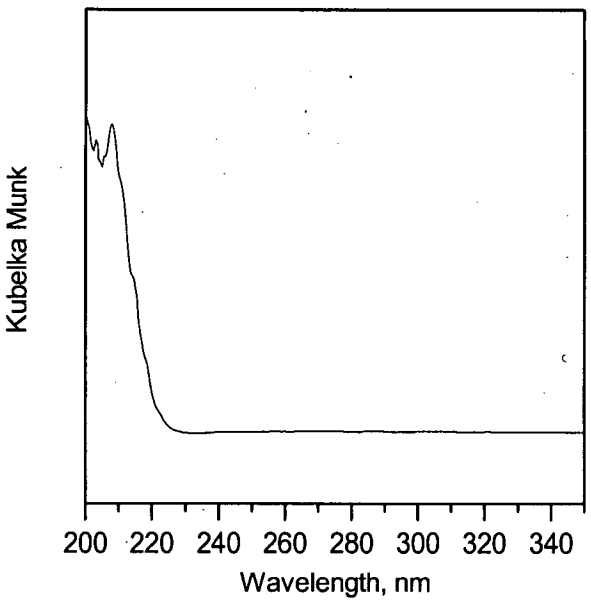
Supporting Information

Photochemical CO_2 Splitting by Metal-to-Metal Charge-Transfer Excitation in Mesoporous ZrCu(I)-MCM-41 Silicate Sieve

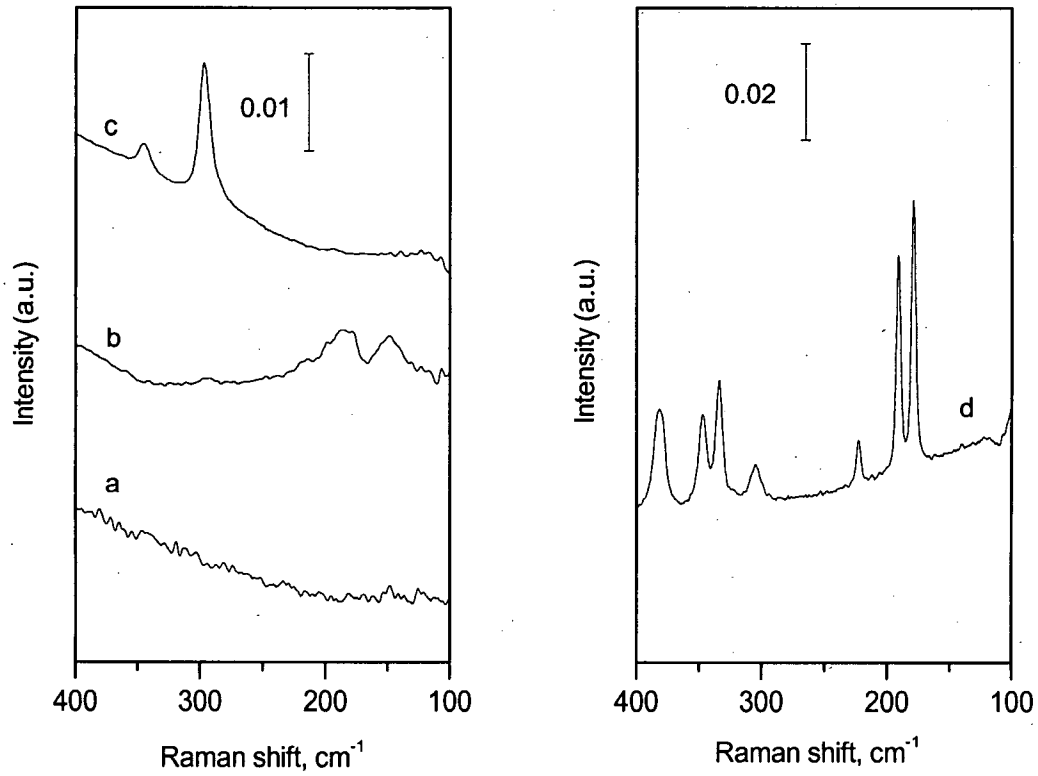
Wenyong Lin and Heinz Frei*

Physical Biosciences Division, Mailstop Calvin Laboratory, Lawrence Berkeley National Laboratory, University of California, Berkeley, CA 94720

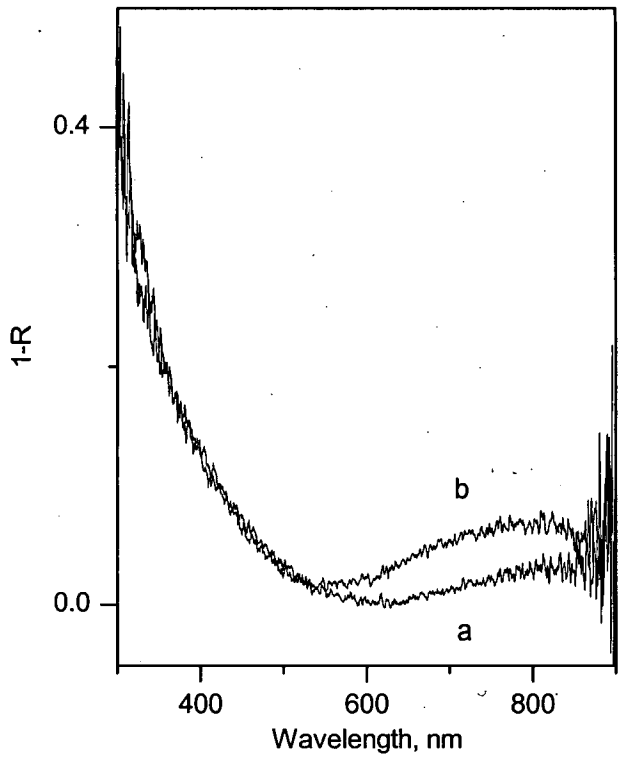
HMFrei@lbl.gov



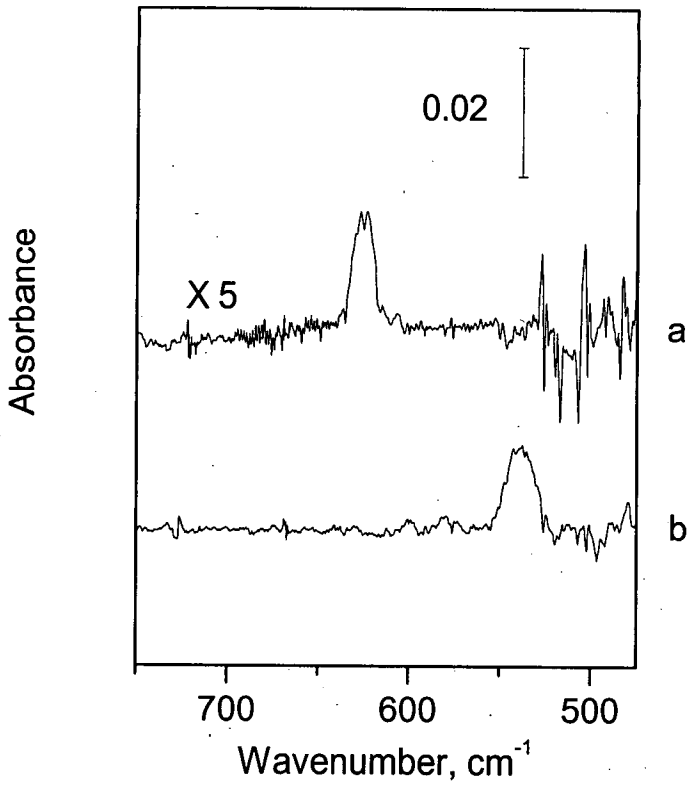
Supplement Fig S1: UV-Vis DRS of Zr(IV)-MCM-41. Absorption at 208 nm is consistent with isolated Zr(IV) tetrahetrally coordinated by oxygen, as can be found in the literature: Morey, M.S.; Stucky, G.D.; Schwarz, S.; Froba, M. *J. Phys. Chem. B* **1999**, *103*, 2037.



Supplement Fig S2: FT-Raman spectra of (a) ZrCu(I)-MCM-41, (b) Cu_2O (2%wt) mechanically mixed with MCM-41, (c) CuO (2%wt) mechanically mixed with MCM-41 and (d) ZrO_2 (2%wt) mechanically mixed with MCM-41. None of the intrinsically intense Raman modes associated with the monometallic oxide moieties are detected in ZrCu(I)-MCM-41. Measurements were conducted on a Bruker model FRA-106/S spectrometer equipped with a Nd:YAG laser source and a LN_2 cooled detector. Data were collected at 2 cm^{-1} resolution.



Supplement Fig S3: UV-vis DRS of Cu(I)-MCM-41 before (a) and after (b) exposure to 1 atm of O_2 for 8 h. By contrast to ZrCu(I)-MCM-41, growth of the Cu(II) d-d transition is not accompanied by absorption decrease in the 300-500 nm region. This supports the assignment of the MMCT transition in ZrCu(I)-MCM-41.



Supplement Fig S4: FT-IR spectra of (a) Cu(I)-ZrO_2 and (b) Cu(II)-ZrO_2. Peaks at 630 cm^{-1} (a) and 540 cm^{-1} (b) are used to confirm the assignment of Cu(I)-OZr and Cu(II)-OZr modes. Cu(I)-ZrO_2 was synthesized by mixing dehydrated ZrO_2 (0.2 g, Aldrich, nanopowder) with 0.3 wt% solution of $Cu(I)(NCCH_3)_4PF_6$ in dichloromethane (100 mL). After stirring under N_2 at RT for 30 min, the solid was collected by filtration, washed with dichloromethane and dried under N_2. In the synthesis of Cu(II)-ZrO_2, dehydrated ZrO_2 (0.2 g) was stirred for 30 min with 0.3 wt% solution of $CuCl_2$ in acetonitrile-dichloromethane = 1:1 mixture (100mL). The solid was collected by filtration, washed with dichloromethane and dried under N_2. The experiments were conducted in a glove box under flow of N_2.