Dalton Transactions

ROYAL SOCIETY OF CHEMISTRY

PAPER

Cite this: *Dalton Trans.*, 2020, **49**, 17243

Dinuclear uranium(VI) salen coordination compound: an efficient visible-light-active catalyst for selective reduction of CO_2 to methanol†

Mohammad Azam, *[a] Umesh Kumar, *[b] Joshua O. Olowoyo,[b] Saud I. Al-Resayes,[a] Agata Trzesowska-Kruszynska,[c] Rafal Kruszynski,[c] Mohammad Shahidul Islam,[a] Mohammad Rizwan Khan,[a] S. F. Adil,[a] Mohammad Rafique Siddiqui,[a] Fahad Ahmed Al-Harthi,[a] Abdul Karim Alinzi,[a] Saikh Mohammad Wabaidur,[a] Masoom Raza Siddiqui,[a] Mohammed Rafi Shaik,[a] Suman L. Jain,[b] M. Amin Farkhondehfal[d] and Simelys Hernàndez[e]

A new dinuclear uranyl salen coordination compound, $[(UO_2)_2(L)_2]\cdot 2MeCN$ [L = 6,6′-((1*E*,1′*E*)-((2,2-dimethylpropane-1,3-diyl)bis(azaneylylidene))-bis(methaneylylidene))bis(2-methoxyphenol)], was synthesized using a multifunctional salen ligand to harvest visible light for the selective photocatalytic reduction of CO_2 to MeOH. The assembling of the two U centers into one coordination moiety *via* a chelating–bridging doubly deprotonated tetradentate ligand allowed the formation of U centers with distorted pentagonal bipyramid geometry. Such construction of compounds leads to excellent activity for the photocatalytic reduction of CO_2, permitting a production rate of 1.29 mmol g^{-1} h^{-1} of MeOH with an apparent quantum yield of 18%. Triethanolamine (TEOA) was used as a sacrificial electron donor to carry out the photocatalytic reduction of CO_2. The selective methanol formation was purely a photocatalytic phenomenon and confirmed using isotopically labeled $^{13}CO_2$ and product analysis by ^{13}C-NMR spectroscopy. The spectroscopic studies also confirmed the interaction of CO_2 with the molecule of the title complex. The results of these efforts made it possible to understand the reaction mechanism using ESI–mass spectrometry.

Received 24th July 2020,
Accepted 25th October 2020

DOI: 10.1039/d0dt02620d

rsc.li/dalton

Introduction

The depletion of fossil fuel reserves and the continuous increase in the CO_2 concentration in the atmosphere have led to various environment-related issues.[1,2] Therefore, the photocatalytic reduction of CO_2 could be a sustainable technology for reducing CO_2 emissions and producing useful chemicals and fuels, subsequently providing environmental remediation to global warming and the future depletion of fossil energy resources.[3,4] Various semiconductor photocatalysts, such as oxide-based semiconductors, have been used for the conversion of CO_2 into useful compounds.[5–9] However, the poor visible light absorbance, low conversion degree, and high charge recombination have limited the usage of these systems.[8,9]However, after tuning the properties of the catalytic system with correct molecular structure, molecular catalysts such as dinuclear rhenium–bipyridine molecular assemblies,[10,11] cobalt–porphyrin compounds,[12] mononuclear iridium hetero-ligand-based molecules (*e.g.*, terpyridine/2-phenylpyridine),[13] iron(0)–porphyrin compounds,[14] cobalt–aminopyridine compounds,[15] and manganese and iron-based coordination polymers with pyridyl-salen ligand can be effective in the photocatalytic reduction of CO_2, especially in CO generation.[16] Similarly, the trinuclear ruthenium polyazine-GO-phen compound,[17] ruthenium trisphenanthroline assemblies,[18] and Mn(I) hydridocarbonyl PNP pincer-type complexes have been developed as photocatalysts for the conversion of CO_2 to MeOH.[19]

Uranium-containing compounds have been used extensively in various catalytic reactions, *i.e.* the alcoholysis of

[a]*Department of Chemistry, College of Science, King Saud University, P. O. Box 2455, Riyadh 11451, Kingdom of Saudi Arabia. E-mail: azam_res@yahoo.com, mhashim@ksu.edu.sa; Tel: +966-1-4675982*
[b]*Chemical Science Division, CSIR-Indian Institute of Petroleum Dehradun, India-248005. E-mail: umesh_kumar@iip.res.in*
[c]*Institute of General and Ecological Chemistry, Lodz University of Technology, Zeromskiego 116, 90-924 Lodz, Poland*
[d]*Center for Sustainable Future Technologies @POLITO, Instituto Italiano di Tecnologia, Via Livorno 60, 10144 Turin, Italy*
[e]*Department of Applied Science and Technology, Politecnico di Torino, C.so Ducadegli Abruzzi 24, 10129 Turin, Italy*

†Electronic supplementary information (ESI) available. CCDC 1567193. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d0dt02620d