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New Re(I)-modified Covalent Organic Frameworks for CO_2 photoreduction

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Recently, great research efforts have been spent to realize solar energy conversion by mimicking natural photosynthesis. This work aims to introduce two new covalent organic framework (COF) modified with Re(I) tricarbonyl complexes, ETTA-BPY-Re(CO)$_3$Cl and DBC-BPY-Re(CO)$_3$Cl (Figure 1), to explore their potential as catalysts for CO_2 photoreduction. The pristine COFs were synthesized from 4,4',4'',4'''-(ethene-1,1,2,2-tetrayl)tetraaniline (ETTA), with 2,2'-bipyridine-5,5'-dicarbaldehyde (BPY) and dibenzo[g,p]chrysene-2,7,10,15-tetraamine (DBC) with BPY using 1,4-Dioxane/Mesitylene (1:1) and acetic acid (10%) for 3 days at 120 °C. Modification with Re(CO)$_5$Cl occurred in toluene under Ar. Both materials underwent initial characterization by PXRD, SEM, N_2 sorption and FTIR spectroscopy confirming the proposed structure. UV-Vis spectroscopy and PL measurements confirmed the electronic interaction between the orbitals of the COF and the Re(I) center. Photocatalytic tests (λ_{irr} > 370 nm; P_{irr} = 100 mW cm^{-2}) were carried out in acetonitrile using 1,3-dimethyl-2-phenyl-2,3-dihydro-1H-benzo[d]imidazole (BIH) as sacrificial agent. The pristine COFs showed no activity for CO_2 photoreduction. ETTA-BPY-Re(CO)$_3$Cl showed a maximum conversion rate of 135 µmol g^{-1} h^{-1}, while the DBC-BPY-Re(CO)$_3$Cl showed a maximum rate of 1168 µmol g^{-1} h^{-1}, which is the highest CO evolution rate for these Re(I) modified COFs in the literature [1]. This highlights the importance of the selection of the building blocks for COF-based CO_2 photocatalysts. DBC, with more unsaturated bonds, possibly acts more efficiently in injecting and collecting light than the ETTA counterpart. Mechanistic studies as well as optimization of the reaction conditions are current in progress aiming at the enhancement of the performance of the new catalyst.

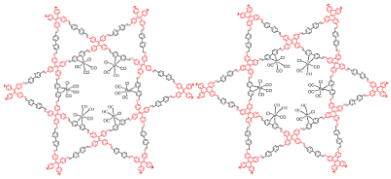

Figure 1. Structures of ETTA-BPY-Re(CO)$_3$Cl (left) and DBC-BPY-Re(CO)$_3$Cl (right).

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