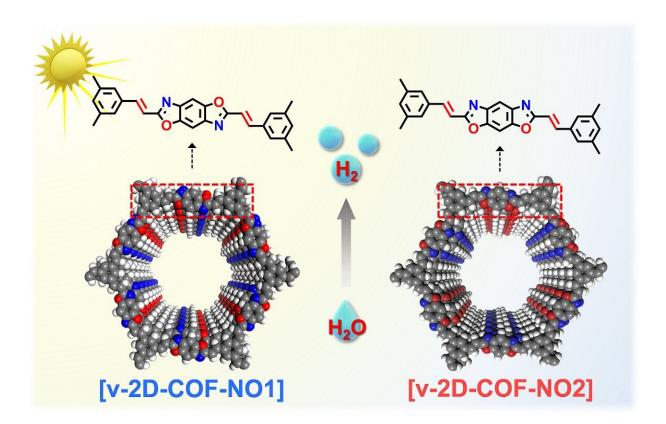


Novel isomeric vinylene-linked covalent organic frameworks developed with distinct photocatalytic properties

September 5 2022, by Zhang Nannan



The isomeric vinylene-linked covalent organic frameworks. Credit: NIMTE

Researchers led by Prof. Zahng Tao at the Ningbo Institute of Materials Technology and Engineering (NIMTE) of the Chinese Academy of



Sciences has synthesized two novel vinylene-linked two-dimensional covalent organic frameworks (v-2D-COFs) with isomeric structures via benzobisoxazole-mediated aldol polycondensation, showing distinct photocatalytic properties. The study was published in *Journal of the American Chemical Society*.

Thanks to their excellent in-plane conjugation and high chemical stability, v-2D-COFs have attracted increasing interest and thus emerged as advanced semiconducting materials. However, exploring new synthesis approaches and delving into the physical and chemical properties of v-2D-COFs remain challenging, due to the limited chemical reactions and monomers applied in v-2D-COFs.

To address this issue, the researchers proposed a solid-state benzobisoxazole-mediated aldol polycondensation reaction. Based on this innovative reaction, two novel isomeric benzobisoxazole-bridged v-2D-COFs (v-2D-COF-NO₁ and v-2D-COF-NO₂) with trans/cis configurations for benzobisoxazole linkages were constructed.

The two synthesized isomeric v-2D-COFs showed similar crystalline structures in terms of molecular formulas, unit cells, and pore sizes. Nevertheless, they exhibit evident differences in optoelectronic and electrochemical properties, such as <u>light absorption</u> and emission and charge-transfer properties, according to the results of the ultraviolet-visible (UV-vis) <u>absorption spectra</u> and ultraviolet photoelectron spectroscopy.

Specifically, under AM 1.5G (solar irradiation standard spectrum) irradiation at -0.3 V vs reversible hydrogen electrode, the v-2D-COF-NO₁ with trans-benzobisoxazole showed better photoelectrochemical performance than v-2D-COF-NO₂.

Employing Pt as cocatalysts, the v-2D-COF-NO₁ showed excellent



photocatalytic hydrogen evolution rate, twice the value of v-2D-COF- NO_2 .

This study provides a novel approach of benzobisoxazole-mediated aldol polycondensation to enrich the family of v-2D-COFs, and sheds light on the isomerization-mediated photocatalytic properties of v-2D-COFs.

More information: Shengxu Li et al, Direct Construction of Isomeric Benzobisoxazole–Vinylene-Linked Covalent Organic Frameworks with Distinct Photocatalytic Properties, *Journal of the American Chemical Society* (2022). DOI: 10.1021/jacs.2c06042

Provided by Chinese Academy of Sciences

Citation: Novel isomeric vinylene-linked covalent organic frameworks developed with distinct photocatalytic properties (2022, September 5) retrieved 15 May 2024 from https://phys.org/news/2022-09-isomeric-vinylene-linked-covalent-frameworks-distinct.html

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