

## Snapshots of some topics of interest of recent notable advances in chemistry

- Conversion of CO<sub>2</sub> to Methane in an Electric Field
- Simple Synthetic Method for Unsymmetrical Tetraarylpyrazine
- Selective Capture of CO<sub>2</sub> by Tunable Active Sites of Light-Responsive Metal-Organic Framework
- Protection of Photoresponsive Diarylethene Crystals Against the Attack of Organic Solvents

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# Snapshots of some topics of interest of recent notable advances in chemistry

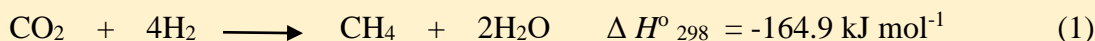
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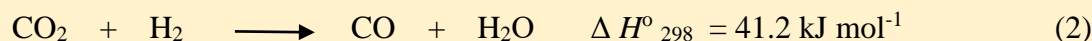
## Conversion of CO<sub>2</sub> to Methane in an Electric Field

The high and stable catalytic activity of 5wt% Ru/CeO<sub>2</sub> promoted the conversion of CO<sub>2</sub> to methane at low temperature in an electric field. This catalytic activity is referred to the low-coordinated Ru sites at the Ru-CeO<sub>2</sub> interface, which contributes to the reverse water gas shift under these reaction conditions.

Carbon dioxide (CO<sub>2</sub>) methanation is the conversion process of CO<sub>2</sub> to methane according to Sabatier reaction (eq. 1).



Considering the thermodynamic equilibrium, operation of CO<sub>2</sub> methanation at low temperatures is favorable to improve CO<sub>2</sub> conversion and CH<sub>4</sub> selectivity because reverse reaction (steam reforming of CH<sub>4</sub>) and side reaction (reverse water gas shift (RWGS), (eq. 2)) are suppressed at low temperatures.



Yamada *et al.* reported a process for CO<sub>2</sub> methanation through imposing an electric field (EF), which activates CO<sub>2</sub> in a non-conventional catalytic mechanism. Employing Ru catalyst supported on CeO<sub>2</sub> exhibited good activity for CO<sub>2</sub> methanation at low temperature in an EF.

The catalyst was prepared using an impregnation method and the process was performed in a fixed bed flow-type reactor. Two stainless steel electrodes were inserted contiguously to the top and bottom of the catalyst bed to impose electric field using DC power supply (5.0 mA, 150 V). The reactant feed gases were CO<sub>2</sub>, H<sub>2</sub>, and Ar in the ratio 1:4:5 respectively, where the gaseous products were CO, CH<sub>4</sub>, and CO<sub>2</sub>. The detected carbon-containing products (CO, CH<sub>4</sub>) with EF at low temperature of 340 K furnace temperature showed that 5wt% Ru/CeO<sub>2</sub> was a suitable catalyst for the conversion of CO<sub>2</sub> and CH<sub>4</sub> selectivity (17.4% and 96.4% respectively) via a different mechanism from that of the conventional catalytic reaction without an EF.

The effects of the contact time on catalytic activity over Ru/CeO<sub>2</sub> in an EF was investigated which showed that as the contact time increased, the CH<sub>4</sub> selectivity increased. This result indicated that CO is an intermediate in CO<sub>2</sub> methanation.

The kinetic investigations and *in-situ* DRIFTS measurements for the mechanistic study of CO<sub>2</sub> methanation over Ru/CeO<sub>2</sub> catalyst with electric field revealed that the methanation process proceeded over

high- and low-coordinated Ru sites by virtue of the promotion of reverse water gas shift (RWGS) reaction at low-coordinated Ru sites. Ru/CeO<sub>2</sub> catalyst exhibited high and stable activity for CO<sub>2</sub> methanation without the hindrance of CO adsorbed onto the Ru particle surface.

## Review

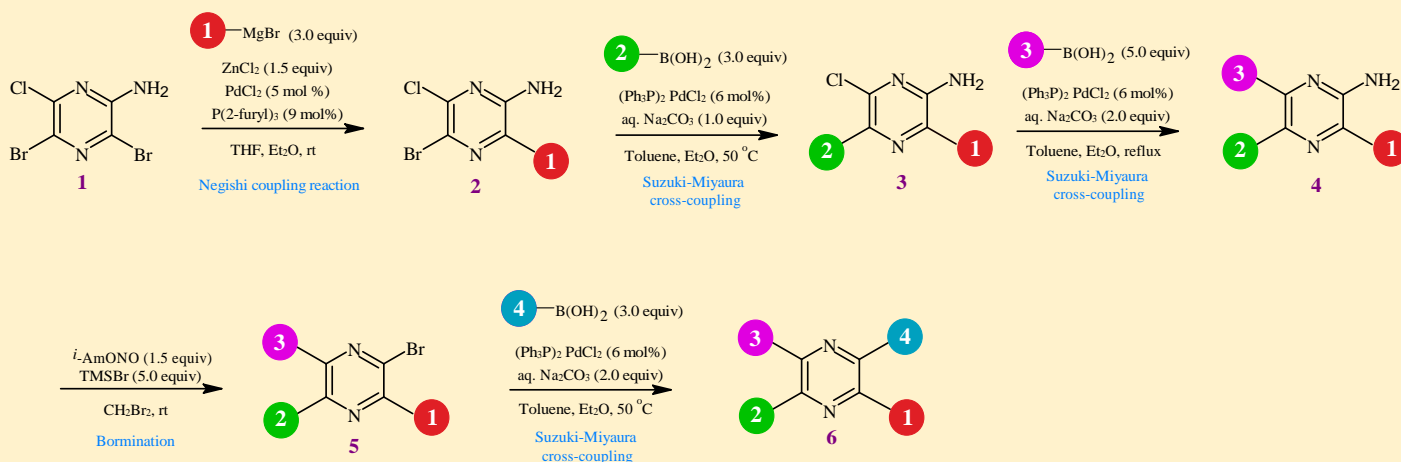
K. Yamada, S. Ogo, R. Yamano, T. Higo, Y. Sekine, *Chem. Lett.*, **2020**, *49*, 303–306.

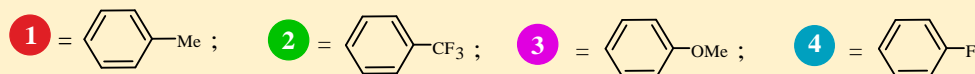
# Simple Synthetic Method for Unsymmetrical Tetraarylpyrazine

A simple 5-step synthetic procedure for unsymmetrical tetraarylpyrazines by sequential cross-coupling is outlined. The method was achieved from 2-amino-3,5-dibromo-6-chloropyrazin through four-fold cross-coupling and diazotization.

Unsymmetrical tetraarylpyrazines are important compounds in material chemistry. Inspired by the elegant studies of the preparation of multiaryl(hetero)arenes in a programmed manner by Itami, Yamaguchi, and coworkers, the team of Yoshida reported a facile synthetic method for unsymmetrical tetraarylpyrazines from 2-amino-3,5-dibromo-6-chloropyrazine **1** through four-fold cross-coupling reaction, which allowed to prepare tetraarylpyrazines bearing different aryl groups, serving in the modulation of properties.

The Negishi coupling reaction of pyrazine **1** with palladium dichloride and tri(2-furyl)phosphine furnished in the selective monoarylation of **1** to provide arylpyrazine **2** in 90% yield (Scheme 1). The ratio of 4-tolylmagnesium bromide to zinc chloride as 2:1 to form di(4-tolyl)zinc was crucial for the efficient Negishi cross-coupling. Treatment of pyrazine **2** with 4-(trifluoromethyl)phenylboronic acid in the presence of sodium carbonate and palladium catalyst at 50 °C gave diarylpyrazine **3** in 85% yield. Subsequent Suzuki-Miyaura cross-coupling between pyrazine **3** and 4-anisylboronic acid at reflux took place smoothly to yield triarylpyrazine **4** in 82% yield. The bromination of 2-aminopyrazine **4** was achieved through diazotization using *i*-amyl nitrite and trimethylsilyl bromide to furnish bromide **5** leaving the pyrazine ring and aryl groups intact. Finally, Suzuki-Miyaura cross-coupling of bromide **5** with 4-fluorophenylboronic acid proceeded smoothly without damaging functional groups to yield the tetraarylpyrazine **6** in 44% overall yield from **1**.

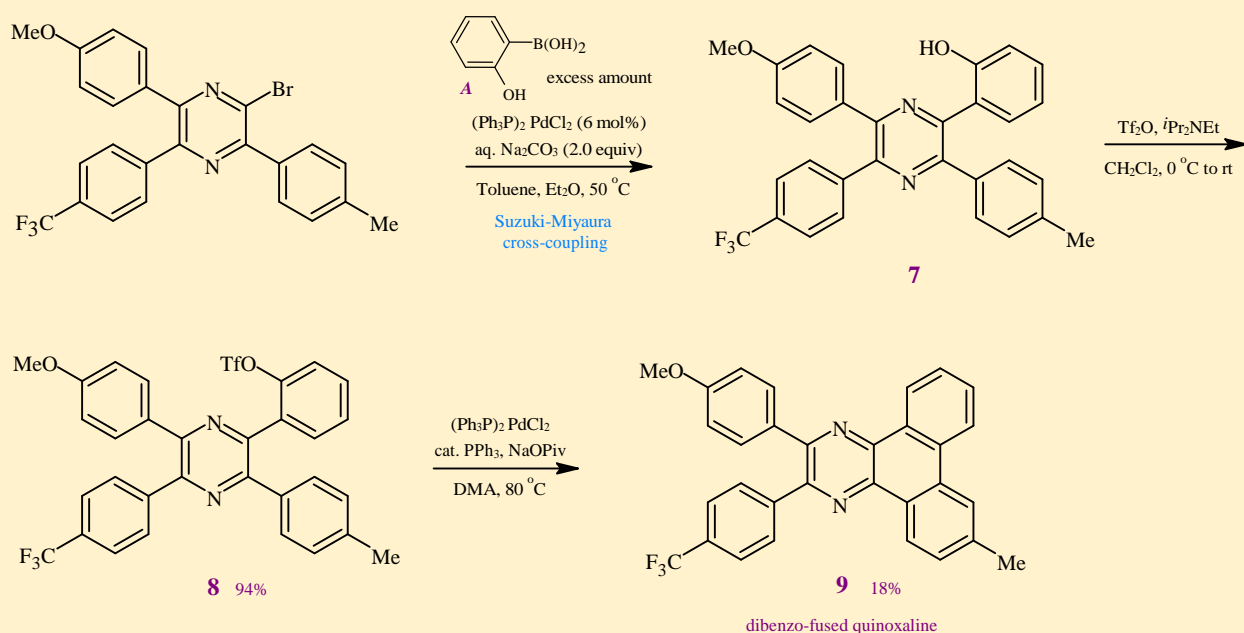




**Scheme 1.** Synthesis of tetraarylpyrazines **6**.

A broad range of pyrazines were successfully prepared by consecutive cross-coupling reactions with various coupling partners providing diverse tetraarylpyrazines with a wide variety of aromatic substituents.

Furthermore, intramolecular C-C formation of tetraarylpyrazine **7** allowed for preparing dibenzo-fused quinoxaline **9** via triflation using triflic anhydride and Hünig's base followed by palladium-catalyzed intramolecular CX/CH coupling of triflate **8** in the presence of sodium pivalate to furnish dibenzo-fused quinoxaline **9** in 18% yield (Scheme 2).



**Scheme 2.** Synthesis of dibenzo-fused quinoxaline **9**. **A** = 2-hydroxyphenylboronic acid.

This approach allowed the selective synthesis of tetraarylpyrazines possessing a wide variety of substituents from simple starting materials.

## Review

Y. Nishiyama, K. Akiyama, Y. Sakata, T. Hosoya, S. Yoshida, *Chem. Lett.*, **2021**, 50, 180–183.

# Selective Capture of CO<sub>2</sub> by Tunable Active Sites of Light-Responsive Metal-Organic Framework

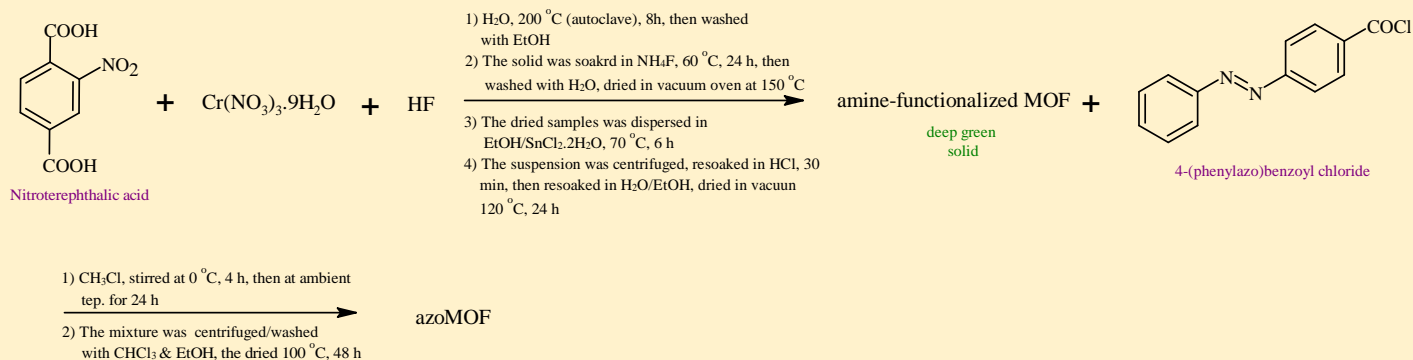
An efficient adsorbent based on metal-organic frameworks with targeted adsorption sites responsive to light for controllable CO<sub>2</sub> capture will be highlighted. This adsorbent has been constructed by incorporating polyethyleneimine into an azobenzene-decorated light-responsive metal-organic frameworks (LMOF). The features of this adsorbent include the adjustability of the surface electrostatic potential around the active sites (amines); high selectivity in the capture of CO<sub>2</sub>; and generating exposed/sheltered adsorption sites upon reversible light irradiation for controllable capture of CO<sub>2</sub> on amines.

Among the processes of mitigating greenhouse gas emissions, various solid porous adsorbents were employed for CO<sub>2</sub> capture. In one adsorption/regeneration cycle in these adsorbents, CO<sub>2</sub> molecules are diffused into the pores of solid adsorbents and combined with active sites via physical or chemical interactions. Subsequently, the adsorbed CO<sub>2</sub> molecules liberated at elevated temperatures or reduced pressures during regeneration, which are energy-consuming processes. To design process with visible economic-viability, metal-organic frameworks (MOFs) are considered ideal porous materials because of their diversified structures and molecular assembly. Among various stimuli-responsive MOFs, light-responsive MOFs (LMOFs) have outstanding properties such as high precision controllability and no byproducts.

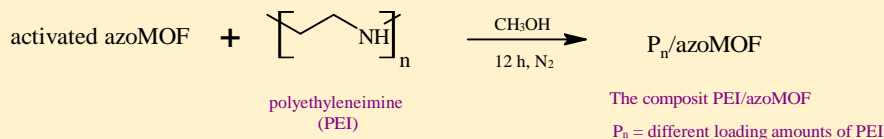
In this context, Jiang *et al.* reported a LMOF-based adsorbent with targeted active sites responsive to light for controllable CO<sub>2</sub> capture taking into consideration the fact that a relatively strong active site is essential for the selective capture of CO<sub>2</sub> over other gases such as N<sub>2</sub> and H<sub>2</sub>. The adsorbent was constructed by incorporating polyethyleneimine (PEI) into the pore of a LMOF (i.e., azobenzene-decorated MOF). PEI is a polymer with high-density amine units that has a strong affinity with CO<sub>2</sub>. The azobenzene-functionalized MOF (azoMOF) was prepared by post-synthetic modification of the amine-functionalized MOF with 4-phenylazobenzoyl chloride (Scheme 1), whereas the synthesis of adsorbent samples with different loading amounts of PEI (P<sub>n</sub>/azoMOF) was accomplished by the wet impregnation method (Scheme 2).

Adsorption studies revealed that the affinity of azoMOF for CO<sub>2</sub> is poor and physisorption is dominant as shown from adsorption isotherms of CO<sub>2</sub> in different samples at 298 K. Whereas, CO<sub>2</sub> can be captured in P<sub>n</sub>/azoMOF samples through chemisorption, which the active sites with PEI effectively enhances the binding affinity to CO<sub>2</sub>. The highest captured amount for CO<sub>2</sub> (65.9 cm<sup>3</sup>·g<sup>-1</sup> at 298K and 1 bar) was realized for the loading amount of PEI 0.98 mmol·g<sup>-1</sup>. Further increasing of the loading amount leads to a decrease of the capture amount, which can be attributed to the serious filling of azoMOF pores. Furthermore, the targeted active sites of amines provide the adsorbent with enhanced adsorption selectively of CO<sub>2</sub> over CH<sub>4</sub> and N<sub>2</sub> with a tunable adsorption capacity upon irradiation.



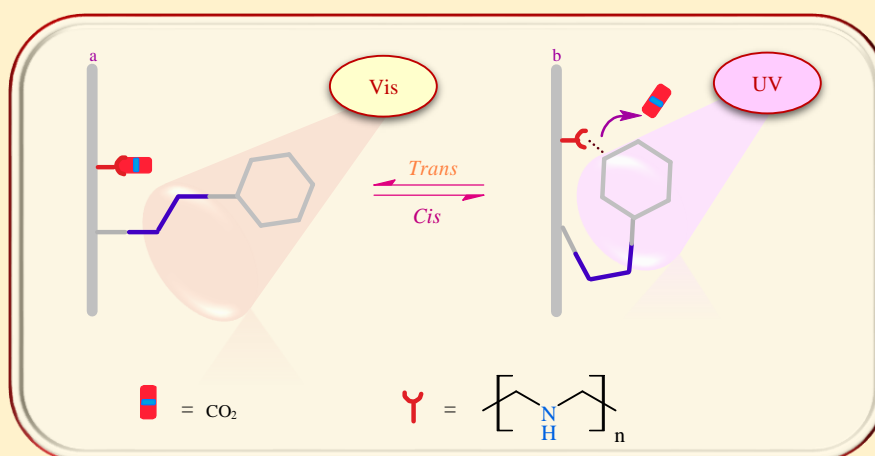


**Scheme 1.** Synthesis of azobenzene-functionalized MOF (azoMOF).



**Scheme 2.** Synthesis of adsorbent samples of P<sub>n</sub>/azoMOF.

Density functional theory (DFT) calculations elucidated that the surface electrostatic potential around the amine active site well correlates with CO<sub>2</sub> capture capacity and is adjustable during the configuration transformation of azobenzene moieties upon light irradiation (Figure 1). In the case of *trans* configuration, there is insignificant interaction between *trans*-azobenzene and amine, and shows little impact on the surface potential around amine ( $-0.048$  eV), thus, a high captured amount of CO<sub>2</sub> is obtained because of the opened active sites. Remarkably, the surface electrostatic potential around amine is increased to  $-0.025$  eV after the isomerization of azobenzene from *trans* to *cis* configuration, i.e., there is a strong interaction between *cis*-azobenzene and amine, and the active sites are sheltered, leading to the decrease of CO<sub>2</sub> adsorption capacity.



**Figure 1.** Schematic diagram for controllable CO<sub>2</sub> capture in the LMOF through the interaction between azobenzene moieties and

amine sites. (a) Upon vis light irradiation, the *trans*-azobenzene isomer is formed, leading to exposed amine sites for CO<sub>2</sub> capture; (b) Upon UV light irradiation, the *cis*-azobenzene isomer is formed, leading to shielded amine sites with reduced CO<sub>2</sub> capture.

This contribution might add new insights into the design and development of new materials with tunable host–guest interactions for adsorptive and catalytic applications.

### Review

Y. Jiang, X-C. Shi, P. Tan, S-C. Qi, C. Gu, T. Yang, S-S. Peng, X-Q. Liu, L-B. Sun, *Ind. Eng. Chem. Res.*, **2020**, *59*, 21894-21900.

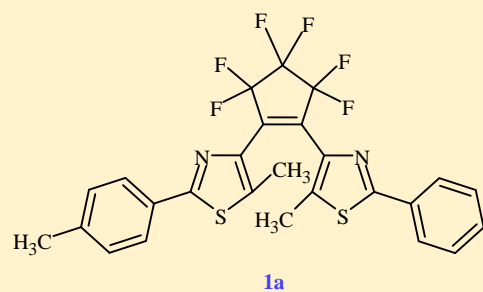
# Protection of Photoresponsive Diarylethene Crystals by Stepwise Assembly of Ultrathin PVA Films

A stepwise assembly method is described to maintain the stability in organic solvents of rodlike two-component mixed crystals composed of diarylethene derivatives, which undergo light-driven bending upon alternating irradiation with ultraviolet (UV) and visible light. The developed method is based on coating the crystal surface with 15 ultrathin poly(vinyl alcohol) (PVA) films, which allowed the stability of the crystal in *n*-hexane without alteration of mechanical properties or any fatigue, resulting in undergoing reversible bending more than 1000 times.

Color changes phenomena of some crystals upon irradiation with UV and visible light are attributed to the photoisomerization of molecules in the crystals, which accompanied by change of both electronic and geometrical structures of these molecules. Among this class of molecules are many diarylethene crystals, which exhibit photobending responses.

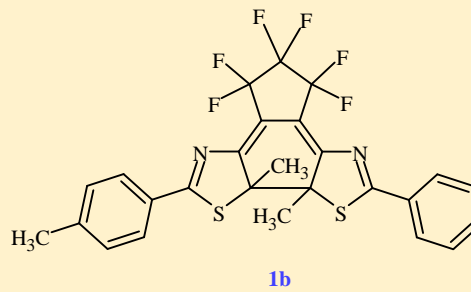
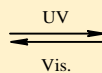
Practically, such photobending response should take place many times under different conditions. To protect the crystal surface against any distortion in organic environment and maintaining its bending response, Chiba *et al.* reported a layer-by-layer stepwise assembly method of ultrathin PVA polymer films. PVA was assembled on the crystal surface by repetitive physical adsorption and drying processes. In the drying process, the adsorbed PVA is stabilized by hydrogen bonding and becomes insoluble in many organic solvents. Two-component mixed crystals composed of **1a** and **2a**, with the molar ratio of 6:4 respectively, were used as the photoresponsive crystals, and were prepared by recrystallization from an ethanol solution containing equimolar amounts of both crystals (Scheme 1).

These rodlike crystals were tested and proven to undergo reversible light-driven upon alternating irradiation with UV and visible light in *n*-hexane and chloroform, and the stepwise assembly of ultrathin PVA films on the crystals ensured stability of the rod-shaped crystals after repeating 15 times. In terms of mechanical properties, they showed no changing, as well as no any fatigue in undergoing reversible bending more than 1000 times.

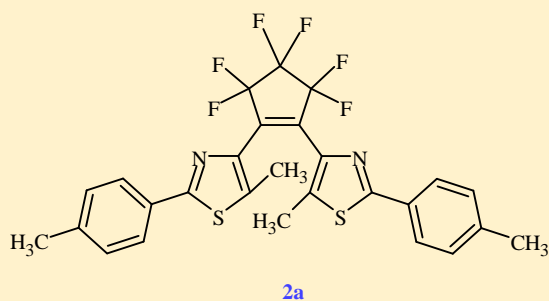


1a

1-(5-methyl-2-phenyl-4-thiazolyl)-2-(5-methyl-2-*p*-tolyl-4-thiazolyl)-perfluorocyclopentene

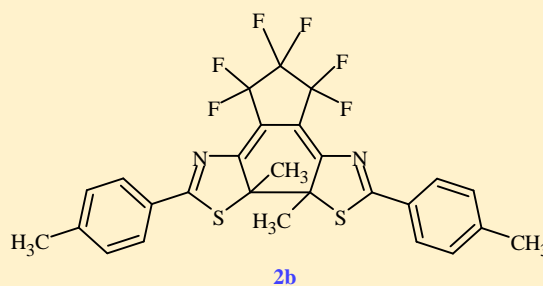
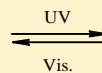


1b



2a

1,2-bis(5-methyl-2-*p*-tolyl-4-thiazolyl)-perfluorocyclopentene



2b

**Scheme 1.** Rodlike crystals that undergo light-driven bending upon alternate irradiation with UV and visible light.

## Review

H. Chiba, M. Morimoto, M. Irie, *Chem. Lett.*, **2021**, *50*, 84–86.