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In Situ Formation of Frustrated Lewis Pairs in a Water-tolerant Metal–organic Framework for the Transformation of CO_2

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Frustrated Lewis pairs (FLPs) consist of sterically hindered Lewis acids and Lewis bases, which provide high catalytic activity towards non-metal-mediated activation of 'inert' small molecules, including CO_2 among others. One critical issue of homogeneous FLPs, however, is their instability upon recycling, leading to catalytic deactivation. Here, we provide a solution toward this issue by incorporating a bulky Lewis acid-functionalized ligand into a water-tolerant metal-organic framework (MOF), named ***SION-105****, and employing Lewis basic diamine substrates for the in situ formation of FLPs within the MOF. Using CO_2 as a C1-feedstock, this combination allows for the efficient transformation of a variety of diamine substrates into benzimidazoles.* ***SION-105*** *can be easily recycled by washing with MeOH and reused multiple times without losing its identity and catalytic activity, highlighting the advantage of the MOF approach in FLP chemistry.*

During the last decade, intensive efforts have been applied to tackle the enormous emissions of CO_2 into the atmosphere; these include the development and promotion of renewable energy sources, improvements in energy efficiency, the reduction of carbon emissions, the development of efficient carbon capture and storage technologies, and the transformation of the emitted CO_2 into valuable products.[1][2] To date, the last approach has attracted a lot of attention, since using CO_2 feedstocks could help to close the carbon cycle and reduce petrochemical consumption. The challenge, however, is that CO_2 is a relatively unreactive molecule.[3]

In recent years, frustrated Lewis pairs (FLPs), comprising Lewis acids and bases sterically hindered in such a way that the acid-base adduct is not formed as in classical Lewis pairs, exhibit outstanding ability for CO_2 non-metal-mediated activation due to their unquenched reactivity.[4][5][6][7] One of the challenges of FLP chemistry, is their high sensitivity towards moisture, although recent studies showed that careful tuning of the steric environment of the acidic center, as well as regulation of basicity of the basic center, affords moisture-tolerant systems.[8][9][10] Indeed, the current research tendency toward FLPs already shifts from the early proof-of-concept investigations to practical applications, with FLPs being facile and powerful tools in chemical conversion.[9][11][12][13] FLPs have been found to be applicable for the conversion of CO_2 to CO, methanol, methane, and formamides among others.[14][15][16] Moreover, CO_2 can be used as a C1-building block for the synthesis of more complicated value-added products, such as the conversion of o-phenylenediamine and CO_2 into benzimidazole using silanes as reducing agents, which proceeds via an FLP-mediated pathway, with $B(C_6F_5)_3$ as a catalyst.[17]

It is worth noting that the majority of industrial chemical processes deploy heterogeneous catalytic systems, as the comparative stability and facile separation of the products from the catalyst facilitates scale-up and continuous production. Therefore, recent progress in FLP-chemistry includes efforts to transfer this concept from homogeneous to heterogeneous environments through the construction of tailorable interfacial FLP-like active sites on solid materials.[18] Recently, Thomas and co-workers created a microporous polymer network based on triphenylphosphine, mimicking the basic sites of FLPs, which, in combination with $B(C_6F_5)_3$, was found to be active for activating H_2.[19] Shaver and co-workers pioneered the first FLP-based self-healing gel,[20] followed by an investigation of its applicability as a catalyst for the *N*-formylation of amines using CO_2 as a C1-feedstock and hydrosilanes as the reductant.[21] Although the FLP-gel catalyst showed good performance for only a few aliphatic amines, it demonstrates the high potential of these materials with

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immobilized FLP sites and inspired us to explore the incorporation of FLPs into metal-organic frameworks (MOFs).

MOFs are crystalline materials formed by the self-assembly of metal ions or clusters with organic ligands and are unique among other porous materials due to their high porosity and structural tunability.[22][23][24] FLP chemistry amalgamated with MOFs should allow the advantages of MOFs as materials with directed assembly to converge with the versatile needs of a catalytic material, and the high potential of FLPs for the activation of small molecules such as CO_2. One of the simplest ways for the FLP concept to be applied with MOFs is the insertion of either a basic or acidic site in the structure of the MOF, followed by a treatment with the complementary part, which will result in the formation of an FLP, providing all the sites are sterically hindered.

Herein, we present a water-stable MOF with a B-based ligand, providing the acidic sites for the *in situ* formation of FLPs upon addition of the basic component. The transformation of a variety of diamines into benzimidazoles using CO_2 as the C1 feedstock and the MOF as the catalyst is then described.

The MOF, $[Eu(tctb)(H_2O)]\cdot$guest molecules (hereafter named **SION-105**), was synthesized by heating $Eu(NO_3)_3\cdot 6H_2O$ and tris(p-carboxylic acid)tridurylborane (H_3tctb) in a 2:1 mixture of DMF:H_2O at 120°C for 72 hours (see Supporting Information). The Eu^{III}_2 dimers in the **SION-105** structure consist of two Eu^{III} atoms separated by 3.9682(1) Å, linked together by two μ_2-bridging H_2O molecules and two tctb^{3-} η^1:η^1-bridging modes, Figure 1. The three duryl groups comprising the tctb^{3-} ligand form the planar blades of a propeller shape; with 61.8(2)°, 52.19(19)°, and 54.04(15)° inclinations with respect to the C9–C20–C31 plane. The carboxylic groups of each tctb^{3-} ligand are involved in Eu^{III} coordination; two of which are in η^2-chelating modes, with the third one in an η^1:η^1-bridging mode. Each tctb^{3-} ligand is therefore connected to a total of four Eu^{III} atoms. Interconnection between Eu^{III}_2 dimers and tetradentate tctb^{3-} ligands results in the formation of a 3 dimensional polymeric framework. Zigzag-shaped structural voids in between of the elements of this framework extend along the [$\bar{1}$01] direction, with periodic ramifications along [101] (Figure 1). These voids, with a volume of 2966.5 Å^3, as calculated with PLATON, comprise 36.6% of the total unit-cell volume. Integrated electron density of 747.5 e$^-$ per unit cell is interpreted as originating from approximately 2 molecules of DMF per symmetric unit, which may be removed upon activation. The acidic B sites are sterically protected by three bulky duryl groups limiting strong covalent binding of B to *p*-donors, such as water, precluding irreversible deactivation of the B sites, typical for FLP chemistry, as well as preventing potential collapse of the whole assembly, which makes **SION-105** an ideal candidate for the development of a bench-stable and sustainable FLP-catalyst. It is worth noting that our approach is distinct to that reported by Ma and co-workers, who incorporated LPs within MIL-101-Cr^{III} by post-synthetic modification.[25] Powder X-ray diffraction (PXRD) confirmed the purity of **SION-105**, which is also stable after immersion in liquid water for 24 hours (Figure S1). Thermogravimetric analysis (TGA) revealed the stability of **SION-105** at temperatures up to 300°C, followed by the loss of DMF lattice solvents within the pores (Figure S2). SEM images (Figure S5) show the rod-shaped morphology of as-made **SION-105** crystals, and B 1s XPS measurements (Figure S6) confirm the presence of B within the MOF structure. Moreover, **SION-105** selectively adsorbs CO_2 over N_2, showing a BET surface area of 216 m^2/g for CO_2 in contrast to <20 m^2/g for N_2 (Figures S3-S4).

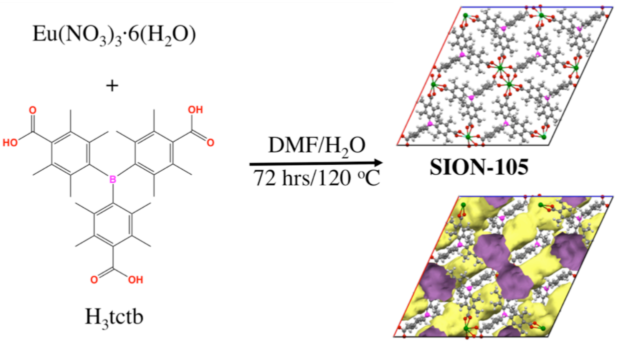


Figure 1. Schematic representation of **SION-105** synthesis. Atom color code: Eu, green; C, grey; O, red; B, magenta; H, white.

In order to assess the potential of **SION-105** in FLP chemistry, we investigated the reaction of aryl o-diamines with CO_2 as a C1-source and silanes as reducing agents, resulting in the formation of the corresponding fused benzimidazoles (Figure 2). This reaction is known to proceed in an FLP-mediated way with $B(C_6F_5)_3$.[17] This particular reaction is of interest since the substrate amine acts as a source of basicity for the formation of a FLP, potentially reducing the cost of the reaction. Sun *et al.* used $PhSiH_3$ as a reducing agent for $B(C_6F_5)_3$-catalyzed cyclization of *o*-phenylenediamines to construct benzimidazoles and, therefore, we started with the same hydrosilane. The reaction was tested in a PTFE-lined

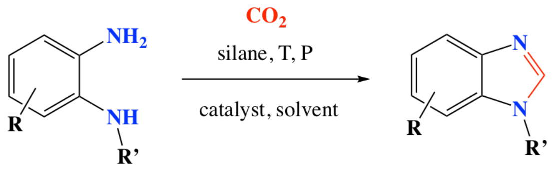
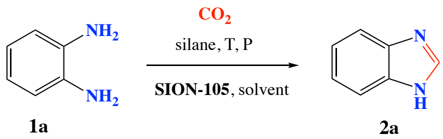


Figure 2. Reaction of aromatic o-diamines with CO_2 as a C1-source.

autoclave under a CO_2 atmosphere. Initial screening (Table 1, Table S2) for a suitable solvent among common aprotic solvents revealed that the reaction proceeds most efficiently in acetonitrile. THF as a solvent showed low reproducibility of conversion (Table 1, Entry 4), while in Et_2O, dioxane, and toluene either only traces of the product were detected or no reaction occurred. Notably, **SION-105** demonstrated good stability in the solvents, preserving its crystallinity after 24 hours at 120°C (Figure S8). The quantity of the reducing agent appeared to influence the conversion drastically, since reducing the amount of hydrosilane to 2 equiv. resulted in conversion falling from 71 to 32% (Table 1, Entries 5-7). Further optimization showed that lowering the temperature of the reaction decreased the yield of benzimidazole (Table 1, Entries 8-10). Lowering the catalyst loading only slightly decreases the conversion, with 3 mol% of **SION-105** being the optimum amount to catalyze the reaction (Table 1, Entry 8). It is important to note that, without **SION-105**, the conversion is only 13% (Table S2, Entry 7), which confirms the role of **SION-105** as a catalyst. Optimization of the CO_2 pressure had minimal effect on the conversion within the range of 0.5-2.0 MPa (Table S2, Entries 11, 14 and 15), giving the potential of using even lower pressures. However, we used 1.0 MPa of CO_2 to provide a sufficient molar quantity for the reaction. Notably, with $PhSiH_3$ as the reducing agent, the highest conversion did not exceed 76% even with prolonged reaction times, which led to side reactions limiting the yield of benzimidazole. Gas chromatography (GC) analysis (Figure S9) revealed the formation of a substantial amount of CO in the reaction mixture (0.545 mmol of CO starting with 0.8 mmol of $PhSiH_3$ and 0.2 mmol of *o*-phenylenediamine), which competes with the cyclization of the diamine. In order to increase the yield of benzimidazole and suppress CO formation and other undesired reactions, different hydrosilane reducing agents were surveyed. With $(EtO)_3SiH$, the conversion achieved was only 13%, whereas using Ph_2SiH_2 resulted in the quantitative conversion of *o*-phenylenediamine into benzimidazole in 24 hours (Table 1, Entry 12).

Table 1. Optimization of the reaction conditions.[a]



entry	hydrosilane (eq.)	temp (°C)	solvent	conv (%)
1	$PhSiH_3$ (4)	120°C	Et_2O	–
2	$PhSiH_3$ (4)	120°C	dioxane	–
3	$PhSiH_3$ (4)	120°C	toluene	–
4	$PhSiH_3$ (4)	120°C	THF	low repr.
5	$PhSiH_3$ (4)	120°C	ACN	76
6	$PhSiH_3$ (2)	120°C	ACN	32
7	$PhSiH_3$ (1)	120°C	ACN	20
8[b]	$PhSiH_3$ (4)	120°C	ACN	70
9[b]	$PhSiH_3$ (4)	100°C	ACN	69
10[b]	$PhSiH_3$ (4)	80°C	ACN	53
11	$(EtO)_3SiH$ (4)	120°C	ACN	13
12	Ph_2SiH_2 (4)	120°C	ACN	99
13[c]	Ph_2SiH_2 (4)	120°C	ACN	22

[a] Reactions were carried out in a PTFE-lined autoclave (20 mL) with **1a** (0.2 mmol), hydrosilane (0.8 mmol) and SION-105 (10 mol%) in solvent (2 mL) under CO_2 (1.0 MPa) atmosphere, 24 h.
[b] Reaction time – 4 h, catalyst loading – 3 mol%.
[c] Reaction time – 4 h

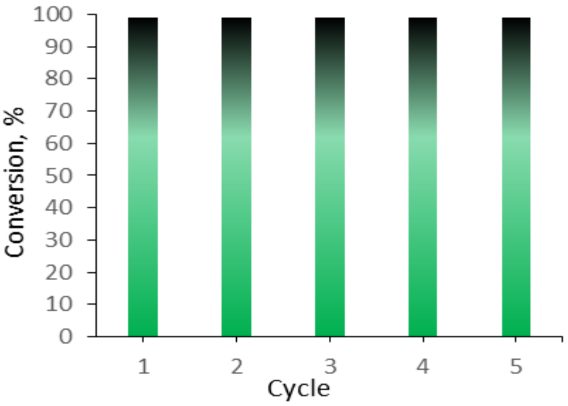
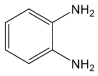
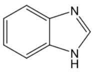
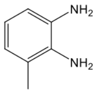
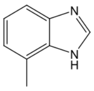
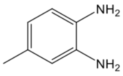
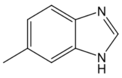
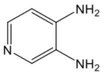
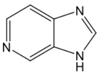
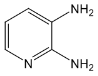
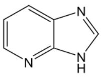
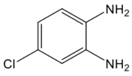
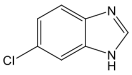
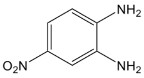
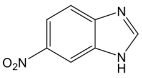
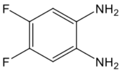
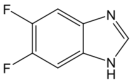
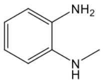
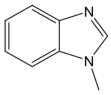
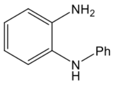
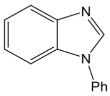
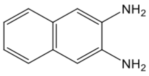
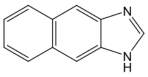
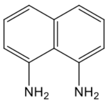
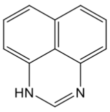


Figure 3. Catalytic activity of **SION-105**, demonstrating quantitative conversion of **1a** after repeated catalytic cycles (**1a** (0.2 mmol), Ph_2SiH_2 (0.8 mmol), **SION-105** (3 mol%), acetonitrile (2 mL), of CO_2 (1.0 MPa), 120°C, 24 h).

Next, we focused on the reusability of **SION-105**. The MOF catalyst, which remains solid, can be easily separated from the products by filtration, and then subsequently washed with methanol and used for the next cycle after drying it in air for 24 h. Recycling experiments with the optimized conditions demonstrated no loss in catalytic activity after five cycles, consistently showing quantitative formation of benzimidazole (Figure 3). ICP-OES revealed negligible (<1 ppb) amount of Eu^{III} leaching in the solution confirming the stability of **SION-105** after five cycles.

Using the optimized conditions, a variety of aromatic *o*-diamine substrates were evaluated (Table 2). The *o*-phenylenediamines with electron-donating groups demonstrated excellent yields, exceeding 90%, along with **1a**, independent on the position of the substituent on the aromatic ring (Table 2, Entries 2-3). The cyclization of heterocyclic pyridine-based diamines proceeded smoothly, giving moderate yields, although for **1e**, the yield was slightly lower, possibly due to the competition between the spatially close basic pyridine nitrogen and the amino group (Table 2, Entries 4-5). Also, a few diamines with electron withdrawing substituents on the aromatic ring were tested (Table 2, Entries 6-8). The yields followed the trend F > Cl > NO_2, correlating with the electron withdrawing effects of the substituents, which decreases the basicity of the amino-groups, but overall the yields were in the range of 60-85%. Introduction of an N-methyl substituent provided a yield of 61% (Table 2, Entry 9), although a more bulky N-phenyl substituent lowered the yield to 33% (Table 2, Entry 10). Also, a good conversion was obtained with the fused naphthalene-based diamine **1k** (Table 2, Entry 11), whereas with naphthalene-1,8-diamine (**1l**) the yield of the corresponding 1H-perimidine was 34% (Table 2, Entry 12).

Table 2. Scope of cyclisation of aromatic o-diamines with CO_2 as a C1-feedstock.[a]

entry	substrate		product		yield (%)[b]
1		**1a**		**2a**	99
2		**1b**		**2b**	96
3		**1c**		**2c**	98
4		**1d**		**2d**	83
5		**1e**		**2e**	69
6		**1f**		**2f**	77
7		**1g**		**2g**	65
8		**1h**		**2h**	84
9		**1i**		**2i**	61
10		**1g**		**2g**	33
11		**1k**		**2k**	83
12		**1l**		**2l**	34

[a] Reactions were carried out in a PTFE-lined autoclave (20 mL) with **1a-l** (0.2 mmol), Ph_2SiH_2 (0.8 mmol) and **SION-105** (3 mol%) in acetonitrile (2 mL) under CO_2 (1.0 MPa) at 120°C, 24 h.
[b] Isolated yields.

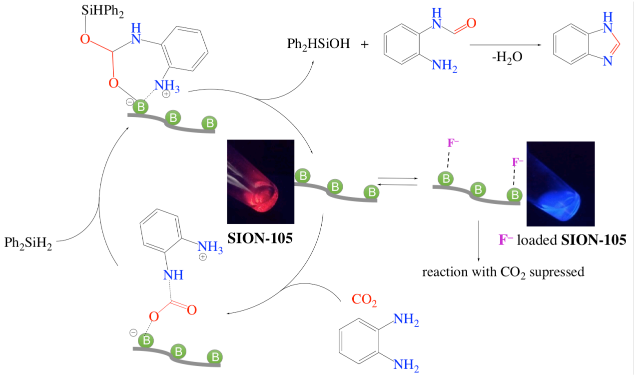


Figure 4. Proposed mechanism for the conversion of CO_2 using **SION-105**.

After testing the substrate specificity, we aimed to delineate mechanistic aspects of the reaction (Figure 4). Since the catalytic system is heterogeneous, direct determination of the catalytic cycle is challenging. Nevertheless, we focused on confirming the non-metal mediated mechanism of the reaction, by demonstrating that the B atoms play the crucial role in the activation of CO_2. It is worth noting that organoboron compounds with structures similar to H_3tctb have been known to selectively bind to fluoride (F^-) anions. For **SION-105**, the introduction of F^- leads to the change of its emission properties.[26][27][28] The luminescence emission of the Eu^{3+} ions within **SION-105** is induced by the antenna effect, in which the tctb^{3-} ligands absorb excitation photons and transfer the energy to the emissive levels of Eu^{3+}. The interaction between the Lewis acidic B atoms of tctb^{3-} and the Lewis basic F^- anions leads to the formation of $[B\cdots F^-]$ pairs creating non-radiative pathways, which result in the quenching of the Eu^{3+} emission.[29] When **SION-105** was immersed in an acetonitrile-water mixture with excess of NaF (30 equiv. compared to B) for 1 hour, its red luminescence emission is quenched, indicative that the B sites are blocked by the F^- ions (Figure S10).[29] The F^- loaded **SION-105** was filtered, dried in air for 24 hours and introduced in the reaction with o-phenylenediamine, diphenylsilane and CO_2. The conversion is reduced to 39% due to the partial deactivation of the B centers. Another Eu-based MOF, EuBTC, which has a relatively high CO_2 capture capacity, was also tested.[30] Under the same reaction conditions as for **SION-105**, the conversion of o-phenylenediamine to benzimidazole is 36%, which is close to the one for **SION-105** quenched with F^--anions. With a conversion of >99%, **SION-105** is apparently a superior catalyst compared to EuBTC. In addition, using H_3tctb itself as a catalyst instead of **SION-105** under the same conditions leads to a 6% conversion of *o*-phenylenediamine to benzimidazole, which might be due to the greater flexibility of H_3tctb compared to the tctb^{3-} ligand in the MOF structure. H_3tctb can adopt a trigonal pyramidal molecular geometry, leading to a possibility of forming the classical tctb^{3-}-amine adduct and hence quenching of the FLP activity. In **SION-105**, the B-C bonds of tctb^{3-} lying in one plane are restricted in movement due to the rigidity of the framework; therefore, strong interactions between the B center and the diamines are prevented. The B 1s XPS spectrum of **SION-105** loaded with o-phenylenediamine showed no interactions between the B centres and amino-groups (Figure S6). These experiments demonstrate the significant impact of B, incorporated in the MOF structure, as the active component, thus confirming the role of B as a Lewis acid for FLP mediated CO_2 activation.

The next question to investigate was whether the catalytic process occurs within the pores of **SION-105** or on its surface. From the X-ray crystal structure, the pore window of **SION-105** is ~4.8 Å (Figure S7), which is smaller than the sizes of the diamine compounds used in this work (~ 5.5 Å for *o*-phenylenediamine). TGA was performed on **SION-105** after immersion in acetonitrile solutions of several representative diamines. As shown in Figure S2, the TGA profiles of the diamine-loaded samples are very similar to that of **SION-105**. Hence, the catalytic reaction occurs on the surface, however **SION-105** still demonstrates high catalytic activity, making it ideal for further investigations using isoreticular approach allowing to increase accessibility to all the B sites.

Further, in order to investigate dependency of the reaction conversion on time and quantity of diphenylsilane, a kinetic study was performed *in situ* using NMR spectroscopy. The reaction was carried out in a 10 mm sapphire NMR tube (0.2 mmol **1c**, 0.2-0.8 mmol Ph_2SiH_2, 3 mol% **SION-105**, 2 mL of CD_3CN, 1.0 MPa CO_2, 120°C). The methyl-substituted substrate **1c** was used since the singlet ^{1}H NMR signal, relevant to the methyl substituent, does not overlap with other signals in the NMR spectrum, allowing to the reaction to be easily monitored. The use of one molar equivalent of Ph_2SiH_2 led to a low reaction rate compared to when four equivalents are used (Figures S11a-b, S12). In the first 2 hours, no conversion was observed in both cases, possibly, due to the generation of the active species from Ph_2SiH_2 (a new peak at 5.58 ppm is observed in the ^{1}H NMR spectrum, which disappears after complete consumption of Ph_2SiH_2). At the same time, the chemical shift of amino-group of the substrate moves to higher frequency, what may tentatively be attributed to the formation of active intermediate from the amine, diphenylsilane and CO_2. The kinetic curves demonstrate conversion of 24% in 24 hours for one molar equivalent of Ph_2SiH_2 and 98% for four equivalents of diphenylsilane. GC-MS for the final reaction mixture revealed formation of $(Ph_2SiH)_2O$ (m/z (relative abundance): 382.3 (2%), 303.2 (24%), 226.1 (100%); exact mass: 382.1209), which might be a product of reaction of diphenylsilane with water (traces are present in the reaction solvent), formed during the reaction, and $Ph_2Si(OMe)_2$ (m/z (relative abundance): 244.0 (26%), 167.0 (100%); exact mass: 244.0920) as a by-product.

In summary, we report a water stable and heterogeneous MOF catalyst for the metal-free and FLP-mediated conversion of CO_2 to value-added benzimidazoles. The introduction of Lewis acidic B centers within the MOF structure provides steric protection, suppressing irreversible binding and deactivation with bases. The high stability of **SION-105** in common organic solvents, CO_2-responsiveness, recyclability, tolerance against a wide variety of functional groups, and catalytic activity achieved through the *in situ* formation of FLPs, highlight the utilization of MOF catalysts for CO_2 conversion. Our findings open the way for the next generation of heterogeneous catalysts, intricately designed via direct assembly and functionalization for the activation of small molecules.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: CO_2 conversion, frustrated Lewis pairs, metal-organic frameworks, heterogeneous catalysis, sustainable chemistry.

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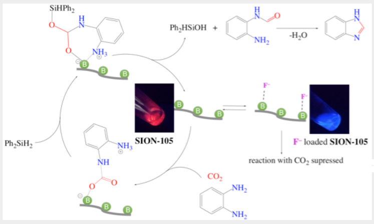
COMMUNICATION

Frustrated Lewis Pairs. A B-based, water stable metal-organic framework heterogenous catalyst (**SION-105**) for frustrated Lewis pair-mediated conversion of CO_2 is reported. Using CO_2 as a C1-feedstock, a variety of different diamine substrates were transformed into value-added benzimidazoles.



Serhii Shyshkanov, Tu N. Nguyen, Fatmah Mish Ebrahim, Kyriakos C. Stylianou and Paul J. Dyson**

In situ formation of Frustrated Lewis Pairs in a Water-tolerant Metal-organic Framework for the Transformation of CO_2