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Polymer Meets Frustrated Lewis Pair: Second-Generation CO_2-Responsive Nanosystem for Sustainable CO_2 Conversion

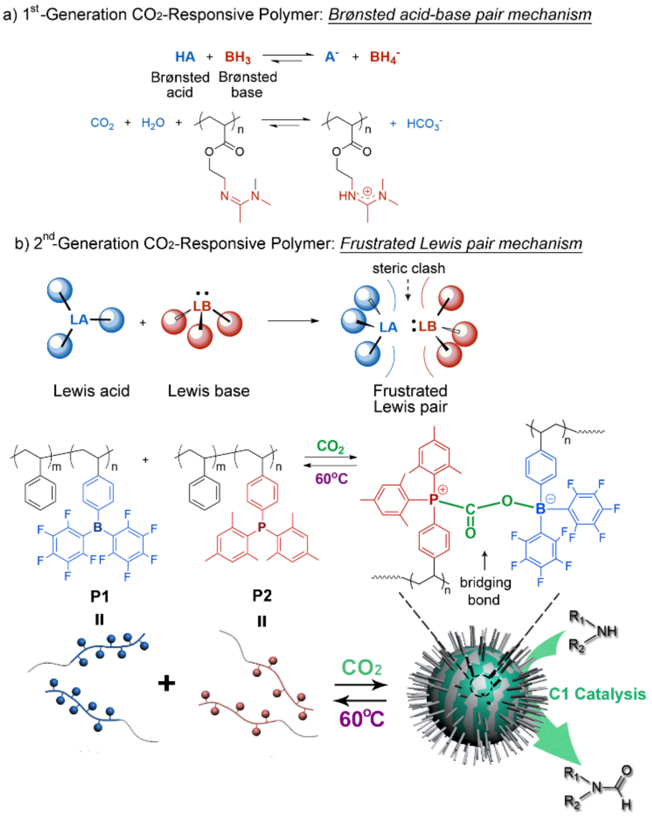
Liang Chen,[†] Renji Liu,[†] and Qiang Yan*

Abstract: Frustrated Lewis pair (FLP), as a couple of sterically encumbered Lewis acid and Lewis base, can offer latent reactivity for activating inert gas molecules. However, their use as a platform for fabricating gas-responsive materials has yet developed. Merging FLP concept and polymers, we report a new generation of CO_2-responsive system, differing from the first-generation ones based on acid-base equilibrium mechanism. Two complementary Lewis acidic and basic block copolymers, installing bulky borane- and phosphine-containing blocks, were built as the macromolecular FLP. They can bind CO_2 to drive the micellar formation, where CO_2 as a cross-linker bridges the block chains. This dative bonding endows the assembly with ultrafast response (< 20 s), thermal reversibility, and excellent reproducibility. Moreover, such micelles bound highly active CO_2 can function as nanocatalysts for recyclable C1 catalysis, opening a new direction of sustainable CO_2 conversion.

Since the advent of carbon dioxide (CO_2)-responsive polymer, it has continued to attract much attention of chemists because CO_2 is a unique gas trigger with mild, non-invasive and contamination-free features.[1] Compare to other chemically responsive polymers, CO_2-responsive polymers manifest irreplaceable advantages in many fields, including cell mimics,[2] latex,[3] switchable surfaces,[4] and gas-guided nanodelivery.[5] Such gas-triggered systems have been increasingly considered as promising candidates for future smart materials.

A seminal work in this theme was derived from Yuan and co-workers.[2a] They have reported an amidine-containing polymer in response to CO_2. In this specific polymer, the basic amidine groups (proton-acceptor) can react with acidic CO_2 gas (proton-donor). Up to now, all the known CO_2-sensitive systems work through this *Brønsted acid-base pair* principle (Scheme 1a).[1-5,6] The essence of this principle is acid-base equilibrium; however, the innate weak acidity of CO_2 causes low responsivity. To solve the bottleneck, seeking a new polymer system with distinct CO_2-sensitive mechanism is pressing.

A fundamental dilemma in enhancing CO_2 responsiveness is its chemical inertness and limited reactivity. In this respect, *frustrated Lewis pair* (FLP) chemistry is possible to become an ideal way for CO_2 activation.[7] FLPs refer to Lewis acids and bases that are sterically prevented from forming Lewis adduct and yet offer latent Lewis acidity and basicity for activation with small molecules,[8] for example, used for H_2 heterolysis.[9] Most recently, Shaver and co-workers pioneered the first FLP-based self-healing gel material.[10] Inspired by these, we wondered if the unique reactivity of FLPs could be used to construct next-generation CO_2-responsive polymer systems, where CO_2 would chemically bridge the FLP-containing polymers and offer dynamic bonding to drive a reversible polymer micellization. Moreover, we postulated that CO_2 species bound in the micelles would be highly active, which could make the micelles function as recyclable nanocatalysts to realize C1 feedstock conversion, as shown in Scheme 1b.



Scheme 1. a) The working principle of first-generation CO_2-responsive polymer based on Brønsted acid-base pair and a typical example of amidine-containing polymer. b) Frustrated Lewis pair (FLP) and the designed FLP-containing block copolymers (**P1** and **P2**) as a second-generation CO_2-responsive system for realizing CO_2-activated micellization and serving as recyclable nanocatalysts for CO_2 catalytic conversion.

To fulfil this goal, we design and synthesize two styrene-based monomers with bulky substituent groups, 4-styryl-di(pentafluorophenyl)borane (**1**) and 4-styryl-dimesitylphosphine (**2**), as the FLP acceptor and donor. Two diblock copolymers consisting of the complementary FLP blocks and common polystyrene block (**P1** and **P2**) are obtained via RAFT polymerizations (the details of copolymer synthesis and characterization are in the Supporting Information, Scheme S1-S2 and Figure S10–S17). Using the

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Gutmann-Beckett method,[11] the Lewis acidity (acceptor number, AN) of the monomer **1** was determined to be 72.4 in toluene-d_8 (Figure S1), close to that of standard reference $B(C_6F_5)_3$ (AN = 75.7).[11b] It suggests that the formation of polymer-type Lewis acid-base pair between **P1** and **P2** can be achievable.

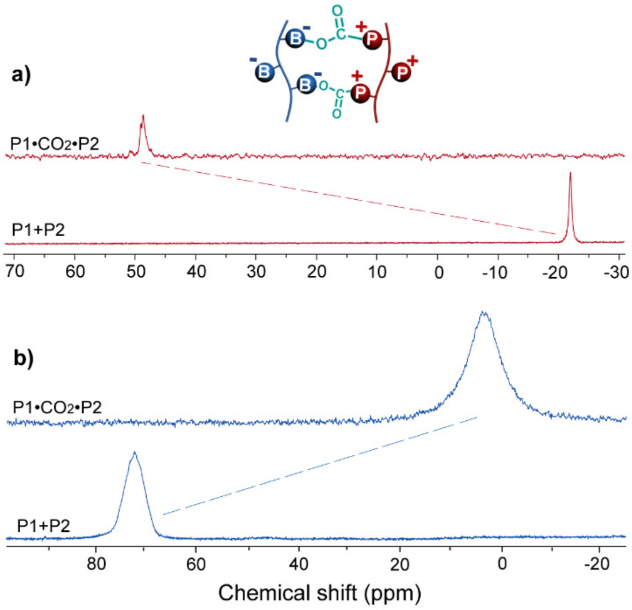

Figure 1. NMR studies of CO_2 binding to complementary FLP polymer (**P1** and **P2**) before and after treatment with CO_2 stimulus: a) ^{31}P NMR spectra change (red line); b) ^{11}B NMR spectra change (blue line). Inset, the structure of CO_2 bridging bonds between the boron-containing frustrated Lewis acidic polymers (**P1**) and the phosphorus-containing frustrated Lewis basic polymers (**P2**)

Mixing equimolar amounts of **P1** and **P2** in toluene (0.6 mM) showed no significant reaction. However, when CO_2 gas (p_{CO2} = 1.0 atm, flow rate = 0.1 mL s^{-1}) was passed through the mixture, a rapid binding reaction occurred, as evidenced by the solution altering from transparent to semiopaque (Figure S2). To elucidate this CO_2-binding mechanism, NMR experiments were carried out to provide detailed information on the polymer structural changes. In the absence of gas stimulus, ^{31}P NMR spectrum of the polymer mixture of **P1** and **P2** gave a single sharp peak, positioning at -22.4 ppm. However, upon addition of CO_2, the ^{31}P NMR signal showed a large downfield shift from -22.4 to 49.2 ppm ($\Delta\delta$ = 71.6 ppm, Figure 1a), suggesting the bonding between phosphorus atom of **P2** and the carbon atom of CO_2. Furthermore, ^{11}B NMR spectral analysis exhibited that **P1** and **P2** mixture had a broad resonance around 74 ppm ascribed to the boron signal of typical three-coordination triphenylborane,[12] whereas this resonance produced a great opposite shift to upfield region from 74 to 2 ppm ($\Delta\delta$ = -72 ppm, Figure 1b) in the presence of CO_2, indicating the formation of a four-coordination borane compound and confirming that CO_2 is covalently bridged with the boron in **P1** and phosphorus in **P2** (Figure 1, inset). The diagnostic ^{19}F NMR spectrum of **P1**•CO2•**P2** adduct corroborate this CO_2-bridged chemical structure (Figure S3).[13] The IR spectrum of product showed a strong vibration at 1692 cm^{-1} ascribed to a characteristic C=O stretch (Figure S4). These data coincide well with the cases in reported small-molecule FLPs.[14] Moreover, this CO_2-binding is highly efficient, since neither free ^{31}P nor ^{11}B resonance was observed. Conductivity experiments support the above results and demonstrate that this CO_2 reactivity is thermally reversible (Figure S5). After treatment with CO_2, the solution conductivity raised remarkably from 7.5 to 680 nS cm^{-1}, indicating that the bridging structure is zwitterionic. As heating up to 60 °C, the conductivity returned back, indicating the cleavage of bridging bonds. This procedure can be repeated at least three cycles, which means that this FLP polymer can reversibly capture and release CO_2.

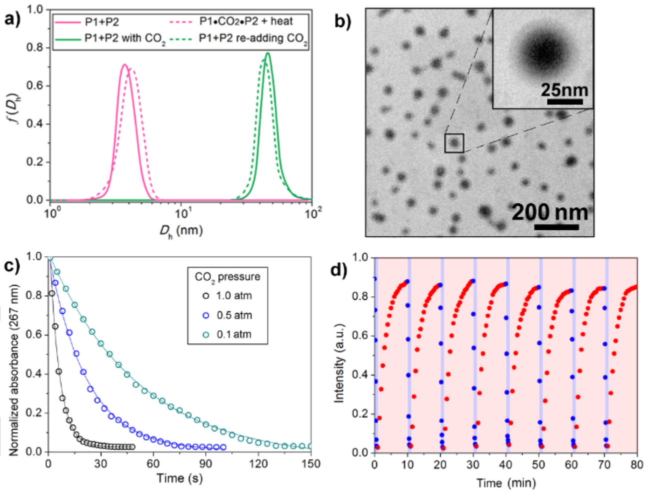

Figure 2. CO_2-responsiveness of FLP polymer: a) Hydrodynamic diameter of FLP polymer solution in the absence (pink solid line) and presence (green solid line) of CO_2 stimulus, and the reversible response upon heating (pink dash line) and re-addition of CO_2 (green dash line) by DLS. b) TEM image illustrating the micellization of FLP polymer upon addition of CO_2 (inset, the detailed core-corona structure). c) Gas response rate of the FLP polymer in various gas partial pressure (1.0 atm, black open circle; 0.5 atm, blue open circle; 0.1 atm, green open circle). d) CO_2 response repeatability monitored by applying an alternating CO_2/thermal cycle: each cycle contains 0.5 min of CO_2 stimulus period (blue circle) and 9.5 min of thermal recovery period (red circle). The concentration of FLP polymer solution (**P1** and **P2**) in all experiments is fixed at 0.6 mM in toluene.

After understanding the CO_2-responsive mechanism, we next aimed to study the responsive self-assembly behavior of the FLP polymer. Prior to CO_2 addition, the hydrodynamic diameter of **P1** and **P2** mixture was 4.2 nm (PDI = 0.14) measured by dynamic light scattering (DLS), consistent with the chain lengths of their unimers (Figure 2a, pink solid line). When we aerated the solution with CO_2 gas, interestingly, their size gave an 11-fold increase up to 46.8 nm (PDI = 0.08, Figure 2a, green solid line), implying the formation of polymer aggregates. Through TEM observation, spherical nanoparticles with a mean size of 40 nm appeared in solution (Figure 2b). Close inspection found that they are typical core-corona micelles (Figure 2, inset): the dark core, accounting for two-third of the total micellar volume, is comprised of the cross-linked FLP-bearing block chains, which induces the micellization; while the polystyrene block chains surround outside as the corona. DLS and TEM results disclosed that these micelles can entirely dissociate upon heating, but rebuild in CO_2 atmosphere (Figure

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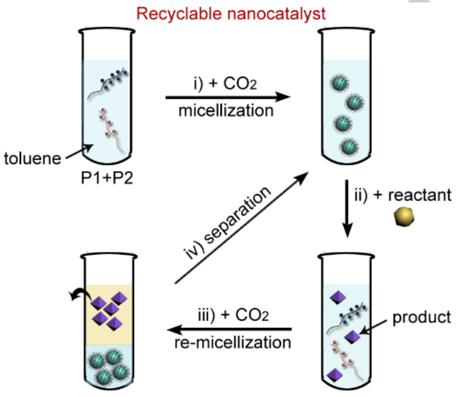
2a, pink and green dashed lines; Figure S6). This confirms the assumption that the dative bonding between FLP polymer and CO_2 is dynamically switchable.

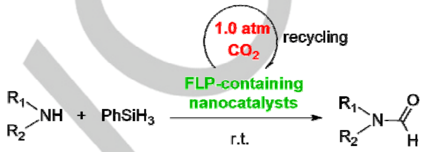
As a new CO_2-responsive system based on FLP chemistry, we wanted to assess its responsive parameters, such as sensitivity, repeatability and chemical tolerance. **P2** showed a strong UV-Vis peak at 267 nm assigned to the absorption band of neutral triphenylphosphine side groups.[15] When the **P1**·CO_2·**P2** adducts formed, the positively charged triphenylphosphonium suppressed this absorption (Figure S7). Thus, monitoring the UV-Vis spectra change upon CO_2 stimulus can determine the above parameters. Keeping the gas flow rate constant at 0.1 mL s^{-1}, we found that the CO_2-binding rate of FLP polymer is dependent on the CO_2 partial pressure. In 1.0 atm, it is clear that the response rate was very fast (18 s, Figure 2c, black open circle), which is 65-fold superior to that of traditional CO_2-responsive systems based on Brønsted acid-base pair principle (>20 min).[2,4,5] Moreover, even though reducing CO_2 partial pressure to 0.1 atm, the response rate remained below 120 s (Figure 2c, blue and green open circles). On the other hand, this CO_2-responsive behavior exhibited satisfactory switchability. After undergoing alternating CO_2/thermal cycle over 8 times, the FLP polymer system can still resist the responsive attenuation (Figure 2d). This, to some extent, addresses the issue of poor reproducibility in the traditional CO_2-responsive systems. A main reason is that this FLP mechanism arises from the covalent interactions between the FLP moieties in polymer and CO_2, circumventing the limit of acid-base chemical equilibrium. In addition, we inspected the applicability of this FLP polymer in different solvents. As expected, it is insusceptible to environmental polarity, allowing to rapidly bind CO_2 regardless if in low polar tetrachloromethane, moderate polar chloroform and high polarity of dimethyl formamide (Figure S8).

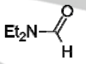
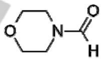
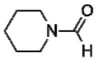
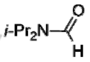
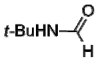
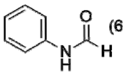
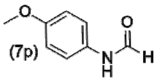
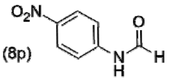
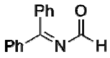
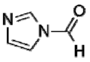
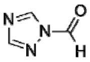


Scheme 2. Schematic illustration of FLP polymer nanoparticles as recyclable nanocatalysts: Step i) FLP polymer micellization triggered by CO_2; Step ii) highly active CO_2 bound nanoparticles catalyse the reactant for C1 catalytic utilization; Step iii) applying a new round of CO_2 gas stimulus to induce re-micellization of FLP polymer; Step iv) separating products and re-dispersing the FLP polymer nanoparticles for a new catalytic cycle.

Utilizing CO_2 as a C1 feedstock to produce other chemicals is one of the most crucial frontiers in sustainable chemistry.[16] A prerequisite to achieve this goal is the efficient activation of inert CO_2 gas. In our micelles, the CO_2 species are highly activated by FLP polymers, we thus speculated that these micelles could be used as recyclable nanocatalysts for C1 catalytic conversion. Our design is as follows: i) **P1** and **P2** dissolve in toluene, and purge with CO_2 to induce the micellization; ii) Upon addition of reactants, they can react with the highly active CO_2 buried in the micelles to yield products, while the micelles that lose the CO_2 cross-linking disassemble into free unimers; iii) After the reaction finished, we can trigger the micellar reconstruction by a new round of CO_2 stimulus; and iv) Finally, a new catalytic cycle can restart after separating the products (Scheme 2 and Figure S9).

Table 1. Catalytic formylation of N-H bonds using CO_2-bound FLP polymer nanocatalysts toward a variety of amine substrates.



Entry	Product		time (h)	yield (%)[a]	TON
1		(1p)	3	99	14800
2		(2p)	3	99	12800
3		(3p)	3	99	12000
4		(4p)	3	78	7800
5		(5p)	3	75	5200
6[b]		(6p)	3	56	4000
7[c]		(7p)	1	70	4500
8[d]		(8p)	12	–	–
9		(9p)	8	65	650
10		(10p)	8	43	480
11		(11p)	8	41	420

[a] Yields are given with respect to the amine substrates;
[b,c] Bi-substituented products (not show) account for <10%;
[d] It is not observed any available products.
All catalytic reactions performed at room temperature

To validate this, we investigated a typical CO_2 hydrogenation as a model catalytic reaction. Conversion of amines to their formamides ($R_1R_2NH \rightarrow R_1R_2NHCHO$) using CO_2 and H_2 is a well-known process.[17] However, this kind of reaction requires metal catalysts working at high temperature and pressure, and the metal catalysts suffer from the problems of deactivation and poisoning. Having in hand the CO_2-bound FLP polymer nanoparticle system, we then surveyed their catalytic ability for the formylation of a variety of N-H bonds with phenylsilane ($PhSiH_3$) as a reductant. Aliphatic secondary amines, such as diethyl amine, morpholine, and piperidine, can be quantitaively converted to their formamides with a turnover number (TON) over 12000 at room temperature within only 3 h, as evaluated by ^1H NMR and mass spectral analysis (Entry 1-3, Table 1 and Supporting Information). Notably, increasing the steric hindrance at nitrogen atom does not shut down the catalytic activity. Diisopropylamine (i-Pr_2NH) and tert-butylamine (t-$BuNH_2$) had 75% formylated yields under the same conditions (Entry 4-5, Table 1). For the cases of aniline derivatives, interestingly, both N-H bonds proved reactive but the bis-formylated products accounted for relatively small. Electron-donating group in aniline (e.g. *p*-methoxy) has a positive influence on the catalytic conversion (in a shorter time, 1 h). On the contrary, electron-withdrawing substituent group (e.g. *p*-nitro) impeded the reaction (Entry 6-8, Table 1). Other less reactive and fragile N-H bonds was also explored. The formylation of benzophenone imine was efficient (65% yield) and the reduction of C=N bond was not observed (Entry 9, Table 1). Similarly, utilizing the nanocatalysts to catalyze N-heterocycles provided delightful results. Imidazole and triazole displayed over 40% yields with a longer reactive time (~8 h), but avoiding the hydrogenation of heterocycles (Entry 10-11, Table 1). On the other hand, we focused on the reusability of the nanocatalysts. By applying CO_2 stimulus to regenerate the micelles for at least 8 times, their catalytic activity towards various categories of amines (diethyl amine, morpholine, aniline, imine and imidazole) retained over 80% (Figure 3). Overall, this CO_2-bound FLP polymer nanoparticles can be regarded as a universal catalytic nanoplatform for recyclable C1 conversion.

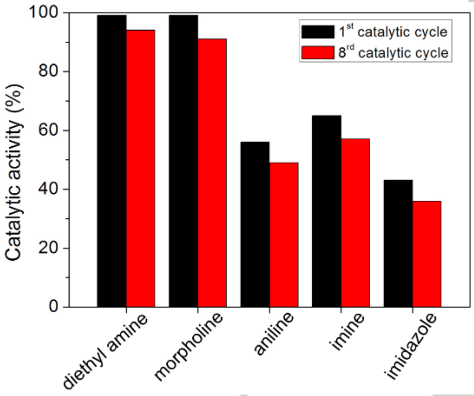


Figure 3. Catalytic activities of the CO_2-bound FLP polymer nanocatalysts after many times of catalytic cycle (black column: the first catalytic cycle; red column: the eighth catalytic cycle) with a various categories of amine substrates.

Conventional CO_2-sensitive systems have to rely on Brønsted acid-base equilibrium principle. This work has broken through this limit and demonstrated a new generation of CO_2-responsive system based on frustrated Lewis pair (FLP) principle. Introducing complementary FLP units into polymer, CO_2 gas can bridge the polymer chains to achieve CO_2-triggered micellization. This dative bonding between CO_2 and FLP units enables the polymers to respond to CO_2 in ultrafast speed, excellent reversibility and wide applicability. Moreover, since CO_2 bound in the micelles are highly active, the FLP polymer nanoparticles can act as nanocatalysts for recyclable CO_2 catalytic conversion. Although there still exists defects, merging of FLP chemistry and polymer will open a new avenue to construct gas-responsive materials, and provide a new outlook in sustainable C1 chemistry.

Acknowledgements

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Keywords: carbon dioxide conversion • frustrated Lewis pair • block copolymer • responsive polymer • nanocatalyst

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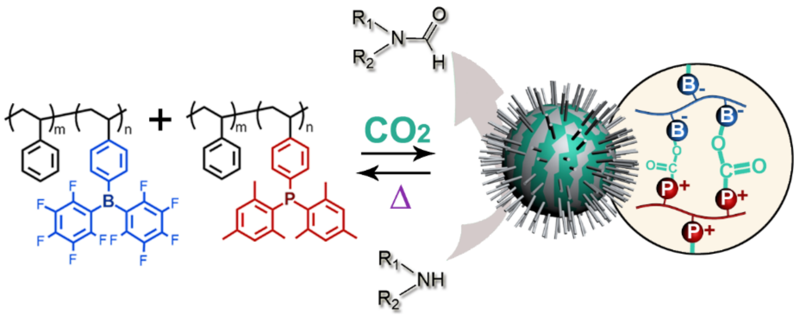

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Polymer Meets Frustrated Lewis Pair: Second-Generation CO_2-Responsive Nanosystem for Sustainable CO_2 Conversion

CO_2 bridged micelles: A second-generation CO_2-responsive polymer system was developed based on frustrate Lewis pair principle. Borane-containing Lewis acidic polymer and phosphine-containing Lewis basic polymer can dynamically bind CO_2, inducing CO_2-triggered micellization. The micelles bound highly active CO_2 species can function as universal nanocatalysts for recyclable C1 conversion.