

Molecular Receptors for Atmospheric Carbon dioxide: Structural and Mechanistic Aspects

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Abstract

Carbon dioxide (CO₂) presents one of the key chemical species and exerts significant influence on diverse environmental sub-systems. It is also an important species in the energy and industrial sector. In natural waters (oceans and rivers), a vital ionic equilibrium exists between ambient CO₂ and carbonate anions (HCO₃⁻ and CO₃²⁻). Thus monitoring of CO₂ in gas phase is a relevant and challenging. Thus the advances in the method development for CO₂ detection are vital. Molecular recognition chemistry based platforms presents one such advancement by providing novel analytical tools in the form of abiotic molecules, "receptors". Such approaches provide rapid and naked-eye based signaling. Most importantly, they are easy to use and provide a cost-effective means of analysis contrary to the bulky and traditional instrumentation based approaches. To the best of our knowledge, and for the first time, crucial molecular receptor platforms for the detection of ambient CO₂ through; (i) covalent bond formation, and (ii) formation of anion activated molecular receptors has been thoroughly reviewed. Some of the crucial design considerations of molecular receptors, such as choice of fluorophore/chromophore and mechanistic aspects are momentarily discussed.

Keywords: Carbon dioxide; Receptor; Chemosensing; Chemodosimetry; Anion; Carbamate

Abbreviations: GHG: Green House Gas; EC: Electrochemical; IR: Infrared; GC-MS: Gas Chromatography-Mass Spectrometry; TPE: Tetraphenylene Ethane; HPS: Hexaphenylsilole; AIE: Aggregation Induced Emission; DPA: Dipropylamine; Carbamate Ionic Liquid; TBBI: Tetrapropyl Benzobisimidazolium.

Introduction

In the past few decades, an increase in the number of

various chemical species (gases, anions, cations, organic and inorganic compounds) has resulted in the degradation of the natural environment [1,2]. Many chemical species in different environmental sub-systems are responsible for various detrimental effects, including degradation of water and air [3]. These detrimental effects continue to accelerate due to urbanization and fossil fuel derived energy generation [4-6]. Thus, there is a growing need to monitor the environment and the sources of contaminants to the environment, in order to control pollution and prevent its rise in the future [7,8].

Development of new and convenient approaches to monitor environmental pollution and understanding of environmental processes is important [9,10]. In this direction, advances in method development for environmentally significant analytes are vital [11,12]. Molecular recognition presents one such advancement via analytical tools, in the form of abiotic molecules, in the form of molecular receptors and optical sensor arrays [13-17]. Such approaches provide rapid and naked-eye based signaling response. Most importantly, they are easy to use and provide a cost-effective means of analysis. [18-22].

Among various chemical species with intense rise and impact on environmental processes, carbon dioxide (CO₂) exerts significant influence on diverse environmental sub-systems. It is also a key species in the energy and industrial sector [23,24]. In natural waters (oceans and rivers), a vital ionic equilibrium exists between ambient CO₂ and carbonate anions (HCO₃⁻ and CO₃²⁻). The maintenance of this equilibrium is crucial for current and future atmospheric CO₂ concentrations [25-29]. Thus, monitoring of atmospheric carbon dioxide is a relevant and challenging problem from the perspective of molecular receptors.

Carbon dioxide

Carbon dioxide is an acidic and chemically stable greenhouse gas (GHG). It is a vital molecular species responsible for over 60% of the enhanced greenhouse effect [30-32]. CO₂ has shown significant rise in the atmosphere, mainly after industrial revolution [33-35]. Emission of significant quantities of CO₂, due to fossil-fuel burning and changes in the land-use practices, is a major issue in managing climatic change. Increase of CO₂ has many negative consequences including greenhouse warming, sea level rise and causing water and food shortages on a global scale [36,37]. Various climate models estimate that the global average temperature may rise by ~1.4-5.8 °C by the year 2100 [38-39]. Thus, rise in climate related disasters, such as melting of polar ice caps and large scale forest loss is expected [31,40]. Moreover, it is unsafe for living beings to be exposed to high concentrations of CO₂, especially, in mines, sewers, wells, tunnels, ships (submarines) and space capsules (~ 0.5%) [41,42].

The alarmingly rising level of CO₂ is due to an increase in global energy requirements and the resulting dependence on burning of the fossil fuels (petroleum, natural gas, and coal)[43-45]. Nonetheless, owing to the economic and safety concerns regarding accessibility to these fuels, a continual dependence on fossils as chemical feedback

sources for decades to come is unavoidable [46,47]. In this regard, CO₂ emissions between 2004 and 2030 are projected to increase by 50%, an annual average rate of increase of 1.7%, which undeniably is a major environmental concern [48-50]. Therefore, development of new strategies for facile monitoring, and selective sequestration of atmospheric CO₂ from anthropogenic mobile or stationary sources, is a primary step of great significance for managing atmospheric CO₂ [51-53].

The most frequent strategy for atmospheric CO₂ monitoring utilizes bulky and sophisticated instrumental based methods (electrochemical (EC), infrared (IR), gas chromatography-mass spectrometry (GC-MS), field effect transistors), requiring time and expertise [54,55,31]. Additionally, many of them (i.e., EC sensors, IR, electrochemiluminescence and others) possess an indirect operating mechanism and thus lack of robustness. Most importantly, current tools are often intolerant to interferences and usually operate under high temperatures (300-800°C). Thus, they are less desirable and power-hungry means of analysis [56,57]. In contrast, molecular receptor based CO₂ sensing mechanism is highly attractive owing to its simplicity in design, cost-effectiveness and ease of detection of CO₂ by naked-eyes [58-60]. Further, such approaches have also demonstrated a potential to display an on-site signal driving quantitative analysis (*in-situ*) [61,62]. Importantly, due to the absorption of ambient CO₂ via bicarbonate anion formation, a secure storage mechanism for atmospheric CO₂ is also appreciable with these receptors.

Molecular recognition

Molecular recognition events yield information about environmental analyte at molecular level through specific binding of substrate by a molecular receptor. Such binding is regulated by geometrical and electronic complementarity between receptor and analyte [63-65]. A receptor can be defined as a molecular entity of abiotic origin that interacts with the analyte (anion, cation or a neutral molecule) and offers a unique response (in the form of photophysical or redox signaling).

Usually, molecular recognition events employ two different strategies to identify molecules, depending upon the mode of binding between the receptor (usually a big molecule) and the analyte (usually a minute structure) [66]. These two strategies have been categorized as chemosensing and chemodosimetry. On one hand, chemosensors utilize interaction of target analyte with the receptor through a non-covalent interaction in order to yield a measurable optical signal with real-time response, usually within seconds. Such basis of

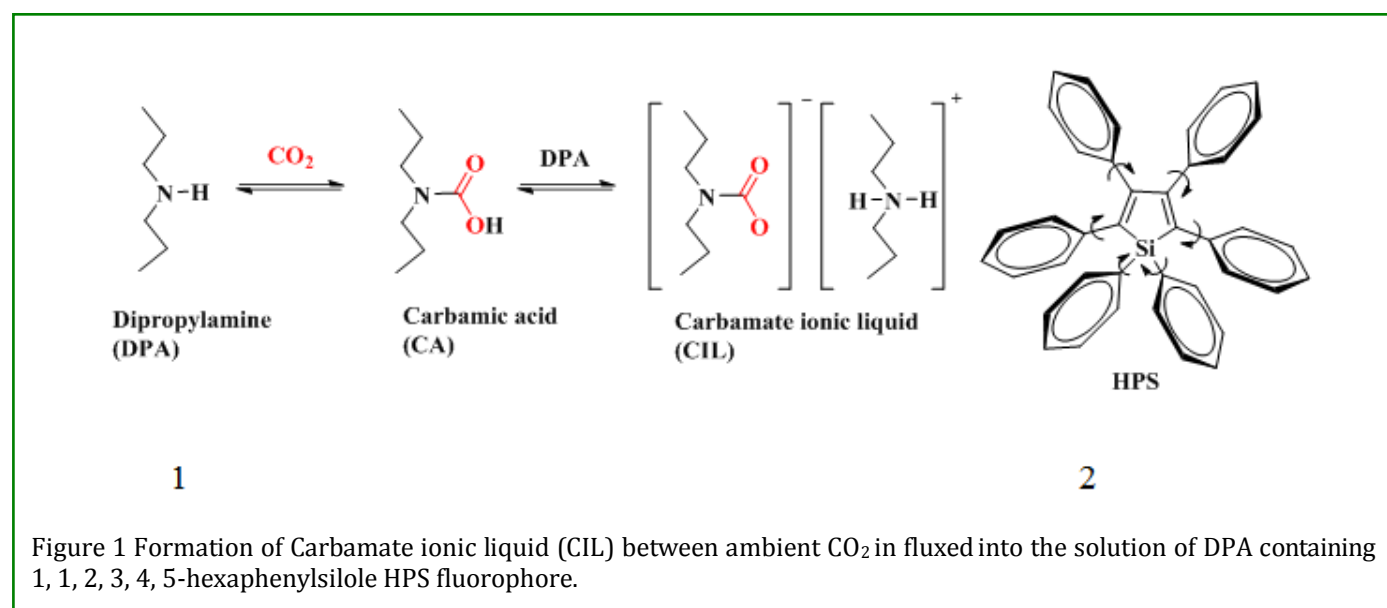
recognition offers them with the advantages of reusability or recyclability. On the other hand, chemodosimetry involves making and breaking of bonds, and events are generally slow and irreversible [67].

Abiotic receptors of carbon dioxide

The approach of abiotic molecules for detection of ambient CO₂ can be via covalent bond formation or formation of anion activated molecular receptors. Among these receptor strategies, anion activated receptor design, has been a subject of great research interest for the past two decades [68,69]. In this regard, naked-eye signaling events in the form of color or fluorescence are widely accepted due to low cost, easy detection and instrument-free analysis. Even though a number of receptors are available, most of them can be classified as acidic-hydrogen containing molecular scaffolds [70,71]. In the covalent bond formation based approach, functional molecular strategies mainly involve direct absorption of CO₂ by the receptor frame work. Here interaction of CO₂ into the solution has been noted with strong optical modulation of receptor either through a chemical reaction or covalent bond formation (Carbamate formation). These processes are assisted by the structure of receptor motif along with operational conditions.

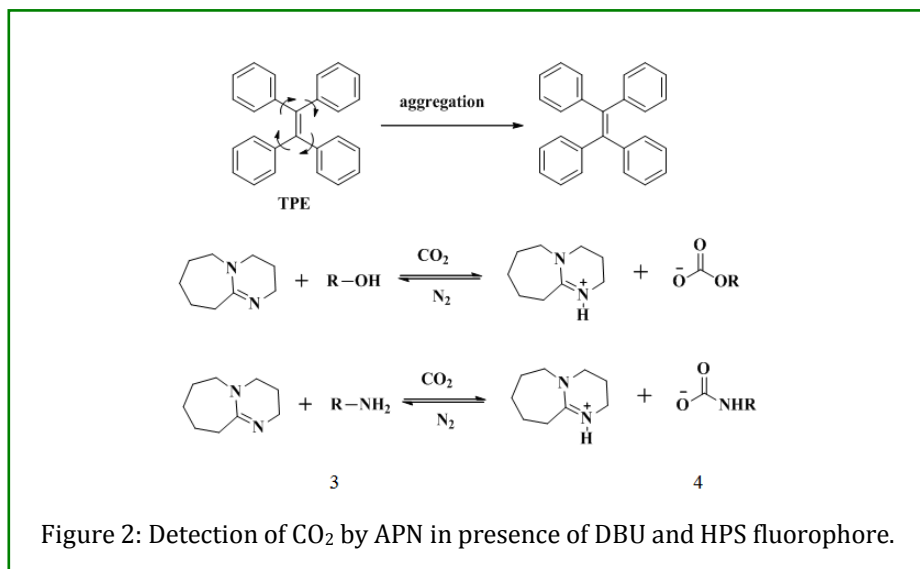
CO₂ recognition through covalent bond formation

In this section, the formation of covalent bond between CO₂ and amines, and the resulting formation of the ionic liquids has been considered. The drastic variation in the photo physical properties of the receptor, viscosity and polarity of the medium alter the fluorescence properties of the fluorescent probe in the solution and that serves as basis for CO₂ detection. Many fluorescent dyes like tetraphenylene ethane (TPE) and 1, 1, 2, 3, 4, 5-hexaphenylsilole (HPS) possessing strong aggregation induced emission (AIE) behavior have been utilized as markers for CO₂ detection. Liu *et al.* [72] achieved fluorescence detection (green light emission) of CO₂ by HPS solution containing dipropylamine (DPA) 1 (Figure 1), due to formation of Carbamate ionic liquid (CIL) 2 (Figure 1). A green light was emitted from a DPA solution of HPS immediately after it had been bubbled with small volume of CO₂ gas (dark at zero concentration) and the brightness increases with CO₂ concentration with an emission λ max 480 nm. It is a simple assay scheme to visualize the presence of CO₂ and permitted the quantification of its amount over the whole concentration range (0-100%). The system enabled quantification of various gas mixtures with high CO₂ contents, such as black damp and volcano damps.



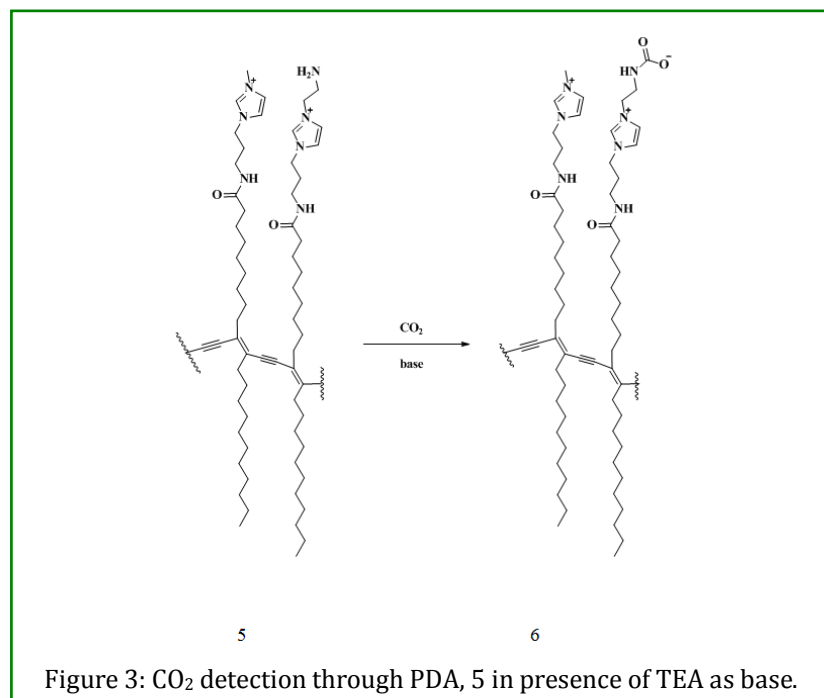
Parallel to this strategy, Tian *et al.* [73] reported fluorescent detection of CO₂ by ionic liquid 4 (Figure 2), mediated emission of TPE through amidine-groups like 5-amino-1-pentanol (APN/R-OH) 3 (Figure 2), in presence of 1, 8-diazabi-cyclo-[5, 4, 0]-undec-ene (DBU). After bubbled with a small volume of CO₂, the TPE contained

mixture of DBU and APN (1:1, v:v) was retained transparent and emitted strong fluorescence immediately. It was illuminated that the fluorescence intensity was enhanced with the increasing of the bubbled volume of CO₂ with an emission λ max 450 nm.



In the similar strategy, Xu *et al.* eliminated the presence of extra fluorophore by tethering of alkyl arms to the imidazolium polydiacetylene backbone (PDA) 5 (Figure 3). He reported the selective sensing of CO₂ in presence of triethylamine (TEA) as a base in order to assist the Carbamate formation. When the CO₂ is bubbled through PDA the presence of TEA solution, the color changes from brilliant blue to red. These features are attributed to the growth of a new absorption peak near 540 nm, together

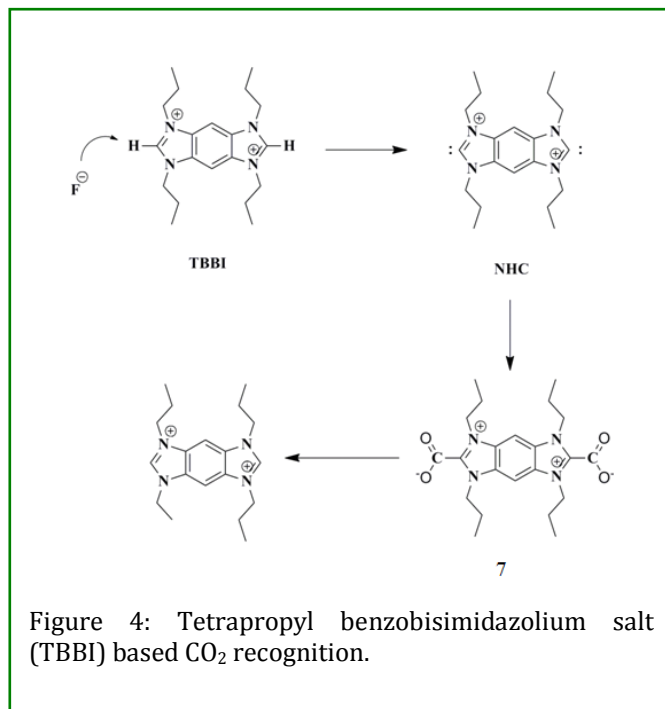
with the decrease in intensity of the absorption maximum of pristine PDA-1 at 623 nm with red shift 83 nm. The PDA-1/TEA system is sufficiently sensitive to allow for detection of atmospheric CO₂ ca. 400 ppm [74]. Here, the confirmation changes of the PDA backbone framework induced blue-to-red phase changes due to formation of carbamate 6 (Figure 3). Further, CO₂ induced phase transition was also monitored by fluorescence spectroscopy.



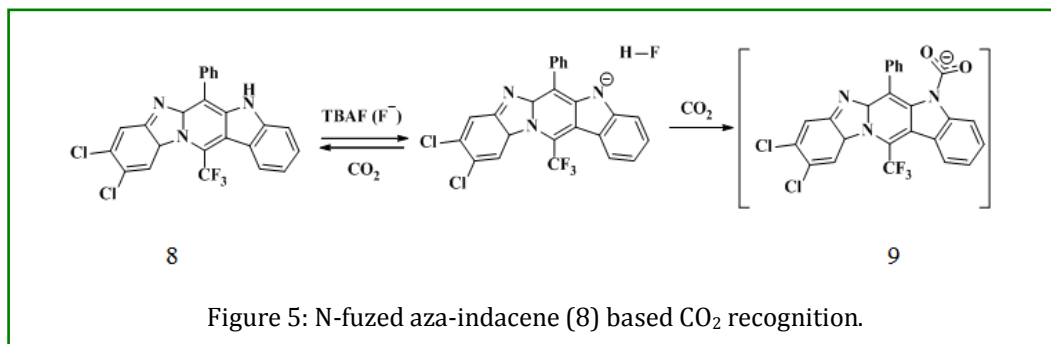
Anion-activated CO₂ recognition

The receptor approach discussed in the previous section is associated with two major shortcomings in the form of delayed signal readout and high temperatures to reverse the CO₂ induced change. However, research interest in the molecular recognition along with highly blown hydrogen-bonding in the field of the supramolecular chemistry, has resulted in the development of quick and reversible means of selective CO₂ absorption/detection [75]. This discovery has shifted the paradigm from Carbamate sensing strategy towards anion-receptor chemistry, for exploration and development of novel anion receptors possessing polar amine (N-H) bonds for recognition of ambient CO₂. It is now established that anion deprotonated receptor species basically possess strong nucleophilic character for activation of ambient CO₂ [76-78]. Along with the generation of characteristic nucleophilic centre, presence of anions with strong hydrogen bonding ability (usually fluoride), assists the formation of carbonate/bicarbonate anion from CO₂ in the presence of trace amount of water or moisture inside the receptor solution. Further, the stability of the anionic species (HCO₃⁻/CO₃²⁻) is guided by structure or configuration of the molecule [79]. However; very few reports exist with anion receptors. Formation of HCO₃⁻/CO₃²⁻ and receptors intermediates or adducts were monitored with modulation in electronic properties of the system and in turn means of their detection for CO₂. Guo *et al.* reported optical recognition of CO₂ by its reaction with *in-situ* generated N-heterocyclic carbene (NHC) from tetrapropyl benzobisimidazolium salt TBBI (Figure 4). The TBBI solution containing F⁻ was exposed to CO₂ gas. When the solution obtained by treatment with 3.0 equiv of TBAF was bubbled with increasing volumes of CO₂ (as governed by a mass flow controller), the intensity of the spectral feature at 290 nm was seen to increase and localized at 312 nm with red shift 22 nm in the absorption spectra. The CO₂ detection limit of this system was calculated to be ca. 30 pp. On the other hand, a marked increase in the fluorescence intensity (λ max = 330 nm) was observed upon exposure to increasing concentrations of CO₂ gas (as inferred from bubbling with increased

volumes at a fixed rate [80]. TBBI detects CO₂ exclusively in presence of fluoride anion in Acetonitrile. Further reversibility and release of carbonate-receptor adduct 7 (Figure 4) is reported to be thermodynamically driven process.



Fluoride assisted deprotonation of N-fused aza-indacenes 8 (Figure 5), for detection of CO₂ was also reported by Ishida *et al.* Such a transformation has been proposed to occur through CO₂ adduct 9 (Figure 5). The decomposition of this adduct allows the use of both absorption and emission changes for CO₂ detection. The detection limit for CO₂ was calculated to be 4.1×10⁻⁷ M. The spectra changes from 376 nm to 493 nm upon the exposure of TBAF solution of NAP-chol 1 to CO₂. The addition of F⁻ ions to a DMSO solution of NAP-chol 1 induced a change from colorless to orange [81]. Both these molecules have been well characterized through single-crystal XRD studies, and were cross checked with a CO₂ analogue (CS₂) which delivered similar products.



Recently, Zhang *et al.* [82] reported the anion promoted colorimetric and fluorescent CO₂ recognition with organic thermo reversible gelator. Exposure of NAP-chol 1 solution to CO₂ gas caused the solution to fade back to colorless. Also the absorption spectra changes from 376 nm to 493 nm with shift 107 nm. CO₂ detection limit of 0.03 bars has been calculated for emission spectra. Here, naphthalimide derivative, NAP-chol 10 (Figure 6), a thermally stable gelator system in DMSO, transforms to a

homogenous solution in presence of fluoride anion (TBAF) via deprotonation of amide (N-H) bond 11 (Figure 6). Detection of CO₂ was envisaged through regeneration of sol to gel. This process resulted in the formation of bicarbonate anion in the solution along with regeneration of receptor 12 (Figure 6). These chromogenic and fluorogenic changes were observed through naked-eyes. The changes were further reflected in the absorption and emission spectra.

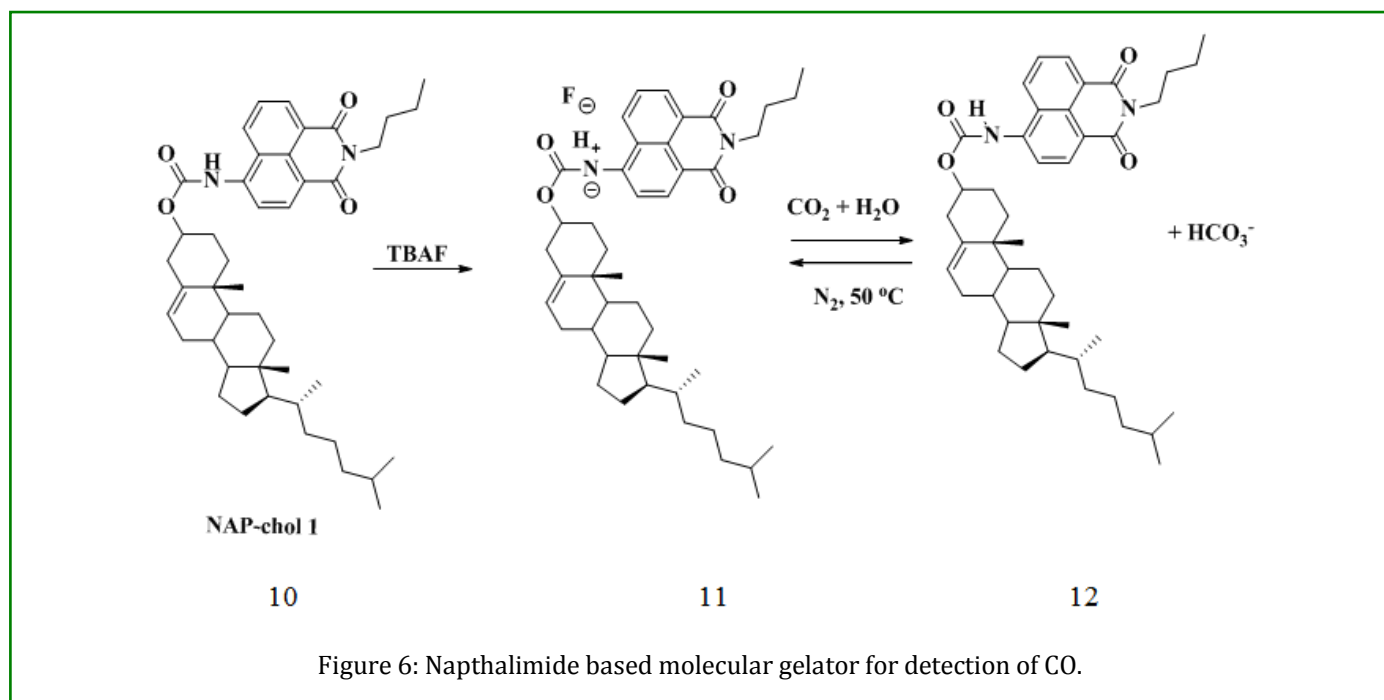


Figure 6: Naphthalimide based molecular gelator for detection of CO₂.

Conclusion

This review summarizes the foremost progress made in the development of abiotic molecular receptors for the detection of CO₂. Emphasis has been given mainly to reports diverted towards practical applications, with lower detection limits, and increased selectivity, and hence reliable in terms of quality assurance. Selected references are being mentioned herein which will provide the ground work for an individual to know quickly strategies and hence their application for CO₂ detection. In this field, research till date has been conducted almost entirely in the academic arena, and little attention has been paid to practical applications. Some of the crucial design considerations, such as choice of fluorophore/chromophore, and mechanism are momentarily discussed. Nevertheless, a substantial progress has been made in developing abiotic molecular receptors for detection of CO₂ over last few decades.

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