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Quinizarin-based Simple and Convenient Colorimetric Sensor for Carbon Dioxide

Quinizarin 색소 기반 간편한

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Abstract

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In search of simple and fast method to estimate the concentration of atmospheric carbon dioxide, the quinizarin and TBD system was discovered and its mechanism was studied and the applications were tried.

From UV-VIS spectrum, the reason behind the change in color of the solution was found to be the different electronic forms of quinizarin. In other words, the color of the quinizarin solution was orange yellow when quinizarin was neutral while its color changed to purple once mixed with TBD as a result of deprotonation. Also, the molar ratio of quinizarin to TBD was 1 to 1 because there was no increase in the strength of the absorption band when TBD was excessive whilst there was a decrease when TBD was deficit. Also, the shift of the absorption band was observed

as a result of TBD binding with carbon dioxide and giving back protons to quinizarin.

From ^{1}H-NMR spectrum, the hydroxyl proton of quinizarin was observed initially but it was soon given to TBD. Also, the fact that TBD bound itself with carbon dioxide was verified by the ^{13}C-NMR spectrum as a new peak was observed at 161 ppm.

In assistance with FT-IR spectrums, the proposed mechanism was supported once more. Quinizarin loses a proton to TBD and the protonated TBD loses the proton as it binds with carbon dioxide. As a result, the color of the solution changed from purple to yellow. The intensity of the vibrational modes for the corresponding functional groups changed accordingly; N-H bond decreased and O-H bond increased.

For the experimental parts, the saturation volume of carbon dioxide was studied; the total volumetric capacity of the detecting system at different concentrations were measured and it was used to estimate the approximate response time and detectable concentration of carbon dioxide for each concentration of the system.

The response time of the system at given concentration of carbon dioxide was figured out in the next step. As predicted, the system with lower concentrations of the chemicals had a shorter response time. However, the systems with the other organic bases such as DBU and piperidine were found to be not fast enough to detect

the concentration of carbon dioxide fast compared to the system with TBD at the same concentration.

Most importantly, the system could be recycled for at least 3 to 5 times and the performance was maintained relatively well. The system could actually be re-used upto 10 times but it became harder and harder to notice the color change when re-used too many times.

Known the properties of the system as sensor, new applications were tried.. For solidification, TBD was physically fixed onto silica and it was successfully done. Nextly, the solid TBD was dipped in the quinizarin solution to become blue. Although the system was seemingly ready, it was not be able to interact with the atmospheric carbon dioxide and did not undergo any color change. Obviously, the solid system failed to interact with carbon dioxide because of too high thermodynamic barrier between solid and gas. The other option was an Agarose gel technique. The quinizarin and TBD solution was made and mixed with hot agarose solution and cooled down. However, the gel had too much viscosity so the response time was significantly increased.

Keywords: Carbon dioxide, Chemical dye, Organic base, Protonation, Deprotonation, Adduct, Colorimetric sensor,

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Chapter 1. Introduction

1.1 Global Warming and Carbon Dioxide

For the last few centuries, global warming has been a major problem as too much carbon dioxide was produced in the atmosphere. This carbon dioxide overload in the atmosphere was mainly caused by the combustion of fossil fuel like coal, natural gas and petroleum. As a result of the combustion, carbon dioxide was always produced because it was the stable and final product. Therefore, the product was slowly accumulated in the atmosphere and played a very important role. As a greenhouse gas, the carbon dioxide molecules in the atmosphere absorbed the heat emitted from the surface of the Earth and emitted it back to the Earth; the heat coming out from the Earth is less than the heat the Earth is gaining. Therefore, the temperature of the Earth would slowly increase and the change leads to other climate and environmental changes all over the world.

There are many kinds of greenhouse gases that trap the heat within the atmosphere of the Earth and induce the increase in the temperature of the Earth such as methane and nitrogen oxides. Most of all, water vapor naturally contributes to greenhouse effect more than any other greenhouse gases. However, the water vapor is often not regarded as greenhouse gas as it occurs naturally and its effect is

inevitable. On the other hand, carbon dioxide is considered to be the most important greenhouse gas because it contributes to the global warming phenomenon more than any other greenhouse gases except for water vapor. The effect of carbon dioxide on climate change was greatly increased ever since 18th century, the Industrial Revolution. People started to build factories and operate a number of machines to produce industrial goods. In consequence, a huge amount of forests were cut down, coals were mined, and oils were collected in order to generate energy. Then, a lot of carbon dioxide was produced as a result of combustion of the fuel and the problem deteriorated as time went by.

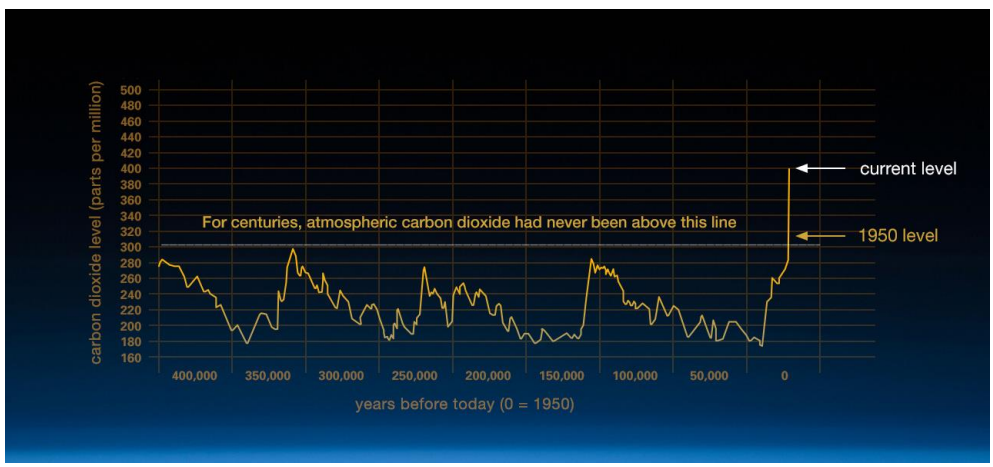


Figure 1.1.1 The graph of carbon dioxide level against year proving that the atmospheric carbon dioxide has increased since the Industrial Revolution.[35]

The actual problem of the global warming is that it is consisted of a positive feedback; the result of the event becomes an additional cause of the event and the effect of the event can only be increased and fastened until the factors wear out. In this case, the carbon dioxide molecules in the atmosphere trap the heat around the Earth and its temperature would gradually increase. Then, the increased temperature would cause the icebergs in both the Antarctic and the Arctic to melt slowly and the carbon dioxide fixed in the ice caps would be released. Only then, a greater volume of the released carbon dioxide gases would contribute more toward global warming and this vicious cycle would repeat itself and get worse and worse.

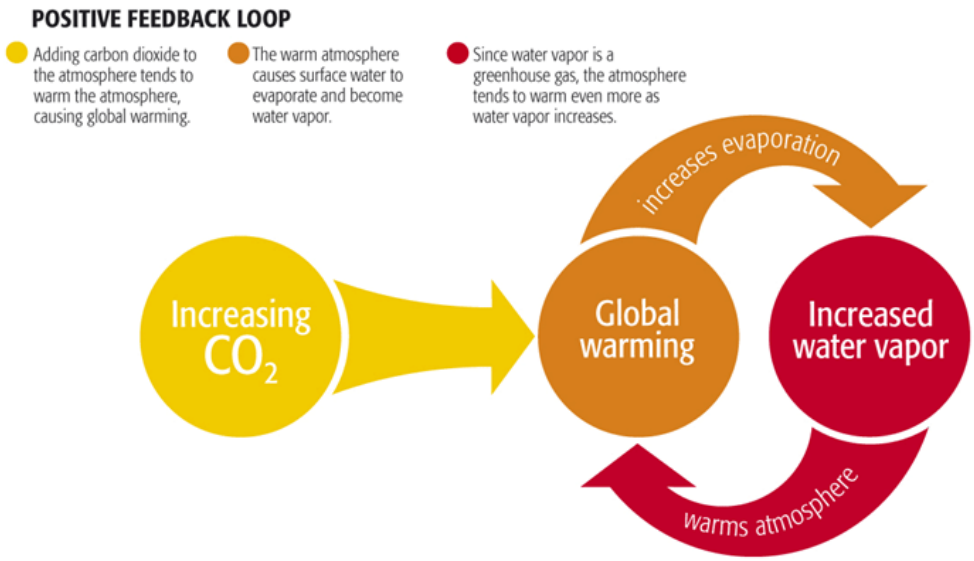


Figure 1.1.2 The diagram showing the greenhouse effect by carbon dioxide and its positive feedback.[36]

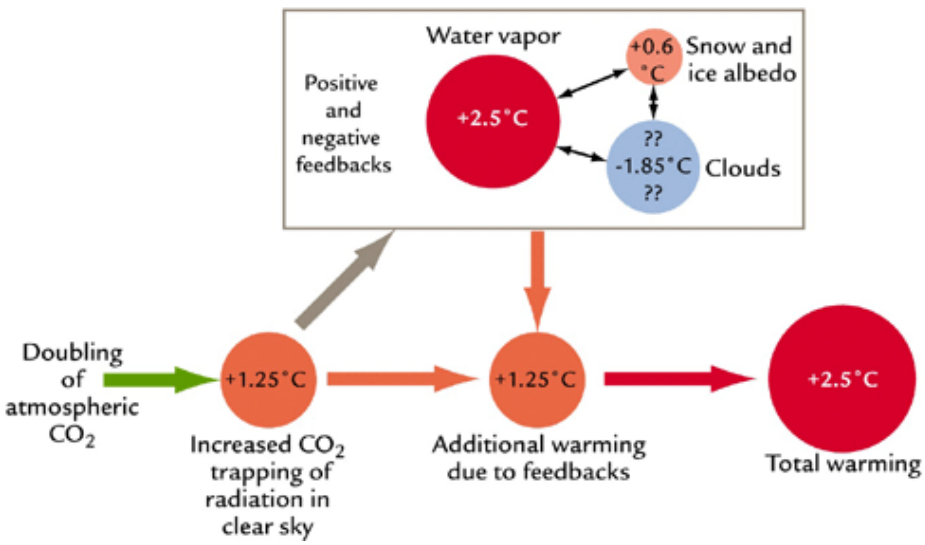


Figure 1.1.3 The level of positive feedback effect on global warming by greenhouse gas and carbon dioxide. [36]

1.2 Attempts to Lower Atmospheric Carbon Dioxide

Later, many countries, organizations and individuals have realized that the global warming was actually happening and the cause for that was mostly man-made carbon dioxide emissions. Regarding this international environmental crisis, the United Nations Framework Convention on Climate Change (UNFCCC) proposed an international treaty to reduce greenhouse gas emissions and eventually to put a stop to the global warming. Fortunately, the treaty was adopted in Kyoto, Japan on 11th December 1997 and 192 parties and countries participated. Then, the next commitments were announced in Doha, Qatar on 21st December 2012 and in Paris, France on 28th November 2016.

Similarly, the Intergovernmental Panel on Climate Change (IPCC) proposed a global climate assessment in 2007 hoping that people could effectively cut down the amount of carbon dioxide produced. The panel discouraged the use of aerosol and investigated the changing trend in land use by people. By measuring the abundance of the greenhouse gases and other climate-changing factors, it could find out the human-induced factors and the level of their influences on the global warming phenomenon. In the figure 1.2.1, carbon dioxide, methane, halocarbons and tropospheric ozone are the most important artificial factors that contribute toward global warming. Methane is one of the fossil fuels and carbon dioxide is a common

product after combusting fossil fuels. Both halocarbons and tropospheric ozone are produced because of industrialization and air pollution.

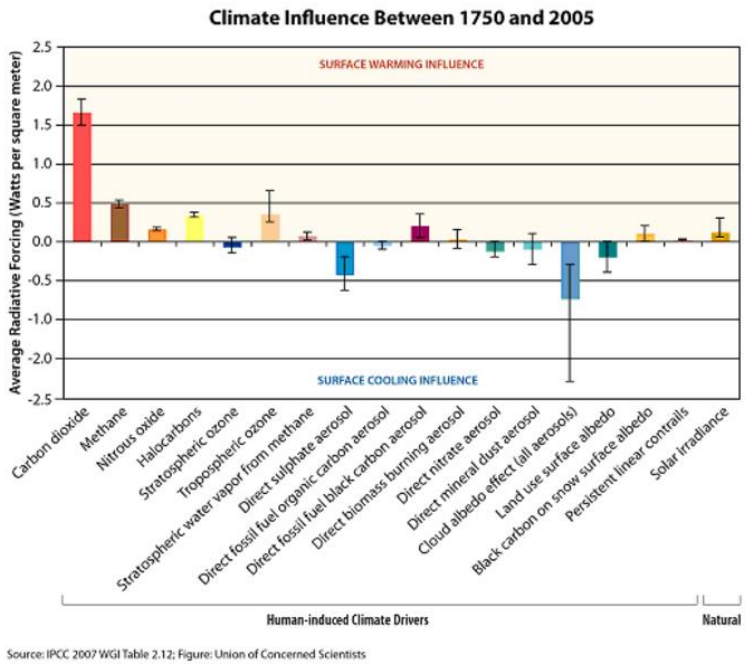


Figure 1.2.1 The list of human-induced climate drivers and their contribution to climate change.[37]

There are many efficient practices that aim to lower the atmospheric carbon dioxide by cutting down the consumption of carbon-based fuels. Indeed, the concerns about global warming is growing too fast that efforts to reduce the carbon dioxide emission is almost mandatory. Thus, politicians encourage both domestic and international firms to produce less carbon dioxide and environmentalists try to raise the awareness on how serious the global warming is and what individuals could possible do to prevent or slower the process. However, just cutting down the carbon dioxide emission can never be an ultimate solution to global warming.[30]

Therefore, scientists try to come up with more fundamental and actual solutions to the problem rather than campaigning. They want to reduce the amount of carbon dioxide in the atmosphere by producing other useful chemicals via chemistry or electro-chemistry, chemical or electro-chemical utilization of carbon dioxide. Additionally, they could try to physically or chemically capture the carbon dioxide molecules in the atmosphere and sequestrate the captured material in safe and stable places such as land or under the ocean, carbon dioxide capture and sequestration.

The first attempt to lower the atmospheric carbon dioxide content is called utilization of carbon dioxide or chemical/electrochemical conversion. It often tries to reduce the carbon dioxide molecules and produce the oxidized forms of carbon dioxide like methane or methanol. This method is widely studied because it is

expected to be the most original and effective as it actually converts carbon dioxide into something useful. There are tons of researches trying to find a way to reduce carbon dioxide and produce useful fuels or products so that the human beings can regulate the carbon cycle just like they do on the nitrogen cycle using the Haber Process. However, none of the techniques studied and developed so far are efficient or economic enough to be applied in everyday life.

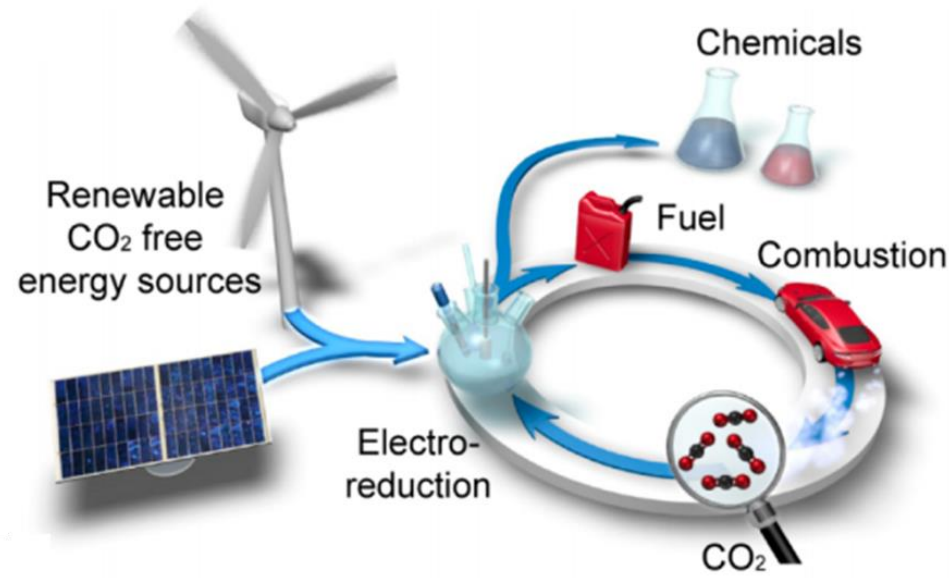


Figure 1.2.2 Electrochemical reduction of carbon dioxide coupled to renewable electricity sources, such as wind or solar, can potentially enable a CO_2-neutral energy cycle in which CO_2 is converted to fuels and industrial chemicals in a renewable and sustainable manner.[34]

The second method for reducing the atmospheric carbon dioxide would be carbon capture and sequestration. The process is consisted of the two steps: capture and sequestration. The technique captures the carbon dioxide chemically or physically with a special chemical or material and bury the captured form under the ocean or the ground. Then, the carbon dioxide in the atmosphere would be reduced and kept in the safe place as long as the material is not exposed to any physical or chemical changes. Nonetheless, this method is not as efficient as the utilization because it cannot be done in a large scale, costs too much, carries too much risks, and takes much time.

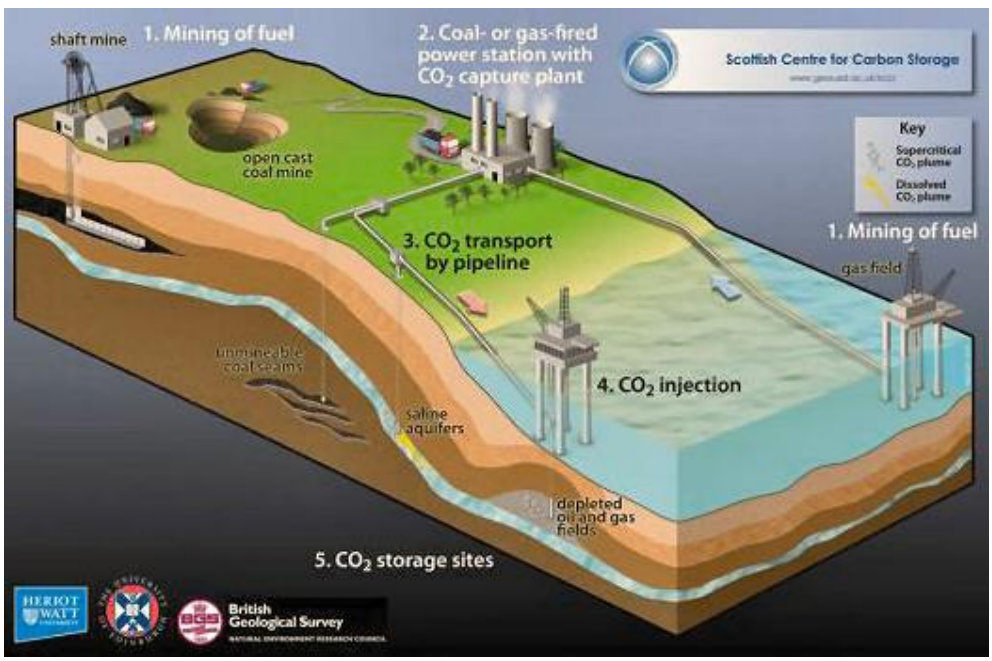


Figure 1.2.3 The diagram showing the steps of carbon capture and sequestration[38]

1.3 Quantitative Measuring and Monitoring of Carbon Dioxide

Compared to the time and resources allocated to researches for utilization of the atmospheric carbon dioxide, too little effort has been made on measuring and monitoring the amount of carbon dioxide accurately. In order to apply the utilization technique of carbon dioxide appropriately, the ability to measure or monitor the carbon dioxide gas should be accurate too. Actually, the concentration of carbon dioxide gas is widely used in so many fields as indicators that distinguish between safe and dangerous.

In the field of personal healthcare, the concentration of carbon dioxide is much more useful than it would seem in everyday life. For one person's inhaled and exhaled breath, the composition of each gas is different and the carbon dioxide content is worthwhile to be monitored. For healthy people, the difference between the arterial blood and the expired carbon dioxide gas partial pressure should be very small. If not, the subject is highly likely to have either lung disease or congenital heart disease and this could be easily noticed by using capnography, monitoring the concentration or the partial pressure of carbon dioxide in the respiratory gases. Then, the diseases could be easily treated as they could be discovered in the early stage.

The capnography measures the amount of carbon dioxide by using non-

dispersive infrared (NDIR) sensor. The spectroscopic method detects carbon dioxide in a gaseous environment by measuring its characteristic absorption in the infrared region. The more the carbon dioxide molecules, the greater the absorption. This technique is advantageous as it is long-term stable, accurate, fast and as sensitive as 20 ppm. However, it is too costly as initial installation requires many expensive and expandable parts and maintenance. Also, its full set-up often occupies too much space and therefore inconvenient.

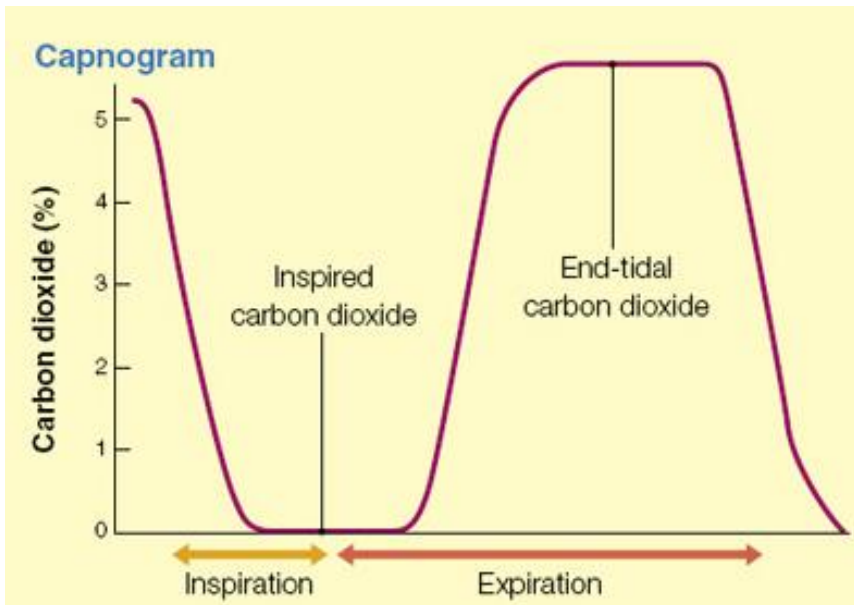


Figure 1.3.1 The capnogram showing the difference in carbon dioxide concentration between inspiration and expiration.[39]

In the meanwhile, an electrochemical carbon dioxide sensor is generally feasible in aqueous solutions and is used in the industrial and academic fields. The Severinghaus electrode is a glass electrode covered by a membrane only permeable to carbon dioxide but not water or electrolyte. When dipped in the liquid or gaseous sample, it measures the partial pressure of carbon dioxide gas based on the pH of the bicarbonate solution. This technique is widely employed in the field of electrochemistry as its response time is few minutes faster than NDIR sensor and more accurate, 10 to 20 ppm scale. However, it also has some holdbacks; the membrane should be kept away from any physical stress and contaminants so stability and hygiene of the system is extremely important. Plus, the measurement of carbon dioxide is not direct as it actually calculates the whole concentration using the partial concentration of the bicarbonate form.

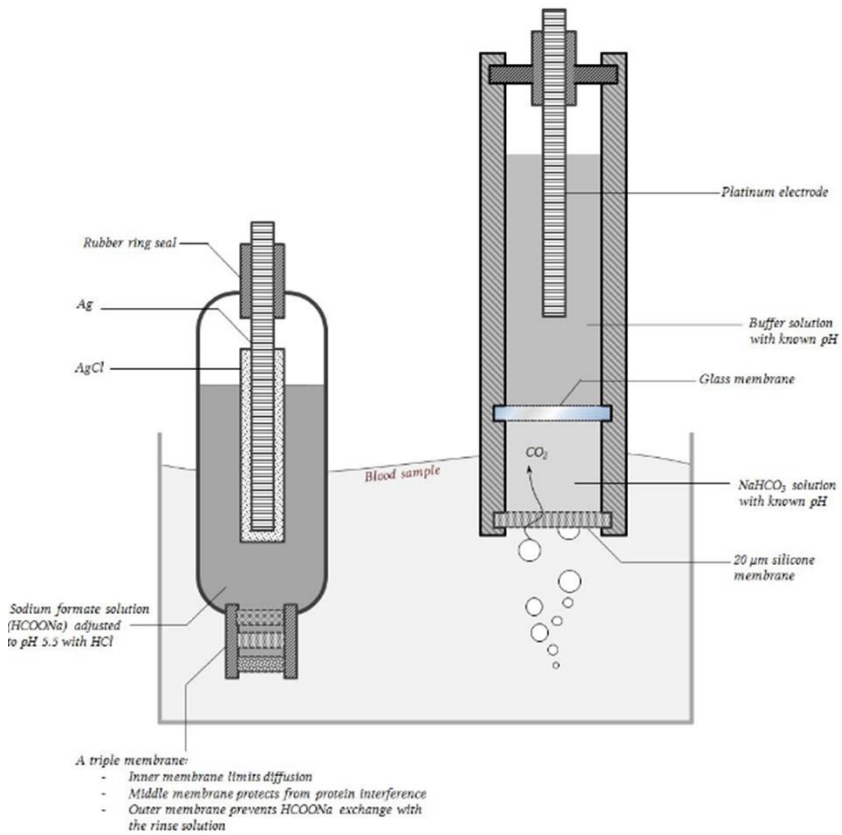


Figure 1.3.2 The capnogram showing the difference in carbon dioxide concentration between inspiration and expiration.[39]

1.4 New Type of Carbon Dioxide Sensor

Typically, carbon dioxide sensors have used a pH-sensitive chemical indicator and detected the change in pH of the system due to the dissolved forms of carbon dioxide.[16] Then, the measurement of carbon dioxide would be indirect and therefore an accountable error could be resulted from even the slightest random errors during the process.

In order to solve this problem, the measuring should be done directly and this could be achieved by using the CO_2-philic molecules bind with carbon dioxide molecules.[32] In other words, a new type of carbon dioxide sensor should have a direct selectivity toward carbon dioxide by employing the molecules or the functional groups that readily bind with carbon dioxide. Then the system would be able to measure the concentration of carbon dioxide based on the concentration of the bound species.

Just like pH papers or litmus papers, it would be very convenient if the concentration of a target chemical could be easily estimated with a glance. In fact, colorimetric sensors could be the best fit here; it is fast, convenient, and economical. Furthermore, it is actually clever because transfer of protons is easy and fast but not that easy and fast.[23] So the change in color of the system can be observed as a result of moving protons.

In the Figure 1.4.1, diethylethanolamine (DEEA) was protonated by the dye, cresol red, and the color of the system became purple as the dye donated its proton to DEEA. When carbon dioxide was introduced to the system, DEEA bound itself with the carbon dioxide molecules and gave back the proton to the dye resulting in a color change to yellow from purple. The analogous phenomenon could also be observed in the Figure 1.4.2; the system of DEEA and phenol red changed its color from red to orange in response to addition of carbon dioxide.[33]

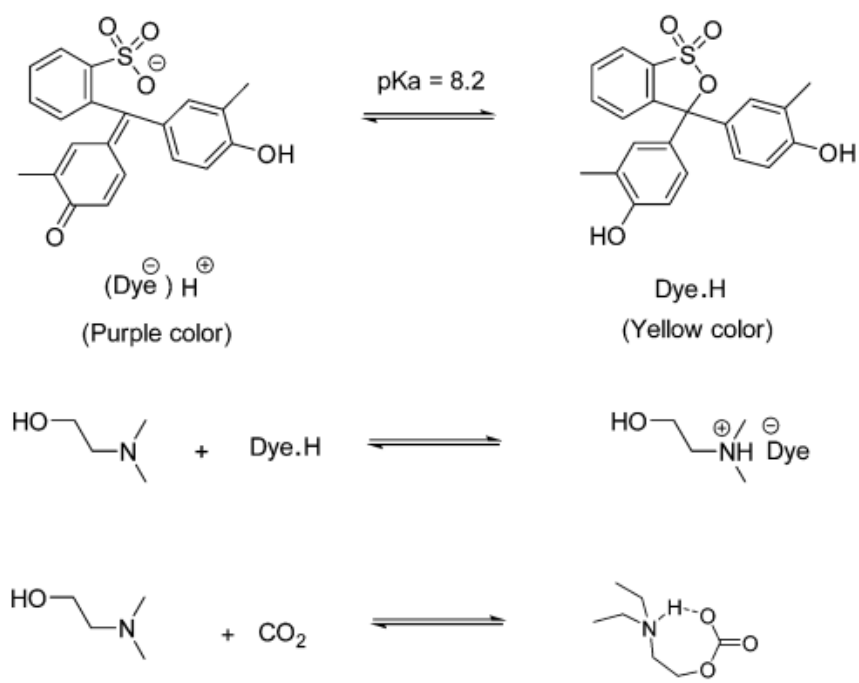


Figure 1.4.1 The proposed reaction sequence which allows the colorimetric response of a pH sensitive dye such as cresol red (CR) to carbon dioxide.[33]

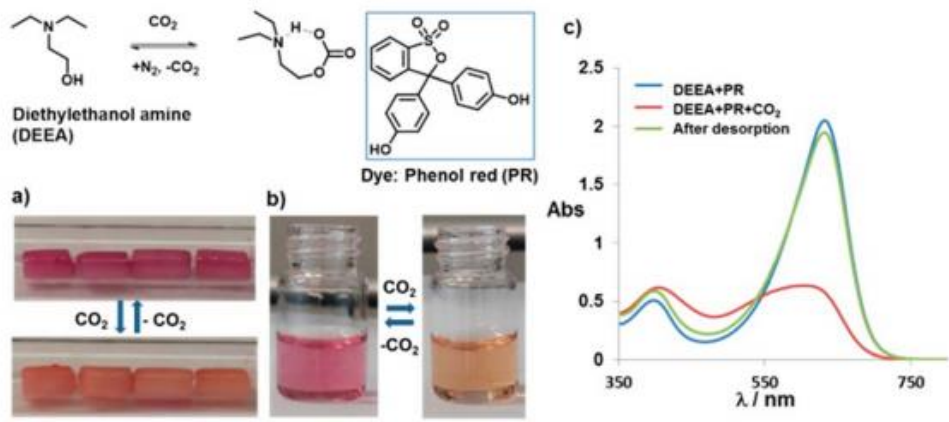


Figure 1.4.2 The observed colorimetric responses of pH sensitive phenol red dye in diethylethanolamine (DEEA) to a flow of pure carbon dioxide at ambient temperature. The color changed from purple to yellow.[33]

However, the ability to easily bind with carbon dioxide molecule is not the only requirement; the binding process should be reversible in relatively mild conditions. If the binding process is almost irreversible, the detection process would not be measuring the concentration of carbon dioxide any more but capturing carbon dioxide. Then, it would be very difficult to recycle the CO_2-bound system and the cost would not be as low as it should be. Also, if and only if the system could establish an equilibrium with a given concentration of carbon dioxide, preferably near its atmospheric one, the system would be more applicable and feasible in everyday use.[27]

Chapter 2. Quinizarin and TBD System

2.1 Experimental

2.1.1 Materials

For the colorimetric sensing system, 1,4-Dihydroxy anthraquinone (Quinizarin, $C_{14}H_8O_4$, >95%) and 1,5,7-Triazabicyclo-[4.4.0]dec-5-ene (TBD, $C_7H_{13}N_3$, >98%) were purchased from TCI. Also, other bases were used for the analogous system instead of TBD.

1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU, $C_7H_{13}N_3$, 98%) was purchased from Sigma-Aldrich, 7-Methyl-1,5,7-triazabicyclo[4.4.0]dec-5ene (MTBD, >95%) was purchased from TCI, and finally piperidine ($C_5H_{11}N$, 99%) was purchased from DAEJUNG Chemicals and Metals.

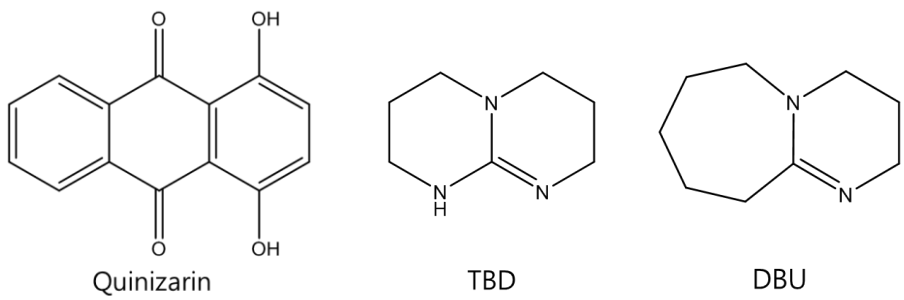


Figure 2.1.1 Chemical Structures and names of the materials

2.1.2 Preparation

The two commercially available chemicals, quinizarin and TBD, were dissolved in acetonitrile to yield each solution. The maximum solubility of quinizarin in acetonitrile is 10 mM concentration. In search of an optimal concentration, any concentration higher than 1 mM was too insensitive to carbon dioxide and took unrealistically long time to observe a color change in common situations, lower than 10,000 ppm of carbon dioxide. On the other hand, any concentration lower than 0.1 mM was too sensible and its color was too dim to be noticed. Therefore, the ideal concentration for the best-working system was set between 0.1 and 1.0 mM quinizarin solution and so was the TBD solution knowing that the molar ratio was one to one.

Then, highly pure argon gas was purged to each solution for 5 minutes to minimize the volume of atmospheric carbon dioxide dissolved in the solutions. The two solutions were mixed together to yield a mixture containing 0.5 mM of each solute. Since both the TBD solution and the mixture readily reacts with the atmospheric carbon dioxide over time, a minimum volume should be prepared for each occasion and should not be stored for later use. The same goes for other bases, especially DBU and MTBD.

When preparing solutions with other bases (DBU, MTBD, and piperidine),

taking density into account is really important because the three bases are liquid.

2.2 Characterization

2.2.1 Ultraviolet-Visible (UV-VIS) Spectroscopy

The UV-VIS spectrum were obtained by using an UV-VIS-NIR spectrophotometer (Cary 500 UV-VIS-NIR, Agilent Technologies). The solvent used for each analysis was acetonitrile (99.8% pure for HPLC) from DAEJUNG Chemicals & Metals.

In the Figure 2.2.1, the quinizarin solution originally had an absorption band at 461 nm and its color was orange yellow, while the TBD solution had no absorption band in the visible region and therefore its color was transparent. However, the quinizarin and TBD mixture had a purple color and its absorption band was observed at 560 and 601 nm.

The reason for the change in color as a result of shift of the band was deprotonation of quinizarin by TBD. Because the TBD solution did not have any absorption band in the visible region whereas the quinizarin solution did, the origin of the color would be the quinizarin solution. Indeed, the positions of the absorption bands of quinizarin were well-known as seen in the table 2.2.1; its neutral form has an absorption band at about 460 nm and the anionic form has one at about 570 nm.

In the Figure 2.2.1, the red-shift was clearly seen from 460 nm to 560 and

601 nm and the positions of the absorption bands well match those of the corresponding forms of quinizarin in the literature[1]. Therefore, the change in color of the solution was caused by the deprotonation process of quinizarin by TBD given the evidence of the shift of the absorption band.

Also, the two bands for the monoanionic forms of quinizarin at 560 and 601 nm could be explained by tautomerism of the monoanionic quinizarin. In the Table 2.2.1, the structures of the two possible tautomers of the monoanionic quinizarin were shown as a result of electron push mechanism and resonance structures.[21]

Then, the prepared system, a mixture of quinizarin and TBD, had a color of purple and its absorption bands were seen at 560 and 601 nm as quinizarin was deprotonated by TBD. In the Figure 2.2.2, however, the quinizarin molecules were re-protonated and therefore its absorption band shifted back to 460 nm when carbon dioxide gas was blown to the system.

The reason for the blue-shift was that the TBD molecules had to bind with the incoming carbon dioxide molecules and therefore had to release the protons they took from the quinizarin molecules. So the quinizarin molecules were re-protonated and as a result, the color of the solution turned back to yellow, absorption band at 460 nm.

Afterwards, the binding process between TBD and carbon dioxide was reversed by purging argon gas and applying some heat with a heat gun to the system.

As seen in the Figure 2.2.3, the detachment of carbon dioxide from the TBD molecule was easily achieved at over 40℃ within a couple of minutes. As a result of the detachment of carbon dioxide, the TBD molecule became capable of taking a proton from the quinizarin molecule and the color of the system turned back to purple, absorption band at 560 and 601 nm.[31]

Interestingly, the system could undergo the whole cycle again and actually its reversibility still remained up to 20 cycles. However, the intensity of the color dimmed away as the process was repeated and it could be also seen in the Figure 2.2.2 since the absorbance slightly decreased after the system was re-newed with Ar gas and hea. Hence, the recommended number for re-use should be between 5 and 10 cycles.

In the next step, the stoichiometric ratio between the quinizarin and the TBD molecules was studied by using a different amount of TBD equivalence in terms of quinizarin. In the Figure 2.2.4, the systems with 1 equivalent TBD showed no difference in absorbance and the band just shifted to the left when carbon dioxide was added. In the Figure 2.2.5, the same phenomenon was observed for the system with 2 equivalent TBD; the intensity of the absorption band barely changed.

On the other hand, the system with 0.5 equivalent TBD showed a difference in the Figure 2.2.6. It showed two absorption bands for both neutral and monoanionic forms of quinizarin because only a half ratio of TBD was present in the system and

only a half of quinizarin was deprotonated. Yet, the absorption band at 560 and 601 nm disappeared when carbon dioxide was purged because all the quinizarin molecules were re-protonated and the absorption band shifted back to 460 nm. Thus, a half of quinizarin stayed at its neutral form not being deprotonated, an absorption band at 460 nm, while the other half was protonated and caused an absorption band at 560 and 601 nm.

In the Figure 2.2.7, the three systems were plotted together for comparison and it could be clearly seen that the de-protonation of quinizarin by TBD was one to one ratio.

In conclusion, the two things were learned from UV-VIS spectroscopy. Firstly, the color of the solution was dependent on the electronic forms of quinizarin. Secoundly, the ratio between quinizarin and was found to be one to one.

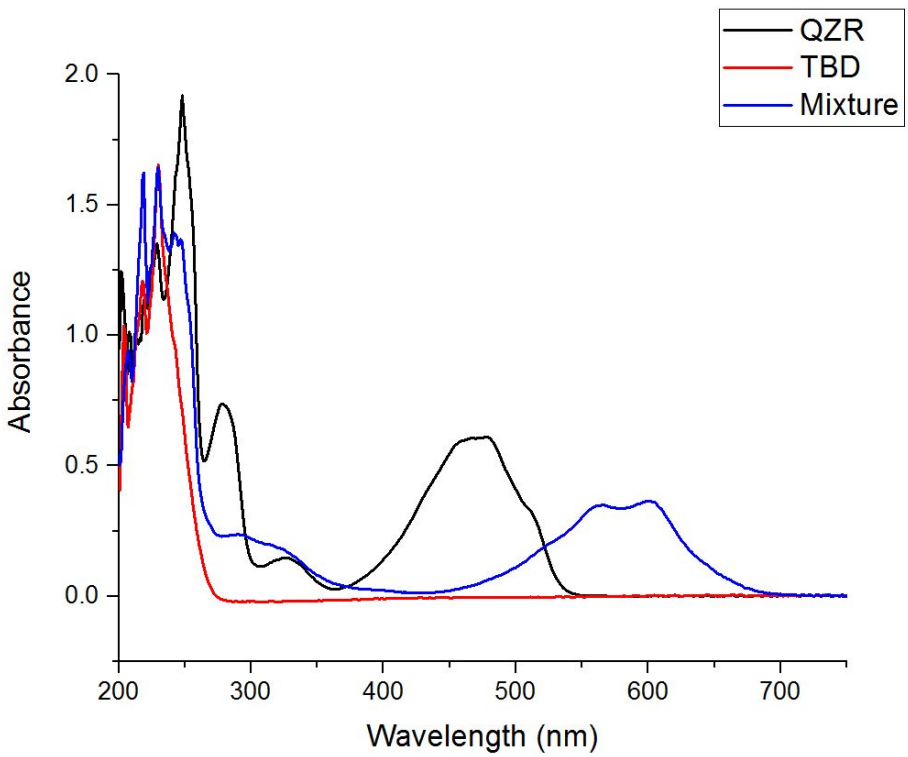
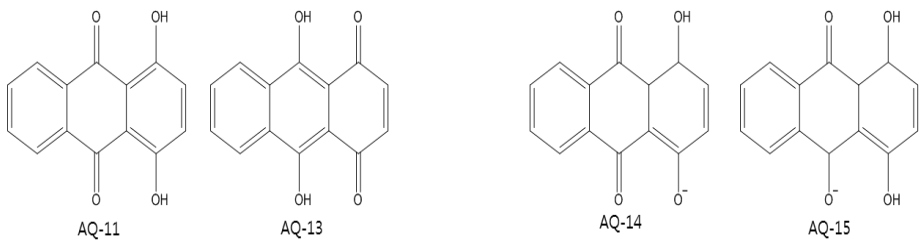


Figure 2.2.1 UV-VIS spectrum of Quinizarin, TBD, and the mixture in CH_3CN



Compounds	ΔG^{taut}	P	λ_{max} [f]		Exp. [21]
	X		PBE0	B3LYP	
Neutral					465
AQ-**11**	0.0	1.0	455 [0.23]	468 [0.22]	
AQ-**13**	6.14	0.0	496		
Monoanionic					540
AQ-**14**	0.0	1.0	554 [0.20]	570 [0.19]	
AQ-**15**	2.26	0.0	569		
Dianionic					594
AQ-**16**	-	-	550 [0.29]	564 [0.27]	
MAE					

Table 2.2.1 Positions of the absorption bands of the different forms of quinizarin[21]

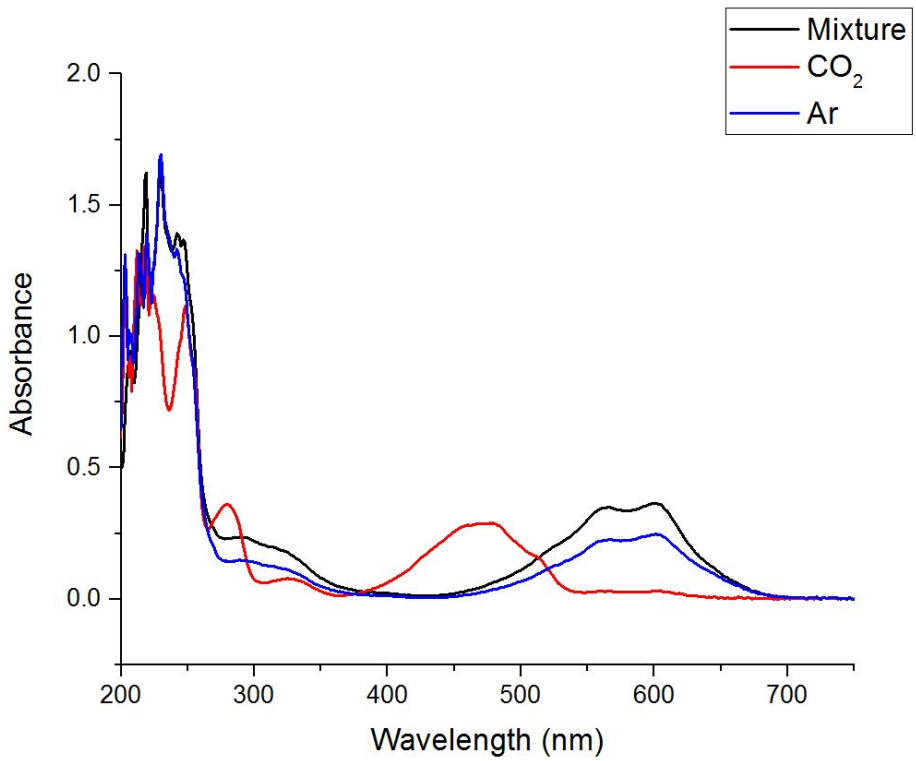


Figure 2.2.2 UV-VIS spectrum of the mixture in CH_3CN in its original condition, after CO_2 purge, and after Ar purge in that order

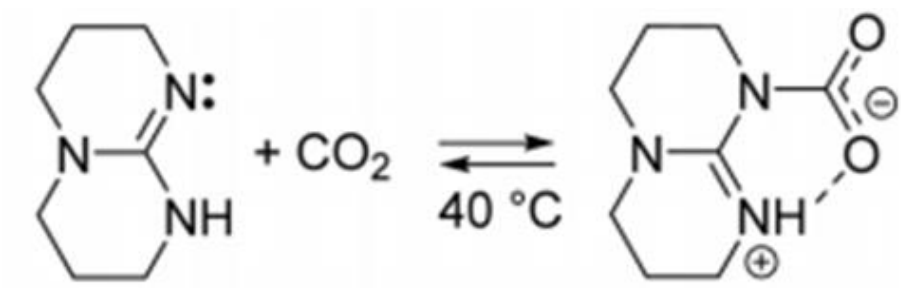


Figure 2.2.3 Reversible chemical binding between TBD and CO_2.[4]

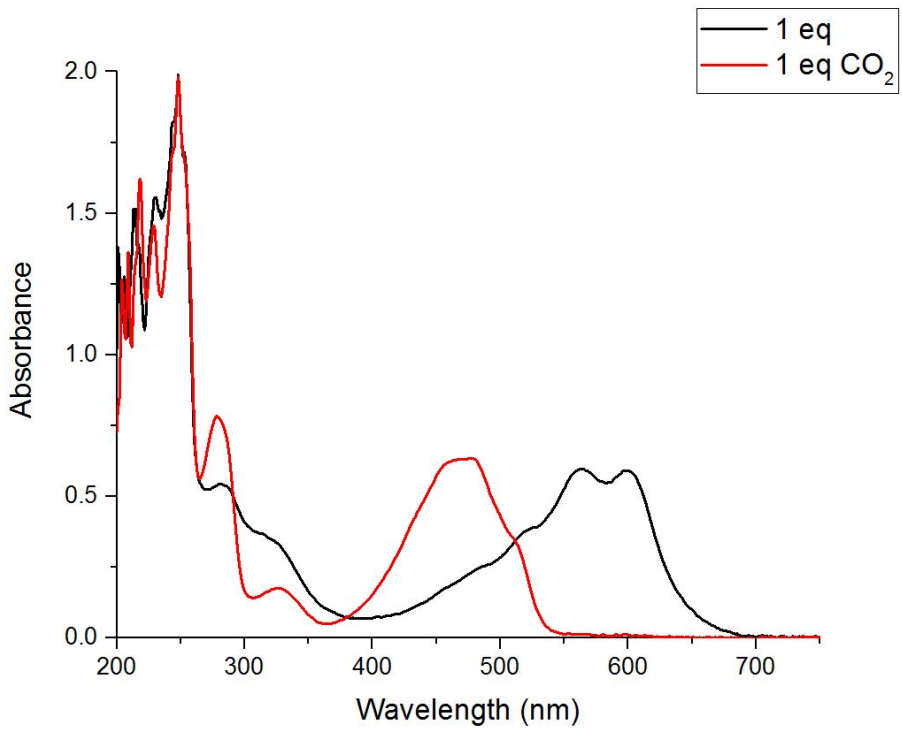


Figure 2.2.4 UV-VIS spectrum of the mixture in CH_3CN before and after CO_2 purge where TBD is 1 equivalent

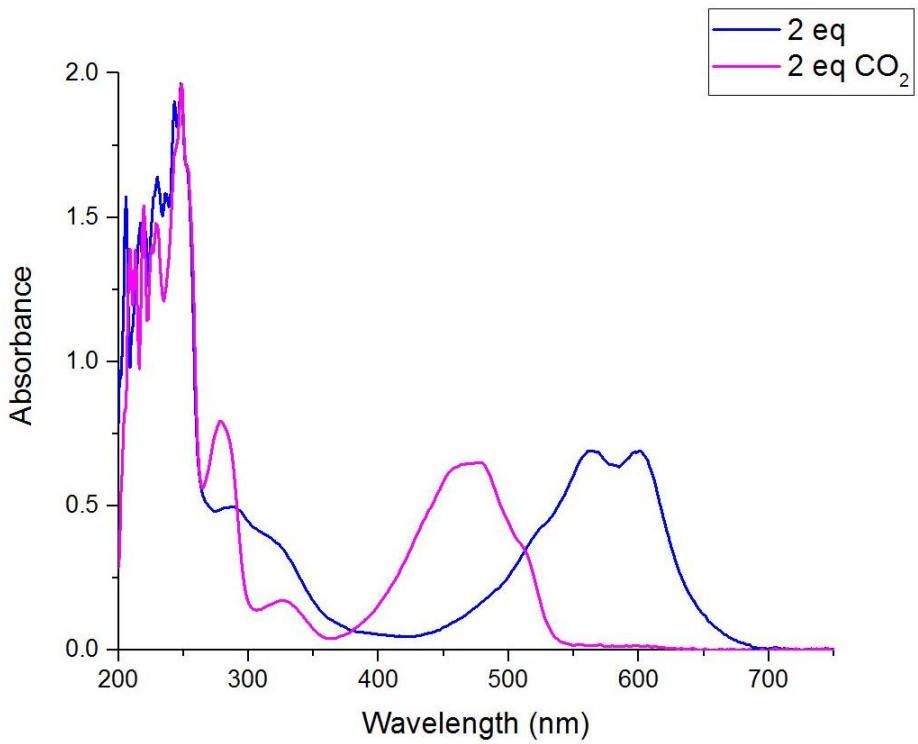


Figure 2.2.5 UV-VIS spectrum of the mixture in CH_3CN before and after CO_2 purge where TBD is 2 equivalent

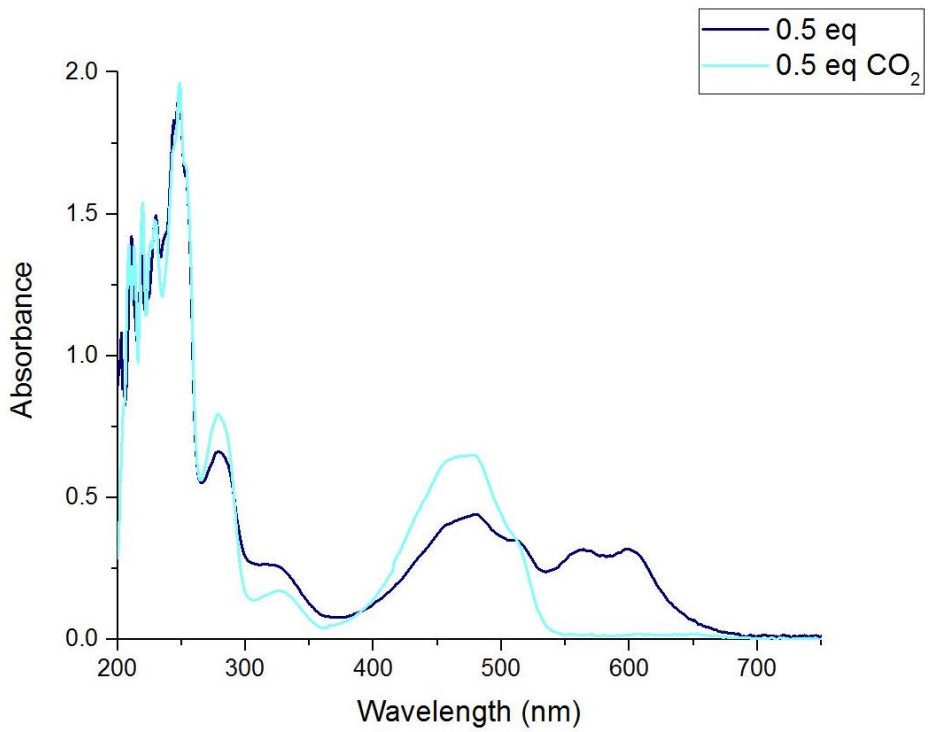


Figure 2.2.6 UV-VIS spectrum of the mixture in CH_3CN before and after CO_2 purge where TBD is 0.5 equivalent

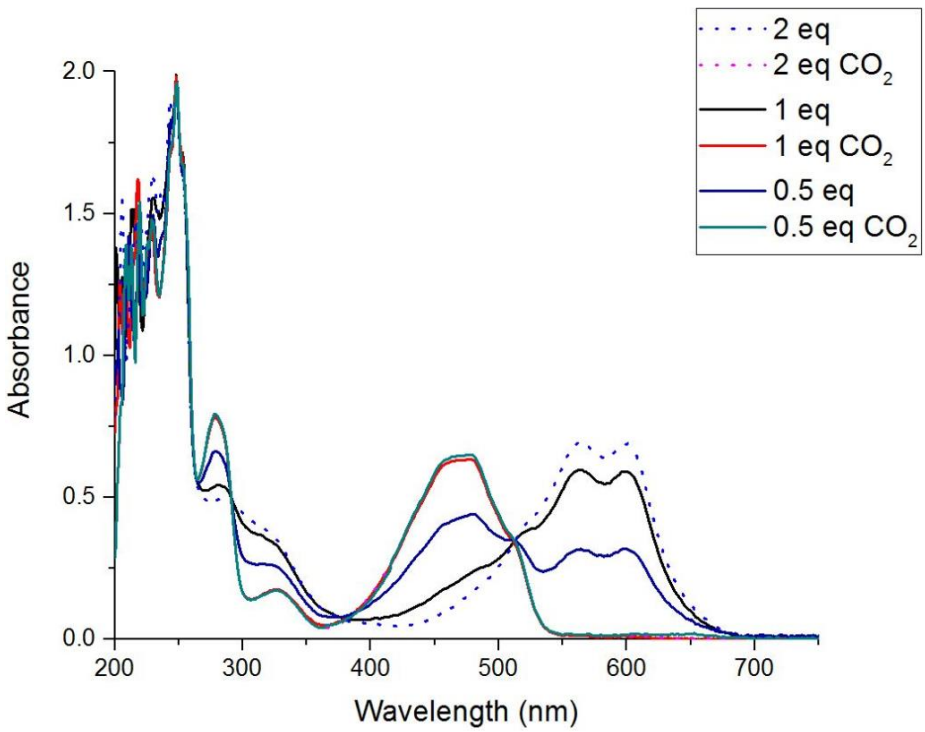


Figure 2.2.7 UV-VIS spectrum of the mixture in CH_3CN before and after CO_2 purge where TBD is 0.5, 1 or 2 equivalent

2.2.2 Nuclear Magnetic Resonance (NMR) Imaging

The NMR spectrum were obtained by using a 400 MHz NMR spectrometer (JNM-LA400 with LFG, Jeol) for ^{1}H-NMR spectrum and a 600 MHz high resolution NMR spectrometer (AVANCE 600, BRUKER) for ^{13}C and ^{15}N – NMR spectrum. The solvent used for ^{1}H-NMR was deuterated water and for ^{13}C and ^{15}N-NMR deuterated water was used (both solvents >99%, Euriso-top).

In the Figure 2.2.8, the ^{1}H-NMR spectra of pure quinizarin solution in deuterated acetonitrile after Ar purge was obtained. The quinizarin molecule had 4 peaks and this meant that there are 4 different chemical environments for the hydrogen atoms. Each hydrogen environment was labelled and the locations were shown in the structure; H_a was at 7.3 ppm, H_b was at 7.9 ppm, H_c was at 8.3 ppm and H_d was at 12.8 ppm. The most important hydrogen environment for quinizarin was the hydroxyl proton, H_d, because it is the one that would be deprotnated by TBD when mixed together.

In the Figure 2.2.9, the ^{1}H-NMR spectra of pure TBD solution in deuterated acetonitrile after Ar purge was obtained. The TBD molecule had 3 peaks and there should be 3 different chemical environments. Actually, the TBD molecule should have 4 different chemical environments for its hydrogen atoms as labelled in its chemical structure but the H_D was not observed in the spectra. So, there were only 3

peaks were shown; H_A caused a triplet at 3.0 ppm, H_B caused a pentet at 1.7 ppm, and H_C caused a triplet at 2.9 ppm.

The reason why the TBD had only 3 peaks and H_D was not seen was that the proton from the amine group rapidly goes through a deuterium exchange and deuterium is ^{1}H-NMR inactive. In order for an atom to be NMR active, it should be able to generate its own magnetic field or magnetic moment. In order to do that, an atom should have an odd number of protons and/or neutrons in its nuclei. However, a deuterium, ^{2}H or ^{2}D, has two subatomic particles, one proton and one neutron, so it is not NMR active. In this case, the deuterium from the solvent is rapidly replaced by the amine proton from the TBD molecule repeatedly and thus the amine proton almost feels like as it is a deuterium that is NMR inactive. The Figure 2.2.10 is an example where TBD underwent a deuterium exchange process with a deuterated solvent, $CDCl_3$ [3].

In the Figure 2.2.11, the ^{1}H-NMR spectra of quinizarin and TBD mixture in deuterated acetonitrile after argon purge was obtained. All the hydrogen peaks appeared at where they used to with slight variations as in pure solutions except for H_d. The hydrogen from the hydroxyl group of quinizarin, H_d, originally appeared at about 12.8 ppm but it was gone in the mixture. This was a strong evidence that the hydroxyl proton from quinizarin was deprotonated by TBD in the mixture. However, there was still no sign of the amine proton in the mixture because the protons

belonging to the amine group of TBD was readily exchanged with the ^{1}H-NMR inactive deuteriums from the solvent.

In the Figure 2.2.12, the ^{1}H-NMR spectra of quinizarin and TBD mixture in deuterated acetonitrile after carbon dioxide purge was obtained. In the spectra, all the previously observed peaks appeared at where they should and most importantly, the hydroxyl proton peak reappeared at near 10 ppm. In fact, the hydroxyl proton of quinizarin originally appeared at around 12.8 ppm but there was a slight shift in the value of the chemical shift.

In the Figure 2.2.13, the ^{13}C-NMR spectra of TBD in deuterated water after Ar purge was obtained. In the spectra, the TBD molecule had 4 different peaks: C_a at 21 ppm, C_b at 39 ppm, C_c at 47 ppm and C_d at 152 ppm. The small noises between 20 and 50 ppm in very low intensity were caused by C-D coupling and could be ignored.

In the Figure 2.2.14, the ^{13}C-NMR spectra of TBD in deuterated water after CO_2 purge was obtained. In the spectra, the TBD molecule had 5 different peaks: C_a at 21 ppm, C_b at 39 ppm, C_c at 47 ppm, C_d at 152 ppm, and C_e at 161 ppm. The important point here was the newly appeared carbon, C_e. Obviously, the new peak was generated at about 11 ppm because the carbon dioxide molecule was attached to the TBD molecule.

In fact, the chemistry of a carbon dioxide adduct form of the TBD molecule

was well studied as shown in the Figure 2.2.3.[1] The binding process of the carbon dioxide molecule onto the TBD molecule can be achieved by simply blowing carbon dioxide gas to the TBD solution even in ambient conditions at RTP.[29] As a result, there was a new peak in the spectra and this well suited the literature too.

For a clearer evidence of the carbon dioxide adduct form of TBD, observing the change in chemical environment of the nitrogen atom before and after carbon dioxide purge was required. Thus, ^{15}N-NMR spectra of TBD solution in deuterated water after argon purge was obtained. Unfortunately, no meaningful spectra was produced due to too low content of isotopic nitrogen atom in the sample.

In conclusion, there were two evidence acquired from NMR spectroscopy. On first, the appearance and disappearance of the hydroxyl proton of quinizarin in ^{1}H-NMR proved that the proton was deprotonated by TBD when mixed and the quinizarin molecule regained the proton as the TBD molecule bound with carbon dioxide when purged with the gas. On second, the existence of the carbon dioxide adduct form of TBD was proven by ^{13}C-NMR as there was a new peak appeared at 161 ppm after purging carbon dioxide gas to the TBD solution.[7]

Figure 2.2.8 ^{1}H-NMR spectra of quinizarin in CD_3CN and its chemical structure with labelled hydrogens

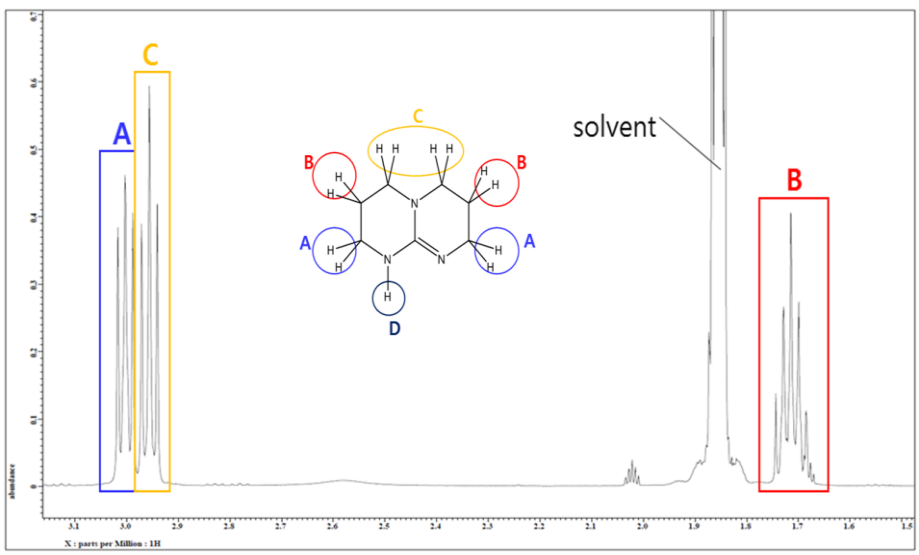


Figure 2.2.9 ^{1}H-NMR spectra of TBD in CD_3CN and its chemical structure with labelled hydrogens

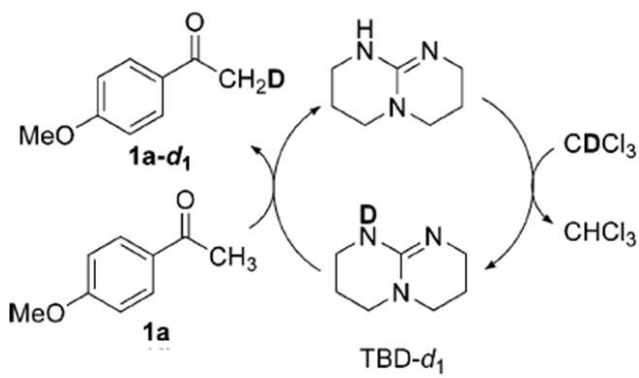


Figure 2.2.10 Deuterium exchange of TBD in deuterated solvent, $CDCl_3$.[40]

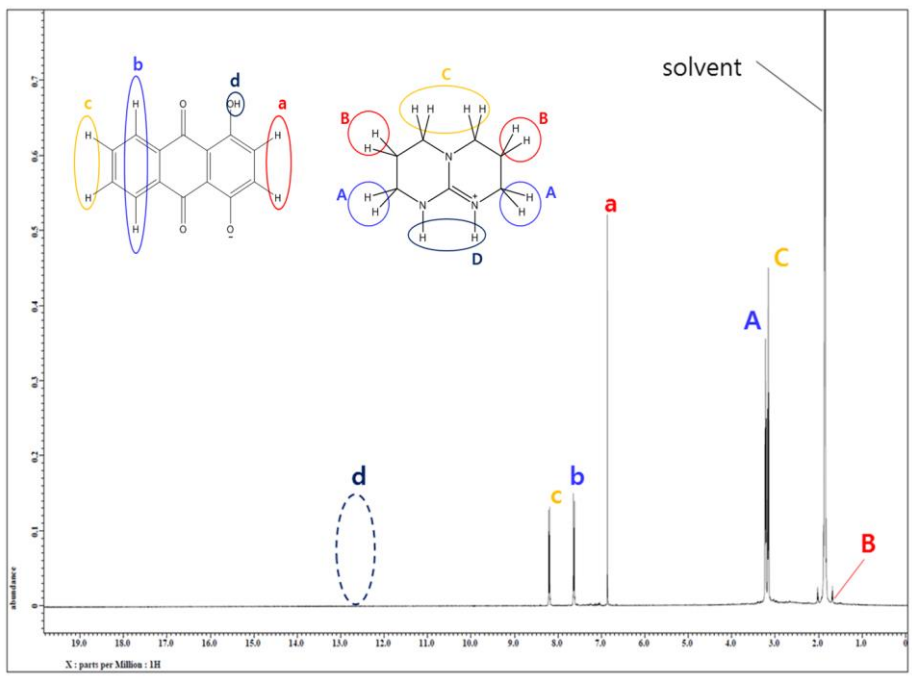


Figure 2.2.11 ^{1}H-NMR spectra of quinizarin and TBD in CD_3CN and their chemical structures with labelled hydrogens

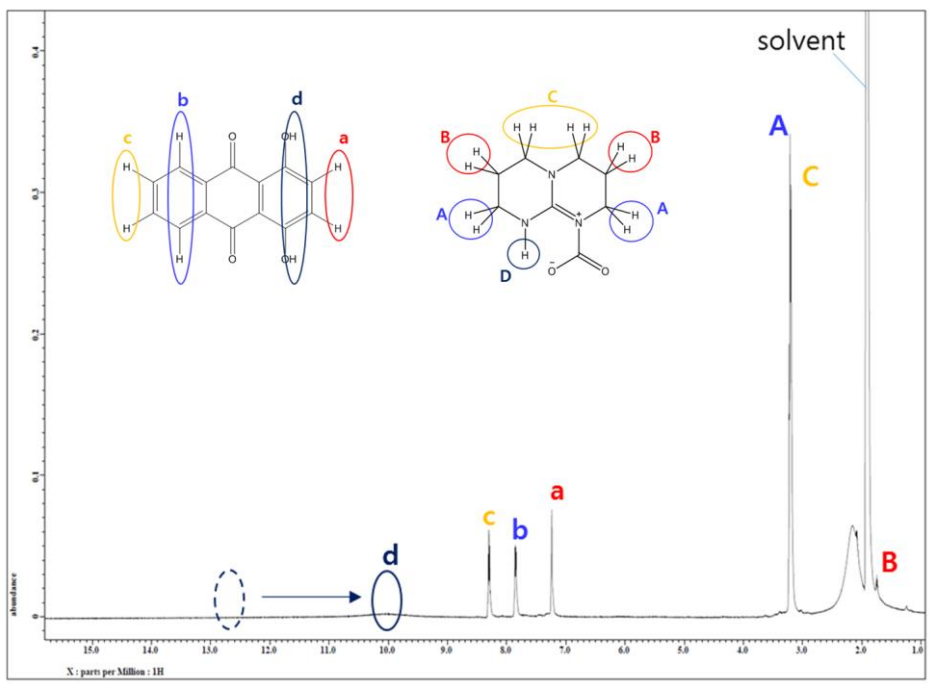


Figure 2.2.12 ^{1}H-NMR spectra of TBD in CD_3CN and their chemical structures with labelled hydrogens

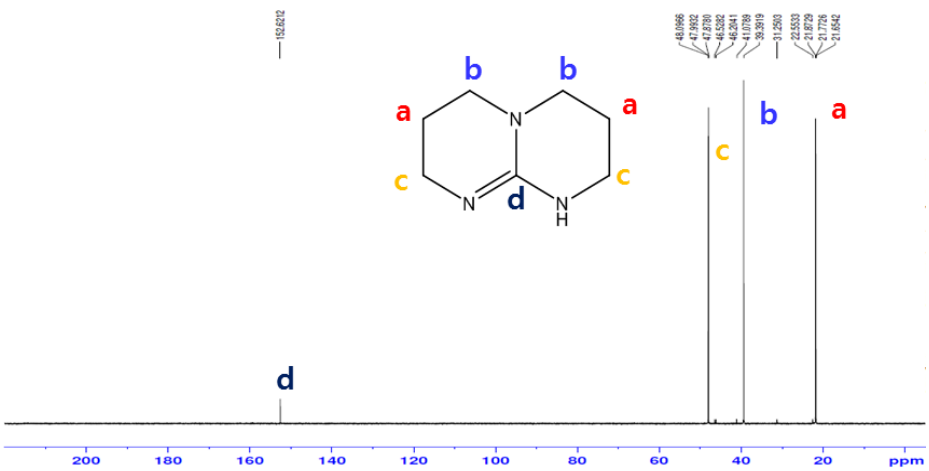


Figure 2.2.13 ^{13}C-NMR spectra of TBD in D_2O and its chemical structures with labelled carbons

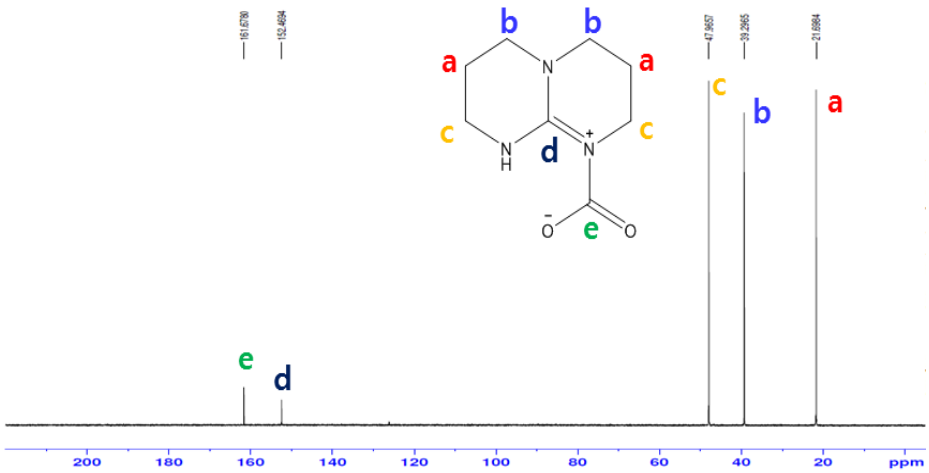


Figure 2.2.14 ^{13}C-NMR spectra of TBD-CO_2 in D_2O and its chemical structures with labelled carbons

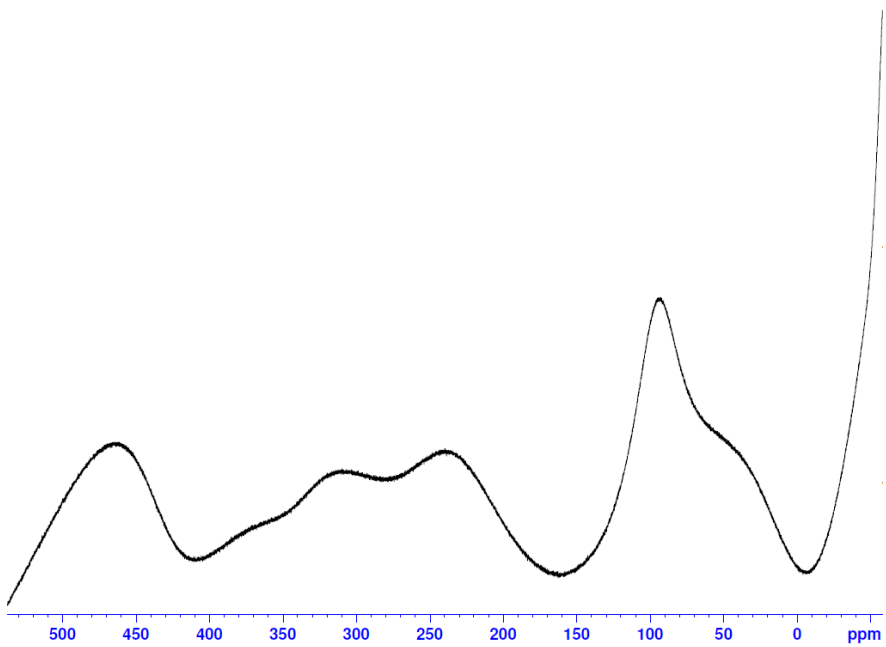


Figure 2.2.15 ^{15}N-NMR spectra of TBD in D_2O

2.2.3 Fourier Transform Infrared (FT-IR) Spectroscopy

The FT-IR spectrum were obtained by using a high resolution vacuum FT-IR spectrophotometer (VERTEX80v, BRUKER) within the wavenumber range of 500 to 4000 cm^{-1}. Each spectra had the resolution of 4 and 32 scans. For ATR (Attenuated Total Reflectance) method, the solid samples were purged with highly pure argon gas before analysis. For KBr pellet method, a couple of drops of the solution were dropped onto the pellet after the solution was prepared and purged with highly pure argon gas.

First, the FT-IR spectrum of the reactant chemicals were obtained by using the ATR method in order to identify the functional groups of the chemicals. In the Figure 2.2.16, the FT-IR spectra of quinizarin crystal was obtained by ATR method. The vibrational mode of O-H bond was observed at 2974 cm^{-1} and this was slightly off the range but relatively well corresponded to the literature value of 3000 - 3300 cm^{-1}. Also, the vibrational mode of C=O bond was found at 1627 cm^{-1} and it was within the suitable range, 1600 - 1800 cm^{-1} too.[6]

In the Figure 2.2.17, the FT-IR spectra of TBD crystal was obtained by ATR method. The vibrational mode of N-H bond was observed at 2814 and 2924 cm^{-1} and they well corresponded to the literature value of 2800 - 3300 cm^{-1}. The splitting could be explained by the resonance structures and the shared charge between the nitrogen

atoms. Also, there were many small peaks appeared over 3000 cm^{-1} region and they were responsible for the vibrational modes of C-H and C-N bonds; they were found at the range of 2900 - 3200 cm^{-1} and 1100 - 1300 cm^{-1} respectively.[17]

With the KBr pellet method, the change in intensity for different functional groups before and after purging carbon dioxide to the mixture system was observed. In the Figure 2.2.18, the FT-IR spectrum of quinizarin and TBD before and after carbon dioxide purge were plotted together for comparison. After purging carbon dioxide to the system, the vibrational mode of N-H bond around 2800 cm^{-1} was decreased since the protonated TBD lost the proton and gave it back to quinizarin. As a result, the vibrational mode of O-H bond at 3200 cm^{-1} was increased as the quinizarin was protonated again. In fact, the TBD chemically bound itself with carbon dioxide and therefore the vibrational mode of C=O bond at 1650 cm^{-1} was increased. On the other hand, the vibrational mode of C-H bonds at 3000 cm^{-1} remained the same indicating that there was no other change.

In conclusion, the two things were proven with FT-IR spectroscopy. Firstly, existence of the important functional groups within the chemicals were confirmed. For quinizarin, the vibrational modes of C=O and O-H bonds were seen and the vibrational modes of N-H and C-N were found for TBD.[18] Most importantly, the quantitative analysis of the increase or the decrease in such functional groups were possible even in an approximate level and the analysis contributed to explanation of

the mechanism.[28] The increase in O-H bond signal around 3300 cm^{-1} and the decrease in N-H bond signal around 2900 cm^{-1} indicated that the quinizarin molecule was re-protonated after carbon dioxide was blown to the system as TBD bound with CO_2. The binding of CO_2 to TBD was also proven by the increase in C-N and C=O bond signals at 1650 and 1150 cm^{-1} respectively.

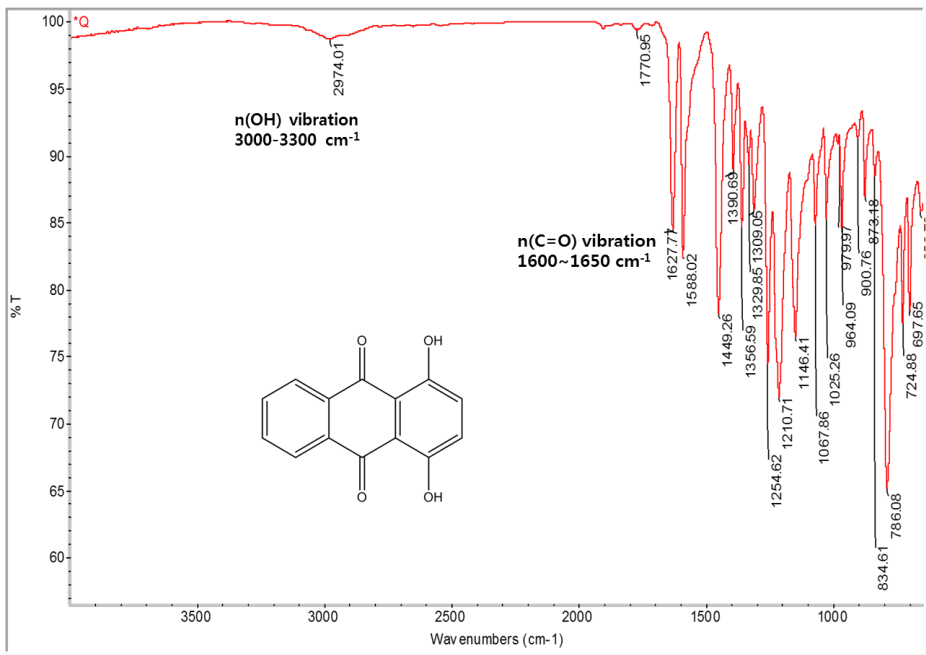


Figure 2.2.16 FT-IR spectra of quinizarin by ATR method

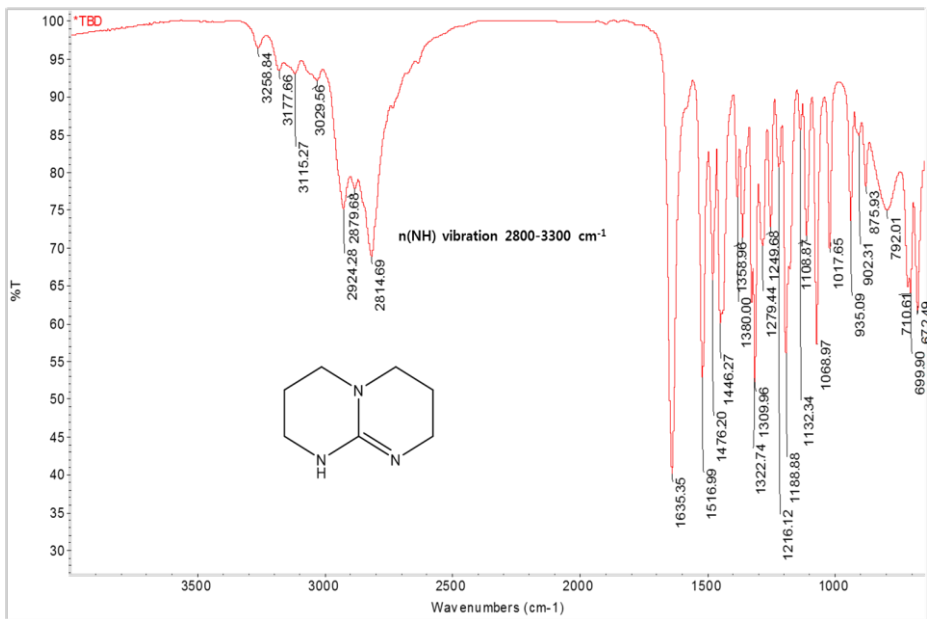


Figure 2.2.17 FT-IR spectra of TBD by ATR method

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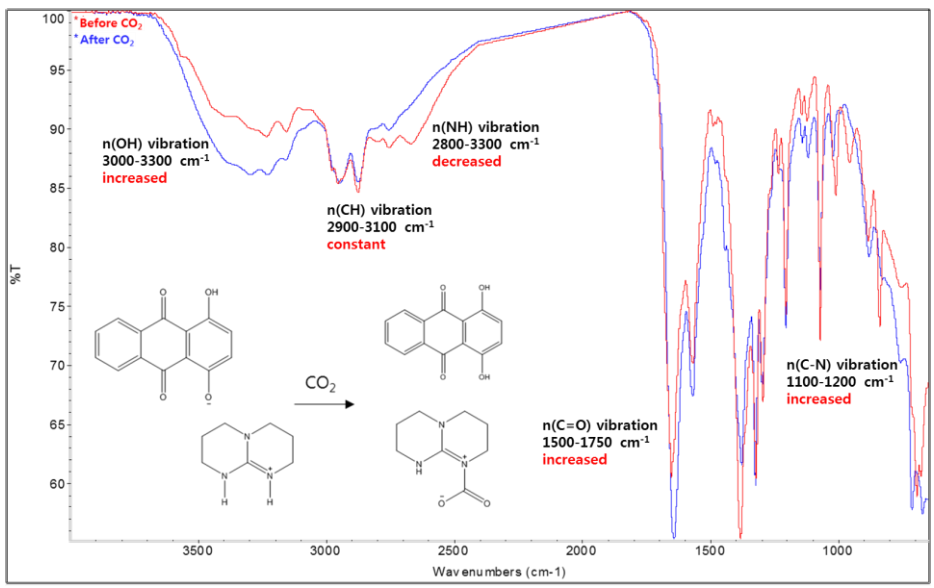


Figure 2.2.18 FT-IR spectra of quinizarin and TBD mixture before/after carbon dioxide purge by KBr pellet method

2.3 Results and Discussion

2.3.1 Interpretation of Data

From UV-VIS spectroscopy, it was learned that the color of the solution came from quinizarin and it was dependent on the electronic forms of quinizarin. To be more specific, the color of the quinizarin solution was orange yellow because the quinizarin molecule was neutral while its color changed to purple when mixed with TBD as a result of deprotonation. So, one molecule of TBD deprotonated a proton from a molecule of quinizarin when mixed and the quinizarin molecule regained its proton when carbon dioxide was purged and bound with TBD.

From ^{1}H-NMR spectrum, the disappearance of a hydroxyl proton peak of quinizarin when mixed with TBD proved that the change in color to purple from orange yellow was caused by the monoanionic form of quinizarin. Also, the ^{13}C-NMR spectrum showed that a new carbon peak was generated at 161 ppm after blowing carbon dioxide gas to the mixture system proved that the stable carbon dioxide adduct form of TBD was produced,[11,12] and the proton was given back to quinizarin as a result.

From the FT-IR spectroscopy, the two things could be supported; the existence of the important functional groups within the chemicals were confirmed

and the change in chemical structures as a result of protonation/deprotonation and attachment/detachment of carbon dioxide. The vibrational modes of C=O and O-H bonds were verified for quinizarin and so were those of N-H and C-N bonds for TBD. Especially, the increase in O-H bond signal around 3300 cm^{-1} and the decrease in N-H bond signal around 2900 cm^{-1} also supported that quinizarin molecule gained its proton back after carbon dioxide was blown to the server.[20] As well, the increase in C-N and C=O bond signals around 1650 and 1150 cm^{-1} respectively well proved that the carbon dioxide adduct form of TBD was formed.

2.3.2 Proposed Mechanism

With all the characterization data, the mechanism of the quinizarin and TBD system was revealed. The color of pure quinizarin solution was orange yellow and its absorption band was seen at 460 nm. After adding a strong organic base, TBD, the quinizarin and TBD mixture had a purple color and its absorption band shifted to 560 and 601 nm. From the previous studies, it was known that the absorption band at 460 nm was responsible for a neutral form of quinizarin whereas the band within 560 to 600 nm was responsible for the monoanionic form of quinizarin.[10,21] Therefore, it could be deduced that the added TBD deprotonated the hydroxyl proton of quinizarin.

In the next step, the mixture was ready to detect carbon dioxide and the TBD molecules readily bound itself with the carbon dioxide molecules present. In return of the binding process between TBD and carbon dioxide, the proton previously detached from quinizarin was returned to its original position and the neutralized quinizarin changed the color of the solution back to orange yellow; the system changes its color from purple to orange yellow when carbon dioxide was purged.

More interestingly, the colorimetric detection process was not a one-time thing but it could be repeated for few times.[24] Application of slight heat over 40℃

for a minute was sufficient to reverse the binding of carbon dioxide molecule and the system could repeat the detection process for a couple of times more.[25] With both heat and argon purge, the whole detection process could be repeated more than 10 times without minimum performance loss.

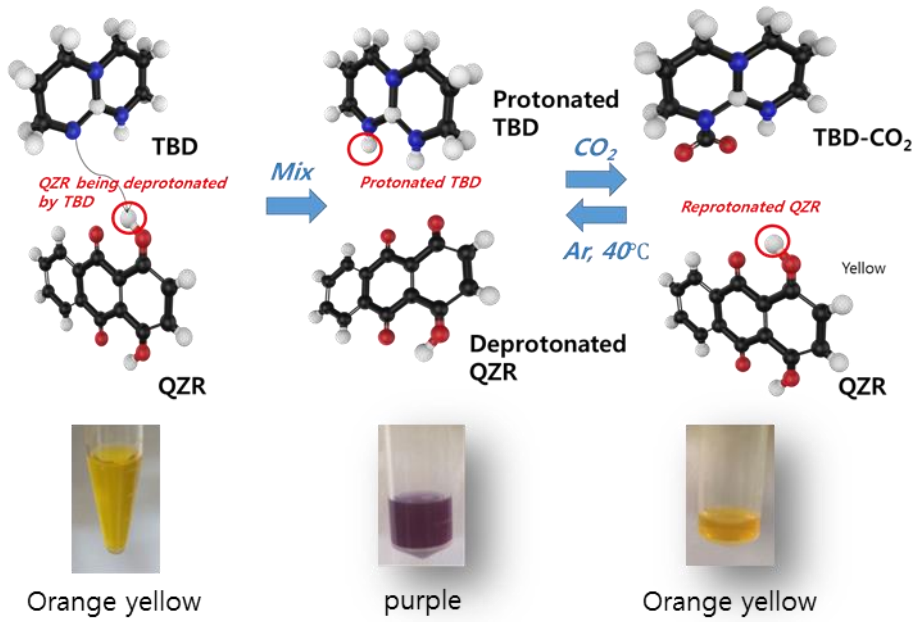


Figure 2.2.19 The proposed mechanism for the system with the colors at each step

Chapter 3. Properties as sensor and applications

3.1 Properties as sensor

3.1.1 Saturation Volume of Carbon Dioxide

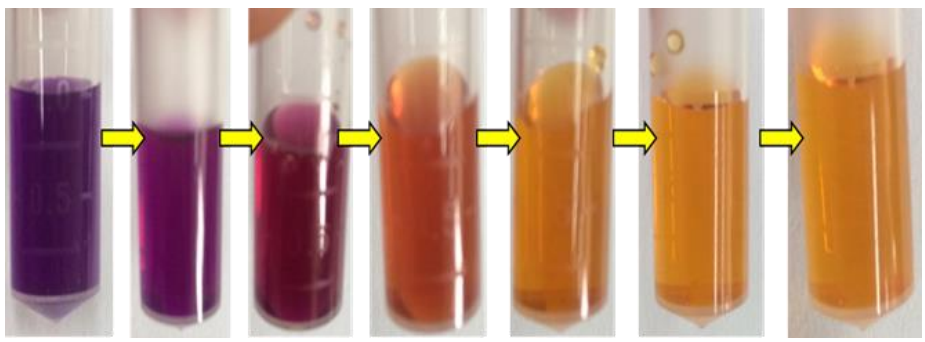
First of all, the organic bases, TBD, and the chemical dye, quinizarin, were used for the detecting system. To measure the maximum volume of carbon dioxide required to change the color of the system, a stream of carbon dioxide gas was blown to the system and the volume of carbon dioxide gas used until the endpoint was recorded.

For the system of 5.0 mM quinizarin and TBD, the original color of the solution was dark purple or violet. As carbon dioxide gas was purged, its color gradually changed to orange through light purple, red orange, and dark orange colors. For the system of 0.5 mM quinizarin and TBD, the initial color of the solution was bright purple and it turned to bright yellow through pale purple, pale magenta, and pale pink as seen in the Figure 3.1.1.

Of course, the system with a greater concentration had a greater capacity for carbon dioxide gas; more volume of carbon dioxide gas had to be purged to induce the endpoint color of the system. The system of 1.0 mM quinizarin and TBD

consumed 1.1 mL of carbon dioxide before being saturated and the saturation volume of carbon dioxide for different systems at different concentrations were shown in the Figure 3.1.2. As well, the other organic bases, DBU and piperidine, were employed but their performance was not as great as the system with TBD.

a)



b)

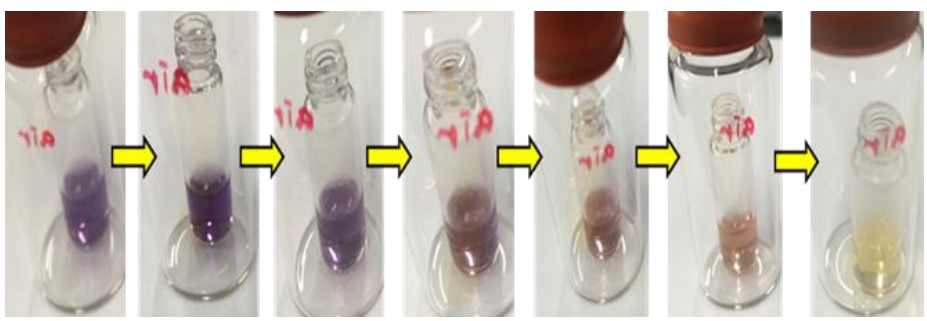


Figure 3.1.1 The changes in color of the system over increased volume of CO_2 added a) 5.0 mM quinizarin and TBD, b) 0.5 mM quinizarin and TBD

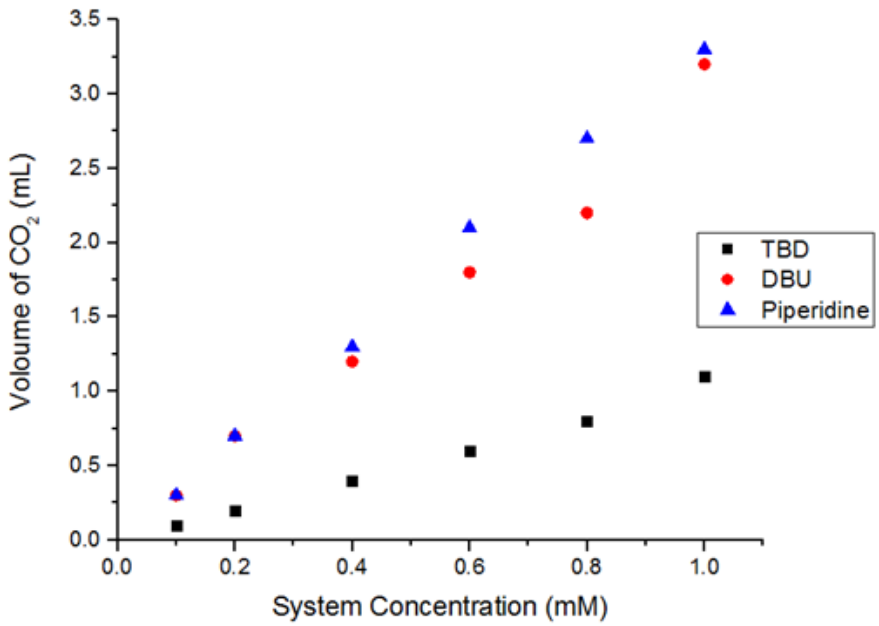


Figure 3.1.2 The saturation volume of CO_2 of the different systems at different concentrations[26]

3.1.2 Response Time

Known that the system with a lower concentration of the chemicals would require a smaller volume of carbon dioxide for saturation, it could be deduced that the sensitive sensor would have low contents of the chemicals. Any concentration greater than 1 mM was too insensitive to go over a color change within half an hour when exposed to reasonable concentrations of carbon dioxide. On the other hand, any concentration lower than 0.1 mM was too dilute that system responded to the atmospheric carbon dioxide too quickly and the changed color was too dim to be noticed easily with bare eyes.

Therefore, the standardized concentration for each system was decided to be 0.1 mM concentration. Each 1.0 mL of the systems with different organic bases, TBD, DBU, and piperidine, was transferred to a 50 mL round-bottom flask and the top was sealed with a rubber septum. Then, the system was purged with argon gas for 5 minutes to remove any atmospheric carbon dioxide and the calculated volume of pure carbon dioxide gas was injected with a syringe to achieve the right concentration of carbon dioxide. (i.e. 49 uL of carbon dioxide was injected to a 50 mL round-bottom flask to achieve 1000 ppm of atmospheric concentration of carbon dioxide)

In the Figure 3.1.3, the system with TBD showed the shortest response time

to the given carbon dioxide concentrations; the system took 433 seconds (about 7 minutes) when exposed to 1000 ppm of carbon dioxide and 43 seconds in 5000 ppm of carbon dioxide. On contrast, the system with DBU took 5820 seconds (about 97 minutes) in 1000 ppm of carbon dioxide and 546 seconds (about 9 minutes) in 5000 ppm of carbon dioxide. For the cases of piperidine, the response time was too long that the system underwent a color change within 3471 seconds (about 58 minutes) even in 5000 ppm of carbon dioxide.

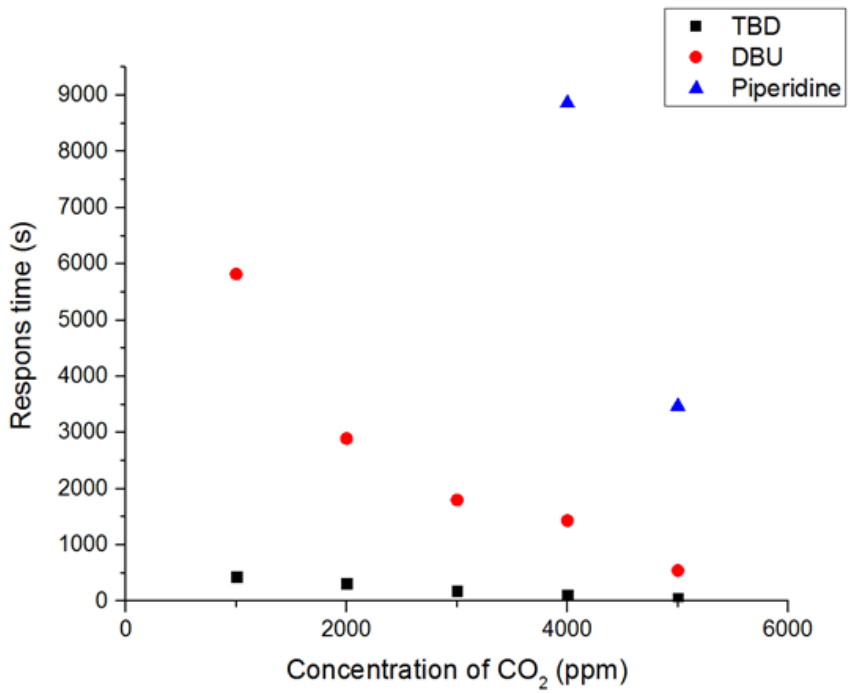


Figure 3.1.3 The response time of the 0.1 mM systems exposed to different concentrations of CO_2

3.1.3 Kinetiecs

The quinizarin and TBD system of 0.1 mM concentration was prepared and its total volume was 3.0 mL; the ratio of quinizarin to TBD was 1 to 1. Then, the system was transferred to a 7 mL quartz cuvette with the air-tight lid and purged with argon gas for 5 minutes. Afterwards, 12 uL of carbon dioxide gas was injected to the closed cuvette in order to achieve 3000 ppm of carbon dioxide and the system was at rest and each UV-VIS spectra was obtained at every 1 minute.

Over time, the absorption band at 600 nm, the monoanionic form of quinizarin, was decreased, while the one at 460 nm, the neutral form of quinizarin, was increased. In about 8 minutes, the color of the system changed wholly from purple to yellow. Also, the color change over time as a result of carbon dioxide injected to the system was clearly shown with the shifts of the band against time.[8,9]

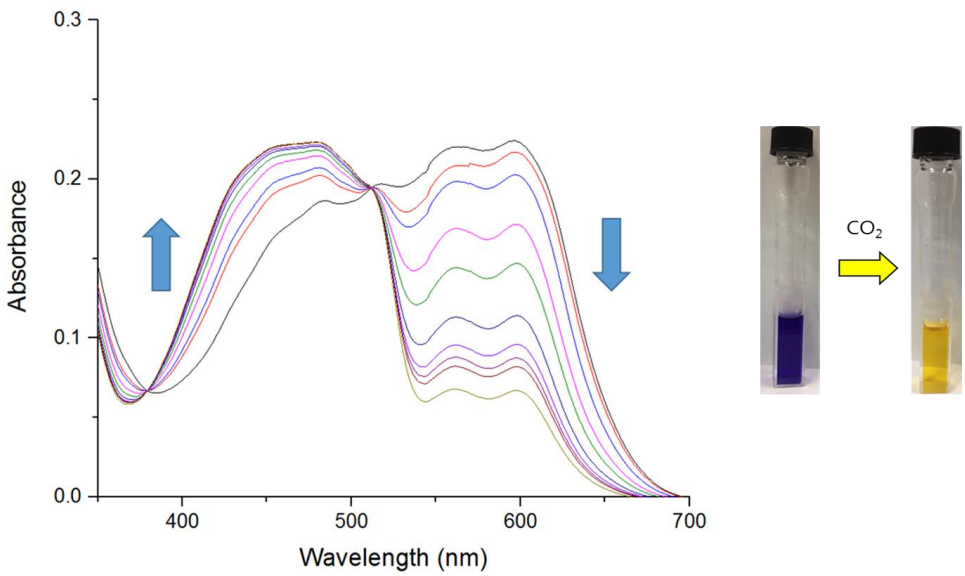


Figure 3.1.4 UV-VIS spectra showing the changes in absorption bands of 0.1 mM quinizarin and TBD system exposed to 3000 ppm of CO_2.[30]

3.1.4 Recyclability

One of the strong advantages of the quinizarin and TBD system was the simple, convenient, and economical detection of carbon dioxide in relatively short time such as few minutes. Another strong benefit of the system could be that the detection process was visible since the color of the system was changed when it was exposed to a certain volume of carbon dioxide. Yet, there was another fascinating advantage of the system, recyclability.

Even though the cost of the disposable system was far lower than that of the long-term carbon dioxide sensor such as the Severinghaus electrode, the total expense of using this quinizarin and TBD system would keep increasing and become more expensive in the long run if the system can be only used once. However, the detection system could be re-used for a multiple times and its performance remained intact for about 3 to 5 detection cycles. In fact, the recyclability of the system could be pushed up to about 10 cycles, but the detection of the color change in response to incoming carbon dioxide gas was rather difficult with bare eyes when reused too many times.

To be more specific, if the system was recycled too many times, the only change that could be observed was the shift of the absorption band and no colorimetric detection was possible after 3 or 5 times of reuse on average. In the

Figure 3.1.5, the cycle of the system was illustrated. The quinizarin and TBD were mixed together to yield a purple solution and its color changed to yellow as a result of carbon dioxide gas introduced to the system. From here, the system can be reversed with a slight heat and argon gas. The reverse reaction, detachment of carbon dioxide from TBD, would rapidly occur at 40℃or higher temperature and the argon purge would remove the carbon dioxide molecules remaining within the system by simply blowing them away.

In one detection cycle, the system ready for sensing carbon dioxide was purple initially and its absorption band appeared at near 600 nm. After purging carbon dioxide, the absorption band shifted to 460 nm and the color changed to yellow. Along with the shift of the band, the intensity of the band was slightly decreased by about 15%. Then, the system was heated with a heat gun for a minute and argon gas was purged for 5 minutes to clear the system. The system recovered its purple color back and was ready to sense carbon dioxide again.

In the Figure 3.1.6, the decrease in absorbance of each peak on the UV-VIS spectrum was observed. As mentioned above, there was a slight decrease in intensity of the absorbance for every shift that was made as a result of blowing either carbon dioxide or argon gas. After 3 full detection cycles, the absorbance was decreased by about 50% and therefore it was not appropriate for any further detection most of the time; the colors were not as clear as they used to be so it became a little tricky to tell

the difference between original and changed colors.

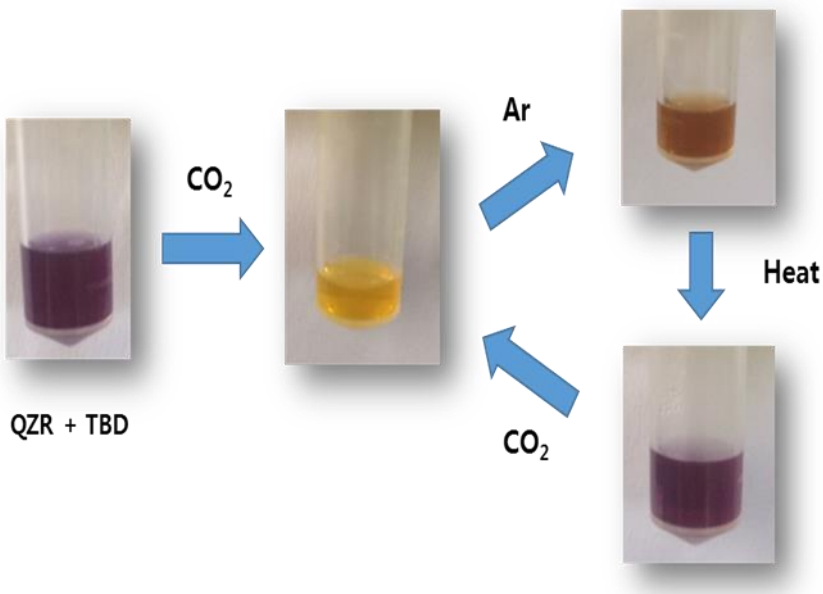


Figure 3.1.5 The system's detection cycle that can be repeated for at least 3 times

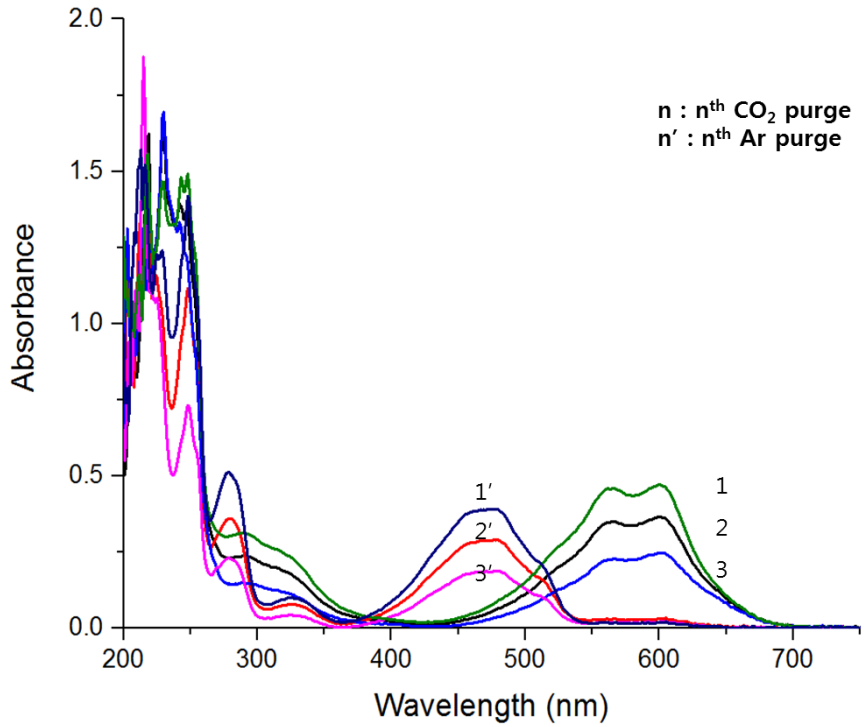


Figure 3.1.6 UV-VIS spectrum of the first three repeated cycles of 0.1 mM QZR and TBD system

3.1.4 Comparison and summary

With the different organic bases, TBD, DBU, and piperridine, the colorimetric detection systems for carbon dioxide were all functional. However, there was a significant difference in performance. The system with TBD showed the best performance while the one with piperridine was the least sensible to incoming carbon dioxide gas.[13] In other words, the pK_a of the organic base determined the performance of the carbon dioxide detecting system.[3]

As TBD was the most basic organic base among the candidates, it readily deprotonated the quinizarin molecules when mixed together resulting in a change in color of the solution. The best system with TBD took only 7 minutes to detect 1000 ppm of carbon dioxide whilst the system with piperridine took more than half an hour to detect 3000 ppm of carbon dioxide.

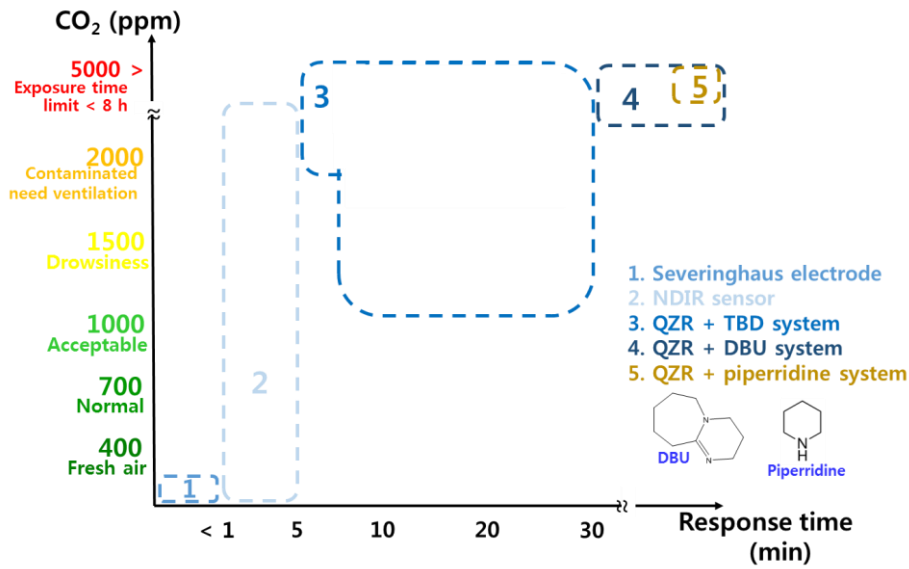


Figure 3.1.7 The diagram of detection range and response time of known CO_2 sensors

3.2 Applications

3.2.1 Physical Fixation on Silica Support for Solid System

With the best conditions known for detecting carbon dioxide gas in a reasonable amount of time, a new attempt to convert the system into solid state was made in order to make it more convenient and tangible. For solidification of the system, physical fixation of TBD was chosen and the silica-TBD was successfully synthesized by employing and modifying the synthetic procedure as described in the Figure 3.2.1.[5]

Then the adsorbed TBD was poured into the quinizarin solution and was allowed to react with the dye. Although the color of the solution was mainly yellow or orange due to the color of quinizarin, the adsorbed TBD turned blue or purple as soon as it was soaked in the solution and was sank at the bottom as seen in the Figure 3.2.2. Then, the solvent was removed from the system and the blue or purple solid powders were collected and dried under vacuum. To be certain, the blue or purple powders were washed with acetonitrile 3 more times but no color came out. Finally, the solidification of the quinizarin and TBD system was successfully carried out.

Nonetheless, this seemingly feasible solid system did not respond to carbon dioxide gas. A stream of carbon dioxide gas was directly blown to the solid system

for few hours but there was still no color change observed with the system. Plus, the solid system was at rest at room temperature and exposed to the air, but the color of the solid system did not change to yellow or any other similar ones in response to carbon dioxide in the atmosphere even after a week. To be sure, the solid system was also dipped in acetonitrile and carbon dioxide gas was purged, however there was still no change. This all indicated that the solid system was incapable of detecting carbon dioxide gas.

From this, it was concluded that the adsorbed TBD was able to interact with quinizarin molecules in liquid phase but was not able to do so with carbon dioxide molecules in gas phase.[19] The reason why the adsorbed TBD could deprotonate quinizarin in liquid but could not adsorb carbon dioxide gas would be the thermodynamic barrier. Heterogeneous systems are much harder to encounter and initiate reactions compared to homogeneous systems due to the difference in the phases of the reactants. The difference between solid and gas is much higher than that between liquid and solid. Therefore, the solid system was not able to detect carbon dioxide gas.

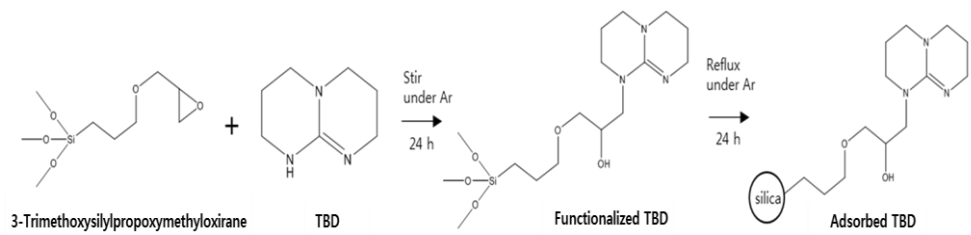


Figure 3.2.1 The reaction scheme of physical fixation of TBD onto silica support.[2, 22]

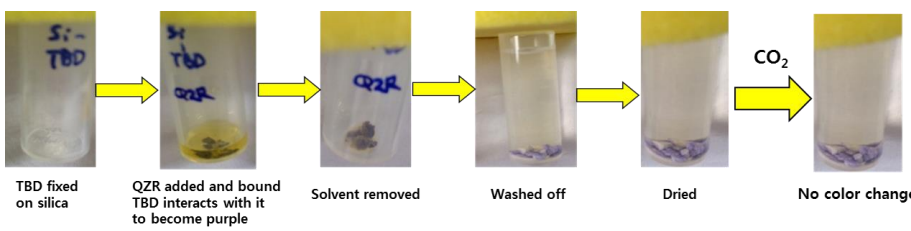


Figure 3.2.2 The physical observations on the changes of the solid system with TBD-silica at each step

3.2.2 Agarose Technique for Gel-like System

A second effort to apply the quinizarin and TBD system was an agarose gel technique. In this procedure, Agarose EP Master (Gel strength : 1.5 % or >1,200 g/cm^2, EEO < 0.12 %, 50 g, reagent grade, BIOSEASANG. INC) was used.

As described in the Figure 3.2.3, a simple agarose gel production method was employed. Agarose gel powder was weighed according to the desired w/w % concentration and dissolved in the corresponding volume of deionized water. (i.e. in order to make 10 mL of 1 w/w % agarose gel, 1 g of the agarose gel powder should be dissoloved in 9 mL of deionized water given that the density of water is equal to 1.0) Then, the aqueous agarose solution would be heated just before boiling and the solution would seem clear and transparent. Depending on the desired portion of the system and agarose gel solution, the volumes of the prepared quinizarin and TBD solution differed and the right volume of it was added to the agarose gel solution. After that, the solution was transferred to a sealed container and purged with argon gas for 5 minutes. In addition, it was at rest for an hour and allowed to cool down to room temperature to become a purple gel. In the Figure 3.2.4, the color of the gel changed to yellow after being exposed to the air for at least 4 hours

As seen in the case of the system with adsorbed TBD, the problem was that the gaseous carbon dioxide molecules were not able to adsorb to the solidified TBD

molecule due to thermodynamic barrier. Here, the gel would have a lower barrier than the solid system but it would still be high enough that there could be no encountering between carbon dioxide and TBD molecules. Further, too slow kinetics would be the next problem even if the gel system successfully captured atmospheric carbon dioxide and underwent a color change. That is because the gel obviously had a higher viscosity compared to acetonitrile solution system and therefore simply there would be much more difficulty for carbon dioxide molecules in the gel system to contact with the TBD molecules than in the solution system; the harder for carbon dioxide molecules to travel, the slower they reach TBD molecules along with a color change into yellow or orange.

Fortunately, the gel system was functional but its performance was not that great regardless of the agarose w/w % concentration. Indeed, the system with a greater agarose content showed a worse performance but even with the slightest content of the agarose gel, the system was too insensitive to carbon dioxide gas compared to the solution system. To be more specific, the gel system showed only a third to tenth performance depending on the agarose gel content compared to the original acetonitrile solution system; the lower the agarose gel w/w % concentration, the better performance.

Therefore, there was a possibility that the quinizarin and TBD system could be turned into a gel state, and there would be more convenience and possible

applications possible. However, gelation of the system obviously deteriorated the sensitivity to carbon dioxide and it should be avoided as it would beat the original purpose of the system as carbon dioxide sensor.

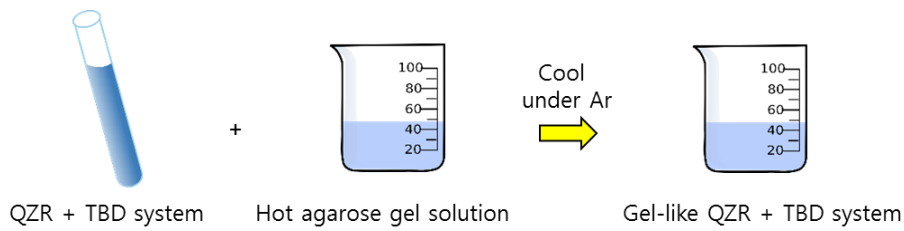


Figure 3.2.3 The schematic diagram of agarose gelation of quinizarin and TBD system

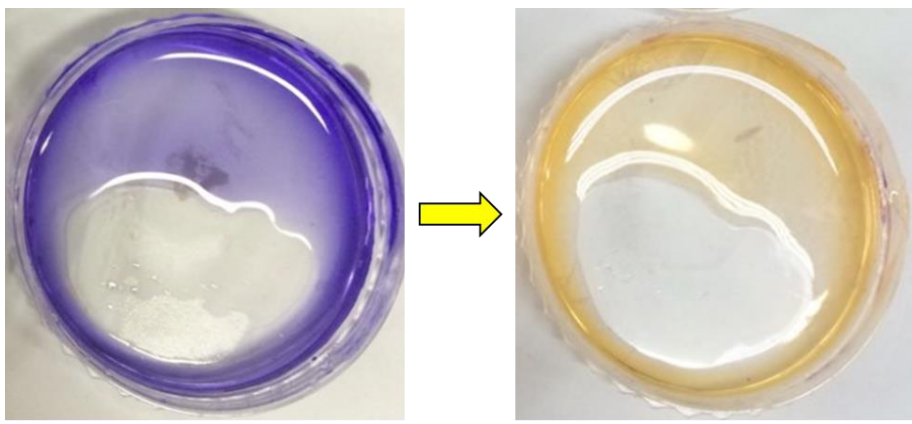


Figure 3.2.4 The color change from purple to yellow of gel-like quinizarin and TBD system in response to atmospheric CO_2

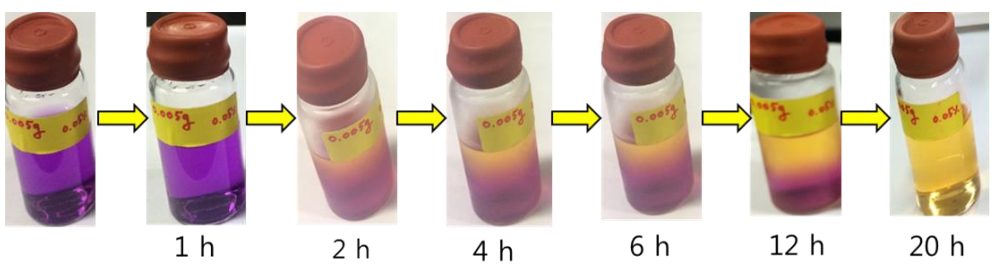


Figure 3.2.5 The changes in color of the 0.05 w/w% gel-like quinizarin and TBD system exposed to 3000 ppm of CO_2

Chapter 4. Conclusion

With a variety of characterization techniques, the mechanism of the quinizarin-based colorimetric sensor for carbon dioxide was revealed. From UV-VIS spectroscopy, the origin of the color change was learned to be the different electronic forms of quinizarin. To be more specific, the color of the quinizarin solution was orange yellow because the quinizarin molecule was neutral while its color changed to purple when mixed with TBD as a result of deprotonation. So, one molecule of TBD deprotonated a proton from a molecule of quinizarin when mixed and the quinizarin molecule regained its proton when carbon dioxide was purged and bound with TBD.

From ^{1}H-NMR spectrum, the evidence of deprotonation of hydroxyl proton of quinizarin by TBD obtained and after addition of carbon dioxide gas to the system, the binding of TBD and carbon dioxide was verified by the ^{13}C-NMR spectrum; a new peak appeared at 161 ppm and it was the carbon atom of the carbon dioxide molecule that attached itself to TBD.

From FT-IR spectrums, the existence of the important functional groups of the chemicals were confirmed and the changes in their intensities supported the mechanism of the detection process; quinizarin loses a proton to TBD to be ready for detecting carbon dioxide and TBD binds with carbon dioxide to protonate

quinizarin back. As a result of the deprotonation, the color of the system changed to yellow from purple and its color went back to purple when purged with argon gas and along with some heat.

From the experiment on the saturation volume of carbon dioxide, the total capacity of the detecting system at different concentrations were learned and based on that the most appropriate concentration for detecting atmospheric carbon dioxide concentration could be chosen. In fact, the quinizarin and TBD system at the concentration of 0.1 mM seemed ideal. Although the other organic bases such as DBU and piperidine had a slightly greater saturation volume of carbon dioxide at given concentrations compared to that of TBD, they also looked as fine as TBD for CO_2-binding moiety within the system.[14,15]

In the next experiments, the response time of the system at given concentration of carbon dioxide was figured out. As expected, the system with smaller concentrations of the chemicals had a shorter response time to a given carbon dioxide concentration. On the other hand, the other organic bases such as DBU and piperidine were found to be inappropriate compared to TBD because their response time were much greater than those of TBD at the same concentration.

Most importantly, the detection system can be re-used for a multiple times and its performance remained intact for about 3 to 5 times. In fact, the recyclability of the system can be pushed up to about 10 times but the detection of incoming

carbon dioxide gas is rather difficult with bare eyes when reused too many times; it can only be noticed as the absorption bands shifts to the left in response to addition of carbon dioxide gas. From the UV-VIS spectra, the intensity of the absorption band decreased as the detecting cycle was repeated.

After a series of tests and experiments, the best conditions for simple and convenient colorimetric detection for carbon dioxide was deduced to be 0.1 mM quinizarin and TBD solution. Also, their working range and corresponding response time were showed in the figure 3.1.7.

With the best conditions, a new attempt to convert the whole system into solid state was made in order to use it more “conveniently”. For solidification of the system, physical fixation of TBD was chosen and the silica-TBD was successfully synthesized. Then the adsorbed TBD reacted with quinizarin solution to yield blue solid system just like the solution one. However, the solid system did not respond to a stream of carbon dioxide gas because the thermodynamic barrier between the solid and gas was too high.

A second effort was an agarose gel technique. With a simple agarose gel production method, the quinizarin and TBD system was mixed with hot agarose solution and cooled down to become a gel. The gel obviously had a higher viscosity and therefore the kinetic for the detection process would be significantly reduced; the more the carbon dioxide molecules has to travel and the harder for them to reach

TBD molecules in the heterogeneous system. Still, the gel-like system was functional but its performance and sensitivity was diminished.

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국문초록

간단하고 편리하게 이산화탄소 농도를 예측할 수 있는 방법을 찾기 위해 노력하다가 quinizarin과 TBD를 이용한 시스템이 발견되었고, 본 연구는 이 시스템의 작용 원리와 특성을 감별하고, 새로운 분야로의 응용을 시도해보았다.

먼저 UV-VIS 스펙트럼을 통해서는 비색감지 센서의 색깔이 어떠한 이유로 변화하는지 알 수 있었고 그 이유는 화학 염료인 quinizarin의 전자 상태 때문이었다. Quinizarin이 양성자를 잃지 않아 중성일 때는 주황색 계열이지만, 유기염기와 만나게 되면 유기 염기에게 양성자를 잃고 이온화 과정을 겪는다. 그러나 이 시스템이 이산화탄소에 노출되면 유기염기는 이산화탄소와 결합하고 양성자를 다시 화학 염료에게 주어 색깔의 변화가 나타난다. 이는 UV-VIS 스펙트럼에서 흡광밴드의 이동을 통해 확인할 수 있다.

핵자기공명 스펙트럼에서는 두 가지의 좋은 근거들을 얻을 수 있었는데, 먼저 ^{1}H-NMR을 통해서는 화학염소의 양성장가 탈양자 반응을 겪어 시스템의 색깔이 변함을 확인하였고, ^{13}C-NMR을 통해서는 유기 염기가 매우 활발하게 이산화탄소와 결합하며 받은 양성자를 내놓는 것을 확인할 수 있었다.

FT-IR 스펙트럼을 통해서는 시스템에 존재하는 화학 물질들의

작용기들을 살펴볼 수 있었고 이를 통해서 시스템이 어떤 순서로 어떻게 작용하며 그 사이사이에 존재하는 화학 물질들의 구조를 예측해 볼 수 있었다. 예를 들어 이산화탄소와 반응하기 전의 시스템에서는 유기 염기인 TBD가 화학 염료인 Quinizarin의 양성자를 빼앗아 각각의 TBD와 Quinizarin에 비해서 N−H 결합의 수는 증가하고, O−H 결합의 수는 감소하였다. 이산화탄소가 시스템에 유입된 후에는 TBD가 이산화탄소와 결합하며 자신이 빼앗았던 양성자를 다시 Quinizarin에게 돌려주어 N−H 결합수가 감소하고 O−H 결합수가 증가하였다.

실험 영역에서는, 각기 다른 농도의 시스템들이 얼마나 많은 부피의 이산화탄소를 포화시킬 수 알아보았고 이를 바탕으로 예측 반응시간과 측정 가능한 최소 농도를 찾아보았다. 뿐만 아니라 작은 공간만을 차지하는 빠르고 간편한 기술이면서도, 이 시스템은 성능의 큰 감소 없이 적어도 3회 이상 재사용이 가능하다.

이 뿐만 아니라, 이런 용액기반 이산화탄소 비색감지 센서를 고체나 젤로 변환 시켜보려는 응용과 노력도 시도되었다. 먼저 TBD 분자를 무거운 실리카에 흡착시켜 고체화 한 후, 화학 염료인 Quinizarin과 반응했을 때 그 시스템이 화학적 변화를 일으키는 지 확인했지만 아무 변화도 일어나지 않았다. 이처럼 Quinizarin과 TBD 시스템의 고체화 작업은 실패가 되었고, 시스템을 젤로 만들기 위한 두번째 기술이 시도되었다. 단순히 뜨거운 아가로스 젤을 섞어준 뒤

상온에 식히는 방법이었지만 성공적으로 젤 특성을 가진 이산화탄소 비새감지 시스템을 만들 수 있었다. 그러나 젤의 점성은 너무 높아 이산화탄소와 결합해 시스템의 색변화를 일으키는 데 소모되는 시간이 너무 늘었고, 일정 시간 내에 이 반응을 지키기 위해 필요한 최소 이산화탄소의 농도 또한 매우 높아졌다.

이처럼 Quinizarin과 TBD를 이용한 이산화탄소 비색감지 시스템은 매우 빠르고 간편하게 이산화탄소의 농도를 예측할 수 있었고, 그 작용 원리 또한 밝힐 수 있었다. 좀 더 편리한 사용을 위한 고체나 젤로의 변형도 시도 되었지만 실패하거나 오히려 성능이 떨어졌다.

주요어 : 이산화탄소, 화학 염료, 유기 염기, 첨양자 반응, 탈양자 반응, 첨가 생성물, 비색감지 센서

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