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Fluorescence Turn-on Chemosensor for the Detection of Dissolved CO_2 Based on Ion-Induced Aggregation of Tetraphenylethylene Derivative

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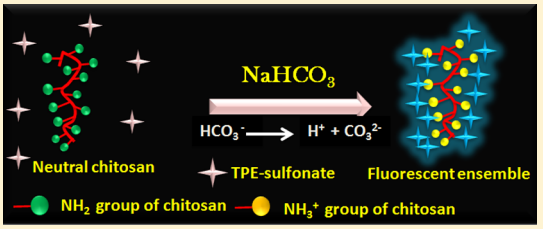
Supporting Information

ABSTRACT: Herein, a sensitive fluorimetric assay for dissolved carbon dioxide (dCO_2) was developed by using ion-induced self-assembly of a tetraphenylethylene derivative by taking advantage of its aggregation induced emission property. Chitosan, a commercially available polymer having amine functionality was utilized for the ion induced assay. In the presence of dCO_2, the amine groups in the chitosan get protonated to convert neutral chitosan to a positively charged species, triggering negatively charged tetraphenylethene derivative (probe **1**) to aggregate with it by electrostatic interaction. The aggregation causes intense blue fluorescence output from the system. The extent of the aggregation is reliant on the charge density of polymer, which is equivalent to dCO_2 concentration. A linear relationship from 5 to 50 μM of dCO_2, with a limit of detection of 5×10^{-6} M (0.00127 hPa) was obtained. This is the first report for detecting dCO_2 utilizing the AIE property.



In recent years, climate change, mainly due to global warming, poses a huge threat to human life as well as causes a large impact on global economy.[1] The emission of CO_2 contributes a good part to the climate change and therefore, monitoring the CO_2 level in the environment has become of utmost interest. Carbon dioxide is most commonly found as either dissolved carbon dioxide (dCO_2) or gaseous carbon dioxide (gCO_2). Dissolved carbon dioxide is naturally abundant in many places like mines,[2] river and lakes,[3] seawater[3−5] and even in human body,[6,7] and is used in many industries for example, food,[8] clinical,[9−11] etc. Monitoring the dissolved carbon dioxide level enhances the efficiency, reproducibility and reduces the cost of many biochemical processes at an industrial level.[12,13] The fermentation of packaged goods can be monitored by detecting the level of dissolved carbon dioxide in the substance.[8] dCO_2 is also found in soft drinks and edible products. Moreover, dCO_2 level is an important indicator for environment study and protection as it provides information about acidity of water which helps in conservation of aquatic life and also to nurture plants and vegetation.[14,15] On the other hand, high concentration of CO_2 is hazardous to living beings and possesses threat to the environment.[16] It is also an important indicator of metabolic distress in the body.[17] Therefore, developing efficient and cost-effective sensors for dCO_2 is very important.

Generally, dCO_2 undergoes a dissociation reaction releasing H^+ ions[18] which can be used to develop sensors of various kinds.[19−22] This dissociation reaction also helps to modulate the pH of biochemical systems (e.g., cellular metabolism inside human body), therefore, a lot of sensors for CO_2 use pH modulation as the method for quantification. There have been numerous efforts to develop efficient and cost-effective sensors for dCO_2 and CO_2 which use various forms of measurement techniques, such as electrochemical,[23] conductometric and coulometric,[15] NIR/IR,[24,25] and optical.[6,26−37] However, sensors based on optical measurements are superior to the rest as they generally use a noninvasive measurement technique and deliver a highly sensitive and accurate signal. The major concern in developing sensors for dissolved CO_2 is eliminating interference from gaseous CO_2; the samples have to be degassed thoroughly for the methods like IR. Hence sensors specifically based on dissociation of dCO_2 in solution will inherently eliminate such interference. The general strategy for preparation of optical sensors for dCO_2 is by introducing a nonfluorescent mediator or luminophore which can be "turned on" by the generation of H^+ ions produced by the dissociation reaction.

In this regard, fluorimetric sensing by attaching appropriate organic probes has drawn much more attention because it is simple, receptive, and cost-effective.[38−45] However, conventional fluorescent probes often endure from the aggregation-caused quenching (ACQ) effect, when dispersed in appropriate solvent or included into solid matrices, ensuing in enormous drop in the performance and sensitivity.[46,47] The ACQ effect

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pretenses huge apprehension in real life applications, particularly, in the in vivo detection of analytes.[46,47] In recent times, a group of molecules, nonemissive in solution, have been bring into being luminescence intensively upon molecular aggregation, showing an aggregation-induced emission (AIE) characteristic.[48,49] Restriction of intramolecular rotation is projected as the main reason behind this observable fact. As their emission is turn-on in nature, instead of quenching, AIE-active materials have found vast application in diverse fields such as proficient sensitive chemo/biosensors, electroluminescent materials, cell imaging, optical devices etc.[50−81] Among the reported AIE active molecules, tetraphenylethylene (TPE), due to its easy synthesis and also for simple functionalization strategies, is one of the most studied luminophore for detection of a variety of analytes[56−81] and other purposes.[50−55] However, to the best of our knowledge, AIEgens have not been utilized to develop a sensor for dCO_2. Herein, as a part of our continued surge toward developing detection tools for biologically/environmentally important analytes,[79−83] we report a label-free assay for dCO_2 using AIE property of a TPE derivative.

The design rationale for this fluorimetric assay is schematically represented below (Figure 1). Probe **1**, a sulfonate

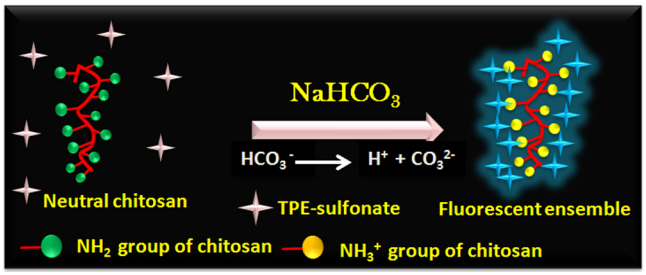

Figure 1. Sensing process of probe **1** based on AIE mechanism.

derivative of tetraphenylethylene was nonfluorescent in 6% THF−water and is anticipated to revive AIE property by pH driven ion-induced aggregation on a polymer support. Commercially available, cheap and biocompatible polymer chitosan having free-NH_2 functionality was used for this purpose. The plausible steps of the sensing event are as follows: (1) dCO_2 dissociates in aqueous solution to produce H^+ ions, (2) amine groups of chitosan immediately capture H^+ present in the solution to make chitosan a positively charged species from neutral one, (3) electrostatic interaction is initiated between protonated chitosan and the negatively charged probe, and (4) several TPE moieties stack with each other in a definite array on a polymeric chain owing to these electrostatic interaction. As anticipated, fluorescence intensity was amplified several folds by the proposed coaggregation pathway in the presence of dissolved CO_2 to realize an effective sensor for dCO_2.

MATERIALS AND METHODS

Chemicals and Reagents. 4-Hydroxybenzophenone, benzophenone, and chitosan were purchased from Sigma-Aldrich (India). $TiCl_4$ was purchased from Spectrochem Pvt. Ltd. Mumbai (India). All other common chemicals and solvents of AR grade were obtained from different commercial suppliers and were used without further purification. All ultrapure water used was purified with a Millipore water system and purged with N_2 for 15 min prior to use.

Instruments and Measurements. NMR spectra were recorded on Bruker Avance (300 MHz) NMR spectrometer. Mass spectra were obtained from Agilent 6400B LC-MS (ESI^-). Fluorescence spectra were taken on a JASCO FP-6300 spectrofluorimeter, the slit width was 5 nm for both excitation and emission. Absorption spectra were recorded on a JASCO V570 UV/vis/NIR spectrophotometer at room temperature. IR spectra were recorded on IR Affinity-1 FTIR Spectrophotometer, Shimadzu. Elemental analysis was carried out on Vario elementar CHNS analyzer.

Synthesis of Sodium 4-(4-(1,2,2-triphenylvinyl)-phenoxy)butane-1-sulfonate (TPE-SO_3^-, 1). 4-(1,2,2-Triphenylvinyl)phenol (**2**) was prepared according to the reported procedure.[80] In a 100 mL round-bottom flask were taken 350 mg (1.0 mmol) of **2** in 5 mL of anhydrous methanol under nitrogen. The mixture was stirred until all solids disappear. A solution of NaOMe (81 mg, 1.5 mmol) in 5 mL of methanol was added dropwise and stirred for 1 h, causing the colorless solution to turn pink-red. Into the solution was added 1,4-butane sultone (204 mg, 1.5 mmol) in 2 mL of methanol. The mixture was vigorously stirred for 8 h, during which time product was precipitated out from the solution. The product was collected by filtration and washed with methanol and acetone twice to afford a white solid. The crude product was purified by Sephadex column chromatography (eluent = 1:1 methanol−water) to afford probe **1** (350 mg, 70% yield). ^1H NMR ($CDCl_3$, 300 MHz): δ (TMS, ppm) 1.55−1.86 (m, 4H), 2.8 (t, 2H, J = 5.6 Hz), 3.47 (m, 2H), 6.42 (d, 2H, J = 8.0 Hz), 6.78−7.01 (m, 17H). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (TMS, ppm) 21.4, 28.3, 50.9, 67.2, 113.6, 126.27, 126.35, 127.6, 127.7, 131.3, 132.5, 136.1, 140.1, 140.4, 143.8, 157.2. ESI-MS (−ve mode): m/z 483 ($M-Na^+$). Anal. Calcd for $C_{30}H_{27}NaO_4S$: C, 71.30; H, 5.37; S, 6.33. Found: C, 71.13; H, 5.44; S, 6.19.

Preparation of Neutral Chitosan Solution. Chitosan (10 mg (0.005% w/v)) was added to 40 mL of 0.1 N HCl and sonicated for about 10 min to uniformly disperse it in solution, followed by stirring for 1 h to dissolve completely. The solution was adjusted to pH 7.0 by adding appropriate volume of 10% aqueous NaOH and stirred for 2 h. Finally, water was added to the aqueous suspension until the total volume reached to 100 mL, and the pH was adjusted again to 7.0.

General Procedure for Fluorescence Measurement. One millimolar stock solution of $NaHCO_3$ was freshly prepared before each experiment. CO_2 free standard solutions were prepared with Millipore water after boiling and purging with nitrogen gas and are stored in closed container. Stock solution of probe **1** (1 mM) was prepared in THF. For each case, required amount of 1 mM $NaHCO_3$ was added to the chitosan containing probe **1** (50 μM) keeping total volume (3 mL) and solvent ratio (94% H_2O-THF) constant (for details see Supporting Information). These solutions were incubated for 30 min before recording the corresponding fluorescence spectrum; the excitation wavelength was 345 nm and the emission was measured from 350 to 600 nm. All the experiments were performed at room temperature.

RESULTS AND DISCUSSION

Synthesis and Characterization of Probe 1. Probe **1** was successfully synthesized following a two-step procedure in high yield (Scheme 1). First, TPE−OH (**2**) was prepared by adopting a reported synthetic route in high yield.[80] The spectra were in good agreement with the reported values. The compound **2** was easily converted to probe **1** by starring it

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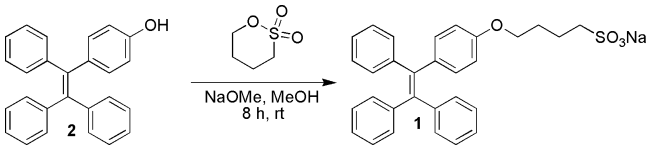
Scheme 1. Synthesis of Probe 1



with a mixture of 4-butanesulfonate and sodium methoxide in anhydrous methanol. Probe **1** was characterized by ^{1}H NMR, ^{13}C NMR, ESI-MS, and CHNS analysis.

Solvent Screening and pH Study of Probe 1. The solvent effect on the aggregation of probe **1** was investigated by using variable proportions of water−THF to identify a suitable solvent system. Probe **1** was completely soluble and non-fluorescent in pure THF and almost insoluble in water. Therefore, by gradually increasing the water to THF ratio, keeping probe concentration fixed at 50 μM, the fluorescence intensity was tuned to obtain a suitable solvent system. The fluorescence intensity of probe **1** upon photoexcitation at 460 nm was plotted with the water volume fraction (Figure 2). It

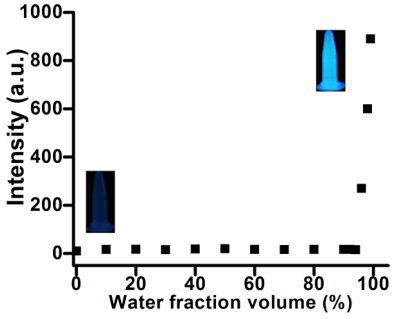


Figure 2. Plot of fluorescence intensity of probe **1** (50 μM) against various proportions of H_2O−THF mixture (λ_{ex} 345 nm, λ_{em} 460 nm).

was quite evident that fluorescence intensity was negligible in pure THF. A sharp rise in intensity was observed over 94% of water−THF which defined the solvent system for probe **1** and also confirmed the AIE activity of the probe.

A separate study was conducted to investigate pH dependency of probe **1**. Therefore, the fluorescence intensity of various solutions of probe **1** within a wide range of pH (3−9) was measured after 1 h of the addition of the probe at 25 °C keeping the solvent proportion same (i.e., 94% H_2O−THF) (Figure S1). Each of the solutions exhibited little or no fluorescence ensuring that the probe is unperturbed within a wide range of pH.

Response of Probe 1 to dCO_2. The whole sensing event was monitored by fluorescence spectrometric study. The competence of the sensing assay was first tested with aqueous solution of measured amount of dissolved CO_2. These specific levels of dCO_2 were attained by altering the amount of standard solution of $NaHCO_3$ in a fixed volume of test solution.

The probe in the working solvent (THF/H_2O = 6:94) showed negligible fluorescence and it remained unaffected upon addition of the neutral chitosan solution (3 mL) (Figure 3) which indicates that the polymer itself could not facilitate the aggregation of the probe. However, after incubation of the above solution mixture with $NaHCO_3$ solution (50 μM) at room temperature for 30 min, it showed ∼18-fold increment in fluorescence intensity at λ= 460 nm (Figure 3). On the other hand, upon direct addition of $NaHCO_3$ to the solution of probe

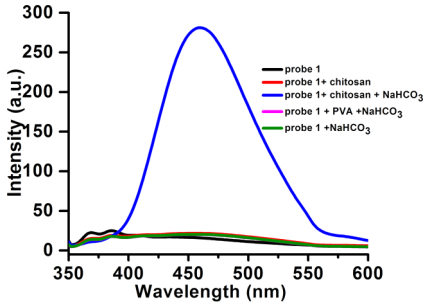


Figure 3. Fluorescence response of probe **1** in the presence of various additives. It shows that the rise in fluorescence intensity is observed only when both chitosan and $NaHCO_3$ are present in the solution.

1, no fluorescence increment was observed (Figure 3). This signifies that the amine functionalized polymer is essential for the ion-induced sensing assay. The role of amine group is further confirmed by carrying out the same experiment with another nonamine polymer, PVA (poly(vinyl alcohol)) by mixing it with probe **1** and $NaHCO_3$ solution (Figure 3). The fluorescence intensity of the above solution remained unchanged which further confirms that the amine group of chitosan plays a key role in the sensing event.

Effect of Polymer Concentration, Incubation Time, and Temperature on Sensing Assay. To find out the effectiveness and to establish the experimental conditions for dCO_2 following parameters such as polymer concentration and incubation time were optimized. To optimize polymer concentration, different concentrations of chitosan were taken. The equimolar concentrations of probe **1** and $NaHCO_3$ were kept constant at 50 μM and fluorescence spectra were recorded. As shown in Figure 4, when

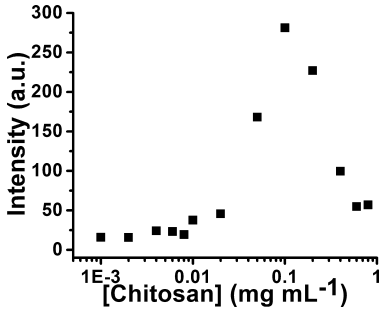


Figure 4. Effect of polymer concentration on sensing assay in the presence of probe **1** (50 μM) upon addition of 1 equiv of $NaHCO_3$ in 94% H_2O−THF after 30 min.

fluorescence spectra was measured with 0.02 mg/mL chitosan, slight change in PL intensity was observed, which further increased with the increment of polymer concentration. However, the fluorescence intensity started decreasing once the concentration of chitosan crossed 0.1 mg/mL. This might be because of the self-assembled structure of chitosan trapping the tetraphenylethylene derivative in its core, which prevents the interaction of the probe and hence assay is turned off. Thus, 0.1 mg/mL chitosan solution was chosen as the optimal concentration for the spectrofluirometric assay. Similarly, the ideal concentration of the probe solution was found to be 50 μM (see Supporting Information for details). The sensing system did not perform to its best below this concentration. To investigate the incubation time, the fluorescence experiment

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was performed keeping concentration of the polymer, probe and analyte fixed at 0.1 mg/mL, 50 μM and 50 μM, respectively. The probe in a solvent system (THF/H_2O = 6:94) showed no change in fluorescence intensity upon addition of the polymer to the solution (Figure 5). When a

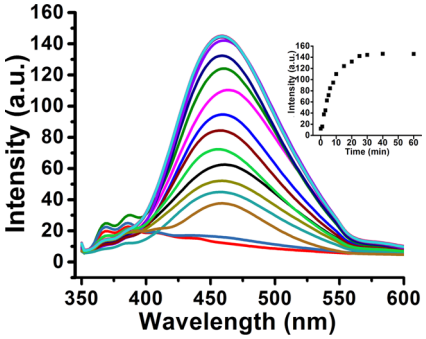

Figure 5. Time dependent fluorescence spectra of probe **1** (50 μM) in the presence of chitosan (0.1 mg/mL) and $NaHCO_3$.

solution of $NaHCO_3$ (50 μM) was added to the above solution a peak at 460 nm appeared after 1 min and its intensity increased with time. After 30 min no palpable change in the spectrum was observed signifying that the reaction had attained equilibrium, therefore, the incubation time for the assay was set as 30 min. To study the effect of temperature, fluorimetric study was performed at four different temperatures (0, 10, 25, and 40 °C) maintaining other conditions same. The assay showed similar fluorescence response at 25 and 40 °C. However, the fluorescence output was low at 10 °C and the response was almost negligible at 0 °C after 30 min (Figure S3). When these solutions were allowed to incubate either for longer time or allowed to reach 25 °C, they gradually revive fluorimetric response. Therefore, suitable experimental temperature was set at 25 °C. Presumably, the delay in signal output is because of the slower dissociation of $NaHCO_3$ at lower temperature.

Spectrofluorimetric Assay of dCO_2. To assess the capability of the probe for sensing of dCO_2, fluorimetric titration with $NaHCO_3$ solution was performed by measuring fluorescence emission of the working solution containing probe **1** in the presence of 0.1 mg/mL of neutral chitosan. Upon gradual addition of 0−2 equiv of bicarbonate with respect to the probe, a significant enhancement of the intensity of characteristic fluorescence peak of tetraphenylethylene moiety at λ_{max} 460 nm was observed (Figure 6). This reiterates that H^+ ions produced by the dissociation of dCO_2 in aqueous medium are captured by the amine groups available in neutral chitosan. As a result the polymer becomes a positively charged entity and forms an ion-induced array with negatively charged probe **1**, hence fluorescence intensity increases by AIE mechanism. The relative fluorescence intensity linearly increased from 5 to 50 μM, that is, 0.001275 hPa to 0.01275 h Pa.

In a separate study, the ability of the sensing system toward the detection of gaseous carbon dioxide was determined by bubbling CO_2 in water (see Supporting Information for details). It was observed that the probe could efficiently sense CO_2 (R^2 = 0.9944) when measured amount of carbon dioxide gas was first bubbled in water followed by addition of probe **1** and chitosan. However, the fluorescene output was much less and inconsistent when gaseous CO_2 was bubbled through an aqueous solution of probe **1** and chitosan. Presumably, this is

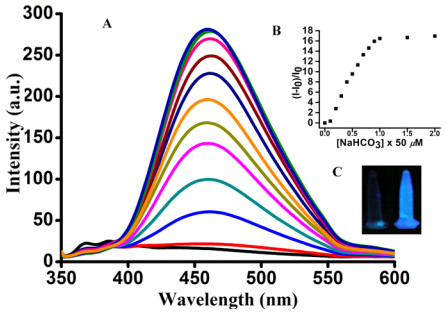

Figure 6. (A) Fluorescence spectra of **1** (50 μM) in 94% H_2O−THF solution in the presence of different amounts of $NaHCO_3$. (B) A plot of relative intensity versus concentration of $NaHCO_3$. (C) Fluorescence change of **1** (50 μM) upon addition 1 equiv of $NaHCO_3$ in 94% H_2O−THF after 30 min.

due to interfering events such as formation of ammonium carbamate in the polymer chain of chitosan (Figure S6).

Selectivity Study for Probe 1. Considering natural water contains a large variety of interfering ions, the detection ability of the probe **1** toward dCO_2 was evaluated in the presence of several other environmentally relevant metal ions and anions. The selectivity of the probe was evaluated by adding 50 μM of different ions, one at a time, into the solution of probe **1** (50 μM) in the presence of neutral chitosan in 94% water−THF and measuring the resulting fluorescence intensity of the system. As shown in Figure 7, the fluorescence intensities of all

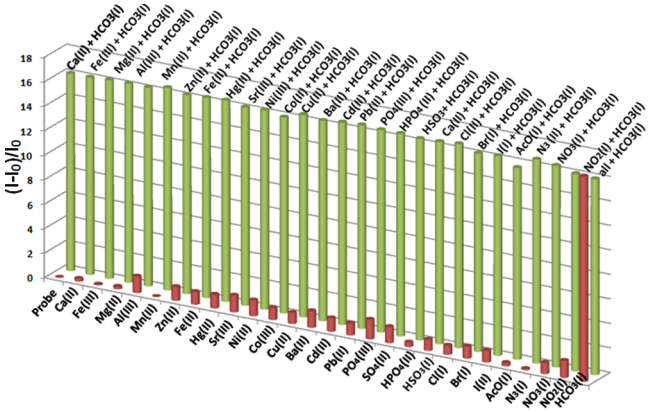

Figure 7. Maximum fluorescence response of probe **1** (50 μM) upon addition of different cation and anions.

the solutions other than $NaHCO_3$ are negligible. In particular, HSO_3^- was selected as the most competing anion to HCO_3^-. It is known that unlike HCO_3^- the dissociation of HSO_3^- in water is very slow.[33] As expected, the fluorescence intensity of probe **1** at 460 nm was changed only slightly upon the addition of similar competence in occurrence of equimolar mixture other ions (Figure 7). These results indicate that the fluorescence assay exhibits satisfactory selectivity toward dCO_2.

DLS Study and Mechanistic Insight. A DLS (Dynamic Light Scattering) study was conducted with four different samples, (a) only probe **1**, (b) neutral chitosan solution, (c) neutral chitosan + $NaHCO_3$ solution, and (d) reaction mixture (probe **1** + neutral chitosan + $NaHCO_3$ solution), to investigate extent of aggregation between protonated chitosan and probe **1** in the presence of dCO_2 (Figure 8). The mean diameter for probe **1** was ~35 nm, whereas, for chitosan, it was

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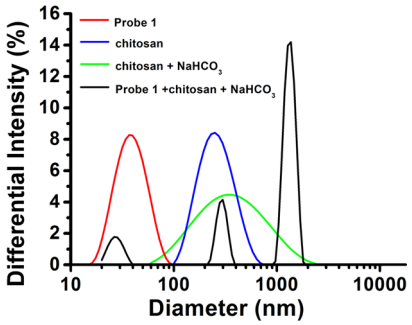

Figure 8. Particle size analysis for different samples in 94% H_2O–THF.

~251 nm, and both showed a fairly monodispersed phase with a very low intensity of scattering. On addition of $NaHCO_3$ to chitosan the mean diameter increased to ~365 nm without any considerable change in intensity indicating minimal aggregation among these molecules. As the intensity of scattering is directly proportional to the extent of aggregation, the nature of DLS graphs for samples a and b can be explained by considering minimal intermolecular interactions among similar molecules. The DLS plot of reaction mixture showed a well-defined polydispersed phase with mean diameters of 40, 250, and 1400 nm. The minimal electrostatic and hydrophobic interactions between probe, chitosan, and $NaHCO_3$ can be attributed to the aggregates with mean diameter of 40 and 250 nm. As these aggregates have quite low intensity of scattering, they do not contribute to the emission signal much. The deferential increment in intensity of aggregates with mean diameter 1400 nm was ~18. This rise in intensity confirms the required elevated agglomeration which is responsible for ion-induced emission.

The DLS results were in agreement with the proposed mechanistic pathway as depicted in Figure 1. In brief, the H^+ ions produced by the dissociation of dCO_2 protonate the amine groups of chitosan and corresponding positively charged species starts interacting with negatively charged probe **1** leading to formation of an array of probe molecules on a polymeric chitosan chain. This is why an intense peak was observed in the DLS plot with mean diameter 1400 nm.

Fluorescence Imaging. The fluorescence imaging technique was employed to get additional insight into the sensing mechanism. Fluorescence images of various solutions were obtained to visually characterize and establish the aggregation induced emissive property of the complexes (Figure 9). Neutral chitosan molecules were clearly inactive species and uniformly dispersed (Figure 9a and 9e). The complex between HCO_3^- and probe was inactive too (Figure 9c and 9g), whereas, complex between probe and chitosan showed small amount of fluorescence (Figure 9b and 9f) caused by aggregation. The complex formed by HCO_3^-, chitosan and probe aggregated readily and led to very high fluorescence compared to others (Figure 9d and 9h). The nature of fluorescence intensities seen in these images also validated the results obtained from the DLS study thus confirming the turn on property of the probe only in the presence of dCO_2 and chitosan molecule.

Measurement of the Detection Limit. Probe **1** responds to $NaHCO_3$ linearly in the micromolar concentration range (Figure 10), and from that, the detection limit of the probe is

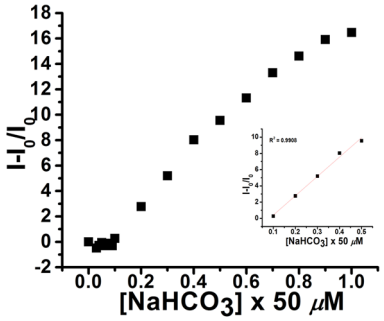

Figure 10. Plot of relative fluorescence intensity of **1** (50 μM) against concentration of $NaHCO_3$. From the graph the detection limit was estimated as 5×10^{-6} M (0.001275 hPa).

estimated to be 5×10^{-6} M of $NaHCO_3$ that corresponds to 0.00127 hPa for pCO_2, which is much lower than previously reported values.

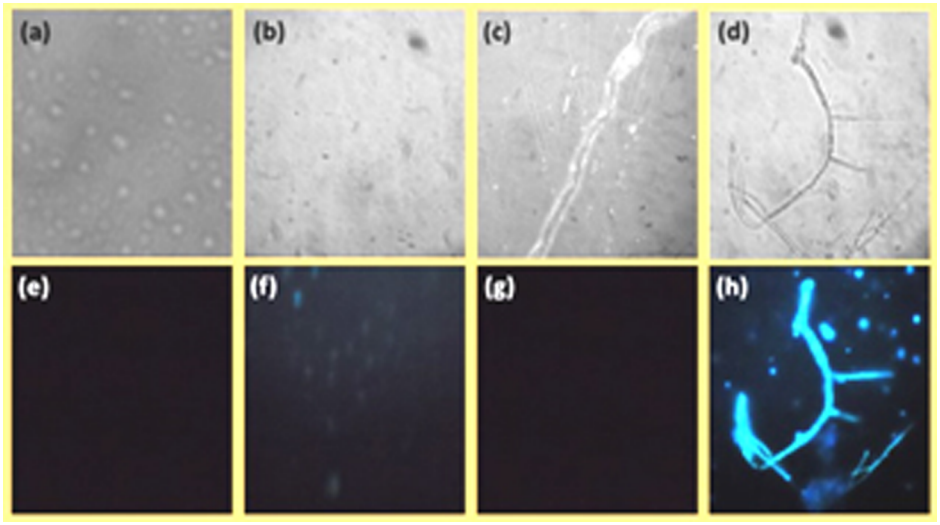

Figure 9. Phase contrast and fluorescent optical micrographs of neutral chitosan solution (a and e), probe **1** in neutral chitosan solution (b and f), probe **1** and HCO_3^- (c and g), and reaction mixture, that is, probe **1** + chitosan + HCO_3^- (d and h).

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Real Sample Analysis. Real sample analysis was conducted on samples obtained from a C_4 type plant *Epipremnum aureum*, algae containing water, aquarium water, and a commercial beverage. Coca Cola Company's Sprite was used as a sample cold beverage. In this sample, the $NaHCO_3$ level was found too high to detect, and hence, the sample was diluted 200 times. Moreover, a sample was obtained by adding algae to a bicarbonate spiked solution (40 μM), and two samples were retrieved after 6 and 12 h. All the samples were further processed by adding chitosan and probe **1** for fluorometric measurements. The measured fluorescence intensities of these samples were plotted to find the amount of dCO_2 in the water (Figure 11). As expected, the dCO_2 level in Sprite (sample A) was much higher than others and in the millimolar range (8.62 mM). The dCO_2 level in aquarium water (sample D) was more than that of plant samples (samples E and F) because of the presence of more aquatic life. Interestingly, dCO_2 level of $NaHCO_3$ spiked sample of algae after 12 h (sample C) was lower than that of the same sample collected after 6 h (sample B) indicating consumption of CO_2 by algae from water.

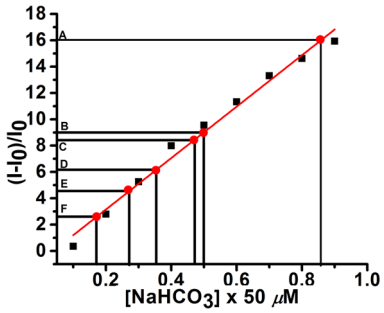

Figure 11. Plot of the relative intensities of different real samples onto standard fluorescence curve to quantify the level of dCO_2 ions in those samples: (A) commercial beverage; (B and C) $NaHCO_3$ spiked solution with algae after 6 and 12 h, respectively; (D) aquarium water; (E) water with algae; (F) C_4 plant (*Epipremnum aureum*) water.

CONCLUSION

In summary, we have successfully developed a continuous assay to detect dissolved carbon dioxide (dCO_2) utilizing the ensemble of TPE-derived probe **1** and a readily available biopolymer, chitosan, by taking advantage of the AIE feature of TPE moiety. The dissociation of dCO_2 leads to generation of H^+ ions and a low pH facilitate the protonation of neutral chitosan to serve as perfect counterion for negatively charged probe **1**. Several probe molecules stack with each other in a definite array on a polymeric chain of chitosan in 94% water-THF owing to the electrostatic interaction between them which thereby, causes aggregation induced emission to educe high fluorescence intensity from the system. The amount of dCO_2 was estimated by measuring the relative fluorescence intensity of probe **1** as the extent of the aggregation is reliant on the charge density of polymer, which is equivalent to dCO_2 concentration. The utility of this fluorimetric assay was validated on several real samples including a C_4 type plant and a cold beverage. The probe showed highly sensitivity with a limit of detection (LOD) defined as 0.00127 hPa. This AIE-based turn-on fluorescent chemosensor method of detection for dCO_2 is a very economic and selective method for the detection of dCO_2. To the best of our knowledge, this is the first report for detecting dCO_2 utilizing the AIE property.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.analchem.5b02339.

Detailed procedure for fluorescence measurements, effect of pH on the probe, effect of probe concentration on sensing assay, effect of temperature on the probe, DLS data with PDI, and response of probe 1 with water bubbled CO_2 and gCO_2 (PDF)

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Notes

The authors declare no competing financial interest.

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