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Complete List of Authors:	Ma, Yun; Hong Kong Baptist University, Chemistry Zeng, Yi; Technical Institute of Physics and Chemistry, Liang, Hua; Nanjing University of Posts and Telecommunications, Ho, Cheuk-Lam; Hong Kong Baptist University, Chemistry Zhao, Qiang; Nanjing University of Posts and Telecommunications, Institute of Advanced Materials Huang, Wei; Singapore-Jiangsu Joint Research Center for Organic/Bio-Electronics and Information Displays & Institute of Advanced Materials (IAM), Nanjing Tech University, Wong, Wai-Yeung (Raymond); Hong Kong Baptist University, Department of Chemistry

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A water-soluble tetraphenylethene based probe for luminescent carbon dioxide detection and its biological application†

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Yun Ma,[a] Yi Zeng,[a] Hua Liang,[b] Cheuk-Lam Ho,[a] Qiang Zhao,[b,*] Wei Huang[b] and Wai-Yeung Wong[a,c,*]

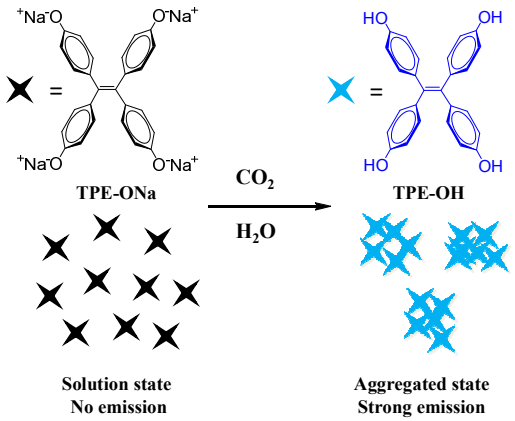
A water-soluble fluorescent CO_2 gas probe based on tetraphenylethene derivative (TPE-ONa) has been developed. After bubbling CO_2 into the detection solution, remarkable color change and fluorescence enhancement could be observed. A porous film was successfully fabricated by mixing the TPE-ONa with sodium carboxymethyl cellulose in water, which can serve as an efficient CO_2 gas detection system. More importantly, TPE-ONa exhibits low cytotoxicity towards live cells and has the ability to monitor the external CO_2 concentration changes of living cells.

Introduction

Carbon dioxide (CO_2) is one of the most important gaseous molecules on earth, which plays a pivotal role in maintaining biosphere homeostasis.[1] It is impossible that the photosynthetic organisms work without CO_2, which provides the basis for the synthesis of organic compounds that supply the necessary nutrients for organisms. In addition, CO_2 is of great importance in global climate change, public health, agricultural production and medicine.[2] Thus, the search for a highly sensitive and selective detection of CO_2 draws much current research attention.

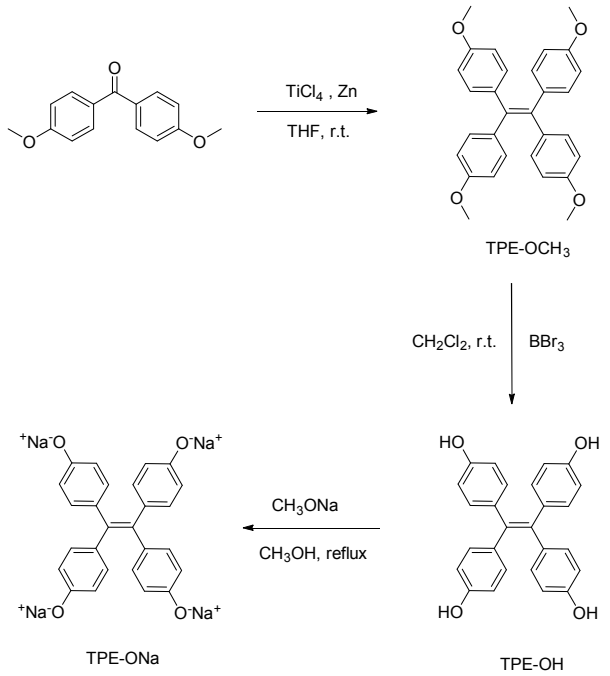
Various traditional methods have been developed to detect CO_2, such as infrared spectroscopic, electrochemical and gas chromatography-mass spectrometric (GC-MS) techniques,[3] which are normally complicated in instrumentation, time-consuming during usage, and require expensive and bulky equipment, and some of them cannot tolerate the interference of carbon monoxide (CO) and water.[4] Recently, luminescent probes have been developed as an alternative approach for CO_2 detection.[5] Such work has attracted considerable interest due to their simplicity, fast speed, safe operation, on-line real time detection, and high visibility to the naked eyes.[6]

CO_2 concentration is critically important in promoting the growth and normal function of living cells. To create an environment suitable for supporting living cells, an atmospheric condition of 5% CO_2 is needed. In order to detect the external/internal CO_2 concentration of living cells, water-soluble luminescent probes are highly desirable. Although excellent CO_2 detection results have been obtained by exploiting luminescent sensors, most of them can only detect CO_2 gas in organic solvents.[5] Therefore, the research on water-soluble luminescent CO_2 probes for the detection of external/internal CO_2 concentration of living cells is still quite rare.[7] In our recent work, a novel iridium(III) complex based probe for time-resolved luminescent sensing of CO_2 gas has been established.[5e] Unfortunately, this phosphorescent probe would suffer severely from the interference of water. Thus, it motivates us to further explore new water-soluble chromophores for CO_2 gas sensing. It is not uncommon to make use of the acidic properties of CO_2 to design water-soluble fluorescent probe. However, there are only few fluorescent pH indicators in the literature that can meet the requirements of pK_a and brightness simultaneously.[8]



Scheme 1 Proposed mechanism of CO_2 gas detection in aqueous solution by using TPE-ONa.

Tang's group discovered the phenomenon of aggregation-induced emission (AIE), and many molecules with AIE properties have been developed in recent years.[9] Tetraphenylethene (TPE) is a typical AIE-active molecule, which possesses the advantages of facile synthesis and flexible structural modification. Up to now, a large number of TPE based molecules have been developed for chemical sensing and bioimaging.[10] In this work, we present a TPE based probe for sensing CO_2 in aqueous solution and measuring the external CO_2 concentration of living cells. Scheme 1 describes the design concept of the detection system. Sodium phenolic salt ($-O^-Na^+$), as a hydrophilic group, is incorporated into the TPE moiety and a new compound (TPE-ONa) is obtained. TPE-ONa is soluble and non-emissive in the aqueous solution. After bubbling CO_2 gas into the aqueous solution, it would be in a chemical equilibrium with the carbonic acid produced. Consequently, the water insoluble and AIE-active TPE-OH can be generated by the reaction between TPE-ONa and carbonic acid. Then, strong fluorescence could be observed in the detecting solution. Moreover, we can load the TPE-ONa into the sodium carboxymethyl cellulose to fabricate a porous film to detect CO_2 gas flow on the surface. Remarkably, TPE-ONa has also been shown to be able to monitor the external CO_2 concentration change of living cells.



Scheme 2. Synthetic routes of TPE-ONa.

Results and discussion

Synthetic procedures

As depicted in Scheme 2, TPE-ONa was synthesized in three steps. Firstly, $TPE\text{-}OCH_3$ was prepared through a McMurry coupling of 4,4'-dimethoxybenzophenone. This was followed by demethylation to give TPE-OH.[11] Finally, the target compound TPE-ONa was prepared by the reaction of TPE-OH with CH_3ONa in methanol. TPE-ONa has good water solubility due to the incorporation of sodium phenolic salt. The desired compounds were characterized by ^1H and ^{13}C NMR spectroscopy, MALDI-TOF mass spectrometry, and elemental analysis.

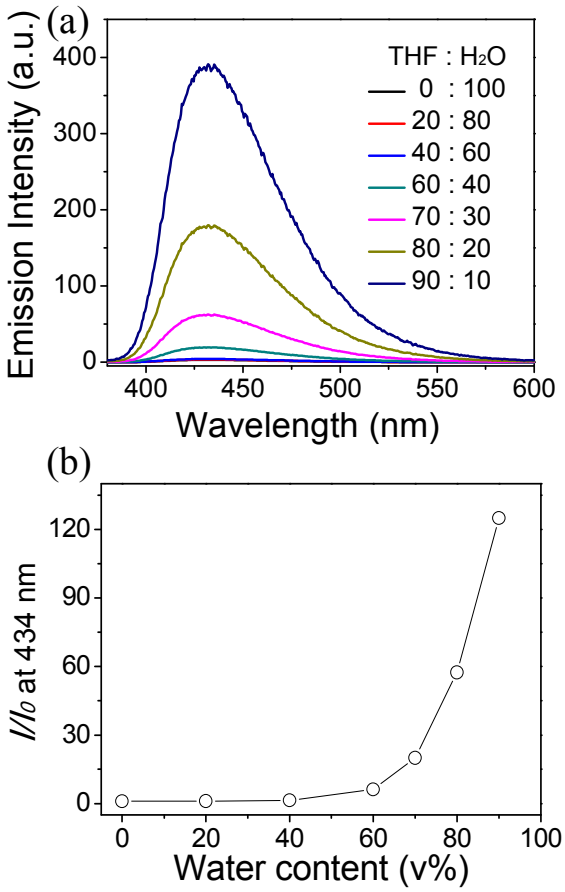


Fig. 1 (a) PL spectra of TPE-OH in THF–water mixtures (50 μM) with different water fractions. (b) Plots of the relative PL intensity (I/I_0) of TPE-OH at 434 nm versus the composition of THF–water mixtures of TPE-OH (I_0 is the PL intensity in pure THF solution).

AIE properties

We first studied the photoluminescence (PL) properties of TPE-OH in both solution and aggregated states. As shown in Fig. 1, TPE-OH is almost non-emissive when dissolved in THF solution, and the blue fluorescence at 434 nm is constantly intensified with increasing water volume fraction in the THF-water mixed solution, clearly demonstrating the AIE effect of TPE-OH. However, for TPE-ONa, it is non-emissive in both solution and aggregated states, which may be attributed to the low-lying charge transfer states of the anionic compound.[12]

CO_2 detection

Firstly, pH response properties of the TPE-ONa were studied in aqueous solution. As shown in Fig. 2, the response of the TPE-ONa is described by a typical sigmoidal dependence. The

fluorescence intensity at low pH value (6) was ca. 101-fold stronger than that at high pH value (13) for TPE-ONa. The p*K*a value of TPE-ONa was measured in aqueous solution by fluorimetric titration as a function of pH value according to the literature method.[13] The measurement of fluorescence intensity change as a function of pH by using the Henderson–Hasselbalch equation:[14] $pKa = pH - \log[(F_{Imax}-F_I)/(F_I-F_{Imin})]$ (where F_I is the fluorescence intensity at 434 nm, F_{Imax} and F_{Imin} are the corresponding maximum and minimum values, respectively), gave a p*K*a of 9.21. This pH-dependent on/off fluorescence properties of TPE-ONa has enabled the potential use of TPE-ONa as an efficient pH probe for the normal pH range. In addition, the p*K*a value of TPE-ONa is high and shows the potential of using TPE-ONa for highly sensitive CO_2 probes.[15a]

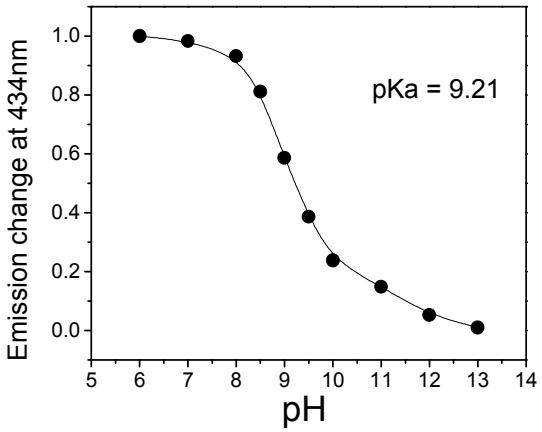


Fig. 2 Plot of $I_{434\ nm}$ versus pH value.

Next, we expect that bubbling of CO_2 gas into the aqueous solution would transform the negatively charged TPE-ONa to the neutral TPE-OH, thus leading to the spectral changes. As shown in Fig. 3a, with the 0.25 mL of CO_2 (as governed by a mass flow controller) bubbled into the solution, the absorbance at 580 nm disappeared and a new peak at 324 nm emerged, suggesting that CO_2 reacted with TPE-ONa in the aqueous solution. Consequently, the solution color was changed significantly from purple black to straw yellow. As shown in Fig. 2b, analogous effects were observed in the corresponding fluorescent emission spectra. A dramatic increase in the fluorescence intensity at 434 nm was observed upon exposure to an increasing volume of CO_2 gas, and it can be increased by up to 91-fold upon further bubbling of CO_2 gas (Fig. 3b). After being bubbled with about 0.32 mL of CO_2 gas, the mixture emitted bright blue light, and no additional change in the emission spectrum was observed. Indeed, the $[H^+]$ can interfere with CO_2 probe based on pH response. However, it is not uncommon to make use of the pH sensors for CO_2 detection and some examples have been reported in the literature.[15] Besides, some other optical probes for CO_2 gas detection are also severely interfered by $[H^+]$.[5c] Other sour gas, such as NO_2, SO_2 and HCl are pungent or colored, which makes them quite distinguishable from CO_2. Besides, there are no apparent changes in the fluorescence intensity upon treatment with colorless and odorless CO, Ar, O_2 and N_2. Thus, we consider that the selectivity of TPE-ONa towards CO_2 is extremely high.

To understand the excellent detection performance, dynamic light scattering (DLS), a powerful tool to study aggregate formation, was employed to investigate the size change of TPE-ONa with CO_2 addition. TPE-ONa is well dissolved as an isolated molecule in aqueous solution, so its particle sizes could not be measured by DLS. Upon bubbling of CO_2 gas, the insoluble compound TPE-OH was generated by the reaction of TPE-ONa and CO_2 in aqueous solution. Thus, the aggregated state was formed, with an average diameter of 458 nm from DLS as displayed in Fig. 4. Consequently, an obvious emission enhancement at 434 nm was found for TPE-ONa after bubbling CO_2. The fluorescence spectra of TPE-ONa in aqueous solution with different amounts of CO_2 gas (0.25, 0.5, 1.0 mL) were recorded. Fig. S1 shows that no apparent change in the fluorescence intensity was observed upon treatment with 0.25 mL CO_2 gas after 180 s. The time-dependent spectral change reveals that after bubbling 0.5 and 1.0 mL CO_2 gas into the detecting solution, the reaction will be completed within 120 s. These results indicate that the response of TPE-ONa to CO_2 is fast. In addition, the detection limit was calculated to be as low as 2.4×10^{-6} M (Fig. S2). Because of the good sensitivity and high selectivity coupled with the fast spectral response, TPE-ONa can be considered as a suitable candidate for the CO_2 detection in practical terms.

Furthermore, to emphasize the practical application of TPE-ONa, a porous film was fabricated as an efficient CO_2 gas detector. TPE-ONa along with sodium carboxymethyl cellulose was dissolved in water to form a rubber matrix, which is highly permeable to CO_2. The concentration of TPE-ONa in sodium carboxymethyl cellulose was calculated in weight percent. We fabricated the film with a concentration of 1.0% of TPE-ONa. The porous film has a clearly visible response to CO_2 gas, which is illustrated in Fig. 3c. The left part shows a photographic image of the film, which is purple black under the daylight and non-emissive after excitation by the UV light (365 nm). The purple black color of the TPE-ONa was faded to colorless when CO_2 gas was purged. In the meantime, the obvious bright blue fluorescence was observed under the UV light after the porous film was exposed to CO_2 gas (Figs. 3c and d). These observations are in accordance with the sensing results in aqueous solution.

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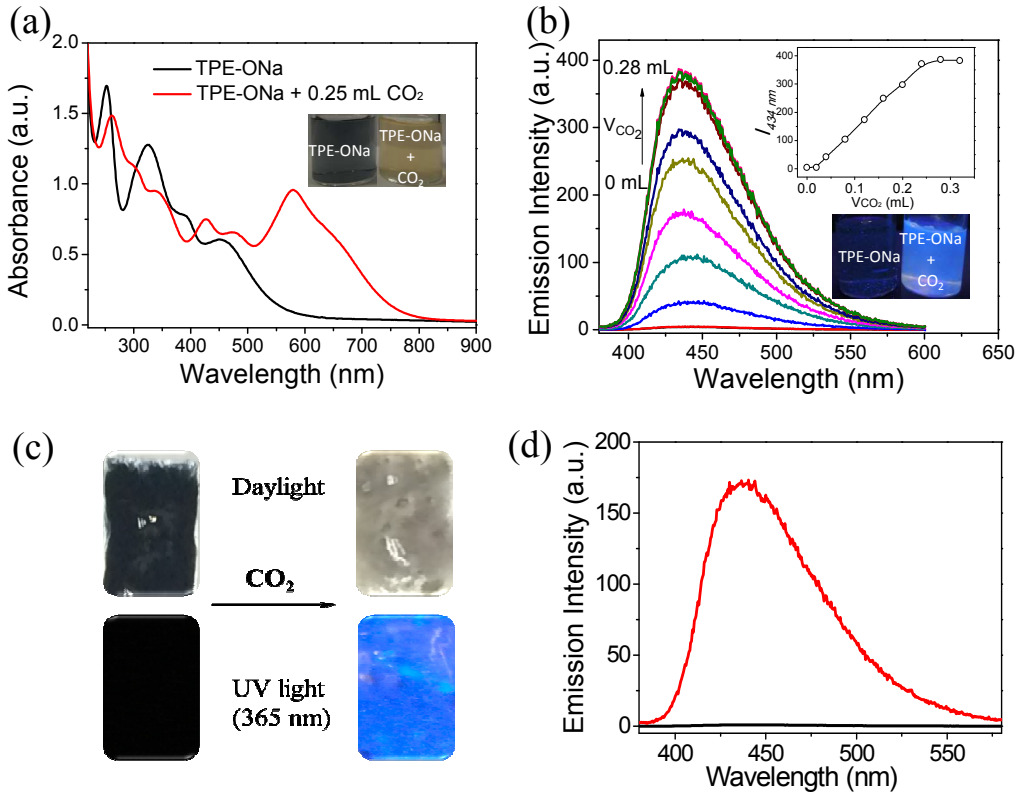

Fig. 3 (a) Changes in the UV-vis spectra of TPE-ONa in aqueous solution (50 μM) with 0.25 mL of CO_2 gas. Inset: photos of the emission of TPE-ONa and TPE-ONa with CO_2 bubbling in aqueous solution. (b) Changes in the fluorescence spectra of TPE-ONa in aqueous solution (50 μM) with different volumes of CO_2 gas (0–0.32 mL). Inset: titration curve of TPE-ONa solution (50 μM) with different volumes of CO_2 gas (0–0.32 mL) and photos of the emission of TPE-ONa and TPE-ONa with CO_2 bubbling in aqueous solution. (c) Photographic images of the porous film under the daylight and UV light. (d) The PL spectra of porous film before (black line) and after (red line) the treatment of CO_2 gas.

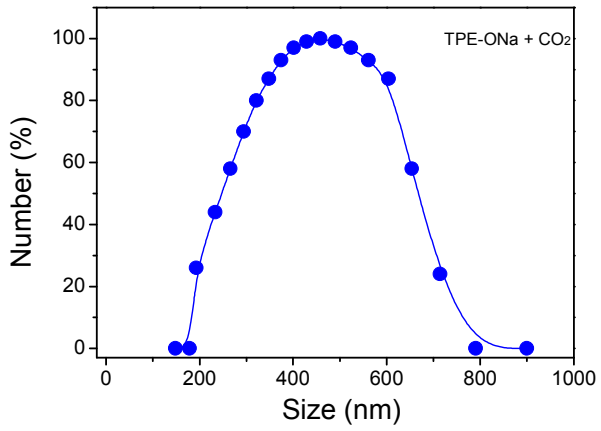

Fig. 4 Dynamic light scattering results for TPE-ONa (50 μM) with CO_2 bubbling in aqueous solution.

Mechanism of CO_2 gas detection

In order to confirm the detection process of CO_2 gas by TPE-ONa, ^{1}H NMR spectroscopic experiments were performed in DMSO-d_6. From Fig. 5, we can see that the resonance signals of protons of TPE-ONa and TPE-OH in the ^{1}H NMR spectra are quite different. The notable change in chemical shifts was observed after the subsequent exposure of TPE-ONa to CO_2 gas, which induced almost complete recovery of the chemical shifts of protons on the phenyl ring, restoring them to the positions observed for TPE-OH. However, the proton signals on the phenol group did not appear after bubbling CO_2 into the solution. The ^{1}H NMR spectral change upon the addition of HCO_3^- into TPE-OH solution indicates that the absence of the proton signals on phenol group might be due to the interaction between HCO_3^- and phenol group (Fig. 5). These results further support the proposal above that the negatively charged TPE-

ONa was transformed to neutral TPE-OH after bubbling CO_2 gas into the solution, thus leading to the remarkable changes in color and photoluminescence.

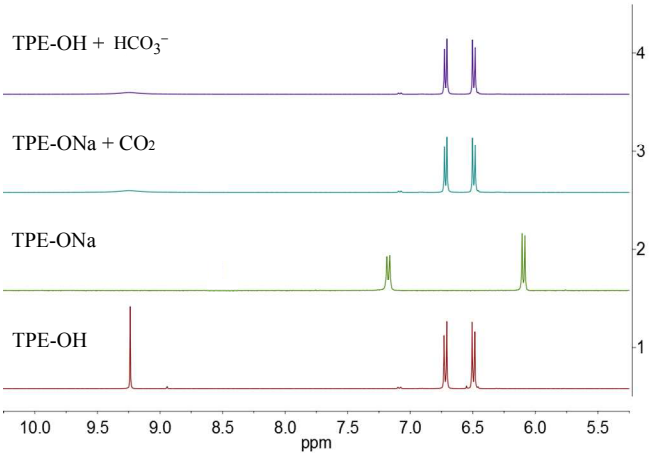

Fig. 5 Partial ^{1}H NMR spectra of TPE-OH, TPE-ONa, TPE-ONa with CO_2 and TPE-OH with HCO_3^- in DMSO-d_6.

Cytotoxicity

The excellent data obtained above in the aqueous solution encouraged us to explore the biological application of TPE-ONa. Firstly, the cytotoxicity towards HeLa cells was evaluated by a standard MTT (MTT = 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl-tetrazolium bromide) assay. The results are illustrated in Fig. 6. After the treatment of the live HeLa cells with different concentrations of TPE-ONa for 24 h, the cellular viabilities were estimated to be approximately 92% at 25 μM, suggesting the low cytotoxicity of TPE-ONa. Thus, it has a good potential to serve as a probe for biological applications.

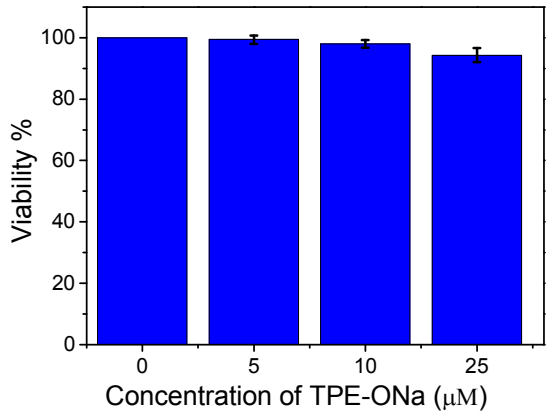

Fig. 6 Cell viability values (%) assessed using a MTT proliferation test versus incubation concentrations of TPE-ONa. HeLa cells were cultured in the presence of 0–25 μM TPE-ONa at 37 ºC for 24 h.

Biological application

The confocal fluorescence microscopy experiment was carried out to explore the capability of TPE-ONa as a specific bioprobe for monitoring the variation of external CO_2 concentration of living cells. Before washing with Roswell Park Memorial Institute 1640 (RPMI 1640) for three times, the live HeLa cells were incubated with 10 μM of TPE-ONa for 2 h at 37 °C and normal atmospheric condition (0.038% CO_2). As shown in Figs. 7a and 7b, only a very weak intracellular fluorescence signal could be observed. Then, the percentage of CO_2 in the incubation chamber was increased from 0.038% to 5% for a further 1h. After the variation, the remarkable intracellular fluorescence signal was subsequently observed (Figs. 7c and 7d). The average intracellular intensity analysis suggests that the emission intensity was enhanced by approximately 4-folds after the concentration of CO_2 increased from 0.038% to 5% (Fig. 7e). These observations suggest that the increase of external CO_2 concentration causes the enhancement of fluorescence emission intensity, revealing the capability of TPE-ONa for measuring the external CO_2 concentration changes of living cells.

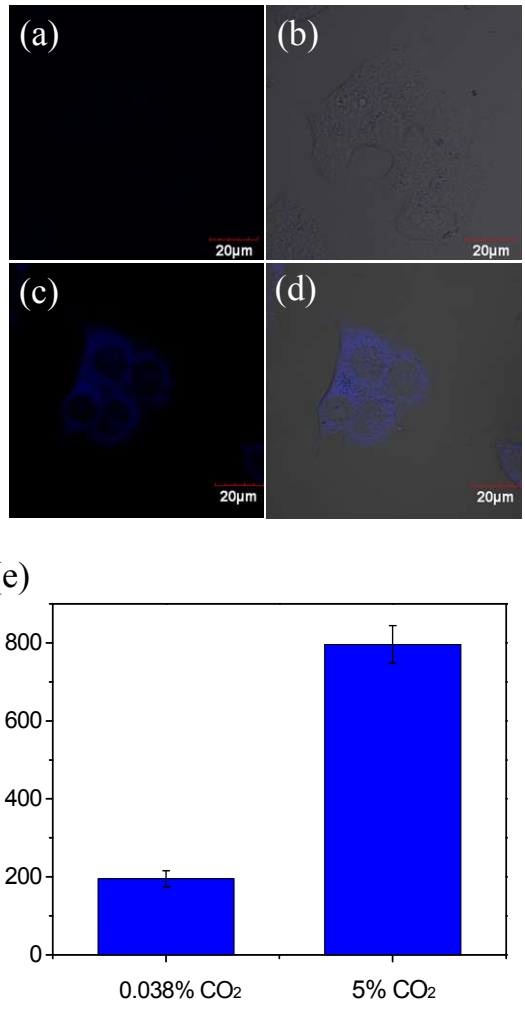

Fig. 7 Fluorescence images of TPE-ONa in HeLa cells. (a, b) HeLa cells incubated with 10 μM TPE-ONa for 2 h at 37 °C and normal atmospheric condition (0.038% CO_2). (c, d) HeLa cells further incubated for 1 h at 37 °C and 5% CO_2. (e) Average fluorescence intensities of TPE-ONa treated with 0.038% CO_2 and further treated with 5% CO_2.

Conclusions

In summary, we have developed a water-soluble fluorescent probe based on tetraphenylethene derivative for CO_2 detection. After bubbling CO_2 into the detection solution, remarkable color change and fluorescence enhancement could be observed. The response of TPE-ONa to CO_2 in aqueous solution is fast and the detection limit is about 2.4×10^{-6} M. To emphasize the practical application of TPE-ONa, a porous film was successfully fabricated by mixing the dye with sodium carboxymethyl cellulose in water, which can serve as an efficient CO_2 gas detector. More importantly, TPE-ONa exhibits low cytotoxicity towards live cells and has the ability to monitor the external CO_2 concentration changes of living cells.

Experimental

General

Commercially available chemical reagents were used without further purification. The solvents were carefully dried and distilled from appropriate drying agents prior to use. NMR spectra were taken on a Bruker Ultrashield 400 MHz FT-NMR spectrometer. Mass spectra were obtained on a Bruker Autoflex matrix-assisted laser desorption/ionization time of flight mass spectrometer (MALDI-TOF MS). UV-vis absorption spectra were recorded using an HP-8453 spectrophotometer. Photoluminescence spectra were measured on an Edinburgh LFS920 fluorescence spectrophotometer.

Synthesis of TPE-OCH_3

Bis(4-methoxyphenyl)methanone (4.84 g, 20 mmol) and zinc powder (2.60 g, 40 mmol) were placed in a round bottomed flask under nitrogen. Dry THF (100 mL) was added and $TiCl_4$ (2.2 mL, 20 mmol) was added dropwise to the solution, and then the mixture was refluxed overnight. After cooling to room temperature, the solution was washed with water, and the mixture was extracted with CH_2Cl_2. Subsequently, the organic layer was collected and evaporated. The resulting crude mixture was subjected to a silica gel column using ethyl acetate/hexane (1/5, v/v) as the eluent to give TPE-OCH_3 in 74% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.97 (d, J = 8.60 Hz, 8H, phenyl group), 6.67 (d, J = 8.71 Hz, 8H, phenyl group), 3.77 (s, 12H, methyl group). MALDI-TOF MS (*m/z*): 453.2 $[M+H]^+$.

Synthesis of TPE-OH

A 5 mL CH_2Cl_2 solution of BBr_3 (53 mmol) was added dropwise to a solution of TPE-OCH_3 (3.0 g, 6.63 mmol) in 20 mL dry CH_2Cl_2 while keeping the mixture at 0 °C. After the addition was complete, the reaction mixture was allowed to stir at room temperature overnight. The reaction mixture was hydrolyzed by dropwise addition of 20 mL H_2O. After the filtration, the precipitate was washed with H_2O and diethyl ether to give TPE-OH in 88% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.24 (s, 4H, phenolic group), 6.70 (d, J = 8.51 Hz, 8H, phenyl group), 6.47 (d, J = 8.55 Hz, 8H, phenyl group). ^{13}C NMR (100 MHz, DMSO-d_6): δ 160.0, 142.3, 139.9, 136.8, 119.3 ppm. MALDI-TOF MS (*m/z*): 397.2 $[M+H]^+$. Elemental analysis (calcd, found for $C_{26}H_{20}O_4$): C (78.77, 78.84), H (5.09, 5.14), O (16.14, 16.02).

Synthesis of TPE-ONa

A solution of TPE-OH (396 mg, 1 mmol) and CH_3ONa (216 mg, 4 mmol) in CH_3OH (10 mL) was heated to reflux. After 2 h, the purple black solution was cooled to room temperature, and then the solution was evaporated to dryness under reduced pressure to give a purple black solid in 97% yield. ^{1}H NMR (400 MHz, DMSO-d_6): δ 7.19 (d, J = 9.2 Hz, 8H, phenyl group), 6.11 (d, J = 8.6 Hz, 8H, phenyl group). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.4, 137.7, 132.3, 123.1, 118.0 ppm. Elemental analysis (calcd, found for $C_{26}H_{16}O_4Na_4$): C (64.47, 64.55), H (3.33, 3.42), O (13.21, 13.09).

CO_2 gas sensing experiments

TPE-ONa dissolved in H_2O and with a concentration of 50 μM was used. CO_2 gas was bubbled into the solution through a 0.5 mm needle. The bubbling rate was fixed and the gas volume was governed by a mass flow controller. 1.5 g sodium carboxymethyl cellulose and 150 mg of TPE-ONa were dissolved in 20 mL water. Then, the mixture was spread onto a glass dish to give a thin film for CO_2 detection.

Cytotoxicity assay

The cytotoxicity of the TPE-ONa towards the cell line Hela has been measured by the methyl thiazolyl tetrazolium (MTT) assay. Before incubated at 25 °C for 24 h, Hela cells in log phase were seeded into a 96-well cell-culture plate at 1×10^4/well. The TPE-ONa (100 μL/well) at the concentrations of 25, 10 and 5 μM was added to the wells of the treatment group. The cells were incubated at 25 °C for 24 h. 20 μL MTT solution (5 mg/mL) was added to each well of the 96-well assay plate, and the solution was incubated for another 3 h under the same condition. A Tecan Infinite M200 monochromator based multifunction microplate reader was used for measuring the OD570 (Absorbance value) of each well referenced at 690 nm. The following formula was used to calculate the viability of cell growth:

$$\text{viability (\%)} = \frac{\text{mean of absorbance value of treatment group}}{\text{mean absorbance value of control}} \times 100$$

In biological studies, the growth of cells in batch culture can be modeled with four different phases: lag phase, log phase, stationary phase, and death phase. The log phase is a period characterized by cell doubling.

Confocal luminescence imaging

The TPE-ONa was dissolved in Roswell Park Memorial Institute 1640 (RPMI 1640) to yield 10 μM solutions. The Hela cells were incubated with the solution of TPE-ONa for 2 h at 37 °C before washing with RPMI 1640. Then, the experiments were performed on an Olympus FV1000 laser scanning confocal microscope and a 60x oil-immersion objective lens. A semiconductor laser was served as the excitation of the Hela cells incubated with TPE-ONa at 405 nm. Emission was collected at 420-480 nm for the Hela cells incubated with TPE-ONa.

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Notes and references

[a] Institute of Molecular Functional Materials, Department of Chemistry and Partner State Key Laboratory of Environmental and Biological Analysis, Hong Kong Baptist University, Waterloo Road, Hong Kong, P. R. China. E-mail: rwywong@hkbu.edu.hk; Fax: +852 34117348; Tel: +852 34117074

[b] Key Laboratory for Organic Electronics & Information Displays (KLOEID) and Institute of Advanced Materials (IAM), Nanjing University of Posts and Telecommunications, Nanjing 210046, P. R. China. E-mail: iamqzhao@njupt.edu.cn; Fax: +86 25 85866396; Tel: + 86 25 85866396

[c] Institute of Polymer Optoelectronic Materials and Devices, State Key Laboratory of Luminescent Materials and Devices, South China University of Technology, Guangzhou 510640, P. R. China.

† Electronic Supplementary Information (ESI) available. See DOI: 10.1039/b000000x/

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Table of Content

A water-soluble tetraphenylethene based probe for luminescent carbon dioxide detection and its biological application

Yun Ma, Yi Zeng, Hua Liang, Cheuk-Lam Ho, Qiang Zhao,* Wei Huang and Wai-Yeung Wong*

A water-soluble tetraphenylethene derivative (TPE-ONa) was developed for luminescent carbon dioxide detection in aqueous solution and porous film, which is able to monitor the variation of external CO_2 concentration of living cells.