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Development of achromatic - chromatic colorimetric sensors for on-off type detection of analytes

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We report the development of achromatic colorimetric sensors; sensors changing their colors from achromatic black to other chromatic colors. An achromatic colorimetric sensor is prepared by mixing a general colorimetric indicator, whose color changes between chromatic colors, and a complementary colored dye with no reaction to the targeted analyte. As the color of an achromatic colorimetric sensor changes from black to a chromatic color, the color change could be much easily recognized than general colorimetric sensors with naked eyes. More importantly, the achromatic colorimetric sensors enable on-off type recognition of the presence of analytes, which have not been achieved from most colorimetric sensors. In addition, the color changes from some achromatic colorimetric sensors (achromatic Eriochrome Black T and achromatic Benedict's solution) could be recognized with naked eyes at much lower concentration ranges than normal chromatic colorimetric sensors. These results provide new opportunities in the use of colorimetric sensors for diverse applications, such as harsh industrial, environmental, and biological detection.

Introduction

Colorimetric sensing is one of the most frequently used analytical methods applicable in various areas including chemical sensing,[1,2] biomolecule sensing,[3-6] temperature monitoring,[7] environmental monitoring,[8,9] health care and safety,[10,11] chemical pollutants,[12,13] and diagnostics.[14,15] As color changes transduced by colorimetric sensors can be easily recognized with human naked eyes, colorimetric sensors can have simple structures and can be operated at negligible power in the absence of complicated instruments. Because of their simplicity and usability, colorimetric sensors can be expanded into array-based sensors (colorimetric sensor array) for multiplexed analysis and have great potential for real time monitoring of anayltes.[16]

Although colorimetric sensors have many important advantages, they also have some critical drawbacks. For most colorimetric sensors, color changes happen between different chromatic colors, such as blue and yellow.

Even though this change of colors can be recognized with naked eyes, it is still difficult for most users to correlate a color and the presence of an analyte because there is no promissory note made to specific chromatic colors. It is also difficult for most users to clearly differentiate two different colors with naked eyes unless the contrast between the two is big enough. As numerous colors can be made by mixing two colors at different ratios, the color change before and after a specific reaction can be ambiguous.[17] One way to solve these problems is to use software programs to analyze the color change before and after the reaction.[18,19] Although this method can provide exact information on the color change, it can still sacrifice many important advantages of colorimetric sensors.

Herein, we report a possible method to solve these critical issues of colorimetric sensors by making sensors that change their colors from achromatic black to other chromatic colors in the presence of analytes. We converted a general chromatic - chromatic color changing sensor to an achromatic - chromatic color changing sensor (achromatic colorimetric sensor) by mixing the former with a complementary colored dye. The complementary colored dye helps the sensor to absorb light over the whole visible wavelength range in the absence of analyte. Through this method, we could make black colored sensors whose colors change to chromatic colors in the presence of analytes. To our knowledge, this is the first study to demonstrate a general method to make an achromatic - chromatic color changing sensor. This study is significant as it not only provides a critical method to solve a major problem of colorimetric sensors but the results can be applied to most colorimetric sensors for broad applications.

Results and discussion

Complementary colors are any two directly opposite color pairs which intensify each other and produce the strongest contrast.[20] As shown in Fig. 1A, color pairs of red and green or blue and orange are a few examples of complementary colors. Two complementary colors have high contrast when they are placed side by side.[21] However, when two complementary colors are mixed together they become dark and will turn black at the right proportions (see parenthesis in Fig. 1B).[22] We adapted this principle of complementary colors to colorimetric sensors to make achromatic colorimetric sensors that change its color from achromatic black to other chromatic colors.

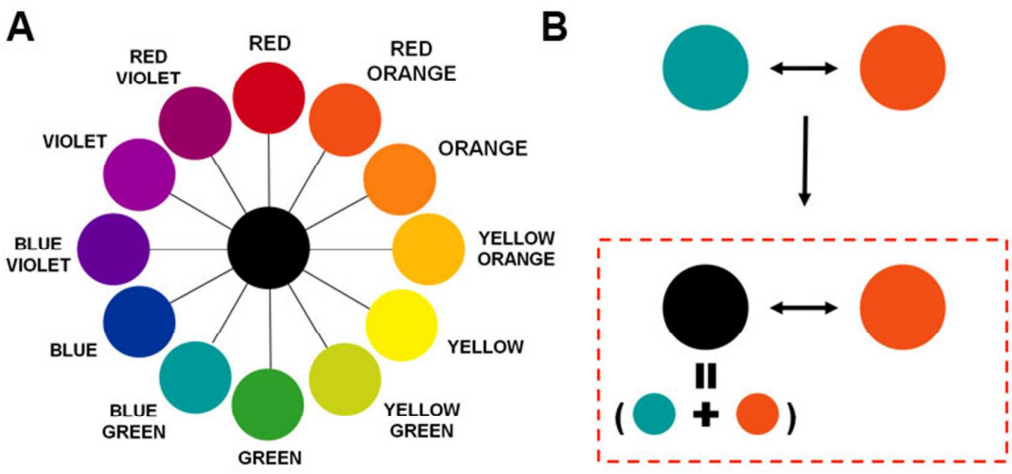

Fig. 1 (A) Color wheel of complementary colors which are directly opposite to each other. The color pairs of red and green, blue and orange, and violet and yellow are representative examples of complementary colors. (B) Schematic representation of the process to make achromatic colorimetric sensors.

Achromatic (black) pH indicator. We first made an achromatic colorimetric pH sensor based on a commercial pH indicator, bromocresol green. Bromocreol green, which belongs to triphenylmethane family, ionizes in aqueous solutions to have a monoanionic form yellow in color; a second proton is lost at higher pH values to yield the dianionic form with a blue color.[23] We observed this color change from blue to yellow (or yellow to blue) depending on the pH value. This color change was also analyzed from a blue (or red)-shift in the absorbance spectra (see Fig. 2A). At pH 7, blue colored bromocreol green has absorbance at 590 - 630 nm (orange range). However, as the pH decreases, the absorbance at 590 - 630 nm decreases while the absorbance at 430 - 480 nm (blue range) increases. Therefore at pH 1, yellow colored bromocreol green has maximum absorbance at 443 nm with no absorbance at 617 nm.

To make a black colored achromatic pH indicator, we prepared an orange colored dye which is complementary to the blue colored bromocresol green at pH 7. This orange complementary dye is prepared by mixing direct red 80 (red color) and tartrazine (yellow color), based on the RYB (red-yellow-blue) color model.[24] To make sure that this orange complementary dye does not have color change at different pH ranges, we varied the pH of the orange complementary dye from pH 7 to pH 1 and monitored its color change. As

shown in Fig. 2B, negligible color change was observed from the orange complementary dye within the pH ranges. This minimal color change could also be verified from insignificant differences in the absorbance spectra. This result indicates that the color of orange complementary dye is not affected by the variation of pH. By combining the bromocresol green and orange complementary dye, we could make an achromatic pH indicator which is black at pH 7. However, when we added small amount of HCl to the indicator, the color of the achromatic pH indicator started to change and it appeared orange at pH 1 (see Fig. 2C).

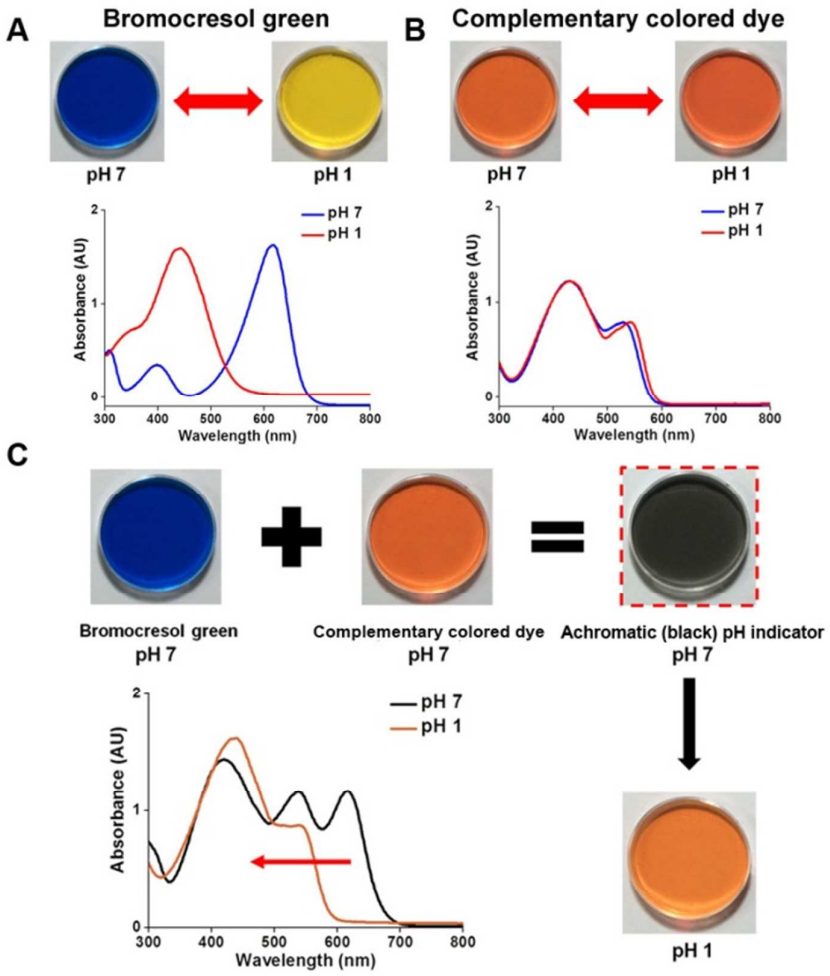

Fig. 2 (A, B) Color changes of the bromocresol green (pH indicator) and complementary colored dye at different pH values. While bromocresol green changes its color from blue to yellow (or yellow to blue), and show a blue (red)-shift in the absorbance spectra, complementary colored dye maintains its color (orange color) and shows no shift in the absorbance spectra within pH 1 and 7. (C) Photograph of the process to make an achromatic (black) pH indicator. At pH 7, achromatic (black) pH indicator

has black color, and absorbs all visible light (400 - 700 nm). As the pH decreases, the achromatic (black) pH indicator changes its color from black to orange, and shows a blue shit of absorbance.

A UV-vis spectrophotometer was used to quantitatively analyze the change of color depending on pH. As expected, the achromatic pH indicator nearly absorbed all visible light (400 - 700 nm) at pH 7 as shown in Fig. 3A. However, as the pH value of achromatic pH indicator decreased, we observed the absorbance of achromatic pH indicator decreasing substantially at the orange range (590 - 630 nm). As a result, only absorbance in blue range (430 - 480 nm) was left within pH 1 and pH 3. We attribute this variation of the absorbance spectra of achromatic pH indicator to the reaction of bromocresol green at different pH. We already observed that bromocreosol green changes its color from blue to yellow (or yellow to blue) and shows a blue (red)-shift in the absorbance spectra according to pH value. In contrast, complementary colored dye maintained its color (orange color) and showed no shift in the absorbance peak regardless of pH value (see Fig. 2A-B). Therefore, when the pH value decreases, only bromocresol green in achromatic pH indicator changes its color from blue to yellow and shows a blue-shift in the absorbance spectra. As a result, the color of achromatic pH indicator is mainly originated from the yellow color of bromocresol green and orange color of complementary dye at low pH range (pH 1 - pH 4). The extent of color change of the achromatic pH indicator is presented by the titration curve as shown in Fig. 3B. In order to quantify the variation of the color of achromatic pH indicator we used the ratio between the absorbance at 430 - 480 nm (blue) and 590 - 630 nm (orange) ranges. When the absorbance ratio between the two ranges is low, the achromatic pH indicator should be colored black. At pH 7, the absorbance ratio between the two ranges was close to 1.35. On the other hand, when the ratio between the two ranges increases the color of the achromatic pH indicator should change. As pH decreased to 6 and 5, there was a small increase in the absorbance ratio and a slight color change was observed. Within the range of pH 3 and pH 5, there is an abrupt increase of absorbance ratio in titration curve. It suggests that the transition pH range of the achromatic pH indicator is approximately from pH 3 to pH 5, similar to the reported transition interval of bromocrseol green (pH 3.4 - pH 5.4).[25] It should be emphasized that the achromatic pH indicator has black color (off-signal) at neutral pH, while it is orange colored (on-signal) at acidic pH. Therefore as the indicator changes its color from black to orange, the achromatic pH indicator helps users to distinguish neutral pH from acidic pH instinctively. It is difficult to achieve this with normal bromocresol green, as the indicator shows multiple chromatic colors of blue, green, and yellow depending on the pH (see Fig. S1).

Even though we have shown an example of an achromatic pH sensor using bromocresol green, it is also possible to make similar achromatic sensors from other pH indicators. We have demonstrated other two examples using metanil yellow and bromocresol purple (see Fig. S2-S3). They not only changed their color from black to purple and black to green depending on the pH variation, respectively, but also preserved the properties of normal pH indicators quite well with the color transition occurring at the normal indicator's transition ranges.

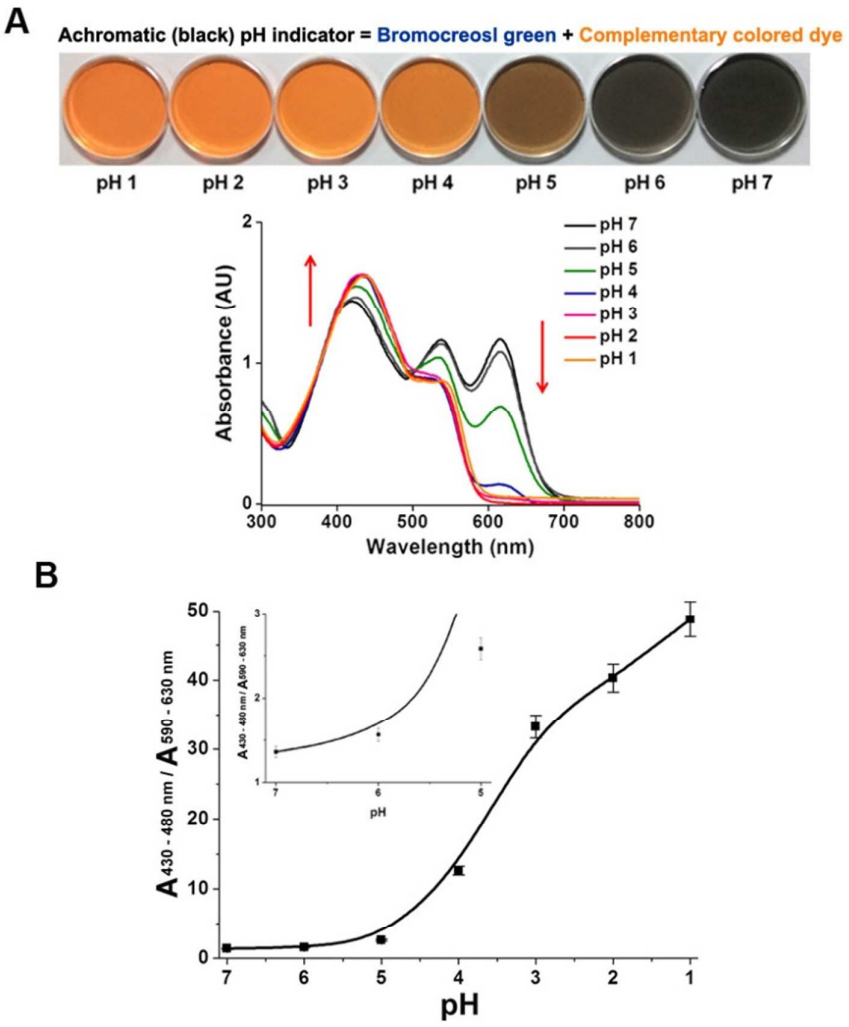

Fig. 3 (A) Color change of the achromatic (black) pH indicator depending on the variation of pH (from pH 7 to pH 1). As the pH decreases, the color of achromatic (black) pH indicator changes from black to orange with a decrease of absorbance at 590 - 630 nm (orange range). (B) Quantification of the

transition pH range of the achromatic (black) pH indicator by monitoring the absorbance ratio between blue (430 - 480 nm) and orange (590 - 630 nm) ranges.

Achromatic (black) Eriochrome Black T. After we found out that it is possible to make an achromatic pH indicator, we next became interested in expanding our concept to sensors used in other applications. A candidate was selected among the indicators whose color cannot be surely differentiated by adding analytes. Eriochrome Black T (EBT) is a colorimetric indicator used to detect the presence of rare earth metal ions,[26] such as calcium[27] and magnesium.[28] We first monitored the color change of normal EBT after treating them with different concentrations of Ca^{2+}. As the concentration of Ca^{2+} increased, the color of EBT changed from red-violet to light pink at pH 6 (see Fig 4). As shown in Fig. S4, red-violet colored EBT had a major absorbance at 496 - 570 nm (green range). However, the absorbance of EBT at 496 - 570 nm substantially decreased when we added Ca^{2+} into the solution. Next, we prepared light green colored complementary dye by combining tartrazine and fast green FCF solutions and investigated whether the complementary dye has response to Ca^{2+}. Through observation with naked eyes and absorbance measurement with UV-vis spectrophotometer, we could verify that the complementary dye has minimal color change in the presence of Ca^{2+} (see Fig. S4A).

EBT was mixed with the light green complementary dye to make achromatic EBT (see Fig. 4A). As Ca^{2+} was added to the achromatic EBT, its color changed from black to green. This color change of achromatic EBT could also be monitored from the variation of absorbance at 496 - 570 nm (green range) depending on the concentrations of Ca^{2+} (see Fig. S4B). This indicates that only EBT can affect the color change of achromatic EBT through reaction with Ca^{2+}, because there is negligible difference of absorbance spectra from light green complementary dye. As the concentration of Ca^{2+} increased, the absorbance of green range (496 - 570 nm) gradually decreased. In result, achromatic EBT changed its color from black to green after reaction with Ca^{2+}. The titration curve of achromatic EBT showed that it had the detection limit of 20 μM (see Fig. 4C).

It should be emphasized that the color change of achromatic EBT is more recognizable with naked eyes at low concentration ranges of Ca^{2+} than the normal EBT. As shown in Fig. 4B, we could identify the color change of achromatic EBT from black to green at the Ca^{2+} concentration of 20 - 30 μM. Surprisingly, this concentration range is comparable to the detection limit obtained with UV-vis spectrophotometer (20 μM). On the other hand, the color change of normal EBT could not be recognized until the Ca^{2+} concentration reached 50 - 100 μM. Since it is much easier for users to distinguish an achromatic color and a chromatic color than two chromatic

colors, achromatic EBT can be very helpful for users to identify the color change in the presence of Ca^{2+}, compared with normal EBT.

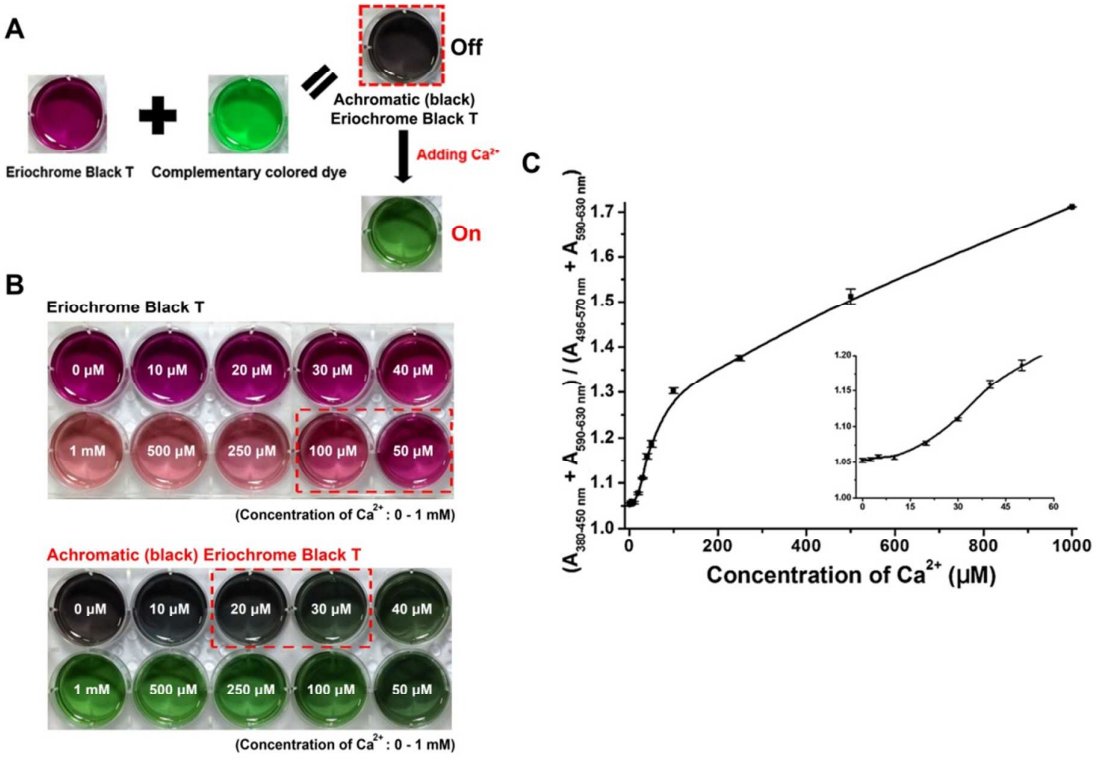

Fig. 4 (A) Photograph of the process to make achromatic (black) Eriochrome Black T (EBT). The color of achromatic (black) EBT changes from black to green in the presence of Ca^{2+}. (B) Color changes of achromatic (black) EBT and normal EBT with different concentrations of Ca^{2+}. In the case of achromatic (black) EBT, its color change can be easily recognized at the Ca^{2+} concentration ranges of 20 -30 μM. On the other hand, color change of normal EBT cannot be recognized until the Ca^{2+} concentration reached 50 - 100 μM. (C) The calibration curve of the achromatic (black) EBT obtained by monitoring the absorbance ratio between red-violet (380 - 450 nm) green (496 - 570 nm) ranges. The detection limit is 20 μM.

Achromatic (black) Benedict's solution. In order to find whether this method can be used for biosensing applications, we prepared an achromatic colorimetric sensor based on Benedict's solution. Benedict's solution is a colorimetric indicator used to detect sugar molecules, such as glucose, fructose, and maltose. Benedict's solution has blue-green color because it contains copper sulfate in water. When it is mixed and heated with a

sugar, its color changes from blue-green to brick red or brown. During this process Cu^{2+} is reduced to Cu^{+} by the oxidization of the aldehyde group of the sugar.[29] So the color of the Benedict' solution changes from blue-green to brown through increase of absorbance at 480 - 530 nm (blue-green range) as shown in Fig. S5.

To make an achromatic Benedict's solution, we prepared a red-orange colored complementary dye using direct red 80 and tartrazine solutions. The red-orange complementary dye did not change its color, and showed no shift of the absorbance peak in the presence of glucose (See Fig. S5). By mixing Benedict's solution and red-orange complementary dye, we made black colored achromatic Benedict's solution. When glucose was added to achromatic Benedict's solution, the color change from black to brownish orange (see Fig. 5A) was observed. This color change could also be verified from the variation of absorbance peak in the presence of different concentrations of glucose (see Fig. S5). As expected, achromatic Benedict's solution nearly absorbed all visible light (400 nm - 700 nm) in the absence of glucose. However, as the concentration of glucose increased, the amount of absorbance at 480 - 530 nm (blue-green range) increased, while the absorbance at 650 - 730 nm (red-orange range) decreased. This variation of absorbance spectra suggests that the color change of achromatic Benedict's solution from black to brownish orange is mainly due to the variation of color in the Benedict's solution. The quantitative analysis of achromatic Benedict's solution was measured by monitoring the absorbance ratio at the wavelengths of 480 - 530 nm (blue-green range) and 650 - 730 nm (red-orange range) after adding various concentrations of glucose. As a result, the detection limit of the achromatic Benedict's sensor was determined to be approximately 2 mM (see Fig. 5C). The color change of achromatic Benedict's solution from black to brownish orange was recognizable with naked eyes within the glucose concentration of 1 - 3 mM. However, the color change of normal Bendict's solution was not recognizable until the concentration reached 10 - 30 mM (see Fig. 5B). This indicates that color change of achromatic Benedict's solution can be much easily recognized than normal Benedict's solution with naked eyes. Furthermore, as black color is conventionally related to information of “off” or “none”, the color change from black to brownish orange helps the user to easily recognize the existence of glucose, compared with normal Benedict solution.

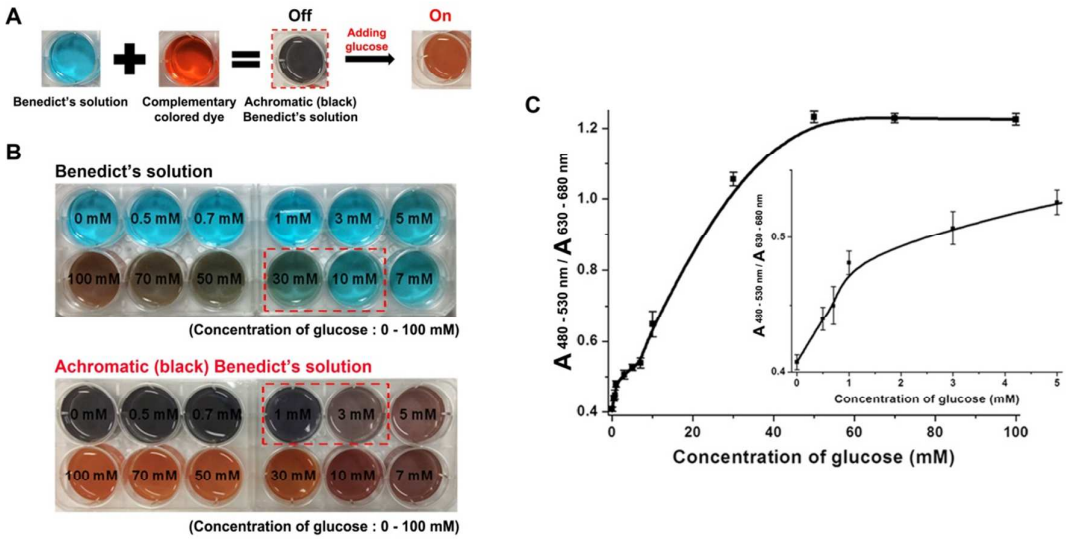

Fig. 5 (A) Photograph of the process to make an achromatic (black) Benedict's solution. In the presence of glucose, the color of achromatic (black) Benedict's solution changes from black to brownish orange. (B) Color changes of achromatic (black) Benedict's solution and normal Benedict's solution with different concentrations of glucose. In the case of achromatic (black) Benedict's solution, its color change from black to brownish orange could be easily recognized at glucose concentration of 1 - 3 mM. However, the color change of normal Benedict's solution could not be distinguished up to 10 - 30 mM of glucose. (C) The titration curve of achromatic (black) Benedict's solution. The detection limit is 2 mM.

Conclusion

In summary, we have successfully made achromatic colorimetric sensors, whose colors change from black to other chromatic colors in the presence of analytes. An achromatic colorimetric sensor could be made by simply mixing a general colorimetric sensor with a complementary colored dye. Through five different examples, we have shown that achromatic colorimetric sensors not only help the users distinguish color changes easily but also allow on-off type signal recognition which is not generally possible with traditional colorimetric dyes. In addition, achromatic colorimetric sensors makes it possible for the users to perceive color changes with the naked eye at low concentration of analytes, and instinctively recognize the existence of analytes. We believe this proposed work is significant as it can be applied to most general colorimetric sensors to significantly improve their properties and also add new functions which were very difficult to be achieved with traditional colorimetric sensors.

Experimental

Preparation of the achromatic pH sensor

a. Bromocresol green (used for pH indicator)

The orange complementary dye was prepared by mixing 4.5 mL of direct red 80 solution (100 μM, Dye content 25%, Sigma-Aldrich) and 6 mL of tartrazine solution (100 μM, Dye content ≥85%, Sigma-Aldrich) at pH 7. The pH of orange complementary dye was measured with a pH meter (SP-2100, SUNTEX). To obtain the achromatic colorimetric pH sensor, we added the orange complementary dye to 4.5 mL of bromocresol green (100 μM, Dye content 95%) solution. After we observed that the achromatic colorimetric pH sensor has black color at pH 7, hydrochloric acid (ACS reagent, 37%, Sigma-Aldrich) or phosphoric acid solution (85 wt. % in H_2O, Sigma-Aldrich) was used to lower the pH of the achromatic colorimetric pH sensor from pH 7 to pH 1. The color change of achromatic colorimetric pH sensor was monitored with the naked eye and a UV-vis spectrophotometer (Hewlett-Packard 8453), respectively.

b. Metanil yellow (used for pH indicator)

The blue-violet complementary dye was prepared by mixing 3 mL of direct red 80 solution (100 μM) and 13 mL of basic blue 31 (100 μM, Dye content 40%, Sigma-Aldrich) at pH 4. 3 mL of metanil yellow (100 μM, Dye content 75%, Sigma-Aldrich) and added to blue-violet complementary dye to make achromatic colorimetric pH sensor which has a black color. Hydrochloric acid was used to decrease the pH value from pH 4 to pH 1. The color change of achromatic colorimetric pH sensor was monitored with the naked eye and a UV-vis spectrophotometer, respectively.

c. Bromocresol purple (used for pH indicator)

The green complementary dye was prepared by mixing three solutions, 0.7 mL of direct red 80 solution (1 mM) and 16 mL of tartrazine solution (1 mM) and 7 mL of basic blue 31 (1 mM) at pH 10. Then, to obtain an achromatic pH sensor, 105 mL of bromocresol purple (100 μM, technical grade, Sigma-Aldrich) was added at the green complementary dye solution. Hydrochloric acid was used to decrease the pH value from pH 10 to pH

1. The color change of achromatic colorimetric pH sensor was monitored with the naked eye and a UV-vis spectrophotometer, respectively.

Preparation of the achromatic Eriochrome Black T (EBT) sensor

The green complementary dye was prepared by mixing 4.5 mL of tartrazine solution (100 μM) and 1.2 mL of fast Green FCF (100 μM, Dye content ≥85%, Sigma-Aldrich). To obtain an achromatic EBT sensor, the green complementary dye was added to 10mL of EBT (140 μM, Reag. Ph. Eur., indicator for metal titration, Sigma-Aldrich) solution. The pH of the achromatic EBT sensor was measured with a pH meter, and controlled using hydrochloric acid and 1 M of sodium hydroxide (ACS reagent, ≥97.0%, Sigma Aldrich). After the achromatic EBT sensor became black in color at pH 6, the stock solution of calcium chloride (ACS reagent, Sigma-Aldrich)was treated with stock solution of achromatic EBT sensor different at concentrations (0 – 1 mM). The color change of achromatic EBT sensor was monitored with the naked eye and a UV-vis spectrophotometer, respectively.

Preparation of the achromatic Benedict's solution sensor

To obtain achromatic Benedict's solution, red-orange complementary dye was mixed with 4 mL of direct red 80 solution (100 μM) and 3 mL of tartrazine solution (100 μM). Red-orange complementary dye solution was added to the 8 mL of Benedict's reagent to make achromatic Benedict's solution which is black in color. After achromatic Benedict's solution became black in color, we treated different concentrations of glucose (D-(+)-Glucose ≥99.5%, Sigma-Aldrich) from 100 to 0.5 mM. The achromatic Benedict's solution was then heated in a boiling water bath for two minutes. A few minutes later, the color of each achromatic Benedict's solution was monitored by the naked eyes and a UV-vis spectrophotometer, respectively.

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Notes and references

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† Electronic Supplementary Information (ESI) available: Photographs, and UV-vis spectra of other black indicators, Eriochrome Black T, and Benedict's reagent. See DOI : 10.1039/b000000x/

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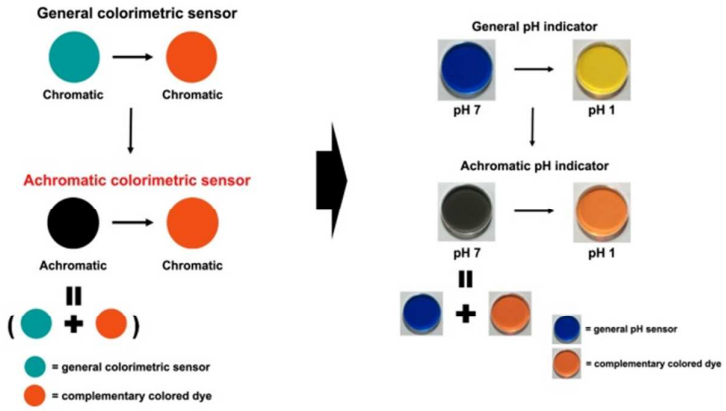

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We developed a method to convert a general colorimetric sensor to an achromatic colorimetric sensor by introducing a complementary colored dye to the sensor. Color change of most colorimetric sensors happens between two chromatic colors. However, the color change of achromatic colorimetric sensor happens between achromatic black and a chromatic color. This achromatic colorimetric sensor can significantly improve traditional colorimetric sensors as they help users distinguish color change easily and allow on-off type signal recognition. In addition, achromatic colorimetric sensor helps users to detect the presence of analytes at much lower concentration and recognize the existence of analytes instinctively.