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A fluorescent light-up platform with "AIE + ESIPT" characteristics for multi-target detection both in solution and on paper strip

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Abstract

We report a fluorescent light-up platform for multi-target detection in aqueous solution and on paper strip. The platform is based on salicylaldazine fluorogen with aggregation-induced emission (AIE) and excited state intramolecular proton transfer (ESIPT) characteristics, which shows distinguished advantages including ease of chemical modifications, free of self-quenching effect, excellent light-up ratio and large Stokes shift. To demonstrate the versatility of the platform, palladium cation and perborate anion, as well as UV light were selected as the targets. The three representative probes of **AIE-Pd**, **AIE-Perborate** and **AIE-UV** light up specifically in the presence of the target both in aqueous solution and on paper strip. The immediate naked-eye response makes the probes ideal for instrument-free and power-free detection.

Key words:

Paper-based detection; Naked-eye sensing; Aggregation-induced emission; Excited state intramolecular proton transfer; Multi-target detection; Light-up sensing

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Introduction

The prevalence of chemicals in daily life leads to the concerns of subsequent pollutions and requires convenient methods to monitor their levels. For instance, palladium plays critical roles in automobile industry, dental crown production, and pharmaceutical manufacture.[1] However, palladium interferes the normal cell metabolism by binding to thiol-containing proteins and DNA.[2, 3] On the other hand, the perborates have been used extensively in cosmetics, medicinal formulations and bleach.[4, 5] Although they are safer alternatives to hydrogen peroxide,[6] mutagenic effect has been found in *in vitro* experiments.[7] Therefore, close monitoring of their usage and residues is of high importance. In addition, many useful products such as medication, developing agents and chemicals are photo-sensitive and should be kept away from light. It is ideal to have an easy and convenient platform, which could be generally used to detect cations, anions and UV light through simple modification.

Fluorescent probes are powerful tools for various detection tasks, which enjoy great promises due to their high sensitivity and selectivity.[8-10] Last several decades have witnessed the prosperity of fluorescent probes in solution detection. Moreover, the concept of "lab-on-paper", for instance, lateral flow assays, has been widely reported with advantages such as low cost, portability and operational simplicity.[11-13] Gold nanoparticles (NPs) and quantum dots (QDs) are typical signal reporters for colorimetric and fluorescent sensing on paper strip.[14] To realize specific analyte detection, recognition elements, such as nucleic acid or antibody are frequently required for nanoparticle modification.[15, 16] The colorimetric and fluorescence changes are usually induced by the aggregation of gold NPs or the separation of a donor from an acceptor in the vicinity in a fluorescence resonance energy transfer (FRET) system. On the other hand, reaction based fluorescent systems which can simultaneously achieve signal recognition and transduction have been less reported on solid support.[17] For example, although palladium species have been intensively studied in solution by probes based on rhodamine,[18-20] fluorescein[21] and other conventional organic fluorogens,[22, 23] very few of them have been further applied on solid substrate.[20, 23] As compared to Pd detection, fluorescent probes for perborate detection are less developed, and the reported assays are limited to solution sensing.[24, 25] In addition, photo-sensitive probes in the form of paper-strip are highly desirable as photo-exposure indicators, but remain limited.[26] Therefore, a platform that can offer fluorescent multi-target detection not only in solution but also on solid substrate is promising for real-life applications.

The development of small molecule based fluorescence light-up paper strip faces a few challenges. It is well known that traditional fluorogens suffer from aggregation-caused quenching (ACQ), which greatly affects the detection sensitivity. In addition, due to the intrinsic fluorescence of most fluorescent probes, additional quencher or fluorescence quenching mechanism must be included on the substrate prior to analyte sensing in order to yield light-up signals.[27-29] Bioprobes based on fluorogens with aggregation-induced emission (AIE) characteristics have attracted increasing attention during the past years, as the AIE fluorogens generally show high fluorescence in aggregate state.[30, 31] This is due to the typical feature AIE fluorogens: they are non-emissive when moleculary dissolved but become highly emissive in the aggregate state.[32-34] It is ideal if one could develop a strategy to quench the fluorescence of AIE fluorogens in solid state, which upon analyte-induced reaction to yield emissive product that

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could fully take advantage of AIE characteristics to offer high detection sensitivity. In this regard, salicylaldazine dye, which shows both AIE and excited state intramolecular proton transfer (ESIPT) properties, offers a unique opportunity for sensing on solid substrate.[35] The salicylaldazine dye generally shows weak blue emission when the excited-state proton transfer from hydroxyl group (proton donor) to nitrogen (proton acceptor) is blocked. In contrast, deprotection of the hydroxyl groups could revert the fluorescence by restoration of the proton transfer and formation of intramolecular hydrogen bond. Together with the restriction of intramolecular motions, this will lead to high fluorescence in the aggregate state.

Herein, we propose a multi-target light-up platform based on the "AIE + ESIPT" fluorogen of salicylaldazine. To demonstrate that the design concept is generally applicable to multiple targets, palladium cation, perborate anion, and UV light are chosen as the representative examples. Three different functional groups are conjugated onto the structure of salicylaldazine to yield three probes, namely, **AIE-Pd, AIE-Perborate** and **AIE-UV**. The three probes are weakly emissive in aqueous solution, which light up in the presence of targets as a result of the functional group deprotection from the hydroxyl groups. Moreover, by drop-casting on paper strip, these probes are ready for naked-eye detection of analyte with the assistance of a portable UV lamp. The visual paper assay offers opportunities for use in resource-limited settings as well as in emergency situation.

Experimental Section

Materials

2-Hydroxybenzaldehyde, 2-(allyloxy)benzaldehyde, 1-(bromomethyl)-2-nitrobenzene, 1,4-dibromobutane, cesium carbonate, hydrazine monohydrate, acetic anhydride, morpholine, ethanol, anhydrous DMF were all purchased from Aldrich. All the other chemicals were purchased from Sigma–Aldrich or Merck. 2,2'-((1*E*,1'*E*)-hydrazine-1,2-diylidenebis(methanylylidene))diphenol was prepared according to the literature.[36]

Equipment and Methods

The UV-vis absorption spectra were obtained using UV-vis spectrometer (Shimadzu, UV-1700, Japan). PL measurements were carried out on a Perkin-Elmer LS-55 equipped with a xenon lamp excitation source and a Hamamatsu (Japan) 928 PMT, using 90° angle detection for solution samples. ^{1}H and ^{13}C NMR spectra were measured on a Bruker ARX 400 NMR spectrometer. The molecular mass was acquired using ion trap-time-of-flight mass spectrometry (MS-IT-TOF) (Shimadzu). The pH values of buffers were adjusted using a Sartorius basic pH-Meter PB-10.

Synthesis and Characterization

Synthesis of 1,2-bis ((*E*)-2-(allyloxy)benzylidene)hydrazine (AIE-Pd):
2-(Allyloxy)benzaldehyde (162 mg, 1.0 mmol) was dissolved in absolute ethanol (10 mL), followed by the addition of hydrazine monohydrate (25 mg, 0.5 mmol), and the mixture was refluxed for 4 h. Precipitates were filtrated under vacuum and washed with absolute ethanol for three times before drying under vacuum. Pure product of 1,2-bis ((*E*)-2-(allyloxy)benzylidene) hydrazine (**AIE-Pd**) was obtained as a yellow powder solid (135 mg, 84% yield). ^{1}H NMR

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($CDCl_3$, 400 MHz): δ 9.14 (s, 2H), 8.14 (d, J = 7.6 Hz, 2H), 7.39 (t, J = 7.6 Hz, 2H), 7.02 (t, J = 7.6 Hz, 2H), 6.93 (d, J = 8.4 Hz, 2H), 6.12–6.04 (m, 2H), 5.45 (d, J = 17.2 Hz, 2H), 5.31 (d, J = 10.4 Hz, 2H), 4.62 (d, J = 4.8 Hz, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 158.1, 157.5, 132.9, 132.3, 127.4, 123.0, 121.0, 117.8, 112.4, 69.2. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{20}H_{20}N_2NaO_2$: 343.1417; found: 343.1422.

Synthesis of ((1*E*,1′*E*)-hydrazine-1,2-diylidene bis(methanylylidene))bis(2,1-phenylene) diacetate (AIE-Perorate):

2,2'-((1*E*,1′*E*)-hydrazine-1,2-diylidenebis(methanylylidene))diphenol (240 mg, 1.0 mmol) was dissolved in DMF (5 mL), followed by addition of Cs_2CO_3 (652 mg, 2.0 mmol), acetic acid anhydride (408 mg, 4.0 mmol), and the mixture was stirred at 60 ^{o}C for 8 h. After cooling to room temperature, the solvent was removed under vacuum, and the residue was extracted with dichloromethane (40 mL × 3). The extracts were washed with brine, dried over anhydrous $MgSO_4$, and concentrated under reduced pressure. The residue was further recrystallized from ethanol/hexane to give **AIE-perborate** as a yellow solid (285 mg, 88% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.73 (s, 2H), 8.11 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.17 (d, J = 8.4 Hz, 2H), 2.39 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): 169.1, 157.1, 150.3, 132.2, 128.5, 126.3, 126.2, 123.1, 21.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{18}H_{16}N_2NaO_4$: 347.1002; found: 347.1011.

Synthesis of 2-((2-nitrobenzyl)oxy)benzaldehyde:

2-Hydroxybenzaldehyde (244 mg, 2.0 mmol) and 1-(bromomethyl)-2-nitrobenzene (428 mg, 2.0 mmol) were first dissolved in DMF (10 mL), followed by the addition of Cs_2CO_3 (652 mg, 2.0 mmol). The mixture was stirred at 60 ^{o}C under nitrogen for 12 h. After cooling to room temperature, the reaction mixture was extracted by dichloromethane (40 mL × 3). The combined dichloromethane fractions were dried over anhydrous $MgSO_4$ and concentrated under reduced pressure. The residue was further separated by column chromatography (silica, petroleum ether: ethyl acetate = 20 : 1, v/v) to give a light yellow solid (447 mg, 87% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 9.26 (s, 1H), 8.20 (d, J = 7.6 Hz, 2H), 7.99 (d, J = 7.6 Hz, 1H), 7.73 (t, J = 7.6 Hz, 1H), 7.52 (t, J = 7.6 Hz, 1H), 7.45 (t, J = 7.6 Hz, 1H), 7.10 (t, J = 7.6 Hz, 1H), 7.02 (d, J = 8.4 Hz, 1H), 5.61 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): 157.7, 157.6, 146.9, 134.2, 133.4, 132.8, 128.6, 128.5, 128.2, 125.1, 123.0, 121.8, 112.8, 67.4.

Synthesis of 1,2-bis((*E*)-2-((2-nitrobenzyl)oxy) benzylidene)hydrazine (AIE-UV):

2-((2-Nitrobenzyl)oxy)benzaldehyde (257 mg, 1.0 mmol) was dissolved in absolute ethanol (10 mL), followed by addition of hydrazine monohydrate (25 mg, 0.5 mmol), and the mixture was refluxed for 4 h. Precipitates were filtrated under vacuum and washed with absolute ethanol for three times, before drying under vacuum. The pure product of 1,2-bis((*E*)-2-((2-nitrobenzyl)oxy)benzylidene) hydrazine (**AIE-UV**) was obtained as a yellow powder solid (237 mg, 89% yield). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 8.93 (s, 2H), 8.14 (d, J = 8.0 Hz, 2H), 8.01 (d, J = 7.6 Hz, 2H), 7.86 (d, J = 7.6 Hz, 2H), 7.79 (t, J = 7.6 Hz, 2H), 7.63 (t, J = 7.6 Hz, 2H), 7.50 (t, J = 7.6 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 7.08 (t, J = 7.6 Hz, 2H), 5.58 (s, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz): 157.3, 156.5, 147.6, 134.0, 133.0, 131.8, 129.5, 129.4, 127.2, 124.8, 122.0, 121.4, 113.3, 67.0. HRMS (ESI): m/z $[M + Na]^+$ calcd for $C_{28}H_{22}N_4NaO_6$: 533.1432; found: 533.1447.

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Solution Sensing

The PL spectra of the probes of **AIE-Pd** and **AIE-UV** were measured in the mixture of THF/H_2O (v/v = 1/99) at excitation wavelength of 365 nm. For detection of palladium species, 10 mM $NaBH_4$ was used as a reducing agent to increase the reaction efficiency. The selectivity of the **AIE-Pd** was verified through screening various metal ions including Cu^{2+}, Fe^{3+}, Hg^{2+}, Ru^{3+}, Pb^{2+} and Mn^{2+}. The cation stock solutions were prepared from $CuSO_4$, $FeCl_3$, $HgCl_2$, $RuCl_3$, $Pb(OAc)_2$, and $MnCl_2$ in aqueous solution with a concentration of 10 mM, respectively. The detection experiments of **AIE-Perborate** responsive to perborate ion were conducted in 1 mL of THF/HEPES (10 mM, pH 5.0) (v/v = 1/99) solution. The selectivity of the **AIE-Perborate** for anions was verified through screening various anions, including F^-, Cl^-, Br^-, I^-, HSO_3^- and $S_2O_3^{2-}$. The anion stock solutions were prepared from KF, NaCl, NaBr, NaI, $NaHSO_3$, and $Na_2S_2O_3$ in aqueous solution with a concentration of 100 mM, respectively. The 10 mM stock solution of **AIE-UV** was first exposed to UV light for increasing time (0, 10, 20, 30, 40, 50, 60 and 70 min, respectively), and 1 μL of the stock solution was dilute to 1 mL (10 μM) before PL measurement.

Solid state Sensing

Whatman filter paper (Advantec, qualitative, 70 mm) was used as the solid substrate for all the solid state sensing. First, 10 μL of THF stock solution of the probe (1.0 mM) was drop-casted onto the filter paper followed by evaporation of THF. Then analytes of different concentrations (as specified in the figure captions) were added onto the spots. All the pictures were taken under UV illumination.

Results and Discussion

Probe design and synthesis. A light-up platform has been designed based on salicylaldazine for multi-target sensing. **AIE-Pd**, **AIE-Perborate** and **AIE-UV** were synthesized with allyl, acetyl and 2-nitrobenzyl group for detection of palladium,[37, 38] perborate ions, and UV light (Scheme 1), respectively. The three probes have unique combination of AIE and ESIPT properties, making them suitable for detection both in solution and on solid substrate. Initially, the probes is only weakly blue-emissive in solution and on paper strip. Deprotection of hydroxyl groups would light up the emission at longer wavelength by restoration of the hydrogen bonds allowing the formation of intramolecular hydrogen bonds**.** The structures and synthetic routes to the three probes are shown in Scheme 1. The probe **AIE-Pd** was synthesized in 84% yield through the condensation reaction between 2-(allyloxy)benzaldehyde and hydrazine monohydrate. The probe **AIE-Perborate** was synthesized in 88% yield through the reaction between salicylaldazine and acetyl anhydride in DMF using Cs_2CO_3 as a base. For the synthesis of the **AIE-UV**, 2-((2-nitrobenzyl)oxy)benzaldehyde was first prepared from 2-hydroxybenzaldehyde and 1-(bromomethyl)-2-nitrobenzene in 87% yield, which was then reacted with hydrazine monohydrate to afford the **AIE-UV** product in 89% yield. The ^1H NMR, ^{13}C NMR and HRMS data confirm their right structures. Detailed spectra are shown in the experimental section and supporting information.

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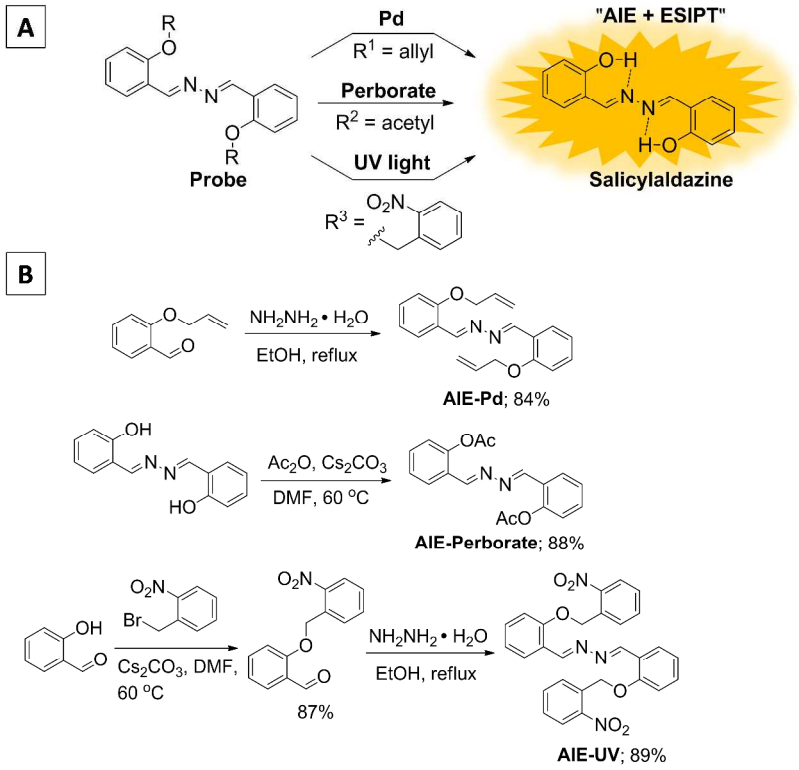

Scheme 1 (A) Design principles of fluorescent light-up probes **AIE-Pd**, **AIE-Perborate**, and **AIE-UV** based on a platform of salicylaldazine with "AIE + ESIPT" characteristics for detection of palladium cation, perborate anion, and UV light and (B) synthetic routes to the probes.

Optical properties. The UV-vis absorption and PL spectra of salicylaldazine were measured in tetrahydrofuran (THF) and the results are shown in Fig. 1A. In THF, the maximum absorption wavelength of salicylaldazine is 365 nm, while its emission intensity is very low. The AIE characteristics of salicylaldazine were studied by measuring its PL intensity changes in a solvent mixture of THF and water. The PL intensity (I) at 542 nm remains very low even when water fraction reaches 90% (I/I_0 is less than 0.07, I_0 is the PL intensity at 542 nm when the water fraction is 99%), while an intense emission was observed at 542 nm when the water fraction reaches 99%, which verifies that salicylaldazine has typical AIE properties. Moreover, the large Stokes shift of 8947 cm^{-1} derived from ESIPT mechanism is also a desired property for solid-state sensing.

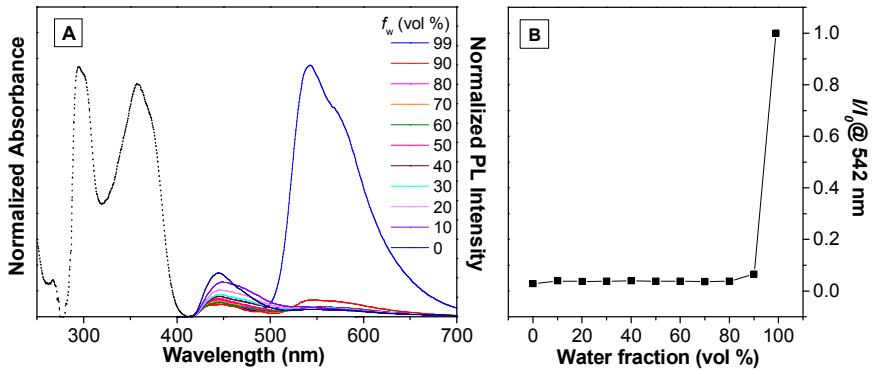

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Fig. 1 (A) UV-Vis absorption spectrum of salicylaldazine in THF (black dashed line); PL spectra of the product in THF and THF-water mixture with different water fractions (f_w); (B) Plot of the relative PL intensity at 542 nm (I/I_0) versus the solvent with different water fractions (f_w). I is PL intensity at any f_w, and I_0 is the PL intensity measured at f_w = 99%. [salicylaldazine] = 10 μM; λ_{ex} = 365 nm.

Pd detection

We designed and synthesized **AIE-Pd** for detection of palladium based on a Pd^0-catalyzed Tsuji-Trost reaction which cleaves allyl group and releases the hydroxyl group,[21, 39] as shown in Fig. 2A. To demonstrate the potential of the probe **AIE-Pd** for quantitative palladium detection, the fluorescence spectra were measured upon addition of increasing concentrations of $Pd(PPh_3)_4$ in the mixture of THF/H_2O (v/v = 1/99). $NaBH_4$ was chosen as a reducing agent because of its ability to reduce Pd(II) to Pd(0), which could prompt the Pd-catalyzed deallylation.[37] As shown in Figs. 2B and 2C, the fluorescence of **AIE-Pd** shows good linear increase with Pd concentration with a correlation coefficient of R^2 = 0.9925 in the range of 0.0 – 8.0 μM. The detection limit was calculated to be 4.97 nM (0.5 ppb Pd content) by (3σ/k), where σ is the standard deviation of the blank measurement and k is the slope of fluorescence intensity over Pd concentration. The results indicate that the probe **AIE-Pd** has high sensitivity with linear response to Pd, which is suitable for detection of trace amount of palladium sample. Filter paper was then used as a substrate to investigate the potential of **AIE-Pd** for solid-state detection. As described in the Experimental Section, the probe **AIE-Pd** was stained onto the filter paper by drop-casting 10 μL of 1.0 mM probe in THF stock solution. As $Pd(PPh_3)_4$ samples (1 μL) with increasing concentrations from 0.1 μM to 1.0 mM were added onto the probe spot, clear fluorescent color change was visualized. Fig. 2D shows photographs taken under UV illumination. The **AIE-Pd** on paper strip gives a very sensitive response to Pd solution even at 1 μM (0.1 ppm Pd content), which clearly satisfies the requirement of governmental restriction limit of Pd in drugs (5-10 ppm).[40] To the best of our knowledge, this probe has the best detection limit for visual sensing of palladium on paper strip reported so far.

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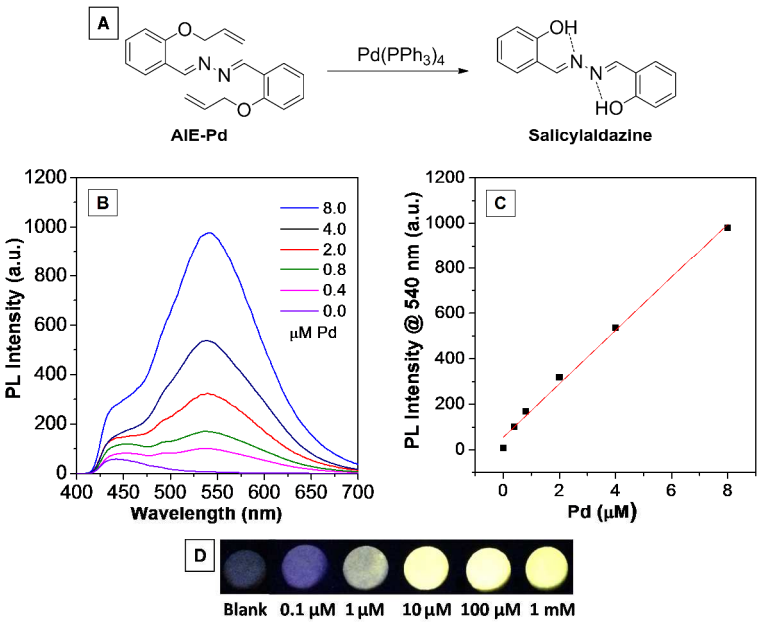

Fig. 2 (A) Detection mechanism of Pd catalyzed deallylation. (B) Changes of the PL spectra of the probe **AIE-Pd** in the presence of increasing concentrations of $Pd(PPh_3)_4$. (C) Plot of the PL peak intensity at 540 nm versus the concentrations of $Pd(PPh_3)_4$ in the mixture of THF/H_2O (v/v = 1/99, with 10 mM $NaBH_4$). [**AIE-Pd**] = 10 μM, λ_{ex} = 365 nm. (D) Solid-state fluorescence response of the **AIE-Pd** with different concentrations of Pd under UV illumination of 365 nm.

The response of **AIE-Pd** toward other metal ions was then explored. In aqueous solution, the fluorescence of the probe hardly shows any change in the presence of other metal ions, including Cu^{2+}, Fe^{3+}, Hg^{2+}, Ru^{3+}, Pb^{2+} and Mn^{2+} even at the concentration of 160 μM (20 equiv. of Pd concentration). In contrast, upon addition of 8 μM $Pd(PPh_3)_4$, the probe lights up significantly as shown in Figs. 3A and 3B. The selectivity experiment was also carried out on the paper strip and the result is shown as the inset of Fig. 3B, demonstrating that other metal ions have negligible response to **AIE-Pd**. The excellent selectivity is due to the specificity of Pd-catalyzed allyl deprotection. Next, the reactivity of probe **AIE-Pd** toward other palladium species including $PdCl_2$, $Pd(OAc)_2$, $PdCl_2(dppf)_2$, and $Pd(PPh_3)_2Cl_2$ was also examined respectively and the results are shown in Fig. 3C. The probe was found to be useful for all the tested sources because Pd (II) can be efficiently reduced to Pd(0) by $NaBH_4$.

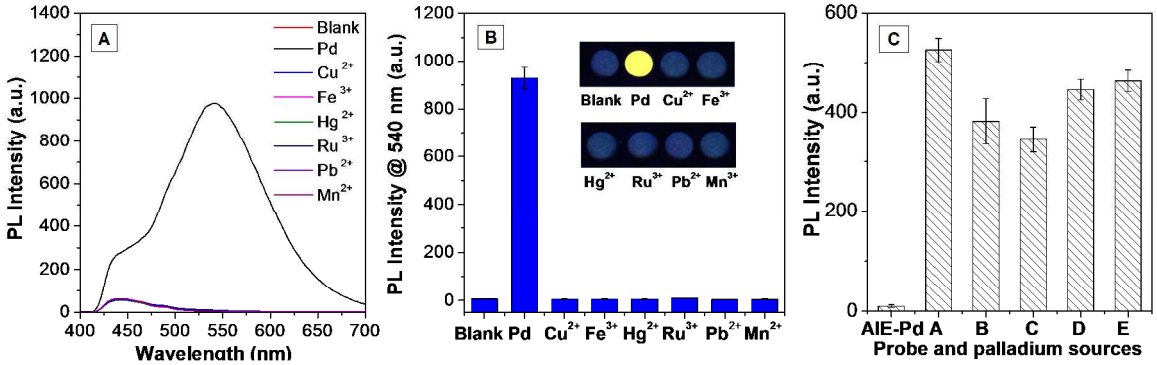

Fig. 3 (A) PL spectra of **AIE-Pd** in the absence and presence of different metal (ions) Pd , Cu^{2+},

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Fe^{3+}, Hg^{2+}, Ru^{3+}, Pb^{2+} and Mn^{2+} (as their Cl^-, $COOH^-$ and SO_4^{2-} salts) in THF/H_2O (v/v = 1/99, with 10 mM $NaBH_4$) solution. (B) Bar chart of PL peak intensity at 540 nm responsive to different metal ions. ([**AIE-Pd**] = 10 μM, [Pd] = 8 μM, [M^{m+}] = 160 μM, λ_{ex} = 365 nm). Inset: Fluorescence response of **AIE-Pd** to various metal cations on paper strip under UV illumination (365 nm). [$Pd(PPh_3)_4$] = 10 μM, [M^{m+}] = 200 μM. (C) Comparison of the fluorescent responses of AIE-Pd toward different palladium species (4 μM) in THF/H_2O (v/v = 1/99, with 10 mM $NaBH_4$), A. $Pd(PPh_3)_4$; B. $PdCl_2$; C. $Pd(OAc)_2$; D. $PdCl_2(dppf)_2$; E. $Pd(PPh_3)_2Cl_2$.

Perborate detection

The sensing of perborate is designed based on selective deprotection of aryl acetates under mild conditions as shown in Fig. 4A. **AIE-Perborate** shows very weak fluorescence at 444 nm in THF/HEPES (10 mM, pH = 5.0) buffer (v/v = 1/99), (Fig. 4B). However, after treatment of the probe with sodium perborate with concentrations ranging from 0 to 50 μM, intense fluorescence turn-on is observed at both 444 and 550 nm. Fig. 4C was obtained by plotting the peak PL intensities of the probe to the concentrations of perborate. The detection limit was calculated to be 0.10 μM, with a correlation coefficient R^2 = 0.998 at the range of 0 – 50 μM, which is similar to that reported by Zheng[24] and better than that reported by Chang.[25] The sensing of perborate on filter paper was subsequently conducted after drop-casting 10 μL of 1.0 mM probe **AIE-Perborate** stock solution in THF and drying. Sodium perborate from 10 μM to 1 mM was added onto the stained filter paper, and pictures were taken under UV illumination, which are shown in Fig. 4D. It is obvious that the **AIE-Perborate** on paper strip gives concentration-dependent turn-on response to perborate, and 50 μM perborate anion can be readily recognized by naked eyes. This represents the first probe which can offer visual detection of perborate on paper strip.

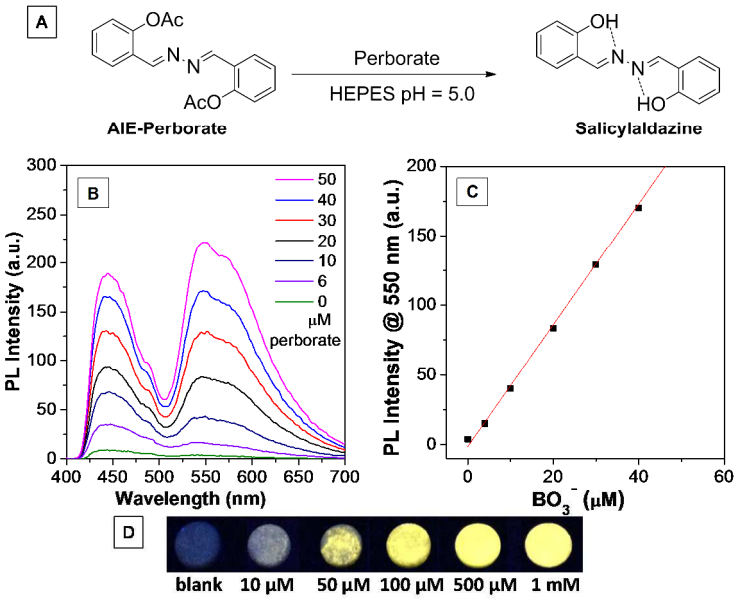

Fig. 4 (A) Detection mechanism of **AIE-Perborate** for BO_3^- through specific deprotection of acetate group. (B) Changes of PL spectra of **AIE-Perborate** in the presence of increasing concentration of BO_3^-. (C) Plot of the PL peak intensity at 550 nm versus the concentration of BO_3^- in the mixture of THF/HEPES (v/v = 1/99). [**AIE-Perborate**] = 20 μM, λ_{ex} = 365 nm. (D)

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Solid-state fluorescence response of the **AIE-Perborate** with different concentrations of perborate under UV illumination at 365 nm.

The selectivity of **AIE-Perborate** to perborate against other anions was also examined in the same solvent medium. The concentrations of other anions are 20-fold as that of perborate. As shown in Figs. 5A and 5B, **AIE-Perborate** can only be lit up by BO_3^-. Other anions including F^-, Cl^-, Br^-, I^-, HSO_3^- and $S_2O_3^{2-}$, at a concentration of 20-fold as that of BO_3^-, do not result in any apparent fluorescent changes of **AIE-Perborate**. The fluorescence changes of the probe stained on paper strip toward BO_3^- and other anions were also studied. The inset of Fig. 5B shows that the probe **AIE-Perborate** is highly specific to perborate, which validates its high sensitivity and selectivity for sensing perborate both in aqueous solution and on paper strip.

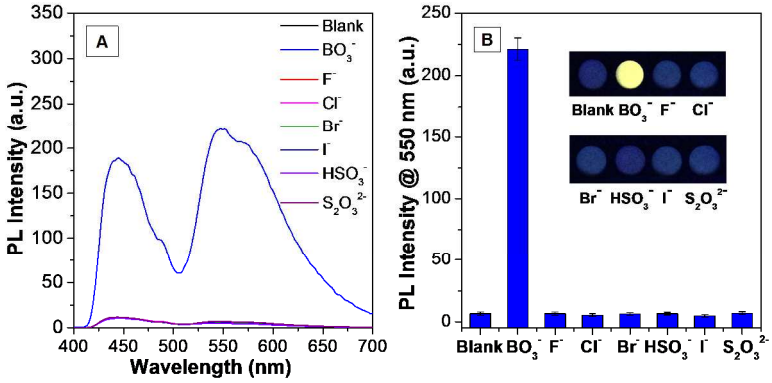

Fig. 5 (A) PL spectra of **AIE-Perborate** in the absence and presence of various anions including BO_3^-, F^-, Cl^-, Br^-, I^-, HSO_3^- and $S_2O_3^{2-}$ (as their K^+ and Na^+ salts) in THF and 10 mM pH = 5.0 HEPES buffer solution (v/v = 1/99). (B) Bar chart of PL peak intensity at 550 nm responsive to different anions. ([**AIE-Perborate**] = 20 μM, [BO_3^-] = 50 μM, [A^{n-}] = 1 mM. λ_{ex} = 365 nm). Inset: Fluorescent response of **AIE-Perborate** to BO_3^- and various anions on paper strip under UV illumination (365 nm).

UV light detection

Nitrobenzyl group has been well established in the literature as a photocleavable protecting reagent for alcohols and amines.[41] The UV responsive probe **AIE-UV** is designed by integration of this reaction and "AIE + ESIPT" mechanism through salicylaldazine core. Based on a similar mechanism as **AIE-Pd** and **AIE-Perborate**, **AIE-UV** should be turned on by deprotection of nitrobenzyl groups as shown in Fig. 6A. To validate the potential of **AIE-UV** for photo-cleavage application, the changes in the PL spectrum were measured after exposure to UV light. From Fig. 6B, as the illumination time increases from 0 to 60 min, the fluorescence intensities of **AIE-UV** show an increasing trend. The peak PL intensity at 554 nm is saturated when exposure time reaches 60 min, providing a 12-fold turn-on compared with the probe without any UV illumination. The sensing on the filter paper strip was also examined. 10 μL of **AIE-UV** (1.0 mM) in THF was used to stain the filter paper. From Fig. 6C, **AIE-UV** shows a quick response to UV light. Even illumination for four minutes is able to yield distinguished fluorescence for naked-eye detection.

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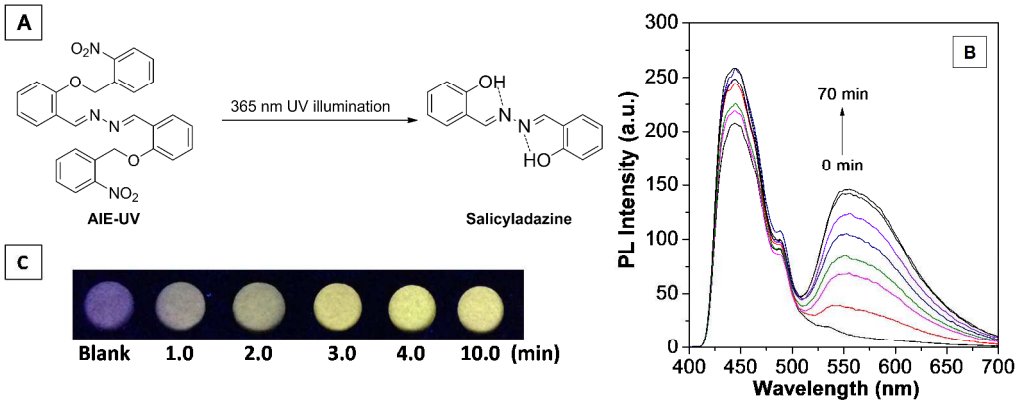

Fig. 6 (A) Schematic illustration of the photo-responsive **AIE-UV** upon UV illumination; (B) The PL spectra of 10 μM probe **AIE-UV** with UV illumination (365 nm) time of 0, 10, 20, 30, 40, 50, 60 and 70 min. (C) Solid-state fluorescence response of the **AIE-UV** with different exposure time to UV illumination at 365 nm.

Because of the ESIPT characteristics of salicylaldazine, it has both enol (E*) (at ~440 nm) and keto (K*) emission (at ~540 nm) (Fig. 7), and the K* emission is formed through excited-state intramolecular proton transfer (ESIPT).[42] According to the literature reports,[43] the ratio of K*/E* emission will decrease because of the disruption on intramolecular hydrogen bonds by polar solvents, which will inhibit the excited-state intramolecular proton transfer process and decrease the K* emission. Because of the aggregation-induced emission (AIE) characteristics of salicylaldazine, at aggregation state, the intramolecular hydrogen bonds of salicylaldazine can be protected from the disruption of polar solvents, and the K*/E* emission ratio will be increased via smooth ESIPT process. However, at non-aggregated state, its intramolecular hydrogen bonds can be disrupted by the polar solvents, and the K*/E* emission ratio will be decreased. To verify that the aggregation extend will affect its emission spectra shape, we have measured the emission spectra of salicylaldazine at different concentrations in THF-water mixture (v/v, 1/99) (Fig. S9). It shows that with decreasing concentration of salicylaldazine (from 10 μM to 1 μM), it shows decreasing K*/E* emission ratio, because the lower concentration of salicylaldazine will lead to lower aggregation extent and the intramolecular hydrogen bonds can be disrupted by the protic water molecules. The reactions between **AIE-Pd**, **AIE-perborate** and **AIE-UV** toward their targets will lead to the same product of salycylaldazine, but their different reaction efficiency will lead to different concentrations and aggregation extent of salycylaldazine product, and the corresponding fluorescence spectra of salicylaldazine with different K*/E* emission ratio have been observed.

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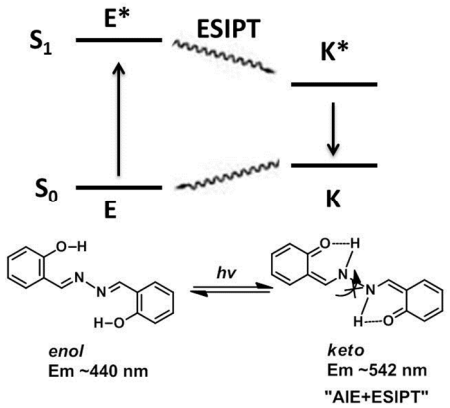

Fig. 7 The emission mechanism of salicylaldazine with both AIE and ESIPT characteristics.

Conclusion

We have designed a fluorescent light-up platform based on salicylaldazine fluorogen with both AIE and ESIPT characteristics. The combination of the two emission mechanisms offers unique optical properties that are highly desirable for sensing in aqueous solution and on solid substrate. Three probes **AIE-Pd**, **AIE-Perborate** and **AIE-UV** have been synthesized to demonstrate the versatility of the platform. Experimental results have shown that the probes can light up linearly by target analytes with increasing concentration or increasing exposure time. To the best of our knowledge, **AIE-Pd** based paper strip offers the best detection limit for visual sensing of palladium. A similar light-up response is also observed for perborate anion and UV light sensing both in solution and on paper strip. This versatile platform has advantages including free of self-quenching effect, excellent light-up ratio and large Stokes shift, which offers new opportunities for convenient visual sensing. Further adjusting the functionalities on the hydroxyl groups could easily yield new probes for different analytes with the same operation mechanism.

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Abstract

We report a fluorescent light-up platform for multi-target detection in aqueous solution and on paper strip. The platform is based on salicylaldazine fluorogen with aggregation-induced emission (AIE) and excited state intramolecular proton transfer (ESIPT) characteristics, which shows distinguished advantages including ease of chemical modifications, free of self-quenching effect, excellent light-up ratio and large Stokes shift. To demonstrate the versatility of the platform, palladium cation and perborate anion, as well as UV light were selected as the targets. The three representative probes of **AIE-Pd**, **AIE-Perborate** and **AIE-UV** light up specifically in the presence of the target both in aqueous solution and on paper strip. The immediate naked-eye response makes the probes ideal for instrument-free and power-free detection.

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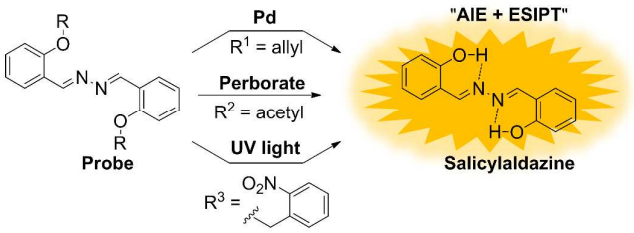

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