

■ Fluorescence

A 1,3-Indandione-Functionalized Tetraphenylethene: Aggregation-Induced Emission, Solvatochromism, Mechanochromism, and Potential Application as a Multiresponsive Fluorescent Probe

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Abstract: A tetraphenylethene (TPE) derivative substituted with the electron-acceptor 1,3-indandione (IND) group was designed and prepared. The targeted IND-TPE reserves the intrinsic aggregation-induced emission (AIE) property of the TPE moiety. Meanwhile, owing to the decorated IND moiety, IND-TPE demonstrates intramolecular charge-transfer process and pronounced solvatochromic behavior. When the solvent is changed from apolar toluene to highly polar acetonitrile, the emission peak redshifts from 543 to 597 nm. IND-TPE solid samples show an evident mechanochromic process. Grinding of the as-prepared powder sample induces a redshift of emission from green (peak at 515 nm) to orange (peak at 570 nm). The mechanochromic process is reversible in multiple grinding–thermal annealing and grinding–solvent-fuming cycles, and the emission of the solid sample switches between orange (ground) and yellow (ther-

mal/solvent-fuming-treated) colors. The mechanochromism is ascribed to the phase transition between amorphous and crystalline states. IND-TPE undergoes a hydrolysis reaction in basic aqueous solution, thus the red-orange emission can be quenched by OH[−] or other species that can induce the generation of sufficient OH[−]. Accordingly, IND-TPE has been used to discriminatively detect arginine and lysine from other amino acids, due to their basic nature. The experimental data are satisfactory. Moreover, the hydrolyzation product of IND-TPE is weakly emissive in the resultant mixture but becomes highly blue-emissive after the illumination for a period by UV light. Thus IND-TPE can be used as a dual-responsive fluorescent probe, which may extend the application of TPE-based molecular probes in chemical and biological categories.

Introduction

Designing and synthesizing organic fluorogens with unique optical and electronic properties has long been a topic of research, due to their wide applications in chemical or biological sensing, imaging, and devices like photovoltaic cells, field-effect transistors, and organic light-emitting diodes (OLEDs).^[1] However, most of the luminogenic molecules are used in their solid states in which the molecules form aggregates. In these

circumstances, their emissions suffer from a troublesome effect termed as “aggregation-caused quenching” (ACQ). In other words, the molecules in aggregates undergo short-range interactions like intermolecular π – π stacking, which generally results in the quenching of the fluorescent emission and thus places great restrictions on their applications in practical situations.^[2] Different from many approaches that have been taken to alleviate the troubles by preventing the molecules from aggregating, another way to tackle the problem is to find certain fluorogens for which the aggregation acts as an advantageous factor to their emissions. In 2001, it was reported by Tang and colleagues that 1-methyl-1,2,3,4,5-pentaphenylsilole molecules were faintly emissive in solutions, but highly luminescent in their aggregates or solid states.^[3] This phenomenon, exactly opposite to the pernicious ACQ, is termed “aggregation-induced emission” (AIE). In addition, it is ascribed to the mechanism of restricted intramolecular rotations (RIR): In a dilute solution, phenyl rings in the 1-methyl-1,2,3,4,5-pentaphenylsilole molecule undergo dynamic intramolecular rotations, which non-radiatively annihilate its excited state and make the molecule non-luminescent. Whereas in the aggregates, the propeller-shaped 1-methyl-1,2,3,4,5-pentaphenylsilole molecules cannot pack through a π – π stacking process, thus the ACQ effect is exempted; and meanwhile the intramolecular rota-

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tions are greatly restricted, which blocks the non-radiative pathways and opens up the radiative channels.^[4]

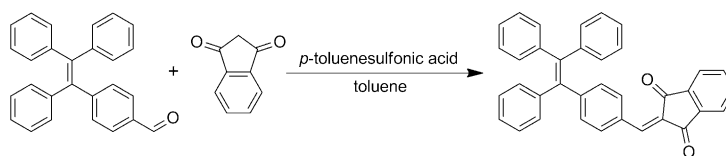
To take advantage of the beneficial emission enhancement, more fluorogens possessing an AIE property have been developed.^[5] Among them, tetraphenylethene (TPE) and its derivatives have received great research attention because of their good AIE performance, simple synthetic routes, and facile modifications with various functionalities.^[6] Up to now, they have been successfully applied to OLEDs, bioimaging systems, and chemical and biological sensors.^[3,4b,5,6] For example, by modifying the TPE core with pyridinyl, aldehyde, boronic acids, thymine, and quaternary amine groups, the obtained TPE derivatives can be used to detect proton and metal cations,^[7a] cysteine over homocysteine,^[7b,c] D-glucose over other mono-saccharides such as D-galactose, D-fructose and D-mannose,^[7d] DNA,^[7e] and proteins.^[7f,g]

However, for TPE derivatives, there is still a large imbalance between the performances and the requirements to be met in applications. To avoid the interference from the autofluorescence of tissues, yellow-to-red-emitting fluorescent probes are in high demand for bioimaging. Besides bioimaging, AIE-based materials with longer emission wavelengths are also crucial in the fabrications of full-color OLEDs and highly sensitive chemosensors. Unfortunately, most of the TPE-based luminogens show blue or green emission, but only a few show red emission. Recently, we modified TPE with strong electron donor (D) and acceptor (A) and the derivatives demonstrated evidently redshifted emission. Meanwhile, these TPE derivatives displayed the expected AIE behavior.^[8] By modifying with TPE moieties, the transformation of classical narrow energy-gap fluorogens such as perylene-3,4,9,10-tetracarboxylic bisimide^[9] and benzothiadiazole^[10] also resulted in AIE-active red-emitting materials. Due to the robust intermolecular π - π interaction in the red-emitting large conjugated systems, these types of AIE molecules were found to easily self-assemble into ordered nano/microstructures.^[9,10]

Another important direction to improve the performance of AIE luminogens in chemo/biosensor applications is to design and prepare fluorescent probes with AIE-activity and dual responses. The ratiometric fluorescent probes are excellent examples, which show a unique merit over normal turn-on/turn-off fluorescent probes. That is, the chemo/biosensing process can be monitored by the changes in both emission intensity and emission color. The change in the ratio of two emission peaks (intensities) provides an inner calibration, thus effectively enhances the detection reliability and sensitivity and eliminates the disturbance from the background or environment species.^[11] In principle, dual fluorescent responses are induced by a specific interaction between the probe and the to-be-detected target, which triggers an intrinsic process such as proton transfer, charge transfer, or bond formation/disruption. So far, all AIE-active fluorescent probes are working on the RIR mechanism. Both deactivation (emission turn-on) and activation (emission turn-off) of the intramolecular rotations of the AIE-active probing molecules have been widely prepared and in-

vestigated. But no dual responsive AIE-type fluorescent probes have been reported.^[3–10,12]

Herein, we report our attempt to design and construct such a fluorescent probe (IND-TPE). The molecular structure of IND-TPE is shown in Scheme 1. The modifier, 1,3-indandione itself is a conjugated system and attaching it onto the TPE core with a conjugated C=C double bond will extend the conjugation



Scheme 1. Synthetic route to the target compound 1,3-indandione-modified tetraphenylethylene (IND-TPE).

system and lead to a redshifted emission. In addition, 1,3-indandione is a moderate electron acceptor and thereby it can further redshift the emission feature by a moderate D–A interaction. More importantly, IND-TPE contains a C=C double bond activated by two adjacent carbonyl groups. It is well-known that an activated C=C bond undergoes a hydrolysis reaction in the presence of base in mild conditions.^[13] We thus expect the hydrolysis reaction will break the conjugation between the 1,3-indandione and TPE moieties, and changes in the emission features (emission intensity and wavelength) will be triggered. As expected, IND-TPE demonstrates evident AIE activity, pronouncedly redshifted emission compared with TPE derivatives without substitution of the D and A groups, and dual fluorescent responses to hydroxyl anion and UV-light illumination.

Results and Discussion

The synthetic route to the IND-TPE conjugate is shown in Scheme 1 and the detailed procedures are described in the Experimental Section. The precursor, an aldehyde-functionalized TPE derivative, was prepared according to our previously published papers.^[7] The target compound IND-TPE was generated from a Knoevenagel condensation between the aldehyde group of the precursor and active methylene part of 1,3-indandione. The structural characterization data of the product by using spectroscopic methods are given in the Experimental Section with satisfactory results (see the Supporting Information, Figures S1–S4).

The thermal properties of IND-TPE were investigated by using thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Figures S5 and S6 in the Supporting Information). The ground sample has a glass transition at around 72 °C and the melting point of the crystalline sample is 268 °C. It possesses high thermal stability with a decomposition temperature (T_d) at 337 °C.

Aggregation-induced emission

It has been found that a variety of TPE derivatives are AIE-active molecules and TPE is a luminogen that can convert classical fluorophores to AIE-active molecules.^[5–10] Thus, TPE can be referred to as an AIE-gen, just like fluorogen and luminogen for traditional emitting compounds. To determine if the 1,3-indandione-modified TPE is an AIE-active molecule, the fluorescent behavior of IND-TPE was examined in the mixture of THF (tetrahydrofuran) and water, which act as a good solvent and non-solvent to IND-TPE, respectively.

As can be seen in Figure 1A, IND-TPE in a dilute THF solution (10 μM) shows a nearly negligible emission, the spectral line is almost parallel to the abscissa, and its FL quantum yield (Φ_F) is measured to be just 0.23% (Figure 1B). When enough

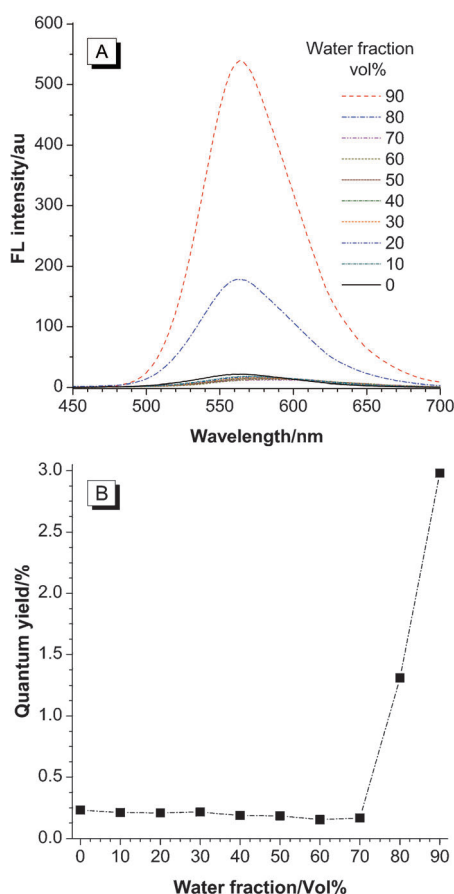


Figure 1. A) Fluorescence (FL) spectra of IND-TPE in THF/water mixtures with different water fractions (f_w). Concentration of IND-TPE: 10 μM ; excitation wavelength: 415 nm. B) Plots of FL quantum yields (Φ_F) of IND-TPE versus f_w in THF/water mixtures. The Φ_F values were estimated by using fluorescein in 0.1 M sodium hydroxide ($\Phi_F=79\%$) water solution as a standard.

water was added into the solution, the resultant mixture emitted evidently enhanced emission. In a water/THF mixture with water fraction (f_w) of 70%, the emission of the solution becomes stronger and an orange emission with a peak at around 564 nm can be observed. When f_w is up to 90%, the emission intensity of the mixture increases sharply and the Φ_F is record-

ed to be 2.98%, which is about 13 times higher than that measured in a dilute solution. Thus, we can draw a conclusion that, like other TPE-derivatives, IND-TPE is an AIE-active molecule.

Solvatochromism

As mentioned above, 1,3-indandione is an electron acceptor. The attachment of an acceptor onto the TPE core offers a pull-push effect to the obtained molecule, thereby it is possible this results in an intramolecular charge-transfer (ICT) process. It is expected that the photophysical properties of IND-TPE in solutions are correlated to the solvent polarity, which is called the solvatochromism effect.^[14]

To examine the solvatochromic behavior of IND-TPE, we measured the absorption and emission spectra in a series of solvents with different polarities. It can be seen in Figure 2A that the absorption spectra almost have no obvious changes with a change in the solvent polarity. From the apolar solvent toluene to the highly polar solvent acetonitrile, the lowest absorption peak has only a small shift. In contrast, the recorded fluorescence (FL) spectra of IND-TPE (Figure 2B) displays evident polarity dependence under the same measurement conditions as the absorption spectra. By changing the solvent from apolar toluene to highly polar acetonitrile, the emission peak of IND-TPE goes through a dramatic redshift from 543 to 597 nm, which indicates a typical solvatochromic effect.

To quantitatively describe the influences of solvent polarity on the emission behavior, the Lippert–Mataga Equation [Eq. (1)],^[14] which directly expresses the relationship between the Stokes shift ($\Delta\nu$) and the solvent polarity parameter (Δf) is used:

$$\Delta\nu = \nu_a - \nu_e = \frac{2\Delta f}{hca^3} (\mu_e - \mu_g)^2 + \text{const} \quad (1)$$

in which, $\Delta\nu$ is the Stokes shift, namely, the difference between the maximum absorbance and emission wavenumbers, ν_a and ν_e ; μ_g and μ_e are the dipole moments in the ground and excited states, respectively, and h , c , and a stand for the Planck constant, the speed of light, and the Onsager solvent cavity radius, respectively. The solvent polarity, Δf , is calculated as follows [Eq. (2)]:

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1} \quad (2)$$

in which ε is the static dielectric constant and n is the optical refractive index of the solvent.

The dependence of $\Delta\nu$ on Δf is given in Figure 1C. As Δf , indicative of solvent polarity, goes up, the Stokes shift $\Delta\nu$ reveals an increasing tendency with the slope of the fitting line being 6277.7. The results indicate that the fluorescent properties of IND-TPE in solutions are bound up with solvent polarity, which exhibits a solvatochromism effect.

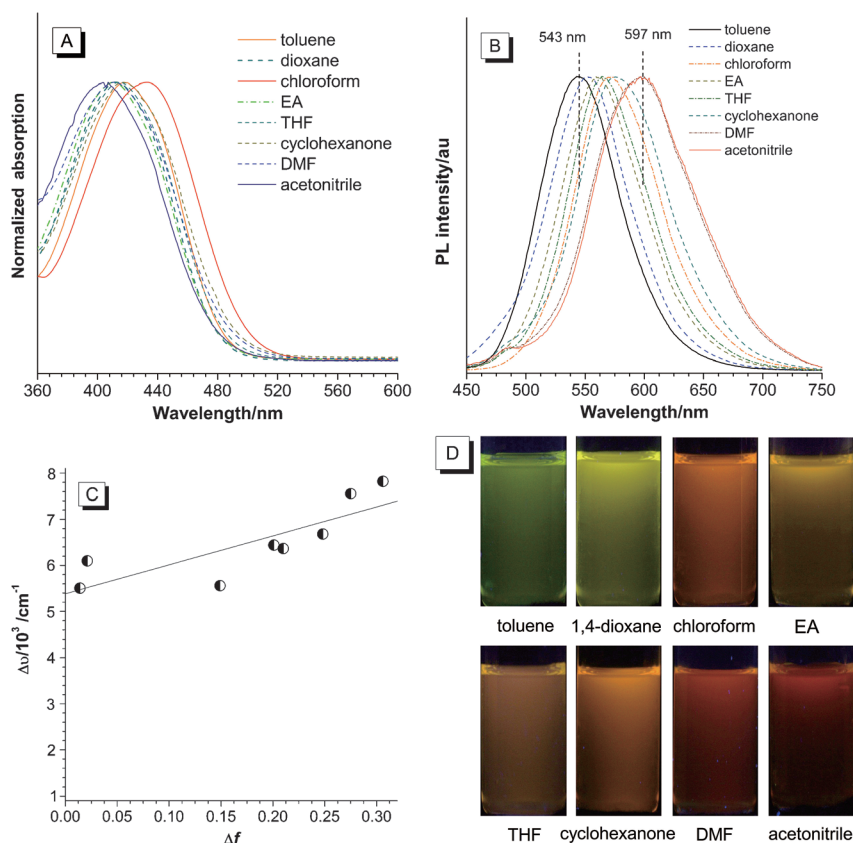


Figure 2. A) Absorption spectra of IND-TPE in different solvents. B) FL spectra of IND-TPE in different solvents. The absorption maximum of each solution was chosen as its excitation wavelength. C) Plot of Stokes shift ($\Delta\nu$) of IND-TPE in each solvent versus Δf of the respective solvent. D) FL images of IND-TPE solutions in different solvents. The photographs were taken under illumination with a 365 nm UV light. Concentration: 10 μM . Solvents: toluene, 1,4-dioxane, chloroform, ethyl acetate (EA), THF, cyclohexanone, dimethylformamide (DMF) and acetonitrile.

Mechanochromism

Mechanochromic fluorogens change their emission colors when a mechanical force like pressure is applied. As a class of “smart” materials, they provide a fundamental basis for FL switches, mechano-history indicators, security papers, information storage, and optoelectronic devices.^[15,16]

The as-prepared IND-TPE is a yellow solid after purifying it with column chromatography and removing the solvent. The powder shows a yellowish-green emission under illumination of a 365 nm UV light. Whereas, after grinding, its color changed to orange with a red-orange emission. Then, through heating at 120 °C for 5 min or fuming with organic solvent vapor (e.g., THF vapor), the ground sample transformed into a deep-yellow powder with a yellow emission (Figure 3 and inset). The chromic processes were further evaluated by using FL spectroscopy. The emission peaks of the as-prepared and the ground solids are located at 510 and 562 nm, respectively; that is, a spectral redshift of 52 nm occurred simply by grinding. Then, through heating or fuming, the emission peak of the ground solid blueshifted to 525 nm. However, it could not be turned back to the original state of the as-prepared solid.

To obtain a further understanding of the observed mechanochromism phenomenon, X-ray diffraction (XRD) measurements were performed on the corresponding samples. In the XRD

patterns (Figure 4A), the as-prepared solid of IND-TPE displays intense and sharp diffraction peaks, indicating the microcrystalline state of the solid. After grinding, some of the sharp peaks become evidently weakened and some blend with the background (Figure 4B), implying that most of the ordered crystalline has been eliminated through the mechanical force and converted into a largely amorphous state. Thermal annealing is a helpful technique to reconstruct the crystalline structure. Upon heating at 120 °C for 5 min, the XRD pattern of the thermal treated sample is nearly identical to that of the as-prepared sample (Figure 4C), indicating that the amorphous ground sample recrystallizes and the polymorph recovers. The XRD experimental data demonstrate that the mechanochromism phenomenon results from the transformation between the crystalline and amorphous states.

Reversible changes in emission colors are considerable features for mechanochromic materials

to be applied in sensors, ambient monitoring, security inks, logic gate units, and so on.^[15,16] Thus, the reversibility of the mechanochromic processes of IND-TPE was analyzed. In a typical grinding–heating cycle, the emission of IND-TPE can

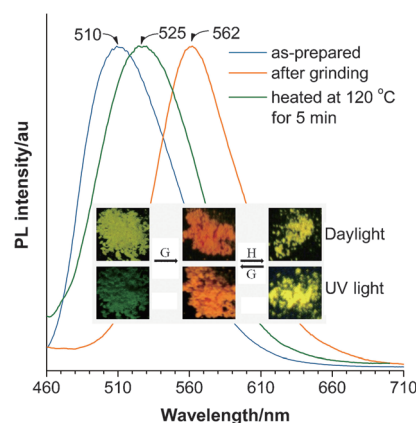


Figure 3. FL spectra of IND-TPE in different solid states: before and after grinding, and heating the ground sample at 120 °C for 5 min. Inset: Photographs of as-prepared (left), ground (middle), and recovered (right) samples of IND-TPE taken under daylight (upper) and UV light (lower). G = grinding; H = heating; λ_{ex} = 365 nm.

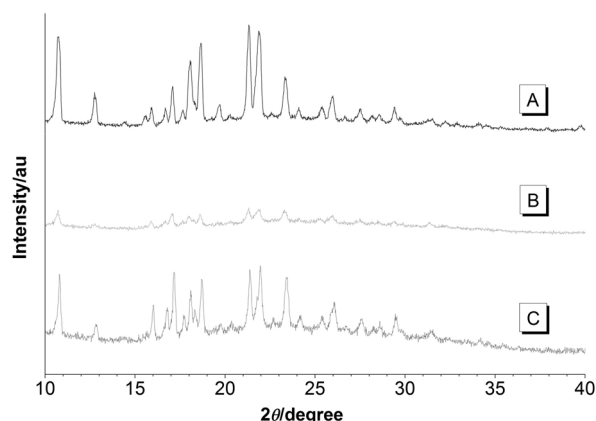


Figure 4. XRD patterns of A) the as-prepared IND-TPE powder sample, B) the ground powder sample, and C) the ground sample after heating at 120 °C for 5 min.

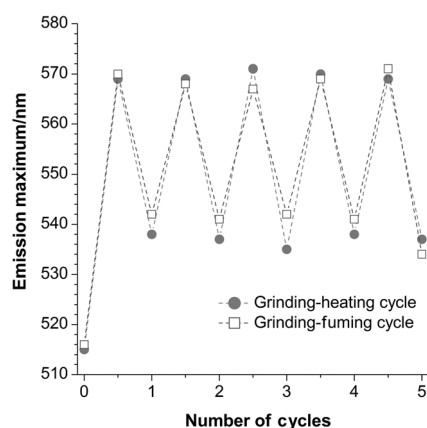
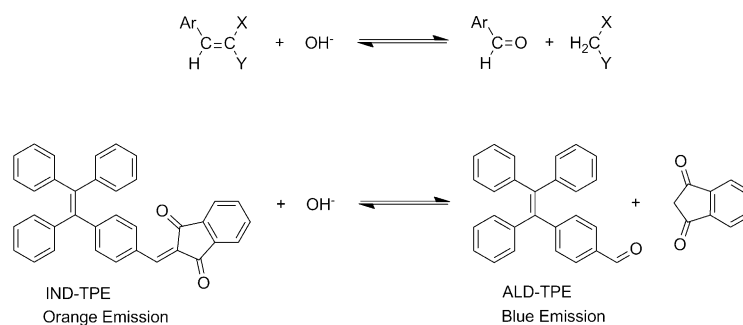


Figure 5. Reversible switching of emission maximum of TPE by repeated grinding–heating (●) or grinding–fuming (□) cycle. Heating: 120 °C for 5 min; fuming: THF vapor; λ_{ex} : 420 nm.

repeatedly switch between two different colors, yellow and orange, and the corresponding emission peaks are at around 536 nm (thermal-treated) and 570 nm (ground). In addition to grinding–heating, grinding–fuming can also trigger the reversible color and emission changes, and the corresponding emission peaks are at around 540 nm (fuming-treated) and 570 nm (ground). As shown in Figure 5, the samples display good and stable reversibility for both grinding–heating and grinding–fuming cycles.

Dual FL responses to hydroxyl

As described in the Introduction, it is well-known that the olefins activated by electron-withdrawing substituents (X and Y, Scheme 2) undergo a hydrolysis reaction in the presence of base in mild conditions.^[13] Given that the olefin is a fluorescent probe composed of two fluorogens (Ar=TPE and X+Y moieties=1,3-indandione), the hydrolysis of the olefin will break the conjugation between the two fluorogens.



Scheme 2. Schematic illustration of the principle of the dual fluorescent response of IND-TPE to hydroxyl anion.

As a result, changes in the emission features (intensity and maximum or color) will be triggered.

We firstly checked the fluorescent responses of IND-TPE to OH^- in THF/buffer solution. The volume fraction (f_b) of the borax buffer was set at $f_b=0.7$ to mimic the conditions of the THF/water mixture solution with $f_w=0.7$. The pH value was adjusted to 9.0 to provide an alkaline environment to IND-TPE. Another reason why $f_b=0.7$ was chosen relied on the fact that IND-TPE began to show its AIE activity at this fraction. Whereas at higher THF fractions, the solution would be non-fluorescent, and at lower THF fractions, only part of IND-TPE could dissolve in the solution and the residual might heavily interrupt the FL measurement. As shown by Figure 6A, at the beginning, the alkaline solution containing IND-TPE emits strong FL with an emission peak at around 595 nm. By extending the reaction time, the FL is quenched gradually. A clear time-dependent decrease in the FL intensity is plotted in Figure 6B.

Figure 6B indicates that FL is heavily quenched after reacting for 40 min. Taking 60 min as the reaction time to ensure the sufficient FL quenching, the fluorescent response of IND-TPE to the pH value in a range from 2.0 to 12.0 has been measured and the derived data are summarized in Figure S7A and B (the Supporting Information). It is found that the FL can be almost completely quenched when the pH is higher than 8.0.

According to the proposed reaction mechanism, the aldehyde-modified TPE (ALD-TPE) will be produced in the hydrolysis process. In THF/buffer solution, ALD-TPE has better solubility than IND-TPE. Thus, the resultant mixture displays only weak FL from residual IND-TPE but without the emission from ALD-TPE aggregates. Interestingly, it was accidentally found that the resultant solution displayed a stronger blue emission after exposure to the UV light in the FL measurement process. Because of the different emission color, we correlated this emission to the presence of ALD-TPE. Then, we exposed the reactant mixture to 330 nm UV light (the light beam used for fluorescent spectrum measurement) for different periods and measured the FL changes at every 2 min interval. The data recorded in a typical run are depicted in Figure 7A and B. Clearly, the intensity of the blue emission increases gradually with the exposure time, although there are intensity fluctuations in a single time-dependent experiment. In addition, the enhancement of the FL intensity does not terminate after an exposure of one hour, indicating that the UV-light-induced reaction has

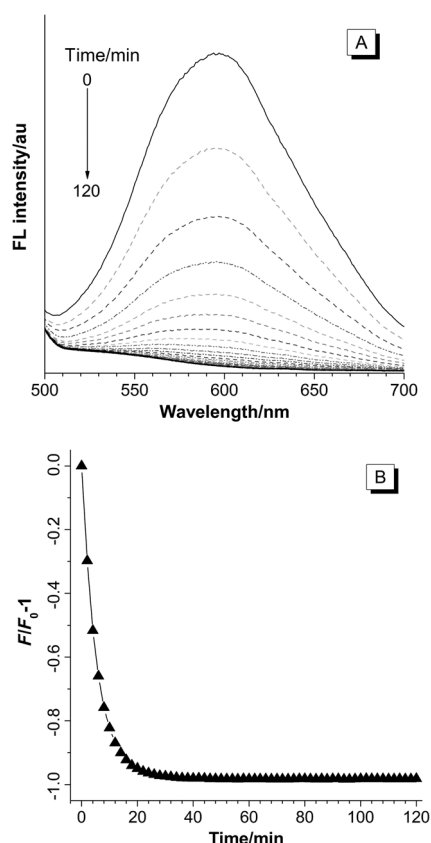


Figure 6. A) Time-dependent FL intensity change of IND-TPE in the mixture of THF and 10 mM borax buffer (3/7 by volume, pH 9.0). B) Variation of the peak intensity of the emission of IND-TPE with reaction time. The data are extracted from (A). F_0 and F : the peak FL intensity at the moment that IND-TPE was added into the solution and after the reaction mixture was kept for a preset time at room temperature, respectively. Concentration of IND-TPE: 10 μM ; λ_{ex} : 420 nm.

not yet ceased. On the contrary, without exposure to the UV light, the reactant mixture shows no FL enhancement at this spectral region (e.g., blue emission, see Figure S8, the Supporting Information). It is noticeable that the UV-light-induced emission band exhibits an evident redshift with the extension of the exposure time. Meanwhile, the vibronic shoulders also vanished after UV-light illumination for a longer time. These behaviors are dissimilar to ALD-TPE; thus, there must be different emissive species in the photo-induced process. We then tried an experiment that involved illuminating the ALD-TPE THF/water solution ($f_w=0.7$) by 365 nm UV light for two hours and observed the enhancement of FL intensity. After several experiments, we collected the resultants by evaporating the solvents and measured the ^1H NMR spectra in deuterated DMSO solution. A few chemical shifts distinct from ALD-TPE appeared in the spectrum (the Supporting Information, Figure S9), indicating the formation of new species other than ALD-TPE. Now, we are trying more experiments to analyze the resultants and to elucidate the underlying mechanism.

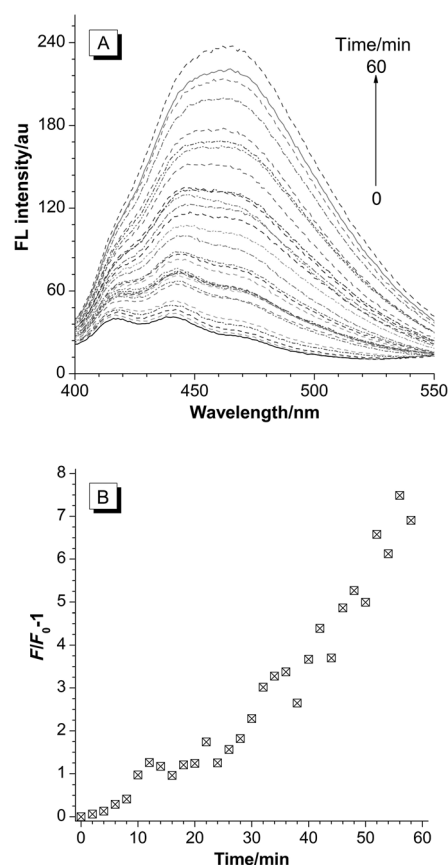


Figure 7. UV-exposure induced FL enhancement. A) Time-dependent FL intensity change of the mixture (THF/buffer = 3/7 by volume, pH 9.0, initial IND-TPE concentration: 10 μM). B) Plot of the relative FL intensity change at 460 nm versus reaction time. F_0 and F are the FL intensity (460 nm) at the moment that IND-TPE was added into the solution and after the reaction mixture was kept for a preset time at room temperature, respectively. λ_{ex} : 330 nm.

FL responses to arginine and lysine

The above observation suggests that IND-TPE has the potential to be used as a dual-responsive fluorescent probe. That is, it is sensitive to both the attack of OH^- anions and the illumination of UV light. Considering that arginine (Arg) and lysine (Lys) are two alkaline amino acids among the 20 common amino acids with pI values of 10.76 and 9.74, respectively (pI values of other used amino acids: His, 7.59; Thr, 6.53; Pro, 6.30; Ala, 6.02; Ile, 6.02; Leu, 5.98; Val, 5.97; Gly, 5.97; Met, 5.75; Ser, 5.68; Tyr, 5.66; Cys, 5.02; Glu, 3.22; Asp, 2.97),^[17] it is expected that Arg and Lys can be selectively detected over other common amino acids by using IND-TPE as a fluorescent probe because it can change its emission features when the pH value is higher than 8.0.

As shown in Figure 8, the fluorescent response starts immediately after the addition of arginine (Arg) into the THF/water mixture. The FL intensity displays a monotonous decrease with the extension of reaction time. In about 60 min, the quenching of the orange emission approaches its steady state. This trend is in consistent with that observed for IND-TPE in alkaline buffer solution, with only a slower declining rate. The interac-

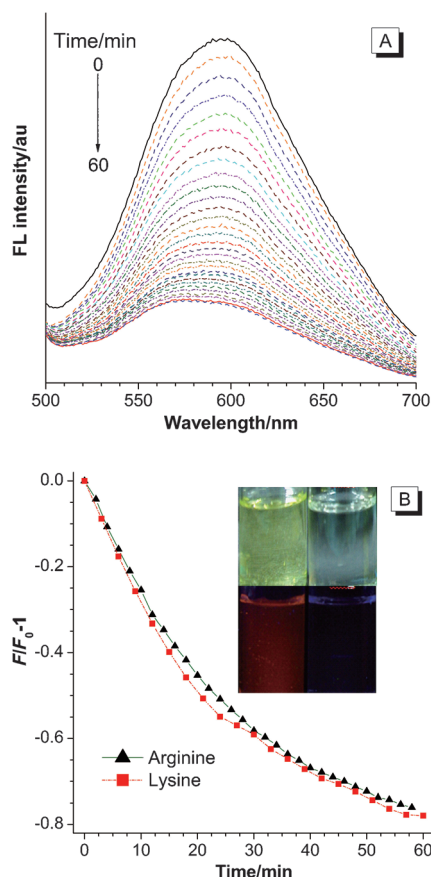


Figure 8. A) Time-dependent FL intensity of IND-TPE + Arg solution. B) Variation of the peak intensity of IND-TPE with reaction time (▲). Also displayed is the FL intensity decrease recorded for IND-TPE + Lys system (■). Inset of (B): Photographs of the solutions of IND-TPE under daylight (upper) and UV light (lower) before and after the addition of Arg. F_0 and F are the peak FL intensity at the moment that Arg was added and after the reaction mixture was kept for a preset time at room temperature, respectively. IND-TPE concentration: 10 μM ; Arg or Lys concentration: 1 mM; λ_{ex} = 420 nm; detection medium: THF/water = 3/7, by volume.

tions between IND-TPE and lysine (Lys) were also tested and the experimental results showed that the fluorescent response of IND-TPE to Lys was quite similar to the response to Arg. The data in Figures 8B and S10 (the Supporting Information) reveal that the decrease of the FL intensity for the system of IND-TPE + Lys goes through a similar time-dependent path to that of IND-TPE + Arg.

Meanwhile, the concentration-dependent fluorescent response of IND-TPE to Lys also shows a similar trend to Arg (Figure 9B and S10B, the Supporting Information). In addition, the sensitivity of Lys to IND-TPE is found to be about 0.1 mM, which is identical to Arg. In comparison with other fluorescent detections of Arg reported in the literature, the performance of IND-TPE is on the moderate level of detection sensitivity.^[18]

To validate that IND-TPE responds specifically to Arg and Lys, we examined the FL responses of IND-TPE to other amino acids. According to the chemical structure of IND-TPE, this probe might be also sensitive to thiol and other strong nucleophilic groups because the bridge C=C double bond is activated

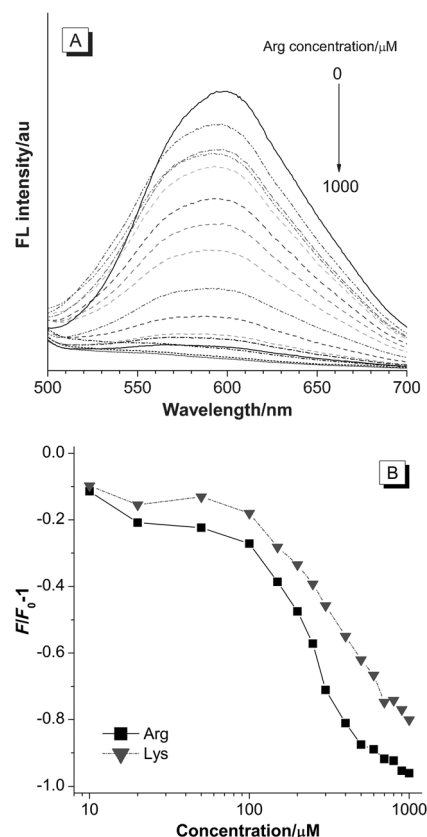


Figure 9. A) Concentration-dependent FL intensity of IND-TPE + Arg system. B) Variation of the peak intensity of IND-TPE with increasing Arg concentration. Also displayed is the change of the peak intensity for IND-TPE + Lys system (▼). Concentration of IND-TPE: 10 μM ; λ_{ex} : 420 nm; detection medium: THF/H₂O = 3/7, by volume; reaction time: 60 min.

by the two adjacent carbonyl groups (α,β -unsaturated ketone). To test this assumption, we analyzed the interaction of cysteine (Cys) with IND-TPE. Upon the addition of Cys into the solutions, no evident changes in the emission features were recorded (Figure S11, the Supporting Information). This observation suggests that the thiol residual on Cys cannot attack the C=C double bond under the experimental conditions. Another potential interference amino acid is histidine (His), which is a basic amino acid with a pI value of 7.59. It was found that the FL features of the system of IND-TPE + His had little changes in comparison with the pristine IND-TPE solution (Figure S12, the Supporting Information). This observation can be explained by the fact that the alkalinity of His is too weak to result in the generation of enough OH^- , thus the hydrolysis of the C=C double bond of IND-TPE cannot be realized.

Besides Arg, Lys, His, and Cys, we also examined the FL responses of IND-TPE to other amino acids and the results are displayed in Figures 10 and S11 (the Supporting Information). Only Arg and Lys showed the ability to alter the emission features of IND-TPE. Based on the experimental results, we can conclude that IND-TPE can specifically respond to Arg and Lys among the examined 16 amino acids.

To confirm that UV-light illumination can also induce the enhancement of blue emission of the IND-TPE + Arg system, we

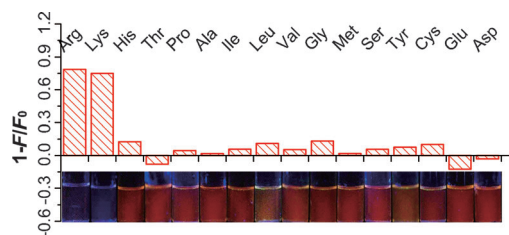


Figure 10. Specific FL response of IND-TPE (10 μM) to diverse amino acids (1.0 mM) in THF/water mixture (3/7 by volume). F_0 and F are the peak PL intensity at the moment that the amino acids were added into the IND-TPE solution and after the reaction mixtures were kept for 60 min at room temperature, respectively. The inset displays the photos of IND-TPE + amino acids taken under UV light ($\lambda_{\text{ex}} \approx 365$ nm).

exposed the reactant mixture under 330 nm UV light for different periods and measured the FL intensity at every 2 min interval (just as described in Figure 7). The data recorded in a typical experiment are depicted in Figure 11 A and B. The blue emission increases with the exposure time. Meanwhile, the intensity fluctuations and redshift of emission features are quite similar to the IND-TPE + borax buffer system, indicating a similar

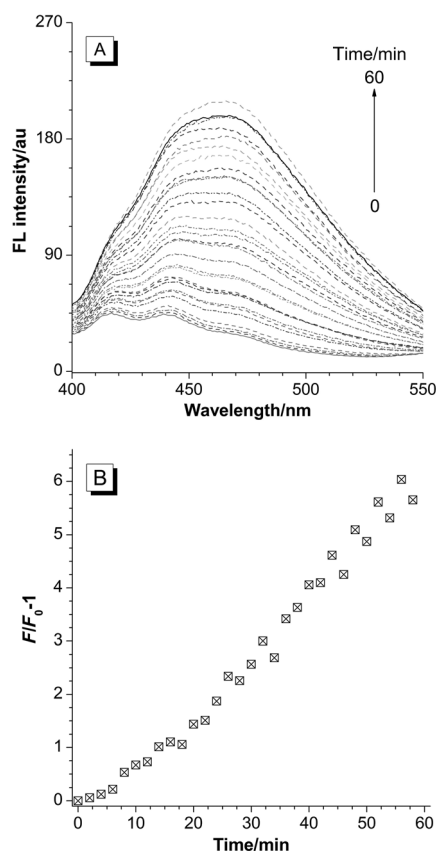


Figure 11. UV-exposure-induced FL enhancement for IND-TPE + Arg system. A) Time-dependent FL intensity change of the mixture (THF/water = 3/7 by volume, pH 9.0, initial IND-TPE concentration: 10 μM); B) Plot of the relative FL intensity change at 460 nm versus reaction time. F_0 and F are the FL intensity (460 nm) at the moment that IND-TPE was added into the solution and after the reaction mixture was kept for a preset time at room temperature, respectively. $\lambda_{\text{ex}} = 330$ nm.

mechanism for the emission change. To validate the OH^- -induced breaking of the conjugation between TPE and 1,3-indandione moieties, we measured the UV-visible absorption spectra of buffer solutions at different pH values. As shown in Figure 12, the absorption band with a maximum at around 425 nm is assigned to the characteristic absorption of IND-TPE. This band remains unchanged for 60 min at pH 4. At pH 7, this band becomes weaker in 60 min, and totally disappears at pH 9. These observations indicate that IND-TPE has been consumed and new fluorogen has generated after 60 min reaction at a pH 9 aqueous solution.

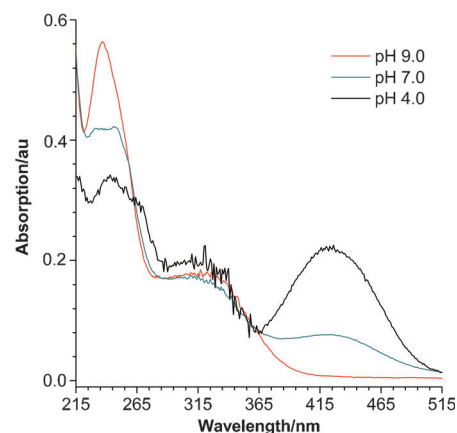


Figure 12. UV/Visible spectra of TPE-IND in the mixture of THF and 10 mM borax buffer with different pH values. Concentration of IND-TPE: 10 μM .

According to the data displayed in Figures 6–10, the red-orange emission of IND-TPE in the aqueous and THF/water mixture solutions can be quenched directly by the OH^- anion and other alkaline species that are capable of inducing the release of OH^- . Moreover, the OH^- -induced hydrolysis of IND-TPE gives rise to a different fluorogen that is blue-emitting and the blue emission can be evidently enhanced by exposure to a suitable source of UV light. Thus, IND-TPE has the potential to be used as a dual-responsive fluorescent probe, which is recognized by both the decrease of the red-orange FL and the increase of the blue FL triggered by UV-light illumination.

Conclusion

A tetraphenylethene derivative decorated with a 1,3-indandione group (IND-TPE) was designed and synthesized. Like many other tetraphenylethene derivatives, IND-TPE displays evident AIE behavior. Due to the electron-withdrawing nature of the 1,3-indandione group, IND-TPE exhibits an intramolecular charge-transfer process from the TPE core and to the peripheral IND groups, which leads to a pronounced solvatochromism effect, a 54 nm redshifted emission from apolar (green FL) to highly polar (red-orange FL) solvents. The conjugation between TPE and 1,3-indandione moieties renders the long-wavelength emission to IND-TPE. Meanwhile, IND-TPE displays evidently mechanochromic responses to external stimuli. The as-prepared powder emits green fluorescence (around

510 nm) and the ground sample emits orange (around 562 nm), which can be changed to yellow-emitting powder (around 525 nm) by thermal-annealing and solvent-fuming treatments. The mechrochromic behavior is reversible in multiple grinding–thermal treating and grinding–solvent-fuming cycles. The mechanism is associated with the reversible crystalline (orange FL)↔amorphous (yellow FL) phase transition, as proved by XRD measurements of the related samples.

Taking advantage of the hydrolysis reaction of the activated C=C double bond between the 1,3-indandione and TPE moieties, we have tried the fluorescent responses of IND-TPE to OH[−] in aqueous solution and mild conditions, and found that the red-orange emission was gradually quenched with the ongoing reaction. The pH-dependent fluorescent responses were also examined in aqueous solution and it was found that the FL quenching occurred in the case of pH ≥ 8. Since Arg and Lys are two basic amino acids with pI values of 10.76 and 9.74, respectively, we applied IND-TPE as a fluorescent probe to the discriminative detection of Arg and Lys from other amino acids. The experimental data indicated that only Arg and Lys showed red-orange FL quenching among 16 different amino acids, and the detection limit for Arg and Lys is about 100 μM. It is interesting that the IND-TPE basic solution (pH 9.0) and IND-TPE + Arg/Lys aqueous solutions demonstrated enhanced blue emission after exposure to 330 nm UV light for a while. The intensity of this blue band increased higher than that of the original red-orange band upon 60 min of UV-light illumination. Without UV light, no blue emission enhancement has been observed. These data indicate that IND-TPE is responsive to both OH[−] and UV-light illumination, thus it can be used as a dual-responsive fluorescent probe. More importantly, the dual responses (red-orange FL quenching and blue FL emerging) can only be detected in the pre-fixed area at which the UV light is focused, just like a spot-light on a stage. Generally, IND-TPE is sensitive to solvent polarity in solutions, sensitive to mechanical force in solid, sensitive to OH[−] in aqueous media, and sensitive to UV light after hydrolyzation, thus, a molecule worthy of the term “multiresponsive fluorescent probe”. The studies on the details of the underlying mechanism of the multiple responses and the related applications in chemical and biological detection are ongoing in our laboratory.

Experimental Section

Materials

Diphenylmethane and 4-bromobenzophenone were purchased from Alfa Aesar. *n*-BuLi was purchased from Acros. Other reagents including *p*-toluenesulfonic acid (TsOH) and toluene were purchased from Sinopharm Chemical Reagent Co., Ltd. Tetrahydrofuran (THF) was distilled under normal pressure from sodium benzophenone ketyl under nitrogen immediately prior to use.

Instrumentation

¹H and ¹³C NMR spectra were measured on a Mercury plus 400 MHz NMR spectrometer in CDCl₃ using tetramethylsilane (TMS; δ = 0 ppm) as internal standard. High-resolution mass spectra

(HRMS) were taken on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. FL spectra were recorded on a Shimadzu RF-5301PC spectrofluorophotometer. UV/Vis absorption spectra were obtained on a Milton Ray Spectrofluorometer.

Synthesis and characterization

IND-TPE was synthesized according to the synthetic routes shown in Scheme 1. A detailed experimental procedure is given below.

2-(4-(1,2,2-Triphenylvinyl)benzylidene)-1H-indene-1,3(2H)-dione (IND-TPE): The TPE-containing precursor 4-(1,2,2-triphenylvinyl)-benzaldehyde (TPE-CHO) was synthesized according to our previously published paper.^[7] A mixture of TPE-CHO (0.720 g, 2 mmol), 1,3-indandione (0.292 g, 2 mmol), and *p*-toluenesulfonic acid (0.020 mg, 0.12 mmol) in toluene (60 mL) was heated to reflux for 24 h. After solvent evaporation, the crude product was purified on a silica-gel column using hexane/ethyl ester (5/1 v/v) as eluent. A yellow solid was obtained in 23.8% yield. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 8.28 (d, 2H; indandione-H), 8.00 (t, 2H; indandione-H), 7.80 (m, 3H; CH=CH and Ph-H), 7.21–7.07 ppm (m, 17H; Ph-H); ¹³C NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 191.11, 189.80, 150.28, 147.33, 143.90, 143.80, 143.70, 143.18, 140.78, 140.67, 135.96, 135.74, 134.58, 132.54, 132.08, 132.02, 131.99, 129.17, 128.63, 128.60, 128.38, 127.80, 127.51, 123.91 ppm; HRMS (MALDI-TOF): *m/z*: calcd for C₃₆H₂₄N₂: 488.18 [M⁺]; found: 488.18.

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