
Triplet-fusion upconversion with oxygen resistance in aqueous media

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ABSTRACT: Triplet fusion upconversion (also called triplet-triplet annihilation, TTA) arouses much attention due to its potential in the fields of biological imaging, optogenetics, and light-harvesting. However, the oxygen quenching remains challenging ahead to restrict their applications in aqueous media. Previous efforts to realizing the aqueous TTA with oxygen resistance have been focused on the core-shell structures and self-assembly, but tedious processes and complicated chemical modification are required. Here, we report a direct and efficient strategy to realize aqueous TTA by controlling the ionic equilibrium of TTA dyad. We find that the ionized organic dyad in physiological buffers and electrolyte-based media show natural aerotolerance without any complicated structure engineering. In particular, the upconversion intensity of this aqueous TTA in Tris buffer under air-saturated condition is more than twice of that under the deaerated condition. We further demonstrate the TTA system for potential applications in pH and temperature sensing with reversible and sensitive performance. We anticipate this facile approach to inspire the development of practical aqueous TTA and broad applications in biological science.

Triplet fusion of organic molecules (also called triplet-triplet annihilation, TTA) triggers numerous interests in catalysis¹, bioimaging², and light-harvesting^{3,4} due to the spectral conversion feature from low to high energy frequencies. It enables low power excitation condition⁵, high upconversion efficiency⁶⁻⁷, and flexible design of platforms⁸⁻¹² based on organic TTA dyad, donor and acceptor. But the solution-based TTA systems are restricted in organic solvents without oxygen molecules because of the intrinsic hydrophobicity of organic dyad and oxygen quenching, although the applications in aqueous media are attractive.

The dioxygen with a triplet ground state consumes the energy of the donor triplets to become singlet oxygen, which will further damage the organic TTA dyad by oxidation. Additional treatments are thus required to isolate them with ambient oxygen molecules in aqueous media. Nano/micro-capsules and self-assembly¹³⁻¹⁴ are common strategies to overcome this challenge. The component, such as surfactant¹⁵⁻¹⁶, polymer¹⁷⁻¹⁸, silica¹⁹⁻²⁰, and bovine serum albumin (BSA)²¹, envelopes TTA dyads to form a dispersible and oxygen-resistant core-shell structure or a tight network in aqueous solutions. Besides, small molecules of antioxidant additive²² and specific acceptors²³ with lower triplet energy than oxygen are also leveraged to suppress the quenching effect of oxygen. However, these indirect strategies induce tedious engineering steps for wrapping and complicated modification.

Here we describe a facile and direct method that can brighten the dark TTA in aqueous media with oxygen. We realize the

water-soluble TTA by controlling the ionic equilibrium of TTA dyad. We find that this TTA system, instead of forming nano/micro-capsule, can remain the upconversion luminescence in air-saturated aqueous media. Moreover, in selective physiological buffers, the TTA upconversion outperforms that under oxygen-deprived conditions. We further explore the potential of this TTA system as a pH and temperature sensor. Our work represents a record situation that realizes stable TTA in an aqueous solution where oxygen is inevitable and sensitive sensing is achievable.

EXPERIMENTAL SECTION

Materials. Solvents were used as received from commercial suppliers (Chem-supply and Sigma-Aldrich). 5,5'-(9,10-anthracenediyl)diisophthalic acid (QCDPA) and meso-tetra(4-carboxyphenyl)porphine tetra methyl ester (H₂TMPP) were bought from Yanshen Technology Co., Ltd. Palladium(II) chloride, dimethyl formamide (DMF) and tetrahydrofuran (THF) were bought from Sigma-Aldrich. PBS and TRIS were purchased from Thermo Fisher Scientific. Unless otherwise indicated, the chemicals used were obtained commercially in high purity and used as received.

Characterization. Absorption spectra were measured with the Agilent Cary 60 UV-Vis spectrophotometer. Fluorescence spectra were recorded on a Shimadzu RF 6000 Fluorimeter with Xenon lamp. Nuclear Magnetic Resonance (NMR) spectra were recorded on an Agilent 500 MHz NMR spectrometer. pH is determined by Oakton pH 700 Benchtop Meter. Upconversion

fluorescence spectra were measured with a home-built system. A fiber-coupled 532 nm (Germ 532 with control software) diode laser work as the excitation source. The emission spectra of the sample were measured by a commercial spectrometer

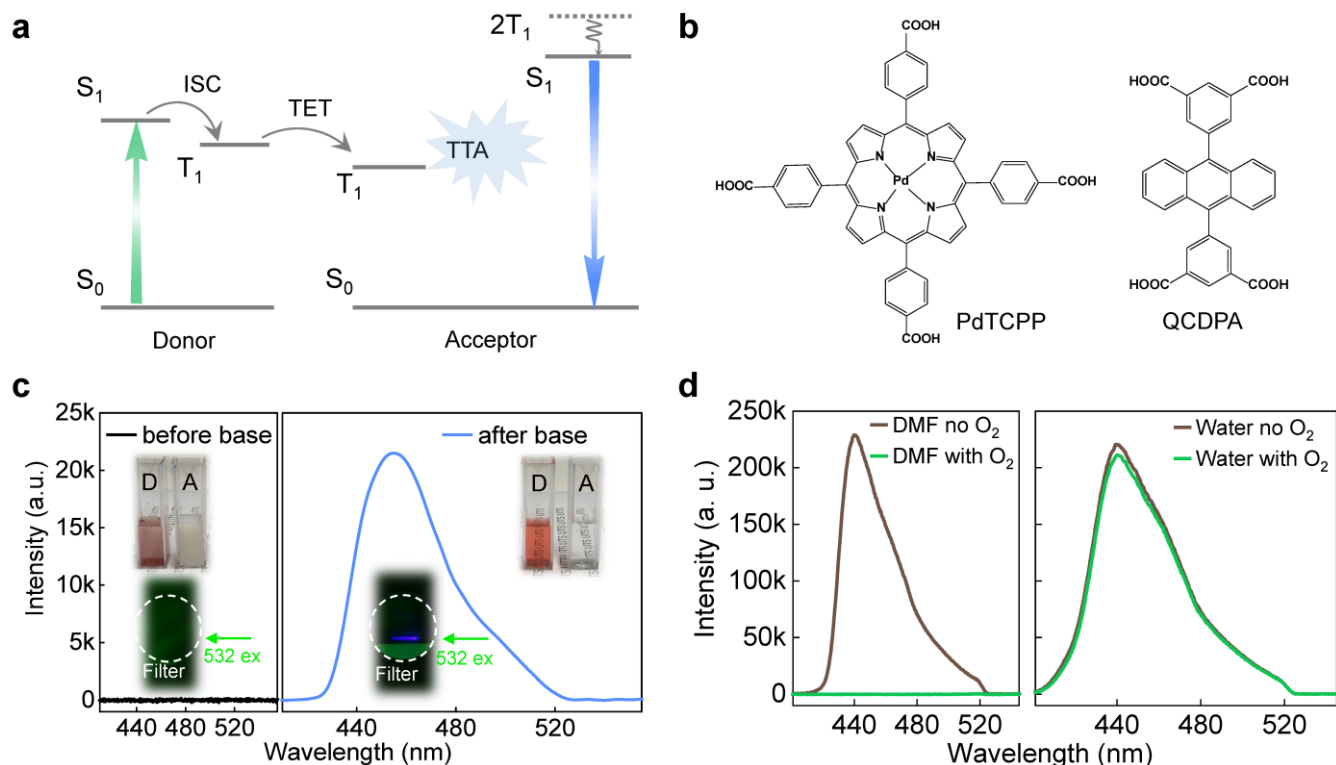


Figure 1. TTA upconversion mechanism and TTA generation with oxygen resistance in aqueous media. (a) The energy level diagram showing the triplet fusion upconversion followed by the intersystem crossing (ISC) and triplet energy transfer (TET) processes in the pair of donor and acceptor. (b) The molecular structure of PdTCPP (donor) and QCDPA (acceptor). (c) The upconversion spectra of the TTA before (left) and after (right) adding base upon 532 nm laser excitation (52 mW cm^{-2}). Insets show the insoluble and soluble statuses of the donor and acceptor molecules in water, and the snapshots behind the 532 nm short-pass edge filter (BSP01-532R-25, Semrock) under excitation of 532 nm laser pen. D means donor, and A represents acceptor. (d) The spectra of TTA in DMF (left) and water (right), the concentrations of acceptor and donor are 5 mM and 0.1 mM, respectively. The excitation power density is 61 mW cm^{-2} .

(Shamrock 193i, Andor) with an EMCCD (iXon Ultra 888, Andor) as the detector. Besides, the emission signal was filtered by a 532 short pass filter (BSP01-532R-25 532 nm EdgeBasic, Semrock). The sample is in a cuvette (i-Quip, $45 \times 12.5 \times 12.5 \text{ mm}$, light length 10mm, light width 5mm) sealed with N_2 .

Upconversion sample preparation. Donor stock solution (5 mM) was prepared by dissolving 8.95 mg PdTCPP in 2 mL aqueous 1 M KOH solution. likewise, acceptor stock solution (50 mM) was prepared using 50.65 mg QCDPA in 2 mL aqueous 1 M KOH solution. Donor and acceptor stock solutions were stored under a dark environment for later use. The information of the samples mentioned in the main text was summarized in Table S1 and S2.

RESULTS AND DISCUSSION

TTA upconversion from organic solvent to water. We take Pd(II) meso-Tetra(4-carboxyphenyl)porphine (PdTCPP) as the donor and 5,5'-(9,10-anthracenediyl)diisophthalic acid (QCDPA) as the acceptor (Figure 1b and Figure S1). Figure 1a shows the energy transfer mechanism of triplet fusion, in which the donor transfers the triplet energy to an acceptor on the ground state after light stimulation (532 nm) and intersystem

crossing (ISC)¹. The collision of the excited acceptor triplets produces upconverted blue emission in higher energy wavelengths. In organic solvents, e.g. DMF, the high solubility makes a quick molecule diffusion of donor and acceptor, resulting in high intensity of upconverting luminescence (Figure 1d). But it fails to produce upconversion in water due to the hydrophobicity of dyad, in which precipitate and turbid solution are observed for the donor and acceptor in water (Figure 1c, left). After adding the base, both the donor and acceptor solutions became soluble and transparent. The corresponding mixture results in blue upconversion emission centred at 455 nm upon the 532 nm laser excitation (Figure 1c, right). This base-induced property transformation is modulated *via* ionic equilibrium of the carboxyl groups on TTA dyad.

To quantify the effect of the solution-phase transfer on TTA, we compare the upconversion emission intensities in DMF and water. When the oxygen has purposely been removed in the solution, the upconversion intensity in water is comparable to that in DMF (Figure 1d). Strikingly, at the atmospheric environment with oxygen, the water-soluble TTA displays neglectable quenching, indicating the strong oxygen resistance of ionized TTA dyad (Figure 1d, right), while completely quenching is observed in the air-saturated DMF (Figure 1d, left). As a simple

TTA dyad that can realize high retention of upconversion emission with an oxygen atmosphere but not relying on micro/nano-capsules, it provides the potential of applicable media, such as biological buffers and media with electrolytes.

We then optimize the upconverting processes by regulating the ratios of acceptor to donor (Figure S2), the concentrations of dyads (Figure S3) and the base concentration used for TTA (Figure S4). The remarkable feature of TTA kinetics as a function of excitation power density confirms the nonlinear process of this aqueous TTA (Figure S5 and S6), which shows an initial

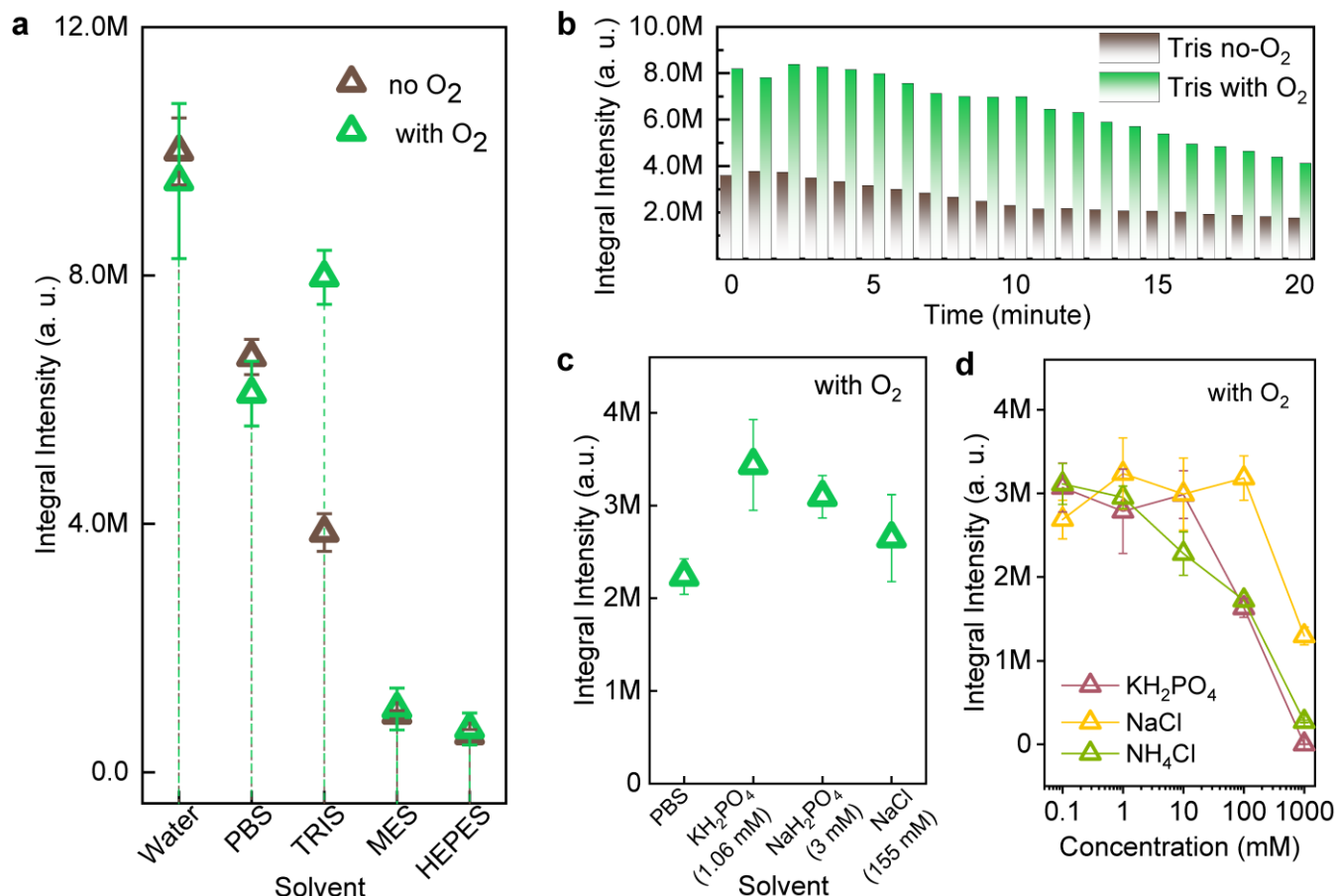


Figure 2. TTA performance in aqueous media. (a) The effect of physiology buffers on the upconversion emission. (b) The durability of TTA in Tris buffer with and without oxygen under 532 nm laser irradiation. (c) The evolution of upconversion intensity in a single-electrolyte medium corresponding to PBS components. (d) The influence of electrolyte concentration on TTA process in the air-saturated conditions. The concentrations of acceptor and donor are 5 mM and 0.1 mM, respectively. The excitation power density is 61 mW cm⁻².

quadratic dependence before saturation^{21,24}. We measure the TTA upconversion efficiency under different excitation power (Figure S7), the efficiency reaches 0.1% in aqueous solution at 138.7 mW cm⁻². Much higher upconversion efficiency is expected to be achieved from the optimized base and dyad types.

TTA performance in air-saturated media. To broaden the range of applicable media, we test the performance of this aqueous TTA in physiological buffers. Taking the optimized acceptor-donor ratio of 501 (see supporting information) as an example, we observe large variations of upconversion intensities in four types of commonly used physiological buffers (Figure 2a). In Tris buffer, we surprisingly find that the oxygen facilitates the upconverting process by showing enhanced intensity up to twice of that in deaerated condition, as well as the appreciable photostability (Figure 2b). By contrast, in PBS, MES and

HEPES, the oxygen barely affects the upconversion performance. It can be concluded that the buffer ingredients determine the upconversion intensity, as a different degree of quenching is observed in these buffers under deaerated condition. The nearly complete quenching in MES and HEPES is due to the significantly suppressed solubility of TTA dyad by the sulfonic acid group from the buffer ingredients.

The influence from the buffer ingredients inspires us to further investigate the upconversion evolution by placing the TTA in electrolyte media, which serve as typical components of a buffer. We prepare single-electrolyte-based media with the concentration corresponding to the ingredients of PBS. As the multi-component buffer involves complex ionization equilibrium, the resultant ions will interfere with the dissolution of TTA dyad and consequently damage the overall upconverting

process. In Figure 2c, we find that TTA in single-electrolyte-based medium outperforms that in PBS buffer.

The tradeoff between the dissolution of TTA dyads and the quenching effect is related with the amount of hydroxyl ions and determines the upconversion process, which is controlled by the ionization equilibrium in a medium. Therefore, careful selection of electrolytes and their concentrations is highly recommended when applying the TTA system in a buffer environment. Here we quantify the ionization effect by tuning the concentration of three representative kinds of electrolytes, basic salt (KH_2PO_4), neutral salt (NaCl) and acid salt (NH_4Cl) (Figure 2d).

The results show that dilute concentrations of all the salts make the upconversion intensity stable while high concentration conditions quench the luminescence. The concentration thresholds for KH_2PO_4 , NaCl , NH_4Cl are 10 mM, 100 mM, and 1 mM, respectively in our experimental condition. We find the products of electrolysis in a solution play a key role in determining the TTA upconversion performance. For neutral salt, NaCl can ionize completely into Na^+ and Cl^- . By contrast, for

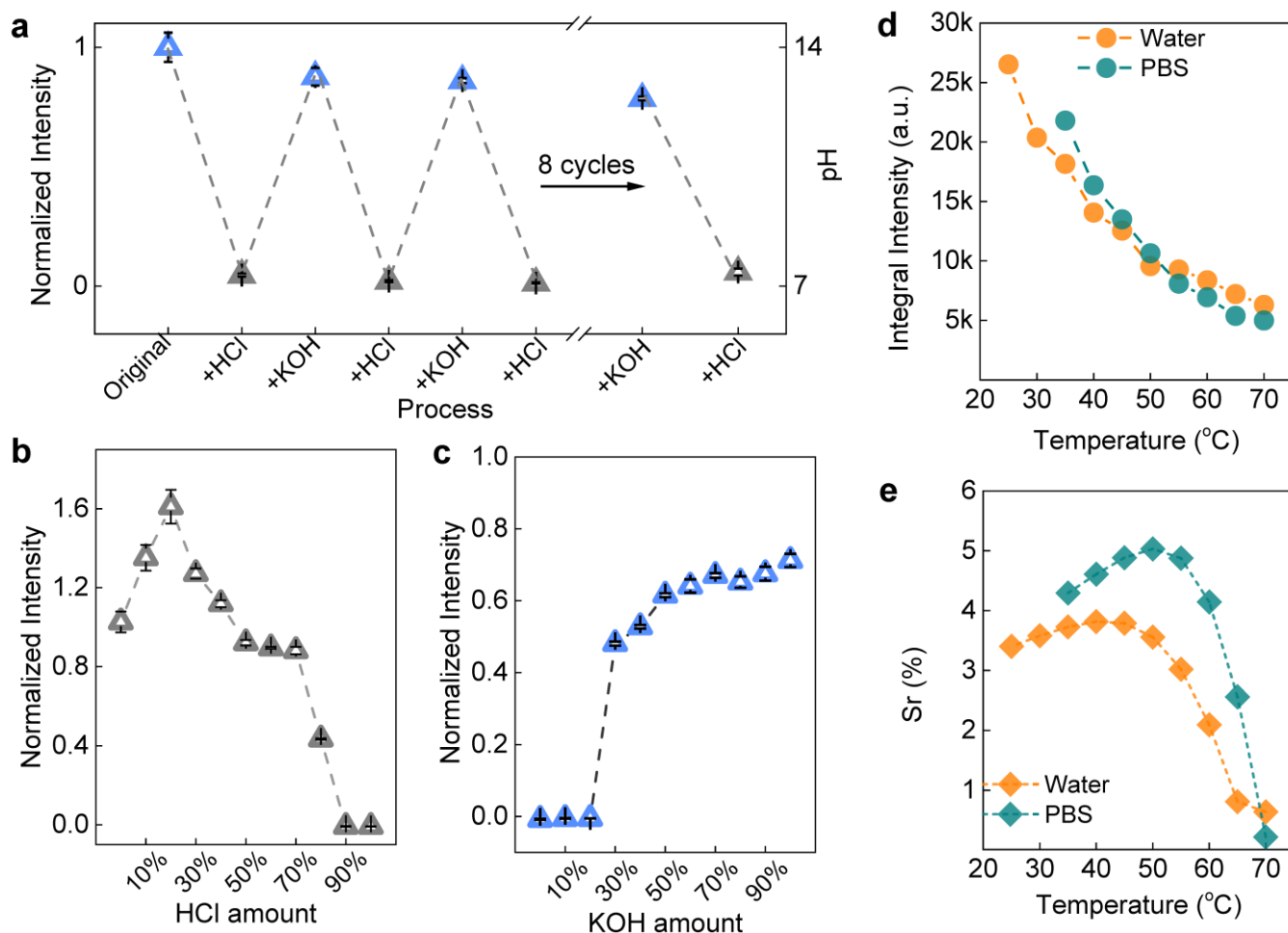
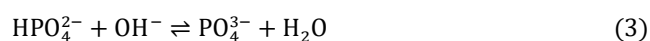
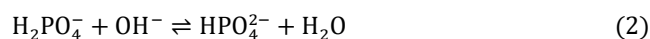


Figure 3. Aqueous TTA systems applied as pH and temperature sensors. (a) Reversibility of TTA as a pH sensor via adding HCl (1 M) and KOH (1 M) solution. (b) The decreased upconversion emission intensity evolution against the gradient adding of HCl (1 M). (c) The increasing trend of upconversion intensity via gradient adding of KOH (1 M). (d) Temperature-sensitive TTA upconversion in water (orange) and PBS (cyan) with inverse intensity evolution compared with traditional TTA systems. (e) The relative temperature sensing sensitivity calculated from data in (d) according to equation (5), $\text{Sr}=(\delta Q/\delta T)/Q$ (5)²⁵. Q is the integral upconversion intensity. The error bars in a, b and c indicate the standard deviation of three measurements. The concentrations of acceptor and donor are 5 mM and 0.1 mM, respectively. The samples were tested under the air-saturated condition. The excitation power density is 61 mW cm^{-2} .

both basic salt and acid salt, their electrolyzations depend on concentration, according to the following equations (1) to (5):



Electrolyzation (equations 1 and 4) firstly facilitate the dissolution of these electrolytes in water. After that, the hydroxyl ions in solution will be immediately consumed by H_2PO_4^- , HPO_4^{2-} and NH_4^+ (equation 2, 3 and 5). In the low concentration regime, the reduction of OH^- quenching for TTA upconversion dominates the contribution over the less dissolution of TTA dyads resulted from the consumption of OH^- . The electrolyte ions accelerate the diffusion of donor and acceptor and benefit to the collision probability for stronger TTA upconversion. In the high concentration regime, the dissolution of TTA dyad is suppressed by excessively consuming OH^- (equation 2, 3 and 5), leading to less molecular diffusion of donor and acceptor and resulting in weaker TTA upconversion.

Oxygen has a slightly negative effect on the TTA intensities in media of electrolytes (Figure S8). But the decrement of intensity is not as significant as that in DMF (Figure 1d). In particular, the TTA intensities in deaerated and aerated NH_4Cl solution are the same, indicating strong oxygen resistance. We test the photostability in solutions of electrolytes and find that the TTA intensities in the media of water, PBS buffer and electrolytes remain good retention after 20 minutes, especially under the condition without oxygen (Figure S9).

Potential in pH and temperature sensing. This upconversion performance is demonstrated to be related with the hydroxyl ions, indicating that the TTA system could be very sensitive to pH. To validate the pH-sensitive property, we design the procedure by alternately adding acid and base into a TTA system to check the possible pH-sensitive property. As shown in Figure 3a, the upconversion of the alkali TTA system completely disappears after adding HCl, and the pH of the final solution becomes close to 7. The intensity of upconversion almost recovers at the initial adding of KOH, and remains nearly 80% even after 11 cycles, indicating the excellent reversibility. To visualize the dynamic variations of upconversion in a single cycle, we divide and add ten units of acid (Figure 3b) and base (Figure 3c) in the TTA systems gradually. The upconversion intensity becomes weak before 7 units of acid adding, followed by a quick reduction until its complete disappearance (Figure 3b). Compared with the trend of fluorescence quenching by acid adding, the recovery tendency of the upconversion intensity by base adding was almost symmetric (Figure 3c), accompanied by the solution status changes from being vague and even precipitate to transparent (Figure S10). Noticeably, the large increase of upconversion in the initial regime of adding acid is speculated to the contribution of diluted concentration of TTA sample (Figure 3b), as the emission intensity increases with the concentration reducing (Figure S3). This implies the transform of TTA dyads forms occurring at the narrow window of acid/base amount.

We further investigate the capability of TTA systems to sense temperature variations both in water and physiology media (PBS). The upconversion intensity, either in water or PBS, displays a declined tendency with the temperature increase (Figure 3d), which is unusual compared with the traditional TTA systems^{18,24,26-29}. We attribute this phenomenon to the TTA dyads dissolution in water, where the electrolytic equilibrium of water, donor/acceptor molecules and the corresponding ions may change with the temperature. Typically, high temperature enables more H^+ and OH^- from the ionization of H_2O ³⁰, which may negatively affect the dissolution of TTA dyads and thus reduce the luminescence intensity. Compared with the properties of temperature sensing in water (from 25 to 70 °C), the dynamic range of temperature monitored in PBS (from 35 to 70 °C) is smaller, while the declined trend of temperature is sharper. We speculate these phenomena are related to the multi-electrolytes existing in PBS. This aqueous TTA system displays high sensitivity of temperature sensing, in particular, in PBS, with the maximum sensitivity of 5.03% °C⁻¹ at 50 °C. This is comparable to the highest record of the reported temperature sensing sensitivity from TTA system^{21,26}.

CONCLUSIONS

We realize the efficient TTA systems in water by modulating the ion equilibrium equation of TTA dyad. The TTA can be applied in many types of aqueous media, especially in physiological buffers and electrolyte-based media. Except for the controllability *via* acceptor-donor ratios, the upconversion intensity of this water-soluble TTA shows apparent dependence of medium. In these media, the ionized TTA dyad display strong aerotolerance, resulting in good retention of upconversion emission in air-saturated conditions. Notably, the upconversion intensity in air-saturated Tris buffer is more than two times of that in deaerated condition, mitigating the general issue of oxygen quenching. We also demonstrate the potential of this aqueous TTA system as a pH sensor and a temperature sensor. This simple strategy may have a profound inspiration for exploring aqueous TTA systems especially considering the possibility in biological applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website.

Detailed experiments, NMR of TTA dyad (S1), upconversion spectra of different acceptor-donor ratios (S2), concentrations (S3) and media pH (S4), power-dependent intensity (S5 and S6), TTA upconversion efficiency (S7), influence of electrolytes (S8), photostability in different media (S9) and digital photos of samples with HCl and KOH (S10) (PDF).

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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