Modulating Room Temperature Phosphorescence by Oxidation of Thianthrene to Achieve Pure Organic Single-Molecule White-Light Emission

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In order to develop pure organic single-molecule white-light emitters (SMWLE), the oxidation of thianthrene (TA) was performed on sulfur atoms at different degrees to tune room temperature phosphorescence (RTP) emission. With increasing degrees of oxidation from 1OTA, 2OTA, 3OTA, to 4OTA, monomeric and aggregative RTP emission was gradually suppressed, due to the gradual disappearance of lone pair electrons on sulfur atoms. Among these compounds, monomers and aggregates of 1OTA demonstrated a better intensity match between fluorescence and RTP. Through partial oxidation of TA, 1OTA exhibited the simultaneous ternary emissions from the lowest singlet state ($S_1$), the lowest triplet state ($T_1$), and the high-lying triplet state ($T_{n}$) in doped film. The single-molecule white-light emission was achieved in 1OTA crystal with a photoluminescence quantum yield (PLQY) of 47.1%. This work not only reports the RTP behavior of TA with different degrees of oxidation, but also provides an example of excited-state modulation to harvest an efficient SMWLE material.

Keywords: single-molecule white light, room temperature phosphorescence, thianthrene, lone pair electrons, spin–orbital coupling
Introduction

Pure organic single-molecule white-light emitters (SMWLE) as single-component systems are attracting growing interest, due to many distinct advantages in contrast with the multicomponent white-light materials, such as absence of phase separation, minimal color aging, good stability, and easy processing. However, the development of pure organic SMWLE is a very challenging task, which essentially involves a systematic and complicated engineering in excited-state design and regulation. Generally, two or three radiative excited states are designed to be responsible for simultaneous dual emission (blue and yellow/orange) or ternary emission (blue, green, and red), corresponding to two-color or three-color white-light strategy in SMWLEs, respectively. In the simplest two-color strategy, one excited state is usually the lowest singlet state ($S_1$) for blue fluorescence emission, and the other excited state can be from the charge-transfer state, proton-transfer state, excimer state, self-assembly state, and the lowest triplet state ($T_1$) for room temperature phosphorescence (RTP) and other methods for low-energy yellow/orange emission. According to the Chroma Theory, a standard two-color white light requires not only wavelength matching but also intensity matching between two emission spectra, indicating a rather intricate modulation between energy level and photoluminescence (PL) efficiency of two excited states. Certainly, the multiple challenges must be met in two-color SMWLE, let alone the more sophisticated three-color mechanism.

Recently, a series of important advances have been made in pure organic RTP materials, which provide a great opportunity and a solid foundation to develop pure organic SMWLE materials through a combined mechanism of fluorescence and RTP. However, pure organic phosphorescence is commonly observed under rigorous conditions (e.g., cryogenic or vacuum) as a result of spin-forbidden transition of $T_1 \rightarrow S_0$, leading to very rare dual-emission real systems of fluorescence and RTP under ambient conditions. Accordingly, some strategies were proposed and applied to achieve the efficient RTP in mild conditions. On the one hand, nonmetallic heavy atoms (e.g., Br, I, and deuterium) and heteroatoms (e.g., B, O, N, S) were introduced to promote spin-orbital coupling (SOC) for efficient intersystem crossing (ISC) to produce triplet excitons. On the other hand, all possible nonradiations (e.g., vibrational and oxygen quenching) of triplet excitons were substantially suppressed by intermolecular interactions and deoxygenation, such as crystallization, H-aggregation, host matrix, metal–organic frameworks (MOF), and so on. Besides, to achieve high performance of pure organic SMWLE, the balance between fluorescence and RTP needs be finely manipulated, which is essentially related to ISC, radiation, and nonradiation processes as mentioned earlier.

In 2018, our group reported a sulfur-based heterocyclic compound, thianthrene (TA), demonstrating dual emission of fluorescence and RTP in both doped film and crystal. Its strong RTP emission was ascribed to a novel mechanism of folding-induced SOC enhancement. However, its RTP was more preponderant than its fluorescence, which made TA emit green color in doped film and crystal, deviating from white light. Inspired by the multiple oxidations of TA, the effect of TA oxidation to different degrees on RTP property (Figure 1) will be systematically investigated to potentially improve the match between fluorescence and RTP for white light. By increasing oxidation degrees from TA to 1OTA, 2OTA, 3OTA, and 4OTA, both energy levels of $S_1$ and $T_1$ were gradually raised, leading to the blue shift of fluorescence and phosphorescence emissions. In the meantime, RTP was gradually decreased and quenched as the oxidation degree increases, due to the gradual disappearance of lone pair electrons on sulfur atoms. Interestingly, 1OTA exhibited not only a better match between fluorescence and RTP intensities in doped film, but also a simultaneous ternary emission from $S_1$, $T_1$, and $T_n$ excited states. Finally, a high-efficiency SMWLE was achieved with a photoluminescence quantum yield (PLQY) of 47.1% in 1OTA crystal. This contribution not only reveals the RTP property of TA with different oxidation degree, but also
suggests an example of excited-state modulation to achieve an efficient SMWLE.

**Experimental Methods**

Oxidation products (1OTA, 2OTA, 3OTA, and 4OTA) were obtained by controllable oxidation reactions (Supporting Information Scheme S1). 1OTA was synthesized as follows: m-chloroperoxybenzoic acid (mCPBA; 2.2 g, 12.7 mmol) was dissolved in dichloromethane (38 mL), and the dissolved solution was added to the TA (2.5 g, 11.6 mmol) solution in dichloromethane, and then the mixture was stirred in an ice water bath for 1 h. The mixture after reaction was extracted with saturated sodium bicarbonate solution. After solvent removal, the crude product was further purified by column chromatography on silica gel using ethyl acetate/n-hexane as the eluent (yield: 68%). The synthesis of 2OTA was similar to 1OTA in which the molar ratio of mCPBA:TA was 2:1 (yield: 39%). 3OTA was synthesized as follows: TA (216 mg, 1 mmol) was dissolved in acetic acid, and then 30% H₂O₂ (6 mL) was added dropwise in the solution at room temperature (RT). The mixture was stirred at 120 °C for 8 h. The mixture after reaction was extracted with dichloromethane. After solvent removal, the crude product was further purified by column chromatography on silica gel using dichloromethane/petroleum as the eluent (yield: 25%). The synthesis of 4OTA was similar to 3OTA in which the excessive amount of 30% H₂O₂ was added (yield: 60%). Their structures were characterized by ¹H NMR, ¹³C NMR, matrix-assisted laser desorption/ionization-time of flight (MALDI-TOF-MS) mass spectra, and elemental analysis. Single crystals of TA derivatives were prepared by crystallization from the solution of dichloromethane and methanol at RT. Detailed experimental procedures and characterizations are shown in the Supporting Information.

**Computational Methods**

All the density functional theory (DFT) calculations were carried out using Gaussian 09 (version D.01) on a Power-Leader cluster. Single-molecule structures of TA derivatives were adopted from optimized ground-state geometries to calculate vertical excitation energy using time-dependent DFT (TD-DFT) at the level of CAM-B3LYP/6-31G (d, p). SOC coefficients were calculated at the level of CAM-B3LYP/6-31G (d, p) by the Beijing density function (BDF) program. In order to examine the nature of electronic transitions, natural transition orbitals (NTOs) were evaluated with the dominant “particle”-“hole” pair contributions.

**Results and Discussion**

These five compounds in dichloromethane solutions showed weak absorption bands in the long-wavelength region of 270–340 nm for TA, 270–335 nm for 1OTA, 270–333 nm for 2OTA, 268–315 nm for 3OTA, and 258–296 nm for 4OTA (Supporting Information Figure S1).
PL spectra of these five compounds in the monomer state [1% wt. doped poly(methyl methacrylate) (PMMA) film] under different conditions were recorded. At RT, these five compounds showed fluorescent emission with PL peaks at 436 nm for TA, 381 nm for 1OTA, 342 nm for 2OTA, 352 nm for 3OTA, and 300 nm for 4OTA, respectively. The PLQY was 3.6% for TA and 4.3% for 4OTA, while 1OTA, 2OTA, and 3OTA showed the PLQY of less than 1.0%. Once at 77 K, all five compounds obviously displayed stronger emission bands in the long-wavelength region, and time-resolved PL spectra revealed long-lived species of 54.4 ms @ 503 nm for TA, 24.2 ms @ 500 nm for 1OTA, 426.1 ms @ 488 nm for 2OTA, 69.5 ms @ 412 nm for 3OTA, and 479.1 ms @ 400 nm for 4OTA, demonstrating the typical phosphorescence characteristic in monomer states of all five compounds (Supporting Information Figures S2 and S3). By increasing the oxidation degree from 1OTA, 2OTA, 3OTA, and 4OTA, the energy levels of both S1 and T1 were raised gradually, leading to the blue shift of fluorescence and phosphorescence emissions relative to those of parent TA. This blue shift may be ascribed to a gradually decreasing p–π conjugation between lone pair electrons on sulfur atoms and π electrons on benzene rings, due to the gradual disappearance of lone pair electrons on sulfur atoms with increasing oxidation degrees (see the following discussion). Furthermore, in order to confirm the phosphorescent properties of monomer states at RT, the PL spectra of 1 wt. % doped PMMA films in vacuum at RT were recorded to verify the oxygen sensitivity. As shown in Figure 2a, TA in vacuum showed enhanced RTP at 520 nm, and 1OTA (446 nm and 500 nm) and 2OTA (446 nm and 490 nm) exhibited weaker RTP relative to TA. However, no phosphorescence emission in the long-wavelength region was observed in 3OTA and 4OTA doped films. To understand the essence of decreased RTP with the increase in oxidation degree from TA to 4OTA, SOC coefficients were calculated using the BDF program \(^{57-60}\) to evaluate the generation of triplet excitons via the ISC process. As illustrated in Supporting Information Figure S4, the SOC coefficients basically showed a decreasing trend from TA to 4OTA with the increase in oxidation degree. Generally, the SOC is dependent on the transition configuration of the excited state, and the difference in transition configurations between singlet and triplet excited states facilitates the enhanced SOC according to the El-Sayed rule.\(^{51,62}\) So natural transition orbitals (NTOs) for S1 and T1 states were used to identify their transition characters and further understand the weakened SOC from TA to 4OTA (Figure 2b, Supporting Information Figures S5 and S6). The T1 state of every compound showed a (n, π*) transition configuration, while their S1 states exhibited the large change in transition configuration from (n, π*) to (π, π*). Specifically, because a sulfur atom in a TA molecule adopts the sp\(^2\) unequal hybridization mode and has two lone pair electrons in its valence shell, there are four lone pair electrons on sulfur atoms in TA when the sulfur atoms are not oxidized. For partial oxidation, there are still three lone pair electrons on sulfur atoms in 1OTA, two lone pair electrons on sulfur atoms in 2OTA, and only one lone pair electrons on sulfur atoms in 3OTA. (The distribution of lone pair electrons was marked in a red dashed rectangle in Figure 2b). TA, 1OTA, 2OTA, and 3OTA show (n, π*) transition configuration in S1 state. Due to the complete oxidation of sulfur atoms, no lone pair electrons remain on sulfur atoms in 4OTA, corresponding to the (π, π*) transition configuration in the S1 state and the smallest SOC coefficients. Therefore, RTP was gradually decreased and quenched as the oxidation degree of sulfur atoms increased, due to the gradual loss of lone pair electrons on sulfur atoms that prevented (n, π*) transition configuration formation in the S1 state (Figure 1 and 2). It can also be inferred that the oxygen atoms in oxidized TA derivatives did not play a substantial role in the SOC. Theoretical optimization of the ground-state geometries demonstrated that these five compounds have folded geometries (Supporting Information Figures S4). It is the cooperation between lone pair electrons and folded geometry that facilitated the enhanced SOC.\(^{56}\)

Interestingly, with increasing delay time, the doped film of 1OTA at 77 K exhibited green afterglow at 500 nm firstly and then longer-lived blue afterglow at 446 nm (Supporting Information Figure S7). The lifetimes at 446 and 500 nm were 33.3 and 24.2 ms, respectively, indicating the different triplet state species of 1OTA in the monomer state at 77 K. Remarkably, similar to the emission behaviors at 77 K, the doped film of 1OTA upon deoxygenation at RT showed emission bands at 446 nm with a lifetime of 16.2 ms and 500 nm with a lifetime of 19.7 ms (Figure 3), corresponding to independent RTP emission from the T1 and high-lying Tn states. This Tn state was further confirmed by temperature-dependent PL spectra. As shown in Figure 3b, both T1 and Tn emissions exhibited high intensity at low temperatures, but the Tn emission at 446 nm showed more sensitive temperature dependence, that is, Tn state showed more vigorous nonradiation vibration with increasing temperature. Temperature-dependent PL spectra also demonstrated that phosphorescence was more temperature-sensitive than fluorescence. So it can be expected that RTP is greatly enhanced by lattice confinement to effectively suppress nonradiative vibrational quenching in crystal. Moreover, theoretical calculations of NTOs of 1OTA showed that T1 and T2 states were the degenerated (n, π*) transition configurations while the T3 state was the (n, π*) transition configuration, and there was a large energy gap between T2 and T3 states (Supporting Information Figure S8). The distinct transition configurations and large energy level difference effectively
suppressed the internal conversion (IC) process from the high-lying triplet state (e.g., T3) to the lower triplet one (e.g., T2 or T1), resulting in the phosphorescent radiation of high-lying triplet state (Figure 3d).25,49 As a result, 1OTA in the monomer state at RT exhibited not only a better match between fluorescence and RTP intensities, but also a simultaneous ternary emission from S1, T1, and Tn excited states, respectively. Besides, 2OTA in the monomer state at RT showed similar photophysical properties to those of 1OTA (Supporting Information Figure S9).

In the crystalline state, the TA showed bright RTP emission peaking at 540 nm with a lifetime of 23.6 ms as well as a weak fluorescence shoulder at 430 nm with a lifetime of 1.8 ns (Supporting Information Figure S10). The PLQY of TA crystal was 25%. The 2OTA crystal showed weakened RTP emission peaking at 518 nm with a lifetime of 66.3 ms (Supporting Information Figure S10), and the PLQY of 2OTA crystal is only 6.8%. However, the crystals of 3OTA and 4OTA showed very weak RTP (0.7 ms @ 520 nm for 3OTA, PLQY ≈ 3.5%; 40.6 ms @ 508 nm for 4OTA, PLQY ≈ 7.8%) (Supporting Information Figure S10). Most importantly, the crystal of 1OTA showed three emission bands, including a bright RTP emission peak at 545 nm with a lifetime of 89.3 ms and two fluorescence shoulders: 2.5 ns @ 381 nm and 4.1 ns @ 446 nm, corresponding to monomer emission and aggregate emission, respectively (Figure 4 and Supporting Information Figure S11). Through the oxidation of TA, 1OTA and 2OTA showed the RTP characteristic in crystal (Supporting Information Figures S11 and S12), but 3OTA and 4OTA showed very weak RTP. What is more, the PLQY of the 1OTA crystal was significantly increased, up to 47.1% relative to those of TA and 2OTA under the excitation of 365 nm. This can be ascribed to the formation of a hydrogen bond network as a result of the introduction of oxygen atoms from TA oxidation, in which one molecule is surrounded by other molecules through C–H···O hydrogen bonding (2.496, 2.544 Å) (Supporting Information Figure S13). Because the central molecular rigidity was greatly enhanced, the nonradiative vibrational quenching was effectively suppressed, resulting in a significant improvement of RTP efficiency.

Using different excitations from 250 to 420 nm, the relative intensities of these three emissions can be finely tuned. Intriguingly, the crystal of 1OTA displayed tunable white-light emission with CIE coordinates of (0.33, 0.40), (0.32, 0.37), and (0.30, 0.35) under the different excitations of 370, 380, and 390 nm, respectively. It can serve as a smart material for tunable white-light illumination,
and its CIE coordinates were recorded under the different excitation wavelengths in Figure 4 and Supporting Information Figure S14. In addition, 1OTA is a good candidate for use in the field of information security. As shown in Figure 4d, the original pattern of a “sun” was made of two kinds of SMWLE materials: one is 1OTA with the characteristic of long-lived RTP, and the other is TX-OCH3 without persistent afterglow. Once the pattern was excited under a 365 nm UV lamp, it initially presented a white “sun.” Switching off the UV light suddenly, the yellow-green “moon” with the long-lived RTP could be readily observed. This behavior at RT makes 1OTA a promising application for information security materials.

Conclusion

In conclusion, a series of TA derivatives were synthesized with different degrees of oxidation on sulfur atoms, and their photophysical properties were carefully characterized and systematically investigated. As the degree of TA oxidation increased, both energy levels of S1 and T1 states showed a gradual rise, corresponding to the blue-shifted fluorescence and phosphorescence emissions relative to those of parent TA, respectively. At the same time, RTP gradually declined and was quenched due to the disappearance of lone pair electrons on sulfur atoms after oxidation. Upon the partial oxidation of sulfur atoms, 1OTA showed not only a better intensity match between fluorescence and RTP in doped film, but also a simultaneous ternary emission from S1, T1, and Tn excited states. As a result, an efficient pure organic SMWLE was harvested with a PLQY of 47.1% in the 1OTA crystal under a certain excitation wavelength. This work not only introduces the effect of TA oxidation at different degrees on RTP property, but also provides a practical case of excited-state modulation for efficient pure organic SMWLE materials based on TA analogues.

Supporting Information

Supporting Information is available.
Conflict of Interest

There is no conflict of interest to report.

Funding Information

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