Spectroscopic study of the authentic emitter of AMPPD chemiluminescence in alkaline aqueous solution†

Langping Tu,[abc] Yu Wang,[abc] Yifei Yang,[ab] Bert H. Bakker,[c] Xianggui Kong,*[a] Albert M. Brouwer,[c] Wybren J. Buma[c] and Hong Zhang*[c]

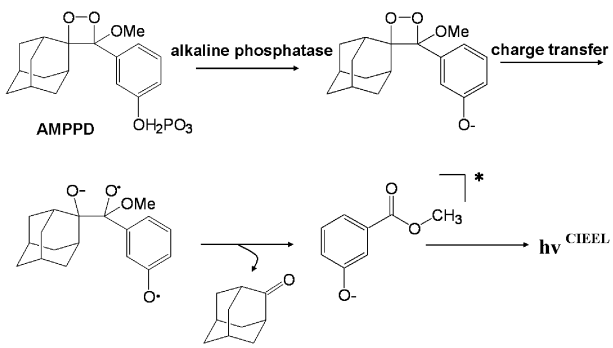
Received 23rd October 2009, Accepted 11th March 2010
First published as an Advance Article on the web 6th May 2010
DOI: 10.1039/b922244h

To design more effective CIEEL (chemically initiated electron exchange luminescence) systems demands a complete picture of the dynamics of the chemiluminescence, which is often a challenge. In this work, photoluminescence of the methyl *m*-oxybenzoate anion – the authentic emitter of AMPPD (3-[2-spiroadamantane]-4-methoxy-4-[3-phosphoryloxy]-phenyl-1,2-dioxetane) in aqueous solvent has been studied. Combining the effect of solvent properties, *e.g.* pH value, and spectroscopic studies employing steady-state and ultrafast time-resolved emission and absorption and ^{1}H NMR techniques, a novel mechanism is proposed. We conclude that the deviation of emission peaks between chemiluminescence and photoluminescence of the authentic emitter of AMPPD *i.e.* the methyl *m*-oxybenzoate anion, in alkaline aqueous solvents is due to its hydrolysis, rather than the hydrogen-bonding effect as has been assumed so far. Besides, the hydrogen-bonding is suggested to play a key role in significantly decreasing the chemiluminescence yield of AMPPD in aqueous solution by shortening the lifetime of the excited authentic emitter to 10 ps order of magnitude – three orders of magnitude shorter than the previously reported value (~10 ns). These results shed light on the chemiluminescence dynamics of AMPPD and facilitate the design of more effective CIEEL systems.

Introduction

Chemiluminescence (CL), a phenomenon of transforming chemical energy into photons, has attracted considerable attention for its diversity of practical applications,[1–4] most prominently in the biochemistry field like immunoassays, nucleic acid identification, measuring enzyme activity, and the detection of small molecules such as O_2^-, H_2O_2, $^1O_2$, NO and ATP,[5–7] *etc*. Dioxetanes, as a typical type of chemiluminescent molecules, have been a focus of research in recent years due to their highly efficient luminescence and special luminescence mechanism.[8–11] It is reported that the solvent properties, *e.g.* viscosity,[12,13] pH value,[14] hydrogen-bonding,[15,16] have a significant impact on the CL of dioxetanes. In the meantime, however, the CL dynamics have not yet been well documented, and a complete picture is still lacking. Taking AMPPD (3-[2-spiroadamantane]-4-methoxy-4-[3-phosphoryloxy]-phenyl-1,2-dioxetane) for example, the significant decrease of its CL yield in protic systems needs to be rationalized. This lack comes partially from the difficulties in determining the fluorescence yield (Φ^{fl}) and the singlet chemiexcitation yield (Φ^S), because the peak positions of CL and the photoluminescence (PL) of its authentic emitter are completely different.[8,15] Furthermore, for some dioxetanes including AMPPD, it is speculated that hydrogen-bonding plays an important role in the decrease of the CL efficiency,[17,18] for which, however, no direct experimental evidence was provided.

In order to design more effective CIEEL (chemically initiated electron exchange luminescence) systems in aqueous solution, it is essential to understand the solvent effect (*e.g.* hydrogen-bonding, pH value) on the luminescence process. The impact of the pH and hydrogen-bonding effects on the authentic emitter of AMPPD, as a representative, has been studied by Adam *et al*., and the CIEEL process of AMPPD was proposed as shown in Scheme 1.[14,15]



Scheme 1 The CIEEL process of AMPPD.

[a] *Key Laboratory of Excited-State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033, China. E-mail: xgkong14@ciomp.ac.cn; Tel: +86-431-86176313*
[b] *Graduate School of Chinese Academy of Sciences, Beijing 100039, China*
[c] *Van't Hoff Institute for Molecular Sciences, University of Amsterdam, Nieuwe Achtergracht 166, 1018 WV Amsterdam, The Netherlands. E-mail: h.zhang@uva.nl; Fax: +31-20-5255604; Tel: +31-20-5256976*

† Electronic supplementary information (ESI) available: Additional data from single-photon counting experiments. See DOI: 10.1039/b922244h

To study the dynamics of the CL process, one approach is to employ the corresponding photoluminescence of the intermediate species. Time-resolved spectroscopy, especially ultrafast spectroscopy, can play a key role in such studies.[19,20] It is reported that the PL of the authentic emitter of AMPPD, which is supposed to be the methyl *m*-oxybenzoate anion, in protic solvents is centered at ~415 nm – ~51 nm blue-shifted compared to the CL of AMPPD. In aprotic solvents, on the other hand, both the PL and CL coincide, peaking at ~466 nm. The blue-shift was attributed to the hydrogen-bonding effect on the methyl *m*-oxybenzoate anion.[15] Although this model has been qualitatively supported by semiempirical AM1 calculations, and employed widely so far to explain similar phenomena of other dioxetanes,[8,16,17,21,22] it cannot explain some observations as mentioned above, more specifically, the solvent dependence of CL yield. Considering that fluorescence yield (Φ^{fl}) should be proportional to the PL lifetime of the authentic emitter,[23] this model leads to a puzzling result: the PL lifetime of the authentic emitter is reported ~10 ns and Φ^{CIEEL} of AMPPD is determined to be $\sim 7.5 \pm 0.3 \times 10^{-6}$ in aqueous system,[14] whereas in aprotic solvent (*e.g.* DMSO), the PL lifetime is only increased approximately twice (~19 ns), but Φ^{CIEEL} is increased by ~39 000 times, to ~0.29.[8,14]

In this work, we have performed steady-state and ultrafast time-resolved spectroscopic studies on the methyl *m*-oxybenzoate anion in various solutions. Our study reveals that hydrolysis plays a key role in unraveling the aforementioned puzzles. The emissions peaking at ~460 nm (in DMSO) and ~412 nm (in alkaline aqueous solvent) are identified as coming from the authentic emitter itself and the hydrolysate of the emitter–3-hydroxybenzoic acid dianion, respectively. Furthermore, the fluorescent lifetime of the authentic emitter is determined to be ~10 ps in aqueous solvent, in contrast with the previous reported ~10 ns, suggesting that hydrogen-bonding effect on the authentic emitter is responsible, to a great extent, for the significant decrease of the chemiluminescence intensity in aqueous solvent.

Experimental section

A Sample preparation

The deviation of the reported emission peaks between PL of the authentic emitter and CL of AMPPD in protic solution is known to be independent of the following parameters: the type of medium (H_2O, D_2O and MeOH), the choice of trigger, the reaction catalyst, and the second dioxetane cleavage fragment.[8,15,16] Therefore, two typical alkaline aqueous solutions in this work were selected: sodium carbonate/sodium bicarbonate solution with pH value about 10, and sodium hydroxide solution with pH value about 14. For the sake of convenience, we name sodium carbonate/sodium bicarbonate (0.05 M, 0.05 M) in deionized water as buffer solution 1 and NaOH (1 M) in deionized water as buffer solution 2 in the following text.

The methyl *m*-oxybenzoate anion in two different pH aqueous solutions, solutions A (pH ~10) and B (pH ~14), were prepared by mixing 1 mM methyl-3-hydroxybenzoate (>99%, Aldrich) 1 mL with 10 mL buffer solution 1 and buffer solution 2, respectively. The hydrolysate of the methyl *m*-oxybenzoate anion–3-hydroxybenzoic acid dianion – in aqueous solutions, named solutions C (pH ~10) and D (pH ~14), were prepared by mixing 1 mM 3-hydroxybenzoic acid (99%, Aldrich) 1mL with 10 mL buffer solution 1 and buffer solution 2, respectively. Finally, the methyl *m*-oxybenzoate anion in DMSO was prepared by adding small portions (0.05–0.08% of volume) of their stock solutions (0.17 mM) in 1 M aqueous NaOH as described previously.[15]

The samples for ^{1}H NMR measurement were prepared as follows: a neutral solution was prepared by dissolving 4.10 mg methyl-3-hydroxybenzoate in 800 μL D_2O, a solution with pH ~10 was prepared by dissolving 3.56 mg methyl-3-hydroxybenzoate in 800 μL D_2O, and adding 0.5 μL 40 wt% NaOD/D_2O. A solution with pH ~14 was prepared by dissolving 3.45 mg methyl-3-hydroxybenzoate in 800 μL D_2O, and adding 5 μL 40 wt% NaOD/D_2O. In the following text they are named as neutral solution, solution E (pH ~10) and solution F (pH ~14), respectively.

B Measurements

Steady-state absorption spectra were measured on a Cary 300 double-beam spectrometer with spectral resolution of 1 nm. Steady-state emission (λ_{ex} = 320 nm) and excitation (λ_{em} = 410 nm) spectra were obtained on the emission spectrometer described previously.[24] The transient spectra of all solutions were recorded by a calibrated time-correlated single photon-counting (TCSPC) system with instrumental response time (IRF) of 17 ps.[24] In the femtosecond transient absorption experiments, the pump pulse (λ_{ex} = 325 nm) was realized by an amplified femtosecond laser system (Hurricane (Spectra-Physics) with OPA-800c, 800 nm pulse, 120 fs pulse duration), while the probe was a white light continuum pulse generated by a small part of the 800 nm beam focusing onto a sapphire plate. The detector was a 2048 pixels CCD camera (Ocean Optics, S2000).[25] IRF, as characterized by the cross correlation, was approximately 300 fs. All the experiments were performed at room temperature and under magic angle conditions. The ^{1}H NMR data were recorded on a Bruken (400 MHz, solvent D_2O; internal standard, TMS) nuclear magnetic resonance spectrometer.

Results and discussion

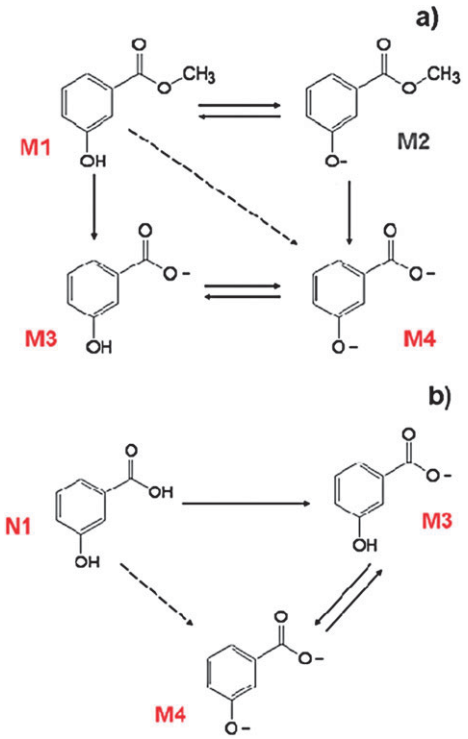
The variation of the emission spectrum of solution A with time is shown in Fig. 1, where the peak remains unchanged at ~412 ± 2 nm, in agreement with the PL peak behavior of the authentic emitter of AMPPD affected by hydrogen-bonding in previous reports (the shoulder at 360 nm is the signal of the scattered light induced by H_2O).[15] It is, however, interesting to note that the emission intensity of solution A increases dramatically with time, implying that some chemical reactions occur continuously. To further investigate this phenomenon, the time evolution of the excitation and emission spectra of solutions A, B, C and D are shown in Fig. 2. It is obvious that the excitation and emission intensities of solutions B, C and D demonstrate much less time dependence, different from that of solution A. To further study the mechanism, we start with the possible reaction channels as depicted in Scheme 2. First of all, considering the high pH value of the solution D (pH ~14) and

the low pK_a values of the phenolic group ($\sim$10) and carboxylic group ($\sim$3.5) in **N1**, it is inferred that **N1** will completely change to **M4** in solution D. Besides, it is noted that in four solutions, all the emission peak ($\sim$412 $\pm$ 2 nm) and excitation peaks ($\sim$316 $\pm$ 2 nm) coincide, revealing that the fluorescence peaks around 412 nm of all four solutions come from the same ion – **M4**. In other words, in the solutions A and B, the fluorescence peaks around 412 nm might have nothing to do with the possible hydrogen bonding effect in **M2** (the authentic emitter of the AMPPD), but simply come from **M4** – the hydrolysate of **M2**. With this in mind, we could further understand the differences in the time behavior of the four solutions with Scheme 2. As it can be readily concluded that the emission of molecules **M1**, **M2**, **M3** and **N1** can be ignored as compared with **M4**, because no other component in the excitation or emission spectra of the four solutions is found during the monitoring period. Besides, it can be assumed that, in solution C, the carboxylic group of **N1** is completely ionized since its pK_a value ($\sim$3.5) is much lower than the pH value of the solution ($\sim$10). Comparing the spectra of solutions C and D, the obviously lower emission intensity of solution C reveals that **M3** and **M4** coexist at pH $\sim$10 which is close to the pK_a of the phenol group. Furthermore, the fact that the emission and excitation spectra of solution C remain unchanged during the monitoring period indicates that, in the solution C, **M3** and **M4** very soon (or even during the preparation process of the sample) reach ionization balance with each other. Similarly, it can be inferred that **M1** and **M2** reach the equilibrium very fast, as well. Therefore, the continuous increase of spectral intensity of solution A with monitoring time can be ascribed to the conversion of transfer from **M1** to **M3** and/or **M2** to **M4**.

The hydrolytic process becomes much faster when the pH value of the solution is 14, as evidenced by the unchanged spectra of solution B during the monitoring period. The time evolutions of the absorption spectra of the solutions A, B, C and D (Fig. 3) also support this argument. It can be seen from Fig. 3 that the absorption peaks of solutions B and D keep constant at 312 nm which is assigned to the absorption of **M4**. The absorption of solution C is apparently composed of two bands, peaking at 288 nm and 312 nm, respectively, from the fitting of a bi-Gaussian function. The latter coincides with that of **M4**. Therefore the former one should be attributed to the absorption of **M3**. At last we come to solution A. Here the absorption band evolves with time and the peak shifts from 327 nm to 322 nm within 72 h. Referenced to Scheme 2, it is clear that this shift is in fact a manifestation of the hydrolytic process – from **M1** to **M3** and/or **M2** to **M4**.

At this point, it is important to emphasise the fact that, in solutions A and B, no PL peak could be observed (Fig. 2) around 466 nm – the maximum of AMPPD CL. This can be rationalized by the extremely low fluorescence yield (Φ^{fl}) of **M2** compared with Φ^{fl} of the hydrolysate-**M4**, which we will discuss later.

In order to further characterize the hydrolytic reaction, time evolution of the ^{1}H NMR spectra of solutions E (pH $\sim$10) and F (pH $\sim$14) are recorded against pH, as displayed in Fig. 4. In both solutions the signals from δ 6.5 ppm to δ 8.0 ppm are assigned to the benzene ring of **M1–4**, the signals at δ 4.6 ppm, δ 3.8 ppm and δ 3.2 ppm correspond to the residual HDO molecule in solvent, the –CH_3 group in the **M1**, **2** and methanol, respectively. It is obvious that, compared with the neutral solution, the signal at δ 3.8 ppm decreases with time (using the signal integral intensity from δ 6.5 ppm to δ 8.0 ppm as a reference) and finally disappears, whereas the signal at δ 3.2 ppm increases in the meantime. This indicates the existence of the hydrolytic process – from **M1** to, **M3** and/or **M2** to **M4**.



Scheme 2 Schematic representation of the possible reactions in four solutions A (pH $\sim$10, solid line arrows) and B (pH $\sim$14, dashed line arrow) (a), C (pH $\sim$10, solid line arrows), and D (pH $\sim$14, dashed line arrow) (b).

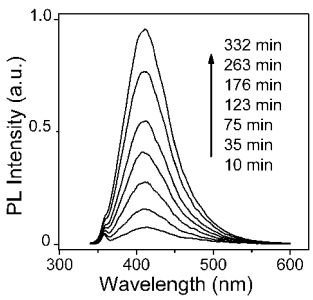


Fig. 1 The PL spectrum of solution A (pH $\sim$10, λ_{ex} = 320 nm) at different times (marked in the Figure) after the preparation of the solution.

And then, to study the dynamics of the hydrolytic process of **M2** in aqueous solutions, the time evolution of the PL decay curves (λ_{em} = 410 nm, 460 nm) of solutions A (pH $\sim$10) and B (pH $\sim$14) are recorded, as shown in Fig. 5. For solution B, both at 410 nm and 460 nm, all the decay curves can be well fitted by an exponential function defined as:

$$I(t) = A \exp(-t/\tau) \quad (1)$$

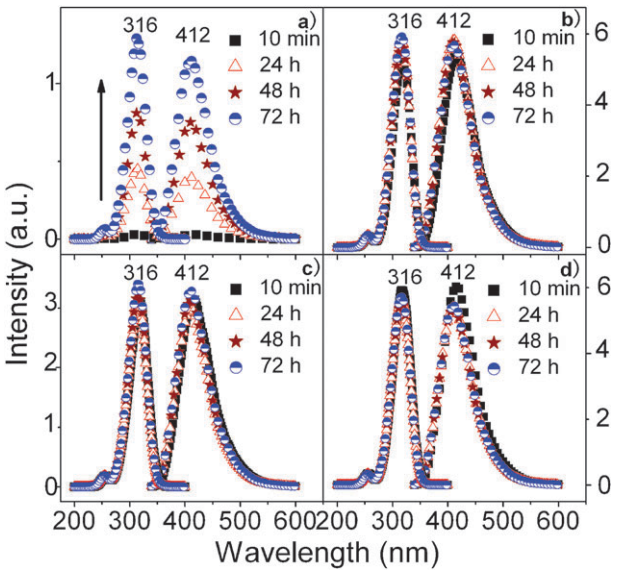


Fig. 2 The excitation (λ_{em} = 410 nm) and emission (λ_{ex} = 320 nm) spectra of the solutions from A to D at different times (marked in the figure) after the preparation of the solutions. (a) pH ~10, (b) pH ~14, (c) pH ~10, and (d) pH ~14.

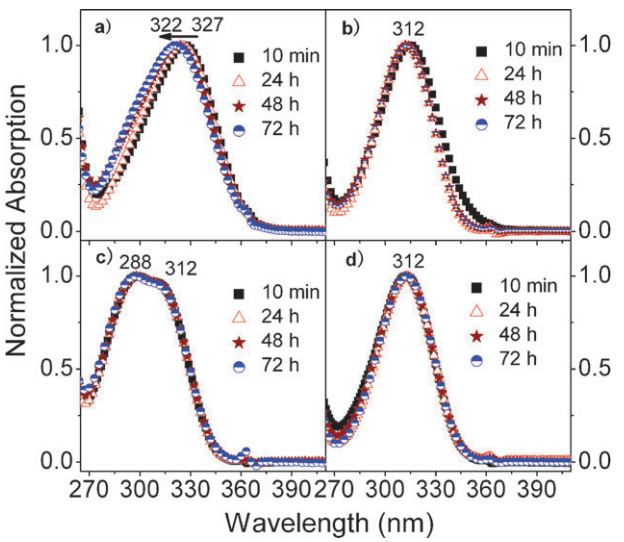


Fig. 3 Normalized absorption spectra of the solutions from A to D at different times (marked in the figure) after the preparation of the solutions. (a) pH ~10, (b) pH ~14, (c) pH ~10, and (d) pH ~14.

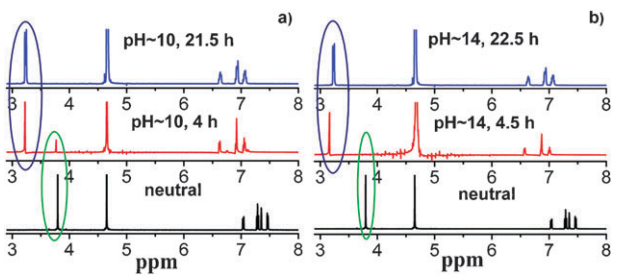


Fig. 4 ^{1}H NMR spectra of solutions E (pH ~10) (a) and F (pH ~14) (b) at different times (marked in the Figure) after the preparation of the solutions, compared with the neutral solution.

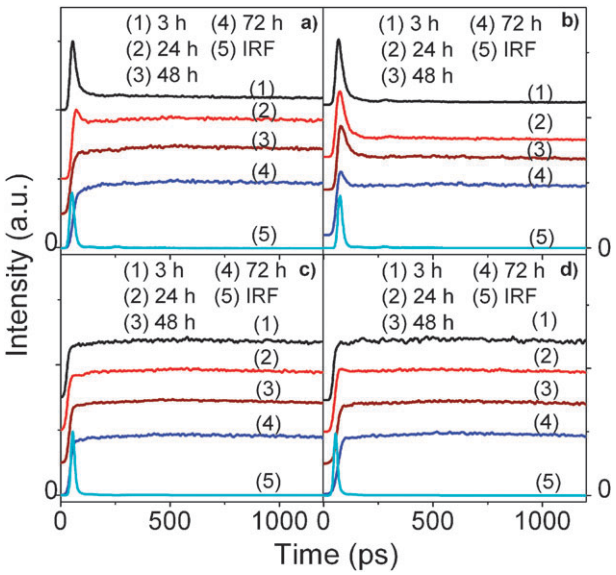


Fig. 5 PL decay curves of solutions A (pH ~10) and B (pH ~14) at different times (marked in the figure) after the preparation of the solutions, λ_{ex} = 320 nm, (a) solution A, λ_{em} = 410 nm, (b) solution A, λ_{em} = 460 nm, (c) solution B, λ_{em} = 410 nm, and (d) solution B, λ_{em} = 460 nm.

where the lifetime is determined to be about 10.5 ns (Fig. 5c and d). In early works, this lifetime was assigned to the excited state of **M2**.[14] However, this long lifetime does not agree with the very low Φ^{CIEEL} of AMPPD (*vide infra*). And based on the experimental results above, we believe that under the conditions of solution B (pH ~14), the hydrolytic process – from **M2** to **M4** – has already finished soon after the sample preparation. Therefore, in this paper, the emission of solution B with the PL lifetime ~10.5 ns is attributed to **M4**, not **M2**.

This assignment is supported by the following observations. For solution A, both at 410 nm and 460 nm, the decay curves show quasi-biexponential behavior and the shorter lifetime component decreases noticeably with a storage time of the sample (*cf.* Fig. 5a and b. Actually, at 410 nm, the shorter lifetime component is almost zero after 48 h).

The decay curves can be well fitted with function:

$$I(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \quad (2)$$

where τ_1, τ_2 are the lifetimes, and A_1, A_2 are the corresponding amplitudes. τ_1 is determined to be ~8.5 ns and τ_2 is ~10 ps. The longer one is related with **M4** and the shorter one should come from **M2**, because, as the hydrolysis evolves with time, only **M1**, **M2** are getting less – which is indeed the observation (see ESI Fig. S1†), since **M1** gives no obvious emission between 400–600 nm both in H_2O and DMSO (λ_{ex} = 320 nm), and **M2** is the recognized authentic emitter of the CL of AMPPD (fluorescence range from 390 nm to 590 nm in aqueous solvent, and from 400 nm to 560 nm in DMSO).[15] It should be reasonable to attribute the shorter lifetime to **M2**. Besides, it will not surprise us that, in the case of solution A, for the same reaction time the amplitude of the shorter lifetime component (**M2**) at 460 nm is always higher than that at 410 nm (see ESI Fig. S1†). Because the CL peak of **M2** is just

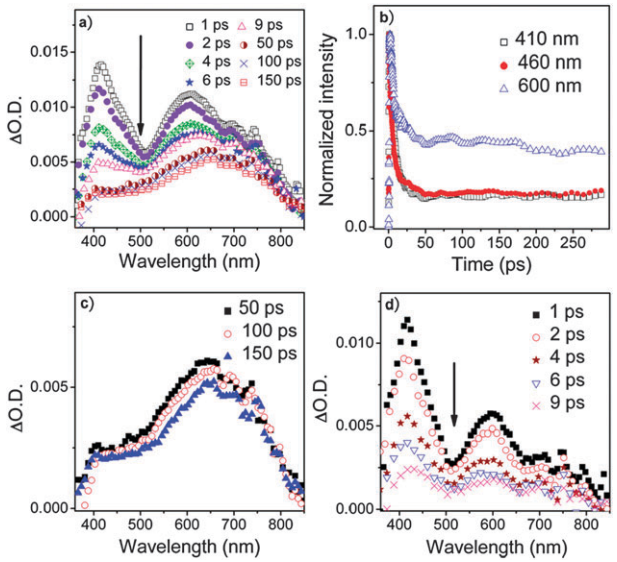


Fig. 6 (a) The transient absorption of the methyl-3-hydroxybenzoate (1 mM) in 0.08 M aqueous Na_2CO_3 solution (pH ~10). (b) The transient absorption change at three wavelengths: 410 nm, 460 nm, 600 nm. (c) Transient absorption of **M4**. (d) Transient absorption of **M2**. The transient absorption experiment was performed between 1 and 3 h after the solution had been prepared.

at ~460 nm and the PL of the longer lifetime component (**M4**) peaks at ~410 nm in aqueous solution, as is described above.

At last, it is worth noting that the lifetime of **M2** measured in our experiment is much shorter than the value reported previously (~10 ns),[14] and is also three orders of magnitude shorter than its lifetime in DMSO (τ_{DMSO} ~ 19 ns) (see ESI Fig. S2†). Because the fluorescence yield (Φ^{fl}) is proportional to the lifetime of the emissive state of the emitter,[23] the huge difference of the AMPPD chemiluminescent efficiency between the aqueous ($\Phi \sim 7.5 \pm 0.3 \times 10^{-6}$) and DMSO ($\Phi \sim 0.29$) solvents can be partly understood in relation with the dramatic changes of PL lifetime in various solvents. The shortening of the PL lifetimes of the emitter in protic solvent is related with the hydrogen-bonding effect, as was proposed in previous reports where the significant decrease of the CL yield of some dioxetanes (*e.g.* AMPPD) was observed in protic solvents (*e.g.* H_2O, D_2O, MeOH) *versus* aprotic solvents (*e.g.* DMSO, MeCN).[8,17,18,21]

To further investigate the dynamics of **M2** in aqueous solution, time-resolved transient absorption measurements were performed with 325 nm excitation, as shown in Fig. 6a. The transient dynamics can be well fitted with a bi-exponential function in the whole spectral range (*cf.* Fig. 6b). The shorter lifetime is determined to be ~8 ps, which is in agreement with the lifetime of **M2** obtained from the TCSPC measurements, and the longer lifetime is in the order of nanoseconds, typical of that of **M4**. Because the lifetimes of two components differ dramatically, the transient absorption spectra of the two components can be well separated: after 50 ps, the shorter lifetime component is attenuated close to zero, and thus, the transient absorption signals after 50 ps should be characteristic of **M4** only (Fig. 6c), whereas the transient absorption of **M2** dominates the change of the obtained transient spectrum within 10 ps. By subtracting the spectrum at 50 ps from the transient spectra as a background, the transient absorption signals of **M2** can be separated from Fig. 6a, as it is seen from Fig. 6d, the spectral profile is time independent, implying that it indeed originates from the same species. As far as **M4** is concerned the transient spectral profile demonstrates a slight time dependence in Fig. 6c, which should not surprise us since various physical and/or chemical processes will have to occur in this long-living electronic state, *e.g.* IVR (instantaneous velocity of reaction), vibrational cooling, *et al.*[26]

Conclusions

An important question in the deviation of the emission peak between PL of the authentic emitter and CL of AMPPD in protic solution has been reconsidered by this work, where the steady-state and time-resolved spectroscopic and ^{1}H NMR studies have been performed, against pH value of the solution on the methyl *m*-oxybenzoate anion – the authentic emitter of the CL of AMPPD. Our results proves that, when the authentic emitter in alkaline aqueous solutions (*e.g.* pH ~10 and ~14), the fluorescence around 412 nm is not induced by the hydrogen-bonding effect on the emitter, but from the hydrolysate of the authentic emitter – the 3-hydroxybenzoic acid dianion. Furthermore, the lifetime of the authentic emitter in aqueous solvent (pH ~10) is determined to be ~10 ps, which is much shorter than previously reported value, and is three orders of magnitude shorter than that in DMSO. This finding leads to the conclusion that the significant decrease of the CL yield of AMPPD in aqueous solvent is mainly caused by the shortening of the emissive state lifetime, and hydrogen-bonding is suggested to play a key role in the decrease of lifetime. These results shall shed light on designing more effective chemiluminescent systems.

Acknowledgements

This work was supported by NSFC of China (60771051, 60601014, 20603035, 60601015), and exchange program between CAS of China and KNAW of the Netherlands.

References

1 R. C. Allen and L. D. Loose, *Biochem. Biophys. Res. Commun.*, 1976, **69**, 245.
2 F. McCapra, *Q. Rev. Chem. Soc.*, 1966, **20**, 485.
3 A. L. Schaefer, B. L. Hanzelka, M. R. Parsek and E. P. Greenberg, *Methods Enzymol.*, 2000, **305**, 288.
4 R. G. Bulgakov, V. P. Kazakov and G. A. Tolstikov, *J. Organomet. Chem.*, 1990, **387**, 11.
5 D. Rieger, *Anal. Biochem.*, 1997, **246**, 67.
6 P. G. Gillespie and A. J. Hudspeth, *Proc. Natl. Acad. Sci. U. S. A.*, 1991, **88**, 2563.
7 R. Creton and L. F. Jaffe, *Biotechniques*, 2001, **31**, 1098.
8 M. Matsumoto, *J. Photochem. Photobiol., C*, 2004, **5**, 27.
9 F. McCapra, I. Beheshti, A. Burford, R. A. Hann and K. A. Zaklika, *J. Chem. Soc., Chem. Commun.*, 1977, **24**, 944.
10 F. McCapra, *J. Chem. Soc., Chem. Commun.*, 1977, **24**, 946.
11 W. Adam, D. V. Kazakov and V. P. Kazakov, *Chem. Rev.*, 2005, **105**, 3371.
12 W. Adam, I. Bronstein, A. V. Trofimov and R. F. Vasil'ev, *J. Am. Chem. Soc.*, 1999, **121**, 958.
13 W. Adam, M. Matsumoto and A. V. Trofimov, *J. Am. Chem. Soc.*, 2000, **122**, 8631.

14 W. Adam, I. Bronstein, B. Edwards, T. Engel, D. Reinhardt, F. W. Schneider, A. V. Trofimov and R. F. Vasil'ev, *J. Am. Chem. Soc*., 1996, **118**, 10400.
15 W. Adam, I. Bronstein and A. V. Trofimov, *J. Phys. Chem. A*, 1998, **102**, 5406.
16 W. Adam, M. Matsumoto and A. V. Trofimov, *J. Org. Chem*., 2000, **65**, 2078.
17 M. Matsumoto, T. Sakuma and N. Watanabe, *Tetrahedron Lett*., 2002, **43**, 8955.
18 N. Watanabe, Y. Matsumoto and M. Matsumoto, *Tetrahedron Lett*., 2005, **46**, 4871.
19 V. Wasselin-Trupin, G. Baldacchino, S. Bouffard, E. Balanzat, M. Gardes-Albert, Z. Abedinzadeh, D. Jore, S. Deycard and B. Hickel, *J. Phys. Chem. A*, 2000, **104**, 8709.
20 N. Chitose, J. A. Laverne and Y. Katsumura, *J. Phys. Chem. A*, 1998, **102**, 2087.
21 M. Matsumoto, Y. Mizoguchi, T. Motoyama and N. Watanabe, *Tetrahedron Lett*., 2001, **42**, 8869.
22 M. Matsumoto, M. Tanimura, T. Akimoto, N. Watanabe and H. K. Ijuin, *Tetrahedron Lett*., 2008, **49**, 4170.
23 T. Hirano, Y. Gomi, T. Takahashi, K. Kitahara, C. F. Qi, I. Mizoguchi, S. Kyushin and M. Ohashi, *Tetrahedron Lett*., 1992, **33**, 5771.
24 Y. L. Zhang, P. T. Jing, Q. H. Zeng, Y. J. Sun, H. P. Su, Y. A. Wang, X. G. Kong, J. L. Zhao and H. Zhang, *J. Phys. Chem. C*, 2009, **113**, 1886.
25 L. J. Tian, Y. J. Sun, Y. Yu, X. G. Kong and H. Zhang, *Chem. Phys. Lett*., 2008, **452**, 188.
26 M. Glasbeek and H. Zhang, *Chem. Rev*., 2004, **104**, 1929.

