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## COMMUNICATION

# A novel chemiluminescence from the reaction of singlet oxygen with $\beta$ -diketonates of europium(III), neodymium(III) and ytterbium(III)

Cite this: DOI: 10.1039/x0xx00000x

Received 00th July 2014,  
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DOI: 10.1039/x0xx00000x

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**Decomposition of 1,4-dimethylnaphthalene endoperoxide, the source of singlet oxygen, in the presence of  $\beta$ -diketonates of europium (III), neodymium (III) and ytterbium (III) is accompanied by bright chemiluminescence (CL) in visible and near infra-red spectral region due to characteristic emission from the lanthanides at  $\lambda_{\text{max}} = 615$  and  $710$  nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  transitions of  $\text{Eu}^{3+}$ ),  $900$  nm ( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$  transition of  $\text{Nd}^{3+}$ ) and  $1000$  nm ( $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$  transition of  $\text{Yb}^{3+}$ ). Singlet oxygen is the key intermediate responsible for the observed CL which is presumably generated by the reaction of  $^1\text{O}_2$  with ligands of the complexes. The herein discovered CL phenomenon paves the way towards development of lanthanide-based CL probe for  $^1\text{O}_2$ .**

Singlet oxygen ( $^1\text{O}_2$ ) has wide applications in organic synthesis and large environmental and biomedical significance<sup>1</sup>. Important role of  $^1\text{O}_2$  in light-emitting chemical reactions (chemiluminescence, CL) is also well documented<sup>2</sup>. Singlet-oxygen based CL systems can be classified into two types. The first one includes reactions where  $^1\text{O}_2$  acts as a direct emitter. In particular, many peroxide reactions (the major chemical source of singlet oxygen) produce characteristic infra-red CL (IR-CL) of  $^1\text{O}_2$  or weak emission in visible spectral region (Vis-CL) derived from its dimol ( $^1\text{O}_2$ )<sub>2</sub>. In the other type of CL transformations, excited oxygen mediates light emission through energy-transfer processes or via oxidation of reactive substrates.<sup>2</sup> Investigation of CL arising during oxidative reactions of  $^1\text{O}_2$  could provide valuable information on mechanisms of chemiexcitation in chemical and biological systems. In addition, these light-generating systems can be potentially used as chemiluminescent probes for singlet oxygen<sup>3</sup>.

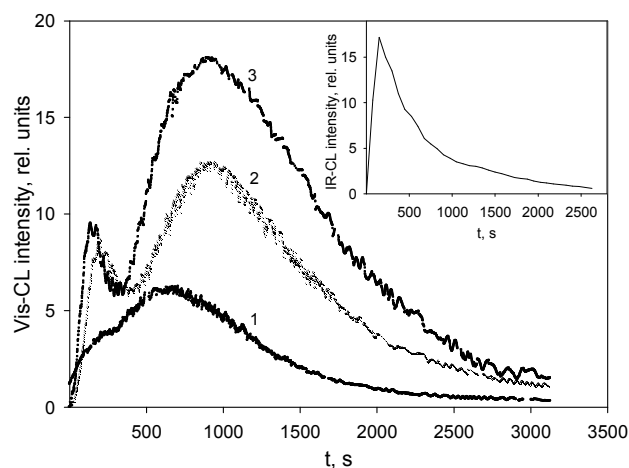
In this context, we report here on novel bright CL from the reaction of singlet oxygen with luminescent  $\beta$ -diketonate complexes of  $\text{Nd}^{3+}$ ,  $\text{Yb}^{3+}$  and  $\text{Eu}^{3+}$ , where  $\beta$ -diketonates are 6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedione (Hfod), 2-thenoyltrifluoroacetone (Htta), and acetylacetone (Hacac). The rare-earth  $\beta$ -diketonates are known to have numerous applications in chemistry and biochemistry including the use in chemiluminescent

studies as light emission enhancers.<sup>4a</sup> To the best of our knowledge CL in the reaction of  $^1\text{O}_2$  with this class of lanthanide chelates is unprecedented. Apart from fundamental scientific significance, our CL findings may serve as a prototype for development of lanthanides-based CL probe for analytical detection of  $^1\text{O}_2$ , since lanthanides compounds possess rather high luminescence quantum yield and enable easy spectral discrimination of their emission bands which span both the visible and near IR ranges.<sup>4</sup>

Endoperoxide of 1,4-dimethylnaphthalene (DMNE) was used as source of singlet oxygen (the yield of  $^1\text{O}_2$  is 76%)<sup>5</sup>. Thermal decay of DMNE in chloroform at  $55^\circ\text{C}$  is accompanied by weak CL in visible spectral region (Vis-CL). When decomposition of the endoperoxide was carried out in the presence of  $\text{Eu}(\text{fod})_3$ , the maximum CL intensity ( $I_{\text{max}}$ ) was increased by a factor of 50 whereas the time-integrated CL signal ( $\text{INT}_{\text{Vis-CL}}$ ) has raised by more than two orders of magnitude. Even higher values of  $\text{INT}_{\text{Vis-CL}}$  and  $I_{\text{max}}$  were observed for the system DMNE/ $\text{Eu}(\text{fod})_3$  in deuterated chloroform and in carbon tetrachloride (Figure 1).

Analysis of the luminescence emission by means of cut-off light filters revealed that the CL released in the system DMNE/ $\text{Eu}(\text{fod})_3$  lies in the spectral region  $\lambda > 570$  nm with maximum between 600 and 620 nm, which corresponds to the photoluminescence of  $\text{Eu}(\text{fod})_3$  (Fig. S-1, ESI). However, intensity of light emission in  $\text{CHCl}_3$  was not enough to record direct CL spectrum. To increase CL signal we have carried decomposition of the endoperoxide in carbon tetrachloride at higher temperature. Under these conditions, we were able to record CL spectrum which is shown in Figure 2: characteristic maxima of europium luminescence at  $\lambda = 615$  ( $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition) and  $710$  nm ( $^5\text{D}_0 \rightarrow ^7\text{F}_4$  transition)<sup>4a-c,6</sup> unambiguously demonstrates that the excited  $\text{Eu}^{3+}$  is indeed the CL emitter.

Similarly, near IR-CL of neodymium (III) and ytterbium (III) was observed when decomposition of  $3 \cdot 10^{-2}$  M of DMNE was carried out in the presence of  $1 \cdot 10^{-2}$  M of  $\text{Nd}(\text{tta})_3 \cdot 2\text{H}_2\text{O}$  ( $55^\circ\text{C}$ ,  $\text{CHCl}_3$ ) and  $\text{Yb}(\text{tta})_3 \cdot 2\text{H}_2\text{O}$  or  $\text{Yb}(\text{fod})_3$  ( $67^\circ\text{C}$ ,  $\text{CCl}_4$ ): characteristic luminescent transitions<sup>4c,d</sup> of  $\text{Nd}^{3+}$  ( $^4\text{F}_{3/2} \rightarrow ^4\text{I}_{9/2}$ ) and  $\text{Yb}^{3+}$  ( $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ ) were measured through interference filters at  $\lambda = 900$  and  $1000$  nm, respectively. Additionally, spectrum of CL was recorded for the system DMNE/ $\text{Yb}(\text{tta})_3 \cdot 2\text{H}_2\text{O}$  (Figure 2). Finding of light emission from neodymium and ytterbium is particularly noteworthy because



**Figure 1.** Time profile of the Vis-CL decay for the decomposition of DMNE in the presence of  $\text{Eu}(\text{fod})_3$ : 1- in  $\text{CHCl}_3$ , 2- in  $\text{CDCl}_3$ , and 3- in  $\text{CCl}_4$ . Conditions:  $[\text{DMNE}] = 3 \cdot 10^{-2} \text{ M}$ ,  $[\text{Eu}(\text{fod})_3] = 1 \cdot 10^{-2} \text{ M}$ ,  $55^\circ \text{C}$ . The insert shows the kinetics of the IR-CL decay for the singlet oxygen formed by thermal decomposition of  $3 \cdot 10^{-2} \text{ M}$  of DMNE in  $\text{CDCl}_3$  at  $55^\circ \text{C}$ .

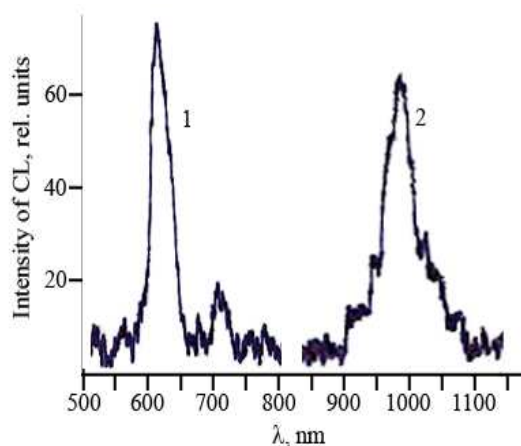
only a few systems have been reported to produce IR-CL of these metals.<sup>7</sup> This work provides yet another rare event (and just second one for  $\beta$ -diketonates of  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$ ) of such an important case of lanthanides chemiluminescent reactions.

Remarkably, similar results have been obtained not only in solution but also on the sorbent surface. In particular, characteristic emission of lanthanides was recorded during decomposition of DMNE adsorbed on a silica gel in the presence of  $\beta$ -diketonates of three-valent neodymium, ytterbium and europium. Experimental details of this solid phase light-emitting reactions will be reported in separate paper.

It is known that decomposition of DMNE is a simple monomolecular reaction which results in the formation of molecular oxygen and parent 1,4-dimethylnaphthalene.<sup>5</sup> This process is accompanied by IR-CL of  $^1\text{O}_2$ <sup>8</sup> and light emission at  $\lambda_{\text{max}} = 633$  and  $703 \text{ nm}$  which belongs to singlet-oxygen dimol.<sup>9</sup> Earlier we have revealed characteristic emission bands of the dimol during decomposition of DMNE in  $\text{CHCl}_3$  and  $\text{CCl}_4$ .<sup>9c</sup> Moreover, careful spectral analysis of the Vis-CL observed in carbon tetrachloride did not disclose any emission bands other than those of  $(^1\text{O}_2)_2$ .<sup>9c</sup> Therefore, it is reasonable to propose that it is  $^1\text{O}_2$  that mediates CL of the lanthanide complexes. To verify this hypothesis, we have studied CL in the system DMNE/lanthanide chelate in the presence of efficient singlet-oxygen quencher 1,4-diazabicyclo[2.2.2]octane (DABCO).<sup>10</sup>

As expected, CL of lanthanides was considerably diminished by DABCO. For example, values of  $I_{\text{max}}$  and  $\text{INT}_{\text{Vis-CL}}$  recorded for the system DMNE/ $\text{Eu}(\text{fod})_3$  in  $\text{CHCl}_3$  were found to be 9 and 17 times lower in the presence of  $1 \cdot 10^{-2} \text{ M}$  of DABCO than in the absence of this diazocompound ( $55^\circ \text{C}$ ,  $[\text{DMNE}] = 3 \cdot 10^{-2} \text{ M}$ ,  $[\text{Eu}(\text{fod})_3] = 1 \cdot 10^{-2} \text{ M}$ ). The quenching effect was even more pronounced in deuterated chloroform where 19- and 56- fold decrease in the maximum CL intensity and time-integrated CL signal was observed in the presence of DABCO. Likewise, near IR-CL of neodymium (III) at  $\lambda = 900 \text{ nm}$  and ytterbium(III) at  $\lambda = 1000 \text{ nm}$  recorded during decomposition of  $3 \cdot 10^{-2} \text{ M}$  of the endoperoxide in the presence of the lanthanide  $\beta$ -diketonates was completely suppressed by  $1 \cdot 10^{-2} \text{ M}$  of DABCO ( $[\text{Yb}(\text{fod})_3]$  or  $[\text{Yb}(\text{tta})_3 \cdot 2\text{H}_2\text{O}] = 1 \cdot 10^{-2} \text{ M}$ ,  $\text{CCl}_4$ ,  $67^\circ \text{C}$ ;  $[\text{Nd}(\text{tta})_3 \cdot 2\text{H}_2\text{O}] = 1 \cdot 10^{-2} \text{ M}$ ,  $\text{CHCl}_3$ ,  $55^\circ \text{C}$ ).

Such a pronounced effect of DABCO could be explained by



**Figure 2.** Chemiluminescence spectra (uncorrected) taken during decomposition of DMNE: 1, in the presence of  $\text{Eu}(\text{fod})_3$  in  $\text{CCl}_4$ ; 2, in the presence of  $\text{Yb}(\text{tta})_3 \cdot 2\text{H}_2\text{O}$  in  $\text{CCl}_4:\text{CH}_3\text{CN}$  4:1 ( $75^\circ \text{C}$ ,  $[\text{DMNE}] = 3 \cdot 10^{-2} \text{ M}$ ,  $[\text{Eu}(\text{fod})_3] = [\text{Yb}(\text{tta})_3 \cdot 2\text{H}_2\text{O}] = 1 \cdot 10^{-2} \text{ M}$ ).

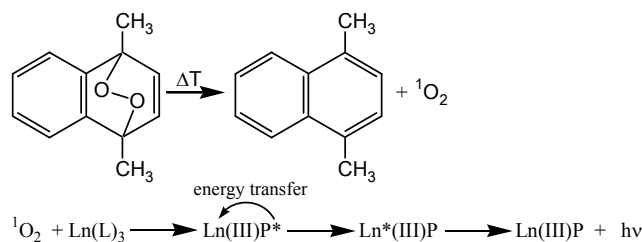
influence of the latter on lanthanides luminescence quantum yield. However, in separate experiments we have shown that the tertiary amine does not extinguish photoluminescence of the  $\text{Eu}(\text{fod})_3$ . In contrast, two-fold increase in photoluminescence intensity of the europium was observed in the presence of DABCO, probably due to complexing of the latter with  $\text{Eu}^{3+}$  (Fig. S-2, ESI).

Unexpected results have been obtained with another efficient singlet-oxygen quencher - tetramethylethylene (TME).<sup>11</sup> It was revealed that TME increases intensity of the light emission evolved during decomposition of DMNE in the presence of  $\text{Eu}(\text{fod})_3$ . These results, however, are only on the first sight surprising. Indeed, singlet oxygen is known to readily react with TME with the formation of hydroperoxide.<sup>12</sup> Therefore it is likely that the latter additionally promotes light emission from the europium chelate, which leads to the overall increase in CL intensity despite the fact that concentration of the other CL mediator,  $^1\text{O}_2$ , is diminished by TME.

If singlet oxygen triggers CL of lanthanides, then quenching of characteristic IR-CL of  $^1\text{O}_2$  at  $\lambda = 1270 \text{ nm}$  should be observed. We have found that this is indeed the case. The ratio of time-integrated intensity of singlet-oxygen IR-CL observed during decomposition of  $3 \cdot 10^{-2} \text{ M}$  of DMNE at  $55^\circ \text{C}$  in the absence and in the presence of  $1 \cdot 10^{-2} \text{ M}$  of  $\text{Eu}(\text{fod})_3$  was found to be equal to 16 and 87, in  $\text{CHCl}_3$  and  $\text{CDCl}_3$  respectively.

Thus, quenching of CL of lanthanides by DABCO as well as extinguishing of IR-CL of singlet-oxygen by  $\text{Eu}(\text{fod})_3$  consistently demonstrate that  $^1\text{O}_2$  is a key intermediate responsible for the light emission recorded during decomposition of DMNE in the presence of  $\beta$ -diketonates of  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$ . The question now arises as to the mode of lanthanides chemiexcitation by  $^1\text{O}_2$ . The following common mechanisms for CL of three-valent lanthanide  $\beta$ -diketonates have been considered so far in literature. First one includes inter- or intramolecular transfer of energy from excited species to the  $\beta$ -diketonate ligand followed by energy transfer to the lanthanide ion with subsequent emission from the latter.<sup>4a,7a,13a</sup> The other one consists in intracomplex energy transfer directly to the 4f levels of the metal.<sup>4a,7a,13</sup> None of these processes are possible for  $^1\text{O}_2$  since its  $^1\Delta_g$  excited state lies only  $22,5 \text{ kcal/mol}$  ( $7867 \text{ cm}^{-1}$ ) above  $^3\text{O}_2$ , which is not enough to populate even triplet excited levels of the  $\beta$ -diketonate ligands in  $\text{Ln}(\text{fod})_3$  ( $22\,500 \text{ cm}^{-1}$ ) and

$\text{Ln}(\text{tta})_3 \cdot 2\text{H}_2\text{O}$  ( $20500\text{ cm}^{-1}$ )<sup>6,7a,b,14</sup> as well as resonance levels of  $\text{Eu}^{3+}$  ( $^5\text{D}_0$ ,  $17\,250\text{ cm}^{-1}$ )<sup>4b</sup>,  $\text{Nd}^{3+}$  ( $^4\text{F}_{3/2}$ ,  $11\,500\text{ cm}^{-1}$ )<sup>4d,e</sup> and  $\text{Yb}^{3+}$  ( $^2\text{F}_{5/2}$ ,  $10\,200\text{ cm}^{-1}$ )<sup>4d,e</sup>. In principal, singlet-oxygen dimol species has sufficient energy<sup>2,15</sup> to populate excited levels of the lanthanides, provided decomposition of DMNE occurs inside of their coordination sphere. In this case the lanthanide  $\beta$ -diketonates would act as an inert CL enhancers and Vis-CL decay would follow simple first-order kinetics. However, complex character of time profile of the Vis-CL attenuation for the system DMNE/ $\text{Eu}(\text{fod})_3$  (Figure 1) testifies against this mechanism of lanthanide chemiexcitation. Taking into account high reactivity of  $^1\text{O}_2$  we propose that the light emission is generated as a result of oxidation of the  $\beta$ -diketonate ligands by singlet oxygen so that lanthanides get excited due to an energy released during this oxidation process (Scheme 1). The broad maximum on kinetic curve in Figure 1 is obviously caused by accumulation of intermediate (presumably peroxide) and its subsequent exothermic decomposition followed by energy transfer to the metal ion. Notably, the similar mechanism was earlier postulated to explain light emission observed during oxidation of some europium  $\beta$ -diketonates with powerful oxidation agent – dimethyldioxirane.<sup>16</sup>



$\text{Ln}(\text{L})_3$ :  $\text{Eu}(\text{fod})_3$ ,  $\text{Yb}(\text{fod})_3$ ,  $\text{Yb}(\text{tta})_3$ ,  $\text{Nd}(\text{tta})_3$ ; P: product of the ligand oxidation by  $^1\text{O}_2$

**Scheme 1.** Proposed mechanism of lanthanides chemiexcitation during decomposition of DMNE in the presence of  $\beta$ -diketonates of  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$  and  $\text{Yb}^{3+}$ .

Additional support for the proposed nontrivial mode of lanthanide chemiexcitation comes from photoluminescence measurements made after diminution of CL in the system  $\text{Eu}(\text{fod})_3/\text{DMNE}$  which disclosed one order of magnitude decrease in intensity of europium photoluminescence. This indicates drastic changes in the europium coordination sphere, presumably associated with oxidation of the ligands by  $^1\text{O}_2$ . Moreover, a new photoluminescence signal of the reaction product at  $\lambda < 600\text{ nm}$  was recorded after excitation of the reaction mixture (Fig. S-3, ESI). Furthermore, oxidation of lanthanide  $\beta$ -diketonates during CL reaction was conclusively confirmed by NMR-spectroscopy.<sup>#</sup>

**In conclusion**, we have found that reaction of singlet oxygen with  $\beta$ -diketonates of  $\text{Eu}^{3+}$ ,  $\text{Nd}^{3+}$ , and  $\text{Yb}^{3+}$  is accompanied by the characteristic light emission of the lanthanide ions in visible and near IR region. Discovered chemiluminescent reactions represent a nontrivial mode of lanthanide chemiexcitation and constitutes rare event of IR-CL of neodymium and ytterbium. It can be anticipated that these light-generating systems will find application for analytical detection of  $^1\text{O}_2$  by CL method.<sup>§</sup>

This work was supported by the Russian Foundation for Basic Research (grant № 14-03-31986). We thank Dr. O.V. Zakiryanova for assistance in NMR measurements which were performed by means of Bruker Avance-III 500 MHz spectrometer (“Chemistry” Collective Use Center of the Institute of Organic Chemistry of USC of the RAS).

## Notes and references

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<sup>†</sup>Electronic Supplementary Information (ESI) available. See DOI: 10.1039/c000000x/

<sup>#</sup>NMR analysis of the crude reaction mixture taken after the CL reaction [ $\text{Nd}(\text{TTA})_3 \cdot 2\text{H}_2\text{O}/\text{DMNE}$  system] revealed at least three main products which were preliminary assigned (data not shown) to the following structures: triketone, carboxylic acid, and ketoaldehyde. We propose that this oxidation process may proceed through dioxetane and/or hydroperoxide intermediates. Precise mechanism of this intriguing case of lanthanide and singlet-oxygen CL awaits further experimentation.

<sup>§</sup>It is pertinent to quote here an excellent review of Binnemans who has made prediction that “wealth of original research will be conducted in the near future” in the field of CL of rare-earth  $\beta$ -diketonate complexes.<sup>4a</sup> We hope that the discovered CL reactions of singlet oxygen will stimulate efforts in this perspective direction of research.

- (a) P.R. Ogilby, *Chem. Soc. Rev.*, 2010, **39**, 3181; (b) J. Cadet, J.-L. Ravanat, G. R. Martinez, M. H. G. Medeiros and P. Di Mascio, *Photochem. Photobiol.*, 2006, **82**, 1219; (c) E. L. Clennan and A. Pace, *Tetrahedron*, 2005, **61**, 6665; (d) A.A. Krasnovsky Jr. *J. Photochem. Photobiol. A: Chem.*, 2008, **196**, 210; (e) L. F. Agnez-Lima, J.T.A. Melo, A. E. Silva, A. H. S. Oliveira, A. R. S. Timoteo, K. M. Lima-Bessa, G. R. Martinez, M. H.G. Medeiros, P. Di Mascio, R. S. Galhardo and C. F.M. Menck, *Mutat. Res.*, 2012, **751**, 15.
- W. Adam, D. V. Kazakov and V. P. Kazakov, *Chem. Rev.* 2005, **105**, 3371.
- (a) H. Wu, Q. Song, G. Ran, X. Lu and B. Xu, *Trend. Anal. Chem.*, 2011, **30**, 133; (b) L.A. MacManus-Spencer, D.E. Latch, K.M. Kroncke and K. McNeill, *Anal. Chem.*, 2005, **77**, 1200; (c) X. Li, G. Zhang, H. Ma, D. Zhang, J. Li and D. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 11543.
- (a) K. Binnemans, Rare-Earth Beta-Diketonates. In *Handbook on the Physics and Chemistry of Rare Earths*; K. A. Gschneidner, Jr., J.-C. G. Bünzli, V. K. Pecharsky, Eds., Elsevier, Amsterdam, 2005, Volume 35, Chapter 225, p 107; (b) K. Binnemans, *Chem. Rev.* 2009, **109**, 4283; (c) J.-C. G. Bünzli, *Chem. Rev.* 2010, **110**, 2729; (d) J.-C. G. Bünzli and S. V. Eliseeva, *J. Rare Earth.*, 2010, **28**, 824; (e) S. V. Eliseeva and J. -C. G. Bünzli, *Chem. Soc. Rev.*, 2010, **39**, 189.
- N.J. Turro, M.-F. Chow and J. Rigaudy, *J. Am. Chem. Soc.*, 1981, **103**, 7218.
- L.S. Villata, E. Wolcan, M.R. Félix and A.L. Capparelli, *J. Phys. Chem. A.*, 1999, **103**, 5661.
- (a) A.I. Voloshin, N.M. Shavaleev and V.P. Kazakov, *J. Photochem. Photobiol. A: Chem.*, 2000, **131**, 61; (b) A.I. Voloshin, N.M. Shavaleev and V.P. Kazakov, *J. Lumin.*, 2000, **91**, 49; (c) A.I. Voloshin, E.V. Zharinova and V.P. Kazakov, *Russ. Chem. Bull.*, 1998, **47**, 2050; (d) A.C. Thomas and A.B. Ellis, *J. Chem. Soc., Chem. Commun.*, 1984, 1270; (e) R. G. Bulgakov, S. P. Kuleshov, Z. S. Kinzyabaeva, A. A. Fagin, I. R. Masalimov and M. N. Bochkarev, *Russ. Chem. Bull.*, 2007, **56**, 1956.
- (a) P.-T. Chou and H. Frei, *Chem. Phys. Lett.*, 1985, **122**, 87; (b) T. Wilson, A.U. Khan and M.M. Mehrotra, *Photochem. Photobiol.*, 1986, **43**, 661.

9. (a) P. Di Mascio, E. J. H. Bechara and J. C. Rubim, *Appl. Spectrosc.* 1992, **46**, 236; (b) Y. Fu, A. A. Krasnovsky, Jr. and C. S. Foote, *J. Am. Chem. Soc.* 1993, **115**, 10282; (c) D.V. Kazakov, V. P. Kazakov, G. Ya. Maistrenko, D. V. Mal'zev and R. Schmidt, *J. Phys. Chem. A.*, 2007, **111**, 4267.
10. F. Wilkinson, W. P. Helman and A. B. Ross, *J. Phys. Chem. Ref. Data* 1995, **24**, 663.
11. R. Schmidt and C. Tanielian, *J. Phys. Chem. A* 2000, **104**, 3177.
12. (a) T. Takabatake, T. Miyazawa, M. Hasegawa and C. S. Foote, *Tetrahedron Lett.*, 2001, **42**, 987; (b) P. Di Mascio, L. H. Catalani and E. J. H. Bechara, *Free Rad. Biol. Med.* 1992, **12**, 471.
13. (a) S. Lis, M. Elbanowski, B. Mąkowska and Z. Hnatejko, *J. Photochem. Photobiol. A: Chem.*, 2002, **150**, 233; (b) V.P. Kazakov, A.I. Voloshin and N.M. Shavaleev, *J. Photochem. Photobiol. A: Chem.*, 1998, **119**, 177; (c) V.P. Kazakov, A.I. Voloshin and S.S. Ostakhov, *Kinet. Catal.*, 1999, **40**, 180.
14. W. R. Dawson, J. L. Kropp and M. W. Windsor, *J. Chem. Phys.*, 1966, **45**, 2410.
15. (a) A. U. Khan and M. Kasha, *J. Am. Chem. Soc.* 1966, **88**, 1574; (b) A.U. Khan and M. Kasha, *J. Am. Chem. Soc.* 1970, **92**, 3293.
16. D.V. Kazakov, G.Ya. Maistrenko, O.A. Kotchneva, R.R. Latypova and V.P. Kazakov, *Mendeleev Commun.*, 2001, 188.