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Quenching of electronically excited Ln^{3+*} ions by C_{60} fullerene

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Quenching of electronically excited states of Ln^{3+*} ions generated upon photoexcitation of toluene solutions of $Ln(acac)_3 \cdot H_2O$ (Ln = Tb, Eu) complexes by C_{60} fullerene at 293 K was detected and investigated. The dependences of quenching efficiency on C_{60} concentration obtained from data on the decrease in the photoluminescence intensity and Ln^{3+*} lifetimes obey the Stern—Volmer law. Quenching is due to inductive—resonant energy transfer from Ln^{3+*} to C_{60} fullerene. The bimolecular rate constants for quenching, the overlap integrals of the Ln^{3+*} photoluminescence spectra with the C_{60} absorption spectra, and the critical energy transfer distances were determined. No sensitized luminescence of C_{60} in the system studied was detected.

Key words: fullerene C_{60}, quencher, photoluminescence of lanthanides.

Processes occurring under photoirradiation of solutions containing fullerene C_{60} have been intensively studied in connection with prospects for the design of novel C_{60}-based photoactive systems for conversion and utilization of solar energy,[1] photodynamic therapy,[2,3] and laser shutters.[4] Irradiation of such systems is accompanied by excitation of C_{60} or other components followed by energy and/or electron transfer between them. In this connection investigations on the efficiency of C_{60} fullerene as acceptor of energy of different types of electronically excited states are topical. Often, photoactive systems include such components as solutions containing C_{60} fullerene and metal compounds, *e.g.*, Fc—ZnP (Fc is ferrocene and P is porphyrin),[1] ZnP,[5] ZnP—H_2P,[6] ZnO,[7] and $[Ru(bpy)_3]^{2+}$ [8] that act as energy donors (D*). Quenching of the donors is attained through formation of complexes between D* and C_{60} followed by electron transfer

$$^1D^* + C_{60} \longrightarrow D^{\cdot+} + C_{60}{}^{\cdot-}.$$

No quenching of metal complexes by fullerene by the mechanism of "pure" energy transfer (with no transfer of an electron and formation of a complex of C_{60} with D) was reported as yet. As to electronically excited states of the metal complexes that luminesce due to transitions between electron energy levels of the metal ion, information on their deactivation by C_{60} fullerene is also unavailable. Here, classical examples are provided by the electronically excited states of lanthanide ions Ln^{3+*} that emit rather bright luminescence over a broad spectral region and can act as both energy donors[9—11] and acceptors.[12] In this work we first detected and studied quenching of Ln^{3+*} ions (Ln = Tb, Eu) generated under photoirradiation of toluene solutions of $Ln(acac)_3 \cdot H_2O$ complexes by fullerene C_{60}.

Experimental

Compounds used in this study were commercially available C_{60} (99.9% purity) and hexahydrates $LnCl_3 \cdot 6H_2O$ (Ln = Tb, Eu) of chemically pure grade. Toluene was purified following a known procedure.[13] Complexes $Ln(acac)_3 \cdot H_2O$ were synthesized following a published procedure;[14] Ln^{3+} and water were determined complexonometrically and according to Fischer,[15] respectively. Argon was purified following a known procedure.[16] Stock solutions of C_{60} (10^{-3} mol L^{-1}) were prepared in the dark by dissolving a weighed sample of fullerite in toluene in argon atmosphere in order to preclude the photochemical oxidation of C_{60}. Solutions of the lanthanide complexes were prepared by dissolving $Ln(acac)_3 \cdot H_2O$ crystals in toluene in argon atmosphere. In order to study quenching of Ln^{3+*}, different amounts of the C_{60} solution were added to the solutions of the lanthanide complexes until a volume of 3 mL ($[Ln(acac)_3 \cdot H_2O] = 3.5 \cdot 10^{-4}$ mol L^{-1}). The content of C_{60} in the solutions before and after excitation of photoluminescence was monitored by HPLC, as reported earlier.[16] Absorption spectra were measured on a Specord M-40 specrophotometer and the lifetimes of Tb^{3+*} and Eu^{3+*} ions were measured using an installation including a LGI-21 pulsed nitrogen laser (λ_{ex} = 337 nm). Photoluminescence spectra with a resolution of 2 nm were measured with an original spectrofluorimeter based on MDR-23 monochromator. Numerical values of the overlap integrals ($\int_{ov}$) of the Ln^{3+*}

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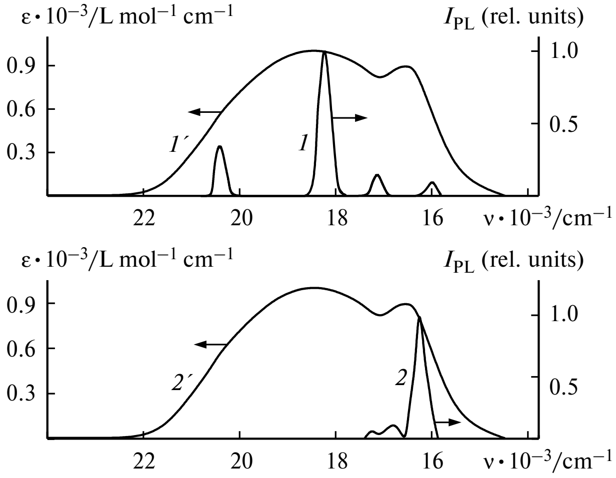

Fig. 1. Normalized photoluminescence (PL) spectra of solutions: $Tb(acac)_3 \cdot H_2O$ (*1*) and $Eu(acac)_3 \cdot H_2O$ (*2*) and the absorption spectra of fullerene C_{60} solutions (*1´*, *2´*) in the visible spectral region (toluene, 293 K, λ_{ex} = 313 (Tb^{3+}) and 325 nm (Eu^{3+})).

photoluminescence spectra with the C_{60} absorption spectrum were obtained using the Origin 7.0 and Maple 7.0 programs that were preliminarily tested on the published[10] photoluminescence spectra of other lanthanide complexes and absorption spectra of several dyes. Differences between our results and the $\int_{ov}$ values reported in Ref. 10 were at most 2%.

Results and Discussion

Positions of maxima in the photoluminescence spectra of the toluene solutions of the Tb and Eu complexes (Fig. 1) match those reported earlier.[7,8] The maxima are due to radiative transitions between 4f-energy levels of these ions (Tb^{3+*}, λ_{max}/cm^{-1}: 20400 ($^5D_4$—$^7F_6$), 18350 ($^5D_4$—$^7F_5$), 17240 ($^5D_4$—$^7F_4$), and 16000 ($^5D_4$—$^7F_3$); Eu^{3+*}, λ_{max}/cm^{-1}: 16300 ($^5D_0$—$^7F_2$), 16780 ($^5D_0$—$^7F_1$), and 17240 ($^5D_0$—$^7F_0$)). The effect of C_{60} fullerene on the photoluminescence intensity of the Ln^{3+*} ions was estimated from the changes in the photoluminescence intensity at two spectral maxima, at 545 nm for Tb^{3+*} and at 613 nm for Eu^{3+*}. The absorption spectrum of C_{60} plotted in the ε—ν coordinates is shown in Fig. 1. The ε values were calculated using the absorption spectrum of C_{60} measured in this work and the relation $A = \varepsilon l c$, where A is absorbance, c is the C_{60} concentration (10^{-5} mol L^{-1}), and l is the cell thickness (1 cm). The photoluminescence spectra of both lanthanide complexes are overlapped with the absorption spectrum of C_{60}.

The addition of C_{60} to the toluene solutions of $Tb(acac)_3 \cdot H_2O$ and $Eu(acac)_3 \cdot H_2O$ is followed by a decrease in the Ln^{3+*} photoluminescence intensity and lifetimes, but positions of the spectral maxima are retained even at low C_{60} concentrations. For instance, the photoluminescence intensity of the Tb^{3+} and Eu^{3+} ions is halved at a C_{60} concentration of $1.1 \cdot 10^{-5}$ mol L^{-1} for the former and $1.9 \cdot 10^{-5}$ mol L^{-1} for the latter. Since C_{60} solutions are photosensitive,[17] a decrease in the Ln^{3+} photoluminescence intensity could be due to the photochemical reactions of C_{60} with Ln^{3+} ions. However, HPLC monitoring revealed no reduction of the C_{60} concentration in the solution on the time scale of photoluminescence detection.

Quenching of Ln^{3+*} by C_{60} fullerene could also be due to trivial reasons,[18] namely, internal filter effect owing to absorption of the excitation light by C_{60}, and reabsorption of the Ln^{3+*} luminescence by C_{60} fullerene. These effects are favored by fact that the C_{60} absorption spans a broad spectral region (200—665 nm) including the spectral range of the excitation light and the region of lanthanide photoluminescence. Specific adjustment of the photoluminescence excitation and detection geometry, which ensured luminescence of thin solution layers (~1.0 mm thick), allowed the internal filter effect to be almost excluded. In the presence of C_{60} we observed an insignificant reduction of the intensity of the excitation light and the corresponding spectral band was detected along with the Ln^{3+*} photoluminescence maxima. Reabsorption of Ln^{3+*} photoluminescence by fullerene estimated by comparing the Tb^{3+*} and Eu^{3+*} photoluminescence spectra and the transmission spectrum of C_{60} (not shown) at the maximum concentration of C_{60} ($6 \cdot 10^{-5}$ mol L^{-1}) was at most 5%.

A characteristic feature of C_{60} fullerene is quenching of various types of electronically excited states by the electron transfer mechanism.[1,5–8] At the same time quenching of Ln^{3+*} ions by such strong electron acceptors as hydrocarbon radical cations[11] involves no electron transfer. In order to estimate the probability of quenching of the Ln^{3+*} photoluminescence by electron transfer in the reaction

$$Ln^{3+*} + C_{60} \longrightarrow Ln^{4+} + C_{60}{}^{\bullet-},$$

we calculated the Gibbs free energy of electron transfer (ΔG) from the Weller equation[19]

$$\Delta G\,(\mathrm{eV}) = E(Ln^{4+}/Ln^{3+}) - E(C_{60}/C_{60}{}^{\bullet-}) - ke^2/\varepsilon r - E^*(Ln^{3+}), \quad (1)$$

where $E(Ln^{4+}/Ln^{3+})$ and $E(C_{60}/C_{60}{}^{\bullet-})$ are respectively the redox potentials of the electron donor and electron acceptor, $E^*(Ln^{3+})$ is the excited-state energy of the donor, e is the charge of electron, ε is the dielectric constant of the solvent (0.59 for toluene, see Ref. 20), and r is the distance between the Ln^{4+} ion and $C_{60}{}^{\bullet-}$ in the radical ion pair formed (0.5 nm, see Ref. 21). The ΔG values for europium and terbium obtained by substituting the corresponding values into Eq. (1) show that electron transfer from the Ln^{3+*} ion is an endothermic process

$$\Delta G(Eu^{3+}) = E(Eu^{4+}/Eu^{3+})^{22} - E(C_{60}/C_{60}^{\bullet -})^{23} - ke^2/\varepsilon r - E^*(Eu^{3+}) =$$
$$= 6.4 - (-0.83) - 1.2 - 2.02 = 4.0 \text{ eV } (392 \text{ kJ mol}^{-1}),$$

$$\Delta G(Tb^{3+}) = E(Tb^{4+}/Tb^{3+})^{22} - E(C_{60}/C_{60}^{\bullet -})^{23} - ke^2/\varepsilon r - E^*(Tb^{3+}) =$$
$$= 3.12 - (-0.83) - 1.2 - 2.53 = 0.22 \text{ eV } (21 \text{ kJ mol}^{-1}),$$

i.e., quenching of Ln^{3+*} ions by fullerene as a result of electron transfer can be excluded.

The aforesaid suggests that the most probable mechanism of Ln^{3+*} quenching is energy transfer to fullerene.

The photoluminescence intensity and excited-state lifetime measurements for the Ln^{3+*} ions showed that the efficiency of quenching of Tb^{3+*} and Eu^{3+*} ions increases in proportion to the C_{60} concentration (Fig. 2) in accord with the Stern—Volmer law

$$I_0/I - 1 = K^1_{St-V}[C_{60}] = k^1_{bim}\tau_0[C_{60}], \quad (2)$$

$$\tau_0/\tau - 1 = K^2_{St-V}[C_{60}] = k^2_{bim}\tau_0[C_{60}], \quad (3)$$

where I_0 (τ_0) and I (τ) are the Ln^{3+*} photoluminescence intensities (lifetimes) in the absence and in the presence of quencher, respectively; $[C_{60}]$ is the quencher concentration; K_{St-V} is the Stern—Volmer constant, and k_{bim} is the bimolecular rate constant for quenching.

The k_{bim} values (Table 1) calculated using Eqs (2) and (3) and the data of measurements of quenching efficiency from a decrease in the photoluminescence intensity (I_0/I) and from reduction of the decay constant (τ_0/τ) of Ln^{3+*} photoluminescence coincide within the limits of experimental error (10%). This indicates[24] a dynamic character of quenching of Ln^{3+*} ions by C_{60} fullerene. The absence of complex formation between C_{60} and $Ln(acac)_3 \cdot H_2O$ in the ground and excited states is also substantiated by the fact that the absorption spectrum of C_{60} and the photoluminescence spectra of Tb^{3+*} and Eu^{3+*} remain unchanged when all compounds are simultaneously present in solutions.

Analysis of the available data[9—12] showed that the best quencher of luminescence of Ln^{3+*} ions is Bengal rose dye ($k^3_{bim} = 5.9 \cdot 10^8$ L mol^{-1} s^{-1} for quenching of Tb^{3+*}).[10] Based on comparison of the k^3_{bim} value and the $k^{1,2}_{bim}$ values obtained in our experiments for quenching of Tb^{3+*} by fullerene, C_{60} can be characterized as efficient quencher of Ln^{3+*} ions. For quenching to occur, the energy of the

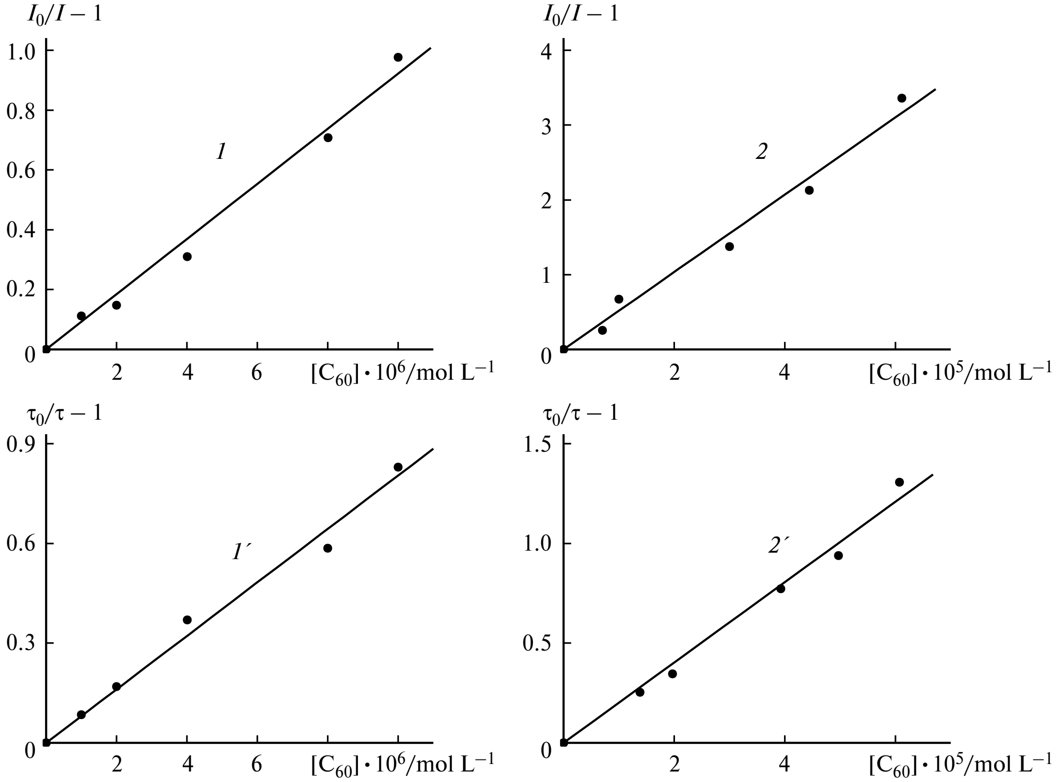

Fig. 2. Photoluminescence intensity (*1*, *2*) and lifetime (*1´*, *2´*) of Ln^{3+*} ions plotted *vs.* C_{60} concentration in toluene at 293 K in the Stern—Volmer coordinates: $Tb(acac)_3 \cdot H_2O$ solution ($3.5 \cdot 10^{-4}$ mol L^{-1}), λ_{ex} = 313 nm (*1*, *1´*) and $Eu(acac)_3 \cdot H_2O$ solution ($3.5 \cdot 10^{-4}$ mol L^{-1}), λ_{ex} = 325 nm (*2*, *2´*).

Table 1. Characteristics of quenching of $Ln(acac)_3 \cdot H_2O$ (Ln = Tb, Eu) complexes by C_{60} fullerene in toluene (293 K)

Ln	$[C_{60}]$ /mol L^{-1}	τ_0 /μs	$k^1_{bim} \cdot 10^{-8}$	$k^2_{bim} \cdot 10^{-8}$	$\int_{ov} \cdot 10^{14}$	$k_{bim}/\int_{ov} \cdot 10^{-22}$	R_0 /Å	$k^1_{theor} \cdot 10^{-8}$	$k^2_{theor} \cdot 10^{-8}$
			L mol^{-1} s^{-1}					L mol^{-1} s^{-1}	
Tb	10^{-6}—10^{-5}	769	1.20±0.12	1.01±0.10	0.67	1.8	22	0.68	0.65
Eu	$7 \cdot 10^{-6}$—$6 \cdot 10^{-5}$	234	2.18±0.22	2.05±0.21	0.72	3.0	21	1.62	1.62

radiative level of the energy donor should be higher than that of the energy acceptor. The energies of the radiative levels of Ln^{3+*} ions estimated from positions of maxima in the photoluminescence spectra shown in Fig. 1 are 2.53 eV (Tb^{3+*}) and 2.02 eV (Eu^{3+*}). Different values of $^1C_{60}{}^*$ energy are available in the literature, namely, 2.0 [25] and 2.2 [26] eV. Comparison of these data shows that the Tb^{3+*} (not Eu^{3+*}) energy is much higher than the $^1C_{60}{}^*$ energy and that energy transfer from Tb^{3+*} can occur at both values of the $^1C_{60}{}^*$ energy. At the same time, energy transfer from Eu^{3+*} is only possible if the $^1C_{60}{}^*$ energy is at most 2.0 eV. Since the experimental results do indicate energy transfer from Eu^{3+*}, the value of 2.0 eV for the energy of the radiative level of $^1C_{60}{}^*$ seems to be more correct.

The overlap integrals of the Ln^{3+*} photoluminescence spectra with the C_{60} absorption spectrum (see Fig. 1) were calculatd using the expression[9]

$$\int_{ov} = \frac{\int_0^\infty F_D(\nu)\varepsilon_A(\nu)\nu^{-4}d\nu}{\int_0^\infty F_D(\nu)d\nu}, \qquad (4)$$

where $F_D(\nu)$ is the quantum intensity distribution in the photoluminescence spectrum of the donor and ε_A is the molar decimal extinction coefficient of the acceptor.

Energy transfer from Ln^{3+*} to C_{60} can proceed by the exchange-resonant or inductive-resonant mechanism. According to published data,[9—11] proportionality between the $k^{1,2}{}_{bim}$ and $\int_{ov}$ values obtained for quenching of Tb^{3+*} and Eu^{3+*} (see above) and similar (according to criteria formulated in Ref. 27) $k_{bim}/\int_{ov}$ ratios (see Table 1) should be treated as substantiation of the inductive-resonant mechanism. This is also confirmed by the absence of complex formation between Ln^{3+*} and C_{60} (see above). Table 1 also lists the critical energy transfer distances (R_0) calculated from a known equation[10]

$$R^6_{0,\text{theor}} = 5.86 \cdot 10^{-25} \frac{q_0(Ln^{3+*})}{n^4} \int_{ov}, \qquad (5)$$

where $q_0(Ln^{3+*})$ is the quantum yield of photoluminescence of the energy donor in the absence of quencher and n is the refractive index of toluene. The $q_0(Tb^{3+*})$ and $q_0(Eu^{3+*})$ values were taken from Ref. 28 and the n value was taken from Ref. 13.

We also calculated the $k^1{}_{theor}$ and $k^2{}_{theor}$ values using the Galanin—Franck (6) and Tunitsky—Bagdasaryan (7) equations (see Ref. 10).

$$k^1_{\text{theor}} = 0.0625 \frac{\ln 10 q_0(Ln^{3+*})}{n^4 \pi^4 \tau_0(Ln^{3+*})} \int_{ov} \Big/ [R(Ln^{3+*}) + R(C_{60})]^3, \qquad (6)$$

where $\tau_0(Ln^{3+*})$ is the excited-state lifetime of the energy donor in the absence of quencher; $R(Ln^{3+*})$ and $R(C_{60})$ are the molecular radii of the energy donor and energy acceptor (molecular radii of $Ln(acac)_3 \cdot H_2O$ (~4.8 Å) were calculated using the relation[10] $4/3\pi R^3 = 0.74V_M/N$ assuming spherical symmetry of the species and close packing of spheres of the same radius and with allowance for voids; the molar volumes (V_M) were determined using the Le Ba relationship;[29] the C_{60} radius (3.5 Å) was taken from Ref. 30).

$$k^2_{\text{theor}} = \frac{4}{3} \cdot 10^{-3} \pi N \frac{R_0^6}{[R(Ln^{3+*}) + R(C_{60})]^3} \frac{1}{\tau_0(Ln^{3+*})}, \qquad (7)$$

where N is the Avogadro constant and R_0 is the critical energy transfer distance (see Table 1).

Comparison of the $k^{1,2}{}_{bim}$ values (see Table 1) with the theoretical values showed good agreement between theory and experiment. The $k^{1,2}{}_{bim}$ and $k^1{}_{theor} = k^2{}_{theor}$ values differ by at most a factor of 1.4 for Eu^{3+} and by a factor of 1.8 for Tb^{3+}. According to Ref. 10, quenching can be treated with certainty as proceeding by the inductive-resonant mechanism of energy transfer (no exchange-resonant transfer) even at fourfold difference between k_{bim} and k_{theor}.

Based on the results obtained and on the published data,[9—11] processes occurring under photoirradiation of solutions containing C_{60} and lanthanide complexes can be described by the following scheme.

$$Ln^{3+} + h\nu_1 \longrightarrow Ln^{3+*} \qquad (8)$$

$$Ln^{3+*} \longrightarrow Ln^{3+} + h\nu_2 \qquad (9)$$

$$Ln^{3+*} + C_{60} \longrightarrow Ln^{3+} + {}^1C_{60}{}^* \qquad (10)$$

$${}^1C_{60}{}^* \longrightarrow {}^1C_{60} + h\nu_3 \qquad (11)$$

$${}^1C_{60}{}^* \longrightarrow {}^3C_{60}{}^* \qquad (12)$$

$${}^3C_{60}{}^* \longrightarrow {}^1C_{60} + h\nu_4 \qquad (13)$$

For brevity, here we show only Ln^{3+} ions and present a simplified description of the Ln^{3+*} excitation. But although the process described by Eq. (8) does occur,[18] initial absorption of light by the ligand followed by energy transfer from the triplet-excited ligand to the Ln^{3+} ion is more efficient. Radiative deactivation of Ln^{3+*} (Eq. (9)) occurs at such C_{60} concentrations that are insufficient for complete quenching of Ln^{3+*} by fullerene, as indicated by retention of the patterns of the photoluminescence spectra of the lanthanide complexes under conditions of partial quenching by C_{60}. Energy transfer from Ln^{3+*} causes fullerene to go to the singlet-excited state $^1C_{60}^*$ (Eq. (10)). This is not accompanied by electron transfer from Ln^{3+*} to C_{60}. We failed to detect fluorescence of C_{60} fullerene (Eq. (11)) because of low quantum yield $(2 \cdot 10^{-4})$[31] and, apparently, insufficiently low sensitivity of the installation for photoluminescence measurements. It should be noted that detection of room-temperature fluorescence of $^1C_{60}^*$ presents some difficulties (pioneering attempts failed[32]); therefore, the first reliable detection of room-temperature photoluminescence of C_{60} in toluene was treated as considerable advance.[32] The yield of the intersystem crossing of $^1C_{60}^*$ to the triplet state (Eq. (12)) approaches unity.[33] At the same time the detection of phosphorescence (Eq. (13)) is even more complicated task. Indeed, room-temperature emission of the $^3C_{60}^*$ state generated under photoexcitation in C_{60} solutions was not observed so far; it was detected[34] only in frozen C_{60} solutions (77 K) in the presence of heavy-atom compounds (EtI). Additionally, we detected room-temperature luminescence of $^3C_{60}^*$ upon generation of $^3C_{60}^*$ in a chemiluminescent reaction of sodium fullerides with a Ce^{4+} complex.[35] Sensitized luminescence of C_{60} fullerene was also not detected by the researchers who studied quenching of photoluminescence of other compounds by fullerene.[6,36] To date, sensitized luminescence of C_{60}^* was detected in a single study[37] and upon energy transfer from the energy donor D* bound in a strong complex with C_{60}.

Summing up, in this work we studied quenching of photoluminescence of lanthanide ions by C_{60} fullerene. We established that fullerene can quench electronically excited states by the energy transfer mechanism without electron transfer and formation of complexes between C_{60} and energy donors.

References

1. M. Fujitsuka, O. Ito, H. Imahori, K. Yamada, H. Yamada, and Y. Sakata, *Chem. Lett.*, 1999, 721.
2. M. A. Yurovskaya and I. V. Trushkov, *Izv. Akad. Nauk, Ser. Khim.*, 2002, 343 [*Russ. Chem. Bull., Int. Ed.*, 2002, **51**, 367].
3. T. N. Yamakoshi, T. Yagami, S. Sueyoshi, and N. Miyata, *J. Org. Chem.*, 1996, **61**, 7236.
4. A. V. Eletskii and B. M. Smirnov, *Usp. Fiz. Nauk*, 1995, **165**, 977 [*Phys.-Usp.*, 1995, **165** (Engl. Transl.)].
5. H. Imahori, K. Hagiwara, T. Akiyama, S. Taniguchi, T. Okada, and Y. Sakata, *Chem. Lett.*, 1995, 265.
6. K. Tamaki, H. Imahori, Y. Nishimura, I. Yamazaki, and Y. Sakata, *Chem. Commun.*, 1999, 625.
7. P. V. Kamat, *J. Am. Chem. Soc.*, 1991, **113**, 9705.
8. A. Polese, S. Mondini, A. Bianco, C. Toniolo, G. Scorrano, D. Guldi, and M. Maggini, *J. Am. Chem. Soc.*, 1999, **121**, 3446.
9. V. L. Ermolaev and T. A. Shakhverdov, *Opt. Spektrosk.*, 1971, **30**, 648 [*Opt. Spectrosc.*, 1971, **30** (Engl. Transl.)].
10. T. A. Shakhverdov and V. L. Ermolaev, *Opt. Spektrosk.*, 1972, **33**, 941 [*Opt. Spectrosc.*, 1972, **33** (Engl. Transl.)].
11. T. A. Shakhverdov, *Opt. Spektrosk.*, 1973, **35**, 168 [*Opt. Spectrosc.*, 1973, **35** (Engl. Transl.)].
12. V. L. Ermolaev, B. M. Antipenko, E. B. Sveshnikova, V. S. Tachin, and T. A. Shakhverdov, *Molekulyarnaya fotonika* [*Molecular Photonics*], Nauka, Leningrad, 1970, 44 (in Russian).
13. A. J. Gordon and R. A. Ford, *The Chemist´s Companion. A Handbook of Practical Data, Techniques, and References*, Wiley, New York—London—Sydney—Toronto, 1973.
14. N. Filipescu, W. F. Sager, and F. A. Serafin, *J. Phys. Chem.*, 1964, **68**, 3324.
15. V. N. Alekseev, *Kurs kachestvennogo khimicheskogo polumikroanaliza* [*A Course of Qualitative Chemical Semimicroanalysis*], Khimiya, Moscow, 1973, 584 pp. (in Russian).
16. R. G. Bulgakov, A. S. Musavirova, A. M. Abdrakhmanov, E. Yu. Nevyadovskii, S. L. Khursan, and S. D. Razumovskii, *Zh. Prikl. Spektrosk.*, 2002, **69**, 192 [*J. Appl. Spectr.*, 2002, **69** (Engl. Transl.)].
17. V. I. Sokolov and I. V. Stankevich, *Usp. Khim.*, 1993, **62**, 455 [*Russ. Chem. Rev.*, 1993, **62** (Engl. Transl.)].
18. C. A. Parker, *Photoluminescence of Solutions*, Elsevier, Amsterdam—London—New York, 1968.
19. A. Weller, *J. Chem. Phys.*, 1967, **46**, 4984.
20. *Khimicheskaya Entsiklopediya* [*Chemical Encyclopedia*], Ed. N. S. Zefirov, Bol´shaya Rossiiskaya Entsiklopediya, Moscow, 1995, **4**, 605 (in Russian).
21. E. I. Kapinus, *Fotonika molekulyarnykh kompleksov* [*Photonics of Molecular Complexes*], Naukova dumka, Kiev, 1988, 256 pp. (in Russian).
22. A. K. Pikaev, V. P. Shilov, and V. I. Spitsyn, *Radioliz Vodnykh Rastvorov Lantanidov i Aktinidov* [*Radiolysis of Aqueous Solutions of Lanthanides and Actinides*], Nauka, Moscow, 1983, 43 (in Russian).
23. D. Dubois, K. M. Kadish, S. Flanagan, and L. S. Wilson, *J. Am. Chem. Soc.*, 1991, **113**, 7773.
24. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*, Plenum Press, New York—London, 1983.
25. J. W. Arbogast, A. P. Darmanyan, C. S. Foote, Y. R. François, M. M. Alvarez, S. J. Anz, and R. L. Whetten, *J. Phys. Chem.*, 1991, **95**, 11.
26. J. P. Hare, H. W. Kroto, and R. Taylor, *Chem. Phys. Lett.*, 1991, **177**, 394.
27. D. L. Dexter, *J. Chem. Phys.*, 1953, **21**, 836.
28. N. M. Shavaleev, Ph.D. (Chem.) Thesis, Institute of Organic Chemistry, Ufa Scientific Center, Russian Academy of Sciences, Ufa, 2000, 115 pp. (in Russian).

29. *Spravochnik khimika* [*A Chemist´s Handbook*], 2nd ed., Ed. B. P. Nikol´skiy, Khimiya, Moscow, 1966, **5**, 658 (in Russian).
30. R. Z. Bakhtizin, T. Hashizume, X.-D. Wang, and T. Sakyrai, *Usp. Fiz. Nauk*, 1997, **167**, 289 [*Phys.-Usp.*, 1997, **167** (Engl. Transl.)].
31. D. Kim and M. Lee, *J. Am. Chem. Soc.*, 1992, **114**, 4429.
32. J. W. Arbogast and C. S. Foote, *J. Am. Chem. Soc.*, 1991, **113**, 8886.
33. J. Catalan and J. Elguro, *J. Am. Chem. Soc.*, 1993, **115**, 9249.
34. Y. Zeng, L. Biczok, and H. Linschitz, *J. Phys. Chem.*, 1992, **96**, 5237.
35. R. G. Bulgakov, R. G. Akhmadieva, A. S. Musavirova, and M. T. Golikova, *Izv. Akad. Nauk, Ser. Khim.*, 2001, 702 [*Russ. Chem. Bull., Int. Ed.*, 2001, **50**, 731].
36. R. N. Nurmukhametov, L. V. Volkova, Yu. I. Kiryukhin, L. V. Romashov, and I. E. Kardash, *Dokl. Akad. Nauk*, 1993, **331**, 323 [*Dokl. Chem.*, 1993 (Engl. Transl.)].
37. T. Yamashiro, Y. Aso, T. Otsubo, H. Tang, Y. Yarima, and K. Yamashita, *Chem. Lett.*, 1999, 443.

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