Fullerene C_{60} as a superefficient quencher of singlet exited states of polycyclic aromatic hydrocarbons

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Quenching of fluorescence of polycyclic aromatic hydrocarbons (PAH), namely, naphthalene, anthracene, 9,10-diphenylanthracene, 9,10-dibromoanthracene by C_{60} fullerene in ethylbenzene at 293 K was found and investigated. The phenomenon is characterized by abnormally high values of bimolecular rate constants for quenching ($k_{bim} = (0.18—6.78) \cdot 10^{12}$ L mol^{-1} s^{-1}) determined from the Stern—Volmer dependence of the PAH fluorescence intensity on the C_{60} concentration and occurs through the inductive-resonance (dominant channel) and exchange-resonance (minor channel) energy transfer from ^{1}PAH* to C_{60}. The overlap integrals of the PAH fluorescence spectra with the C_{60} absorption spectrum and the critical energy transfer distances were calculated.

Key words: C_{60} fullerene, quencher, naphthalene, anthracene, 9,10-diphenylanthracene, 9,10-dibromoanthracene, fluorescence.

Research on the deactivation of electronically excited states (EES) of various classes of compounds by C_{60} fullerene is of great importance in connection with the design of novel C_{60}-based materials promising for solar energy storage, photodynamic therapy, optical (optical switches), and other applications.[1—4] Deactivation through electron transfer from the EES of various types of donors (D*) to C_{60} involving production of short-lived species (radical cation $D^{\bullet +}$ and radical anion $C_{60}^{\bullet -}$) detected from short-lived absorption spectra has been better studied.[1—4] The deactivation of the EES of other compounds by C_{60} fullerene as a result of pure physical energy transfer has been much less studied. Meanwhile, the spectral characteristics of C_{60} fullerene suggest its ability to serve a universal quencher of EES of different chemical nature, which deactivates these states by the energy transfer mechanism. Indeed, the absorption spectrum of C_{60} spans the range from 200 to 680 nm and thus overlaps with the fluorescence spectra of the majority of luminescent compounds and metal ions. Additionally, the singlet and triplet EES of C_{60} fullerene lie below the emitting energy levels of these compounds on the energy scale. The results of our preliminary communication[5] substantiate the conclusion that C_{60} can act as universal acceptor of the energy of EES. The sole example of such a deactivation reported so far is concerned with quenching of anthracene fluorescence by fullerene without measuring quantitative parameters and identification of the type (inductive-resonance or exchange-resonance) of quenching mechanism.[6]

The aim of this work was to study the ability of fullerene C_{60} to deactivate the EES through energy transfer taking the quenching of fluorescence of polycyclic aromatic hydrocarbons (PAH) in ethylbenzene as an example, to determine quantitative characteristics of the process, and to establish its mechanism.

Experimental

Experiments were carried out with commercially available fullerite C_{60} (synthesized at the G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences, Nizhny Novgorod). The purity of the material (99.9%) was checked by UV and IR spectroscopies and by HPLC. The PAH set included naphthalene, 9,10-diphenylanthracene, 9,10-dibromoanthracene ("chemically pure" grade) and anthracene ("scintillation" grade). Ethylbenzene[7] and argon[8] were purified following known procedures. Stock solutions of C_{60} ($(1.0—6.4) \cdot 10^{-4}$ mol L^{-1}) and PAH ($(2.8—5.0) \cdot 10^{-4}$ mol L^{-1}) were prepared by dissolving crystalline samples in ethylbenzene in the dark under argon. In the fluorescence quenching studies, solutions of C_{60} in ethylbenzene were added to the PAH solutions and the decrease in the intensity of the fluorescence maxima of naphthalene, anthracene, 9,10-diphenylanthracene and 9,10-dibromoanthracene at 30960, 24735, 23070, and 22745 cm^{-1}, respectively, was measured at 293 K.

The fluorescence of the solutions was measured in 1-cm quartz cells by detecting the thin-layer (~1.0 mm) fluorescence of the solution in order to reduce the internal filter effect to the highest possible extent; the effect is due to absorption of excitation light and fluorescence by C_{60}. To allow for absorption of excitation light, the corresponding band was detected along

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with the fluorescence maxima. The internal filter effect for naphthalene, anthracene, 9,10-diphenylanthracene, and 9,10-dibromoanthracene was at most 14.3, 13.3, 13.6, and 12.6% at $[C_{60}]_{max} = 3.8 \cdot 10^{-5}$, $1.0 \cdot 10^{-4}$, $3.2 \cdot 10^{-4}$, and $1.8 \cdot 10^{-4}$ mol L^{-1}, respectively. These data were used for correction and subsequent determination of the true intensity of PAH fluorescence

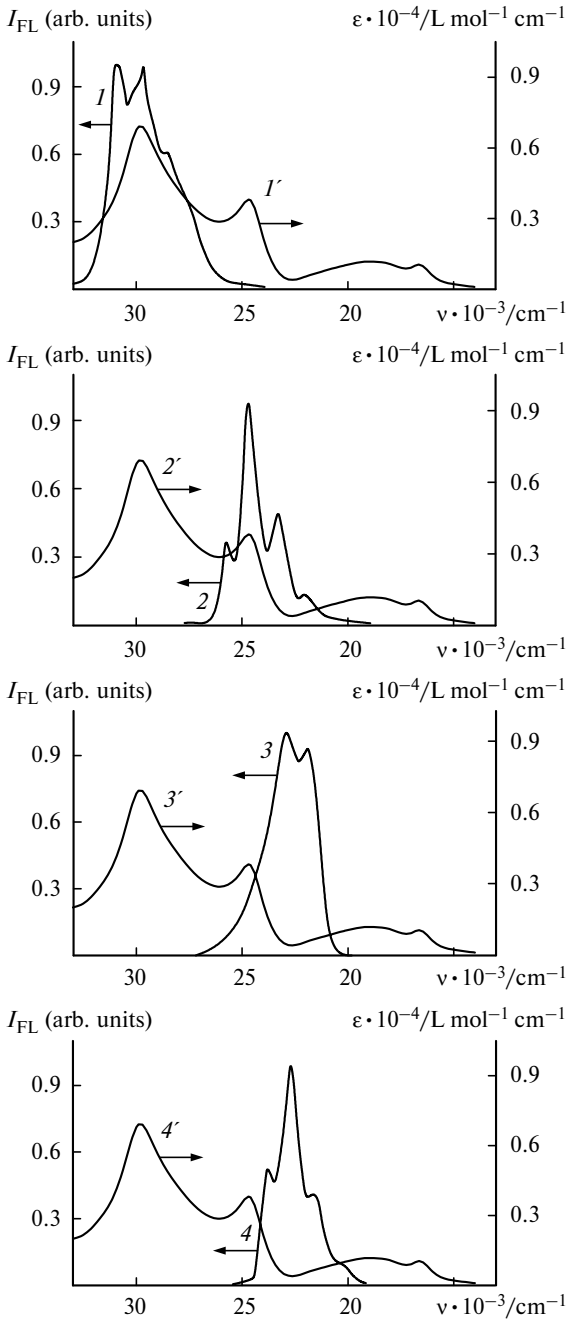

Fig. 1. Normalized fluorescence spectra of naphthalene (*1*), anthracene (*2*), 9,10-diphenylanthracene (*3*), and 9,10-dibromoanthracene (*4*) solutions and absorption spectra (*1′—4′* respectively) of these solutions in the presence of C_{60} in ethylbenzene (293 K) in the UV and visible spectral regions; λ_{exc} = 295, 388, 366, and 348 nm, respectively.

by the expression $I_x^{real} = I_x + (I_0^{exc} - I_x^{exc})$, where I_x is the observed fluorescence intensity and I_0^{exc} and I_x^{exc} are the excitation line intensities in the absence and in the presence of the quencher. The overlap integrals of the PAH fluorescence spectra with the C_{60} absorption spectrum were calculated using the Origin 7.0 and Maple 7.0 programs preliminarily tested with the known[9] fluorescence spectra and absorption spectra of other energy donor—acceptor pairs. The overlap integrals calculated in this work and those reported earlier[9] differed by at most 2%.

The HPLC procedure was reported earlier.[8] The absorption spectra of the PAH and C_{60} solutions were measured on a Specord M-40 spectrophotometer (UV and visible spectral regions) and the absorption spectrum of fullerite was measured on a Specord IR-75 IR spectrophotometer (IR spectral region). Fluorescence spectra with a 2 nm resolution were recorded on an original spectrofluorimeter based on an MDR-23 monochromator and FEU-100 photomultiplier.

Results and Discussion

The fluorescence spectra of the PAH solutions in ethylbenzene (Fig. 1) match those measured in other solvents.[10—13] The PAH fluorescence intensity decreases in the presence of C_{60}. In the course of fluorescence quenching measurements the C_{60} fullerene concentration in the solution remained unchanged, as indicated by constant intensity of the C_{60} peak in the HPLC chromatogram and by the C_{60} maxima in the absorption spectrum in ethylbenzene (λ_{max} = 335, 406, 541, 601 nm). This means that the decrease in the PAH fluorescence intensity is not a result of a known[14] photochemical reaction between C_{60} and PAH. The decrease in the fluorescence intensity due to the internal filter effect was also excluded, because we recorded thin-layer fluorescence of the solutions. Additionally, the decrease in the fluorescence intensity can not be attributed to possible reabsorption caused by absorption of the PAH fluorescence by fullerene because the quenching efficiency I_0/I (I_0 and I are the PAH fluorescence intensities in the absence and in the presence of quencher) changed by at most 3.4 (naphthalene), 4.0 (anthracene and 9,10-diphenylanthracene), and 5.2% (9,10-dibromoanthracene) even upon a more than tenfold dilution of the PAH and C_{60} solutions.

Thus, the decrease in the PAH fluorescence intensity is governed by the quenching of singlet-excited states ^{1}PAH* by fullerene through electron transfer (this is typical of C_{60})[1,15—18] or energy transfer. The Gibbs free energies of electron transfer were calculated using the expression[19,20]

$$\Delta G \text{ (kcal mol}^{-1}) = 23.06[E(\text{PAH}^{\bullet+}/\text{PAH}) - E(C_{60}/C_{60}^{\bullet-}) - ke^2/(\varepsilon r)] - E^*(^1\text{PAH}^*), \quad (1)$$

where $E(\text{PAH}^{\bullet+}/\text{PAH})$ and $E(C_{60}/C_{60}^{\bullet-})$ are the redox potentials of the donor and acceptor, respectively,[21—23] e is the electron charge, k is the Boltzmann constant, r is the average distance between PAH and C_{60} in the radical

ion pair (0.5 nm),[24] $\varepsilon = 2.403$ is the dielectric constant of ethylbenzene at 293 K, and $E^*(^1\text{PAH}^*)$ is the excited-state energy of the donor.[25]

The ΔG values for naphthalene, anthracene, 9,10-diphenylanthracene, and 9,10-dibromoanthracene are 359.0, 159.4, 176.4, and 317.4 kcal mol^{-1}, respectively. This excludes the quenching of ^{1}PAH* through electron transfer to C_{60}, because this process is endothermic.

Energy transfer can proceed by the exchange-resonance mechanism as a result of the orbital overlap between the energy donor and energy acceptor or by the inductive-resonance mechanism (long-range energy transfer). The case in point is the dynamic quenching of PAH fluorescence by fullerene, because no complexation between C_{60} and PAH occurs in the ground state and in the EES, as indicated by the unchanged absorption spectrum of C_{60} and the PAH fluorescence spectra when both components are present in solution. The dynamic character of quenching also follows from the linear dependence of the efficiency, I_0/I, of the PAH fluorescence quenching on the C_{60} concentration in the coordinates of the Stern—Volmer equation (Fig. 2):

$$I_0/I - 1 = K_{S-F}[C_{60}] = k_{bim}\tau_0[C_{60}], \quad (2)$$

where $[C_{60}]$ is the concentration of quencher, K_{S-F} is the Stern—Volmer constant, k_{bim} is the bimolecular rate constant for quenching, and τ_0 is the excited-state lifetime of the energy donor in the absence of quencher.

The K_{S-F} values were determined from the slopes of the Stern-Volmer plots and then used for calculating the k_{bim} constants (Table 1) using Eq. (2). The high k_{bim} values obtained, $(0.181—6.78)\cdot10^{12}$ L mol^{-1} s^{-1}, were quite unexpected. Indeed, they are much higher than the k_{bim} constants for other donor—acceptor pairs[26] and the rate constants for diffusion-controlled processes (*cf.* $k_{dif} = 1.0\cdot10^{10}$ L mol^{-1} s^{-1} at $T = 293$ K for a related solvent, benzene[27]). If a rate constant for fluorescence quenching is two- to tenfold higher than the diffusion rate constant, the former is usually treated as very high constant. In our case the k_{bim}/k_{dif} ratios are much higher,

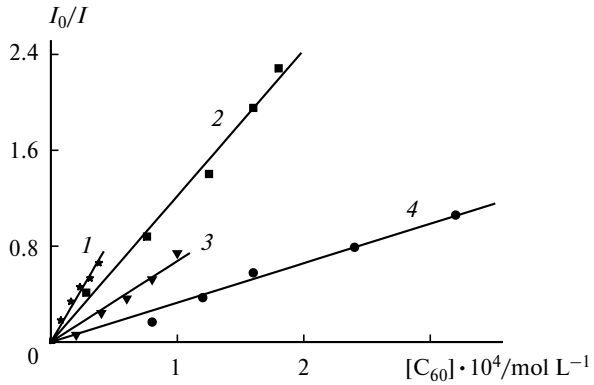

Fig. 2. Stern—Volmer plots of the PAH fluorescence intensity *vs.* C_{60} concentration for naphthalene ($2.4\cdot10^{-4}$ mol L^{-1}), λ_{exc} = 295 nm (*1*), 9,10-dibromoanthracene ($1.4\cdot10^{-4}$ mol L^{-1}), λ_{exc} = 348 nm (*2*), anthracene ($2.5\cdot10^{-4}$ mol L^{-1}), λ_{exc} = 388 nm (*3*), and 9,10-diphenylanthracene ($1.0\cdot10^{-4}$ mol L^{-1}), λ_{exc} = 366 nm (*4*); ethylbenzene, 293 K.

being about 18, 23, 40, and 660 for naphthalene, anthracene, 9,10-diphenylanthracene, and 9,10-dibromoanthracene respectively. Because the C_{60} molecule (d = 7.1 Å)[28] is much larger than other molecules, we calculated the k_{dif} constants for various pairs C_{60}—PAH using the Smoluchowski equation

$$k_{dif} = 4\pi RDN_A/1000 = \\ = 4\pi N_A\cdot10^{-3}\cdot(R_A + R_D)(D_A + D_D), \quad (3)$$

where $R = 8.3144$ L mol^{-1} K^{-1} is the universal gas constant and R_A, D_A, R_D, D_D are the molecular radii and the diffusion coefficients of the energy acceptor (C_{60}) and energy donor (PAH), respectively. The coefficients D_A and D_D were determined by the Stokes—Einstein equation

$$D = kT/(6\pi\eta R_M), \quad (4)$$

where R_M is the molecular radius (in Å) and η is the solvent viscosity (0.637 cP for ethylbenzene).

Table 1. Characteristics of PAH fluorescence quenching by C_{60} fullerene in ethylbenzene at 293 K

PAH	[PAH]	[C_{60}]	k_{bim} /L mol^{-1} s^{-1}	τ_0 /ns	$\int_{Ov}\cdot10^{14}$	R_0 /Å	$k_{bim}/\int_{Ov}\cdot10^{-25}$	$k_{bim}/\int_{Ov}{}'^*$	$\Sigma\zeta_i^2$
	mol L^{-1}								
Naphthalene	$2.4\cdot10^{-4}$	$(0.8—3.8)\cdot10^{-5}$	$(1.81\pm0.06)\cdot10^{11}$	100	0.50	22.3	3.6	1.0	$1.3\cdot10^3$
Anthracene	$2.5\cdot10^{-4}$	$(2—10)\cdot10^{-5}$	$(2.25\pm0.30)\cdot10^{11}$	30	0.29	22.0	7.8	0.6	$1.8\cdot10^4$
9,10-Diphenylanthracene	$2.5\cdot10^{-4}$	$(0.4—3.2)\cdot10^{-4}$	$(4.10\pm0.23)\cdot10^{11}$	7.3	0.15	22.9	27.3	1.3	$3.4\cdot10^4$
9,10-Dibromoanthracene	$1.4\cdot10^{-4}$	$(0.28—1.8)\cdot10^{-4}$	$(6.78\pm0.15)\cdot10^{12}$	1.8	0.09	14.7	753	0.6	$1.2\cdot10^7$

* The ratio for naphthalene was taken to be 1.0.

The R_M values for PAH were calculated using the expression $(4/3)\pi R_M^3 = 0.74 V_M/N$ (with inclusion of voids assuming[9] a close packing of spherical molecules of the same radius). The molar volumes (V_M) were determined according to Le Ba:[29] R_M = 3.5, 3.9, 5.0, and 4.2 Å for naphthalene, anthracene, 9,10-diphenylanthracene, and 9,10-dibromoanthracene, respectively. The value $R_M(C_{60})$ = 3.5 Å was taken from Ref. 28.

We found that all the PAHs under study are characterized by almost the same k_{dif} values equal to $(1.00\pm0.03)\cdot10^{10}$ L mol^{-1} s^{-1}.

Usually, the root-mean-square displacement $(\Delta x^2)^{0.5}$ of a molecule over the time interval τ_0 in the course of diffusion-controlled fluorescence quenching differs from the critical energy transfer distance R_0 by several orders of magnitude. In contrast to this the $(\Delta x^2)^{0.5}$ values (139, 43, 33, and 17 Å for naphthalene, anthracene, 9,10-diphenylanthracene. and 9,10-dibromoanthracene, respectively) calculated using the Einstein equation $\Delta x^2 = 2D\tau_0$ (D is the diffusion coefficient expressed in cm^2 s^{-1}) are much smaller than the R_0 values obtained from expression (5) and listed in Table 1. This also points to insignificant effect of diffusion on quenching.

$$R_0^6 = 5.86\cdot10^{-25}\,\frac{q^0(^1\mathrm{PAH}^*)}{n^4}\int_{Ov}, \qquad (5)$$

where $q^0(^1PAH^*)$ is the quantum yield of fluorescence of energy donor in the absence of quencher,[25] n = 1.4958 is the refractive index of ethylbenzene, and $\int_{Ov}$ is the overlap integral between the fluorescence spectrum of PAH and the absorption spectrum of fullerene C_{60}.

Thus, the quenching does not occur under diffusion control of the energy donor (^{1}PAH*) and energy acceptor (C_{60}); rather, it occurs at long distances.

Table 1 also lists the overlap integrals of the PAH fluorescence spectra with the C_{60} absorption spectrum calculated according to Förster

$$\int_{Ov} = \int_0^\infty F_d(\nu)\varepsilon_A(\nu)\nu^{-4}d\nu \Big/ \int_0^\infty F_d(\nu)d\nu, \qquad (6)$$

where $F_d(\nu)$ is the quantum intensity distribution in the fluorescence spectrum of the energy donor and ε_A is the molar decimal absorption coefficient of the energy acceptor.

The numerical values of the overlap integrals and the very high constants k_{bim} point to deactivation of ^{1}PAH* through singlet-singlet energy transfer by the inductive-resonance mechanism. At the same time no direct proportionality between the k_{bim} values and overlap integrals was found. This indicates[30] that energy transfer by the exchange-resonance mechanism also contributes to quenching and substantiates the correlation between the constants k_{bim} and the overlap integrals corrected with allowance for spin selection rules[30,31] (see Table 1). The corrected overlap integrals $\int_{Ov}^{corr}$ were calculated as follows:

$$\int_{Ov}^{corr} = \frac{B}{\sum\zeta_i^2}\lambda\int_{Ov}^{'} + \frac{\sum\zeta_i^2}{B}(1-\lambda)\int_{Ov}^{'}, \qquad (7)$$

where $\int_{Ov}^{'} = \int_0 F_d(\nu)\varepsilon_A(\nu)d\nu$, $B/\Sigma\zeta_i^2$ is the coefficient, which allows for removal of the intercombination forbiddenness in the donor molecule in the case of exchange-resonance energy transfer; B is a constant equal to $11\cdot10^6$ cm^{-2}; $\Sigma\zeta_i^2$ is the spin-orbit coupling constant, i = 18—44; and λ is the fraction of the overlap with the intercombination bands in the spectrum of acceptor.

The $\Sigma\zeta_i^2$ values for anthracene, 9,10-diphenylanthracene, and 9,10-dibromoanthracene (see Table 1) were taken from Ref. 23 and the corresponding coefficient for naphthalene was obtained from the linear dependence of the $\Sigma\zeta_i^2$ coefficients of anthracene, 9,10-dimethylanthracene, 9,10-dipropylanthracene, and 9,10-diphenylanthracene on the total number of atoms in these molecules. The data in Table 1 show that the $k_{bim}/\int_{Ov}^{corr}$ ratios for different PAH are similar in the sense of the criteria reported in Ref. 30. Energy transfer in the PAH—C_{60} system only by the exchange-resonance mechanism is hardly probable. Indeed, here quenching should occur under diffusion control, but the abnormally high k_{bim} values we have obtained suggest that this is not a unique mechanism of PAH deactivation.

The results obtained and the aforesaid shows that quenching of ^{1}PAH* by fullerene proceeds by two mechanisms, namely, the inductive-resonance (dominant channel) and exchange-resonance (minor channel) energy transfer. In the latter case, energy transfer can occur with or without conservation of the spins of the particles involved in the process (singlet-singlet or singlet-triplet energy transfer, respectively, for the ^{1}PAH*—C_{60} pair). Singlet-triplet energy transfer is only possible[31] if the singlet-singlet energy transfer is energetically impossible and the triplet energy level of the energy acceptor lies lower than the singlet energy level of the energy donor on the energy scale. A unique feature of the electronic structure of C_{60} fullerene consists in that its excited singlet and triplet energy levels have lower energies than the singlet energy levels of all the PAH studied. Therefore, energy transfer from ^{1}PAH* to C_{60} is possible to both these levels.

In determining the multiplicity of energy transfer from ^{1}PAH* to C_{60} we were guided by the published data,[31] according to which proportionality between the k_{bim} and $\Sigma\zeta_i^2$ values proves singlet-triplet energy transfer from ^{1}PAH* to naphthalene. Quenching of ^{1}PAH* (9,10-diphenylanthracene and 9,10-dibromoanthracene) by fullerene is also characterized by an increase in the k_{bim}

constant with an increase in the spin-orbit coupling constant $\Sigma\zeta_i^2$.

We can conclude that quenching of the singlet excited state of naphthalene is due to singlet-singlet energy transfer by the inductive-resonance mechanism (Eqs (I) and (II)), whereas in the case of anthracene, 9,10-diphenylanthracene, and 9,10-dibromoanthracene the process occurs through both singlet-singlet and singlet-triplet energy transfer (Eqs (I)—(III)). The efficiency of singlet-triplet energy transfer increases in the order anthracene < 9,10-diphenylanthracene < 9,10-dibromoanthracene.

$$PAH + h\nu_1 \longrightarrow {}^1PAH^* \qquad (I)$$

$$^1PAH^* + C_{60} \longrightarrow PAH + {}^1C_{60}^* \qquad (II)$$

$$^1PAH^* + C_{60} \longrightarrow PAH + {}^3C_{60}^* \qquad (III)$$

Equations (I)—(III) show that energy transfer from ^{1}PAH* to fullerene causes transition of the latter to an electronically excited state. We failed to detect sensitized luminescence of C_{60}*. We believe this is due to low quantum yields of fluorescence ($2\cdot10^{-4}$)[32] and phosphorescence[33,34] of fullerene and to low sensitivity of our fluorimeter. More detailed treatment of the problem of recording fullerene fluorescence and phosphorescence faced by us and other authors[6,16] has been reported elsewhere.[35]

Thus, fullerene C_{60} can efficiently deactivate the EES of various luminescent chromophores, namely, triplet states of ketones and aldehydes,[5] singlet PAH, and electronically excited lanthanide ions Ln^{3+}* (see Ref. 35) through transfer of their energy. Therefore, transfer of electronic excitation energy to C_{60} can contribute largely to complex processes occurring under photoirradiation of fullerene-containing systems.

Summing up, at present we can only give a tentative explanation for abnormally high efficiency of PAH fluorescence quenching by C_{60} fullerene. The predominant contribution to quenching comes from long-range energy transfer treated[26] as resonance interaction of two oscillators (energy donor and energy acceptor), each of them acting as inductor disturbing the electronic structure of the other. Probably, the electron ensemble of the C_{60} molecule, which includes a total of 240 electrons, is a more powerful inductor compared to other molecules and has a strong effect on the electronic structure of the energy donor molecules, thus inducing nonradiative deactivation of these species.

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