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NEW TYPE OF MAGNETICALLY SENSITIVE FLUORESCENCE PRODUCED BY EXCITATION OF TETRACENE ON THE SURFACE OF AN ANTHRACENE CRYSTAL

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A study is reported of the fluorescence produced by exciting tetracene deposited on single-crystal anthracene. The fluorescence quantum yield is high and its spectrum is very different from the spectrum of tetracene dissolved in an anthracene crystal. The fast fluorescence is quenched by 2–3% by a magnetic field $H \sim 20$ Oe. The anisotropy of the magnetic quenching indicates that the magnetically sensitive excited states are oriented by the anthracene crystal. The data are interpreted as a result of the interaction between singly excited states of the tetracene molecules and the anthracene accompanied by the formation of an excited complex with charge transfer. The magnetic field modifies the distribution of the singlet component of the complex over its spin states and the intensity of its fluorescence.

THE effect of a magnetic field on photoprocesses in molecular crystals, first demonstrated in the case of the photoconductivity of anthracene and tetracene,[1,2] is connected with the change in the distribution of the singlet and triplet components of the pair of interacting particles with nonzero spin over the spin states, for example, an electron and a hole,[4] two triplet excitons,[3] a triplet and a radical,[5] and an oxygen molecule and a triplet exciton.[6] The discovery in recent years of the effect of a magnetic field on the delayed fluorescence of anthracene and the fluorescence of tetracene[7,8] has been attributed to the magnetic sensitivity of the triplet-triplet interaction[9] and the converse process of singlet-excitation decay into two triplet states.[10,11]

We have found that a weak magnetic field ($H \sim 20$ Oe) produces a 2–3% quenching of the fast fluorescence which is emitted during the excitation of a thin film of tetracene on the surface of an anthracene single crystal. The experimental data cannot be interpreted in terms of the magnetic sensitivity of the triplet-triplet interaction (including nonequivalent triplets) and the decay of the singlet excitation into two triplets, and leads to the conclusion that the magnetic field affects the excited state with charge transfer (exciplex[12]), which is formed during the interaction of the excited tetracene molecule with the anthracene molecule within the framework of the model proposed in[4].

EXPERIMENTS

The fluorescence of the specimen was excited by an incandescent lamp using suitable filters (3 cm of water and interference filters for the region 400–500 nm, in combination with the SZS-9 and SS-5 filters) or by the SPM-2 monochromator which had a resolution of 2–5 nm/mm in the wavelength band 400–500 nm. For $\lambda = 482$ nm ($\Delta\lambda = 10$ nm) the maximum intensity of the exciting light was $I = 6 \times 10^{14}$ photons/cm^{2}sec.

The fluorescence was detected with an FÉU-11B or FÉU-79 photomultiplier. Threshold filters (OS-11, OS-12, KS-10) with a blue transmission limit $\lambda \geq 540$ nm were placed in front of the photomultiplier. The specimen was placed inside a light-tight chamber placed between the poles of a dc electromagnet, or inside a solenoid when an alternating magnetic field was employed. Magnetic fields of $H \leq 600$ Oe were used. Since the magnetic effect reached its limiting value in very weak fields ($H \sim 20$ Oe), special measures were taken to compensate the residual magnetization of the core material.

To minimize the effect of the fringe magnetic field on the photomultiplier, the latter was placed at a distance of 1.5 m from the magnet and was surrounded by a steel envelope. The fluorescence intensity was found to be stable to within 0.1%.

The photomultiplier signal was fed either into the ÉPPV system, which had a long time constant (1 sec), in the case of the constant magnetic field measurements, or into the V6-4 tuned amplifier in the case of the alternating magnetic field. In the latter case, the time constant of the recording circuits was less than 10^{-5} sec. A signal compensation system was employed for the precise measurement of small changes in the fluorescence intensity.

Single crystals grown from zone-melted anthracene and tetracene purified by vacuum sublimation were employed. The tetracene was deposited on the surface of the crystal in acetone or benzene solution. The solvent was then evaporated in air. No change in the intensity of the fluorescence nor any effect on the final data was found when the specimens were placed in a vacuum of 10^{-2} Torr during measurements. After the removal of the solvent by evaporation from the surface of the crystal the latter was covered by a thin film of tetracene with an optical density $D \geq 0.3$ for $500 > \lambda > 420$ nm. In the spectral region in which the fluorescence was recorded ($\lambda \geq 540$ nm) the increase in the signal intensity after the deposition of tetracene was by a factor of about ten in the case of excitation by radiation transmitted through a filter with a transmission window between 340 and 450 nm. When the tetracene was deposited in the same way on the surface of glass, the fluorescence produced by excitation in the same wavelength region was weaker by at least an order of magnitude,

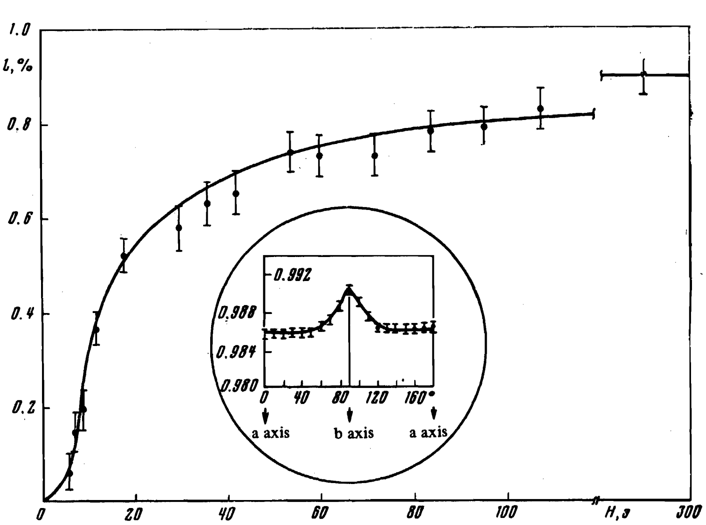

FIG. 1. Relative change in the fluorescence intensity as a function of the magnetic field. The exciting wavelength is 482 nm and the fluorescence was recorded for $\lambda > 540$ nm. The inset shows the relative intensity of fluorescence in a magnetic field of 65 Oe as a function of the direction of the magnetic field in the ab plane of the crystal.

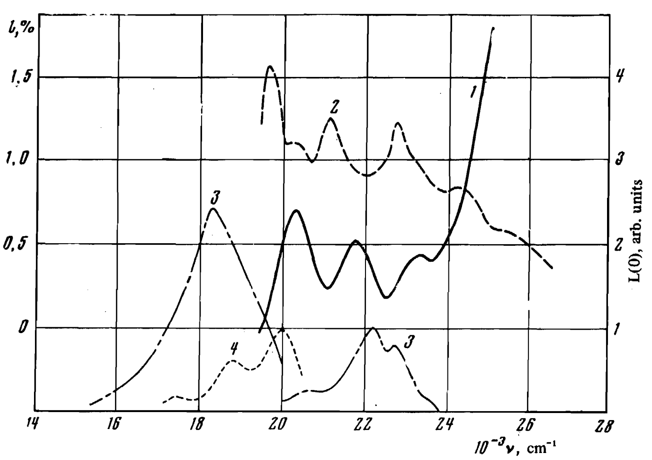

FIG. 2. Curve 1—fluorescence excitation spectrum with allowance for the spectrum of the source of light. Curve 2—relative fluorescence quenching l as a function of the wave number of exciting radiation in a magnetic field of 65 Oe. Curve 3—fluorescence spectrum of the specimen. The ordinates for curve 3 in the region 20 000-24 000 cm^{-1} (anthracene fluorescence) are reduced by a factor of 5. Curve 4—fluorescence spectrum of the solid solution of tetracene in anthracene, taken from [13].

and did not depend on the strength of the magnetic field for H = 60 Oe. We also prepared films by simultaneous evaporation of tetracene and anthracene. In this case, the fluorescence yield produced by excitation in the same wavelength band was found to increase rapidly, as compared with the film of tetracene on glass, but the intensity did not change in the magnetic field H = 60 Oe.

The fluorescence spectra were recorded with the LKPI spectrofluorimeter, which was constructed at the Academy of Medical Sciences and had a resolution of 1.8 nm/mm.

RESULTS

We have discovered for the first time the magnetic quenching of fast fluorescence which appears during the excitation of tetracene deposited on the surface of an anthracene crystal. Figure 1 shows the relative fluorescence quenching

$$l = \frac{\Delta L}{L} = \frac{L(0) - L(H)}{L(0)}$$

as a function of the magnetic field, where L(0) is the fluorescence intensity in zero field and L(H) is the intensity in a field H. The wavelength of the exciting light is $\lambda = 482$ nm and lies within the absorption band of tetracene.

It is clear from Fig. 1 that the magnetic effect reaches its limiting value in very weak magnetic fields (the field strength $H_{1/2}$ at which the effect reaches half the limiting value was 16 Oe). The ratio l does not depend on the intensity of the exciting light ($\lambda = 482$ nm) in the range $6 \times 10^{12} - 6 \times 10^{14}$ photons/cm^{2}sec. To elucidate the nature of the fluorescence and its magnetic quenching, we recorded the fluorescence excitation spectra and the relative quenching l in the magnetic field, and the emission spectra, for different excitation wavelengths (Fig. 2).

Analysis of these spectra and comparison with the fluorescence spectrum emitted by a solid solution of tetracene and anthracene showed the following:

a) The absorption of light on the surface of anthracene covered with a tetracene film obtained from solution is due to the tetracene molecules and the anthracene crystal.

b) The emission spectrum consists of two bands—one with three resolved peaks ($\nu_1 = 22\ 700$ cm^{-1}, $\nu_2 = 22\ 200$ cm^{-1}, and $\nu_3 = 20\ 600$ cm^{-1}) which coincides with the fluorescence spectrum of the pure anthracene crystal (right-hand part of curve 3 in Fig. 2) and this differs from the published spectra,[13] probably as a result of reabsorption, since the crystal thickness is 1 mm, and a second band which has no structure and whose maximum lies at $\nu_m = 18\ 200$ cm^{-1} (left-hand part of curve 3 in Fig. 2). The second band is, in general, different from the emission spectrum of tetracene in the anthracene matrix[13,14] which contains three peaks ($\nu_1 = 20\ 000$ cm^{-1}, $\nu_2 = 18\ 800$ cm^{-1}, and $\nu_S = 17\ 450$ cm^{-1}). The observed emission spectrum with $\nu_m = 18\ 200$ cm^{-1} is similar to the emission spectrum of the tetracene dimer, reported in[15], at high tetracene concentrations in solution.

c) The relative fluorescence quenching ($\lambda > 540$ nm) in the magnetic field (H = 65 Oe) depends on the exciting wavelength as follows: in the region in which anthracene crystals absorb ($\lambda < 420$ nm) the effect is quite small in absolute magnitude (0.3—0.5%) and increases with

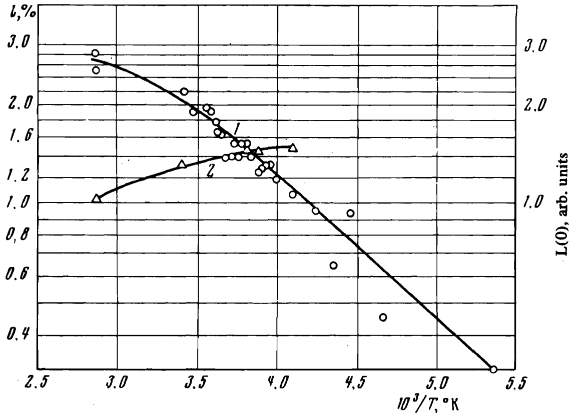

FIG. 3. Fluorescence intensity (curve 2) and the relative change in the fluorescence intensity in a magnetic field of 65 Oe (curves 2 and 1, respectively) as functions of the reciprocal temperature.

wavelength, whereas in the region in which tetracene alone absorbs ($420 < \lambda < 500$ nm) the effect also increases in absolute magnitude with increasing exciting wavelength but there is, in addition, a certain modulation of its magnitude. The modulation is such that, as the fluorescence intensity increases, the magnitude of the effect decreases (curve 2, Fig. 2).

The wavelength dependence of the magnetic quenching can be explained by assuming that, in addition to the magnetically sensitive emission, there is a small contribution due to the ordinary emission of tetracene molecules, and that the emission by the tetracene molecules which are in immediate contact with the anthracene crystal is magnetically sensitive. The fact that the anthracene crystal plays an important role in the quenching process is shown by anisotropy of the effect when the direction of **H** is varied in the plane ab of the crystal, which is shown in Fig. 1 (within the circle where the relative fluorescence intensity L(H)/L(0) in the magnetic field H = 65 Oe is plotted along the ordinate axis and the angle between **H** and the direction of the a axis in the crystal is plotted along the abscissa axis). It is clear that magnetic quenching is a minimum when the direction of the magnetic field lies along the b axis of the anthracene crystal, i.e., it depends on the orientation of **H** relative to the crystal axis. No change in the effect was found when **H** was rotated through 180°.

When an alternating field $H = H_0 \sin 2\pi ft$ of frequency f and amplitude up to 200 Oe is applied to the specimen, the fluorescence modulation amplitude is frequency-independent up to 4 kHz. This means that the lifetime of the magnetically sensitive excited states is less than 10^{-5} sec.

Figure 3 shows the fluorescence intensity and magnetic effect as functions of the specimen temperature. The specimen was cooled by a jet of nitrogen gas boiled off the surface of liquid nitrogen by a special heater. The temperature was recorded by a copper—constantan thermocouple. This method could be used to cool the specimen down to 182°K. A hot-air jet was used to heat it up to 350°K. It is clear that the magnetic effect decreases with decreasing temperature, and at low temperatures it is described by the Arrhenius formula

$$|l| = c \exp(-\Delta E / kT)$$

with $\Delta E = 0.08$ eV. At the same time, L(0) increases with decreasing temperature, but much more slowly than l. The fluorescence was excited in this case by 443 nm radiation and the magnetic field was 65 Oe.

DISCUSSION

It is well known that in films and crystals of tetracene the process which is sensitive to the magnetic field at room temperature is the decay of the singlet excitation into two triplets,[10,16] according to the scheme

$$^1T^* + T_0 \rightarrow (^3T^* {}^3T^*) \rightarrow {}^3T^* + {}^3T^*. \tag{1}$$

For weak fields H < 500 Oe the fluorescence intensity falls by 5%, whereas in strong fields (H ~ 2000 Oe) it increases by up to 40% (for suitable orientations of H). A characteristic feature of this mechanism is that the increase in the fluorescence efficiency (usually equal to 0.002) with decreasing specimen temperature or increasing exciting intensity leads to a reduction in the magnetic effect, since the magnetically sensitive channel (1) is, at the same time, the fluorescence quenching channel.[10,17] In principle, judging by the sign of the effect, this mechanism can also be responsible for the effect observed in our own work, i.e., the quenching of the fluorescence of tetracene in weak magnetic fields, associated with the formation of the thin film of tetracene on the surface of the crystal.

To verify this possibility, we compared the fluorescence intensity from two crystals: on one of them the tetracene was deposited from solution, as described above, and on the other it was vacuum-evaporated onto the crystal up to a thickness of 1000 Å. The exciting wavelength was 482 nm in both cases. The intensity of the fluorescence emitted by the film deposited in vacuum was lower by a factor of 20, as compared with the film obtained from solution. Next, light with a broad spectral range ($340 < \lambda < 450$ nm; FS-6 and FS-7 filters) was used for excitation, and equal fluorescence intensity was produced in both cases by varying the light source output, and a field of 60 Oe was applied to the specimens. In the case of the specimen with a tetracene film deposited from solution, the fluorescence was quenched by 0.6%, whereas for the vacuum evaporated film, a field of 60 Oe had no effect on the fluorescence, and only the usual magnetic effect was observed,[10] which was due to the process described by Eq. (1) (in strong fields H > 1000 Oe). These facts suggest that (a) for the specimen prepared by deposition from solution the fluorescence quantum yield is higher by a factor greater than 20 as compared with the case of the vacuum evaporated film, and (b) the magnetic field H = 60 Oe which we used is too weak to produce the effect due to the decay of the singlet into two triplet excitations in accordance with Eq. (1).

The fluorescence quantum yield of tetracene in the case of the film produced from solution is found to be comparable with the fluorescence yield of anthracene. This is indicated by the fluorescence spectra shown in Fig. 2 and recorded at the same time using an excitation wavelength of 400 nm. The ratio of the areas under the spectra for tetracene and anthracene is 0.5. The fact that Eq. (1) is not valid is shown also by the temperature dependence of the fluorescence. Its intensity L is practically independent of T, whereas transition to the (TT) state in accordance with Eq. (1) will quench the luminescence, and L varies with T in accordance with the Arrhenius law with an activation energy of 0.16 eV.[10]

The observed facts can be explained by assuming that a special excited state (TA)*, known as the exciplex,[12,18] is magnetically sensitive. This state is formed during the interaction of the excited tetracene molecule $^1T^*$ and an anthracene molecule in the ground[1] state A_0:

$$^1T^* + A_0 \rightarrow (TA)^* \xrightarrow{h\nu} (TA)_0 \rightarrow T_0 + A_0. \tag{2}$$

In the ground state, the exciplex dissociates into the unexcited molecules T_0 and A_0. The formation of exciplexes was observed mainly in liquid solution, for example, during the excitation of anthracene plus diethylaniline[19], or indole and its derivatives in polar solvents.[20] The formation of the exciplex was also observed between related aromatic compounds in the solid state (pyrene and perylene).[21]

In our case, the formation of the exciplex (or excimer) is confirmed by the fluorescence and excitation spectra (Fig. 2). They have a characteristic form: while the excitation and absorption spectra are not different from the absorption spectrum of tetracene (obtained for a film evaporated in vacuum together with anthracene), the fluorescence spectrum differs from the fluorescence spectrum of tetracene dissolved in anthracene—it has no structure and is shifted toward lower frequencies (Fig. 2), which is characteristic for the emission spectrum of an exciplex.[18-21]

According to[12], a considerable contribution to the binding energy of the exciplex is provided by the interaction with charge transfer (T^+A^-), where the charge separation can be more or less substantial.[22] The existence of a singlet and a triplet state of the exciplex is possible.[22] If the lifetimes of these states, τ_1 and τ_3, are different, for example, $\tau_1 < \tau_3$, and do not exceed the spin-lattice relaxation time, whereas the fluorescence is determined by the decay of the singlet state (as, for example, in[22]), the mixing of these states in the magnetic field, according to the model developed for excitons with charge transfer,[4] leads to an enhancement of the exchange between them and, consequently, to a reduction in the fluorescence intensity.

The fluorescence intensity L is determined by the rate of formation of singlet excited states of the complex and the distribution of the singlet component over the spin states:

$$L = \sum_i G f_i \tau_i' \frac{f_i}{\tau_1}. \tag{3}$$

Here F_i is the fraction of the singlet component in the i-th spin state, $\sum_i f_i = 1$, τ_i' is the total lifetime of the i-th state, Gf_i is the rate of population of the i-th state as a result of the singlet-singlet transition, τ_1 is the radiative lifetime of the purely singlet state, and f_i/τ_1 is the probability of a radiative transition in the i-th state.

In zero magnetic field there is only one singlet state: $\tau_i = \tau_1$, $f_1 = 1$, and L = G. In a nonzero magnetic field H there is a singlet contribution to the triplet spin state with m = 0. For these two states we have

$$f_1 = 1 - x^2, \quad f_2 = x^2,$$

$$\tau_1' = \left[\frac{1}{\tau_1}(1 - x^2) + \frac{1}{\tau_3}x^2\right]^{-1}, \quad \tau_2' = \left[\frac{1}{\tau_1}x^2 + \frac{1}{\tau_3}(1 - x^2)\right]^{-1}.$$

Here $x = \mu_B H \Delta g/\Delta W$, Δg is the g-factor difference between the positive and negative charges forming the exciplex, μ_B is the Bohr magneton, H is the magnetic field, and ΔW is the energy difference between the triplet and singlet states. Summation over the two states yields

$$L(H) = G\left[\frac{(1 - x^2)^2}{1 - x^2 + \tau_1 x^2/\tau_3} + \frac{x^4}{x^2 + (\tau_1/\tau_3)(1 - x^2)}\right] < G, \tag{4}$$

$$l \equiv \frac{\Delta L}{L} = \frac{\tau_1}{\tau_3}\frac{x^2}{\tau_1/\tau_3 + x^2}. \tag{5}$$

It is clear from Eq. (5) that the effect reaches its limiting value for $x^2 > \tau_1/\tau_3$, and that its maximum magnitude is

$$l_{x^2 > \tau_1/\tau_3} = \tau_1 / \tau_3. \tag{6}$$

Since it is found experimentally that

$$l_{x^2 > \tau_1/\tau_3} = 2 \cdot 10^{-2},$$

it follows from Eq. (6) that

$$\tau_1 / \tau_3 = 2 \cdot 10^{-2}. \tag{7}$$

It can be shown, by using Fig. 1, that the magnetic field $H_{1/2}$, for which

$$l(H_{1/2}) = {}^1\!/_2\, l_{x^2 > \tau_1/\tau_3},$$

is 16 Oe. Using this value of $H_{1/2}$ in Eq. (5), we obtain

$$\Delta W / \Delta g = \mu_B H_{1/2} \sqrt{\tau_3 / \tau_1} = 7 \cdot 10^{-7}\ \text{eV} \tag{8}$$

Δg cannot be determined without knowing the detailed electron structure of the exciplex, but it may be supposed that, owing to the strong Coulomb interaction, the exciplex exhibits spin-orbit coupling and Δg is in the range 10^{-2}—10^{-1}. This leads to $\Delta W = 10^{-7}$—10^{-8} eV.

This model cannot be used to explain the anisotropy of the magnetic effect by using the anisotropy of the zero field of the triplet, as in the case of the triplet-triplet interaction.[23] However, the anisotropy of *l* may be due to the anisotropy of the Zeeman interaction. The dependence of the magnetic effect on the angle between the directions of the field vector and the a axis of the crystal, observed in the present work (Fig. 1), has only one peak at 180° and is very different from the anisotropy of the triplet-triplet interaction in anthracene and tetracene.[23,24]

A possible explanation of the anisotropy is as follows. It is well known (see, for example,[12]) that the exciplex is formed only for a strictly defined mutual disposition of the interacting molecules.[2] One of its components,

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[1] It is possible, at least in principle, that if the molecules in the tetracene layer are oriented by the anthracene crystal, then A_0 can be an unexcited tetracene molecule T_0 and the excimer (TT)* is formed instead of the exciplex (TA)*.

[2] This may explain why the magnetically sensitive state which we are considering is formed only on the surface of the crystal when the tetracene film is produced from solution, and is not formed within the body of the crystal or during vacuum evaporation.

i.e., the anthracene molecule, is oriented in a definite fashion relative to the crystal axes, and this leads to the conclusion that the exciplex axis along which the binding electric field is directed is also oriented.

If there is a sufficiently strong spin-axis interaction, the spin magnetic moment will have a definite component along this axis.[25] If the axis is not perpendicular to the ab plane of the crystal, the projection of this moment onto the ab plane can be resolved into two mutually perpendicular components, one of which is a constant and the other oscillates between zero and the maximum value. Since the operator representing the interaction between the magnetic moment $\boldsymbol{\mu}$ and the magnetic field $\mathbf{H}$ is of the form $\mu H \cos \alpha$, where α is the angle between $\boldsymbol{\mu}$ and $\mathbf{H}$, it is clear that, in this case, the operator will be $\mu' H \cos \alpha$, where μ' is a constantly oriented part of the projection of the moment onto the ab plane. This means that x in Eq. (5) must be replaced by $x \cos \alpha$, and this gives the dependence of l on α with one resonance peak at $\alpha = 90°$. The form of the peak in this case is given by

$$l(\alpha) \sim \frac{H^2 \cos^2 \alpha}{\mathrm{const} + H^2 \cos^2 \alpha}. \tag{9}$$

The width of the peak decreases with increasing H. The experimentally determined position of this peak enables us to conclude that the exciplex axis has a projection on the ab plane which lies along the a axis, i.e., it lies in the ac plane and, in this respect, it is similar to the c axis of the anthracene crystal.

In conclusion, it is important to note that, in a previous paper,[2] we reported a magnetic effect in the surface photoconductivity of anthracene single crystals in which the photoconductivity increases when the magnetic field is applied in a way similar to that shown in Fig. 1 with $H_{1/2} \approx 20$ Oe. The above model leads to an increase in the total concentration of excited complexes when the magnetic field is introduced, and provides a unified explanation of the fluorescence quenching and the increase in photoconductivity. The formation of current carriers on the surface of the anthracene crystal is preceded by the appearance of an excited complex of anthracene and an impurity molecule on the surface. The dissociation of these complexes, which does not depend on their spin states, determines the current-carrier concentration. A similar mechanism is probably operative in the case of the "positive" magnetic effect in the photoconductivity of tetracene.[26] The formation of an excited state with charge transfer may act as a channel which competes with the decay of the singlet into two triplets and determines the quenching of the tetracene fluorescence at low temperatures, when the singlet decay channel does not operate.

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