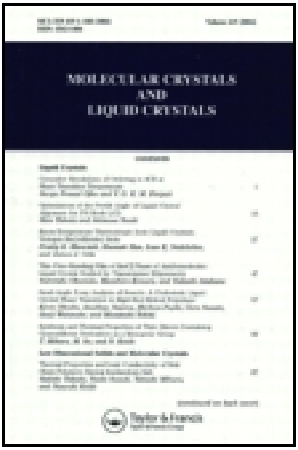

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Delayed Reikbination Fluorescence and Production of Triplet Charge Transfer and Exciton States in VUV-Excited Molecular Crystals

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DELAYED RECOMBINATION FLUORESCENCE AND PRODUCTION OF TRIPLET CHARGE TRANSFER AND EXCITON STATES IN VUV-EXCITED MOLECULAR CRYSTALS

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Abstract At sufficiently high excitation energies, the molecular crystals exhibit a new, slowly decaying magnetic field sensitive fluorescent component. The experimentally observed properties of this special luminescence component in anthracene and p-terphenyle are discussed, considering in particular the excitation spectra of the intensity for energies up to 40 eV. According to the characteristic magnetic modulation of the intensity, the light emission follows the recombination of long lived electron-hole pairs created initially in a triplet spin state via a deep valence hole. The nature of the photodynamic processes responsible for such recombination fluorescence precursors is suggested to be connected with the well documented mechanism of photoinduced exciton fission in triplet pair states, which involves intermolecular charge transfer transitions within a pair of neighboring molecules. It is shown that the measured excitation spectra are fairly interpreted on the whole explored energy domain; at the higher excitation energies, the expected onset of a new relaxation channel for the deep valence holes, producing singlet excitons, is indeed detected.

Keywords: anthracene, p-terphenyl, VUV, molecular crystals, exciton fission, recombination fluorescence, magnetic modulation

INTRODUCTION

High energy excited state evolution in dense molecular media involves, in addition to the common intramolecular mechanisms, a variety of electronic relaxation phenomena induced by intermolecular exciton and charge transfer (CT) interactions. In such photoexcited processes, the final states are essentially exciton or electron-hole (e,h) pairs, which can be detected by special fluorescence measurements. Experimental studies in this field have been made with organic molecular crystals photoexcited in the UV and VUV spectral ranges: the main results are concerned with the excitation spectra of:

- the yield of singlet exciton pair states, detected by coincidence measurements of two correlated fluorescence photons,[1-3]
- the yield of triplet exciton pair states, observed via "fine structure" (FS) magnetic field modulated fluorescence,[1-3]
- the formation of long lived (e,h) pair states detected by "hyperfine structure" (HFS) magnetic sensitive recombination fluorescence,[4-7]
- the total fluorescence quantum yield.[7,8]

In the present contribution, we shall focus on the last two of these phenomena and discuss our results obtained with crystalline anthracene (Ac) and p-terphenyl (pTP) excited with photons up to 40 eV.

In HFS magnetic field modulated recombination fluorescence, the emitting singlets are formed by neutralization of geminate (e,h) pairs, initially created with a definite spin correlation.[9-11] The efficiency depends on the probability for the ion pair to be singlet at the recombination time, which is determined by spin motion in the pair under the influence of the Zeeman and HFS interactions: HFS modulation of recombination fluorescence takes place for fields in the 10-100 G range and requires times larger than the hyperfine singlet-triplet mixing periods, i.e., $t \geq 10$ ns. Therefore, it is only observable for sufficiently long lived geminate (e,h) pairs.

In the case of liquid alkane solutions of aromatic compounds, the process is well documented:[9-12] the positive magnetic modulation of a slowly decaying fluorescence component indicates that initial photoionization in the alkane solvent produces (e,h) pairs in a singlet spin state. After rapid trapping of the charge carriers by the fluorescent solute molecules, the resulting singlet ion pairs undergo the observed $t^{-3/2}$ dependent recombination process via relative diffusion of the molecular ions. The exact characterization of the kinetic and magetic sensitive properties enabled us to use recombination fluorescence for the detection of photoionization and for the study of the corresponding excitation spectra in the liquid alkanes.[13,14]

We have undertaken similar investigations with the neat Ac and pTP crystals. The main results are presented in the next section; they exhibit a notable difference with those obtained for the liquid solutions: beyond a well defined threshold energy, primary photoionization in the crystal generates long lived CT excitations in an initial triplet spin state. The sequence of electronic transitions invoked to describe the photodynamic process thus detected is discussed in the third section: after the initial radiative transition from a deep valence electronic orbital to a highly excited level, further evolution of the primary excitation proceeds in a fashion related to the well known exciton fission transitions producing triplet exciton pairs; it thereby involves intermolecular CT within pairs of adjacent molecules, but following special features that will be considered in detail.

EXPERIMENTAL RESULTS

The Ac and pTP single crystals were excited by the synchrotron radiation pulses of the DORIS II (HASYLAB, DESY, Hamburg) and SUPER-ACO (LURE, Orsay) storage rings. Following the procedures described before,[4-7] the fluorescence intensity curves I(t,E) have been measured under nanosecond time resolution conditions, for photon energies E up to 40 eV, in the absence (I^0) and in the presence (I^B) of a 0.05 tesla magnetic field. In previous work,[5,6] we already reported that, at excitation energies higher than a threshold value E_0, a new fluorescence component arises, which slowly decays following a $t^{-3/2}$ law and is magnetic field sensitive, with a negative modulation ratio $(I^B-I^0)/I^0$ having the characteristic HFS modulation properties of recombination fluorescence. The negative sign of the modulation ratio is in contrast with the positive effect for the alkane solutions, meaning that the recombining geminate (e,h) pairs are initially created with triplet character in the crystals.

At times larger than tens of nanoseconds, the observed temporal intensity decay is known to be controlled by the rate of recombination, according to the expression:[9,10]

$$I^B(t,E) = \eta_F \rho_S^B R(t,E) \qquad (1)$$

where η_F is the molecular fluorescence efficiency; ρ_S^B represents the constant asymptotic value of the probability $\rho_S^B(t)$ for the ion pair to be singlet at the recombination time, a well defined quantity depending upon the magnetic field strength and the initial spin alignment of the ion pair.[7,9-11] The function $R(t,E)$ is the neutralization rate that reflects the recombination kinetics and the yield of the photoinduced relaxation channel detected in these experiments. To obtain a measure for the exci-tation spectra, it is convenient to consider the normalized integrated intensities $J^0(E)$ and $J^B(E)$ defined as

$$J^{B,0}(E) = \frac{1}{Q_F(E)} \int_{50\ \text{ns}}^{300\ \text{ns}} dt\ I^{B,0}(E,t) \qquad (2)$$

where $Q_F(E)$ is the absolute fluorescence quantum yield of the crystal excited by the photons of energy E.

We have measured the absolute excitation spectra $Q_F(E)$ for the Ac and pTP crystals using the common method with sodium salicylate as a reference.[7,15]

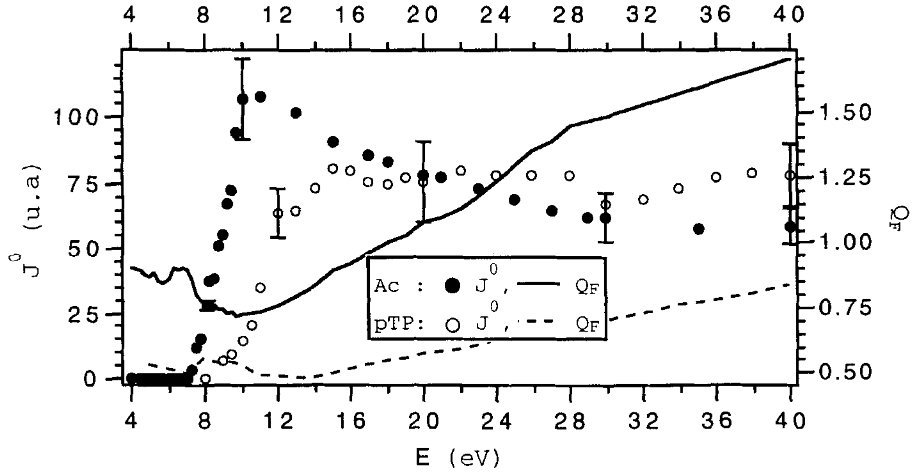

FIGURE 1 Ac and pTP crystals: Excitation spectra of the recombination intensity J^0 and of the total fluorescence quantum yield Q_F.

The data obtained for the excitation spectra of the formation of long lived (e,h) pairs in the triplet spin state (J^0) and of the total fluorescence quantum yield (Q_F) are presented in Figure 1, for both the Ac and pTP crystals. In the two cases, it is noteworthy that two energy domains, separated by a critical value E_c, may be distinguished: at the lower energies, between the threshold E_0 (7.1 ± 0.2 eV in Ac; 8.0 ± 0.2 eV in pTP) and E_c (≈10 eV in Ac; 14 eV in pTP), $J^0(E)$ increases steeply with E while $Q_F(E)$ decreases; at the higher energies, beyond E_c, $J^0(E)$ decreases for Ac and remains constant for pTP, whereas $Q_F(E)$ increases monotonously.

DISCUSSION

The photodynamic relaxation channel in the molecular crystals detected in these fluorescence experiments involves a sequence of electronic processes ending with (e,h) pair states, characterized by:
(i) an initial triplet character: therefore, the concomitant formation of another triplet excitation is necessary during the primary stages of the photoprocess; this points to a similarity with the well studied photoinduced singlet fission transitions leading to triplet exciton pairs in the crystals;[1-3]
(ii) a long lifetime (≥100 ns): under common conditions for thermalized charge carriers diffusion in the crystals, recombination of geminate (e,h) pairs takes place on a subnanosecond time scale, fixed by r_c^2/D in terms of the Onsager radius r_c (≈170 Å in Ac) and the relative diffusion coefficient D (≈10^{-2} cm^{2}s^{-1} in Ac);[7,16,17] much longer times hence require specific trapping mechanisms for the carriers. Also the accompanying triplet presumably acts as a trapping center since the delayed recombination is only observed for the (e,h) pairs in the triplet state;
(iii) an efficiency with the energy dependence given by $J^0(E)$, showing a steep increase at the relatively high threshold energy E_0, followed by a decrease or a saturation of the effect after the still higher energy E_c.

In order to account for all these observations, we begin with a regard on item (i) and look for a mechanism connected with those commonly envisaged for photoinduced exciton fission in triplet exciton pairs.[1,7,18,19] These are recalled in Figure 2. They involve two virtual or real CT transitions between neighboring molecules according to the

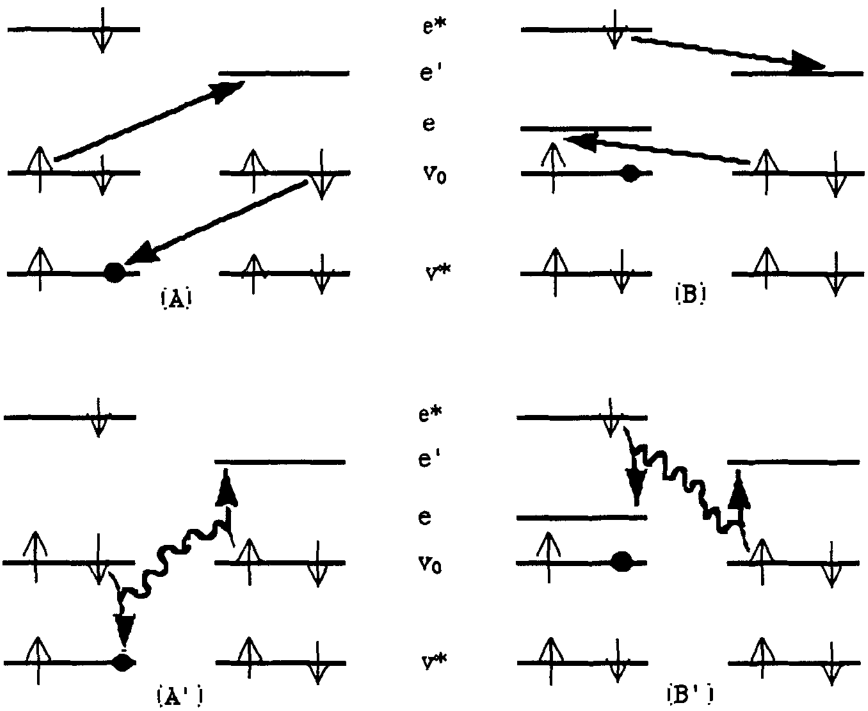

FIGURE 2 Transition schemes for singlet exciton fission:
A & B: fission in triplet exciton pairs: the transitions involve intermolecular electron transfers within a molecular pair.
A' & B': fission in singlet exciton pairs: the transitions involve intermolecular excitation transfer within a molecular pair.

two possibilities (A) and (B), where either the hole (in A) or the electron (in B) of the initial singlet photoexcitation takes part in the transition. As a necessary condition for process (A), we note that the primary hole must be in a sufficiently deep valence orbital state (v^*).

Considering next the features (ii) of the experimental findings, we argue that these are fairly explained by a mechanism of class (A), for which the primary excited electron (e^*) is prepared by the photon in a superexcited or a continuum molecular orbital. By means of the CT transitions in process (A), the hole and the triplet exciton are preferably created on molecular sites that are connected by the largest intermolecular transition amplitudes, i.e., the nearest neighbors in the (a,b) planes of the Ac and pTP crystals.[20] Such a spatial correlation then favors efficient stabilization of a complex binding the hole and the triplet exciton by the strong attractive interaction potential related to the charge of molecular polarizability upon excitation in the triplet state.[21,22] While in the doublet spin state of the hole-triplet complex, the lifetime is severely limited by the annihilation of the exciton, such reactions are forbidden in the quartet state;[23] the complex can then live as long as the natural lifetime of an isolated triplet exciton, with the consequence that the hole is quasi-immobile for times over several milliseconds. The primary electron (e^*) acts as a spectator of the foregoing intermolecular electron transfer transitions, but follows its own relaxation channels: via autoionization or direct ionization, it enters the conduction band with excess kinetic energy. After energy relaxation per emission of molecular and lattice phonons, it localizes at finite distances from the initially excited site; these are distributed around a "mean thermalization length" estimated of the order of several tens of Å-units[24] and encompassing therefore several crystalline (a,b) planes. It follows that mechanism (A), together with the subsequent relaxation phenomena, indeed produces efficiently well separated (e,h) pairs with triplet character and having the hole trapped by the concomitant triplet exciton in a (a,b) plane of the Ac and pTP crystals.

But the observed delay over hundreds of nanoseconds in the recombination of the correlated triplet (e,h) pairs, controlled by relative diffusion of the charges carriers cannot be explained by trapping of the hole alone: in the migration of the electron towards the fixed hole, its mobility must be sufficiently reduced as well. This may be justified by analyzing in some detail the transport anisotropy of the electron in the crystal, e.g., by considering its transfer from site to site in the lattice towards the hole complex, as done in reference.[25] The recombination ladders thus followed are determined by the spatial configuration of the (e,h) pairs. Whenever the charges are created in the same (a,b) plane, recombination is governed by fast migration within the plane on a subnanosecond time scale, which prevents observation in these experiments. By contrast, in the more common situation where the primary electron is thermalized in a plane different from that containing the hole-exciton complex, the recombination ladder involves one or several steps with interplanar electron transfers. These steps have small transition amplitudes[20] and form kinetic bottlenecks for all such ladders. Each can introduce a temporal delay exceeding 100 ns; but the main retarding contribution is certainly due to the last step, engaging the electron on the site nearest to the hole complex in the adjacent (a,b) plane: this corresponds to the neutralization of charges located on the relatively distant neighbors along the c axis, a transition also slowed down by the large electronic energy gap due to the Coulomb interaction and the relaxation energy of the hole-exciton complex.[5,25] Therefore, together with the immobilization of the photoexcited hole by the accompanying triplet exciton, the thermalization of the photoexcited electron in a distant (a,b) plane is sufficient to account for the long lifetimes of the recombining CT states detected in our experiments.

The discussion must proceed with part (iii) of the above mentioned experimental information, concerned with the influences of excitation energy on the intensity of magnetic sensitive recombination fluorescence for the two crystals. In line with the proposed interpretation, the variation of $J^0(E)$ is expected to reflect the excitation spectrum of the electronic process (A), photoinduced via an initial singlet excitation having the electron (e^*) on an energy level above the bottom of the conduction band and the hole (v^*) in a valence level below the highest occupied molecular orbital (HOMO, v_0) by an amount larger than the lowest triplet exciton energy E_T in the crystal.

The threshold energy E_0 is hence determined as

$$E_0 = E_G + \varepsilon_{v_0} - \varepsilon_{v^*} \quad , \quad \varepsilon_{v_0} - \varepsilon_{v^*} > E_T \qquad (3)$$

where E_G is the band gap between the conduction band and the HOMO, while $\varepsilon_{v_0} - \varepsilon_{v^*}$ is the energy difference of the valence orbitals that may be regarded as the excitation energy of the hole. These energies can in principle be deduced from photoconduction and photoemission measurements.[16] They are known for Ac,[26] where $E_G=4.4$ eV and $E_T=1.8$ eV; also the first inner valence orbital satisfying fully the condition necessary for producing the triplet exciton is $v^* \equiv v_3$, for which $\varepsilon_{v_0} - \varepsilon_{v^*}=2.7$ eV; this then yields $E_0=4.4+2.7=7.1$ eV, which is in perfect agreement with the observed threshold value (cf figure 2). For pTP, we are not aware of a directly measured E_G value, but will estimate it knowing the photoemission threshold energy, $I_c=6.2$ eV,[27] and assuming that the energy V_0 of stabilization, with respect to vacuum, of the lowest conduction band edge is the same as for Ac, i.e., $V_0=1.3$ eV:[7,26] using $E_G=I_c-V_0$, one gets $E_G=4.9$ eV; with $E_T=2.5$ eV, the first inner valence state satisfying the foregoing condition is found to be $v^*=v_3$, for which $\varepsilon_{v_0} - \varepsilon_{v^*}=3.0$ eV; the threshold energy in pTP is hence estimated as $E_0=4.9+3.0=7.9$ eV, again in fair agreement with the observed value.

In the lower energy part of the excitation spectra in Figure 1, the steep rise of $J^0(E)$ beyond the threshold energies E_0 has similarities with the excitation spectra of photoemission in the crystals and is likewise interpreted in terms of the densities of states in the relatively sharp v^* band and the wider conduction band.[7,16]

For the higher photon energies, when still deeper valence orbitals (v^{**}) participate to the radiative transitions, the valence excitation energy $\varepsilon_{v_0} - \varepsilon_{v^{**}}$ begins to exceed the lowest singlet excitation energy E_S in the crystal. The primary hole then also relaxes by emitting singlet excitons, following a process of class (A') in Figure 2. Such intermolecular excitation transfers, that are governed by the strong direct Coulomb transition matrix elements, are known to have much larger probabilities than the electron transfers; therefore, they necessarily act as strong competitors of process (A). The above mentioned critical energy E_c, beyond which $J^0(E)$ saturates or decreases, is interpreted as corresponding to the onset of this new relaxation channel. In the case of Ac, the observed value, E_c=10 ± 0.5 eV, is found to coincide with the energy of a strong absorption transition that involves initial valence levels with $\varepsilon_{v_0}-\varepsilon_{v^{**}}$=6.5 eV:[26] since E_S=3.15 eV, the necessary condition for the competing process (A') to be operative is amply satisfied. In pTP, where E_S=3.9 eV, the observed energy, E_c=14 ± 0.5 eV, is so high that the inner valence levels engaged in the radiative transitions are expected to be so that $\varepsilon_{v_0}-\varepsilon_{v^{**}}\leq$ 10 eV, meaning that the relaxation channel via mechanism (A') is largely open as well.

The interpretation of E_c as a demarcation energy between a low energy domain controlled by the triplet excitation producing process (A) and a high energy range, where the singlet excitation producing process (A') progressively becomes dominant is further confirmed by the excitation spectra of fluorescence quantum yield in Figure 1: since the transitions (A) and (A') respectively quench and promote the formation of fluorescent singlets, the Q_F(E) functions should have minima for E=E_c, which is indeed the case for the two crystals.

At this point, it is worthwhile to establish a connection with the earlier studies of exciton fission in Ac, made by G. Klein, who measured the quantum yields Q_{TT}(E) and Q_{SS}(E) of the photoproduction of triplet and singlet exciton pairs, repectively.[1-3,29] Theses results are presented in Figure 3.[28] The mechanisms that have essentially been invoked are those of the classes (B) and (B') in Figure 2, which emphasing the role of the excitation energy of the electron rather than of the hole: together with the direct fission transitions, the secondary excitation of triplet and singlet states by the hot photoelectrons has in particular been considered.[7,29] In fact, however, the yields Q_{TT} and Q_{SS} include respectively the additional contributions from the processes (A) and (A'), meaning that definite correlations with the excitation spectra of the present work may be expected. This appears to be clearly the case in Figure 3: at the same critical energy E_c=10 eV as for J^0(E) and Q_F(E), the graphs Q_{TT}(E) and Q_{SS}(E) indeed undergo slope changes, indicating that, at the higher energies, the production of triplets progressively decreases while that of the singlets steadily increases. In a more quan-

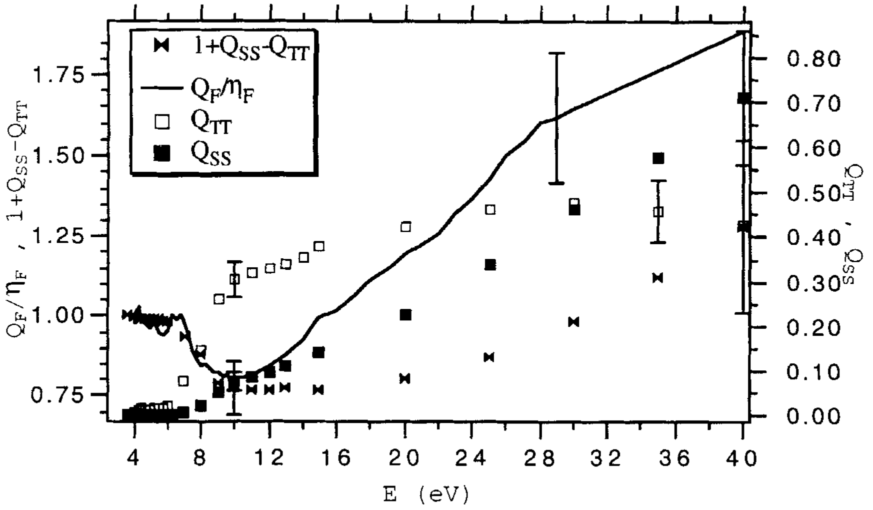

FIGURE 3 Ac crystal: comparaison of the excitation spectra for exciton fission in triplet and singlet pairs and for the total fluorescence yield .

titative comparaison, we may assume that the main decay modes of the primary photoexcited singlet states include, in addition to the fission phenomena represented in Figure 2, the internal conversion and geminate (e,h) recombination processes populating isolated fluorescing singlets. Denoting the yield of these monomolecular processes by $Q_S(E)$, one then has the equation $Q_S(E)+Q_{TT}(E)+Q_{SS}(E)=1$, while the total fluorescence quantum yield is written as $Q_F(E)=\eta_F[Q_S(E)+2Q_{SS}(E)]$. From this one deduces the relationship

$$Q_F(E)/\eta_F = 1 + Q_{SS}(E) - Q_{TT}(E) \tag{4}$$

which enables us to compare the measured excitation spectra for exciton fission to that of the total fluorescent quantum yield. The result is shown in Figure 3: the agreement is excellent in the low energy domain ($E<E_C=10$ eV). For the higher energies, the foregoing relationship reproduces the measured rise of $Q_F(E)$, but underestimates the actual values. Understanding of the possible reasons, including the eventual role of

electronic processes here ignored, like multiexciton spur formation, requires further work, which is currently in progress.

CONCLUDING REMARKS

The high energy photon induced effect detected via magnetic sensitive recombination fluorescence in organic molecular crystals is found to result predominantly from the electronic relaxation of excited holes rather than of the excited electrons. Whenever energetically possible, the intermolecular decay modes induced by CT and singlet excitation transfer interactions are highly efficient and thereby strongly competitive with the intramolecular decay transitions (internal conversion, autoionization, Auger ...). In the electronic relaxation of highly excited molecular states in condensed matter, the intermolecular radiationless processes engaging the holes in inner valence orbitals, as the electrons on the excited orbitals, certainly play a role more important than hitherto recognized.

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