

## Triplet exciton caging in two dimensions

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It is proposed that the bimolecular process of triplet exciton fusion to form singlet excitons can be enhanced by reducing the size of the domain in which the triplet exciton pair is free to move. These small domains, or exciton cages, are much more effective when the host material is highly anisotropic, and the triplet excitons are constrained to move in one or two dimensions. In the present case, the host material is tetracene crystal in which triplet exciton diffusion is essentially two dimensional. The exciton caging is produced by introducing relatively high concentrations of a guest molecule that can reflect the triplet exciton rather than trap it; in the present case, 2,3-benzocarbazole (BC) is used. Polycrystalline mixtures of BC in tetracene were prepared in the mol fraction range 0%–50%. In tetracene, the mode of decay of the first excited singlet state is by fission into two neighboring triplet excitons that can undergo geminate recombination. The introduction of BC is found to increase the tetracene fluorescence lifetime at room temperature from 100 psec at 0% BC to 360 psec at 50% BC, while the lifetime at 77°K is relatively constant. In addition, the characteristic increase in the tetracene fluorescence quantum efficiency with increasing excitation intensity is found to diminish as the BC concentration is increased. The lifetime and the relative fluorescence efficiency experiments are interpreted in part by invoking the concept of exciton caging, in which the geminate recombination of the original triplet exciton fission pair is enhanced by the presence of exciton reflectors that reduce the size of the domain in which the excitons can freely move. A computer simulation is made of the fission and fusion process in an ideal mixed crystal containing randomly distributed exciton reflectors, and the response of the model agrees well with the observed results.

### I. INTRODUCTION

A distinguishing feature of excited crystal states of aromatic hydrocarbons like anthracene and tetracene is the prevalence of an extraordinary variety of excitonic phenomena.<sup>1</sup> The creation and movement of excitons is also important in the early stages of photosynthesis.

One important question that can be asked about these excitonic phenomena as observed in macroscopic crystal systems is whether one can expect a significant alteration of diffusion-mediated rate processes as the size of the crystal is progressively diminished. This is the question that we addressed ourselves to, and the particular phenomenon we chose to study was that of triplet-triplet ( $T-T$ ) exciton fusion. As a bimolecular process,  $T-T$  fusion depends on the concentration of excitons and hence on the volume of the domain. The occurrence in nature of small crystal domains is not an unusual phenomenon. In all crystals, particularly the soft molecular crystals, there are edge dislocations in which an extra half-plane of molecules is in-

serted into the crystal lattice. If this half-plane is limited in extent, it becomes a raft of molecules lying between the normal lattice planes, and as such it can represent a region of confinement or a cage for excitons. This question of domain size also has special relevance to biological systems where one typically deals with small heterogeneous structural units either surrounded by a membrane or separated from its environment by virtue of insolubility; structures in the size range of a few tens to a few hundreds of angstroms are not uncommon.

Ordinarily, one must produce rather high concentrations of triplet ( $T$ ) excitons in order to study the  $T-T$  fusion process. In tetracene, for example, the  $T-T$  fusion process becomes comparable to the first-order  $T$  decay process at exciton densities of  $\sim 10^{13}/\text{cm}^3$ . Based on a direct production of  $T$  excitons by the spin-forbidden transition from the ground state, a light intensity of  $10^{21}$  photon  $\text{cm}^{-2} \cdot \text{sec}^{-1}$  would be required to generate a  $T$  exciton density of  $\sim 10^{13}/\text{cm}^3$ ; this is a very high light

intensity. Fortunately, it is not necessary to use such a high light intensity to study  $T$ - $T$  fusion processes in crystalline tetracene. Virtually every singlet exciton produced in this material fissions into two  $T$  excitons<sup>2</sup>; since these excitons are generated as near neighbors, the local concentration of  $T$  excitons is huge. The situation is analogous to that of ionization in particle tracks in which positive and negative carriers are produced in close proximity to each other; the local concentration of carriers is very high, although the average concentration in the crystal may be vanishingly small.<sup>3</sup> In short, fission bears the same relation to excitons as ionization does to carriers. A dominant early process in ionization is geminate recombination, and the same process occurs in the exciton fission process.

As for the problem of producing small volumes in which to generate the triplet excitons, several techniques are available. One could grow small crystallites inside frozen glasses, or evaporate incomplete films of tetracene on a suitable substrate or disperse tetracene crystals of colloidal size inside a suitable medium. The method we used was to try to divide the tetracene crystal into small cells or cages by means of exciton reflecting molecules. This technique is a variation of one used by Hochstrasser and Whiteman<sup>4</sup> in their work with "one-dimensional" crystals. In anthracene and tetracene, the  $ab$  planes are relatively distant from each other as compared with the  $ac$  and  $bc$  planes, so the short range  $T$  exciton migration tends to be confined in a given  $ab$  plane. Although no measurement has been made yet on the anisotropy of the  $T$  exciton in the  $ab$  plane in tetracene, calculations have shown that this diffusion should be essentially isotropic.<sup>5</sup> In the present study we have doped tetracene with 2,3 benzocarbazole (BC) in order to construct an approximately two-dimensional system with  $T$  exciton reflectors. None of the low-lying excited electronic states of BC is accessible from either low-lying excited electronic state of tetracene. The  $T$  energy level of 2,3 benzocarbazole (BC) lies at  $18\,200\text{ cm}^{-1}$  (2.26 eV),<sup>6</sup> which is 1 eV higher than the tetracene  $T$  energy (1.27 eV) and is just below that of the singlet level of tetracene ( $\sim 2.35\text{ eV}$ ).<sup>2</sup> It is highly improbable that there is significant inter-system crossing from a tetracene singlet to a BC triplet since the transition singlet (tetracene)-triplet (BC) is spin forbidden. In addition, the competing reaction of host singlet exciton hopping is fast, in all likelihood exceeding  $10^{13}\text{ sec}^{-1}$ . The singlet level of BC lies at 3.2 eV,<sup>7</sup> which is thermally inaccessible to the tetracene singlet exciton. Most important, BC was chosen because there was a good likelihood that it would form solid solutions with tetracene; this compound is virtually impossible to remove from tetracene by vapor zone refining.<sup>8</sup> The concentrations we used were 7, 14, 29, and 50 mol%. This use of a solid solution of BC in tetracene has the virtue of simplicity of preparation, but it has drawbacks. The cages that are formed are not completely isolated, so a good deal of leakage of excitons out of one cage into another can occur. Obviously, this reduces the magnitude of the effect to be expected. In addition, as will be discussed, the mere replacement of tetracene molecules by BC molecules

has an effect that mimics exciton caging, and must be accounted for.

The principle of the experiment was to generate  $T$  exciton pairs inside the cells of the BC/tetracene system and to study the recombination process by measuring both the changes in the lifetime of the prompt fluorescence, and the changes in the fluorescence efficiency of the mixed crystal. In the mixed crystal, the generation of  $T$  exciton pairs inside a small domain should enhance geminate recombination and hence tend to increase the lifetime of the total singlet exciton population. In neat tetracene crystal it is shown that the fluorescence efficiency increases with increasing light intensity, reaching a maximum ( $F^H$ ) of about 2.9<sup>9</sup> times the low light intensity ( $F^L$ ) value. This increase in fluorescence efficiency is caused by the fusion of the  $T$  excitons produced in the singlet exciton fission process.<sup>10</sup> In effect, the high  $T$  exciton concentration partially blocks the fission channel and thereby increases the fluorescence efficiency. If exciton caging exists, the effective concentration of  $T$  excitons inside the cage should be high enough to produce a heightened recombination and hence an increase in the prompt fluorescence efficiency *even at low incident light intensity*. The net effect of this caging would manifest itself as a decrease in the ratio  $F^H/F^L$ , and an increase in the lifetime of the singlet exciton. Finally, in view of the fact that incompletely isolated small domains were being studied, it was important to determine whether it was possible in principle for such systems to demonstrate caging. It is conceivable that leaky cages could have the opposite effect of reducing geminate recombination. To investigate this possibility, we constructed what we considered to be a realistic, simple computer model of exciton fission and fusion processes in mixed BC/tetracene crystals, and obtained results that could then be compared with the experimental findings. Good quantitative agreement was found between the simulation, the kinetic analysis, and the experimental results, thus supporting the notion that exciton caging occurs.

## II. EXPERIMENTAL

To prepare the 2,3-benzocarbazole/tetracene mixtures, vapor zone refined powder of the two materials were introduced into a Pyrex glass capsule which was then evacuated to  $5 \times 10^{-5}$  torr, and sealed off. The various mixtures were then heated in an oven at 220 °C and allowed to remain at this temperature for 10 h. After this period the oven was turned off and the encapsulated material cooled to room temperature in 2 h. The various compositions were prepared by weighing the BC and tetracene powders to a precision of 2%. The largest concentration of BC was 50%.

Measurements were made of the following:

1. quantum efficiency of fluorescence as a function of light intensity;
2. the prompt fluorescence lifetime at room temperature and 77 °K;
3. fluorescence emission spectra;
4. delayed fluorescence lifetime.

The techniques used for each of these measurements are described below.

The relative quantum efficiency was calculated from the ratio of the intensity of the luminescence to that of the incident excitation. The incident excitation was provided by an argon laser at 4880 Å and monitored by a 1P21 photomultiplier through neutral density filters. The intensity of the excitation was varied in a similar manner to that employed by Ern *et al.*<sup>9</sup>

The fluorescence emission spectra were measured with a Hitachi Fluorescence Spectrophotometer (MPF-2A). Because the samples were in the form of powders, the fluorescence spectra were measured from the front surface at right angles to the direction of the excitation. All spectra were corrected for the sensitivity of the emission monochromator and photomultiplier.

The delayed fluorescence lifetime was computed from the relatively long-lived decay in the tail of the prompt fluorescence. The sample excitation was provided by an argon laser at 4880 Å followed by a high speed mechanical chopper with a turn-off time of about 15 μsec.

The technique for direct measurement of the lifetime of the prompt fluorescence has been discussed previously.<sup>11</sup>

### III. RESULTS

#### A. Fluorescence efficiency measurements

As may be seen in Fig. 1, the expected decrease in the ratio  $F^H/F^L$  with increasing BC concentration is observed. In addition, the light intensity at which the fluorescence efficiency starts to rise tends to increase as the BC concentration increases. This is to be expected if caging occurs because the effective concentration of  $T$  excitons inside the cages at any given light intensity is what normally would be encountered at higher light intensities in neat crystals; it is therefore necessary to go to even higher light intensities in order to generate a  $T$  exciton density in excess of that already present in the cages. However, there are other pro-

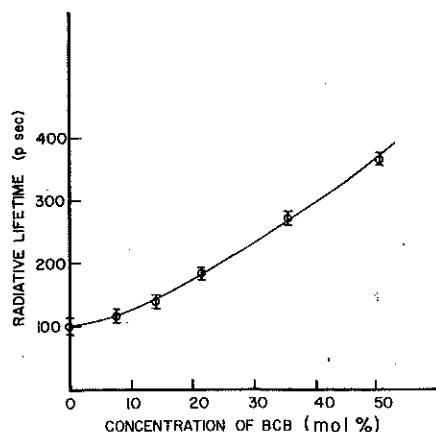


FIG. 2. Lifetime of the prompt fluorescence vs BC concentrations.

cesses that could produce the same effects. Thus, the trapping of singlet excitons can prevent their fission, but still permit them to decay radiatively with a higher fluorescence efficiency; trapping can account for at least part of the decrease in the ratio  $F^H/F^L$  shown in Fig. 1 and also accounts for the reduced ratio of 2.15 for  $F^H/F^L$  in the neat crystals instead of 2.9.<sup>9</sup> The trapping effect must therefore be evaluated and this is best done by specifically including trapping in the kinetic equations.

#### 1. Kinetic analysis of steady-state fluorescence in BC/tetracene crystals including trapping

The work of Smith and Weiss<sup>12</sup> (hereinafter referred to as SW) on tetracene single crystals and evaporated films showed that there are two fluorescing states, one of which was fast (~300 psec) and the other slow (~12 nsec). In our own work, we verified the observation of the two lifetimes, except that our technique for measuring the fast lifetime was more direct and precise and did not depend upon a convolution of source response function with the fluorescence response function. As may be seen in Fig. 2, the fast fluorescing state of

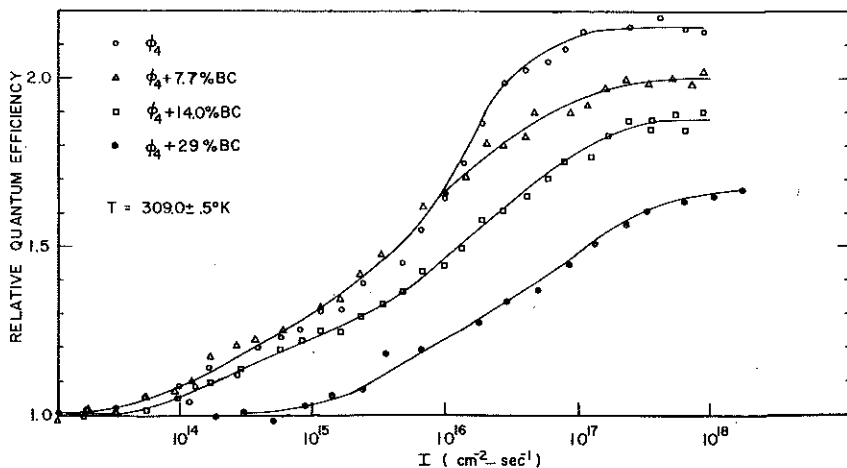
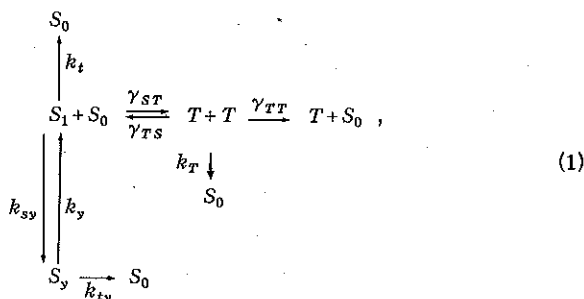


FIG. 1. Relative quantum efficiency  $F^H/F^L$  vs excitation intensity for four concentrations of BC in tetracene ( $\phi^4$ ) powder samples.

the neat tetracene had a lifetime of 100 psec. From temperature studies, SW also determined that the energy of separation of the two fluorescing states was  $440 \text{ cm}^{-1}$ ; they assumed that the lower energy state had the 12 nsec lifetime, and did not fission. SW also assumed that the trap was present in low concentration and was filled by energy transfer from the host, rather than by direct optical pumping. It may be that the trap is an excimer state with a binding energy of  $440 \text{ cm}^{-1}$ . In the kinetic scheme developed below, we use a single trapping site in addition to the other assumptions employed by SW. An experimental check on the validity of the hypothesis of a single trapping site would be the relative independence of the low temperature lifetime on the concentration of BC. At low temperatures, fission is frozen out, leaving only the radiative, nonradiative, and trapping modes to deplete the excited singlet excitons. As will be seen, this low temperature lifetime is relatively insensitive to the BC concentration.

The overall reaction may be written as



where  $S_1$ ,  $S_0$ ,  $T$ ,  $S_y$  are, respectively, the first excited singlet state, ground state, first excited  $T$  state, and trapped singlet state;  $\gamma_{ST}$  is the singlet fission rate constant;  $\gamma_{TS}$ ,  $\gamma_{TT}$  are, respectively, the fusion rate constants that form singlet and triplet states;  $k_t$  is the total rate constant for the decay of the tetracene singlet exciton excluding fission (includes radiative  $k_r$ , and nonradiative  $k_{nr}$ );  $k_{sy}$  is the rate constant for trapping the singlet exciton;  $k_y$  is the rate constant for detrapping the trapped singlet exciton;  $k_{ty}$  is the total rate constant for the decay of the trapped singlet exciton (includes radiative  $k_r$ , and nonradiative  $k_{nr}$ );  $k_T$  is the unimolecular decay rate for  $T$ . Note should be made of the fact that no account is taken of the process



in which a lone  $T$  exciton is generated by the geminate recombination of the correlated  $TT$  pair after spin relaxation has occurred. It is therefore assumed that out-of-plane hopping is fast compared to the spin relaxation of the pair state, which appears to be the case for anthracene.<sup>13</sup>

Under steady-state conditions, in one dimension, it can be shown that at high light intensity, where the  $T$  concentration is determined only by the  $T+T$  fusion rate, the quantum efficiency of fluorescence from the higher energy state for impurity concentration  $x$ ,  $F_x^H$  is

$$\begin{aligned}
 F_x^H &= \frac{k_r \int_0^\infty [S_1] dz}{I_0^H} \\
 &= \frac{k_r}{\gamma_{ST}[S_0] \left[ 1 - 2\gamma_{TS}/(\gamma_{TT} + 2\gamma_{TS}) \right] + k_t + k_{sy} \left[ 1 - k_y/(k_y + k_{ty}) \right]}, \quad (3)
 \end{aligned}$$

where  $k_r$  is the radiative rate constant from the upper state, and the intensity distribution  $I(z)$  is taken to be  $I_0^H e^{-\alpha z}$ . The superscript  $H$  denotes high light intensity at room temperature. Finally, a quantity  $f$  will be defined as

$$f = 2\gamma_{TS}/(\gamma_{TT} + 2\gamma_{TS}). \quad (4)$$

In the work of Ern *et al.*,<sup>9</sup>  $f$  is defined as a branching ratio for the formation of singlets from the exciton fusion reaction, and the expression (4) connects the nomenclature adopted in this paper to that used by Ern *et al.*<sup>9</sup>

Similarly, for the case of trapped singlet exciton, the quantum efficiency of fluorescence is

$$F_y^H = \frac{k_{ry} \int_0^\infty [S_y] dz}{I_0^H} = \frac{k_{ry} k_{sy}}{k_{ty} + k_y} \frac{F_x^H}{k_r}, \quad (5)$$

or

$$F_x^H + F_y^H = \left( 1 + \frac{k_{ry} k_{sy}}{k_r (k_{ty} + k_y)} \right) F_x^H. \quad (6)$$

At low light intensity where there is essentially no delayed fluorescence contribution to the total fluorescence, it can be shown that

$$F_x^L = \frac{k_r}{\gamma_{ST}[S_0] + k_t + k_{sy} \left[ 1 - k_y/(k_y + k_{ty}) \right]} \quad (7)$$

and

$$F_y^L = F_x^L \left( \frac{k_{ry} k_{sy}}{k_r (k_{ty} + k_y)} \right). \quad (8)$$

Here the superscript  $L$  refers to low light intensity at room temperature. Combining Eqs. (7) and (8), and using Eq. (6), one forms the ratio

$$\frac{F_x^H + F_y^H}{F_x^L + F_y^L} = \frac{\gamma_{ST}[S_0] + k_t + k_{sy} \left[ 1 - (k_y/k_y + k_{ty}) \right]}{\gamma_{ST}[S_0] (1-f) + k_t + k_{sy} \left[ 1 - k_y/(k_y + k_{ty}) \right]}, \quad (9)$$

$$\frac{F_x^L + F_y^L}{F_x^H + F_y^H} = 1 - \frac{\gamma_{ST}^x [S_0] f}{\gamma_{ST}^x [S_0] + k_t + k_{sy} \left[ 1 - k_y/(k_y + k_{ty}) \right]}. \quad (10)$$

In Eq. (10), special superscripts have been added to the quantities which are dependent on BC concentrations. The superscript  $x$  on  $\gamma_{ST}^x$  in Eq. (10) indicates that this quantity is *expected* to vary with BC concentration. The superscript  $\gamma$  on  $[S_0]$  indicates that no correction has been made for the replacement affect (described in Sec. III. C).

The quantity to the left of the equality sign in Eq. (10) is measured in the steady-state experiment. The results are shown in Fig. 1. The quantity  $(\gamma_{ST}^x [S_0] + k_t + k_{sy})^{-1}$  is measured as the room temperature fluorescence lifetime (see Sec. III. B). The quantity  $(k_t + k_{sy})^{-1}$  is measured at low temperatures as a fluorescence lifetime (see Sec. III. B),

TABLE I. Fluorescence lifetime and relative quantum efficiency measurements in BC/tetracene mixed crystals.

	A	B	C <sup>a</sup>	D <sup>b</sup>	E <sup>c</sup>	F <sup>d</sup>	G <sup>e</sup>
BC <sup>f</sup> (mol%)	Fluorescence decay rate (298°K)(sec <sup>-1</sup> × 10 <sup>9</sup> )	Fluorescence decay rate (77°K)(sec <sup>-1</sup> × 10 <sup>9</sup> )	Fission rate uncorrected (A - B)(sec <sup>-1</sup> × 10 <sup>9</sup> )	Replacement effect factor (σ <sup>x</sup> )/⟨σ <sup>0</sup> ⟩	Fission rate corrected (C × D)(sec <sup>-1</sup> × 10 <sup>9</sup> )	F <sup>h</sup> /F <sup>i</sup>	Branching ratio <i>f</i>
0	10 ± 1	1.9 ± 0.3	8.1 ± 0.8	1	8.1 ± 0.8	2.15	0.66 ± 0.09
7.7	8.7 ± 1	(1.7 ± 0.2) <sup>g</sup>	(7.0 ± 0.2) <sup>b</sup>	1.06	(7.4 ± 0.8)	2.0	(0.62 ± 0.1)
14.0	7.2 ± 0.7	1.5 ± 0.2	5.7 ± 0.6	1.14	6.5 ± 0.7	1.88	0.6 ± 0.1
29	4.5 ± 0.5	1.4 ± 0.2	3.1 ± 0.3	1.33	4.1 ± 0.4	1.7	0.6 ± 0.1
50	2.8 ± 0.3	...	...	...	...	...	...

<sup>a</sup>Column C: The fission rate (uncorrected for replacement) is found by subtracting the result in Column B from that in Column A.

<sup>b</sup>Column D: Replacement effect factor is calculated from a computer simulation of exciton fission; see Sec. III, C and Table II for details.

<sup>c</sup>Column E: These data are produced by multiplying C × D; the data are thereby corrected for replacement effect.

<sup>d</sup>Column F: This is the ratio of the total steady-state fluorescence at high light intensity to that at low light intensity. See Fig. 2.

<sup>e</sup>Column G: This is calculated from experimental data in A, B, using Eq. (15) and F; see Sec. III, A for definition of terms.

<sup>f</sup>BC = 2,3-benzocarbazole.

<sup>g</sup>This decay rate was obtained by interpolation between the 0% and 7.4% BC values. All values depending on this decay rate are placed in parentheses.

$$k_y = k_{sy} \exp(-E_y/kT); \quad E_y = 0.055 \text{ eV.} \quad (11)$$

The values for  $k_{sy}$  and  $k_y$  at room temperature will be taken from the work of SW. These values are  $k_{sy} = 2 \times 10^8 \text{ sec}^{-1}$  and  $k_y = 3 \times 10^7 \text{ sec}^{-1}$ .

We shall use Eq. (10) to calculate a value of  $f$  for three BC concentrations. The value for the denominator in the fraction on the right in Eq. (10) is given in Table I, Column A neglecting the contribution of the term  $k_{sy}k_y/(k_y + k_{ty})$ . It should be noted that the fluorescence lifetimes are measured in a time too short to permit trap filling equilibrium, so the term  $k_{sy}k_y/(k_y + k_{ty})$  was evaluated from the data supplied by SW, where  $k_{sy} = 2 \times 10^8 \text{ sec}^{-1}$ ,  $k_y = 3 \times 10^7$ , and  $k_{ty} = 8 \times 10^7 \text{ sec}^{-1}$ . In general, the correction to the fluorescence rate constant measurement was insignificant, being about  $0.01 \times 10^9 \text{ sec}^{-1}$  or about 1% of the fluorescence rate.

For the four concentrations used,  $f$  is a constant to within the experimental error. This is shown in Table I, Column G. For the neat tetracene,  $f = 0.66 \pm 0.09$ , in excellent agreement with the work of Ern *et al.*,<sup>9</sup> who obtained a value of  $f = 0.66 \pm 0.06$  for a single crystal. The magnitude of  $f$ , and its independence on BC concentration, has important implications, which we discuss in Sec. IV, A.

## B. Lifetime measurements

As may be seen in Fig. 2, there was a substantial increase in the lifetime of the prompt fluorescence in going from the neat sample (100 psec) to the 50% sample (360 psec). However, there are other processes that could produce these same effects that have nothing to do with caging. For example, the mere replacement of tetracene molecules by BC molecules diminishes the opportunity for tetracene to find a fission partner. This so-called replacement effect produces an increased singlet exciton lifetime and must be accounted for.

In terms of the definition given in Sec. III, A, the

fluorescence lifetime at room temperature  $\tau_h^x$  can be written as

$$(\tau_h^x)^{-1} = \gamma_{ST}^x [S_0^*] + k_t + k_{sy}. \quad (12)$$

The excitation pulsewidth is so narrow ( $\sim 5$  psec) and the entire measurement time so short ( $< 10^{-9}$  sec) that the detrapping rate constant  $k_y$  can be neglected. The term  $\gamma_{ST}^x [S_0^*]$  is the overall fission rate and includes all processes leading to a disappearance of  $S_1$  by fission. At low temperatures (77°K), this term is negligible. The lifetime at low temperature is thus given by

$$(\tau_h^x)^{-1} = k_t + k_{sy}. \quad (13)$$

By subtracting Eq. (13) from Eq. (6) for each BC concentration, one obtains the results shown in Column C in Table I. The values of  $\gamma_{ST}^x [S_0^*]$  so obtained contain the replacement factor (indicated by the presence of the superscript  $r$  on the  $S_0$ ) and the caging factor (indicated by the superscript  $x$  on  $\gamma_{ST}^x$ ). The replacement factor is estimated as described in Sec. III, C, and its values are recorded in Column D of Table I.

The caging factor is defined as the quantity

$$1 - \frac{\gamma_{ST}^x [S_0^*]}{\gamma_{ST} [S_0]} = \text{caging factor} = K, \quad (14)$$

where the asterisk superscript indicates that a correction has been made for the replacement effect. The experimentally inferred caging factors are given in Column D in Table IV. For complete caging,  $K = 1$ ; for no caging,  $K = 0$ .

## C. Computer simulation

### 1. Estimation of replacement effect in fission of tetracene singlet exciton in BC/tetracene crystals

In order to get an estimate of the effect of replacing fissionable tetracene molecules in the crystal by BC molecules we resorted to computer modeling of fission in the BC/tetracene system. We constructed a planar grid consisting of 22 801 sites, upon which we placed a random distribution of BC molecules in the appropriate

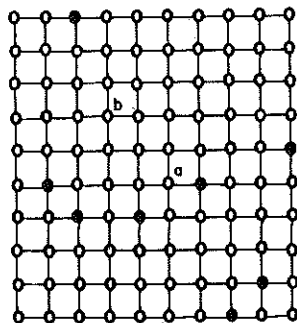


FIG. 3. Random distribution of BC molecules in a simulated tetracene crystal. The solid circles represent the BC molecules and the open circles represent the tetracene molecules.

mol fraction. A small sample of this grid is shown in Fig. 3, where the BC molecules are represented by solid circles and the tetracene molecules by the open circles. The straight lines represent the only directions in which triplet excitons can hop.<sup>13</sup> Singlet excitons are not restricted to a hopping process and move by a longer range dipole-dipole process. In this com-

puter simulation, singlet excitons were generated at random on a tetracene site anywhere in the grid, and they had a choice of fissioning, transferring, or decaying (radiatively or nonradiatively as represented by  $k_f$ ). The fission rate was taken to be about 10 times the decay rate, as is approximately the case found experimentally. Trapping was ignored because trapped singlet excitons decay *in situ*. This effect is corrected by the low temperature lifetime measurement. The coherent transfer rate was assumed to be approximately 100 times the fission rate, although this rate is not crucial in determining the replacement effect. The singlet exciton was permitted to transfer at random to any tetracene molecule within a radius of about four sites until it either fissioned or decayed. A singlet exciton landing on site *a* in Fig. 3 had a fission probability three-quarters that of site *b*.

The number of steps to fission is a measure of the fission rate constant, and in the absence of caging effects the replacement effect factor is defined as

$$\text{Replacement effect factor} = \frac{\text{number of steps to fission in mixed crystal}}{\text{number of steps to fission in a pure crystal}} = \frac{\langle \sigma^x \rangle}{\langle \sigma^0 \rangle} \quad (15)$$

The replacement effect factors determined in this manner are given in Table II. By multiplying the estimated fission rate  $\gamma_{ST}^x[S_0^*]$  by the replacement factor, one arrives at the fission rate normalized to zero replacement effects  $\gamma_{ST}^x[S_0^*] = (\langle \sigma^x \rangle / \langle \sigma^0 \rangle) \times \gamma_{ST}^x[S_0^*]$ . As can be seen in Column E of Table I, replacement effects are not sufficiently large to account for the observed effect of BC on the singlet exciton lifetime (Column C).

## 2. Simulation of triplet-triplet geminate recombination in BC/tetracene crystal

In simulating the geminate recombination process, the same kind of grid is used as is shown in Fig. 3. A

singlet exciton fissions in a randomly chosen portion of the grid. The two *T* excitons formed by fission start out on neighboring sites and each hops randomly to any other available molecular sites. One step consists of a hop by one *T* exciton followed by a hop by the other. A collision occurs if the *T* excitons land on neighboring sites after they start out from their points of origin. A game consists of permitting the fission pair of *T* to hop around until they recollide or die. A death is defined as an out-of-plane hop by one of the *T* excitons. The choice of the ratio of the average number of hops within the plane to the number out of the plane is an important assumption in the simulation. The average game length was chosen to satisfy some physically

TABLE II. Computer simulation of replacement factor.

BC (mol)	Number of singlet excitons generated	Number of fissions	Number of decays	Average number <sup>a</sup> of steps to fission $\langle \sigma^x \rangle$	Replacement effect <sup>b</sup> factor $\langle \sigma^x \rangle / \langle \sigma^0 \rangle$
0	10 000	9146	854	101.27	1
	1 000	916	84	102.58	
	2 000	1814	186	99.31	
			Mean	101 ± 1	
7.5	2000	1825	175	105.26	1.06
	2000	1801	199	108.09	
				Mean	
13.5	2000	1788	212	116.29	1.14
	2000	1803	197	113.17	
				Mean	
28	2000	1760	240	135.67	1.33
	2000	1747	253	131.47	
				Mean	

<sup>a</sup>  $\langle \sigma^x \rangle$  = Average number of steps to fission in crystal of BC mol fraction *x*.

<sup>b</sup> Replacement effect factor =  $\frac{\text{fission rate in pure crystal}}{\text{fission rate in mixed crystal}} = \frac{\text{Steps to fission in mixed crystal}}{\text{steps to fission in neat crystal}}$ .

TABLE III. Computer simulation of geminate recombination of correlated triplet exciton pair state.

BC (mol%)	A <sup>a</sup> Number of (TT) generated = (games)	B <sup>b</sup> Number of games ending in collision $\bar{s}_c^2$	C <sup>c</sup> Number of games ending in (TT) dissociation $\bar{s}_d^2$	D <sup>d</sup> Average number of steps to collision $\langle s^2 \rangle$	E <sup>e</sup> Average number of steps per game	F <sup>f</sup> $\langle s^2 \rangle / \langle s^2 \rangle$	G <sup>g</sup> $\langle s_d^2 \rangle / \langle s_c^2 \rangle$	H <sup>h</sup> $\langle s_d^2 \rangle / \langle s_c^2 \rangle$
100 Step Game Length								
0	50 000	42 572	7428	5.36 ± 0.1	19.57	1.00	1.00	1.00
7.5	40 000	34 474	5526	4.97 ± 0.02	18.24	0.92	0.74	0.93
13.5	40 000	35 182	4818	4.63 ± 0.05	16.24	0.86	0.65	0.83
28	40 000	36 983	3017	4.09 ± 0.06	11.40	0.76	0.41	0.58
500 Step Game Length								
0	40 000	35 291	4709	13.89 ± 0.64	71.23	1.00	1.00	1.00
7.5	40 000	35 929	4071	12.75 ± 0.12	62.44	0.92	0.86	0.88
13.5	40 000	36 290	3710	11.69 ± 0.3	57.07	0.84	0.79	0.80
28	40 000	37 833	2167	9.20 ± 0.2	35.84	0.66	0.46	0.50
1000 Step Game Length								
0	40 000	35 797	4203	22.55 ± 0.32	125.36	1.00	1.00	1.00
7.5	40 000	36 298	3702	20.67 ± 0.35	111.40	0.92	0.88	0.89
13.5	40 000	36 750	3250	19.07 ± 0.66	98.85	0.85	0.77	0.79
28	35 000	33 225	1775	13.07 ± 0.32	63.13	0.58	0.48	0.50

<sup>a</sup>Column A: A game starts when a (TT) pair is generated on neighboring sites. See Fig. 4 for lattice description. The length (maximum number of steps permitted) of the particular game is shown at the heading for each group of data.

<sup>b</sup>Column B: A collision results when the triplet excitons land on neighboring sites; game stops.

<sup>c</sup>Column C: These games ended in (TT) dissociation prior to any collision.

<sup>d</sup>Column D: The collision precedes a dissociation.

<sup>e</sup>Column E: These include games that end both in collision and in dissociation prior to collision.

<sup>f</sup>Column F: Relative number of steps to a collision in mixed crystal (prior to a dissociation) compared with neat crystal results.

<sup>g</sup>Column G: Ratio of number of games ending in dissociation (prior to collision) in neat crystal to those in mixed crystal.

<sup>h</sup>Column H: Ratio of average number of steps per game (Column E) in mixed crystal to that in neat crystal.

reasonable bound.

It has been estimated from indirect experiments that the anisotropy of the triplet exciton diffusion  $D_{ab}/D_c$  in tetracene is approximately 200<sup>11</sup> and the hopping time in the *ab* plane is approximately 10<sup>-13</sup> sec.<sup>11</sup> On the basis the rate of hopping out of the *ab* plane would be about 5 × 10<sup>10</sup> sec<sup>-1</sup>. This rate is an order of magnitude faster than the time for the pair-state spin character to relax in anthracene.<sup>13</sup> This relatively fast out-of-plane hopping rate in tetracene implies that the correlation time of the pair state will be controlled by out-of-plane hopping. Therefore, the number of steps per game was chosen to be of the order of magnitude of the diffusion anisotropy; thus, game lengths of 100, 500, and 1000 steps were chosen in order to check the effect of game length variations.

When the particles (*T* excitons) hop, they can either undergo a geminate recombination before the execution of *L* steps (whereupon the game stops, and the number of steps to collision is recorded), or the particles may hop out of the plane before recombining. The latter process results in a death in *L* steps. The results of this computer simulation are shown in Table III.

#### D. Fluorescence emission spectra

In view of the high concentrations of BC that are added to the tetracene, and the accompanying possibility of lattice distortions and trapping, it would be expected that there would be observable changes in the

absorption and emission spectra. We did not make any absorption spectrum measurements because the sample was in the form of a powder for which light scattering effects were large. Fluorescence emission spectra were taken, and a comparison of the spectra of the neat and mixed crystals in Fig. 4 does not show any large differences.

The association of a red shift in the fluorescence spectrum in tetracene with a decrease in the fission rate is found in high pressure experiments.<sup>14</sup> Although adding BC to tetracene does measurably decrease the fission rate, a red shift in the fluorescence spectrum is not observed. The lack of such an association is therefore evidence that the decrease in the fission rate is not caused by energy level displacements associated with a strained lattice.

#### E. Lifetime of the delayed fluorescence

The lifetime of the delayed fluorescence is equivalent to half the *T* lifetime and is therefore sensitive to *T* quenching. Since the quenching of a member of the pair of geminate triplets would certainly increase the overall fission rate, it is important to investigate the triplet lifetimes for various concentrations of BC.

The delayed fluorescence lifetimes of samples with BC concentrations of 0%, 14.0%, and 21.6% were found to be 17.5 ± 1.0, 19 ± 2, and 20 ± 2 μsec, respectively. All of these measurements are consistent with a *T* lifetime of 36 μsec. Since the prompt fluorescence mea-

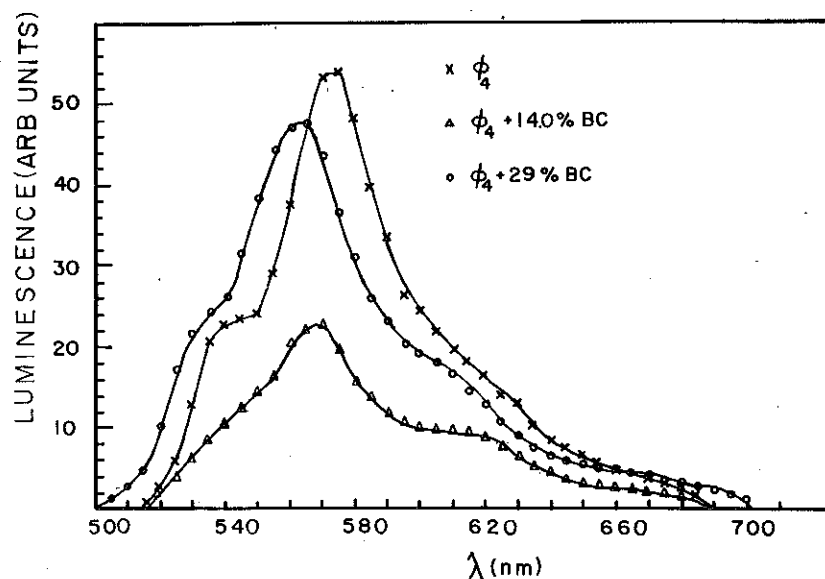


FIG. 4. Fluorescence emission spectra for three concentrations of BC in tetracene ( $\phi^4$ ). The relative magnitudes of the fluorescence intensities between various concentrations of BC are unrelated.

measurements at room temperature are made in less than 1 nsec after excitation,  $T$  quenching with a time constant of 36  $\mu$ sec is too slow to affect the measured prompt fluorescence lifetimes. Therefore we may conclude that the lowering of the overall fission with added BC concentration is not due to the destruction of geminate pairs by triplet quenching.

#### IV. DISCUSSION

The prompt fluorescence lifetime measurements shown in Fig. 2 and the measurements of the steady-state intensity dependence of the fluorescence quantum efficiency shown in Fig. 1 are consistent with what would be expected if the  $T$  exciton pairs produced by singlet exciton fission were forced to undergo enhanced geminate recombination because of spatial constraints on their motion. This conclusion is based on an analysis of the kinetics of the steady-state fluorescence experiments including the lifetime measurements, and a computer simulation of the caging process. We shall present the kinetic analysis first.

##### A. Kinetic scheme

In Sec. III. A, a kinetic scheme was presented for the analysis of the steady state fluorescence and its light intensity dependence for different concentrations of BC. This scheme was based on the same assumptions as those employed by SW.<sup>12</sup> In conjunction with the lifetime data obtained as described in Sec. III. B, in addition to the data in Fig. 1, it is possible to calculate the branching ratio  $f$  using Eq. (10). As is seen in Table I, Column G, the branching ratio  $f$  is constant within experimental error ( $\sim 16\%$ ) over the concentration range from the neat sample to a 29% BC mixture. The agreement between  $f$  for the neat sample (0.66) and that obtained by Ern *et al.*<sup>9</sup> for a pure single crystal (0.66) provides support for the validity of the kinetic scheme. The invariance of  $f$  with BC concentration has special meaning in tetracene because the magnitude of  $f$  is

somewhat anomalous. On the basis of simple spin statistics,  $f$  should have a value of 0.4, and this is the case with anthracene.<sup>15</sup> However, in the case of tetracene,  $f \approx 0.7$  implies that the actual ratio for the formation of singlets relative to triplets is not  $\frac{1}{3}$  but almost 1, which in turn implies that fewer  $T$  states, or more singlet states, or both, are being formed. There is reason to favor the conclusion that fewer triplets are being formed, because in tetracene, the  $T$  pair state ( $TT$ ) lies at 2.54 eV, which is above that of the singlet state at  $\sim 2.4$  eV but is very close to and may be below that of the crystal  $T_2$  state; in the tetracene molecule, the  $T_2$  state has been located at 2.56 eV.<sup>16</sup> If  $T_2$  lies above ( $TT$ ), then  $T_2$  can only be a final state for the fusion channel if one of the triplets is in a suitable vibronic state. On the other hand, passage from the ( $TT$ ) to the vibrationally excited  $T_1$  state would be inefficient because of unfavorable Franck-Condon factors. The overall effect of this disposition of energy levels would be to diminish the ratio of triplets formed relative to singlets.

Since  $f$  is relatively constant and the same as in the pure crystal, the results shown in Fig. 1 support the hypothesis of caging because the changes in the ratio of the fluorescence efficiencies  $(F_x^L + F_y^L)/(F_x^H + F_y^H)$  shown in Eq. (10) are therefore restricted to changes in the value of  $\gamma_{ST}^x$ . These changes have been attributed to the replacement effect and to the caging effect.

In summarizing, the kinetic analysis is supported by the essential constancy of  $f$  and its agreement with the pure crystal values. Based on the kinetic analysis, we have subtracted  $(\tau_T^x)^{-1}$  from  $(\tau_T^H)^{-1}$  (see Sec. III. A) to obtain  $\gamma_{ST}^x[S_0^x]$ , corrected this rate for replacement, and obtained the relative caging factors shown in Table IV, Column D. We now examine the results of the computer simulation.

In order to determine the connection between the computer simulated geminate recombination process and



TABLE IV. Comparison of computer simulated exciton caging effect with observed caging effect.

BC <sup>a</sup> (%)	A <sup>b</sup> Average number of steps to collision (s <sup>x</sup> )	B <sup>c</sup> (s <sup>x</sup> )	C <sup>d</sup> $\frac{\gamma_{ST}^x[S_0^*]}{\gamma^x[S_0]}$	D <sup>e</sup> Experimental caging factor K $1 - \frac{\gamma_{ST}^x[S_0^*]}{\gamma^x[S_0]}$	E <sup>f</sup> Simulated caging factor $1 - \frac{\langle s^x \rangle}{\langle s^0 \rangle}$
100 Step game length					
0	5.36	1	1	0	0
7.5	4.97	0.92	0.91 ± 0.1	0.09	0.08
13.5	4.63	0.86	0.80 ± 0.1	0.20	0.14
28	4.09	0.76	0.51 ± 0.1	0.49	0.24
500 Step game length					
0	13.89	1	1	0	0
7.5	12.75	0.92	0.91 ± 0.1	0.09	0.08
13.5	11.69	0.84	0.80 ± 0.1	0.20	0.16
28	9.20	0.66	0.51 ± 0.1	0.49	0.34
1000 Step game length					
0	22.55	1	1	0	0
7.5	20.67	0.92	0.91	0.09	0.08
13.5	19.07	0.85	0.80	0.20	0.15
28	13.02	0.58	0.51	0.49	0.42

<sup>a</sup>The concentration of BC is in mol % for computer simulated parameters and in mass % for parameters estimated from experiments. The mass % and mol % units are within 4% of each other.

<sup>b</sup>Column A: Same as Column D in Table III.

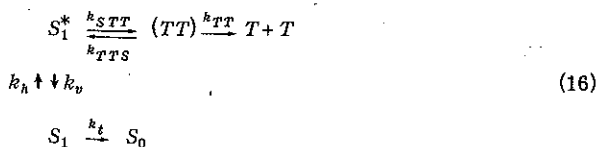
<sup>c</sup>Column B: Same as Column F in Table III.

<sup>d</sup>Column C: Same as Column E in Table I.

<sup>e</sup>Column D: Defined using data in Column C. Maximum error is ± 20.

<sup>f</sup>Column E: Defined using data in Column B. Average error is ± 4%; maximum error is 8%.

the experimental results, we construct the following kinetic scheme for an ideal BC/tetracene crystal:



where  $S_1^*$  is a vibrationally excited singlet state that is isoenergetic with the  $(TT)$  state;  $k_{STT}$  is the fission rate of  $S_1^*$ ;  $k_v$  is the vibrational relaxation rate of  $S_1^*$ ;  $k_h$  is the rate of thermal activation from  $S_1$  to  $S_1^*$ ;  $k_{TTs}$  is the rate of geminate collision of the correlated  $(TT)$  pair state. The other terms were previously defined in Sec. III. A. In the ideal mixed crystal there are no trapping sites. Keeping in mind that Eqs. (1) and (16) must coincide, the overall fission rate for this ideal mixed crystal can be expressed as

$$\gamma_{ST}^x[S_0^*] = k_h \frac{k_{STT}^*}{k_v + k_{STT}^* [k_{TT} / (k_{TT} + k_{TTs}^*)]} \frac{k_{TT}}{k_{TT} + k_{TTs}^*}, \quad (17)$$

where the asterisk superscript indicates that the replacement effect has been taken into account. In Eq. (17) one must note that the only rate constant that is sensitive to BC concentration is  $k_{TTs}^*$ . It will be assumed, following Suna,<sup>17</sup> that the out-of-plane hopping rate dominates the  $(TT)$  dissociation process; thus,  $k_{TT}$  is to be interpreted as an out-of-plane hopping rate. It is true that to some extent,  $k_{TT}$  is also affected by

the presence of reflecting sites in the planes that lie above and below the plane of exciton motion, but calculations have shown that this contribution is negligible. If  $k_{STT}^*$  is corrected for the replacement effect, then neither  $k_{STT}^*$  nor  $k_v$  nor  $k_h$  depends on the BC concentration.

As for the relative magnitudes of  $k_{TT}$  and  $k_{TTs}$ , these can be ascertained by referral to Column D in Table III. For the 100 step game and the 1000 step game, the number of steps between geminate collisions of a correlated  $(TT)$  pair is about 5 and 20, respectively. There are thus, on the average, about 20 geminate collisions/100 step game and 50 geminate collisions/1000 step game. By definition, the game length is determined by the out-of-plane hopping rate, so there is on the average only 1 out-of-plane hop/100 steps in plane. Since  $k_{TTs}$  is the geminate collision rate to yield the state  $S_1^*$  (not to be confused with the rate of forming  $S_1$ ), and  $k_{TT}$  is out-of-plane hopping rate, it appears that  $k_{TTs}^* \gg k_{TT}$ ; if, in addition,  $k_v > k_{STT}^* (k_{TT} / k_{TTs}^*)$ , then from Eq. (17) one gets

$$\frac{\gamma_{ST}^x[S_0^*]}{\gamma_{ST}^x[S_0]} = \frac{k_{TTs}^0}{k_{TTs}^x} = \frac{\langle s^x \rangle}{\langle s^0 \rangle}, \quad (18)$$

where  $\langle s^x \rangle$  and  $\langle s^0 \rangle$  are the average number of steps to collision in the mixed and pure samples, respectively, and where  $1/\langle s^x \rangle$  is directly proportional to the geminate collision rate. If instead of  $k_v > k_{STT}^* (k_{TT} / k_{TTs}^*)$  we used the relation  $k_v < k_{STT}^* (k_{TT} / k_{TTs}^*)$ , then in Eq. (17),  $\gamma_{ST}^x[S_0^*]$  would depend only on  $k_h$ . Since  $\gamma_{ST}^x[S_0^*]$  is known to be strongly magnetically sensitive<sup>10</sup> and  $k_h$  is not magnetically sensitive then  $k_v > k_{STT}^* (k_{TT} / k_{TTs}^*)$ . Furthermore,  $k_{STT}^*$  is magnetically sensitive, so our assumption regarding the relative magnitude of  $k_v$  in Eq. (17) is reasonable. In Eq. (18), the ratio on the left refers to an experimental measurement in an ideal crystal, but we shall use the experimental values shown in Column E, Table I, and the computed simulated values for  $\langle s^x \rangle / \langle s^0 \rangle$  from Column F, Table III, to construct Table IV. As may be seen in Table IV, for example, in the 1000 step game, the agreement between the simulated and experimental values is essentially within the experimental error of both methods. While it is gratifying to find this close qualitative and quantitative agreement between simulation and experiment for the 1000 step game, we do not feel that it is appropriate at this time to conclude that the 1000 step game length is what actually occurs in the real mixed crystal. What is evident in Table IV and in Fig. 5 is that there is excellent qualitative agreement and surprisingly good quantitative agreement between the predictions of caging in the simple computer simulation and in the real mixed crystal.

Since the computer simulation deals with an ideal crystal that excludes trapping, one must conclude that trapping plays a minor role in determining the experimental ratio of the fission rate constants. This is indeed the case, because the ratio of fission rate constants shown in Eq. (18) is about the same as the ratio of the total fluorescence rate constants (corrected for replacement effects). Another aspect of the derivation

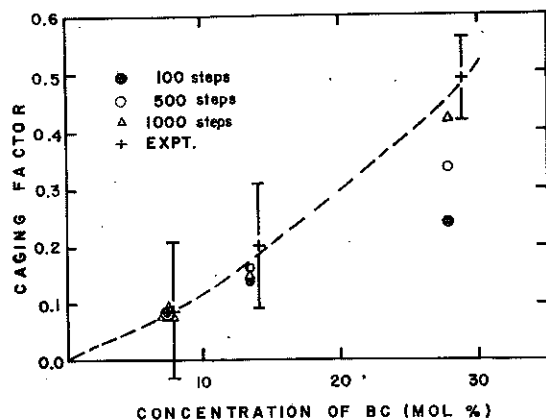


FIG. 5. Caging factor vs BC concentration. See text equation (19) for definition of caging factor.

of Eq. (18) is the requirement that the geminate recombination rate  $k_{TTS}$  be greater than the out-of-plane hopping rate  $k_{TT}$  and that  $k_v > k_{STT}^*(k_{TT}/k_{TTS}^*)$ . For the 1000 step game, as we have seen, the ratio  $k_{TT}/k_{TTS}^*$  is about 0.1. Using Eq. (17) and the assumption made on the magnitude of the terms therein, we arrive at

$$\gamma_{ST}^*[S_0^*] \approx k_h \frac{k_{STT}^*}{k_v} \frac{k_{TT}}{k_{TTS}^*} \approx 0.1 k_h \frac{k_{STT}^*}{k_v} \quad (19)$$

From the work of Alfano *et al.*,<sup>11</sup>  $\gamma_{ST}^0[S_0]$  is  $10^{10} \text{ sec}^{-1}$  at room temperature. Using this value in Eq. (19), we get  $k_h k_{STT}^*/k_v \approx 10^{11} \text{ sec}^{-1}$ ; this is about as much as one can deduce, assuming that the 1000 step game is a valid model of the real mixed crystal.

The comparison between the computer simulated and experimental caging factor in Fig. 5 provides strong support for the conclusion that we have observed two-dimensional triplet exciton caging in BC doped tetracene crystals. The slight shift in concentration between the experimental and computer simulated points in Fig. 5 is due to the fact that the experiments were done on samples having concentrations of  $X \text{ mass}\%$  and the simulation was for  $X \text{ mol}\%$ .

## V. CONCLUSIONS

In view of the agreement between the computer simulated process of two-dimensional triplet-exciton caging and the experimental results, we can draw the following conclusions:

1. The incorporation of 2,3-benzocarbazole in concentrations up to 28% into the tetracene crystal lattice creates a system of cells or cages that partially restricts the motion of triplet excitons without trapping them.
2. The motion of the triplet excitons is essentially two dimensional, being restricted to the  $ab$  plane. The assumption of one out-of-plane hop for every 1000 in-plane hops generates data that are in excellent agreement with the experimental results. Agreement is also good (within a factor of 2) for the assumption of 500 and 100 in-plane hops for every out-of-plane hop.

3. The geminate recombination of the triplet excitons produced by singlet exciton fission can be enhanced by almost 50% by caging the triplet excitons so that they are physically forced to remain spatially correlated.

4. The caging effect varies approximately linearly with BC concentration over the concentration 0%–29% BC.

5. The presence of BC molecules should normally act as a barrier to the geminate recombination of two  $T$  excitons because they block a site upon which fusion normally occurs. Nevertheless, it has been found that the addition of BC increases the geminate recombination rate. It must therefore be concluded that the improvement in the efficiency of geminate recombination produced by restricting the space in which the  $T$  excitons may diffuse has a greater effect than the decrease in efficiency of geminate recombination produced by blocking the fusion sites. This is an important result and is not one that could easily have been predicted.

6. As caging approaches 100%, the room temperature fluorescence lifetime of the mixed crystal approaches that of the low temperature fluorescence lifetime, i. e., exciton fission becomes inoperative.

7. The average number of steps to geminate recombination is approximately 5 in the case of 100 step game. Most recombinations take place quickly. In the 1000 step game, the average number of steps for geminate recombination is about 18. Under these circumstances, there can be as many as 4 or 5 lattice sites between the randomly hopping correlated excitons at some point during the evolution of the pair; this represents a distance of about 25–30 Å. If one member of this pair is quenched, then there is no longer any possibility for geminate recombination to restore the singlet state. Then the possibility exists that there will be enhanced quenching of singlet fluorescence induced by quenchers, such as trapped or free carriers. Such pseudo-three-body collisions may be important in the quenching of electroluminescence in tetracene and in other aromatic hydrocarbon crystals.<sup>18</sup>

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