Anomalous Excimer Fluorescence from Anthracene Derivatives crystallizing in Chiral Crystal Structures

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Summary Achiral anthracene derivatives crystallizing in excimer-forming, chiral crystal structures exhibit two excimer emissions; the high-energy emission may arise from molecules at the boundary between domains of opposite enantiomeric form.

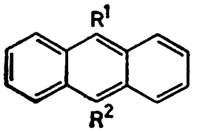
THE fluorescence spectra of excimer-emitting single crystals of known[1] structures of five anthracene derivatives were measured around 5 K. The results are summarized in the Table.

TABLE. Fluorescence of single crystals of various excimer-emitting anthracene derivatives.

Compound	Space group	Z	Excimer emission(s)[a] λ_{max}/nm	τ/ns
(**1**)	$P2_12_12_1$	4	552 520	156 70
(**2**) (β-form)	$P2_12_12_1$	4	515 490	70 30
(**3**) (α-form)	$P2_1/c$	4	540	123
(**4**)	$P2_1$/c	4	528	190
(**5**) (β-form)	$P\bar{1}$	2	538	95

[a] λ_{max} = wavelength of fluorescence maximum; τ = fluorescence lifetime. For compounds exhibiting two excimer emissions the emission listed first is the dominant one. Full crystal structures are known only for (**1**), (**4**), and (**5**); however, (**2**) and (**3**) are isostructural with (**1**) and (**4**) respectively.

It is seen that the two compounds crystallizing in the chiral space group[†] $P2_12_12_1$ exhibit two excimer emissions (broad, structureless emissions with large Stokes shifts and long fluorescence lifetimes) at low temperatures, while the three compounds crystallizing in either of the achiral space groups $P2_1/c$ or $P\bar{1}$ exhibit only one excimer emission at all temperatures. The existence of two overlapping emissions in the first two crystals is revealed by fluorescence polarization measurements and by observation of biexponential decay (see Figure). The relative contributions of the two excimer emissions were evaluated from the results of these measurements. In both cases where dual excimer emission was observed, the emission at shorter wavelength contributed 3—5% of the total integrated fluorescence intensity.



(**1**) R^1 = CN, R^2 = H
(**2**) and (**3**), R^1 = Cl, R^2 = H
(**4**) R^1 = Me, R^2 = H
(**5**) R^1 = R^2 = Cl

The anomalous (weaker) emission cannot arise from impurities owing to the absence of energy transfer at these temperatures[2] and the high purity of samples. Also, dual emission appears in only one of the two polymorphic forms of 9-chloroanthracene, which were grown from the same sample but using different solvents (see Figure).

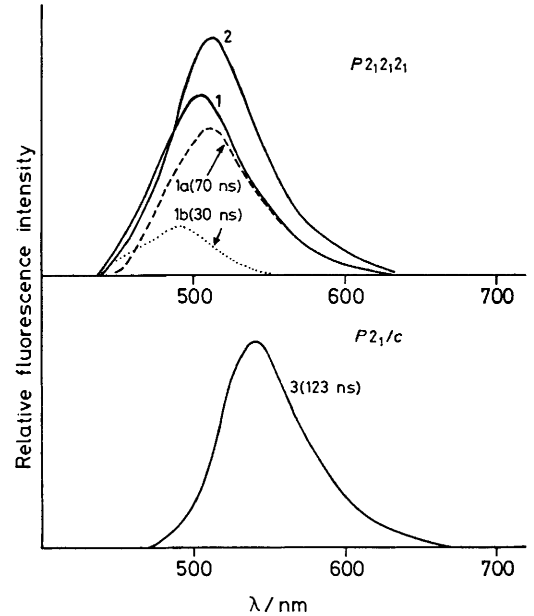


FIGURE. Fluorescence of 9-chloroanthracene (**2**) and (**3**) single crystals at 5 K grown from different solvents. Fluorescence lifetimes in nanoseconds are given in parentheses. The spectral distribution of fluorescence from orthorhombic β crystals (grown from methanol) depends on the polarization direction. The emissions polarized parallel and perpendicular to the crystallographic c axis are shown in curves 1 and 2 respectively. The fluorescence can be resolved into two excimer emissions of different lifetimes (curves 1a and 1b). Monoclinic α crystals (from hexane) exhibit a single monoexponential fluorescence whose bandshape is independent of polarization direction (curve 3).

Dual excimer fluorescence of 9-cyanoanthracene[3] and of racemic anthroates[4] have been reported previously.[‡] The weaker 9-cyanoanthracene excimer emission was later attributed to 'incipient *trans*-dimers'[6] but we suggest here an alternative more general explanation, similar to our proposals for the 9-anthroates.[4]

It has been shown[7] by electronic microscopic diffraction that single crystals of some inorganic molecules which pack in chiral space groups can consist of domains of enantiomorphous structure which cannot be distinguished by conventional X-ray diffraction. Although such direct verifica-

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[†] A space group whose symmetry operations do not involve inversions or reflections.

[‡] A recent time-resolved study[5] suggested that the fluorescence of 9-cyanoanthracene crystals also contains monomer fluorescence. Such emission was not observed in either steady-state fluorescence or decay time measurements of our samples, which were stored in the dark after purification. It is well known[3] that these crystals dimerize and emit monomer fluorescence upon irradiation.

tion of similar phenomena in organic crystals has not been reported, since racemic and enantiomerically pure β-phenylglyceric acid[8] and several optically active polymers[9] were shown to crystallize in the same chiral crystal structure, it was concluded that these racemates consist of enantiomorphous domains. In addition, low optical rotations from dissolved hexahelicene single crystals were shown[10] to result from lamellar growth of enantiomorphous domains in the crystals.

It is known also that excimer emission is very sensitive to external constraints such as the crystal packing, as demonstrated by the different excimer emissions of the two crystal forms of 9-chloroanthracene (see Figure), and as reviewed elsewhere.[11]

It is therefore suggested that the dominant excimer emission arises from the bulk of the crystal, and that the minor excimer emission may arise from possible interfacial regions between enantiomorphous domains. At high temperatures (above about 100 K) energy transfer in excimer-forming crystals is efficient[2] and thus only the lower-energy emission is observed. At lower temperatures, however, both emissions are present owing to inefficient energy transfer. Assuming the same absorption for all anthracene monomers and equal fluorescence quantum yields for the two excimers, we deduce from the 5 K spectrum that the average distance between two successive interfaces along the stack axis is about 50 unit cells, or about 200 Å.

We believe that such a domain structure in chiral molecular crystals is not rare. However, unequivocal confirmation of this in organic crystals is thus far lacking.

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