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# FRACTAL-LIKE EXCITON TRANSPORT AND FUSION IN DISORDERED NAPHTHALENE*

Laurel A. HARMON and Raoul KOPELMAN
Department of Chemistry, The University of Michigan, Ann Arbor, MI 48109

Steady-state fluorescence and phosphorescence spectra of semi-crystalline naphthalene are presented. Singlet and triplet exciton transport are strongly dependent on temperature and degree of annealing. Analysis of delayed fluorescence decays reveals fractal-like transport in the more disordered samples.

Spatially disordered molecular solids provide excellent examples of energy transport in energetically disordered media.[1] In pure semi-crystalline solids, differing molecular environments produce a distribution of site energies, disrupting resonance interactions. We report here spectroscopic studies of energy transport in disordered naphthalene.

High purity naphthalene (N-$h_8$) and perdeuteronaphthalene (N-$d_8$) were prepared by zone-refining and potassium fusion. Samples were formed by evaporation onto a quartz substrate (60-80 K) under reduced pressure. Annealing was accomplished by either warming to 130 K for 3-5 h or warming slowly to 175 K over 8-10 h, after which samples were recooled with liquid helium. Shuttered 1000 W Xenon arc lamp excited emission spectra (PAR model 1110 photon counter) and decays (PAR model 4202 signal averager) were collected via a 1 m Jobin Yvon double monochromator.

Emission from a freshly prepared sample of 100% naphthalene-$h_8$ is shown in Fig. 1. At low temperatures, fluorescence dominates; increasing temperature allows transport into defect sites which produce broad excimer emission as in polymeric films.[2] Singlet emission of a fresh film at liquid He temperatures is seen in Fig. 2 (bottom). With increasing temperature, the maximum of each vibronic band shifts to lower energy and the band broadens. The absorption does not change in this temperature regime; changes seen must be ascribed to increased transport populating lower energy sites. The upper trace of Fig. 2 shows the same band at 7.5 K after annealing. Most striking is the appearance of the BMN 0-0 peak, indicating the presence of domains in which transport is efficient enough to reach a $< 10^{-6}$ impurity. The annealed naphthalene vibronic band is shifted to slightly lower energy and the intensity reduced, as with increasing temperature.

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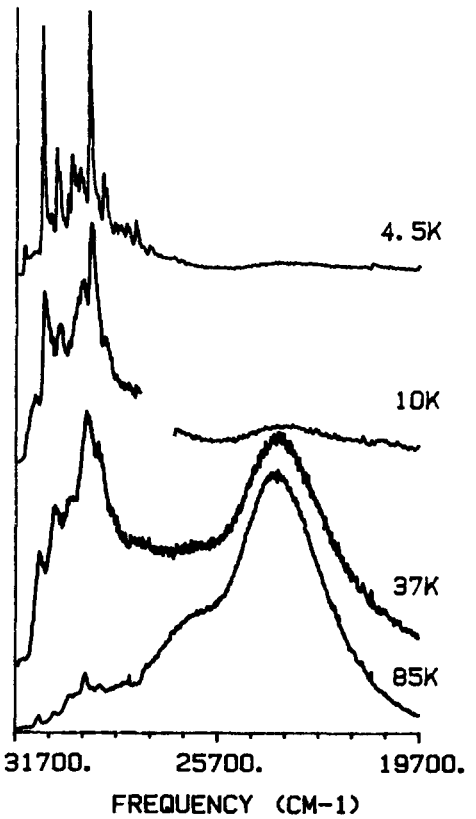


FIGURE 1
T-dependence of freshly-deposited 100% H-$h_8$ emission. Singlet excimer emission appears below 27,000 $cm^{-1}$.

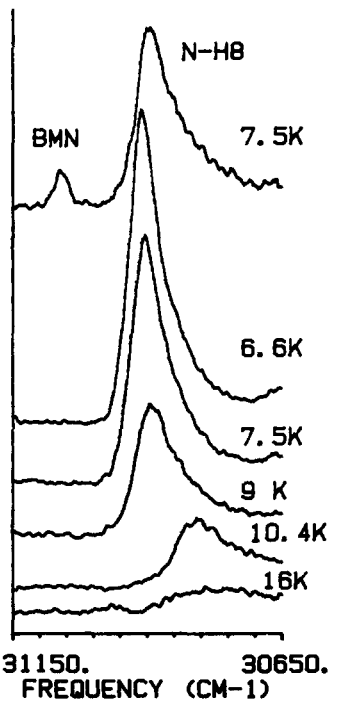


FIGURE 2
T-dependence of freshly-deposited (bottom five) and annealed (top) 100% N-$h_8$ vibronic ("512") emission. (BMN denotes β-methylnaphthalene impurity band.)

The other extreme of transport effectiveness is seen in phosphorescence from a 4.9% N-$h_8$ in N-$d_8$ sample at 5K, Fig. 3. In spite of the long triplet lifetime[2] and high concentration of the "trap" (N-$h_8$), 150 $cm^{-1}$ wide emission is observed only from the N-$d_8$ triplet in the fresh film, indicating that transport is limited to very small regions. When annealed, only N-$h_8$ emission is seen.

Analysis of triplet exciton homofusion in mixed naphthalene single crystals[3] has shown the transport to be fractal with exponent -h. When hetero-

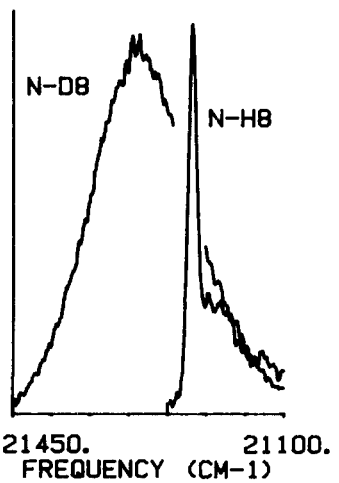


FIGURE 3
Phosphorescence from a 4.9% N-$h_8$ in N-$d_8$ sample at 5 K before (N-D8) and after (N-H8) annealing.

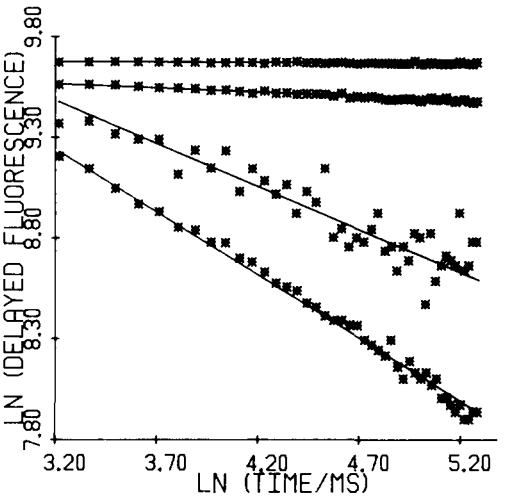


FIGURE 4
Ln(DF) vs. ln (time) from 100% N-$h_8$ samples. Straight lines were obtained from $I_{DF} \propto t^{-h}$, with slopes -h. Bottom to top: fresh, 5K (h=0.62); fresh, 6.2K (h=0.42); fresh, 7.5K (h=0.04) and annealed, 6.2 K (h=0.00).

fusion dominates, the early delayed fluorescence is proportional[4] to $t^{-h}$. Short time delayed fluorescence decays from our vapor-deposited 100% naphthalene-$h_8$ samples are shown in Fig. 4. At higher temperatures and after annealing, the behavior is classical (h=0). However, the freshly-deposited samples exhibit temperature-dependent fractal behavior: the exponent h increases up to 0.6 with reduced temperature, paralleling the increase in h with decreasing concentration in mixed crystals.[3]

In conclusion, steady state and time-resolved studies of the emission from disordered naphthalene samples at low temperatures have demonstrated a temperature- and annealing-dependent exciton transport which ranges from fractal to classical behavior.

REFERENCES

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4) P. Evesque and J. Duran, J. Chem. Phys. 80 (1984) 3016.