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Solid state effects on the photophysics of π -conjugated polymer thin films ALOK SHUKLA, Indian Institute of Technology Bombay, ZHENDONG WANG, SUMIT MAZUMDAR, University of Arizona — The photophysics of thin films of π -conjugated polymers (PCPs) are remarkably different from that of dilute solutions. The difference is generally ascribed to interchain interactions and disorder in films. Microscopic understanding of the consequences of interchain interactions has remained incomplete in spite of intensive investigations. We present a theory of the complete energy spectrum of interacting PCP chains that leads to correct qualitative, and perhaps even semiquantitative description of the photophysics of PCP films. Within our theory branching of photoexcitations occurs to excimers that occur both below and above the optical exciton. Emission, as well as ultrafast photoinduced absorption (PA) in films are from the lower excimer. The lowest energy PA at 0.35 - 0.4 eV corresponds to the allowed transition from the lower excimer to the lowest polaron-pair. We explain why the energies of the PA at ~ 1.0 eV and higher are the same in films and solutions, even though the origins of these PAs are different. Finally, we give consistent explanations of the peculiarities associated with emission in films, including delayed emission, its quenching by electric field and the reappearance of the delayed emission upon removal of the field.¹

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