Ordered films of organic conjugated polymers offer an ideal scenario for the study of electronic and excitonic confinement, being composed of quasi-one-dimensional systems arranged in a three-dimensional crystalline environment. So far, experiments are usually interpreted in terms of a single-chain model, thereby neglecting any effect of solid-state arrangement and interchain interaction. We investigate [1,2] the importance of these effects in two prototypical systems, such as poly-para-phenylenevinylene (PPV) and poly-thiophene (PT), in both isolated chain and different possible crystalline packings. We employ an \textit{ab initio} density matrix scheme to include electron-hole interaction on top of a density functional theory calculation: this allows us to use the reciprocal-space representation and consequently to study infinite periodic systems, which can not be accessed through quantum chemistry methods. The details of crystalline arrangement dramatically alter the optical properties and lead to a richer excitonic structure: each excitonic state splits into two direct components (with electron and hole on the same chain), one for each non-translationally-invariant chain in the unit cell. For both PPV and PT crystals, we find that the optical inactivity of the lowest component drastically quenches the photoluminescence efficiency. Also, charge transfer states (electron and hole on adjacent chains) are induced at energy just above the lowest direct states, and can therefore enhance photoconductivity. Our results suggest that control of interchain interaction and solid-state packing are essential for photoluminescence properties and can act as tunable parameters for the design of efficient optical devices.