The morphology of organic active layer plays a crucial role in the performance of organic solar cell devices. Understanding of charge carrier mechanism governed by the distinct morphologies of the active blend systems is required to enhance the power conversion efficiencies in solar cells. In this work, we have investigated the ultrafast photophysics in a wide range of active blend systems and correlated with their nano-morphology and optoelectronic properties in solar cell devices. External electric field treatment, inclusion of the solvent additive and solvent vapour annealing of the active layer were adopted as three different processing methods to modify the morphology of the active blend system in bulk heterojunction solar cells. External electric field treatment on the active layers based on semicrystalline donor polymers (i.e. P3HT and P3BT) promotes self-organization in the system and enhances the exciton/polaron generation, which results in improved device efficiency. On the other hand, inability of self-organization, complex molecular structure and larger molecular size of the amorphous donor polymers (i.e. PTB7 and PCPDTBT) make this approach unsuitable, resulting in invariant optoelectronic performance. Addition of a small fraction of poor solvent in P3HT:PCBM blend system is a room temperature processing approach to improve the device efficiency, which is suitable for roll-to-roll applications. The performance enhancement by solvent additive is comparable to the thermally annealed devices, however certain additives cause strong phase separation of the donor and acceptor, which result in higher charge carrier recombination. Similar to conjugated polymer systems, the suppression of charge carrier losses is also important in solution processed small molecule blend system. Solvent vapour annealing of DRCN5T:PCBM active blend layer helps to reduce the predominant monomolecular recombination in the finely mixed system. Hence, this improved the performance from 3.3 % to 10%. This work provides new in-depth understanding on the morphology dependent charge carrier dynamics, which will lead to further improvements in organic solar cell devices.