

Time-resolved photoluminescence in α -PTCDA single crystals: evidence for recombination via Frenkel excitons, charge transfer states, and excimers

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Abstract

The radiative recombination channels in α -PTCDA are analysed with time-resolved PL techniques in the 50 ns range between temperatures of $T=10$ and $T=300$ K. The resulting PL spectra are interpreted with calculations based on the transfer of Frenkel excitons and with time-dependent density functional theory applied to different deformed geometries of molecular dimers as microscopic models for self-trapped excitons. At low temperature, the lineshape and radiative lifetime of the most important PL channel can be assigned quantitatively to a vertical transition from the indirect minimum of the Frenkel exciton dispersion towards the electronic ground state. In an intermediate regime below about $T=100$ K, charge transfer states involving an anionic and a cationic molecule dominate the PL spectra. Radiative recombination from an excimer state in a stack geometry has a rather weak temperature dependence, and due to non-radiative quenching of the other PL channels, this excimer PL band predominates above about $T=200$ K.