Delayed Fluorescence in a Chiral Perylene-3,4,9,10-bis(dicarboximide) Organic Cage

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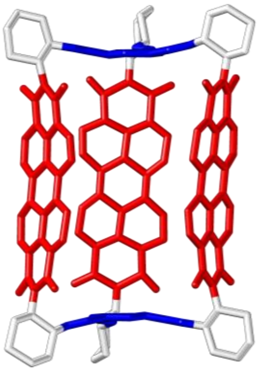
Porous organic materials discovered a little more than a decade ago have developed rapidly because they offer a number of attractive properties as gas storage or separation materials.[1-2] They can display high porosities but are processable unlike zeolites or covalent organic frameworks. The spatial shape of organic cages represents a promising platform to study phenomena associated with electronic materials. However, studies of photophysical or electronic properties using organic cages are rare. Previously,[3a] we reported a synthesis of a chiral covalent organic cage with three built-in redox-active naphthalene-1,4:5,8-bis(dicarboximide) units by dynamic imine chemistry.[4] We found that intracage photoinduced charge separation provided a long-lived charge separated state and that electrons could migrate between individual redox units demonstrating the potential of organic cages as interesting organic electronic materials.

Here, we present a new cage with three perylene-3,4,9,10-bis(dicarboximide) (PDI) units that displays a delayed fluorescence in a solution unlike a monomeric compound with a single PDI unit.[3b] The measured quantum yields and the fluorescence lifetimes suggest a formation of a non-emissive state on a nanosecond time-scale that is in a dynamic equilibrium with the bright monomer-like excited state. The observed interconversion rates and the equilibrium between these states depend on the polarity of the solvent. The spatial arrangement of the PDI units revealed by single-crystal X-ray diffraction and DFT calculations allows only for a weak coupling between the individual PDI units as probed by cyclic voltammetry, and steady-state optical spectroscopies. Our data hint that the new non-emissive state is formed either via a PDI–PDI charge separation or a singlet fission event.



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