# Laser-Induced Fluorescence Spectroscopy of PTCDA and PDI in Helium Nanodroplets

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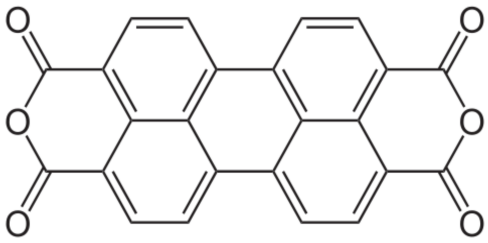
**Synopsis** Electronic spectra of the $S_1 \leftarrow S_0$ transition of the perylenetetracarboxylic dianhydride (PTCDA) and perylene diimide (PDI) embedded in helium nanodroplets have been measured by laser-induced fluorescence. These two neutral species preserve the central perylene chromophore; however, the two oxygens in the aromatic ring of the former are exchanged for N–H. The spectral signatures of PTCDA and PDI are compared to each other and presented.

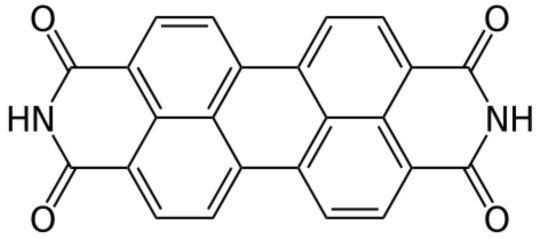
Perylene dyes are useful for the absorption of intense visible light, high structural stability, electron accepting ability, and near-unity quantum yields. [1] The physical properties of these molecules make them attractive for optoelectronic and photovoltaic devices, thermographic processes, energy-transfer cascades, light-emitting diodes, and near-infrared-absorbing systems. [2] By chemical substitution, these dyes can be engineered to absorb or emit throughout the whole visible spectrum.

Perylenetetracarboxylic dianhydride (PTCDA) and perylene diimide (PDI) are two such molecules that belong to the class of perylene dyes (Figure 1). PTCDA monomer and oligomers embedded in helium nanodroplets has been previously studied by laser-induced fluoroscence (LIF). [3, 4] The origin band of the $S_1 \leftarrow S_0$ transition of PTCDA monomer in a helium droplet is at 20 987.8 $cm^{-1}$, while no clear origin in the electronic spectrum of dimers and larger clusters is discernible. By exchanging the two central oxygens on the ends of PTCDA with N–H, one has the molecular geometry of PDI. The monomer of PDI in a helium droplet has an origin band of the $S_1 \leftarrow S_0$ electronic transition at 20 681.6 $cm^{-1}$, being redshifted to PTCDA by $\approx 300\,cm^{-1}$.

Furthermore, in the electronic spectrum of PDI, there are absorption features redshifted to the origin band. Some of these increase in intensity upon heating and are attributed to dimers of PDI; however, not all bands to the red are due to dimers formed in the helium nanodroplet. An assignment of the electronic spectrum of PDI and a comparison of PDI with PTCDA will be presented.



perylenetetracarboxylic dianhydride (PTCDA)




perylene diimide (PDI)
Pigment Violet 29

**Figure 1**. Planar molecular structures of 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) and perylene diimide (PDI). The central perylene chromophore is preserved in both PTCDA and PDI.

## References

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