

Controlling Photoinduced Processes in Oligophenylenevinylene-C₆₀ Arrays

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In recent years several fullerene arrays containing amine-type subunits have been synthesized. They may exhibit photoinduced electron transfer, which can be controlled by pH or solvent polarity (1-4).

Following the first preparation of photovoltaic devices from fullerene/oligophenylenevinylene (OPV) conjugates (5) a great deal of attention has been devoted to the study of the excited state properties of such arrays (6-9).

We have carried out photophysical investigations on the fullerene derivatives **1** and **2** in which an oligophenylenevinylene trimeric subunit (3PV) is attached to C₆₀ through a pyrrolidine or a pyrazoline ring. In **2** both an amine and an OPV function are integrated with the fullerene chromophore

The electronic ground and excited-state properties of the multicomponent arrays **1** and **2** have been studied in solution using 3PV, fulleropyrrolidine **3**, and fulleropyrazoline **4** as reference compounds.

In **1** quantitative OPV→C₆₀ photoinduced singlet-singlet energy transfer has been observed. Population of the lowest fullerene singlet excited state is followed by nearly quantitative intersystem crossing to the lowest fullerene triplet excited state in CH₂Cl₂ and toluene, whereas OPV→C₆₀ electron transfer is able to significantly compete in more polar benzonitrile solvent. In the case of **2**, the excited-state properties are more complex due to the electron donating ability of the pyrazoline ring. As observed for **1**, quantitative OPV→C₆₀ photoinduced singlet-singlet energy transfer occurs in **2**. However, in this case, the population of the lowest fullerene singlet excited state is followed by an efficient electron transfer from the pyrazoline ring in CH₂Cl₂ and benzonitrile. In **2**, studies of the dependence of photoinduced processes on solvent polarity, addition of acid, and temperature also reveal that this compound can be considered as a fullerene-based molecular switch, the switchable parameters being the photoinduced processes.

1 and **2** have been tested as active materials in photovoltaic devices and the differences of light to energy conversion efficiencies found for the two compounds rationalised on the basis of their photophysical properties.

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