Organic host–guest systems for blue emission

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Abstract

The photoluminescence (PL) quantum yields (QYs) and lifetimes of the 1,6-diphenyl-1,3,5-hexatriene (DPH) blue emitter and of the acceptor–donor system, DPH and *p*-terphenyl (P3), are investigated embedded in the nanochannels of a perhydrotriphenylene (PHTP) matrix. In the co-inclusion system, light emission takes place from DPH, due to the efficient resonant energy transfer (RET) from the P3 donor molecules. The host matrix stabilizes the guest molecules against photooxidation degradation. The largest quantum yield, up to 100%, has been found in the co-inclusion compound (IC), where excitations are localized at the emissive acceptor sites.
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1. Introduction

Self-organized host–guest systems are materials where the host imposes a specific spatial organization to selected active molecules (guests). A proper design of such systems allows to achieve a specific function in energy transport and conversion for artificial antenna systems. Host–guest systems obtained with dye-loaded zeolites displaying efficient energy transfer properties have been recently reported [1]. All-organic host–guest systems, as inclusion compounds (ICs) of active conjugated molecules in perhydrotriphenylene (PHTP), possess similar energy transfer properties [2].

ICs of conjugated chromophores in PHTP have been reported for both oligothiophenes (Tn) [3] and oligophenylenevinylenes [4] molecules. The major effect of the inclusion is the strong suppression of the intermolecular interactions [5], which drastically reduce the emission quantum efficiency of the isolated molecules [6]. Moreover, with respect to molecules dissolved in solution, ICs offer the advantage of more planar and rigid molecular conformations, which increase the emission efficiency [7]. Recently, we have shown that very efficient resonant energy transfer (RET) takes place in co-inclusion compounds obtained by the inclusion of two chromophores possessing proper optical properties, thanks to the optimal chromophore orientation imposed by the host. Those systems give emission from the lower energy gap molecule even when its relative concentration is well below 1% [2]. The advantages of these co-inclusion compounds are (i) chemical stability of the active molecules, (ii) efficient conversion of light, and (iii) emission with reduced self-absorption effects.

In this work we report a complete CW and time-resolved photoluminescence (PL) analysis of the inclusion 1,6-diphenyl-1,3,5-hexatriene (DPH) compound and of the co-inclusion donor–acceptor DPH/P3 system. We show that ICs are stable and efficient emitters providing excellent light converters from the UV to the visible.

2. Experiment

PHTP has been prepared as reported elsewhere [5]. DPH and P3 bought from Aldrich are used without further purification. Inclusion and co-inclusion compounds are obtained both by melting and successively cooling the molecules with PHTP [5], by simultaneous vacuum sublimation of PHTP and P3 chromophores, and by slow solvent evaporation [8]. The chromophores are accommodated into the crystalline matrix of PHTP which forms

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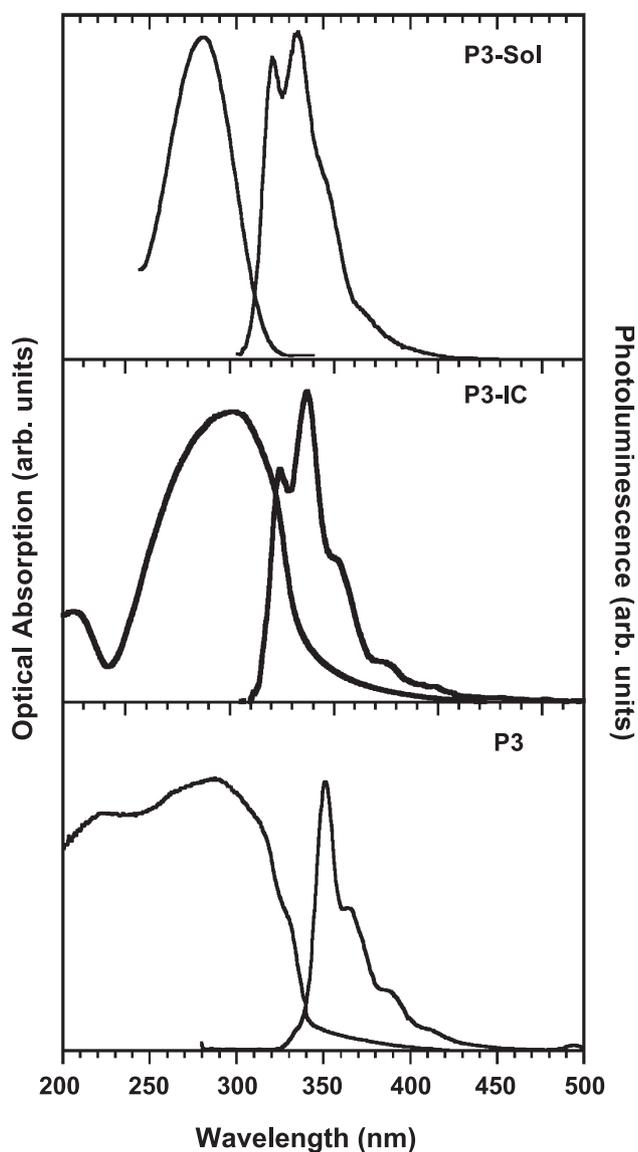*E-mail address:* chiara.botta@ismac.cnr.it (C. Botta).

Fig. 1. Absorption and photoluminescence spectra of P3 molecules in CH$_2$Cl$_2$ solutions (P3-Sol), IC films (emission) and powders (absorption) (P3-IC), and P3 vacuum sublimated films (P3).

the excitation pulses is centred at 382 nm and the pulse duration (FWHM) is around 150 fs. The excited region of the sample is about 10^4 μm^2. The PL is time-resolved by using a Hamamatsu optical oscilloscope with 30-ps time resolution.

3. Results

The optical properties of P3 and DPH molecules are reported in Figs. 1 and 2 for the solutions, ICs obtained by vacuum sublimation techniques or by melting, and aggregate molecules obtained by vacuum sublimation or by powder dispersion in KBr. For both the molecules, the PL
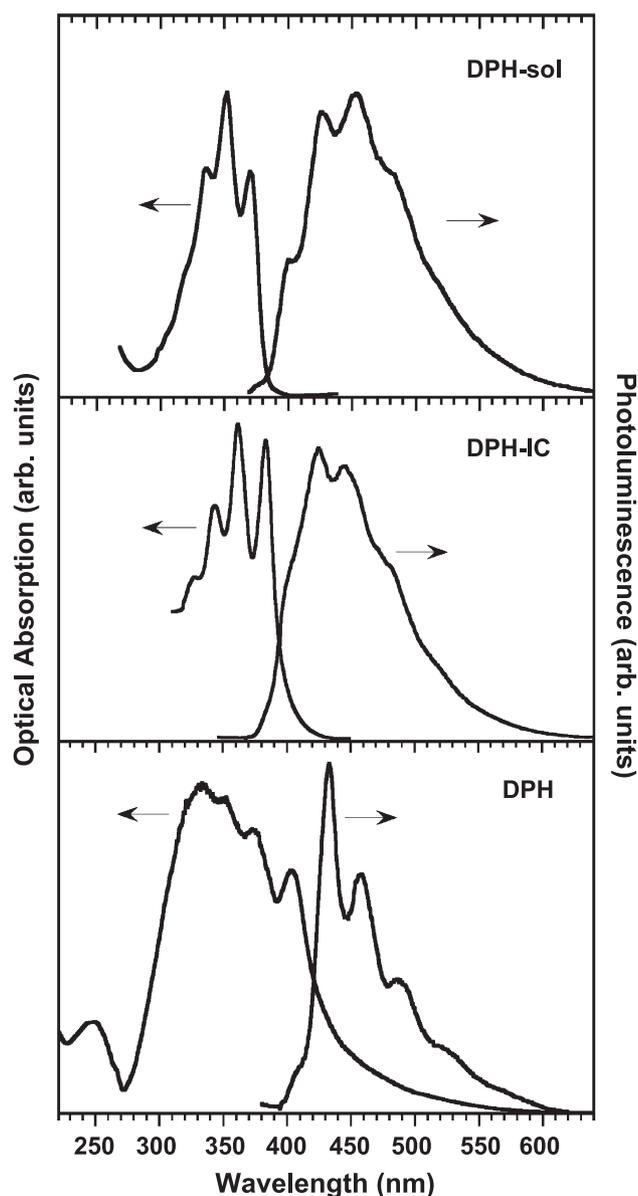

Fig. 2. Absorption and photoluminescence spectra of DPH molecules in ether solutions (DPH-Sol), IC (DPH-IC) and powder (DPH) KBr pellets.

channels of about 7 Å of diameter, at a distance of about 12 Å. The absorption spectra are recorded with a Perkin Elmer spectrometer on films or pellets of KBr dispersed powders. The PL measurements are performed using a SPEX 270M monochromator equipped with a N$_2$-cooled CCD detector and excited by a monochromated Xe-lamp. PL quantum yields (QYs) are measured with a homemade integrating sphere following the procedure of Ref. [9], with errors in the range of 5–10%. QYs in dilute solution are measured by using quinine sulfate as a reference. The relative concentration of the molecules in the co-inclusion compounds is deduced from the optical analysis. The time-resolved PL is measured by exciting the samples with the frequency double-pulsed output of a mode-locked Ti:Sapphire laser system operating at 80 MHz. The wavelength of
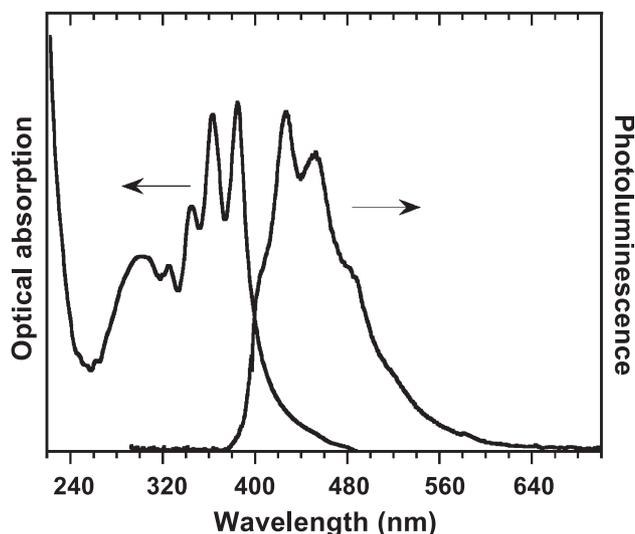
Fig. 3. Optical absorption and photoluminescence of DPH:P3 co-inclusion compounds. The excitation wavelength is centred at 290 nm.

spectra of ICs are similar to those of the solutions, while the aggregated materials display red-shifted emission. The absorption spectra of the ICs are slightly red-shifted with respect to the solution because of the higher planarity of the conjugated backbones in the solid state.

In a previous paper we have shown that co-inclusion of two thiophene molecules (T3 and T5) provides a host–guest system where the resonant energy transfer from the short wavelength (T3) to the longer wavelength (T5) emitter is very efficient [2]. By using both CW and femtosecond spectroscopy, we made a quantitative analysis of the energy transfer process showing that homotransfer (RET from T3 to T3) was important in the long time dynamics and could increase the overall RET efficiency from T3 to T5.

Here we report a co-inclusion compound where two chromophores (P3 and DPH) are included in PHTP in order to (i) extend the absorption region up to the UV, and (ii) substitute the T3 molecule with a molecule (DPH) with similar spectral properties, but higher PL efficiency. In order to maximise the energy transfer efficiency, a complete spectral superposition between the emission of the spectra at higher energy (donor) and the absorption of the lower energy (acceptor) molecules is necessary. This condition is fulfilled for the P3/DPH samples.

In Fig. 3 we report the absorption–emission spectra of a co-inclusion compound of the two molecules DPH and P3 with molar ratio of DPH/P3 close to 1. Only the emission from DPH molecules is detected by exciting P3 chromophores. Emission from DPH also occurs for much lower molar ratio of DPH/P3, in agreement with the presence of an efficient RET [8].

In Fig. 4 the time-resolved PL of DPH is shown for the CH_2Cl_2 solution, the IC, and the co-inclusion compound. The inclusion and co-inclusion compounds decay with lifetime constants of 4.5 and 5.8 ns, respectively. The decay of the solution is non-exponential due to aggregation effects
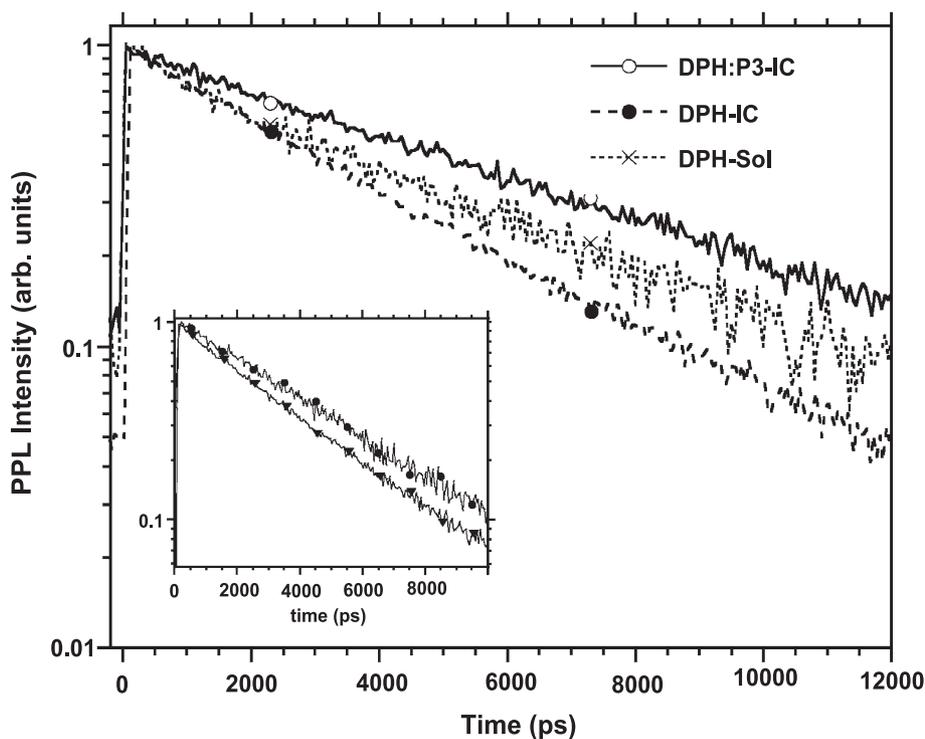

Fig. 4. Time-resolved PL of DPH molecules in CH_2Cl_2 solutions (DPH-Sol), inclusion compound (DPH-IC) and co-inclusion compound (DPH:P3-IC) with DPH/P3 = 0.43 molar ratio. In the inset is shown the time dependence of the PL of DPH-IC for two different excitation densities: 1.5×10^{-11} J per pulse (solid squares) and 1.5×10^{-12} J per pulse (solid triangles).

which give rise to a faster initial decay [10]. In order to determine the origin of the different decay times of the PL in the inclusion and co-inclusion compounds, we have recorded the PL decays at different excitation intensities. The decay kinetics of the DPH:P3 IC is found density-independent. Conversely, the PL lifetime of DPH IC increases slightly up to 4.5 ns when the pump intensity is attenuated by a factor 20. For lower excitation rates, the decay time remains almost constant.

The small dependence of the decay rate on the pump intensity could be accounted for by bimolecular annihilation of the excitations. Since the rate of this process is proportional to the excitation diffusion constant, resonant homotransfer (both intra- and inter-channels) between DPH moieties is not negligible in the IC [2,10]. Conversely, homotransfer is strongly inhibited in DPH:P3-IC, where acceptors are dispersed among larger energy gap donors. In this latter case, quenching effects are thus suppressed.

The PL QYs of the DPH chromophores in the co-inclusion compounds show values of about 94–100% for co-inclusions with DPH/P3 molar ratios below 0.4, reduced to 87% for a 0.5 DPH/P3 molar ratio. ICs of DPH show lower PL QYs of about 62–72%, indicative of the fact that diffusion of the excitations towards residual chemical impurities quenches the PL at the weak excitation intensity used for QY measurements. This result is consistent with the faster low-intensity PL decay of DPH with respect to DPH/P3. A QY of 53% is measured in CH_2Cl_2 solution. This value is unusually low, as compared to the long PL lifetime measured. It should be noted that the PL QY of DPH in solution depends strongly on the solvent (Ref. [1] reports a value of 27% for methanol solution). Photodegradation of DPH molecules as well as solvent polarizability dependences are probably the reasons for this behaviour. In the inclusion compound photodegradation effects are suppressed and QY values as high as 100% can be obtained when the excitation is confined in the PHTP matrix, thanks to the co-inclusion with molecules possessing larger energy gap.

4. Conclusion

We have prepared host–guest compounds of conjugated chromophores in an organic matrix able to form parallel nanochannels. These materials are able to convert very efficiently light from the UV to the visible spectral region. In particular, we have prepared a two-molecule co-inclusion material where excitations are localized at the emissive species, which are stabilized by the matrix against photooxidation processes. Photoluminescence quantum yields reaching 100% have been obtained, with lifetimes of about 6 ns.

Acknowledgements

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