Photophysics of Pentacene-Doped Picene Thin Films

Tullio Toccoli,* Paolo Bettotti,§ Antonio Cassinese,‖ Stefano Gottardi,* † Yoshihiro Kubozono,⊥ Maria A. Loi,‡ Marianna Manca,‡ and Roberto Verucchi†

†Trento Unit, IMEM–CNR, Institute of Materials for Electronics and Magnetism, Via alla Cascata 56/C, Povo, 38123 Trento, Italy
‡Photophysics and OptoElectronics, Zernike Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands
§Nanoscience Laboratory, Department of Physics, University of Trento, 38123 Trento, Italy
‖SPIN-CNR and Physics Department, University of Naples, P.le Tecchio 80, I-80125 Naples, Italy
⊥Research Institute for Interdisciplinary Science, Okayama University, 700-8530 Okayama, Japan

ABSTRACT: Here, we report a study on picene nanocrystalline thin films doped with pentacene molecules. The thin films were grown by supersonic molecular beam deposition with a doping concentration that ranges between less than one molecule of pentacene for every $10^4$ picene molecules and up to about one molecule of pentacene for every $10^8$ picene molecules.

1. INTRODUCTION

Acenes and phenacenes are two different series of polycyclic aromatic hydrocarbon compounds with a fused benzene ring arranged in a linear and zigzag sequence, respectively. Picene and pentacene are isomeric forms that show contrasting electronic and optical properties because of different arrangements of the rings that modifies the energetic levels of the conjugation system. Molecules of the acenes series have been known for a long time to exhibit outstanding transport properties, so that they became model systems for organic electronics. The ultrapure single crystals of anthracene, tetracene, and pentacene demonstrated semiconducting properties with high carrier mobility values comparable to those of amorphous inorganic materials, (up to $40 \text{ cm}^2/(\text{V s})$ for pentacene) and rubrene. Some of these molecules also displayed an ambipolar transport with appreciable charge carrier mobilities. Thin films of acenes have been grown using different techniques including evaporation, supersonic molecular beam deposition (SuMBD), and even by solution processing through molecular modification. Besides their superb transport properties, members of the acene family were recently investigated also for the singlet exciton fission due to the relative positions of their singlet and triplet excited states. This phenomenon is currently gaining interest not only in the photovoltaic community to enhance the efficiency of organic solar cells but also for the realization of room temperature solid-state microwave amplification by stimulated emission of radiation (MASER) as it was recently reported for the case of pentacene included in $p$-terphenyl crystals. For these reasons, we herein present a study of a promising host–guest system based on picene and pentacene. The choice of picene as a host molecule was made due to its stability under ambient conditions and its electronic, optical, and electrical characteristics. Pentacene is a well-known molecule for organic electronics that is believed to have a good affinity with picene due to the structural similarities and optical complementarities. We show in the following how the host–guest system made by picene and pentacene could be interesting both for the possible use in the fabrication of optoelectronic and microwave devices and for the study of the molecular properties that are otherwise not accessible in the isolated molecular form. In this article, we demonstrate a strong enhancement in the photoluminescence (PL) intensity of pentacene once embedded into a picene matrix. The PL increase is shown to originate from a very fast energy transfer process between picene and...
pentacene that seems to be of the Förster type. The probable distortion of pentacene molecules embedded in the picene matrix could also favor their emission. In fact, the doping of a picene matrix allows to effectively access the energy levels of the isolated pentacene molecules, overcoming the problem of its poor solubility and low emission intensity. The high efficiency of the energy transfer could also enable access to the optical levels of pentacene (i.e., triplet state) without the need of a strong optical excitation that could damage the material. In the following, we correlate the material optoelectronic properties with the growth conditions and film morphologies by means of atomic force microscopy (AFM) analysis, ultraviolet photoelectron spectroscopy (UPS), absorbance, and PL and time-resolved photoluminescence spectroscopy.

2. EXPERIMENTAL SECTION

2.1. Thin Film Growth. Pentacene-doped picene thin films were grown by supersonic molecular beam deposition (SuMBD) in an ultra-high vacuum (UHV). A detailed description of the SuMBD set-up can be found elsewhere. Two separate crucibles were loaded inside the SuMBD source: one with picene powder acquired from Asahi Kasei, 99%, and one with pentacene powder (Sigma-Aldrich, 99.995% pure). The temperature gradient inside the supersonic source can be controlled by acting on two separate heating stages positioned at the nozzle and around the body of the source. The relative concentration of the compounds in the molecular beam can be regulated within a certain range and precision (see hereafter) by controlling the temperature gradient inside the source and by considering the different vapor pressure of the two materials. Additionally, the system is provided with a time of flight mass spectrometer that permits to measure the mass spectra and the flux of the molecules in the beam. The molecular beam was seeded in He carrier gas and characterized by a kinetic energy per molecule of about 7 eV. All depositions were performed in UHV (background pressure $10^{-9}$ mbar) on thermal silicon oxide (50 nm thick) on silicon or on quartz substrates kept at room temperature, with a growth rate of about 0.3 ML/min. In this study we fabricated three sets of samples with different pentacene concentrations. Set 1, where the pentacene concentration was estimated to be lower than one molecule for every $10^4$ molecules of picene. Set 2, where the pentacene concentration was 10 times higher with respect to sets 1 and 3 with a pentacene concentration of about one molecule for every 100 molecules of picene. To determine the stoichiometry of the films is the same as that present in the supersonic molecular beam. Picene and pentacene are stereoisomers and their peaks in the mass spectrum collected with our spectrometer are at the same position; for these reasons, we do not have a direct access to their relative concentration in the supersonic beam. To do this we worked with only one crucible filled alternatively with one of the two materials and maintained the same conditions used for growing the thin films. The value for the concentrations was calculated from the ratio between the area underlying the picene and pentacene peaks in the mass spectra.

2.2. Thin Film Characterization. The morphology of the films was characterized by AFM in air, using a Sema SFC050 scanning head by NTMDT. Measurements were carried out by AFM in semi-contact mode (using NSG11 silicon cantilevers by NTMDT). The detailed analysis of the AFM data was performed with the WSxM software (version 5.0 Develop 1.1, Nanotec electronica).

Organic thin films have been characterized ex situ by UPS, using the He II photon emission at 40.82 eV, produced by a Helium discharge lamp. The hemispherical electron energy analyzer (VSW HA100, interfaced with a PSP power supply unit) had a total energy resolution of 0.86 eV. The binding energy (BE) position for the valence band was calibrated using the Au Fermi level (0 eV) as a reference. All analyzed films were deposited on a 50 nm SiO$_2$ layer on Si, to properly compare with all other analysis. However, this lead to strong charging effects during UPS measurements at photon flux typical for He I emission. We use He II emission working conditions, thus greatly reducing the photon flux, to avoid sample charging and achieve reliable UPS spectra, although with a lower signal to noise ratio.

The UV–vis–near-infrared spectra were recorded using a Varian Cary 5000 spectrometer in the range of 1000–200 nm with a scan rate of 150 nm/min and a bandwidth of 2 nm in a double beam configuration.

Photoluminescence measurements were performed on a Cary-ECPLISE fluorometer in the spectral range of 350–600 nm, the excitation wavelength was set to 350 nm. Both excitation and emission slit widths were 10 μm and a scan rate of 120 nm/min was used. An automatic excitation filter was used to reduce the effect of higher diffraction orders. Time-resolved PL measurements were performed by exciting the samples with the second harmonic (380 nm) of a mode locked Ti:sapphire femtosecond laser (Coherent), tunable in the range of ~720–980 nm, characterized by pulses of ~150 fs and a repetition frequency of ~76 MHz. The PL spectra were detected with a monochromator coupled with an Image EM CCD camera (Hamamatsu Photonics). The spectra were corrected for the spectral response of the set-up. Time-resolved traces were recorded with a streak camera (Hamamatsu Photonics) working in synchroscan mode.

3. RESULTS AND DISCUSSION

The picene–pentacene host–guest system (pentacene inside a picene matrix) is an interesting reference system for the study of small-molecule nanocrystalline compounds.

The singlet energy levels of these molecules (Figure 1) are well-positioned to expect efficient transfer of excitation energy from the host to the guest. Both molecules in the thin film show a similar crystal structure, with a similar interplane distance (about 1.4 nm for picene and about 1.5 nm for pentacene) and their molecular dimensions are very close (1.15 nm for picene and 1.22 nm for pentacene) and also their thin film packing, it is possible for pentacene molecules to substitute picene molecules while maintaining the same crystal packing, and thus minimizing phase segregation in the thin film. We can expect, based on their crystalline structures and molecular dimensions, that under these conditions pentacene will be distorted by the crystal field of picene by modifying its symmetry and consequently some of its chemical and physical properties.

We know that during the growth of the thin film (in terms of nucleation, island formation, and coalescence) these two molecules follow different pathways resulting in different morphologies. However, due to the low concentration of pentacene in the thin film, the growth and the final morphology are expected to be determined by the host component. This is confirmed by the comparison of thin film...
Figure 2. Scheme of the excitonic levels of picene and of pentacene and their molecular structures. We indicate the singlet energy level of picene in the thin film (about 3.23 eV) and the one of molecular pentacene (about 2.1 eV). The process of the energy transfer from the host (picene) to the guest (pentacene) is represented: optical excitation (violet arrow), energy transfer (black dashed arrow), and radiative decay (yellow arrow).

Figure 1. Scheme of the excitonic levels of picene and of pentacene and their molecular structures. We indicate the singlet energy level of picene in the thin film (about 3.23 eV) and the one of molecular pentacene (about 2.1 eV). The process of the energy transfer from the host (picene) to the guest (pentacene) is represented: optical excitation (violet arrow), energy transfer (black dashed arrow), and radiative decay (yellow arrow).

morphologies reported in Figure 2. Here, we show the morphological characterization of a pure picene film (a), mixed films of sets 1, 2 and 3 (b−d), and pure pentacene (e). All films were grown on the thermal silicon oxide surface (50 nm thick). As we have reported previously, the early-stage morphology of pure picene films shows that the molecules nucleate in islands that develop in a three-dimensional growth. The crystallites are several hundred of nanometers wide with sharp edges and very regular shape; the average height of the crystallites is about 70 nm. Doping picene with a concentration of pentacene <10⁻⁴ (set 1 samples) does not significantly change the growth of the thin film (Figure 2b), but the crystallites seem to be less regular (we observe that the typical sharp edges present for pure picene are not so evident anymore). The average height of the crystallite before reaching percolation is about 70 nm for pure picene on silicon oxide. The trend is confirmed when we increase the pentacene concentration (set 2 samples Figure 2c), where the crystallites result to be little larger and less regular. Upon further increasing the pentacene concentration (set 3 samples Figure 2d), the crystallites become little larger and exhibit a “quasi” pyramidal structure. In every case, the typical morphology observed for the doped films are more close to that observed for pure picene films (Figure 2a) with respect to the typical morphology of pentacene (Figure 2e). From the AFM characterization, we were not able to observe the presence of crystallites displaying the typical pentacene growth (Figure 2c), and thus we exclude the possibility of phase segregation.

Figure 3 reports the analysis of the valence band (using He II emission at 40.82 eV as the photon source) for pure pentacene and picene films, as well as the picene film with two different pentacene doping concentrations (sets 1 and 3). The lineshape of the spectra shows differences in the reported data in the literature. Nevertheless, the highest occupied molecular orbital (HOMO) features for pentacene and picene pure films at about 0.9 and 2 eV can be easily identified, in agreement with previous results. Other differences between the two molecule’s valence bands can be found in the 6–11 eV energy region. Upon comparing picene films with those doped by

Figure 2. AFM micrograph: (a) pure picene; (b) set 1 samples; (c) set 2 samples; (d) set 3 samples; and (e) pure pentacene. In the mixed film no phase segregation is visible. The morphology is substantially the same as that of the pure picene film.
different amounts of pentacene, apparently no significant energy shifts occur for their HOMO and main features. The overall lineshape is partially altered, with features becoming less defined and broader. By comparison with the valence band of pure pentacene, the observed changes could be attributed to the appearance of bands related to the guest molecules. At the higher concentration, the appearance of a broad peak at about 1 eV can be identified (see Figure 3 right), i.e., in the BE region of the pentacene HOMO.

This structure can be definitely attributed to the pentacene HOMO, whereas more detailed considerations are not possible due to the low intensity and large width of this peak. Its energy position is strictly similar to that of the pristine pentacene film, this suggests a simple superposition of the two valence bands with a Fermi level alignment. We can conclude that the pentacene HOMO and lowest unoccupied molecular orbital (LUMO) levels are inside the HOMO–LUMO gap of picene.

The position of the levels of the two molecules suggests that an efficient energy transfer from picene to pentacene is possible. With this host–guest system it may be possible to access excited states of the pentacene molecule that are not easily accessible otherwise. This opens the possibility to use such a host–guest system for several applications like lighting, photovoltaics, and solid-state MASER.
The main change in the photophysics of the doped samples becomes visible from the PL spectra. In Figure 5, we report the spectra of the doped samples and the PL of pure picene and pure pentacene for comparison. The black curve shows the emission spectra of picene,27 with a structured emission band in the spectral range between 3.4 and 2.7 eV characterized by the presence of peaks at 3.21, 3.06, 2.89, and 2.71 eV, due to the singlet–singlet transitions and the peaks at 2.53, 2.38, and 2.09 eV due to the triplet–singlet transition.28 The extended and well-defined vibronic progression of this sample, underlines the high quality and crystallinity of the sample deposited by the supersonic molecular beam.22

Therefore, the emission spectra relative to the samples doped with pentacene show completely different emission spectra and the spectra are also completely different with respect to the typical emission of the pure pentacene film.28,39 We note an almost complete suppression of the picene emission for all sets of samples and at the same time the formation of a strong and sharp emission band at about 2.09 eV (with replicas at about 1.92 and 1.76 eV). We assign these bands to the emission coming from a single pentacene molecule dispersed inside the picene matrix.34,40 The absolute intensity of the emission that we observed for the samples doped with pentacene seems to be perceptibly larger than that of pure picene and we observe that the doped samples under UV illumination (i.e., the mercury lamp) change their color from blue (as of pure picene) to orange. This observation is already an indication of the presence of energy transfer from picene to pentacene and to the trapping of the photoexcitation.

Figure 5. Photoluminescence spectra of different samples excited at a wavelength of 300 nm. Black curve: pure picene; blue curve: set 1 sample; red curve: set 2 sample; green curve: set 3 sample; and orange curve: pure pentacene (in this case the excitation was made with a laser at 568 nm).

The progressive suppression of the picene emission and the enhancement of the pentacene optical features at the same time can be interpreted as the first indication of an efficient energy transfer between the picene and pentacene molecules.31,32

To shed light on the energy transfer between the picene matrix and the pentacene dopants, we performed time-resolved photoluminescence measurements. In Figure 6a, the PL dynamics recorded at 2.75 eV (∼450 nm) for pure picene, set 2 samples and set 3 samples, are reported. At this energy, we observe a remarkable reduction of the lifetime of the excited state of picene in the host–guest system in comparison with the reference case of a pure picene film, reduction that is more pronounced for the sample of set 3. The PL of pure picene (black dots) at 445 nm displays a monoexponential decay with time constant up to 10 ns. On the other hand, the set 2 sample displays a biexponential decay with time constants equal to 30 and 300 ps. Further reduction of the picene lifetime is demonstrated by samples with a larger amount of pentacene dopant (set 3 sample). The strong quenching of the picene emission in the presence of pentacene and its dependence with respect to the pentacene concentration can be due to the resonant transfer of the excitation energy from picene to pentacene and to the trapping of the photoexcitation on the latter.

Table 1 presents the decay times determined for the different sets of samples at 2.75 and 2.09 eV. The rise time calculated at 2.09 eV for the samples at a lower pentacene concentration are also reported.

To better understand these observations, in Figure 6b we report the time-resolved photoluminescence decay of the samples of sets 1–3 and pure pentacene for wavelengths corresponding to the main peak (0–0) of the pentacene optical emission (∼2.09 eV). Looking into detail at different dynamics, we note that the samples of set 1 (lower pentacene concentrations) show a monoexponential behavior. This is also maintained for the sample of set 2 with the lower pentacene concentration (Figure 6b). Here, we found a lifetime of: τ ∼ 1
can be explained again with the formation of small clusters of pentacene, and with the opening of nonradiative channels due to the intermolecular interaction in the clusters. The formation of aggregates of pentacene in these samples is in agreement with that concluded from the analysis of the absorption spectra reported in Figure 4. Looking into detail the dynamics of the decay reported in Figure 6b, we observe the evidences for the samples at the lower pentacene concentration of a rise time. In particular, we obtain a rise time up to 5.5 ps for the samples of set 1 at a lower pentacene concentration. Shorter rise times were measured for samples with intermediate concentrations (set 2 samples). Here, we measure a rise time of 12 ps for the samples with a pentacene concentration lower than 10^{-3} molecules (the red thin dashed line in the inset of Figure 6b) and a rise time of 4 ps for the samples with the pentacene concentration higher than 10^{-3} molecules (the red bold line in Figure 6b).

The presence of the rise time and its dependence with respect to the pentacene concentration is an indication of an indirect excitation of the pentacene molecules. Förster energy transfer is the best mechanism to explain such an indirect excitation due to the fast processes involved. The resonant energy level of the picene excited state with the singlet of pentacene molecules and the overlap of the emission and absorption spectra of the host and guest, respectively, indicate that a dominant contribution to the energy transfer is of the Förster type. At the same time the high degree of crystallinity of these films increases the delocalization of the exciton, favoring in this way the energy transfer from the host to the guest molecules.

When the percentage of pentacene is increased, the rise time becomes faster. This can be due to the lower average distance between the photoexcited picene and the pentacene molecules; the direct photoexcitation of pentacene is less probable as the absorption of pentacene at the excitation wavelength is rather weak. In fact, when we use an excitation energy lower than the picene optical gap, no luminescence is visible for all the set of samples reported.

The quenching of the picene emission in the doped samples indicates a high efficiency in the energy transfer process from picene to pentacene. The energy transfer gives rise to an unusually strong PL coming from pentacene molecules; we believe that this is due to the breaking of the molecular symmetry of pentacene triggered by the crystalline field of picene. This system is thus very appealing for studying singlet fission in pentacene-molecules and opens interesting possibilities for studying the photophysics of other excited states of pentacene (e.g., triplet state). The approach presented in this work may also be extended to other acenes.

The biexponential behavior presented by the photoluminescence dynamics of set 3 samples and of set 2 samples

### Table 1. Decay Time Calculated at 2.7 and 2.09 eV. Rise Time Calculated at 2.09 eV

|          | decay time @2.75 eV (450 nm) τ (ps) | @2.09 eV (590 nm) τ (ps) |
|----------|------------------------------------|-------------------------|
|          | decay time | rise time | decay time | rise time |
| picene   | monoexponential | 5800 ± 200 | not calculated | not calculated |
| set 1 samples | not calculated | | | |
| set 2 samples | biexponential | 44 ± 5 | 345 ± 16 | 1165 ± 122 | 55 ± 2 |
| set 3 samples | biexponential | 7 ± 1 | 224 ± 20 | 850 ± 13 | 12.8 ± 0.5 |
| pentacene | biexponential | not calculated | not calculated | 72 ± 7 | 661 ± 14 | 5 ± 1 |
|          |          |          | biexponential | 16 ± 0.3 | 265 ± 8 | not calculated |
|          |          |          | biexponential | 3.2 ± 0.4 | 52 ± 4 | not calculated |

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4. CONCLUSIONS

In this work, we report a study of pentacene-doped picene thin films that are grown by supersonic molecular beam deposition. It is found that the pentacene–picene host–guest system can be an optimal system to become a reference in the study of doped nanocrystalline thin films made with small-molecules due to the complementary electronic and optical properties of these two molecules and the high similarities of the two stereoisomers. The photoluminescence spectra and time-resolved measurements at room temperature and atmospheric pressure revealed an efficient energy transfer from the host matrix (picene) to the dopant molecules (pentacene) and the high photostability of this host–guest system. The electronic and excitonic energy levels of the two molecules favor an efficient energy transfer from the host to the guest. We attributed this energy transfer to a long-range Förster resonant energy transfer, which is favored by the superposition of picene emission with pentacene absorption. Moreover, we explain the strong emission coming from pentacene (a molecule that usually shows a very low luminescence intensity) due to its distortion in the crystalline field of picene. High population of singlets on the pentacene molecules also enhance the probability to have a transfer of the excitation energy, via inter system crossing, to the triplet state of pentacene which might be interesting for the study of the solid-state MASER based on pentacene. From the results presented in this work, we also conclude that the wide optical-gap of the picene matrix could be a robust tool to investigate singlet fission in pentacene single molecules. The air stability and high mobility properties of picene, and the sharp emission peaks observed for this nanocrystal host–guest system paves the way to its application as an active material for light-emitting diodes, light-emitting transistors as well as light down-converters systems. Finally, the approach presented in this work may also be applied to other acenes and acene derivative molecules.

AUTHOR INFORMATION

Corresponding Author
*E-mail: tullio.toccoli@unitn.it.

ORCID
Tullio Toccoli: 0000-0001-5758-4613
Maria A. Loi: 0000-0002-7985-7431

Present Address
Simbeyond B.V., P.O. Box 513, 5600 MB Eindhoven, The Netherlands (S.G.).

Author Contributions
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