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Dibenzanthanthrene in N-Hexadecane, Dibenzoterrylene in Naphthalene: Two New Systems for Single Molecule Spectroscopy

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DIBENZANTHANTHRENE IN N-HEXADECANE, DIBENZOTERRYLENE IN NAPHTHALENE: TWO NEW SYSTEMS FOR SINGLE MOLECULE SPECTROSCOPY

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Abstract We report on two new highly fluorescent aromatic compounds for single molecule spectroscopy, dibenzanthanthrene, studied in a n-hexadecane matrix and dibenzoterrylene in a naphthalene crystal. The very weak triplet yields and short triplet lifetimes make the molecules nearly perfect optical two-level systems, with negligible buildup of triplet population.

INTRODUCTION

Fluorescence excitation spectroscopy of single molecules at low temperatures is an alternative method to spectral hole-burning that displays intense and narrow homogeneous lines [1,2]. However, the conditions required to observe narrow single molecule lines with a high signal-to-noise ratio are rather stringent. The host-guest system must present the following features:

i) a strongly allowed optical transition of the guest, with a high fluorescence yield,

ii) favourable photophysical parameters of the guest, leading to a low buildup of triplet population under strong excitation of the singlet-singlet transition,

iii) intense and narrow zero-phonon lines, requiring a good fit between host and guest and low electron-phonon coupling,

iv) high photostability of both guest and host, allowing sufficiently long accumulation times (typically, seconds).

These requirements have been met so far by a handful of systems only, with very few guest molecules, most of them polycyclic aromatic hydrocarbons. The guest molecules studied so far are pentacene [3], perylene [4], terrylene [5], and a derivative of perylene with heteroatoms. They were included in molecular crystals like p-terphenyl, in Shpol'skii matrices like n-hexadecane [6] or in polymers such as polyethylene or polyvinylbutyral [7]. Here, we describe two new aromatic guests which give intense and narrow single molecule lines. One of them, dibenzoterrylene (DBT), absorbs in the near infrared (730 nm in alkane solutions, 760 nm in naphthalene crystal), a spectral range accessible to cheap single mode diode lasers. Of the two new systems presented, one is a Shpol'skii matrix, the other a crystal.

EXPERIMENT

Since 2.3,8.9-dibenzanthanthrene [8] (DBATT, structure shown on Fig1) absorbs at about 589 nm, it was excited with a single-frequency dye laser. For single-molecule measurements, a drop of a saturated solution of DBATT in n-hexadecane was placed at the end of a single mode optical fiber, as first done in [3], and the fluorescence was collimated by a parabolic mirror. The setup was that described in [9] for pentacene (which absorbs in the same spectral range). Intensity correlation functions were recorded using an ALV-5000 pseudo-logarithmic correlator [10].

7.8,15.16-dibenzoterrylene [8] (DBT, see structure in Fig2) was included in a naphthalene crystal by rapid Bridgman growth from a melt. The concentration obtained was very low (we estimate it to 10^{-9} mole/mole or less), but sufficient to study single molecules. The excitation source at about 760 nm was a single-frequency Ti-sapphire laser, and the optical setup was the confocal design described in [11], based on a high-quality parabolic reflector. The fluorescence counts were filtered from the exciting light by a notch filter (Kaiser 752) and detected using an avalanche photodiode (EG&G, SPCM-AQ131).

DIBENZANTHANTHRENE IN N-HEXADECANE [12]

The 0-0 fluorescence excitation line of DBATT in n-hexadecane shows a dominant Shpol'skii site at 589.1 nm, with an inhomogeneous breadth of about 15 cm^{-1}. Spectral holes can be burned in this absorption band, giving an extrapolated hole width of about 50 MHz at low fluence, consistent with the fluorescence lifetime of DBATT (9.4 ns).

Lines of single DBATT molecules were studied mainly in the wings of the inhomogeneous profile. Their dependence on laser intensity shows a clear saturation, with a homogeneous width of 17 MHz on average and a saturation intensity of the order of 1 mW/cm^2 (the exact saturation intensity, depending on the molecular position and orientation, was unknown).

Intensity auto-correlation functions of the single molecule fluorescence showed photon bunching for all molecules studied. The observed bi-exponential decay can be attributed to intersystem crossing (ISC) toward the triplet manifold, which can be modelled using two effective triplet sublevels. The study of the contrast and time constants of the two components in the correlation function as the excitation intensity is varied allowed us to determine the ISC rates toward and from the triplet sublevels:

T_X, T_Y sublevels:	S_1 to T_1: 1250 s^{-1};	T_1 to S_0: 4500 s^{-1};
T_Z sublevel:	S_1 to T_1: 40 s^{-1};	T_1 to S_0: 750 s^{-1}.

The intersystem crossing yield of DBATT is therefore extremely low, while

triplet lifetimes are still rather short. The bottleneck effect of the triplet being practically negligible, DBATT is a nearly perfect optical two-level system (even better than terrylene [13]), which can be used to test quantum optical effects.

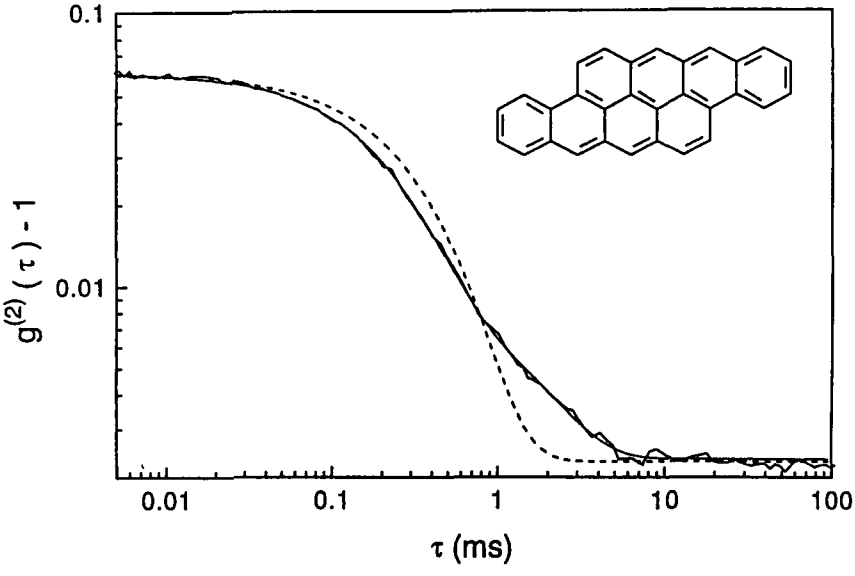

FIGURE 1 : Normalized auto-correlation function of the fluorescence intensity of a single DBATT molecule in n-hexadecane. The dashed and solid lines resp. are single- and bi-exponential fits to the data.

DIBENZOTERRYLENE IN NAPHTHALENE [14]

DBT in a benzene solution absorbs around 740 nm. When it is included in a naphthalene crystal matrix, its absorption band is shifted to 757.1 nm, where a sharp single site is visible.

Since the concentration of DBT in the crystal was very low, the single molecular lines studied lay very close to the center frequency of the site. The background in these spectra was very low because of the high purity of the matrix material, and because very few impurity molecules can absorb and fluoresce in the near-infrared. No spectral jumps were observed, as may be expected in a crystalline matrix.

The saturation and correlation studies of single DBT molecules in naphthalene give a homogeneous width of about 34 MHz (no lifetime measurement was performed on DBT), and show no trace of photon bunching between 10 microseconds and seconds. Since the triplet state of DBT must be very low, we think that the triplet lifetime is so short that no effect ofthe triplet can be detected on the experimental correlation functions.

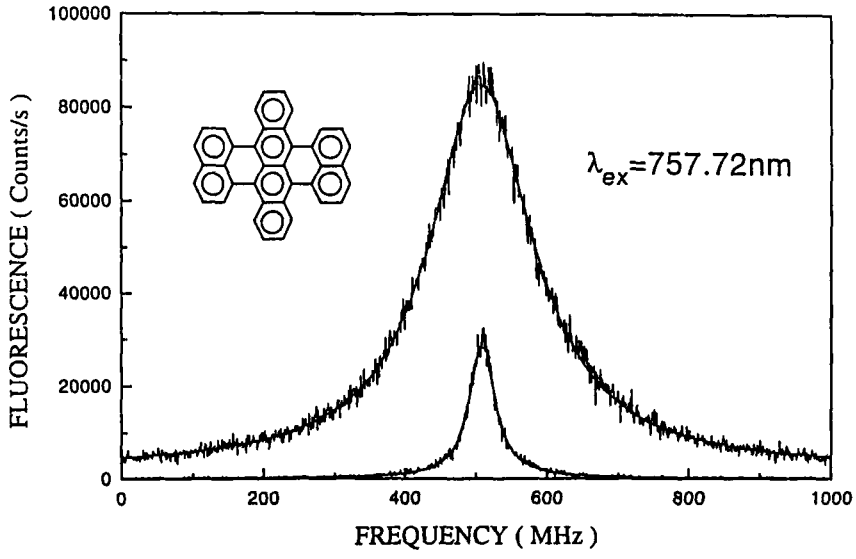

FIGURE 2: Example of a single DBT molecule line, showing the high signal-to-background ratio. The upper spectrum was recorded at a 50 times higher intensity than the lower one. The solid lines are Lorentzian fits.

In conclusion, the two new molecules DBATT and DBT present all the desired features for a high signal-to-background ratio in single molecule spectra: narrow, very photostable lines, with high fluorescence efficiency and negligible triplet bottleneck. These molecules are well suited to future quantum optical experiments [15]. DBT, absorbing at around 758 nm in a naphthalene crystal, is particularly interesting because it can be excited with cheap diode laser sources rather than a Ti-sapphire laser.

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