



Photophysical properties of new bis-perylene dyads for potential upconversion use



Marcos R. Ribas^{a,*}, Ronald P. Steer^b, Ricardo R  ther^a

^aUniversidade Federal de Santa Catarina – UFSC, Centro Tecnol  gico – CTC, Departamento de Engenharia Civil, Campus Reitor Jo  o David Ferreira Lima, Rua Jo  o P  o Duarte da Silva, 205, Bairro C  rrego Grande, Florian  polis, Santa Catarina CEP 88037-000, Brazil

^bDepartment of Chemistry, University of Saskatchewan, Saskatoon, SK S7N 5C9, Canada

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ABSTRACT

Two new bis-perylenes, BPC with a *meta*-disubstituted benzene linker, and BPD with a *p,p'*-disubstituted biphenyl linker, have been synthesized and their photophysical parameters measured. Their singlet and triplet energies decrease incrementally in the order perylene, BPC, BPD, making them ideally matched with C₆₀ for triplet–triplet energy transfer in sensitized photon upconversion schemes. Following photosensitization by triplet C₆₀, BPC exhibits strong fluorescence upconversion by triplet–triplet annihilation, indicating that these bis-perylene dyads (and the multimers that can be constructed from them) will be interesting candidates for use in organic devices such as bulk-heterojunction and dye-sensitized solar cells employing non-coherent photon upconversion.

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1. Introduction

Increasing global pressure to replace fossil fuels with renewable energy sources together with the increasing costs of conventional energy generation technologies and the decreasing costs of solar photovoltaics (PV) in particular, have prompted an increase in attempts to improve the efficiencies and longevities of all forms of PV devices [1–5]. All conventional single-threshold devices are subject the Shockley–Queisser power conversion efficiency (PCE) limit of *ca.* 30% [6]. Silicon-based and other inorganic PV technologies are nevertheless now well-established commercially, and some have even achieved efficiencies close to their theoretical limits, but still suffer from high costs of manufacture, despite the massive cost reductions resulting from economies of scale (with single PV module manufacturing plants in the gigawatt/year level) in recent years. In this context, the drive to produce a new generation of stable and lower cost solar PVs, with improved efficiencies using robust organic, organometallic and/or organic–inorganic hybrid materials has been intense [7–13].

Two of the novel proposed means of improving PV efficiencies involve circumventing the Shockley–Queisser limit by employing singlet exciton fission (in which one high energy absorbed photon yields more than one electronic state capable of electron transfer) [14], or non-coherent photon upconversion (NCPU, in which two low energy photons are absorbed and by excited state annihilation

produce one higher energy electronic state capable of electron transfer) [15,16]. Dyads of polycyclic aromatic hydrocarbons have been used in elucidating the basic photophysics of both processes [17,18]. Resulting increases in efficiency have in practice, however, been limited to a few fractions of a percent so far [19].

In this report we focus on a new, all-hydrocarbon, potentially very robust, sensitized NCPU system based on a bis-perylene upconverter. NCPU is now known to occur in a wide variety of materials, and has received particular attention because of its potential use in tandem dye-sensitized solar cells (DSSCs), where the energy-pooling process is triplet–triplet annihilation (TTA) [20]. So far the impact on the PCE of PVs using NCPU based on TTA has been small, but the fundamentals of the photophysics are known and improvements in efficiency are frequently being demonstrated [15,21].

Perylene itself has been recognized for some time as a very useful upconverting agent in sensitized systems. Castellano and co-workers [15] have characterized these systems thoroughly and have also used an all-hydrocarbon system, perylene plus C₆₀, with good results [22]. However, other all-hydrocarbon sensitized upconverters have been shown, under some conditions, to exhibit even better upconversion efficiency [23], particularly when the triplet energies of the sensitizing donor and acceptor are carefully tuned. Tuning of the molecular energy spacings in the photoactive components of DSSCs is not new, but can lead to significant efficiency improvements. In the bis-tetracene system, the energy spacings of the lowest singlet and triplet states of a series of dyads were tuned via the structure of the aromatic linker so as to

* Corresponding author.

E-mail address: marcosribas@gmail.com (M.R. Ribas).

promote singlet exciton fission [17]. Here we use the same approach to tune the energies of the upconverting and triplet energy accepting states of a series of bis-perylene dyads so that an excellent match is made with the triplet state of C_{60} as a sensitizer in NCPU. The structures of the newly-synthesized dyads examined in this report are shown in Chart 1.

2. Materials and methods

The bis-perylene dyads were synthesized in two steps: (i) perylene bromination to 3-bromoperylene and (ii) Suzuki–Myamura coupling of 3-bromoperylene with 1,3-phenylene and 4,4'-biphenylene diboronic acid, as described in detail in the accompanying Supporting Information. Toluene (Aldrich, spectroscopic grade) was selected as a solvent because it promotes NCPU and does not form charge transfer complexes with C_{60} ; it was used as received. All solutions involving triplet energy transfer or TTA were thoroughly deoxygenated by purging with dry, oxygen-free nitrogen followed by repeated freeze-pump-thaw cycles on a grease and mercury-free high vacuum line. All experiments were carried out at room temperature.

Absorption spectra were measured on a Cary 6000i (Agilent) spectrophotometer operating in dual beam mode. Spectra were taken in 10 mm \times 10 mm matched fused silica cuvettes with pure solvent as a reference, usually with a spectral bandpass of 2 nm and a step size of 1 nm for data acquisition. Steady-state fluorescence measurements were obtained on a Photon Technology International Quantmaster spectrofluorometer fitted with double excitation and emission monochromators. Samples were excited along the long path of a 10 mm \times 2 mm fluorescence cuvette and emission collected on the short path to minimize fluorescence reabsorption. Fluorescence and fluorescence excitation spectra were digitally corrected for spectral variations of the detection and excitation systems respectively. Fluorescence quantum yields were measured by the relative method using the quantum yield of perylene as a standard. (Note that there is some discrepancy in the literature concerning the fluorescence quantum yield of perylene; we used $\phi_f = 0.89$ for dilute solutions in benzene [24].) Upconversion experiments were conducted in a custom-modified Spex spectrofluorometer refit by Olis, Inc. with a single-photon counting detection system. Excitation was provided by a cw frequency-doubled Nd:YAG laser (WSTech, TECGL-30) and the incident power density delivered to degassed samples in a 10 mm \times 10 mm fused silica cuvette was adjusted through the use of a set of calibrated neutral density filters (Edmund Optics). A 532 nm notch filter was placed in the emission collection optics to eliminate excitation laser scatter.

Fluorescence decay times were measured as described in detail previously [25]. Briefly, samples were excited with a ps, mode-locked, frequency-doubled, pulse-picked, Ti:sapphire laser at 400 nm, and emission was observed at the wavelength of the maximum emission intensity and magic polarization angle. Temporal decays were obtained by time-correlated single photon counting detection. Fluorescence lifetimes were obtained by

iterative reconvolution of test decay functions with the instrument response function until an acceptable fit was obtained using the reduced χ^2 value and the distribution of weighted residuals as criteria.

An Edinburgh Instruments LP920 ns laser flash system, previously described in detail [23], was used to obtain transient absorption spectra and transient decay kinetics information in the C_{60} -sensitized bis-perylene TTA experiments.

3. Results and discussion

The spectra and photophysical properties of the two newly synthesized bis-perylene dyads will be compared with those of the parent perylene monomer. Wherever possible these comparisons are made under the same or similar conditions of solvent, temperature and solute concentration and spectral measurement parameters to obtain meaningful trends. The absorption, emission and emission excitation spectra and the fluorescence lifetime of degassed samples of pure perylene in toluene at room temperature were measured (cf. Supporting Information) and accurately reproduced reliable literature reports [22,26,27].

The UV–visible absorption and emission spectra of BPC and BPD in toluene at room temperature are shown in Figure 1. The corrected fluorescence excitation spectra (Supporting Information) accurately reproduced the absorption spectra. As expected, these spectra are similar, but not identical to those of perylene itself, and exhibit interesting trends when examining the structure of the linker, in the order: perylene, BPC, BPD. All three spectra are well-structured, but the breadths of the absorption features increase within the above sequence, perhaps indicating the presence of excitonic broadening and/or conformational diversity in the bis-perylenes. In each case, the band envelope is strongest in both the absorption and emission spectra, with two or three additional vibronic features of successively lower intensity attached to this electronic origin in a progression with intervals of ca. 1300–1500 cm^{-1} . These vibronic features can be assigned to C–C ring stretching vibrations, which exhibit the largest Franck–Condon factors in the electronic transitions, consistent with slight ring expansions in these electronic excited states. The Stokes shifts are small, of the order of 300–600 cm^{-1} , indicative of the rigid structure of the parent chromophore, but increase from perylene to BPC to BPD as the flexibilities of the molecules increase. The 0–0 bands exhibit a red-shift in the same order, as do the precise electronic origin energies obtained from the intersection of the red side of the 0–0 band in absorption and the blue side of the 0–0 band in the normalized emission spectrum. These data are summarized in Table 1.

The phosphorescence spectra of perylene and its dyads are extraordinarily weak due to the high symmetry of the chromophore, the large singlet–triplet energy spacing and the lack of heavy atoms in the molecule. Consequently, the exact triplet energies of BPC and BPD could not be measured accurately in the present experiments. However, the energies of the triplet states of BPC and BPD can be estimated from the spacings of the S_1 and T_1 states

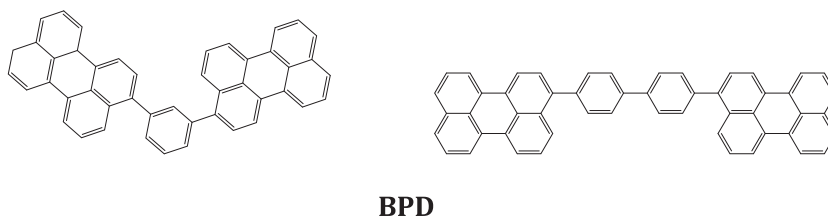


Chart 1. Structures of the bis-perylene dyads.

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