

Electronic Supplementary Information

Amplifying the Reactivity of BODIPY Photoremovable Protecting Groups

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Additional Figures

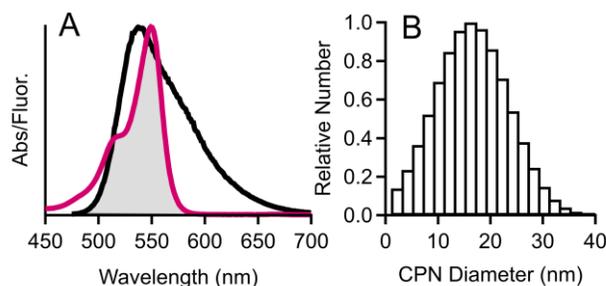


Figure S1. (A) Absorbance of **1DNB** (pink) and fluorescence of PFBT CPNs (black) with shaded donor-acceptor spectral overlap. (B) Size distribution of **1DNB**-doped CPNs measured by dynamic light scattering in aqueous suspension.

Experimental Section

Materials

All chemicals were obtained from Acros or Sigma-Aldrich and used as received unless otherwise specified. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-*co*-1,4-benzo-{2,1'-3}-thiadiazole] (PFBT) with an average molecular weight of 107,000 and polydispersity 3.5 was obtained from American Dye Source (Quebec, Canada). 4,4'-Dimethyltriphenylamine (TPA) was obtained from TCI America. The dye **1DNB** was synthesized as described previously.¹

Spectroscopy and Photochemistry

Absorption and fluorescence measurements were made with Agilent Technologies Cary 60 UV-Vis and Varian Eclipse Fluorimeter, respectively. All fluorescence experiments used an excitation wavelength of 455 nm. Fluorescence kinetics were collected at 568 nm. CPNs were studied in both aerated and degassed aqueous suspension in semi-micro quartz cuvettes (Starna, 10 mm × 4 mm interior dimensions). Samples were degassed in micro quartz cuvettes with septum screw tops for 30 minutes via argon bubbling. Small sample volumes (300 μ L) were used to maximize consistency of the visible irradiation intensity throughout the sample. Visible irradiation (455 nm or 530 nm) was provided by a four-wavelength high-power LED Source (ThorLabs, DC4100). Irradiation was delivered to the top of the sample cuvette in the absorbance and fluorescence instruments by a liquid light guide (ThorLabs, LLG0538). Photon flux values for 455 nm and 530 nm irradiation were determined by chemical actinometry² using Aberchrome 670.³ The photon flux ranges employed in this work (1 – 8 $M s^{-1}$) are approximately equivalent to 0.5 – 4.5 mW/cm^2 at 455 nm and 0.2 – 1.2 mW/cm^2 at 530 nm.

Nanoparticle Preparation

CPNs were prepared by a literature procedure.⁴ Separate stock solutions of conjugated polymer PFBT (1 mg/mL) and antifade agent TPA (0.2 mg/mL) in anhydrous tetrahydrofuran (THF) were stirred under argon for at least two hours before use. A small amount of **1DNB** was dissolved in THF (10 mL), and the concentration of the solution was determined by absorbance. A precursor solution was prepared by combining portions of the PFBT and TPA stock solutions with additional THF to final yield concentrations of 0.04 mg/mL PFBT and 0.0046 mg/mL TPA. This precursor solution was filtered through a 0.7 μm filter to remove any aggregates and then sonicated for 30 seconds to ensure homogeneity. A 1 mL portion of the precursor solution was injected into 8 mL of sonicating ultrapure water, which was then sonicated for an additional 2 minutes. For doped CPNs, a small volume of **1DNB** stock solution was then injected into the mixture, which was sonicated for an additional 15 s. The volume of **1DNB** stock was adjusted to give a dye concentration of 15 wt % relative to PFBT. THF was removed via argon bubbling for 60 minutes, and the aqueous suspension of CPNs was filtered through 0.7 μm and 0.22 μm filters. The **1DNB**-doped CPNs were tested for leakage of dye into the aqueous medium using a centrifugal filtration device (Amicon Ultra-4 centrifugal filter with an MW cutoff of 100,000). The absorbance spectrum of the aqueous filtrate showed no features, indicating that **1DNB** dyes are stably doped onto the CPN surface.

Nanoparticle Composition Estimates

The number of polymer chains per CPN was estimated by Eq S1,

$$n = \frac{V \cdot d}{M_w} \cdot N_A \quad (\text{S1})$$

where V is the CPN volume computed using the particle radius obtained from dynamic light scattering, d is a typical organic density of 0.8 g/mL, M_w is the molecular weight of the polymer (107,000), and N_A is Avogadro's number. This method yielded an estimate of 7 polymer chains per particle for the PFBT CPNs reported in this work. Absorbance values for the conjugated polymer and **1DNB** dye in the doped CPNs were used to calculate the average number of dyes per polymer chain using Beer's law. This value was then multiplied by the average number of polymer chains per nanoparticle obtained above to yield the estimated number of dyes per nanoparticle.

Kinetic Analysis

The fluorescence intensity at 568 nm was monitored as a function of time during continuous LED irradiation ($\lambda = 455$ nm for FRET-sensitization, $\lambda = 530$ nm for direct excitation) to obtain kinetic traces. FRET-sensitized reactions ran to completion during the data collection period and were analyzed by Eq S2

$$F_t = F_{max} \cdot (1 - e^{-k_{pr}t}) + B \quad (\text{S2})$$

where F_t is the fluorescence intensity at 568 nm at time t , F_{max} is the maximum emission intensity, k_{pr} is the photorelease rate constant, and B is an offset that accounts for the non-zero value of the initial fluorescence intensity. We previously determined that the energy transfer efficiency can change over the course of a FRET-sensitized reaction due to photoselection phenomena.⁵ Accordingly, only the first 75% of each FRET-sensitized kinetic trace was used in the fitting process. Photorelease reactions under direct excitation conditions were too slow to obtain empirical values for F_{max} . Alternatively, plots of $\ln(F_{max} - F_t)$ vs. t were constructed for a wide

range of possible F_{max} values and linear fits were performed.⁶ The F_{max} value that yielded a minimum in the standard deviation of the fit was used to fit the kinetic traces by Equation S2. The obtained value was consistent with those observed experimentally for sensitized reactions that ran to completion. Because energy transfer efficiency depends on both the dye concentration and the particle size of individual samples,⁵ it is not possible to obtain k_{pr} values in triplicate. The values presented in Fig. 2C in the main text are for one sample divided into aliquots for the different photon fluxes and irradiation colors. The experiment was repeated numerous times to ensure that the presented values represent typical behavior for this system.

References

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