

Electronic Supplementary Information

Visible Light Photoswitching of Conjugated Polymer Nanoparticle Fluorescence

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Supplemental Figures

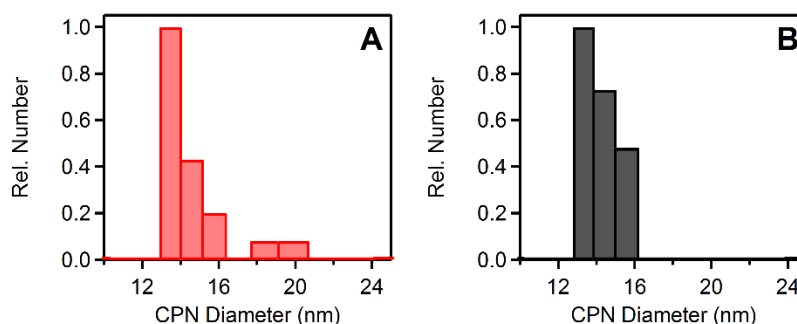


Figure S1. Size distributions of CPNs measured in aqueous suspension by dynamic light scattering. (A) APESO-doped, coated CPNs. The distribution shown represents 100% of CPNs and has a mean diameter of 13.4 ± 0.8 nm. (B) Undoped, coated CPNs. The distribution shown represents 96% of CPNs and has a mean diameter of 13.6 ± 0.7 nm. The remaining 4% of CPNs are a population of larger CPNs with mean diameter 46.3 ± 3.8 nm.

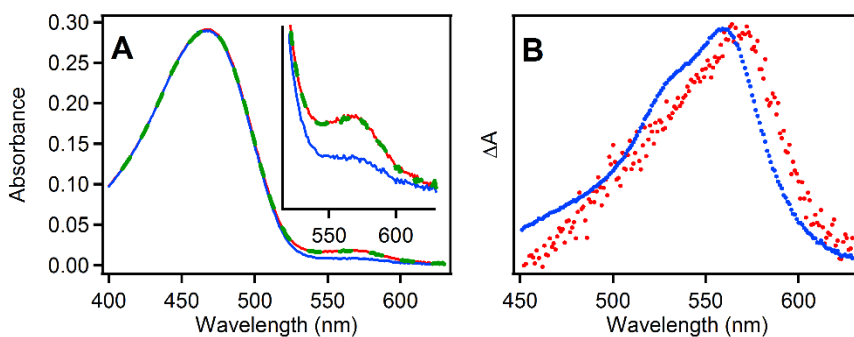


Figure S2. (A) Absorption spectra of APESO-doped, coated CPNs in aqueous suspension before (red) and immediately after (blue) visible light irradiation (5 s, 455 nm, 2.2 mW/cm^2) and after 1 min. dark thermal recovery (red). Inset: red-edge expansion of the 3 spectra. (B) Difference spectrum (red) created by subtracting the spectrum obtained immediately after irradiation from that obtained prior to irradiation superimposed with the absorption spectrum of APESO in dilute THF solution (blue).

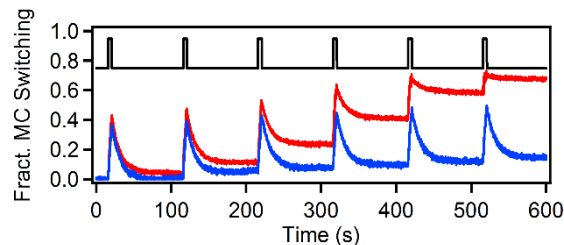


Figure S3. Fraction of MC isomers switching to the SO form in APESO-doped, uncoated CPNs in aerated (red) and degassed (blue) aqueous suspension during irradiation following the square wave pattern depicted at the top of the figure. These results show that APESO-doped CPNs without the coating experience massive photochromic fatigue, with more than 60% of dyes lost to fatigue after 6 cycles in aerated aqueous suspension. When the same aqueous suspension of uncoated CPNs is degassed, just 14% of dyes experience fatigue. This degree of fatigue is similar to that observed in the coated CPNs in Figure 2B in the main text, which lose 12% of the MC dyes to fatigue after 7 cycles in aerated suspension. The coating appears to protect the dyes from oxygen, enabling repeated cycling of the photochromic conversion and fluorescence intensity.

Calculation of Fraction of MC Switching to SO

For APESO-doped CPNs, the absorbance at 565 nm (A_{565}) is due to the absorbance of MC (A_{MC}) and the conjugated polymer chromophores (A_{CPN}) with no contribution from SO, as it absorbs only in the UV (Eq. S1). The value of A_{CPN} was determined by recording A_{565} before and after deliberately photobleaching of all the MC dyes in a sample. A_{MC} was then calculated by Eq. S1.

$$A_{565} = A_{MC} + A_{CPN} \quad (S1)$$

At any time t during the experiment, the concentrations of MC and SO can be calculated by Beer's Law (Eq. S2), where ϵ is the extinction coefficient of MC and l is the path length. The concentration of [SO] at any time t is given by the loss of MC from the initial population prior to visible irradiation ($[MC]_0$) (Eq. S3).

$$[MC]_t = \frac{A_{MC,t}}{\epsilon \cdot l} \quad (S2)$$

$$[SO]_t = [MC]_0 - [MC]_t \quad (S3)$$

The fraction of MC isomers that convert to SO at a given time t is then given by Eq. S4.

$$\frac{[SO]_t}{[MC]_0} = \frac{[MC]_0 - [MC]_t}{[MC]_0} = \frac{\frac{A_{MC,0}}{\epsilon \cdot l} - \frac{A_{MC,t}}{\epsilon \cdot l}}{\frac{A_{MC,0}}{\epsilon \cdot l}} = \frac{A_{MC,0} - A_{MC,t}}{A_{MC,0}} \quad (S4)$$

The values for $[SO]_t/[MC]_0$ expressed in the main text were determined at the end of the visible irradiation period, $t = 5$ s.

Estimation of Number of Polymer Chains per CPN

The volume of the CPNs is calculated as for a sphere (Equation S5), using size information from dynamic light scattering measurements for the radius.

$$V = \frac{4}{3}\pi r^3 \quad (\text{S5})$$

The number of polymer chains per CPN is then estimated by Equation S6, where d is a typical organic density of 0.8 g/mL, M_w is the molecular weight of the polymer, and N_A is Avogadro's number.

$$n = \frac{V \cdot d}{M_w} \cdot N_A \quad (\text{S6})$$

The CPNs reported herein are prepared from the conjugated polymer PFBT with molecular weight 138,000, which gives $n = 4.4$ for APESO-doped CPNs and $n = 4.6$ for undoped control CPNs. Given the polydispersity (3.1) of PFBT, these values are considered estimates and presented in the main text as rounded values.

Estimation of Number of APESO Dyes per CPN

To estimate the number of APESO dyes per CPN, the ratio of APESO dyes to conjugated polymer chains was first calculated. This calculation was performed twice for each CPN sample, once based on the amounts and concentrations of components that were added to produce the CPNs (input) and again based on the absorption spectra of as-prepared CPNs (output). For the input calculation, PFBT concentration was quantified based on the amounts of solid polymer and solvents added as described in the Experimental Section below. The concentration of the APESO stock solution in THF was calculated by Beer's Law using the absorbance at 565 nm and the measured extinction coefficient value of $5 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ (MC form). The number of APESO dyes per PFBT chain was calculated to be 10 by this method. For the output calculation, the concentrations of APESO and PFBT in the CPNs were calculated from absorbance spectra using Beer's Law, with the polymer concentration assessed using the absorbance at 460 nm and the literature extinction coefficient value¹ of $1 \times 10^7 \text{ M}^{-1}\text{cm}^{-1}$ and the APESO concentration calculated as described above after correction for contribution of the conjugated polymer to the absorbance at 565 nm. This procedure yielded a value of 10 APESO dyes per polymer chain, demonstrating consistency between the input and output values. Calculation of the number of polymer chains per CPN as described above enabled calculation of the number of dyes per CPN, yielding an estimate of 40 dyes/CPN.

Estimation of Photoinduced Electron Transfer Energetics

The change in free energy for charge separation (ΔG_{CS}) produced by photoinduced electron transfer can be estimated by Equation S7, where E_{ox} and E_{red} are the first one-electron oxidation potential of the donor and first one-electron reduction potential of the acceptor, respectively, $E_{0,0}$ is the energy of the 0,0 transition to the lowest excited singlet state, and C is the Coulomb interaction energy, which is solvent-dependent and can be neglected in a solvent of moderate polarity.²

$$\Delta G_{CS} = E_{ox} - E_{red} - E_{0,0} + C \quad (\text{S7})$$

For APESO, the MC form is more easily oxidized and reduced than the SO form with E_{ox} (MC) = 0.61 V and E_{red} (MC) = -0.59 V vs. SCE. For PFBT in acetonitrile, E_{ox} = 1.16 V and E_{red} = -1.68 V vs. SCE.³ The energy of the charge separated species $MC^{\bullet+}-PFBT^{\bullet-}$ is 2.29 V above the ground state while that of the charge separated species $MC^{\bullet-}-PFBT^{\bullet+}$ is 1.75 V above the ground state. Following Lakowicz, we obtained an E_{00} value of 2.43 eV (510 nm) from the intersection of the normalized CPN absorption and fluorescence spectra.⁴ Using this value, both PET processes described above would be thermodynamically possible, but formation of $MC^{\bullet-}-PFBT^{\bullet+}$ would be the most favored with a ΔG_{CS} value of -0.68 V.

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 138,000 and polydispersity 3.1 was obtained from American Dye Source (Quebec, Canada) and used as received. Granular poly(vinyl butyral-co-vinyl alcohol-co-vinyl acetate) (PVB-VA-VA) was obtained from Sigma-Aldrich. Spiro[azahomoadamantane-phenanthrene-oxazine] (APESO) was synthesized as described previously.⁵

Nanoparticle Preparation and Characterization. CPNs were prepared by a literature procedure.⁶ Stock solutions of PFBT (1 mg/mL) and PVB-VA-VA (1 mg/mL) in anhydrous tetrahydrofuran (THF) were stirred overnight under argon. A precursor solution was prepared by combining portions of the PFBT and PVB-VA-VA solutions with additional THF to a final concentration of 0.04 mg/mL PFBT and 0.008 mg/mL PVB-VA-VA. This precursor solution was filtered through a 0.7 μ m filter to remove any aggregates and then sonicated for 30 s 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 min. For undoped control CPNs, the THF was then removed by a high vacuum pump, and the resulting aqueous suspension of CPNs was filtered through a 0.22 μ m filter. For APESO-doped CPNs, a stock solution of APESO in THF was freshly prepared and its concentration determined by absorption spectroscopy using the extinction coefficient value of 50,000 $M^{-1}cm^{-1}$. Typical APESO stock solution concentrations were ca. 2×10^{-6} M. To prepare APESO-doped CPNs, a portion of the stock solution was added to the aqueous suspension of CPNs while sonicating, and sonication was continued for an additional 15 s. The volume of APESO stock solution added was adjusted for each preparation so that the concentration of APESO in CPNs would be 2.7 wt. % relative to PFBT. The THF was removed by a high vacuum pump, and the aqueous suspension of APESO-doped CPNs was filtered through a 0.22 μ m filter.

APESO-doped CPNs were tested for dye leaching by a literature procedure.⁷ Aqueous suspensions of CPNs were spun at 5000 rpm for 2 min. in a centrifugal filtration device (Amicon Ultra-4 centrifugal filter with a molecular weight cutoff of 100,000). The absorbance of the filtrate was recorded, and no evidence of APESO was found in the spectra, demonstrating that the dyes do not leach into the surrounding aqueous medium. Nanoparticle size distributions were measured in aqueous suspension by dynamic light scattering using a Nicomp N3000 Submicron Particle Sizer (Particle Sizing Systems).

Spectroscopy and Photochemistry. Absorption and fluorescence measurements were made with a Varian Cary 50 and Varian Eclipse instruments, respectively. All fluorescence experiments used an excitation wavelength of 455 nm. CPNs were studied in aerated aqueous suspension in semi-micro cuvettes (10 mm x 4 mm interior dimensions). Small sample volumes

(150 μ L) were used to maximize consistency of the visible irradiation intensity throughout the sample. Visible irradiation (455 nm) was provided by a 4-Wavelength High-Power LED Source (ThorLabs, DC4100) with square wave input from a function generator. Irradiation was delivered to the top of the sample cuvette in the absorbance/fluorescence instrument by a liquid light guide (ThorLabs, LLG0538).

References

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