

Supporting Information

for

Driving Charge Separation for Hybrid Solar Cells: Photo-induced Hole Transfer in Conjugated Copolymer and Semiconductor Nanoparticle Assemblies

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1. Synthesis of PDPPPV alternating conjugated copolymers

1.1. Synthesis of (-)PDPPPV

Poly(potassium 1,4-diketo-2,5-bis(4-sulfonylbutyl)-3,6-diphenyl-pyrrolo(3,4-c)pyrrole-alt-divinyl-1,4-bis(ethoxy)benzene), denoted as (-)PDPPPV, was synthesized by Heck-coupling of monomer (**5**) with monomer (**9**), as illustrated in Figure S1.

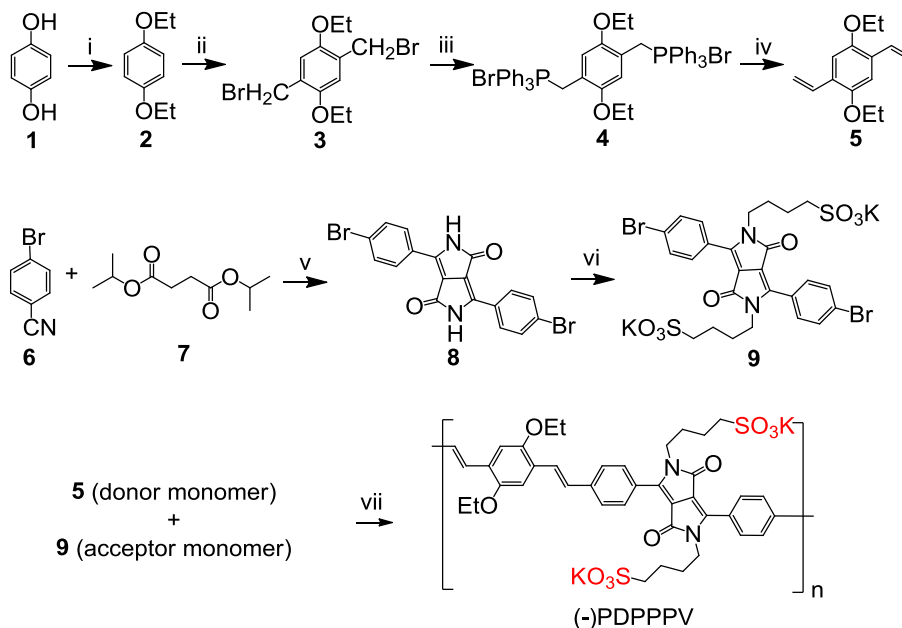


Figure S1. Synthetic route of (-)PDPPPV: (i) NaOH, DMSO, EtBr;¹ (ii) NaBr, HOAc, H₂SO₄, (CH₂O)_n;² (iii) PPh₃, toluene;³ (iv) CH₂Cl₂, HCHO;⁴ (v) Na, tert-amylalcohol, FeCl₃, HOAc;² (vi) t-BuOK, DMF, 1,4-butane sultone; (vii) P(o-tolyl)₃, Pd(OAc)₂, NEt₃, DMSO, H₂O.⁵

Monomer 5. Under an argon atmosphere, compound **4** (2,5-diethoxy-1,4-xylylene-bis(triphenyl phosphonium bromide)) (6.5748 g, 7.5 mmol) was stirred at 0 °C in dichloromethane (100 mL) and formaldehyde (30 mL), to which a 25 mL aqueous solution of NaOH (20 wt %) was added drop-wise over a time period of 1 h, and the reaction mixture was stirred for 24 h. Afterward phase separation was allowed to occur

and the aqueous layer was extracted. The resultant non-aqueous layer was dried with anhydrous sodium sulfate, and then the solvent was removed by rotary evaporation. The residue obtained afterward was purified by recrystallization in ethanol to yield pale yellow Yield: 1.05 g, 64.1 %. NMR (300 MHz, CDCl₃): δ (ppm) 7.10–7.00 (dd, $J = 11.1$, 17.8 Hz, 2H, vinyl-H), 7.00 (s, 2H, Ar-H), 5.73 (d, $J = 17.7$ Hz, 2H, vinyl-H(terminal)), 5.26 (d, $J = 11.1$ Hz, 2H, vinyl-H(terminal)), 4.04 (q, $J = 7.0$ Hz, 4H, O-CH₂), 1.43 (t, $J = 7.0$ Hz, 6H, -CH₃).

Monomer 9. Under an argon atmosphere, compound **8** (4.46 g, 10 mmol) and potassium *t*-butoxide (1.76 g, 22 mmol) were heated at 60 °C in dry DMF (150 mL), and 1,4-butane sultone (3.1 mL, 30 mmol) was slowly added. The reaction mixture was stirred at 90 °C for 12 h, and then it was poured into ethanol (1L) to obtain a precipitate that was collected by filtration and redissolved in hot water. The resultant water solution was filtered, concentrated, and dried under vacuum to give an orange-red solid. Lastly the product was purified by recrystallization in an aqueous solution of potassium chloride (50g/L) and dried under vacuum at 120 °C for 24 h to obtain a red-brown powder. Yield: 1.55 g, 19.5 %. ¹H NMR (300 MHz, D₂O): δ (ppm) 7.60 (d, $J = 8.5$ Hz, 4H, DPP aromatic H), 7.44 (d, $J = 8.4$ Hz, 4H, DPP aromatic H), 3.67 (t, $J = 6.0$ Hz, 4H, N-CH₂), 2.69 (t, $J = 7.3$ Hz, 4H, S-CH₂), 1.49 (m, 8H, -CH₂-).

(-)PDPPPV. Under an argon atmosphere, monomer **5** (0.2183 g, 1 mmol), monomer **9** (0.7946 g, 1 mmol), palladium(II) acetate (0.0135 g, 0.06 mmol), tri(*o*-tolyl)phosphine (0.0730 g, 0.24 mmol), and triethylamine (5 mL) were placed in a three-neck round-bottom flask with H₂O (3 mL) and dimethylsulfoxide (8 mL). The reaction mixture was allowed to stir at 100 °C for 18 h and subsequently cooled and then filtered.

The filtrate was poured into the mixed solvent (ethyl ether/acetone/methanol =5/4/1), after which a precipitate was formed and isolated by filtration. It was then re-dissolved in deionized water (10 mL). The resultant solution was dialyzed in deionized water for three days using a 4kD MWCO cellulose membrane (*Spectra/Por* Cellulose Ester Membrane). Finally the solvent was removed by rotary evaporation and the crude product was further dried under vacuum with P₂O₅ at 50 °C for 2 days to obtain a dark purple powder. Yield: 0.34 g, 40%. ¹H NMR (300 MHz, D₂O): δ (ppm) 7.57–7.22 (vinyl-H and DPP aromatic H), 3.96 (O-CH₂), 3.65 (N-CH₂), 2.75–2.59 (S-CH₂), 1.47–1.37 (-CH₃ and -CH₂-).

1.2. Synthesis of (+)PDPPP

1.2 Poly(1,4-diketo-2,5-dipropyl-3,6-diphenyl-pyrrolo(3,4-c)pyrrole-alt-divinyl-1,4-bis(2-(N,N,N-triethylammonium)ethoxy)benzene bromide), namely, (+)PDPPP, was synthesized by Heck-coupling of monomer **2** and monomer **8**, as shown in Figure S2. Note that the compound labels here should not be confused with those for (-)PDPPP.

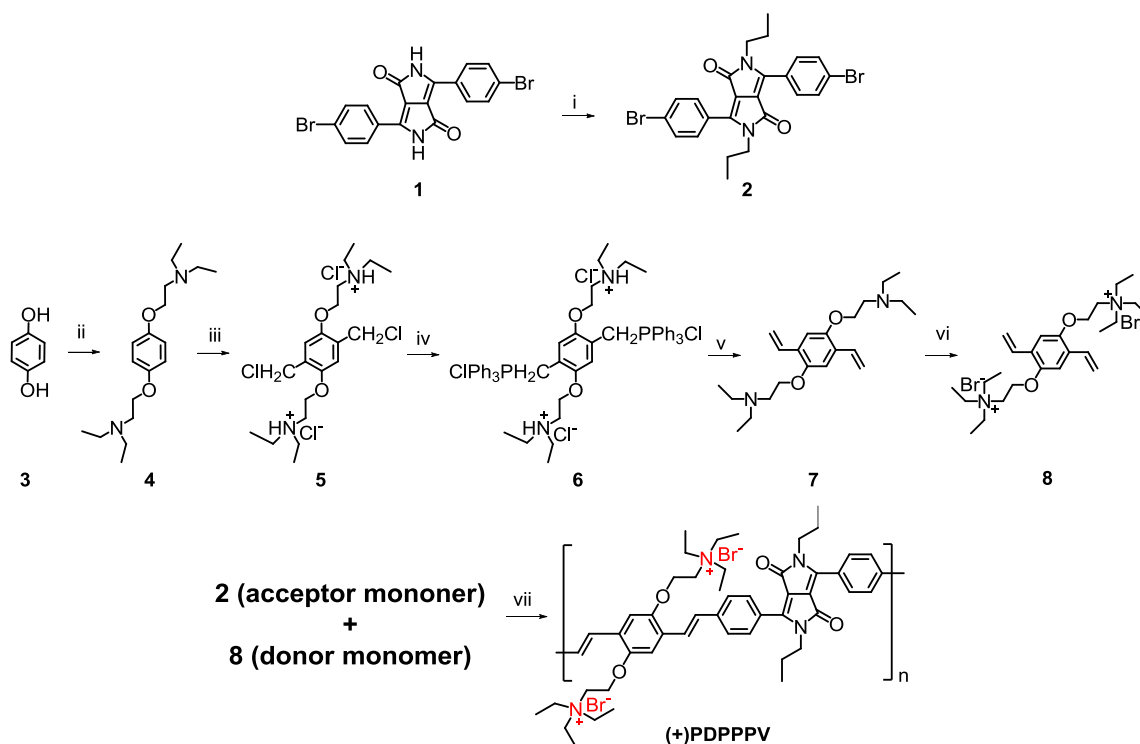


Figure S2. The synthesis for (+)PDPPP. (i) $t\text{-BuOK}$, NMP, 1-iodopropane;⁶ (ii) K_2CO_3 , acetone, 2-chlorotriethylamine hydrochloride;⁷ (iii) HCl, HCHO, dioxane;⁷ (iv) PPh_3 , H_2O , DMF;⁸ (v) NaOH, HCHO; (vi) EtBr, acetone; (vii) $\text{P}(\text{o-tolyl})_3$, $\text{Pd}(\text{OAc})_2$, NEt_3 , DMSO.⁵

Monomer 2. Under an argon atmosphere, compound **1** (1,4-diketo-3,6-bis(4-bromophenyl)pyrrolo[3,4-c]pyrrole) (0.892 g, 2 mmol), potassium tert-butoxide (0.494 g,

4.4 mmol), and anhydrous 1-methyl-2-pyrrolidinone (15mL) were heated at 60 °C. 1-iodopropane (2.04g, 12mmol) was added slowly and the mixture was stirred at 60 °C for 24 h. After cooling to room temperature, 25 mL of toluene was added to the reaction mixture, which was then washed with water to remove the NMP. The solution was concentrated by using a rotary evaporator. The crude product was purified by column chromatography on silica using dichloromethane as the eluent, and the final product was an orange powder. Yield: 0.221 g, 21%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 7.72–7.64 (m, 8H, DPP aromatic H), 3.74–3.67 (m, 4H, N-CH₂), 1.59 (dd, J = 15.0, 7.5 Hz, 4H, -CH₂-), 0.85 (t, J = 7.4 Hz, 6H, -CH₃).

Monomer 8. Under an argon atmosphere, compound **7** (1,4-bis[N,N-diethylamino]-1-oxapropyl]-2,5-divinyl-benzene benzene) (crude product, 2.095 g), bromoethane (2 g), and acetone (10 mL) was stirred and heated for two days to obtain a white precipitate. The solid was filtered, washed with bromoethane and hot acetone repeatedly, and finally dried under vacuum to obtain a white powder. Yield: 714 mg, 43% (6→8, 2 steps total yield). ¹H NMR (300 MHz, D₂O): δ (ppm) 7.22 (s, 2H, Ar-H), 7.02 (dd, J = 17.7, 11.2 Hz, 2H, vinyl-H), 5.85 (d, J = 17.7 Hz, 2H, vinyl-H(terminal)), 5.41 (d, J = 11.3 Hz, 2H, vinyl-H(terminal)), 4.53–4.43 (m, 4H, O-CH₂), 3.81–3.72 (m, 4H, N-CH₂), 3.46 (q, J = 7.2 Hz, 12H, N-CH₂(ethyl)), 1.35 (t, J = 7.2 Hz, 18H, -CH₃).

(+)PDPPPv. Under an argon atmosphere, monomer **8** (115.7 mg, 0.2 mmol), monomer **2** (106 mg, 0.2 mmol), palladium(II) acetate (2.8 mg, 0.012 mmol), tri(o-tolyl)phosphine (14.6 mg, 0.048 mmol), and triethylamine (2 mL) were placed in a three-neck round-bottom flask with dimethylsulfoxide (8 mL). The reaction mixture was stirred at 80 °C for 6 h; then the mixture was poured into a mixed solvent (ethyl

ether/acetone/methanol=5/4/1). A precipitate was formed and isolated by filtration. The crude product was dried under vacuum to obtain a dark purple powder. ^1H NMR (400 MHz, DMSO- d_6): δ (ppm) 7.96–7.36 (vinyl-H and phenyl-H), 4.60–4.50 (O-CH₂), 3.89–3.47 (N-CH₂), 1.48–1.31 (-CH₂-), 1.05–0.78 (-CH₃).

2. Molecular weight determination for PDPPPV copolymers

Table S1 shows the molecular weight results for the two PDPPPV copolymers determined by using gel permeation chromatography (GPC) and polyethylene oxides as a standard in either DI water or DMSO. The solvent was selected based on the polymer's solubility in order to reach a concentration required to obtain reasonable signal intensity and reproducible results. It has been reported that accurate determination of the molecular weight for these copolymers is problematic, because its self-aggregation leads to an overestimation of the molecular weight.⁹⁻¹² For example, the (-)PDPPPV has a Mn of 25,700 and a Mw of 266,400. A high polydispersity index (Mw/Mn) suggests a large size distribution, which is likely caused by the polymer self-aggregation. Similar observations have been reported for other donor-acceptor copolymers.^{11, 12} Note that the GPC measurements required a relatively high polymer concentration (~ 1 mg/ml), which is about 300 times higher than that used in the spectroscopic measurements. Figure S4A shows absorbance spectra for these two copolymers and does not indicate features of aggregation. Thus, the self-aggregation does not pose a serious problem for the charge transfer studies at low concentrations in solution.

Table S1. The GPC results for the molecular weight of the two PDPPPV copolymers.

Polymer	M_w	M_n	PDI (M_w/M_n)	Solvent
(-)-PDPPPV	266,400	25,700	10.4	0.1 M Na ₂ SO ₄ aqueous solution at 30 °C
(+)-PDPPPV	58,500	24,200	2.4	DMSO at 80 °C

3. Synthesis of anionic and cationic CdTe nanoparticles

CdTe nanoparticles (NPs) (~ 5 nm in diameter, see Figure S3) were originally synthesized in octadecene at 280 °C by the hot-injection method with oleic acid (OA) as the capping ligand.¹³ The resulting OA-CdTe NPs in CHCl_3 were injected at 100 °C into an aqueous solution of $\text{CdCl}_2/2$ -(dimethylamino) ethanethiol hydrochloride (DEA) to obtain water-soluble, highly fluorescent, and cationic DEA-CdTe NPs ((+)NPs). The molar ratio of OA-NP and DEA ligand is 1:2, and the molar concentration of the OA-NP is about 1 μM . Anionic CdTe NPs ((-)NPs) were prepared by using 3-mercaptopropionic acid (MPA) in the ligand exchange, instead of DEA. MPA-CdTe and DEA-CdTe NPs have very similar absorption spectra with that of the parent OA-CdTe NPs, as shown in Figure S4B.

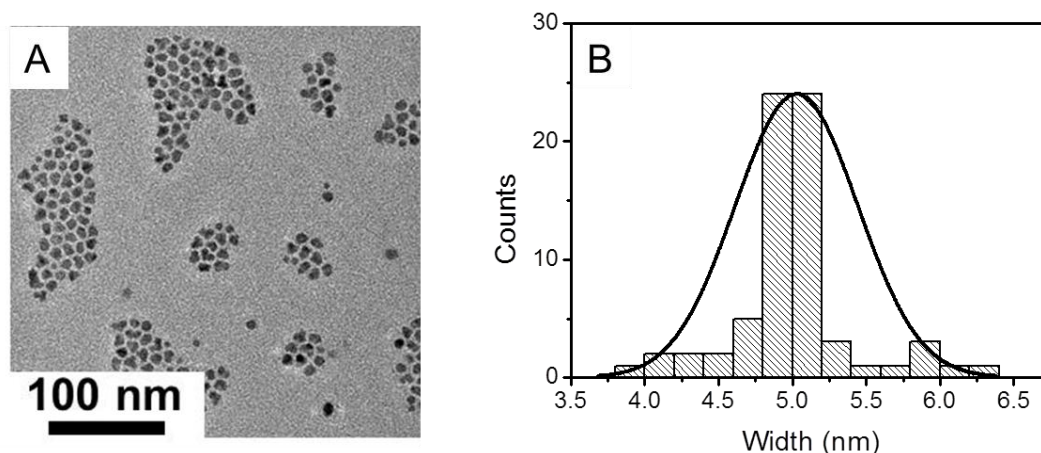


Figure S3. Panel A shows a TEM image for the OA-CdTe NPs used in this study. Panel B shows the size distribution for the OA-NPs obtained by using Image J software to analyze more than 60 NPs.

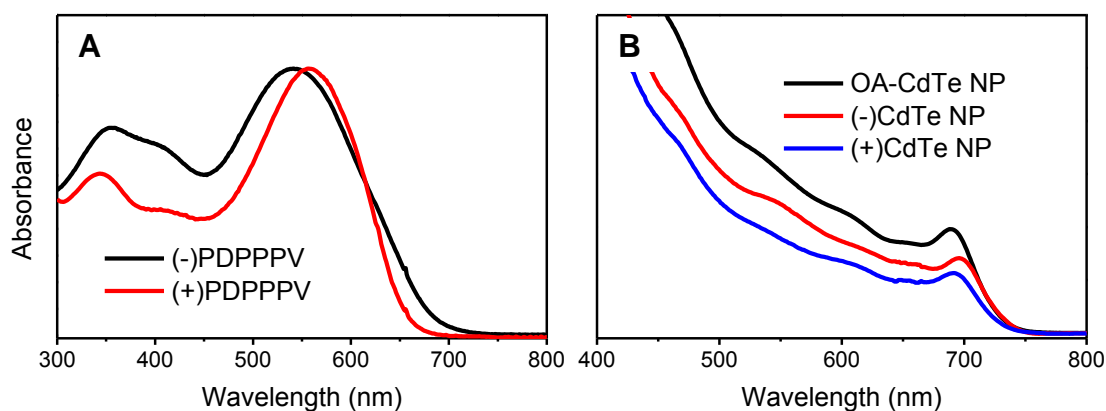


Figure S4. Panel A compares the steady-state absorption spectra for (-)PDPPPV and (+)PDPPPV. Panel B compares the steady-state absorption spectra for the parent OA-CdTe NPs and (-)/(+) CdTe NPs.

4. Cyclic Voltammetry

A three-electrode electrochemical cell was used to determine the energetics of the NPs and polymers. Films of the NPs and polymers were drop-cast from their aqueous solution onto a glassy carbon electrode. The electrochemical cell also included a Pt counter electrode and a Ag/AgNO₃ reference electrode (0.1 V vs. Fc/Fc⁺), to which the potential is referenced. The electrolytes were an acetonitrile solution with 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆).

Because the oxidation onset can be directly related to the charge transfer with the valence band edge,¹⁴ cyclic voltammetry (CV) was used to determine the band edge position for the CdTe NPs and PDPPPV copolymers. Figure S5 shows the CV results for (+)/(-) PDPPPV copolymers, (+)/(-) CdTe NPs, and a control polymer, poly[5-methoxy-2-(3-sulfopropoxy)-1,4-phenylenevinylene] (denoted as (-)PPV). As described previously,¹⁵ the onset oxidation potentials can be used to place the valence band edges

for these materials and they are found to be at -5.50 ± 0.1 eV for CdTe NPs, -5.10 ± 0.1 eV for PDPPPV copolymers, and -5.60 ± 0.1 eV for (-)PPV. Errors were determined from the standard deviation of the data obtained from three separated measurements. These results agree well with other literature reports for similar materials.¹⁶⁻¹⁸ If one uses their optical bandgap calculated from the absorption spectrum and the electrochemical valence band edge value to estimate the conduction band edge, then we obtain the energy level diagram shown in Figure S5D. This energy level scheme predicts that 1) a type-II (donor-acceptor) heterojunction is formed between the PDPPPV copolymers and CdTe NPs; and 2) a type-I heterojunction is formed between the (-)PPV and CdTe NPs.

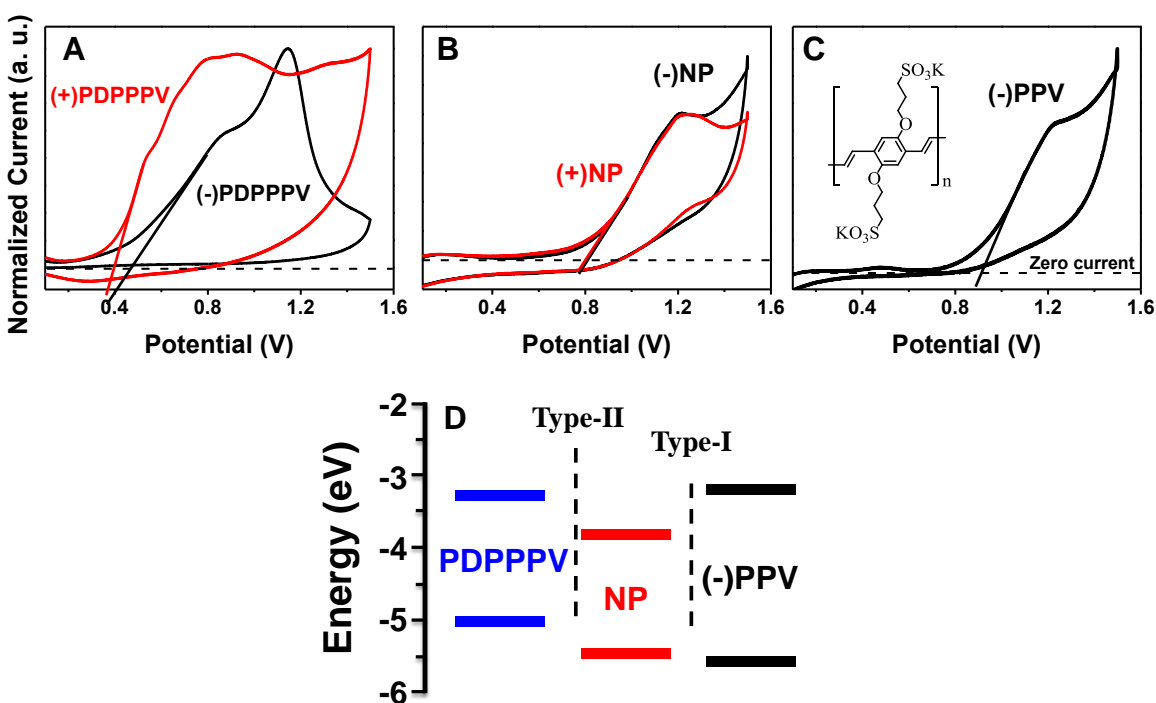


Figure S5. Panels A to C show cyclic voltammograms for (+)/(-) PDPPPV copolymers, (+)/(-) CdTe NPs, and (-)PPV. The background from the electrolytes has been subtracted from all voltammograms shown here. The dashed line marks the position of zero current in each panel. The crossing point between the zero current and onset tangent gives the

oxidation onset potential. Panel D shows an energy diagram with the final CV results for all samples.

5. Dynamic light scattering (DLS) and Zeta-potential measurements

DLS measurements were performed on solutions of the NP/polymer assemblies at room temperature in a 90° geometry and analyzed by using particle sizing software with a 532 nm laser (Brookhaven Instrument Co.). Zeta-potential measurement were performed on the same instrument at room temperature with an electrical field strength of 10 V/cm by using a Zeta Plus potential analyzer.

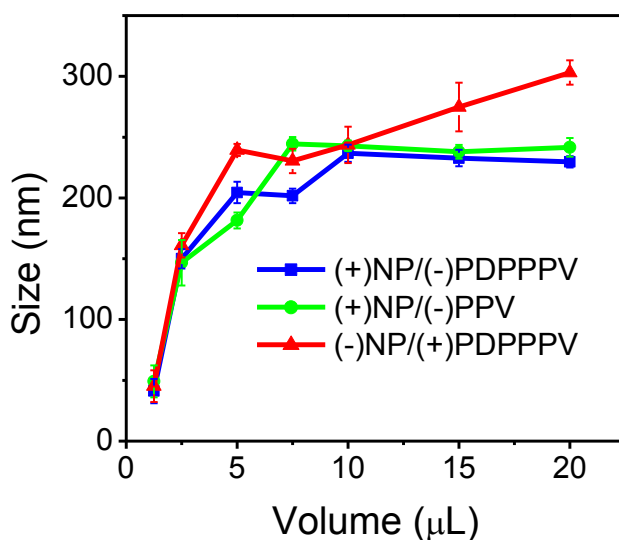


Figure S6. The aggregation size measured by dynamic light scattering for the three CP/NP combinations.

Table S2. Zeta-potential values for the polymers and NPs involved in this study.

Polymers	Zeta-potential (mV)	NPs	Zeta-potential (mV)
(-)PDPPP	-36.24 ± 1.34	(-)NP	-24.59 ± 2.92
(+)PDPPP	36.91 ± 2.31	(+)NP	20.45 ± 3.28
(-)PPV	-27.81 ± 1.22		

6. PL quenching

Steady-state absorption and emission spectra were measured by an Agilent 8453 spectrometer and a Horiba J-Y Fluoromax 3 fluorescence spectrophotometer. Steady-state photoluminescence quenching measurements were carried out while continuously adding 0.05 wt% aqueous polymer solution (20 μ L in total) into a 3 mL NP phosphate buffer solution (pH=7). The optical density (OD) is \sim 0.1 for both NP and PDPPPV at their absorption peaks after titration, which corresponds to a NP/polymer molar ratio of 3 to 1. The NP/polymer PL quenching experiments were performed in both DI water (where the counter ion for the (+)NP is solely Cl^- , which is from the surface ligands), and pH=7 potassium phosphate buffer (where the counter ions for the NP are Cl^- , H_2PO_4^- and HPO_4^{2-}). The results were very similar in both cases, and thus we believe that the counter ion effect on the QD PL yield and PL quenching is minimal

The time-resolved fluorescence data were collected using the time-correlated single photon counting (TCSPC) method. The instrument response function was measured using a sample of colloidal BaSO_4 . The samples were excited at 660 nm using a dye laser (DCM) at a 1 MHz repetition rate, and fluorescence counts were collected until 6000 counts in the peak channel for each sample. Experiments were also performed with a 300 kHz repetition rate, at which the lifetime values were found to be nearly identical to those collected at a 1 MHz repetition rate in all the systems studied. The kinetics were extracted by fitting the fluorescence decay curves by using a Edinburgh FAST lifetime distribution software.

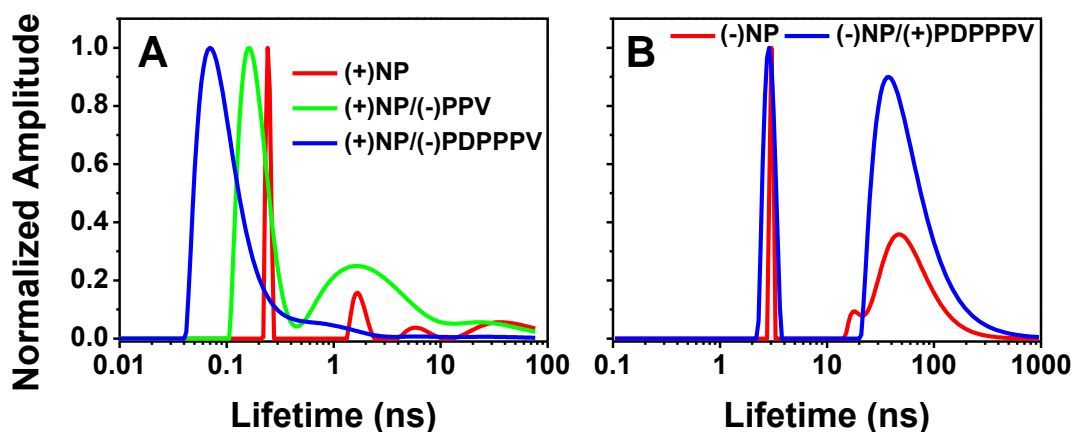


Figure S7. Lifetime distribution fitting for the PL decays shows in Figure 3D and Figure 5B.

By following previously published methods,¹⁹ hole transfer rate constant (k_{CT}) can be estimated as:

$$k_{CT} = 1/\tau - 1/\tau_0$$

where, τ is the short lifetime component for the (+)NP/(-)PDPPP assembly, and τ_0 is that for the (+)NP/(-)PPV assembly as a reference system.

7. Ultrafast transient absorption spectroscopy

Ultrafast transient absorption spectroscopy measurements were carried out at the Notre Dame Radiation Lab by using a Clark-MXR 2010 Ti:sapphire laser system (775 nm, 1 mJ pulse⁻¹, full width at half maximum of 130 fs, and 1 kHz repetition rate) equipped with a CCD spectrograph (Ocean Optics, S2000-U-UVvis). Five percent of the fundamental was used to generate a probe pulse, while 95% of the laser beam was

utilized by a second harmonic generator to produce a pump laser pulse (387 nm). For details of the instrument and measurement, please refer to reference 19-20.^{19,20}

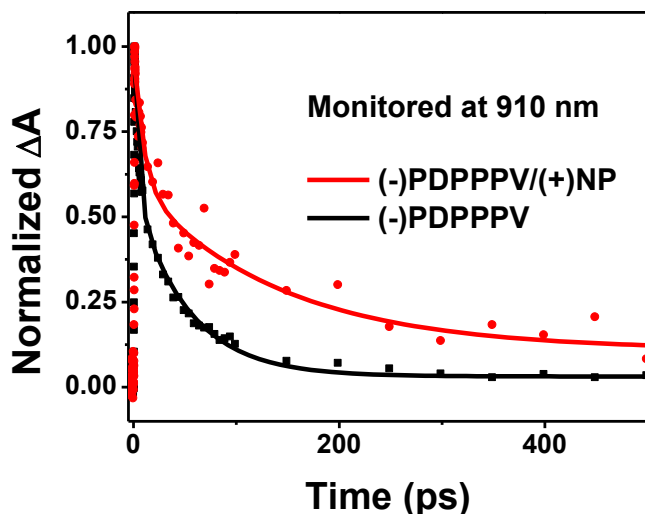


Figure S8. This figure compares the fitted kinetic traces monitored at 910 nm for the (-)PDPPPV-only and (-)PDPPPV/(+)NP samples.

8. Spectroelectrochemistry

The measurement was performed with a drop-cast (-)PDPPPV thin film on an ITO working electrode in a three-electrode spectroelectrochemical cell that has a Au wire counter electrode and a Ag/Ag⁺ reference electrode. The voltage was applied by a CHI 618B potentiostat, and the spectra were collected on an Agilent 8453 spectrometer.

9. NP intrinsic photoluminescence decay law

Note that the intrinsic decay rate of the NPs can change somewhat between batches, and this was accounted for by control experiments. The figure below compares time-resolved photoluminescence decay for (-)NP and (-)NP/(+)PDPPPV with that for a control, (-)NP/(+)PPV. The data clearly show that the control polymer can quench the

photoluminescence lifetime for (-)NP more than the (+)PDPPPV can. This result is in sharp contrast with that for the (+)NP/(-)PDPPPV system (Figure 3); thus it supports the effect of the internal electric field (Figure 6). Note that, compared to the (-)NP/(+)PDPPPV assembly, stronger lifetime quenching is observed in the (-)NP/(+)PPV assembly (or (+)NP/(-)PPV assembly). The reason for this difference is not clear at this point, but it may be related to the structural difference in the polymers and/or NP/polymer packing within the electrostatic aggregates, as control polymers ((+)/(-)PPV) have a smaller repeat unit than do the PDPPPV copolymers.

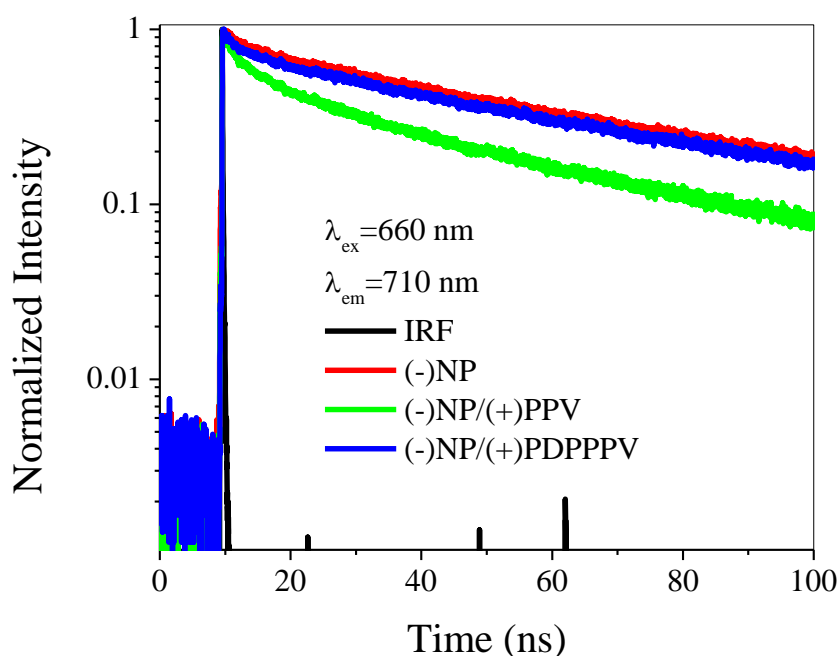


Figure S9. This figure shows time-resolved photoluminescence decays for (-)NP, (-)NP/(+)PPV, and (-)NP/(+)PDPPPV.

10. References

1. D. A. M. Egbe, H. Tillmann, E. Birckner and E. Klemm, *Macromolecular Chemistry and Physics*, 2001, **202**, 2712-2726.
2. K. Liu, Y. Li and M. J. Yang, *Journal of Applied Polymer Science*, 2009, **111**, 1976-1984.
3. S. X. Xiao, S. Wang, H. J. Fang, L. Y. L., S. Z. Q., C. M. Du and D. B. Zhu, *Macromolecular Rapid Communications*, 2001, **22**, 1313-1318.
4. S. L. Lu, M. J. Yang, J. Luo, Y. Cao and F. L. Bai, *Macromolecular Chemistry and Physics*, 2005, **206**, 664-671.
5. B. H. Xie, M. Bagui, R. R. Guo, K. Li, Q. Wang and Z. H. Peng, *Journal of Polymer Science Part A: Polymer Chemistry*, 2007, **45**, 5123-5135.
6. A. R. Rabindranath, Y. Zhu, I. Heim and B. Tieke, *Macromolecules*, 2006, **39**, 8250-8256.
7. K. Liu, Y. Li, G. Q. Zhang, X. Lv and M. J. Yang, *Sensors And Actuators B-chemical*, 2009, **135**, 597-602.
8. Q. L. Fan, S. Lu, Y. H. Lai, X. Y. Hou and W. Huang, *Macromolecules*, 2003, **36**, 6976-6984.
9. H. Bronstein, Z. Chen, R. S. Ashraf, W. Zhang, J. Du, J. R. Durrant, P. Shakya Tuladhar, K. Song, S. E. Watkins, Y. Geerts, M. M. Wienk, R. A. J. Janssen, T. Anthopoulos, H. Sirringhaus, M. Heeney and I. McCulloch, *Journal of the American Chemical Society*, 2011, **133**, 3272-3275.

10. J. C. Bijleveld, V. S. Gevaerts, D. Di Nuzzo, M. Turbiez, S. G. J. Mathijssen, D. M. de Leeuw, M. M. Wienk and R. A. J. Janssen, *Advanced Materials*, 2010, **22**, E242-+.
11. J. D. Yuen and F. Wudl, *Energy & Environmental Science*, 2013, **6**, 392-406.
12. L. Biniek, B. C. Schroeder, C. B. Nielsen and I. McCulloch, *Journal of Materials Chemistry*, 2012, **22**, 14803-14813.
13. W. W. Yu, Y. A. Wang and X. Peng, *Chemistry of Materials*, 2003, **15**, 4300-4308.
14. S. K. Haram, B. M. Quinn and A. J. Bard, *Journal of the American Chemical Society*, 2001, **123**, 8860-8861.
15. Y. Wang, Z. Xie, G. Gotesman, L. Wang, B. P. Bloom, T. Z. Markus, D. Oron, R. Naaman and D. H. Waldeck, *The Journal of Physical Chemistry C*, 2012, **116**, 17464-17472.
16. Q. Liu, X. Lü, L. Geng and C. Lü, *Polymer International*, 2011, **60**, 1514-1520.
17. G. Zhang, H. Xu, K. Liu, Y. Li, L. Yang and M. Yang, *Synthetic Metals*, 2010, **160**, 1945-1952.
18. S. K. Haram, A. Kshirsagar, Y. D. Gujarathi, P. P. Ingole, O. A. Nene, G. B. Markad and S. P. Nanavati, *Journal of Physical Chemistry C*, 2011, **115**, 6243-6249.
19. J. H. Bang and P. V. Kamat, *Acs Nano*, 2011, **5**, 9421-9427.
20. K. Tvrđy, P. A. Frantsuzov and P. V. Kamat, *Proceedings of the National Academy of Sciences*, 2011, **108**, 29-34.