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Supplementary Information[†]- Polymer Nanoparticle Photocatalysts Realized in Non-Aqueous Solvents

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S1 oNP Solvent-Transfer Characterization:



Figure S1: (a) Normalized absorption spectra and (b) dynamic light scattering (DLS) size distributions of 1:1 PTB7-Th : N2200 oNPs throughout the solvent transfer process - in water (Z-Avg = 72.7 nm, PDI = 0.192), then oleic acid (Z-Avg = 164.3 nm, PDI = 0.115), and finally DMF (Z-Avg = 149.7 nm, PDI = 0.218).



Figure S2: DLS size distributions of 1:1 PTB7-Th : N2200 oNPs in DMF, transferred by centrifuging the oNP/oleic acid solution (with and without acetone anti-solvent) at 22,000 rpm for 3 hours, as opposed to 16,000 rpm for 2 hours + 18,000 rpm for 1 hour. The sample without anti-solvent (dark blue trace) has a Z-Avg diameter = 158 nm & PDI = 0.107, while the sample with anti-solvent (light blue trace) has a Z-Avg diameter = 149 nm & PDI = 0.101.

Residual Oleic Acid Quantification To determine the concentration of residual oleic acid in the oNP/DMF spectrum, the UV-Vis absorption spectrum of the oNP/DMF sample was fit using a linear combination of the spectra of oleic acid and PTB7-Th (**ESI Figure S3**). The oleic acid spectrum (yellow) and PTB7-Th spectrum (pink) are each derived from samples of known concentration and serve as basis spectra to fit the composition of the oNP/DMF spectrum (orange; solid trace = sample, dashed trace = fit). Due to vibronic differences between free PTB7-Th in solution and the oNPs in DMF, only the spectral region between 265 nm and 575 nm was used for the fitting process. The analysis indicates that the oNP/DMF sample (characterized in **Figure 3** of the main text) contains approximately 1.8

mg/mL of oleic acid. If each oleic acid molecule were bound to the nanoparticle surface, this would correspond to a surface density of roughly 2,900 molecules per square nanometer. However, this density is physically improbable, and oleic acid's high solubility in DMF suggests that the majority of residual oleic acid molecules remain free in solution.

Notably, the fit poorly captures the shape of the oNP/DMF spectrum between 300–350 nm due to a shoulder present in the oleic acid basis spectrum but absent in the oNP/DMF spectrum. Technical grade oleic acid sourced from Millipore Sigma is known to include impurities from other lipid species.¹ Previous studies have shown that these lipid contaminants contribute a shoulder to the red of oleic acid's main UV absorption peak and can be removed via repeated recrystallization.^{1,2} Although the oleic acid in this study was ultracentrifuged at 22,000 rpm for 3 hours to remove trace colloidal contaminants, this process does not effectively eliminate alternative lipid species. The inability to account for this shoulder region in the oNP/DMF sample implies that oleic acid selectively survives the transfer process, while the lipid contaminants do not. This conclusion is supported by the gray trace in **ESI Figure S3b**, which represents the difference spectrum between the actual oNP/DMF spectrum and the estimated contribution of bulk PTB7-Th. This difference spectrum notably lacks the low-energy shoulder absorption characteristic of contaminant lipids in the oleic acid basis spectrum.



Figure S3: a) UV-Vis absorption spectra of PTB7-Th oNPs in DMF (orange trace), oleic acid in DMF (yellow trace), and bulk PTB7-Th in CHCl₃ (pink trace). b) Zoomed-in view of (a) additionally showing the fit of the oNP/DMF spectrum (orange dashed trace) as well as the difference spectrum (grey trace) between the actual oNP/DMF spectrum and the estimated contribution of the bulk PTB7-Th.

	Value	Units	Value	Units
Density of PTB7-Th	1.15	g/mL	1150	g/L
Mass Concentration in DMF Sample from fit	0.0043	mg/mL	0.0043	g/L
OA concentration in DMF sample from fit	1.8	mg/mL	1.8	g/L
OA Molar mass	282.46	g/mol		
Diameter of oNPs in water	65	nm	6.50E-08	m
Diameter of swollen oNPs in DMF	127	nm	1.27E-07	m
Volume of DMF sample	3	mL	0.003	L
Avogadro's number	6.02E+23			
Volume of 1 oNP in water (m^3)	1.44E-22	m^3		
Volume of 1 oNP in water (L)	1.44E-19	L		
Mass of 1 oNP in water	1.65E-16	g		
Mass of 1 oNP in DMF	1.65E-16	g		
Volume of 1 oNP in DMF (m^3)	1.07E-21	m^3		
Volume of 1 oNP in DMF (L)	1.07E-18	L		
Density of oNPs in DMF	154.18	g/L		
Surface area per oNP in DMF	5.07E-14	m^2		
Mass of PTB7-Th in DMF sample	1.29E-05	g		
Volume of PTB7-Th in DMF sample (L)	8.37E-08	L		
Number of oNPs in DMF sample	7.80E+10	еа		
Total surface area of all oNPs in DMF (m^2)	3.95E-03	m^2		
Total surface area of all oNPs in DMF (nm^2)	3.95E+15	nm^2		
Total mass of OA in solution	0.0054	g		
Total moles of OA in solution	1.91178E-05	mol		
Total # molecules of OA in solution	1.15E+19	ea		
Total # molecules per surface area of oNPs	2.91E+03	nm^-2		
Volume of PTB7-Th in DMF sample (nm^3)	8.37E+16	nm^3		
Total # molecules per volume of oNPs	137.5987832	nm^-3		

Table S1: Calculations to determine concentration of oleic acid relative to concentration of oNPs

S2 oNP Composition Optimization:

To ensure that the samples analyzed using transient absorption and TRMC produced sufficient charge signal, we optimized the donor-acceptor blend ratios for both oNP and bulk film samples using steady-state microwave conductivity (SSMC) measurements. Similar to time-resolved microwave conductivity (TRMC), SSMC employs a resonant microwave cavity to measure the yield of free charge carriers as well as their mobility, but in this case, the samples are measured under frequency-tuned chopped illumination.

oNP samples were prepared at a range of PTB7-Th:N2200 compositions and embedded into an inert hydroxypropyl cellulose thin film, following the same procedure outlined in the "Thin Film Preparation" methods section of the main text. SSMC results for the oNP samples show that most intermediate blend ratios yield similar photoconductance signals, regardless of composition (**Figure S5 a & c**). However, oNPs with a 50:50 (by mass) blend of PTB7-Th:N2200 exhibit the highest photo-conductance, as measured at high (7-8 kHz) frequency where the signal is least influenced by trapping phenomena.

For bulk blend samples, the photoconductance signal is again relatively consistent across most blend ratios but peaks at approximately 15:85 PTB7-TH:N2200 (**Figure S5 b & d**). Across all blend ratios, both bulk thin films and oNP thin films produce comparable photoconductance signals (within a factor of 2, **Figure S5d**). Within this work, we selected samples with a 50:50 blend ratio for TRMC experiments, while samples with a composition of approximately 70 PTB7-Th:30 N2200 were used for transient absorption measurements. Based on the SSMC results, we expect bulk and oNP thin films to be comparable to one another at each of these compositions.



Figure S4: UV-Vis Absorption Spectra for a) oNP blend films and b) bulk blend film. In each case, the spectrum of the lamp used for illumination during SSMC experiments is shown as a black dashed trace and corresponds to the right hand axis.



Figure S5: a) oNP blend films' relative photoconductance vs. lamp chopping frequency; b) Bulk blend films' relative photoconductance vs. lamp chopping frequency; c) oNP blend films' relative photoconductance at 7429 Hz vs. oNP composition; d) oNP & bulk blend films' relative photoconductance at 7429 Hz & 625 Hz vs. sample composition. All photoconductance signals are scaled by the fraction of incident lamp photons absorbed by each sample.

S3 Time-Resolved Photoluminescence

Non-normalized UV-Vis absorption spectra of the samples used for PL and TRPL are shown in Figure S32.



Figure S6: Normalized time-resolved photoluminescence spectra averaged over early time (0.4 - 0.5 ns), late time (0.5 - 2 ns), and all time (0.4 - 2 ns) for (a) PTB7-Th oNPs in DMF; (b) PTB7-Th oNPs in water; (c) bulk PTB7-Th in CHCl₃; and (d) a bulk PTB7-Th thin film.



Figure S7: Normalized time-resolved photoluminescence transients (log scale y-axis) of bulk PTB7-Th in $CHCl_3$ (spectrum shown in **Figure S6c**). Transients are averaged over the whole spectrum (640 nm - 860 nm), over the small mass fragment (640 nm - 700 nm), and over the main peak (700 nm - 860 nm).

S4 Transient Absorption



Figure S8: a)UV-Vis absorption spectra and b) DLS size distribution for PTB7-Th/N2200 blend samples studied by transient absorption spectroscopy (Z-Avg = 147.2 nm, PDI = 0.131)



Figure S9: (a) Visible and (b) NIR transient absorption spectra of a mixture of neat PTB7-Th oNPs combined with neat N2200 oNPs in water in a 2:1 ratio. Sample serves as a negative control and shows minimal evidence of long-lived charge generation, explained by the fact that PTB7-Th and N2200 phases are not in physical contact with one another.



Figure S10: UV-Vis absorption difference spectrum of PTB7-Th cation. PTB7-Th (0.01 mg/mL) is p-doped with triethyloxonium hexachloroantimonate ($8.4 \times 10^{-10} \text{ mg/mL}$) in 1:2 dichloroethane : chloroform. Ground-state PTB7-Th spectrum is subtracted out prior to dopant addition.



Figure S11: (a) Normalized transient absorption spectra (visible) for each sample taken at the ground-state bleach signal maximum (0.3 ps); (b) Normalized transient absorption spectra (NIR) for each sample taken at the PTB7-Th cation signal maximum (8 ps).



Figure S12: Transient absorption kinetics averaged over (a) 616 - 652 nm (bluer bleach peak); (b) 688 - 727 nm (redder bleach peak); (c) 816 - 857 nm (N2200 anion and PTB7-Th cation PIA); and (d) 1184-1160 nm (PTB7-Th cation PIA).



Figure S13: Normalized transient absorption kinetics averaged over (a) 616 - 652 nm (bluer bleach peak); (b) 688 - 727 nm (redder bleach peak); (c) 816 - 857 nm (N2200 anion and PTB7-Th cation PIA); and (d) 1184-1160 nm (PTB7-Th cation PIA).

S5 Time-Resolved Microwave Conductivity

Solution-phase TRMC transients (oNPs in DME and oNPs in 1,4-dioxane) contained high-frequency noise interference from the excitation laser. This noise was removed by performing a Fourier transform on the data, smoothing the interference peaks located between 210 - 250 MHz, then performing an inverse Fourier transforming on the modified waveform.



Figure S14: TRMC transients corresponding to changes in real conductivity ($\Delta\sigma'$) for (a) PTB7-Th:N2200 blend oNPs in DME and (b) PTB7-Th:N2200 blend oNPs in 1,4-dioxane before and after the removal of high frequency noise caused by the excitation laser.



Figure S15: (a) TRMC transients corresponding to changes in imaginary conductivity ($\Delta \sigma$) for PTB7-Th:N2200 blend oNPs cast from water as a cellulose thin film (light blue trace), a PTB7-Th:N2200 bulk blend thin film (dark purple trace), PTB7-Th:N2200 blend oNPs in 1,4-dioxane (red trace), PTB7-Th:N2200 blend oNPs in DME (green trace), and a 1:1 mixture of bulk PTB7-Th + bulk N2200 in Benzene (gray trace); (b) DLS size distribution of oNPs in DME studied by TRMC (Z-Avg = 260 nm, PDI = 0.114). The size distribution of the aqueous oNP stock solution from which they were transferred is also shown for reference (Z-Avg = 70 nm, PDI = 0.157). DLS data for the oNPs in dioxane is not shown because its PDI value was too large, making these data unsuitable for quantitative size analysis; (c) UV-Vis absorption spectra for all samples studied by TRMC in (a); (d) Zoomed-in view of (c).

S6 Ionic Contamination Troubleshooting

During the solvent-transfer procedure, the aqueous oNP stock solution is sonicated into a water-in-oil emulsion and then heated to evaporate off the water, resulting in the transfer of all contents into the oil. We observe that ionic contaminants, which are often soluble in water but insoluble in oil, will precipitate into solid microstructures throughout this process.³ We identify 3 possible major sources of ionic contamination: (1) the water source used to originally prepare the oNP aqueous stock solution, (2) the polymers themselves, and (3) materials that come into contact with the aqueous stock solution, including glass vials and the ultrasonicator tip:

(1) The water source used to originally prepare the oNP aqueous stock solution: oNPs are prepared in MiliQ water, as it has been shown to have a low concentration of dissolved ions.

(2) The polymers themselves: Many commercially available semiconducting polymers are synthesized via a Stille coupling, which involves an organotin compound and a palladium catalyst.⁴ It has been shown that semiconducting polymers produced through this route often contain trace palladium, and that this palladium can be active for HER.⁵ We observe this residual Pd through STEM/EDS imaging, often in the form of individual small (≈ 1 nm) spheres (Figure S16 b & g) or larger clusters of many small spheres (Figure S17 a & b). Several ICP-MS runs confirm Pd concentrations ≈ 1000 ng/mg of polymer. In addition to Pd and Sn from the Stille coupling, we hypothesize that our commercially purchased stocks of PM6, PTB7-Th, and N2200 all contain trace Cu and Ca contamination, which likewise appear as contaminants in the EDS imaging (Figures S16 & S17). We observe that Cu contamination is co-spatial with Pd, while the Ca contamination phase separates into rod-like structures. Though the process was not undertaken for this work, it is possible to purify trace contaminants such as Pd out of a polymer through gel permeation chromatography and repeated washes with a chelating agent, such as diethyldithiocarbamate.⁵

(3) Materials that come into contact with the aqueous stock solution: A third class of contaminants, including Al and Si, are not present in any of the starting materials in any significant amounts and are instead believed to be introduced through surface contact throughout the transfer process. When glass comes into contact with water, silicate species are known to diffuse into the water, though the kinetics of this process vary depending on the type of glass.⁶ Silicon is thought to be introduced when aqueous oNP solutions are stored in glass vials for extended periods, as evidenced by the large Si peak that appears in the EDS spectrum of the aqueous oNP sample after synthesis and storage in glass (**Figure S18**). Solvent-transferring these same oNPs that have been stored in glass vials results in the creation of Si_xO_y NPs (**Figure S17 a, c & g**). To avoid this, all aqueous dispersions of the oNPs are prepared and stored in Teflon vials to minimize the leeching of Si from the glass into the solution. When this change is incorporated, we observe significantly less incorporation of Si into the final solvent-transferred oNPs (**Figure S19**).

The inclusion of aluminum was empirically traced to an ultrasonication step that was initially used to generate the oil-water emulsion in the solvent transfer process, but was later replaced with a gentler bath sonication step. Ultrasonication relies on the rapid vibration of a metal tip that is inserted into a solution. In this case, the metal tip is composed of an aluminum (Al)/vanadium (V) alloy and we noted the inclusion of both Al and V following ultrasonication of the oil/water mixture (**Figure S17 k**, V EDS results not available). Interestingly, using ultrasonication to create a CHCl₃/water emulsion in the original oNP synthesis does not appear to indroduce Al to the sample, suggesting that oleic acid plays a role in incorporating Al from the tip into the solution. In addition to incorporating aluminum, this ultrasonication step was also too harsh and resulted in poor oNP morphology in the solvent-transferred product. For this reason, the oil/water ultrasonication step was replaced with a gentler bath sonication step, which yielded the desired oNP morphology and eliminated Al contamination.



Figure S16: (a) HAADF image of PTB7-Th oNPs in DMF, solvent-transferred according to the procedure reported in the main text; (b) HAADF image of rod structures found in PTB7-Th oNP/DMF sample; (c) sulfur; (d) oxygen; (e) calcium; (f) carbon; and (g) palladium EDS images of rod shown in (b). Results indicate that rods are composed of $Ca_xO_yS_z$ and small bright spots are composed of Pd.



Figure S17: (a) HAADF image of PTB7-Th oNPs 7 days after transfer into THF, prepared using tip-ultrasonication instead of bath sonication to generate the oil/water emulsion in the solvent-transfer process; (b) - (l) Pd, O, Si & S, F, C, Si, Na, Mg, S, Al, and Cu EDS images corresponding to image shown in (a). PTB7-Th oNPs are no longer intact, evidenced by the absence of fluorine signal structure. However, impurity Si_xO_y NPs and Pd clusters remain stable long-term.



Figure S18: EDS spectrum of PTB7-Th oNPs in water that have been synthesized in glass and subsequently stored in glass for 4 days. Note the prominent Si peak.



Figure S19: (a) HAADF image of PTB7-Th oNPs in DMF, solvent-transferred according to the procedure reported in the main text; (b) fluorine; (c) sulfur; (d) silicon; (e) carbon; (f) palladium; (g) oxygen; and (h) copper EDS images of oNP shown in (a). Note the reduced structure of Si EDS signal upon exchanging glass vials for Teflon vials for all steps.

S7 Unsuccessful Solvent-Transfer Attempts

Several methods from the inorganic nanomaterial solvent-transfer literature were adapted and tested for transferring organic nanoparticles. However, these attempts were unsuccessful, and are included here for reference.

- Standard precipitation and re-suspension: Aqueous oNPs are very colloidally stable in solution and do not
 precipitate out easily with ultracentrifugation. Ultracentrifuging a solution of aqueous oNPs at high speeds
 (Beckman Ultracentrifuge, SW 32 TI swinging bucket rotor, 24,000 rpm) for for several hours does not result
 in substantial oNP precipitation. The addition of ethanol prior to centrifugation does marginally increased precipitation. However, oNPs do not re-suspend in 'bad' solvents (*i.e.*, solvents in which the polymer is insoluble,
 such as DMF), regardless of whether or not they are precipitated with the use of ethanol. Addition of a 'good'
 solvent (such as toluene) to the pellet results in oNPs disassembling fully.
- 2. Separate oNPs out of water using octadecylamine (ODA), wash, then re-dispered in new solvent environments, as described by Wang *et al.*:⁷ This method was successful at initially removing the oNPs from water as a greasy film that sits atop the aqueous layer. However, upon washing and re-suspending, the resulting colloidal stability of the oNPs in their new solvent was poor and the oNPs appeared to rapidly chemically degrade, evidence by their change in color from blue to pink. This color change is believed to indicate photo-oxidation of the polymer backbone, likely by ODA's reactive amine moiety.
- 3. Liquid-Liquid Interfacial Transport: In this technique, oNPs are intended to transit from water into an adjacent immiscible non-aqueous liquid phase which contains a stabilizing surfactant.⁸ As oNPs migrate to the liquid-liquid interface, their surface becomes covered by the new, more stabilizing surfactant, allowing for preferential migration from water into the new solvent. This method has been shown to be successful for transferring inorganic nanoparticles into organic solvents, likely because the strong metal-ligand interactions that exist between the nanoparticle and its surfactant can be leveraged to drive the transfer. However, the nature of particle-surfactant interactions for organic nanoparticles is less understood as it is for inorganic materials. These interactions are believed to be weaker in organic systems, relying on van der waals interactions between neutral organic species as opposed to stronger electrostatic interactions that often exist between inorganic nanomaterials and their ligands, making this ligand-exchange-driven transfer process less thermodynamically favorable for organic oNPs. Indeed, we tuned a number of factors in attempting this method, and in each case the oNPs remained within the aqueous phase making the transfer unsuccessful.

Factors tuned include:

- (a) Ligand identity: Octanethiol, dodecanethiol,⁹ 3-decylthiophene, 1-butanol¹⁰ and sodium oleate/oleic acid
- (b) Ligand concentration
- (c) Organic solvent identity (limited to solvents that are immisible with water): Toluene, CHCl₃, DCM, Hexanes
- (d) Temperature
- (e) Sample agitation: tried shaking mixtures vigorously to generate an emulsion, stirring over several days, or leaving biphasic mixtures completely undisturbed. oNPs remained in the aqueous phase in all cases.
- (f) Use or absence of illumination paired with the use of a charged stabilizing surfactant. We hypothesized that adding illumination may generate surface charges on the oNP surface, increasing the strength of the oNP - surfactant interaction.

- 4. Mixed Solvent Systems: In this technique, an aqueous solution of oNPs is diluted with a miscible non-aqueous solvent. While the water is not removed, this method can still increase opportunities for driving diverse chemistry due to chemical species' expanded solubility in mixed solvent systems. This method showed some success; oNPs were colloidally stable in a 1:1 mixture (v:v) of water and acetonitrile for up to 1 week. However, this method is limited to creating dilute samples using solvent that are miscible with water, and water is never removed from the reaction mixture.
- 5. Scaling up the volumes in the reported solvent-transfer procedure: Scaling up the solvent-transfer procedure beyond the reported volumes was unsuccessful because the efficiency of both bath sonication and sample heating decrease as sample volume increases. When all volumes were doubled, the water phase was not fully incorporated into the oleic acid during the initial bath sonication step. Rather, some water was incorporated into the oil as an emulsion but large droplets of water remained at the bottom of the teflon vial. Upon heating this mixture, the larger volume warmed up more slowly, presumably giving the emulsified water droplets time to coalesce with one another. This resulted in larger particle sizes (aggregates) post-transfer, which ultimacy crashed out of solution.

S8 Covalent Cross-Linking Attempts

S8.1 Introduction

Significant efforts were made to incorporate a covalent cross-linking step that could enable the oNPs to be transferred into 'good' solvents, *i.e.*, solvents in which the polymer is soluble, without unraveling. Currently, our transfer procedure as well as other methods described in the literature only permit polymer oNPs to be transferred into 'bad' solvents (solvents in which the polymer is *insoluble*) because oNP are held together as aggregates by hydrophobic forces. By incorporating a covalent cross-linking step, we aimed to "lock" the oNPs into their spherical shape by irreversibly bonding together adjacent polymer chains within the oNP. While the incorporation of this cross-linking step appeared to grant the oNPs some promising resistance against dissolution in good solvents, our results are ultimately inconclusive. More work is needed to tune this process such that oNPs remain intact and colloidally and chemically stable in good solvents.

For simplicity, we have chosen to demonstrate the cross-linking procedure on single-phase oNPs composed entirely of either PTB7-Th or PM6 (**Figure S20 a & b**), both high-performance semiconducting polymers for organic photovoltaic applications. We transfer cross-linked oNPs ($oNPs_{x-Linked}$) and non-cross-linked oNPs ($oNPs_{Non-Linked}$) into DMF (bad solvent), MeOH (bad solvent), and THF (good solvent) and characterize their colloidal stability with dynamic light scattering (DLS), Transmission Electron Microscopy (TEM) imaging, and UV-Vis absorption spectroscopy. We also use photoluminescence (PL) and time-resolve photoluminescence (TRPL) to study how the exciton environment changes when cross-linked oNPs and non-cross-linked oNPs are transferred from water into a nonaqueous environment. We find that the addition of the covalent cross-linking step may extend the window of colloidal stability for oNPs in both THF and MeOH, but makes no difference for oNPs in DMF. PL and TRPL data show that cross-linked oNPs in THF have more quenched emission than non-cross-linked oNPs in THF, as expected for polymer chains that are aggregated into a nanoparticle as opposed to free in solution, but the effect is minimal. More work is needed to optimize the concentration of cross-linker used, understand how the cross-linking process impacts free charge generation within a semiconducting polymer oNPs, and ensure that the solvent-transferred oNPs remain intact and colloidally stable.

The covalent cross-linker used in this study is a fluorinated tetrakis-azide linker, pentaerythritol tetra(4-azido-2,3,5,6-tetrafluorobenzoate) (**Figure S20c**), termed 'FL4' in this report, and was synthesized according to ref. 11. The cross-linking mechanism is shown in **Figure S20d** and begins when the cross-linker is illuminated with UV light ($\lambda = 275$ nm). Once illuminated, the azide moiety releases a molecule of N₂, yielding a highly reactive nitrene species. The nitrene can then insert into C-H bonds, including within alkyl side chains of semiconducting polymers. This cross-linking process has been shown to be highly efficient and proceed to completion in under 3 minutes of UV-illumination.¹² The presence of 4 azide groups per cross-linker molecule allows for a high cross-linking efficiency at low cross-linker concentrations. Herein, we use 10 wt% cross-linker relative to the semiconducting polymer, though this quantity could likely be optimized to a lower value. This family of covalent cross-linker has previously been used to successfully insolubilize polymeric hole transport layers in organic semiconducting thin film devices, ¹² but this is the first time it's been used to immobilize polymer chains within an organic nanoparticle.

S8.2 Methods

S8.2.1 Cross-Linked oNP Synthesis

The procedure for synthesizing cross-linked oNPs is similar to the miniemulsion procedure used in previous reports.^{13,14} However, several changes were incorporated to include the cross-linking step, including lowering the evap-



Figure S20: Chemical structures of (a) PTB7-Th, (b) PM6, (c) the covalent Cross-Linker (FL4), and (d) the UV-mediated covalent cross-linking mechanism.

oration temperature to 55 $^{\circ}$ C to avoid premature reactivity of the cross-linker and working with a more concentrated polymer stock solution. This reduction in evaporation temperature was incorporated in the non-cross-linked oNP synthesis (below) for uniformity.

Stock solutions of each bulk semiconducting polymer (PTB7-Th or PM6) in chloroform (2 mg/mL) are stirred at 80 °C for 8 hours, then stirred at room temperature for another 7 hours. A stock solution of the cross-linker FL4 is prepared in chloroform (2 mg/mL), wrapped in foil to avoid exposure to light, and stirred at room temperature for 30 minutes immediately prior to use. A stock solution of TEBS surfactant in MiliQ water (0.5 wt%) is prepared in a teflon vial and used fresh on the day of preparation. Polymer/CHCl₃ stock solution (0.625 mL) is combined with FL4/CHCl₃ solution (0.0625 mL), stirred for one minute, then loaded into a 5 mL syringe and spray-coated into a shallow glass dish as a 1 inch x 1 inch thin film. Neat chloroform (1 mL) is loaded into the same syringe and sprayed again over the same area to minimize material loss. The resulting film is illuminated with a 275 nm LED (Thor Labs M275L4, 75 mA) for 5 seconds from a height of 1 cm. The film is redissolved in chloroform (3 mL), combined with 0.5 wt% aqueous TEBS surfactant solution (5 mL) in a 30 mL Teflon vial, then tip-sonicated at 30% amplitude for 1.5 minutes (Cole-Parmer CP 750 Ultrasonic Processor, 1/4 inch tapered tip). The resulting emulsion is stirred for 30 minutes at 55 °C in an aluminum heating block while being bubbled with nitrogen to evaporate the organic phase, yielding a surfactant-stabilized suspension of oNPs in water. The aqueous oNP solution is transferred again to a shallow dish and illuminated with a 275 nm LED (Thor Labs M275L4, 75 mA) for 3 minutes from a height of 1 cm, then stored in a clean lidded Teflon vial. Aqueous $oNP_{x-Linked}$ are approximately 45 nm in diameter, as determined by DLS (Figure S22, Table S2 & Table S3).

S8.2.2 Non-Linked oNP Synthesis

 $oNP_{Non-Linked}$ are synthesized from the same polymer stock solutions as the $oNP_{x-Linked}$. A dilution step is incorporated in order to match this procedure with the one described in the methods section of main text of this manuscript.

Stock solutions of each bulk semiconducting polymer (PTB7-Th or PM6) in chloroform (2 mg/mL) are stirred at

80 °C for 8 hours, then stirred at room temperature for another 7 hours. A stock solution of TEBS surfactant in MiliQ water (0.5 wt%) is prepared in a teflon vial and used fresh on the day of preparation. Polymer/CHCl₃ stock solution (0.625 mL) is diluted with chloroform (1.875 mL) to a concentration of 0.5 mg/mL, then combined with aqueous TEBS surfactant solution (5 mL) in a 30 mL Teflon vial, and tip-sonicated at 30% amplitude for 1.5 minutes (Cole-Parmer CP 750 Ultrasonic Processor, 1/4 inch tapered tip). The resulting emulsion is stirred for 30 minutes at 55 °C in an aluminum heating block while being bubbled with N₂ to evaporate the organic phase, yielding a surfactant-stabilized suspension of oNPs in water. The aqueous oNP stock is transferred into a clean, lidded teflon vial for storage. Aqueous $oNP_{Non-Linked}$ are approximately 65 nm in diameter, as determined by DLS (**Figure S22, Table S2 & Table S3**).

S8.2.3 Why use 2 UV Doses for the Cross-Linking?

The cross-linking process is followed by FT-IR (**Figure S21**) to tune doses of UV and confirm that the cross-linker azide moiety reacts fully, evidence by the loss of the azide stretching peak at 2130 cm⁻¹. The initial short dose of UV is used to 'dock' the cross-linker onto the polymer to prevent it from phase segregating from the polymer during the subsequent oNP synthesis procedure. FTIR data indicate that this initial dose reacts only about 25% of the azide moieties within FL4, which is supported by the observation that this "partially-cross-linked" thin film readily re-dissolves into chloroform, while a fully-cross-linked film cannot.¹² The initial UV dose is done on a thin film rather than in solution to prevent the cross-linker from reacting with C-H bonds within the solvent (chloroform). Once the oNPs are transferred into water, they are illuminated for a further 3 minutes to fully react the cross-linker, evidenced by the complete loss of the azide peak by FTIR. This second dose of UV is believed to "lock" the oNP into it's spherical confirmation by cross-linking adjacent polymer chains. Note that the drop in peak intensity moving from the first dose of UV (orange trace) to after formation of the nanoparticles (light blue trace) arises because the sample has been diluted in water and normalizing by peaks specific to the polymer was a challenge due to the addition of overlapping peaks corresponding to the TEBS surfactant.

S8.3 Colloidal Stability Results - DLS, TEM, and UV-Vis Absoprtion Data

Aqueous and solvent-transferred oNPs were analyzed with DLS, UV-Vis Absorption, and TEM to evaluate their longterm colloidal stability. Aqueous solutions of non-cross-linked oNPs made from either PTB7-Th or PM6 are colloidally stable for at least 6 weeks (**Figure S22, Table S2, & Table S3**), with an average diameter of 65 nm in both cases. Aqueous cross-linked oNPs made from PTB7-Th are also colloidally stable for at least 6 weeks, with an average diameter of 46 nm, indicating that the cross-linking step does not hinder oNP formation. Aqueous cross-linked oNPs made from PM6 also have an average diameter of 46 nm, but their polydispersity increases after 1 week, after which point the DLS data become unsuitable for analysis.

Interpreting DLS Data: The Z-Avg diameter reported in DLS measurements is a harmonic mean calculated from the intensity-weighted size distribution. Therefore, the DLS Z-avg size can be thought of as approximating the upper limit of particle sizes within a solution, since larger particles scatter more photons and the measurement therefore tends to underestimate the contribution of smaller particles.¹⁵ While this approximation is imperfect, Z-avg is the standard value for reporting spherical nanomaterial diameter in the literature, and we therefore use it to aid correlation with materials reported elsewhere in the literature. The quality of the DLS data can be confirmed from the polydispersty index (PDI). Assuming a single size population following a Gaussian distribution, which appears to be the case for these samples, then the PDI can be defined as the square of the standard deviation of the gaussian distribution divided by the square of the mean.¹⁶ Samples with a PDI value of less than 0.2 are generally considered "monodisperse".¹⁶



Figure S21: (a) Raw FTIR transmission data tracking the loss of the covalent cross-linker's azide stretching peak (@ 2130 cm⁻¹) throughout the oNP synthesis procedure; (b) Same FTIR data converted to absorption spectra and offset vertically to overlay at 2130 cm⁻¹. Inset shows zoomed-in view of the loss of the azide stretching peak.

Throughout this report, DLS data time points are reported only as long as the data is considered 'suitable for analysis' by the zetasizer fitting software (*i.e.*, single-modal with a polydispersity index (PDI) < ca. 0.3).

UV-Vis absorption spectra for both PTB7-Th and PM6 non-cross-linked and cross-linked oNPs in water (**Figure S22 c & d**) remain largely unchanged over the course of 6 weeks. Normalized spectra for non-cross-linked and cross-linked oNPs overlay closely with one another (**Figure S23**), which together with the DLS data confirm that the incorporation of the cross-linker does not hinder the formation of the oNP. Successful incorporation of the cross-linker does not hinder the formation of the oNP. Successful incorporation of the cross-linker (**Figure S23**). Solutions of cross-linked oNPs tend to be smaller in diameter and less optically dense than equivalent solutions of non-cross-linked oNPs, in the case of both the PM6 and PTB7-Th systems (**Figure S22**). We attribute this to loss of polymer starting material during the spray-coating step of the cross-linker synthesis, resulting in less polymer in an equivalent volume of aqueous surfactant solution and therefore a less concentrated solution of smaller oNPs.

The structural integrity of solvent-transferred oNPs is characterized using TEM, DLS, and UV-Vis absorption data,



Figure S22: DLS (a & b) and UV-Vis absorption spactra (c & d) of PTB7-Th oNPs (a & c) and PM6 oNPs (b & d) over the course of several weeks.



Figure S23: Normalized UV-Vis absorption spectra for non-cross-linked and cross-linked (a) PTB7-Th oNPs and (b) PM6 oNPs alongside the spectrum of the covalent cross-linker, FL4



Figure S24: HAADF (High-angle annular dark-field) and bright-field TEM images of non-cross-linked (a - f) and cross-linked (g - m) PTB7-Th oNPs in water, DMF, THF and methanol. oNPs were imaged both on the day they were solvent-transferred (1st and 3rd rows) and after 1 week of aging (2nd and 4th rows), when possible.

which are summarized below in **Figures S24 - S30**. Results for each sample (cross-linked vs. non-cross-linked in each solvent) are discussed separately in the following sections.

S8.3.1 Non-cross-linked oNPs in DMF (Bad Solvent):

PTB7-Th oNPs: As stated in the main text, non-cross-linked PTB7-Th oNPs in DMF are colloidally stable by DLS for up to 6 weeks, with an average diameter of 127 nm (**Figure S26a & Table S2**). TEM data taken both on the day of the transfer and after 1 week of aging confirm that the oNPs survive the transfer process intact (**Figure S24b & e**), often forming small multi-particle clusters. UV-Vis absorption spectra bleach slightly over time but otherwise remain the same shape, confirming that the non-cross-linked PTB7-Th oNPs in DMF are chemically stable over time (**Figure S28a**). As discussed in the main text, absorption spectra for the oNPs in DMF most closely that of the bulk thin film and suggest a mixture of H- and J-aggregate contributions.



Figure S25: Bright-field TEM images of non-cross-linked (a - g) and cross-linked (h - n) PM6 oNPs in water, DMF, THF and methanol. oNPs were imaged both on the day they were solvent-transferred (1st and 3rd rows) and after 1 week of aging (2nd and 4th rows).

PM6 oNPs: Stability results for the non-cross-linked PM6 oNPs in DMF are very similar to those of the PTB7-Th analogue. Non-cross-linked PM6 oNPs in DMF are colloidally stable by DLS for up to 6 weeks, with an average diameter of 145 nm (**Figure S27a & Table S3**) and TEM data taken both on the day of the transfer and after 1 week of aging confirm that the oNPs survive the transfer process intact (**Figure S25b & e**). UV-Vis absorption spectra bleach slightly over time but otherwise remain the same shape and closely resemble that of the bulk thin film (**Figure S29a**), suggesting a mixture of H- and J-aggregate contributions.

S8.3.2 Cross-linked oNPs in DMF (Bad Solvent):

PTB7-Th oNPs: Cross-linked PTB7-Th oNPs in DMF behave similarly to the non-linked oNPs in DMF; they are colloidally stable by DLS for around 5 weeks, with an average diameter of 175 nm (**Figure S26b & Table S2**). As before, TEM confirms the presence of small clusters of intact spherical NPs (**Figure S24h & k**). As in the non-linked case, absorption spectra of the cross-linked PTB7-Th oNPs in DMF show only slight bleaching over the course of



Figure S26: DLS data of solvent transferred PTB7-Th oNPs over the course of several weeks. (a) Non-cross-linked PTB7-Th oNPs in DMF, (b) Cross-linked PTB7-Th oNPs in DMF, (c) Cross-linked PTB7-Th oNPs in MeOH, and (d) Cross-linked PTB7-Th oNPs in THF. Cross-linked PTB7-Th oNPs in THF gave suitable DLS results only on the day of the transfer prior to filtration.

	Non-Cross-Linked PTB7-Th oNPs in DMF		Cross-Linked PTB7-Th oNPs in DMF		Cross-Linked PTB7-Th oNPs in THF		Cross-Linked PTB7-Th oNPs in MeO H		Non-Cross-Linked PTB7-Th oNPs in Water		Cross-Linked PTB7-Th oNPs in Water	
	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI
Day 1												
Pre-Filter	127.9	0.139	178.9	0.224	183.9	0.331	202.3	0.251	65.0	0.142		
Day 1												
Post-Filter	136.0	0.155	182.7	0.211			177.1	0.162				
Day 2											45.9	0.221
Day 3	134.9	0.141	177.6	0.208			177.5	0.140			46.5	0.222
Day 5	126.8	0.155	174. 1	0.310			179.0	0.181			45.5	0.223
Day 7	127.4	0.189	173.2	0.297			180.3	0.178			46.1	0.246
2 weeks	124.9	0.141	172.4	0.260			182.2	0.183			45.8	0.229
3 weeks	127.1	0.201	165.4	0.236			189.0	0.218				
4 weeks	125.0	0.147					193.0	0.210				
5 weeks	126.9	0.183	172.2	0.288			197.1	0.207				
6 weeks	127.5	0.210							66.5	0.159	47.2	0.265

Table S2: Z-Average diameter (Z-Avg (nm)) and polydispersity index (PDI) of aqueous and solvent-transferred PTB7-Th oNPs over the course of several weeks. Green boxes indicate that the scattering data is considered suitable for analysis (single-modal with a polydispersity index (PDI) < ca. 0.3), while red boxes indicate that the scattering data is unsuitable for analysis (multimodal or too polydisperse). Grey boxes indicate that the measurement was not attempted on that day. Samples are color-coded to correspond to DLS plots shown in **Figure S26**. Samples not shown (*i.e.*, non-cross-linked oNPs in THF and non-cross-linked oNPs in MeOH) did not produce any suitable DLS data.



Figure S27: DLS data of solvent transferred PM6 oNPs over the course of several weeks. (a) Non-cross-linked PM6 oNPs in DMF, (b) Cross-linked PM6 oNPs in DMF, (c) Cross-linked PM6 oNPs in MeOH, and (d) Non-cross-linked PM6 oNPs in MeOH. Non-cross-linked PM6 oNPs in MeOH gave suitable DLS results for only the first 5 days post-transfer.

	Non-Cross-Linked PM6 oNPs in DMF		Cross-Linked PM6 oNPs in DMF		Non-Cross-Linked PM6 oNPs in MeOH		Cross-Linked PM6 oNPs in MeOH		Non-Cross-Linked PM6 oNPs in Water		Cross-Linked PM6 oNPs in Water	
	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI	Z-Avg (nm)	PDI
Day 1 Pre-Filter	137.5	0.240	153.9	0.200	173.4	0.153	153.9	0.143	61.3	0.204	47.0	0.253
Day 1 Post-Filter	143.6	0.241	151 9	0 170	165.7	0.096	147.4	0.097				
Day 3	143.0	0.241	153.6	0.170	260.1	0.195	150.8	0.081				
Day 5	144.2	0.217	154.6	0.156	362.2	0.312	154.4	0.098	61.7	0.197	46.0	0.224
Day 7	145.2	0.214	155.1	0.167			160.9	0.100	61.6	0.198	46.6	0.229
2 weeks	146.6	0.202	153.1	0.155			223.6	0.166	62.9	0.222		
3 weeks	149.7	0.223	153.4	0.151			299.0	0.250				
4 weeks			147.5	0.166								
5 weeks	149.5	0.269	146.7	0.161								
6 weeks	145.2	0.239	147.1	0.182					66.1	0.240		

Table S3: Z-Average diameter (Z-Avg (nm)) and polydispersity index (PDI) of aqueous and solvent-transferred PM6 oNPs over the course of several weeks. Green boxes indicate that the scattering data is considered suitable for analysis (single-modal with a polydispersity index (PDI) < ca. 0.3), while red boxes indicate that the scattering data is unsuitable for analysis (multimodal or too polydisperse). Grey boxes indicate that the measurement was not attempted on that day. Samples are color-coded to correspond to DLS plots shown in **Figure S27**. Samples not shown (*i.e.*, non-cross-linked oNPs in THF and cross-linked oNPs in THF) did not produce any suitable DLS data.



Figure S28: UV-Vis Absorption spectra of solvent-transferred PTB7-Th oNPs over the course over several weeks. (a) Non-cross-linked oNPs in DMF, (b) Cross-linked oNPs in DMF, (c) Non-cross-linked oNPs in MeOH, (d) Cross-linked oNPs in MeOH, (e) Non-cross-linked oNPs in THF, (f) Cross-linked oNPs in THF. Spectra for non-cross-linked PTB7-Th oNPs in MeOH (c) are not collected after the first day because the oNPs did not survive the filtration step.



Figure S29: UV-Vis Absorption spectra of solvent-transferred PM6 oNPs over the course over several weeks. (a) Non-cross-linked oNPs in DMF, (b) Cross-linked oNPs in DMF, (c) Non-cross-linked oNPs in MeOH, (d) Cross-linked oNPs in MeOH, (e) Non-cross-linked oNPs in THF, (f) Cross-linked oNPs in THF.



Figure S30: UV-Vis Absorption spectra of (a) bulk PTB7-Th and (b) bulk PM6 sonicated in THF, collected over the course over several weeks.

several weeks, and have a vibronic pattern and peak position that most closely resembles that of the bulk thin film (Figure S28b).

PM6 oNPs: Stability results for the cross-linked PM6 oNPs in DMF are again similar to those of the PTB7-Th analogue. Cross-linked PM6 oNPs in DMF are colloidally stable by DLS for up to 6 weeks, with an average diameter of 150 nm (**Figure S27b & Table S3**) and TEM data taken both on the day of the transfer and after 1 week of aging confirm that the oNPs survive the transfer process intact (**Figure S25i & I**). UV-Vis absorption spectra bleach slightly over time and closely resemble that of the bulk thin film (**Figure S29b**).

We conclude that the cross-linker is not necessary when transferring the oNPs from water into DMF, based on the similarity of results for the cross-linked and non-cross-linked samples. This result is explained by the fact that both PTB7-Th and PM6 are insoluble in DMF and therefore polymer chains tend to remain coiled to minimize contact with the solvent environment.

S8.3.3 Non-cross-linked oNPs in MeOH (Bad Solvent):

PTB7-Th oNPs: Non-cross-linked PTB7-Th oNPs are initially suspended into methanol but produce only poor quality DLS data and are removed entirely in the filtration process. Prior to filtration, the non-cross-linked oNPs in MeOH have a significant baseline offset by UV-Vis, suggesting the presence of large aggregates (**Figure S28c**). After filtration, the solution no longer absorbs within the visible region, indicating the the NP aggregates are too large to pass through the 0.45 um filter pores. This is confirmed by TEM imaging, which shows large clusters of intact, spherical oNPs in the unfiltered sample (**Figure S24c**).

PM6 oNPs: Unlike the PTB7-Th oNPs, the non-cross-linked PM6 oNPs survive the transfer process into methanol and subsequent filtration step. These oNPs are colloidally stable in methanol for up to 5 days, with their diameter increasing from 173 nm on Day 1 to 362 nm on Day 5 (Figure S27c & Table S3). TEM imaging shows large clusters of intact, spherical oNPs on both Day 1 and Day 7 (Figure S25c & f). UV-Vis absorption spectra of the non-cross-linked PM6 oNPs in methanol show a gradual bleach and positive baseline offset over time, indicating that the oNPs are slowly aggregating and precipitating out of solution (Figure S29c).

We conclude that transferring non-cross-linked oNPs into methanol was initially successful, but PTB7-Th oNPs were too aggregated to survive the filtration step and PM6 oNPs gradually aggregated and precipitated out of solution over time. We understand this difference to mean that the transfer procedure conditions may need to be tailored slightly to each polymer and will likely requires some optimization to ensure a mono-disperse population of single oNPs in all destination solvents. As with nanoparticles in DMF, the absorption spectra of the oNPs in methanol resemble those of the bulk thin film, suggesting a similar transition from H- to J- aggregates in methanol.

S8.3.4 Cross-linked oNPs in MeOH (Bad Solvent):

PTB7-Th oNPs: Unlike the non-linked oNPs, cross-linked PTB7-Th oNPs in MeOH survive the filtration process and are colloidally stable for up to 5 weeks, with an average size of approximately 200 nm by DLS (**Figure S26c & Table S2**). UV-Vis absorption spectra for this sample resemble the bulk thin film due to the equal S_{00} and S_{10} peak intensities and, like the DLS data, remains invariant over time (**Figure S28d**). We hypothesize that the cross-linker may be inserting into C-H bonds within the TEBS surfactant in addition to the polymer, thereby covalently binding some surfactant to the surface of the polymer oNP. Given the surfactant's solubility in methanol, we suspect this process may improve colloidal stability in a solvent environment that would otherwise strip ligands from the oNP

surface and destabilize a colloidal suspension. TEM imaging confirms the presence of *ca*. 200 nm clusters of oNPs both initially after transfer and after 1 week of aging (**Figure S24i & I**).

PM6 oNPs: With the exception of a longer window of colloidal stability, results for cross-linked PM6 oNPs are very similar to results for the non-cross-linked PM6 oNPs. These oNPs are colloidally stable in methanol for up to 3 weeks, with their diameter increasing from 154 nm on Day 1 to 300 nm on week 3 (**Figure S27d & Table S3**). TEM imaging shows large clusters of intact, spherical oNPs on both Day 1 and Day 7 (**Figure S25j & m**). UV-Vis absorption spectra of the non-cross-linked PM6 oNPs in methanol show a gradual bleach and positive baseline offset over time, indicating that the oNPs are slowly aggregating and precipitating out of solution (**Figure S29d**).

We conclude that the addition of a covalent cross-linking step aids long-term colloidal stability for oNPs that have been transferred into methanol. Rather than holding the oNPs together, which is likely unnecessary since methanol is an antisolvent for the polymers, we hypothesize that the the cross-linker may be covalently tethering some surfactant to the surface of the oNPs, improving long-term colloidal stability and reducing the tendency of the oNPs to aggregate.

S8.3.5 Non-cross-linked oNPs in THF (Good Solvent):

PTB7-Th oNPs: Non-cross-linked PTB7-Th oNPs transferred into THF show no scattering signal by DLS, indicating that the oNPs disassemble and dissolve in the surrounding solvent. Interestingly, HAADF images taken shortly after the transfer into THF still show intact oNPs (**Figure S24d**). However, after one week of aging, these oNPs disappear, likely as they dissolve into the solvent (**Figure S24f**). Although the oNPs are not colloidally stable over the long term, it is possible that the initial survival of the oNPs after solvent transfer is due to the protective oleic acid coating on their surface, or because the dissolution of the polymer into THF occurs slowly. It is important to note that DLS detects light scattered from the interface between the oNPs and the solvent. If the oNPs become highly swollen with solvent or if the solvent's dielectric constant closely matches that of the polymer, the system may not scatter light effectively, making it unsuitable for DLS analysis.

Early-time (Day 1 - 7) absorption spectra of the non-cross-linked PTB7-Th oNPs in THF are nearly identical to that of the bulk polymer in CHCl₃; both are 'J-aggregate-like' due to the larger magnitude of the S_{00} peak relative to the S_{10} peak (**Figure S28e**). Absorption spectra of the oNPs in THF bleach and blue-shift significantly over the course of a couple days, indicating rapid deterioration of the polymer backbone, possibly by a low concentration of peroxide species within the air-exposed THF. Interestingly, absorption spectra for the solvent-transferred oNPs bleach more quickly than that of the bulk polymer in THF (**Figure S30a**), indicating that the polymer backbone may be predisposed to damage after undergoing the oNP fabrication or solvent-transfer processes.

PM6 oNPs: Non-cross-linked PM6 oNPs transferred into THF similarly show no scattering signal by DLS, again indicating that the oNPs disassemble and dissolve in the surrounding solvent. Unlike the non-cross-linked PTB7-Th oNPs, TEM imaging of the non-cross-linked PM6 oNPs is unclear and does not seem to show intact oNPs at any point (**Figure S25d & g**). Similar to the PTB7-Th oNPs, early-time (Day 1 - 5) absorption spectra of the non-cross-linked PM6 oNPs in THF are nearly identical to that of the bulk polymer in CHCl₃; both are 'J-aggregate-like' due to the larger magnitude of the S_{00} peak relative to the S_{10} peak (**Figures S29e**). Absorption spectra of the PM6 oNPs in THF similarly bleach and blue-shift significantly over the course of a couple days, degrading more rapidly than that of the bulk polymer in THF (**Figure S30b**).

We conclude that neither the PTB7-Th nor PM6 non-cross-linked oNPs remain intact upon transfer into THF, as expected for polymer oNPs dispersed in a good solvent.

S8.3.6 Cross-linked oNPs in THF (Good Solvent):

PTB7-Th oNPs: Cross-linked PTB7-Th oNPs transferred into THF initially show a scattering signal by DLS, but these data include a significant small (≈ 1 nm) size peak and become too polydisperse for analysis after the sample is filtered (**Figure S26d & Table S2**). As before, oNPs appear intact by TEM immediately after transfer into THF, but dissolve after the sample ages for 1 week (**Figure S24j & m**). As in the non-cross-linked case, the absorption spectra for the cross-linked PTB7-Th oNPs in THF closely resembles that of the free bulk polymer in CHCl₃ (**Figure S28f**), and bleach and blue-shift more rapidly than the bulk polymer in THF (**Figure S30a**). Interestingly, cross-linked oNPs in THF experience a greater drop in absorption through the filtration process than non-cross-linked oNPs in THF do. This may indicate that the cross-linking process was partially successful, resulting in larger polymer aggregates that are unable to easily pass through the 0.45 μ m filter

PM6 oNPs: Cross-linked PM6 oNPs transferred into THF show no scattering signal by DLS, but TEM imaging reveals that the oNPs are intact immediately after the transfer (Day 1) and potentially after 1 week of aging (Day 7) (**Figure S25k & n**). As was the case for the PTB7-Th oNPs, absorption spectra for the cross-linked PM6 oNPs in THF resemble the bulk free polymer in CHCl₃ but experience a greater drop in absorption through the filtration process than non-cross-linked PM6 oNPs in THF do, indicating successful aggregation (**Figure S29f**).

We conclude that the addition of a covalent cross-linking step may give the polymer oNPs some added colloidal stability within good solvents like THF. However, the degree to which the particle integrity is maintained remains unclear.

S8.4 PL and TRPL

Steady-state photoluminescence (PL) and time-resolved photoluminescence (TRPL) data both provide insights into the exciton environment of cross-linked and non-cross-linked oNPs in different solvents. PL and TRPL data were collected on "Day 1" of the solvent transfer and samples prepared in methanol were excluded because they were too dilute. The PL spectra shown in **Figure S31** reveal two distinct cases: oNPs in THF, both cross-linked and non-cross-linked, exhibit high emission with a narrow peak around 750 nm, resembling the bulk free polymer in CHCl₃. These samples show J-aggregate-like behavior, characterized by a larger intensity in the S_{00} peak relative to the S_{01} peak. In contrast, oNPs in water and DMF, both cross-linked and non-cross-linked, show H-aggregate-like behavior with a broad, quenched emission peaking around 820 nm and reduced intensity of the S_{00} peak.

Emission spectra shown in (**Figure S31a & b**) have all been scaled by sample absorption at the excitation wavelength, 600 nm, (**Figure S32**) so the relative intensities of each spectrum can be compared. We find that incorporation of the cross-linker consistently reduces emission intensity by at least half in all cases, including in THF, suggesting that the cross-linking process preserves a higher degree of H-aggregation, even in the presence of a good solvent like THF. This implies that cross-linking helps stabilize the polymer chains into a compact spherical structure, preventing dissolution into the surrounding solvent, at least temporarily. This cross-linking-induced reduction in emission could also indicate that the polymer backbone is damaged in the cross-linking process, leading to more rapid exciton quenching, but this explanation is ruled out by time-resolved microwave conductivity (TRMC) data in the following section.

TRPL data, shown in **Figure S31d**, support the steady-state PL findings, further clarifying the nature of exciton dynamics in these samples. Both cross-linked and non-cross-linked oNPs in DMF and water exhibit short exciton lifetimes and multi-exponential decay kinetics, which are typical of H-aggregated polymers. In contrast, oNPs in THF, both cross-linked and non-cross-linked, show long exciton lifetimes and single-exponential decay kinetics, similar to

bulk free polymer in chloroform. Interestingly, the TRPL data for cross-linked oNPs in THF (pink trace) display some biexponential decay behavior, evidenced by a slight sub-linearity of this trace at short times. This indicates that these particles retain some H-aggregate-like structure, suggesting that cross-linking partially stabilizes the oNPs against dissolution into THF. As seen in the PL data, this reduction the exciton lifetime is seen across all cross-linked samples and supports the hypothesis that cross-linking promotes a higher degree of aggregation. While both PL and TRPL are limited to detecting only emissive species, these results confirm that no free polymer exists in solution in water or DMF, but cannot rule out the presence of polymer aggregates in THF.



Figure S31: (a) Steady-state photoluminescence spectra of cross-linked and non-cross-linked PTB7-Th oNPs (aqueous and solvent-transferred). Spectra are normalized relative to the sample absorption at 600 nm; (b) Zoom-in of (a) to compare spectral magnitude of the quenched species; (c) Normalized steady-state photoluminescence spectra of cross-linked and non-cross-linked PTB7-Th oNPs (aqueous and solvent-transferred); (d) Normalized time-resolved photoluminescence (TRPL) transients of cross-linked and non-cross-linked PTB7-Th oNPs (aqueous and solvent-transferred).



Figure S32: Uv-Vis absorption spectra for samples studied by PL and TRPL.

S8.5 TRMC

Time-Resolved Microwave Conductivity (TRMC) measurements confirm that the cross-linking process does not substantially impair charge generation in blended donor-acceptors systems. TRMC is a perturbative technique for directly quantifying the yield and mobility of photo-generated free charges in low-dielectric (organic) materials. Our TRMC methodology has been described in detail previously.^{17,18} Briefly, TRMC photoconductivity transients (**Figure S33**) are collected for oNP and bulk blended thin films over a range of excitation fluence values from $10^{12} - 10^{16}$ cm⁻². Transients are fit with a biexponential global fitting procedure and the initial (time t = 0 ns) carrier yield-mobility product ($\phi \Sigma \mu_{t=0}$) is determined from the sum of the fit's exponential pre-factors. $\phi \Sigma \mu_{t=0}$ is plotted at each fluence measured and the resulting curve is fit with the "Exciton-Charge Annihilation" (ECA) model (**Figure S34**), described in previous reports.¹⁴ Low-Fluence yield-mobility product values, ($\phi \Sigma \mu_{LF}$), are determined by extrapolating the ECA fit to a fluence of 10^9 cm⁻² (y-intercept in **Figure S34**), which approximates solar flux.

In this study, we compare cross-linked and non-cross-linked oNPs and bulk blend thin films, all made up of a 2 : 1 (by mass) ratio of PTB7-Th:N2200, with either 10 wt% or 0 wt% cross-linker. The cross-linked oNPs are made according to the above reported process, while the cross-linked bulk blend thin film is spray-coated then illuminated with 275 nm UV light for 3 minutes. TRMC is a thin-film measurement, so oNP samples are suspended in hydroxypropyl cellulose (HPC) (500 μ L oNPs per 30 mg HPC), drop-cast onto a quartz substrate, then dried at 60 °C for 30 minutes. The resulting thin film is made up of blended donor/acceptor oNPs suspended in a hydrated inert HPC matrix. As shown in **Figure S34**, the incorporation of a covalent cross-linking step only minimally reduces $\phi \Sigma \mu_{LF}$ (y- intercept) in both the oNP and bulk systems, indicating the neither the yield of free carriers nor their mobilities are negatively impacted by the cross-linker. This suggests that the covalent cross-linker is primarily binding to the alky side chains of the semiconducting polymers rather than their conjugated cores, which are responsible for their electronic properties.

To confirm the effectiveness of the cross-linking process in bulk blend films, we soaked the bulk blend films in toluene for 1 minute and monitored the drop in absorption as material dissolved off. As shown in **Figure S35**, the cross-linked film lost significantly less material compared to the non-cross-linked film during the soaking process. Notably, the material removed from the cross-linked film came off as macroscopic tendrils and chunks that did not redissolve in toluene, in contrast to the non-cross-linked film, which dissolved cleanly. This observation confirms that the cross-linked bulk blend thin film measured via TRMC was, indeed, effectively cross-linked.



Figure S33: Photoconductivity transients at various fluence values. (a) Non-cross-linked PTB7-Th/N2200 bulk blend thin film; (b)



Figure S34: $\phi \Sigma \mu_{t=0}$ vs. fluence for a non-cross-linked bulk blend thin film (green), cross-linked bulk blend thin film (yellow), non-cross-linked oNPs in HPC thin film (blue), and cross-linked oNPs in HPC thin film (red), all composed of a 2:1 PTB7-Th:N2200 ratio (by mass). Points are fit with the with the "Exciton-Charge Annihilation" (ECA) model and extrapolated to a fluence of 10^9 cm⁻² to approximate $\phi \Sigma \mu_{LF}$ (y-intercept)



Figure S35: UV-Vis absorption of 2:1 PTB7-Th:N2200 Bulk Blend Thin Films studied by TRMC. Spectra for cross-linked (yellow) and non-cross-linked (green) bulk blend thin films are shown both before (solid trace) and after (dashed trace) being rinsed with toluene for 1 minute.

S8.6 Conclusions from Covalent Cross-Linking Attempts

In conclusion, both the solvent-transfer and cross-linking processes are versatile and can be applied to oNPs composed of various polymers, such as PTB7-Th, PM6, and PTB7-TH/N2200 blends. While oNPs can be successfully transferred into DMF without the use of a cross-linker, the cross-linker may provide added stability, particularly when transferring oNPs into poor solvents like methanol, possibly by covalently bonding the surfactant to the oNP surface. Interestingly, TEM imaging reveals that both cross-linked and non-cross-linked oNPs initially retain their spherical shape when transferred into THF, despite the solubility of the polymers in this good solvent. However, this effect is short-lived, with both types of oNPs dissolving after one week, though cross-linked oNPs demonstrate a longer stability window as observed by DLS. PL and TRPL data further suggest that cross-linked oNPs exhibit more quenched emission than their non-cross-linked counterparts, including in THF, indicating that the cross-linker may help maintain a higher degree of H-aggregation by "locking" the polymer into a spherical nanoparticle structure rather than allowing it to dissolve freely in solution. Encouragingly, TRMC measurements show that cross-linked oNPs and cross-linked bulk thin films maintain nearly unchanged charge generation efficiency, indicating that the cross-linking process does not compromise the functionality of the system. Despite these findings, the effect of the cross-linker on colloidal stability remains modest. Specifically, it's unclear whether the cross-linker is connecting separate neighboring polymer chains, as intended, or merely causing an individual chain to coil upon itself. These two processes would produce indistinguishable vibronic spectroscopic signatures. Additional studies are necessary to optimize the cross-linking conditions, understand the structural integrity of solvent-transferred oNPs, and investigate the impact of cross-linking on free charge generation in semiconducting polymer oNPs.

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