



Cite this: DOI: 10.1039/d0cp04819d

How to reprogram the excitonic properties and solid-state morphologies of π -conjugated supramolecular polymers†‡

Kaixuan Liu,^a Victor Paulino,^a Arindam Mukhopadhyay,^a ^a Brianna Bernard,^a Amar Kumbhar,^b Chuan Liu^a and Jean-Hubert Olivier^a *^a

The development of supramolecular tools to modulate the excitonic properties of non-covalent assemblies paves the way to engineer new classes of semiconducting materials relevant to flexible electronics. While controlling the assembly pathways of organic chromophores enables the formation of J-like and H-like aggregates, strategies to tailor the excitonic properties of pre-assembled aggregates through post-modification are scarce. In the present contribution, we combine supramolecular chemistry with redox chemistry to modulate the excitonic properties and solid-state morphologies of aggregates built from stacks of water-soluble perylene diimide building blocks. The n-doping of initially formed aggregates in an aqueous medium is shown to produce π -anion stacks for which spectroscopic properties unveil a non-negligible degree of electron–electron interactions. Oxidation of the n-doped intermediates produces metastable aggregates where free exciton bandwidths (E_{BW}) increase as a function of time. Kinetic data analysis reveals that the dynamic increase of free exciton bandwidth is associated with the formation of superstructures constructed by means of a nucleation-growth mechanism. By designing different redox-assisted assembly pathways, we highlight that the sacrificial electron donor plays a non-innocent role in regulating the structure–function properties of the final superstructures. Furthermore, supramolecular architectures formed via a nucleation-growth mechanism evolve into ribbon-like and fiber-like materials in the solid-state, as characterized by SEM and HRTEM. Through a combination of ground-state electronic absorption spectroscopy, electrochemistry, spectroelectrochemistry, microscopy, and modeling, we show that redox-assisted assembly provides a means to reprogram the structure–function properties of pre-assembled aggregates.

Received 11th September 2020,
Accepted 3rd December 2020

DOI: 10.1039/d0cp04819d

rsc.li/pccp

Introduction

Molecular aggregates that feature stacks of π -conjugated building blocks (π -stacks) are important classes of semiconducting materials relevant to organic electronics, spintronics, and solar energy capture, conversion, and storage.^{1–10} Knowledge acquired over the last few decades has unambiguously underscored the critical role played by molecular order in dictating the linear and non-linear optical properties in addition to the exciton, charge and spin transport properties of organic nanoscale compositions.^{11–16} For example, while delocalized charge transfer excitons have been shown to facilitate the formation of free

charge carriers in organic solar cells, their formation is contingent upon the existence of strongly interacting frontier molecular orbitals and is intimately related to the conformation of molecular aggregates at the nanoscale dimension.^{17,18}

The pioneering theoretical studies by Bredas, Ratner, Spano, and others have highlighted the importance of interchromophore electronic coupling in non-covalent π -conjugated assemblies and the extent to which it can be leveraged to modulate the (opto)-electronic properties of organic semiconducting materials.^{19–25} From a theoretical perspective, maximizing the frontier molecular orbital overlap between adjacent π -conjugated cores paves the way to increase the electronic coupling between chromophores, but it requires the formation of a parallel stack geometry (co-facial) that is associated with experimental limitation. In this regard, attractive electrostatic and dispersion energies are well-recognized parameters that regulate the conformation of supramolecular constructs and, consequently, their functions.^{26,27} In solvated π -stacks, also termed as π -conjugated supramolecular polymers (SPs), complex interplays of hydrophobic and quadrupole–quadrupole interactions among

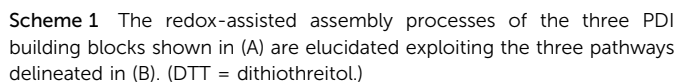
^a Department of Chemistry, The University of Miami, 1301 Memorial Drive, Cox Science Building, Coral Gables, FL 33146, USA. E-mail: Jh.olivier@miami.edu

^b Chapel Hill Analytical and Nanofabrication Laboratory, Department of Applied Physical Sciences, University of North Carolina, 243 Chapman Hall, Chapel Hill, NC 27599, USA

† This manuscript is dedicated to J.-H. Olivier's father.

‡ Electronic supplementary information (ESI) available. See DOI: 10.1039/d0cp04819d

To deliver a general understanding of the synergistic role played by the building block structure and the chemical reductant employed, we engineered the three PDI cores shown in Scheme 1A. While each of the PDI units feature two cationic functional groups placed at an equal distance from the aromatic core by a propyl linker, these building blocks differ in: (1) the structure of the peripheral cationic groups (ammonium and imidazolium), and (2) the terminal side chains which are expected to equip the initial



Solvent-dependent aggregation studies reveal that an isodesmic supramolecular polymerization mechanism regulates the formation of the [PDI-C₃Am-C₂OH]_{lfa}, [PDI-C₃Am-C₃]_{lfa}, and

[PDI-C₃Im-C₂]_{Iffa} assemblies in an aqueous medium. Fig. 1A and Fig. S1A, S2A (ESI†) chronicle the spectral evolution, as a function of solvent composition, of the PDI-C₃Am-C₂OH, PDI-C₃Am-C₃, and PDI-C₃Im-C₂ building blocks, respectively. In pure water, the ratio of the 0–1 and 0–0 vibronic transitions centered at 500 and 542 nm is below one for the representative PDI-C₃Am-C₂OH unit shown in Fig. 1A; the PDI-C₃Am-C₃ and PDI-C₃Im-C₂ platforms share similar spectral properties (Fig. S1 and S2, ESI†). These well-established spectroscopic signatures indicate that the [PDI-C₃Am-C₂OH]_{Iffa}, [PDI-C₃Am-C₃]_{Iffa}, and [PDI-C₃Im-C₂]_{Iffa} building blocks exist under an aggregated state best described as H-like aggregates. We have previously shown that PDI-derived building blocks sharing related structural attributes engender the formation of H-like aggregates in water.⁴⁵ The addition of a good solvent (DMF) to a solution of PDI aggregates solvated in a poor solvent (H₂O) is accompanied by a drastic change of spectroscopic features indicative of the formation of individualized

building blocks. Fig. 1A highlights the simultaneous rise and hypsochromic shifts of the 0–0 and 0–1 vibronic transitions in addition to an inversion of the 0–0 and 0–1 ratio reaching 1.5 in pure DMF. Furthermore, in pure DMF, the 0–0, 0–1 and 0–2 vibronic transitions are consistently separated by 180 meV (1452 cm^{−1}, aromatic C=C bond stretching), an additional hallmark of molecularly dissolved PDI building blocks.^{46,47}

The degree of aggregation as a function of solvent composition is analyzed using the equilibrium model developed by Korevaar and Meijer.^{48,49} It provides important insights into the thermodynamic parameters governing the assembly of the PDI building blocks. We exploited the 0–0/0–1 ratio as a function of DMF ratio in water to construct the “denaturation” curve for the representative PDI-C₃Am-C₂OH unit shown in Fig. 1B. The denaturation curves for the PDI-C₃Am-C₃ and PDI-C₃Im-C₂OH units are shown in Fig. S1B and S2B (ESI†), respectively. In the equilibrium model, the Gibb's free energy is made dependent on the DMF volume fraction following eqn (S3) (ESI†) where ΔG^0 represents the gain of Gibb's free energy upon monomer addition in pure water, and the m -value accounts for the change of ΔG as a function of DMF volume fraction (f). Please refer to Section S3 of the ESI† for a more detailed discussion. The thermodynamic parameters that regulate the assembly of [PDI-C₃Am-C₂OH]_{Iffa}, [PDI-C₃Am-C₃]_{Iffa}, and [PDI-C₃Im-C₂]_{Iffa} constructs are presented in Table 1. For the three studied PDI building blocks, the degree of cooperativity (σ) is equal to one signalling that the growth of the respective aggregates is dictated by a monomer addition sharing an identical elongation constant, K_e , as represented in the inset of Fig. 1A. It is interesting to note that the elongation constant of the PDI-C₃Im-C₂ building block is modestly lower than that calculated for the ammonium-derived PDI-C₃Am-C₂OH, and PDI-C₃Am-C₃ units. This observation can be rationalized from the steric hindrance imposed by the imidazolium groups that can potentially destabilize the aggregation of the PDI-C₃Im-C₂ building blocks when compared to the PDI-C₃Am-C₂OH and PDI-C₃Am-C₃ analogues flanked with less sterically demanding ammonium side chains.

Concentration-dependent and variable-temperature studies are traditionally leveraged to probe the assembly mechanisms of supramolecular polymers. However, experimental challenges exist. To ensure the sampling of the entire aggregation process in variable-temperature studies, a solvated building block should exist as molecularly dissolved at high temperatures and under a fully aggregated state at low temperatures. The physical property of the solvent may impose a temperature window that hampers the accurate elucidation of a self-assembly mechanism. An appealing

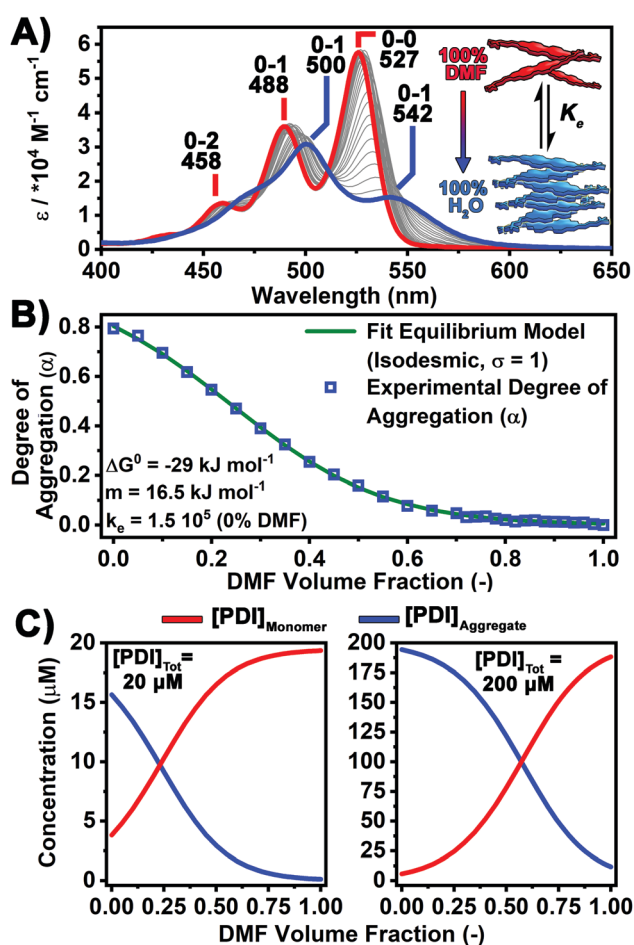


Fig. 1 (A) Solvent-dependent UV-vis ground-state electronic absorption spectra of a 20 μ M solution of the representative PDI-C₃Am-C₂OH building block in water upon the addition of DMF. (B) Experimental degree of aggregation (empty blue square) as a function of DMF volume fraction. The solid green line represents the best fit using the equilibrium model detailed in the ESI†. Correction factor p used is 1.25. (C) Evolution of the concentration of the free monomer ([PDI]_{Monomer}) and the monomers that construct the aggregates ([PDI]_{Aggregate}).

Table 1 Thermodynamic parameters extracted from the global fitting of the solvent-dependent UV-vis data

	PDI-C ₃ Am-C ₂ OH	PDI-C ₃ Am-C ₃	PDI-C ₃ Im-C ₂
σ	1	1	1
ΔG^0 (kJ mol ^{−1})	−29	−28.75	−28
m (kJ mol ^{−1})	16.5	17.15	14
K_e (mol ^{−1})	1.4×10^5	1.3×10^5	10^5
DP at 200 μ M	5.8	5.6	5

aspect of the equilibrium model developed by Korevaar and Meijer is the introduction of a correction factor p that accounts for an incomplete aggregate formation, or lack of saturation, under a given set of experimental conditions.

Fitting the denaturation curve of the three PDI building blocks required correction factors varying from 1.25 to 1.3 suggesting that these building blocks do not exist under a fully aggregated state in water at room temperature with a $[PDI] \sim 20 \mu\text{M}$. Please see Section S3 in the ESI† for more details. Fig. 1C illustrates this observation and chronicles the evolution of the concentration of PDI cores that are under an aggregated state ($[PDI]_{\text{Aggregate}}$) and molecularly dissolved ($[PDI]_{\text{Monomer}}$) as a function solvent composition for the representative **PDI-C₃Am-C₂OH** units. For a total concentration of PDI units $C_{\text{tot}} = 20 \mu\text{M}$, a non-negligible population of the monomer exists as molecularly dissolved in pure water and suggests a non-complete polymerization process. The concentration distribution for the **PDI-C₃Am-C₃** and **PDI-C₃Im-C₂OH** units are shown in Fig. S1 and S2 (ESI†), respectively. Because ΔG^0 and m are independent of the total monomer concentration, the simulated curves showing the evolution of $[PDI]_{\text{Aggregate}}$ and $[PDI]_{\text{Monomer}}$ at $C_{\text{tot}} = 200 \mu\text{M}$ are shown in Fig. 1C-(right panel). This concentration is representative of the building block concentration exploited during the redox-assisted process (*vide supra*) allowing us to confirm the aggregated states of the initial formed assemblies. As expected, a higher initial concentration of PDI building blocks leads to a drastic decrease of the total monomer population (less than 2%) that exists as molecularly dissolved at room temperature, in pure water. The **PDI-C₃Am-C₃** and **PDI-C₃Im-C₂** building blocks demonstrate identical concentration-dependent aggregation profiles as detailed in Section S3 of the ESI†. Further assessment of the degree of polymerization for the three assemblies indicates that an average of 5 to 6 repeating units comprise the aggregates at a concentration of $200 \mu\text{M}$.⁵⁰

Potentiometric characterization of n-doped PDI supramolecular polymers

The potentiometric properties elucidated for the **[PDI-C₃Am-C₂OH]_{if}**, **[PDI-C₃Am-C₃]_{if}**, and **[PDI-C₃Im-C₂]_{if}** assemblies reveal that these π -conjugated supramolecular polymers evidence complex electronic structures in solution. Cyclic voltammetry (CV) experiments were performed on the three assemblies in 100% H₂O at $C_{\text{tot}} = 200 \mu\text{M}$, and the corresponding data are shown in Fig. 2 and Fig. S3 (ESI†). A common first reduction potential at $\sim -0.27 \text{ V vs. SCE}$ is evidenced, and it indicates that these PDI-derived supramolecular polymers have some similarities in their electronic structure. While the **[PDI-C₃Am-C₂OH]_{if}** assembly exhibits a distinct first reduction wave as shown in Fig. 2A, the **[PDI-C₃Am-C₃]_{if}**, and **[PDI-C₃Im-C₂]_{if}** assemblies are characterized by broad cathodic and anodic transitions that sample the 0 to -0.9 V electrochemical window. These observations suggest a non-negligible level of structural heterogeneity, in addition to a different solvation environment, that translates to electronic states that are distributed across a wide energy window. It is interesting to note that cyclic voltammograms

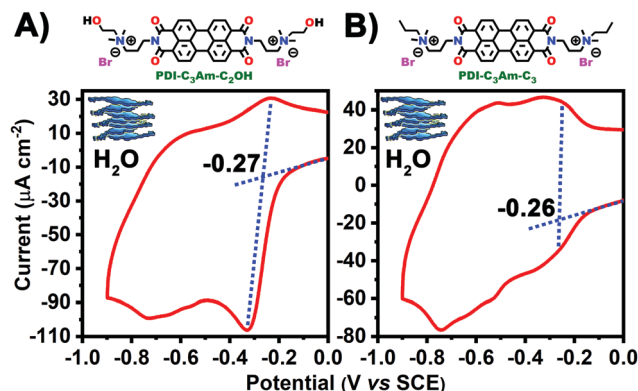


Fig. 2 Cyclic voltammograms recorded for the initially formed assemblies **[PDI-C₃Am-C₂OH]_{if}** (A) and **[PDI-C₃Am-C₃]_{if}** (B) in H₂O solvent under argon atmosphere. Experimental conditions: [analyte] = $200 \mu\text{M}$, $1 \times$ PBS buffer, scan rate = 50 mV s^{-1} , glassy carbon working electrode.

recorded in a solvent mixture in which the assemblies exist primarily as molecularly dissolved (90% DMF-Fig. S4, ESI†) show more resolved cathodic and anodic transitions reminiscent to these of individualized building blocks.⁵¹ The chronocyclic potentiometric properties confirm that sacrificial electron donors characterized by an oxidation potential more negative than -0.30 V vs. SCE are potential candidates to n-dope the PDI-derived supramolecular polymers in an aqueous solution.

The electronic spectral properties of the n-doped assemblies in an aqueous medium are examined and reveal the existence of π -anion stacks. Exploiting the inorganic (NaSH/pathway 1 – Scheme 1) and organic (DTT/pathway 2/3 – Scheme 1) sacrificial electron donors, reductive titrations of the initially formed assemblies **[PDI-C₃Am-C₂OH]_{if}**, **[PDI-C₃Am-C₃]_{if}**, and **[PDI-C₃Im-C₂]_{if}** were conducted and the associated EAS are shown in Fig. 3A and Fig. S9–S12 (ESI†). As shown in Fig. 3A, the addition of up to 0.3 eq. of NaSH to a solution of the **[PDI-C₃Am-C₂OH]_{if}** assembly initiates the formation of reduced PDI aggregates as diagnosed by the emergence of the spectroscopic signatures centred at 990 nm, 816 nm, 733 nm, and 616 nm.^{44,52} A similar observation is made by gleaning the EAS of **[PDI-C₃Am-C₃]_{if}** and **[PDI-C₃Im-C₂]_{if}** n-doped with 0.3 eq. NaSH (Fig. S9, ESI†). Furthermore, it is important to note the apparition of a broad NIR band that covers the 1050-to-2500 nm spectral window that is initially centred at 1563 nm, 1576 nm, and 1565 nm for the **[PDI-C₃Am-C₂OH]_{n-doped}**, **[PDI-C₃Am-C₃]_{n-doped}**, and **[PDI-C₃Im-C₂]_{n-doped}** intermediates, respectively.

As shown in Fig. 3A and Fig. S9 (ESI†), the further addition of up to 1 eq. of NaSH is accompanied with profound modifications of the EAS sharing similar features among the three n-doped assemblies under investigation. For the exemplary **[PDI-C₃Am-C₃-C₂OH]_{n-doped}** assembly, while one of the spectroscopic fingerprints of an aggregated PDI radical anion centered at 991 nm vanishes as the equivalency of reductant is increased from 0.3 eq. to 1 eq., the loss of the resolved absorptive features observed in the visible to NIR spectral windows gives rise to a broad transition centered at 567 nm with two shoulders at 410 nm and 785 nm. The most striking observation is the evolution of the NIR transitions bathochromically

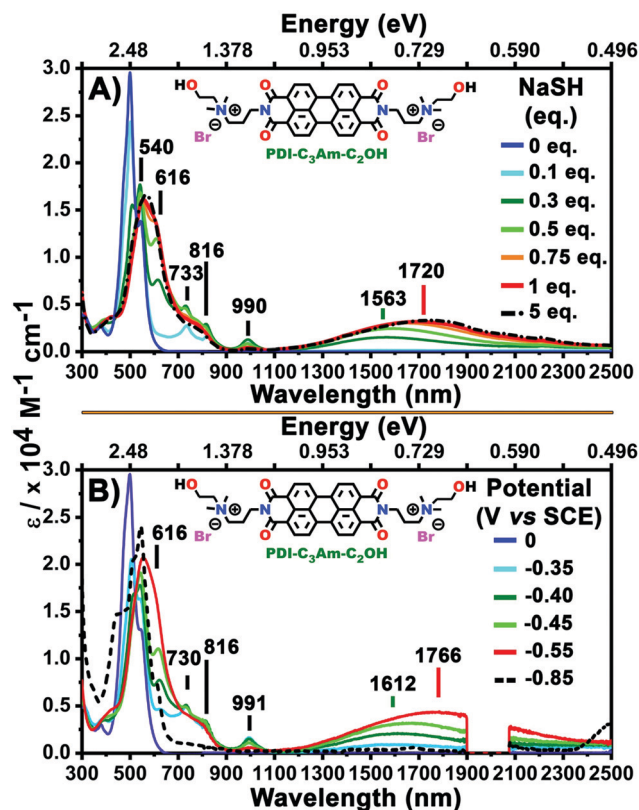


Fig. 3 UV-vis-NIR ground state electronic absorption spectra that narrate the: (A) reductive titration of the initially formed $[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{Ira}}$ assembly in deuterated water solvent exploiting sodium hydrosulfide (NaSH) as sacrificial electron donor, and (B) the electrochemically generated spectra in deuterated water. Experimental conditions: $[\text{PDI}] = 200 \mu\text{M}$ (A and B); argon atmosphere; $T = 20^\circ\text{C}$; optical pathlength = 2 mm (A) and 1 mm (B); gold working electrode (B).

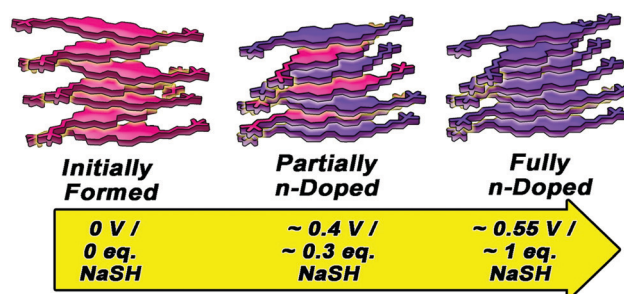
shifted from 1563 nm to 1720 nm upon the addition of 1 eq. of the sacrificial electron donor NaSH. Furthermore, while the spectral evolutions of $[\text{PDI-C}_3\text{Am-C}_3]_{\text{n-doped}}$ and $[\text{PDI-C}_3\text{Im-C}_2]_{\text{n-doped}}$ intermediates share a similar trend to that underscored for $[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{n-doped}}$, the n-doped $[\text{PDI-C}_3\text{Im-C}_2]_{\text{n-doped}}$ assembly evidences a more modest bathochromic shift of the NIR band (51 meV) when compared to those established for $[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{n-doped}}$ (61 meV) and $[\text{PDI-C}_3\text{Am-C}_3]_{\text{n-doped}}$ (66 meV). The spectra acquired upon the addition of up to 5 eq. of NaSH mimic those recorded after the addition of 1 eq. of sacrificial electron donor, suggesting completion of the n-doping process.

Exploiting the organic reductant dithiothreitol (pathway 2 – Scheme 1) does not alter the electronic properties of n-doped assemblies mimicking those observed when using NaSH as a sacrificial electron donor. As gleaned from the reductive titration and associated EAS chronicled in Fig. S10–S12 (ESI †), similar spectral evolutions to those evidenced when using NaSH as a sacrificial electron donor are witnessed upon n-doping the initially formed $[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{Ira}}$, $[\text{PDI-C}_3\text{Am-C}_3]_{\text{Ira}}$ and $[\text{PDI-C}_3\text{Im-C}_2]_{\text{Ira}}$ assemblies. Spectroscopic signatures that indicate the formation of aggregated radical PDI states are followed by the emergence of absorptive features in the 400-to-900 nm spectral window concomitant with the red shift of the broad

NIR transitions. All taken together, the NaSH and DTT reductive titrations suggest the emergence of similar electronic states in the n-doped $[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{n-doped}}$, $[\text{PDI-C}_3\text{Am-C}_3]_{\text{n-doped}}$ and $[\text{PDI-C}_3\text{Im-C}_2]_{\text{n-doped}}$ intermediates that diagnose a substantial degree of PDI–PDI interaction. To confirm that the NIR absorptive features are intrinsic spectroscopy properties of the n-doped aggregates, an exemplary reductive titration utilizing a molecular surfactant was conducted on the $[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{Ira}}$ assembly and is presented in Fig. S14 (ESI †). Following the formation of the n-doped intermediate, the addition of 100 eq. of the molecular surfactant sodium dodecyl sulfate (SDS) triggers the formation of individualized PDI radical anions as indicated by the recovery of the well-resolved spectroscopic signatures located at 962, 720, and 602 nm.

To gain more insights into the electrochemical potentials associated with the spectroscopic signatures of the n-doped intermediates, electrochemically generated spectra of the $[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{n-doped}}$, $[\text{PDI-C}_3\text{Am-C}_3]_{\text{n-doped}}$ and $[\text{PDI-C}_3\text{Im-C}_2]_{\text{n-doped}}$ intermediates are acquired and are shown in Fig. 3B and Fig. S5–S7 (ESI †), respectively. For the three assemblies, the spectroscopic profiles of the n-doped intermediates, generated with 1 and 5 eq. of chemical reductant (NaSH or DTT), are perfectly reproduced at a potential of -0.55 V vs. SCE . The apparent redshifts of the NIR transitions when comparing the electrochemically (1766 nm) with the chemically (1720 nm) induced spectra may originate from the nature of the cations paired with the nascent negative charges. It is interesting to note that the spectrum recorded at a potential of -0.60 V vs. SCE mimics that monitored at -0.55 V , suggesting the saturation of the n-doped intermediates with electrons. Incrementing the potentials to -0.65 V is accompanied with the decrease of the NIR transitions in addition to the apparition of new spectroscopic features centered at 540 nm and 448 nm. Further excursion towards more cathodic potentials (-0.85 V vs. SCE) reinforce the absorptive signatures characteristic of the PDI dianion species (Fig. S5–S7, ESI †).

The reductive titration experiments combined with the UV-vis-NIR spectroelectrochemistry experiments deliver preliminary conclusions on the origin of the NIR transitions characterizing the n-doped intermediates. As suggested by the electrochemically generated spectra, a first n-doped state is formed up to a potential of -0.40 V and is represented schematically in Scheme 2. A similar state is accessed when using a low



Scheme 2 Representation of the level of n-doping of an initially formed assembly as a function of applied cathodic potential and concentration of sacrificial electron acceptor.

equivalency of sacrificial electron donor (~ 0.3 eq. vs. PDI units). For the exemplary **PDI-C₃Am-C₂OH** building block, the corresponding n-doped intermediate is characterized by the transitions centered at 1612 nm, 991 nm, 816 nm, 730 nm and 616 nm. It is fair to assume that increasing the potential to -0.55 V enables the formation of highly doped intermediates at the origin of the NIR transition lying lower in energy when compared to that of the species formed at -0.35 V. A similar pattern is observed in the reductive titration experiments. Furthermore, an increase of only 0.05 V towards cathodic potentials (-0.60 V to -0.65 V) initiates the formation of PDI dianions which become the major reduced species at -0.85 V. All taken together, this data suggests that the negatively charged intermediates formed at -0.55 V can be described as heavily n-doped where most of the PDI units comprising the aggregates exist under a reduced state.

We postulate that the NIR transition observed at -0.55 V originates from novel electronic states formed by interaction of the PDI radical anions in the n-doped SPs. In this regard, it is interesting to note that n-doped **[PDI-C₃Im-C₂]_{n-doped}** intermediates feature the highest NIR transition energy among the three PDI systems under investigation. Concomitantly, the **PDI-C₃Im-C₂** building block evidences the lowest elongation constant at room temperature. Less likely to be coincidental, these observations may originate from the steric hindrance imposed by the imidazolium side chains that decrease the degree of interchromophore interaction both in the neutral and in the n-doped state. Seminal work by Miller has reported closely related phenomena for n-doped water-soluble naphthalene diimides derivatives.^{53–55}

Tuning the excitonic properties

Because weak, non-covalent interactions regulate the conformation of supramolecular constructs, stacks of π -conjugated cores are fragile matter compositions where minor perturbations of the interchromophore geometry can perturb the excitonic properties at the assembly level. Pioneering studies by Spano have unambiguously demonstrated that Angstrom-level displacement engenders a drastic modification of the excitonic coupling in PDI-based H-like aggregates.^{24,56,57} To glean further insights into the extent to which the n-doping of π -stacks can be exploited to tune the electronic properties of non-covalent assemblies, the model developed by Spano for H-like aggregates was exploited to calculate and compare the E_{BW} of the initially formed assemblies **[PDI-C₃Am-C₂OH]_{ifa}**, **[PDI-C₃Am-C₃]_{ifa}**, and **[PDI-C₃Im-C₂]_{ifa}** to those of the final, redox-treated superstructures formed by aerating the n-doped intermediates over 48 hours. Because excitonic properties in non-covalent assemblies are intimately related to interchromophore interactions and building block conformations, elucidating the E_{BW} for each of the pathways shown in Scheme 1 provides a means to evaluate potential structural reconfigurations throughout the redox-assisted assembly pathways.

The electronic spectral properties of the redox-treated PDI assemblies **[PDI-C₃Am-C₂OH]**, **[PDI-C₃Am-C₃]**, and **[PDI-C₃Im-C₂]** differ as a function of the chemical reductants (pathway 1–3, Scheme 1). Fig. 4 chronicles the representative EAS for the initially

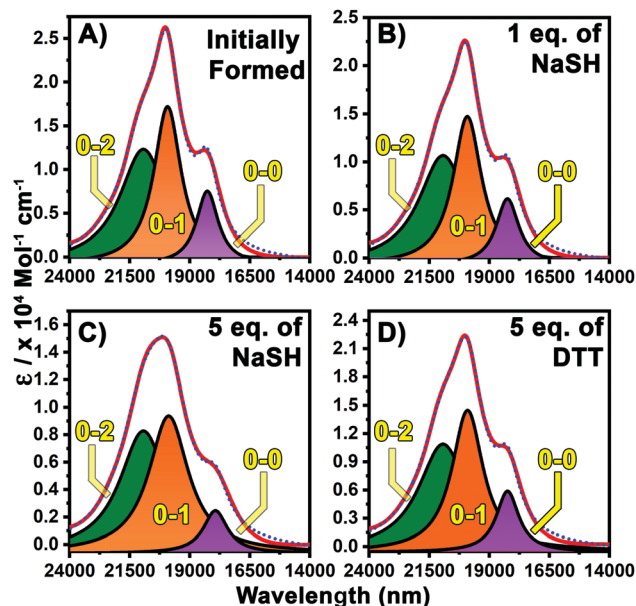


Fig. 4 Representative electronic absorption spectra recorded for the initially formed **[PDI-C₃Am-C₂OH]_{ifa}** assembly (A), and the neutral, redox-treated **[PDI-C₃Am-C₂OH]_{Rta}** assemblies generated after oxidizing the n-doped intermediates initially formed with 1 eq. of NaSH (B), 5 eq. of NaSH (C), and 5 eq. of DTT (D). The area under curve in purple, orange and green have been calculated using a nonlinear regression fitting (Lorentzian) and correspond to the 0–0, 0–1, and 0–2 vibronic transitions, respectively. The reconstructed absorption spectra from the fit are shown in dotted blue line.

formed **[PDI-C₃Am-C₂OH]** assembly and the related redox-treated superstructures formed after oxidizing the n-doped state. Please note that 48 hours separates the data collection from the oxidation of the reduced intermediates. While the EAS recorded for the redox-treated superstructures formed with 1 eq. of NaSH and 5 eq. of DTT evidence spectroscopic features similar to those that characterize the initially formed assembly, non-negligible perturbations of the absorptive properties are diagnosed for the superstructure engendered using 5 eq. of NaSH. A pronounced redistribution of the oscillator strength of the 0–0 vibronic transition into the 0–1 and 0–2 vibronic transition is evidenced, in addition to a ~ 300 cm^{-1} hypsochromic shift of the 0–0 transition. Congruent with these spectroscopic features, an increase of more than 33% of the E_{BW} is evidenced in the redox-treated superstructure **^{NaSH}[PDI-C₃Am-C₂OH]_{Rta}** formed through pathway 1. Table 2 summarizes the calculated E_{BW} as a function of n-dopant equivalency and chemical properties. To rule out that the reported increase of E_{BW} originates solely from the interaction of salts produced during the oxidation of the excess of NaSH reductant, the E_{BW} of the control samples was investigated. These control samples were generated by adding an aerated solution comprising oxidized NaSH (5 eq.) to a solution of the initially formed assembly **[PDI-C₃Am-C₂OH]_{ifa}**. As can be seen in Fig. S15, ESI,† and Table 2, no noticeable perturbation of the EAS is witnessed, and the calculated E_{BW} for the controlled assembly **[PDI-C₃Am-C₂OH]_{ifa}** remains virtually unperturbed ($< 4\%$) when compared to that of the pristine **[PDI-C₃Am-C₂OH]_{ifa}** assembly.

Table 2 Calculated free exciton bandwidth (E_{BW}) in meV for the three assemblies as a function of the n-doping conditions used in the redox-assisted assembly pathway 1–2

	PDI-C ₃ Am-C ₂ OH	PDI-C ₃ Am-C ₃	PDI-C ₃ Im-C ₂
Initially formed	280	281	283
Control	290	290	292
DTT (5 eq.)	323	310	325
NaSH (1 eq.)	310	309	303
NaSH (5 eq.)	395	395	375
DTT/Na ₂ SO ₃	396	n/a	n/a

The redox-treated superstructures [PDI-C₃Am-C₃]_{RTS}, and [PDI-C₃Im-C₂]_{RTS} formed through pathway 1 exhibit similar electronic spectral properties to those elucidated for the analog PDI-C₃Am-C₂OH building blocks, as shown in Fig. S16 and S17 (ESI†). As gleaned in Table 2, a non-negligible increase of E_{BW} is observed for assemblies n-doped with 5 eq. of NaSH while only a modest evolution of the E_{BW} is notable when 1 eq. of NaSH and 5 eq. of DTT are exploited. Furthermore, it is important to note that, as confirmed by the control experiment, the sole products generated from the oxidation of NaSH are not responsible for the increase of E_{BW} . All taken together, the data presented thus far indicate that: (1) the imidazolium side chains flanked on the PDI cores engender superstructures equipped with a lower E_{BW} when compared to superstructures that feature ammonium groups, (2) the formation of n-doped intermediates is critical to increase the E_{BW} , and (3) additional parameters have to be accounted for to rationalize the increase of E_{BW} exclusively evidenced in the reaction pathway 1 that exploits 5 eq. of NaSH.

As shown in Fig. 5, which chronicles the evolution of the E_{BW} , as a function of time recorded for the ^{NaSH}[PDI-C₃Am-C₂OH]_{RTS}, ^{NaSH}[PDI-C₃Am-C₃]_{RTS}, and ^{NaSH}[PDI-C₃Im-C₂]_{RTS} superstructures, the E_{BW} measured for assemblies that are n-doped using 5 eq. of NaSH (pathway 1 – Scheme 1) increases over the 48 hours following redox treatment. The three assemblies share a similar trend: the modest increase of E_{BW} (<7%) witnessed within the first 8 hours after neutralizing the n-doped intermediates is followed by a drastic augmentation between 8 to 40 hours that plateaus afterwards. In sharp contrast, the control samples do not evidence a meaningful evolution of the recorded E_{BW} , but instead, fluctuates in the 280-to-290 meV energy range. Because the functions of non-covalent assemblies are defined by their structure, the dynamic increase of E_{BW} suggests that the conformation of the redox-treated superstructures, created immediately after oxidation, evolves as a function of time.

A nucleation-growth mechanism, exclusive to pathway 1, governs the aggregation of the redox-treated ^{NaSH}[PDI-C₃Am-C₂OH]_{RTS}, ^{NaSH}[PDI-C₃Am-C₃]_{RTS}, and ^{NaSH}[PDI-C₃Im-C₂]_{RTS} superstructures. The sigmoidal shape that characterizes the increase of E_{BW} as a function of time, shown in Fig. 5, is reminiscent to kinetic data reported for protein aggregation. More specifically, the general 2-step kinetic model introduced by Finke and Watzky (F-W) has been widely applied to fit protein aggregation and features a nucleation step followed by an autocatalytic growth step.^{58–61} This model is exploited to successfully fit ($R^2 > 0.99$)

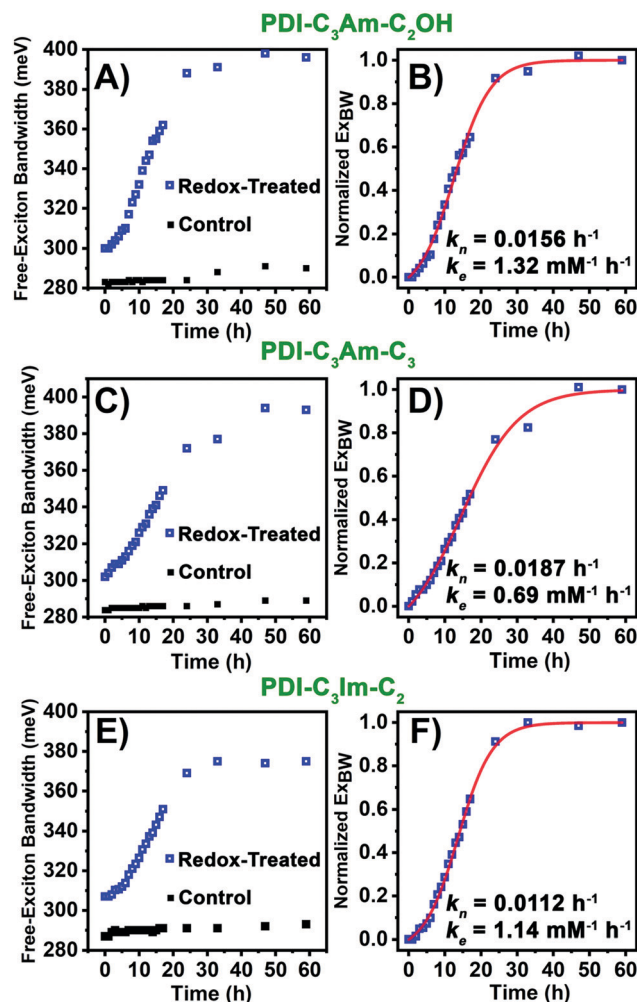


Fig. 5 (A, C and E) Evolution of the free-exciton bandwidth as a function of time for the control assemblies and the redox-treated superstructures formed with 5 eq. of NaSH. (B, D and F) Normalized E_{BW} as a function of time calculated for the redox-treated assemblies. The experimental data (open blue square) is fitted using the nucleation-growth 2-step model introduced by Finke and Watzky. Please refer to Section S6 of the ESI† for more details.

the normalized increase of E_{BW} as a function of time in Fig. 5. For the three assemblies, a similar nucleation rate constant bracketed between 0.01 and 0.02 h^{-1} (k_n) is evidenced where the elongation rate constant (k_e) varies from 0.69 $\text{mM}^{-1} \text{h}^{-1}$ for the [PDI-C₃Am-C₃]_{RTS} superstructure to 1.32 $\text{mM}^{-1} \text{h}^{-1}$ for the [PDI-C₃Am-C₂OH]_{RTS} superstructure. While we acknowledge that the 2-step F-W mechanism is a simplified model that condenses and averages a plethora of steps into two pseudo-elementary steps, it provides valuable insights into the possible mechanisms that regulate the growth of the redox-treated superstructures. It is important to note that perturbation of the structure–function properties of neutral, water-soluble PDI assemblies upon redox treatment has also been reported by Hermans and further bolsters our analysis.⁴²

To rationalize the data presented thus far, we postulate that pathway 1 in Scheme 1B enables the creation of metastable architectures initiated immediately after the oxidation step;

their further nucleation and growth engender superstructures with increased Ex_{BW} . It is interesting to note that at $t = 0$ h, the redox-treated assemblies are characterized by an Ex_{BW} modestly larger than that recorded for the control samples. This change in excitonic properties further confirms the formation of supramolecular constructs that differ from the initially formed assemblies. In addition, the fact that 5 eq. of NaSH are necessary to record a substantial change in the excitonic properties indicates that the oxidized NaSH products are necessary to promote the growth of the final superstructures. While the oxidation of NaSH can generate several byproducts, sodium sulfite Na_2SO_3 salt is one of the predominant species. We hypothesized that this byproduct may participate in the growth of the superstructures.

Reductive titration experiments that combine the sacrificial electron donor DTT and the addition of sodium sulfite (Na_2SO_3) provide insights into parameters that regulate the increase of Ex_{BW} in PDI assemblies solvated in an aqueous medium. Because n-doping the initially formed PDI assemblies with the organic reductant DTT does not enforce the same increase of Ex_{BW} elucidated in pathway 1, we leveraged this condition to unveil the potential role played by the sulfite anion in the redox-assisted assembly process. To test our hypothesis, we exploited the $[PDI-C_3Am-C_2OH]$ building blocks as an exemplary platform. In this experiment, the $[PDI-C_3Am-C_2OH]_{n-doped}$ intermediate was generated by the addition of 5 eq. of DTT and 5 eq. of Na_2SO_3 (pathway 3 in Scheme 1B). The associated EAS are chronicled in Fig. S13 (ESI ‡) and demonstrate identical spectroscopic signatures to those recorded for the n-doped assemblies formed using 5 eq. of NaSH. This observation suggests that these two pathways, namely DTT/ Na_2SO_3 and NaSH (5 eq.), generate n-doped intermediates equipped with similar electronic structures.

The EAS and Ex_{BW} presented in Fig. S18 (ESI ‡) underscore the non-negligible role played by the sulfite anion in regulating the electronic spectral properties of the redox-treated superstructures $[PDI-C_3Am-C_2OH]_{Rts}$. As gleaned in Fig. S18C (ESI ‡), the reductive titration of the $[PDI-C_3Am-C_2OH]_{Rts}$ assembly with DTT/ Na_2SO_3 leads to the formation of the redox-treated assembly $[PDI-C_3Am-C_2OH]_{Rts}$ that evidences an Ex_{BW} (396 meV) after 48 hours, similar to that observed in the titration that exploits 5 eq. of NaSH (pathway 1). Please note that control samples for pathway 3 are shown in Fig. S18A and B (ESI ‡) and do not suggest that the increases of Ex_{BW} stem solely from Na_2SO_3 . The kinetic data shown in Fig. S19 (ESI ‡) chronicles the change of Ex_{BW} as a function of time for the $[PDI-C_3Am-C_2OH]_{Rts}$ assembly formed exploiting pathway 3 (Scheme 1B) and reveals that an alternative aggregation process, rather than a nucleation-growth mechanism, dictates the formation of these supramolecular architectures. Please refer to the Section S7 of the ESI ‡ for a more detailed discussion. From these preliminary kinetic analyses, it is fair to infer that the chemical composition of the salts produced during the redox treatment process plays an important role in assisting the reconfiguration of the parent assemblies. In all likelihood, the oxidation of the excess of NaSH reductant engenders the formation of a more complex salt mixture involved in the growth of the final redox-treated

superstructures. Analysis of the solid-state morphologies confirms this hypothesis.

Solid-state morphologies

Interrogating the solid-state morphologies of the redox-treated $NaSH[PDI-C_3Am-C_2OH]_{Rts}$, $NaSH[PDI-C_3Am-C_3]_{Rts}$, and $NaSH[PDI-C_3Im-C_2]_{Rts}$ superstructures reveals the formation of hierarchical mesoscale objects exclusively detected in the redox-assisted assembly pathway 1 that exploits 5 eq. of NaSH. Fig. 6 chronicles the SEM images recorded for the three redox-treated superstructures after dropcasting the parent aqueous solutions on a silicon-oxide-coated substrate. While the $NaSH[PDI-C_3Am-C_2OH]_{Rts}$ and $NaSH[PDI-C_3Am-C_3]_{Rts}$ superstructures initiate the creation of ribbon-like materials which can span more than 65 μm in length with an associated width of 14 μm , as shown in Fig. 6D, E, G and H, the $NaSH[PDI-C_3Im-C_2]_{Rts}$ superstructure evolves toward high-aspect ratio fiber-like materials. To validate reproducibility, additional SEM images are shown in Fig. S20 (ESI ‡). The fact that both $NaSH[PDI-C_3Am-C_2OH]_{Rts}$ and $NaSH[PDI-C_3Am-C_3]_{Rts}$ superstructures enable the formation of seemingly 2D objects whereas the $NaSH[PDI-C_3Im-C_2]_{Rts}$ superstructure evolves into 1D microstructures, highlights the non-innocent role played by the cationic side chains in dictating the solid-state morphologies of the superstructures. Because the mesoscale

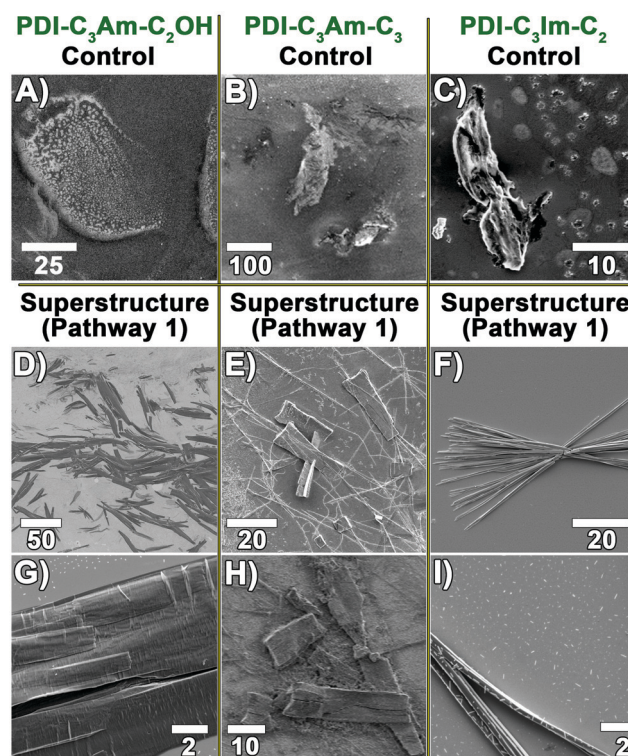


Fig. 6 SEM images recorded for the control assemblies $[PDI-C_3Am-C_2OH]_{Cont}$ (A), $[PDI-C_3Am-C_3]_{Cont}$ (B), and $[PDI-C_3Im-C_2]_{Cont}$ (C). Hierarchical solid-materials that characterize the redox-treated superstructures $[PDI-C_3Am-C_2OH]_{Rts}$ (D and G), $[PDI-C_3Am-C_3]_{Rts}$ (E and H), and $[PDI-C_3Im-C_2]_{Rts}$ (F and I). These SEM images correspond to the solid-state morphologies formed by dropcasting the parent, water solution on a silicon wafer. Scale bar units are in μm .

objects shown in Fig. 6 derived from lateral interactions between π -stacks, we postulate that the imidazolium side chains hamper the growth of the ribbon-like materials exclusively engendered when the PDI cores are flanked with small ammonium cationic groups.

In sharp contrast, the SEM images chronicled in Fig. S22 and S23 (ESI ‡) indicate that assemblies treated with 1 eq. of NaSH and 5 eq. of DTT lack the ability to form hierarchical solid-state materials, as do the control assemblies shown in Fig. 6 and Fig. S21 (ESI ‡). Similarly, the $\text{DTT/Na}_2\text{SO}_3[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{Rts}}$ assemblies formed using pathway 3 (DTT/Na₂SO₃) do not initiate the formation of organized solid-state constructs as shown in Fig. S24 and S25 (ESI ‡). All taken together, these findings indicate that: (1) the formation of hierarchical materials is exclusive to superstructures formed *via* a nucleation-growth mechanism (pathway 1 – Scheme 1), and (2) the drastic change of solid-state morphologies signals a reconfiguration of the initially formed assemblies only observed when pathway 1 in the redox-assisted assembly process is taken.

To glean more insights into the solid-state morphologies at the nanoscale dimension, TEM images were recorded for the representative $\text{NaSH}[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{Rts}}$ superstructures and are shown in Fig. 7. Characterized by fiber-like materials, the images in Fig. 7 suggest that the ribbon-shaped materials observed by SEM in Fig. 6D and G are composed by interacting 1-dimensional subcomponents. Furthermore, elementary fibers can be detected on the zoom-in region in Fig. 7B and C and demonstrate a width varying from 15 to 21 nm. Local crystalline domains with substantially ordered phases within the fibrous nanostructures are detected by electron diffraction, as shown in Fig. 7F. Further corroboration of this fact emerges from the presence of well-resolved periodic lattice fringes, known as ‘moiré fringes’, with the periodic distance of ~ 3 nm in the nanostructures shown in Fig. 7D and E.^{62–66} This observation confirms the presence of local crystalline domains, and

consequently periodicity in the long-range ordering of the 1D π -conjugated supramolecular polymeric chains that are constituents of the overall hierarchical fiber-like superstructures. The rod-like morphologies easily discerned in Fig. 7D and E are characterized by a width of ~ 3 nm that matches the size of one **PDI-C₃Am-C₂OH** building block as indicated by the energy-minimized structure performed at the DFT level of theory (Section S9 of the ESI ‡). This relationship indicates that the observed nanoscale objects correspond to elementary stacks of π -conjugated building blocks.

Structure–function relationships

Correlating the reductive titration experiments with the change of excitonic properties, and the solid-state morphologies evidenced by the redox-treated superstructures formed during pathway 1, delivers important consideration to modulate the structure–function relationships of redox active supramolecular polymers. Not only is the formation of n-doped intermediates a required step, but the nucleation-growth step of the redox-treated assemblies appears equally important to access superstructures that demonstrate an increase of E_{BW} and are capable of forming hierarchical materials.

It is fair to consider that a structural reorganization of the π -conjugated supramolecular polymers accompanies the injection of negative charge carriers. Preliminary DFT calculations performed on a model aggregate built from three truncated PDI repeating units supports this hypothesis. Fig. 8A compares the electrostatic potential map of an energy minimized PDI trimer structure under a neutral state ($[\text{PDI}]_3$), and in an n-doped state ($[\text{PDI}]_3^{3-}$). As can be

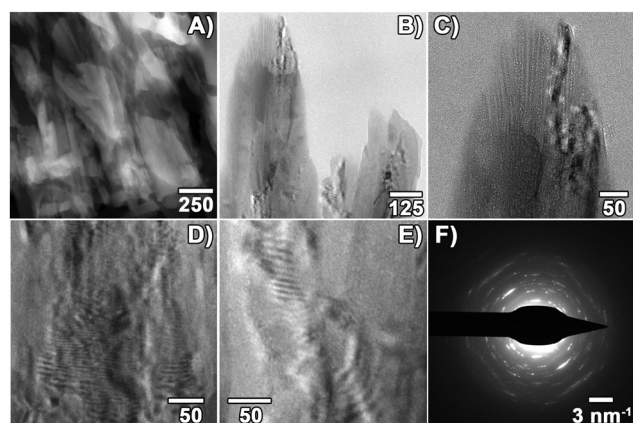


Fig. 7 TEM images of the redox-treated superstructure $[\text{PDI-C}_3\text{Am-C}_2\text{OH}]_{\text{Rts}}$ (A–E). The rod-like nanostructures observed in panel D and E are characterized by a width of 3 nm and correspond to the elementary π -conjugated supramolecular polymer (π -stack) comprising the assemblies shown in (A–C). (F) Selected area electron diffraction acquired on the hierarchical superstructures shown on A. Scale bar units are in nm.

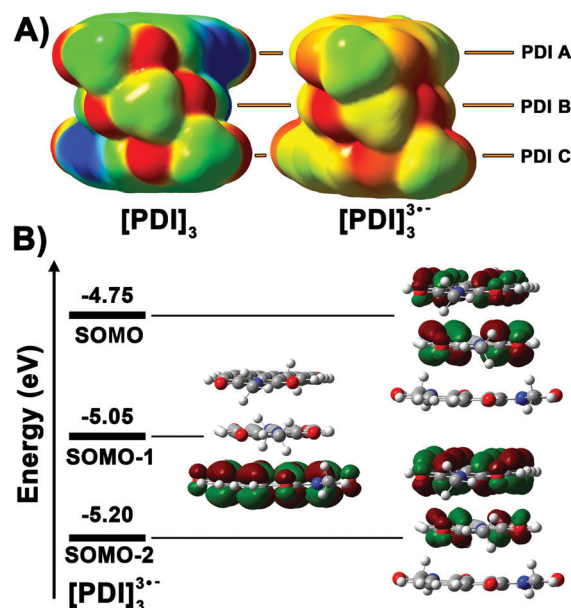


Fig. 8 (A) Energy-minimized structures of a representative π -conjugated supramolecular polymer that features three PDI repeating units. The neutral $[\text{PDI}]_3$ and fully n-doped $[\text{PDI}]_3^{3-}$ are represented. Please note that a truncated PDI unit where the side chains have been replaced by a methyl group is used. (B) Frontier orbital diagram for $[\text{PDI}]_3^{3-}$. Computational method: DFT = ω B97X-D, basis set = cc-pvdz, solvent = water.

gleaned for $[PDI]_3$, a slipped geometry best describes the conformation of this representative neutral trimer where: (1) a distance of 3.45 Å separates the PDI planes, and (2) a twist angle of 23.4° defines the rotational offset between the repeating units. Electrostatic interactions between the carbonyl groups of the imide functions and the methyl side chains may be a major contributor to the apparent slipped geometry. As shown in Fig. 8A, the energy-minimized structure calculated for the n-doped PDI trimer $[PDI]_3^{3-}$ underscores a non-negligible degree of structural reorganization. More specially, the conformation of PDI A and PDI B is characterized by a twist angle of 13.2° that contrasts the 23.4° angle delineated by the parent, neutral trimer. It is also interesting to note that while a distance of 3.4 Å separates PDI A and PDI B, PDI B and PDI C are separated by 3.6 Å. This increase of interplanar distance may underscore the existence of electrostatic repulsion between PDI radical anions comprising this model aggregate.

To glean more insights into the electronic structure of the model n-doped aggregate, Fig. 8B chronicles the frontier molecular orbitals computed for $[PDI]_3^{3-}$. Notably, the wavefunctions characterizing the SOMO and the SOMO–2 are delocalized over the PDI A and B repeating units. This observation may diagnose a non-negligible degree of interaction between the PDI radicals comprising the n-doped trimer model that may be at the origin of the broad NIR transitions observed for the n-doped intermediates. While we acknowledge that the DFT calculation performed on the trimer model aggregate oversimplifies the structure–function complexity of the n-doped intermediates reported in this study, we suggest that it provides further evidences that structural reorganization accompanies electron injection into the conduction band of neutral PDI-derived supramolecular polymers.

The species formed following oxidation of the n-doped intermediates are likely to bear some of the conformational modifications dictated by the reduced π -conjugated SPs. Note that the slight increase of Ex_{BW} evidences from all the reductive titration experiments support this claim. Furthermore, the increase of Ex_{BW} as a function of time for the reductive titration that exploits 5 eq. of NaSH reveals that the products formed by oxidation of the excess of NaSH further assist the growth of the reconfigured superstructures. The dynamic increase of Ex_{BW} diagnoses a non-negligible change of superstructure conformation that is further confirmed by the formation of hierarchical mesoscale materials in the solid-state.

While evidencing an increase of Ex_{BW} comparable to that of the reconfigured $^{NaSH}[PDI-C_3Am-C_2OH]_{Rts}$ superstructure formed through pathway 1, the redox treated $[PDI-C_3Am-C_2OH]_{Rta}$ assembly generated with DTT/ Na_2SO_3 (pathway 3 – Scheme 1) takes an alternative aggregation route. This assumption is supported by the kinetic analysis tracing the increase of Ex_{BW} as a function of time and the corresponding solid-state morphologies. The redox-assisted assembly pathway 3 does not engender the formation of hierarchical mesoscale materials comparable to those delineated by the reconfigured superstructure $^{NaSH}[PDI-C_3Am-C_2OH]_{Rts}$. This observation indicates that the nucleation–elongation mechanism, exclusively monitored for the assemblies treated with 5 eq. of

NaSH, is a required step to access organized solid-state materials. While a matter of speculation at this time, we hypothesize that the conformation of the reconfigured superstructures in solution (pathway 1 – Scheme 1) may, to some extent, differ from that of the redox-treated assembly (pathway 3 – Scheme 1) consequently leading to different packing configurations formed during the dropcasting process.

Conclusions

In conclusion, we provide the first, general understanding of the parameters required to modulate the excitonic properties of π -conjugated supramolecular polymers through redox-assisted assembly. The properties of the initially formed assemblies are characterized using a solvent-dependent equilibrium model and reveals that an average of 5 to 6 PDI building blocks comprise the H-like aggregates. The electrochemical and chemical reduction of these non-covalent assemblies enable the formation of n-doped π -stacks that present significant degree of electron–electron interaction as indicated by the rise of novel spectroscopic transitions in the NIR spectral window. Oxidation of the n-doped intermediates produces redox-treated assemblies which Ex_{BW} increases as a function of time. Kinetic data analysis reveals that a nucleation–elongation mechanism governs the growth of assemblies formed immediately after neutralization of the n-doped stacks. This finding indicates that electron injection into the conduction bands of the PDI-derived supramolecular polymers opens a new pathway in the aggregation energy landscape and yields superstructures demonstrating a non-negligible level of structural reconfiguration.

Interrogation of the solid-state morphologies recorded for the redox-treated assemblies using HRTEM and SEM unveils the formation of hierarchical mesoscale materials that are exclusively evidenced for the superstructures formed by a nucleation-growth mechanism. We elucidate that the modulation of the structure–function relationships evidenced by the PDI-derived assemblies is intimately correlated to the sacrificial electron donor properties and underscores a synergistic effect between the products formed during the redox-assisted assembly process. Not only does this study deliver a general tool to regulate the excitonic properties of PDI-based aggregates, but it also refines the rules and principles to orchestrate the creation of hierarchical organic matter compositions. In addition, increasing excitonic coupling of organic assemblies paves the way to engineer materials composition relevant to solar energy capture, conversion, and storage.^{8,10,67–69}

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The work was funded by the National Science Foundation through the CAREER award CHE-1941410. TEM analysis was

performed at the Chapel Hill Analytical and Nanofabrication Laboratory, CHANL, a member of the North Carolina Research Triangle Nanotechnology Network, RTNN, which is supported by the National Science Foundation, Grant CCS-1542015, as part of the National Nanotechnology Coordinated Infrastructure, NNCI. The authors are grateful to BioNIUM.

Notes and references

- 1 M. R. Wasielewski, *Acc. Chem. Res.*, 2009, **42**, 1910–1921.
- 2 J. M. Mativetsky, E. Orgiu, I. Lieberwirth, W. Pisula and P. Samori, *Adv. Mater.*, 2014, **26**, 430–435.
- 3 J. R. Caram, S. Doria, D. M. Eisele, F. S. Freyria, T. S. Sinclair, P. Rebentrost, S. Lloyd and M. G. Bawendi, *Nano Lett.*, 2016, **16**, 6808–6815.
- 4 N. Liang, K. Sun, Z. Zheng, H. Yao, G. Gao, X. Meng, Z. Wang, W. Ma and J. Hou, *Adv. Energy Mater.*, 2016, **6**, 1600060.
- 5 D. Di Nuzzo, C. Kulkarni, B. Zhao, E. Smolinsky, F. Tassinari, S. C. J. Meskers, R. Naaman, E. W. Meijer and R. H. Friend, *ACS Nano*, 2017, **11**, 12713–12722.
- 6 G. Bullard, F. Tassinari, C.-H. Ko, A. K. Mondal, R. Wang, S. Mishra, R. Naaman and M. J. Therien, *J. Am. Chem. Soc.*, 2019, **141**, 14707–14711.
- 7 J.-H. Olivier, J. Park, P. Deria, J. Rawson, Y. Bai, S. Kumbhar Amar and J. Therien Michael, *Angew. Chem., Int. Ed.*, 2015, **54**, 8133–8138.
- 8 J. Sung, A. Nowak-Król, F. Schlosser, B. Fimmel, W. Kim, D. Kim and F. Würthner, *J. Am. Chem. Soc.*, 2016, **138**, 9029–9032.
- 9 C. Kulkarni, A. K. Mondal, T. K. Das, G. Grinbom, F. Tassinari, M. F. J. Mabesoone, E. W. Meijer and R. Naaman, *Adv. Mater.*, 2020, **32**, 1904965.
- 10 J. Sung, P. Kim, B. Fimmel, F. Würthner and D. Kim, *Nat. Commun.*, 2015, **6**, 8646.
- 11 A. K. Le, J. A. Bender and S. T. Roberts, *J. Phys. Chem. Lett.*, 2016, **7**, 4922–4928.
- 12 A. K. Le, J. A. Bender, D. H. Arias, D. E. Cotton, J. C. Johnson and S. T. Roberts, *J. Am. Chem. Soc.*, 2018, **140**, 814–826.
- 13 A. T. Haedler, K. Kreger, A. Issac, B. Wittmann, M. Kivala, N. Hammer, J. Köhler, H.-W. Schmidt and R. Hildner, *Nature*, 2015, **523**, 196–199.
- 14 V. Coropceanu, J. Cornil, D. A. da Silva Filho, Y. Olivier, R. Silbey and J.-L. Brédas, *Chem. Rev.*, 2007, **107**, 926–952.
- 15 M. Mas-Torrent and C. Rovira, *Chem. Rev.*, 2011, **111**, 4833–4856.
- 16 O. Ostroverkhova, *Chem. Rev.*, 2016, **116**, 13279–13412.
- 17 S. Gélinas, A. Rao, A. Kumar, S. L. Smith, A. W. Chin, J. Clark, T. S. van der Poll, G. C. Bazan and R. H. Friend, *Science*, 2014, **343**, 512.
- 18 A. A. Bakulin, A. Rao, V. G. Pavelyev, P. H. M. van Loosdrecht, M. S. Pshenichnikov, D. Niedzialek, J. Cornil, D. Beljonne and R. H. Friend, *Science*, 2012, **335**, 1340.
- 19 X.-K. Chen, M. K. Ravva, H. Li, S. M. Ryno and J.-L. Brédas, *Adv. Energy Mater.*, 2016, **6**, 1601325.
- 20 H. M. Heitzer, B. M. Savoie, T. J. Marks and M. A. Ratner, *Angew. Chem., Int. Ed.*, 2014, **53**, 7456–7460.
- 21 N. E. Jackson, K. L. Kohlstedt, B. M. Savoie, M. Olvera de la Cruz, G. C. Schatz, L. X. Chen and M. A. Ratner, *J. Am. Chem. Soc.*, 2015, **137**, 6254–6262.
- 22 J. Vura-Weis, M. A. Ratner and M. R. Wasielewski, *J. Am. Chem. Soc.*, 2010, **132**, 1738–1739.
- 23 M. Zubiria-Ulacia, J. M. Matxain and D. Casanova, *Phys. Chem. Chem. Phys.*, 2020, **22**, 15908–15918.
- 24 N. J. Hestand and F. C. Spano, *Chem. Rev.*, 2018, **118**, 7069–7163.
- 25 N. J. Hestand and F. C. Spano, *Acc. Chem. Res.*, 2017, **50**, 341–350.
- 26 S. Grimme, *Angew. Chem., Int. Ed.*, 2008, **47**, 3430–3434.
- 27 C. A. Hunter and J. K. M. Sanders, *J. Am. Chem. Soc.*, 1990, **112**, 5525–5534.
- 28 F. Cozzi, F. Ponzini, R. Annunziata, M. Cinquini and J. S. Siegel, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 1019–1020.
- 29 L. M. Salonen, M. Ellermann and F. Diederich, *Angew. Chem., Int. Ed.*, 2011, **50**, 4808–4842.
- 30 F. J. M. Hoebe, P. Jonkheijm, E. W. Meijer and A. P. H. J. Schenning, *Chem. Rev.*, 2005, **105**, 1491–1546.
- 31 T. F. A. De Greef, M. M. J. Smulders, M. Wolffs, A. P. H. J. Schenning, R. P. Sijbesma and E. W. Meijer, *Chem. Rev.*, 2009, **109**, 5687–5754.
- 32 C. Liu, K. Liu, A. Mukhopadhyay, V. Paulino, B. Bernard and J.-H. Olivier, *Organometallics*, 2020, **39**, 2984–2990.
- 33 C. Liu, K. Liu, J. Klütke, A. Ashcraft, S. Steefel and J.-H. Olivier, *J. Mater. Chem. C*, 2018, **6**, 11980–11991.
- 34 P. A. Korevaar, S. J. George, A. J. Markvoort, M. M. J. Smulders, P. A. J. Hilbers, A. P. H. J. Schenning, T. F. A. De Greef and E. W. Meijer, *Nature*, 2012, **481**, 492–497.
- 35 P. A. Korevaar, T. F. A. de Greef and E. W. Meijer, *Chem. Mater.*, 2014, **26**, 576–586.
- 36 A. T. Haedler, S. C. J. Meskers, R. H. Zha, M. Kivala, H.-W. Schmidt and E. W. Meijer, *J. Am. Chem. Soc.*, 2016, **138**, 10539–10545.
- 37 T. Fukui, S. Kawai, S. Fujinuma, Y. Matsushita, T. Yasuda, T. Sakurai, S. Seki, M. Takeuchi and K. Sugiyasu, *Nat. Chem.*, 2016, **9**, 493–499.
- 38 A. Aliprandi, M. Mauro and L. De Cola, *Nat. Chem.*, 2015, **8**, 10.
- 39 S. Ogi, C. Grzeszkiewicz and F. Würthner, *Chem. Sci.*, 2018, **9**, 2768–2773.
- 40 M. F. J. Mabesoone, A. J. Markvoort, M. Banno, T. Yamaguchi, F. Helmich, Y. Naito, E. Yashima, A. R. A. Palmans and E. W. Meijer, *J. Am. Chem. Soc.*, 2018, **140**, 7810–7819.
- 41 F. Fennel, S. Wolter, Z. Xie, P.-A. Plötz, O. Kühn, F. Würthner and S. Lochbrunner, *J. Am. Chem. Soc.*, 2013, **135**, 18722–18725.
- 42 J. Leira-Iglesias, A. Sorrenti, A. Sato, P. A. Dunne and T. M. Hermans, *Chem. Commun.*, 2016, **52**, 9009–9012.
- 43 K. Liu, A. Mukhopadhyay, A. Ashcraft, C. Liu, A. Levy, P. Blackwelder and J.-H. Olivier, *Chem. Commun.*, 2019, **55**, 5603–5606.
- 44 K. Liu, A. Levy, C. Liu and J.-H. Olivier, *Chem. Mater.*, 2018, **30**, 2143–2150.
- 45 D. Görl, X. Zhang and F. Würthner, *Angew. Chem., Int. Ed.*, 2012, **51**, 6328–6348.

- 46 A. Ashcraft, K. Liu, A. Mukhopadhyay, V. Paulino, C. Liu, B. Bernard, D. Husainy, T. Phan and J.-H. Olivier, *Angew. Chem., Int. Ed.*, 2020, **59**, 7487–7493.
- 47 F. Würthner, C. Thalacker, S. Diele and C. Tschierske, *Chem. – Eur. J.*, 2001, **7**, 2245–2253.
- 48 P. A. Korevaar, C. Schaefer, T. F. A. de Greef and E. W. Meijer, *J. Am. Chem. Soc.*, 2012, **134**, 13482–13491.
- 49 R. Appel, J. Fuchs, S. M. Tyrrell, P. A. Korevaar, M. C. A. Stuart, I. K. Voets, M. Schönhoff and P. Besenius, *Chem. – Eur. J.*, 2015, **21**, 19257–19264.
- 50 M. M. J. Smulders, M. M. L. Nieuwenhuizen, T. F. A. de Greef, P. van der Schoot, A. P. H. J. Schenning and E. W. Meijer, *Chem. – Eur. J.*, 2010, **16**, 362–367.
- 51 S. K. Lee, Y. Zu, A. Herrmann, Y. Geerts, K. Müllen and A. J. Bard, *J. Am. Chem. Soc.*, 1999, **121**, 3513–3520.
- 52 R. O. Marcon and S. Brochsztain, *J. Phys. Chem. A*, 2009, **113**, 1747–1752.
- 53 L. L. Miller and K. R. Mann, *Acc. Chem. Res.*, 1996, **29**, 417–423.
- 54 L. L. Miller, C. J. Zhong and P. Kasai, *J. Am. Chem. Soc.*, 1993, **115**, 5982–5990.
- 55 C. J. Zhong, W. S. V. Kwan and L. L. Miller, *Chem. Mater.*, 1992, **4**, 1423–1428.
- 56 F. C. Spano and C. Silva, *Annu. Rev. Phys. Chem.*, 2014, **65**, 477–500.
- 57 J. Clark, J.-F. Chang, F. C. Spano, R. H. Friend and C. Silva, *Appl. Phys. Lett.*, 2009, **94**, 163306.
- 58 L. Bentea, M. A. Watzky and R. G. Finke, *J. Phys. Chem. C*, 2017, **121**, 5302–5312.
- 59 A. M. Morris, M. A. Watzky and R. G. Finke, *Biochim. Biophys. Acta, Proteins Proteomics*, 2009, **1794**, 375–397.
- 60 M. A. Watzky and R. G. Finke, *J. Am. Chem. Soc.*, 1997, **119**, 10382–10400.
- 61 A. M. Morris, M. A. Watzky, J. N. Agar and R. G. Finke, *Biochemistry*, 2008, **47**, 2413–2427.
- 62 V. K. Maka, A. Mukhopadhyay, G. Savitha and J. N. Moorthy, *Nanoscale*, 2018, **10**, 22389–22399.
- 63 A. Mukhopadhyay, V. K. Maka, G. Savitha and J. N. Moorthy, *Chem*, 2018, **4**, 1059–1079.
- 64 D. N. Bunck and W. R. Dichtel, *J. Am. Chem. Soc.*, 2013, **135**, 14952–14955.
- 65 Y. Ding, Y.-P. Chen, X. Zhang, L. Chen, Z. Dong, H.-L. Jiang, H. Xu and H.-C. Zhou, *J. Am. Chem. Soc.*, 2017, **139**, 9136–9139.
- 66 I. Berlanga, M. L. Ruiz-González, J. M. González-Calbet, J. L. G. Fierro, R. Mas-Ballesté and F. Zamora, *Small*, 2011, **7**, 1207–1211.
- 67 H. A. M. Ardoña, E. R. Draper, F. Citossi, M. Wallace, L. C. Serpell, D. J. Adams and J. D. Tovar, *J. Am. Chem. Soc.*, 2017, **139**, 8685–8692.
- 68 C. Kaufmann, W. Kim, A. Nowak-Król, Y. Hong, D. Kim and F. Würthner, *J. Am. Chem. Soc.*, 2018, **140**, 4253–4258.
- 69 J. Mei, K. R. Graham, R. Stalder, S. P. Tiwari, H. Cheun, J. Shim, M. Yoshio, C. Nuckolls, B. Kippelen, R. K. Castellano and J. R. Reynolds, *Chem. Mater.*, 2011, **23**, 2285–2288.