Charge-Transfer Nanostructures

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Biocatalytic Self-Assembly of Supramolecular Charge-Transfer Nanostructures Based on n-Type Semiconductor-Appended Peptides**

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Abstract: *The reversible in situ formation of a self-assembly building block (naphthalenediimide (NDI)–dipeptide conjugate) by enzymatic condensation of NDI-functionalized tyrosine (**NDI-Y**) and phenylalanine-amide (**F-NH$_2$**) to form **NDI-YF-NH$_2$** is described. This coupled biocatalytic condensation/assembly approach is thermodynamically driven and gives rise to nanostructures with optimized supramolecular interactions as evidenced by substantial aggregation induced emission upon assembly. Furthermore, in the presence of dihydroxy/alkoxy naphthalene donors, efficient charge-transfer complexes are produced. The dynamic formation of **NDI-YF-NH$_2$** and electronic and H-bonding interactions are analyzed and characterized by different methods. Microscopy (TEM and AFM) and rheology are used to characterize the formed nanostructures. Dynamic nanostructures, whose formation and function are driven by free-energy minimization, are inherently self-healing and provide opportunities for the development of aqueous adaptive nanotechnology.*

There is significant current interest in supramolecular approaches to produce functional nanomaterials for biomedical and technological applications.[1] In many of these systems, and in particular for photonic/electronic nanostructures, function is a direct consequence of the supramolecular order. In water, the building blocks are generally poorly soluble, which may result in the formation of (route-dependent) kinetic aggregates rather than the thermodynamically optimized structures, resulting in reproducibility issues and suboptimal performance. In here, we address this issue by using biocatalytic peptide condensation to reversibly control the assembly of charge-transfer nanostructures, thus producing free-energy-optimized functional electronic nanostructures in water.

One-dimensional (1D) self-assembly of π-conjugated building blocks provides an attractive approach for the production of supramolecular wires that possess intermolecular charge delocalization of the π-electron cloud.[2] Effective intermolecular charge transport and energy migration can be achieved by incorporating π-electron-deficient (acceptor) and π-electron-rich (donor) components to produce charge-transfer complexes.[3] A number of strategies have been developed using various π-conjugated molecules, including organic semiconductors of both *p*-[4] and *n*-type[5] chromophores, typically in organic solvents. One increasingly investigated approach, which is especially of interest in aqueous systems, is to take advantage of conjugates of self-assembling peptides[6] and functional aromatics, where the assembly of the peptides (typically through H-bonding) is used to precisely control the positioning of the aromatics for optimum π–π overlap.[7] Clearly, the self-assembly of organic semiconductors appended with short peptides provides opportunities for the construction of functional biomaterials that may be of use in interfacing biology with electronics/photonics.[8]

Naphthalenediimides (NDIs) are considered to be among the most promising *n*-type organic semiconductors,[9] with potential applications in organic-field-effect transistors, solar cells, photovoltaic devices and artificial light-harvesting systems.[5a,10] Recent reports have demonstrated the self-assembly of NDI-appended peptides into various nanoscale assemblies, such as 1D nanotubes,[11] ribbons[12] belts,[13] and fibers,[14] as well as supramolecular polymers and microspheres.[15] Furthermore, it is well-known that π-electron-deficient NDI (acceptor) forms strong charge-transfer complexes with various positional isomers of π-electron-rich dihydroxy/alkoxy naphthalene derivatives (donor).[16] Although there are reports on hydrogels based on *n*-type NDI-appended peptides,[11b,13] to our knowledge charge-transfer structures have not been described in aqueous medium.

As mentioned above, the difficulty of producing such structures in water relates to their poor aqueous solubility and slow dynamics of building blocks in the gel state. Conventional self-assembly approaches, in which the assembly is typically induced by changes in temperature or solvent polarity in combination with mechanical mixing (shaking, stirring, commonly assisted by sonication), can lead to the formation of kinetically aggregated metastable states that may be difficult to reverse. Indeed, it is increasingly clear that self-assembly is highly sensitive to temporal/mechanical/environmental factors.[17]

We set out to produce structure-optimized peptide-based charge-transfer nanostructures by catalytic formation of the self-assembling NDI–peptide building blocks in situ by reversible, covalent condensation. While peptide hydrolysis (not condensation) is favored under dilute aqueous solution-phase conditions, the change in free energy associated with hydrol-

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ysis is relatively small (approximately $-4.0\ kJ\ mol^{-1}$),[18] so that the gain in free energy associated with assembly and structure formation can provide the driving force to overcome the preference for hydrolysis, in some cases favoring amide condensation.[18,19] By using a nonselective protease and a small library of amino acid building blocks, various peptide sequences are produced and their thermodynamic selection is possible, with the most stable peptide structure formed preferentially.[20] We recently used this approach to identify optimized peptide sequences for the production of donor/acceptor (naphthoxy/dansyl) peptide nanostructures.[21]

Herein, we investigate whether enzymatic condensation and self-assembly can be used to produce energy-minimized peptide-based NDI structures (as well as co-assembly with di-alkoxy/hydroxy naphthalene donors) in water (Figure 1). This approach addresses substantial challenges in the bottom-up fabrication of aqueous electronic nanostructures: 1) The NDI bioconjugates are substantially hydrophobic and prone to kinetic aggregation, compared to the precursors of previously studied 9-fluorenylmethoxycarbonyl (Fmoc)-,[18,19] Nap-[21] or azobenzene-[22] peptide conjugates. 2) Effective charge-transfer nanostructures require alternating stacks, which is particularly challenging in co-assembly with poorly soluble building blocks (unlike energy-transfer nanostructures, in which efficient energy transfer occurs even below 1–3 mol% doping with the acceptor).[22] 3) Finally, optimal donor/acceptor pairing in terms of molecular structure of alkoxy/hydroxy naphthalene donors is currently not straightforward to predict, particularly in the gel state.[16c,23] Thermodynamically controlled condensation and assembly allow for facile identification of the most stable structures based on condensation yields.

We employed the largely nonspecific endoprotease, thermolysin from *Bacillus thermoproteolyticus rokko*, to catalyze the condensation reaction between the NDI–amino acid conjugate, that is, NDI–tyrosine (**NDI-Y**; see the Supporting Information for synthesis and characterization details) and a two-fold excess of phenylalanine amide (**F-NH_2**) to produce the NDI–dipeptide conjugate (**NDI-YF-NH_2**). The **YF** peptide sequence was selected as a suitable peptide motif based on our previous results[21] and its similarity to the widely employed **FF** sequence.[24] The first objective was to investigate the biocatalytic condensation and self-assembly of the NDI–dipeptide conjugate (Figure 1c). The precursor **NDI-Y** (10 mM) alone formed a yellow-orange self-supporting hydrogel (Figure 2a) in 100 mM phosphate buffer (pH 8) within two minutes. This gel was stable for several months. In the presence of **F-NH_2** (20 mM), a slight color change to orange was observed. Transmission electron microscopy (TEM) revealed twisted nanofibers with lengths on a micrometer scale for **NDI-Y/F-NH_2** precursor (Figure 2a and Figure S1 in the Supporting Information). Tapping-mode atomic force microscopy (AFM) imaging of the gel samples also indicated the formation of a network of entangled nanofibers of several micrometers in length (Figure 2c).

Interestingly, upon the addition of thermolysin, the orange color of the gel gradually faded and turned into a pale yellow gel after about three hours. The time-dependent

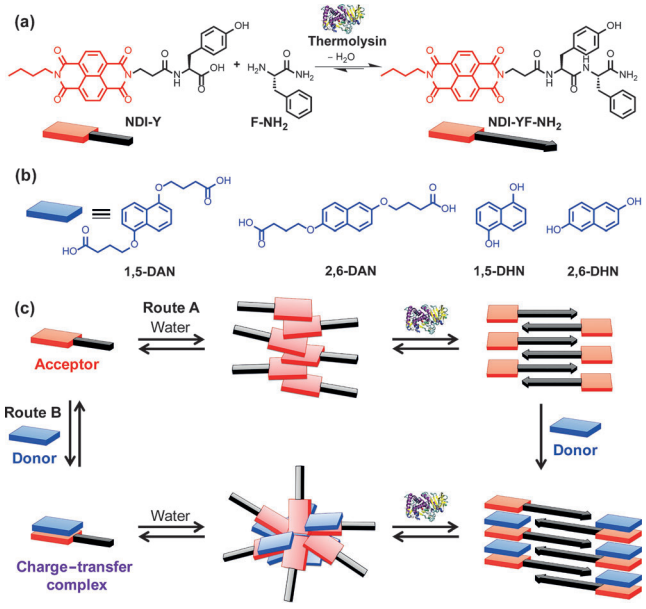

Figure 1. a) Thermolysin-catalyzed condensation to form *n*-type naphthalenediimide–dipeptide conjugate acceptor (**NDI-YF-NH_2**). b) Molecular structures of various di-alkoxy/hydroxy–naphthalene (DAN/DHN) donors used in this study. c) Schematic illustration of the proposed differential supramolecular organization of **NDI-Y**/**NDI-YF-NH_2** acceptors in the absence and presence of various DAN/DHN donors. The biocatalytic condensation and assembly combined with charge-transfer interactions favor the formation of highly ordered chiral 1D supramolecular charge-transfer nanofibers.

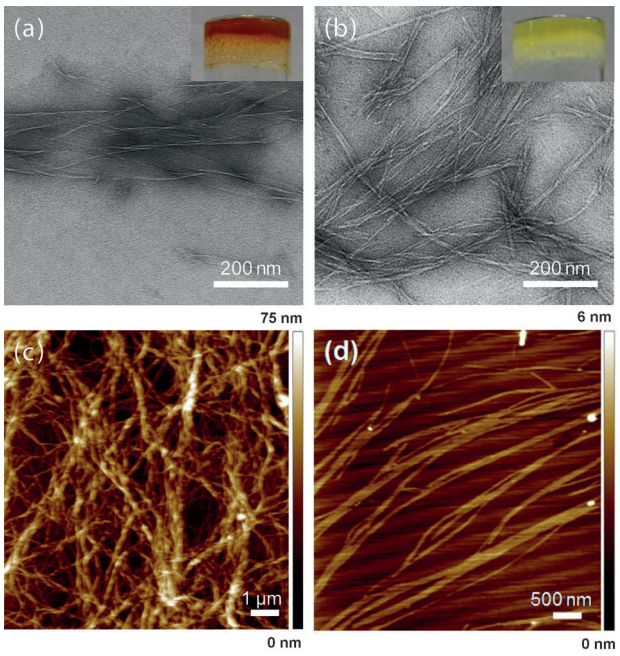

Figure 2. Microscopy images of **NDI-Y/F-NH_2** hydrogel samples before (a, c) and after (b, d) exposure to thermolysin for 24 hours. TEM images (on a carbon-coated copper grid) of hydrogels before (a) and after (b) the addition of thermolysin; insets show the digital photographs of the corresponding gel samples. Tapping-mode AFM height images (on freshly cleaved mica) of hydrogels before (c) and after (d) the addition of thermolysin.

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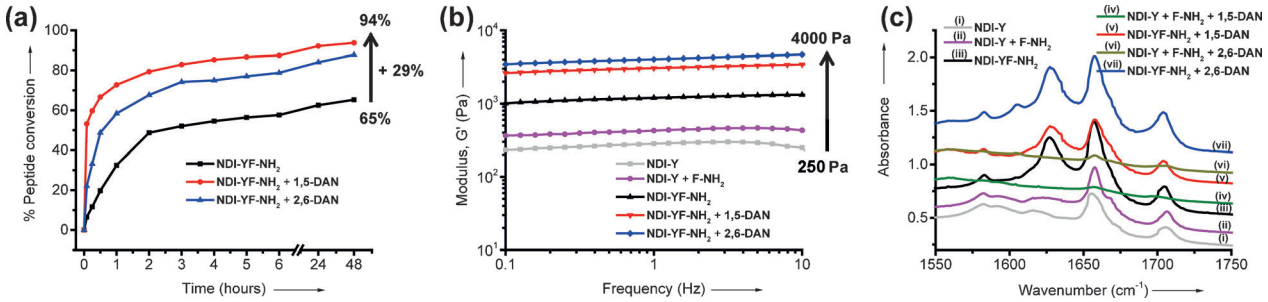

Figure 3. Thermolysin-catalyzed supramolecular self-assembly of *n*-type **NDI-Y**/**NDI-YF-NH$_2$** conjugate acceptors (10 mM) in both the absence and presence of various DAN donors (10 mM). a) HPLC data showing the time-dependent percentage conversion of **NDI-Y** into **NDI-YF-NH$_2$** and its substantial enhancement of condensation yields in the presence of various DAN donors. b) Stiffness of acceptor-only hydrogels and charge-transfer donor–acceptor hydrogels, as measured by rheology. c) FTIR spectra of the corresponding gel/sol samples, revealing the presence of intermolecular β-sheet-like structures.

enzymatic conversion of **NDI-Y** into **NDI-YF-NH$_2$** was analyzed by HPLC. The formation of **NDI-YF-NH$_2$** progressed over time and reached a constant conversion of up to 65 % after 48 hours (Figure 3 a). The corresponding TEM and AFM imaging of the gel sample shows the formation of a dense network of chiral nanofibers of several micrometers in length (Figure 2 b,d). The mechanical properties of the gels were determined by oscillatory rheology. The frequency sweep measurements performed on the gels showed a gel stiffness of 250 Pa for **NDI-Y** and 400 Pa for **NDI-Y**/**F-NH$_2$**, while the addition of thermolysin significantly increased the stiffness up to 1200 Pa for **NDI-YF-NH$_2$** after 24 hours (Figure 3 b). This increase in stiffness is related to the difference in network properties, with the biocatalytic system showing enhanced bundling of fibers.

To assess the mechanism governing the molecular self-assembly of **NDI-Y** and **NDI-YF-NH$_2$** conjugates, we further employed fluorescence emission, Fourier-transform infrared (FTIR) and circular dichroism (CD) spectroscopy on the hydrogels before and after the addition of thermolysin. Fluorescence emission of a dilute solution of **NDI-Y** in DMSO (as a non-assembling reference sample at 100 μM)[15] exhibited an emission maximum at 410 nm with a shoulder at 440 nm, which is a characteristic peak for monomeric *N*,*N*-dialkyl-substituted NDIs (Figure 4 a).[25] The aqueous solution of **NDI-Y** (or **NDI-Y** + **F-NH$_2$**) exhibits a more intense red-shifted (by about 150 nm) broad emission maximum at around 558 nm with two different weak shoulder peaks at around 432 nm and 468 nm. The combination of these emission bands attributes to the intermolecular excimer emission emerging from the long-range charge delocalization among closely packed NDI chromophores within the twisted nanofiber assemblies.[11b,12] The addition of thermolysin to this gel caused two pronounced changes in the emission spectra, which were monitored over time. The weak peaks at 432 and 468 nm were gradually increasing over time and after 3 h, the peak at 468 nm dominates the slightly blue-shifted (by about 10 nm) broad emission peak at 558 nm with a concomitant increase in the relative emission intensity that remained relatively constant after 24 h (Figure 4 a). This aggregation-induced enhanced emission (AIEE) for NDI–peptide conjugates was so far observed only in organogels.[13,14] Notably,

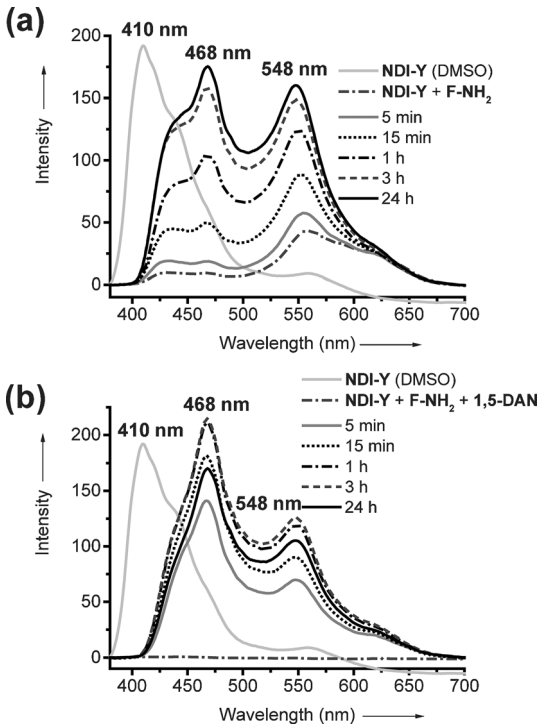

Figure 4. Time-dependent fluorescence emission spectra of **NDI-Y**/**NDI-YF-NH$_2$** conjugate acceptors (10 mM) in both the absence (a) and the presence (b) of **1,5-DAN** donor (10 mM). The acceptor excitation wavelength (λ_{ex} = 360 nm) was used for all measurements and the time shown here was monitored immediately after the addition of thermolysin.

time-correlated single photon counting experiments (TCSPC) further confirmed the loss of monomer emission at 410 nm and the formation of excimer emission at 468 nm (Figure S2). These time-dependent spectroscopic changes, in combination with the morphological changes observed, provide clear evidence indicating that the molecular self-assembly of **NDI-YF-NH$_2$** is different from **NDI-Y**. This difference is thought to be related to the reversible formation of the NDI–dipeptide derivative, producing a more ordered structure that results in the dramatic changes in fluorescence emission.

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There is a likely role of the intermolecular hydrogen-bonding network in this enzymatic reconfiguration, which was investigated by FTIR. H-bonding contributions for the **NDI-Y** and **NDI-YF-NH$_2$** systems were investigated by monitoring the absorption of gels in the amide I region of the spectra in D_2O (Figure 3c). The precursor gels (**NDI-Y** or **NDI-Y** + **F-NH$_2$**) showed a weak peak at 1616 cm^{-1}, while the product dipeptide gel of **NDI-YF-NH$_2$** showed a dramatically enhanced peak at 1627 cm^{-1}, demonstrating the formation of a significant β-sheet-like intermolecular hydrogen-bonding network within the self-assembled nanofibers of **NDI-YF-NH$_2$**.[13,26] The additional peaks observed at 1583, 1657, and 1704 cm^{-1} for all gels correspond to the symmetric and asymmetric stretching of the imide carbonyl of NDI chromophores.[12] CD spectroscopy was performed to gain insights into the supramolecular chiral environment of aromatic NDI chromophores within the self-assembled nanostructures (Figure S3). The precursor gel (**NDI-Y** alone) displayed a weak signal in the band I region (300–400 nm) of π–π* transitions polarized along the long *z*-axis, while a strong positive Cotton effect in the band II region (220–260 nm) of π–π* transitions polarized along the short *y*-axis of NDI chromophores.[27] The gel of **NDI-YF-NH$_2$** remarkably showed negative Cotton effects in both band I and band II regions, suggesting a left-handed, *M*-type chiral orientation of NDI chromophores[11a,15] within the nanofiber assemblies of **NDI-YF-NH$_2$**. The combined microscopic and spectroscopic observations consistently indicate that the biocatalytic assembly of NDI–dipeptide conjugates led to the formation of hydrogels composed of the more ordered assemblies of chiral nanofibers.

We then investigated the charge-transfer interactions of electron-deficient NDI–amino acid/dipeptide conjugate acceptors with electron-rich DAN/DHN donors. To achieve this, we selected various donors, such as the water-soluble compounds 1,5-dialkoxy naphthalene (**1,5-DAN**) and 2,6-dialkoxy naphthalene (**2,6-DAN**), and the less water-soluble compounds 1,5-dihydroxy naphthalene (**1,5-DHN**) and 2,6-dihydroxy naphthalene (**2,6-DHN**). Remarkably, the addition of **1,5-DAN** donor (10 mM) to **NDI-Y** acceptor (10 mM) completely transformed the yellow-orange hydrogel into a dark-plum-colored solution (Figure S4). The change in color suggests the formation of a characteristic charge-transfer complex between NDI acceptors and DAN donors. The gel–sol transition[16e] indicates that the charge-transfer interactions disturb the delicate balance between hydrophobic and hydrophilic interactions of self-assembled **NDI-Y** hydrogelator.[28] UV/Vis absorption spectroscopy confirmed the appearance of a broad absorption band between 450 and 700 nm, which is typical for the formation of a charge-transfer complex (Figure S5).[16,29] The fluorescence emission of the donor/acceptor solution was completely quenched and no emission was observed when either NDI acceptor (Figure 4b) or DAN donor was excited (Figure S6). TEM and AFM imaging of the **NDI-Y/F-NH$_2$/1,5-DAN** solution showed the complete transition of morphology from chiral nanofibers (Figure 2a,c) to spherical aggregates of variable diameters (Figure 5a,d and Figure S7). DLS and SLS experiments further confirmed the presence of such spherical aggregates

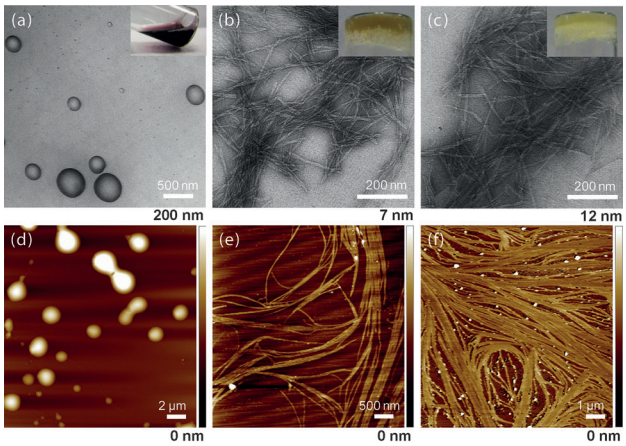

Figure 5. TEM images (a and b) and AFM height images (d and e) of **NDI-Y** acceptor and **1,5-DAN** donor mixture (1:1) before (a and d) and after (b and e) exposure to thermolysin for 24 hours. The corresponding TEM (c) and AFM (f) images of the charge-transfer hydrogel of **NDI-Y** acceptor and **2,6-DAN** donor mixture (1:1) after exposure to thermolysin for 24 hours. Insets in (a–c) show the digital photographs of the corresponding gel/sol samples.

(Figure S8). FTIR spectra did not show any peaks in the amide I region (1610 to 1640 cm^{-1}), suggesting the absence of a β-sheet-like hydrogen-bonding network (Figure 3c and Figure S9). Similarly, no peaks were observed in both band I and band II regions of the CD spectra, which suggests that NDI and DAN chromophores were not present in a supramolecular chiral environment (Figure S3).[30] All these observations consistently indicate that the charge-transfer **NDI-Y** acceptor and **1,5-DAN** donor pair clearly lacks the ability to form the elongated supramolecular charge-transfer nanofibers.

The observed structural reconfiguration of **NDI-Y/F-NH$_2$**/donors prompted us to investigate the biocatalytic assembly of NDI-dipeptide conjugate acceptors in the presence of various DAN/DHN donors. The addition of thermolysin to the precursor solution (**NDI-Y/F-NH$_2$/1,5-DAN**) resulted in the formation of a self-supporting charge-transfer hydrogel. The dark-plum-colored solution immediately turned into a pale-pink viscous gel, which was then transformed into a pale-yellow-brown gel after about two hours (Figure S4).[31] The obtained hydrogels showed increased stiffness, apparently reinforced by the charge-transfer nanostructures, with **NDI-YF-NH$_2$** hydrogels having a stiffness of 3000 and 4000 Pa in the presence of **1,5-DAN** and **2,6-DAN**, respectively (Figure 3b). Also, the time-dependent formation of **NDI-YF-NH$_2$** in the presence of **1,5-DAN** was investigated by HPLC, and the conversion was substantially amplified to 94% after 48 hours, which corresponds to about 29% amplification, as only 65% was obtained in the absence of any donor (Figure 3a). Similar amplification was also observed in the presence of other donors and was found to be 88, 85, and 86% conversions for **2,6-DAN**, **1,5-DHN** and **2,6-DHN** donors, respectively (Figure 3a and Figure S9). In analogy with our recent findings,[21] it can be assumed that thermolysin-catalyzed amide formation reaction is driven by self-assembly under thermodynamic

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control and the self-assembly of the NDI–dipeptide conjugate acceptors is more favorable in the presence of donors because of the strong charge-transfer interactions between NDI acceptors and DAN/DHN donors. This hypothesis was further reinforced by the fact that the percentage amplification of the formation of **NDI-YF-NH$_2$** is entirely dependent on the overall ratio of donor and acceptor components present in the system. For instance, the percentage conversions in the presence of **1,5-DAN** were calculated by adding varying amounts of donor (2, 6, 10, and 20 mM) to a fixed concentration of the acceptor (10 mM), and it was found to be 73% at 1:5, 90% at 3:5, 94% at 1:1, and 94% at 2:1 donor–acceptor ratios (Figure S10–S13), thus demonstrating that the process is equilibrium driven. Strikingly, such amplification was also observed when **1,5-DAN** was added (at 5 h after adding thermolysin) to preassembled **NDI-YF-NH$_2$**, further highlighting that this process is indeed caused by charge-transfer interactions and is fully reversible in nature (Figure S9). As **1,5-DAN** and **2,6-DAN** gave rise to the highest condensation yields, these systems were studied in more detail. TEM and AFM imaging of the charge-transfer samples, after the addition of thermolysin, gave rise to a morphology transition from spherical aggregates (Figure 5a,d) to a dense network of nanofibers with lengths on a micrometer scale (Figure 5b,e). A similar nanofiber-like morphology was also observed for all the other donor–acceptor combinations (Figure 5c,f and Figure S14). CD spectra of the gel in the presence of **1,5-DAN** showed strong negative excitonic Cotton effects in both band I and band II regions, representing a left-handed, *M*-type chiral arrangement of **NDI-YF-NH$_2$** acceptors and **1,5-DAN** donors within the self-assembled nanofibers (Figure S3). Moreover, the addition of thermolysin caused distinct changes to the fluorescence emission spectra and the observed reorganization of morphology from spherical aggregates to chiral nanofibers enhanced the emission instantaneously (which was completely quenched before adding thermolysin).[32] The two broad emission peaks with maxima at 467 and 548 nm reappeared within five minutes (Figure 4b). The relative emission intensity of both these peaks gradually increased in the first three hours and then slightly reduced after 24 hours, indicative of the formation of more stable, extensive charge-transfer aggregates within the self-assembled nanofibers. Replacing **1,5-DAN** by **2,6-DAN** led to similar observations, with a more pronounced enhancement of emission observed (Figure S15). All these results once again consistently indicate that the presence of charge-transfer interactions between DAN/DHN donors and **NDI-YF-NH$_2$** acceptors within the self-assembled nanofibers give rise to supramolecular chiral charge-transfer nanofibers.

In summary, we have successfully demonstrated the use of biocatalytic self-assembly of *n*-type NDI–dipeptide conjugate acceptors and various DAN/DHN donors into two-component 1D chiral charge-transfer nanofibers in aqueous medium by exploiting a fully reversible enzyme-catalyzed amide formation reaction. This approach holds great promise for the development of functional nanomaterials with enhanced long-range charge-transfer properties and fewer defects. The presence of the catalyst in the system ensures that any disruption of the system through external factors can be dynamically corrected through the fully reversible nature of this system. The full scope of catalytic self-healing in response to mechanical and chemical factors is currently being investigated.

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[28] It is interesting to note that the remarkable gel–sol transition behavior was only observed for the **1,5-DAN** system, while the systems with other donor/acceptor pairs formed a viscous liquid/gel.

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[31] Strikingly, the chemically synthesized (instead of enzymatic) dipeptide amide (**NDI-YF-NH$_2$**) formed amorphous precipitates, and thus no gelation, upon cooling a heated solution in buffer (see Figure S16). This in turn indicates that the in situ formation of **NDI-YF-NH$_2$** using biocatalytic methodology described here provides a pathway to obtain such 1D supramolecular charge-transfer chiral nanofibers, which cannot be achieved using direct self-assembly.

[32] It is expected that during morphology reorganization, a small fraction of donor/acceptor molecules may partially undergo a transition from a charge-transfer state to a self-sorted state. Nonetheless, our data clearly suggest that this effect is thermodynamically not favorable.

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