Supporting Information

Oligoaniline-Assisted Self-Assembly of Polyaniline Crystals

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Table S1. Abbreviations

PANI	Polyaniline
TANI	Tetraaniline
TAS-PANI	Tetraaniline-assisted self-assembled polyaniline
TAS-PANI-5k	Tetraaniline-assisted self-assembled polyaniline (M_W ~ 5k Da)
TAS-PANI-10k	Tetraaniline-assisted self-assembled polyaniline (M_W ~ 10k Da)
TAS-PANI-20k	Tetraaniline-assisted self-assembled polyaniline (M_W ~ 20k Da)
TAS-PANI-50k	Tetraaniline-assisted self-assembled polyaniline (M_W ~ 50k Da)
TAS-PANI-65k	Tetraaniline-assisted self-assembled polyaniline (M_W ~ 65k Da)
TAS-PANI-100k	Tetraaniline-assisted self-assembled polyaniline (M_W ~ 100k Da)

Synthesis of phenyl/amine-capped tetraaniline (Ph/NH_2 TANI)

Ph/NH_2 TANI was synthesized following previously reported procedure with modified purification steps.[1] 50 mmol of *N*-phenyl-1,4-phenylenediamine that was crushed using a mortar and pestle, was sonicated for 2 hours in a 250 mL 0.1 M HCl solution. A stoichiometric amount of iron(III) chloride was dissolved in a 50 mL 0.1 M HCl solution, and was rapidly added to the dimer mixture while being stirred strongly with a mechanical stir rod. The mixture was allowed to react for 2 hours. Centrifugation was then used to wash the mixture with 300 mL 0.1 M HCl, followed by 450 mL 0.1 M NaOH to dedope tetraaniline and 3 L of deionized water. The crude product was dried under high vacuum. The dedoped crude product was reduced by dissolving it in 200 mL of 200 proof ethanol, followed by the addition of four equivalents of hydrazine monohydrate, which was allowed to stir overnight. The mixture was precipitated by adding 2 L deionized water, and the solid was collected using filtration. Impurities were removed by repeated mixing with 200 proof ethanol, centrifugation, and removal of the supernatant until the leucoemeraldine tetraaniline was isolated. Ethanol was then removed using high vacuum. The reduced tetraaniline was oxidized to the emeraldine base form by crushing and sonication in a 1

M HCl solution, followed by rapid addition of a solution of one equivalent of ammonium persulfate in 10 mL 1 M HCl, which was then stirred overnight. The mixture was dedoped by adding 1 M ammonium hydroxide, followed by repeated centrifugation with deionized water until the pH was neutral. The product was dried, then purified by filtering over a large plug of silica eluting with hexane, then ethyl acetate, and was repeated until the product was pure. The product was confirmed using thin layer chromatography (TLC) and UV-vis-NIR (near-infrared) spectroscopy.

Chemical characterization of phenyl/amine-capped tetraaniline (Ph/NH_2 TANI)

The Ph/NH_2 TANI oligomer displayed FT-IR signals that are characteristic to polyaniline and many other aniline oligomers.[2,3,4] The characteristic peaks include the quinoid C=C stretching at around 1587 cm^{-1}, the benzoid C=C stretching at 1494 cm^{-1}, the C-N stretching of secondary aromatic amines at 1293 cm^{-1}, and the aromatic C-H out-of-plane bending at 831 and 744 cm^{-1}. A notable strong N-H stretching signal is present at 3372 cm^{-1}, which can be attributed to TANI's secondary amines, as well as the terminal primary amine groups. Although the sample was vacuum dried before analysis, there is still a trace amount of water which appears as a broad peak from the O-H stretching at 3324 cm^{-1}.

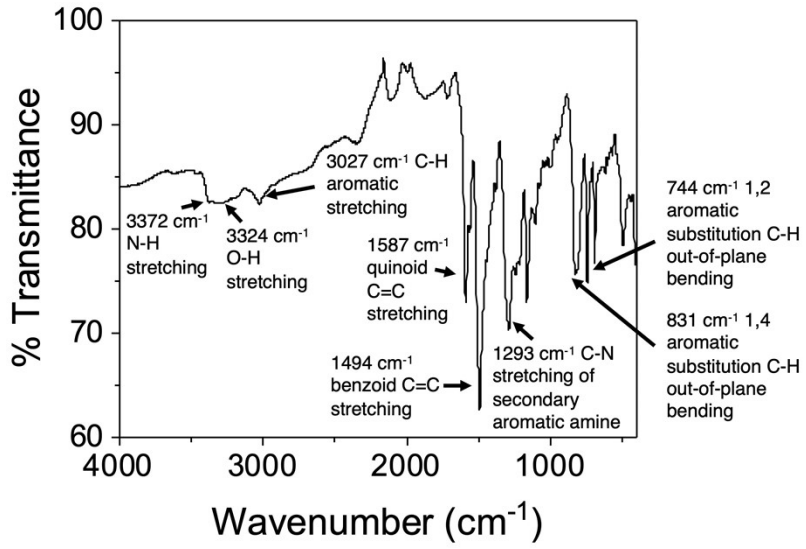


Figure S1. FT-IR spectrum with peak assignments of phenyl/amine-capped TANI.

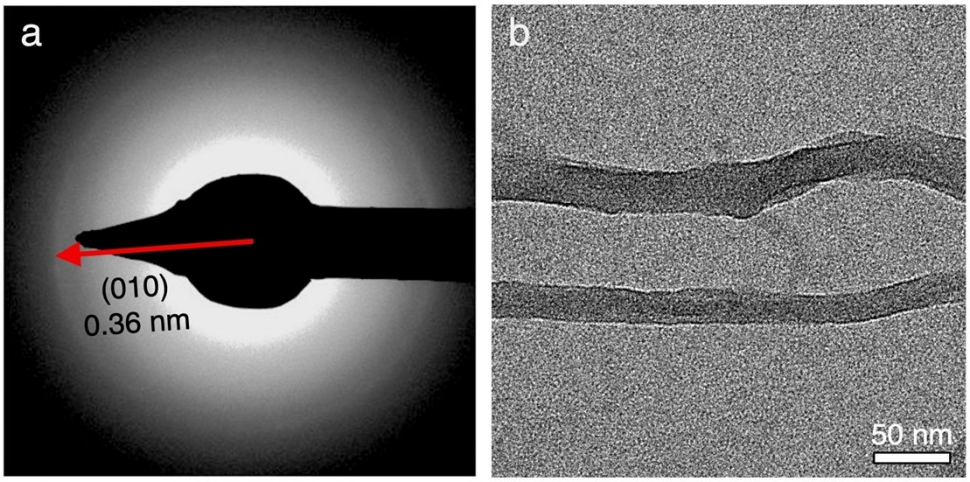
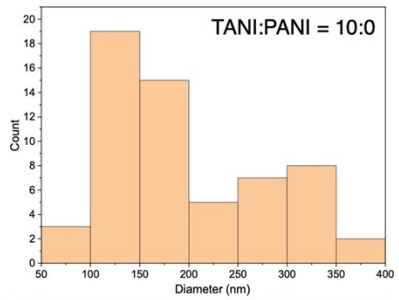
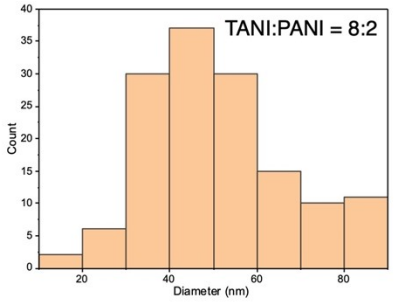


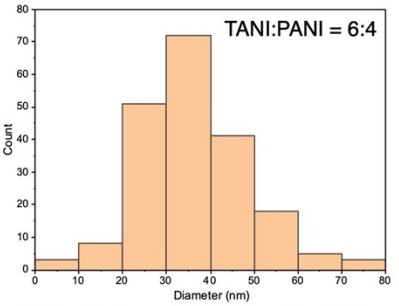
Figure S2. (a) Selected area electron diffraction (SAED) pattern and (b) the corresponding TEM image for self-assembled TAS-PANI-NF (PANI NF with 20% TANI). The packing diagram in Fig. 1i is schematized based on the SAED data here. The scattering arcs have a spacing of 0.36 nm, corresponding to π-π stacking, indicating that TANI and PANI interact and assemble perpendicular to the long axis of the nanowires through π-π stacking. The weak scattering arcs indicate that the degree of order is likely not strong. However, polymeric materials are sensitive to electron beams, so a certain level of beam damage may have also led to the weak scattering.



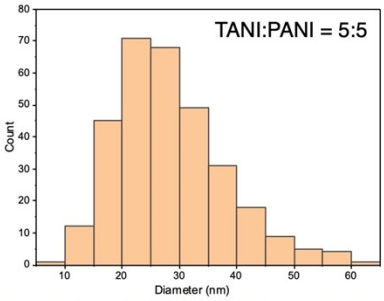
Mean (nm)	Standard Deviation (nm)	Median (nm)
201.0	83.58	179.5



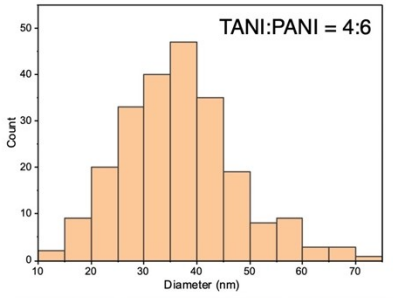
Mean (nm)	Standard Deviation (nm)	Median (nm)
50.57	16.80	49.00



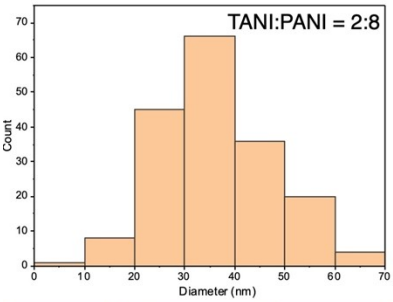
Mean (nm)	Standard Deviation (nm)	Median (nm)
36.48	11.97	37.00



Mean (nm)	Standard Deviation (nm)	Median (nm)
28.08	9.590	27.00

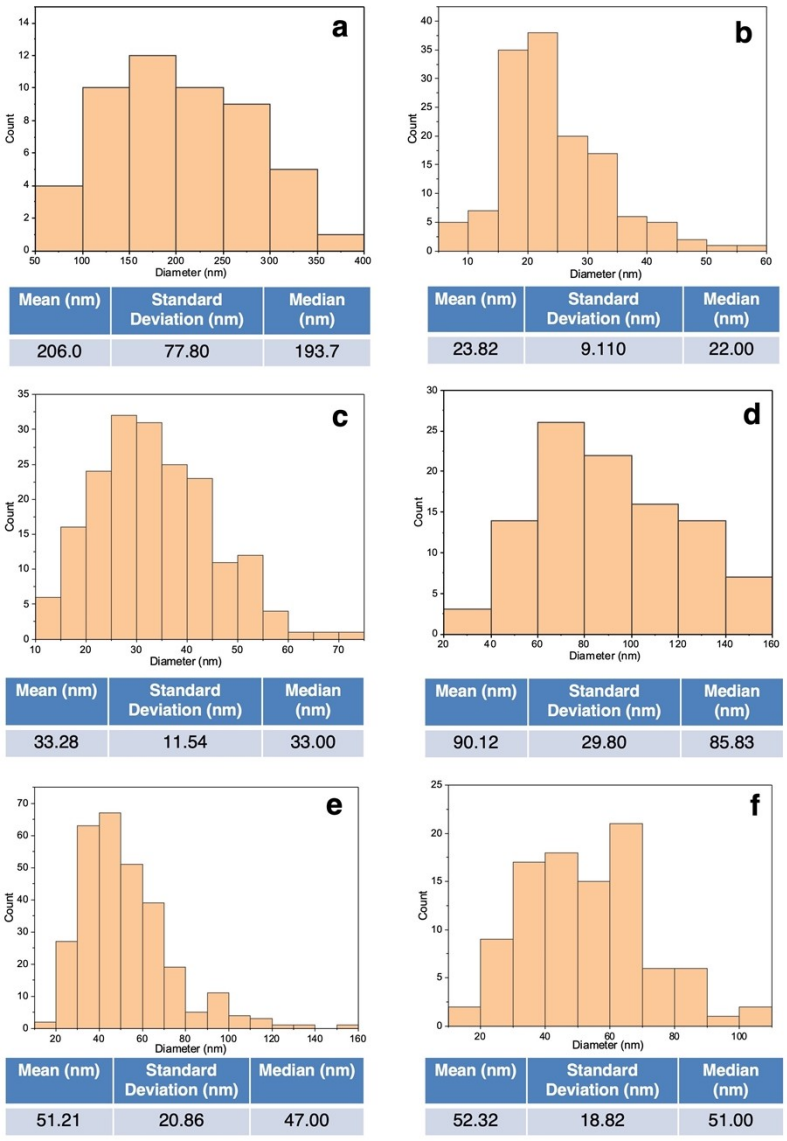


Mean (nm)	Standard Deviation (nm)	Median (nm)
36.22	11.02	35.00



Mean (nm)	Standard Deviation (nm)	Median (nm)
35.89	11.13	34.00

Figure S3. Diameter analysis of TAS-PANI self-assembled at different TANI:PANI ratios (Fig. 2). Samples corresponding to TANI:PANI ratios of 9:1 (Fig. 2b), 1:9 (Fig. 2h), and 0:10 (Fig. 2i) exhibit agglomerated morphology, so their diameter analyses are not included here.



Mean (nm)	Standard Deviation (nm)	Median (nm)
206.0	77.80	193.7

Mean (nm)	Standard Deviation (nm)	Median (nm)
23.82	9.110	22.00

Mean (nm)	Standard Deviation (nm)	Median (nm)
33.28	11.54	33.00

Mean (nm)	Standard Deviation (nm)	Median (nm)
90.12	29.80	85.83

Mean (nm)	Standard Deviation (nm)	Median (nm)
51.21	20.86	47.00

Mean (nm)	Standard Deviation (nm)	Median (nm)
52.32	18.82	51.00

Figure S4. Diameter analysis of 20% TANI-assisted self-assembled nanostructures of PANI with defined molecular weight (Fig. 3): (a) 5,000 Da, (b) 10,000 Da, (c) 20,000 Da, (d) 50,000 Da, (e) 65,000 Da, (f) 100,000 Da.

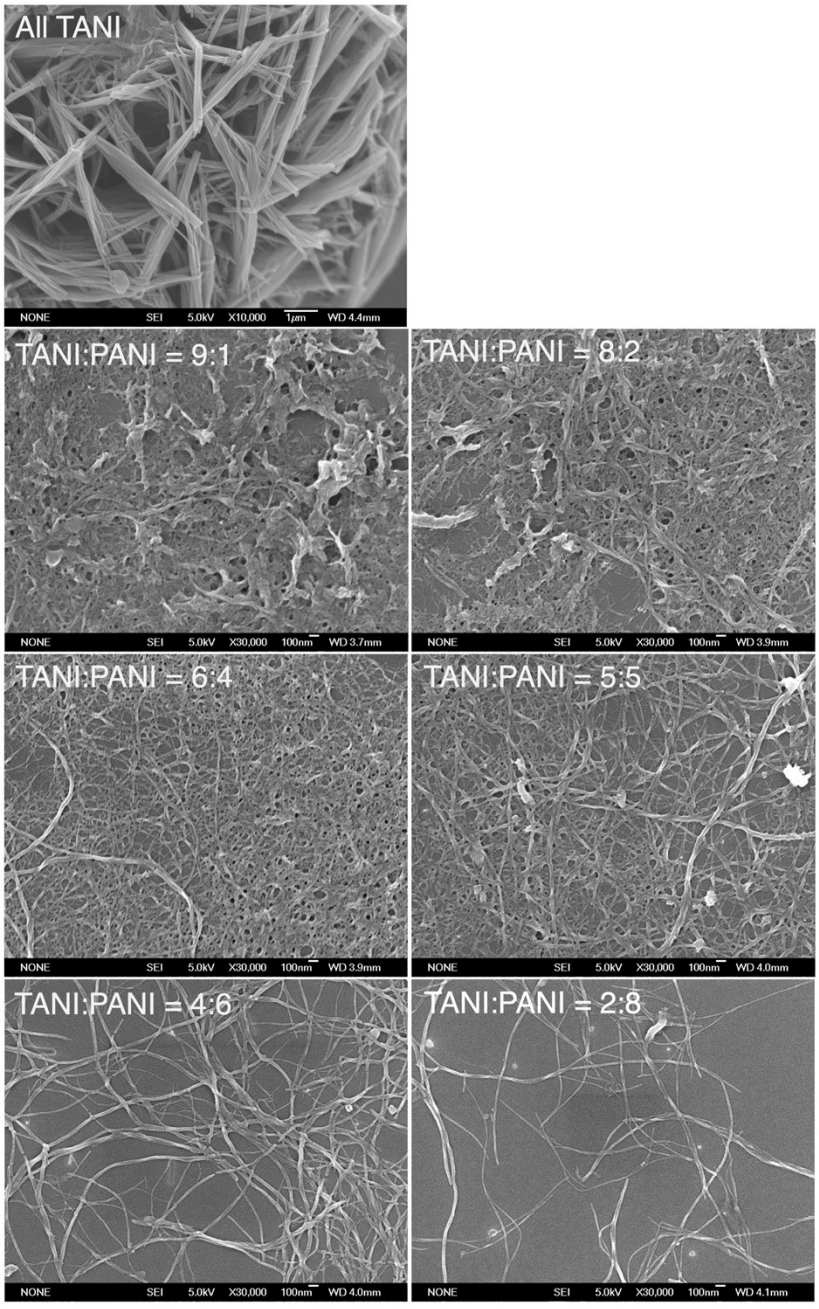


Figure S5. SEM images of TANI and TAS-PANI-NF self-assemble at different TANI:PANI ratio in a solvent mixture of 20% DMSO and 80% 0.1 M $HClO_4$.

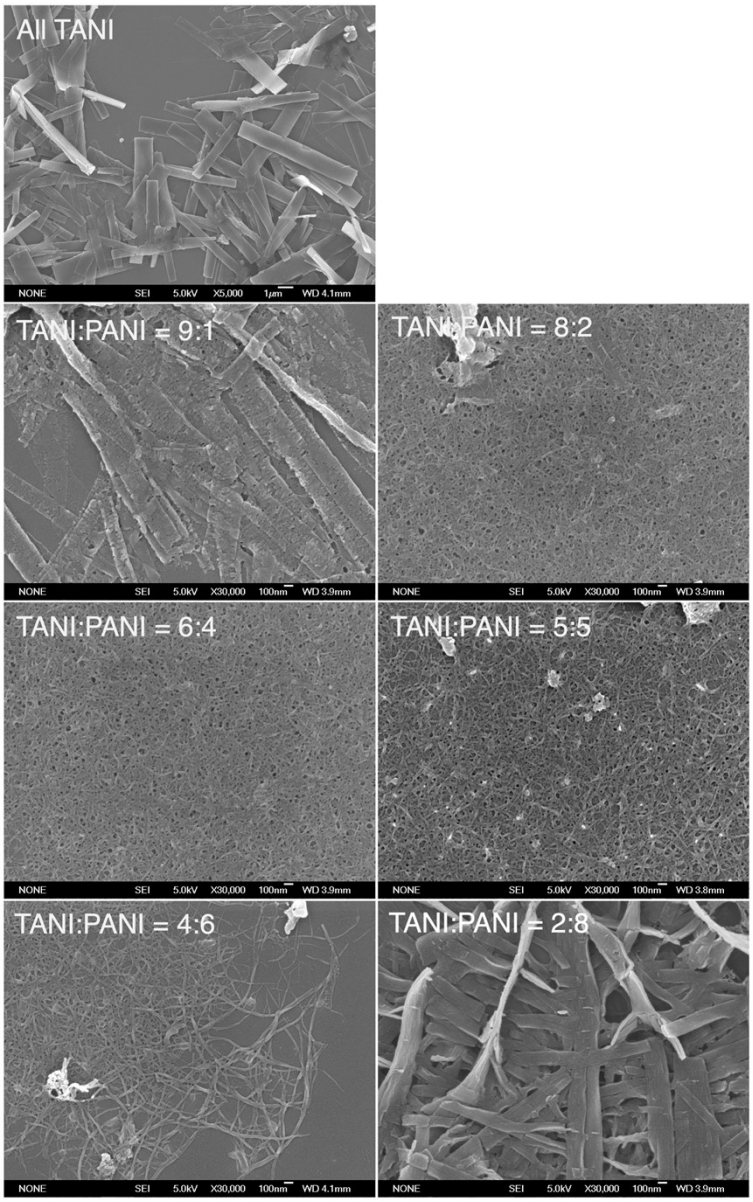


Figure S6. SEM images of TANI and TAS-PANI-NF self-assemble at different TANI:PANI ratio in a solvent mixture of 20% ethanol and 80% 0.1 M $HClO_4$.

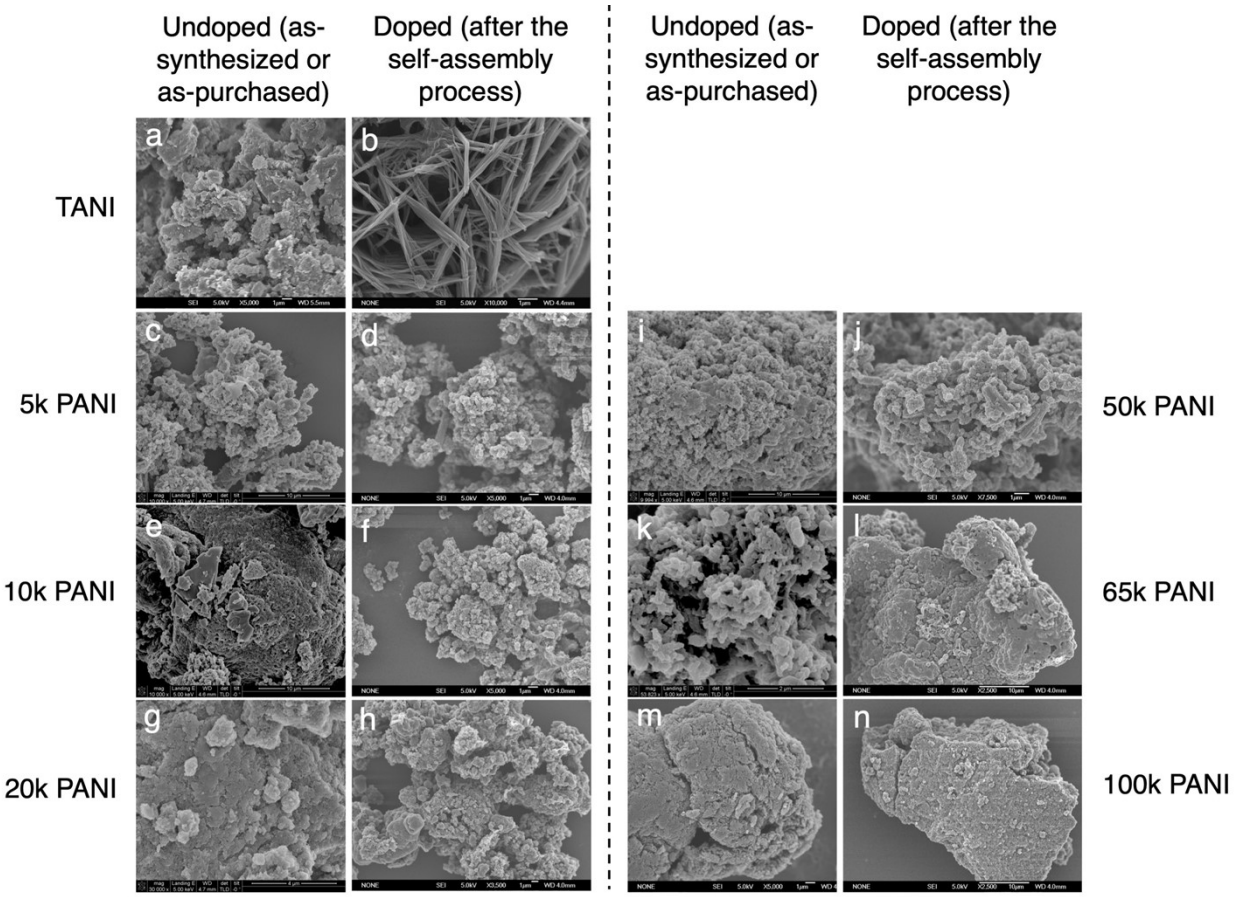


Figure S7. SEM images of TANI and PANI with various molecular weights in the as-synthesized (TANI) or as-purchased (PANI) forms vs. after self-assembly in a solvent mixture of either 20% THF and 80% water (the undoped columns) or 20% THF and 80% 0.1 M $HClO_4$ (the doped columns).

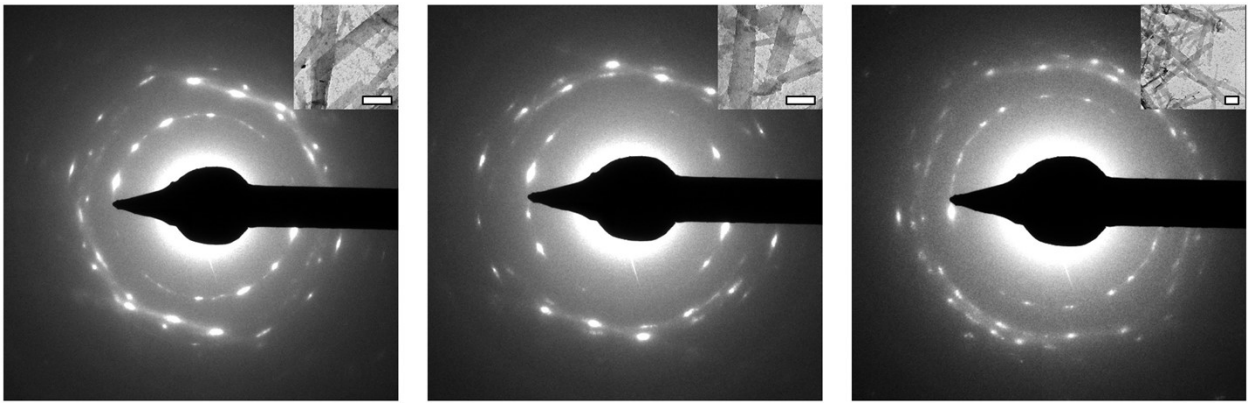


Figure S8. Select area electron diffraction (SAED) patterns of clusters of TAS-PANI-5k nanoribbon from different areas and samples. Insets show the corresponding TEM images. Scale bar = 500 nm. The SAED for a single TAS-PANI-5k nanoribbon is shown in Fig. 4a, which indicates that these nanoribbons are single crystals. Similar results are obtained for over ten nanoribbons across multiple samples. To further confirm the representativeness of such results, we collected SAED patterns over large areas that contain multiple overlapping TAS-PANI-5k nanoribbons (insets in this figure). In all these SAED patterns, spotty rings are observed, which are results of the overlapping diffraction patterns of individual nanostructures. The discrete diffraction spots in these patterns confirm that a very high percentage, if not all, of the TAS-PANI-5k nanoribbons are single crystalline.

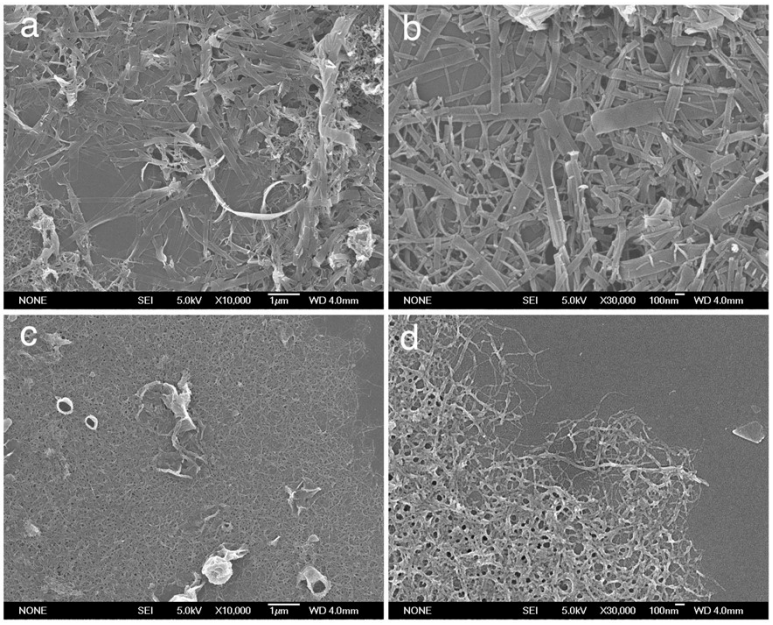


Figure S9. PANI-NF assembled with the assistance of aniline dimer. (a) and (b) SEM images of the assembled structure with a 60% PANI and 40% aniline dimer composition. (c) and (d) SEM images of the assembled structure with an 80% PANI and 20% aniline dimer composition.

References

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4. Wang, Y., Tran, H. D., Kaner, R. B., Template-Free Growth of Aligned Bundles of Conducting Polymer Nanowires. *J. Phys. Chem. C*, **113**, 10346–10349 (2009).