Supplementary Information

Arginine as a 'Molecular Glue' for Robust Hierarchical Supramolecular Assembly

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Section 1. Impact of Environmental Changes on NTs and b-NTs

Overview: ***Background and Significance.***

The fundamental limitations on the performance of supramolecular assemblies in device-based applications is their robustness under environmental stress such as (a) light exposure, (b) changing solvent conditions, and (c) elevated temperatures—all distorts the weakly interacting molecular network within the assembly's supramolecular structure. In contrast to fluorescence lifetime, the hierarchical assembly process did not show any impact on the assemblies' lack of robustness towards light exposure or reduced monomer concentration upon dilution.

Summary and Result: ***b-NTs as fragile as NTs***

Steady-state absorption spectroscopy from solution samples revealed that there is no significant difference of individual NTs and b-NTs under light exposure from 30 min up to 6 hours (**Fig. S1a and S1b**), and against methanol dilution (**Fig. S1c and S1d**). Both, NTs and b-NTs exhibited loss of excitonic character after 4 and 6 hours of exposure to visible light, while complete disassembly into monomers occurred upon dilution by a factor of 1.72 with methanol.

While there is no significant difference in instability against light exposure and upon dilution, however, the b-NTs are less instable against heat stress compared to NTs, which can be rationalized as follows. Dilution of the aqueous solution of NTs and b-NTs with methanol reduces not only monomer concentration but also the solvent's polarity, both leading to the disassembly of supramolecular assemblies into free monomers. The hydrogen bonding network between water and the supramolecular assemblies is disrupted upon methanol addition, as water preferentially forms hydrogen bonds with methanol. Light exposure can lead to the degradation of optoelectronic properties by causing bond cleavage, oxidation [1].

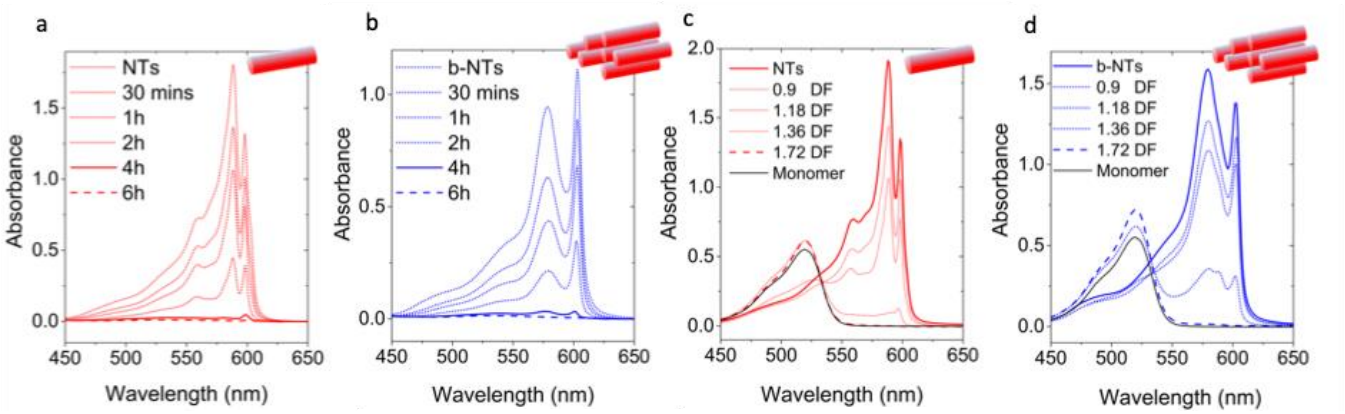


Figure S1: Steady state absorption spectra taken from solution samples (a) of neat double-walled nanotubes (NTs) and **(b)** neat bundled nanotubes (b-NTs) exposed to visible light of 5 min, 30 min, 1h, 2h, 4h and 6h, respectively. The NTs and b-NTs lost their excitonic character after exposed to visible light for 4h and 6h (red-solid and red-dashed spectra for NTs, and blue-solid and blue-dashed spectra for b-NTs). Steady-state absorption spectra of **(c)** double-walled nanotubes and **(d)** b-NTs diluted with methanol at different dilution factors 0.9, 1.18, 1.36, and 1.72. NTs and b-NTs are completely disassembled into monomers with a complete loss of the nanotubes' excitonic properties at dilution factor 1.72 (red-dashed spectrum for NTs, and blue-dashed spectrum for b-NTs). The absorption spectra of double-walled and b-NTs, which diluted with methanol at dilution factor 1.72 compared with the black-solid spectrum, which shows the steady state absorption spectrum of free cyanine dye monomer (C8S3).

Section 2. Interaction of Amino Acids with NTs

Overview: ***Background and Significance.*** In nature, many amino acids exist, each possessing different properties based on their chemical structure. We performed both hydrophilic and hydrophobic, polar and apolar, aromatic and aliphatic and basic and acidic amino acids. Specifically, we utilized lysine, histidine, aspartic acid, glutamic acid, isoleucine, asparagine, and arginine at several concentrations and different time points (**Table S1**).

Table S1. A list of the amino acids used in this study, along with their respective properties.

Amino Acid	Side Chain	Hydrophobic	PKa	Polar	Aromatic or Aliphatic	pH
Lysine	$-(CH_2)_4NH_2$	✗	10.40	✓	-	basic
Histidine	$-CH_2C_3H_3N_2$	✗	6.54	✓	aromatic	weak basic
Aspartic Acid	$-CH_2COOH$	✗	3.67	✓	-	acidic
Glutamic Acid	$-CH_2CH_2COOH$	✗	4.25	✓	-	acidic
Isoleucine	$-CH(CH_3)CH_2CH_3$	✓	-	✗	aliphatic	-
Asparagine	$-CH_2CONH_2$	✗	-	✓	-	-
Arginine	$-(CH_2)_3NH-C(NH)NH_2$	✗	12.3	✓	-	strongly basic

Summary and Result:

Lysine. We evaluated different concentrations of lysine and incubation times for their interaction with NTs to determine the optimal conditions. At 9.00 mM lysine, free monomers are driven to participate in the nanotubular assembly within 5 min interaction of lysine with NTs most efficiently compared to lower concentrations (0.18, 0.45. 0.90, 4.50 mM). This is evidenced by a decrease in the peak intensity corresponding to the broad monomer peak at approximately 520 nm, accompanied by an increase in the intensity of the peaks associated with the outer and inner cylinders at 589 nm and 599 nm, respectively (**Fig. S2.a**). Incubation time is a critical determinant in the bundling process. At a lysine concentration of 9.00 mM, the formation of bundled nanotubes (NTs) was observed after 24 hours of incubation (**Fig. S2.b**). NTs interacted with lysine (Fig S3.a) shows the evidence of spectroscopic signature of bundled NTs in aqueous solution: the narrow exciton band at 603 nm and a broad absorption feature around 580 nm (**Fig. S3.a**). The absorption spectra of bundled NTs in presence of lysine and neat bundled NTs were nearly similar (**Fig. S3.a**). The peak at 580 nm, accompanied by a shoulder peak, suggests that the bundling process is still ongoing. This indicates that lysine is less effective than arginine in accelerating the hierarchical self-assembly of NTs, though it still exerts a significant influence. Bundled NTs in presence of lysine exposed to 1-cycle and 10-cycle heat stress; overall spectral shape and energy position of exciton bands changed (**Fig. S3.b** and **Fig. S3.c**). Upon heat stress, lysine interaction with NTs significantly increases robustness of overall excitonic character but change in spectral shape indicates changes in details of molecular packing within supramolecular structure.

Histidine. Unexpectedly, within 5 min interaction, at lower concentrations of histidine, the spectral contribution of the outer cylinder (at 589 nm) disappeared (**Fig. S4.a**). However, at higher concentrations, the spectroscopic signatures of both NTs (589 nm and 599 nm) and bundled NTs (580 nm and 603 nm) were observed, indicating that

histidine accelerates bundling formation at higher concentrations, particularly at 4.50 and 9.00 mM in a very short time manner (5min) (**Fig. S4.a**). Histidine at a concentration of 9.0 mM interacted with NTs for 24 h, leading to the formation of bundled NTs, as evidenced by the characteristic spectroscopic signatures at 580 nm and 603 nm (**Fig. S4.b**). Although the relative intensities of the two peaks changed, their exact positions remained consistent with those of bundled NTs, confirming the formation of bundled structures (**Fig. S4.b**). However, bundled NTs in the presence of histidine are not robust against a single cycle of heat stress, as evidenced by the degradation of excitonic bands after annealing. (**Fig. S4.c**).

Aspartic acid and Glutamic Acid. NTs interacted with aspartic acid and glutamic acid at concentrations of 0.09, 0.18, 0.36, and 0.72 mM. The spectral contribution of the outer cylinder decreased with increasing amino acid concentration and completely disappeared at 0.36 mM within 5 minutes (**Fig. S.5a** and **Fig. S.6a**). Similarly, the spectral contribution of the inner cylinder began to decrease at 0.72 mM (**Fig. S5.**and **Fig. S6.a**). The NTs interacted with 0.36 mM amino acid—optimum concentration for selective alteration of the outer cylinder— were incubated for 24 h, which leaded to the formation of complex structures (**Fig. S5.b**, **Fig S6.b** and **Fig. S6.c**). As a result, both negatively charged acidic amino acids failed to control the hierarchical process; instead, their interaction disrupted the intact structure of the NTs.

Isoleucine. The determined concentration of isoleucine (9.00 mM) interacting with NTs for both 5 min and 24 h has no effect on the bundling process. Instead, the interaction of isoleucine with NTs leads to their degradation, as evidenced by an increase in the intensity of the monomer signature around 520 nm (**Fig. S7.a**). The hydrophobic nature of isoleucine prevents its interaction with the hydrophilic sulfonate groups on the surface of NTs.

Asparagine. The interaction of asparagine (9.00 mM) led to a significant loss of the excitonic character of NTs after 5 min. Additionally, after 24 h of incubation, changes in the molecular packing of NTs were observed, as indicated by the emergence of new spectroscopic signatures (**Fig. S7.b**).

Conclusion: The amino acids; histidine, aspartic acid and glutamic acid, isoleucine and asparagine, do not have an acceleration effect on hierarchical self-assembly like arginine instead they alter the supramolecular structure of the NTs. Lysine is the only amino acid that mediated hierarchical self-assembly toward formation of b-NTs within 24h like arginine did. However, the Lysine mediated b-NTs are not robust under heat stress.

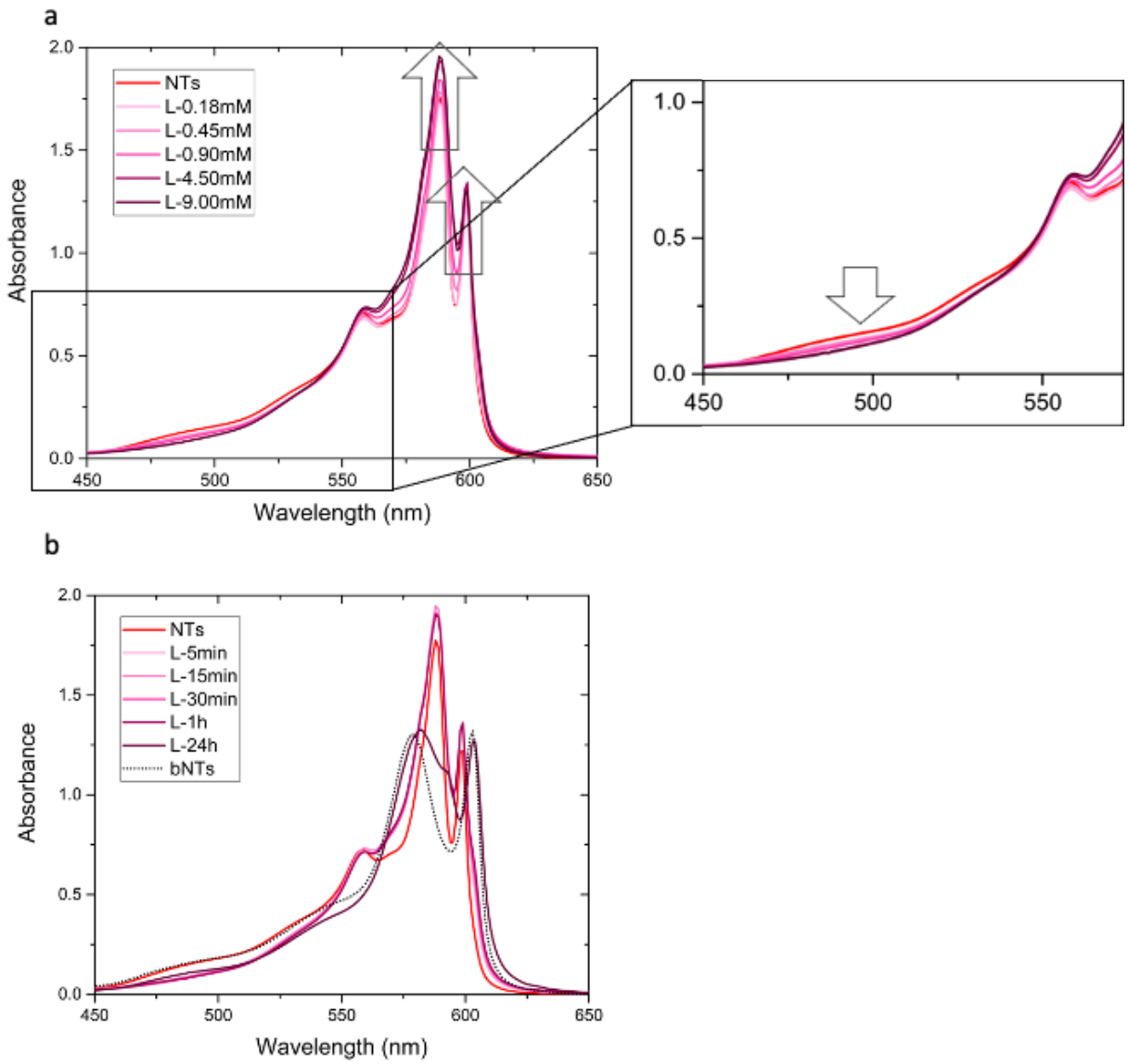


Figure S2. (a) Steady state absorption spectra of pristine NTs (red) and NTs interacted with lysine at different concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM, and 9.00 mM (the spectra illustrate the transition of pink from light to dark). The NTs interacted with different concentrations of lysine for 5 min. **(b)** Steady state absorption spectra of pristine NTs (red), b-NTs obtained incubation for a month at room temperature (black dotted) and NTs interacted with lysine (9.00 mM) at incubation times 5 min, 15 min, 30 min, 1 h and 24 h (the spectra illustrate the transition of pink from light to dark). The NTs interacted with lysine at 9.00 mM for 24 h resulted with formation of b-NTs.

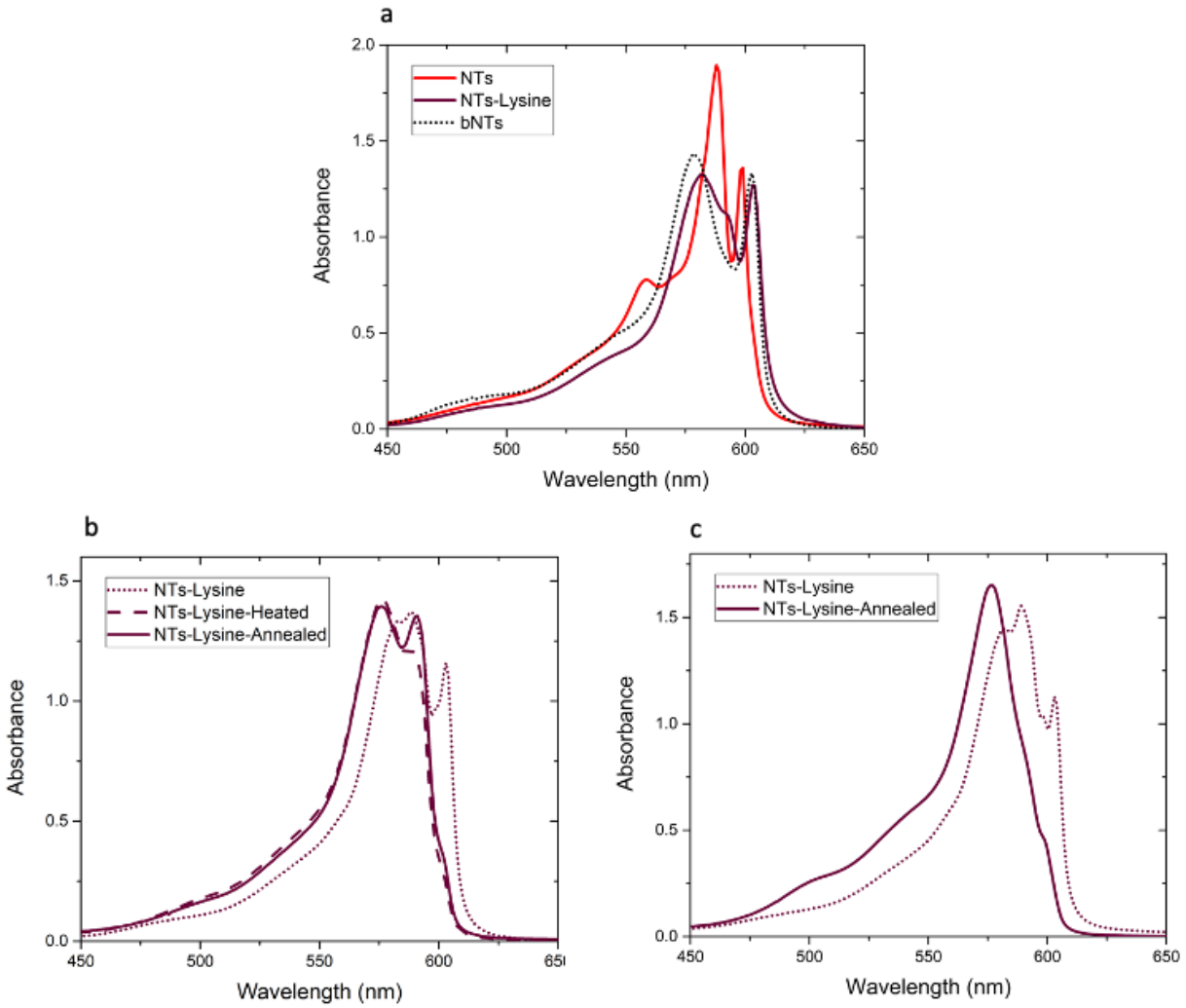


Figure S3. (a) Steady state absorption spectra of pristine NTs (red solid), b-NTs obtained by incubation for a month at room temperature (black dotted) and b-NTs prepared with interaction of double-walled NTs with lysine for 24 hours (claret red solid). **(b)** Heat stress (one-cycle, heating to 95 ºC and then cooling down to 23 ºC) applied to b-NTs prepared with interaction of NTs with lysine. Steady state absorption spectra obtained at 95 ºC (claret red dashed) and the spectra obtained at 23 ºC after annealing (claret red solid) show overall spectral shape and energy position of exciton bands changed compared to spectrum obtained from b-NTs (NTs-lysine) before applying heat stress (claret dotted). **(c)** Heat stress (10-cycles, heating to 95 ºC and then cooling down to 23 ºC in one cycle) applied to b-NTs prepared with interaction of NTs with lysine. Steady state absorption spectrum obtained from annealed b-NTs (NTs-Lysine) after exposed to 10-cycles heat stress (purple solid) show overall spectral shape and energy position of exciton bands changed compared to b-NTs (NTs-lysine) before applying heat stress (claret red dotted).

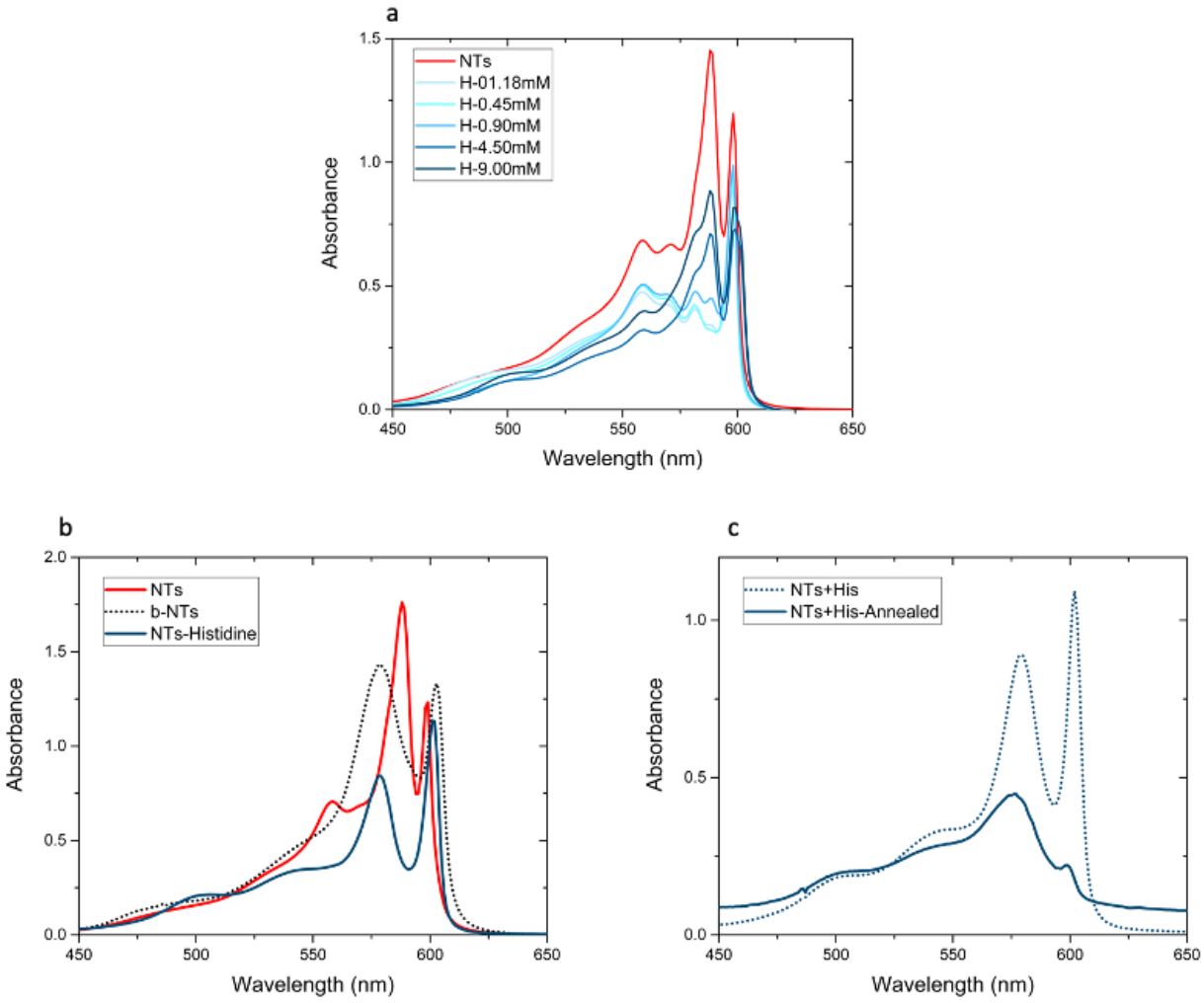


Figure S4. (a) Steady state absorption spectra of pristine NTs (red solid), and NTs interacted with histidine at concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM and 9.00 mM for 5 min (the spectra illustrate the transition of blue from light to dark). **(b)** Steady state absorption spectra of pristine NTs (red solid), b-NTs prepared incubation for a month at room temperature (black dotted), and b-NTs prepared by incubation NTs interaction with 9.00 mM histidine for 24h (dark blue solid). **(c)** Heat stress (one-cycle, heating to 95 ^{o}C and then cooling down to 23 ^{o}C) applied to b-NTs prepared with interaction of NTs with histidine for 24 h, before heat stress (dark blue dotted) and after annealing (dark blue solid).

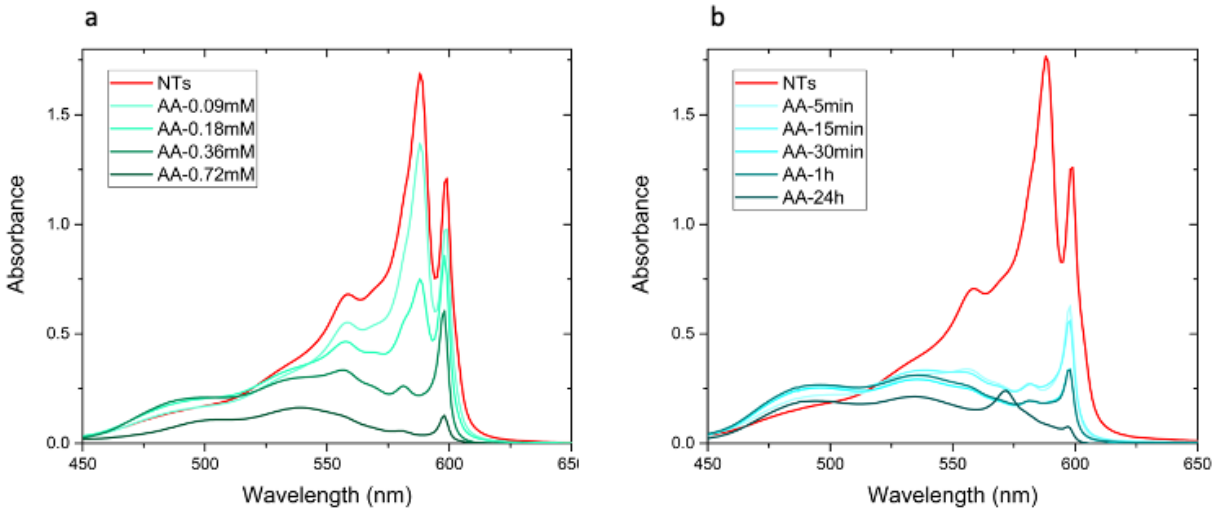


Figure S5. (a) Steady state absorption spectra of pristine NTs (red), and NTs interacted with aspartic acid at concentrations: 0.09 mM, 0.18 mM, 0.36 mM, and 0.72 mM for 5 min (the spectra illustrate the transition of aquamarine from light to dark). **(b)** Steady state absorption spectra of pristine NTs (red), and NTs interacted with aspartic acid at 0.36 mM concentration for 5 min, 15 min, 30 min, 1h and 24 h (the spectra illustrate the transition of aquamarine from light to dark).

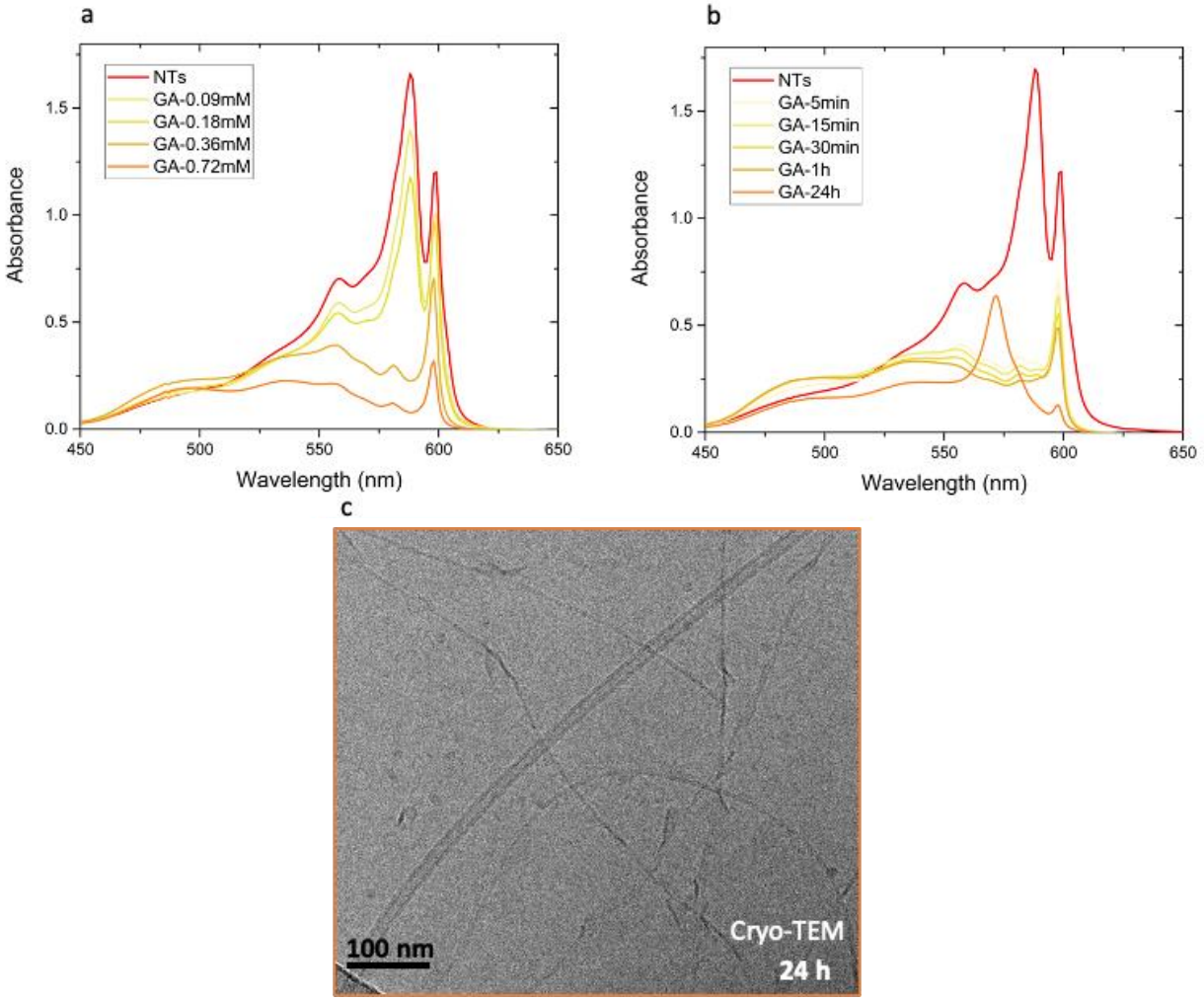


Figure S6. (a) Steady state absorption spectra of pristine NTs (red), and NTs interacted with glutamic acid at concentrations: 0.09 mM, 0.18 mM, 0.36 mM, and 0.72 mM for 5 min (the spectra illustrate the transition of yellow from light to dark). **(b)** Steady state absorption spectra of pristine NTs (red), and NTs interacted with glutamic acid at 0.36 mM concentration for 5 min, 15 min, 30 min, 1h and 24 h (the spectra illustrate the transition of yellow from light to dark). **(c)** Cryo-TEM image of NTs interacted with 0.36 mM glutamic acid for 24 h. Formation of complex structures can be clearly seen from the Cryo-TEM image.

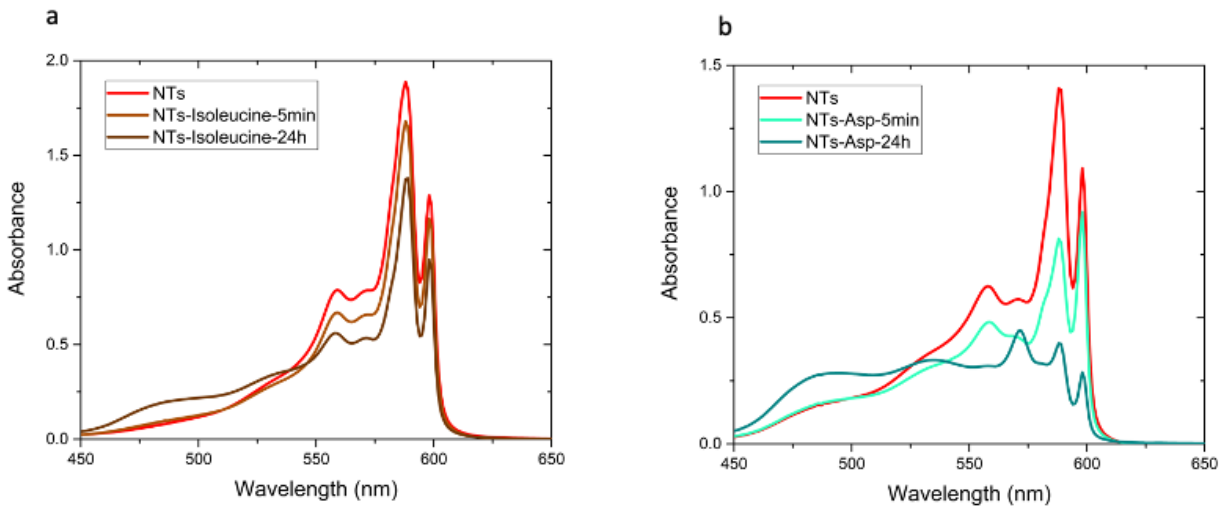


Figure S7. (a) Steady state absorption spectra of pristine NTs (red solid), NTs interacted with 9.00 mM isoleucine for 5 min (light aquamarine) and for 24 h (dark aquamarine). **(b)** Steady state absorption spectra of pristine NTs (red solid), NTs interacted with 9.00 mM asparagine for 5 min (light brown) and for 24 h (dark brown).

Section 3. Concentration & Time Dependent Effect of Arginine-NT Interaction

Overview: ***Background and Significance***. Optimizing the conditions for interaction of biomolecules with NTs is essential for controlling their structural organization and functional properties. Arginine, with its positively charged guanidinium group, plays a critical role in mediating hierarchical self-assembly. However, the optimal concentration and incubation time required for effective interaction remain unclear. This experiment focuses on determining the ideal arginine concentration and incubation duration for mediating the hierarchical self-assembly. By analyzing spectroscopic signatures, we identify how arginine influences monomer integration and bundling over time.

Summary and Result:

Concentration Dependent Effect of Arginine. We investigated the interaction of arginine with NTs across different concentrations (0.18, 0.45, 0.90, 4.50, 9.00 mM) for 5 min. At a concentration of 9.00 mM, arginine facilitates the efficient incorporation of free monomers into the nanotubular assembly within 5 min. This is evidenced by a reduction in the monomer-associated broad peak at around 520 nm (highlight), along with a corresponding increase in the intensity of peaks at 589 nm and 599 nm, which are characteristic of the outer and inner cylinders, respectively (**Fig. S8.a**).

Time Dependent Effect of Arginine The incubation duration plays a crucial role in the bundling process. The NTs incubated with 9.00 mM arginine for 5min, 15min, 30min, 1h and 24h. After 24 h of incubation at 9.00 mM arginine, the formation of bundled NTs was observed (**Fig. S8.b**). Spectroscopic analysis of NTs interacting with arginine further confirms this structural transformation, as indicated by the presence of a narrow exciton band at 603 nm and a broad absorption feature around 580 nm in aqueous solution (**Fig. S8.b**).

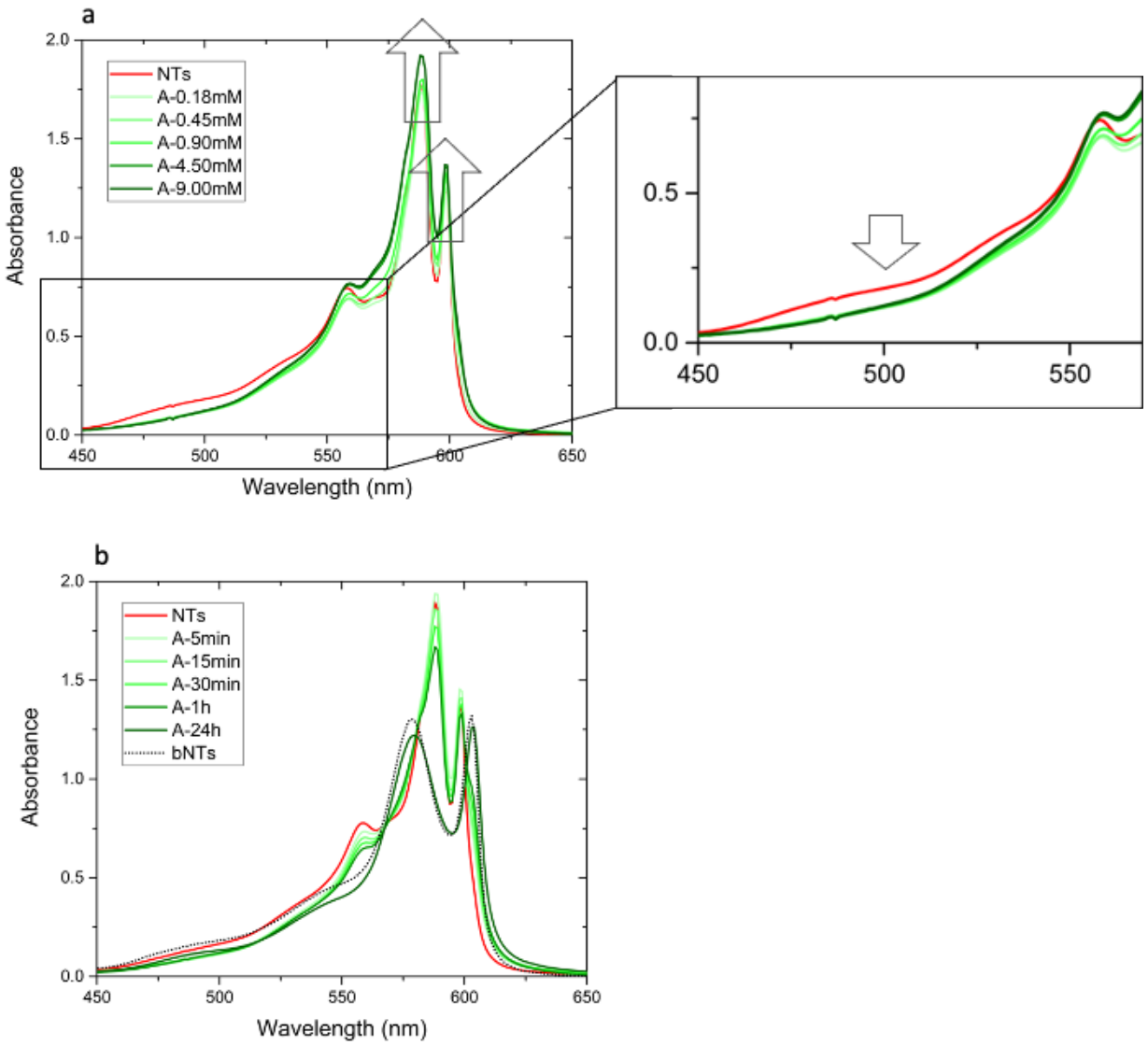


Figure S8. (a) Steady state absorption spectra of pristine NTs (red) and NTs interacted with arginine at different concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM, and 9.00 mM (the spectra illustrate the transition of green from light to dark). The NTs interacted with different concentrations of arginine for 5 min**. (b)** Steady state absorption spectra of pristine NTs (red), b-NTs obtained incubation for a month at room temperature (black dotted) and NTs interacted with arginine (9.00 mM) at incubation times 5 min, 15 min, 30 min, 1 h and 24 h (the spectra illustrate the transition of green from light to dark). The NTs interacted with arginine at 9.00 mM for 24 h resulted with formation of b-NTs.

Section 4: Impact on Environmental Changes on Arginine mediated b-NTs

Overview: ***Background and Significance.***
The fundamental limitations on the performance of supramolecular assemblies in device-based applications is their robustness under environmental stress such as (a) light exposure, (b) changing solvent conditions, and (c) elevated temperatures—all distorts the weak non-covalently interacting molecular network within the assembly's supramolecular structure. In contrast to florescence lifetime, the arginine-mediated hierarchical assembly process did not show significant impact on the assemblies' lack of robustness towards light exposure or reduced monomer concentration upon dilution compare to NTs and b-NTs.

Summary and Result: Steady-state absorption spectroscopy from solution samples revealed that b-NTs in presence of arginine against methanol dilution (**Fig. S9.a**) and under light exposure from 30 min up to 6 hours (**Fig. S9.b**). b-NTs in presence of arginine exhibited loss of excitonic character after 6 hours of exposure to visible light, while complete disassembly into monomers occurred upon dilution by a factor of 2.09 with methanol.

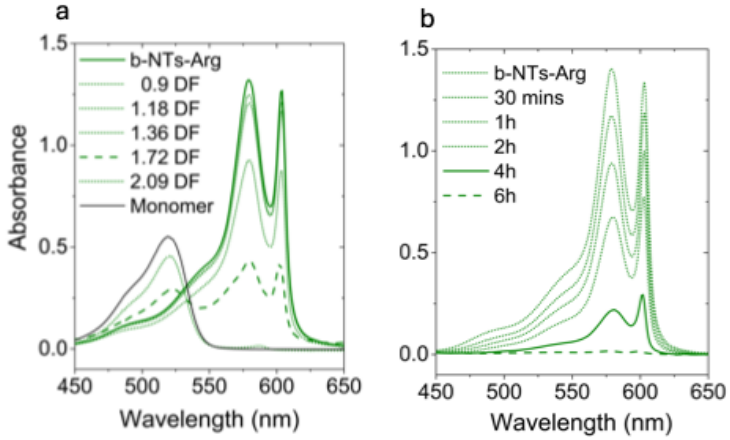


Figure S9: Steady state absorption spectra taken from solution samples (a) b-NTs assembled in presence of arginine diluted with methanol at dilution factors 0.9, 1.18, 1.36, 1.72, and 2.09. The b-NTs disassembled into monomers with a complete loss of the system's excitonic properties at dilution factor 2.09 (black-dotted spectrum). The absorption spectra of nanotubes diluted with methanol at dilution factor 2.09 compared with the black-solid spectrum, which shows the steady state absorption spectrum of free cyanine dye monomer (C8S3). Steady-state absorption spectra of **(b)** b-NTs assembled in presence of arginine exposed to visible light of 5 min, 30 min, 1h, 2h, 4h and 6h, respectively. The nanotubes lost their excitonic character after exposed to visible light for 6h (green-dashed spectrum).

Section 5. Interaction of Ionic Compounds with NTs

Overview: ***Background and Significance***. The hierarchical self-assembly in nature enables the formation of multifunctional and efficient systems through the self-assembly of molecular subunits into closely packed structures [2]. Molecular organization is controlled by Van der Waals forces, hydrophobic interactions, and electrostatic interactions [3,4] Solvent conditions—such as surfactants, pH of the solution, impurities, and counterions—play an important role in the self-assembly process by affecting the fundamental dynamics of molecular subunits [5]. In aqueous solutions, inorganic salts dissociate into counterions, which increase the dielectric constant of the solution. This, in turn, enhances Coulomb interactions between counterions and molecules, suppressing the repulsive forces between identically charged molecules and leading to aggregation [6]. Additionally, ionic compounds play a role in altering the ionic balance of the solution, which influences hierarchical self-assembly [7].

Concentration Dependent Effect of Ionic Compounds. We investigated the interaction of ionic compounds with NTs at different concentrations (0.18, 0.45, 0.90, 4.50, 9.00 mM) for 5 min.
Time Dependent Effect of Counterions. The NTs incubated with 9.00 mM ionic compounds for 5 min, 15 min, 30 min, 1 h and 24 h.

Summary and Result: ***Concentration Dependent Effect of Ionic Compounds.*** We investigated the interaction of ionic compounds with NTs at different concentrations (0.18, 0.45, 0.90, 4.50, 9.00 mM) for 5 min.

Time Dependent Effect of Ionic Compounds. The NTs incubated with 9.00 mM counterions for 5 min, 15 min, 30 min, 1 h and 24 h. For both ionic compounds—Sodium Hydroxide, Sodium Chloride, Cesium Hydroxide, Potassium Hydroxide— at a concentration of 9.00 mM, they supported contribution of free monomers into the nanotubular assembly within 5 min. The intensity of monomer-associated peak at around 520 nm decreased significantly, along with an increase in the intensity of peaks at 589 nm and 599 nm belong to the outer and inner cylinders, respectively (**Fig. S10.a**, **Fig. S.11.a**, **Fig. S12.a**, **Fig. S13.**a). It was found that, after 24 hours of incubation at 9.00 mM ionic compounds, the formation of bundled NTs was observed by the presence of a narrow exciton band at 603 nm and a broad absorption feature around 580 nm in aqueous solution (**Fig. S10.b**, **Fig. S11.b**, **Fig. S12.b**, **Fig. S13.b**).

The b-NTs in presence of sodium hydroxide and potassium hydroxide are not robust after one cycle heat stress (23ºC-95ºC-23ºC). The annealed samples (solid spectra in **Fig. S14.a** and Fig. **S14.d**) showed significant degradation of their exciton bands. The bundled NTs, in the presence of sodium chloride and cesium hydroxide, preserve their excitonic properties after one cycle of heat stress; however, the overall spectral shape and the energy position of the exciton bands changed (solid spectra in **Fig. S14.b** and **Fig. S14.c**).

Conclusion: The ionic compounds, ionized in aqueous solution, accelerate the hierarchical self-assembly, however b-NTs in presence of ionic compounds are not robust against heat stress. The electrostatic interaction between ions and NTs is sufficient to accelerate the formation of b-NTs; however, it is not enough to obtain highly robust supramolecular assemblies. These results demonstrate that interactions beyond electrostatics, such as hydrogen bonding, play a key role in providing structural robustness.

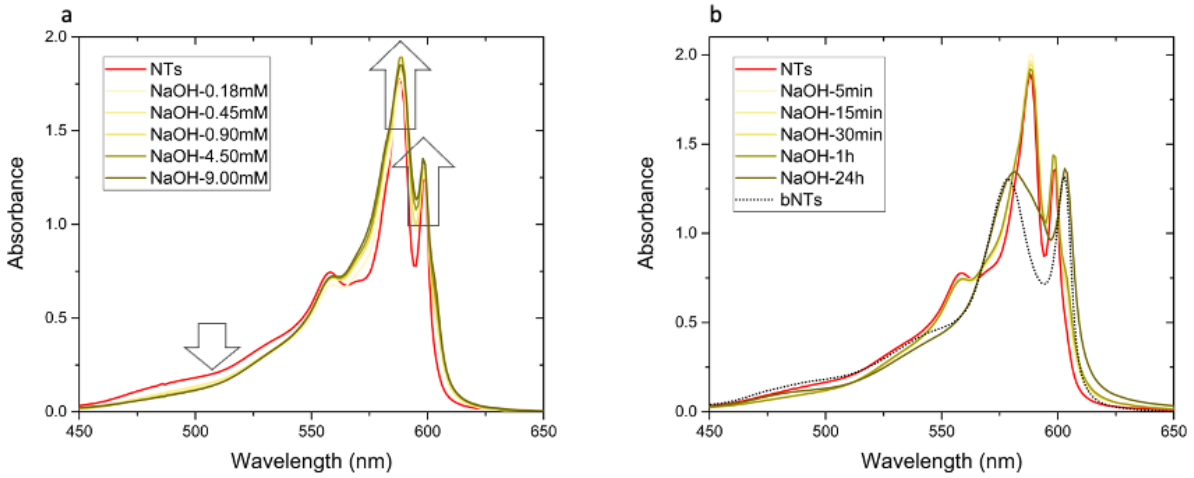


Figure S10. (a) Steady state absorption spectra of pristine NTs (red) and NTs interacted with NaOH at different concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM, and 9.00 mM (the spectra illustrate the transition of yellow from light to dark). The NTs interacted with different concentrations of NaOH for 5 min. **(b)** Steady state absorption spectra of pristine NTs (red), b-NTs obtained incubation for a month at room temperature (black dotted) and NTs interacted with NaOH (9.00 mM) at incubation times 5 min, 15 min, 30 min, 1 h and 24 h (the spectra illustrate the transition of yellow from light to dark). The NTs interacted with NaOH at 9.00 mM for 24 h resulted with formation of b-NTs.

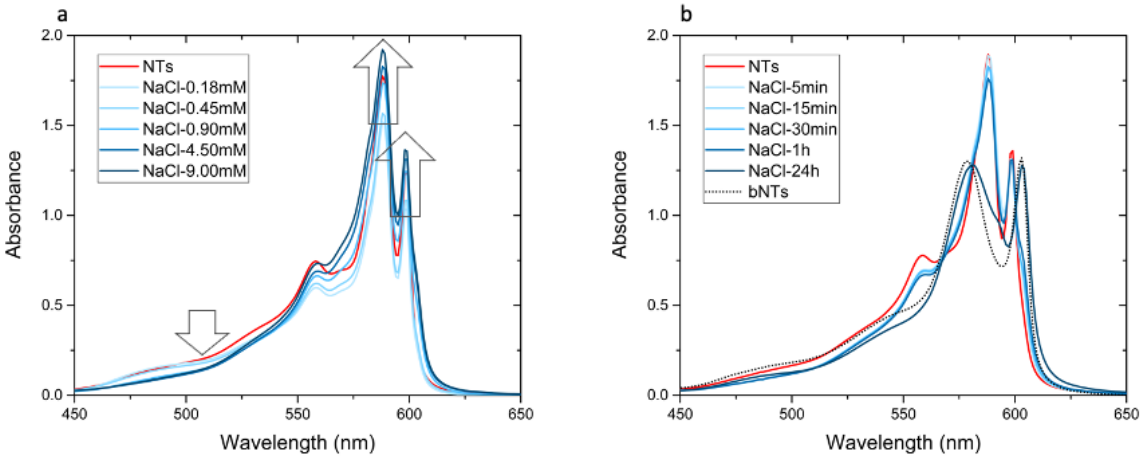


Figure S11. (a) Steady state absorption spectra of pristine NTs (red) and NTs interacted with NaCl at different concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM, and 9.00 mM (the spectra illustrate the transition of blue from light to dark). The NTs interacted with different concentrations of NaCl for 5 min. **(b)** Steady state absorption spectra of pristine NTs (red), b-NTs obtained incubation for a month at room temperature (black dotted) and NTs interacted with NaCl (9.00 mM) at incubation times 5 min, 15 min, 30 min, 1 h and 24 h (the spectra illustrate the transition of blue from light to dark). The NTs interacted with NaCl at 9.00 mM for 24 h resulted with formation of b-NTs.

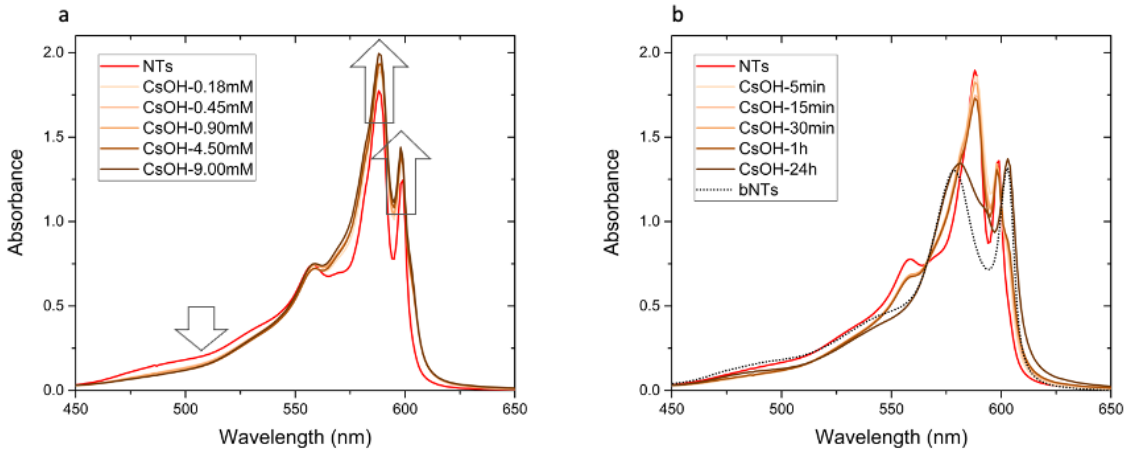


Figure S12. (a) Steady state absorption spectra of pristine NTs (red) and NTs interacted with CsOH at different concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM, and 9.00 mM (the spectra illustrate the transition of orange from light to dark). The NTs interacted with different concentrations of CsOH for 5 min. **(b)** Steady state absorption spectra of pristine NTs (red), b-NTs obtained incubation for a month at room temperature (black dotted) and NTs interacted with CsOH (9.00 mM) at incubation times 5 min, 15 min, 30 min, 1 h and 24 h (the spectra illustrate the transition of orange from light to dark). The NTs interacted with CsOH at 9.00 mM for 24 h resulted with formation of b-NTs.

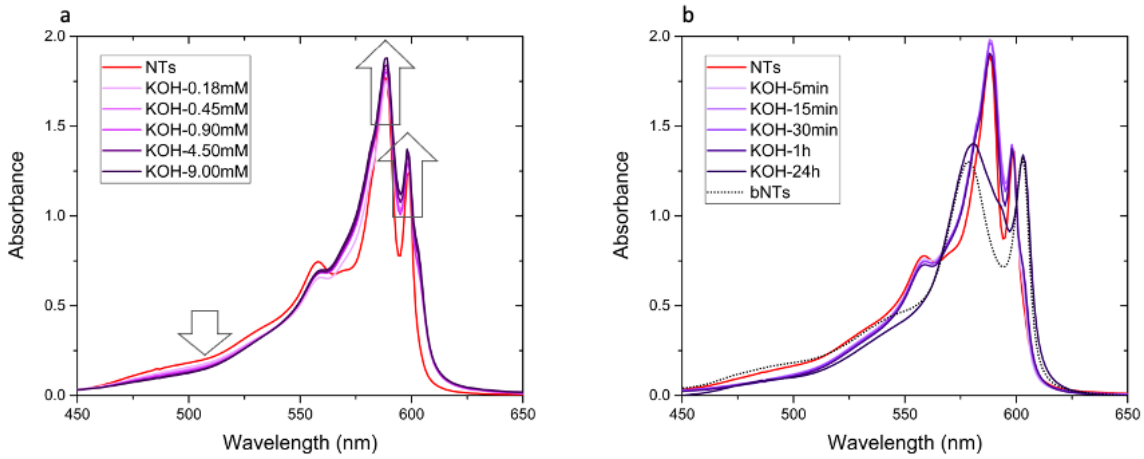


Figure S13. (a) Steady state absorption spectra of pristine NTs (red) and NTs interacted with KOH at different concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM, and 9.00 mM (the spectra illustrate the transition of pink from light to dark). The NTs interacted with different concentrations of KOH for 5 min. **(b)** Steady state absorption spectra of pristine NTs (red), b-NTs obtained incubation for a month at room temperature (black dotted) and NTs interacted with KOH (9.00 mM) at incubation times 5 min, 15 min, 30 min, 1 h and 24 h (the spectra illustrate the transition of pink from light to dark). The NTs interacted with KOH at 9.00 mM for 24 h resulted with formation of b-NTs.

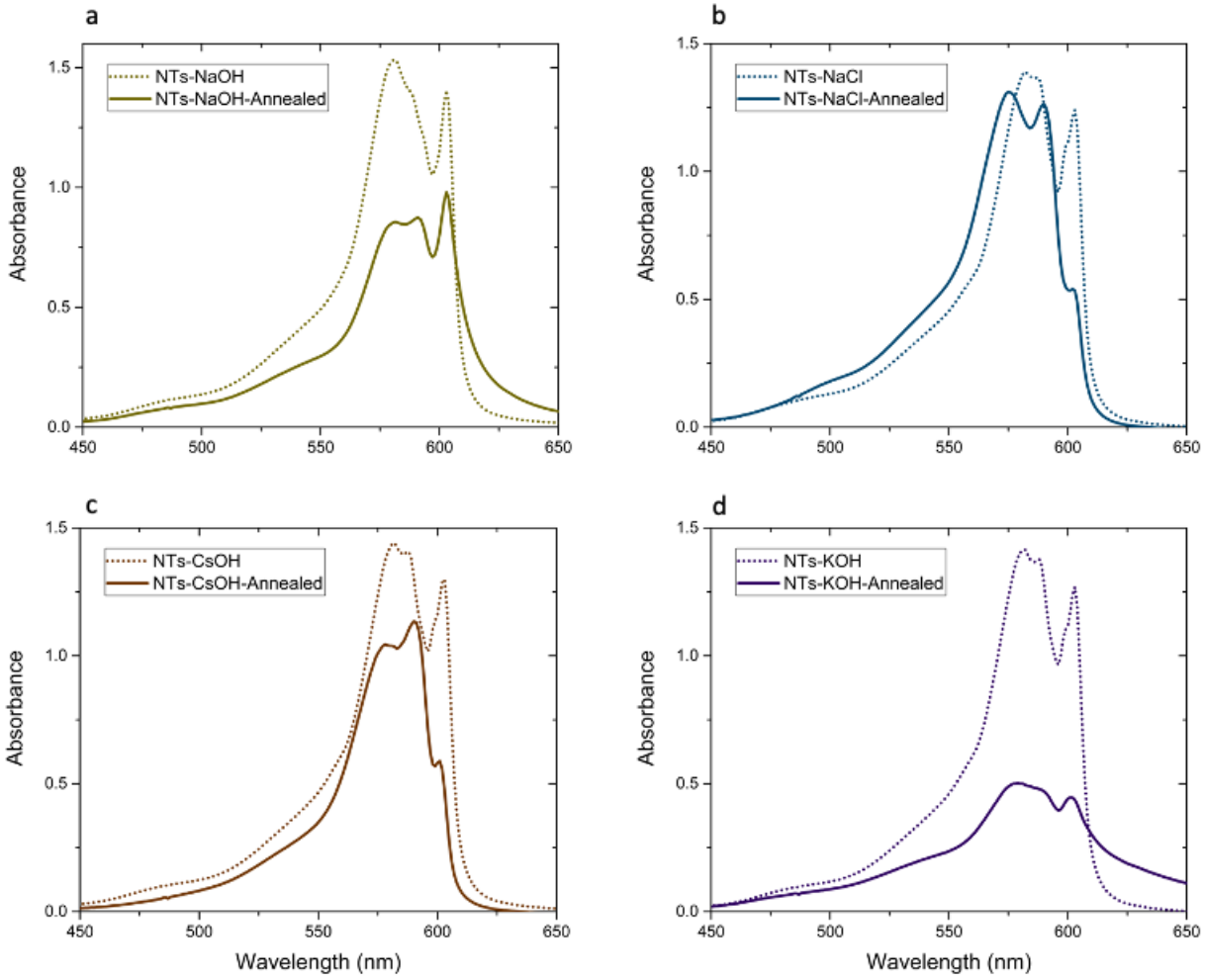


Figure S14. Heat stress (One-cycle heat stress, heating to 95 ºC and then cooling down to 23 ºC) applied to b-NTs prepared with interaction of bNTs obtained interaction of **(a)** NTs with NaOH, **(b)** NTs with NaCl, **(c)** NTs with CsOH, **(d)** NTs with KOH. The dotted spectra show the b-NTs before heat stress, the solid spectra show the b-NTs after annealing (one-cycle heat stress).

Section 6. Interaction of Arginine with NTs

6.1 Stoichiometry between Arginine and NTs—Considering *only* Electrostatic Interaction

Overview: ***Background and Significance***. The sulfonate groups not only impart hydrophilicity but also play a crucial role in the structural organization of NTs. Specifically, sulfonate chains in both the inner-wall and outer-wall cylinders of NTs exhibit a highly conserved interlocked arrangement with the polymethine chromophore [8]. In each monomer forming the NTs, one sulfonate group is interlocked with the polymethine chromophore, while the other remains free (**Fig. S15**).

Here, given this structural arrangement, if we consider *only* the electrostatic interaction between arginine and cyanine dye, it is expected to follow a specific stoichiometry. Each arginine molecule contains a single positively charged -NH_2 group on its side chain (**Fig. S15**), which can interact with the free sulfonate groups of NTs. As a result, under these conditions, the expected stoichiometry between NTs and arginine is [1:1].

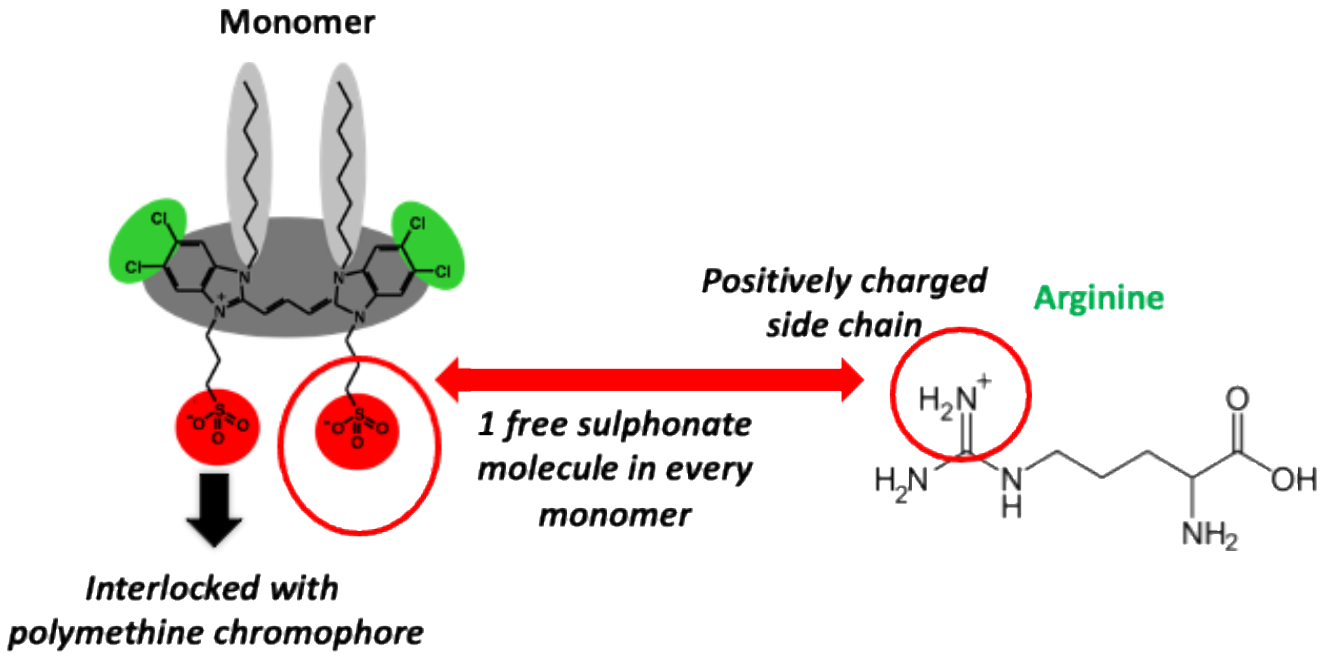


Figure S15. The illustration of chemical structure of cyanine dye monomer (3,3′-bis(2-sulfopropyl)-5,5′,6,6′ -tetrachloro-1,1′-dioctylbenzimidacarbo-cyanine). One molecule of cyanine dye includes two negatively charged sulphonate groups. One of the sulfonate groups is interlocked with polymethine chromophore [8], and one of the sulfonate groups is free in every monomer. The illustration of chemical structure of arginine shows the positively charged side chain (-NH_2).

Summary and Result: ***Stoichiometry between Arginine and NTs for Bundling.*** Arginine concentrations of 0.18, 0.45, 0.90, 4.50, and 9.00 mM were incubated for 24 hours to determine the experimental stoichiometry between monomer and arginine molecules. The NTs hierarchically assembled to bundled NTs at 0.90 mM as minimum within 24h (**Fig. S16**).

Calculation of the number of **arginine** molecules in 275 µL of a 0.90 mM solution:

1. Conversion of the concentration to moles per liter (M)

   $0.90\ mM = 0.90 \times 10^{-3}\ M = 0.0009\ M$

2. Conversion the volume from µL to liters:

   $275\ \mu L = 275 \times 10^{-6}\ L = 2.75 \times 10^{-4}\ L$

3. Calculation the moles of arginine:

   Moles of arginine = Concentration x Volume

   $= 0.0009\ mol/L \times 2.75 \times 10^{-4}\ L$

   $= 2.475 \times 10^{-7}\ mol$

4. Conversion moles to molecule

   Number of molecules = Moles x Avogadro's number (6.022×10^{23} molecules/mol)

   $= 2.475 \times 10^{-7}\ mol \times 6.022 \times 10^{23}\ molecules/mol$

   $=$ **1.49×10^{17} molecules**

Calculation the number of **cyanine dye monomers** in 250 µL of a 0.36 mM solution:

1. Conversion of the concentration to moles per liter (M)

   $0.36\ mM = 0.36 \times 10^{-3}\ M = 0.00036\ M.$

2. Conversion the volume from µL to liters:

   $250\ \mu L = 250 \times 10^{-6}\ L = 2.50 \times 10^{-4}\ L$

3. Calculation the moles of cyanine dye monomer:

   Moles of cyanine dye monomers = Concentration x Volume

   $=0.00036\ mol/L \times 2.50 \times 10^{-4}\ L$

   $=9.0 \times 10^{-8}\ mol$

4. Conversion moles to molecule

   Number of molecules = Moles x Avogadro's number (6.022×10^{23} molecules/mol)

   $= 9.0 \times 10^{-8}\ mol \times 6.022 \times 10^{23}\ molecules/mol$

   $=$ **5.42×10^{16} molecules**

Stoichiometry Calculation:

Stoichiometry = Number of arginine molecules/ Number of cyanine dye monomer

$= 1.49 \times 10^{17} / 5.42 \times 10^{16}$

$= \approx 3$

The experimental stoichiometric ratio of **arginine to cyanine dye monomer** is approximately [**3:1].** The experimental stoichiometry between arginine and the cyanine dye monomer is three times higher than the expected stoichiometry based on arginine's side-chain interaction with negatively charged sulfonate groups. This suggests that arginine not only interacts electrostatically with the negatively charged sulfonate groups but may also participate in hydrogen bonding and van der Waals interactions with both NTs and the aqueous solution [9].

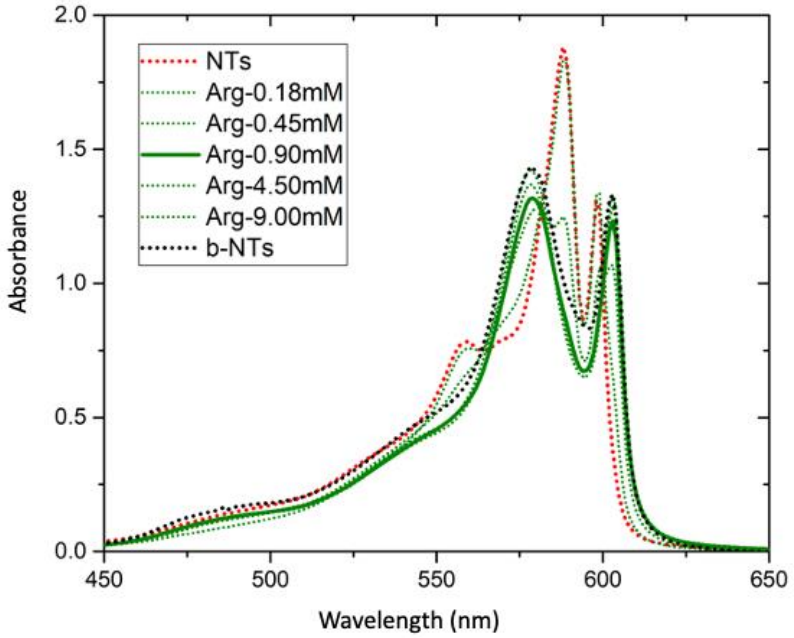


Figure S16. Steady state absorption spectra of pristine NTs (red dotted), b-NTs obtained by incubation for a month at room temperature (black dotted) and NTs interacted with arginine at different concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM, and 9.00 mM for 24 h. The green solid spectrum shows the critical (the minimum) concentration of arginine is 0.90 mM to obtain b-NTs within 24h.

Stoichiometry between Arginine and NTs for Robustness. b-NTs in presence of arginine at concentrations 0.18, 0.45, 0.90, 4.50, and 9.00 mM exposed to extreme heat stress (10-cycle heat stress). We determined the experimental stoichiometry between arginine and NTs for the robust material. The Bundled NTs are robust in the presence of a minimum of 4.50 mM arginine (**Fig. S17**).

Calculation of the number of **arginine** molecules in 275 µL of a 4.50 mM solution:

1. Conversion of the concentration to moles per liter (M)

   $4.50\ mM = 4.50 \times 10^{-3}\ M = 0.0045\ M$

2. Conversion the volume from µL to liters:

   $275\ \mu L = 275 \times 10^{-6}\ L = 2.75 \times 10^{-4}\ L$

3. Calculation the moles of arginine:

   Moles of arginine = Concentration x Volume

   $= 0.0045\ mol/L \times 2.75 \times 10^{-4}\ L$

   $= 1.2375 \times 10^{-6}\ mol$

4. Conversion moles to molecule

   Number of molecules = Moles x Avogadro's number (6.022×10^{23} molecules/mol)

   $= 1.2375 \times 10^{-6}\ mol \times 6.022 \times 10^{23}$ molecules/mol

   $=$ **7.45×10^{17} molecules**

Calculation the number of **cyanine dye monomers** in 250 µL of a 0.36 mM solution:

1. Conversion of the concentration to moles per liter (M)

   $0.36\ mM = 0.36 \times 10^{-3}\ M = 0.00036\ M.$

2. Conversion the volume from µL to liters:

   $250\ \mu L = 250 \times 10^{-6}\ L = 2.50 \times 10^{-4}\ L$

3. Calculation the moles of cyanine dye monomer:

   Moles of cyanine dye monomer = Concentration x Volume

   $=0.00036\ mol/L \times 2.50 \times 10^{-4}\ L$

   $=9.0 \times 10^{-8}\ mol$

4. Conversion moles to molecule

   Number of molecules = Moles x Avogadro's number (6.022×10^{23} molecules/mol)

   $= 9.0 \times 10^{-8}\ mol \times 6.022 \times 10^{23}$ molecules/mol

   $=$ **5.42×10^{16} molecules**

Stoichiometry Calculation:

Stoichiometry = Number of arginine molecules / Number of cyanine dye monomers

$= 7.45 \times 10^{17}$ molecules / 5.42×10^{16}

$=$ **≈ 14**

The experimental stoichiometric ratio of arginine to cyanine dye monomer for a robust material is approximately [14:1**]**, which is nearly five times higher than the experimental stoichiometry between arginine and the cyanine dye monomer required for the formation of bundled NTs. This suggests that the formation of bundled NTs alone is not sufficient for a robust material; more arginine molecules are needed to support the hierarchical assembly network of bundled NTs.

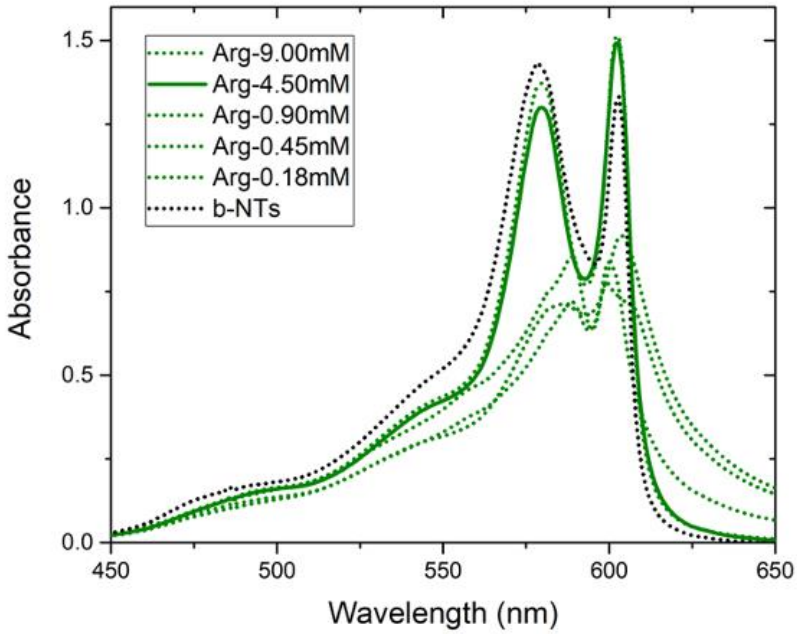


Figure S17. Steady state absorption spectra of b-NTs obtained by incubation for a month at room temperature (black dotted) and the annealed NTs interacted with arginine at different concentrations: 0.18 mM, 0.45 mM, 0.90 mM, 4.50 mM, and 9.00 mM for 24 h after exposed to 10-cycles heat stress. The green solid spectrum shows the critical (the minimum) concentration of arginine is 4.50 mM to obtain robust b-NTs against 10-cycles heat stress.

Arginine Effect on Surface Charge. The NTs have negatively charged sulfonate groups on their outer layer, which interact with the aqueous solution. The zeta potential of double-walled NTs was measured as -55.74 ± 0.42 mV, while the surface charge of hierarchically assembled bundled NTs was -47.95 ± 0.48 mV. The interaction with arginine had a slight effect on the surface charge of bundled NTs, which was measured as -38.13 ± 0.85 mV as shown in **Table S2**. This result supports our stoichiometry calculations, indicating that arginine not only interacts with sulfonate groups via electrostatic side chain interactions but also possible hydrogen bonding and van der Waals interactions.

Table S2. Zeta potential (mV) of NTs, b-NTs and b-NTs in presence of arginine.

	Zeta Potential (mV)
NTs	-55.74±0.42
b-NTs	-47.95±0.48
b-NTs-Arginine	-38.13±0.85

6.2 Hydrogen Bonding Effect on Excited-State Properties.

<u>Overview:</u> Background and Significance.

In J-aggregates, responsible for the decreased fluorescence lifetime of the superradiant emission is the coherent coupling of excitations between the closed-packed dye monomers within the supramolecular assembly that leads to Frenkel excitons delocalized over 25 monomers [10], pivotal for their unique optoelectronic properties [10].

In purple photosynthetic bacteria, pigments are responsible for absorbing light energy and converting it into excitation energy. This excitation energy is then transferred to the reaction center, a pigment-protein complex known as antenna complex, where it is ultimately converted into a charge-separated state [11].

Hydrogen bonding interactions between pigments and the protein surrounding play a crucial role in driving the assembly of the antenna complex while also contributing to its stability [12]. The pigments engage in hydrogen bonding interactions with the side chains of the surrounding amino acids within the protein surrounding, facilitating the structural organization and function of the complex [13].

In the antenna complex of purple photosynthetic bacteria, hydrogen bonding between the pigments and the protein plays a significant role in inducing the spectral red-shift in their absorbance, alongside pigment-pigment interactions [14]. The energy of the excited state is influenced by hydrogen bond interactions, with the extent of the effect depending on the strength of the interaction. An increase in the strength of the hydrogen bond can reduce the excitation energy of the associated excited state, leading to a red shift in the electronic spectrum as seen in purple photosynthetic bacteria [15]. Conversely, it is also possible that, a weakening of the hydrogen bonding results in a blue shift in the electronic spectrum [15].

Time-resolved fluorescence spectroscopy is a powerful technique for elucidating hydrogen bonding dynamics by monitoring changes in fluorescence decay upon photoexcitation. Since hydrogen bonds significantly influence excited-state relaxation, variations in fluorescence lifetime provide critical insights in effects of the possible interaction of arginine with sulfonate groups of NTs [15].

Hydrogen bond mediated supramolecular assemblies between light-harvesting chromophores and complimentary hydrogen bonding molecules have been known to exhibit triplet photosensitizing properties [16]. Hydrogen bonding allows intersystem crossing (*ISC*), a transfer of excited carriers from the singlet to the triplet states. Consequently, such transfers increase the rate of non-radiative recombination ($\gamma_{non\text{-}rad}$) involving the triplet-triplet ($T_n \rightarrow T_o$) transitions (**see Fig. S18**). The total rate of relaxation can be expressed as an additive of the radiative and non-radiative components, Eq. (1) [17].

$$\gamma_{total} = \gamma_{rad} + \gamma_{non-rad} \quad \text{.....(1)}$$

Lifetime is inversely proportional to the rate of recombination ($\gamma_i = 1/\tau_i$); therefore, Eq. (1) can be expressed as the following (2) [2]:

$$\frac{1}{\tau_{total}} = \frac{1}{\tau_{rad}} + \frac{1}{\tau_{non-rad}} \quad \text{.....(2)}$$

In the presence of non-radiative relaxation, the observable lifetime (τ_{total}) is expected to be shorter than the purely radiative case as the observable lifetime is an additive of the reciprocal radiative and non-radiative lifetimes.

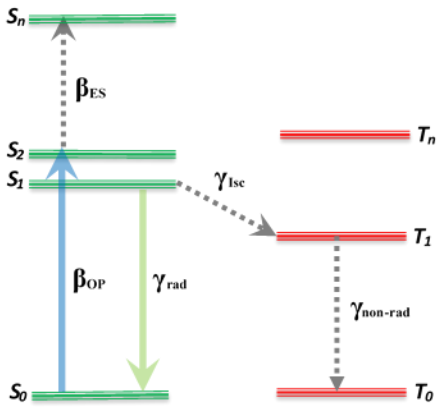


Figure S18. An energy level diagram showing quenching effects. [key: singlet states: S_n; triplet states T_n; one-photon absorption coefficient: β_{OP}; excited state absorption coefficient: β_{ES}; radiative recombination rate: γ_{rad}; non-radiative recombination rate: $\gamma_{non-rad}$, rate of inter system crossing (ISC): γ_{ISC}.

Summary and Result: ***Hydrogen Bonding Effect on Steady State Absorption Spectrum.*** The spectra of bundled NTs (1month incubation) and bundled NTs in presence of arginine (24h incubation) were normalized based on the inner cylinders. A very slight red shift (around 1 nm, seen in **Fig. S19**) suggests a potential effect of hydrogen bonding, which should be further investigated using additional spectroscopic techniques, as steady state absorption alone may not provide sufficient insight to fully observe this difference. To further investigate this effect, we examined the lifetime using time-resolved spectroscopy to clarify the possible hydrogen bonding effect.

Hydrogen Bonding Effect on Lifetime. Fluorescence lifetime of Frenkel excitonic materials was determined by time-resolved spectroscopy: time-resolved emission was collected using a custom-built apparatus with a Hamamatsu Streak Scope (C4334). Briefly, a chirped-pulse regenerative amplifier (Spectra-Physics Spitfire F) is pumped using the output of a Ti:sapphire Oscillator (Spectra-Physics Tsunami) to produce 800 nm laser pulses at a 1 kHz repetition rate. In the main manuscript in Figure 1M, it is seen that cyanine dye monomer has a (129±1.75) ps fluorescence lifetime. As expected, upon the assembling of the free monomers into double-walled NTs, the fluorescence life time significantly reduced to 63.62±0.65 ps (Figure 1N). As it is known, free dye molecules interact with each other through weak interactions, leading to a collective electronic state called an exciton [19]. This interaction causes a delocalization of the excited state over multiple molecules, which can alter the way the

energy is transferred and dissociated within the system. This results in a shortening of the excited-state lifetime because the energy is rapidly transferred from one molecule to another, leading to faster relaxation processes [19]. As a further step, double-walled NTs hierarchically self-assembled into the bundled NTs (1 month incubation) with a fluorescence lifetime (81.85±1.57) ps (Figure 1O). While double-walled NTs hierarchically self-assembled into bundled NTs in the presence of arginine (24 h incubation), the fluorescence lifetime dramatically reduced to (40.58 ± 0.56) ps (Figure 2L). We observed a significant reduction in the fluorescence lifetime of the bundled nanotubes in the presence of arginine ($\tau_{bn\text{-}t\ Arg} \sim \tau_{bn\text{-}t\ /\ 2}$). The quenching effect of arginine could be indicative of H-bond formation between the sulfonate groups of NTs and the arginine molecules, which in turn could be the driving mechanism behind the bundling process.

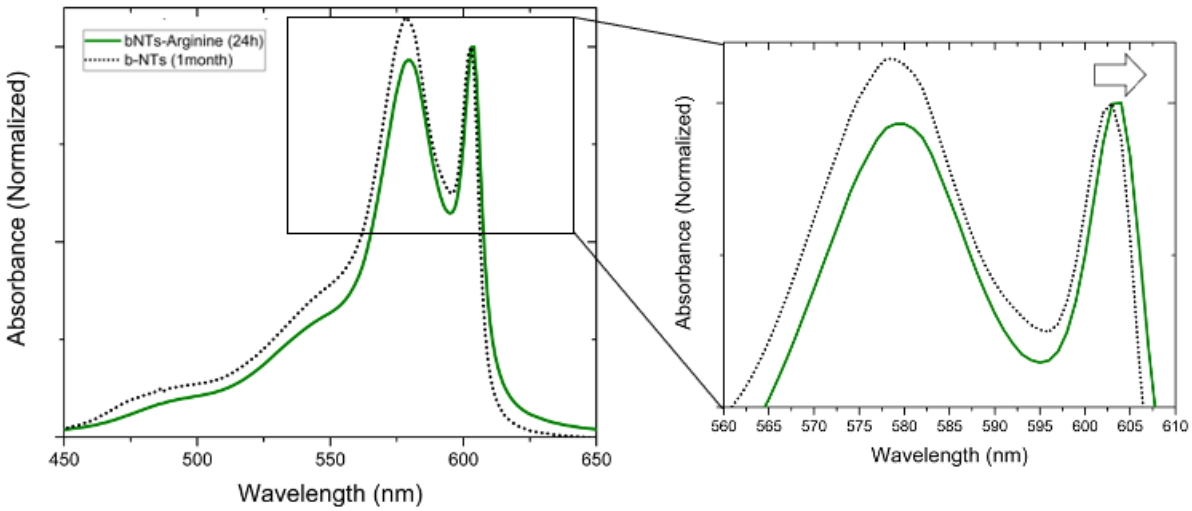


Figure S19. Steady State Absorption spectrum of b-NTs-Arginine (prepared within 24h, green solid spectrum), and b-NTs (prepared within a month, black dotted spectrum).

Conclusion: Concentration-dependent experiments reveal the critical concentrations of arginine required to form b-NTs and to provide robustness under heat stress are 0.90 mM and 4.50 mM, respectively. However, the expected stoichiometry between NTs and arginine [1:1] do not align with these findings, as the expected stoichiometry was determined by considering only the electrostatic interactions between arginine molecules and NTs. The stoichiometry between arginine and NTs was determined as [**3:1**] **and** [**14:1**] for b-NTs formation and robustness, respectively, according to experimental results. Furthermore, the surface charge of the NTs after interaction with arginine supports the idea that the intermolecular interactions between them cannot be explained only by electrostatic forces, as the surface charge of the NTs only decreases from (-55.74 ± 0.42) mV to (-38.13 ± 0.85) mV. This indicates that arginine not only interacts with sulfonate groups via electrostatic side chain interactions but also possible hydrogen bonding and van der Waals interactions. Hydrogen bonding is evidenced by the significant reduction in the fluorescence lifetime of the b-NTs in the presence of arginine, which results from a quenching effect caused by arginine.

Section 7. Control Experiment: *Interaction of NTs with Guanidine*

Overview: ***Background and Significance.*** Arginine is a unique amino acid that contains a guanidine group in its side chain, making it highly basic and hydrophilic. Guanidine is a strong hydrogen bond donor and exhibits a high pKa (~13.6), rendering it readily protonated under correct solvent conditions. This strong basicity enables guanidine to engage in hydrogen bonding with water and as well as hydrogen bonding and electrostatic interactions with negatively charged functional groups, such as sulfonates ($-SO_3^-$) [18]. The delocalization of charge within the guanidinium cation further enhances its affinity for anionic species, making it a crucial functional moiety in various biological and chemical systems. To assess the specific contribution of the guanidine group to the effects of arginine, we conducted a control experiment in which double-walled nanotubes (NTs) were interacted with guanidine.

Summary and Result: ***Guanidine has the same impact on NTs as Arginine.*** The prepared NTs interacted with guanidine (final concentration is 0.90 mM) for 24h. NTs interacted with guanidine (purple solid) shows the evidence of spectroscopic signature of bundled NTs in aqueous solution: the narrow exciton band at 603 nm and a broad absorption feature around 580 nm (**Fig. S20.a**) [2]. Specifically, the absorption spectra of bundled NTs with guanidine and neat bundled NTs were nearly identical (**Fig. S20a**), demonstrating that guanidine can control the hierarchical self-assembly of NTs in the same way as arginine. The presence of guanidine significantly provides robustness to the NTs, as evidenced by the absence of notable alterations in the overall spectral profile, indicating that the supramolecular structure remained largely intact after heat stress (One cycle-heating to 95 ^oC, after that cooling (annealing) to 23 ^oC) (**Fig. S20.b**). Notably, in the presence of guanidine, neither thermal degradation nor disassembly of the supramolecular assembly occurred, even when the assembly solution was subjected to boiling (dashed spectrum in **Fig. S20.b**). Additionally, **Fig. S20.c** demonstrates the remarkable resilience of bundled NTs when exposed to extreme thermal fluctuations and multiple heating cycles (10 cycles), particularly in the presence of guanidine. The intensity difference in the absorption spectra of bundled NTs-guanidine before and after heat stress is influenced by the concentration change resulting from the evaporation of the aqueous solution during boiling.

Conclusion: Guanidine exhibits the same effect as arginine, indicating that the interaction of arginine with NTs is primarily attributed to its guanidine group, which provides robustness to the NTs. Guanidine contributes strong hydrogen-bond donor properties to the structure of arginine and directly interacts with sulfonate groups on the surface of NTs. This interaction both accelerate hierarchical self-assembly process and provide robustness to the supramolecular assemblies even under extreme heat stress.

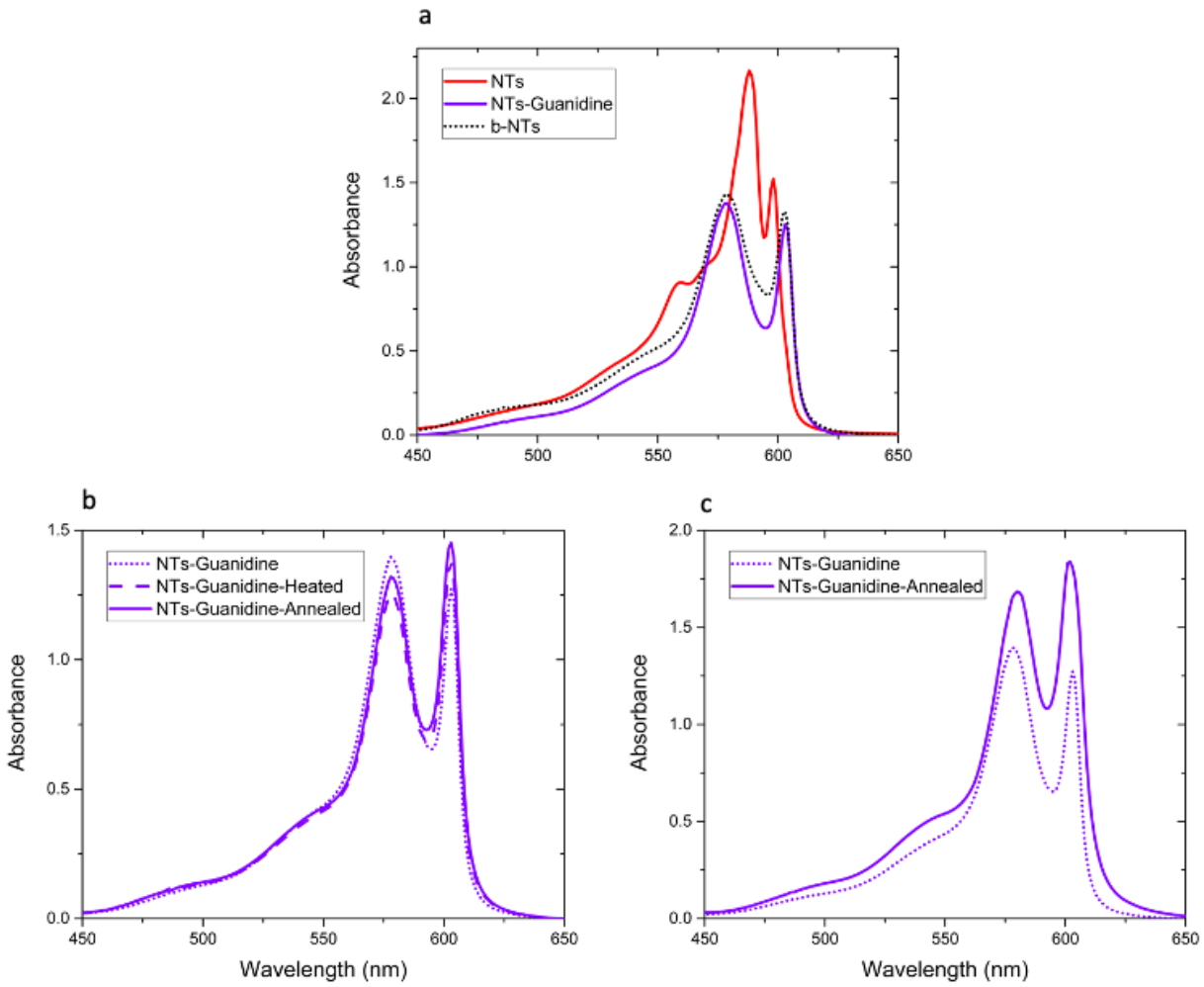


Figure S20. Steady state absorption spectra taken from solution samples (a) of pristine NTs (red solid), b-NTs obtained by incubation for a month at room temperature (black dotted) and b-NTs prepared with interaction of double-walled NTs with guanidine for 24 hours (purple solid). **(b)** Heat stress (one-cycle, heating to 95 ºC and then cooling down to 23 ºC) applied to b-NTs prepared with interaction of NTs with guanidine. Steady state absorption spectra obtained at 95 ºC (purple dashed) and the spectra obtained at 23 ºC after annealing (purple solid) show no significant difference compared to spectrum obtained from b-NTs (NTs-guanidine) before applying heat stress (purple dotted). **(c)** Heat stress (10-cycles, heating to 95 ºC and then cooling down to 23 ºC in one cycle) applied to b-NTs prepared with interaction of NTs with guanidine. Steady state absorption spectrum obtained from annealed b-NTs (NTs-Guanidine) after exposed to 10-cycles heat stress (purple solid) has no significant difference in the peak positions compared to b-NTs (NTs-guanidine) before applying heat stress (purple dotted). The intensity difference between the samples is caused by the evaporation of water during the boiling process.

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