Supporting Information

Supramolecular nanochannels self-assembled by helical pyridine-pyridazine oligomers

Tengfei Yan, Feihu Yang, Shuaiwei Qi, Xiaotong Fan, Shengda Liu, Ningning Ma, Quan Luo, Zeyuan Dong* and Junqiu Liu*

* To whom correspondence should be addressed.

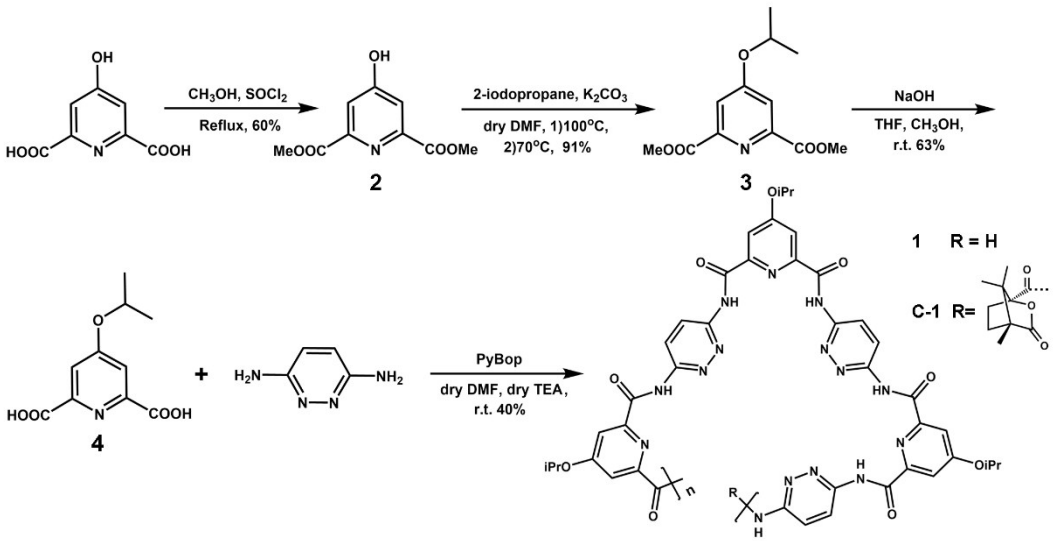
E-mail: zdong@jlu.edu.cn

junqiuliu@jlu.edu.cn

1. General information

Materials and instrumentations: N, N-dimethylformamide (DMF) and triethylamine (TEA) were dried by distillation with CaH_2. Other chemicals and solvents were purchased from commercial suppliers without further purification unless otherwise stated. Characterization instruments including NMR of 500 MHz, AVANCEIII500 from Bruker. Chemical shifts were reported in ppm relative to the residual solvent peak (D_2O: 1H, 4.79, DMSO-*d6*: 1H, 2.50) or tetramethylsilane (TMS) peak. Multiplicity was indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), quin (quintet), m (multiplet), br (broad singlet). ESI-MS Agilent1290-microTOF Q II from Bruker, MALDI-TOF MS Autoflex speed TOF from Bruker, GPC is from Waters 2414. FTIR VERTEX 80V from Bruker. Circular Dichroism (CD) PMS450 from Biologic Company, Ultraviolet-Visible (UV-Vis) Absorption Spectrometry UV-2450 from Shimadzu Company, AFM NanoScope Multimode is from Bruker, NanoScope Analysis software by the tapping mode. TEM JEM-2100F from JEOL, Fluorescence Spectrometer 5301PC from Shimadzu, DLS Zetasizer Nano Series from Malvern Company.

2. Synthetic procedures of the helical oligomers



Scheme S1. Synthetic routes of oligomer **1** and oligomer **C-1**.

Compound **2** and **3** were synthesized according previous reported methods and fully characterized.[1]

Synthesis of compound **4**

Disperse compound **3** (500 mg, 2.0 mmol) and NaOH (800 mg, 20 mmol) in 50 mL CH_3OH. After 12 h, evaporate the solvent at reduced pressure. Neutralize the superfluous NaOH with diluted HCl (1.2 mmol/L) solution then the hydrolyzed product was separated out. We can obtain 280 mg white powder (yield 63.1 %) after filtering and drying strategy. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ = 7.86 (s, Ar-H), 5.16-5.09 (m, OCH), 1.47 (d, CH_3). ^{13}C NMR (500 MHz, $CDCl_3$, 293 K) δ = 172.74, 162.90, 146.17, 113.90, 75.52, 20.53. HR-MS (ESI): *m/z* calcd for $C_{10}H_{12}NO_5$ $[M+H]^+$: 226.0715, found: 226.0713.

Synthesis of oligomer **1**

Dissolve compound **1** (80 mg, 0.36 mmol), 3,6-diamine-pyridazine (39.1 mg, 0.36 mmol) and PyBop (462 mg, 0.89 mmol) in 2 mL dry DMF, and then inject TEA (0.5 mL, 3.6 mmol) into the solution. Evaporate the solvent after stirring for one week at room temperature. Add 2 mL CH_3OH to the residue and place the mixture at -20 ^{o}C overnight. There will appear precipitant (our product) and then filter it with a small Buchner funnel. Greyish product (43 mg, yield 40.6 %) was obtained. ^{1}H NMR (500 MHz, $CDCl_3$, 293 K) δ = 7.09-7.06 (m, Ar-H), 6.83 (br, Ar-H), 5.03-4.94 (m, OCH), 1.37-1.32 (m, CH_3).

Synthesis of oligomer **C-1**

Add oligomer **1**(13 mg) and (1*S*)-(-)-camphanic chloride (25 mg, 0.12 mmol, which is a common chiral inducer) to dry $CHCl_3$ (2 mL), then inject 0.5 mL TEA as acid-binding agent. Stirring at room temperature for three days. We can get gray product **C-1** (6.2 mg, yield 44.3 %) ^{1}H NMR (500 MHz, $CDCl_3$, 293K) δ= 8.76-8.29 (br, Ar-H), 7.85-7.26 (m, Ar-H), 5.01 (br, OCH), 1.35 (br, CH_2). 1.26-1.16 (m, CH_3).

3. Figures mentioned in manuscript

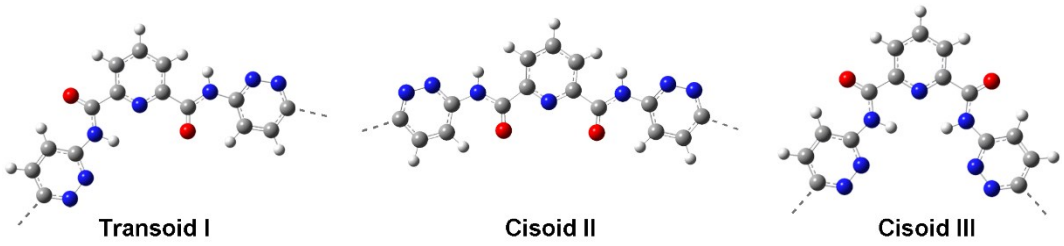


Figure S1. Three possible conformations of pyridazine-pyridine-pyridazine sequence with significant Gibbs energy barriers ($\Delta G_{I\text{-}III}$ = 29.05 kJ/mol, $\Delta G_{II\text{-}III}$ = 71.02 kJ/mol). Calculated at B3LYP/6-31G* level by using Gaussian03 program, presented by GaussView5.0 software.

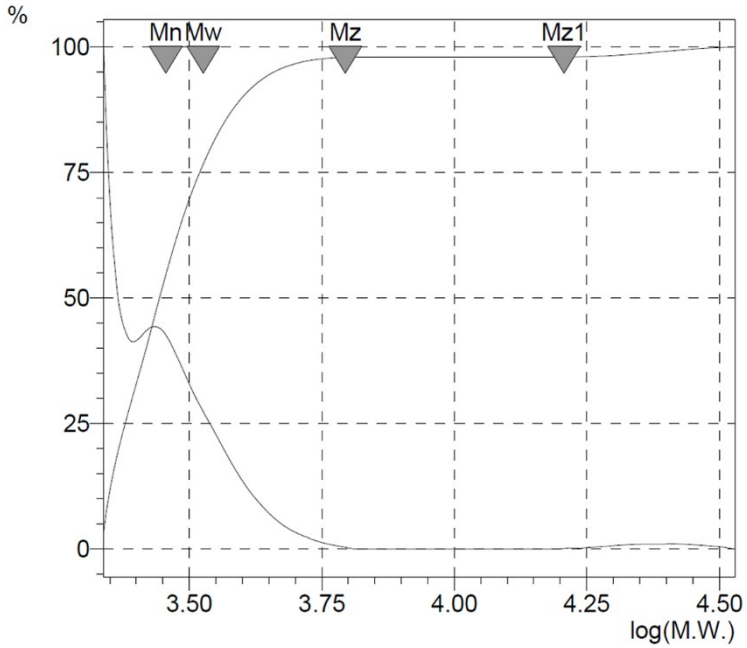


Figure S2. GPC spectrum of oligomer **1** in THF. The Mn and PDI was estimated to be 3000 and 1.17, respectively.

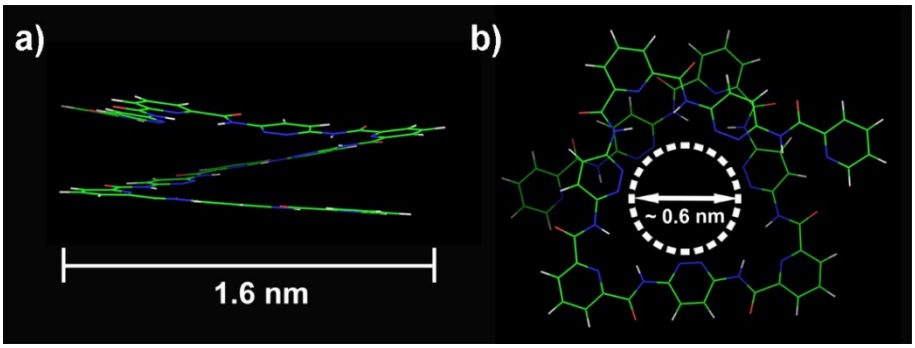


Figure S3. a) Side view and b) Top view of the most stable conformation of the designed

oligomeric model with 5.5 repeating units calculated by Gaussian03 program, presented by PyMOL software. Isopropoxy side chains were omitted for clarity.

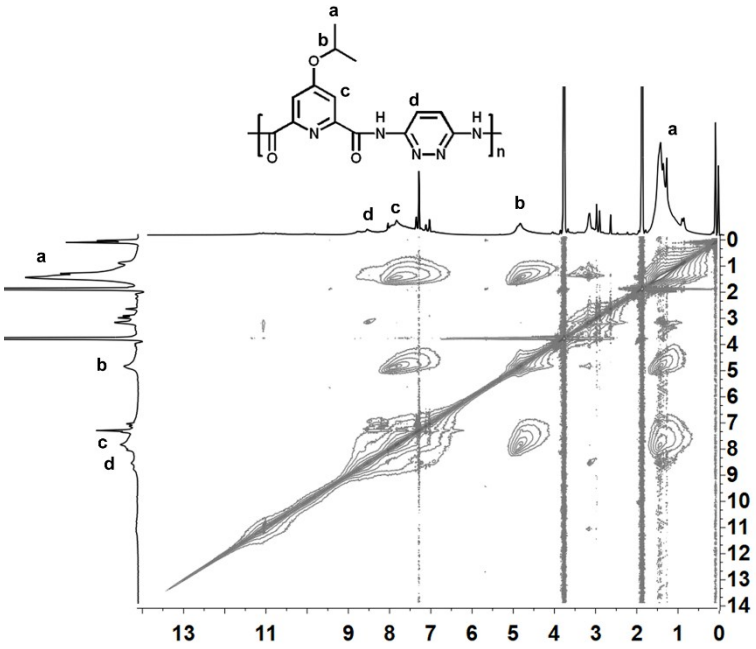


Figure S4. 2D NMR spectra of oligomer **1** in $CDCl_3$ at 293 K.

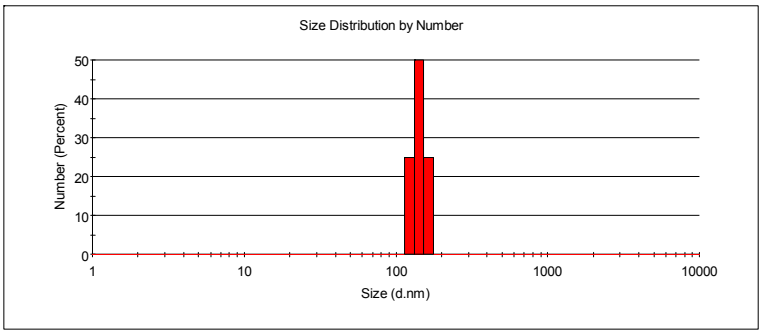


Figure S5. DLS analysis of supramolecular tubular assemblies formed by oligomer **1** at the concentration of 0.01 mg/mL in THF.

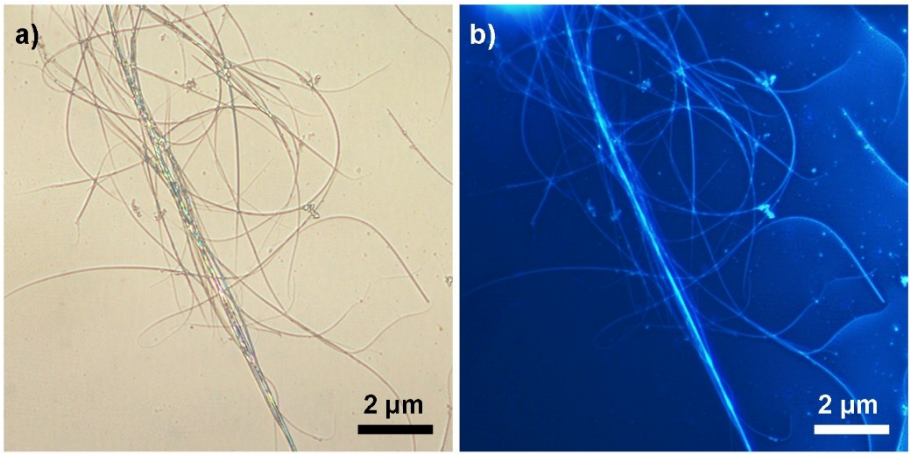


Figure S6. a) Optical and b) Fluorescence images of large-scale microfibers aggregated by oligomer **1** at the concentration of 0.5 mg/mL in THF.

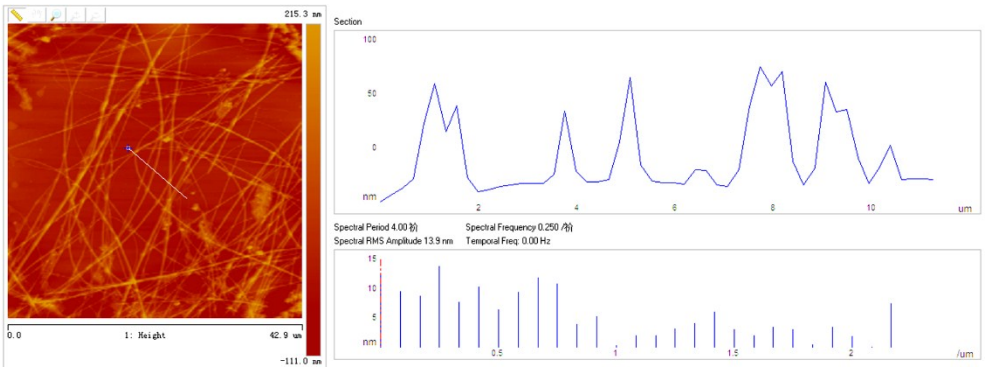


Figure S7. AFM image and high profile of the microfibers detected on the surface of wafer.

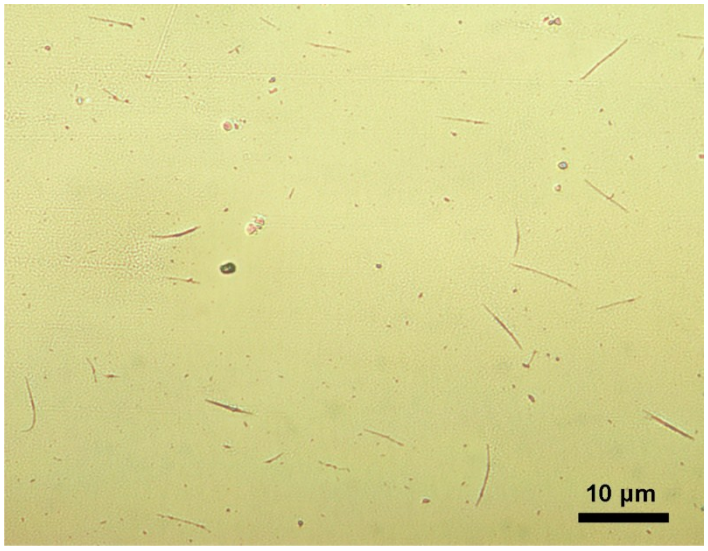


Figure S8. Optical image of small supramolecular microfibers detected from freshly dissolved oligomer **1** in THF at the concentration of 0.5 mg/mL.

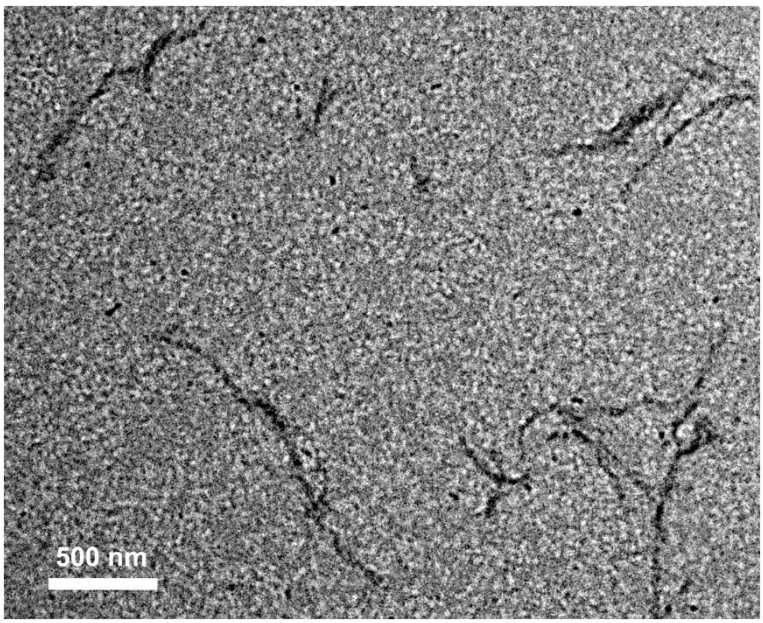


Figure S9. TEM image of small supramolecular microfibers self-assembled by oligomer **1**.

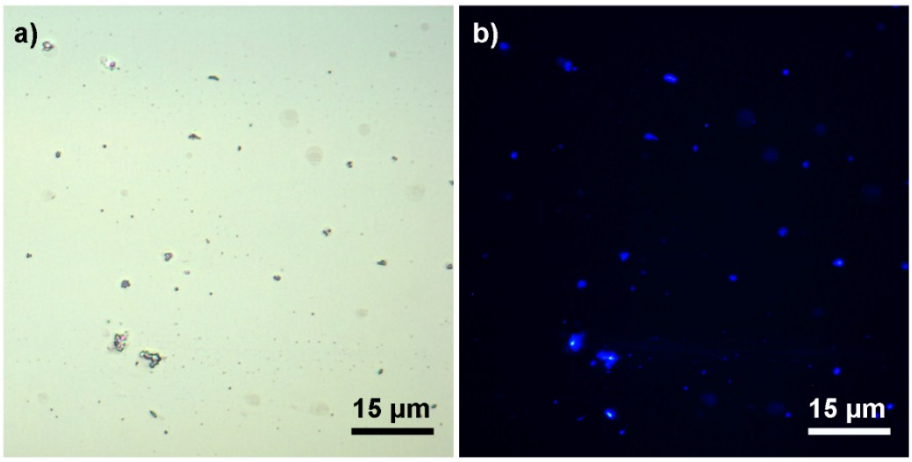


Figure S10. a) Optical and b) Fluorescence images of TFA-treated (5‰ in volume) oligomer **1** at the concentration of 0.5 mg/mL in THF.

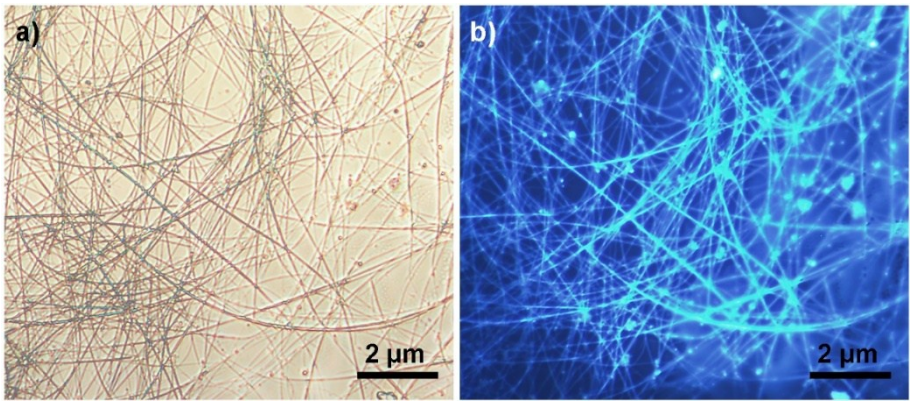


Figure S11. a) Optical and b) Fluorescence images of supramolecular microfibers aggregated by oligomer **1** treated by TFA and TEA, respectively.

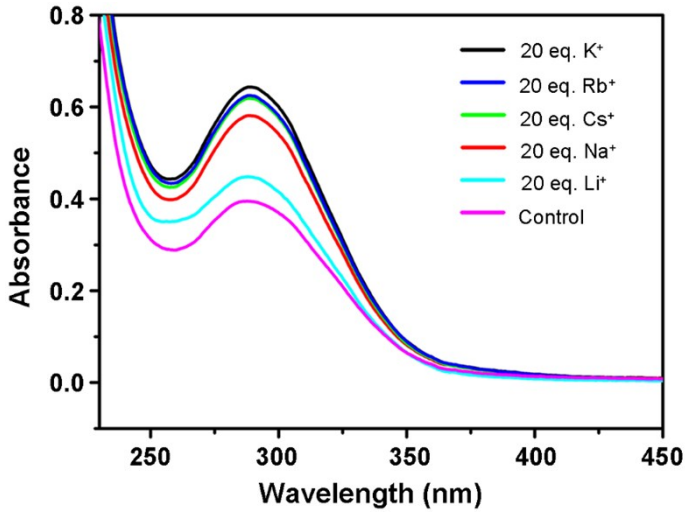


Figure S12. UV/Vis titration spectra of oligomer **1** with different alkali metal in the mixed solvents of MeCN and water (1:50, vol:vol) at the concentration of 5 μM.

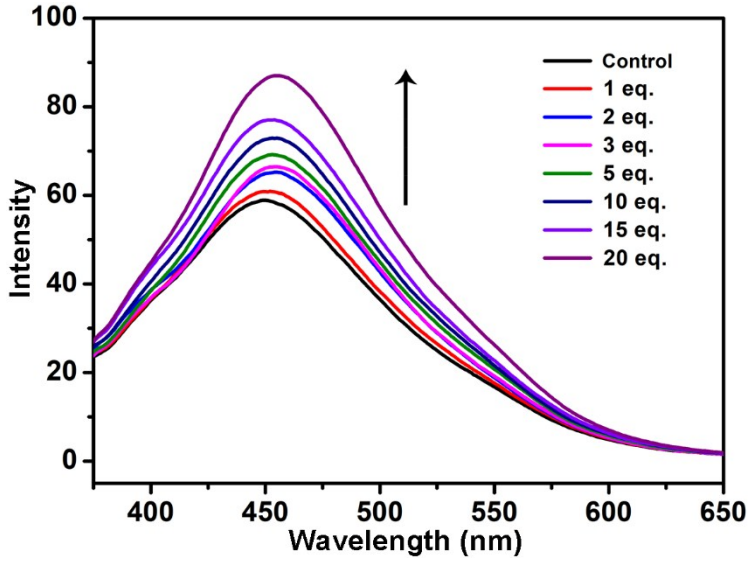


Figure S13. Fluorescence titration spectra of oligomer **1** with different ratio of KCl in the mixed solvents of MeCN and water (1:50, vol:vol).

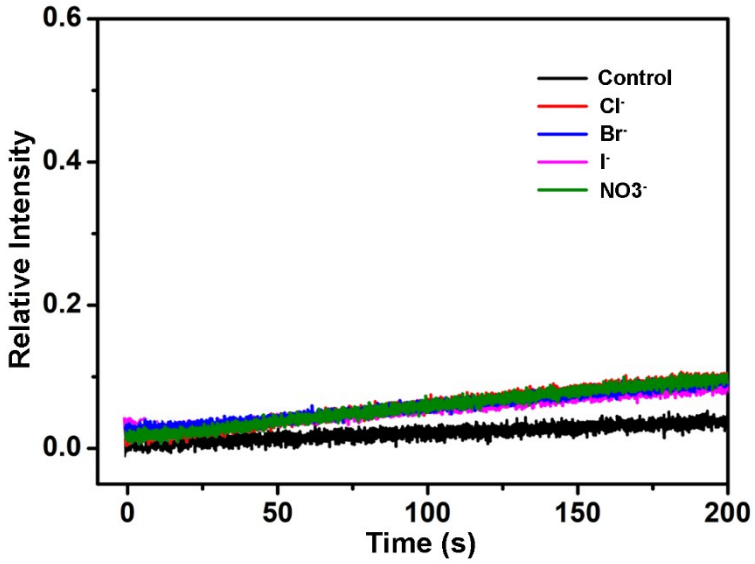


Figure S14. Determine anion selectivity of oligomer **1** by the fluorescence change of Safranin O in a solution containing 100 mM NaA (A = Cl^-, Br^-, I^-, NO_3^-). The activities were very low and similar, indicating **1** was not sensitive to anions.[1]

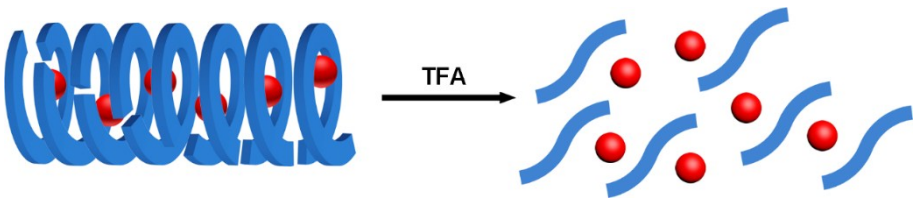


Figure S15. Schematic representation of triggered release behaviors of ions-loaded supramolecular nanotubular assemblies.

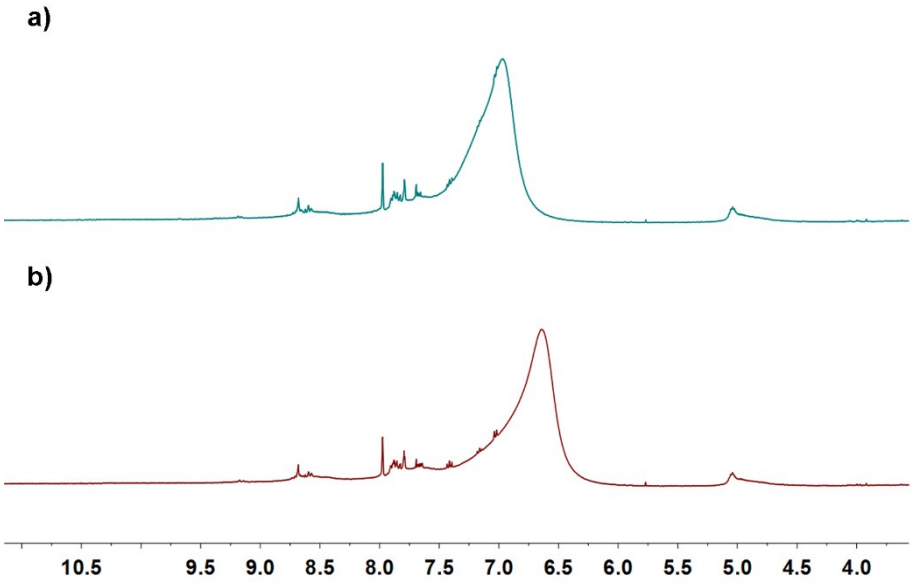


Figure S16. Partial NMR spectra of a) oligomer **1** and b) oligomer **1** + 5 eq. KCl in DMSO-*d6* after adding 0.5 % TFA.

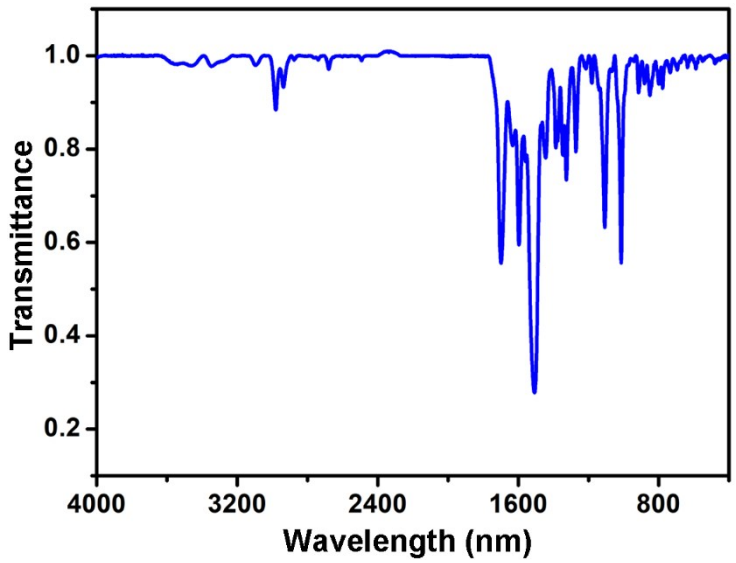
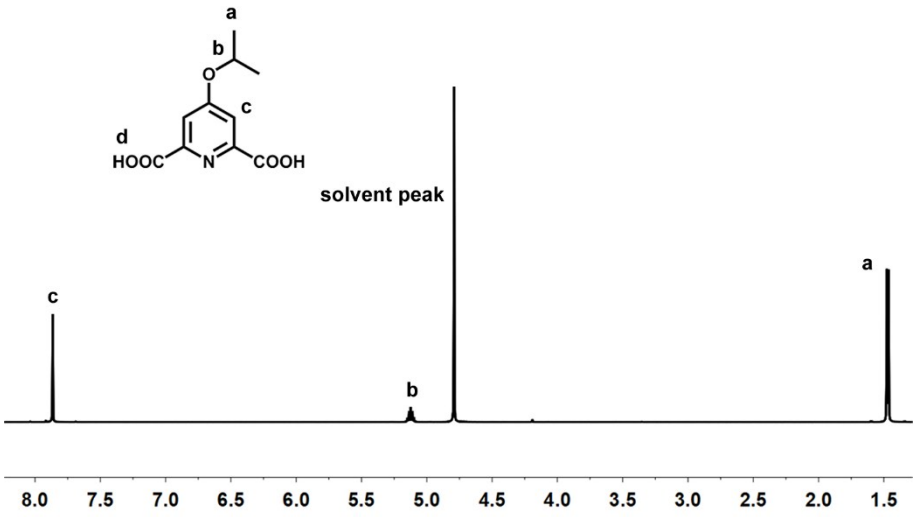


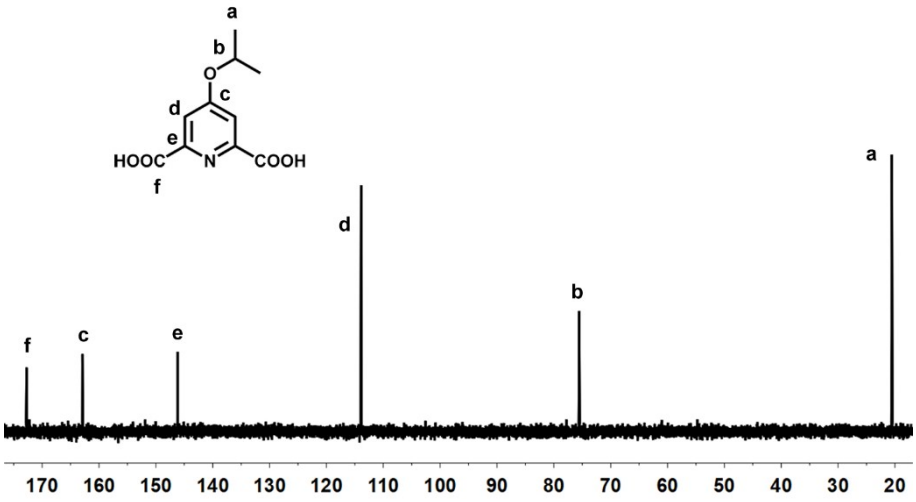
Figure S17. TFIR spectrum of oligomer **1**.

4. Supplementary notes

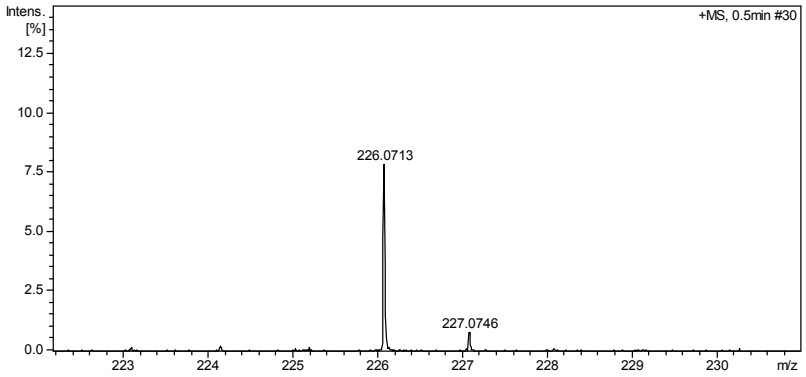
Note S1. NMR and MS spectra of main products.



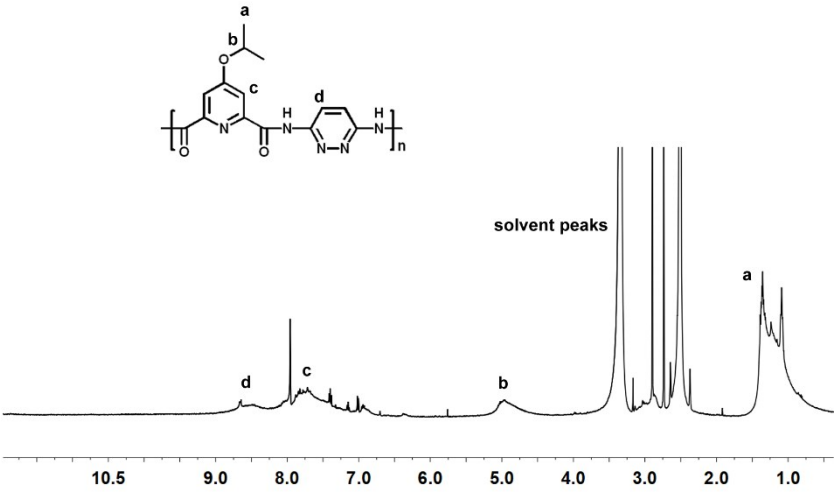
^{1}H NMR of compound **4** in D_2O.



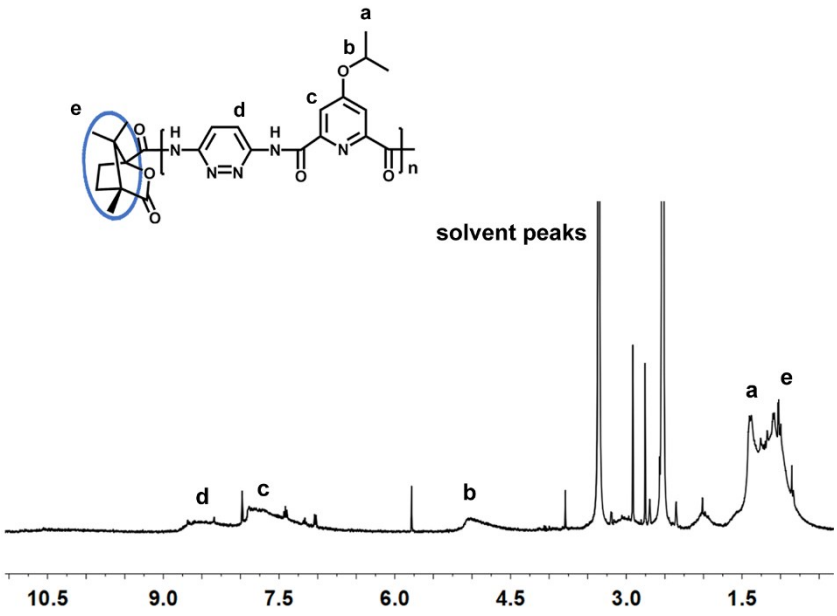
^{13}C NMR of compound **4** in D_2O.



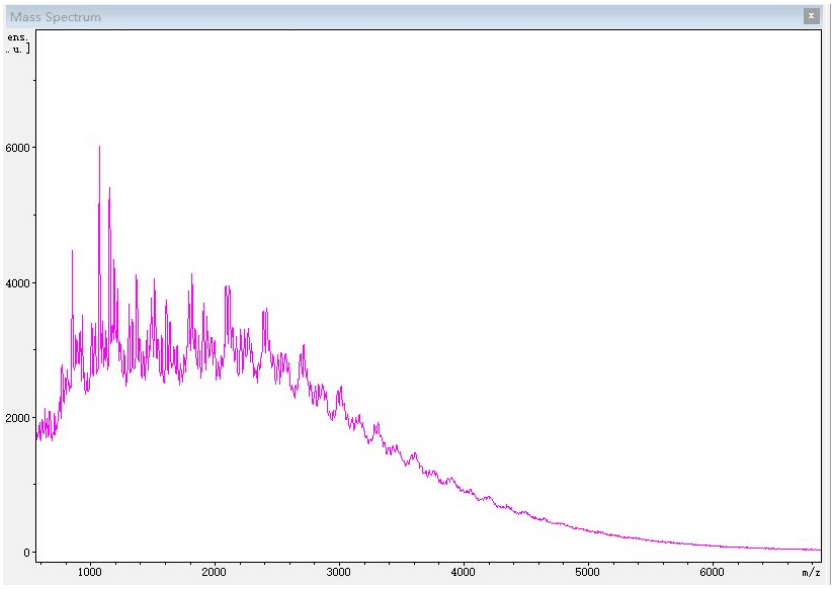
HR-MS (ESI) spectrum of compound **4** in MeCN.



^{1}H NMR spectrum of oligomer **1** in DMSO-*d6* at 293 K.



^{1}H NMR spectrum of oligomer **C-1** in DMSO-*d6* at 293 K.



MALDI-TOF mass spectrum of **C-1** in THF.

Note S2. OM measurements

Optical micrograph was acquired from Olympus Fluoview FV1000. The sample were prepared by depositing a droplet (ca. 5 μL) of the solution of oligomer **1** (in THF, c= 0.5 mg/mL) on a slide glass surface and dried under air flow at room temperature.

Note S3. SEM measurements

SEM micrograph was recorded on FESEM 6700F from JEOL with operating voltage of 10kV. The sample films were prepared by depositing a droplet (ca. 3 μL) of the solution of oligomer **1** (in THF, c= 0.5 mg/mL) on a silicon wafer surface and dried under air flow at room temperature.

Note S4. TEM measurements

TEM micrograph was recorded on a JEM-2100F instrument with an accelerating voltage of 120 kV. Sample for TEM measurement was prepared by depositing a droplet (ca. 3 μL) of the solution of oligomer **1** (in THF, c= 0.5 mg/mL) on a freshly formvar carbon-coated copper surface. The sample was dried under air flow at room temperature.

Note S5. AFM measurements

AFM experiment was performed on a Bruker NanoScope Multimode AFM using the tapping mode. Sample was prepared by depositing a droplet (ca. 3 μL) of the solution of oligomer **1** (in THF, c=0.01 mg/mL) on a silicon wafer surface followed by drying in air.

Note S6. Ion transport with HPTS assay and planer lipid bilayer conductance experiments

The ion transport with HPTS assay and planer lipid bilayer conductance experiments were conducted according to previously reported methods.[2]

5. References

1. C. Lang, X. Deng, F. Yang, B. Yang, W. Wang, S. Qi, X. Zhang, C. Zhang, Z. Dong and J. Liu, *Angew. Chem. Int. Ed.*, 2017, **129**, 12842.
2. C. Lang, W. Li, Z. Dong, X. Zhang, F. Yang, B. Yang, X. Deng, C. Zhang, J. Xu and J. Liu, *Angew. Chem. Int. Ed.*, 2016, **55**, 9723.