

Supporting Information

Fluoride binding modulated supramolecular chirality of urea-containing triarylamine and photo manifestation

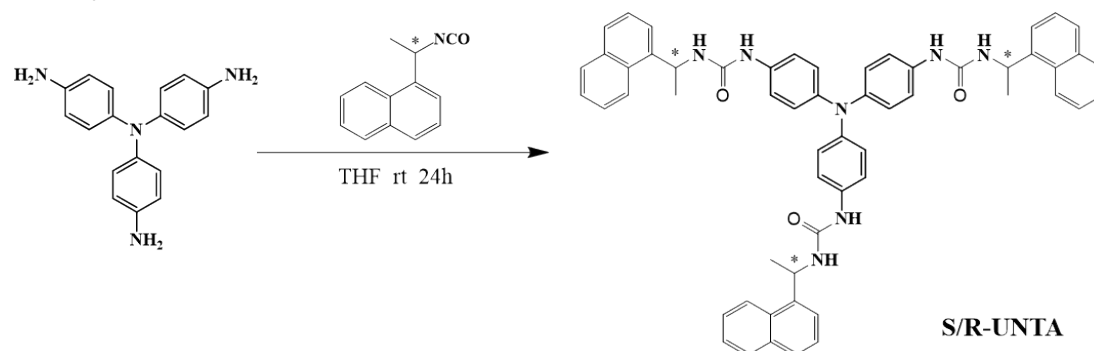
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S1. Synthetic Procedures.



Scheme S1. Synthetic routes of **S/R-UNTA**

S/R-UNTA, 1,1',1''-(nitrilotris(benzene-4,1-diyl))tris(3-(1-(naphthalen-1-yl)ethyl)urea)

Add 4,4',4''-Triaminotriphenylamine (580mg, 2mmol) and (S)-(+)-1-(1-naphthyl) ethyl isocyanate (1305.5mg, 6.6mmol) to a round-bottom flask, followed by the addition of tetrahydrofuran (THF). Heat the mixture under reflux with stirring in an oil bath for 24 hours. Once the reaction is complete, filter and collect the precipitate. Subsequently, recrystallize the filter cake from DMF and DCM, then dry under vacuum for 24 hours to yield a white solid in 65.2% **S-UNTA**. **R-UNTA** was synthesized by following the same procedure as **S-UNTA**, with the exception of using (R)-(-)-1-(1-naphthyl) ethyl isocyanate.

S-UNTA

^1H NMR (400 MHz, DMSO- d_6) δ 8.27 (s, 3H), 8.15 (d, $J = 8.4$ Hz, 3H), 7.94 (d, $J = 7.7$ Hz, 3H), 7.83 (d, $J = 8.0$ Hz, 3H), 7.61 – 7.47 (m, 12H), 7.23 (d, $J = 8.8$ Hz, 6H), 6.78 (d, $J = 8.8$ Hz, 6H), 6.66 (d, $J = 7.9$ Hz, 3H), 5.65 – 5.55 (m, 3H), 1.50 (d, $J = 6.8$ Hz, 9H).

^{13}C NMR (100 MHz, DMSO- d_6) δ 154.84, 142.08, 141.21, 135.52, 133.90, 130.80, 129.11, 127.72, 126.68, 126.08, 124.10, 123.63, 122.51, 119.36, 45.07, 22.64.

MS (MALDI-FTICR MS): m/z (%): 881.41 $[\text{M}]^+$.

R-UNTA

^1H NMR (400 MHz, DMSO- d_6) δ 8.27 (s, 3H), 8.15 (d, $J = 8.4$ Hz, 3H), 7.94 (d, $J = 7.7$ Hz, 3H), 7.83 (d, $J = 8.0$ Hz, 3H), 7.61 – 7.48 (m, 12H), 7.23 (d, $J = 8.8$ Hz, 6H), 6.76 (d, $J = 8.8$ Hz, 6H), 6.66 (d, $J = 7.9$ Hz, 3H), 5.65 – 5.55 (m, 3H), 1.50 (d, $J = 6.8$ Hz, 9H).

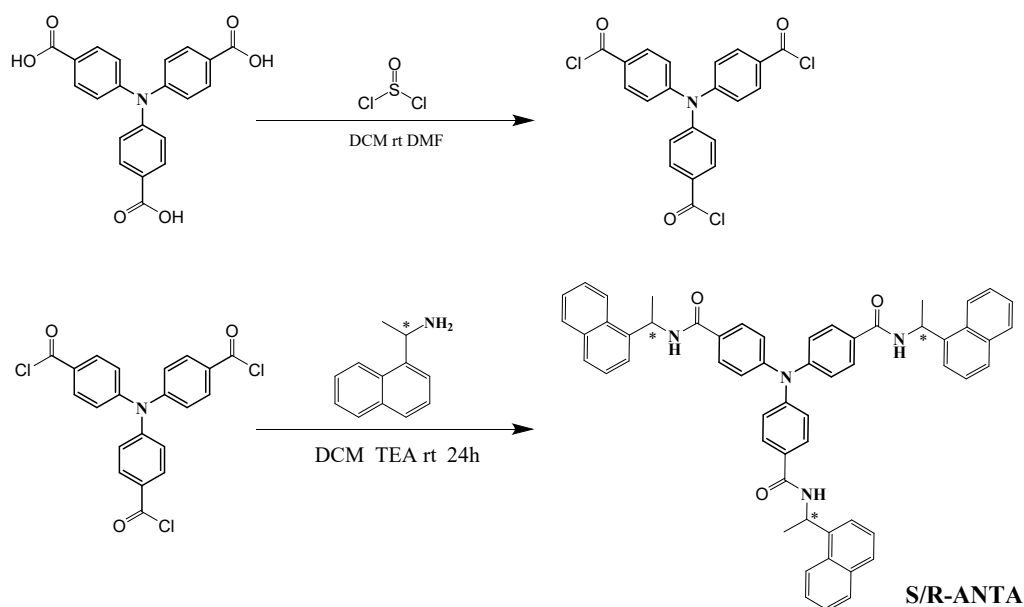
^{13}C NMR (100 MHz, DMSO- d_6) δ 154.83, 142.06, 141.20, 135.53, 133.91, 130.80, 129.14, 127.70, 126.67, 126.08, 125.95, 124.10, 123.63, 122.53, 119.35, 45.06, 22.63.

MS (MALDI-FTICR MS): m/z (%): 881.41 $[\text{M}]^+$.

ANTA, 4,4',4''-nitrilotris(N-(1-(naphthalen-1-yl)ethyl)benzamide)

4,4',4''-Nitrilotribenzoic acid (754 mg, 2 mmol) was dissolved in anhydrous dichloromethane

(60 mL) and treated with oxalyl chloride (1 mL, 11.7 mmol). The resulting solution was stirred at ambient temperature for 24 hours. The organic solvent was then removed under reduced pressure on a rotary evaporator at a temperature not exceeding 40 °C. The residual solid was subsequently dissolved in a minimal volume of anhydrous dichloromethane (5 mL) for subsequent use.



Scheme S2. Synthetic routes of S/R-ANTA

1-(1-Naphthyl) ethylamine (1.367 g, 8 mmol) was dissolved in extra-dry dichloromethane (150 mL) with triethylamine (5 mL) and placed in ice water bath. Add 2 ml DMF as catalyst. The mixture in step 1 was slowly added dropwise, and then stirred at room temperature in dark for 5 days. The dropping process should be completed within half an hour after the preparation of mixture in step 1. Extraction by adding water (Mini Q, 18.2 MΩ·cm), to the reaction solution, the precipitate was collected by filtration. Then the filter cake was recrystallized with DMF and H₂O, dried under vacuum for 24 h. The product yield was 85%.

ANTA

¹H NMR (400 MHz, DMSO) δ 8.84 (s, 3H), 7.89 (s, 18H), 7.56 (d, J = 8.5 Hz, 3H), 7.48 (s, 6H), 7.11 (d, J = 8.6 Hz, 6H), 5.33 (s, 3H), 1.57 (d, J = 7.0 Hz, 9H).

¹³C NMR (100 MHz, DMSO-d₆) δ 165.11, 149.21, 140.84, 133.84, 130.95, 129.79, 129.60, 129.12, 127.72, 126.64, 126.06, 125.93, 123.78, 123.64, 123.07, 45.10, 21.86.

MS (MALDI-TOF): m/z (%): 836.37 [M]⁺.

S1. Supplementary Figures and Data.

Table S1. The incorporation of varying concentrations of F^- results in alterations in the g_{abs} values of the samples.

sample	g_{abs}
R-UNTA	1.17×10^{-4}
R-UNTA- $1.0F^-$	8.76×10^{-4}
R-UNTA- $2.0F^-$	1.51×10^{-3}
R-UNTA- $3.0F^-$	1.72×10^{-3}
R-UNTA- $4.0F^-$	1.78×10^{-3}
R-UNTA- $5.0F^-$	1.76×10^{-3}

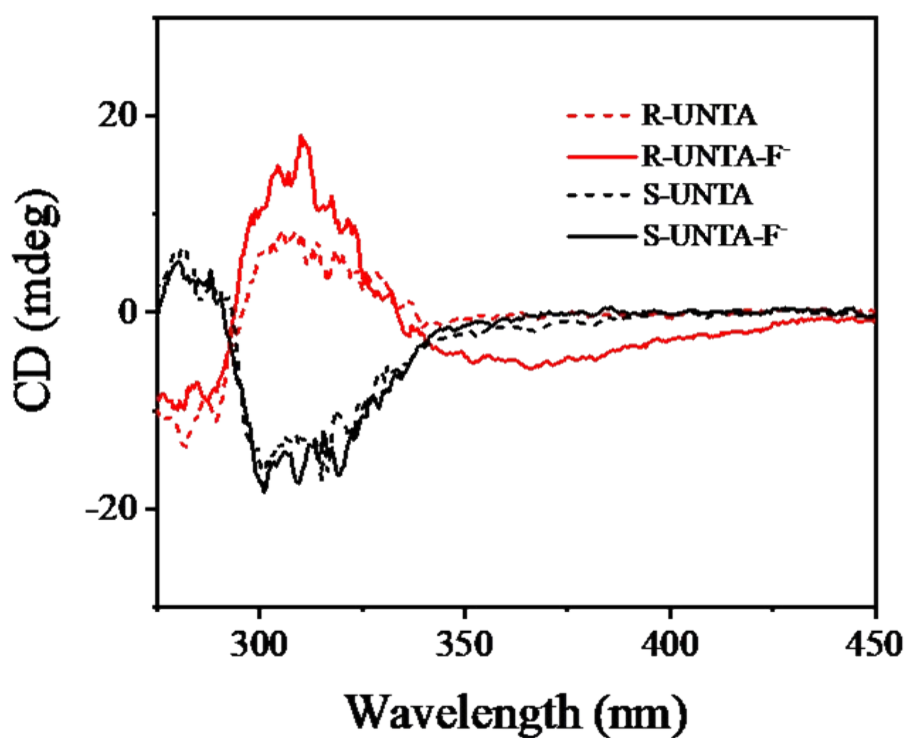


Figure S1. CD spectra of the R-UNTA (red dashed line), S-UNTA (black dashed line), and the R-UNTA co-assembly with F^- (red solid line), S-UNTA co-assembly with F^- (black solid line). (the solvent of DMF: DCM=2:8, concentration of 1×10^{-5} mol/L).

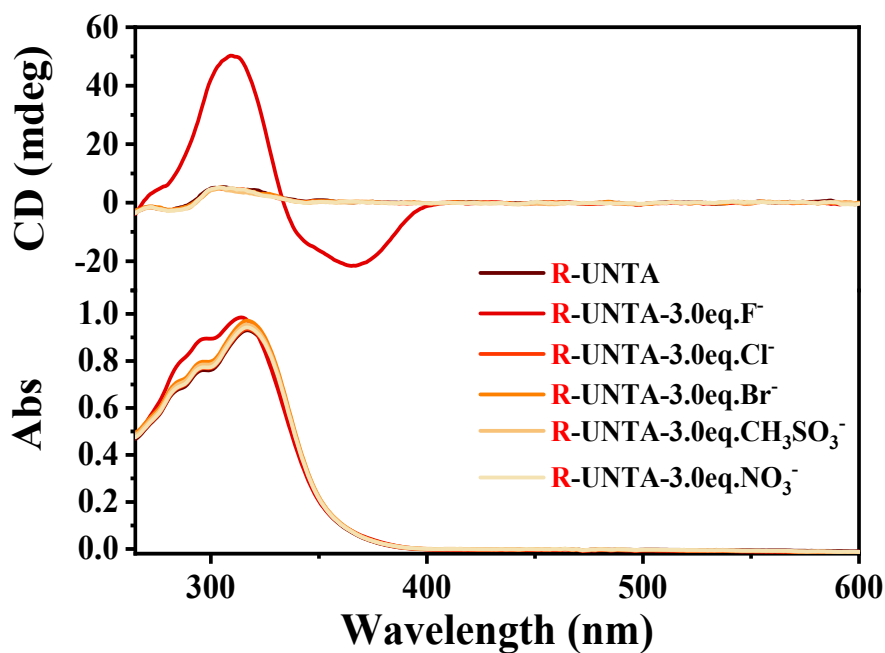


Figure S2. CD spectra of R-UNTA upon the addition of different anions. (DMF: DCM =2:8).

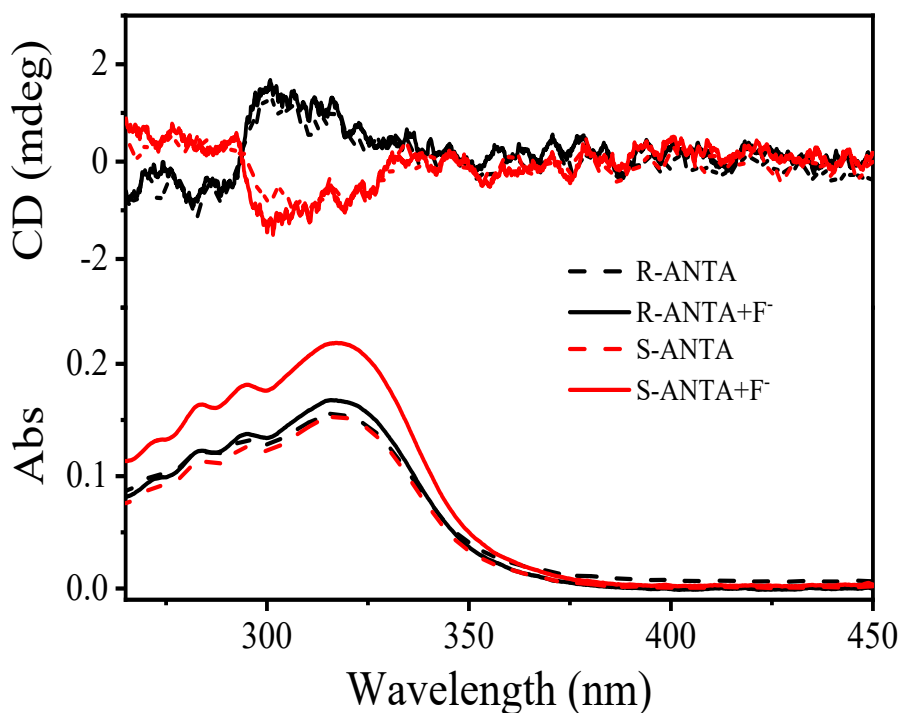


Figure S3. CD spectra of the S-ANTA (red dashed line), R-ANTA (black dashed line), and the S-ANTA co-assembly with F⁻ (red solid line), R-ANTA co-assembly with F⁻ (black solid line). (the solvent of DMF: DCM=2:8, concentration of 1×10^{-3} mol/L).

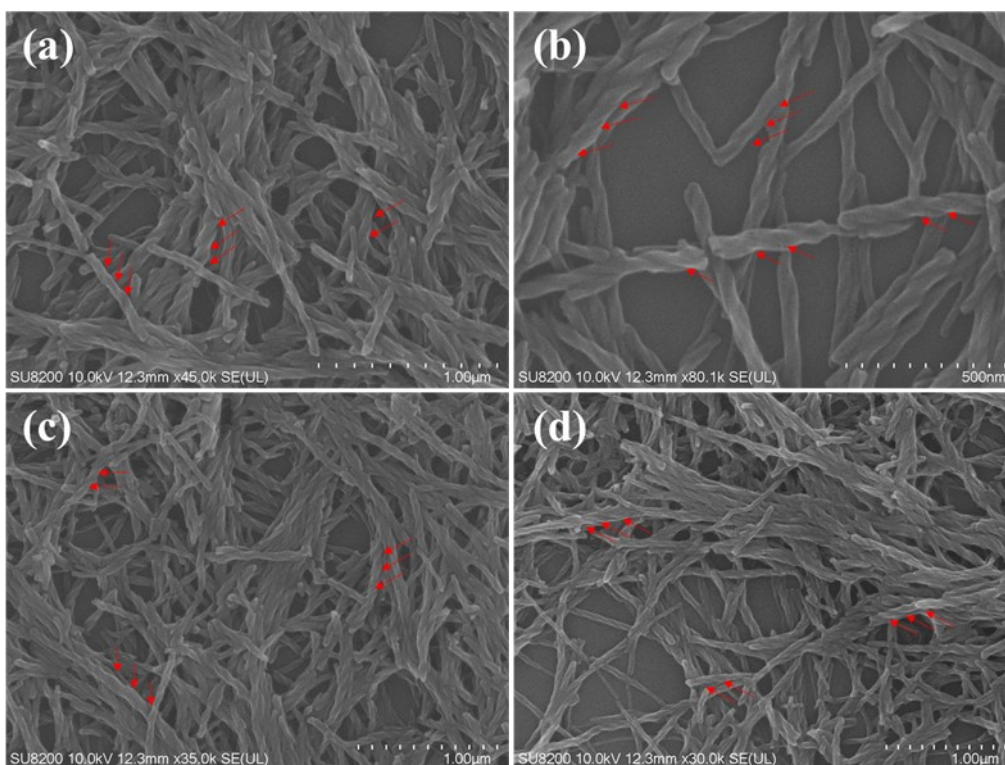


Figure S4. SEM image of (a-d) **R-UNTA** co-assembly with 3eq. F^- (Solvent ratio DMF:DCM=2:8, concentration of **R/S-UNTA** are 5×10^{-4} mol/L)

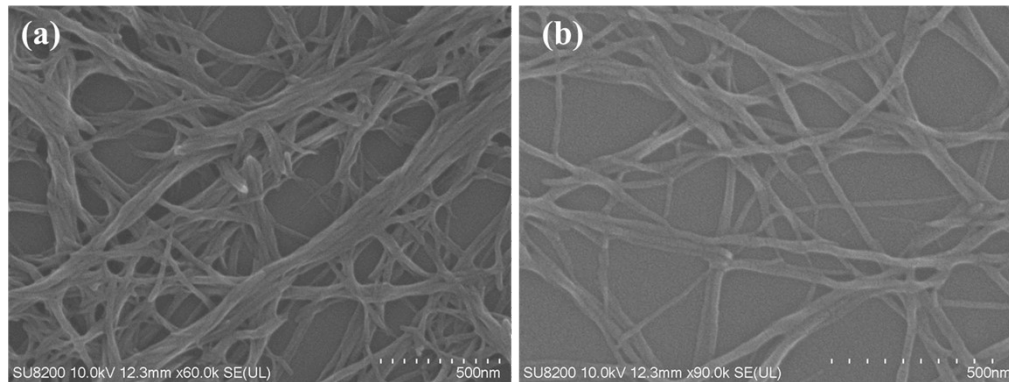


Figure S5. SEM image of (a) **R-UNTA** co-assembly with 0.1eq. F^- , (b) **S-UNTA** co-assembly with 0.01eq. F^- , (Solvent ratio DMF:DCM=2:8, concentration of **R/S-UNTA** are 5×10^{-4} mol/L)

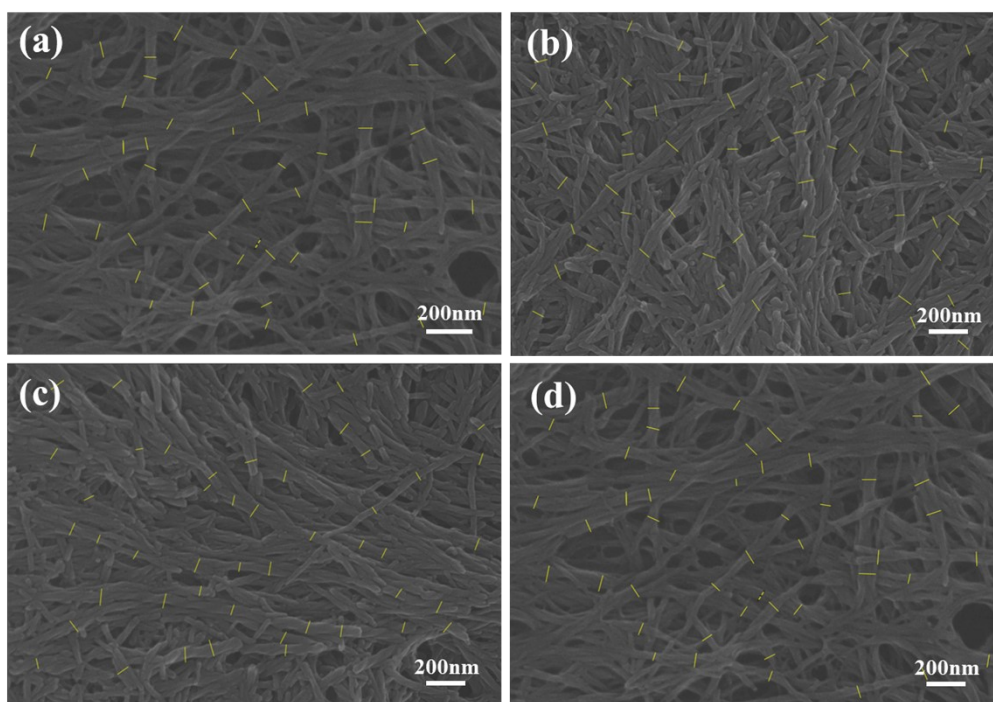


Figure S6. SEM image of (a) (b) **R-UNTA** self-assembly, (c) **R-UNTA/F⁻** co-assembly, (d) **S-UNTA/F⁻** co-assembly

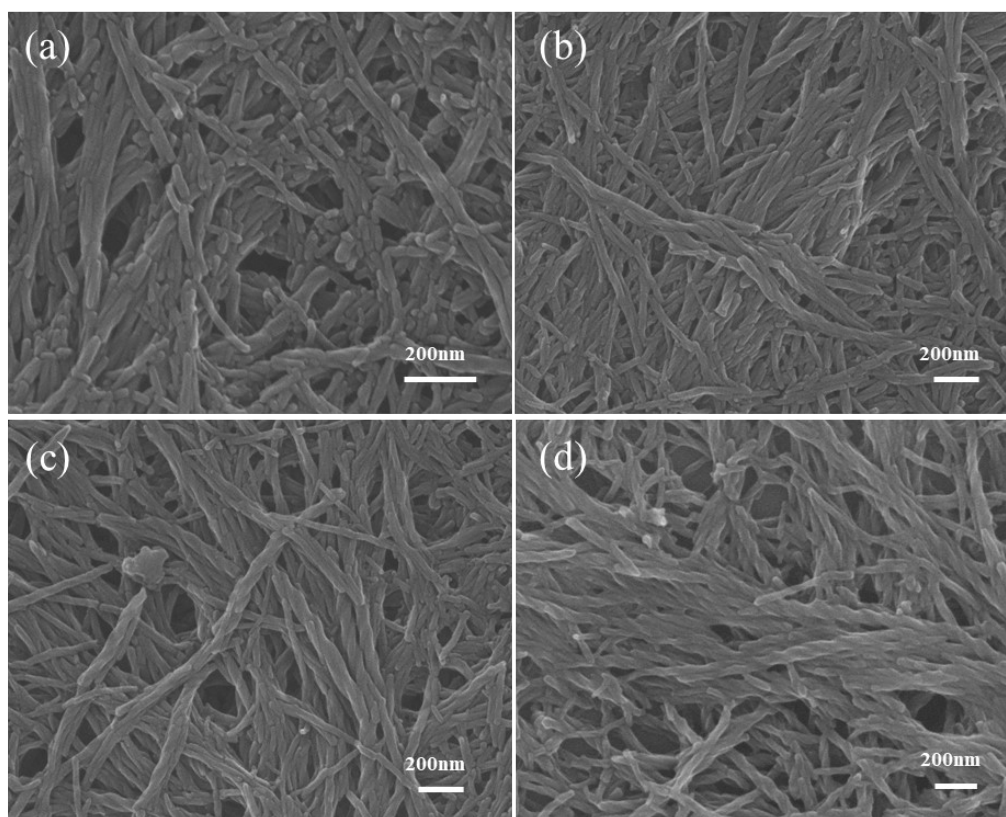


Figure S7 SEM image of **R-UNTA** co-assembly with (a) 0.5eq. F⁻ (b) 1.0 eq. F⁻ (c) 2.0 eq. F⁻ and, (d) 3.0 eq. F⁻.

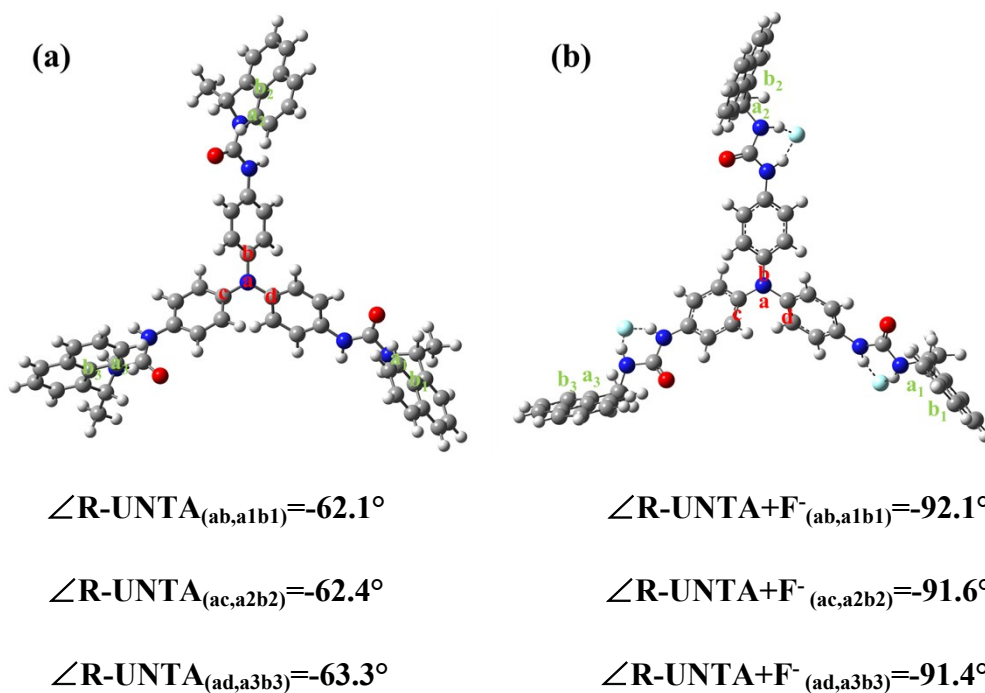


Figure S8. The snapshot of R-UNTA dimer and R-UNTA/F⁻ co-assembly dimer in mixed solvent (DMF: DCM=2:8).¹

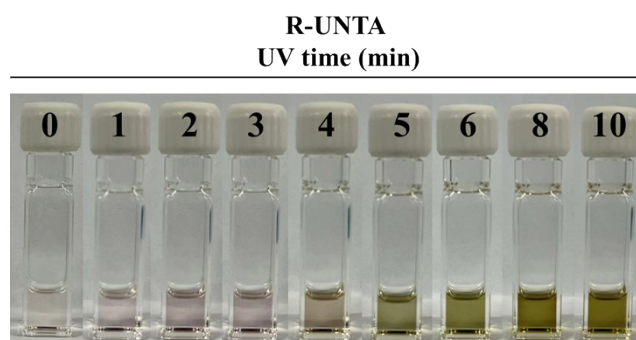


Figure S9. Photo picture of R-UNTA upon UV-irradiation. (concentration of R-UNTA is 1×10^{-3} mol/L, Solvent ratio DMF:DCM=2:8).

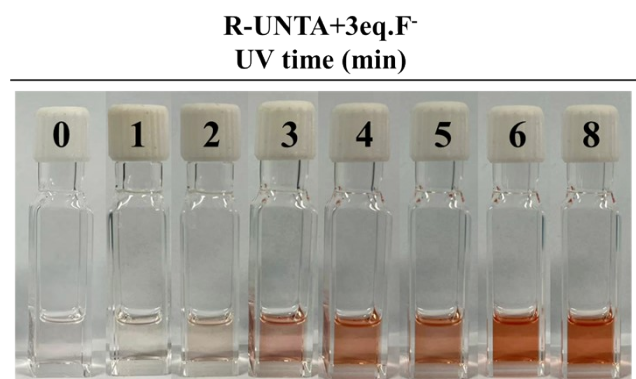


Figure S10. Photo picture of **R-UNTA/F⁻** co-assembly upon UV-irradiation. (concentration of **R-UNTA** is 1×10^{-3} mol/L, Solvent ratio DMF:DCM=2:8).

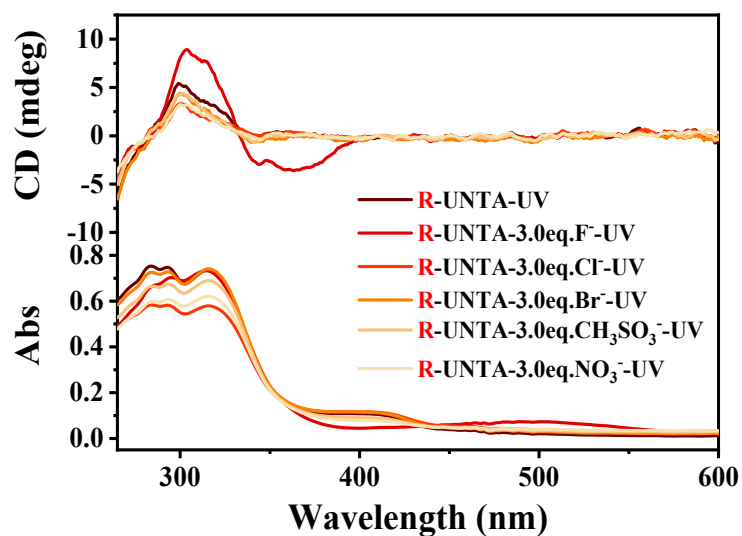


Figure S11. CD spectra of **R-UNTA** after adding different anions and irradiating with 365nm ultraviolet light for 10 minutes. (DMF: DCM =2:8).

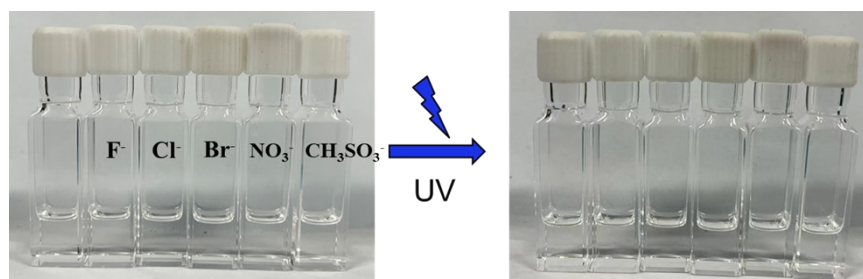


Figure S12. Colorimetric response of **R-UNTA** upon the addition of different anions.

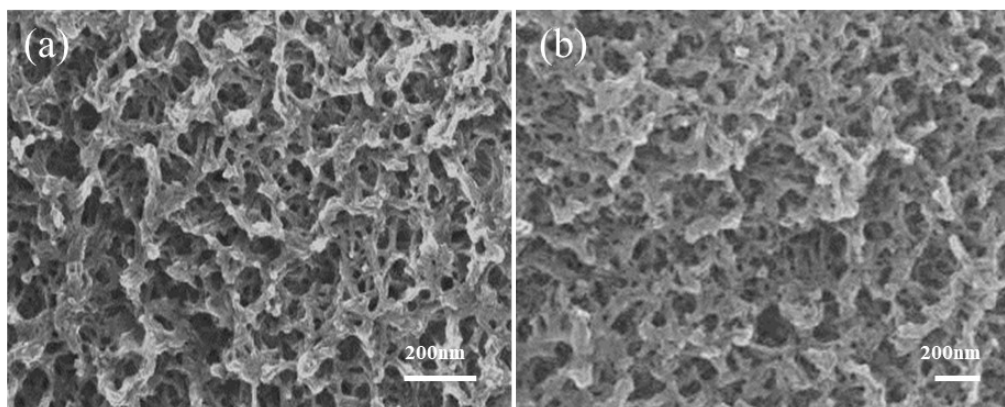


Figure S13. SEM image of **R-UNTA** following exposure to UV irradiation for (a) 10min and (b) 30min.

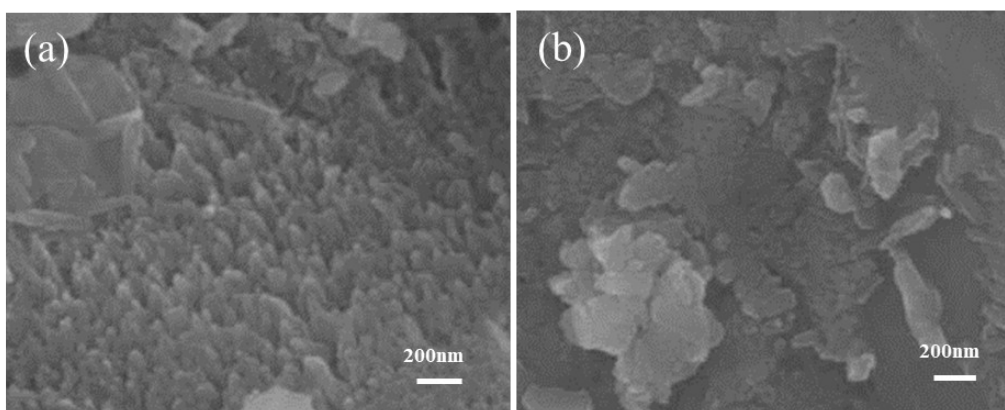


Figure S14. SEM image of **R-UNTA** co-assembly with F^- following exposure to UV irradiation for (a) 10min and (b) 30min.

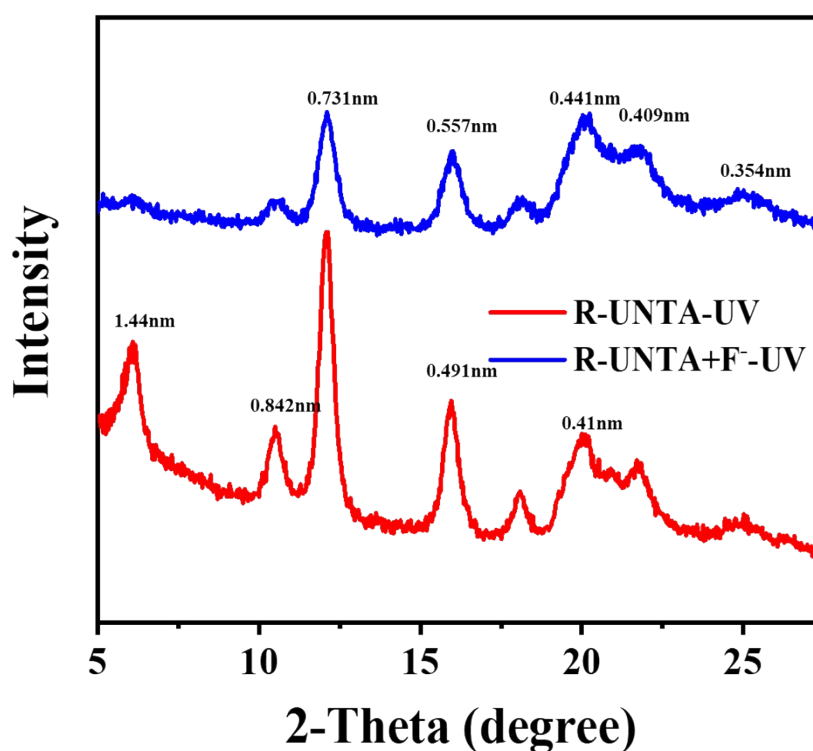


Figure S15. XRD pattern of **R-UNTA** based assembly, **R-UNTA** based assembly and **R-UNTA/F⁻** co-assembly irradiating with 365nm UV.

We subjected the **UNTA** molecules to heat treatment in the solvent and prepared SEM samples while they were still at elevated temperatures. Our SEM analysis revealed that heating induced disassembly of the assembled structures, as shown in Figure S16.

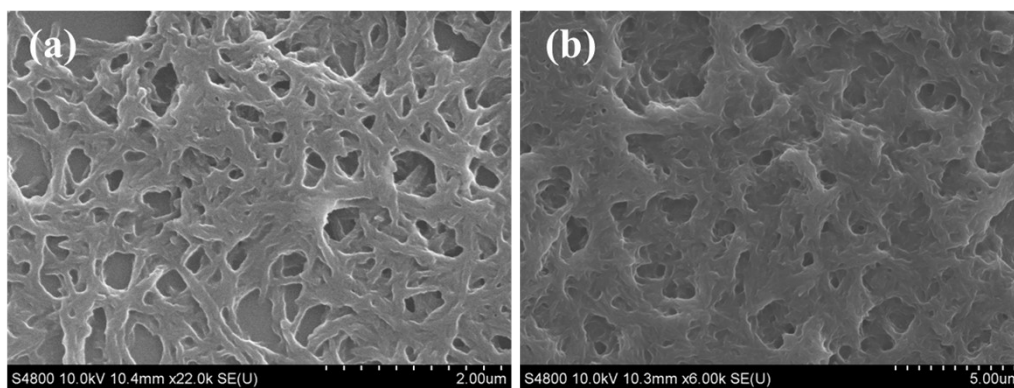


Figure S16. SEM image of (a) **R-UNTA** and 3eq. **F⁻** (b) **S-UNTA** and 3eq. **F⁻** co-assembly. (The sample preparation temperature is 45°C, solvent ratio DMF:DCM=2:8, concentration of **R/S-UNTA** are 5×10^{-4} mol/L).

Moreover, we also added triethylamine and trifluoroacetic acid to the above system, adjusted the pH value of the system, and characterized the SEM morphology. We found that when triethylamine (3eq.) was added, the microstructure of the sample didn't change significantly and remained as a nanofiber structure. However, the morphology was disrupted after the addition of trifluoroacetic acid (3eq.). By adjusting the pH, the microstructure of the assembly can be altered.

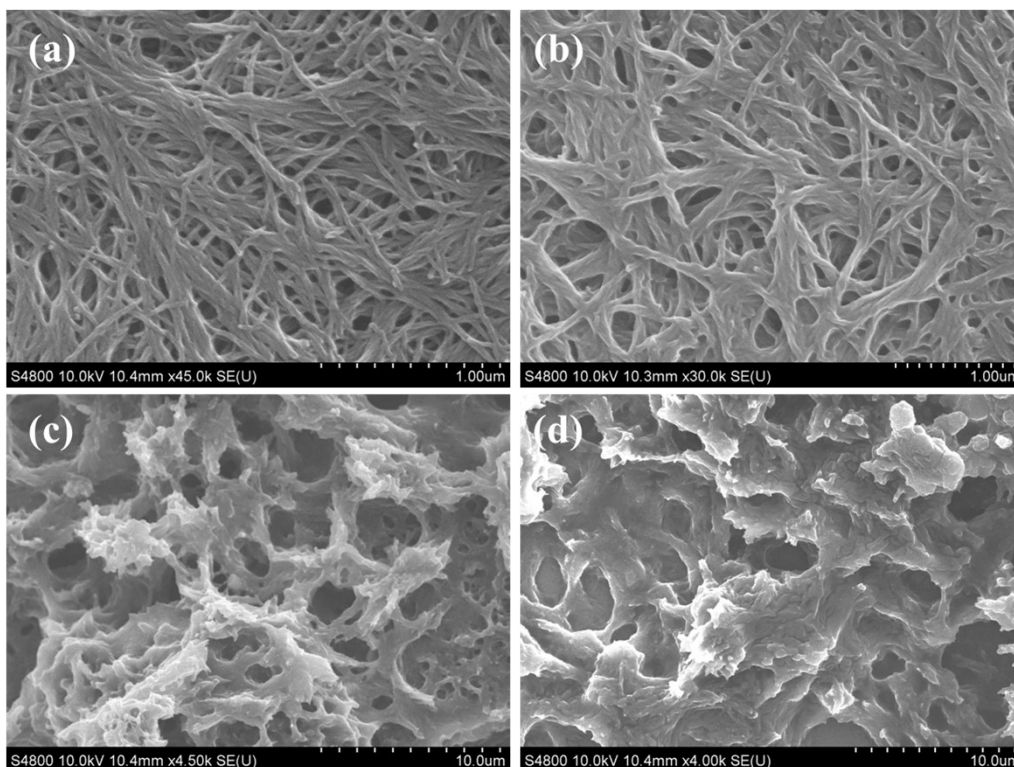


Figure S17. SEM image of (a) **R-UNTA** and 3eq. **F⁻** co-assembly+3eq.TEA, (b) **S-UNTA** and 3eq. **F⁻** co-assembly+3eq.TEA, (c) **R-UNTA** and 3eq. **F⁻** co-assembly+3eq.TFA, (d) **S-UNTA** and 3eq. **F⁻** co-assembly+3eq.TFA (Solvent ratio DMF:DCM=2:8, concentration of **R/S-UNTA** are 5×10^{-4} mol/L).

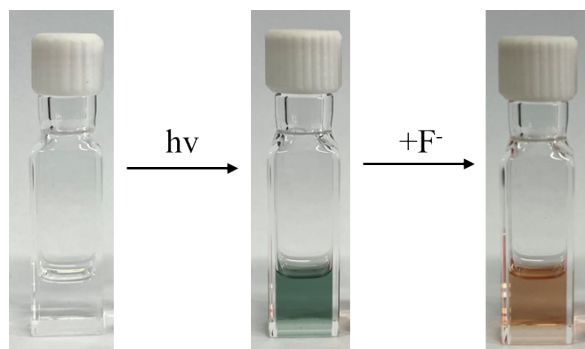


Figure S18. The impact of the sequence in which F^- are introduced to the **R-UNTA** system on the evolution of its chromatic properties.

References

1. M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian 16, Revision A.03, Gaussian, Inc., Wallingford, CT, 2016.