Electronic Supplementary Material (ESI) for Dalton Transactions.

Syntheses of water-soluble acyclic naphthalene oligomers and their applications in water

Yang Wang,[†] Tianyin Liu,[†] Jie Jiang,[†] Yanmei Chen, Moupan Cen, Dou Lu, Leyu Cao, Siyu Sun and Yong Yao*

College of Chemistry and Chemical Engineer, Nantong University, Nantong, Jiangsu, 226019, P.R. China.

Email address: yaoyong1986@ntu.edu.cn.

[†] Yang Wang, Tianyin Liu and Jie Jiang contributed equally to this work.

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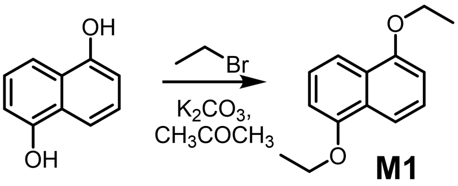
1. Materials/General Methods/Instrumentation

All reagents were commercially available and used as supplied without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratory (Andover, MA). NMR spectra were recorded on a BRUKER VANCE III HD 400 MHz spectrometer. ^{1}H and ^{13}C NMR chemical shifts are reported relative to residual solvent signals. TEM images were obtained using a Philips TECNAI-12 instrument with an accelerating voltage of 120 kV. Mass spectra were recorded on a Micromass Quattro II triple-quadrupole mass spectrometer using electrospray ionization with a MassLynx operating system. UV-vis spectra were taken on a Shimadzu UV-2550 UV-vis spectrophotometer. The fluorescence experiments were conducted on a RF-5301 spectrofluorophotometer (Shimadzu Corporation, Japan).

2. Synthetic Protocols

*2.1 Synthesis of **M1***



1,5-Dihydroxynaphthalene (16.0g, 100 mmol), CH_3CH_2Br (44g, 400 mmol), and K_2CO_3 (27.6g, 200 mmol) were refluxed in 250 mL CH_3COCH_3 over night under N_2 atmosphere . After removal of the inorganic salts by filtration, the solvent was evaporated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, v/v 100:1) to give **M1** as a light yellow solid (19.3 g, 89%). The ^{1}H NMR spectrum of **M1** is shown in Figure S1. ^{1}H NMR ($CDCl_3$, room temperature, 400 MHz) δ (ppm): 7.86 (d, $J = 8$ Hz, 2H), 7.35 (t, $J = 8$ Hz, 2H), 6.82 (d, $J = 8$ Hz, 2H), 4.22-4.16 (m, 4H), 1.54 (t, $J = 8$ Hz, 6H). LR-ESI-MS: m/z 239.1 [**M1** + Na]$^+$.

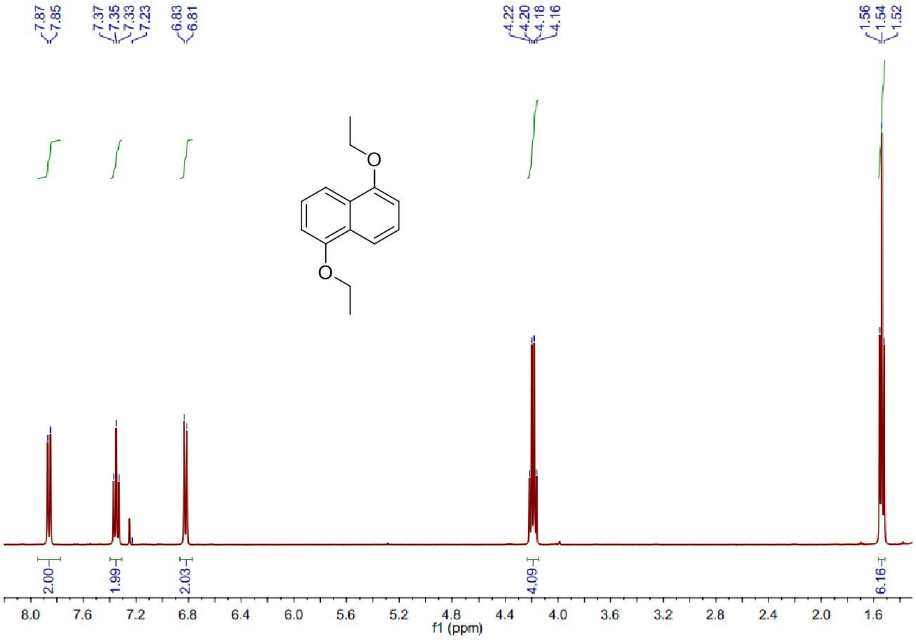
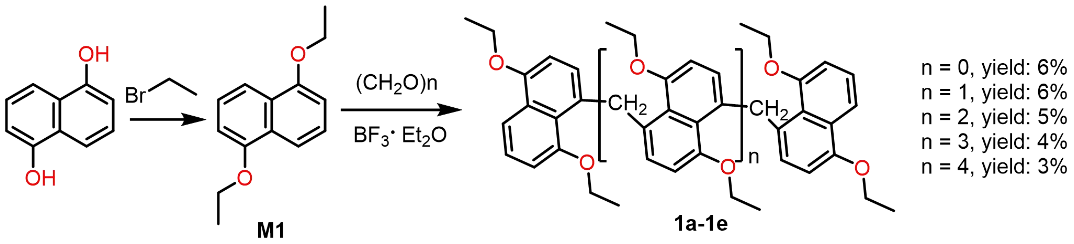


Figure S1. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **M1**.

2.2 Syntheses of ***1a-1e***



A solution of **M1** (5.32 g, 20.0 mmol) and paraformaldehyde (0.6 g, 20 mmol) in dichloromethane (250 mL) was cooled with ice bath. Boron trifluoride etherate (3.26 g, 23.0 mmol) was added to the solution and the mixture was stirred at room temperature for 5 min. The reaction mixture was then washed by water (250 mL × 2) and dried with Na_2SO_4. The solvent was evaporated to provide a crude product, which was purified by column chromatography (eluent: petroleum ether/ethyl acetate, 100:1) to give five solid **1a** (0.274 g, 6%), **1b** (0.272 g, 6%), **1c** (0.22 g, 5%), **1d** (0.18 g, 4%), **1e** (0.13 g, 3%). The proton NMR spectrum of **1a-1e** is shown in Figure S2.

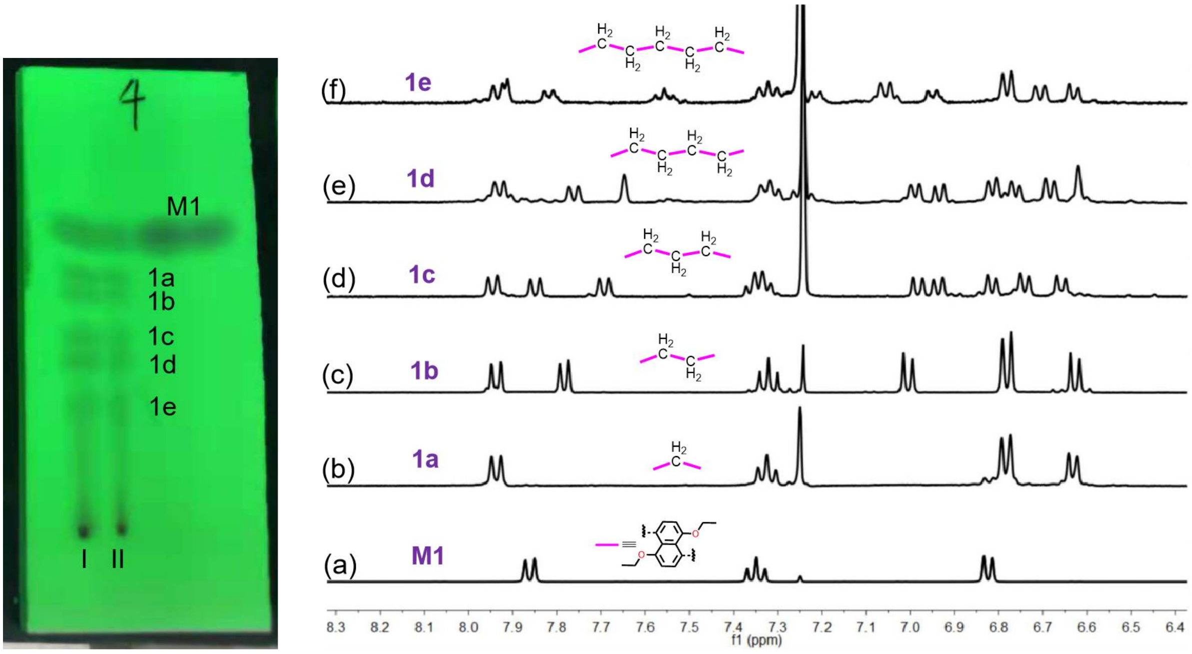
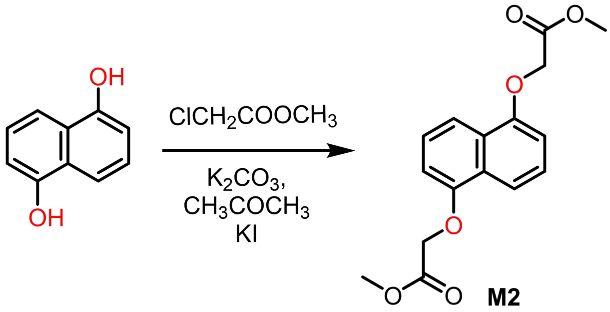


Figure S2. The photo of thin-layer chromatography of the reaction mixture and **M1** (left) and ^{1}H NMR ($CDCl_3$, room temperature, 400 MHz) spectrum of **1a-1e** (right).

Table S1. Total yield of **1a-1e** with different catalysts

Catalyst:	HCl	F_3CCOOH	*p*-TsOH	$FeCl_3$	$ZnCl_2$
Yield:	10%	19%	25%	23%	18%

*2.3 Synthesis of **M2***



1,5-Dihydroxynaphthalene (16.0g, 100 mmol), $ClCH_2COOCH_3$ (43.4g, 400 mmol), and K_2CO_3 (27.6g, 200 mmol) were refluxed in 250 mL CH_3COCH_3 fover night under N_2 atmosphere. After removal of the inorganic salts by filtration, the solvent was evaporated and the residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate, *v*/*v* 10:1) to give **M2** as a light yellow solid (19.3 g, 89%). The ^1H NMR spectrum of **M2** is shown in Figure S3. ^1H NMR ($CDCl_3$, room temperature, 400 MHz) δ (ppm): 7.99 (d, J = 8 Hz, 2H), 7.37 (t, J = 8 Hz, 2H), 6.76 (d, J = 8 Hz, 2H), 4.82 (s, 4H), 3.83 (s, 6H). LR-ESI-MS: m/z 327.2 [**M2** + Na]$^+$.

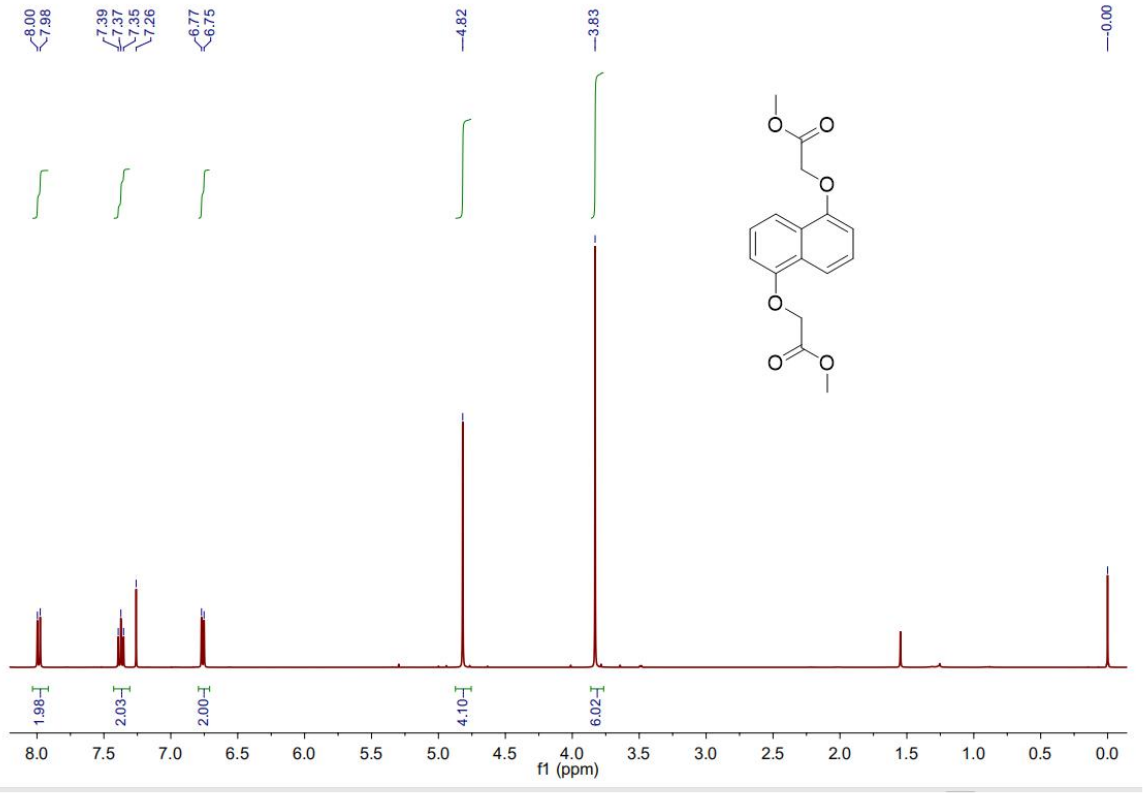
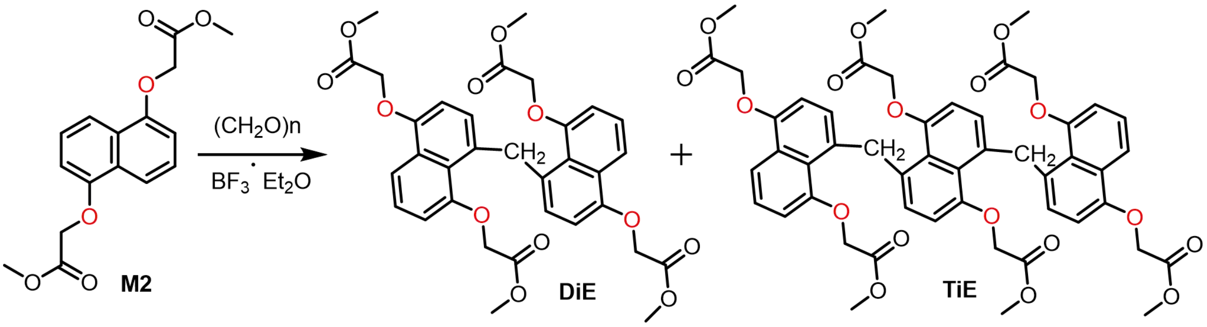


Figure S3. ^1H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **M2**.

2.4 Syntheses of ***DiE*** *and* ***TiE***



A solution of **M2** (5.32 g, 20.0 mmol) and paraformaldehyde (0.6 g, 20 mmol) in dichloromethane (250 mL) was cooled with ice bath. Boron trifluoride etherate (3.26 g, 23.0 mmol) was added to the solution and the mixture was stirred at room temperature for 5 min. The reaction mixture was then washed by water (250 mL × 2) and dried with Na_2SO_4. The solvent was evaporated to provide a crude product, which was purified by column chromatography (eluent: petroleum ether/ethyl acetate, 10:1) to give two solid **DiE** (2.6 g, 42%), **TiE** (1.43 g, 23%). The ^{1}H NMR spectrum of **DiE** is shown in Figure S4. ^{1}H NMR ($CDCl_3$, room temperature, 400 MHz) δ (ppm): 8.09-8.06 (m, 2H), 7.35 (t, J = 8 Hz, 2H), 6.83 (d, J = 8 Hz, 2H), 6.74 (d, J = 8 Hz, 2H), 6.57 (d, J = 8 Hz, 2H), 5.36 (s, 2H), 4.76 (s, 4H), 4.44 (s, 4H), 3.81 (s, 6H), 3.57 (s, 6H). The ^{13}C NMR spectrum of **DiE** is shown in Figure S5. ^{13}C NMR (100 MHz, $CDCl_3$, 293K) δ (ppm): 169.44, 169.26, 155.96, 151.62, 132.58, 128.20, 127.56, 125.91, 124.97, 116.24, 108.07, 105.73, 66.10, 65.76, 52.24, 51.94, 43.27. The ^{1}H NMR spectrum of **TiE** is shown in Figure S6. ^{1}H NMR ($CDCl_3$, room temperature, 400 MHz) δ (ppm): 8.07 (d, J = 8Hz, 2H), 7.35 (t, J = 8Hz, 2H), 6.88 (d, J = 8Hz, 2H), 6.82-6.74 (m, 4H), 6.56 (t, J = 8Hz, 4H), 5.39 (s, 4H), 4.49 (s, 4H), 4.30 (s, 4H), 3.81 (s, 6H), 3.66 (s, 6H), 3.52 (s, 6H). The ^{13}C NMR spectrum of **TiE** is shown in Figure S7. ^{13}C NMR (100 MHz, $CDCl_3$, 293K) δ (ppm): 169.46, 169.35, 156.05, 154.26, 151.50, 133.17, 132.66, 128.27, 128.17, 127.59, 127.19, 125.78, 124.94, 116.20, 107.92, 105.73, 66.17, 66.04, 65.78, 52.23, 52.05, 51.85, 44.05. LR-ESI-MS of **DiE** is shown in Figure S8: m/z 659.0 [**DiE** + K]$^{+}$. LR-ESI-MS of **TiE** is shown in Figure S9: m/z 959.3 [**TiE** + Na]$^{+}$ (100%).

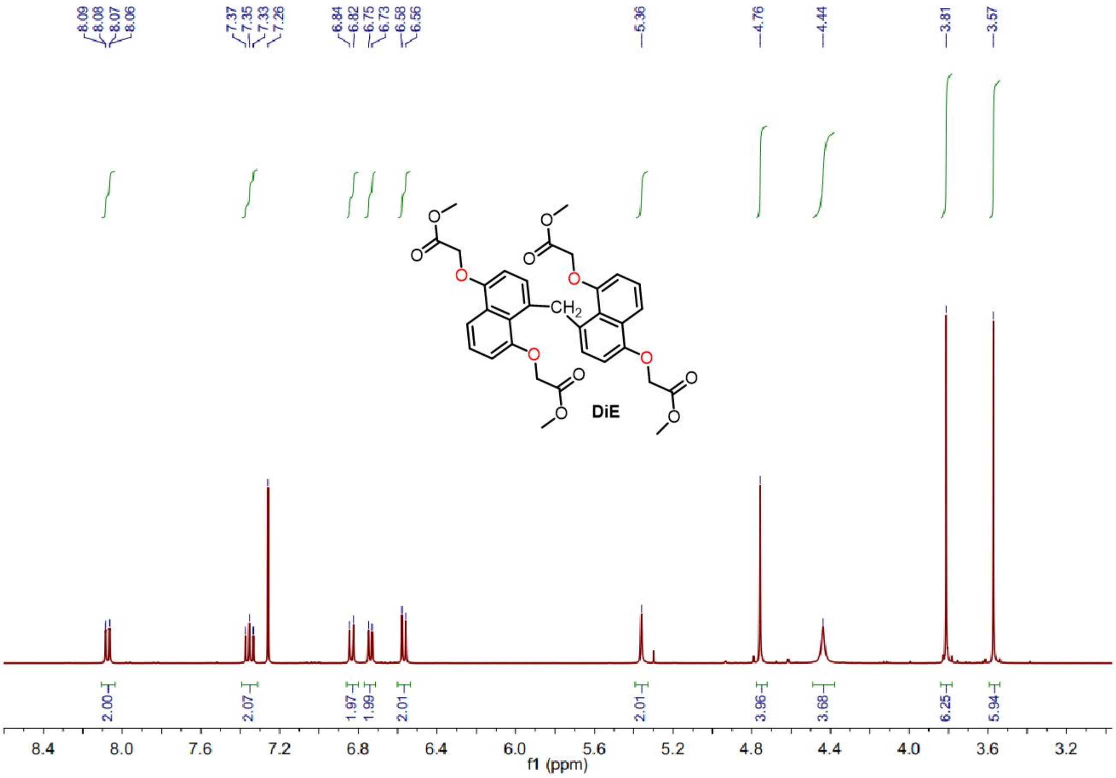


Figure S4. ^{1}H NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **DiE**.

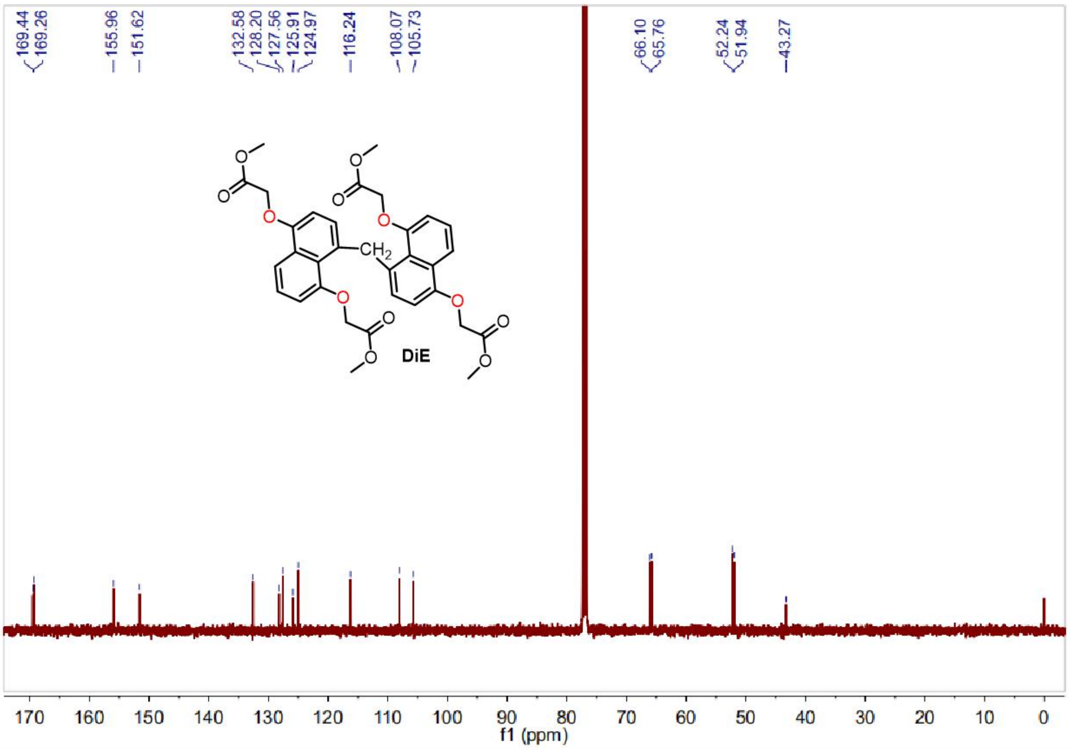


Figure S5. ^{13}C NMR spectrum ($CDCl_3$, room temperature, 400 MHz) of **DiE**.

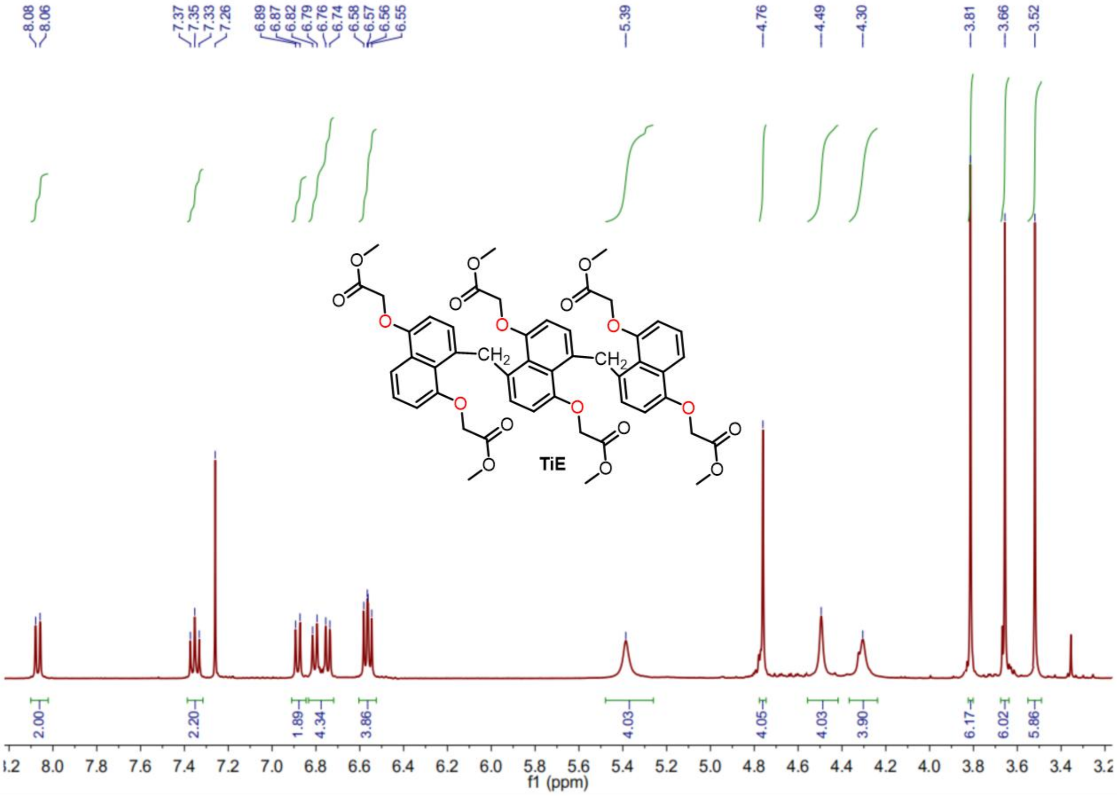


Figure S6. ^{1}H NMR spectrum (acetone, room temperature, 400 MHz) of **TiE**.

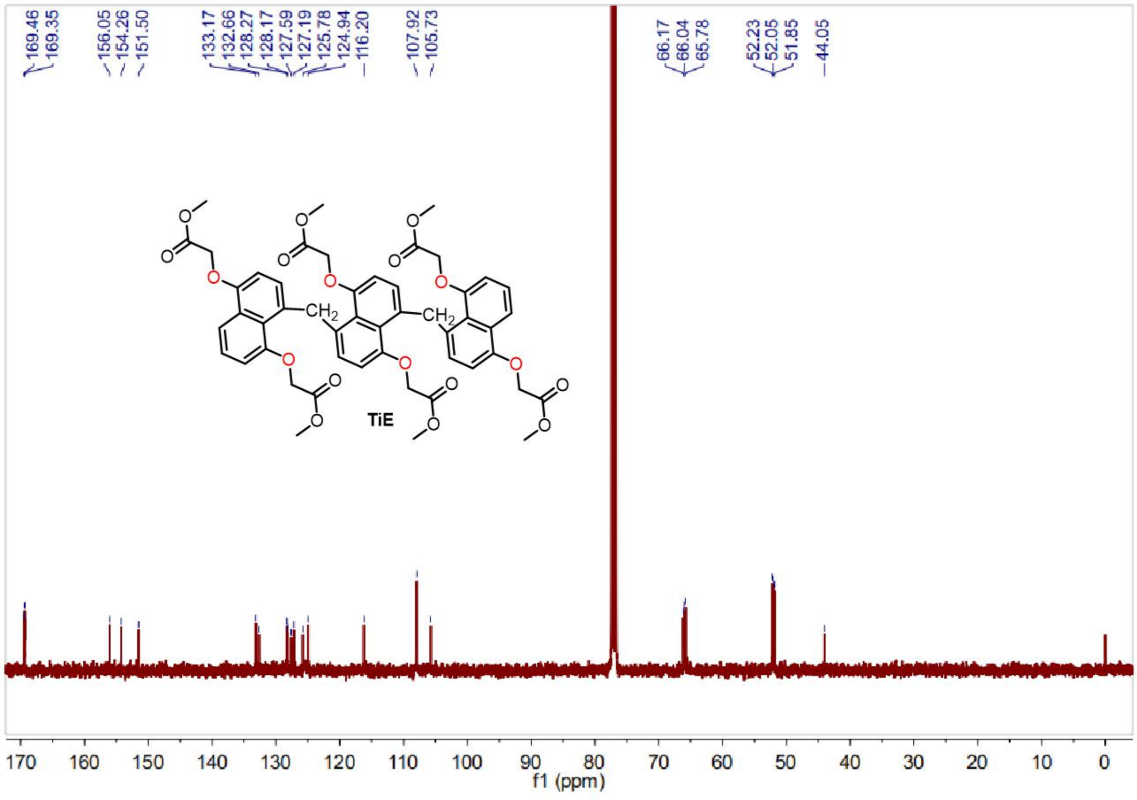


Figure S7. ^{13}C NMR spectrum (CDCl$_3$, room temperature, 400 MHz) of **TiE**.

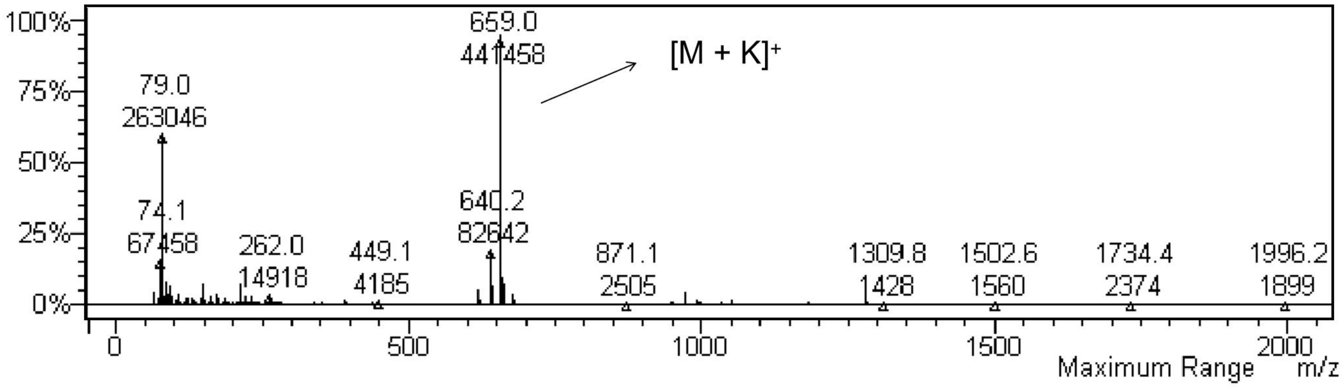


Figure S8. Electrospray ionization mass spectrum of **DiE**. Assignment of main peak: m/z 659.0 $[M + K]^{+}$(100%)

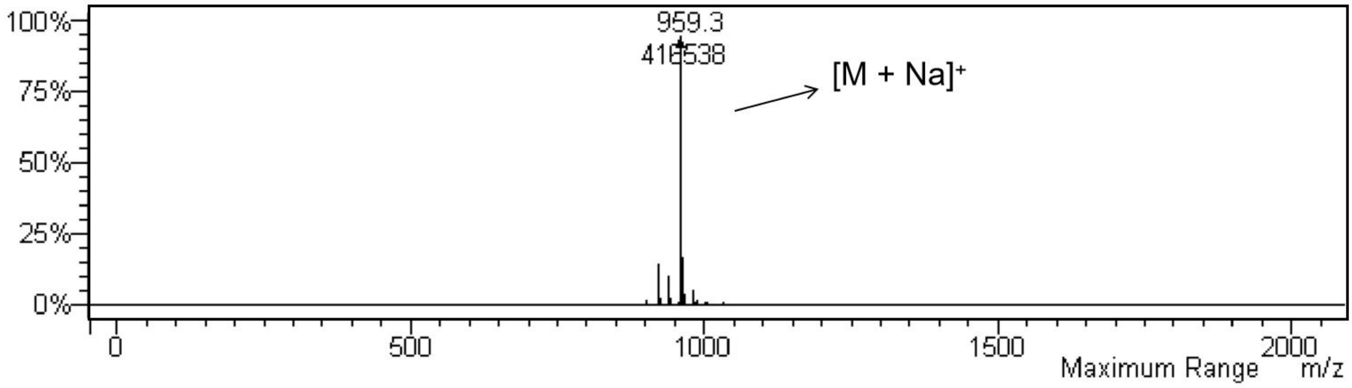
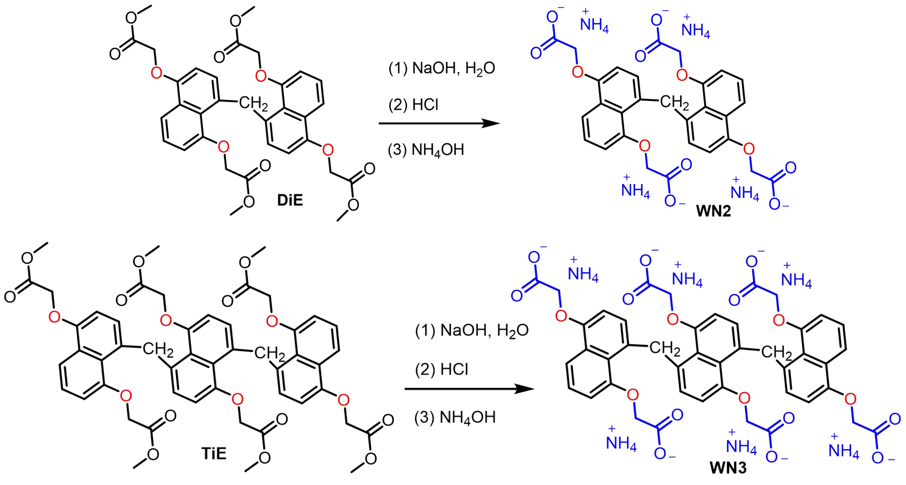


Figure S9. Electrospray ionization mass spectrum of **TiE**. Assignment of main peak: m/z 959.3. $[M + Na]^{+}$(100%)

*2.5 Syntheses of **WN2** and **WN3***



Compound **DiE** (0.2 g, 0.322 mmol), NaOH (0.300 g) and water (50 mL)were refluxed for 24 h. To the solution, diluted aqueous HCl was added. The precipitated solid was collected by filtration. The solid was washed with water several times and dried under reduced pressure. Then aqueous ammonia solution (0.30 mL) was added. The heterogeneous suspension became a homogeneous solution by adding aqueous ammonia solution. The resulting solution was evaporated to give the salt **WN2**, quantitatively. The ^{1}H NMR spectrum of **WN2** is shown in Figure S10. ^{1}H NMR (D_2O, 400 MHz, ppm): δ 7.92 (d, *J* = 8Hz, 2H), 7.34 (t, *J* = 8 Hz, 2H), 6.79 (d, *J* = 8 Hz, 2H), 6.72 (d, *J* = 8 Hz, 2H), 6.57 (d, *J* = 8 Hz, 2H), 5.20 (s, 2H), 4.50 (s, 4H), 4.07 (s, 4H). The ^{13}C NMR spectrum of **WN2** is shown in Figure S11. ^{13}C NMR (D_2O, 100 MHz, ppm): δ 176.91, 156.38, 151.62, 132.03, 127.79, 127.57, 125.67, 125.38, 115.10, 108.87, 105.92, 67.91, 67.31, 42.43. LR-ESI-MS of **WN2** is shown in Figure S14: m/z 298.5 [**WN2** - 2 NH_4]$^{2-}$, 192.7 [**WN2** - 3 NH_4]$^{3-}$. HR-ESI-MS: m/z calcd for [**WN2** - 2 NH_4]$^{2-}$ C29H28N2O12, 298.0827; found, 298.0809; error -6 ppm.

Compound **TiE** (0.2 g, 0.213 mmol), NaOH (0.300 g) and water (50 mL)were refluxed for 24 h. To the solution, diluted aqueous HCl was added. The precipitated solid was collected by filtration. The solid was washed with water several times and dried under reduced pressure. Then aqueous ammonia solution (0.30 mL) was added. The heterogeneous suspension became a homogeneous solution by adding aqueous ammonia solution. The resulting solution was evaporated to give the salt **WN3**, quantitatively. The ^{1}H NMR spectrum of **WN3** is shown in Figure S12. ^{1}H NMR (D_2O, 400 MHz, ppm): δ 7.42-7.16 (m, 6H), 6.78-6.53 (m, 8H), 5.17 (s, 2H), 4.56 (s, 8H), 4.39 (s, 4H), 4.17 (s, 2H). The ^{13}C NMR spectrum of **WN3** is shown in Figure S13. ^{13}C NMR (D_2O, 100 MHz, ppm): δ 176.83, 157.27, 155.07, 154.90, 152.03, 151.82, 137.09, 131.78, 129.18, 127.19, 126.99, 125.29, 125.10, 115.83, 109.35, 108.73, 107.57, 105.28, 105.02, 71.50, 68.10, 67.55, 67.04, 66.88, 42.83, 35.65. LR-ESI-MS of **WN3** is shown in Figure S15: m/z 458.6 [M - 2 NH_4]$^{2-}$(100%), 300.1 [M - 3 NH_4]$^{3-}$, 220.6 [M - 4NH_4]$^{4-}$. HR-ESI-MS: m/z calcd for [**WN3** - 3 NH_4]$^{3-}$ C44H42N3O18, 300.0827; found, 300.0831; error 1.3 ppm.

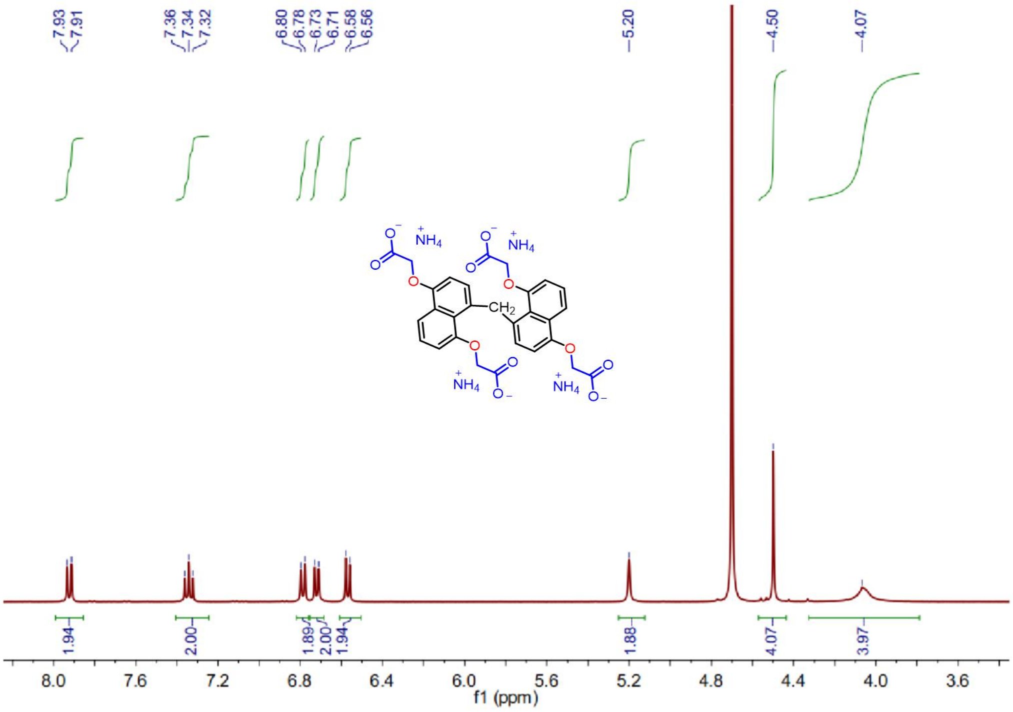


Fig. S10. ^{1}H NMR spectrum (D_2O, room temperature, 400 MHz) of **WN2**.

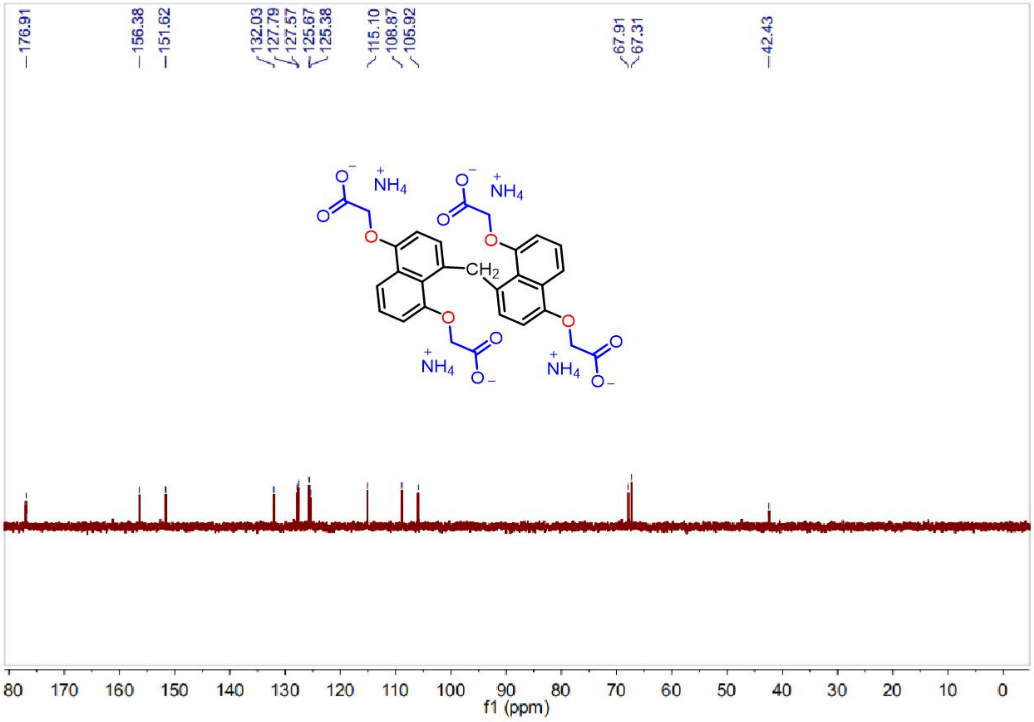


Fig. S11. ^{13}C NMR spectrum (D_2O, room temperature, 100 MHz) of **WN2**.

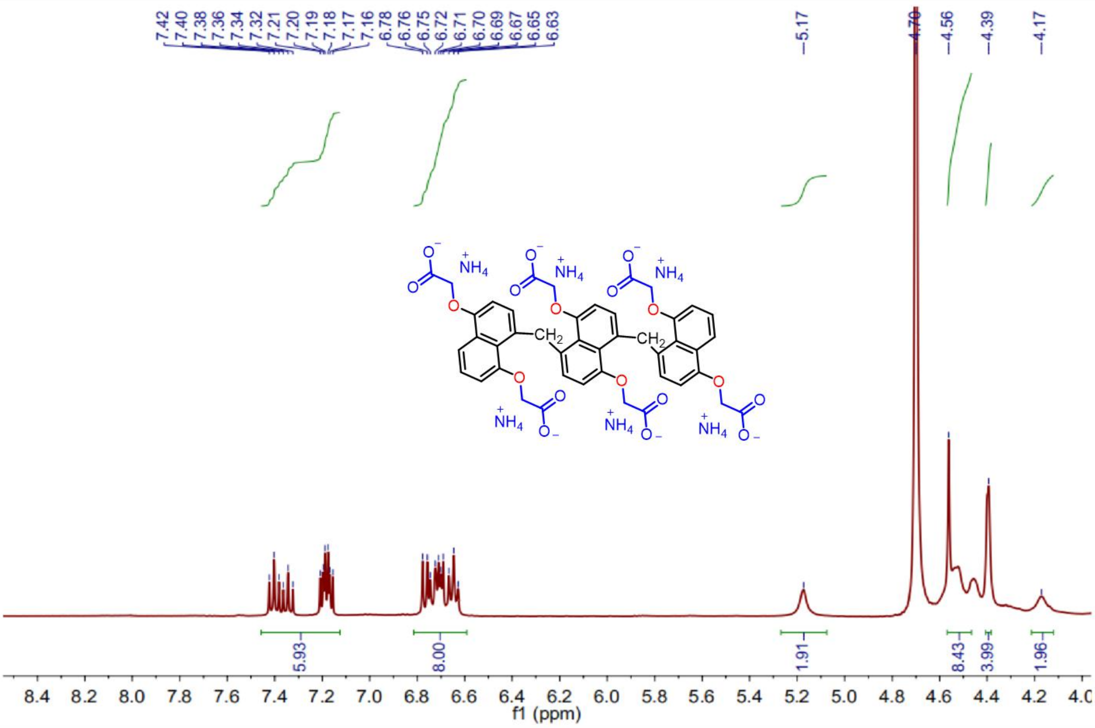


Fig. S12. ^{1}H NMR spectrum (D_2O, room temperature, 400 MHz) of **WN3**.

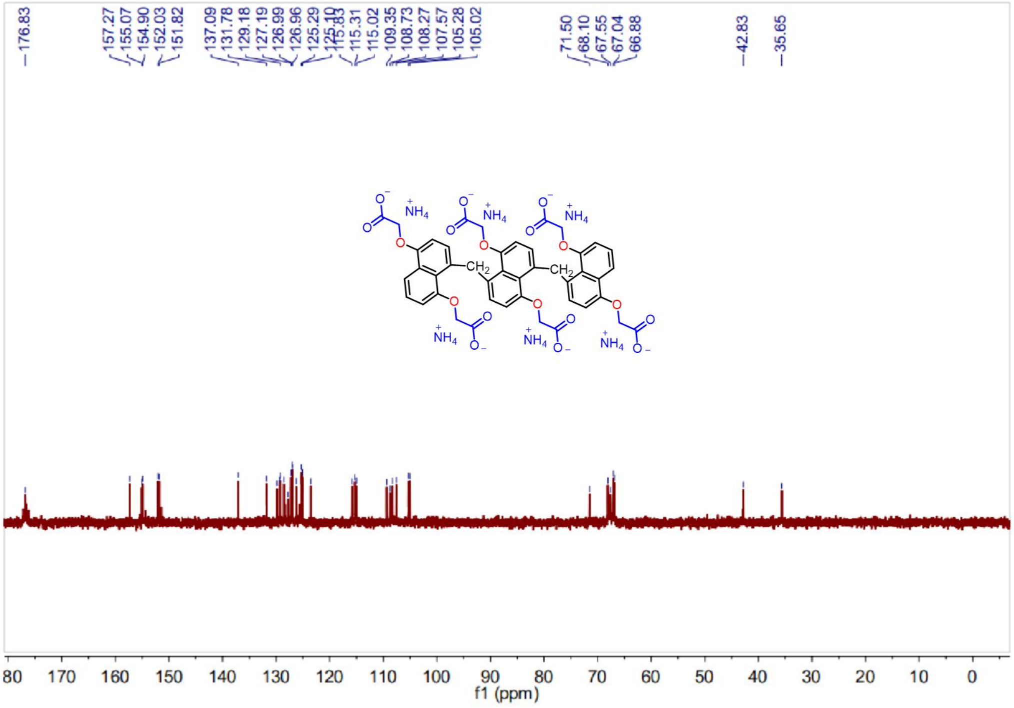


Fig. S13. ^{13}C NMR spectrum (D_2O, room temperature, 100 MHz) of **WN3**.

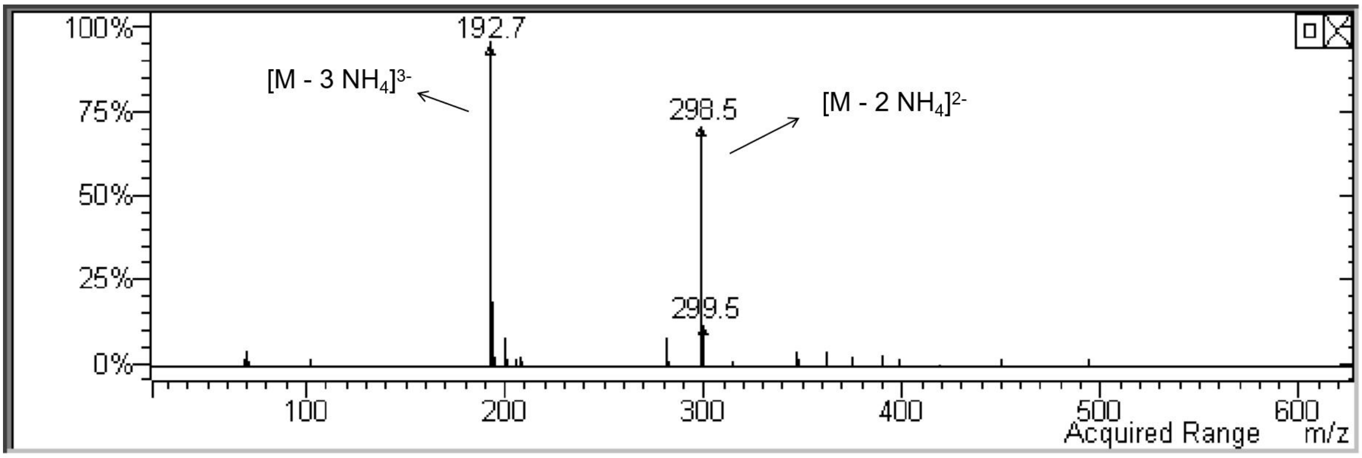


Figure S14. Electrospray ionization mass spectrum of **WN2**. Assignment of main peak: m/z 192.7 $[M - 3\ NH_4]^{3-}$ (100%), 298.5 $[M - 2NH_4]^{2-}$.

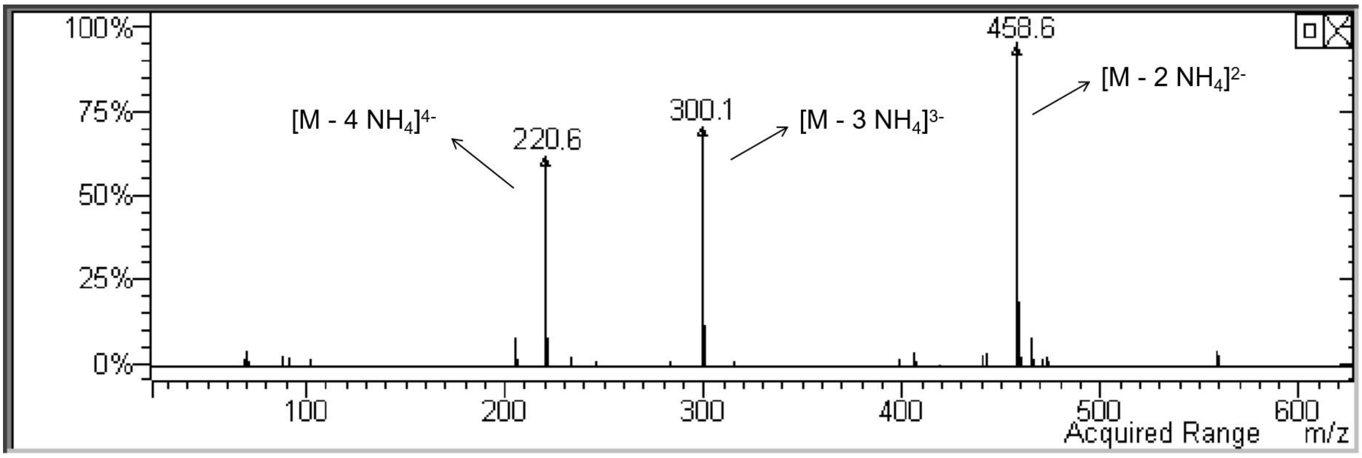


Figure S15. Electrospray ionization mass spectrum of **WN3**. Assignment of main peak: m/z 458.6 $[M - 2\ NH_4]^{2-}$ (100%), 300.1 $[M - 3\ NH_4]^{3-}$, 220.6 $[M - 4NH_4]^{4-}$.

3. X-ray single-crystal datas of DiE

Crystallographic data: block, colorless, 0.32 × 0.28 × 0.31 mm^3, $C_{33}H_{32}O_{12}$, *FW* 620.58, monoclinic, space group $P\ 2_1/n$, a = 11.823(2) , b = 24.855(4) , c = 10.5044(16) Å, α = 90°, β = 100.333(6)°, γ = 90°, V = 3036.7(9) Å^3, Z = 4, D_c = 1.357 g cm^{-3}, T = 296 (2) K, μ = 0.104 mm^{-1}, 28435 measured reflections, 5954 independent reflections, 410 parameters, 7 restraints, $F(000)$ = 1304, $R(\text{int})$ = 0.0826, R_1 = 0.1638, wR_1 = 0.1628 (all data), R_2 = 0.0644, wR_2 = 0.1295 $[I > 2\sigma(I)]$, max. residual density 1.009 e•Å^{-3}, and goodness-of-fit (F^2) = 1.016.

4. Disperse of multi-wall nanotubes in water

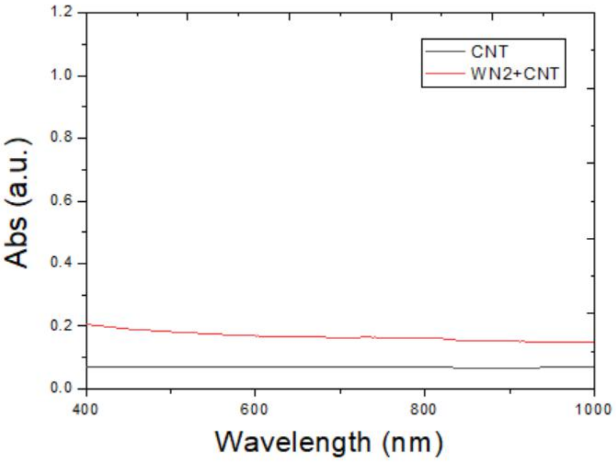


Fig. S16 UV-Vis-NIR spectra ([**WN2**] = 1 mg/10mL) of the aqueous solution of **CNT** (black line), **WN2&CNT** (blue line).

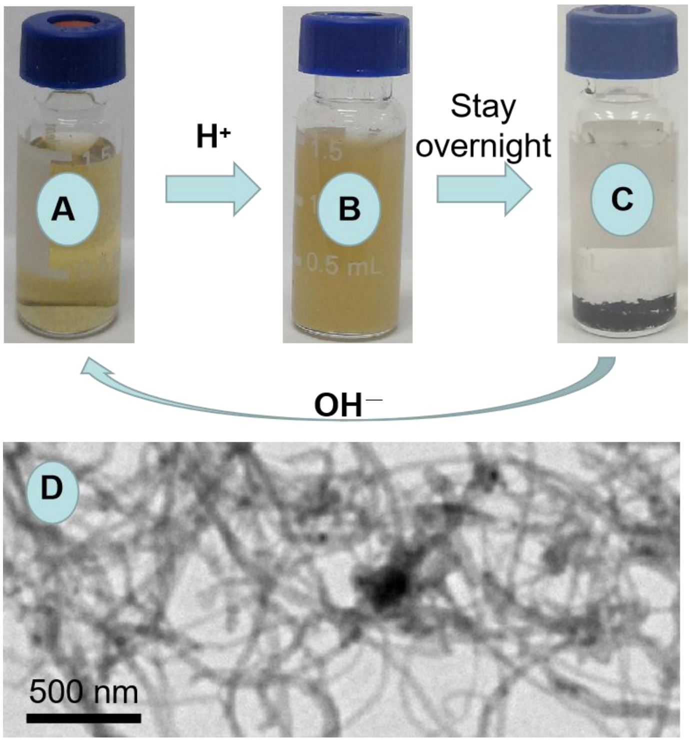


Fig. S17 Photographs of : A) multi-wall nanotubes with **WN3**; B) multi-wall nanotubes with **WN3** after addition of H^+; C) Sample **B** was stay overnight. D) TEM image of multi-wall nanotubes with **WN3** after addition of H^+.