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Supporting Information

Self-assembled Organic Nanotube Promoted Allylation of Ketones in Aqueous Phase

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General information

Characterizations. The ^{1}H NMR spectra were recorded on a Bruker Avance III 400 (400 MHz) spectrometer. CD spectra were obtained using JASCO J-1500 spectrophotometer. Analytical high-performance liquid chromatography (HPLC) was done with a Waters instrument using a chiral column (4.6 mm×250 mm, Daicel CHIRALCEL OJ-H). Atomic Force Microscope (AFM) measurements were performed on a Bruker FastScan system. The samples were suspended on the surface of mica. GC analysis was done with a Shimadzu Nexis GC-2030 instrument with a flame-ionization detector using nitrogen as a carrier gas.

Reagents. All reagents and solvents were used as received. Tetraallyltin and Allyltriphenyltin were purchased from TCI (Shanghai) Development Co., Ltd. Allylboronic acid pinacol ester, 4-Methylacetophenone, 4-Methoxyacetophenone, 4-Nitroacetophenone, 4-Fluoroacetophenone, 4-Bromoacetophenone, and 2-Acetonaphthone was purchased from Inno-Chem Science and Technology Co., Ltd. Acetophenone and allyltributylstannane were purchased from J&K.

General procedure

Catalytic ketone to homoallylic alcohol

HDGA was self-assembled into nanotube first. In doing this, 1.65 mmol of HDGA was added into 45 mL of water and heated to dissolve, and a transparent hydrogel was obtained after cooling to room temperature. Then tetraallyltin (471 mg, 1.66mmol) and ketone (1.66mmol) was injected into the dispersion under vigorous stirring, the reaction was proceed for about 24 h at 25℃. The resulting product was added into water, extracted with ethyl acetate and purified by silica column chromatography (hexane : ether = 50 : 1) to afford the homoallylic alcohol as clear oil.

2-Phenyl-4-penten-2-ol : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 1.55 (s, 3 H), 2.05 (s, 1 H), 2.50 (dd, J =13.7 Hz, 8.3 Hz, 1 H), 2.69 (dd, J = 13.7 Hz, 6.4 Hz, 1 H), 5.13 (m, 2 H), 5.62 (m, 1H), 7.25 (m, 1 H), 7.34 (m, 2 H), 7.45 (m, 2 H).

2-p-tolylpent-4-en-2-ol : ^{1}H NMR (400 MHz, $CDCl_3$) δ = 7.33 (d, J = 7.9 Hz, 2H), 7.15 (d, J = 7.9 Hz, 2H), 5.63 (m, 1 H), 5.12 (m, 2 H), 2.67 (dd, J = 13.8 Hz, 6.4 Hz, 1 H), 2.49 (dd, J = 13.7 Hz, 8.2 Hz, 1 H), 2.34 (s, 3 H), 2.00 (s, 1 H), 1.53 (s, 3 H).

2-(4-Methoxylphenyl)-4-penten-2-ol : ^{1}H NMR (400 MHz, CDCl3) δ = 7.36 (d, J = 8.4 Hz, 2 H), 6.87 (d, J = 8.4 Hz, 2 H), 5.63 (m, 1 H), 5.13 (m, 2 H), 3.81 (s,3 H), 2.66 (dd, J = 13.7, 6.5 Hz, 1 H), 2.48 (dd, J = 13.7, 8.2 Hz, 1 H), 2.00 (s, 1 H), 1.53 (s, 3 H).

2-(4-nitrophenyl)-pent-4-en-2-ol : ^{1}H NMR (400 MHz, CDCl3) δ = 8.22 (d, J = 8.6, 2 H), 7.64 (d, J = 8.6, 2 H), 5.61 (m, 1 H), 5.18 (m, 2 H), 2.70 (dd, J = 13.8, 6.6 Hz, 1 H), 2.56 (dd, J = 13.8, 8.2 Hz, 1 H), 1.60 (s, 3 H).

2-(4-Fluorophenyl)-4-penten-2-ol : ^{1}H NMR (400 MHz, CDCl3) δ = 7.40 (m, 2 H), 7.02 (m, 2 H), 5.61 (m, 1 H), 5.14 (m, 2 H), 2.65 (dd, J = 13.8, 6.5 Hz, 1 H) 2.49 (dd, J = 13.8, 8.2 Hz, 1 H), 1.95 (s, 1 H), 1.54 (s, 3 H).

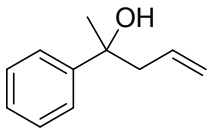
2-(4-Bromophenyl)-4-penten-2-ol : ^{1}H NMR (400 MHz, CDCl3) δ = 7.46 (d, J = 8.4Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 5.60 (m, 1H), 5.14 (m, 2H), 2.64 (dd, J =13.7, 6.5 Hz, 1H) 2.48 (dd, J = 13.7, 8.3 Hz, 1H), 2.00 (s, 1H), 1.52 (s, 3H).

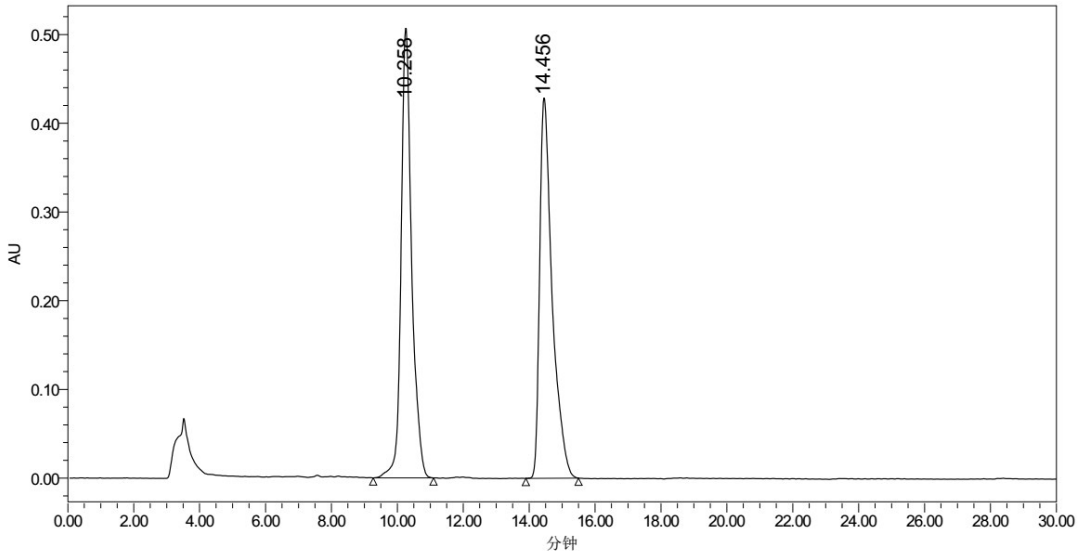
2-(Naphthalen-2-yl)-4-penten-2-ol : ^{1}H NMR (400 MHz, CDCl3) δ = 7.91 (s, 1 H), 7.83 (m, 3 H), 7.54 (d, J = 8.6 Hz, 1 H), 7.46 (m, 2 H), 5.61 (m, 1 H), 5.14 (m, 2 H), 2.80 (dd, J = 13.7, 6.3 Hz, 1 H) 2.58(dd, J = 13.8, 8.4 Hz, 1 H), 2.19 (s, 1 H), 1.63 (s, 3 H) .

General Procedure for the Asymmetric Allylation of Ketones

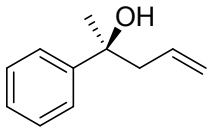
10 mg (18.4μmol) of HDGA was added into 1 mL of solvent and heated to dissolve, after cooling to room temperature, tetraallyltin (4.4μl, 18.4μmol) and acetophenone (2.14μl, 18.4μmol) was injected into the mixture under vigorous stirring, the reaction was proceed for about 24 h at 25℃. The result product was added into 10ml water, extracted with ethyl acetate and concentrated in vacuo. which was then subjected to chiral HPLC for determination of enantiomer excess. Enantiometric excess was determined by HPLC with a Chiralcel OJ-H column (98:2 hexane:2-propanol), 1 mL/min; minor enantiomer tr = 10.3 min, major enantiomer tr = 14.5 min.

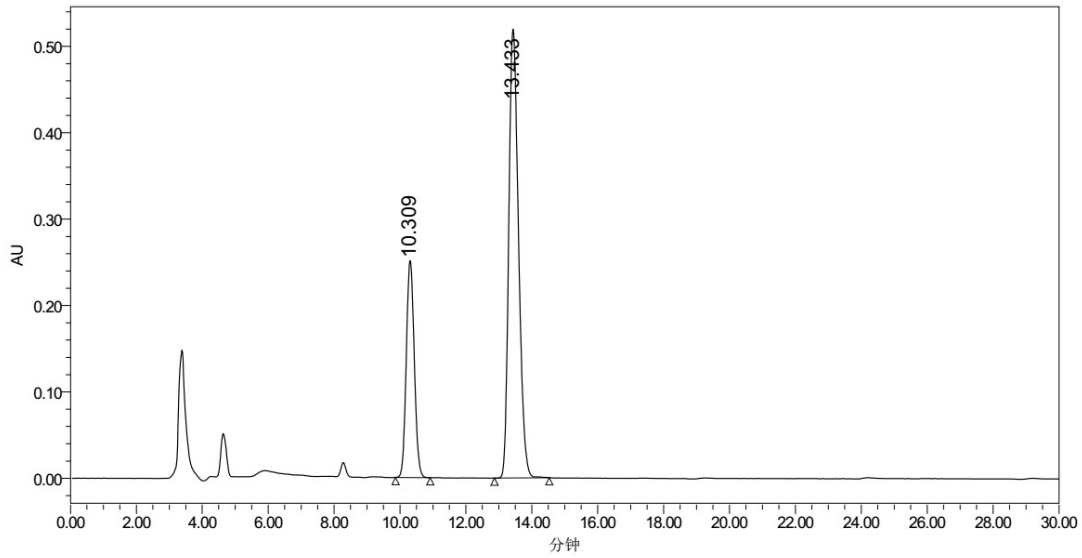
HPLC Trace





Peak #	RetTime (min)	Area (mAu*s)	Area %	Height (mAu)	Height %
1	10.258	11297473	50.02	507714	54.19
2	14.456	11288809	49.98	429119	45.81





Peak #	RetTime (min)	Area (mAu*s)	Area %	Height (mAu)	Height %
1	10.309	4225293	28.43	251391	32.62
2	13.433	10637428	71.57	519355	67.38

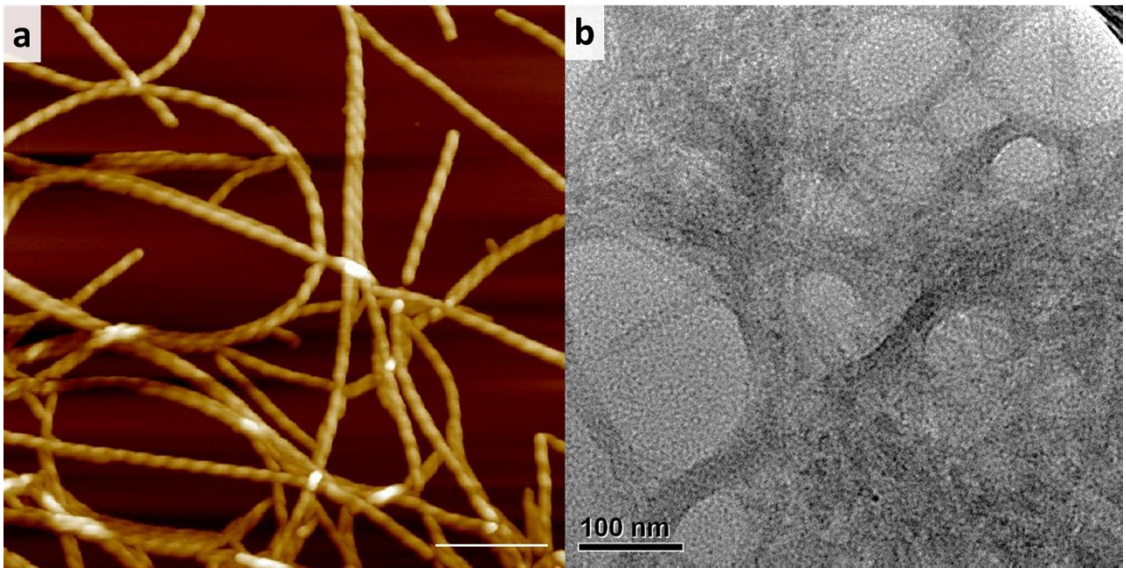


Figure S1. a) AFM (scale bar 200 nm) and b) TEM image of **HDGA** and tetraallyltin assembly.

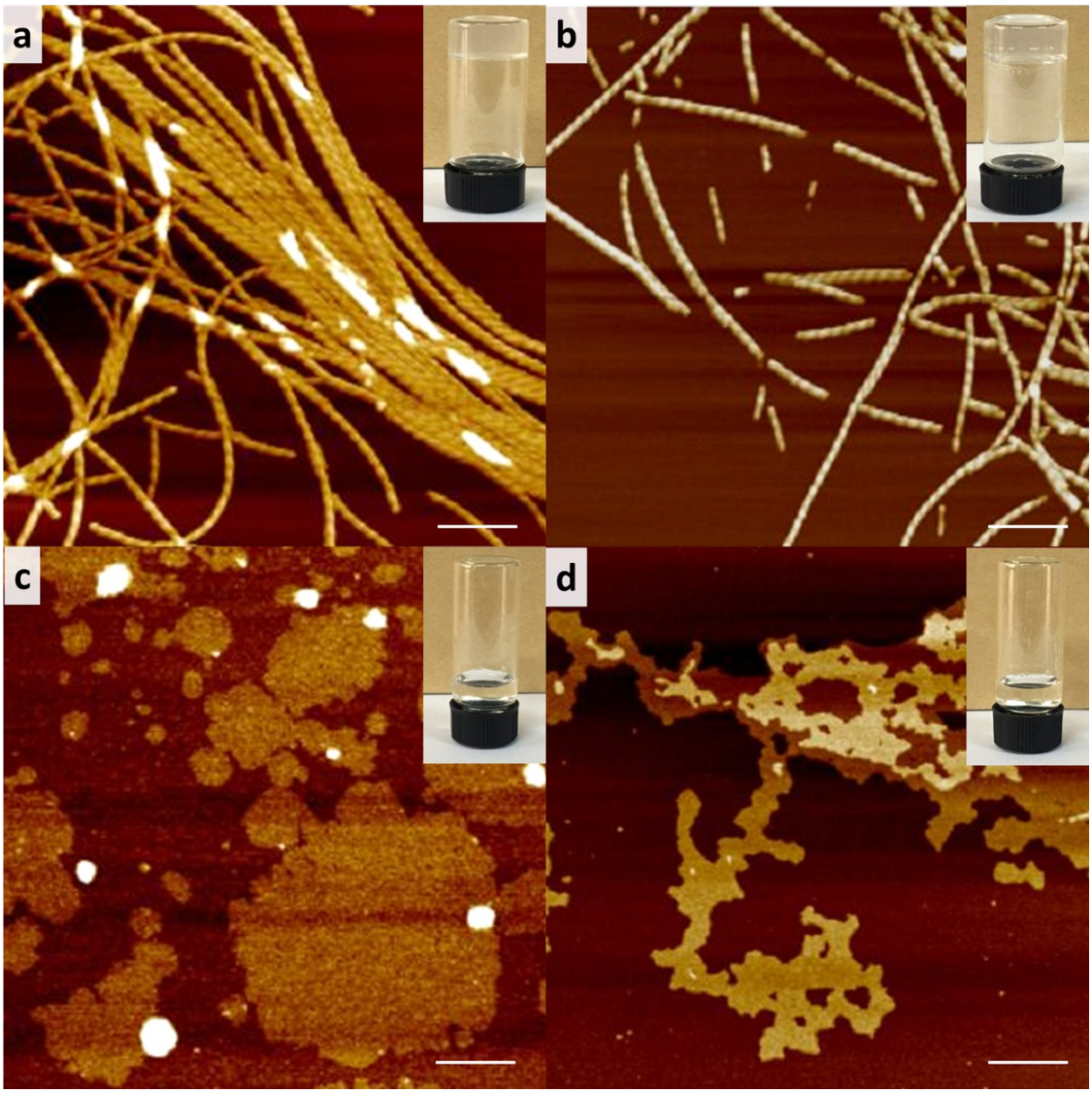


Figure S2. AFM image of HDGA assembly in different volume ratio methanol and water: a) MeOH: H_2O=0: 1; b) MeOH: H_2O=1: 2; c) MeOH: H_2O=1: 1; d) MeOH: H_2O=2: 1. The inserted pictures in all the figures were the optical photographs of assembly in aqueous media. Scale bars: 200 nm

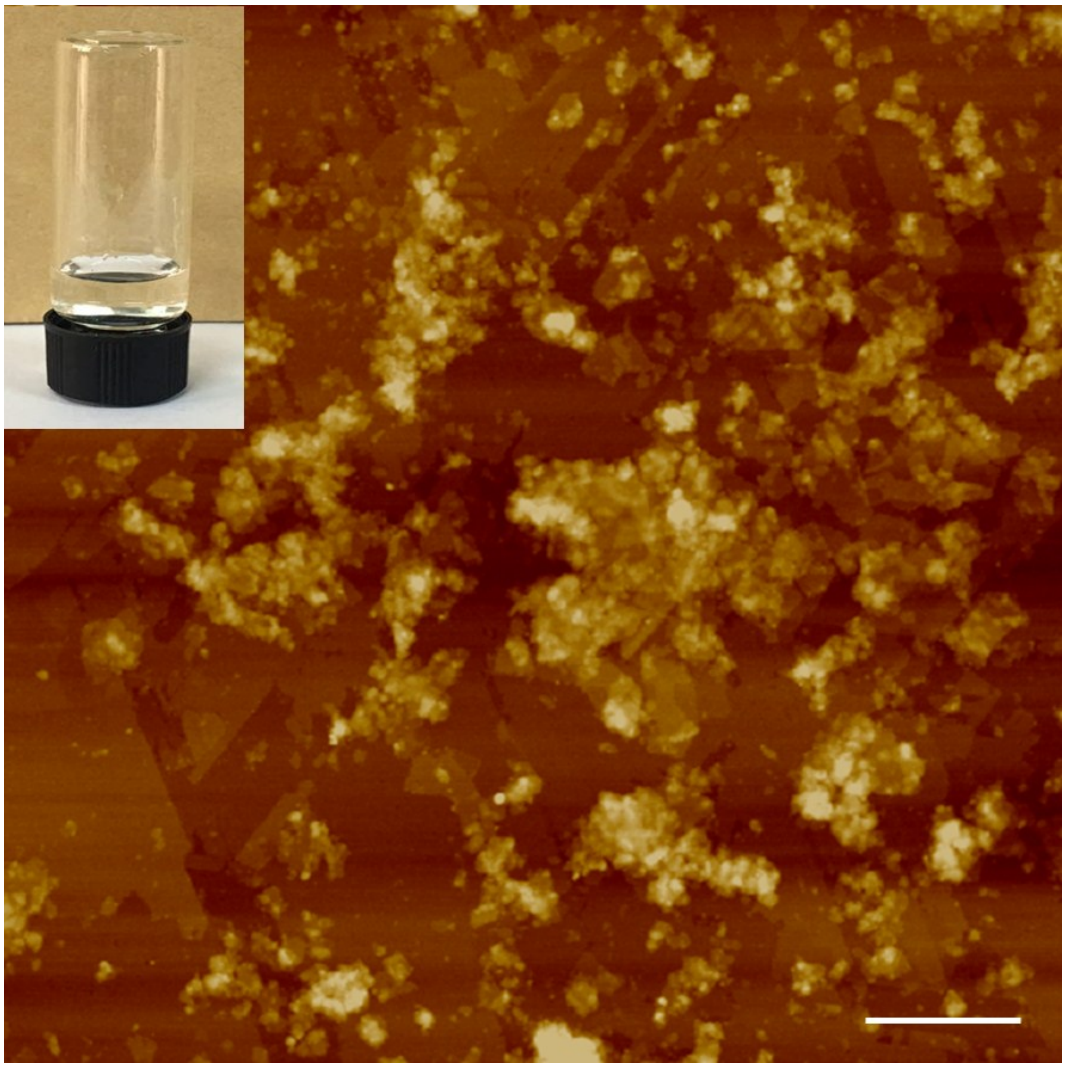


Figure S3. AFM image of **HDGA** gel after adding 3 equiv of NaOH. The inserted picture was the optical photographs of assembly in aqueous media. Scale bars: 200 nm.