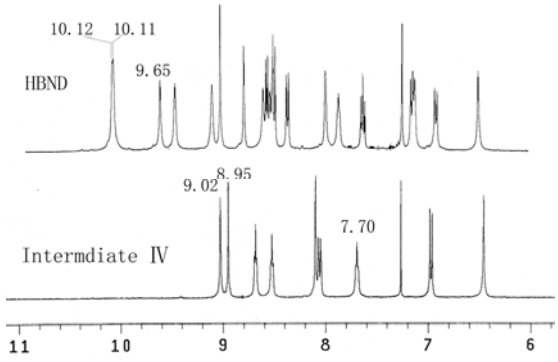

Fig.1. The ^{1}HNMR spectra (downfield region) of **HBND** and **Ⅳ**.

It can be seen from the ^{1}H NMR spectrum of the self-assembly duplex **HBND** (25 mM in $CDCl_3$) that there exist three amide NH protons with higher chemical shifts in the region of 9.6-10.2 ppm; in contrast, the chemical shifts of the amide NH protons of the intermediate **Ⅳ** are shifted to upfield (9.02, 8.95, and 7.70 ppm) (shown in **Fig. 1**).

This confirms the existence of intense intermolecular H-bonds between the two strands, and the signals in the spectrum of **HBND** at chemical shift of 10.12, 10.11 and 9.65 ppm can be assigned to protons **j**, **e**, and **n**, respectively, convincing the successful dimerization of . These NMR data are in good coincidence with those reported in the literatures.[1, 2]

[1] H. Q. Zeng, X. W. Yang, A. M. Brown, S. Martinovic, R. D. Smith, B. Gong, *Chem. Commun*. **2003**, 1556.
[2] H. Q. Zeng, H. Ickes, R. A. Flowers, B. Gong, *J. Org. Chem.* **2001**, *66*, 3574.

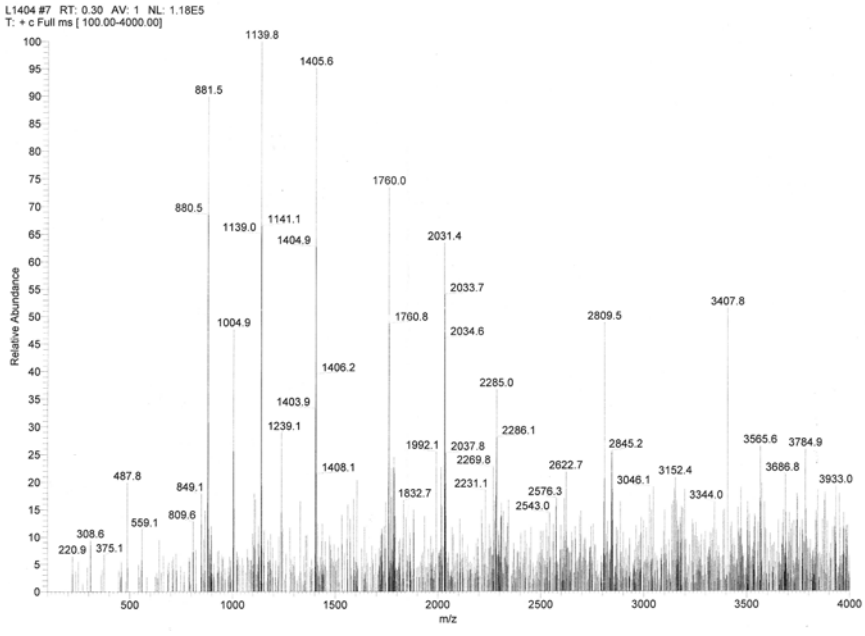

Fig 2. ESI-MS spectrum of **HBND**, determined by FINNIGAN-LCQ^{DECA} from chloroform solution

ESI-MS spectrum (**Fig. 2**) affords additional evidence confirming the formation of duplex **HBND**. The peaks of 2809 and 1404 can be assigned to the molecular ion of $[M+H]^+$ ($C_{162}H_{224}N_{16}O_{26}$) and $[M/2]^+$ respectively.

Synthesis of the intermediates as well as the target molecules:

Synthesis of 3-amino-5-nitrobenzoic acid (**1a**): To a boiling solution of 3,5-dinitrobenzoic acid (1.7 g, 8 mmol) dissolved in 10 mL CH_3OH was added a solution of NaHS in CH_3OH/H_2O (prepared from 6.1 g of $Na_2S{\cdot}9\ H_2O$ and 2.1 g of $NaHCO_3$). The reactant was refluxed for 20 min., then methanol was evaporated and the residue was poured into 100 mL of water. Acidification with conc. hydrochloric acid followed by recrystalization with water afforded dark red needles. Yield: 69.5%. Mp 209-210°C; EIMS (*m*/*z* (%)): 182 (70) [M^+].

Synthesis of 3-hexanamido-5-nitrobenzoic acid (**1b**): To a mixture of **1a** (0.18 g, 1 mmol) and triethylamine (0.1 g) dissolved in dioxane (50 mL) was added a solution of hexanoyl chloride (0.15 g, 1.3 mmol) in anhydrous dioxane (20 mL). The reactant was stirred overnight followed by reflux for 2 h, then cooled down and filtered. The solvent was evaporated and the residue was dissolved in ethyl acetate, washed with dilute hydrochloric acid and water, after removal of ethyl acetate, the crude product was purified via recrystallization with ethanol to give white needles. Yield: 58.5%. Mp 177.5-179□; ^{1}H NMR (400 MHz, DMSO-d_6, δ): 13.19(s, 1H), 10.56 (s, 1H), 8.82 (s, 1H), 8.51 (s, 1H), 8.26 (s, 1H), 2.34-2.38 (t, *J*=7.6 Hz, 2H), 1.56-1.65 (m, 2H), 1.28-1.34 (m, 4H), 0.86-0.89 (m, 3H); EIMS (*m*/*z* (%)): 279.1 (100) [M-1]$^+$, 280.1 (15) [M^+].

Synthesis of 4-bromo-*N*-(2-hydroxyethyl)-1,8-naphthalimide (**1c**): To a mixture of 4-bromo-1,8-naphthalenedicarboxylic anhydride (4.0 g, 16 mmol) and water (54 mL) was added 2-aminoethanol (1 g, 16 mmol). The reactant was stirred and refluxed for 3 h, then cooled down and filtered. The filter cake was washed with water and recrystallized with ethanol to give white needles. Yield: 68.7%. Mp 202.5-204°C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.67(dd, J=7.2Hz, J=0.8Hz, 1H), 8.59(dd, J=8.4Hz, J=0.8Hz, 1H), 8.43(d, J=7.6Hz, 1H), 8.06(d, J=8Hz, 1H), 7.86 (t, J=8.4Hz, 1H), 4.46(t, J=4.8Hz, 2H), 3.99(t, J=4.8Hz, 2H) ; EIMS (*m*/*z* (%)): 320 (40) [M^+].

Synthesis of *N*-(2-hydroxylethyl)-4-piperidinyl-1,8- naphthalimide (**1d**): To a mixture of **1c** (1.28 g, 4 mmol), piperidine (1.1 g, 4 mmol) and 30 mL monoethyl ether of glycol was added Cu_2Cl_2 (0.21 g) under protection of N_2. The reactant was refluxed for 5 h under stirring. After evaporation of the solvent, the residue was added into 40 mL chloroform, then washed with dilute hydrochloric acid and water. Evaporation of solvent followed by recrystalization from 95% ethanol resulted in yellow crystal. Yield: 70.2%. Mp 148.5-149.5°C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.58(dd, J=7.2Hz, J=0.8Hz, 1H), 8.50(d, J=8Hz, 1H), 8.43(dd, J=8.4Hz, J=0.8Hz, 1H), 7.71(t, J=8Hz, 1H), 7.20 (d, J=8Hz, 1H), 4.46(t, J=4.8Hz, 2H), 3.99(t, J=4.8Hz, 2H), 3.29(t, J=5.2Hz, 4H), 1.90(m, 4H), 1.75(m, 2H); ESI-MS (*m*/*z* (%)): 325.3 (100) [M+1]$^+$.

Synthesis of *N*-[2-(3-hexanamido-5-nitrobenzoyloxy) ethyl]-4-piperidinyl-1,8- naphthalimide (**1e**):**1b** (0.56 g, 2 mmol), 1-ethyl-3-[3-(dimethylamino)propyl] carbodiimide hydrochloride (EDCI) (0.6 g, 3 mmol), and 1-hydroxybenzotriazole (HOBT) (0.4 g, 3 mmol) were added together with 20 mL DMF under stirring for 30 min. Then **1d** (0. 65 g, 2 mmol) was added and stirred overnight at r. t. The reactant was poured into 150 g of cracked ice, and the crude product was collected, dissolved with THF, and purified through column chromatography (eluent: ether/ethyl acetate, 3/1) to obtain yellow solid, yield: 43%. Mp 77-78.5°C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.93(t, J=2Hz, 1H), 8.57(d, J=7.2Hz, 1H), 8.49(d, J=8Hz, 1H), 8.39-8.48(m, 2H), 8.14(s,1H), 7.84(s,1H) , 7.66-7.67 (t, J=7.2Hz, 1H), 7.17(d, J=8Hz, 1H), 4.69-4.62(m, 4H), 3.24(t, *J*=5.6 Hz, 4H), 2.41(t, *J*=7.6 Hz, 2H), 1.84-1.92(m, 4H), 1.70-1.78(m, 4H), 1.24-1.43(m, 4H), 0.78-0.95(m, 3H); ESI-MS (*m*/*z* (%)): 585.4 (100) [M-1$^+$], 586.4 (40) [M^+].

Synthesis of *N*-[2-(3-amino-5-hexanamidobenzoyloxy) ethyl]-4-piperidinyl-1,8- naphthalimide (**I**): **1e** (0.24 g, 0.40 mmol) was reduced by catalytic hydrogenation in a media of 10 mL methanol and 3 mL THF with 0.05 g of

Pd/C (10%, water: 65 wt %) as the catalyst at room temperature. The reaction time was monitored and determined by TLC. Removal of catalyst and solvent gave the crude product, which was used for the next step without further purification.

Synthesis of ethyl 2-{5-[2-([5-hexylcarbamoyl-2,4-bis (octyloxy)]benzamido) acetamido}-2-(octyloxy)benz amido acetate (**IV**): To a mixture of **II** (2.64 mmol) and 60 mL DMF was added EDCI (2.64 mmol) and HOBT (2.64 mmol). After stirring for 30 min., a solution of 2.64 mmol **III** in 50 mL DMF was added under protection of N_2. Then the reactant was stirred overnight, poured into ice-water, and the crude product was recrystalized with methanol to afford white solid, yield: 89%. M.p. 198-199°C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.02(s, 1H), 8.95(s, 1H), 8.70(t, *J*=7.2 Hz, 1H), 8.52 (t, *J*=7.2 Hz, 1H), 8.10 (m, 1H), 8.06(m, 1H), 7.70(t, *J*=7.2 Hz, 1H), 6.96 (d, *J*=9.2 Hz, 1H), 6.46 (s, 1H), 4.1-4.4 (m. 12H), 3.42 (m, 2H), 1.9-2.0(m, 6H), 1.25-1.61(m, 41H), 0.86 (m, 12H); ESI-MS (*m*/*z* (%)): 893.8 (20) [M^+], 930.1 (100) [M+K^+-2]$^+$.

Synthesis of 2-{5-[2-([5-hexylcarbamoyl-2,4-bis(octyl oxy)]benzamido) acetamido} -2-(octyloxy)benzamido acetic acid (**V**): To a solution of **IV** (2.23 mmol) in 60 mL hot DMSO was added 9.2 mL of 0.37 M aqueous NaOH. The mixture was refluxed and the reaction was monitored *via* TLC. After the hydrolysis was finished, the mixture was poured into 300 mL of ice-water, and filtered. The filtrate was acidified with conc. hydrochloric acid and white precipitate was collected and recrystallized from methanol to afford white crystal. Yield: 85.1%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 9.83(s, 1H, NH), 9.10(s, 1H, NH) ,8.98(s, 1H, NH) ,8.86(s, 1H, ArH), 8.48(d ,1H, *J*=9.2Hz, ArH), 7.93(d, 1H, *J*=1.6Hz, ArH), 7.66(s, 1H, NH), 6.91(d, 1H, *J*=9.2Hz, ArH), 6.41(s, 1H, ArH), 4.42(s, 2H, -CH_2), 4.33(s, 2H, -CH_2), 4.03-4.20(m, 6H, -OCH_2), 3.41(q, 2H, *J*=6Hz, -CH_2), 1.85-2.08(m, 6H, -CH_2), 1.25-1.58(m, 38H, -CH_2), 0.84-0.92(m, 12H, -CH_3).

Synthesis of the duplex VI·VI (**HBND**): To a mixture of **V** (2.64 mmol) and 60 mL DMF was added EDCI (2.64 mmol) and HOBT (2.64 mmol). After stirring for 30 min., a solution of **I**(2.64 mmol in 50 mL DMF) was added under protection of N_2. The reactant was gently heated until all the solid dissolved, then cooled down to room temperature and stirred overnight, poured into ice-water, and the crude yellow solid was collected, dissolved in 5 mL CH_2Cl_2, then dropped into ethanol, this procedure was repeated for three times to remove the reactant, and the resulted yellow solid was recrystallized from $CHCl_3$/EtOH. Yield: 75%. Mp 228-229°C; ^{1}H NMR (400 MHz, $CDCl_3$, δ): 10.12 (s, 1H, NH), 10.10 (s, 1H, NH), 9.65 (s, 1H, NH), 9.50 (s, 1H, NH), 9.13 (s, 1H, NH), 9.05 (s, 1H, Ar H), 8.82 (s, 1H, Ar H), 8.63 (s, 1H, Ar H), 8.59 (d, *J*=7.2 Hz, 1H, Ar H), 8.57 (d, *J*=9.6 Hz, 1H, Ar H), 8.52 (d, *J*=8 Hz, 1H, Ar H), 8.36 (d, *J*=8.4 Hz, 1H, Ar H), 8.02 (s, 1H, Ar H), 7.89 (s, 1H, NH), 7.65 (t, *J*=7.6 Hz, 1H, Ar H), 7.17 (s, 1H, Ar H), 7.15 (s, 1H, Ar H), 6.93 (d, *J*=8.8 Hz, 1H, Ar H), 6.51 (s, 1H, Ar H), 4.62 (m, 4H, H_2C-CH_2), 4.42 (s, 2H, CH_2), 4.32 (s, 2H, CH_2), 4.05-4.16 (m, 6H, OCH_2), 3.40 (m, 2H, CH_2), 3.20 (m, 4H, CH_2), 2.40 (t, *J*=6.8 Hz, 2H, CH_2), 1.17-2.01 (m, 56H, CH_2), 0.74-0.90 (m, 15H, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$, δ): 172.05, 166.47, 166.38, 166.19, 164.58, 164.41, 163.87, 163.69, 161.51, 160.59, 157.29, 153.70, 139.48, 139.38, 136.01, 132.84, 132.72, 131.21, 130.57, 130.12, 129.46, 126.34, 125.27, 124.48, 123.08, 121.18, 120.20, 117.95, 116.77, 115.93, 115.39, 114.65, 114.03, 113.70, 113.63, 112.96, 96.75, 70.61, 70.02, 69.80, 61.86, 54.53, 45.70, 45.60, 40.49, 38.77, 36.78, 32.08, 31.83, 31.77, 31.72, 29.61, 29.51, 29.49, 29.33, 29.29, 28.90, 28.79, 27.14, 26.39, 26.31, 26.22, 25.09, 24.34, 22.80, 22.70, 22.68, 22.64, 14.19, 14.04, 14.01; ESI-MS (*m*/*z* (%)): 1405.6 (95) [*M/2* +1]$^+$, 1404.9 (65) [*M/2*]$^+$,2809.5 (50) [M^+]; Anal. calcd for $C_{162}H_{224}N_{16}O_{26}$: C 69.23, H 7.98, N 7.97; found:

C 69.26, H 8.01, N 7.95.)

Synthesis of the naphthalimide counterpart (**ND**): **1d** (1 g, 3 mmol) and 30 mL of acetic anhydride was mixed and refluxed for 2 h. After cooled down to r. t., it was filtered to obtain yellow powder. The crude product was washed with water, acetone and water, then recrystallized form ethanol to get yellow crystal. Yield: 88%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 8.58(dd, J=7.2Hz, J=0.8Hz, 1H), 8.50(d, J=8Hz, 1H), 8.43(dd, J=8.4Hz, J=0.8Hz, 1H), 7.71(t, J=8Hz, 1H), 7.20(d, J=8Hz, 1H), 4.49(t, J=5.2Hz, 2H), 4.43(t, J=5.2Hz, 2H), 3.29(t, J=5.2Hz, 4H), 2.01(s, 3H), 1.90(m, 4H), 1.75(m, 2H)